Controlled Growth of Zinc Oxide Nanorod Array in Aqueous Solution by Zinc Oxide Sol-gel Thin Film in Relation to Growth Rate and Optical Property

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Abstract- Our work provides a systematic study of controllable morphology, crystallinity and photoluminescence (PL) of ZnO nanorod array. Our investigation demonstrates that the pre-treatment conditions of the ZnO sol-gel thin-film have strong influences on the morphology, crystalline and PL of the ZnO nanorod arrays grown thereon. The annealing temperature of the sol-gel thin film plays an important role on the microstructure of the ZnO grains and then the growth of the ZnO nanorod arrays. As the annealing temperature increases from 130 to 900 °C, the grain size of the thin films increases, and the diameter of the ZnO nanorod arrays increases from 60 to 250 nm. The scanning electron microscopy image show that the growth rate of ZnO nanorod along c-axis direction is very sensitive to the size of ZnO grains, and then influences the PL peak at 380 nm. The thin film annealed at the low temperature of 130 °C is amorphous, but the thereon nanorod arrays are high-quality single crystals growing along the c-axis direction with a high consistent orientation perpendicular to the substrates. The as-synthesized ZnO nanorod arrays via all solution-based processing enable the fabrication of next-generation nano-devices at low temperature.

Keywords-Zinc oxide; annealing; nanorods; hydrothermal method; sol-gel method; thin films; photoluminescence; X-ray diffraction; nucleation

I. INTRODUCTION

Zinc oxide (ZnO) nanorods, with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, are suggested promising applications in transparent electronics, solar cells and optoelectronics devices [1-4]. Over the past few years, ZnO nanorods have been synthesized with various methods including vapor-liquid-solid (VLS) epitaxy, chemical vapor deposition (CVD), pulse laser deposition (PLD), hydrothermal synthesis, and so on [5-7]. Unlike CVD and VLS techniques which are high temperature processes requiring costly equipment, the hydrothermal method has been found a simple process for growth of ZnO nanorods due to its low growth temperature below 100 °C and easy scale-up [8]. Recently, numerous efforts have been employed in controlling the sizes and shapes of ZnO nanorods, because it provides a better model for investigating the dependence of electronic and optical properties on the size confinement and dimensionality [9-11]. It had been reported that the size of ZnO nanowire arrays could be controlled at different growth temperatures [12]. It also had been reported that the growth of different morphologies of ZnO nanowires was dependent on substrate temperature in the PLD process [13]. Ma et al. had studied the effects of annealing substrates on the density of the ZnO nanorod arrays [14]. However, there was no study of the annealing effect on the crystallinity and photoluminescence (PL) of ZnO nanorod arrays. Moreover, the annealing temperature lower than 300 °C had not been explored in this report. Also, the growth rate of ZnO nanorod arrays influenced by the characteristics of ZnO sol-gel thin films has not been addressed in those reports.

In this work, controllable morphology, crystallinity and PL of ZnO nanorod array prepared on ZnO thin film with different annealing conditions were systematically studied. In particular, we reported the relation between annealed thin film and the growth mechanism of nanorod. Our investigations indicated that the thin film annealed at the low temperature of 130 °C was amorphous, but the thereon nanorod arrays were high-quality single crystals growing along the c-axis direction with a high consistent orientation perpendicular to the substrates.

This paper is organized as follows. In Sec. II, we brief the experiments including preparation and annealing treatment of ZnO sol-gel thin films and the growth of thereon ZnO nanorod arrays. In Sec. III, the experimental results are reported and discussed. Room temperature PL spectrum, field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) pattern, and were applied to analyze the produced ZnO nanorod arrays. Finally, we draw conclusions.

II. EXPERIMENTAL DETAILS

A. ZnO thin films: Sol-gel method

The ZnO thin films served as the seed layers were deposited on silicon substrates by a sol-gel method. A coating solution was prepared by dissolving zinc acetate dehydrate [Zn(OAc)₂] (Merck, 99.5% purity) and equivalent molar monoethanolamine (MEA) (Merck, 99.5% purity) in 2-methoxyethanol (2MOE) (Merck, 99.5% purity). The concentration of zinc acetate was 0.5 mol. The resulting solution was then stirred at 60 °C for 2 h to yield a homogeneous and stable colloid solution, which served as the
coating solution after being cooled to room temperature. Then the solution was coated onto $p$-type silicon (100) wafers by a spin coater at the rate of 1000 rpm for 20 s and then 3000 rpm for 30 s at room temperature. Subsequently, the gel films were preheated for 10 minutes to remove the residual solvent. The procedures from coating to preheating were repeated 10 times. Then the 10-layer films were annealed in a furnace at different temperatures ranging from 130 °C to 900 °C for 1 h. Fig. 1 shows the flow diagram for ZnO thin films prepared from sol-gel process using the spin-coating method.

B. ZnO nanorod arrays: Hydrothermal growth

After uniformly coating the silicon substrates with ZnO thin films, hydrothermal growth of ZnO nanorod arrays was achieved by suspending these ZnO seed-coated substrates upside-down in a glass beaker filled with aqueous solution of 50 mM zinc nitrate hexahydrate (Sigma Aldrich, 98% purity) and 50 mM hexamethylenetetramine (HMT) (Sigma Aldrich, 99.5% purity). During the growth, the glass beaker was heated with a laboratory oven and maintained at 90 °C for 4 hours. At the end of the growth period, the substrates were removed from the solution, then immediately rinsed with de-ionized water to remove any residual salt from the surface, and dried in air at room temperature. The general morphologies of the ZnO thin films and thereon ZnO nanorod arrays were examined by FESEM. The crystal phase and crystallinity were analyzed at room temperature by XRD using Cu $K\alpha$ radiation. The room temperature PL, measured using a Nd:YAG laser at 266 nm as the exciting source, was used to characterize the optical properties of the ZnO nanorod arrays.

III. RESULTS AND DISCUSSION

A. Photoluminescence of ZnO nanorod arrays

Fig. 2 shows the room temperature PL characteristics of as-grown ZnO nanorod arrays as a function of annealing temperatures of the thin films. They were grown at a fixed temperature of 90 °C, while the thin films were annealed at 130, 300, and 900 °C, respectively. A strong peak and a board peak could be observed, which are located in UV and visible region, respectively. The strong PL peak centered at about 380 nm, corresponding to the near band gap edge emission due to the recombination of free excitons through an exciton-exciton collision process. At the temperature of 900 °C, in addition to the UV emission, an obvious green band ~570 nm also appears in the PL spectrum of ZnO nanorod arrays. It has been suggested that the green band emission caused by the impurities and structural defects corresponds to the singly ionized oxygen vacancies in ZnO. It indicates a low concentration oxygen vacancy in ZnO nanorod arrays grown by this method.

It is interesting to note that the UV peak increases with annealing temperature of the ZnO thin films as shown in Fig. 2. To further understand the reason behind the increase in the UV band emission, morphologies of these as-grown ZnO nanorod arrays with different annealing temperature of thin films were analyzed by SEM as shown in Fig. 3. For the ZnO thin film annealed at 130 °C, thereon ZnO nanorods had a diameter of 60 nm and a length of 700 nm in average as shown in Fig. 3(a). At the temperature of 300 °C, the ZnO nanorods with a larger diameter of about 75 nm and a longer length of about 950 nm was shown in Fig. 3(b). As the annealing temperature of thin films increased to 900 °C, the diameter and length of thereon ZnO nanorod increased to 250 nm and 2600 nm, respectively, as shown in Fig. 3(c). It shows that the size of the ZnO nanorod arrays increases with the annealing temperature of ZnO thin films, which results in the increase in UV band emission of PL spectra.

B. Growth rate of ZnO nanorod arrays

The length of ZnO nanorods increased with the annealing temperature of the ZnO thin film, as mentioned previously. It indicates that the 3 samples, which were grown together in the same solution, experienced different growth rate of nanorods. Here we defined the growth rate as growing length per growing time. In this experiment, the growing time was 4 hours for the 3 samples. For the thin films annealed at 130, 300, and 900 °C, the growth rates were 175, 238, and 650 nm/h, respectively.
Fig. 4 shows the growth rate of the ZnO nanorod as a function of the annealing temperature of the ZnO thin films. It indicates that a high annealing temperature of thin films leads to a fast growth rate of the ZnO nanorod arrays, and vice versa. The reason could be further explained by the surface structure of the thin films as shown in Fig. 5.

Fig. 5 shows the top view FESEM images for the surface morphologies of the ZnO thin films with increasing annealing temperatures from 130 to 900°C. At the annealing temperature of 130 °C, no grain forms and the surface is smooth. At the annealing temperature of 300 °C, the film contains fine grains and the particle size is about 80nm. Once the annealing temperature increases, the grains become larger and densely packed. It demonstrates that the grain size of the ZnO thin film was changed due to re-distribution of crystalline grain by supplying sufficient thermal energy and the small grain has been joined into great crystalline surface.

We now examine the reason for the difference in the growth rate. It is believed that the crystal structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated Zn$^{2+}$ and O$^{2-}$ ions, stacked alternately along the c-axis, exhibiting an unique characteristic in terms of polar surfaces [15]. The oppositely charged ions produce positively charged Zn and negatively charged O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis, as well as a divergence in surface energy. As a result, the nanostructure is arranged in such a configuration to minimize the electrostatic energy. This is the driving force for growing the nanostructures. In addition, the interfacial free energy determines the growth rates on the different crystal faces [16]. Because larger grains have more surface polar charges at the surface, resulting in higher electrostatic surface energy, they are neutralized by absorbed more ions to redistribute their surface charges and lower their free energy. This accounts for the enhancement of growth rate in our ZnO growth.

C. Crystallinity of ZnO nanorod arrays

Fig. 6 gives the XRD patterns of the ZnO nanorod arrays corresponding to those shown in Fig. 3. The peaks in the XRD patterns are indexed to the hexagonal phase of ZnO. It is found that no other characteristic peaks corresponding to the impurities of the precursors such as zinc nitrate and zinc hydroxide are observed in the XRD patterns. At the temperature of 130 and 300 °C, only a very strong (002) diffraction peak and a very weak (101) peak are observed, indicating that the three ZnO samples are all of high c-axis orientation. It is noticeable that for the sample annealed at 130 °C, the XRD pattern shows only the (002) diffraction peak. In addition, the intensity of (002) diffraction peak is strongest, compared to other samples annealed at higher temperatures. This implies its perfect c-axis orientation and this result is in accordance with its SEM image. On the other hand, for the...
sample annealed at 900 °C, the (002) diffraction peak becomes weak, and at the same time, the (100) and (101) peaks become strong, indicating its tendency toward random orientation. It means that the films annealed at 900 °C has worse morphology and hence results in the relatively random orientation of nanorod arrays as observed in the Fig. 3. It is reasonable to expect that the ZnO nanorod orientation is determined by the nucleation and growth of the first few layers of zinc and oxygen atoms.

The previous investigation of the thin films annealed at 130 °C indicates that it is nearly amorphous (no shown here). However, the growth of ZnO nanorod arrays on amorphous ZnO thin films along the (002) plane is even more notable than that on poly-crystalline thin films. It may be because the polycrystalline ZnO grains with a certain orientation limit the growth along the (002) plane. In comparison, the amorphous ZnO seed layer does not limit the growth along the (002) plane. This indicates that the ZnO nanorod arrays prepared by the hydrothermal method have preferential orientation along the (002) plane, in particular on the thin films without a certain orientation.

IV. CONCLUSIONS

This work provides a systematic study of controlled growth of ZnO nanorod arrays by using the hydrothermal method. Our investigation demonstrates that the annealing treatment of ZnO sol-gel thin films have strong influences on the diameter and orientation of the ZnO nanorod arrays grown thereon. The annealing temperature of the ZnO thin films can affect the microstructure of the ZnO grains and then the growth of the ZnO nanorod arrays. As the annealing temperature increases from 130 to 900 °C, the grain size of the thin films increases, and the diameter of thereon ZnO nanorod arrays increases. The thin films influence the nucleation of the ZnO and subsequently affect the diameter and orientation of the thereon nanorod arrays. At the temperature of 130 °C, the ZnO nanorod arrays align very vertically with growth along the c-axis direction. This work provides a route to fabrication of low-cost highly oriented ZnO nanorod arrays at low temperature. These vertical nanorod arrays are highly suitable for use in ordered nanorod-polymer devices, such as solar cells and light emitting diodes.

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REFERENCES


