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Indirect optical transition due to surface band bending in ZnO nanotubes

L. L. Yang^{1,2,a)} Q. X. Zhao,¹ M. Q. Israr,¹ J. R. Sadaf,¹ M. Willander,¹ G. Pozina,³ and J. H. Yang²

¹Department of Science and Technology (ITN), Linköping University, SE-60174 Norrköping, Sweden

²Institute of Condensed State Physics, Jilin Normal University, Siping, 136000, People's Republic of China

³Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

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ZnO nanotubes (ZNTs) have been successfully evolved from ZnO nanorods (ZNRs) by a simple chemical etching process. Two peaks located at 382 and 384 nm in the UV emission region has been observed in the room temperature photoluminescence (PL) spectrum of ZNTs since the surface band bending in ZNTs induces the coexistence of indirect and direct transitions in their emission process. In addition, a strong enhancement of total luminescence intensity at room temperature in ZNTs has also be observed in comparison with that of ZNRs. Both temperature-dependent PL and time-resolved PL results not only further testify the coexistence of indirect and direct transitions due to the surface band bending but also reveal that less nonradiative contribution to the emission process in ZNTs finally causes their stronger luminescence intensity. © 2010 American Institute of Physics. [doi:10.1063/1.3511345]

I. INTRODUCTION

One-dimensional (1D) nanostructures of ZnO has been widely investigated for a decade since the first report about ZnO nanowires was published in 2001.¹ It is obvious that 1D nanostructures of ZnO with a wide band gap ($E_g = 3.37$ eV) and a large exciton binding energy (60 meV) have become important nanomaterials owing to their special properties and potential applications in nanoscale electric and optoelectronic devices.^{1–7} During the past decade, different 1D ZnO nanostructures such as nanotubes,^{8–15} nanowires,¹ nanorods,¹⁶ nanobelts,^{17,18} tetrapods,¹⁹ and nanoribbons²⁰ have been successfully fabricated by different methods. Among these 1D structures, the tubular structures of ZnO become particularly important since numerous applications, such as dye-sensitized photovoltaic cells²¹ and bio/gas sensors,^{22,23} are required their high porosity and large surface area to fulfill the demand for high efficiency and activity. Although the synthesis of ZnO nanotubes (ZNTs) have been successfully realized by a few groups, the systematical investigations on their optical properties, especially temperature-dependent photoluminescence (PL) and time-resolved PL (TRPL), are still limited.^{13–15} It is well known that both temperature-dependent PL and TRPL are very sensitive tools for characterizing the radiative and nonradiative recombination process in the materials, which are very helpful in understanding the optical performance and mechanism of the materials. Therefore, the investigation on the temperature-dependent PL and TRPL properties of ZNTs are necessary and urgent to be done for prompting their applications.

To date, ZnO nanotubes has been synthesized by electrochemical method,^{10–12} low temperature solution method,^{8,9,13,14} vapor phase growth¹⁵ and so on. As a com-

mon knowledge, the reproducibility and control of growth in synthesis of ZnO nanostructures are a major issue. Among these methods, we prefer the simple chemical etching process to convert the ZnO nanorods (ZNRs) into ZNTs. One reason is that our technique to control the growth of ZNRs is already mature,^{24,25} which can provide the precursor with appropriate size and good crystal quality for the conversion of ZNTs. The other reason is that previously we have not only already investigated the optical properties of ZNRs in detail but also optimized their optical properties by effectively suppressing the surface recombination.^{26–29} In this way, it is relative easier for us to reveal the luminescence mechanism of ZNTs through comparing the optical properties between ZNRs and ZNTs.

In this paper, we use a simple wet chemical approach to fabricate the ZNRs and ZNTs. An anomalous stronger luminescence intensity can be observed from the room temperature PL spectrum of ZNTs in comparison with that of ZNRs. In order to reveal the optical mechanism of ZNTs both temperature-dependent PL and TRPL spectra of ZNTs and ZNRs have been investigated in detail.

II. EXPERIMENTS

The ZNTs used in this investigation were synthesized by two-step process, i.e., growth of ZNRs and chemical etching process for converting ZNRs into ZNTs. First, ZNRs were grown on Si substrates by the chemical bath deposition (CBD) method, which also includes a two-steps process, i.e., a substrate treatment prior to the CBD growth. The pretreatment of the substrates, by coating the substrate for different times with a 5 mM solution of zinc acetate dihydrate $[\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}]$ dissolved in pure ethanol, was used to control the diameter of ZNRs. In the CBD growth, the 0.1M aqueous solutions of zinc nitrate hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, 99.9% purity and 0.1M aqueous solutions of methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$, 99.9% purity) were first

^{a)}Electronic mail: lili.yang@itn.liu.se.

FIG. 1. (Color online) [(a) and (b)] SEM images of ZNRs and ZNTs with average diameter of 120 nm; [(c) and (d)] SEM images of ZNRs and ZNTs with average diameter of 280 nm. (e) TEM image of ZNTs average diameter of 280 nm. (f) HRTEM images corresponding to the region marked by the dotted box in (e).

prepared and mixed together. The pretreated Si substrates were immersed into the aqueous solution and kept at 93 °C for 3 h with sealing the beaker. Subsequently, two ZNRs samples with the diameter of 100 nm and 200 nm were, respectively converted into ZNTs by chemical etching process. The chemical etching process was carried out by suspending the ZNRs sample upside down in 100 ml aqueous solution of potassium chloride (KCl) with 5M concentration for 10 h at 95 °C.

Scanning electron microscopy (SEM) pictures were recorded by using a JEOL JSM-6301F. ZNTs were scratched off the substrate to analyze their structural properties by transmission electron microscopy (TEM) using a high-resolution microscope of JEM-2100HR from Japan operating at 200 kV. A drop of an ethanol suspension containing the nanotubes was deposited on a copper grid with lacey carbon for TEM observations. Room temperature PL measurements were carried out. A charge coupled device detector (Spectrum One) and monochromator HR460 from Jobin Yvon-Spex were used to disperse and detect the ZnO emission. Laser line with a wavelength of 266 nm from a diode laser (Coherent Verdi) pumped resonant frequency doubling unit (MBD 266) was used as excitation source. Time resolved PL was performed by using an excitation laser line from a frequency tripled sapphire:Ti laser emitting at 266 nm, a 0.3 m monochromator and a streak camera. The spectral resolution is about 1 meV and the time resolution is 7 ps. The measurements were done under weak excitation conditions (0.5 W/cm²).

III. RESULTS AND DISCUSSIONS

SEM and TEM were used to characterize the structures of ZNRs and ZNTs. SEM images of the as-grown ZNRs with 120 and 280 nm diameters and corresponding converted ZNTs are shown in Figs. 1(a)–1(d). The hexagonally shaped

nanorods uniformly cover the entire Si(001) substrate with high density as shown in Figs. 1(a) and 1(c). In Fig. 1(d), we can observe that all the ZNRs have been converted into nanotubes and the average wall thickness of the nanotubes is ~40 nm. Whereas, in Fig. 1(b), only small part of ZNRs just starts to be etched into nanotube shape. This phenomenon can be explained by the etching mechanism as discussed in Ref. 12. Elias *et al.* pointed out that the selective etching to form hollow structures should be related with initial crystal structure of ZNRs due to no assistant reagents existed in the etching solution. Two main factors will determine the conversion process from ZNRs to ZNTs. On one hand, the distinctive ZnO crystal habit exhibits a polar basal (000 $\bar{1}$)/top (0001) planes and six nonpolar (10 $\bar{1}$ 0) planes parallel to c-axis. The two polar planes are metastable due to the high surface energy, while the nonpolar (10 $\bar{1}$ 0) planes are the most stable ones due to the lower surface energy. So the Cl[−] ions might be preferentially adsorbed onto the top polar (0001) surface of the nanorods, which may result in the formation of a highly water-soluble zinc chloride complex such as ZnCl⁺, inducing the gradual dissolution of the nanorods core from the tip toward the bottom. As a whole effect, the etching rate is faster along polar plane than nonpolar planes. On the other hand, the defects in the ZNRs preferentially located near the crystal center, so that the preferential etching occurs from the center to form the tubular structures. It is well known that the smaller diameter of the nanorods, the more stable of the surface. Therefore, the ZNRs with less than 100 nm diameter are harder to be etched into tubular structures. Furthermore, the etching conditions can be optimized by varying the temperature, concentration of KCl solution as well as etching time to realize the transformation from nanorods to nanotubes. In addition, in our case, we would like to point out that the two ZNRs samples with diameter of 120 and 280 nm are obtained in the same chemical solution with growing for the same time. The details on controlling the size of ZNRs through manipulating seeding layer can be found in our earlier report.^{24,25} So the average defect concentration in both of them should be similar. Thus we can conclude that the defect concentration is not the main factor to influence the etching process, supporting the conclusion that the diameter plays an important role when ZNRs were converted into ZNTs. In the following experiments, ZNRs with 280 nm diameter and ZNTs with 280 nm diameter and 40 nm wall thickness were characterized to obtain the detailed information about structural and optical properties.

The structure of ZNTs is also characterized by TEM and high-resolution TEM (HRTEM). The TEM image in Fig. 1(e) shows the hollow structure of two single ZNTs. The HRTEM image in Fig. 1(f) was taken out at the top area marked by red dot box in Fig. 1(e). It clearly reveals a lattice spacing of 0.52 nm which corresponds to the distance of the (001) crystal plane of wurtzite ZnO (hexagonal structure with cell constants of $a=3.249$ Å and $c=5.206$ Å).

The room temperature PL spectra of ZNRs and ZNTs are illustrated in Fig. 2(a), both samples show a dominant UV emission at ~382 nm and a weak deep level emission

FIG. 2. (Color online) (a) Room temperature PL spectra of ZNRs and ZNTs. (b) Room temperature TRPL spectra of ZNRs and ZNTs.

(DLE) centered at ~ 520 nm. The UV emission band is related to a near band edge transition of ZnO, namely, the recombination of the free excitons (FXs) (376 nm). The room temperature PL peak position can be different, for example the transition energy from 375 (Ref. 30) to 383 nm,³¹ and the exact energy position depends on the contribution between the FX, FX-phonon replica and the transition between free electrons to acceptor bound holes.^{32–35} The DLE band had recently been identified and at least two defect origins (V_O and V_{Zn}) with different optical characteristics were claimed to contribute to this DLE band.^{36–38} As seen from Fig. 2(a), the integrated UV emission intensity of the ZNTs is about 3.8 factor higher in comparison with the ZNRs. Room temperature TRPL spectra have been illustrated in Fig. 2(b). It is obvious that the lifetime of ZNTs is about four times longer than that of ZNRs. The longer lifetime is inconsistent with observed enhancement of total PL intensity, indicating that the contribution of nonradiative process is different between ZNTs and ZNRs materials. In addition, we also find in Fig. 2(a) that, besides the intensity enhancement, the UV peak position (384 nm) of ZNTs exhibits a redshift compared with that of ZNRs (382 nm). In particular, a small left shoulder at 382 nm presented in the PL spectrum of ZNTs is obviously corresponding to the peak position of ZNRs, which can be clearly seen in the insert of Fig. 2(a). Through careful analysis, we propose that the surface band bending due to the large surface-to-volume ratio in ZNTs is responsible for all the abnormal phenomena in the PL spectrum of ZNTs.

Although as-synthesized ZnO nanostructures are usually n-type, both donor- and acceptorlike states are present within

the band gap.³⁹ In this case, some donor electrons in the conduction band will reduce their energy by occupying the acceptorlike surface states. A negative surface charge is generated, counterbalanced by a positive space charge that originates from ionized donors within a depletion width d away from the surface, such that overall charge neutrality is maintained. Consequently, a built-in electric field and the corresponding electrostatic potential will built up so that the energy bands bend upwards as they approach the surface and finally results in a surface depletion layer, which will strongly influence the PL properties of ZnO nanostructures.^{40–45} Since ZnO nanostructures usually have a very large surface-volume ratio, the band bending due to near surface on the PL process become more significant. The smaller a nanostructure is, the larger surface-volume ratio and stronger band bending effect it will have. In our case, the ZNTs with 40 nm wall thickness exhibit intrinsic high surface-to-volume ratio compared with ZNRs with 280 nm diameters. Hence, the band bending near surface will play an important role to influence the PL properties in ZNTs.

We can simply estimate band bending effect and its impact on PL of ZNRs and ZNTs in a detail. The width of the surface depletion region can be described as^{45,46}

$$d = \left[\frac{2\epsilon_{ZnO}\epsilon_0\Phi_S}{e^2N_D^+(T)} \right]^{1/2}, \quad (1)$$

where ϵ_{ZnO} is the relative dielectric constant of ZnO, ϵ_0 is the permittivity of vacuum, Φ_S is the height of potential barrier, e is the electronic charge, and $N_D^+(T)$ is the temperature-dependent activated donor concentration, which can be described as follows:

$$N_D^+(T) = \frac{N_D}{1 + 2 \exp\left(\frac{E_F - E_D}{k_B T}\right)}. \quad (2)$$

Using $N_D^+(T) \sim 10^{17} \text{ cm}^{-3}$ at room temperature, $\epsilon_{ZnO} \sim 8.7$, and Φ_S is of the order of 0.5 eV,⁴⁴ the calculated width of depletion region is ~ 69 nm. In our case, the ZNTs have been converted from ZNRs. Therefore, to make it easy, we assume that the donor concentration, permittivity and potential barrier height for ZNTs are the same as that in the original ZNRs. That is to say, ZNRs and ZNTs have the same width of depletion region. If $D > 2d$, both the depletion region and nondepletion region can exist in the nanostructure, as shown in Fig. 3(a). It is obvious that the ZNRs with ~ 280 nm diameter fit this situation well. If the nanostructure diameter $D < 2d$, however, the nanostructure will be thoroughly depleted, as shown in Fig. 3(b). Since the wall thickness of ZNTs is only ~ 40 nm, it should belong to this case.

Under laser excitation, the photogenerated electrons and holes will be created. But they will be separated and swept in opposite directions by the built-in electric field. For ZNRs, as shown in Fig. 3(a), the photogenerated electron-hole pairs created deeply within the bulk of ZNRs have to diffuse through the bulk before reaching the surface depletion region. Since the photogenerated minority holes have a shorter diffusion length than the much more numerous majority elec-

FIG. 3. (Color online) Sketch of the energy band of the ZNRs and ZNTs with different type of surface depletion region. (a) ZNRs is partially depleted (b) ZNTs is thoroughly depleted.

trons in ZNRs, all of them will radiatively recombine with electrons before they can reach the surface depletion region. Therefore, although the depletion region exists in ZNRs, as shown in Fig. 3(a), the chance of indirect recombination (E_{ID}) is quite smaller. So the direct radiative recombination (E_D) in the bulk materials is the dominating recombination channel. On the contrary, in the case of ZNTs as shown in Fig. 3(b), since the nanostructure will be thoroughly depleted, the photogenerated electrons and holes already in the surface depletion layer can be effectively separated and accumulated at the edge of conduction band and valence band without radiative recombination in the diffusion process. Besides, if the energy difference between E_{ID} and E_D is smaller (in our case only ~ 17 meV) than the thermal excitation energy of carriers ($KT \sim 25$ meV) at room temperature, both indirect E_{ID} and direct E_D recombination will contribute to the UV emission, which finally result in two emission peaks in the PL spectrum of ZNTs (384 and 382 nm) and the peak located at 382 nm is corresponding to the peak position of ZNRs, as seen in Fig. 2. Usually, the existence of indirect radiative recombination will strongly suppress the emission intensity due to reduced electron-hole wave function overlapping. However, in our case, the PL intensity of ZNTs is much higher than that of ZNRs. As mentioned above, the ZNTs are evolved from ZNRs so that the average defect concentration inside the ZNTs and ZNRs should be same. Besides, the surface recombination of ZNRs has been effectively suppressed as reported in our previous paper.²⁹ Even for the TRPL spectra obtained from ZNTs in Fig. 2(b), the decay exhibit a single exponential curve, which apparently indicates no surface recombination exist in the ZNRs.²⁶⁻²⁹ Hence, we can reach the conclusion that, under the identical excitation conditions, the nonradiative recombination contribution to the emission process in ZNTs is much less than that in ZNRs, which will be further proved in the following experimental results.

To support the effect of surface band bending theory on the PL properties of ZNRs and ZNTs, we further studied the temperature evolution of UV emission. The temperature-dependent PL measurements were performed between 80 and 300 K, which has been illustrated in Fig. 4. The spectrum for each temperature is displaced vertically for clarity. As observed in Fig. 4(a), the dominant peak at 3.362 eV is known as the donor bound exciton (D^0X) emission.^{47,48} The emis-

sion observed at 3.378 eV on the higher energy shoulder of the D^0X peak is assigned to the FX emission.^{47,48} The variations in D^0X and FX peak position with the increase in measurement temperature are illustrated by the dot curves in Fig. 4(a). It is obvious that the exciton emission shifts to lower energy and the FX become gradually stronger in intensity relative to the D^0X peak with increasing temperature. In addition, as temperature raises, the D^0X emission decrease rapidly than the FX emission due to thermal dissociation of the donor bound excitons. Thus, the FX emission finally becomes prominent when the temperature is above 200 K. In the contrast, although the variation in peak shape and intensity for ZNTs in Fig. 4(b) is quite similar to that of ZNRs in Fig. 4(a), the peak is obvious much broader for the former one since both indirect FX (FX_{ID}) and direct FX (FX_D) transitions coexist in the emission process as discussed above in Fig. 3. However, it is hard to investigate the variation in FX and D^0X in indirect and direct transition separately when the temperature is lower than 150 K, since the D^0X play the dominant role in the emission process. But it can be observed that at least two peaks contribute to the PL spectrum measured above 150 K in Fig. 4(b). In particular, when temperature reaches up to 200 K, the separation of two peaks become obvious. Hence, we assume that they independently come from indirect FX_{ID} and direct FX_D transitions. Then, we use Gauss function to deconvolute all the experimental curves

FIG. 4. (Color online) Temperature-dependent PL spectra for (a) ZNRs and (b) ZNTs.

FIG. 5. Temperature-dependent photon energy of FX_{ID} and FX_{D} . Inset is the energy difference between FX_{ID} and FX_{D} .

into FX_{ID} and FX_{D} peaks. As shown in Fig. 4(b), the variation in FX_{D} peak position located at higher energy is illustrated by the black dot curve. While, the red dot curve reveals the variation in FX_{ID} peak position. The photon energy of FX_{ID} and FX_{D} as the function of the temperature is summarized in Fig. 5. The energy difference between FX_{D} and FX_{ID} is also illustrated in the insert of Fig. 5. It can be seen from both Fig. 4(b) and insert in Fig. 5 that the energy difference between FX_{D} and FX_{ID} become bigger with increasing the temperature. As we know that FX_{ID} transition is related to the surface band bending, with increasing the temperature, more and more electron bound to donors are thermally dissociated into free carriers. So the Fermi level will move upward to the conductive band. As a result, the band bending increases and photon energy of FX_{ID} transition decreases, which finally results in the bigger energy difference between FX_{D} and FX_{ID} at higher temperature.

In addition, we can also observe from Fig. 4 that the intensity quenching behavior of ZNRs and ZNTs are quite different. Grabowska *et al.* pointed out that the quenching behavior of band edge emission is very important in evaluating the effect of nonradiative centers in ZnO nanostructure materials.^{49,50} Under optical excitation, two competitive carrier quenching processes exist in the materials, one is radiative and the other is nonradiative. Nonradiative recombination rates are generally thermally activated. If there is only one nonradiative recombination channel, one can obtain^{49,50}

$$I = I_0 [1 + a \exp(-E_a/kT)], \quad (3)$$

where I is the PL intensities, a is the process rate parameter, k is the Boltzmann constant, and E_a is the activation energy.

Figure 6 shows the integrated PL intensity of ZNRs and ZNTs as a function of reciprocal temperature. All the experimental results have been fitted with Eq. (3) to extract the activation energy. The fitting curves and the corresponding fitting formulas have been illustrated in the Fig. 6. The activation energy of the temperature quenching is evaluated to be about ~ 58 meV for ZNRs. The average activation energy of the temperature quenching is evaluated to be about ~ 74 meV for ZNTs. Lin *et al.* points out that the lower activation energy is mainly due to the existence of more nonradiative contributions in the materials, which also can be deduced from Eq. (3).⁵⁰ Therefore, we can conclude that more nonradiative recombination contribute to the emission process in ZNRs than that in ZNTs. This is also consistent

FIG. 6. (Color online) Reciprocal temperature-dependent entire intensities of the ZNRs and ZNTs. The formulas and the solid lines in the figure are the result of simulation.

with the results shown earlier, i.e., longer lifetime and stronger PL intensity in ZNTs in comparison with ZNRs.

PL intensity is sensitive to radiative and nonradiative recombination lifetimes, τ_{R} and τ_{NR} , respectively. To further prove that more nonradiative contribution in ZNRs than ZNTs, we utilized TRPL technique to get the lifetime information. The temperature evolution of decay curves from ZNRs and ZNTs are shown in Fig. 7. All the results obtained can be satisfactorily fitted by a single exponential decay function: $I(t) = I_0 \exp(-t/\tau)$, where τ is the decay time constant. The fitting values of τ for ZNRs and ZNTs as the function of temperature are summarized in Fig. 8.

Generally, the PL decay rate of a semiconductor includes two components, i.e., radiative and nonradiative decay rates with a relationship of $\tau_{\text{PL}}^{-1} = \tau_{\text{NR}}^{-1} + \tau_{\text{R}}^{-1}$, where τ_{PL} , τ_{NR} , and τ_{R} are the time constants of PL, nonradiative and radiative decay, respectively.^{51,52} The measured effective PL decay τ_{PL}

FIG. 7. (Color online) Temperature-dependent TRPL spectra of ZNRs (a) and ZNTs (b). All the logarithmic decay behaviors have been fitted by a single exponential function of $I(t) = I_0 \exp(-t/\tau)$. The solid lines in the figure are the fitting curves.

FIG. 8. The fitted decay time constants τ from ZNRs and ZNTs as a function of temperature.

will strongly depend on relative value of nonradiative τ_{NR} and radiative time τ_R . As summarized in Fig. 8, we can see that the life time is only around 8–16 ps in the whole temperature range for both ZNTs and ZNRs. Zhang *et al.* reported an exciton radiative lifetime of about 340 ps measured at 4.3 K in ZNRs fabricated by a vapor transport method.⁵³ Recently, Mohanta *et al.* revealed an exciton radiative lifetime of about 432 ps in ZNRs prepared by metal organic chemical vapor deposition.⁵⁴ Our results are even shorter than that (70 ps) from the samples prepared by the other low temperature (90 °C) aqueous chemical growth technique.⁵⁵ Apparently, the value of τ in our case is so much shorter compared to other reports on the ZNRs. Therefore, we can incipiently conclude that nonradiative recombination process dominates the life time in our case. The further evidence can be obtained from temperature-dependent exciton lifetimes. If the recombination process was dominated by nonradiative channels, the lifetime would decrease with increasing temperature, since the nonradiative channels would play a more important role with temperature. As shown in Fig. 8, decay time constant τ of ZNRs and ZNTs first decreases with temperature until 100–150 K and then slightly increases when the temperature further increases up to 300 K. This behavior is similar to the results obtained by Robin *et al.*,⁵⁶ which can be explained by a thermal quenching of the nonradiative recombination due to a limited number of nonradiative defects. As increasing the temperature below 150 K, the donor bound excitons are thermalized into free carriers or FXs gradually, which enlarge the carrier quantity trapped by the nonradiative centers. That is also to say, more nonradiative recombinations contribute to the emission process as the temperature increasing from 80 to 150 K. However, the number of nonradiative centers is limited after all. When all the nonradiative centers have been occupied by the carriers, the decay time reaches the minimum. When the temperature further increases from 150 to 300 K, the limited number of nonradiative centers and the exciton band will be thermally redistributed, which reduces the occupation probability of the nonradiative states and slightly increases the decay time. On the basis of the discussion above, we can conclude that nonradiative recombination does play the dominated role in the emission process in our ZNTs and ZNRs samples.

In addition, it is also worth to note that the value of τ from ZNTs is apparently longer than that from ZNRs as

shown in Figs. 7 and 8. In principle, the decay time of indirect transition should be longer than that of direct transitions due to reducing overlapping of electron-hole wave function.⁵⁷ Without taking into account of nonradiative recombination process, we should expect a longer decay time for ZNTs. However, as we discussed above, in our case the nonradiative recombination process become a dominating factor to determine the measured decay time τ_{PL} , the observed slight longer decay time in ZNTs means less nonradiative contribution to its emission process.

IV. CONCLUSIONS

ZNTs have been successfully evolved from ZNRs by a simple chemical etching process. The results of room temperature PL reveal that indirect and direct transitions coexist in the emission process of ZNTs due to the surface band bending. Moreover, the integrated UV emission intensity of the ZNTs is about 3.8 times higher than that of the ZNRs at room temperature. Both temperature-dependent PL and TRPL results not only further testify the coexistence of indirect and direct transitions due to the surface band bending, but also reveal that less nonradiative contribution in ZNTs which induces the stronger luminescence intensity in the PL spectra of ZNTs. These results will stimulate more investigation on ZNTs and finally pave a way for ZNTs in the application of photoelectronic devices.

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- ¹M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science* **292**, 1897 (2001).
- ²Z. L. Wang and J. H. Song, *Science* **312**, 242 (2006).
- ³M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. D. Yang, *Nature Mater.* **4**, 455 (2005).
- ⁴X. Zhang, Y. Zhang, J. Xu, Z. Wang, X. Chen, D. Yu, P. Zhang, H. Qi, and Y. Tian, *Appl. Phys. Lett.* **87**, 123111 (2005).
- ⁵H. Faber, M. Burkhardt, A. Jedaa, D. Kalbalein, H. Klauk, and M. Halik, *Adv. Mater. (Weinheim, Ger.)* **21**, 3099 (2009).
- ⁶C. H. Liu, J. A. Zapien, Y. Yao, X. M. Meng, C. S. Lee, S. S. Fan, Y. Lifshitz, and S. T. Lee, *Adv. Mater. (Weinheim, Ger.)* **15**, 838 (2003).
- ⁷M. Willander, L. L. Yang, A. Wadeasa, S. U. Ali, M. H. Asif, Q. X. Zhao, and O. Nur, *J. Mater. Chem.* **19**, 1006 (2009).
- ⁸L. Vayssieres, K. Keis, A. Hagfeldt, and S. E. Linquist, *Chem. Mater.* **13**, 4395 (2001).
- ⁹H. D. Yu, Z. P. Zhang, M. Y. Han, X. T. Hao, and F. R. Zhu, *J. Am. Chem. Soc.* **127**, 2378 (2005).
- ¹⁰L. F. Xu, Q. Liao, J. P. Zhang, X. C. Ai, and D. S. Xu, *J. Phys. Chem. C* **111**, 4549 (2007).
- ¹¹G. W. She, X. H. Zhang, W. S. Shi, X. Fan, J. C. Chang, C. S. Lee, S. T. Lee, and C. H. Liu, *Appl. Phys. Lett.* **92**, 053111 (2008).
- ¹²J. Elias, R. Tena-Zaera, G. Y. Wang, and C. Lévy-Clément, *Chem. Mater.* **20**, 6633 (2008).
- ¹³Q. J. Yu, W. Y. Fu, C. L. Yu, H. B. Yang, R. H. Wei, M. H. Li, S. K. Liu, Y. M. Sui, Z. L. Liu, M. X. Yuan, G. T. Zou, G. R. Wang, C. L. Shao, and Y. C. Liu, *J. Phys. Chem. C* **111**, 17521 (2007).
- ¹⁴Y. H. Tong, Y. C. Liu, C. L. Shao, Y. X. Liu, C. S. Xu, J. Y. Zhang, Y. M.

- Lu, D. Z. Shen, and X. W. Fan, *J. Phys. Chem. B* **110**, 14714 (2006).
- ¹⁵Y. J. Xing, Z. H. Xi, Z. Q. Xue, X. D. Zhang, J. H. Song, R. M. Wang, J. Xu, Y. Song, S. L. Zhang, and D. P. Yua, *Appl. Phys. Lett.* **83**, 1689 (2003).
 - ¹⁶L. Vayssieres, *Adv. Mater. (Weinheim, Ger.)* **15**, 464 (2003).
 - ¹⁷Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science* **291**, 1947 (2001).
 - ¹⁸W. Z. Wang, B. Q. Zeng, J. Yang, B. Poudel, J. Y. Huang, M. J. Naughton, and Z. F. Ren, *Adv. Mater. (Weinheim, Ger.)* **18**, 3275 (2006).
 - ¹⁹Y. Qiu and S. Yang, *Adv. Funct. Mater.* **17**, 1345 (2007).
 - ²⁰X. Fan, M. L. Zhang, I. Shafiq, W. J. Zhang, C. S. Lee, and S. T. Lee, *Adv. Mater. (Weinheim, Ger.)* **21**, 2393 (2009).
 - ²¹Q. F. Zhang, C. S. Dandeneau, X. Y. Zhou, and G. Z. Cao, *Adv. Mater. (Weinheim, Ger.)* **21**, 4087 (2009).
 - ²²K. Yang, G. W. She, H. Wang, X. M. Ou, X. H. Zhang, C. S. Lee, and S. T. Lee, *J. Phys. Chem. C* **113**, 20169 (2009).
 - ²³Z. H. Jing and J. H. Zhan, *Adv. Mater. (Weinheim, Ger.)* **20**, 4547 (2008).
 - ²⁴L. L. Yang, Q. X. Zhao, and M. Willander, *J. Alloys Compd.* **469**, 623 (2009).
 - ²⁵L. L. Yang, Q. X. Zhao, M. Willander, and J. H. Yang, *J. Cryst. Growth* **311**, 1046 (2009).
 - ²⁶Q. X. Zhao, L. L. Yang, M. Willander, B. E. Sernelius, and P. O. Holtz, *J. Appl. Phys.* **104**, 073526 (2008).
 - ²⁷L. L. Yang, Q. X. Zhao, M. Willander, J. H. Yang, and I. Ivanov, *J. Appl. Phys.* **105**, 053503 (2009).
 - ²⁸L. L. Yang, Q. X. Zhao, M. Willander, X. J. Liu, M. Fahlman, and J. H. Yang, *Appl. Surf. Sci.* **256**, 3592 (2010).
 - ²⁹L. L. Yang, Q. X. Zhao, M. Willander, X. J. Liu, M. Fahlman, and J. H. Yang, *Cryst. Growth Des.* **10**, 1904 (2010).
 - ³⁰Y. Chen, N. T. Tuan, Y. Segawa, H. Ko, S. Hong, and T. Yao, *Appl. Phys. Lett.* **78**, 1469 (2001).
 - ³¹W. I. Park, S. J. An, G. C. Yi, and H. M. Jang, *J. Mater. Res.* **16**, 1358 (2001).
 - ³²B. P. Zhang, N. T. Binh, K. Wakatsuki, Y. Segawa, Y. Kashiwaba, and K. Haga, *Nanotechnology* **15**, S382 (2004).
 - ³³K. Maejima, M. Ueda, and S. Fujita, *Jpn. J. Appl. Phys., Part 1* **42**, 2600 (2003).
 - ³⁴Q. X. Zhao, M. Willander, R. E. Morjan, Q. H. Hu, and E. E. B. Campbell, *Appl. Phys. Lett.* **83**, 165 (2003).
 - ³⁵W. I. Park, Y. H. Jun, S. W. Jung, and G. C. Yi, *Appl. Phys. Lett.* **82**, 964 (2003).
 - ³⁶Q. X. Zhao, P. Klason, M. Willander, H. M. Zhong, W. Lu, and J. H. Yang, *Appl. Phys. Lett.* **87**, 211912 (2005).
 - ³⁷T. M. Børseth, B. G. Svensson, A. Y. Kuznetsov, P. Klason, Q. X. Zhao, and M. Willander, *Appl. Phys. Lett.* **89**, 262112 (2006).
 - ³⁸P. Klason, T. M. Børseth, Q. X. Zhao, B. G. Svensson, A. Y. Kuznetsov, P. J. Bergman, and M. Willander, *Solid State Commun.* **145**, 321 (2008).
 - ³⁹T. Heinzel, *Mesoscopic Electronics in Solid State Nanostructures* (Wiley-VCH, Weinheim, 2007), p. 76.
 - ⁴⁰I. Shalish, H. Temkin, and V. Narayanamurti, *Phys. Rev. B* **69**, 245401 (2004).
 - ⁴¹J. D. Ye, S. L. Gu, F. Gin, S. M. Zhu, S. M. Liu, X. Zhou, W. Liu, L. Q. Hu, R. Zhang, Y. Shi, and Y. D. Zheng, *Appl. Phys. A: Mater. Sci. Process.* **81**, 759 (2005).
 - ⁴²X. L. Wu, G. G. Siu, C. L. Fu, and H. C. Ong, *Appl. Phys. Lett.* **78**, 2285 (2001).
 - ⁴³B. Lin, Z. Fu, and Y. Jia, *Appl. Phys. Lett.* **79**, 943 (2001).
 - ⁴⁴Z. M. Liao, K. J. Liu, J. M. Zhang, J. Xu, and D. P. Yu, *Phys. Lett. A* **367**, 207 (2007).
 - ⁴⁵Z. M. Liao, H. Z. Zhang, Y. B. Zhou, J. Xu, J. M. Zhang, and D. P. Yu, *Phys. Lett. A* **372**, 4505 (2008).
 - ⁴⁶K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, and J. A. Voigt, *J. Appl. Phys.* **79**, 7983 (1996).
 - ⁴⁷D. W. Hamby, D. A. Lucca, M. J. Klopstein, and G. Cantwell, *J. Appl. Phys.* **93**, 3214 (2003).
 - ⁴⁸B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck, and A. V. Rodina, *Phys. Status Solidi B* **241**, 231 (2004).
 - ⁴⁹J. Grabowska, A. Meaney, K. K. Nanda, J. P. Mosnier, M. O. Henry, J. R. Duclere, and E. McGlynn, *Phys. Rev. B* **71**, 115439 (2005).
 - ⁵⁰S. S. Lin, H. P. He, Z. Z. Ye, B. H. Zhao, and J. Y. Huang, *J. Appl. Phys.* **104**, 114307 (2008).
 - ⁵¹J. Y. Shi, J. Chen, Z. C. Feng, T. Chen, X. L. Wang, P. L. Ying, and C. Li, *J. Phys. Chem. B* **110**, 25612 (2006).
 - ⁵²C. P. Li, L. Guo, Z. Y. Wu, L. R. Ren, X. C. Ai, J. P. Zhang, Y. Z. Lv, H. B. Xu, and D. P. Yu, *Solid State Commun.* **139**, 355 (2006).
 - ⁵³X. H. Zhang, S. J. Chua, A. M. Yong, H. Y. Yang, S. P. Lau, S. F. Yu, X. W. Sun, L. Miao, M. Tanemura, and S. Tanemura, *Appl. Phys. Lett.* **90**, 013107 (2007).
 - ⁵⁴S. K. Mohanta, S. Tripathy, X. H. Zhang, D. C. Kim, C. B. Soh, A. M. Yong, W. Liu, and H. K. Choi, *Appl. Phys. Lett.* **94**, 041901 (2009).
 - ⁵⁵C. Bekeny, T. Voss, B. Hilker, J. Gutowski, R. Hauschild, H. Kalt, B. Postels, A. Bakin, and A. Waag, *J. Appl. Phys.* **102**, 044908 (2007).
 - ⁵⁶I. C. Robin, B. Gauron, P. Ferret, C. Tavares, G. Feuillet, L. S. Dang, B. Gayral, and J. M. Gérard, *Appl. Phys. Lett.* **91**, 143120 (2007).
 - ⁵⁷U. Cebulla, A. Forchel, G. Trankle, S. Subbanna, G. Griffiths, and H. Kroemer, *Phys. Scr.* **35**, 517 (1987).