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Annealing effect on structure and green emission of ZnO nanopowder by decomposing precursors*

Zhong Hong-Mei(钟红梅)[a)b)†], Liu Qian(刘 茜)[a)], Sun Yan(孙 艳)[b)], and Lu Wei(陆 卫)[b)]

[a)] *State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai* 200050, *China*

[b)] *National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai* 200083, *China*

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ZnO nanopowder is successfully synthesized by annealing the precursors in oxygen gas using the chemical precipitation method. Structural and optical properties of thus synthesized ZnO nanopowder are characterized by scanning electron microscopy (SEM) and photoluminescence (PL). The morphology of ZnO nanopowders evolves from nanorod to cobble as annealing temperature increases from 500 to 1000 °C, while spiral structures are observed in the samples annealed at 900 and 1000 °C. The PL spectra of ZnO nanopowder consist of largely green and yellow emission bands. The green emission from ZnO nanopowder depends strongly on the annealing temperature with a peak intensity at a temperature lower than 800 °C while the yellow emission is associated with interstitial oxygen O_i.

Keywords: ZnO, nanopowder, annealing effect, green emission

PACC: 7280E, 6140M, 8140G, 7855E

1. Introduction

ZnO is a direct-band gap semiconductor with excellent optical properties including its large exciton binding energy (60 meV) and wide bandgap (3.3 eV). It has been receiving extensive attention due to its promising potential applications in low-voltage and short wavelength (green or green/blue) electro-optical devices such as light emitting diodes, laser diodes, chemical sensors and varistors.[1,2] To explain the green emission from ZnO, various physical models have been proposed. For example, the green emission involved copper impurities,[3] oxygen vacancies,[4−5] interstitial oxygen atoms,[6−8] and zinc vacancies.[8] But the eventual identification of the green emission, even other emissions in the visible range, from ZnO remains rather ambiguous. Naturally, it is of great importance to clarify and understand the mechanism of the green emission for successful optical applications of ZnO.

In the present paper, we concentrate on the fabrication of ZnO nanopowder samples and the annealing effects on the structures and the green emission of ZnO nanopowder samples to understand the green emission mechanism.

2. Experiment

The synthesis of ZnO precursors was carried out by using the chemical precipitation method. Stoichiometric $ZnCl_2$ was added into a solution of NH_4HCO_3 mixed with lauryl sodium sulfate ($C_{12}H_{25}NaO_4S$). The solution was filtered and the resulting solids were washed with alcohol 3–4 times. Precursors were then dried out at 50–60 °C for 3–4 h, and finally the precursors were annealed at different temperatures of 500, 600, 700, 800, 900, and 1000 °C, separately, for one hour in an oxygen atmosphere.

Structural and optical properties were characterized by x-ray diffraction (XRD, Rigaku D/max-rotating target x-ray diffractometer from Hitachi), scanning electron microscopy (SEM, FEI Sirion 200 FESEM), and photoluminescence (PL, SPEX 1403 Spectrometer).

3. Results and discussion

Figure 1 shows XRD spectra of ZnO nanopowder samples annealed at different temperatures from 500 to 1000 °C. Sharp diffraction peaks labelled (100),

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†Corresponding author. E-mail: hmzhong@mail.sic.ac.cn

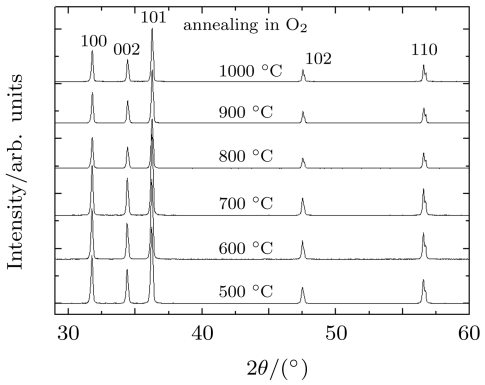


Fig.1. XRD patterns of ZnO nanopowder samples annealed at different temperatures.

(002), (101), (102), and (110) can be indexed as the crystalline hexagonal wurtzite structure (JCPDS No 36-1451). No other crystal phases are observed. The relative intensity of the (002) peak increases with annealing temperature increasing from 500 to 700 °C, it then decreases after the annealing temperature has further increased above 700 °C as shown in Fig.2. The correlated increase of the (002) peak intensity and annealing temperature below 700 °C was reported by Fujimura *et al* who believed that the (001) orientation lay in the lowest surface energy as compared with other orientations which need more thermal energies for developments.[9] On the other hand, the decrease of the (002) peak observed in our experiments at temperatures higher than 700 °C can most likely be due to the development of other orientations or the generation of new phases, as Kang *et al* pointed out that it was possible to develop other orientations by high-temperature annealing.[10]

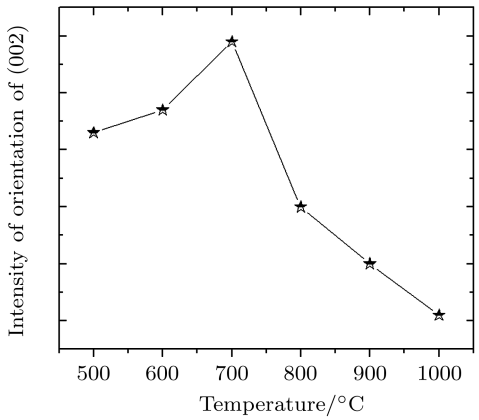


Fig.2. Dependence of the relative intensity of the (002) peak on annealing temperature.

Figure 3 shows SEM images of ZnO nanopowder samples annealed at different temperatures from 500 to 1000 °C, separately. One can see that the ZnO nanopowder morphologies evolve, in general, from nanorod to cobble as the annealing temperature increases from 500 to 1000 °C. Additionally, it is interesting to notice

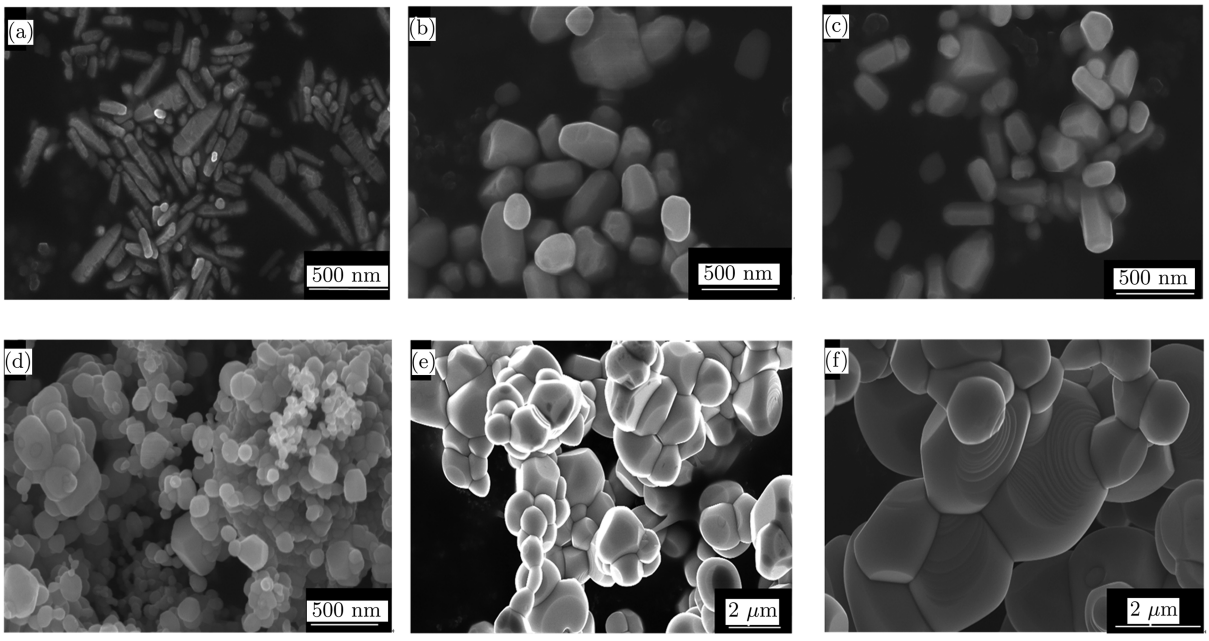


Fig.3. SEM morphologies of ZnO nanopowders annealed, separately, at (a) 500, (b) 600, (c) 700, (d) 800, (e) 900, and (f) 1000 °C.

that many small particles are congregated around big particles at 800 °C and spiral structures begin to appear at 900 and 1000 °C. The formation of small particles at 800 °C is most likely associated with the reaction between zinc atoms evaporated on the surface of large particles and oxygen atoms in atmosphere. Hence, the intensity of the (002) peak becomes reduced due to the formation of these small particles, as clearly confirmed by the XRD results discussed in the previous paragraph.

The spiral structures have been observed in both ZnO tubes on a sapphire substrate[11] and films of $YBa_2Cu_3O_7$[12] in past years. The spiral structure is closely associated with the screw dislocation according to the mechanism of spiral growth which is also called the Frank mechanism, after Frank who was the first to develop this theory.[13]

Figure 4 shows the annealing-temperature-dependent PL spectra of ZnO nanopowder samples, where UV near-band edge emission and the visible emission are observed from all samples annealed at different temperatures. However, the UV near-band edge emission at about 3.2 eV tends to be replaced by two emission peaks at 3.11 and 3.27 eV when the annealing temperature increases to 900 and 1000 °C. The emission at about 3.2 eV originates from the band-edge-exciton-related transition, which is in agreement with the previously reported results.[14] It is interesting to note that the twin peaks at 3.11 and 3.27 eV are observed only in the spiral-structured samples, which suggests a possible correlation between the twin peaks and those small particles. Further investigation however is needed for confirmation.

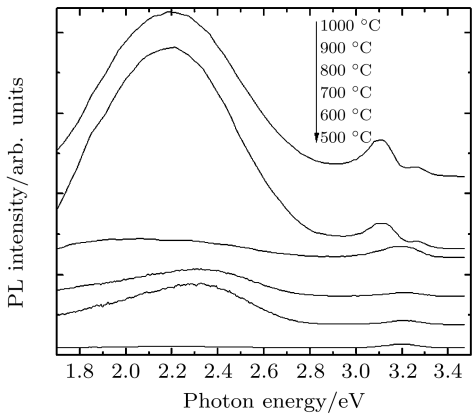


Fig.4. Room temperature PL spectra of ZnO nanopowder samples varying with annealing temperature. The spectrum curves for all annealing temperatures have been shifted up vertically for display clarity.

Broad-band emission in the visible range was observed in all ZnO nanopowder samples. The emission band is asymmetric which indicates a multiple-emission-peak composition. Figure 5 shows the fitting results by Gaussian line distributions for all samples annealed at 500, 600, 700, 800, 900, and 1000 °C, separately. The broad band contains two emission subbands in the yellow and the green regions, separately. The yellow emission is observed in all samples, while the green emission is observed only in samples annealed at 600, 700, and 800 °C separately. Furthermore, the ratio of the green to yellow integral intensities increases with the increase of annealing temperature as shown in Fig.6. This suggests that the green and the yellow emissions originate from two different defect centres which compete with each other between 600 and 800 °C. The yellow emission was assigned to interstitial oxygen O_i^-.[15,16] The green emission may result from two different sources: intrinsic defects and surface defects: Xiong *et al*[17] proposed that the green emission originated from the intrinsic defects in bulk crystal, Shalish *et al*[18] and Dijken *et al*[19] suggested, on the other hand, that the green emission originated from the surface defects. In order to clarify the origin of the green emission, Djuriši *et al*[20] coated the fabricated ZnO nanostructures with surfactant and compared the PL spectra of coated ZnO nanostructures with those of an un-coated one. A significant reduction in green emission intensity was obtained from the coated nanostructure, which strongly

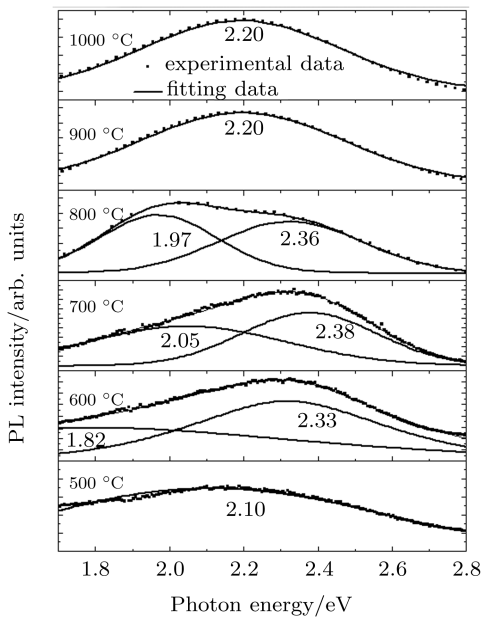


Fig.5. Visible emission spectra of ZnO nanopowders at different annealing temperatures.

suggests that surface centres should be responsible for the green emission, for the surface defects are significantly reduced by the coating.[17]

In order to further confirm the origin of the green emission, we have added the same quantity of surfactants into the precursors during the chemical synthesis for all annealing-temperature samples. However, the eventual concentration of the surfactants on the ZnO nanostructure is expected to be small when the annealing temperature is high because of decomposition of the surfactants. This means that the concentrations of the surface defects are high in the high-temperature-annealed ZnO samples. Moreover, a large number of small particles are observed (see the SEM picture of Fig.3(d)) on the surfaces of large ZnO particles at 800 °C. Therefore, the density of surface states per volume reaches its maximum value at 800 °C, resulting in the strongest intensity of the green emission as demonstrated in our experiment in Fig.6. For samples annealed at 900 and 1000 °C,

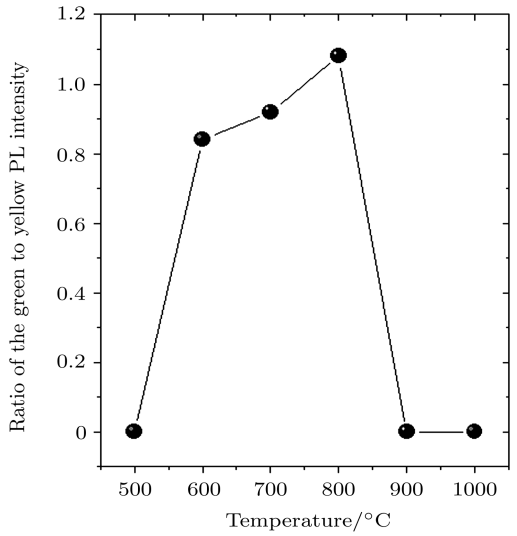


Fig.6. Ratio of the green to yellow PL integral intensity.

the green emission totally disappears and the yellow emission dominates. The most probable physical mechanism is that the surfaces of large particles are now in the O-rich mode due to the evaporation of zinc atoms at high annealing temperatures, and thus the visible emission is now dominated by the yellow emission from O_i^-. This is in good agreement with the result recently reported by Djurišić *et al.*[19]

4. Conclusion

We prepared ZnO nanorods in oxygen gas by annealing the precursors, which were produced by the chemical precipitation method. The structural and optical properties of the thus synthesized ZnO nanopowder were characterized by scanning electron microscopy (SEM) and photoluminescence (PL). The SEM pictures show that the morphology of ZnO nanopowders evolves from nanorod to cobble as the annealing temperature increases from 500 to 1000 °C, while spiral structures are observed in the ZnO nanopowder samples annealed at 900 and 1000 °C separately. The PL spectra are composed of two broad emission subbands, i.e. the green and the yellow ones. The green emission depends strongly on annealing temperature: a peak intensity appears at 800 °C. Our studies indicate that the yellow emission is associated with interstitial oxygen O_i^-, while the green emission most likely involves surface defect complexes in the samples. However, it is difficult to clearly associate the green emission in ZnO nanpowder with the exact type(s) of the surface defect complexes, for the defect complexes strongly depend on synthesis conditions. Further investigation in this respect is needed.

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