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Synthesis and cathodoluminescence of ZnO tetrapods prepared by a simple oxidation of Zn powder in air atmosphere

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Abstract

Tetrapod-shaped ZnO crystals were synthesized by an oxidation process of Zn powder at temperatures over 930 °C in air. The ZnO crystals were formed in an alumina crucible in which metallic Zn powder was put. X-ray diffraction patterns revealed that the tetrapods were ZnO with wurtzite structure. Any impurities including Zn were not detected, indicating that the ZnO crystals were of high quality. As the oxidation temperature increased, the size of tetrapods was getting larger and longer. However at 1100 °C, tetrapod morphology was disappeared and changed to irregular shape. Strong UV emission at 380 nm was observed in the CL spectra taken for the ZnO tetrapods. The increase in the intensity of green emission at 510 nm was also observed with increased oxidation temperature.

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

1. Introduction

ZnO has been attracted as a promising material for the application in electric and optoelectronic devices. It has a wide bandgap of 3.37 eV, which results in ultraviolet (UV) light emission. In addition, its large exciton binding energy leads to an effective excitonic emission of UV region even at room temperature. These properties make ZnO one of the most promising candidates for the potential applications in photonic devices such as short wavelength light emitting diodes, laser diodes and waveguides [1].

In recent, UV lasing action has been observed from ZnO nanocrystals. This has stimulated the studies on the synthesis of ZnO nanocrystals because of the possible application in nanoscale optoelectronic devices.

The synthesis of ZnO nanocrystals has been achieved through many techniques, including thermal evaporation [2], chemical vapor deposition [3], metalorganic chemical vapor deposition [4], pulsed laser deposition [5], hydrothermal method [6], and sol–gel method [1]. However vacuum and(or) catalyst are required in the most of the techniques, and thus results in a difficult process using complex apparatus. Accordingly, the synthetic methods capable of synthesizing easily ZnO nanocrystals have received particular attention. One of the simplest methods for the synthesis of ZnO nanocrystals is via the oxidation of Zn source materials in air without any catalysts. There are some reports on the synthesis of ZnO nano-/micro-crystals by oxidation of Zn source in air. But, in the synthetic approaches, Si wafers were used as a substrate to collect ZnO nano-/micro-crystals and the mixtures of Zn and carbon, or Cu were used as a source material [7–9].

In this paper, we report the effect of oxidation temperature and time on the morphology and cathodoluminescence (CL) property of the ZnO nanocrystals synthesized in a crucible by oxidation of pure Zn powder in air without using the substrate such as Si wafer, and the additive like carbon powder.

2. Experimental procedure

Metallic Zn powder with a purity of 99.9% and an average diameter of 4 μm was used as the source material. Zn source materials of 0.5 g were put into alumina crucibles. The alumina crucibles without any lid were inserted into an oxidation furnace and heated to the temperatures in the range of 870–1100 °C with a heating rate of 10 °C/min. Then the furnace was kept at the above temperatures for 1–60 min in air. After the

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oxidation process, the furnace was turned off and cooled down to room temperature. The white products were observed on the surface of the oxidized source materials in the crucibles. The products were collected from the sample surfaces using tweezers for characterization.

The crystal structure and the morphology of the products were investigated by X-ray diffractometry with Cu K_α radiation and scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) and CL spectroscopes, respectively. The components of the products were verified by the EDX. CL measurements were performed with an electron beam energy of 10 KeV at room temperature in the UV–visible spectral range.

3. Results and discussion

Fig. 1 shows the photographs of the white colored products synthesized by thermal oxidation of Zn powder in air with different oxidation temperatures ranging from 870 °C to 1100 °C. For the sample oxidized at 870 °C, white product was not found. White products were formed uniformly on the surface of the Zn powders oxidized at temperatures over 930 °C in air.

Fig. 2 shows the XRD patterns of the products. The white products were collected from the surface of the oxidized Zn source materials for XRD measurement. All the peaks of the XRD patterns can be indexed to hexagonal wurtzite structure of ZnO, which reveals that the white products were ZnO wurtzite crystals. The lattice parameters of the ZnO crystals were calculated from the XRD spectrum. The lattice constants of *c*- and *a*-axis were estimated to be 0.520 nm and 0.325 nm, respectively, which are in very good consistent with the reported standard values of bulk ZnO. Any peaks from impurities including Zn are not found in the XRD patterns, which is indicative of high quality ZnO crystals. As shown in Fig. 2(b), the EDX spectrum shows that the products are composed of Zn and O irrespective of oxidation temperature, which proves that the ZnO is of high purity.

Fig. 3 shows the SEM images of the ZnO crystals synthesized after oxidation for 60 min at different oxidation temperatures of 870, 930, 1000 and 1100 °C. ZnO crystals begin to be formed from the temperature of 930 °C. The morphology of the as-synthesized ZnO crystals is a typical tetrapod shape with four legs protruding from the center. For the ZnO tetrapods synthesized at 930 °C, the tetrapods have an

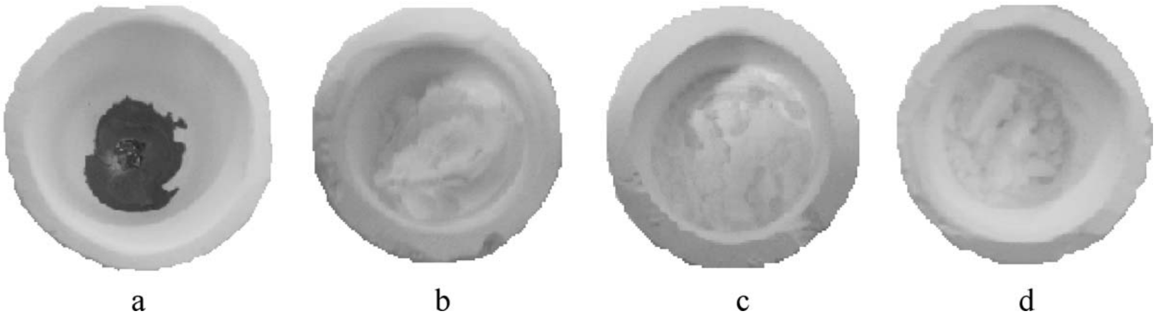

Fig. 1. Photographs of the white colored products synthesized by thermal oxidation of Zn powder in air with different oxidation temperatures; (a) 870 °C, (b) 930 °C, (c) 1000 °C and (d) 1100 °C.

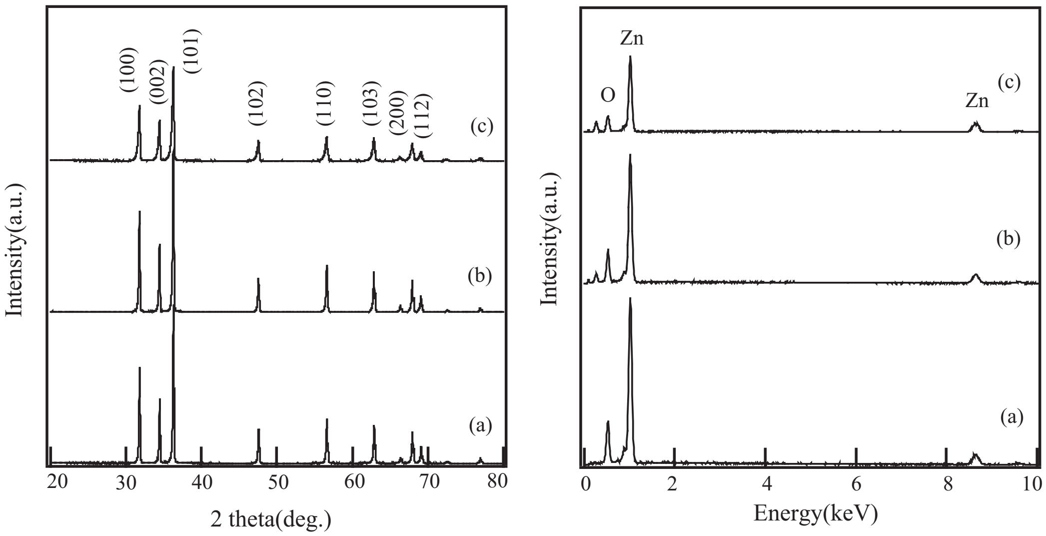

Fig. 2. X-ray diffraction patterns and EDX spectrum of the white products synthesized by thermal oxidation of Zn powder in air with different oxidation temperatures; (a) 930 °C, (b) 1000 °C and (c) 1100 °C.

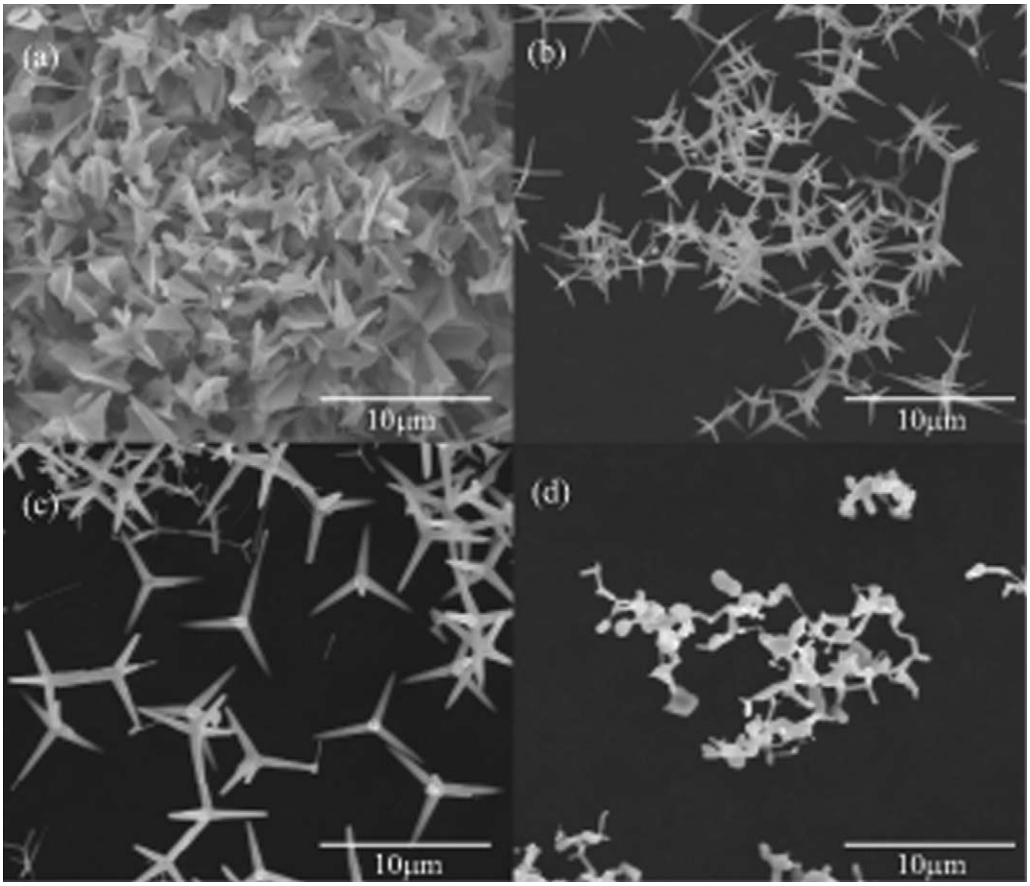

Fig. 3. SEM images of the ZnO crystals synthesized after oxidation for 60 min in air at different oxidation temperatures; (a) 870 °C, (b) 930 °C, (c) 1000 °C and (d) 1100 °C.

average leg width of 200 nm and leg length of 1 μm. When the oxidation temperature increases, the tetrapods grow longer and larger. The average size of the tetrapods fabricated at 1000 °C are about 350 nm in width and 2.5 μm in length, respectively. However, when the oxidation temperature is 1100 °C, the tetrapod shape is not found and changes to irregular shape. ZnO tetrapods began to be formed at a temperature around the boiling point of Zn (907 °C), at which metallic Zn would be easily evaporated. The Zn vapor would react with oxygen in the furnace chamber, resulting in the formation of tetrapod shaped ZnO crystals. At the oxidation temperature of 1100 °C, the oxidation rate of Zn to ZnO is so fast that the growth species of Zn and O atoms cannot diffuse to stable growth sites on the surface of ZnO nuclei. Accordingly, the ZnO nuclei may grow to crystals with irregular shape. From the experimental results, it can be concluded that proper oxidation rate is required for the formation of tetrapods.

Fig. 4 shows the SEM images of the ZnO crystals synthesized at 930 °C with different oxidation time of 0, 1, 5, 10, 30 and 60 min. Fig. 4(a) shows the morphology of Zn source powder. The Zn powder has ball-shape with an average diameter of 4 μm. ZnO tetrapods were easily formed even by oxidation for 10 min. With increasing oxidation time, the size of the tetrapods increases gradually. This suggests that the size of tetrapods can be controlled by adjusting oxidation time of metallic Zn. On the other hand, it is suggested that the tetrapods grew via vapor-solid growth mechanism because any catalysts were not used.

Fig. 5 shows the room temperature CL spectra from the ZnO crystals synthesized by oxidation of Zn powder for 60 min in air at different temperatures of (a) 930 °C, (b) 1000 °C and (c) 1100 °C. All spectra show a high intensity narrow UV emission peak centered at 380 nm and a low intensity broad green emission peak at 510 nm. The UV emission corresponds to the near bandgap transition, the recombination of free excitons [10]. The green emission is attributed to the recombination of a photogenerated hole with an electron occupying the oxygen vacancies in ZnO [11]. Thus, high intensity of UV emission indicates high crystalline quality of ZnO crystals. Strong UV emissions are observed for the all samples, suggesting that the ZnO tetrapods are of high quality. The inset in Fig. 5 shows the visible luminescence spectra as a function of the oxidation temperature. The intensity of green emission increases with increased oxidation temperature, which indicates that oxygen vacancies can be easily produced with oxidation temperature. This can be explained that when the oxidation temperature is too high, the oxidation rate of Zn to ZnO is too fast, which leads to the thermodynamically unstable oxidation reaction of Zn with oxygen. The unstable oxidation reaction would cause the increase in the concentration of oxygen vacancy in ZnO crystal. In order to remove the visible emission which is detrimental for application, the density of oxygen vacancy in ZnO crystal must

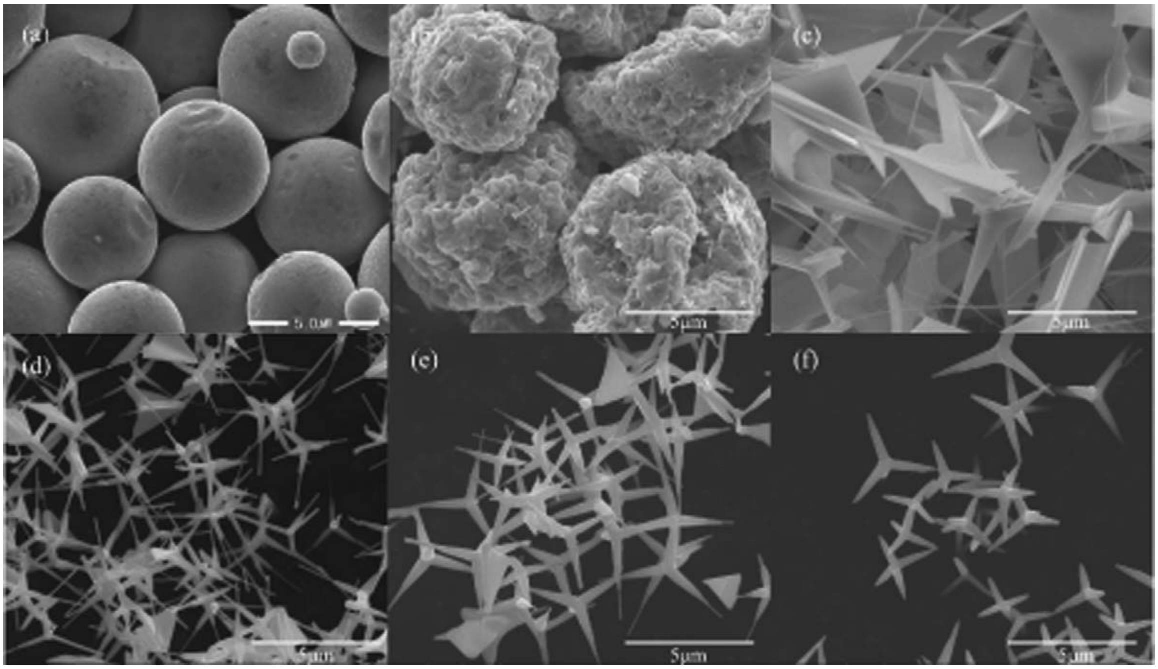

Fig. 4. SEM images of the ZnO crystals synthesized at 930 °C with different oxidation time; (a) 0, (b) 1, (c) 5, (d) 10, (e) 30 and (f) 60 min.

be reduced. Ha et al. reported that when ZnO nanowires were annealed in oxygen atmosphere, oxygen vacancies were reduced in the ZnO nanowires, leading to the decrease in the intensity of visible emission peak [12]. Wang and Zhang demonstrated that oxygen vacancies in ZnO nanowires were removed after the ZnO nanowires being exposed to air, resulting in the disappearance of visible emission [13]. They suggested that when ZnO nanowires were annealed under oxygen atmosphere or exposed to air, oxygen ions diffused into the oxygen vacancies in the ZnO nanowires, which leaded to the reduction of oxygen vacancies. Thus annealing of ZnO nanowires in oxygen ambience is an effective process for the improvement of the crystalline quality of ZnO nanowires.

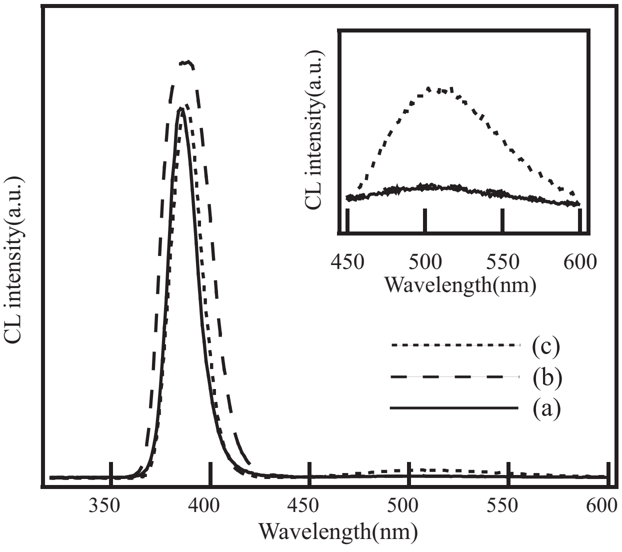

Fig. 5. CL spectra of the ZnO crystals synthesized after oxidation for 60 min in air at different oxidation temperatures; (a) 930 °C, (b) 1000 °C and (c) 1100 °C.

4. Conclusions

ZnO tetrapods were formed by a simple oxidation of metallic Zn powder at temperatures over 930 °C in air. The higher the oxidation temperature was, the larger the size of the tetrapods was. At the oxidation temperature of 1100 °C, ZnO crystals grew into irregular shape, which is assumed that the oxidation rate is faster than the diffusion rate of Zn vapor on the surface of ZnO nuclei. The size of the tetrapods increased with a prolonged oxidation time. CL spectra revealed a sharp strong UV emission at 380 nm for the ZnO tetrapods regardless of oxidation temperature. Meanwhile, the intensity of green emission at 510 nm increased with oxidation temperature due to the increase of oxygen vacancy in ZnO crystals.

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