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Physical characterization of ZnO nanorods grown on Si from aqueous solution and annealed at various atmospheres

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High-density ZnO nanorods were vertically grown on Si coated with ZnO film (ZnO/Si substrate) from aqueous solution at low temperatures. The ZnO nanorods after annealed in various atmospheres still present good *c*-axis crystalline character but exhibit remarkable differences in photoluminescence (PL) properties. Enhancement of PL properties due to N_2-atmosphere annealing for ultraviolet emission can be attributed to the reduction of defect density because the nonparamagnetic singly ionized state (N^-) can easily occupy the oxygen vacancies as evidenced by Raman spectroscopy and electron paramagnetic resonance spectrometry. The extended x-ray absorption fine structure reveals that the annealing atmosphere shows no apparent influence on the deep-level defects of ZnO nanorods except that some ions are possibly trapped or adsorbed on the surface of the ZnO nanorods. © *2005 American Vacuum Society.* [DOI: 10.1116/1.2102967]

I. INTRODUCTION

Wide band gap semiconductors such as ZnO have attracted much attention because of their potential for optoelectronic devices in the blue and ultraviolet spectral regions due to its wide direct band gap of 3.37 eV and a relatively large exciton binding energy of 60 meV. In the recent years, one-dimensional (1D) nanostructures (nanowires or nanorods) are expected to further lower the lasing threshold because of quantum effects that result in the enhancement of density of states near the band edges and radiative recombination due to carrier confinement.[1] Different approaches have been used to synthesize 1D solid nanostructures including metal-organic-chemical vapor deposition method,[2] vapor-liquid-solid growth,[3] solution-liquid-solid method,[4] template-mediated growth method,[5] electron-beam lithography.[6] However, so far, no systematical studies were performed to investigate the effect of annealing atmospheres on the relationship between the structure and optoelectronic properties of the ZnO nanorods grown in liquid solution. Therefore, in this study, Raman spectroscopy, x-ray diffraction (XRD), electron paramagnetic resonance spectrometry (EPR), and extended x-ray absorption fine structure (EXAFS) technique will be used to characterize ZnO nanorods and investigate the effect of annealing atmosphere on the photoluminescence (PL) properties of ZnO nanorods.

II. EXPERIMENT

Both precursors of methenamine ($C_6H_{12}N_4$) and zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] were used for preparing the solution to grow ZnO nanorods (ZNs). The ZnO thin films were deposited on Si substrates by rf magnetron sputtering following our previous report.[7] The ZnO_f/Si substrates were then placed inside the aqueous solution at 75 °C for 10 h. After that, the substrates were removed from the aqueous solutions, rinsed with distilled water, and dried at room temperature overnight. After annealed at 850 °C in various atmospheres, the structural characteristics of the ZnO nanorods were analyzed by scanning electron microscopy (SEM/EDX, JEOL-6500F), and transmission electron microscopy (Philips Tecnai 20). The crystal structure was determined using x-ray diffraction (XRD) with CuKα radiation. Photoluminescence of the ZnO nanorods were performed by the excitation from 325 nm He–Cd laser at room temperature. Zinc K-edge x-ray absorption spectra were recorded at the wiggler beamline BL17C at NSRRC. The electron storage ring was operated at energy of 1.5 GeV and a current of 120–200 mA. The EXAFS function, so-called $\chi(k)$ data, was obtained by subtracting the post-edge background from the overall absorption data followed by normalization with respect to the edge step. A polycrystalline ZnO powder (Cerac, 99.9%) was used as a reference standard. The EPR measurements were performed using a *X*-band (9.776 GHz) Bruker spectrometer at room temperature. Raman spectroscopy was also conducted as a supplementary tool to identify structural information.

III. RESULTS AND DISCUSSION

A. Microstructure and phase evolution

Figure 1 shows the top-view field-emission scanning-electron microscope image of the ZnO nanorods annealed at 850 ° for 1 h in different atmospheres. It can be observed that some ZnO nanorods tend to be aggregated and lose the hexagonal shape especially for the sample annealed in O_2 and air atmospheres. The space group of the hexagonal wurzite ZnO belongs to C_{6V}^4 ($P6_3\,mc$) with two formula units per primi-

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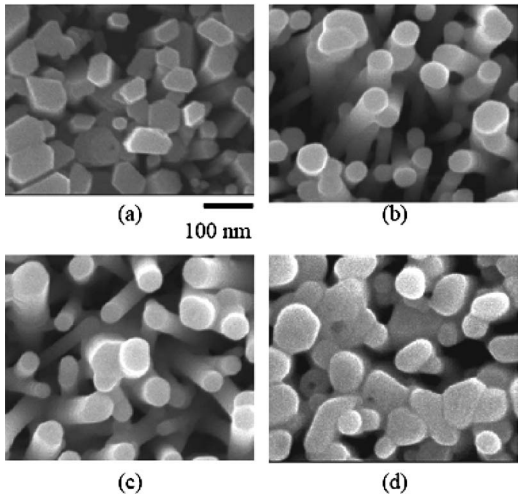

FIG. 1. Morphology of annealed ZnO nanorods. (a) Not annealed ZnO nanorods, and annealed in (b) N_2, (c) O_2, and (d) air at 850 °C/1 h.

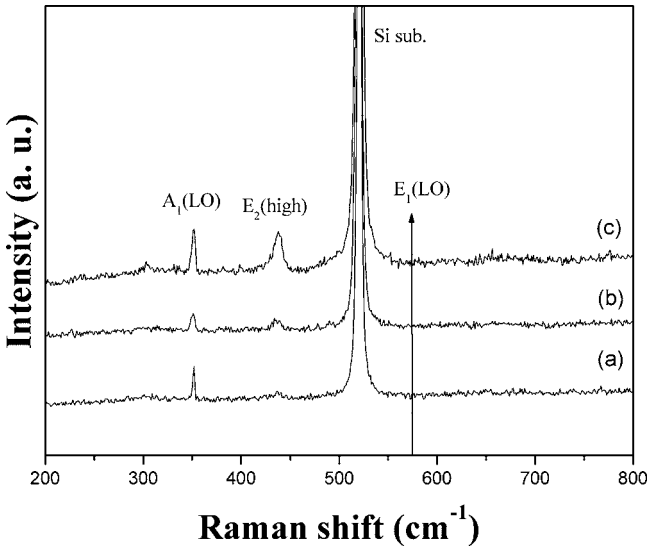

FIG. 2. Room-temperature Raman spectrum of the ZnO nanorods annealed in (a) N_2, (b) O_2, and (c) air atmospheres.

tive cell, all atoms occupying $2b$ sites of symmetry C_{3V}. Therefore, there are Raman-active phonon modes E_2 (low), E_2 (high), A_1 longitudinal optical (LO), A_1 transverse optical (TO), E_1 (LO), E_1 (TO). According to group theory, single-crystalline ZnO has three optical phonon modes at point of the Brillouin zone, classified as Raman active modes ($A_1+E_1+2E_2$), Raman silent modes ($2B_1$), and infrared active modes (A_1+E_1). E_2 mode is only Raman active and the $B1$ mode is inactive. Figure 2 shows the room-temperature Raman spectrum of the ZnO nanorods annealed at different atmospheres of (a) N_2, (b) O_2, and (c) air. The observed photon frequencies are E_2 (high)$=437$ cm^{-1} and A_1 (LO) $=351$ cm^{-1}. The spectrum was recorded with the incident light exactly perpendicular to the top surface of the ZnO nanorods arrays, that is to say, the incident light is parallel to the c-axial direction of the ZnO nanorods.[8] In this case, only both E_2 and A_1 (LO) modes are allowed, while the A_1 (TO) and E_1 (TO) modes are forbidden according to the Raman selection rules. Thus, the absence of the TO mode in the measurements further confirms that the ZnO nanorods are highly c-axis oriented.

The peak at 437 cm^{-1} is attributed to ZnO nonpolar optical phonons E_2 vibration mode, which is typical of the one of Raman active branches. The E_2 peak in Fig. 2 is more sharpened when the ZnO nanorods annealed in air compared to that in other conditions. According to the report of Tzolov *et al.*,[9] a significant increase in the defect number of Zn rich and oxygen vacancies enhances the Raman activity of this phonon mode. It means that the defect density of the ZnO nanorods annealed in air is more than that annealed in both O_2 and N_2 atmospheres.

Generally, at higher temperatures, Schottky disorder may occur as follows:

$$\text{Nill} \rightarrow V''_{\text{Zn}} + V^{\cdot\cdot}_{\text{O}}. \tag{1}$$

When the ZnO was annealed at a higher temperature, a large number of zinc element could be vaporized from the ZnO and induce the formation of defects as illustrated in Eq. (1). Therefore, it is possible for the formation of a certain amount of Zn interstitials and oxygen vacancies on the surface of the ZnO nanorods after air annealing.

When annealed in nitrogen atmosphere at a high temperature, the as-grown ZnO nanorods can be considered as annealed in reductionlike atmosphere (a much lower oxygen pressure). Although the oxygen could be evaporated from the ZnO and many oxygen vacancies were produced, in this condition, it is possible for a certain amount of nitrogen ions to occupy oxygen sites especially on the surface of the ZnO nanorods. Therefore, the defect density could be reduced for the ZnO nanorods after nitrogen annealing.

$$\text{ZnO} \xrightarrow{\text{N}_2} \text{Zn}_{\text{Zn}} + \text{N}_{\text{O}} + 1/2\text{O}_2. \tag{2}$$

A similar phenomenon was reported by Wang *et al.*, that with the incorporation of nitrogen into ZnO film, the intensity of E_2 peak decreased.[10]

However, if the annealing atmosphere was exchanged using the oxygen atmosphere for annealing the ZnO nanorods, the oxygen vacancies will be reduced according to Eq. (1). Therefore, the defect density can be also decreased, leading to a decreased E_2 peak intensity.

B. Spectroscopic characterization

Figure 3 shows the photoluminescence spectra of the ZnO nanorods annealed at different atmospheres (N_2, O_2, and air). The UV emission corresponds to the near band-edge emission, and the green emission peak is commonly referred to as a deep-level or trap-state emission. The green transition has been attributed to the singly ionized oxygen vacancy in ZnO and the emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy.[11] The spectrum is usually characterized by a sharp UV band and small green light emission. It was found that the ZnO nanorods annealed in N_2 atmosphere dis-

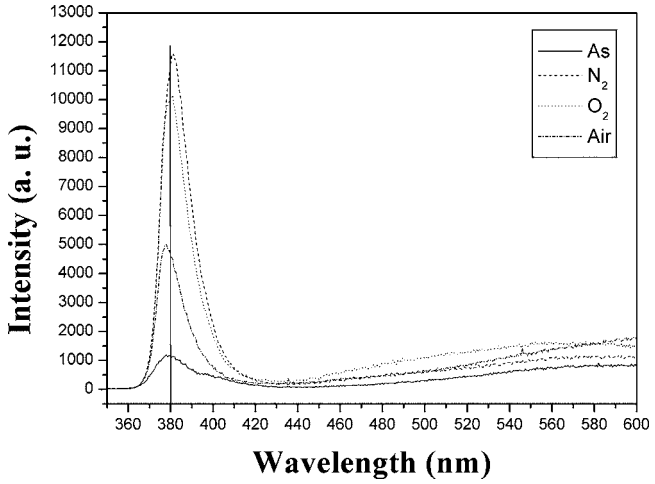

FIG. 3. PL spectra of as-grown ZnO nanorods annealed in various atmospheres at 850 °C for 1 h.

play a maximum UV peak because the near band edge may represent transition from singly ionized nitrogen acceptors to shallow donor. The nitrogen ions probably have the opportunity to be in the nonparamagnetic singly ionized state (N^-) for the N_2-annealed sample in the high temperature.[12] Furthermore, because the nitrogen has a smaller ionic radius than oxygen, it can be easily trapped in the ZnO nanorods to reduce intrinsic defects. Therefore, the surface defects can be reduced and thus the UV peak intensity can be further enhanced compared to the sample annealed in air.

The electron paramagnetic resonance spectrometry (EPR) is an effective method for investigating the electron spin state and the structure of the surface of nanosized crystallines. The ZnO is generally antimagnetic, as can be proved from theory or experiments; that is, the undoped ZnO does not have the EPR signal. However, the ZnO nanorods show a strong EPR signal with a g factor of 1.96. The $g \approx 1.96$ signal is attributed to singly ionized oxygen vacancy defects (V_O^+) in the ZnO matrix.[13] Qualitative observation of the

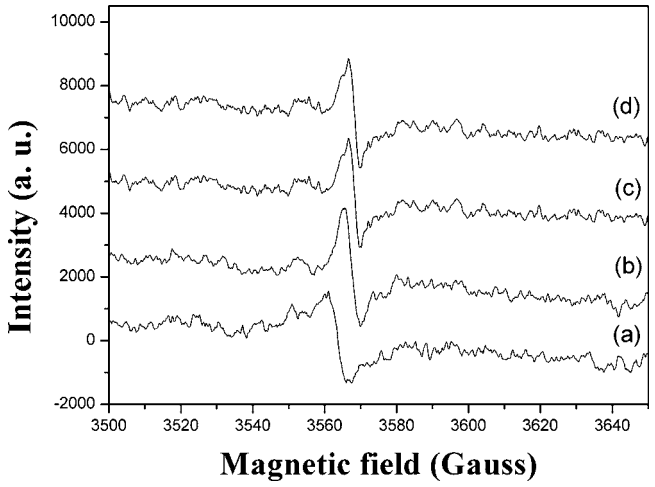

FIG. 4. EPR spectra of (a) as-grown and annealed ZnO nanorods in (b) N_2, (c) O_2, and (d) air at 850 °C/1 h.

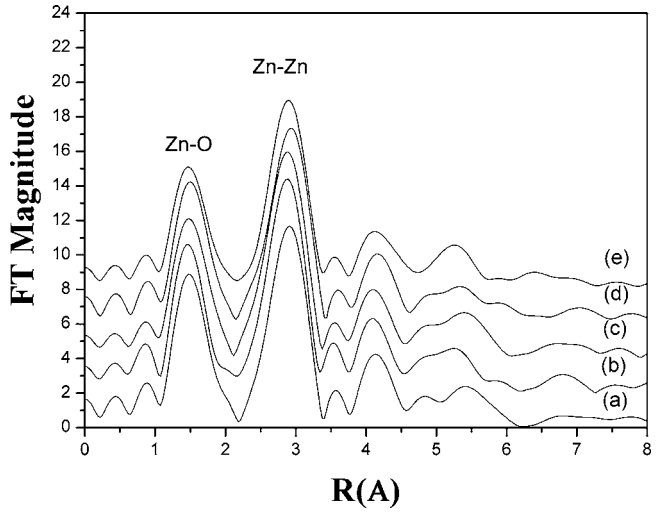

FIG. 5. Fourier transform of the EXAFS function at the Zn K edge for (a) as-grown and annealed ZnO nanorods annealed at 850 °C for 1 h in (b) N_2, (c) O_2, and (d) air atmosphere; (e) ZnO powder standard.

850 °C-annealed ZnO nanorods reveals that the EPR spectra are not significantly different for those samples annealed under different atmospheres as shown in Fig. 4. This may be attributed to the fact that the ZnO nanorods structure are not apparently changed compared to the as-grown sample at room temperature. However, from the oxygen vacancy defects (V_O^+), the intensity of the g factor (≈ 1.96) is $N_2 < O_2 <$ air, because the nitrogen ion in the annealed sample could be in the nonparamagnetic singly ionized state (N^-) which can easily occupy the oxygen vacancies.[12] This can further support the PL spectra of ZnO nanorods shown in Fig. 3. The ZnO nanorods annealed in N_2 atmosphere exhibit a weaker green emission peak than that in air atmosphere. In other words, a stronger UV peak was detected for the ZnO nanorods annealed in N_2 atmosphere.

Figure 5 shows pseudoradial distribution functions obtained from k^3-weighted Fourier transforms of the as-grown ZnO nanorods annealed at 850 °C for 1 h in various atmospheres. The local structural parameters, such as the interatomic distance, coordination number, and Debye–Weller factor are measurements of disorder of neighboring atoms around an absorbing atom that can be extracted from the EXAFS function. From the Fourier transform of the EXAFS function shown in Fig. 5, the first shell bond distance around Zn^{2+} is ~1.47 Å which is close to the Zn–O bond length (~1.47 Å) of a standard ZnO sample. A second intense peak, labeled Zn–Zn, is observed for ZnO. It was found that those peaks are not significantly different. This indicates that the local structure around Zn^{2+} ions in those samples is similar. In other words, the annealing atmosphere shows no apparent influence on the deep-level defects of ZnO nanorods except that some ions are possibly trapped or adsorbed on the surface of the ZnO nanorods.

IV. CONCLUSIONS

High-density ZnO nanorods can be vertically grown on Si substrate from aqueous solution via a simple low-

temperature process. After annealed in various atmospheres, the ZnO nanorods exhibit different PL spectra. A maximum UV emission was observed for the ZnO nanorods annealed in N_2 atmosphere which may be correlated with the decrease in defect density as evidenced in Raman and EPR. However, the EXAFS analysis demonstrates that the effect of annealing atmosphere on the deep-level defects of ZnO nanorods is confined in local surface area.

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