

Linköping University Post Print

On the origin of suppression of free exciton no-phonon emission in ZnO tetrapods

Shula Chen, Sun Kyun Lee, Weimin Chen, H X Dong, L Sun, Z H Chen and Irina Buyanova

N.B.: When citing this work, cite the original article.

Original Publication:

Shula Chen, Sun Kyun Lee, Weimin Chen, H X Dong, L Sun, Z H Chen and Irina Buyanova, On the origin of suppression of free exciton no-phonon emission in ZnO tetrapods, 2010, APPLIED PHYSICS LETTERS, (96), 3, 033108.

<http://dx.doi.org/10.1063/1.3292027>

Copyright: American Institute of Physics

<http://www.aip.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-53938>

On the origin of suppression of free exciton no-phonon emission in ZnO tetrapods

S. L. Chen,¹ S. K. Lee,¹ W. M. Chen,¹ H. X. Dong,² L. Sun,² Z. H. Chen,² and I. A. Buyanova^{1,a)}

¹Department of Physics, Chemistry, and Biology, Linköping University, 58183 Linköping, Sweden

²Department of Physics, Surface Physics Laboratory, Fudan University, Shanghai 200433, People's Republic of China

(Received 4 November 2009; accepted 21 December 2009; published online 19 January 2010)

Temperature dependent photoluminescence and cathodoluminescence (CL) spectroscopies are employed to investigate free exciton (FX) emissions in ZnO tetrapods. The intensity of the no-phonon line is found to be largely suppressed as compared with longitudinal optical phonon assisted transitions, in sharp contrast to bulk ZnO. From spatially resolved CL studies, this suppression is shown to strongly depend on structural morphology of the ZnO tetrapods and becomes most significant within areas with faceted surfaces. A model based on reabsorption due to multiple internal reflections in the vicinity of the FX resonance is suggested to account for the observed effect. © 2010 American Institute of Physics. [doi:10.1063/1.3292027]

ZnO, with a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, has drawn enormous research interest in the last decade as one of the most promising materials for future ultraviolet (UV) optoelectronic and spintronic devices.^{1–3} Moreover, ZnO can be easily synthesized in a large variety of interesting morphologies that potentially allows deliberate tailoring of material properties and adds to its versatility in optoelectronic and sensing applications.^{4–7} Radiative recombination of high quality ZnO is usually governed by free exciton (FX) transitions at room temperature (RT), as a result of the large binding energy. However, it has been pointed out that whereas the no-phonon (NP) FX emission usually prevails in bulk ZnO, it is often weak in microstructures and nanostructures where longitudinal optical (LO) phonon-assisted FX transitions dominate.^{8–12} This has often been attributed to enhanced exciton-phonon coupling, though its exact mechanism remains unclear. Also lacking is a direct correlation between exciton-phonon coupling strength and local morphology of individual nanostructure, as the previous studies based on macro photoluminescence (PL) primarily probed integrated optical properties from an ensemble of nanostructures. The purpose of the present study is to clarify this issue by employing PL and cathodoluminescence (CL) measurements. The former will be used to evaluate overall optical properties of the tetrapod ensemble, whereas the latter will be utilized to spatially correlate optical and structural properties of single tetrapods.

ZnO tetrapods studied in this work were synthesized on a Si substrate by a thermal evaporation method at ~ 900 °C under atmospheric pressure. A comparison with a single-crystal bulk material was made by using a ZnO substrate from Cermet Inc. PL spectra were excited by the 266 nm line of a solid state laser and detected by a charge-coupled device assembled with a monochromator. Topographic images of the ZnO tetrapods were investigated by scanning electron microscopy (SEM). CL measurements were performed at RT

using a monochromatic CL system equipped with a photomultiplier tube.

A typical PL spectrum at 5 K from an ensemble of tetrapods is shown in Fig. 1(a), together with a PL spectrum from the bulk ZnO sample for comparison. In both structures, the PL spectra are dominated by excitonic transitions due to a surface exciton (SX) (Refs. 13–15) and a neutral donor bound exciton (BX) at 3.367 and 3.361 eV, respectively. The SX is less pronounced in the bulk ZnO with a lower surface-to-volume ratio. The FX transition at 3.377 eV

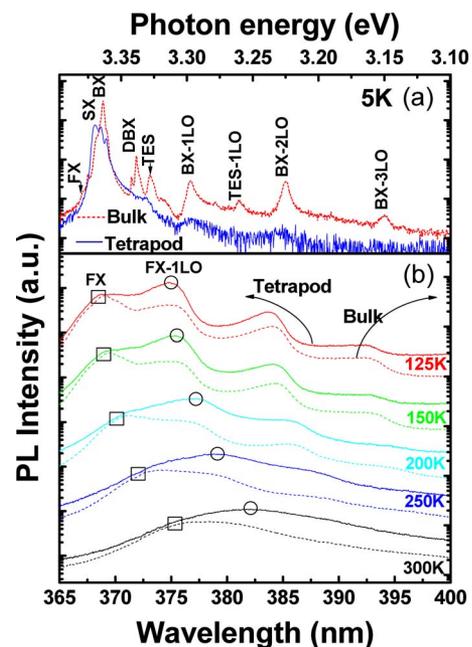


FIG. 1. (Color online) (a) Typical PL spectra at 5 K from bulk ZnO (the dashed line) and an ensemble of tetrapods (the solid line). TES denotes two-electron-satellite transitions of the BX. The peaks denoted as SD are from BX transition occurring at structural defects. (b) Temperature dependent PL spectra measured from the same samples as in (a). The spectra are normalized to the same FX intensity at each temperature and are offset vertically, for clarity. Open squares (circles) denote the maximum positions of the FX (FX-1LO) transitions.

^{a)}Author to whom correspondence should be addressed. Electronic addresses: irb@ifm.liu.se and iribu@ifm.liu.se.

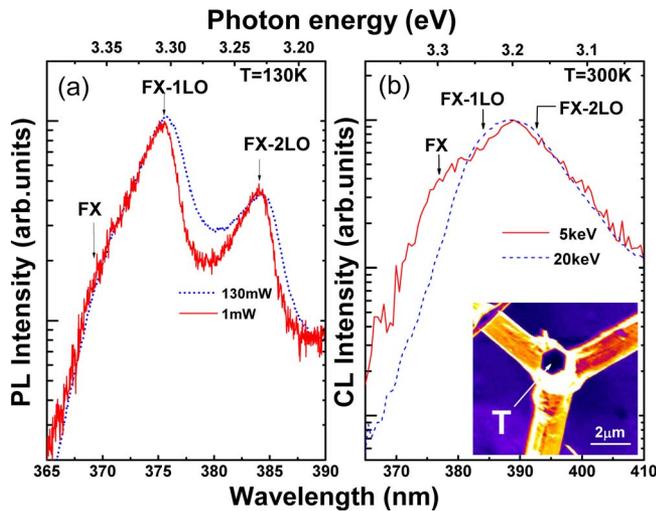


FIG. 2. (Color online) (a) PL spectra from an ensemble of tetrapods measured at 130 K with light excitation powers of 1 mW (the solid line) and 130 mW (the dashed line). (b) RT CL spectra recorded at a facet of a hexagonal leg (denoted as T) with acceleration voltages of 5 keV (the solid line) and 20 keV (the dashed line). The spectra are normalized to the same peak intensity. The indicated positions of the FX, FX-1LO and FX-2LO transitions are based on the reported data in Ref. 1.

is very weak at 5 K in both tetrapods and bulk. In addition, the LO-phonon replicas of the BX (denoted as BX-nLO) are observed. The SX and BX transitions are rapidly quenched with increasing temperature due to low binding energies of the involved states. Simultaneously, the FX transitions, i.e., the NP FX and FX-1LO lines, gain intensity and become dominant above 100 K—see Fig. 1(b). The intensity of the FX-1LO emission in the tetrapod structures exceeds that of the NP FX line, in sharp contrast to the bulk ZnO. This results in an overall redshift of the RT PL in the tetrapods as compared with bulk ZnO, consistent with the previous findings.^{8–12} The observed high intensity of the FX-1LO emission may reflect either enhanced exciton-phonon coupling or suppression of the NP FX transition in the tetrapods.

Let us first discuss the first alternative. In principle, LO-assisted excitonic transitions are expected for highly polar semiconductors such as ZnO, promoted by a strong Fröhlich interaction. According to the Huang–Rhys theory,¹⁶ the exciton-phonon coupling strength strongly depends on spatial distributions of electron and hole charge densities and becomes larger when their overlap is reduced. It can, therefore, increase in nanostructures because a significant fraction of excitons reside in proximity to the surface (due to a large surface-to-volume ratio), experiencing a built-in electric field caused by surface band bending.¹⁷ To evaluate importance of this effect, we have performed PL measurements under considerably different excitation powers that can alter surface band bending due to screening of the surface built-in field by photogenerated carriers. The results from such measurements performed at 130 K, i.e., under conditions when both the FX and FX-1LO transitions are clearly seen, are shown in Fig. 2(a). Evidently, relative intensities of the transitions remain practically constant in spite of a change by 130 times in the excitation power. This implies that the surface band bending and the associated exciton-phonon coupling cannot be the origin of the strong FX-1LO transitions observed in our tetrapod structures.

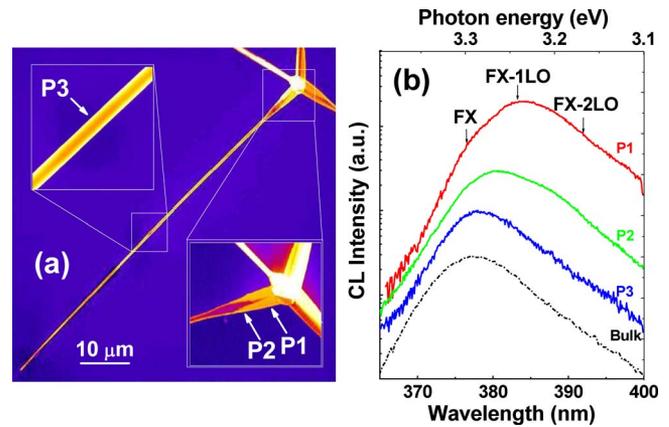


FIG. 3. (Color online) (a) An SEM image of a single tetrapod. (b) RT CL spectra measured at the P1, P2, and P3 positions of the tetrapod shown in (a), together with a typical CL spectrum from the reference bulk ZnO. SEM and CL measurements were performed with an electron beam acceleration voltage of 5 keV, to ensure a high spatial resolution ($\sim 0.2 \mu\text{m}$).

The same conclusion can also be drawn from CL measurements of individual tetrapods, as shown in Fig. 2(b). Here, relative contributions of the FX-related emissions from the near-surface region and the bulk of the tetrapods were controlled by varying acceleration voltage of the electron beams from $V_a=5$ to 20 keV. According to our Monte Carlo simulations, this change corresponds to a change in excitation depth from 0.2 to $2 \mu\text{m}$. As shown in Fig. 2(b), the intensity of the FX transition is enhanced when the excitons are generated closer to the surface. This is opposite to the trend expected when the coupling with LO phonons is facilitated by the surface band bending, further ruling out the surface band bending as being responsible for the intense FX-1LO emission in the studied tetrapods.

In order to clarify its origin, high resolution CL and SEM measurements from single tetrapods were performed. A representative SEM image is presented in Fig. 3(a) and shows that legs of the tetrapod are tapered with a diameter continuously decreasing from several micrometers close to a core (i.e., legs junction) down to 300–500 nm at the apex of the tip. Moreover, shape of the tetrapod legs is distinctively different in the areas close to the core, where it has a well defined multifaceted surface structure. In the main part of the leg, on the other hand, it becomes round. These structural changes are accompanied by a substantial change of CL spectra, see Fig. 3(b). For example, whereas the FX-1LO emission dominates in the area close to the core (position P1) and is also intense in the faceted regions of the tetrapod legs (position P2), the NP FX emission prevails in the middle part of the tetrapod leg (position P3).

In principle, exciton-phonon coupling could be promoted in the faceted regions leading to formation of exciton-polarons, and thus the experimentally observed higher intensity of the FX-1LO replica.¹⁸ Such polaron formation is possible in ZnO as the FX binding energy of 60 meV is nearly resonant with the LO-phonon energy ($\sim 72 \text{ meV}$).⁸ It can also be enhanced at rough (e.g., steplike) surfaces.¹⁹ However, the polaron formation is expected to be more pronounced at low temperatures as it decays into phonon continuum at elevated temperatures,¹⁸ which is opposite to our observation.

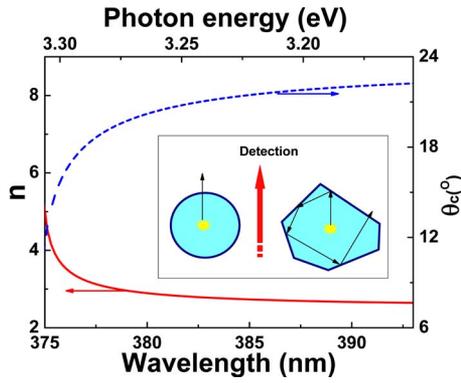


FIG. 4. (Color online) Calculated refractive index and critical angle of ZnO within the spectral range of the FX transition and its phonon replica. The inset schematically shows light propagation in the tetrapods with round and faceted surfaces.

We are, therefore, left with the second alternative, i.e., that the NP FX emission is in fact suppressed in the tetrapods. A probable reason is FX reabsorption. This reabsorption cannot be simply related to the increasing thickness close to the core regions, however, as this effect should be even more pronounced in the bulk ZnO which is not observed experimentally—see Fig. 3(b). We notice that the NP FX emission is suppressed in the regions where the tetrapod legs have faceted structures making probable multiple total internal reflections (TIR) of the emitted light. Based on ray optics, light generated inside ZnO will indeed have a higher probability to be internally reflected from a flat surface (i.e., ZnO/air interface) than from a curved one, as shown schematically in the inset in Fig. 4. This is because most of photons will transmit through a curved surface as they propagate radially along the direction normal to the surface. In contrast, only a small fraction of photons incident on a flat surface at an angle smaller than the critical angle can transmit. Multiple TIRs will enhance light absorption, especially in the FX range of strong absorption, significantly suppressing the FX emission.

To further elucidate importance of this effect in the vicinity of the FX resonance, refractive index n and the critical angle for TIR were calculated over the spectral range of interest. Taking into account that the FX transitions at RT contain contributions from three valence band states split due to crystal-field and spin-orbit interactions (the so-called A-B and C-excitons), the refractive index can be calculated from the following expression:²⁰

$$n^2 = \epsilon_\infty \left(1 + \sum_{j=A,B,C} K_j \frac{\omega_{j,L}^2 - \omega_{j,T}^2}{\omega_{j,T}^2 - \omega^2 - i\omega\gamma_j} \right). \quad (1)$$

Here ϵ_∞ is the background dielectric constant, $\omega_{j,T}^2$ and $\omega_{j,L}^2$ are transverse and longitudinal resonance frequencies of the FX, ω is a photon frequency, and γ_j is a damping constant. K_j is a prefactor defined in Ref. 20. Spectral dependence of the refractive index n , determined from Eq. (1) with the values of all parameters taken from Ref. 18, is shown in Fig. 4

together with a spectral dependence of the critical angle Θ_c for TIR. It is found that the conditions for light transmission are further restricted in the vicinity of the FX resonances. Indeed, whereas the critical angle is $\sim 22^\circ$ for light originating from the FX-nLO transitions, it decreases down to $\sim 11^\circ$ in the vicinity of the FX resonances. This will further facilitate multiple TIR and reabsorption of the NP FX emissions, diminishing their contribution to the emitting light. Moreover, a high density of the photon field due to these reflections and strong exciton-photon coupling may promote formation of exciton-polaritons, often observed in ZnO nanostructures acting as microcavities.^{5,21} As group velocity of exciton polaritons suffers strong retardation in the vicinity of the FX resonance,²² the corresponding polaritons will not be able to effectively propagate toward the surface and escape as photon emission. This will additionally reduce the contribution of the NP FX emission.

In summary, by employing temperature dependent PL and spatially resolved CL studies we have shown that the NP FX transition is suppressed in ZnO tetrapod structures. The suppression is not affected by changes in surface band bending but depends on the structural morphology of the tetrapods and is the most pronounced in the faceted regions. This is attributed to enhanced reabsorption due to multiple internal reflections, which become especially pronounced in the vicinity of the FX resonance.

- ¹Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho, and H. Morkoc, *J. Appl. Phys.* **98**, 041301 (2005).
- ²C. Klingshirn, *Phys. Status Solidi A* **244**, 3027 (2007).
- ³S. J. Pearton, C. R. Abernathy, G. T. Thaler, R. M. Frazier, D. P. Notron, F. Ren, Y. D. Park, J. M. Zavada, I. A. Buyanova, W. M. Chen, and A. F. Hebard, *J. Phys. Condens. Matter* **16**, R209 (2004).
- ⁴M. 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).
- ⁵M. C. Newton and P. A. Warburton, *Mater. Today* **10**, 50 (2007).
- ⁶A. B. Djurišić and Y. H. Leung, *Small* **2**, 944 (2006).
- ⁷L. Sun, Z. Chen, Q. Ren, K. Yu, L. Bai, W. Zhou, H. Xiong, Z. Q. Zhu, and X. Shen, *Phys. Rev. Lett.* **100**, 156403 (2008).
- ⁸H.-C. Hsu and W.-F. Hsieh, *Solid State Commun.* **131**, 371 (2004).
- ⁹T. Voss, C. Bekeny, L. Wischmeier, and H. Gafsi, *Appl. Phys. Lett.* **89**, 182107 (2006).
- ¹⁰X. Q. Gu, K. Huo, G. X. Qian, J. J. Fu, and P. K. Chu, *Appl. Phys. Lett.* **93**, 203117 (2008).
- ¹¹W. K. Hong, G. Jo, M. Choe, T. Lee, J. I. Sohn, and M. E. Welland, *Appl. Phys. Lett.* **94**, 043103 (2009).
- ¹²C. H. Ahn, S. K. Mohanta, N. E. Lee, and H. K. Cho, *Appl. Phys. Lett.* **94**, 261904 (2009).
- ¹³V. V. Travnikov, A. Freiberg, and S. F. Savikhin, *J. Lumin.* **47**, 107 (1990).
- ¹⁴L. J. Grabowska, A. Meaney, K. K. Nanda, J. P. Mosnier, M. O. Henry, J. R. Duclère, and E. McGlynn, *Phys. Rev. B* **71**, 115439 (2005).
- ¹⁵L. Wischmeier, T. Voss, S. Börner, and W. Schade, *Appl. Phys. A: Mater. Sci. Process.* **84**, 111 (2006).
- ¹⁶K. Huang and A. Rhys, *Proc. R. Soc. London, Ser. A* **204**, 406 (1950).
- ¹⁷M. W. Allen, P. Miller, R. J. Reeves, and S. M. Durbin, *Appl. Phys. Lett.* **90**, 062104 (2007).
- ¹⁸J. C. Hermanson, *Phys. Rev. B* **2**, 5043 (1970).
- ¹⁹H. Sun and S.-W. Gu, *Phys. Rev. B* **40**, 11576 (1989).
- ²⁰J. Lagois, *Phys. Rev. B* **23**, 5511 (1981).
- ²¹L. E. Li and L. D. Demianets, *Opt. Mater.* **30**, 1074 (2008).
- ²²C. G. B. Garrett and D. E. McCumber, *Phys. Rev. A* **1**, 305 (1970).