Morphology control of ZnO crystals through design of the source material

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ZnO crystals with controllable morphology were synthesized by employing the different source materials. A simple thermal evaporation technique was employed to synthesize ZnO crystals. Morphologies such as tetrapods and inverted cone-shaped rods were realized experimentally through thermal evaporation of Zn and ZnS powder, respectively. The morphology of ZnO crystals could also be controlled by designing the source material. Peculiar ZnO tetrapods with inverted cone-shaped legs were obtained via thermal evaporation of a mixture of Zn and ZnS powder mixed with a certain ratio. The intensity of green emission in the photoluminescence spectrum increased with the increase in the ratio of ZnS to Zn in the source material.

Key-words : Zinc oxide, Nanomaterials, Thermal evaporation, Morphology control, Desired source material

1. Introduction

Currently, the study on semiconductor nanomaterials has gained significant attention due to their unique electrical or optical properties distinct from those of bulk materials. In particular, metal-oxide semiconductor nanomaterials have unique properties such as wide bandgaps, high dielectric constants, and good electric and optical characteristics, which make them potential candidates of various applications in electronic and optoelectronic devices. Among the metal oxide nanomaterials, zinc oxide (ZnO) nanomaterial is one of the most interesting materials owing to its variety of morphologies. ZnO is an important material for applications in optoelectronic devices due to its wide bandgap (3.37 eV) and large exciton binding energy (60 meV). Its wide bandgap provides the possibility for use as ultraviolet (UV) emitting devices and its large exciton binding energy ensures highly efficient excition UV lasing under low excitation intensity even at RT. Recently, much of the work has been focused on preparation of various morphologies of ZnO nanomaterials. Although ZnO nanomaterials with diverse morphologies including wires, tubes, combs, tetrapods, belts has been synthesized, it is still a significant challenge to selectively synthesize ZnO nanomaterials with designed morphology. The properties of nanomaterials depend on the shape as well as the size of nanomaterials. Hence the control of morphology can usefully modulate the properties of nanomaterials. Thus, controlled growth of ZnO nanomaterials is of great significant.

In this paper, we report the controlled synthesis of ZnO crystals with desired morphology through appropriate design of the source material.

2. Experimental procedure

ZnO crystals were synthesized by thermal evaporation of various source materials in air atmosphere. Zn powder, ZnS powder, and mixtures of Zn and ZnS powder were used as the source materials. The mixtures were prepared by mixing Zn and ZnS powder with different ratios of Zn/ZnS = 1.0/0.5, 0.5/0.5 and 0.5/1.0. The purity and the average diameter of the Zn and ZnS powder were 99.9% and 4 μm, respectively. The source materials were put in different alumina crucibles. Then the crucibles were taken out from the furnace and cooled down to room temperature. The white products were collected for the further analysis and characterization.

The morphology of the as-synthesized products was observed by scanning electron microscope (SEM) operated at a voltage of 15 kV. The crystal structure was characterized by X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.54 Å) operated at a power of 40 kV × 30 mA. The components and composition of the products were studied by energy dispersive X-ray (EDX) spectroscopy. The photoluminescence (PL) properties were measured by using He–Cd laser as an exciting light source.

3. Results and discussion

The XRD measurement was carried out to investigate the crystallographic structure of the products. Figure 1 shows the XRD patterns of the products synthesized with different source materials of (a) Zn powder, (b) ZnS powder and (c) Zn-ZnS mixture with a ratio of Zn/ZnS = 0.5:0.5, respectively. The products prepared with different source materials show similar XRD patterns, in which the diffraction peaks appear at the same diffraction angle. The XRD diffraction peaks are in good agreement with the standard peaks of hexagonal wurtzite structure of ZnO (JCPDS 36-1451). The XRD data reveal that all the products are ZnO with wurtzite crystallographic structure.

The components of the products were detected by EDX. Figure 2 shows the EDX spectra of the as-synthesized products with different source materials of (a) Zn powder, (b) ZnS powder, and (c) Zn-ZnS mixture with a ratio of Zn/ZnS = 0.5:0.5, respectively. The EDX spectra of all the products are
also very similar. The EDX spectra reveal that the products are composed of zinc and oxygen elements without any Zn and S impurities indicating the high purity of ZnO.

The morphologies of the products synthesized in the crucibles were observed with the SEM. Figure 3 shows the SEM images of the as-synthesized products. Figures 3(a)–3(e) show the images of the products synthesized with different source materials of Zn powder, ZnS powder and Zn–ZnS mixtures with different ratios of Zn to ZnS: 1.0/0.5, 0.5/0.5, 0.5/1.0, respectively. From these images, it could be found that the morphology of products is considerably dependent on the source material. The products show three types of morphologies depending on the source materials. When Zn is used as the source material, the ZnO crystals show the typical tetrapod-like morphology with four legs extending from the center. The diameter of the legs gradually decreases from the center to top, which forms a cone shape. The legs are several micrometers in length. When ZnS was used as the source material, the ZnO crystals formed the rod-like morphology. However, the rods display inverted-cone-like morphology of which the diameter gradually increases from the center to outside.

Employing a mixture of Zn and ZnS powder, we realized the controlled growth of ZnO crystals with tetrapod and inverted cone-shaped rod morphologies. After oxidation of the mixture of Zn and ZnS powder with a ratio of Zn:ZnS = 0.5:0.5 in air, ZnO crystals with an interesting morphology of the tetrapod-like crystals with inverted cone-shaped legs could be obtained as shown in Fig. 3(d). When the mixture of Zn and ZnS powder with a ratio of Zn:ZnS = 0.5:1.0 is used as a source material, ZnO crystals reveals multipod and rod morphologies. The legs of the multipods also exhibit the inverted-cone shape as shown in Fig. 3(e). The inverted cone shaped legs with well-defined hexagonal facets are clearly observable in the image.

Generally, it is well known that crystal plane with fast growth rate tends to disappear, while slow growing plane tends to leave. According to the well-known growth habit of ZnO crystal, the growth rate in the [0001] direction is the fastest. Therefore legs of tetrapod are grown along the [0001] direction. However, as the fast growing plane tends to disappear, the diameter of the leg gradually decreases from the center to tip and so leg with cone-like morphology is formed. But the morphology of tetrapod was controlled by designing the source material. When a mixture of Zn and ZnS powder was used, Zn vapor was first produced from the evaporation of metallic Zn powder while the furnace temperature was rising to 1200°C. This is because the melting point of Zn (419°C) is lower than that of ZnS (1185°C). Hence we suppose that the morphology of ZnO crystals must have been affected by the concentration of Zn vapor produced from metallic

Fig. 1. XRD patterns of the products prepared with different source materials of (a) Zn powder, (b) ZnS powder and (c) Zn–ZnS mixture with a ratio of Zn/ZnS:0.5/0.5.

Fig. 2. EDX spectra of the products prepared with different source materials of (a) Zn powder, (b) ZnS powder and (c) Zn–ZnS mixture with a ratio of Zn/ZnS:0.5/0.5.

Fig. 3. SEM images of the ZnO products prepared with different source materials of (a) Zn powder, (b) ZnS powder, and Zn–ZnS mixtures with different ratios of Zn/ZnS: (c) 1.0/0.5, (d) 0.5/0.5 and (e) 0.5/1.0.
Zn powder, which resulted in the formation of tetrapod-like ZnO crystals. After reaching 1200°C, the concentration of Zn vapor would be abruptly increased because Zn vapor is also produced from the evaporation of ZnS powder. Usually, at high vapor concentration, three dimensional growth tends to occur on the growing surface of crystals. Therefore the top area of the tetrapod legs grows not only in the longitudinal direction but also in the transverse direction, inducing the enlargement of the top area. This results in the formation of tetrapod and multipod crystals with inverted cone-shaped legs.

Figure 4 shows the photoluminescence spectra of the ZnO crystals at room temperature. Figures 4(a)–4(c) represent the PL spectrum of the ZnO structures prepared by thermal evaporation of Zn–ZnS mixtures with different weight ratios of Zn to ZnS: 1.0/0.5, 0.5/0.5 and 0.5/1.0, respectively. In the spectrum of all the samples, two main emission peaks are observed: an UV emission peak at 380 nm and a green emission peak at 510 nm. The relative intensity of UV emission peak decreases with the increase in the ratio of ZnS to Zn. Further increase in the ratio of ZnS to Zn results in the observation of only a strong intensive green emission. The UV emission is known to be attributed to a free excitonic transition and the green emission is ascribed to the intrinsic defects such as oxygen vacancies, oxygen interstitials, zinc vacancies, and zinc interstitials. The PL spectra show that the defect density in ZnO crystals increases as increasing the ratio of ZnS to Zn in the source material.

4. Conclusions

ZnO crystals with controlled morphology were synthesized through selective design of source material. When Zn powder was used as source material, typical tetrapods whose leg diameter decreases with the distance from tetrapod core were obtained. Rods with inverted cone shape were obtained when ZnS powder was employed as a precursor. Employing the Zn and ZnS powder as mixed source, tetrapods or multipods with inverted cone-shaped legs were synthesized. The diameter of the legs gradually increased with distance from core. These results establish that ZnO crystals with controlled morphology could be fabricated by adopting the right source materials.

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