

Influence of surface structure on the phonon-assisted emission process in the ZnO nanowires grown on homoepitaxial films

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We carried out temperature-dependent photoluminescence measurements to investigate the influence of surface roughness on the phonon-assisted emission of the surface-tailored ZnO nanowires (NWs). For the rough ZnO NWs, the observation of strong defect emission with vibration peaks by the exciton-phonon coupling reflects the presence of a high density of surface defects, resulting in a rapid shift to lower energy region of free exciton emission and a strong contribution of the first order phonon-assisted free exciton in ultraviolet emission. This investigation indicates that the surface defects associated with roughness have a significant influence on the phonon-assisted exciton emission. © 2009 American Institute of Physics.

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Recently, the photoluminescence (PL) properties of ZnO nanostructures, which usually exhibit ultraviolet (UV) emission and defect emission, have been intensively studied due to their potential applications in the nanoscale devices.^{1,2}

In the ZnO nanostructure systems, exciton-phonon interactions can differ significantly from the bulk counterpart and, in particular, their interactions have a significant influence on the optical properties in emission processes as well as electrical properties.³ In addition, the size- and surface-related effects on the emission properties of ZnO nanostructures are much stronger than those of ZnO bulk crystals due to the large surface-to-volume ratio.^{4,5} Recently, we reported that the optical and electronic transport properties of ZnO nanowires (NWs) are considerably influenced by roughness and NW size, which depend on the growth condition, growth substrates, stress/strain, catalysts, and other factors.⁶ The growth of such surface-tailored ZnO NWs facilitates the fabrication and fundamental study of nanoscale devices with unique optical and electrical properties. Therefore, it is essential to understand the role of roughness, which is associated with the surface defects, in the emission processes and electronic transport properties for the practical purpose of designing functional devices.

In this Letter, we investigate the influence of roughness in the emission process using the temperature-dependent PL spectra of the surface-tailored smooth and rough ZnO NWs grown on different homoepitaxial ZnO films. The results show that the presence of surface defects associated with roughness strongly affects the exciton emission process and the peak position in the UV emission band.

Vertically well-aligned ZnO NWs were grown on *c*-plane sapphire substrates coated with gallium-doped ZnO (GZO) and aluminum-doped ZnO (AZO) films by a vapor transport method without using metal-catalysts [Figs. 1(a) and 1(d)]. The general growth method for ZnO NWs has been described in detail elsewhere.⁶ The ZnO NWs were characterized using scanning electron microscopy (SEM)

and transmission electron microscopy (TEM). The micro-photoluminescence (μ PL) spectra were measured using a He-Cd laser (325 nm) as an excitation source at room temperature. Temperature-dependent PL measurements were carried out at temperatures of 10–300 K from the ZnO NWs transferred to a silicon wafer.

The low magnification TEM images show the distinct difference in the surface morphology between the ZnO NWs grown on two different substrates. Compared with the ZnO NWs grown on the GZO film [Fig. 1(b)], the ZnO NWs grown on the AZO film [Fig. 1(e)] are significantly rougher across the surfaces parallel to the growth direction and have a smaller diameter. The high-resolution TEM (HRTEM) images show the lattice fringes and the corresponding fast Fourier transformation patterns of ZnO NWs, which confirm that two types of ZnO NWs are single crystalline with a preferred growth direction of [0001].

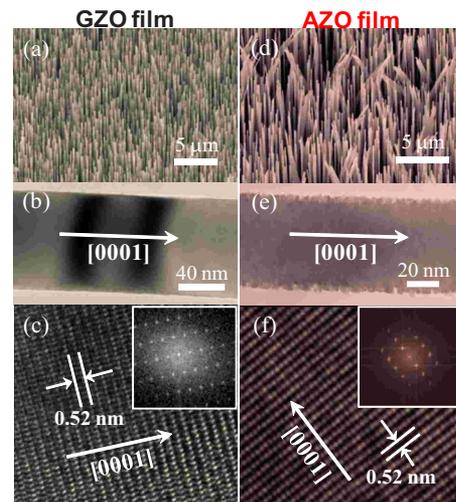


FIG. 1. (Color online) SEM [(a) and (d)] and TEM images [low magnification: [(b) and (e)] and high resolution: [(c) and (f)]] of ZnO NWs grown on two different types of substrates. The insets of (c) and (f) show fast Fourier transformation patterns corresponding to the lattice fringes from the NWs.

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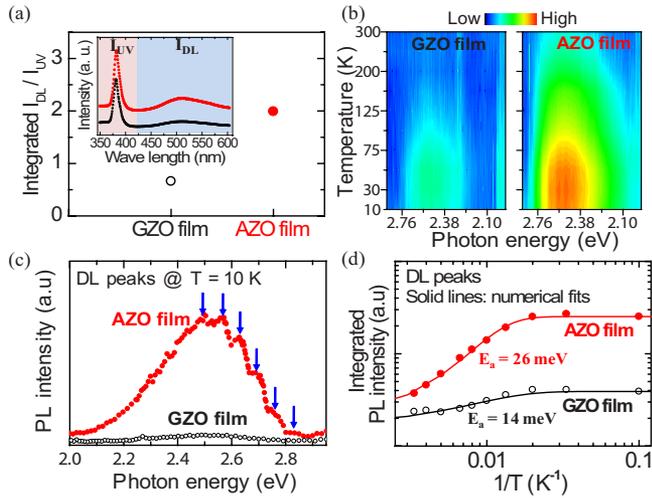


FIG. 2. (Color online) (a) PL intensity I_{DL}/I_{UV} ratios and μ PL spectra (inset) at room temperature, (b) PL contour plot of temperature-dependent defect emissions, and (c) PL spectra (at $T=10$ K) of the defect emissions of ZnO NWs grown on two different substrates. (d) Temperature dependence of intensity of the defect emission band. The solid lines show the results of parameter fitting to Eq. (1).

Figure 2 shows the influence of surface defects associated with roughness on the defect emission for two types of ZnO NWs. Figures 2(a) and 2(b) show the integrated PL intensity ratio (defect emission intensity to UV emission intensity I_{DL}/I_{UV}) and the PL contour plots of temperature-dependent defect emissions of two types of ZnO NWs, respectively. The rough ZnO NWs show a relatively strong defect emission, indicating that the rough ZnO NWs have a significantly greater number of surface defects.^{1,2} Interestingly, in the PL data on the high-energy side at low temperature for the rough ZnO NWs [Fig. 2(c)], we observed a series of sharp peaks with vibration characteristics related to the strong electron-LO-phonon coupling.^{7,8} In these vibration peaks, the energy separation between any two adjacent fine peaks was found to be 69–72 meV. Figure 2(d) shows an Arrhenius plot of the integrated PL intensity of the defect emissions. The observed temperature-activated behavior of defect emission can be described by

$$I_{DL} = \frac{I_0}{[1 + C \exp(-E_a/k_B T)]}, \quad (1)$$

where E_a is the activation energy, k_B is Boltzmann's constant, I_0 is the emission intensity at 0 K, T is the temperature, and C is a constant.^{9,10} The good fits (solid lines) yielded E_a values of ~ 14 and ~ 26 meV for the ZnO NWs grown on GZO and AZO films, respectively. All these results (Figs. 2) indicate the presence of different defect densities and different energy levels of defects as well as different types of defects between two types of ZnO NWs. Although the origin of the commonly observed defect emissions is still controversial, the defect emissions can originate from multiple defects and/or defect complexes involving oxygen vacancies, oxygen interstitials, Zn vacancies, Zn interstitials, and anti-site defects in ZnO NWs.^{1,2,10-12} These defects create shallow levels or deep trap levels in the bandgap, and may act as recombination centers by trapping charge carriers during photoexcitation.^{1,10,12} Therefore, the surface defects of ZnO NWs have a significant influence on their optical properties. Also the relatively large concentration of the surface defects

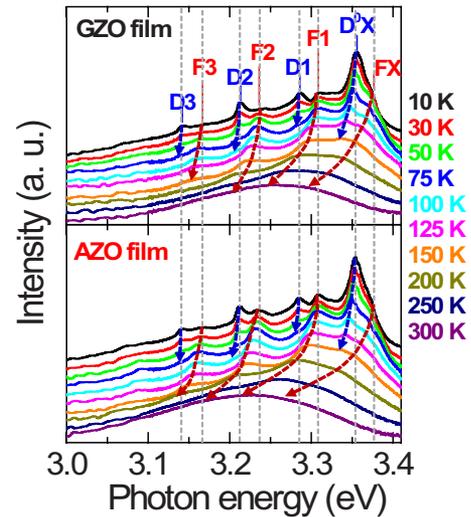


FIG. 3. (Color online) Temperature-dependent PL spectra of UV emissions showing the excitons and their LO-phonon replicas for ZnO NWs grown on two different substrates (see text for details).

in the rough ZnO NWs can play an important role in ZnO NW electronic devices.⁶

Figure 3 shows the UV emission spectra of two types of ZnO NWs for selected temperatures between 10 and 300 K. It is well known that the UV emission of ZnO nanostructures is commonly attributed to the direct recombination of excitons through an exciton-exciton scattering.¹ Despite many PL studies,^{1,13,14} the exact mechanisms of UV PL in ZnO nanostructures are still controversial. For example, the origin of UV PL in ZnO quantum dots (QDs), depending on the fabrication methods and ZnO QD surface quality, is explained by recombination of confined excitons or surface-bound ionized acceptor-exciton complexes.¹³ In particular, in undoped-ZnO nanowires, it is likely that the UV PL originates mainly from the recombination of free and donor bound excitons although there can exist acceptor defects, whereas in doped-ZnO nanowires, the UV PL is dominant mainly by the acceptor-bound exciton emission.¹⁴ For our two types of undoped-ZnO NWs, it can clearly be seen that a free exciton (FX), a neutral-donor-bound exciton (D^0X), and their LO-phonon replicas are located at the same energy positions (indicated by the vertical dashed lines) at low temperature. The LO-phonon replicas of FX and D^0X are labeled FX-1LO (F1), FX-2LO (F2), FX-3LO (F3), D^0X -1LO (D1), D^0X -2LO (D2), and D^0X -3LO (D3). For two types of ZnO NWs, the separation between them were observed as 70–72 meV, which corresponds to the characteristic energy of LO-phonon ($\hbar\omega_{LO} = \sim 72$ meV) in ZnO.^{7,15,16} These pronounced replicas originate from the strong exciton-phonon coupling effect due to the high ionicity and polarity of ZnO.¹⁵⁻¹⁷ The exciton emission shifts to lower energy with increasing temperature and the FX and its LO-phonon replicas become stronger in intensity relative to the D^0X -related peak. In addition, as temperature increases, the D^0X -related emissions decrease more rapidly than the FX-related emissions due to thermal dissociation of the donor-bound excitons, and thus the FX and its two phonon replicas (F1 and F2) emission remain at room temperature (Fig. 3). Therefore, all these results indicate that for the UV emissions of two types of ZnO NWs D^0X -related transitions are dominant at

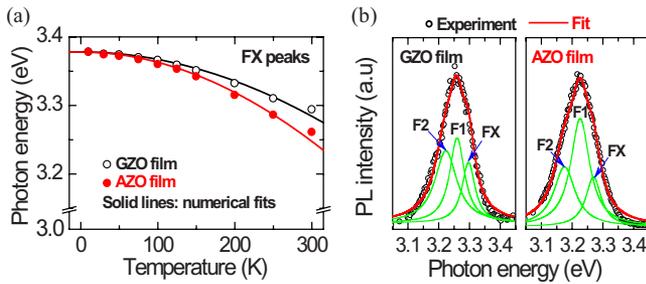


FIG. 4. (Color online) (a) Temperature dependence of FX peak position. The solid lines are the fitting curves of the experimental data by Varshni's formula [Eq. (2)]. (b) Lorentzian curves for the room-temperature UV emissions showing the contributions from the FX, F1, and F2 emission curves. The sums of the three Lorentzians are indicated by the solid curves (red).

low temperature, whereas FX-related transitions are dominant at high temperature.

Figure 4(a) summarizes the temperature-dependent FX peak positions in the range of 10–300 K for two types of ZnO NWs, which can be successfully described by Varshni's empirical formula,^{16,17}

$$E(T) = E(0) - \frac{\alpha T^2}{T + \beta}, \quad (2)$$

where α and β are constants and $E(0)$ is an exciton energy at $T=0$ K. The fits are plotted as solid lines through the data points in Fig. 4(a). The fitting parameters $E(0)$, α , and β are 3.378 eV, 0.0065 eV/K⁻¹, and 5940 K for the smooth ZnO NWs and 3.378 eV, 0.00778 eV/K⁻¹, and 5070 K for the rough ZnO NWs. The interesting finding here is that the energy position of the FX peak for the rough ZnO NWs shifts to lower energy region rapidly with increasing temperature than for the smooth ZnO NWs. This shift can be attributed to the influence of surface defects on exciton-phonon interaction as well as laser-induced heating in nanostructure ensembles.^{18–20} However, based on the TEM images and defect emissions (Figs. 1 and 2), it is more likely that the surface defects greatly contribute to the observed peak shift. Thus, in order to further investigate the effects of surface defects on the exciton-LO-phonon interaction, the shape of each room-temperature PL spectrum was fitted using Lorentzian functions, which are a good approximation to determine the relative contribution of FX, F1, and F2 peaks as shown in Fig. 4(b). It can clearly be seen that the emission of both smooth and rough ZnO NWs is composed of FX, F1, and F2 peaks merging into one broad peak. Interestingly, the relative contribution of the F1 line to the UV emission peak at room temperature is stronger in the rough ZnO NWs than in the smooth ZnO NWs, leading to a shift of the UV emission peak to lower energy region. These observations suggest that the crystal environment near surface in the rough ZnO NWs is different from in the smooth ZnO NWs. It has been known that in semiconductors with polarity and ionicity such as ZnO and GaN, the interaction between free excitons and LO-phonons can be mainly occurred by the Fröhlich interaction, which is a Coulomb interaction between electrons and the longitudinal electric field produced by the LO-phonons.^{21–23} In particular, the first order phonon-assisted free exciton emission (F1) in the Fröhlich interaction is vanishingly small for a perfect crystal due to parity

conservation.^{21–23} However, since the Fröhlich interaction can be mainly influenced by the incorporation of defects in a crystal, the strength of exciton-phonon coupling can be remarkably changed.^{21–23} Therefore, we believe that the strong contribution of F1 line for the rough ZnO NWs is attributed to a high density of surface defects associated with the rough surface of ZnO NWs, which is consistent with previous report.²³

In conclusion, we carried out temperature-dependent PL to investigate the influence of surface roughness on the phonon-assisted emission of the ZnO NWs. We found that the surface defects associated with roughness lead to a strong contribution of the first order phonon-assisted free exciton (FX-ILO) and a peak shift of the UV emission band at room temperature to lower energy region. This work will help us to understand the influence of the surface roughness on the optical emission properties as well as the transport properties for practically useful applications in ZnO material nanoscale devices.

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