Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp258-259

P-7-21

Structural and luminescence properties of highly crystalline ZnO nanoparticles prepared by sol-gel method

Wiem Bousslama[1], Habib Elhouichet[1,2], Bernard Gelloz[3,*], Brigitte Sieber[4], Myriam Moreau[5], Mokhtar Férid[1], and Nobuyoshi Koshida[3]

[1] Laboratoire de Physico-Chimie des Matériaux Minéraux et leurs Applications, Centre National de Recherches en Sciences des Matériaux, B.P. 95 Hammam-Lif, 2050, Tunisia.
[2] Département de Physique, Faculté des Sciences de Tunis, Campus ElManar 2092, Tunisia.
[3] Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan.
[4] UMET, UMR CNRS 8807, Université Lille 1, 59655 Villeneuve d'Ascq Cédex, France.
[5] LASIR UMR CNRS 8516, Université Lille 1, 59655 Villeneuve d'Ascq Cédex, France.
[*] Phone: +81-4-2388-7433 E-mail: bgelloz@cc.tuat.ac.jp

1. Introduction

ZnO is used in ultraviolet optoelectronic devices due to its wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature (RT)[1-3]. There has been an increased interest in nanocrystalline ZnO powders for photonic, chemical and electro-magnetic applications. However, there is a compromise in the development of a method for preparing low cost ZnO nanoparticles on a large scale and with the high crystalline quality required for optoelectronic applications.

In this paper, we report the synthesis of ZnO nano-powders (NPs) using the sol-gel method. The key advantages of this technique are: the low processing temperatures, short annealing times, high purity of materials and good control of the size and shape of the particles. The as-grown ZnO nanoparticles were annealed at various temperatures to optimize the crystalline quality and nanoparticle sizes.

The structure and optical properties of the ZnO NPs were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy, Raman spectroscopy, and photoluminescence (PL).

2. Preparation of ZnO powders

The ZnO nanopowders (NP) were grown from sol-gel method. The sol was prepared using zinc acetate dehydrate ($Zn(CH_3COO)_2 2H_2O$) as the starting material, methanol as the solvent, and citric acid ($C_6H_8O_7$) as the stabilizer. The powders obtained from the dried sol were annealed at different temperatures (400, 500, 650 and 800 °C) for 2 h in ambient air.

3. Results and Discussion

Structure of ZnO nano-powders

The XRD patterns of the as-synthesized ZnO nanoparticles and those annealed at temperatures of 400–800 °C for 2 h are shown in **Fig. 1**. The three pronounced diffraction peaks at about 2θ =31.8°, 34.5° and 36.3° are identified, respectively, as the (100), (002) and (101) peaks of ZnO. The results confirm the hexagonal wurtzite structure of the calcined ZnO NP. By increasing the calcination temperature, these three peaks showed enhanced intensity with reduced full-width at half-maximum, showing that both crystalline quality and nanoparticle size are improved with annealing temperature.

Raman scattering was used here to clarify the quality and structure of ZnO nanoparticles. **Figure 2** shows the Raman spectra of the ZnO NP excited by the 532 nm line. For the excitation line 532 nm, the peaks located at 332, 380, 437, and 564.5 cm^{-1} can be observed. The peaks located at 332, 380, and 437 cm^{-1} can be assigned to second-order Raman spectrum $2E_2(M)$, $A_1(TO)$, and $E_2(H)$, respectively. The strongest peak, centered at about 437 cm^{-1}, is characteristic mode (E_{2H}) for the hexagonal phase of ZnO. It indicates the good crystallization of the nanoparticles and further testifies the results from XRD patterns.

Photoluminescence

Figure 3 shows the RT PL of the ZnO NP annealed at 800ºC. The PL spectrum is composed of a strong emission line, centered at 385.65 nm (3.215 eV) with a FWHM of 5.31 nm, characteristic of excitonic recombination in ZnO. In addition, a weak visible emission broadband (mainly due to structural defects which are related to deep-level emissions, such as zinc vacancies, oxygen vacancies, interstitial zinc and interstitial oxygen) was observed.

The optical quality of ZnO is expressed as the ratio R of the peak intensities of the near band-edge emission to that of the deep-level emission at around 502 nm (2.47 eV). It is a key aspect for studying the applications of ZnO film in the UV region [4]. R was as high as 160 even at RT, much higher than values reported in the literature (*e.g.* 60 [5]; 122 [6]). Thus, our ZnO NPs have good optical properties with very few structural defects.

The results of the evolution of the integrated UV PL intensity versus temperature are shown in **Fig. 4**. The integrated PL intensity of the near band edge emission measured at RT was 2% of that observed at 15 K. R reached 15000 at 15 K. The UV PL intensity exhibits a thermal quenching with an activation energy E_a of 51.3 meV, which is of the same order than the value 47 meV obtained by

Him et al. [7] and which is related to the presence of hydrogen.

4. Conclusions

ZnO nanoparticles were prepared using the cost-effective sol–gel method. Single-phase formation of the sample with hexagonal crystal symmetry was obtained. Annealing enhanced the crystalline quality. After annealing at 800°C, the particle size was estimated to be around 50-70 nm. A sharp, strong and dominant UV emission with a suppressed green emission has been observed which confirms that the synthesized ZnO NPs have good optical properties with very few structural defects.

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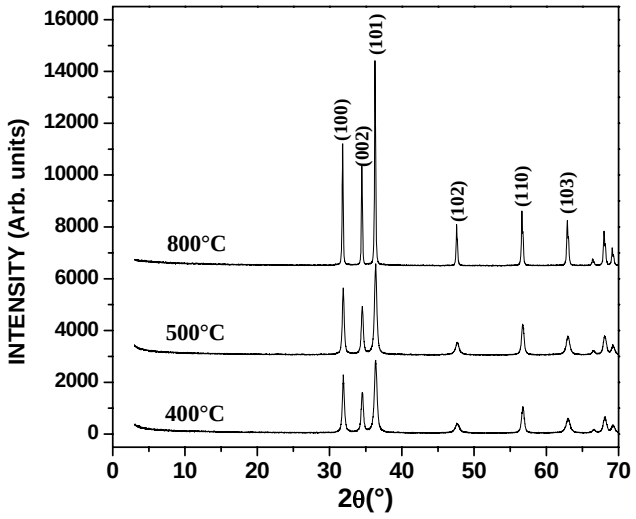

Fig. 1 XRD patterns of ZnO nanoparticles annealed at different temperatures.

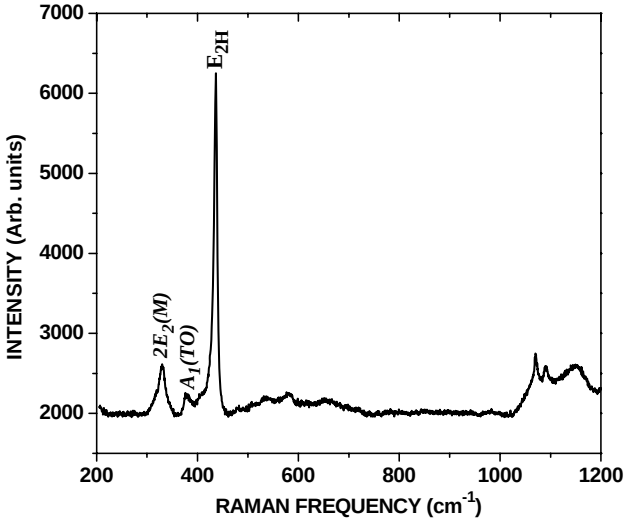

Fig. 2 Raman spectrum of ZnO nanoparticles for 532 nm excitation wavelength.

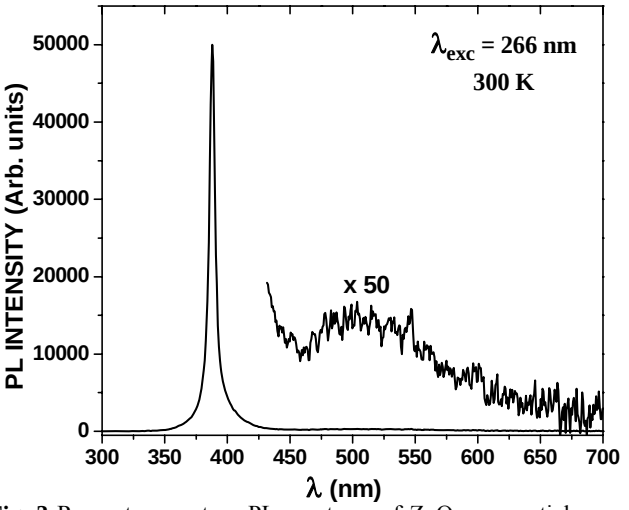

Fig. 3 Room temperature PL spectrum of ZnO nanoparticles annealed at 800°C. The low intensity region for energies below that of the main peak was plotted again with a factor 50 enlargement.

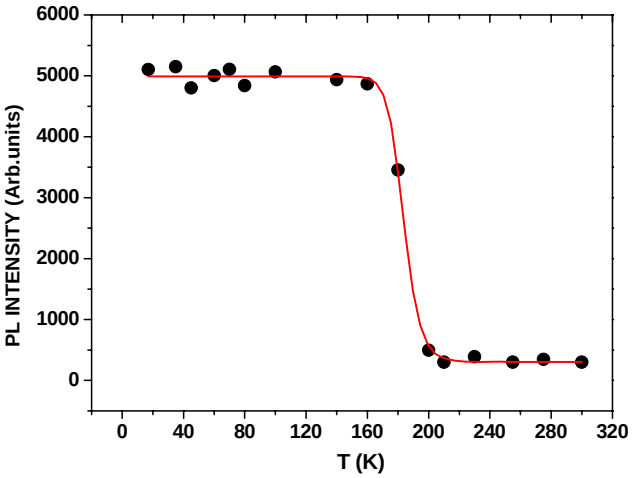

Fig. 4 Integrated UV PL intensity versus temperature. The solid line is a fit to a thermally-activated quenching: $I(T)=I_0/[1+Cexp(-E_a/kT)]$, with Ea=51.3 meV.