Preparation of vertically aligned ZnO crystal rods in aqueous solution at external electric field

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In this study, an external electric field was used to facilitate the growth of vertically aligned ZnO crystal rods on the surface of indium tin oxide (ITO) glass substrates in an aqueous solution. We used $\text{Zn}(\text{NO}_3)_2$ and $\text{C}_6\text{H}_{12}\text{N}_4$ as precursor and reagent. We found that the external electric field generated by DC potential of 5 kV between two electrodes that were placed outside the bottle could facilitate the growth of homogeneous, high density and vertically aligned ZnO crystal rods. Position of the substrate during the growth of crystal was found to be important to obtain well aligned crystal. The crystals that were grown near the negative electrode had the best properties. Photoluminescence measurement at room temperature revealed sharp peaks at around 360 and 380 nm and a broad peak around 420 nm that indicated good properties of ZnO crystals grown with external electric field.

Keywords: *aqueous solution deposition; ZnO rods; external electric fields; photoluminescence*

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1. Introduction

Zinc oxide (ZnO) is one of II – VI compound semiconductors that receive a lot of attention due to their interesting properties and potential applications. Zinc oxide is known to have a wide direct band gap of 3.37 eV [1] and large exciton binding energy of 60 meV at room temperature [2]. This oxide material could be applied in many devices such as light-emitting devices [3, 4], transparent conducting layer for solar cells [5], field effect transistors [6] and gas sensors [7]. Among one-dimensional (1D) structures such as nanorods, ZnO has the most interesting properties due to quantum confinement effect in reduced dimension.

ZnO crystal rods that grow vertically and homogeneously on a substrate are very important for many applications such as lasing systems, solar cells and others. Several attempts have been

made to produce ZnO crystal rods that grow homogeneously and are vertically aligned. There are many papers that report the preparation of vertically aligned ZnO crystal rods using metal organic chemical vapor deposition (MOCVD) [8], pulsed laser deposition [9], molecular beam epitaxy (MBE) [10] and simple chemical solution methods [11]. The chemical solution method drew our attention since it is very simple and can be carried out with very cheap equipments. However, this method needs some improvement since in the X-ray diffraction (XRD) pattern, the diffraction peaks from other than (002) reflection plane still could be observed. In order to facilitate the proper growth along the c-axis and to obtain vertically aligned crystals using chemical solution method, the template layer of ZnO film [12] or Au nanoparticles, which act as nucleation sites [13] should be prepared on the glass substrate. These additional procedures prolong and complicate the fabrication process. Therefore, another method to obtain

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vertically aligned ZnO nanostructure needs to be explored.

Zinc oxide has a wurzite structure at ambient conditions. In this structure, Zn and O layers are separated along the c-axis direction. In the crystal, Zn has a positive charge and O has a negative one. This arrangement produces separated layers with different charges and therefore, it gives strong polarity or dipole moments along the c-axis. Since the dipoles could be aligned using electric field, we could assume that the growth direction of ZnO 1D nanostructure can be controlled by applying high external electric field during the deposition or growth. The application of external electric field during the fabrication of ZnO thin film has been carried out and reported. Hirose *et al.* [14] applied high electric field during the preparation of ZnO film by pulsed laser deposition (PLD) technique and reported that highly improved crystallinity could be found in the area on the substrate that was exposed to high electric field. Liu *et al.* [15] also reported on the effect of electric field on the growth of ZnO films using atomic layer deposition method and found highly epitaxial growth of the films that were prepared under electric field. However, to our best knowledge, there is no report on the application of external electric field to the growth of ZnO crystals in aqueous solutions.

In this paper, we report the results of our study on the effect of external electric field on the growth of ZnO crystals on an indium-tin oxide (ITO) glass substrate. The ZnO crystals were grown by simple chemical solution deposition methods, where zinc nitrate was used as a precursor. We intended to prepare well-aligned c-axis oriented ZnO crystal on the ITO glass substrate without an additional treatment of the substrate in order to study the effect of external electric field on the growth of the ZnO crystals.

2. Experimental

First, we prepared solutions of 0.1 mol/L of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 98 %) and 0.1 mol/L of hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) (Aldrich, 99 %) with demineralized water as a solvent. The chemicals were used as received without further

treatments. The pH of the solution was found to be 6.8. The ITO glass substrates were cut into $5 \times 5 \text{ mm}^2$ pieces, cleaned using acetone, ethanol and demineralized water in an ultrasonic cleaner and then dried. The ITO glass substrates were then placed vertically inside a rectangular glass bottle. In the experiments, all substrates were placed at the center of the bottle wall. The bottle was then filled with the prepared solution and then sealed. Outside the bottle, we placed two stainless steel electrodes that covered the bottle's flat sides. The distance between the two electrodes was the same as the width of the bottle, which was 2 cm. The electrodes were connected to the high voltage DC power supply, capable of producing electric potential of 0 – 20 kV. The bottle and electrodes were put into a laboratory oven at 95 °C for 8 hours. We prepared 3 different samples. The first sample was ZnO crystal grown without an external electric field, which was used as a control. Two others samples were prepared under DC voltage of 5 kV. Sample A was placed on the side of positive electrode whereas sample B was placed adjacent to the negative electrode. The experimental apparatus and detailed electrodes configuration are shown in Fig. 1. Sample A and B were not prepared in the same process. After preparation of sample A, sample B was prepared in a fresh solution. During the process, the substrates were placed at the same position but the polarity of electrodes was reversed. After the process, the sample was taken out from the solution, washed with demineralized water and then dried at room temperature.

Morphology of the samples was examined by scanning electron microscope (JEOL, JSM 5360LA). The crystal structure of the samples was characterized by X-ray diffractometer using Cu-K α radiation (PAN-analytical PW3373) and spectrofluorometer (Shimadzu, RF-5301PC) was used to investigate its photoluminescence (PL) properties. All measurements were carried out at room temperature.

3. Results and discussion

The X-ray diffraction patterns of ZnO crystals that were grown on the ITO glass without and with

Fig. 1. A schematic diagram of the chemical solution deposition method and the arrangement of substrates and electrodes used in the experiment.

external electric field are shown in Fig. 2. For ZnO sample that was prepared without an external electric field, we could clearly observe the presence of (100), (002), (101) peaks and other reflection peaks at higher 2θ value. In this sample, the intensity of (002) peak is lower than the intensity of (100) peak and slightly higher than the intensity of (101) peak. The X-ray diffraction pattern of ZnO crystals in sample A, which was grown on the substrate placed at the positive electrode and under electric field produced by a potential difference of 5 kV, shows an increasing intensity of (002) peak compared with the previous sample. Different XRD pattern was observed from sample B, which was grown at the negative electrode at the same potential difference. In this XRD pattern, sharp and high (002) peak is clearly observed. However, other reflection peaks still can be observed but their intensity is remarkably smaller compared with the (002) reflection peak. This gives indication that the ZnO crystals in this sample grew mainly along the c-axis.

The morphology of ZnO crystals grown on ITO glass was examined by scanning electron microscope and the results are shown in Fig. 3. In

Fig. 2. X-ray diffraction pattern of ZnO crystal grown on ITO substrates for sample A, placed near the positive electrode, sample B, placed near the negative electrode and ZnO crystals that were grown without an external electric field.

those figures, we show images taken at two different magnifications for each sample. In all samples, ZnO crystals mostly grew as hexagonal rods. For ZnO crystals that were grown without external electric field, there is a large variation in the diameter of the crystal rods. This sample is similar to the ZnO crystals grown using the same method and conditions as reported earlier [11]. We can observe that in our sample, the length of hexagonal sides is not uniform and the rods are fairly vertically aligned also. In sample A, the ZnO crystals clearly form hexagonal crystal rods. It also has smoother crystal surface compared with the ZnO crystals that were grown without an external electric field. We could mention also that the rods are not quite vertically aligned. In the sample B, we can observe higher number of ZnO crystals formed as hexagonal rods which grew almost vertically. This observation is consistent with the XRD pattern, which shows high intensity of (002) orientation peak indicating that most of ZnO crystals are well-aligned vertically. There are several crystals that did not grow vertically and this may explain the small intensity of (100) and (101) peaks as observed in the XRD pattern.

The SEM images let us observe the differences in the crystals morphologies and diameters. On their basis we then calculated the diameters of the

Fig. 3. Scanning electron microscope images of ZnO crystals of (a) sample that was grown without an external electric field, (b) sample A and (c) sample B at two different magnifications. The external electric field is given by potential difference of 5 kV at the distance between two electrodes of 2 cm.

crystal rods and studied their distribution quantitatively. The results are shown in Fig. 4. For the ZnO crystal that grew without the external electric field, ZnO rods have diameters from about 100 nm to 1200 nm and the population of the crystal with diameters of around 500–700 nm is found to be the largest. Meanwhile, the average diameter of ZnO crystal rods that were grown without the external electric field is around 600 nm. For crystals that were grown with the external electric field of sample A, the crystal rod average diameter is 1060 nm and in sample B, it is of 720 nm. This indicates that the electric field narrowed the distribution of diameters of the grown ZnO crystal rods or it enabled us to produce more homogenous crystals on the substrate. We also can state here that the external electric field also caused the increase in the diameters of ZnO crystal rods. Sample A has larger diameter of crystal rods compared with sample B

and in these two samples the average of the rod diameter is still larger than the rod diameter of ZnO crystals grown without the external electric field. From the SEM images we could also determine the surface density of ZnO rods on the substrate. The surface density of ZnO rods that were grown on the substrate without the external electric field is about $9.0 \times 10^7/\text{cm}^2$. In the sample B, the surface density increases to about $1.3 \times 10^8/\text{cm}^2$ but it decreases to about $3.6 \times 10^7/\text{cm}^2$ in sample A.

Fig. 4. Distribution of ZnO crystal rod diameters in samples A, B and in a sample that was grown without an external electric field.

Based on the previous results, we tried to study the effect of higher voltage. We prepared also ZnO crystals in the same conditions as we grew sample B, except that the electric potential differences between the electrodes were set at 7.5 kV and 10 kV. The SEM images of ZnO crystal grown in DC potentials of 7.5 kV and 10 kV are shown in Fig. 5. As the electric field was increased to the value higher than 5 kV, the ZnO crystals mostly did not align vertically and tended to have different orientations. Here, we could conclude that the higher voltage (>5 kV) could not promote the growth of vertically aligned ZnO crystals. We could observe also that the diameter of ZnO rods became smaller as the voltage increased from 7.5 kV to 10 kV. The most notable fact is that the surface density decreased as the applied voltage increased above 5 kV. The surface densities of the samples grown at the potentials of 7.5 kV and 10 kV were $1.8 \times 10^7/\text{cm}^2$ and $1.4 \times 10^7/\text{cm}^2$, respectively.

Fig. 5. Scanning electron microscope images of ZnO crystals that were grown near the negative electrodes at potential difference of (a) 7.5 kV and (b) 10 kV at a distance between electrodes of 2 cm.

From the above results, we could see that the external electric field could significantly affect the growth of ZnO crystals on the ITO substrate. Now, let us discuss the growth of ZnO rods in the aqueous solution under the influence of external electric field. In the aqueous solution with pH below 7, hydration of Zn^{2+} ions occurs and they start to be surrounded by water molecules, which could be written as $\text{Zn}(\text{OH}_2)_4^{2+}$ [16]. The oxygen atom of a water molecule will attach to the positive Zn^{2+} ion since oxygen atom in the water molecule has partially negative charge. The electric charge of hydrated molecules is the same as Zn^{2+} ion since water molecules have neutral charge. The route from the hydrated ion to the oxide is through the process known as hydrolysis, in which hydrated ions

lose its water molecules [16]. In this case, water molecules are not always removed but some water molecules release H^+ in the higher pH environment or at higher OH^- concentration since OH^- may attract positive ions like H^+ to form H_2O molecules. After the hydrolysis, $\text{Zn}(\text{OH}_2)_4^{2+}$ can transform into different molecules. Above pH = 7, the most dominant species is $\text{Zn}(\text{OH})_2$, which, by the further dehydration process, can be transformed into zinc oxide [17] as described in the following equilibrium reactions:

This high pH environment is provided by hexamethylenetetramine which is known as a weak base since its molecules decompose at higher temperature ($\sim 95^\circ\text{C}$) to release OH^- in the water [16].

In the presence of strong electric field, the $\text{Zn}(\text{OH}_2)_4^{2+}$ molecule, which has positive charge, will tend to move to the negative electrode and it will accumulate in the region close to the negative electrode. This might explain the higher surface density found on the sample B and the lower one on the sample A in comparison to the sample that was grown without an external electric field. Meanwhile, the OH^- ions, which have negative charge will tend to concentrate in the region near the positive electrode, therefore, the pH in that region could increase locally. At high pH environment, zinc ions in the water solution could be found as complex molecules of $\text{Zn}(\text{OH})_4^{2-}$, which have a negative charge and tend to concentrate near the positive electrode. These complex molecules could decompose into ZnO at high temperature ($\sim 95^\circ\text{C}$) [18] according to the following equation:

Two different growth routes then could be expected in the solution near the positive electrode and the other near the negative one. This could lead to different morphology of the ZnO crystal grown on different regions in the solution.

Let us discuss our results that show smaller surface density of ZnO crystals in the samples grown at potential above 5 kV. We propose an explanation as follows: in water we could expect the presence of H_3O^+ species from the auto-ionization of water as a solvent. These positive molecules are easily dragged to the region near the negative electrodes and make the region near the negative electrode become more acidic. It could shift the chemical balance to the left side in the reaction (1) and (2) and lead to the stabilization of $\text{Zn}(\text{OH})_2$ and $\text{Zn}(\text{OH}_2)_4^{2+}$ molecules. This could explain smaller surface density of the ZnO crystals grown at higher potential.

Fig. 6. Photoluminescence spectra of samples A, B and a sample that was grown without an external electric field. All samples were irradiated with light at a wavelength of 325 nm.

Finally, we studied the photoluminescence of our samples. The photoluminescence spectra taken at room temperature for ZnO crystals that were grown without electric field and in external electric field of sample A and B are shown in Fig. 6. The measurements were conducted at excitation with light at 325 nm using Xe lamp as a source. It could be seen clearly that the intensity of PL spectra of ZnO crystals grown without an external electric field is the lowest compared to the other samples. In all the spectra, we can observe a wide distribution from around 390 nm to about 650 nm and two relatively noticeable peaks centered around 380 nm as well as a smaller one at around 360 nm. In all samples, the peak at around 360 nm is observed.

The emission at 360 nm was also observed in ZnO nanowires [19] and it may be attributed to the direct recombination of photo-generated electron-hole pairs [20]. However, the peak at 380 nm is strongly suppressed in sample A. Emission peak at 380 nm is the near-band-edge photoluminescence and can be assigned to the donor electron and free hole recombination [21, 22]. To explain the suppression of this peak, further study is needed but we could add as a comment here that different growth routes play an important role since sample B is expected to be grown in the environment rich of OH^- species and H^+ trapped in ZnO crystal could compensate the concentration of donor defects in the crystals.

4. Summary

In brief, the external electric field could be used to produce vertically grown and well-aligned ZnO crystal rods on ITO substrate in an aqueous solution. The average diameter of ZnO crystal rods grown under the influence of external electric field is larger than that of the ZnO crystals that were grown without the external electric field. We observed significant differences in average rod diameter and surface density of ZnO crystals between samples that were grown near the positive and negative electrodes. Crystals that were grown near the negative electrode tend to have high surface density, smaller rod diameter while the opposite behavior is observed in the sample that was grown near the positive electrode. The PL spectra also reveal different features of these two samples (sample A and B) and a sharp peak at around 380 nm is strongly suppressed in the sample that was grown near the positive electrode (sample A).

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