Photoluminescence of ZnO Fine Powders Synthesized by Sol–Gel Process

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ZnO powder, which was composed of sub-micrometer particles, was synthesized by sol–gel method. SEM image shows that the mean size of the particles was about 70 nm. X-ray diffraction patterns revealed that the particles had hexagonal structure with the c-axis and a-axis lattice constants of 0.520 nm and 0.324 nm, respectively. The lattice constants are in well accordance with those of ZnO single crystal. Photoluminescence spectra at room temperature showed the green emission with the peak at 500 nm. In addition, the intensity of the green emission increased upon increasing the heating temperature.

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1. Introduction

At recent, the synthesis and characterization of low dimensional nanoscale materials are attracting considerable attention due to their unique properties determined by the restricted size. A great deal of effort has been made to develop the efficient processes for the growth of nanosized materials. To date, a lot number of studies on the fabrication of low dimensional structures of ZnO have been performed.1–5

ZnO is one of the most attractive materials for the potential application in optoelectronic devices. Its wide band gap of 3.37 eV and large exciton binding energy of 60 meV enable to use as UV light emitting devices. In addition, the exciton binding energy is much greater than thermal energy at RT (26 meV), which leads to an efficient excitation of UV region even at room temperature (RT). Room temperature UV lasing has been observed for ZnO thin films. However, for low dimensional structures of ZnO with high surface area to volume ratio, the different photoluminescence (PL) characteristics have been reported. ZnO nanowires exhibit strong green light emission, which suggests that the luminescence of ZnO is very sensitive to its surface state. This PL characteristics of ZnO to exhibit UV emission and size-dependent green emission should promise its potential application in optoelectronic devices.

Many methods such as MOCVD, thermal evaporation,6 electrochemical deposition,7 and sol–gel method8–10 have been used to produce the ZnO nanostructures with many different morphology. Among them, it has been reported that sol–gel process is suitable for the production of ZnO nanoparticles. In order to compare with the PL characterization of the sub-micron particles synthesized by other methods, it is worth investigating the PL characteristic of the particles synthesized by sol–gel process.

In this paper, we report the structure and the PL characterization of ZnO powder synthesized by sol–gel process.

2. Experimental

ZnO powder was synthesized by sol–gel process at room temperature. Zinc acetate dihydrate \( (\text{Zn(CH}_2\text{CO}_2)_2 \cdot \text{H}_2\text{O}) \) of 5 mol was dissolved in distilled water of 1000 ml and the solution was stirred vigorously for 1 h to yield a transparent and homogeneous solution. Then 28% aqueous ammonia \( (\text{NH}_3 \text{aq.}) \) was added to the solution. The pH value was adjusted approximately to 8 by titration of \( \text{NH}_3 \text{aq.} \) and the solution was stirred continuously for 16 h. The resultant precipitate was filtrated from the suspension, rinsed with distilled water, and then dried at 110°C for 24 h in air to form as-prepared powder. The powder was calcined at 450°C for 2 h in air. A part of the powder was again thermally treated at 1200°C for 2 h in air. The crystal structure of the powder was examined by X-ray diffractometer with Cu Kα radiation operated at 40 kV and 30 mA. The surface morphology was observed with using scanning electron microscope (SEM). The photoluminescence (PL) at room temperature was measured with using a He–Cd laser with the wavelength of 325 nm as an excitation source. The PL spectra were detected through a cooled charge coupled device with a monochromator.

3. Results

X-ray diffraction (XRD) patterns were taken to examine the crystal structure of the powder. Figure 1 shows the XRD patterns measured at each step when the powder was dried at 110°C, calcined at 450°C and annealed at 1200°C.
patterns of the powders measured at each step when the powder was dried at 110°C, calcined at 450°C and heated at 1200°C. Similar XRD patterns were also taken for all samples measured at each temperature step. In comparison with JCPDS data card, the diffraction patterns can be well indexed to hexagonal structure of ZnO. The lattice constants calculated from the diffraction peaks are $a = 0.324$ nm, $c = 0.519$ nm, respectively. These are in well agreement with those of ZnO single crystal ($a = 0.324$ nm, $c = 0.519$ nm), which is indicative of single phase ZnO. In addition, no peaks from other impurities except ZnO were detected in the patterns even for the powder dried at 110°C, which also proves high purity of the ZnO powder. An increase in the diffraction peak intensity was observed upon increasing the heating temperature, which means that the crystallinity of the ZnO powder was enhanced at higher temperature.

The morphology and size of the powder were observed by scanning electron microscope (SEM). Typical SEM images at (a) low magnification and (b) high magnification on the powder dried at 110°C and then calcined at 450°C are shown in Fig. 2. The images show that the powder is composed of submicrometer ZnO particles with clear spherical shape and their mean size of about 70 nm. This indicates that ZnO particles with sub-micrometer size can be synthesized by sol-gel process. In order to investigate the variation of morphology and PL characterization of the powder with heating temperature, the powder was heated at 1200°C for 2 h in air. Figure 3 represents a SEM image of the powder dried at 110°C, calcined at 450°C, and then finally heated at 1200°C. Higher temperature induced the growth of particles, because which the particle size became as large as several micrometer in diameter. That is, higher temperature caused the powder with lower surface area to volume ratio.

The room temperature PL spectra were measured for two samples. One is the powder dried at 110°C and then calcined at 450°C. The other is the powder dried at 110°C, calcined at 450°C and finally heated at 1200°C. The PL patterns show a strong green emission with peak at around 500 nm (Fig. 4). Weaker near-band-edge emission around 380–390 nm is also detected. The PL peak intensities increase with the final heating temperature.

4. Discussion

The XRD patterns prove that the powder synthesized by sol-gel method is single phase ZnO without any impurity and has wurtzite structure. SEM image shows that the ZnO powder is composed of sub-micrometer particles with a spherical shape. The mean particle size is 70 nm. With increasing the heating temperature, the particle size became larger due to the grain growth of particles.

On the other hand, strong green emission was observed for the sub-micrometer ZnO particles with the mean size of 70 nm. It is well known that the green emission of ZnO is as-
sociated with singly ionized oxygen vacancy in ZnO lattice and the emission results from the recombination of a photogenerated hole with an electron occupying the singly ionized oxygen vacancy. The green emission has been generally observed for nanostructures of ZnO. When compared with bulk crystal, nanostructure has higher density of surface and thus nano-sized ZnO particles must have higher density of subsurface oxygen vacancy. Hence, the strong green emission should be observed for nano-sized ZnO particles, which is the characteristic of ZnO nanostructures. From the fact that the intensity of PL for the ZnO particles heated at 1200°C is stronger than that for the particles calcined at 450°C, it is supposed that the ZnO particles heated at higher temperature have a greater fraction of oxygen vacancy.

The reason why the density of oxygen vacancy in sub-micrometer ZnO particles increases upon increasing the heating temperature can be suggested as follows. The particles were heated in a furnace under atmospheric pressure in air. Then the quantity of air in the furnace at higher temperature would be lower than that at lower temperature according to the ideal gas equation

\[ PV = nRT \]

where \( P \), \( V \), \( T \), \( n \), and \( R \) are the pressure, volume, temperature, molar number, and gas constant, respectively. That is, higher temperature decreases the oxygen quantity in the furnace, in turn lowered oxygen content results in the higher density of oxygen vacancy in ZnO due to the reductive environment. As shown in Figs. 2 and 3, the particle size increased as the heating temperature increased. Therefore an enhanced green emission for larger particles proves that the green emission is not attributed to higher level of surface oxygen vacancies, but to higher density of oxygen vacancies in particles.

5. Conclusions

ZnO particles with sub-micrometer size were successfully synthesized by sol-gel process. The particles were ZnO with hexagonal wurtzite structure. The particle shape was sphere and the most of the particles had the size in the range of 40–80 nm. Strong deep-level green emission was observed at RT, which was caused by high surface area to volume ratio of nanostructures. As the particles were heated at higher temperature, the green emission intensity increased. This suggests that the density of ionized oxygen vacancies in ZnO particles increased with the heating temperature.

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References