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Long lifetime of free excitons in ZnO tetrapod structures

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Time-resolved photoluminescence (PL) is employed to characterize optical quality of ZnO tetrapods. PL decay of free excitons (FE) is concluded to contain two components with time constants of 1 and 14 ns at room temperature. The fast PL decay is attributed to nonradiative recombination whereas the slow decay is suggested to mainly represent FE radiative lifetime, based on correlation between thermally induced increases in the PL linewidth and FE lifetimes. The results underline superior optical quality of the tetrapods as the decay time of the slow PL component is comparable to the longest lifetimes reported to date for ZnO. © 2010 American Institute of Physics. [doi:10.1063/1.3328099]

ZnO is an excellent candidate material for use in visible, ultraviolet (UV), and white light emitting devices owing to its wide band gap and large exciton binding energy which allows free exciton (FE) emission even at room temperature (RT). The desire for efficient light emitters has motivated considerable interest in exciton dynamics^{1–10} as it provides information both on efficiency of radiative recombination, determined by oscillator strength of the corresponding optical transitions, and also on material quality reflected by contributions of nonradiative recombination in lifetimes of photogenerated carriers. The decay time of excitonic photoluminescence (PL) reaches several nanoseconds at RT in high quality ZnO single crystals^{1,5} but is substantially shorter (\sim hundreds of picoseconds) in ZnO nanostructures.^{2–4,6–9} It has been suggested that the exciton lifetime is largely determined by nonradiative (NR) recombination even in the case of bulk ZnO as the radiative lifetime has been deduced to be \sim 20 ns, from an analysis of quantum efficiency of the excitonic emissions.⁵ The reported stronger NR recombination in ZnO nanostructures reflects their degraded optical quality presumably due to a high defect density and detrimental surface recombination.

Most recently, however, it has been reported¹⁰ that NR recombination can be suppressed in ZnO tetrapods by optimizing temperature during growth subjected to a humid Ar gas flow. This resulted in a long PL decay time of tens of nanoseconds at RT due to predominance of the radiative recombination, though the observed improvements in material quality were only possible within a very narrow growth window of 940 ± 5 °C. In this work, we demonstrate that ZnO tetrapods with superior optical quality can be readily fabricated by thermal evaporation in air. By investigating temperature dependent FE dynamics, the PL decays in these structures are shown to be governed by radiative recombination.

The studied tetrapod ZnO nanostructures were synthesized on a (111) silicon substrate by a thermal evaporation method at a temperature of \sim 900 °C and atmospheric pres-

sure under a flow of high-purity Ar as carrier gas and air as reaction gas. No catalyst was employed during the growth. To reduce tetrapod density and also to avoid contributions of ZnO films which may form between the tetrapods, the tetrapods were then removed from their native substrate and transferred onto another Si wafer by ultrasonic technique. A representative scanning electron microscopy (SEM) image of a tetrapod is shown in the inset in Fig. 1. For comparison, a single-crystal ZnO substrate from Cermet Inc. was also studied. Time resolved PL experiments were performed within the temperature range of 4–300 K. The PL was excited by third-harmonic pulses of a mode-locked Ti:sapphire laser, with an excitation wavelength of 294 nm and a repetition rate of 80 MHz. The resulting transient PL was recorded by

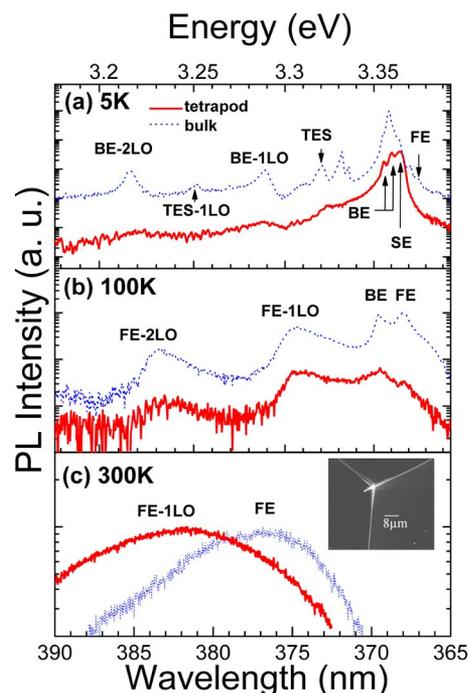


FIG. 1. (Color online) Normalized PL spectra from tetrapods (solid lines) and bulk ZnO (dotted lines) measured at 5 K (a), 100 K (b), and 300 K (c). The spectra are offset vertically, for clarity. The inset in (c) shows a representative SEM image of the tetrapod.

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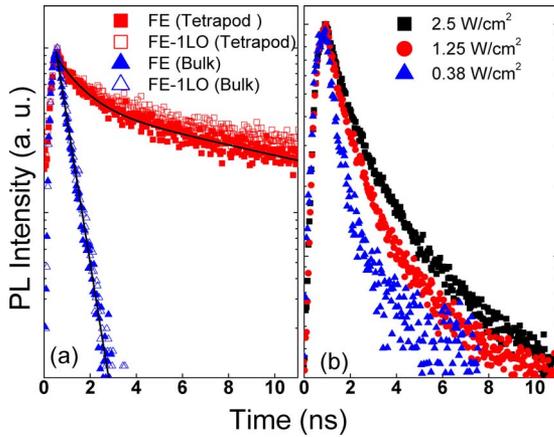


FIG. 2. (Color online) (a) PL transients measured for the FE emissions at 280 K. Symbols represent experimental data. The solid lines are fitting curves assuming $\tau=0.5$ ns for the bulk ZnO and biexponential decay with slow ($\tau_s=14$ ns) and fast ($\tau_f=1$ ns) decay components of equal intensity for the tetrapods. (b) PL decays of the FE-1LO emission from the tetrapods measured at RT with the specified excitation powers.

a streak camera system. The response time of the entire system was about 20 ps.

Typical PL spectra from the tetrapods and bulk ZnO are shown in Fig. 1 and are governed by excitonic transitions within the UV spectral range. At 5 K, a surface exciton (SE) (Ref. 11) and two neutral donor-bound excitons (BEs) are responsible for the main peaks at 3.367, 3.361, and 3.358 eV—see Fig. 1(a). The peaks around 3.323 eV can be assigned to two-electron-satellite transitions of the BEs, as its position is consistent with the energy separation of 39 meV between the $1s$ and $2p$ energy states of the neutral BE.¹² In addition, longitudinal optical (LO)-phonon replica of the BEs are observed within the 3.1–3.4 eV spectral range. A weak transition at 3.377 eV originates from FE recombination. The transitions from the SE and BEs rapidly quench with increasing temperature as a result of thermal ionization—see Fig. 1(b). This leads to the dominance of the FE emission at $T>140$ K and its first and second LO-phonon replicas (denoted as FE-1LO and FE-2LO in Fig. 1). The latter become especially pronounced at RT [see Fig. 1(c)] due to reabsorption of the no-phonon transitions, as discussed in detail elsewhere.¹³ The same behavior was also found for the bulk ZnO except for the higher intensity of the no-phonon FE transitions. The results of the PL measurements shown in Fig. 1 indicate very good quality of the investigated tetrapod structures. First of all, the excitonic peaks at 4 K are rather narrow with a typical full width at half-maximum of around 2–4 meV for the BEs. These values are somewhat larger than the BE linewidths in the bulk ZnO (0.6 meV) which is expected due to inhomogeneous broadening in the tetrapods caused, e.g., by nonuniformities in local strain. Second, the FE emissions remain the dominant radiative process at elevated temperatures indicating a low density of radiative defects.

To further characterize the tetrapod structures, transient PL measurements were performed. The decays of the FE and FE-1LO PL emissions from the ZnO tetrapods are found to be biexponential with time constants of $\tau_s=14$ ns and $\tau_f=1$ ns at 280 K for the slow and fast components, respectively—see Fig. 2(a). In sharp contrast, the PL decay in bulk ZnO is much faster and is described by a single

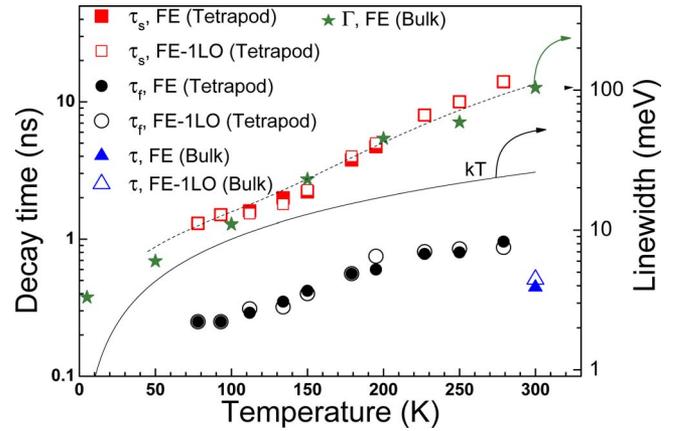


FIG. 3. (Color online) Temperature dependence of the PL decay constants for the FE and FE-1LO emissions, as well thermal variation in the excitonic linewidth. The symbols represent experimental data. The dotted line is a fitting curve of the $\Gamma(T)$ dependence by using Eq. (2) with the parameters specified in the text. For easy reference, thermal energies are shown by the solid line.

decay time of 0.5 ns. This may indicate superior optical quality of the investigated tetrapod structures as the decay time of the slow PL component is comparable to the largest values of 14 and 27 ns reported so far in the literature for bulk¹ and nanostructured ZnO,¹⁰ respectively.

To fully understand the FE dynamics in the ZnO tetrapods, the PL transients were measured at different excitation powers and also at different lattice temperatures. We found that τ_s and τ_f remain practically constant for excitation powers (W_{ex}) up to 2.5 W/cm². However, the fast PL decay component prevails at low excitation conditions whereas both components acquire the same intensity when W_{ex} is raised—see Fig. 2(b). The decay times strongly depend on the lattice temperature, especially in the case of τ_s which increases superlinearly (almost exponentially) with increasing T —Fig. 3.

Let us now discuss the origin of the two decay components in the PL transient. The FE emission is expected to have a single decay time (τ) determined by interplay of radiative and NR recombination processes as $1/\tau=1/\tau_r+1/\tau_{nr}$, where τ_r and τ_{nr} denote the intrinsic radiative and defect-mediated NR lifetimes of the FE, respectively. This is indeed observed in the bulk ZnO where the short FE lifetime points toward predominance of the NR recombination. For the ZnO tetrapods, on the other hand, the existence of two components of the FE emission with distinctly different lifetimes implies that the emission occurs within different spatial regions. Possibly, the slow PL decay component originates from regions far from the NR recombination centers whereas the fast component arises from the areas in the vicinity of these centers. This NR recombination in the tetrapod structures, which could be surface-related, is expected to saturate at high excitation conditions as confirmed by power-dependent transient PL measurements [Fig. 2(b)].

As to the slow decay time τ_s , it may represent the radiative lifetime of the FE emission. It is well known that the radiative lifetime is expected to increase with increasing temperature T , as indeed observed experimentally—see Fig. 3. To further ascertain the physical process governing the lifetime, we carry out a detailed analysis of its dependence on measurement temperature. The temperature dependence of

exciton radiative lifetime is determined by thermally induced exciton redistribution in momentum space and depends on dimensionality of the investigated structures and also on a ratio between homogeneous FE linewidth, Γ , and thermal energy kT . Under conditions $\Gamma < kT$ the radiative lifetime has been shown^{14,15} to change as $\tau_r = \tau_0/r(T)$, where τ_0 is the radiative lifetime at $T=0$ and $r(T)$ is a fraction of FEs with kinetic energy smaller than kT . For three-dimensional systems such as the studied ZnO tetrapods and assuming a Maxwell–Boltzmann distribution, $r(T)$ is roughly proportional to $T^{-3/2}$ and is given by

$$r(T) = \frac{2}{\sqrt{\pi}} \int_0^{\Gamma/kT} \sqrt{E} \exp(-E) dE. \quad (1)$$

Here E denotes the FE energy. This results in the characteristic $\tau_r \propto T^{3/2}$ dependence, often reported in bulk semiconductors.¹⁴ In the opposite case of $\Gamma > kT$, however, τ_r is proportional to the homogenous linewidth and, therefore, changes with temperature as $\Gamma(T)$ where the $\Gamma(T)$ dependence is mainly determined by interactions of excitons with acoustic and optical phonons as follows:¹⁵

$$\Gamma(T) = \Gamma_0 + \gamma_a T + \Gamma_{LO} [\exp(\hbar\omega_{LO}/kT) - 1]. \quad (2)$$

Here $\hbar\omega_{LO} = 72$ meV is the energy of a LO phonon, Γ_0 is the zero temperature broadening parameter, γ_a is the coupling strength of an exciton–acoustic phonon interaction and Γ_{LO} is a parameter describing exciton–LO–phonon interaction.

To find out which scenario is applicable to our structures, we have analyzed temperature dependence of the FE linewidth. This was performed for the bulk ZnO, to minimize contributions of nonhomogenous broadening which is significant in the tetrapods, as revealed by the low-temperature PL measurements [Fig. 1(a)]. We assume that this dependence will remain essentially the same in the tetrapods. The deduced values of the FE linewidths are shown by stars in Fig. 3 and are comparable to the previously reported ones based on reflectance and PL studies,^{16,17} e.g., ~ 100 meV at RT.¹⁷ The $\Gamma(T)$ dependence can be fitted using Eq. (2) assuming $\Gamma_0 = 2$ meV, $\gamma_a = 0.08$ meV/K, and $\Gamma_{LO} = 1.14$ eV. Also shown in the figure is the thermal energy (solid line), for an easy reference. It is seen that the FE linewidth exceeds kT , especially at elevated temperatures. A rapid increase in the homogenous broadening with T is not surprising, taking into account polar nature of ZnO which promotes strong exciton–LO phonon coupling via the Fröhlich interaction.¹⁸ Most importantly, we see that the FE broadening and exciton lifetime follow exactly the same trend with increasing temperature so that $\tau_s \propto \Gamma(T)$. This suggests that the slow PL decay is mainly determined by the radiative lifetime τ_r and

that the radiative recombination is among the dominant processes that control carrier recombination in the ZnO tetrapods even at RT.

In conclusion, by employing temperature dependent time-resolved PL spectroscopy we have shown that high quality ZnO tetrapods can be fabricated by a thermal evaporation method in air. It is found that the PL transient measured for the FE emissions is significantly longer in the tetrapods than in the reference bulk ZnO, indicating better quality of the former. The PL decay in the tetrapods is shown to contain two decay components with the time constants of 1 and 14 ns at RT. The former is attributed to nonradiative recombination whereas the latter is suggested to mainly represent radiative lifetime of the FE, based on the observed correlation between thermally induced increases in the PL linewidth and lifetimes of the FE. The obtained results underline superior optical quality of the tetrapod structures, even grown by a simple method, and show great potential of nanostructured ZnO for optoelectronic applications.

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