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Optical anisotropy of near band-edge transitions in zinc oxide nanostructures

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ABSTRACT

Optical anisotropy of the below and above band-edge transitions in three samples of well-aligned and tilted ZnO nanorods has been characterized using thermoreflectance (TR) and photoluminescence (PL) measurements in the temperature range between 30 and 300 K. The TR and PL spectra of the well-aligned nanorods with the largely top planes of {0 0 0 1} show considerable difference in energy with respect to those of the other tilted nanorods with the largely side planes of {1 0 $\bar{1}$ 0}. Optical-axial anisotropy of the defects and band-edge excitonic transitions in the well-aligned and tilted ZnO nanorods are observed. Temperature dependences of transition energies of the defect emissions and band-edge excitons for the ZnO are analyzed. The crystallinity for the as-deposited ZnO thin films is also discussed.

1. Introduction

ZnO is a direct semiconductor that derives more interests for application in wide band-gap optoelectronics. Among them, the zinc oxide nanostructures received much attention for being room-temperature lasers, light-emitting diodes, transparent field-effect transistors, ultraviolet photodetectors, and solar cells. Especially, the ZnO nanorods gain increasing interest since they offer a unique opportunity for fabrication of nanoscale opto-electronic devices such as field-emission device [1], field-effect transistor [2], and light-emitting device [3]. Although various potential applications for the ZnO nanorods have been proposed, the experimental understanding on the optical anisotropy of the ZnO nanocrystal with different crystal axes is still rather incomplete.

In this paper, three samples of two well-aligned and one tilted ZnO nanorods have been characterized using TR and PL. Optical anisotropy of the defect and excitonic transitions in between the two different types of well-aligned and tilted nanorods is observed. The origins for the near band-edge transitions of the ZnO nanorods are evaluated and discussed.

2. Experiment

Three samples of ZnO nanorods were grown on Si and sapphire by metallorganic chemical-vapor deposition (MOCVD). Different setting of substrate temperature may result in lower growth rate and higher sintering rate, which can change the direction of ZnO nanorods from well-aligned vertical to tilted structures during the MOCVD growth [4]. Displayed in Fig. 1 are the field-emission scanning electron microscope (FESEM) images of the as-grown ZnO nanorods on different substrates of (a) sample A (ZnO/Si), (b) sample B (ZnO/sapphire), and (c) sample C (ZnO/sapphire), respectively. The diameters of the nanorods are estimated to be about 20–120 nm. For samples A and B, the ZnO were grown as the individual nanorods largely along the [0 0 0 1] direction, whereas most of the as-grown nanorods were closely contacted and even bended and merged demonstrated in sample C. X-ray diffraction measurements also showed that samples A and B have more strong (0 0 0 1) peak intensity than that of sample C. PL and TR were performed in two distinct spectral measurement systems. The experimental

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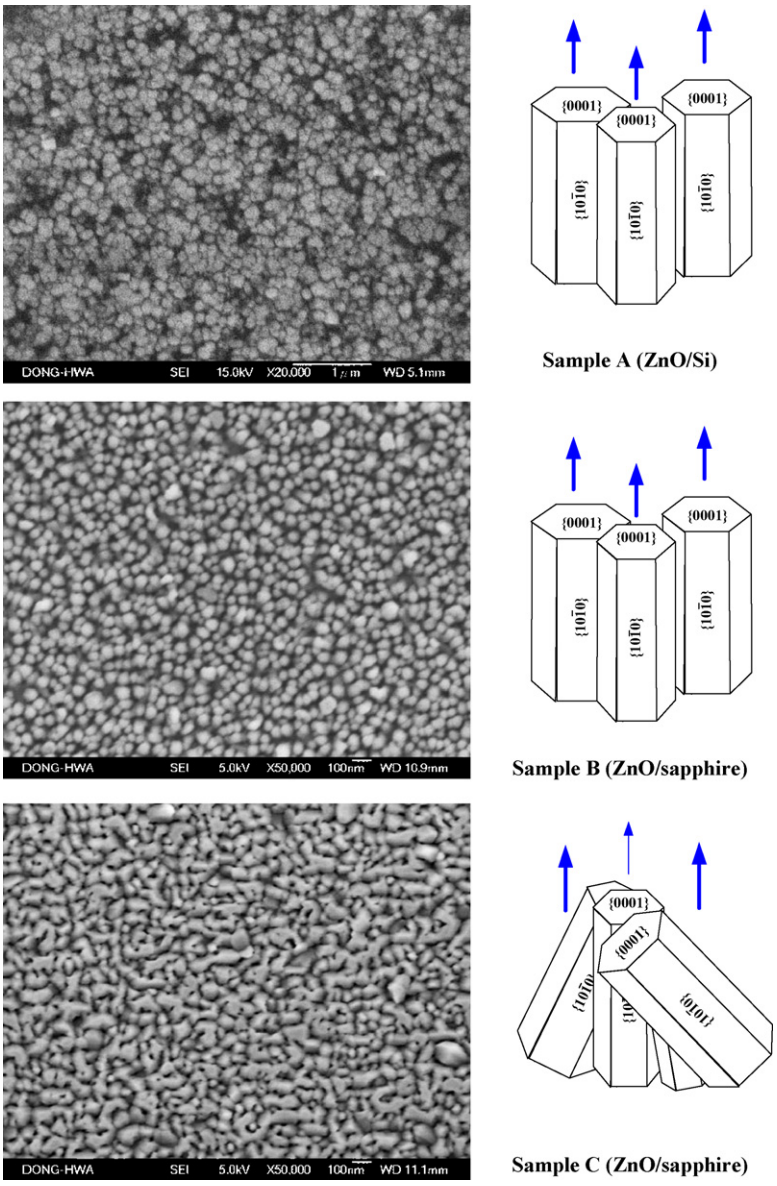

Fig. 1. The SEM images of three samples of two vertical-aligned and one tilted ZnO nanostructures. The light emissions from the surfaces of two different types of ZnO nanorods are also shown.

details of PL and TR measurements were described elsewhere [5]. Both measurements were done in the temperature range between 30 and 300 K.

3. Results and discussions

Temperature-dependent TR spectra of the well-aligned and tilted nanorods of (a) sample A, (b) sample B, and (c) sample C are shown in Fig. 2. The dashed lines are the experimental TR spectra and solid lines are the least-square fits to a first derivative Lorentzian line-shape function appropriate for the excitonic transitions [6]. The obtained transition energies of the band-edge free excitons (FXs) of A, B, and C indicate by arrows. As shown in the TR spectra of 30 K, the transition amplitudes for the FX series A–C in the well-aligned (samples A and B) and tilted (sample C) nanorods show different optical anisotropic behavior due to the geometric selection rule applied in different crystal planes of $\{0\,0\,0\,1\}$ or $\{1\,0\,\bar{1}\,0\}$. The optical-axial anisotropy is similar to that observed in the bulk ZnO crystal [7,8]. From Fig. 2, it is also found that all the excitonic transitions of FXs A_1, B_1, A_2, B_2, C_1, C_2, and C_∞ are clearly detected in the TR spectrum of sample C at 30 K while incomplete exciton series of A and B (missing A_1' and B_2') are observed in the TR spectrum of samples A and B. It also means that the binding energies and direct gaps for the A–C excitons in sample C can be analyzed from the Rydberg series using $E_n = E_\infty - R_y/n^2$. The values of binding energy R_y for the A–C excitons in sample C are determined to be 64, 60, and 61 meV. The threshold energies (i.e. E_∞) for the A–C excitons are determined to be 3.407, 3.421, and 3.481 eV at 30 K. As shown in Fig. 2(a), the TR spectra seem to contain two parts of contribution: one is coming from the A–C excitons, and the other is contributed by a broadened feature (~3.4 eV at 30 K). The broaden feature is coming from a E_0' transition in the silicon substrate. Also seeing from the TR spectra of 300 K in Fig. 2(a) and (b), for the well-aligned nanorods of sample A and sample B, the TR spectrum of sample B presents higher resolution and hence better crystallinity for the ZnO nanorods with respect to those shown in sample A. It is also evident from the SEM images of the well-aligned nanorods shown in Fig. 1, where sam-