Defect states of ZnO nanoparticles: Discrimination by time-resolved photoluminescence spectroscopy

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ZnO nanoparticles with different shapes and sizes were prepared by changing coordinating ligands. Hexagonal cones presented UV and green (≈500 nm) emissions, which originated from excitons and defects, respectively. Oxygen vacancies were found to be major defects in the hexagonal cones. Blue emission at ≈440 nm was observed for hexagonal plates, and analyses of time-resolved photoluminescence spectra showed that two transitions were responsible for this blue emission, because transitions from Zn to the valence band (430 nm) and from Zn to VZn (480 nm) were distinguished by emission wavelengths and lifetimes. The visible emissions from defects were related to the roles of coordinating ligands. © 2010 American Institute of Physics.

[I. INTRODUCTION]

Semiconductor nanocrystals prepared using colloidal chemistry techniques allow electronic and optical properties to be “tuned” by changing the crystal sizes and shapes.1–3 Recently, tremendous advances in colloidal chemistry have led to the productions of high quality nanocrystals for several II–VI and III–V semiconductors. Of these, zinc oxide (ZnO) has attractive properties, such as a wide band gap (3.37 eV) and a large exciton binding energy (60 meV). Generally, the photoluminescence (PL) spectrum of ZnO exhibits UV emission from exciton states and visible emission from defects. This visible emission can be explained by several types of defects,4–18 because the wavelengths and intensities of visible emissions depend on the preparation methods used. An understanding of the defects in ZnO is fundamental, because competition between exciton and defect emission is important for applications of UV/blue emitters. However, the exact mechanism is still a subject of controversy because of the intrinsically broad nature of visible emissions and coexistence of several defects, although there have been many reports on the mechanism of visible emissions. In previous studies, the defects were carefully examined by the deconvolution of broad visible emission data assuming Gaussian distributions and by the temperature dependence of visible emissions.4–9 However, it remains difficult to understand the exact mechanism responsible for visible emissions, when several defects coincide in a sample.

We report an effective method to distinguish the defects of ZnO using time-resolved PL (TRPL) spectroscopy, which showed a clear characteristic of defects with time-dependent peak positions and time constants. ZnO nanoparticles prepared with different coordinating ligands had different sizes (30 and 100 nm) and shapes (hexagonal plate and hexagonal cone). In addition, the PL spectra of these two differently shaped ZnO nanoparticles were totally different, which implied that coordinating ligands controlled not only nanoparticle sizes and shapes but also their photophysical properties. The defects in ZnO nanoparticles were separated and distinguished by time-dependent peak positions and distinctive lifetimes in TRPL spectra despite the broad nature of visible emission and coexistence of multiple defects.

II. EXPERIMENT

The synthesis of ZnO nanoparticles has been described elsewhere,19–21 and only a brief overview is given here. In order to produce hexagonal cones, 1,12-dodecanediol was reacted with a solution of zinc/ligand complex, which was prepared by reacting zinc acetate with oleic acid and trioctylphosphine oxide (TOPO). 1-Hexadecylamine (HDA) was used instead of TOPO to produce hexagonal plates, and all other reagents and conditions were identical. The synthesized nanoparticles were characterized by transmission electron microscopy. The hexagonal cones had an average size of 100 nm, whereas the hexagonal plates were smaller (≈30 nm), as shown in Fig. 1. These observations suggested a facile route to control the sizes and shapes of ZnO nanoparticles that involves exchanging ligands (TOPO and HDA).

Hexagonal cones and hexagonal plates drop-coated on glass substrates were excited using a He–Cd laser (325 nm, Kimmon) to obtain time-integrated PL spectra [Fig. 1(c)]. For comparison purposes, PL spectra of ZnO bulk powders purchased from Aldrich were also obtained. The emission peak of the hexagonal cones in the UV region, which was attributed to exciton recombination, occurred at 382 nm. In addition, a broad green emission at 500 nm was observed for the hexagonal cones. On the other hand, blue emission centered at 440 nm was observed for hexagonal plates, but exciton emission was barely evident. In addition to the difference in the wavelength of the visible emission, the full width at half maximum (FWHM) of the blue emission (≈0.7 eV) was broader than that of the green emission (≈0.5 eV). In order to study defects of ZnO in more detail, TRPL spectra were obtained, because green and blue emission of ZnO have

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been reported to originate from various defects.\textsuperscript{4–18} The nanoparticles were excited by the second harmonic of a cavity-dumped oscillator (Mira/PulseSwitch, Coherent, 1 MHz, 710 nm, 150 fs) using a UV microscope objective. Emission was collected using the same objective, spectrally resolved using a monochromator, detected using a photomultiplier, and recorded using a time-correlated single photon counter (TimeHarp, PicoQuant). The instrumental response of the entire system was 0.5 ns, which resulted in a resolution of 0.1 ns with the use of deconvolution.

III. RESULTS AND DISCUSSION

A. Photodynamics of exciton states in bulk powders

In order to test a possibility of discrimination between emissive states, TRPL spectra of bulk powder were investigated. Figure 2(a) shows the decay profiles of the exciton emission of the bulk powder. Although the decay profiles seemed similar each other, at first glance, a close look revealed the wavelength dependence of the decay profiles, as shown in the inset of Fig. 2(a). The time profile at 420 nm decayed slower than that at 370 nm, suggesting that more than one state was involved in the exciton emission. In addition, TRPL spectra became slightly redshifted with time [Fig. 2(b)], when TRPL spectra were reconstructed from decay profiles measured at 2 nm intervals.\textsuperscript{10} The peak position was 382 nm at 0 ns, which shifted to 383 nm at 10 ns, as shown in the inset of Fig. 2(b). The existence of two emissive states was also found in the decay profile at 382 nm in Fig. 2(c). The decay profile was fitted most reasonably by a double-exponential model, rather than a single exponential one,

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \]  

where \( I(t) \) is intensity, \( \tau_1 \) and \( \tau_2 \) are decay times, and \( A_1 \) and \( A_2 \) are relative magnitudes. The decay profile shows two time constants (1.0 and 4.7 ns) with respective magnitudes (0.82 and 0.18). The fast decay component (1.0 ns) might include free and bound exciton states, because the lifetime of a free exciton state was <0.1 ns (below the limit of resolution) and that of an impurity- and/or defect-bound exciton state was ≤1 ns\textsuperscript{22–25} although these features were not distinguishable.

FIG. 1. (a) Transmission electron microscopy (TEM) image of uniformly sized ZnO hexagonal cones with an average size of 100 nm. The inset shows a cone shape (side view). (b) TEM image of ZnO hexagonal plates with an average size of 30 nm. (c) Photoluminescence spectra of ZnO bulk powders, hexagonal cones, and hexagonal plates.

FIG. 2. (Color online) (a) Selected decay profiles of the exciton emission of the ZnO bulk powder among decay profiles measured at 2 nm intervals, which are obtained using the time-correlated single photon counter technique. The inset shows the slight wavelength dependence of the decay profiles. Intensities are normalized for comparison purposes. (b) TRPL spectra of bulk powder as a function of detection time. From top to bottom, the emission spectra are shown with increasing detection times. The inset shows the slight wavelength dependence of the decay profiles measured at 2 nm intervals. Time constants were obtained by fitting and the numbers in parentheses represent the relative contributions of the time components. The thin line at time zero represents an instrumental response function (IRF) for the entire system.
in Fig. 2(c) due to resolution limitations. The lifetime of the exciton state (1 ns) was longer than, or at least comparable to, the previously reported values, which indicated the good quality of the bulk powder. We note that another emissive state was discernable with our temporal resolution, which contributed to the UV emission with a time constant of 4.7 ns. The relatively long time constant of UV emission has been explained with exciton localization due to the disorder created by the random strain field. Thus, a slight redshift of UV emission with increasing time was ascribed to a long-lived exciton state (localized exciton), the emission of which was redshifted as compared with the free and bound exciton states. This result proved that an emissive state could be distinguished from other emissive state by a shift of peak position and an indication of a time constant in the TRPL spectra, even when the center wavelength and time constant of the emissive state were similar to those of other emissive state.

B. Photodynamics in hexagonal cones

Photodynamics in the hexagonal cones was studied in order to identify the defects responsible for the visible emission centered at 500 nm in Fig. 1(c). The decay profiles of the visible emission were almost identical each other, as clearly found in the inset of Fig. 3(c). In addition, the TRPL spectra in Fig. 3(b) barely shifted with increasing time. (The TRPL spectra of hexagonal cones in the UV regime are not shown here, because they were virtually identical to those of the bulk material.) Although a shift was observed between 0 and 5 ns in the inset of Fig. 3(b), it turned out to be due to exciton emission centered at 382 nm. As the intensity of the exciton emission was much larger than that of the defect emission during the early time [see the TRPL spectrum at 0 ns in Fig. 3(b)], the defect emission appeared a little blue-shifted. But the deconvolution of the defect emission from the exciton emission confirmed that the defect emission was not shifted until 30 ns. Thus, the identical shape implied that one defect was mainly responsible for the green emission centered at 500 nm until 30 ns. In other words, other defects in hexagonal cones, if present, were not emissive states or their contributions were negligible. This was also supported by the decay profile of 500 nm in Fig. 4(a), which was more reasonably fitted by a triple-exponential model than a double-exponential one,

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3),
\]

where \(\tau_1\), \(\tau_2\), and \(\tau_3\) are decay times and \(A_1\), \(A_2\), and \(A_3\) are relative magnitudes. The best fit by the triple-exponential model suggested three emissive states, because the overall contribution of multiple relaxation pathways determined the lifetime of a single state by the following equation:

\[
\tau = \frac{1}{k_{rv} + k_{nr}}.
\]

FIG. 3. (Color online) (a) Selected decay profiles of the visible emission of the ZnO hexagonal cones among decay profiles measured at 2 nm intervals. The inset shows the negligible wavelength dependence of the decay profiles. Intensities are normalized for comparison purposes. (b) TRPL spectra of hexagonal cones as a function of detection time. From top to bottom, the emission spectra are shown with increasing detection times. The inset shows a negligible shift of the visible emission with increasing time. Intensities are normalized for comparison purposes.

defect. Thus, three time constants in Eq. (2) indicated that three states were involved in the emission of 500 nm. The two fast time constants (0.9 and 3.8 ns) at 500 nm were similar to those at 382 nm in Fig. 4(a), suggesting that two time constants were related to the exciton states. Naturally, the remaining component (25 ns) presented the lifetime of defect, which confirms that the green emission was dominated by one defect in the hexagonal cones.

We note that the value of \(A_3\), which was as small as 0.30, seems to be confused, because the green emission was well separated from the exciton emission in Fig. 1(c) and thus the effect of exciton emission around 500 nm was expected to be negligible. However, the overall integration over 1 \(\mu\)s (time-window of the time-integrated PL spectra) with the estimated contribution (\(A_1\), \(A_2\), and \(A_3\)) answered that the overall intensity affected by the time constant of 25 ns was about ten times larger than other emission affected by the fast time constants such as 0.9 and 3.8 ns. Thus, the seemingly large values of \(A_1\) and \(A_2\) implied that the exciton emission predominated only at early time, as observed in Fig. 3(b).

Another thing to be noted is the lifetimes of exciton states. As a matter of fact, the lifetime of the exciton state resulted from the overall contribution of the radiative and nonradiative decay to the valence state in addition to the
nonradiative decay to the defect, which is assumed to be negligible in the bulk powder. Thus, the exciton lifetime of the hexagonal cone can be different from that of the bulk powder as following:

$$\tau_{HC} = \frac{1}{k_{rv} + k_{nrv} + k_{nrd}},$$ \hspace{1cm} (4)$$

$$\tau_{BP} = \frac{1}{k_{rv} + k_{nrv}},$$ \hspace{1cm} (5)$$

where $\tau_{HC}$ is the exciton lifetime of the hexagonal cone and $\tau_{BP}$ is the exciton lifetime of the bulk powder. If other rate constants ($k_{rv}$ and $k_{nrv}$) of the hexagonal cone are not different from those of the bulk powder, because these are the intrinsic properties of ZnO materials, the rate of nonradiative decay to defect ($k_{nrd}$) can be estimated by measuring $\tau_{HC}$ and $\tau_{BP}$. In addition, the efficiency ($\phi_{HC}$) of the nonradiative decay from exciton to defect in the hexagonal cone can be calculated by the following equation:

$$\phi_{HC} = \frac{k_{nrd}}{k_{rv} + k_{nrv} + k_{nrd}}.$$ \hspace{1cm} (6)$$

Because the lifetimes of bound exciton ($\tau_{HC}$ and $\tau_{BP}$) was measured to be 0.9 and 1.0 ns, respectively, the nonradiative decay of bound exciton to defect was estimated to be 0.10 (10%) with the assumption that other rate constants ($k_{rv}$ and $k_{nrv}$) were unchanged in the hexagonal cone from the bulk powder. Likewise, the nonradiative decay of localized exciton to defect was calculated to be 0.19 (19%) from the lifetimes of the hexagonal cone (3.8 ns) and the bulk powder (4.7 ns). It is noted that the overall intensity of the visible emission was two times larger than the exciton emission in Fig. 1(e), which could not be explained only by the occupation of the defect through the nonradiative decay from the exciton. In addition, the rise component in the time profile of 500 nm was nearly identical to that of 382 nm in Fig. 4(a), which suggested that the rise of defect emission was not strongly affected by the decay of the exciton state. Thus, the occupation of most defects was not attributed to be from the exciton but rather directly from the conduction band.

Various assignments of visible emission involve vacancies and interstitial atoms, including cationic and anionic sites in ZnO, while some of them reported completely different theoretical and experimental results. At this point, the origin of the defect responsible for the green emission cannot yet be definitely determined only with the experimental results, because visible spectra were greatly affected by preparation methods, environmental conditions, and roles of the coordinating ligands. In general, most defects are considered as a result of the surface states located in the band gap of the nanocrystals, which act as trapping states for the photogenerated carriers, while the surface states of the nanoparticles might be investigated by x-ray photoelectron spectroscopy. A certain type of surface structure or surface reconstruction of thin films grown by the gas phase techniques can be accomplished by providing the system with a biased ratio of the precursors and annealing treatments. On the other hand, the surface reconstruction in a solution reaction with a defined number of monomeric units takes place only for a short period of time due to the rapid variation in the concentrations of the monomers, the precursors, and ligands in the solution. The monomers on the surface of nanocrystals should collaborate and compete with the ligands to form stable crystallinity during the surface reconstruction and the growth. If the surface ligands could provide a good passivation for the surface states, some or all surface trapping states can be removed. Consequently, the nature and density of the surface trapping states should depend on the surface structure of the nanocrystals and the surface ligands. Thus, we pay our attention to the coordinating ligands in the generation/suppression of defects such as the surface trapping states. TOPO is a well-known base ligand, which can bind strongly to zinc atoms. At the surface of the ZnO nanoparticles, TOPO interacted with zinc atoms located at the surfaces with a help of polarized bonds between oxygen and phosphorous atoms, reducing the surface defect densities. On the other hand, the oxygen-related defects were not expected to be completely quenched by TOPO, which suggested oxygen-related defects for the surface trapping states in the hexagonal cones. The green emission due to a recombination between an electron in single positively charged oxygen vacancy ($V_{O}^+$) and a hole in the valence band was reported and $V_{O}^+$ was predicted to lie at 2.48 eV above the...
valence band. In addition, the lifetimes of the green emission assigned to oxygen-related defects also agreed with our results, which led us to attribute $V_{\text{O}}^{\text{+}}$ to the defect in hexagonal cones. The dynamics of photoexcited hexagonal cones is schematically summarized in Fig. 4(b). Photogenerated electrons and holes formed the excitons (BX), and some of these were localized (LX), which resulted in UV emissions (382 and 383 nm) with lifetimes of 0.9 ns and 3.8 ns, respectively. The electrons in the deep level ($V_{\text{O}}^{\text{-}}$) also recombined with the holes in the valence band, emitting the green light (500 nm, 2.48 eV) with a lifetime of 25 ns.

C. Photodynamics in hexagonal plates

The exciton emission around 382 nm was hardly discernable in hexagonal plates with totally different shape of PL spectrum in Fig. 1(e). The absence of exciton emission implied a fast nonradiative decay of the exciton state to the distinctive defect in hexagonal plates, because exciton emission was clearly observed in the bulk powders and the hexagonal cones. To study the defects responsible for the absence of exciton emission, TRPL spectra of the hexagonal plates were obtained. Figure 5(a) shows the decay profiles of the visible emission of the hexagonal plates. The decay profiles exhibited the strong wavelength dependence, as observed in the inset of Fig. 5(a), suggesting that more than one state was involved in the visible emission. In addition, the emission peak in the TRPL spectra showed significant redshift with the increase in time in Fig. 5(b). The emission at 0 ns was dominated by blue emission at 430 nm, which shifted to 480 nm at 30 ns, supporting the existence of more than one defect.

The number of emissive states was thus estimated by fitting decay profiles in Fig. 6(a), where the best fits were obtained by a double-exponential model [Eq. (1)]. Time constants at 430 nm were 1.7 and 6.5 ns, while those at 480 nm were 1.7 and 6.5 ns. Despite the near identical values of these time constants, the relative contributions ($A_1$ and $A_2$) of the two components were not similar, which confirmed that the two components originated from different defects. In other words, the visible emission centered at 430 nm was due to a fast decaying defect (1.7 ns), whereas the emission at 480 nm was from a slow decaying defect (6.5 ns), although these are not well-separated due to the broad spectral nature of defect emission. Thus, a broad spectrum centered at 440 nm with an FWHM of ~0.7 eV [Fig. 1(c)] was not caused by a single defect but by two kinds of defects. Figure 6(b) shows a clearer view for the existence of two defects. The upper panel was fitted with a single Gaussian function, while the lower panel was deconvoluted with two Gaussian functions at the center wavelengths of 430 and 480 nm, which reproduces the PL spectrum more reasonably.

We note that the distinctive defect responsible for the absence of exciton emission exists in hexagonal plates, which were synthesized by the identical reagents and conditions to the hexagonal cones except HDA used instead of TOPO. Accordingly, the nature of the defects must have the relationship with the coordinating ligands. Amines are known as weaker bases than phosphine oxide, while amines also reduce the surface defects by linking to the surface with the lone pair of nitrogen atoms, and thus, to supply electrons to the defects. Thus, it is expected that HDA removes electron-deficient defects such as a positively charged oxygen vacancy ($V_{\text{O}}^{\text{+}}$) effectively, while HDA might reduce specific defects due to the selective binding to surface, as at the surface of CdSe nanoparticles. In other words, the presence of HDA reduced defects related to the green emission [Fig. 1(c)], whereas HDA was not effective to remove the defects for the blue emission, because HDA bound less strongly and interacted less efficiently with zinc atoms. As a consequence, it is suggested that HDA could not remove the zinc-related defects completely. Since the interstitial zinc (Z$_i$), which lies at ~0.3 eV below the conduction band, is the energetically-matched defect responsible for the blue emission centered at 430 nm, the shallow electron level is assumed to be Z$_i$. In addition, the zinc vacancy ($V_{\text{Zn}}$) might be the most probable shallow hole level related to the emission at 480 nm, which is located at ~0.3 eV above the valence band.
The lifetime of 1.7 ns was related to the state composed of \( \text{Zn}_i \) (electron level) and \( \text{V}_\text{Zn} \) (hole level). The time constants obtained in this study (1.7 and 6.5 ns) were similar to previously determined values (2 and 9 ns) in \( \text{ZnO} \) nanoparticles prepared using octylamine, but only the 9 ns time constant was assigned to the blue-emitive defect in \( \text{ZnO} \) nanoparticles.\(^{11}\) We note that it was difficult to figure out the defects responsible for the blue emission only with the time-integrated PL spectrum [Fig. 1(c)], whereas two types of defect emissions (transitions from \( \text{Zn}_i \) to the valence band and to \( \text{V}_\text{Zn} \)) could be separated in \( \text{ZnO} \) hexagonal plates by time-dependent peak positions [Fig. 5(b)] and distinctive lifetimes [Fig. 6(a)] in TRPL spectra.

### IV. SUMMARY

We prepared two types of \( \text{ZnO} \) nanoparticles, namely, hexagonal cones (100 nm) and hexagonal plates (30 nm). The shapes and sizes of nanoparticles were changed by the substitution of one coordinating ligand (TOPO versus HDA), while all other reagents (1,12-dodecanediol, zinc acetate, and oleic acid) and conditions were unchanged. In addition to the obvious differences between the two in terms of size and shape, the totally different PL spectra of nanoparticles showed that defects related to the photophysical properties were also influenced by the coordinating ligands. Although it was not easy to estimate defects only by the time-integrated PL spectra mainly due to the intrinsically broad nature of visible emissions, TRPL spectra clearly distinguished defects through the time-dependent peak positions and the distinctive lifetimes. The green emission in the hexagonal cones was mainly related to \( \text{V}_\text{Zn} \). In hexagonal plates, most of the photogenerated electrons were captured at the shallow electron level (\( \text{Zn}_i \)), and recombined with holes located in the valence band and in the shallow hole level (\( \text{V}_\text{Zn} \)).

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