ZnO micro/nanocrystals synthesized via a thermal evaporation of Al–Zn mixtures

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ZnO micro/nanocrystals with different morphologies were synthesized through thermal evaporation of Al–Zn mixtures under air atmosphere. The Al–Zn mixtures were put into alumina crucibles and then inserted into an electric furnace. The effect of synthesis temperature and time on the morphology of ZnO crystals was investigated. At temperatures below 900°C, no ZnO crystals were synthesized. When the temperature was 1000°C, ZnO crystals with a hexagonal pillar shape were found. With the increase in the temperature from 1000 to 1100°C, the morphology of the crystals changed to wire and granular shapes. As the synthesis time increased at 1000°C, tetrapod-shaped ZnO crystals started to be formed. As a result, the synthesis temperature and time were key factors in the morphological control of ZnO crystals. Because no catalyst particles were observed at the tips of the micro/nanocrystals, it is suggested that the ZnO crystals were grown via a vapor–solid mechanism.

Key-words : ZnO crystals, Thermal evaporation, Al–Zn mixture, Synthesis temperature, Synthesis time

1. Introduction

ZnO is an attractive material for the application in electric and optoelectronic devices. Its wide bandgap of 3.37 eV results in ultraviolet (UV) light emission and its large exciton binding energy leads to an effective excitonic emission of UV region even at room temperature. Because of these properties, ZnO has been paid attention as the most promising candidate for the potential applications in photonic devices such as short wavelength light emitting diodes, laser diodes and waveguides.\(^1\)

With the advent of nanotechnology, the prospects for using nanomaterials in industrial applications have developed rapidly. Over the past few decades, much effort has been focused on the synthesis of various nanomaterials. In particular, since UV laser was observed from ZnO nanocrystals, the synthesis of ZnO nanocrystals with different morphologies has been the focus of intense research due to their possible applications in nanoscale optoelectronic devices.

Many methods have been used in the synthesis of ZnO nanocrystals with a variety of morphologies. The methods include thermal evaporation,\(^2\) chemical vapor deposition,\(^3\) sputtering,\(^4\) pulsed laser deposition,\(^5\) hydrothermal method,\(^6\) and sol–gel method.\(^7\) Among them, thermal evaporation is one of the simplest methods for the synthesis of ZnO nanocrystals. So far, ZnO nanocrystals with various morphologies have been synthesized via thermal evaporation of different source materials. It has been reported that the morphology of ZnO nanocrystals is highly dependent on source material in thermal evaporation method. In recent years, micro/nanocrystals of ZnO were simply synthesized through a thermal evaporation of Al–Zn mixed source even in air atmosphere. According to the Kim group,\(^8\) in case that Al–Zn mixture was used as a source material, Al was firstly oxidized at the top of the surface of the melted source material because Al has a lower specific gravity than that of Zn, resulting in the formation of Al

6 g of Al ingot and 0.2 g of Zn powder with a purity of 99.9% were mixed well, and the mixture was put into an alumina crucible. The alumina crucible without any lid was inserted into a furnace for oxidation. First, the furnace was heated to a temperature of 700°C. Al and Zn were melted at 700°C and the melt was stirred. Next, the furnace was reheated in the range of 900–1100°C with a heating rate of 10°C/min for the oxidation process. Then the furnace was kept at the above temperatures for 60–180 min in air atmosphere. After the 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 for characterization.

The crystal structure and the morphology of the products were examined by X-ray diffractometry using Cu Kα radiation and scanning electron microscope (SEM) equipped with energy

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dispersive X-ray (EDX), respectively. The components of the products were verified by the EDX.

3. Results and discussion

Figure 1 shows the XRD patterns of the white products prepared at 1000 and 1100°C for 120 min in air at atmospheric pressure. The peaks of the XRD patterns can be indexed to hexagonal wurtzite structure of ZnO, indicating that the white products are ZnO 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 and 0.325 nm, respectively, which were in good consistent with the reported standard values of bulk ZnO. Some metallic Zn peaks and Al$_2$O$_3$ peak with very weak intensity are also observed. The Al$_2$O$_3$ peak is supposed to come from the Al$_2$O$_3$ collected together when ZnO samples were collected from the surface of the oxidized source material for characterization. For the product prepared at 900°C, white product was not found on the surface of the oxidized source material. SEM observation showed that no ZnO crystals were observed on the surface. EDX result revealed that no Zn signals were detected. The SEM and EDX results indicated that ZnO crystals were not formed on the surface of the oxidized source material at a temperature of 900°C. This is because the concentration of Zn vapor was not large enough to form ZnO crystals at a temperature lower than the boiling point of Zn (907°C).

Figure 2 shows the SEM images of the white colored products synthesized at different temperatures of 900, 1000 and 1100°C. Because the synthesis temperature of 900°C was lower than the boiling point of Zn, Zn vapor pressure was not high enough to form ZnO nuclei. The product prepared at 1000°C consists of many hexagonal pillar shaped crystals as shown in Fig. 1(b). In particular, a detailed observation of the hexagonal pillar crystals shows the growth of needle-shaped crystals on the pillars. The needle-shaped crystals were grown on one side of the pillars, while any needle-shaped crystals were not observed on the other side of the pillars. The diameter of the crystals gradually reduces from the bottom to the tip, showing the needle shape. In case of the product synthesized at 1100°C, wire and granular shaped crystals are observed. It is supposed that the granular shaped crystals were produced by the spheroidizing behavior of rods and wires to reduce the surface free energy at high temperature.

Figure 3 shows the EDX spectra of the white products prepared at 1000 and 1100°C. The EDX spectra reveal that the white products are ZnO materials. To investigate the effect of synthesis time on the morphology of ZnO crystals, the source materials were oxidized at 1000°C with different times of 60, 120 and 180 min. For the sample prepared after oxidation for 60 min, white product was not obtained. Figures 4(a) and 4(b) are the SEM images of the surface of the oxidized source material after oxidation for 60 min. The surface is not dense and rugged, on which no crystals with regular shape are observed. Figures 4(c) and 4(e) display the low magnification images of the ZnO crystals synthesized on the surface of the oxidized source materials after oxidation for 120 and 180 min, respectively. As the time increases from 120 to 180 min, the size of the ZnO crystals decreases slightly. It is known that ZnO micro/nanostructures contain a large density of surface defects such as oxygen vacancies or deficiencies. Thus when the growth time was too long, Zn sub-oxide (ZnO$_x$ where $X < 1$) would sublimate to Zn vapor, resulting in the decrease in the size of the ZnO crystals. Figures 4(d) and 4(f) demonstrate the high magnification images of the ZnO crystals obtained after oxidation for 120 and 180 min. The ZnO crystals synthesized after oxidation for 120 min adopt a hexagonal pillar shape, on which needle-shaped crystals were grown. It is found that from the hexagonal pillar shape, the ZnO crystals were grown along the $c$-axis of crystal structure. As the crystals became larger, secondary nucleation and growth were occurred on $c$-plane of the pillar, leading to the formation of needle-like crystals. On the other hand, ZnO with wurtzite structure has the non-central symmetry, and thus the ZnO crystal with pillar shape has $+c$ plane terminated with Zn cations and $-c$ plane terminated with oxygen anions. It is known that the Zn terminated surface is chemically active and the oxygen terminated surface is relatively

**Fig. 1.** XRD patterns of the products prepared through thermal evaporation of Al-Zn mixtures at (a) 1000°C and (b) 1100°C in air.

**Fig. 2.** SEM images of the products prepared through thermal evaporation of Al-Zn mixtures at (a) 900°C, (b) 1000°C and (c) 1100°C in air.
Thus, secondary nucleation can be occurred on only Zn terminated surface of the hexagonal pillar. This is the reason of asymmetric growth of the needle-like crystals on the hexagonal pillars. Tetrapod-shaped crystals as well as hexagonal pillar-shaped crystals are observed in the product prepared through oxidation for 180 min. Tetrapod shaped crystal is made up of a core and the four legs extending from the core.

Figure 5 shows the XRD patterns of the products prepared through thermal evaporation of Al–Zn mixtures at 1000°C for (a) 120 min and (b) 180 min in air. The most diffraction peaks are in agreement with those of hexagonal wurtzite structure of ZnO. The peaks of Zn and Al₂O₃ are also detected. However, the intensity of the peaks is too low, reflecting small amount of Zn and Al₂O₃ phases.

Figure 6 shows the EDX spectra of the white products synthesized after oxidation for 120 and 180 min. The EDX spectra show that the white products are ZnO. There are two crystal growth mechanisms through evaporation-condensation process; vapor–liquid–solid (VLS) mechanism and vapor–solid (VS) mechanism. The VLS mechanism is a growth mechanism to be assisted by a metal catalyst. Metal catalyst forms liquid alloy droplets at a process temperature, so the metal catalyst particles are observed at the tips of crystals. In the present work, the ends of the ZnO crystals showed no catalyst particles at their tips. It is assumed that the ZnO crystals were grown without catalysts. For this reason, it is suggested that the ZnO crystals were grown via vapor–solid growth mechanism.

4. Conclusions

ZnO micro/nanocrystals were formed by a thermal evaporation of Al–Zn mixture in air atmosphere. ZnO crystals formed at 1000°C showed a hexagonal pillar shape. In addition, needle-shaped crystals were grown on the Zn terminated surface of the pillar shaped crystals. Wire and granular shaped ZnO crystals were observed for the product prepared at 1100°C. As the synthesis temperature increased, the shape of the ZnO crystals changed from pillar shape to wire and granular shape. On the other hand, with the increase in synthesis time, tetrapod shaped ZnO crystals started to be formed. Based on the results presented here, we concluded that the synthesis temperature and time had...
an important effect on the morphology of ZnO crystals, and so the morphology of ZnO crystals can be controlled by adjusting the synthesis temperature and time.

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