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Effect of the O_2/N_2 ratio on the morphology of ZnO nanostructures grown by a thermal evaporation technique

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Abstract

ZnO nanostructures were synthesized by thermal evaporation of Zn powder in an oxygen and nitrogen gas environment at 1000 °C. No substrates or catalysts were used for the formation of the ZnO nanostructures. The ZnO nanostructures were synthesized inside crucibles with Zn source powder. ZnO nanoneedles began to be found at O_2/N_2 ratios of less than 60/40. As the O_2/N_2 ratio increased to 80/20, the ZnO nanostructures mainly grew in the longitudinal direction. Upon increasing the O_2/N_2 ratio to 100/0, the ZnO nanostructures grew mainly in the transverse direction. CL spectra showed that ZnO with a high crystalline quality was obtained at a O_2/N_2 ratio of 80/20.

Keywords: A. Powders: gas phase reaction; B. Whiskers; C. Optical properties; D. ZnO

1. Introduction

Semiconductor nanostructures have attracted great interest because of their unique physical and chemical properties. Among semiconductor nanostructures, zinc oxide (ZnO) is considered as a potential material for the applications in electronic and optoelectronic devices due to its wide bandgap and large exciton binding energy. Its bandgap of 3.37 eV and large exciton binding energy of 60 meV allow for ultraviolet (UV) excitonic emission under low excitation intensity even at room temperature (RT). So far, ZnO nanostructures have been synthesized in various ways, including thermal evaporation [1], metal organic chemical vapor deposition [2] and hydrothermal method [3].

Among these methods, the thermal evaporation method has been widely employed because of low cost and simplicity. ZnO nanostructures with various morphologies have been realized by changing the parameters of temperature and pressure in a thermal evaporation technique. However, there have been few reports on the effect of other experimental parameters on the morphology and optical properties of ZnO nanostructures. The synthesis process in the thermal evaporation technique generally has been carried out using O_2 and N_2 (or Ar) as reactant and carrier gas, respectively. However, the effect of the O_2/N_2 ratio on the morphology of ZnO nanostructures has not been studied extensively. So far, there have been a few studies on the effect of ambient gas on the morphology of ZnO nanostructures, but the studies were performed with a small amount of oxygen [4] or air and argon gas [5]. Furthermore, in the previous studies, ZnO nanostructures were synthesized on the substrates placed apart from the source materials. The substrates were placed in the low temperature zone in a furnace, which provided the nucleation sites for the growth of ZnO nanostructures.

In this paper, we report on the effect of the O_2/N_2 ratio on the morphology of ZnO nanostructures. In order to investigate the effect of the O_2/N_2 ratio under oxygen-rich as well as oxygen-poor conditions, the O_2/N_2 ratio was varied over a wide range. Although no substrates or catalysts were used in our experiment, ZnO nanostructures were synthesized inside a crucible. The morphology and optical properties of the ZnO nanostructures synthesized inside the crucible were characterized.

2. Experimental procedure

Zn powder with a purity of 99.99% was used as the source material for synthesizing ZnO nanostructures. The Zn powder

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was put in an alumina crucible and inserted into an alumina tube furnace. The alumina crucible was placed at the center of the furnace. No substrates were used. One end of the tube was connected to a rotary pump. The other end of the tube was connected to the gas supply system. The furnace system was evacuated to a base pressure of 1×10^{-1} Torr. Then N_2 and O_2 gas were introduced into the furnace until it reached a pressure of 100 Torr. Subsequently, the furnace was heated to 1000 °C with a heating rate of 10 °C/min and the source material was oxidized at this temperature for 1 h. After the oxidation process, the furnace was turned off and cooled to RT. White products were found in the crucibles. The ratio of O_2/N_2 was changed in the range of 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0.

The morphology of the as-synthesized product was studied by a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectroscope. The crystal structure was characterized by X-ray diffractometry (XRD) with Cu Kα radiation. The components were studied by the EDX. The cathodoluminescece (CL) properties were characterized by CL spectroscopy.

3. Results and discussion

First, the effect of pressure on the synthesis and morphology of the ZnO nanostructures was investigated to find the optimal pressure for synthesizing ZnO nanostructures. Zn powders were oxidized at different pressures in an O_2 gas atmosphere at 1000 °C for 1 h. Fig. 1 shows the morphologies of the as-synthesized products. Fig. 1(a), (b), (c) and (d) display the morphologies of the products synthesized at pressures of 1, 10, 100, and 900 Torr, respectively. When the pressure is 1 Torr, the spherical Zn granule is converted to spherical ZnO particles. No nanostructures are observed. As the pressure is increased to 10 Torr, nanowires begin to be formed. At the pressure of 100 Torr, ZnO nanowires with hexagonal shape are obtained. When the pressure is further increased to 900 Torr, again no nanostructures are obtained. These results confirmed that ZnO nanostructures were not formed when the pressure was either much lower or much higher than 100 Torr.

Then experiments were carried out at 100 Torr. The effect of the O_2/N_2 ratio on the synthesis and morphology of the ZnO nanostructures was investigated. Fig. 2 (a)–(f) shows the morphologies of the products prepared at different ratios of O_2 to N_2: 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0, in turn. No nanostructures are observed for the products prepared at O_2/N_2 ratios of less than or equal to 40/60. When the O_2/N_2 ratios are 50/50 and 60/40, nanostructures with needle shape start to appear. For the product prepared at a O_2/N_2 ratio of 80/20, needle-like nanostructures with a uniform diameter of 50–100 nm and a length of several tens of microns were observed more distinctly. When the O_2/N_2 ratio is 100/0, rod-like nanostructures are obtained. The diameter and the length of the nanorods are about 500 nm and several tens of microns respectively. The SEM observation revealed that the ZnO nanostructures mainly grow in the longitudinal direction as the O_2/N_2 ratio increases from 50/50 to 80/20, while the ZnO nanostructures mainly grow in the transverse direction upon increasing the O_2/N_2 ratio to 100/0.

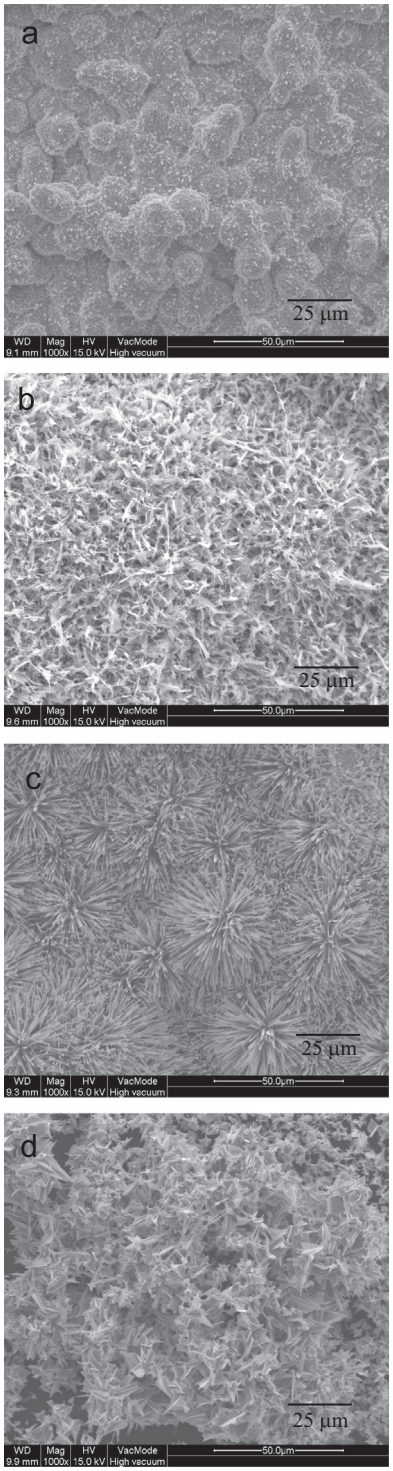

Fig. 1. SEM images of the products synthesized in the crucibles through thermal evaporation of Zn powder at different pressures under an O_2 gas atmosphere at 1000 °C for 1 h: (a) 1 Torr, (b) 10 Torr, (c) 100 Torr and (d) 900 Torr.

XRD patterns of ZnO nanostructures were taken for the products prepared at the O_2/N_2 ratios of 80/20 and 100/0. The XRD patterns of the ZnO nanoneedles and nanorods are shown

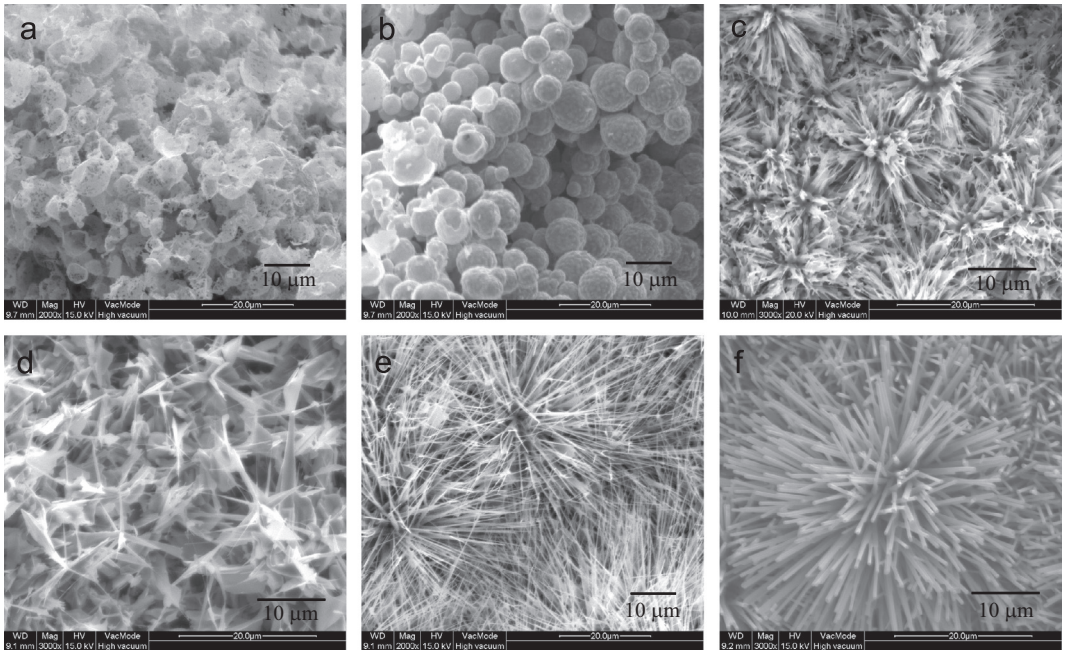

Fig. 2. SEM images of the products prepared at different O_2/N_2 ratios of (a) 20/80, (b) 40/60, (c) 50/50, (d) 60/40, (e) 80/20 and (f) 100/0.

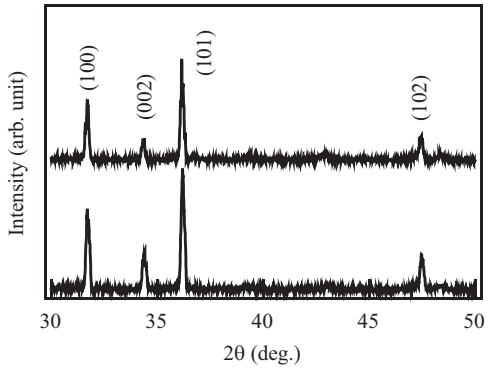

Fig. 3. XRD patterns of the products prepared at different O_2/N_2 ratios of (a) 80/20 and (b) 100/0.

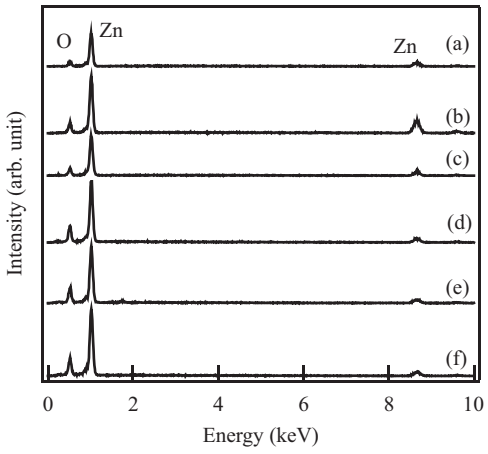

Fig. 4. EDX patterns of the products prepared at different O_2/N_2 ratios of (a) 20/80, (b) 40/60, (c) 50/50, (d) 60/40, (e) 80/20 and (f) 100/0.

in Fig. 3. The XRD patterns are well indexed to the standard hexagonal wurtzite structure of ZnO (JCPDS 36-1451). The positions of XRD peaks are in well agreement with those of the standard hexagonal structure of ZnO. The components of ZnO were examined by EDX. Fig. 4(a)–(f) shows the EDX patterns of the products synthesized at different O_2/N_2 ratios, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0. The EDX analysis reveals that all the products are composed of Zn and O elements. No impurities, including Zn are detected, which indicates that the ZnO is of high purity.

The room temperature CL spectra of the products synthesized at different ratios of O_2/N_2 are shown in Fig. 5. Fig. 5(a)–(f) shows the CL spectra of the ZnO products synthesized at different O_2/N_2 ratios, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0. When the O_2/N_2 ratio is less than 50/50, only a broad green emission peak at 510 nm is observed. It should be noted that the ZnO prepared at a O_2/N_2 ratio of 80/20 exhibits a high-intensity sharp UV emission peak centered at 380 nm and a low-intensity broad green emission peak at 510 nm. However, although both of the emission peaks are still observed in the CL spectrum of the ZnO grown at a O_2/N_2 ratio of 100/0, the intensity of the green emission peak is relatively higher than that of the UV emission. Generally, it is well known that the UV emission originates from a recombination of free excitons [6] and the green emission is attributed to intrinsic defects such as single ionized oxygen vacancies [7] and antisite oxygen atoms [8] in ZnO. Thus, it is obvious that the higher the UV-to-green emission ratio, the better the crystal quality of the ZnO.

In the ZnO samples produced at O_2/N_2 ratios of less than 60/40, the UV-to-green emission ratio in the CL spectra is very low, which suggests that the concentration of oxygen vacancy in the ZnO is very high. When the ZnO samples are synthesized at relatively low O_2/N_2 ratios, the green emission is related to oxygen vacancies. When the O_2/N_2 ratio is 80/20, the highest UV-to-green emission ratio is obtained in this

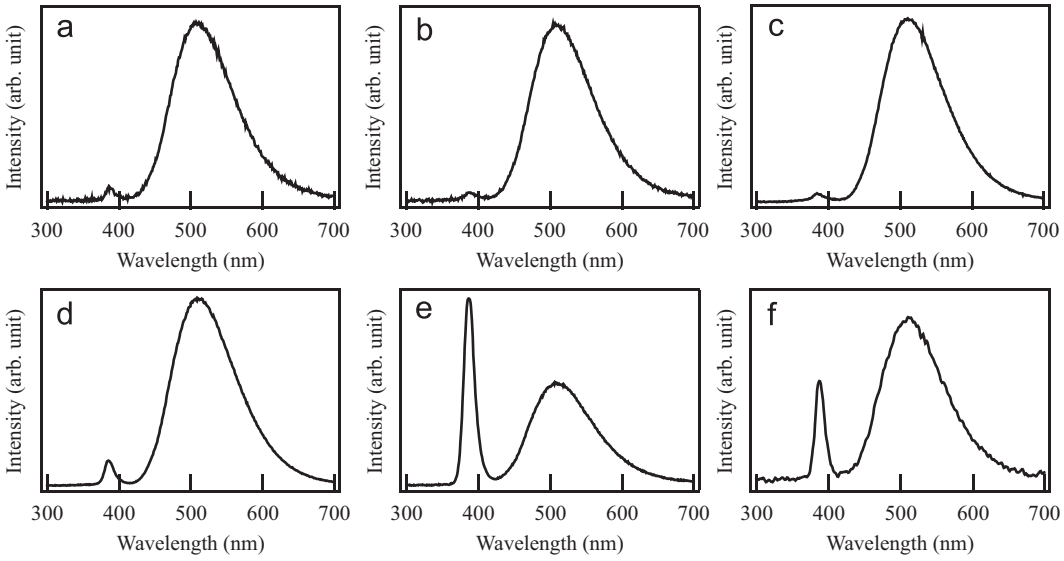

Fig. 5. Room temperature CL spectra of the products prepared at different O_2/N_2 ratios of (a) 20/80, (b) 40/60, (c) 50/50, (d) 60/40, (e) 80/20 and (f) 100/0.

experiment, which means that the ZnO has a low concentration of defects. On the other hand, the UV-to-green emission ratio decreases again when the O_2/N_2 ratio increases from 80/20 to 100/0. This can be explained by the increase in the concentration of antisite oxygen.

4. Conclusions

ZnO nanostructures were synthesized through thermal evaporation of Zn powder in crucibles with Zn powder when O_2/N_2 ratio was above 50/50. Under the conditions of O_2/N_2 ratios less than 80/20, the ZnO nanostructures had a needle-like morphology. When the O_2/N_2 ratio increased from 80/20 to 100/0, the morphology of the ZnO nanostructures evolved from needles to rods. Particularly, it is noted that the ZnO nanostructures grew in the longitudinal direction when the O_2/N_2 ratio increased from 50/50 to 80/20, whereas the nanostructures grew in the transverse direction when the O_2/N_2 ratio increased from 80/20 to 100/0. CL properties of the ZnO nanostructures depended on the O_2/N_2 ratio. When the O_2/N_2 ratio was 80/20, the UV-to-green emission ratio was the highest, indicating the ZnO had a high crystalline quality.

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