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Shape controlled ZnO nanoparticle prepared by microwave irradiation method

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ZnO nanoparticle was successfully prepared by microwave irradiation method in various oxygen/nitrogen ratio atmospheres. In the present method, steel wool was used as a heat generator by microwave irradiation. The highest heating rate of ~200°C/sec for the reaction was achieved under the highest oxygen concentration, 80%, whereas the lowest hating rate was ~40°C/sec. The product prepared in a low oxygen ratio atmosphere showed tetra pod shape with high aspect ratio, *c/a*. On the other hand, the product prepared under high oxygen ratio atmosphere was relatively isotropic. PL spectra of the products with the higher aspect ratios showed higher UV emission intensity than the products with low aspect ratios i.e. isotropic shape.

Key-words : ZnO, Nanoparticle, Microwave, Photoluminescence, Rapid heating

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1. Introduction

Microwave irradiation method for ceramic materials is expected as a fast, low energy loss method. Microwave irradiation to bulk ceramic materials is used for sintering Al_2O_3. Advantage of the microwave use is low temperature and short time preparation as well as reduced crystal growth during preparation. After a significant finding by R. Roy et al.[1] about the microwave sintering for metal powder, microwave irradiation for metal particle attracts attention. The reaction under microwave irradiation for the metal causes induction current on the surface of the metal and it generate the Joule heat.

Zinc oxide (ZnO) nanoparticles attract attention in the field of luminescence as well as transparent conductive material. ZnO shows two different luminescence peaks: UV light (~380 nm) and green light (~510 nm) attributed to near the band edge and oxygen defects, respectively. The peak intensity ratios between the two generally reflect the crystallite shape and size. The rod shape ZnO nanoparticle grown along the [0001] direction has a potential for a laser device application. Dijken et al.[2] reported ZnO nanoparticle prepared by solution process showed a drop in quantum efficiency of luminescence from 20% to 12% with increasing the particle size from 0.7 nm to 1 nm. Shalish et al.[3] reported ZnO nanowire prepared by thermal evaporation method showed a relationship between the diameter of the rod and photoluminescence properties; the UV luminescence decreased with decreasing the diameter. As described above, it is quite important to understand the relationship between luminescence properties and shape of the ZnO nanoparticles.

In the present paper, we fabricated ZnO nanoparticles by the microwave irradiation method. We also found that oxygen concentration of the reaction atmosphere affect particle shapes (aspect ratios) of the obtained ZnO nanoparticles.

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2. Experimental procedure

In this work, we prepared ZnO nanoparticles using microwave irradiation method under various oxygen/nitrogen ratio atmospheres (O_2/N_2 = 20/80, 40/60, 60/40, and 80/20). Experimental setup is schematically shown in the **Fig. 1**. Zn metal powder as Zn source for the ZnO nanoparticle was placed on the steel wool (0.2 g) put on the bottom of an aluminum crucible. A glass plate used as a substrate was placed on the aluminum crucibles so that the surface of the glass plate faced to the Zn source side (faced to the bottom of the crucible).

The crucible with these setups was placed in an atmosphere-controllable PFA jar in a microwave oven. In the present method, the steel wool was used as a heat generator by the microwave irradiation, where the steel wool was heated by the Joule heat which evaporated Zn metal particle and precipitated ZnO nanoparticles. Reaction temperature during the reaction measured by a pyrometer at different oxygen concentration was shown in **Fig. 2**. The oxygen concentration of the reaction atmosphere strongly affected the heating rate although the power of the microwave was constant (1000 W). Due to high specific surface area of the steel wool, quite high heating rate (~200°C/sec) was achieved at high oxygen concentration, whereas relatively low heating rate

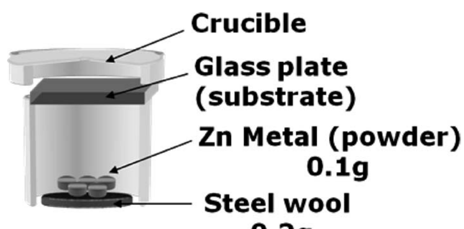

Fig. 1. Experimental setup for microwave irradiation method. The steel wool was heated by the induction current caused by microwave.

(~40°C/sec) was achieved at low oxygen concentration. O_2/N_2 ratio of the reaction atmosphere was detected using a zirconium oxide oxygen sensor.

Photoluminescence (PL) spectra of the ZnO nanoparticles were measured at room temperature with excitation light of He-Cd laser. Morphology of the products were observed by SEM and TEM. For the TEM observation, the ZnO nanoparticles deposited on the glass plate were peeled off by scratching. Crystallographic analyses were performed by XRD and TEM electron diffraction.

3. Results and discussion

3.1 Morphology of ZnO particles

By means of the microwave irradiation method, single phase ZnO nanoparticle was successfully prepared as shown in **Fig. 3** independent of the oxygen/nitrogen ratios.

Figure 4 and **5** shows SEM and TEM images of the ZnO nanoparticles prepared in different oxygen concentration atmospheres, respectively. Morphologies of the ZnO nanoparticles were dependent of the oxygen concentrations; the higher concentration resulted in thicker rods as obviously seen in the 80% oxygen concentration sample which consisted of thick particles rather than rod shapes, whereas the samples prepared in the lower oxygen concentration showed rod shapes. The TEM images indicated that the growth direction of the ZnO nanoparticles was c axis in all of the four samples. Relationship between aspect ratios of the particles shape (*c*/*a*) and percentage of the particles was shown in **Fig. 6**, which obviously indicated the atmosphere effect on the ZnO particles morphology. High oxygen concentration, i.e. high heating rate, might lead to homogeneous nucleation and resulted in isotropic morphology.

3.2 Crystal growth mechanism and photoluminescence spectra

Morphology of the samples showed different crystallization behaviors between high oxygen and low oxygen atmospheres as seen in the SEM and TEM images. In the high oxygen atmosphere, high heating rate was achieved due to rapid oxidation of the steel wool. The high heating rate, which implies high supersaturation of ZnO in the reaction atmosphere, might enhance crystal growth rate and yield isotropic crystal growth. On the other hand, in the low oxygen atmosphere, the heating rate and the supersatulation of ZnO becomes low. It results in anisotropic growth i.e. growth along with *c*-axis of the ZnO, and the whisker shapes were mostly obtained.

PL spectra of the products showed a significant effect of reaction atmosphere to their photoluminescence intensities at I_A (~380 nm) and I_B (~510 nm) as shown in **Fig. 7**(a). As shown in Fig. 7(b), the intensity ratio $I_A/(I_A + I_B)$ became the highest at the

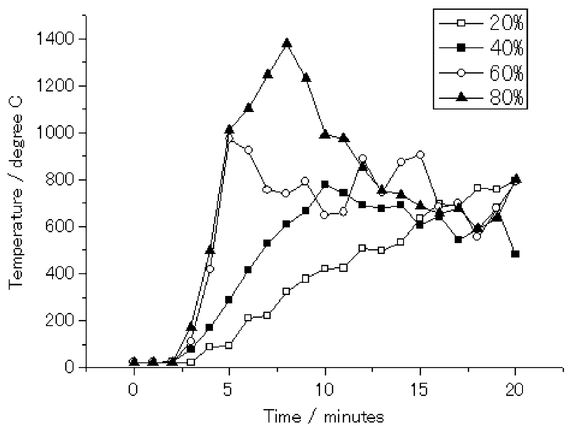

Fig. 2. Reaction temperature of the microwave irradiation method at different oxygen concentration. The higher oxygen concentration resulted in higher heating rate and higher maximum temperature.

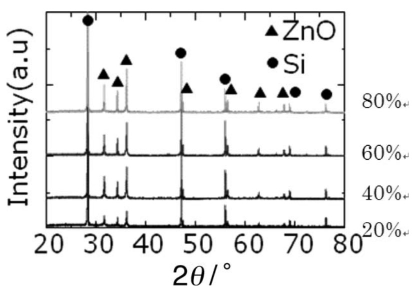

Fig. 3. XRD patterns of the products obtained by the microwave irradiation method. Si powder was used as a standard. Percentage values indicate oxygen contents in the atmosphere.

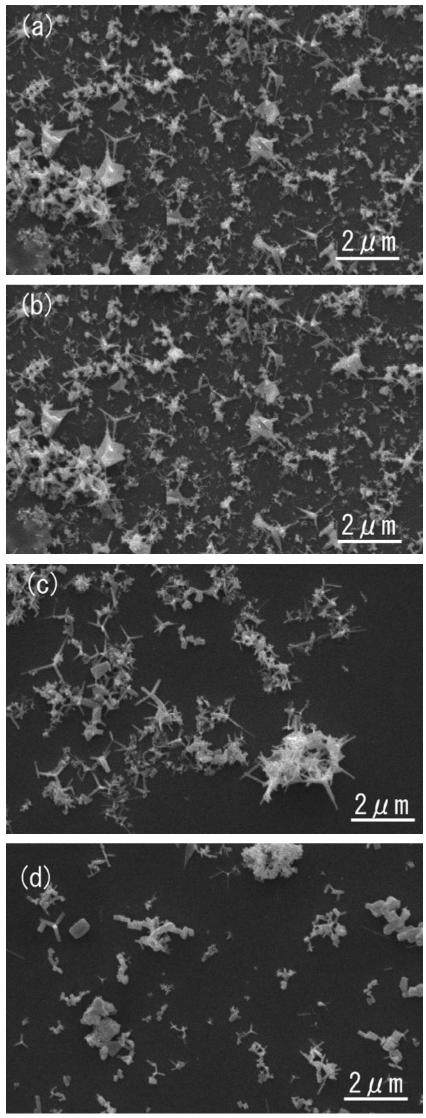

Fig. 4. SEM images of the ZnO nanoparticles prepared in different oxygen concentration atmospheres. Higher oxygen concentration resulted in thick particles.

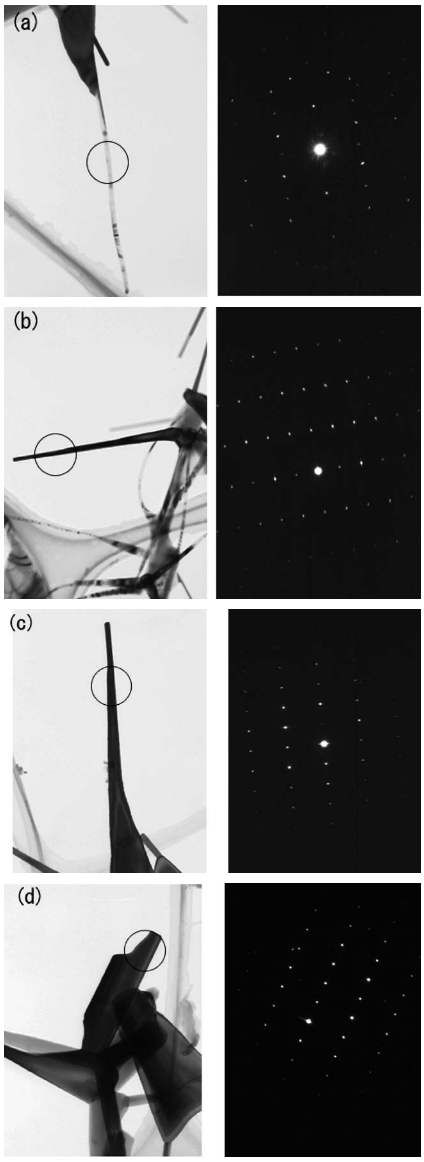

Fig. 5. TEM bright field images (left) and selected area diffraction patterns (right) of the ZnO nanoparticles prepared in different oxygen concentration atmospheres ((a) 20%, (b) 40%, (c) 60% and (d) 80% O_2). The areas selected were indicated with the circle in the bright field images. Electron diffraction patterns obviously indicated the growth direction of [0001].

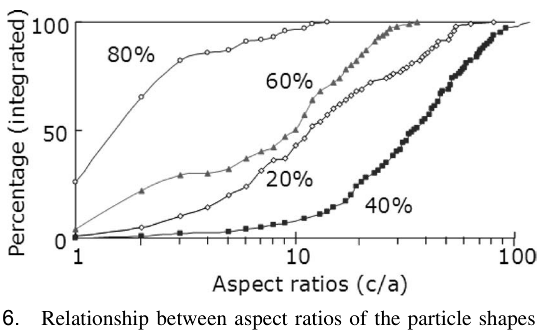

Fig. 6. Relationship between aspect ratios of the particle shapes (*c*/*a*) and percentage of the particles. The highest aspect ratios were achieved in the sample prepared in 40% O_2 atmosphere.

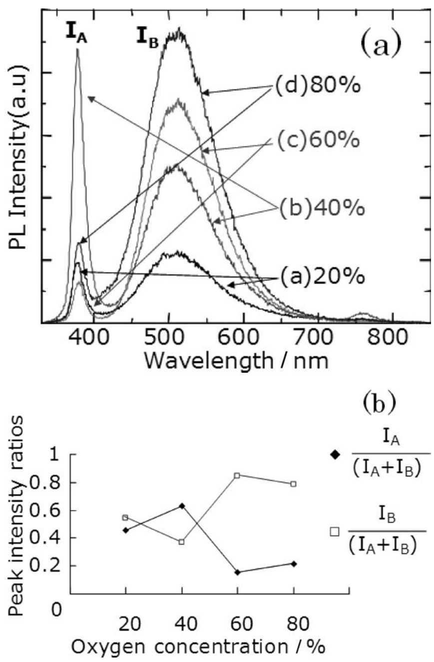

Fig. 7. Photoluminescence spectra (a) and peak intensity ratios of I_A and I_B (b) of the ZnO nanoparticles prepared in various oxygen atmosphere. The sample prepared in 40% O_2 showed the highest peak intensity ratios, $I_A/(I_A + I_B)$.

oxygen concentration of 40%. On the other hand, the I_B became the strongest at the oxygen concentration of 60%. It should be noticed that the intensity I_B increased with increasing oxygen concentration although the luminescence ~510 nm was caused by the oxygen defects. This might be explained by the crystal growth rate under each oxygen concentration. Low oxygen concentration (low growth rate) may result in low defect concentration in the ZnO crystal, and vice versa. From these results regarding PL spactra, we can conclude that the peak intensity of the two luminescence peaks can be varied by controlling the oxygen concentration in the atmosphere.

4. Summary

In the present work, we successfully fabricated the ZnO nanoparticles with controlled morphologies and PL properties by controlling oxygen concentration of reaction atmosphere in the microwave irradiation method. The microwave irradiation method for ZnO nanoparticles has a significant interest both scientifically and technologically. The rapid heating ~200°C/sec at maximum, which can not be achieved the other heating device, might affect crystal growth mechanisms of ZnO nanoparticles in different oxygen atmospheres.

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