Effect of the O$_2$/N$_2$ Ratio on the Growth of ZnO Nanostructures on c-Plane Sapphire Substrate via Thermal Evaporation Technique

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ZnO nanostructures were grown on c-plane sapphire substrate in an oxygen and nitrogen gas environment at 1000°C by thermal evaporation of Zn powder without using catalyst. The ZnO nanostructures were synthesized at different O$_2$/N$_2$ ratios in order to investigate the effect of O$_2$/N$_2$ ratio in ambient gas on the morphology, crystal structure and cathodoluminescence of ZnO nanostructures. No nanostructures were grown on the substrate in a N$_2$ environment. As the ratio of O$_2$ to N$_2$ increased, ZnO nanostructures with wire shape began to be grown on the substrate. In addition, tilted nanowires, which were grown with tilt angles with respect to the substrate plane, were observed. With further increasing the ratio of O$_2$ to N$_2$, the size of nanostructures increased. The intensity of visible emission in CL spectra increased with the increase in the ratio of O$_2$ to N$_2$.

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1. Introduction

ZnO is a semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, which ensures an efficient ultraviolet (UV) excitonic emission under low excitation intensity even at room temperature (RT). Its excellent optical and electrical properties make ZnO a promising material for applications in UV light emitting devices, photo detectors, electron field emitters, gas sensors and solar cells.

On the other hand, semiconductor nanostructures have attracted great interest due to their unique physical and chemical properties, and potential applications in nanoelectronics and nano-photronics. Among them, the nanostructures of ZnO semiconductor is particularly promising for the applications in nanodevices and nanosystems including nanolasers, nanosensors, nanocantilevers, transistor and nanoresonators.

Sapphire substrate has been widely used in the growth of ZnO nanostructures and thin films owing to its high crystalline perfection, high stability at high temperature and transparency. So far, ZnO nanostructures have been synthesized on sapphire substrates by various methods, including sputtering, metal organic chemical vapor deposition, hydrothermal method and thermal evaporation. Among these methods, the thermal evaporation method has been widely employed because of low cost and simplicity. In thermal evaporation method, the morphology and phase structure of oxide nanostructures also depend on carrier gas (ambient gas). The synthesis process in thermal evaporation method generally has been carried out using O$_2$ and N$_2$ (or Ar) as reactant and carrier gas.

In this paper, we report on the effect of the O$_2$/N$_2$ ratio on the morphology and the luminescence property of ZnO nanostructures. In addition, the epitaxial relationship between ZnO nanostructures and sapphire substrate was studied.

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2. Experimental Procedure

Zn powder with a purity of 99.99% was used as the source material for synthesizing ZnO nanostructures on c-plane sapphire substrate. The Zn powder was put in an alumina boat and the sapphire substrate was placed at the downstream end of the boat with a distance of 20 mm away from Zn powder. Then the alumina boat containing the Zn powder and the substrate was inserted into an alumina tube furnace and placed in the center of the furnace. Before the process, the alumina tube was evacuated to a base pressure of 1.33 × 10$^{-5}$ Pa by a rotary pump. Then N$_2$ and O$_2$ gas were introduced into the furnace until it reached a pressure of 1.33 × 10$^{-3}$ Pa. Subsequently, the furnace was heated to 1000°C and kept at this temperature for 1 h. After the oxidation process, the furnace was turned off and cooled to room temperature. The ratio of O$_2$/N$_2$ was changed in the wide range of 0/100, 25/75, 50/50, 75/25 and 100/0.

The morphology of the as-synthesized product was observed by scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectroscope. The crystal structure was studied by X-ray diffractometry (XRD) with Cu K$_\alpha$ radiation. The components were investigated by the EDX. The cathodoluminescence (CL) properties were characterized at room temperature by CL spectroscopy.

3. Results and Discussion

Figure 1 shows SEM images of the as-synthesized products grown on sapphire substrates at different pressures of 1.33 × 10$^2$, 1.33 × 10$^3$ and 1.33 × 10$^4$ Pa in an O$_2$ gas atmosphere at 1000°C for 1 h. At a pressure of 1.33 × 10$^2$ Pa, zinc oxide nanowires are grown on the substrate. The diameter of the nanowires is about 40 nm. When the pressure is 1.33 × 10$^3$ Pa, nanowires with diameters ranging from 300 nm to 800 nm are observed. Whereas no product are formed on the substrate at 1.33 × 10$^4$ Pa as shown in the EDX spectrum (the inset in Fig. 1(c)). At an oxygen pressure as high as 1.33 × 10$^4$ Pa, the surface of Zn source powder
was likely to be quickly oxidized by the abundant oxygen, resulting in an abrupt decrease of Zn vapor. As a result, no ZnO crystals were formed on the substrate. Based on this result, then experiments were carried out under a pressure of $1.33 \times 10^3$ Pa.

The effect of the O$_2$/N$_2$ ratio on the synthesis and morphology of the nanostructures was investigated. Figures 2(a)–(e) show the morphologies of the products prepared at different ratios of O$_2$ to N$_2$: 0/100, 25/75, 50/50, 75/25 and 100/0, respectively. When the O$_2$/N$_2$ ratios are less than or equal to 25/75, no nanostructures are formed on the substrates. When oxygen content in the gas mixture is low, it is difficult to form ZnO nuclei on the substrate. According to the nucleation theory, nucleation density of ZnO is determined by the following equation:

$$N = A \exp(-\Delta G^*/RT)$$

where $N$ is the nucleation density, $T$ is growth temperature, $A$ is a constant, and $\Delta G^* = \Delta G_v + \Delta G_s$ is the activation energy of nucleation. $\Delta G_v$ is the volume free energy and $\Delta G_s$ is the surface free energy. $\Delta G_v$ is related to the oxygen concentration as: $\Delta G_v \propto -\ln P(O_2)$. Thus $\Delta G_v$ increases with the decrease in oxygen concentration, which leads to the increase in the activation energy of nucleation. As a result, it is difficult to nucleate ZnO on the substrates. As the O$_2$/N$_2$ ratio increases to 50/50, nanostructures with wire shape are found. The diameters of the nanowires are in the range of 50–120 nm with a length of 600 nm. The nanowires are high density and uniform on a large area. In particular, it should be noted that the nanowires were grown in three directions with tilt angles with respect to the substrate plane. For the product prepared at a O$_2$/N$_2$ ratio of 75/25, the diameter of the nanowires increases to about 300 nm. When the O$_2$/N$_2$ ratio is 100/0, the diameter of the nanowires further increases to about 500 nm.

XRD measurement was carried out in order to identify the component and crystal structure of the nanostructures. XRD patterns were taken for the products prepared at the O$_2$/N$_2$ ratios of 0/100, 50/50, 75/25 and 100/0. Figure 3 shows the XRD patterns of the products. All the diffraction peaks are well indexed to the standard hexagonal wurtzite structure of ZnO (JCPDS 36-1451). For the product prepared at a O$_2$/N$_2$ ratio of 0/100, ZnO was not formed on the substrate. When the O$_2$/N$_2$ ratio is 50/50, a remarkably strong ZnO (002) diffraction peak is observed. The observation of the strong (002) peak indicates that the ZnO nanowires grown on the c-plane sapphire substrate are highly oriented in the c-axis direction. While a weak ZnO (101) peak as well as ZnO (002) peak is observed at the O$_2$/N$_2$ ratios of 75/25 and 100/0. For all the products, no peaks related to unreacted Zn or impurities are found in the spectra.

The components of ZnO were examined by EDX. Figures 4(a)–(e) show the EDX patterns of the ZnO synthesized at different O$_2$/N$_2$ ratios, 0/100, 25/75, 50/50, 75/25 and 100/0. The EDX analysis reveals that no ZnO was formed on the substrates under the conditions of O$_2$/N$_2$ gas ratios of 0/100, 25/75, whereas ZnO with high purity was synthesized on the substrates when the O$_2$/N$_2$ ratios were more than or equal to 50/50.

Let us consider the epitaxial relationship between the substrate and the nanowires. Figure 5 shows a high
magnification SEM top-view image of the ZnO nanowires grown on a c-plane sapphire substrate at a O2/N2 ratio of 50/50. XRD result indicated that the ZnO nanostructures were grown along the c-axis direction on the c-plane sapphire substrate. The c-axis [0001] direction in ZnO has the fastest growth rate and thus ZnO grows along the c-axis, resulting in the formation of one-dimensional nanowires. On the other hand, as shown in the SEM image of Fig. 5, a large number of the ZnO nanowires were grown tilted to the substrate. As indicated by the white lines in the SEM image, the tilted nanowires were grown in three different directions. The three directions have a rotation angle of 120° to one another. The ZnO (0001) plane and the sapphire (0001) plane have lattice misfit of about 18%, while the ZnO (0001) plane and the sapphire (1014) plane have the misfit less than 2.7%. The three sapphire (1014) plane directions have a rotation of 120° to one another, which is in well agreement with the angle between the growth directions of the tilted nanowires in the Fig. 5. Thus the titled ZnO nanowires could be grown on c-plane sapphire substrate to reduce the in-plane lattice mismatch.

Figures 6(a)–(d) show the room temperature CL spectra of the ZnO products synthesized at different O2/N2 ratios, 0/100, 25/75, 50/50, 75/25 and 100/0. Because no ZnO was formed at a O2/N2 ratio of 0/100, any emission peak...
was not observed. When the O$_2$/N$_2$ ratios are higher than or equal to 50/50, there are two emission peaks: ultra-violet (UV) emission peak at 380 nm and green emission peak at 510 nm. It is known that the UV emission originates from a recombination of free excitons$^6$ and green emission is related to singly ionized oxygen vacancies$^7$ and (or) antisite oxygen atoms.$^8$ As shown in Fig. 6, the intensity of green emission peak increases with the increase in the ratio of O$_2$ to N$_2$, which indicates that more oxygen defects exist in the ZnO nanostructures. The growth rate of ZnO crystals will increase with increasing the oxygen content and ZnO adatoms onto the surface of ZnO crystals do not have sufficient time to diffuse to thermodynamically stable sites on the surface of ZnO crystals. Consequently, this leads to an increase of structural defect density in the crystals.

On the other hand, no metal catalyst droplets were observed on the tips of the nanowires. This suggests that the ZnO nanowires were grown via the vapor-solid mechanism.

4. Conclusions

When the O$_2$/N$_2$ ratios in ambient gas were higher than or equal to 50/50, ZnO nanowires were grown on c-plane sapphire substrates via thermal evaporation of Zn powder. At the O$_2$/N$_2$ ratios of less than 50/50, no ZnO products were formed on sapphire substrates. The ZnO nanowires were grown preferentially along the c-axis direction on the c-plane sapphire substrate, indicating the epitaxial growth of the ZnO nanowires on the c-plane sapphire substrates. On the other hand, a large number of the nanowires tilted to the substrate surface were observed. The tilted nanowires had the rotation of 120° to one another, from which it was found that the wires grew in three preferred orientation with ZnO(0001)∥Al$_2$O$_3$(1014). The intensity of the green emission related to oxygen defects increased with increasing the O$_2$/N$_2$ ratio.

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REFERENCES