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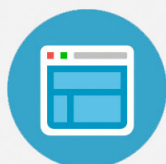
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# Luminescent and structural characteristics of ZnO nanorods fabricated by postannealing

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Well-aligned ZnO nanorods grown on silicon substrates buffered with ZnO film were postannealed at 200–1000 °C in various atmospheres. The optical properties of ZnO nanorods were much improved by annealing at high temperatures in both atmospheres of N<sub>2</sub> and O<sub>2</sub>. This improvement was ascribed to the decrease in structure defects as compared to as-grown ZnO nanorods. However, for the ZnO nanorods annealed in H<sub>2</sub>/N<sub>2</sub>, a stronger UV emission occurs at 600 °C; above that the UV emission rapidly disappeared, which was attributed to the collapse of the ZnO nanorods due to H<sub>2</sub> etching during a higher-temperature annealing in H<sub>2</sub>/N<sub>2</sub>. The crystallinity and optical properties of the ZnO nanorods can be controlled by postannealing treatment. © 2006 American Vacuum Society. [DOI: 10.1116/1.2163893]

## I. INTRODUCTION

ZnO has a wide band gap of 3.3 eV at room temperature, making it promising for potential applications in manufacturing electronic and optoelectronic devices, especially ultraviolet (UV) laser devices.<sup>1–3</sup> Recent investigations have demonstrated that directionally grown ZnO nanorods can effectively reduce the threshold power, achieving UV lasing emission at room temperature.<sup>4</sup> The photoluminescence (PL) spectra of ZnO typically exhibit UV and visible PL peaks. UV emission has been considered to be caused by exciton-related activities, but the exact mechanism of visible emission remains controversial.<sup>5</sup> Vanheusden *et al.* reported that the singly ionized oxygen vacancy is responsible for the green emission in zinc oxide<sup>6</sup> but it was also hypothesized that interstitial zinc and oxygen vacancies are the luminescent centers responsible for green luminescence.<sup>7</sup> It is well known that both physical characterization and optoelectronic properties are strongly influenced by the defect concentration of native defect in ZnO and this can be modified via thermal treatment under different atmospheres and annealing conditions.<sup>8</sup> Therefore, it is important to investigate the effect of postannealing on the crystallinity and optical properties of ZnO nanorods. The variation of structural and optical properties of ZnO nanorods with thermal annealing conditions will be discussed in detail in this work.

## II. EXPERIMENT

A ZnO-buffered layer (with a thickness of around 100 nm) was deposited on Si substrate by radio-frequency (rf) magnetron sputtering using 99.99% ZnO as the target. The ZnO nanorods were grown on the substrate. Then, the

ZnO-coated Si substrates were placed in an equimolar (0.01M) aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and hexamethylenetetramine (HMT) at 75 °C for 10 h. Subsequently, the substrates were removed from the aqueous solutions, rinsed in distilled water, and dried overnight at room temperature. After growth, the ZnO nanorods were annealed at 200–1000 °C for 30 min in different atmospheres of H<sub>2</sub>/N<sub>2</sub> (5%/95%), N<sub>2</sub>, and O<sub>2</sub> to investigate the effect of postannealing on the crystallinity and optical properties of ZnO nanorods. The structural characteristics of the ZnO nanorods were analyzed by scanning electron microscopy/energy-dispersive x-ray (SEM/EDS)(JEOL-6500F) and transmission electron microscopy (Philips Tecnai 20). The crystal structure was elucidated using Siemens D5000 x-ray diffraction (XRD) with Cu K $\alpha$  radiation and a Ni filter. The photoluminescence of the ZnO nanorods was measured from the excitation from a 325 nm He–Cd laser at room temperature.

## III. RESULTS AND DISCUSSION

Figure 1 plots the room-temperature photoluminescence spectra of the ZnO nanorods annealed under various conditions. Only two emission peaks at 377 nm (UV emission) and 595 nm (visible emission) were observed. It was found that UV emission intensities increase with annealing temperature, but the visible emission in postannealed samples tends to disappear, suggesting that the native defects or non-radiative recombination can be reduced by postannealing treatment in O<sub>2</sub> and N<sub>2</sub> atmospheres as shown in Figs. 1(a) and 1(b). However, the ZnO nanorods annealed in N<sub>2</sub> show stronger visible emission peaks compared to that annealed in oxygen atmosphere because the oxygen vacancies become the predominant point defects in N<sub>2</sub> atmosphere. In addition, a unique phenomenon was observed for the sample annealed in H<sub>2</sub>/N<sub>2</sub> atmosphere, as presented in Fig. 1(c). An optimal UV emission occurs at the 600 °C. It was believed that

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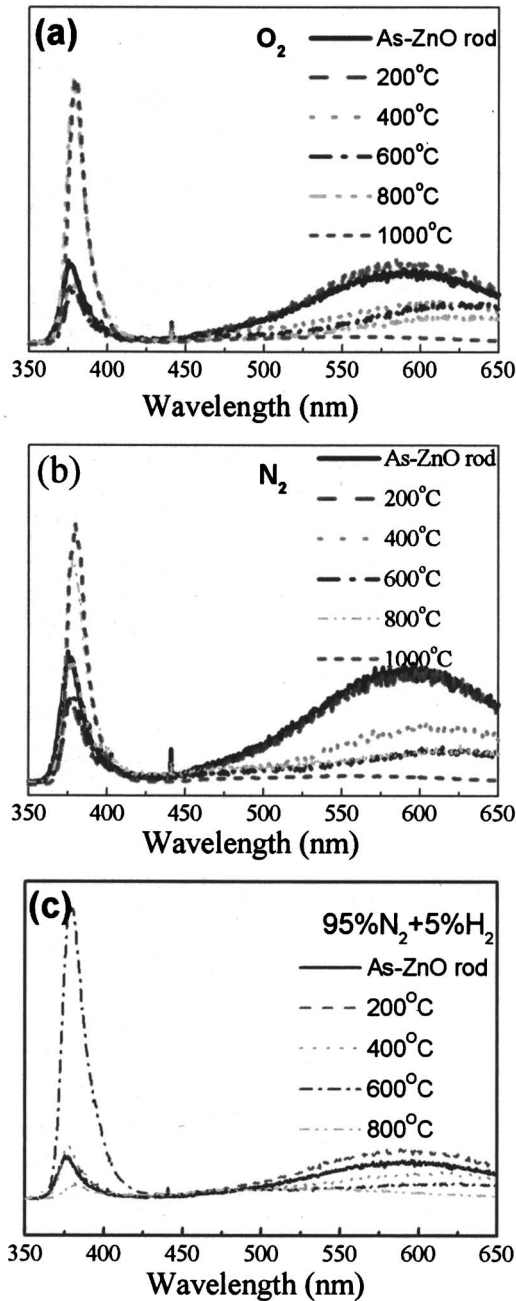


FIG. 1. Room-temperature PL spectra of ZnO nanorods annealed at various temperatures in (a)  $O_2$ , (b)  $N_2$ , and (c)  $H_2/N_2$  atmospheres.

$H_2/N_2$  treatment is able to passivate native defects or impurities that contribute to visible transition, because the hydrogen atoms can be situated in various lattice positions. However, when the sample was exposed to  $H_2/N_2$  at 800 °C, the UV emission almost disappeared. This marked change can be attributed to the fact that a high-temperature reduction environment of  $H_2/N_2$  could damage the crystal structure of the ZnO nanorods by surface etching.<sup>9</sup> It was also observed that the peak position of the longer-wavelength visible emission band shifted with different treatments. The peak position of the visible (deep level) emission is related to the predominant defects in the ZnO nanorods and both defects of zinc

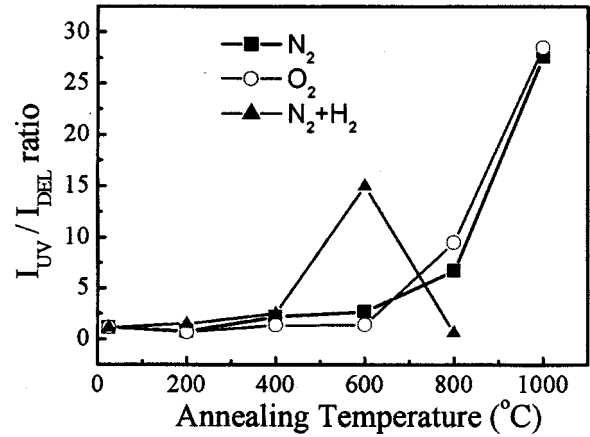


FIG. 2.  $I_{UV}/I_{DEL}$  of the annealed ZnO nanorods dependent on various annealing conditions.

interstitials and oxygen vacancies are strongly modified by changing annealing temperature and using different atmospheres.<sup>5</sup> The relative PL ratios ( $I_{UV}/I_{DLE}$ ) of the samples as a function of various atmospheres can be further summarized and are presented in Fig. 2, revealing that the improvement in the optical quality of postannealed ZnO nanorods is not only dominated by the annealing temperature but also by the annealing atmosphere.

Figure 3(a) shows that the as-grown ZnO nanorods are perpendicular to the substrate with a uniform length of 900–950 nm. When annealed at 600 °C in  $H_2/N_2$ , the cross-sectional morphology of the annealed ZnO nanorods in Fig. 3(b) is slightly different from that of the as-grown ZnO nanorods. It was found that the diameter of the annealed ZnO nanorods was locally necked, as shown in the set of Fig. 3(b). When the ZnO nanorods were annealed at 800 °C in  $H_2/N_2$ , the surface image in Fig. 3(c) shows that all the ZnO nanorods collapsed on the substrate, probably because of surface etching. These results may elucidate why the UV peak rapidly and suddenly disappeared at 800 °C in Fig. 1(c). In contrast, as the ZnO nanorods were annealed at 800 °C in both  $O_2$  and  $N_2$  atmospheres, the morphology of the ZnO nanorods remained almost unchanged as compared to that of the as-grown ZnO nanorods [Figs. 4(a) and 4(c)]. At 1000 °C in  $N_2$  and  $O_2$ , the surface morphology of ZnO nanorods changed from “rodlike” to irregular shape as shown in Figs. 4(b) and 4(d), perhaps because of the melting and regrowth of the nanorods.

High-resolution transmission electron microscopy (HR-TEM) was further used to study the ZnO nanorods annealed at 1000 °C in  $N_2$  to elucidate the variation in the local structure. Figure 5(a) reveals that the ZnO nanorods shortened to 300–400 nm, and became partially joined to their neighbors. The split diffraction spots in the central region of the selected area electron-diffraction (SAED) pattern suggest that the merged ZnO nanorods are not perfectly aligned in either the  $a$  (or  $b$ ) or  $c$  direction, as presented in the inset of Fig. 5(b). Moreover, HR-TEM images of the ZnO nanorods in Fig. 5(c) demonstrate that partial amorphous formed in the single-crystal ZnO nanorod. In addition, several lattice

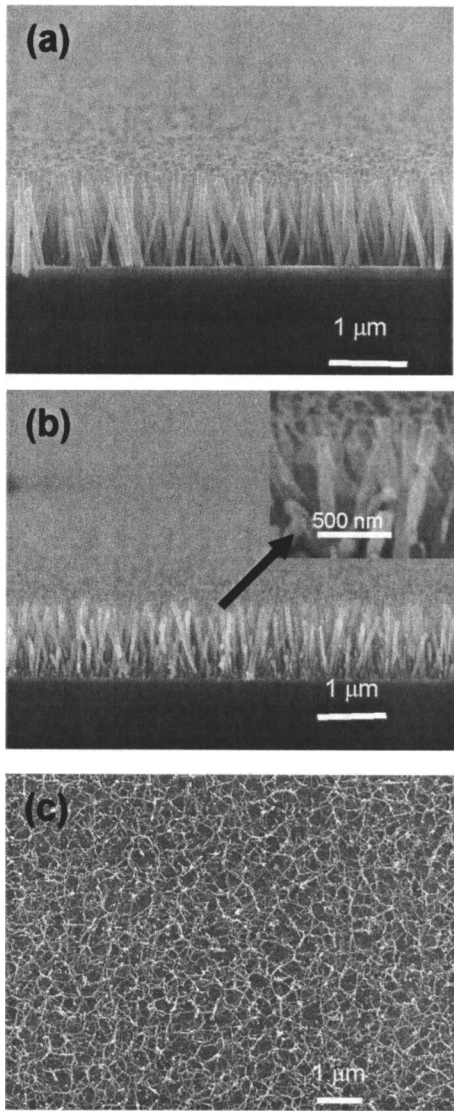


FIG. 3. SEM images of (a) the as-grown ZnO and annealed ZnO nanorods at (b) 600 °C and (c) 800 °C in  $H_2/N_2$ . The inset in Fig. 3(b) shows the ZnO nanorods become locally necking.

fringes (marked with arrows) appear in the edge of the ZnO nanorod in Fig. 5(d). Furthermore, according to x-ray photoelectron spectroscopy (XPS) analysis (not show here), the atomic ratio of O to Zn was approximately 0.9 for the nanorods and the single of  $O^{2-}$  ions in the oxygen-deficient regions were almost covered by the background signal, indicating that these amorphous regions appeared to contain some structural defects. The primary defect type in the region may be considered as oxygen vacancies as evidenced by PL spectra.

#### IV. CONCLUSIONS

The photoluminescence spectra indicate that the optical quality of the ZnO nanorods can be changed and controlled by annealing the ZnO nanorods in various atmospheres at different temperatures. For the sample annealed in both  $O_2$  and  $N_2$  atmospheres, the room-temperature UV emission of

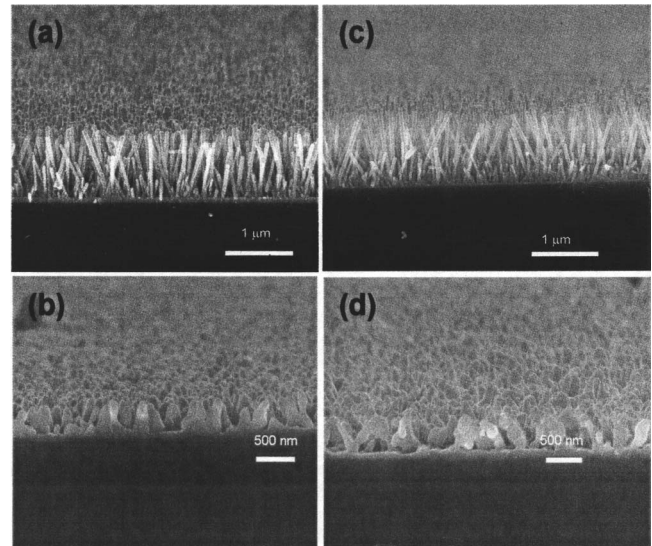


FIG. 4. SEM images of the annealed ZnO nanorods at (a) 800 °C and (b) 1000 °C in  $O_2$ , and (c) 800 °C and (d) 1000 °C in  $N_2$ .

the ZnO nanorods increases with the increase of temperature due to the reduction of structure defects. In contrast, in  $H_2/N_2$  atmosphere, a stronger UV emission occurs at 600 °C, above that the ZnO nanorods would collapse on the substrate and their optical property would deteriorate by  $H_2$  etching process during a higher-temperature annealing treat-

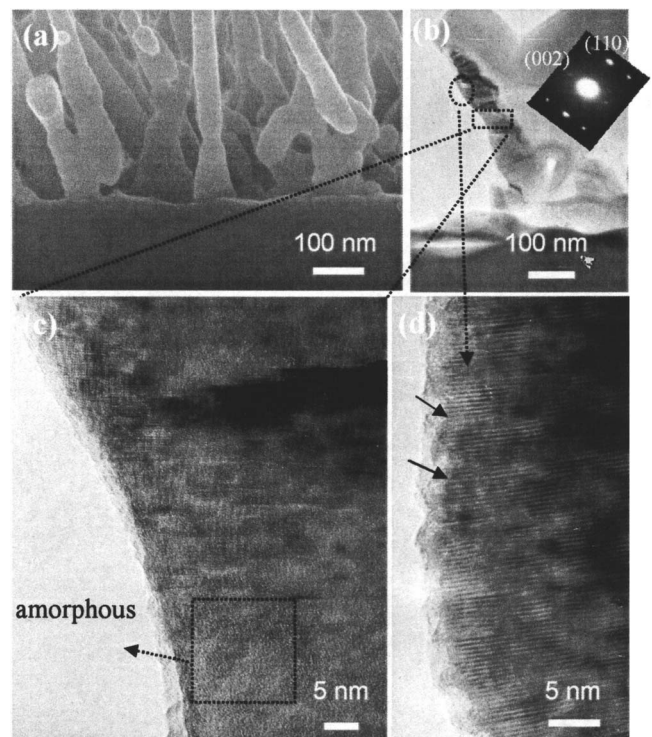


FIG. 5. (a) High-magnification SEM and (b) low-magnification TEM images of ZnO nanorods annealed at 1000 °C in  $N_2$  ambient with a corresponding diffraction pattern in the inset. A high-resolution TEM image of (b) showing the selected area in the (c) neck and (d) top of the ZnO nanorods.

ment. The above-mentioned results may suggest that the crystallinity and optical properties of the ZnO nanorods can be improved by postannealing treatment.

#### ACKNOWLEDGMENT

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