

ZnO nanorod arrays grown under different pressures and their photoluminescence properties

Xiuqing Meng^{a,b}, Dongxu Zhao^{a,*}, Dezhen Shen^a, Jiying Zhang^a, Binghui Li^a,
Xiaohua Wang^c, Xiwu Fan^a

^aKey Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 East Nan-Hu Road, Open Economic Zone Changchun 130033, PR China

^bGraduate School of the Chinese Academy of Sciences, PR China

^cNational Key Laboratory of High Power Semiconductor Laser, Changchun University of Science and Technology, 7089 Weixing Road Changchun, PR China

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Abstract

The ZnO nanorod arrays were synthesized via a simple vapor deposition method on Si (1 1 1) substrates at a low growth temperature of 520 °C. By selecting different source materials under different growth pressures, well-aligned hexagonal-shaped ZnO nanorod arrays were obtained under both conditions. X-ray diffraction (XRD) analysis confirmed the nanorods are *c*-axis orientated. Selected area electron diffraction (SAED) and transmission electron microscopy (TEM) analysis demonstrated the individual nanorod is single crystal. Photoluminescence (PL) analyses show the superior optical properties of the nanorod arrays.

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1. Introduction

One-dimensional nanostructures have attracted great attention in recent years, owing to their potential applications as basic building blocks in nanosciences and technologies. Among the variety of nanostructures, ZnO nanostructures are the focus of study, because ZnO has a wide band-gap and large binding energy of excitons and biexcitons [1]. Due to their particular electrical and optical properties, well aligned ZnO nanorod arrays can find applications in Schottky diode [2], ZnO-based nanorod heterojunctions [3] and sensors [4]. Different methods were used to fabricate ZnO nanorod arrays, including vapor–liquid–solid (VLS) process [5], chemical physics deposition [6] and template-induced method [7]. Until now, people have studied the synthesis, property study and application of the nanorods. But to our knowledge, no one reported on the synthesis of ZnO nanorod arrays with similar

morphologies under different growth pressures, and on the study of their physical properties.

In this letter, ZnO nanorod arrays were synthesized via a simple vapor deposition method on Si (1 1 1) substrates at a low temperature of 520 °C, by selecting different source materials under different growth pressures. The nanorods grown under ambient pressure possess larger size and better optical properties.

2. Experimental

The growth was carried out in a horizontal tube furnace by vapor transport process for 30 min. Equal amount of zinc powder (99.99%) and mixture of ZnO:Zn (mass ratio 2:1) loaded in a quartz boat served as source material for the growth processes under 1 and 760 Torr, respectively. The details are discussed elsewhere. The as-grown samples were investigated by field-emission scanning electron microscopy (FESEM), energy-disperse X-ray (EDX) attached to the SEM, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Photoluminescence (PL) and resonant

*Corresponding author. Tel.: +86 431 6176322; fax: +86 431 4627031.
E-mail address: dxzhao2000@yahoo.com.cn (D. Zhao).

Raman measurements were performed using a He–Cd laser line of 325 nm as excitation source.

3. Result and discussions

Figs. 1 (a) and (b) present the FESEM images of ZnO nanowire arrays synthesized at 520 °C under low (1 Torr) and ambient (760 Torr) pressure, respectively. In both images, well-aligned hexagonal-shaped ZnO nanorod arrays with flat top are observed to grown vertically on the substrate surface. In Fig. 1(a), the nanorods have a uniform length of 1 μm , with diameter range from 40 to 120 nm. The nanorods grown under ambient pressure show larger size with an equal length of 2 μm and diameters range from 200 to 300 nm, as shown in Fig. 1(b). EDX analyses demonstrate the nanorods grown under both conditions consist of zinc and oxygen element only (figures not given).

Fig. 2 show the XRD spectra of the as-synthesized samples, which reveal the nanorods are ZnO wurtzite structure with lattice parameters of $a = 0.325$ nm, $c = 0.520$ nm. Both samples are c -axis oriented. Especially for the sample grown under low pressure only [002] diffraction peak is observed in the spectra. For the sample grown under ambient pressure, very weak peaks related to other orientation appear, which can only suggest the orientation of the nanorods grown under ambient pressure is not as good as those grown under low pressure.

TEM images shown in Fig. 3 were explored to observe the nanorod microstructures. In both cases the nanorods have smooth surface and uniform size distribution from the root to the top. The SAED patterns and high-resolution TEM images in both cases illuminate a nanorod is single crystal, the interplanar spacing (inset of Fig. 3) is about 0.26 nm corresponding to the (002) plane of hexagonal ZnO, which indicates the growth direction of the nanorod is c -axial.

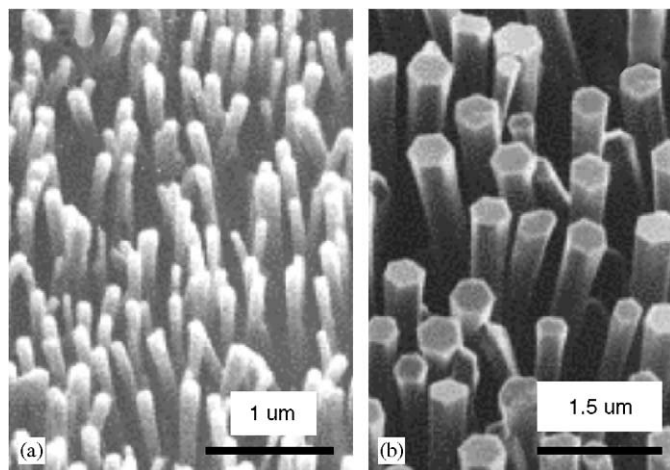


Fig. 1. FESEM images of nanorods grown (a) at low pressure and (b) under ambient pressure.

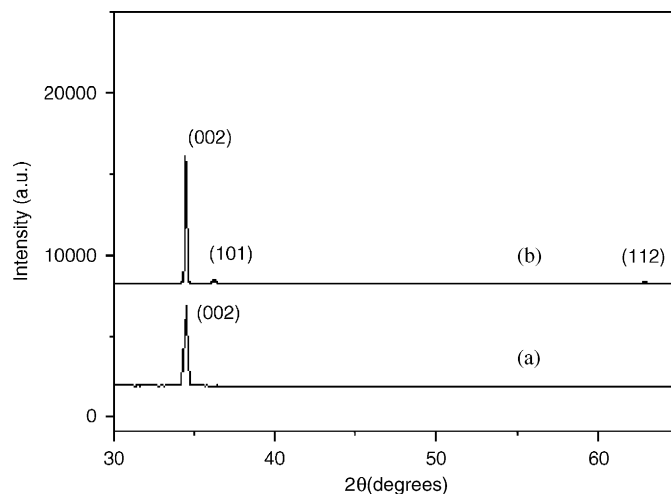


Fig. 2. XRD analysis of nanorods grown (a) at low pressure and (b) under ambient pressure.

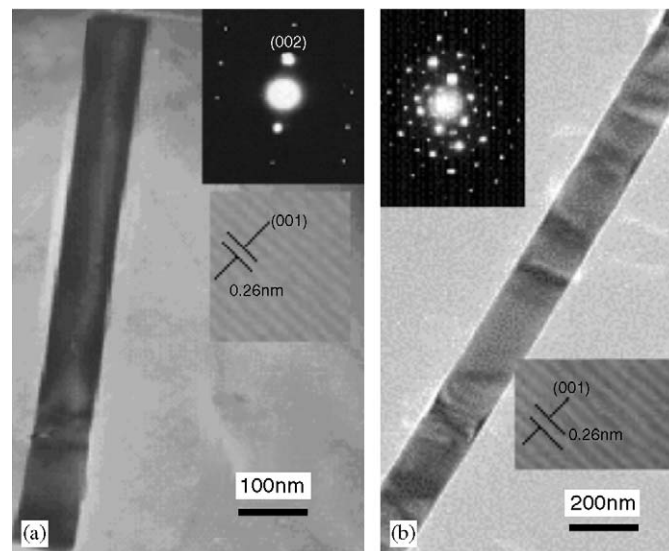


Fig. 3. TEM images of nanorods grown (a) at low pressure and (b) under ambient pressure.

The PL spectra (Fig. 4) of the nanorods grown under both conditions show a strong UV emission and a weak deep-level emission. The dominant UV emission, located at 379 nm, is the exciton recombination related near-band edge emission of ZnO and the deep-level emission usually results from the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy [8]. Since the nanorods were grown under low temperature and no catalyst was used, unintentional incorporation of metal impurities can be avoided and intrinsic defects such as oxygen vacancies are weak, correspondingly the deep-level emissions are weak. The intensity of the UV to visible emission of the sample grown under ambient pressure is larger than that of the sample grown under low pressure.

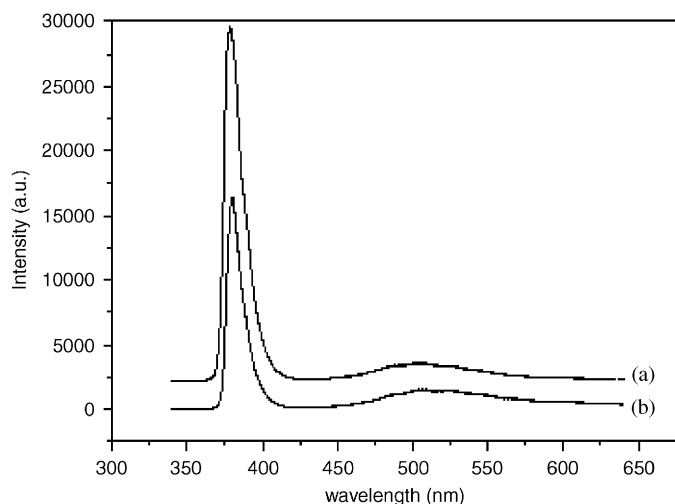


Fig. 4. PL spectra of nanorods grown (a) at low pressure and (b) under ambient pressure.

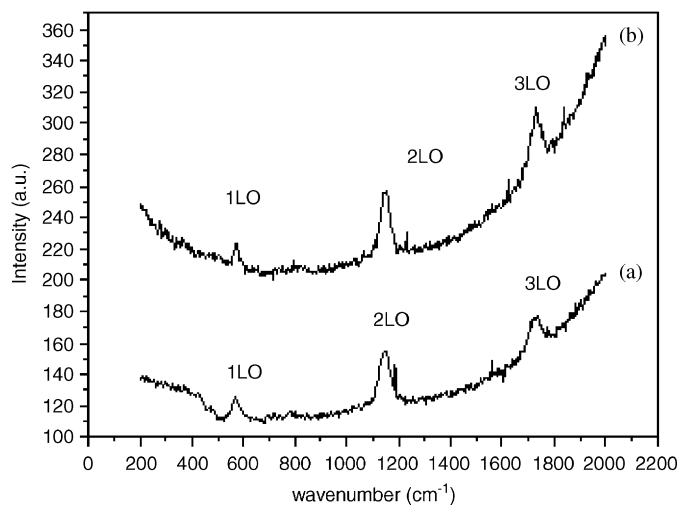


Fig. 5. Resonant Raman spectra of ZnO nanorods grown (a) at low pressure and (b) under ambient pressure.

To investigate the vibrational properties of the nanowires, the UV resonant Raman scattering were measured at room temperature (shown in Fig. 5), the energy of the laser line (325 nm) is about 440 meV higher than the band gap of ZnO, indicating a possibility that the laser line is in resonance with an interband electronic transition [9]. The observed Raman shifts centered at 571, 1144, 1723 and 571, 1146, 1729 cm^{-1} of the nanorods grown at low pressure and under ambient pressure, respectively, are both attributed to Raman A_1 LO phonon scattering and their overtones [10,11]. ZnO crystal material has large polaron coupling coefficient and a large phonon frequency. Hence enormous frequency shifts are observed. The larger Raman shifts of the nanorods grown under low pressure than that grown under ambient pressure demonstrate the nanorods grown at low-pressure possess larger deformation energy.

[11] The width of the multiphonon scatterings of the nanorods grown at low pressure of the 1LO, 2LO, 3LO phonons are 28, 43, and 63 cm^{-1} , respectively, while the line widths of the nanorods grown under ambient pressure of the 1LO, 2LO, 3LO phonons are 27, 33, and 61 cm^{-1} , respectively. All the ZnO multiphonon line widths are broader compared with the formula $\lambda \text{ (nLO)} = 9n \text{ cm}^{-1}$ [11]. The main reason for this may be attributed to oxygen deficiency and residual stress presented in that the nanorods [10]. From this point, we can deduce the nanorods grown under ambient pressure have less oxygen deficiency and stress than those grown under low pressure.

The growth mechanism of the nanorods can be described as the vapor–solid (V–S) process [12]. For the nanorods grown under low pressure, most of the zinc vapor was drained with the gas flow, leaving a small part of the zinc vapor that reached the substrate, nuclei and grew along the *c*-axis, according to ‘low energy’ principle. For the ones grown under ambient pressure, the gas flow was smooth, though the source was diluted by zinc oxide (which can avoid too high concentration of the source), the concentration was still high, when the desired temperature was reached, zinc evaporated from the mixture, and most of the zinc vapor reached the substrate to start the nanorods growth. So the size of the nanorods grown under this condition is larger than those grown under low pressure.

4. Conclusions

In conclusion, we obtained ZnO nanorod arrays both under low and ambient pressure by simple vapor–solid process. The hexagonal-shaped ZnO nanorod arrays without catalyst impurity will benefit further device fabrications based on ZnO nanostructures. And the nanorods grown at ambient pressure condition is much easier to control. We believe it brings up a convenient way to grow ZnO nanorod arrays using simple vapor–solid process under ambient pressure.

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