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Morphology controlled synthesis of ZnO particles through the oxidation of Al–Zn mixture

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Abstract

ZnO particles with different morphologies were synthesized through a simple oxidation process of Al–Zn mixtures in air. The morphologies significantly depended on the Zn content in Al–Zn mixture and the oxidation time. Rod-based brushes, typical tetrapods, and novel tetrapods with triangular wedges were synthesized with the increase of Zn content in Al–Zn mixture. The morphology was also changed from rod to tetrapod shape with oxidation time. The results indicate that the concentration of Zn and the oxidation time might be responsible for the different morphologies of ZnO particles. XRD spectra showed that the ZnO particles were a hexagonal wurtzite structure.

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

1. Introduction

Zinc oxide (ZnO) becomes one of the most attractive materials for applications in optoelectronic devices due to its wide bandgap and large exciton binding energy. Its bandgap of 3.37 eV provides the possibility for use as ultraviolet (UV) emitting devices as well as transparent conducting electrodes in display devices and solar cells. Its large exciton binding energy of 60 meV leads to stability of excitons at room temperature (RT), resulting in highly efficient excitonic UV lasing under low excitation intensity even at RT.

Because of the attractive properties of ZnO, extensive studies have been recently carried out on the synthesis of ZnO nanostructures with various different morphologies. Furthermore the observation of lasing and high efficient electron emission from the ZnO nanostructures has stimulated the studies on the synthesis of ZnO nanostructures with different morphologies. So far, various kind of interesting morphologies including nanowires, nanotubes, nanocombs, and nanobelts have been synthesized by a variety of methods such as thermal evaporation [1], sputter-deposition [2], hydrothermal method [3], chemical vapor deposition [4], catalytic growth [5], and electrochemical deposition [6].

On the other hand, since the properties of nanostructures depend significantly on their morphology and size, the synthetic methods capable of controlling easily the morphology and size have received particular attention.

In this paper, we report a simple method to synthesize ZnO nano-/micro-structures with high yield by oxidation of Al–Zn mixtures in air and morphology control by adjusting Zn content in Al–Zn mixtures.

2. Experimental procedure

The source materials for synthesizing ZnO nanostructures were prepared by mixing Al block and Zn powder. A commercial Al alloy containing a small amount of Mg was used as the Al source material. Zn powder was mixed in the range of 1–7 wt% to examine the effect of Zn on the morphology of ZnO nanostructures. The oxidation time changed in the range of 1–3 h for Al–3 wt% Zn mixture in order to investigate the influence of oxidation time on the morphology.

The Al metal block and Zn powder were put in an alumina crucible and inserted into a furnace. The Al and Zn were melted and stirred using an alumina rod at 700 °C. After the furnace

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was cooled down to room temperature (RT), the furnace was again heated to 1100 °C with a heating rate of 10 °C/min and the mixture in the alumina crucible was oxidized at this temperature in air. The furnace was turned off and cooled down abruptly after the oxidation process. White colored product was found on the surface of the oxidized source materials. The white product was easily collected from the surface of the oxidized source materials using tweezers for the characterization.

The morphology of the as-synthesized product was studied by scanning electron microscope (SEM) equipped with 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.

3. Results and discussion

Fig. 1 shows the photographs of the white products synthesized in the crucibles through the oxidation of the Al–Zn mixtures with different Zn contents of 1, 3, 5, and 7 wt%. The white product was not found on the surface of the Al–Zn mixture with 1 wt% Zn content.

The crystallographic structure of the products was characterized by XRD. Fig. 2 shows the XRD patterns of the products synthesized by the oxidation for 2 h from (a) Al–3 wt% Zn, (b) Al–5 wt% Zn and (c) Al–7 wt% Zn mixtures, respectively. Similar XRD patterns are observed for the products prepared with different Zn contents. The XRD diffraction peaks can be indexed to the hexagonal wurtzite structure of ZnO according to the diffraction standard card (JCPDS 36-1451). Any diffraction peaks from Zn and other impurities were not detected, which indicates the product is ZnO with high purity. In the initial stage of the oxidation process, Al was oxidized at the top surface of the melted source materials and then solid Al_2O_3 oxide layer was formed. As the oxidation proceeded, the volume difference between the oxide layer and the molten metal leaded to the development of stress in the oxide layer. This resulted in the formation of micro-channels within the oxide layer. Zn was evaporated upward the oxide layer through the micro-channels because of its high vapor pressure (boiling point: 907 °C). The evaporated Zn was oxidized on the surface of the Al_2O_3 layer and formed ZnO. Thus the ZnO product could be simply separated from the surface of the oxidized source materials.

The morphology of the products was examined by SEM. Fig. 3 shows the low and high magnification SEM images of the products synthesized from Al–Zn mixtures with different Zn contents: (a) and (b) 3 wt%, (c) and (d) 5 wt%, and (e) and (f) 7 wt%. Depending on the Zn contents, the remarkable change in morphology is observed. There are three morphologies along the Zn contents. When the Zn content is 3 wt%, the morphology is a rod-based brush shaped structure, which is composed of ZnO nanowires on micro-sized hexagonal ZnO stem. As the Zn content is increased up to 5 wt%, the ZnO particles represent the typical tetrapod morphology with four legs extending from the center. The legs have a length of several micrometers and a conical shape to grow smaller from center to edge. When the Zn content is further increased to 7 wt%, a novel tetrapod morphology with triangular wedges on the side surfaces of the tetrapod legs is observed. The SEM images reveal that in our experiment, Zn content in source material is an important parameter in modulating the morphology of ZnO particles.

It has been reported that the different vapor pressure (or supersaturation) of Zn is correlated to the formation of different morphologies of ZnO. In the present experiment, the vapor pressure of Zn would increase with the increase in Zn content. When the Zn content is 3 wt%, the vapor pressure of Zn is relatively low. The low vapor pressure means the formation of a small number of growth species. The small number of species induces the low density of ZnO nuclei. According to the rule of growth habit of ZnO crystal, the growth rate in the [0 0 0 1]

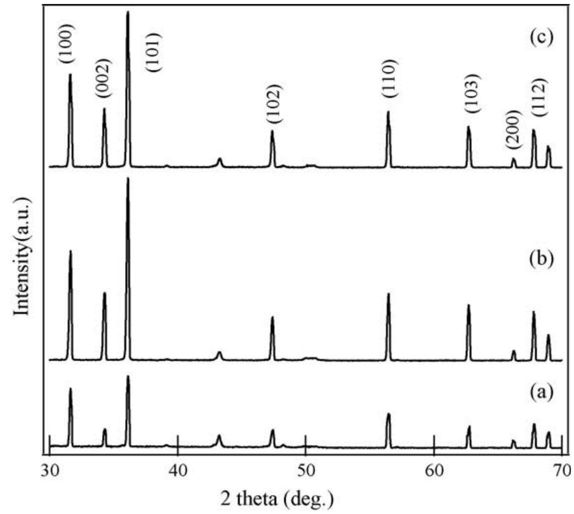

Fig. 2. X-ray diffraction patterns of the white products synthesized by thermal oxidation of Al–Zn mixtures with different Zn contents: (a) 3, (b) 5 and (c) 7 wt%.

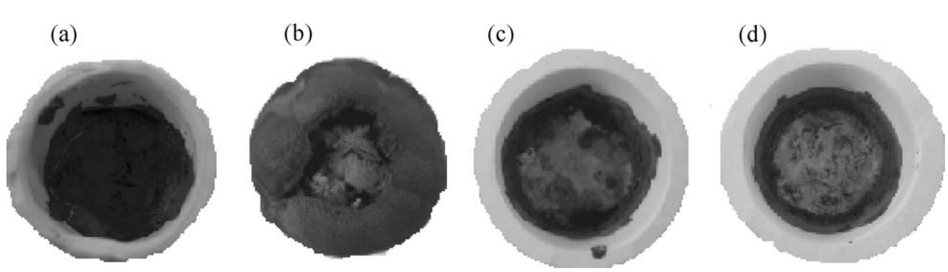

Fig. 1. Photographs of the white products synthesized in the crucibles through the oxidation of the Al–Zn mixtures with different Zn contents: (a) 1, (b) 3, (c) 5 and (d) 7 wt%.

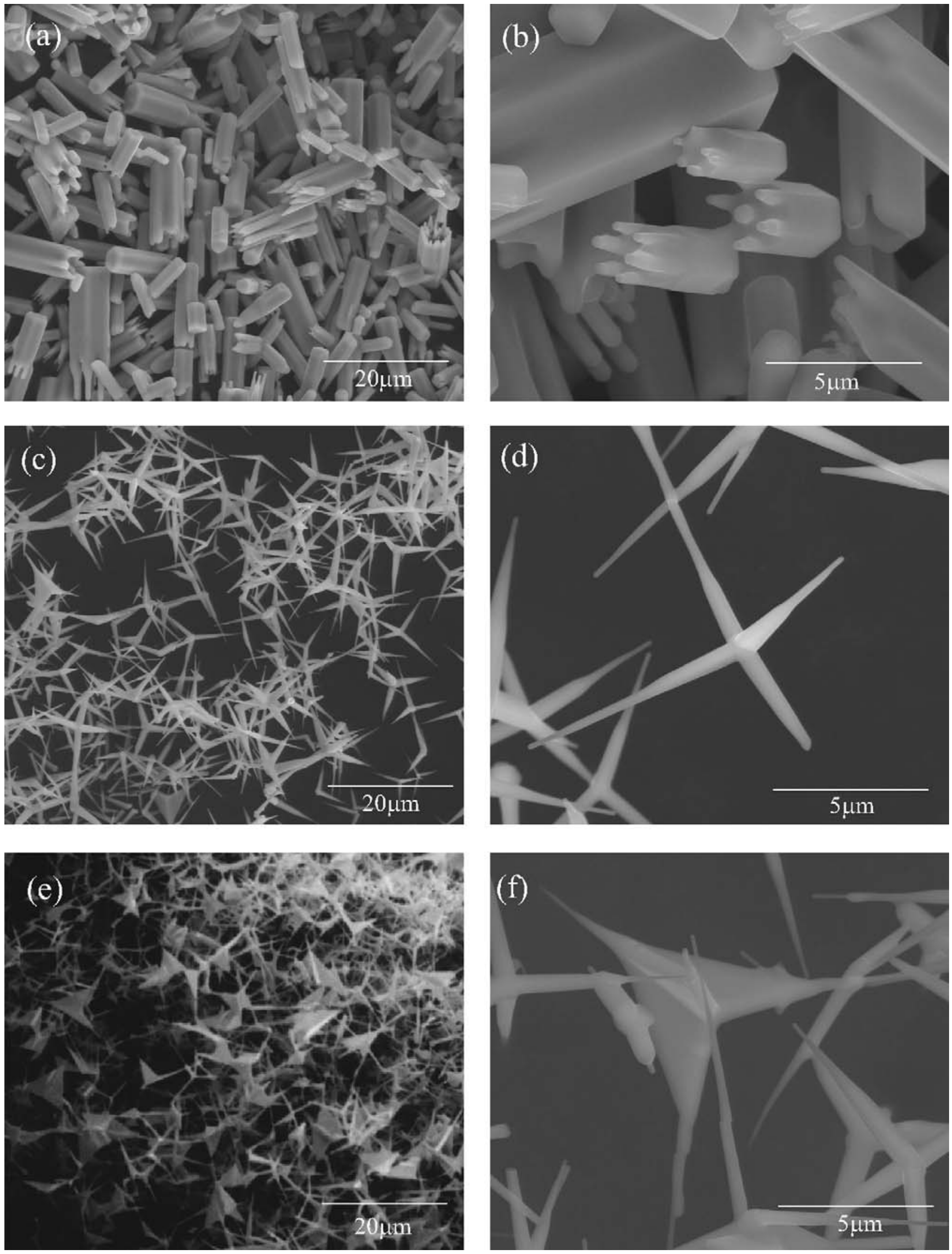

Fig. 3. Low and high magnification SEM images of ZnO particles synthesized from Al–Zn mixtures with different Zn contents: (a) and (b) 3, (c) and (d) 5, (e) and (f) 7 wt%.

direction is the fastest, resulting in rod-based structures. In the case of Zn content of 5 wt%, the vapor pressure of Zn is relatively high. The high vapor pressure or supersaturation favors the formation of a large number of nuclei. It was reported that the density of nuclei had an influence on the formation of different morphology of ZnO structures [7,8]. The formation of rod-based nanowires is attributed to low nucleation density, while high nucleation density leads to the formation of multipod or tetrapod structures [7]. Large amounts of ZnO nuclei would provide the aggregation of some nuclei. Then each nucleus in the aggregate grows along the c-axis with the fastest growth rate, which forms multipod structures [8]. Similar result was obtained in our present experiment.

When the Zn content increases to 7 wt%, the vapor pressure of Zn is very high. The tetrapods with three triangular wedges are found. Gong et al. reported that when nanorod grows to a larger size than a critical size, nucleation occurs on the side surfaces of the nanorods, resulting in the growth of the triangular nanosheets [9]. When the vapor pressure or supersaturation level is very high, new nucleation would be induced on the side surfaces of the nanorods [9]. By adjusting the Zn content in Al–Zn mixture, we could synthesize ZnO particles with three different morphologies.

Fig. 4 shows the low and high magnification SEM images of the ZnO particles synthesized from Al–3 wt% Zn mixture with different oxidation time: (a) and (b) 1 h, (c) and (d) 2 h, and (e)

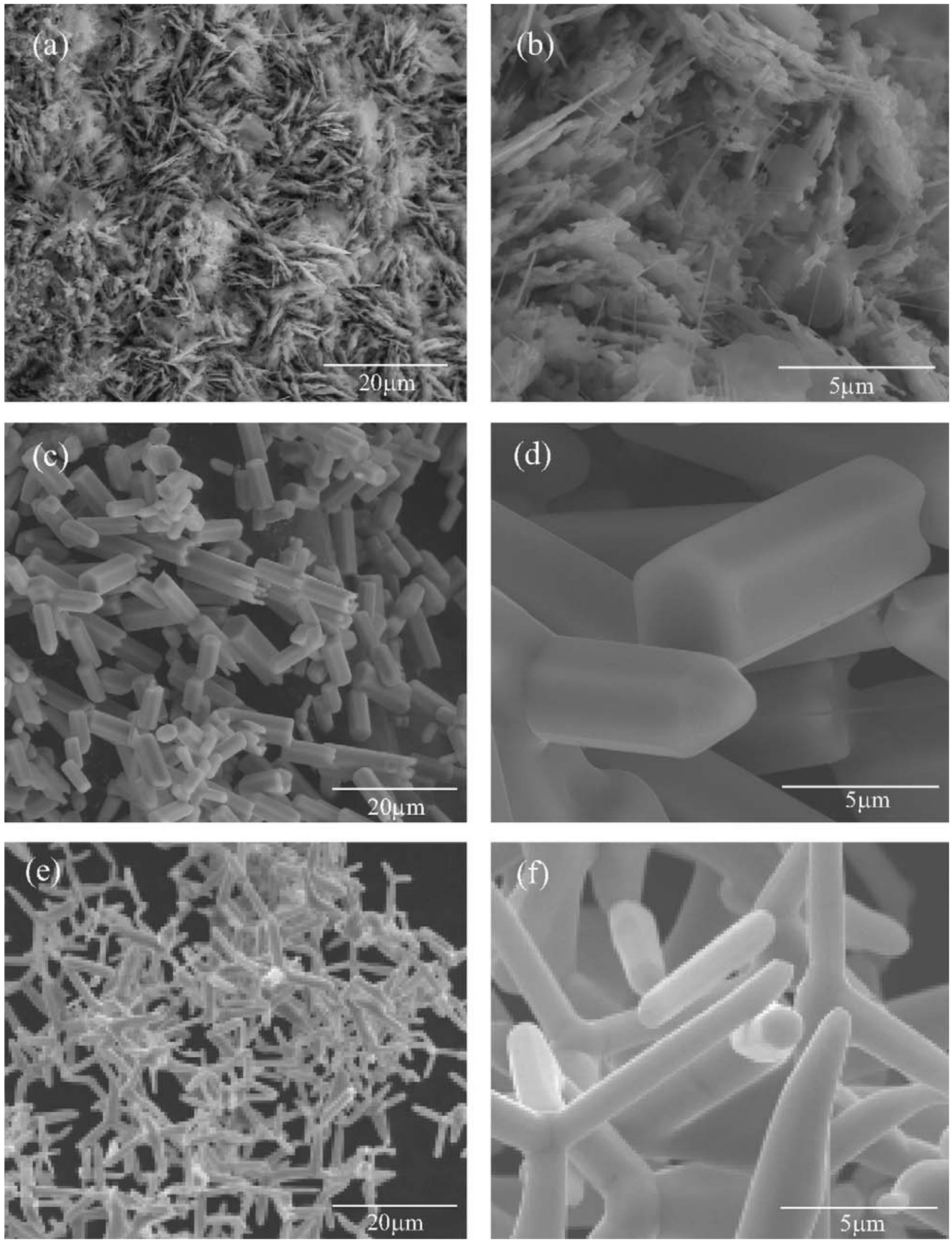

Fig. 4. Low and high magnification SEM images of ZnO particles synthesized from Al–3 wt% Zn mixtures with different oxidation times: (a) and (b) 1 h, (c) and (d) 2 h, and (e) and (f) 3 h.

and (f) 3 h. When the oxidation time is 1 h, the flake-like ZnO is found on the surface of the oxidized source material. After the oxidation for 2 h, rod-based brush shaped ZnO particles are formed. As the oxidation time increases to 3 h, tetrapod-shaped particles start to be found. This result indicates that the vapor pressure of Zn increases with oxidation time. Vapor–solid (VS) growth mechanism is suggested for the formation of the ZnO particles because no catalyst and impurity were used in this process.

4. Conclusions

In the synthesis of ZnO particles by oxidation of Al–Zn mixtures, ZnO rod-based brushs, tetrapods and novel tetrapods with triangular wedges were synthesized by adjusting the Zn content in Al–Zn mixtures. The vapor pressure or supersaturation of Zn during the growth would increase as the Zn content increases, which leads to the high density of nuclei. The rod-based structures were formed under the condition of low nucleation density. The high density of nuclei may induce the aggregation of some nuclei, which is responsible for the formation of tetrapods. Higher vapor pressure of Zn for the sample with 7 wt% Zn content would provide a second nucleation on the side surfaces of tetrapod legs, leading to the formation of novel tetrapods with three triangular wedges on the sides. The Zn content could be used to modulate the morphology of ZnO structures.

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