Photoluminescence property of ZnO nanoparticle prepared by microwave irradiation method

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Abstract

ZnO nanoparticle was successfully prepared by microwave irradiation method in various oxygen/nitrogen ratio atmospheres. The product prepared in a low oxygen ratio atmosphere showed tetra pod shape with high aspect ratio, c/a. PL spectra of the products showed higher UV emission intensity than the others when it was prepared in the atmosphere oxygen/nitrogen=40/60.

1. Introduction

Zinc oxide (ZnO) nanoparticle attracts attention in the field of luminescence as well as transparent conductive material. ZnO shows two different luminescence peaks: UV light (~380nm) from near the band edge and green light (~510nm) from oxygen defects. 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. A. V. Dijken et al. [1] 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 0.7nm to 1 nm. I. Shalish et al. [2] 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 significant to understand the relationship between luminescence properties and shape of the ZnO nanoparticles.

Microwave irradiation to ceramics material 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. [3] 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. Objective of the present work is to find a relationship between reaction atmosphere and photoluminescence properties of ZnO particle prepared by the microwave irradiation method.

2. Experimental

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 (0.2g) 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 (1000W). 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 (~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. Chemical composition and chemical bonding state of the products were measured by XPS.

3. Results and discussion

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

Figure 4 shows SEM images of the ZnO nanoparticles prepared in different oxygen concentration atmospheres. 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. Relationship between aspect ratios of the particle shapes (c/a) and percentage of the particles were 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.

Lattice spacing of (100) and (002) planes were precisely analyzed using Si standard. As shown in Fig. 4, the lattice spacing was strongly dependent of oxygen concentration of the reaction atmosphere. (100) lattice spacing dropped at the oxygen concentration of 40%, whereas (200) spacing showed the highest value at the same oxygen concentration. From these results, 40% of oxygen concentration seemed to be a boundary of two different nucleation & crystal growth mechanisms. This is obviously shown in the PL spectra of the samples.

PL spectra of the products showed a significant effect of reaction atmosphere to their photoluminescence intensities at I_A (~380nm) and I_B (~510nm) as shown in Fig. 7. As shown in Fig. 8, the intensity ratio $I_A/(I_A+I_B)$ became the highest at the oxygen concentration of 40%. On the other hand, the I_B became the strongest at the oxygen concentration of 60%. From these results, we can conclude that the peak intensity of the two luminescence peaks can be varied by controlling the oxygen concentration in the atmosphere.

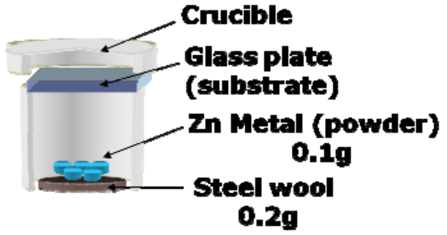

Fig. 1. Experimental setup for microwave irradiation method. The steel wool was heated by the induction current caused by microwave.

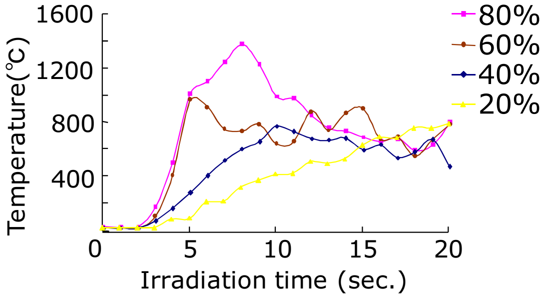

Fig. 2. Reaction temperature of the microwave irradiation method at different oxygen concentration. The higher oxygen concentration resulted in higher heating rate.

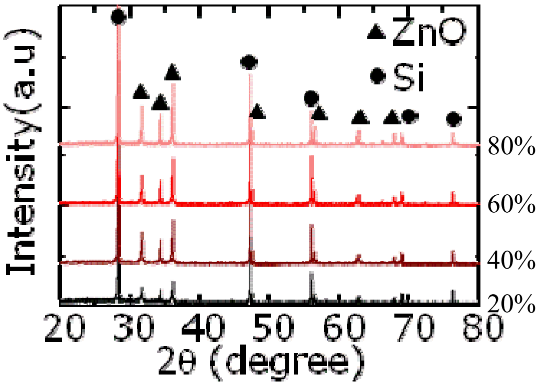

Figure 3. XRD patterns of the products obtained by the microwave irradiation method. Si powder was used as a standard. Percentage values indicate oxygen contents in the atmosphere.

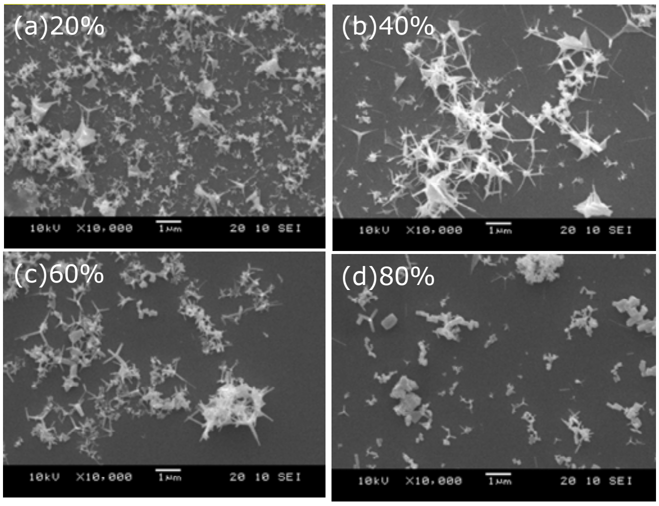

Figure 4. SEM images of the ZnO nanoparticles prepared in different oxygen concentration atmospheres. Higher oxygen concentration resulted in thick particles.

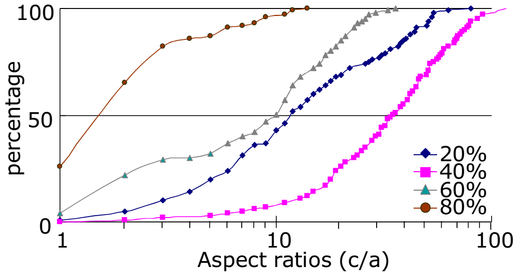

Figure 5. R Relationship between aspect ratios of the particle shapes (c/a) and percentage of the particles were shown in Fig. 6.

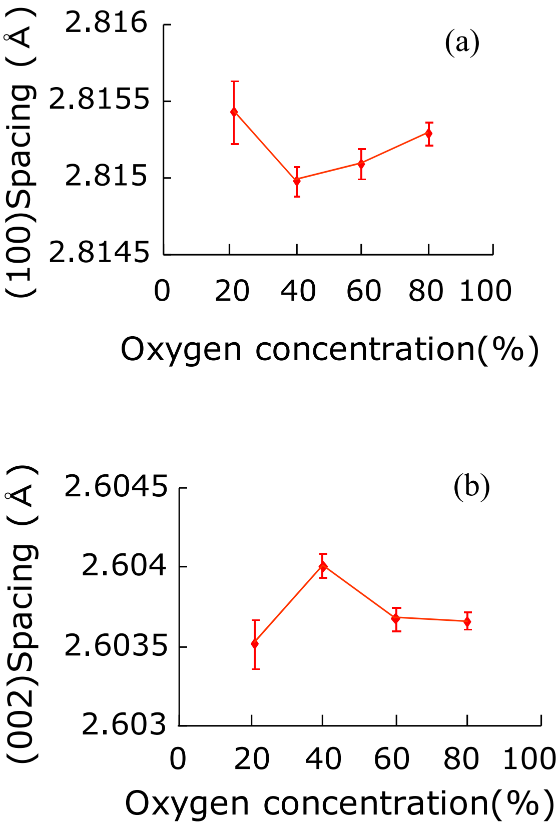

Figure 6. (a) (100) and (b) (002) lattice spacing of the ZnO nanoparticles prepared in different oxygen concentration atmosphere. (100) spacing showed lowest value at 40% oxygen atmosphere, whereas (200) spacing showed highest.

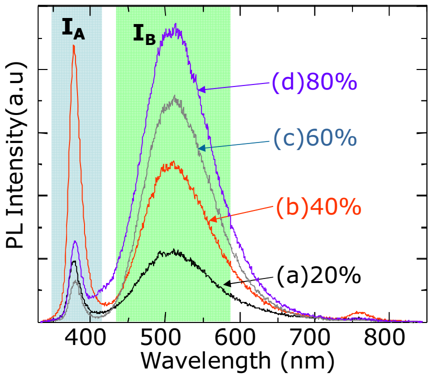

Figure 7. PL spectra of the ZnO nanoparticles prepared in different oxygen concentration atmospheres. The 40% oxygen concentration resulted in the highest UV light intensity compared to the other samples.

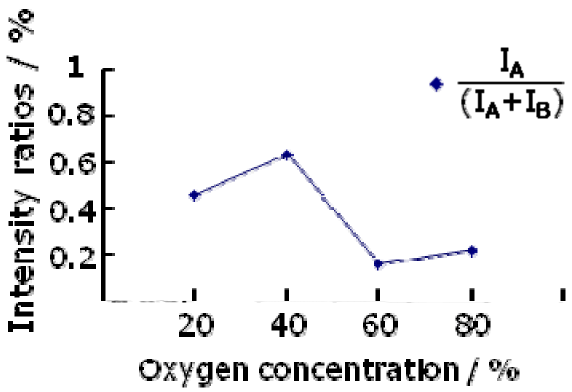

Figure 8. Relationship between oxygen concentration of the reaction atmosphere and the PL peak intensity ratios, $I_A/(I_A+I_B)$. The highest value was achieved at the 40% oxygen atmosphere.

4. Summary

In the present work, we have succeeded to fabricate ZnO nanoparticles with different 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. For the scientific interest, the rapid heating ~ 200 ^{O}C/sec at maximum, which can not be achieved the other heating device, might affect nucleation and growth mechanisms of ZnO nanoparticles in different oxygen atmospheres. For technological interest, the present method can yield ZnO nanoparticles in short time without expensive setup. High productivity compared to the other fabrication methods, e.g. CVD, VLS, sol-gel, etc. is a significant advantage when considering the technological meaning.

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6. References

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