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Temperature-dependent studies of defect-assisted light emission and excitation processes in crystalline ZnO nanowire phosphors

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A series of photoluminescence and photoluminescence-excitation spectroscopies have been performed to probe the processes regulating defect-assisted light emission from one-dimensional ZnO nanowire phosphors in a wide temperature range of 123–463 K. The observed nonmonotonic change of the integral defect-photoluminescence intensity as well as its peak position with temperature are explained based on the interplay of competing effects of thermal quenching and carrier redistribution over radiative channels. A temperature-induced broadening of the defect photoluminescence band is observed and attributed to the appearance of ~2.1 eV band, the intensity of which is also found to quench quickly with the onset of higher temperature. The results of photoluminescence-excitation measurements show that band-to-band excitations remain a primary excitation channel of defects especially at low and moderate temperature range, whereas the role of direct, one-photon absorption channel is found to progress as temperature approaches ~500 K. © 2010 American Institute of Physics. [doi:10.1063/1.3462432]

I. INTRODUCTION

Despite their very large band gap, oxides remain an important class of visible range luminescent materials ubiquitously implemented in many low-cost, light-emitting devices and display technologies and are a subject of continued research.1–3 Nanostructured nonagglomerated phosphors generally demonstrate such advantages as increased brightness and reduced voltage requirements, and have a lower perdevice fabrication cost. Likewise, with their small size and ability in certain cases to up-convert infrared radiation to a visible one, luminescent nanophosphors also can play a role in a host of biomedical applications such as molecular tagging, sensing, and detection.

Among different classes of recently emerged nanophosphor materials, ZnO nanorods, and nanowires are known to yield very strong, visible-range, defect-assisted emissions as a result of their large surface-to-volume ratio.4,5 These, ZnO nanophosphors also have been found to emit in three primary colors: red, green, and blue, making them of high technological importance.6–8 Importantly, free electron densities can be easily controlled by doping ZnO-phosphors with, for example, Al, to protect against aging and degradation of the luminescent characteristics of ZnO-based, light-emitting devices.9

Light emission from ZnO phosphors can be categorized based on the defect-assisted radiative recombinations mostly involving donor/acceptor bound excitons, shallow/deep donor-acceptor pair (DAP), and free-to-bound transitions, effectively covering UV-near-IR spectral range. At the same time, the green-color luminescence is known to dominate the defect-assisted PL from ZnO nanowires and involve such point defects as Zn, O", V", and V. Doping can also strongly affect the luminescence characteristics of both bulk and nanostructured ZnO. The results of early studies by Dingle10 and more recent ones by us11 suggest that the presence of Cu-impurities that form acceptor states within the band gap of II-VI compound,10,12,8 can enhance visible-range luminescence in ZnO materials, including nanowires. Despite many published reports on light emission characteristics of ZnO nanostructures, most of the studies were performed at low-temperature (T) range, whereas many fundamental aspects such as the influence of high-T conditions on defect-assisted emission from ZnO nanophosphors remain uninvestigated and not well understood. In this letter, we present the details of high-T photoluminescence (PL) and photoluminescence-excitation (PLE) based investigations of the carrier recombination and excitation pathways based on the model of ZnO-nanowire phosphors, which is critical from the standpoint of developing a host of novel visible-range light emitting and sensing devices that implement nanostructured-ZnO.

II. EXPERIMENTAL

In this work, highly luminescent ZnO nanowires were grown on a top surface of 1×1 cm² (100) c-Si wafer that was covered with an ordered, ultradense array of Au-nanodisks prepared by e-beam deposition using an ordered alumina nanotemplate as a shadow nanomask as reported previously.5,13 Next, the synthesis was carried out in a single-zone, horizontally-oriented quartz tube furnace. A ZnAs₂ polycrystalline micropowder was heated to ~450 °C to generate Zn vapors. A laminar flow of Ar gas was set in the tube to transfer produced Zn-vapors to the growth substrate, whereas an array of ~90 nm diameter Au-islands catalyzed the growth of ZnO nanowire array. A postgrowth inspection of the Si substrate with scanning electron microscope (SEM), (Fig. 1, inset a) revealed an array of semialigned, individual ZnO nanorods/wires with an average diameter of ~90 nm.
and areal density of $\sim 10^{12}$ cm$^{-2}$. Energy dispersive x-ray spectroscopy (EDS) has been further performed on the nanowire samples and the results confirm the presence of O, Zn, and Au, Fig. 1, the inset b. No As was detected, which suggests that under the growth conditions used in this study As is unlikely to incorporate into ZnO nanocrystals. This also requires us to exclude this impurity from playing any role in the defect emission from ZnO nanorods to be discussed below. At the same time, EDS spectrum revealed Al and Si signals, both originating from the growth substrate. The presence of Au-particles on top of individual nanowires, which has been also verified by a point EDS analysis suggests that the growth mechanism is a vapor-liquid-solid one, with the vertical growth rate of 10 nm/min. While the temperature of the growth remained low, the nanorods fabricated under these conditions are typically found to consist of a single crystal core surrounded by a small, $\sim 10$ nm thick amorphous layer. Furthermore, the field-effect transistor measurements performed on individual nanowires confirmed that the nanowires are n-type.

III. RESULTS AND DISCUSSIONS

The subgap luminescence from the samples was excited with a $\sim 320 \pm 5$ nm light generated by a 450 W Xenon lamp and filtered out with the help of a double-grating monochromator. The light was focused into a $\sim 10$ $\mu$m diameter spot with an Olympus 51 $\times$ microscope, whereas the emitted radiation was collected and analyzed using another double-grating (emission) monochromator. A photomultiplier tube operating in a photon counting mode served as a detector. The temperature of the samples was varied with the help of an Instec HCS302 heating/cooling stage that uses liquid nitrogen and a resistive heating element for cooling and heating, respectively. To minimize the effect of moisture condensation, the sample compartment was continuously purged with an Argon gas. The spectral resolution of the instrument was set to 2 nm, with the detector integration time of $\sim 0.5$ s for each spectral acquisition. To minimize the sample exposure to Argon ambient at high T, the spectra were acquired at varied T-intervals of $\sim 20$ K at temperatures less than 300 K and of $\sim 60$ K at temperatures above 300 K.

As-grown ZnO nanowire samples revealed a strong luminescence, Fig. 1 at both ultraviolet (UV) and visible parts of the electromagnetic (EM)-spectrum, attributed to exciton and defect emissions that originate from two physically separate regions: the crystalline core and the surface layer, respectively. A large lattice mismatch of c-Si from c-ZnO is believed to be a leading cause for the increased defect emission observed in our samples, whereas a green fluorescence could be easily registered by the naked eye by exciting the samples with a UV-lamp ($\sim 5$ mW/cm$^2$, 360 nm). Figure 2 displays the defect-related part of PL spectra acquired at T range of 123–463 K. Compared with the excitonic band, the defect band is very broad, with its full width at half maximum approaching $\sim 0.45$ eV at T of $\sim 123$ K and $\sim 0.5$ eV at T of 463 K (Fig. 3) which suggests that multiple defect bands contribute to the subgap, i.e., defect-assisted luminescence. The individual bands were extracted by performing a multipeak Gaussian decomposition of the obtained spectra. At low T range, the decomposition gave satisfactory results using three bands with the peaks at 467, 492, and 537 nm, whereas at T $>340$ K four bands with peaks at 446, 478, 525, and 585 nm were needed to fit the data. Figure 3, left

FIG. 1. PL spectrum of ZnO nanorods obtained at $\sim 140$ K; the insets (a) and (b) present top-view SEM image and EDS spectrum of the nanorods, respectively. The scale bar is 0.5 $\mu$m. A weak emission band at $\sim 420$ nm stems from a lens autofluorescence.

FIG. 2. (Color online) Defect PL spectra obtained for the temperature range of 123–463 K from ZnO nanorods; the inset shows the peak position as a function of temperature.

FIG. 3. (Color online) Shows results of decomposing the defect band into three Gaussian peaks at 467, 492, and 537 nm (123 K, left) and four Gaussian peaks at 446, 478, 525, and 585 nm (463 K, right), referred to as peaks 1, 2, 3, and 4, respectively.
and right shows the fitting results for two different T acquisitions: 123 K and 463 K, respectively. Given that the three primary bands experience little to no broadening, the T-induced broadening of the integral PL peak is mainly attributed to the appearance of a new, red-color band with its peak positioned at ~585 nm (Fig. 3, right). This also requires us to exclude free-to-bound transitions as possibly contributing to subgap PL, contrary to what has been previously suggested in Ref. 15.

Room temperature time-resolved PL measurements were next performed to verify the mechanism of the defect emission at this temperature range. The samples were excited with a 340 nm light-emitting diode, and the results are presented in Fig. 4. As the experimental data exactly followed a \( \sim t^{-3/2} \) dependence, this confirms that the rate-limited mechanism is a direct tunneling between the radiative recombination centers (known as DAP recombination, or DAP mechanism), rather than the release of an electron (hole) from a shallow donor (acceptor) state followed by its diffusion to the hole (electron) trapped on a remote center; whereas in the latter case, the recombination is known to instead yield a \( t^{-2} \) decay. The role of the diffusion process is expected to stay minimized in the nanowires even at elevated T mostly due to the existence of the upward band bending near the surface of the nanowires induced by a negative surface charge. As screening effects are to remain subdued in ZnO, there will exist a strong electrical field inside of the wires, that will sweep the released holes quickly toward the surface of the wires, where the concentration of recombination sites is the largest.

Excitation-power dependent PL measurements have been additionally performed and across the whole T range the obtained dependences were linear with the results for T of 463 K presented in Fig. 4, the inset. According to the PLE results to be discussed below, the over-band-gap excitations remain a primary excitation channel of the defect PL over the whole T range. Taking into consideration that some of the photogenerated electron-hole pairs are to be lost due to band-to-band transitions, we can then write the following balance equation for the minority carriers,\textsuperscript{16,17}

\[
\frac{\partial p}{\partial t} = G - \frac{p n}{\tau_{bb}} - \frac{p N_{nr}}{\tau_{nr}} - \frac{p (N_{A} - N_{A})}{\tau_{A} N_{A}},
\]

(1)

where \( G \) is electron-hole pair generation rate; \( p \) and \( n \) are hole and electron densities, respectively; \( \tau_{nr} \) is characteristic capture time of holes by radiative centers and \( \tau_{bb} \) is the time of band-to-band recombinations involving free excitons in our case. \( N_{A} - N_{A} \), and \( N_{nr} \) stand for the effective concentrations of deep-acceptor impurities, deep-acceptor bound holes, and nonradiative centers, respectively. For low injection conditions that prevail in our case, \( n = n_{0} \), where \( n_{0} \) is equilibrium electron density, and the above equation can be then rewritten as follows:

\[
\frac{\partial p}{\partial t} = G - \frac{p n}{\tau_{G}} + \frac{p N_{A}^{0}}{\tau_{A} N_{A}},
\]

(2)

where \( \tau_{G} \) now stands for a characteristic lifetime of holes in the valence band. A similar rate equation can be also written for the holes bound on deep-acceptors

\[
\frac{\partial N_{A}^{0}}{\partial t} = \frac{p (N_{A} - N_{A})}{\tau_{A} N_{A}} - \frac{N_{A}^{0}}{\tau_{r}},
\]

(3)

where \( \tau_{r} \) is a characteristic recombination time of acceptor-bound holes. In the steady-state, \( \partial p/\partial t = \partial N_{A}^{0}/\partial t = 0 \). Now, by solving Eqs. (3) and (2) together, one obtains the following expression for the defect PL intensity:

\[
I_{\text{defect}} \sim \frac{N_{A}^{0}}{\tau_{r}} = 0.5 \left( \frac{N_{A} \tau_{A}}{\tau_{G} \tau_{r}} + G \right) \pm 0.5 \left( \frac{N_{A} \tau_{A}}{\tau_{G} \tau_{r}} + G \right)^{2}
\]

\[
- \frac{G N_{A}^{0}}{\tau_{r}} \left( \frac{G N_{A}^{0}}{\tau_{r}} \right)^{0.5}.
\]

(4)

As \( I_{\text{defect}} \) is zero for \( G=0 \), at the limit of the high excitation intensity, the defect intensity becomes insensitive to the excitation optical powers and is to saturate to \( I_{\text{defect}} \sim N_{A} / \tau_{0} \). On the other hand, at low excitation intensity, \( G \sim 0 \), Eq. (4) now yields a linear dependence of the emission intensity on the excitation intensity with \( I_{\text{defect}} \sim G \tau_{G} / \tau_{r} \), which is in a good agreement with the experimental findings.

A T-induced blueshift of the integral PL band can be further noticed in Fig. 1, the inset. As multiple defect bands contribute to the defect emission, a nonmonotonic change of the peak position arises from a complex evolution of each defect band and a change in their contribution to the PL signal with T. At the same time, we note the spectral peak positions of the three primary bands consistently exhibited a blueshift; which suggests that the trend is intrinsic. We now discuss the observed blueshift of the defect bands within the framework of the DAP emission mechanism. As most of the DAP emission from nanowires originates on surface-defect states, the radiative recombination involves carriers localized in spatially-separated potential wells via direct tunneling. The photon energy, \( h \omega \) emitted by DAP in this case is known to be given by the following expression:\textsuperscript{18}
\[ \hbar \omega = E_e - (E_D + E_A) - 2\zeta, \]

where \( E_e, E_D, E_A \) represent the band gap, donor energy, and acceptor energy, respectively. The last term represents the reduction in the photon energy due to carrier localization effects, with \( \zeta \) representing the effective potential well energy.

Previously, we investigated the evolution of free exciton band with \( T \) in ZnO nanowire samples produced similarly. The results confirmed that a strong band gap renormalization effect is responsible for a \( T \)-induced redshift of the excitonic band in our samples,\(^6\) therefore, the energy of DAP emission peak is expected to exhibit a redshift as \( T \) increases. Likewise, the depth, \( \zeta \) is known to increase with the impurity/defect density and as carrier compensation effects become stronger. As the capture probability of the excess carriers by the impurity is expected to stay low for both low \( T \) and deep-lying state, any increase in \( T \) should be accompanied by a redshift of DAP bands.\(^{18} \) On the other hand, as the density of free carriers, \( n \) is to increase strongly (exponentially) with \( T \), and given that \( \zeta \sim n^{-1/3} \), the depth of the potential well is expected to undergo an exponential-like reduction as \( T \) increases, thus explaining a net blueshift obtained experimentally in our case.

To further clarify the origin of the nonmonotonic \( T \)-evolution of the defect PL intensity, integral PL intensities were calculated for each spectral acquisition and the results are presented in Fig. 4. The inset in Fig. 5 clearly reveals a nonmonotonic response, in particular, the presence of local minimum at \( \approx 180 \) K which we associate with a complex interplay/change in the relative PL contributions of the three primary defect bands. This nonmonotonic decay has not been confirmed in other type of samples such as molecular beam epitaxy-grown GaN, which suggests that the behavior is intrinsic to ZnO nanowire samples. From Fig. 5, one can see that the increase in the emission intensity at \( T \approx 180 \) K is primarily associated with the increase in amount of the emission coming from band no. 3. Based on its peak position of \( \approx 2.34 \) eV, we attribute the origin of this band to electronic transitions involving shallow delocalized donor states such as neutral oxygen vacancy \( V_O \) and interstitial zinc \( Zn_i \) and an antisite defect state such as \( O_{Zn} \). At the same time, the amount of PL emission originating from the band no. 2 (peak position at \( \approx 2.59 \) eV) is seen to strongly decrease with \( T \). A strong thermal quenching of the emission of the first and second bands is expected to be accompanied by the release of free holes into the valence band, some of which are to be recaptured by the ionized deep acceptors, thus partially offsetting the losses of the defect PL as \( T \) increases. Moreover, the appearance of the defect band no. 4 is likely induced by a thermal quenching of the band no. 3 as \( T \) approaches 340 K. Similar behavior has been previously reported for the defect-assisted yellow luminescence in GaN samples.\(^{17} \) We also note that compared with excitonic PL, the defect luminescence is expected to quench much faster with \( T \) owing to a relatively large exciton binding energy and thus drastically increased stability of free exciton emission against thermal excitations in ZnO nanocrystals.

To probe the role the defect states play behind the visible-range excitation, micro-PLE spectra were collected at the similar temperature range of 143–463 K. The excitation wavelength was changed from 300 to 400 nm, whereas the emission wavelength was set to 480 nm. The cut-off of the PLE bands observed for the wavelengths below \( \approx 300 \) nm is associated with a limited optical transparency of the microscope beam-splitter for the light wavelength less than 300 nm. The results presented in Fig. 6 clearly suggest that over the band gap excitation processes play a key role behind the excitation of the subband gap luminescence. A quick reduction in the PLE intensity observed at the onset of high temperatures regardless of the excitation energy is induced by a thermal quenching of defect emission rather than change in the absorption/excitation characteristics of the samples. The effect is accompanied by a pronounced redshift of the PLE band. The position of the band gap was calculated as a function of temperature as indicated by the arrow marks in Fig. 6.
and it is evident that the observed PLE spectral shift is a result of the band gap renormalization with T. As can be easily seen, the amount of defect PL generated as a result of the direct excitation of defects remains relatively low for both low and moderate T. At the same time, as T increases and approaches ~500 K, the PLE spectral profile starts to exhibit more of a band-like profile (Fig. 6, the inset). This is a direct a result of the increased availability of optically-excitable defect states in the vicinity of the band edges as the transformation is also accompanied by increased smearing of the PLE edge around band gap at high T. We also note the direct excitation pathway remains effective only at very high T and under low excitation optical densities (away from saturation) in ZnO nanowires.

IV. CONCLUSION

The processes and mechanisms regulating defect emission from one-dimensional ZnO nanophosphors were investigated at an extended temperature range. The defect-assisted PL emission exhibited a highly complex, nonmonotonic evolution with T which is explained based on detailed consideration and change in the relative contribution of different defect bands. Among other findings presented above, we note that spectral broadening and blueshifting of integral PL emission take on different physical origins: the development of a new red-color defect emitting band at T ~ 400 K and a change in the potential well energy associated with deep-defect states as T increases. The PLE measurements performed also confirm that indirect, i.e., over the band gap excitation of carriers remains a primary excitation channel of defect PL, whereas the role of direct excitation channel is found to increase as T approaches ~500 K range.

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