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

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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. 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. 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. 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) and a neutral donor bound exciton (BX) at 3.367 eV, respectively. The BX is less pronounced in the bulk ZnO with a lower surface-to-volume ratio. The FX transition at 3.377 eV

![Figure 1](image.png)

**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 due to spatially resolved CL studies. (b) Temperature dependent CL 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.
The origin of the strong FX-1LO transitions observed in our tetrapods can be attributed to exciton-phonon coupling or suppression of the NP FX transition in the tetrapods. 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 indicates that the surface band bending is 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. Such polaron formation is possible in ZnO as the FX binding energy of 60 meV is nearly resonant with the LO-phonon energy (~72 meV). It can also be enhanced at rough (e.g., steplike) surfaces. However, the polaron formation is expected to be more pronounced at low temperatures as it decays into phonon continuum at elevated temperatures, which is opposite to our observation.

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 μm. 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.
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 the 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:\textsuperscript{20}

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

(1)

Here $\varepsilon_\infty$ is the background dielectric constant, $\omega_{j,T}$ and $\omega_{j,L}$ are transverse and longitudinal resonance frequencies of the FX, $\omega$ is a photon frequency, and $\gamma_j$ 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 $\Theta_c$ 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.\textsuperscript{5,22} As group velocity of exciton polaritons suffers strong retardation in the vicinity of the FX resonance,\textsuperscript{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.