

Anomalous blueshift in emission spectra of ZnO nanorods with sizes beyond quantum confinement regime

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Cathodoluminescence (CL) spectroscopy has been employed to study the electronic and optical properties of well-aligned ZnO nanorods with diameters ranging from 50 to 180 nm. Single-nanorod CL studies reveal that the emission peak moves toward higher energy as the diameter of the ZnO nanorod decreases, despite that their sizes are far beyond the quantum confinement regime. Blueshift of several tens of meV in the CL peak of these nanorods has been observed. Moreover, this anomalous energy shift shows a linear relation with the inverse of the rod diameter. Possible existence of a surface resonance band is suggested and an empirical formula for this surface effect is proposed to explain the size dependence of the CL data. © 2006 American Institute of Physics. [DOI: 10.1063/1.2211047]

Nanometer-sized materials have a high surface-to-volume ratio, which critically affects the electronic and optical properties, especially near the band gap of such materials.¹ The quantum confinement effect has often been inferred by a shift in the band gap of nanometer-sized materials with geometric dimensions smaller than a threshold.^{2–4} The effect is expected to be weak when the size of the nanomaterial exceeds that of the exciton Bohr radius, which is, for instance, about 2 nm for ZnO.⁵ This work presents the results regarding the anomalous energy shift of cathodoluminescence (CL) emission spectra of the ZnO nanorods with various diameters ranging from 50 to 180 nm. The “anomaly” refers to the unexpected large blueshift in the CL emission spectra of ZnO nanorods with the decrease of their diameters, even though the sizes (50–180 nm) considered here are far beyond the quantum confinement regime. A surface effect is thus proposed to explain the experimental data. The dependence of the electronic structure of the ZnO nanorods on their diameters is consistent with those determined by x-ray absorption near-edge spectroscopy (XANES) and scanning photoelectron microscopy (SPEM).⁶

The formation of the highly oriented ZnO nanorods on Si(100) substrates has been described in detail elsewhere.⁷ In brief, ZnO nanorods were formed via H₂ post-treatment of the ZnO films in the absence of metal catalysts. As-grown ZnO films were formed at a temperature of 400 °C using zinc acetylacetonate and oxygen in a two-temperature-zone furnace. H₂ post-treatments of the as-grown ZnO films were further performed at 400–450 °C and 200 Torr using a

H₂/N₂ flow. Diameter control of the ZnO nanorods has been achieved via varying the conditions of the H₂ post-treatments, such as the temperature, the ratio of the H₂/N₂ flow, and the period of the treatment. The size distribution of the nanorods was examined by a field-emission scanning electron microscope (FESEM) (JEOL 6700) and a high-resolution transmission electron microscope (HRTEM) (JEOL 4000-EX). Five samples were determined to have average diameters d of 50, 65, 100, 120, and 180 nm. These well-aligned nanorods had a hexagonal (wurtzite) structure and were oriented along the c axis with lattice spacing of 0.26 nm, as shown by the representative FESEM and HRTEM micrographs for the 50 nm nanorod in Figs. 1(a) and 1(b), respectively. CL measurements were made at room temperature for ZnO nanorods with diameters of 50–180 nm, using a Gatan Mono-CL3 system attached to the FESEM, operated with an accelerating voltage of 5 kV and a beam current of 3 nA.

Figures 2(a) and 2(b) show the typical FESEM and CL images, respectively, of a single ZnO nanorod with a diameter of 100 nm. Figure 2(c) presents the room-temperature

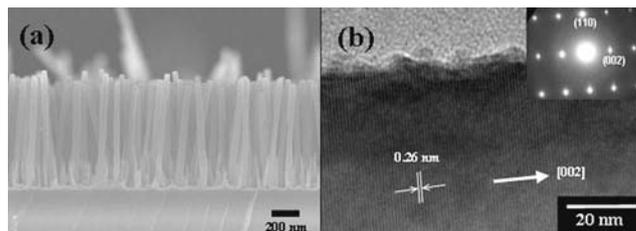


FIG. 1. (a) FESEM image of well-aligned ZnO nanorods. (b) HRTEM image and the corresponding electron diffraction pattern (inset) of ZnO nanorods.

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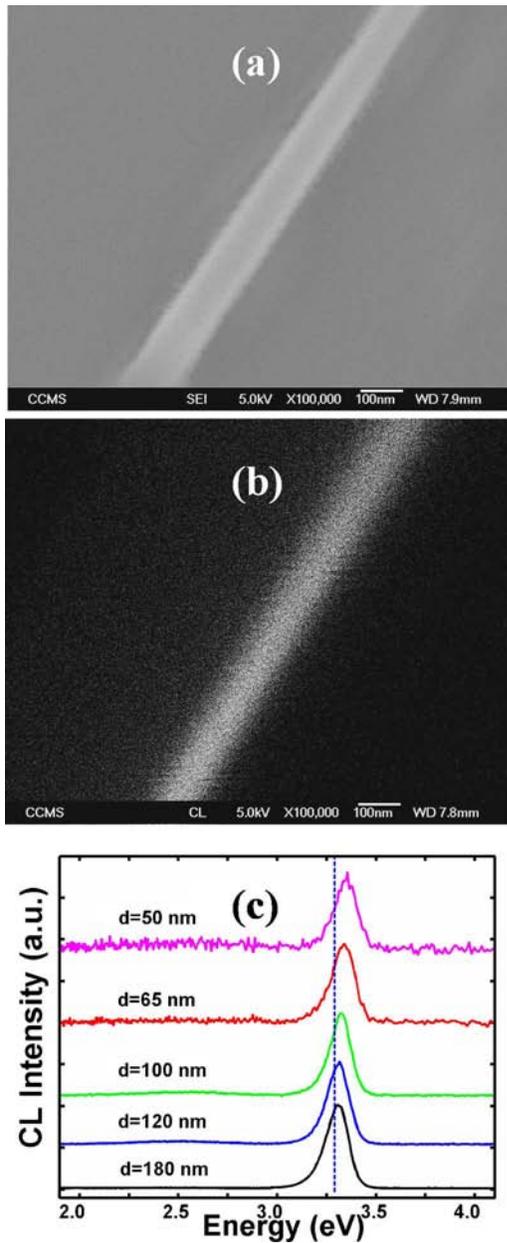


FIG. 2. (Color online) The (a) FESEM and (b) CL images of a single ZnO nanorod with a diameter of 100 nm. (c) Intensity normalized CL emission spectra of a single ZnO nanorod measured at room temperature, for diameters of 50, 65, 100, 120, and 180 nm. The dash line indicates the emission peak position of the bulk ZnO film, which is at 3.29 eV (Ref. 10).

CL spectra of a series of single ZnO nanorods with various diameters d ranging from 50 to 180 nm. The CL spectra exhibit a strong UV emission peak at about 3.3 eV, which is related to the direct recombination of photon-generated charge carriers (excitonic emission). An additional green band at ~ 2.5 eV caused by the intrinsic defects or oxygen vacancies in the ZnO is also observed,^{8,9} but is extremely weak, implying that the ZnO nanorods are almost defect-free and of high quality. Interestingly, the peak position of the UV emission shifts toward the higher energy side from 3.31 to 3.36 eV as the diameters of ZnO nanorods decrease from 180 to 50 nm. Notably, the energy of the UV emission peak of the single ZnO nanorod exceeds that of the bulk, which is at 3.29 eV. A similar blueshift of the emission peak in the CL spectra as the diameter is decreased from 120 to 80 nm in GaN nanorods has been reported by Kim

*et al.*¹¹ However, they controversially attributed their observation to the quantum confinement effect, even though the diameters of the GaN nanorods were far beyond the threshold. Various potential origins, such as localized strain, the interface effect, and defects may influence the electronic and optical properties of nanomaterials.^{12,13} Here, we suggest that the surface resonance effect for the relatively high surface-to-volume ratio of ZnO nanorods¹⁴ is primarily responsible for this anomalous blueshift in the CL peak position as the diameter is decreased.

It has been revealed from TEM measurement in Fig. 1(b) that the ZnO nanorods are oriented in the c -axis direction. Therefore, the tip surface is in either the $[0001]$ or $[000\bar{1}]$ orientation, which exhibit polar nature with Zn or O termination, respectively. The sidewall surface is in the $[10\bar{1}0]$ direction and is nonpolar with equal numbers of Zn and O atoms on the surface. Angle-resolved photoemission spectroscopy¹⁵ of the surface band structure of the ZnO $[10\bar{1}0]$ surface indicates that the O $2p$ dangling-bond band lies below the upper edge of the valence band. This suggests that the energy band is associated with surface resonance with no states within the band gap, which also agrees quite reasonably with the theoretical calculations.¹⁶ The ionic resonances occur at the ZnO $[10\bar{1}0]$ surface, resulting in the surface band structure lying well within the projection of the bulk valence and conduction bands. Similar surface effect has been reported in other II-VI semiconductors, such as CdS and CdSe $[10\bar{1}0]$ surfaces.¹⁷⁻¹⁹ The excitonic recombination from the surface band, and the subsequent emission of a photon, is associated with a higher energy than that of the bulk band. Accordingly, the overall CL emission spectra of ZnO nanorods can be regarded as the superposed radiative recombination signals from both the surface and bulk. In particular, when the ZnO nanorods have smaller diameters, their surface-to-volume ratios are high and the surface effect is expected to be stronger; the UV emission peak thus gradually moves toward higher energy in the CL spectra as the diameter of ZnO nanorods decreases, as displayed in Fig. 2(c).

A simple description based on the variation of the surface-to-volume ratio of ZnO nanorods with their diameter is proposed to elucidate the origin of the “anomalous” energy shift in the emission spectra. For a rod of height h and radius r , the surface-to-volume ratio R (considering only the sidewall surface) can be expressed as

$$R = \frac{V_{\text{surface}}}{V_{\text{bulk}}} = \frac{(2\pi rh)t}{\pi r^2 h} = \frac{2t}{r} = \frac{4t}{d}, \quad (1)$$

where t represents the effective thickness of the surface recombination layer. Surface recombination states can be associated only within the very few top monolayers. Hence, the contribution of surface recombination can be assumed to be effective within a certain diffusion length, i.e., a distance, t . According to our assumption, the energy shift of the CL emission peak depends on the change in the surface-to-volume ratio (R), which can be expressed as

$$\Delta E_g(\text{shift}) = E_g^{\text{CL}} - E_g^{\text{bulk}} \propto R = 4t/d, \quad (2)$$

where E_g^{CL} and E_g^{bulk} represent the CL emission energy and the bulk band gap of ZnO nanorods, respectively. Moreover, the CL energy shift, ΔE_g , also depends on ΔE_g^{s-b} , the energy

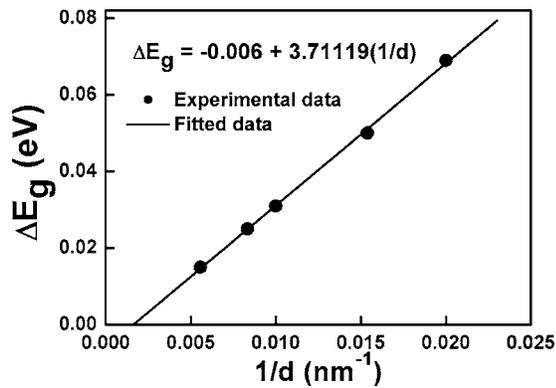


FIG. 3. Experimental (solid circle) and fitted data (solid line) of the energy shift, ΔE_g , of the CL emission peak energies as a function of $1/d$.

difference between the surface and bulk band gaps and can be expressed as

$$\Delta E_g(\text{shift}) = E_g^{\text{CL}} - E_g^{\text{bulk}} \propto \Delta E_g^{s-b} = E_g^{\text{surface}} - E_g^{\text{bulk}}, \quad (3)$$

where E_g^{surface} represents the surface band gap. Combining Eqs. (2) and (3), we can obtain

$$\Delta E_g(\text{shift}) = -\gamma + \Lambda/d, \quad (4)$$

where γ is a constant and $\Lambda = 4Ct\Delta E_g^{s-b}$ (C is a constant of proportionality). The constant γ can be used to determine the critical dimension of the nanorod, beyond which they will exhibit the bulk properties, so that no energy shift will be observed. Equation (4) is an empirical formula for the relation between the energy shift in ZnO nanorods with their size, which is in excellent agreement with the experimental data as depicted below.

Figure 3 shows the CL energy shift (ΔE_g), obtained from the CL spectra in Fig. 2(c), as a function of the inverse of d . A linear relationship is found to exist between ΔE_g and $1/d$ with a slope of 3.711. The linear fit in Fig. 3 results in zero-energy-shift diameter d_0 and γ of 620 nm and 0.006 eV, respectively. Hence, according to our description, ZnO nanorods having diameters $d \geq 620$ nm will exhibit the bulk properties and no energy shift will be observed. Below this critical dimension d_0 , the limited number of surface recombination centers becomes very effective and, with the decrease of dimensions, their contribution gradually becomes significant over the bulk part. Therefore, d_0 can be considered as the upper limit of the nanorod diameter, below which the energy shift will show a linear relation with the inverse of diameter, as per our description.

In a previous publication,⁶ the XANES and SPEM spectra yielded from the sidewall surface of ZnO nanorods with different diameters were presented. The analysis of the XANES spectra revealed increased numbers of O $2p$ and Zn $4p$ unoccupied states with the downsizing of the nanorods, which reflects the dominance of surface states when the diameter is decreased. In the SPEM spectra, all the spectra showed two peaks corresponding to the occupied O $2p$ -Zn $4sp$ states and O $2p$ -Zn $3d/4sp$ hybridized states, wherein higher intensity was observed for the nanorods with smaller diameters. The dominance of the surface density of states as

the diameter of the ZnO nanorods decreases is clearly correlated to the anomalous energy shift in their CL emission spectra. It should also be emphasized that this anomalous energy shift observed here is not originated from the strain of the sample. In fact, the x-ray diffraction (XRD) data in our earlier report⁶ showed a tensile stress along the growth direction, which will result in a redshift of the optical spectra. Therefore, the reported blueshift will be even more pronounced considering the presence of tensile stress in the nanorods.

In conclusion, anomalous energy shift in CL emission spectra of individual ZnO nanorods with diameters ranging from 50 to 180 nm was observed. This energy shift of nanorods with diameters far beyond the quantum confinement regime is attributed to the surface effect due to the increased surface-to-volume ratio. A linear relationship between the ΔE_g and $1/d$ is established, which is in excellent agreement with the experimental data. Meanwhile, the electronic structures determined by the XANES and SPEM measurements also support the surface effect beyond the quantum confinement regime.

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