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Synthesis of Bottle-Shaped ZnO Particles through the Oxidation of a Mixture of Al-Zn-Au

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ZnO particles with a bottle-like morphology were synthesized by direct melt oxidation of a source material mixed with Al, Zn, and Au in air at atmospheric pressure. The particles were synthesized when the source material contained Au. Without Au, only ZnO particles with a tetrapod shape were identified. The bottle-shaped particles consisted of a well-defined hexagonal faceted micro-rod stem and a bottleneck. It is proposed that the bottle-shaped morphology forms through a vapor-solid growth mechanism as no catalyst was used during the synthesis process. [doi:10.2320/matertrans.M2009137]

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1. Introduction

ZnO is among the most promising of optical materials. It has a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, resulting in an efficient excitonic emission of UV region even at room temperature. Hence, a significant amount of research has focused on ZnO, especially ZnO-based nano-/micro-particles. Nano-/micro-particles have attracted considerable attention due to the unique physical and chemical properties that are ascribed to the restricted size of these particles. Recently, ZnO nano-/micro-particles in various forms including needles,[1] tetrapod,[2] wires,[3] tubes,[4] belts,[5] and combs[6] have been synthesized by a wide range of techniques.

The authors reported the synthesis of ZnO nanowires by oxidation of an Al-Zn mixture in air at atmospheric pressure.[7] Zn vapor was oxidized upon the microchannels in Al_2O_3/Al matrix formed by the oxidation of molten Al, resulting in the ZnO nanowires. The microchannels in the Al_2O_3 matrix played an important role in the formation of the ZnO nanowires. The fabrication method is relatively simple because ZnO particles are synthesized over a large area in air.

The present study reports the fabrication of novel bottle-shaped ZnO particles by oxidation from an Al-Zn-Au mixture in air at atmospheric pressure.

2. Experimental Procedure

Al, Zn, and Au were mixed at a weight ratio of 50 : 5 : 1 as a source material. The source material was placed in an alumina crucible and then inserted into an oxidation furnace. The furnace was heated to 1000°C at a heating rate of 10°C/min and kept at 1000°C for 2 h in air at atmospheric pressure. After the oxidation process, the furnace allowed to cool naturally to room temperature.

The crystallographic structure of the product was examined by X-ray diffractometry using Cu K_α radiation. The morphology was characterized using a scanning electron microscope (SEM), and the chemical characterization was done via energy dispersive X-ray (EDX) spectroscopy.

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3. Results and Discussion

After the oxidation process, a white color powder was observed on the surface of the oxidized source material. The white powder was collected from the surface of the source materials for its characterization and measurement.

Figure 1(a) shows the XRD pattern of this powder, which indicates that it is ZnO with a hexagonal wurtzite structure. The lattice constants of the a- and c-axis were estimated to be 0.325 nm and 0.520 nm, respectively, from the pattern. These values are very consistent with the standard values of bulk ZnO. No peaks of metallic Zn were detected. As shown in Fig. 1(b), the EDX spectrum reveals that the powder is ZnO material with an atomic ratio of 1 : 1. The quantitative result was obtained from the relative x-ray counts at the characteristic energy levels for Zn and O without standard. The quantification was performed with automatic background subtraction, matrix correction, and normalization to 100% for all of the elements.

The morphology of the ZnO was examined using SEM. Figures 2(a), (b) show high magnification and low magnification images, respectively. The bottle-shaped particles are

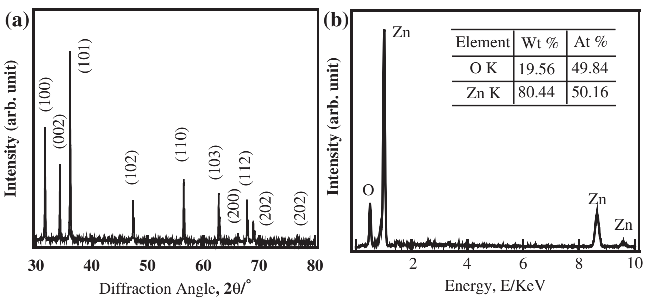

Fig. 1 (a) X-ray diffraction pattern and (b) Energy dispersive X-ray spectrum of ZnO particles synthesized by thermal oxidation of Al-Zn-Au mixture at 1000°C for 2 h in air.

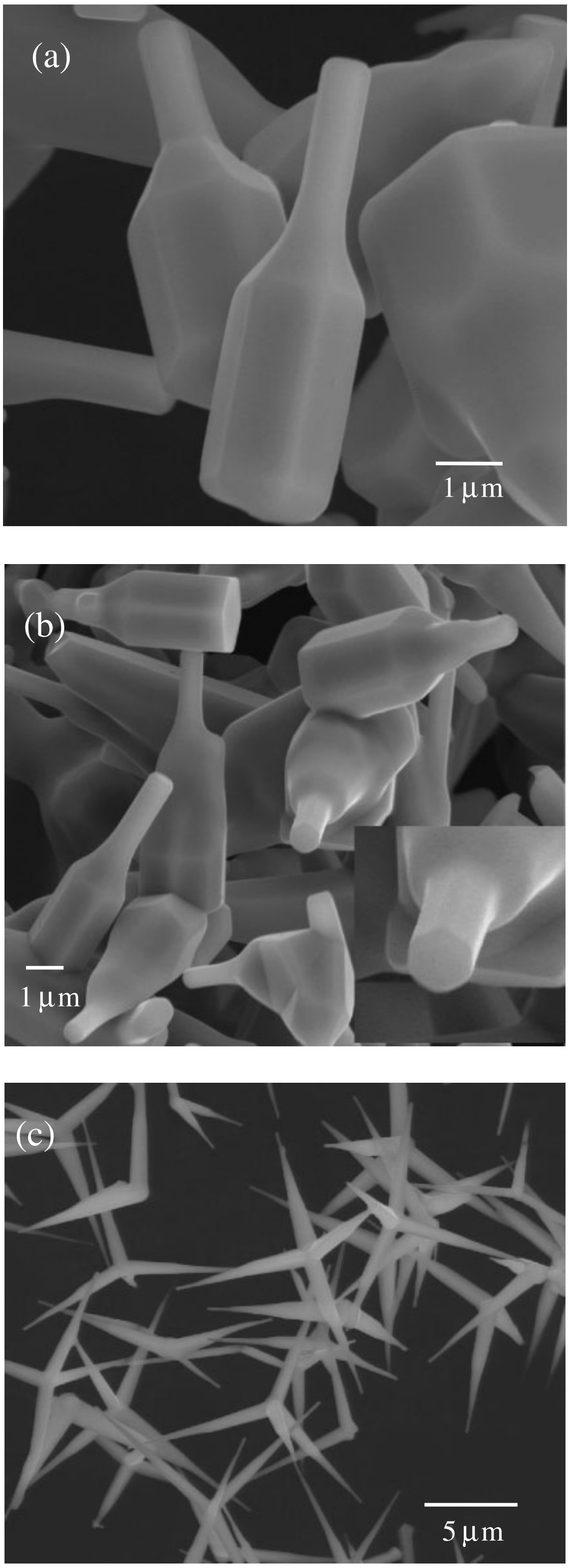

Fig. 2 SEM images of ZnO particles synthesized from source material with mixing Au ((a) high magnification image and (b) low magnification image), and (c) from source material without mixing Au.

clearly observable in these images. The particle consists of two parts; a hexagonal micro-rod base stem and a hexagonal bottleneck. The bottle-shaped particle has well defined hexagonal facets, which demonstrates that the growth occurred along the [0001] direction. The bottleneck grew in

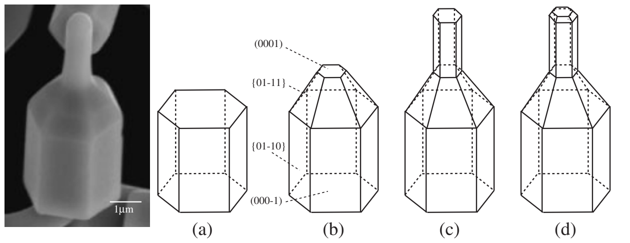

Fig. 3 SEM image and schematic growth model of bottle-shaped ZnO particles.

the same [0001] orientation as the micro-rod base stem with six-facet side surfaces. The hexagonal end plane of the bottleneck can be observed clearly in the inset of the SEM image in Fig. 2(b). Other catalysts were not observed at the tips of the ZnO particles, which implies that the growth of the ZnO particles proceeded via a self-catalyzation process or through a vapor-solid (VS) mechanism.

To investigate the effect of Au on the morphology of the ZnO particles, the morphology of ZnO particles synthesized by the oxidation of an Al-Zn mixture without Au is presented in Fig. 2(c). In this case, the ZnO morphology has a tetrapod shape. This suggests that Au plays an important role in the formation of the bottle-like ZnO particles. It was recently reported that different vapor pressures(or concentrations) of Zn during the growth process contributed to the formation of different morphologies of ZnO particles.[8,9] In the present experiment, when the source material was mixed with Au, Zn vapor atoms were able to diffuse into the Au melt at an oxidation temperature of 1000°C, as Au has solubility relative to Zn. This led to a decrease in the concentration of the Zn vapor. This can explain the formation of the ZnO particles with a novel bottle-like shape as opposed to the tetrapod shape.

A schematic of the growth model of the bottle-shaped ZnO particle is given in Fig. 3. During the first stage of growth, the hexagonal base rod is formed and grows along the [0001] direction, maintaining a uniform size (Fig. 3(a)). As the growth proceeds, the morphology of the rod tip takes on a hexagonal pyramid-like shape (Fig. 3(b)). This can be understood by the growth habit of ZnO, which arises from the different growth rates of the crystal planes. The relationship between the velocities of the crystal growth to the different directions is known to be: [0001] > [01-1-1] > [01-10] > [01-11] > [000-1].[10] From the growth habit of ZnO crystal, the crystal face (0001) with its rapid growth rate is likely to disappear easily. In contrast, crystal faces {01-11} and {01-10}, with their slow growth rates, will appear easily and will not disappear. Consequently, as shown in Fig. 3(b), the area of the (0001) plane disappears gradually, whereas the {01-10} planes remain and the {01-11} planes begin to appear. The elongated pyramid-like morphology is identical to that described as the idealized growth habit of a ZnO single crystal.[10] For the formation of the bottleneck on the hexagonal pyramid-like rod, the pyramid growth of the rod should stop, and the growth of a finer rod along the [0001] direction must then occur on the top (0001) surface of the pyramid rod. Similar growth behavior was observed in the growth of ZnO nanowires,[11] the teeth of the ZnO nano-combs[12] and in the legs of the tetrapod ZnO nanocrystals.[13] This growth behavior takes place due to the change of the concentration of Zn vapor during the growth. This finer rod-pyramid rod structure was proved to be a single crystal from the TEM observations.[13] Tam *et al.* suggested that the base rod is formed in the early stage of the growth when the concentration of the Zn vapor is very high. As the growth proceeds, the decrease of the Zn supply favors the growth of the finer rod on the base rod.[11]

In the present experiment, the bottleneck may be formed by the cooling process. Wang *et al.* showed that when the concentration of the source vapor decreased due to the lowering of the furnace temperature, the lower concentration as a result can induce a new nucleus on a large ZnO plate, leading to the vertical growth of one dimensional nano-structures.[9] During the cooling stage, the growth of the hexagonal micro-rods formed during the first growth process stops due to the low concentration (or low supersaturation) of the source vapor, and new nuclei are formed on account of the lower mobility of the atoms at lower temperatures on a large hexagonal micro-rod. This causes the growth of a new finer rod on top of the micro-rod to form the bottleneck (Fig. 3(c)).

4. Conclusion

Bottle-shaped ZnO particles were synthesized via a simple method of the oxidation of an Al-Zn-Au mixture in air. The particles were formed in the presence of Au, indicating that Au plays a key role to the formation of the bottle-like morphology. The formation of bottleneck is ascribed to the different concentrations of Zn vapor during the growth process. When the growth mechanism is clearly elucidated, it is expected that various morphologies of ZnO particles can be synthesized by this method.

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