Abrupt and tunable quenching of photoluminescence in ZnO

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The abrupt and tunable quenching of photoluminescence (PL) in bulk ZnO samples is reported, a phenomenon which has been previously observed only in GaN and a few phosphorescent materials. ZnO samples grown by the hydrothermal method contain Li defects responsible for the orange luminescence (OL) band with a maximum at 2.0 eV. The Li_{Zn} acceptor is well studied, but there is some disagreement in the literature on the value of its ionization energy. Here we show that the ionization energy of the Li_{Zn} acceptor responsible for the OL band is 0.65 ± 0.10 eV. The thermal emission of holes from the Li_{Zn} acceptor to the valence band and their subsequent capture by unknown nonradiative centers causes the abrupt quenching of PL, the temperature of which is tunable by excitation intensity.

Keywords: ZnO, photoluminescence, Li acceptor, thermal quenching

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1. Introduction

ZnO is a promising material for optoelectronic applications such as white light-emitting devices or UV laser diodes due to its direct and wide bandgap of 3.437 eV at low temperature [1]. A major obstacle to achieving these technological developments is the lack of a clear understanding of point defects in ZnO. Typically, ZnO crystals exhibit *n*-type conductivity, but, thus far, reliable *p*-type conductivity has not been obtained in the sense that the results are reproducible or sustainable [2-4]. Since the conductivity in ZnO has always been difficult to control, a better understanding of defects and their effect on the electrical and optical properties of ZnO would substantially increase the progress in this field.

Many initial attempts to acquire *p*-type conductivity in ZnO involved the use of group-I elements, since these impurities substituting for Zn were expected to create shallow acceptor levels. For many years, the question of whether Li introduces a shallow or deep acceptor level in ZnO remained the focus of discussions. Early experimental works provided evidence that Li_{Zn} is a deep acceptor [5-8]. The frequently cited value of 800 meV for the binding energy of the Li_{Zn} acceptors [9-11] originates from a pioneer work by Schirmer and Zwingel [7], where this value was estimated from the position and shape of the thermoluminescence band attributed to Li. Photoluminescence (PL) studies show an identical band which will be called the orange luminescence (OL) band hereafter, because it has a maximum at 2.0 eV (615 nm) [8]. By analyzing the shape, position, and activation energy of the thermal quenching of the OL band, the binding energy of the Li_{Zn} acceptor has been estimated to be 0.5-0.6 eV in [12]. A higher value of 0.86 eV was found for the Li_{Zn} acceptor from PL excitation and temperature-dependent electrical resistivity experiments [13]. In addition to the deep Li_{Zn} acceptor responsible for the OL band, Meyer *et al.* [14] reported on a

shallow acceptor, with a binding energy of 0.3 eV, which is responsible for a PL peak at 3.05 eV and could be attributed to a complex involving Li and H.

First-principles calculations also produce controversial results for the energy level of the Li_{Zn} acceptor in ZnO. In early theoretical works, using density functional theory (DFT), the Li_{Zn} acceptor level was calculated to be very shallow. In particular, Park *et al.* [15] calculated that Li in Zn site has a binding energy of 0.09 eV, and Wardle *et al.* [16] predicted that the Li_{Zn} transition level is located at about 0.2 eV above the valence band. However, the prediction of the shallow acceptor level was a consequence of the underestimated bandgap of ZnO in early DFT calculations. Newer approaches, such as hybrid density functional schemes, have demonstrated that Li_{Zn} produces a deep acceptor level, but the exact value of the binding energy varies between 0.4 and 1.1 eV in different works. In particular, Lany and Zunger, [17,18] by employing a Koopmans corrected density functional method, have calculated that the Li_{Zn} acceptor binding energy is 0.86 eV [17] or 0.64 eV [18]. They also predicted that the Li_{Zn} defect in ZnO may have a dual nature, where, in addition to the deep localized state, a shallow acceptor state may exist at about 0.21 eV above the valence band and be revealed in certain experimental conditions [18]. DFT calculations based on hybrid functional schemes predicted a binding energy of 0.75 eV [19,20] and 0.46 eV [21] for the Li_{Zn} acceptor in ZnO. Carvalho *et al.* [22] concluded that, by using different pseudopotentials and functionals, the calculated binding energy of the Li_{Zn} acceptor varies between 0.6 and 1.1 eV. Thus, an accurate and reliable experimental value of the Li_{Zn} binding energy would aid in the development of more accurate theoretical calculation methods.

In PL studies, the binding energy of an acceptor in a conductive n -type semiconductor can be determined from the slope of the thermal quenching of the related PL band [23]. The intensity of the OL band in n -type ZnO decreases considerably above 200 K. From the temperature dependence of the PL intensity, the binding energy E_A for the related acceptor is determined to be in the range of

0.45- 0.68 eV for different samples [24,25]. However, this determined activation energy from the Arrhenius plot should be regarded with caution, because in high-resistivity semiconductors the thermal quenching of PL is sometimes abrupt, and the slope of the dependence has no relation to the acceptor binding energy [26,27]. Abrupt thermal quenching was reliably detected only in high-resistivity GaN up to date. It occurs when the PL intensity drops substantially within a relatively small range of temperatures. Traditional simple models fail to explain the abrupt quenching behavior and instead predict unrealistic and absurd parameters for the defects causing PL bands [26]. A characteristic feature of the abrupt quenching is that the temperature T_0 , at which the PL quenching begins, increases with increasing electron-hole generation rate G ; i.e., the quenching is tunable by the laser power. Remarkably, the binding energy of the acceptor can be found from the $T_0(G)$ dependence. In this work, we report on the first observation of abrupt and tunable thermal quenching of PL in ZnO. From the analysis of this phenomenon, the binding energy for the Li_{Zn} acceptor is estimated to be 0.65 ± 0.10 eV.

2. Experimental

The undoped bulk ZnO samples used in this work were grown by the hydrothermal method by the MTI Corporation (Richmond, CA). The hydrothermal method is known to produce high-resistivity ZnO samples with a low concentration of free electrons [28]. The high resistivity is attributed to the compensation of shallow donors by the Li_{Zn} acceptors originating from the mineralizer which is typically LiOH and KOH [29,30]. PL measurements were performed using a continuous-wave HeCd laser (photon energy of 3.81 eV). The excitation power density, P_{exc} , was varied between 1.9×10^{-4} and 0.19 W/cm^2 using calibrated neutral density filters to attenuate the laser intensity. A closed-cycle cryostat was used for the temperature range of 15 – 320K. The PL spectra were corrected to account for the response of the optical system. The absolute quantum efficiency of the PL, η , is given by the expression, $\eta = I^{\text{PL}} / G$, where I^{PL} is the PL intensity

integrated over the region of the PL spectrum specific to the PL band, and G is the concentration of electron hole pairs created by the laser, per unit volume, per second. For other experimental details, refer to [26].

3. Results

3.1. PL spectrum

The evolution of the PL spectrum with increasing temperature from 15 to 300 K for one of the ZnO samples is shown in Fig. 1. A very broad band at low temperatures is composed of the OL band with a maximum at 2.0 eV and the green luminescence (GL) band with an unresolved maximum at ~ 2.4 eV. The OL and GL bands can be better resolved in time-resolved PL

Fig. 1. PL spectra from undoped ZnO (sample M27) where $P_{\text{exc}} = 0.023 \text{ W/cm}^2$ for select temperatures. The defect-related OL and GL bands (the shapes are indicated with dashed lines) contribute to a broad band at low temperatures. With increasing temperatures, the GL band quenches and disappears by 200 K, after which the quenching of the OL band begins.

measurements because they have very different characteristic lifetimes [31]. The Gaussian shapes of the OL and GL bands, shown in Fig. 1 with dashed lines for temperatures 15 and 100 K, are nearly identical to the shapes revealed in [31] from time-resolved PL measurements. The OL band is caused by transitions between a shallow donor (at low temperature) or the conduction band (at

higher temperatures) and the Li_{Zn} acceptor. The origin of the GL band in ZnO is unclear, yet it is most likely the same as the GL1 band studied in [31]. The GL band is quenched at low temperatures and has a negligible contribution at 100 K to the PL intensity in the region of the OL maximum (2.0 eV), similar to the temperature behavior of the GL1 band reported in [31]. The quenching of the OL band begins above 200 K.

3.2. Thermal quenching of the OL band

The quantum efficiency of the OL band is shown in Fig. 2 as a function of inverse temperature. At low temperature (100-200 K), η is about 8% for the lowest excitation intensity and decreases with increasing excitation intensity due to saturation of the Li_{Zn} acceptors with holes. The quenching of the OL band begins at 210 K for $P_{\text{exc}} = 1.9 \times 10^{-4} \text{ W/cm}^2$.

Fig. 2. Temperature dependence of the PL quantum efficiency, η , for the OL band in ZnO (sample M6) at several excitation intensities. The solid lines are numerical solutions of rate equations [26] using the following parameters: $N_s = 2 \times 10^{17} \text{ cm}^{-3}$, $N_A = 2.3 \times 10^{17} \text{ cm}^{-3}$, $N_D = 0.9 \times 10^{17} \text{ cm}^{-3}$, $C_{nD} = 10^{-10} \text{ cm}^3/\text{s}$, $C_{nS} = 3 \times 10^{-10} \text{ cm}^3/\text{s}$, $C_{pS} = 4 \times 10^{-5} \text{ cm}^3/\text{s}$, $C_{pA} = 7 \times 10^{-6} \text{ cm}^3/\text{s}$, $C_{nA} = C_{DA} = 10^{-14} \text{ cm}^3/\text{s}$, $E_D = 50 \text{ meV}$, $E_A = 600 \text{ meV}$, $G = 1.6 \times 10^{23} \times P_{\text{exc}} \text{ cm}^{-3}\text{s}^{-1}$. Vertical arrows indicate positions of T_0 for $P_{\text{exc}} = 1.9 \times 10^{-4}$ and 0.19 W/cm^2 .

The characteristic temperature of quenching, T_0 , can be found by extrapolating the slopes and finding the intersection of the low and high temperature dependences of η in an Arrhenius plot [26]. It can be seen from Fig. 2 that T_0 shifts to higher temperatures with increasing excitation intensity; i.e., the quenching is tunable. The largest slope of the temperature dependence in the Arrhenius plot in the region of PL quenching corresponds to an activation energy of about 650 meV for $P_{exc} = 1.9 \times 10^{-4} \text{ W/cm}^2$ (at $T = 240\text{-}260 \text{ K}$). At higher temperatures (260-320 K), the slope is smaller for this excitation intensity (corresponds to about 330 meV).

However, according to theory [26], the “slope” of the PL quantum efficiency temperature dependence in the region of abrupt PL quenching has no relation to any binding or activation energy. The abrupt and tunable quenching of PL is caused by a sudden redirection of the recombination flow from a defect-related radiative recombination channel to a nonradiative recombination channel [26]. This happens when the concentration of holes thermally emitted from the radiative defect to the valence band becomes comparable to the concentration of photogenerated holes. Using the simplest PL model (assuming that electron-hole pairs are generated with uniform density only in an active region near the surface, which has a width equal to the inverse of the optical absorption coefficient α), the “slope” of the abrupt quenching may reach several eV. However, in a more realistic model [assuming that the concentration of photogenerated holes decreases exponentially as $\alpha \exp(-\alpha x)$, where x is the distance from the surface], the “slope” is significantly smaller [26]. According to the theory [26], all radiative channels (which involve free electrons) are abruptly quenched at $T \approx T_0$, because the concentration of electrons in the conduction band suddenly drops at $T \approx T_0$.

3.3. Thermal quenching of the exciton band

To verify the assumption that the quenching of the OL band is abrupt and tunable, we have plotted the temperature dependence of η for the exciton emission (Fig. 3). The quantum efficiency of the exciton PL band was calculated from the PL intensity integrated over the region from 3.1 to 3.45 eV. In this Arrhenius plot, the quenching of the exciton luminescence occurs with two slopes. The

Fig. 3. Temperature dependence of the PL quantum efficiency, η , for the exciton luminescence band in ZnO (sample M6) at several excitation intensities. The solid lines are calculated using Eq. (1) with $E_{exc} = 60$ meV and $C = 36$. The dashed lines are calculated using Eq. (2) with $E^* = 350$ meV. PL quenching occurs with two slopes: the first part corresponding to the dissociation energy of the excitons in ZnO, and the second resulting from the abrupt thermal quenching of the OL band and the relative drop in intensity of all channels. A vertical arrow indicates the position of T_0 for $P_{exc} = 0.19$ W/cm².

first, low-temperature portion of the quenching (for $T < T_0$) is a result of exciton dissociation, and it can be fit with the following expression

$$\eta = \frac{\eta_0}{1 + C \exp(-E_{ex} / kT)}, \quad (1)$$

where η_0 is the exciton emission quantum efficiency as $T \rightarrow 0$, C is a constant, E_{ex} is the exciton binding energy, and k is Boltzmann's constant. From the fit, $E_{ex} \approx 60$ meV, which agrees with the

binding energy of free excitons in ZnO [1]. The second portion of the quenching (for $T > T_0$) is a result of abrupt thermal quenching. It can be formally fit with the following expression

$$\eta = \eta_{\infty} \exp(E^* / kT), \quad (2)$$

where η_{∞} is the exciton emission quantum efficiency for $T \rightarrow \infty$, and the constant E^* characterizes the dependence of the slope in this region, but its physical meaning is uncertain. The intersections of the low-temperature and high-temperature dependences give the values of T_0 . It is clear that the PL quenching is tunable by excitation intensity, which is very similar to the OL band. In the region after the abrupt quenching of PL, the quantum efficiency of the exciton emission becomes nearly independent of temperature (Fig. 3) as can be seen for $P_{exc} = 0.00019$ and 0.00097 W/cm².

3.4. Dependence of PL intensity on the excitation intensity

To further support the assumption about the mechanism of PL quenching, we studied the dependence of the PL quantum efficiency on the excitation intensity at selected temperatures. At low temperatures ($T < T_0$), the quantum efficiency of the OL band decreases with increasing excitation intensity (Fig. 2). Such behavior indicates that the Li_{Zn} acceptors become saturated with photogenerated holes, and the new photogenerated holes find other channels such as a nonradiative recombination channel. The exciton luminescence quantum efficiency increases with increasing excitation intensity at low temperature (Fig. 3). The dependence is a power dependence of the form $\eta \propto (P_{exc})^m$, with $m \approx 0.3$ for $T = 100$ -200 K. For a bimolecular law (when excitons are formed from independent electrons and holes), we expect $m = 1$, while for a monomolecular law (when an exciton is formed immediately after an electron-hole pair is generated and the separation of the electron and hole does not occur), we expect $m = 0$. We can speculate that, at low temperatures,

both mechanisms take place, yet the exact explanation of the power dependence of the exciton luminescence efficiency is beyond the scope of this work.

The PL quantum efficiency for both the OL band and the exciton luminescence in the region of the PL quenching (at $T = 280$ K) is plotted as a function of excitation intensity in Fig. 4. At low excitation intensity (up to $P_{exc} \approx 10^{-3}$ W/cm²), the quantum efficiency for both bands is constant. At

Fig. 4. PL quantum efficiency as a function of excitation power density for the OL and exciton emission bands in ZnO (sample M27).

higher excitation intensities (between 10^{-3} and 3×10^{-2} W/cm²), the quantum efficiency for both bands increases in a similar way. Finally, at $P_{exc} > 3 \times 10^{-2}$ W/cm², the exciton PL efficiency approaches a plateau, while the OL quantum efficiency decreases due to saturation of the related defects with photogenerated holes. The rise of the PL quantum efficiency, observed for both PL bands between 10^{-3} and 3×10^{-2} W/cm² can be explained within the model of abrupt and tunable quenching of defect-related PL [32].

4. Discussion

4.1. Abrupt and tunable quenching of PL

Abrupt and tunable quenching of PL is a relatively new phenomenon found in high-resistivity GaN samples, where the thermal quenching of PL occurs in a much narrower temperature range than Boltzmann's statistics predict. In this case, simple formulas derived for conductive n -type semiconductors fail and may produce unreasonable and unphysical parameters. A new model has been suggested for high-resistivity semiconductors, which accurately describes the observed experimental behavior [26].

In the model explaining abrupt and tunable quenching, at least three types of defect centers must be involved [26]. For the studied ZnO samples, these are the following: the Li_{Zn} acceptor responsible for the OL band (with concentration N_A , electron- and hole-capture coefficients C_{nA} and C_{pA} , respectively, and the ionization energy E_A), an unknown nonradiative center (a deep donor with concentration N_S and electron- and hole-capture coefficients C_{nS} and C_{pS} , respectively), and a shallow donor (with concentration N_D , electron-capture coefficient C_{nD} , and the ionization energy E_D). The shallow donor, possibly substitutional hydrogen, is responsible for n -type conductivity with the room-temperature concentration of free electrons on the order of 10^{14} cm^{-3} in bulk ZnO samples grown by the hydrothermal method [33]. While the identity of the nonradiative center remains unknown, it plays an important role in the abrupt and tunable thermal quenching of PL [26].

At low temperatures and under above-bandgap illumination, the acceptors become saturated with photo-generated holes even at very low excitation intensities, and the nonradiative centers become saturated with photo-generated electrons. For this to happen, the nonradiative defects should have large capture cross-sections for both electrons and holes. The preferential capture of

free electrons by nonradiative centers results in the partial blocking of this recombination channel and the accumulation of a significant amount of free electrons in the conduction band. As a result, a population inversion (the saturation with electrons of a higher-lying nonradiative defect energy level and the saturation with holes of a lower-lying energy level of the acceptor) occurs at low temperatures, below the critical temperature T_0 . When the thermal energy is sufficient to release the acceptor-bound holes to the valence band (at $T \approx T_0$), the nonradiative centers efficiently capture the holes, and the nonradiative recombination channel becomes unblocked. Because of the sudden drop in the concentration of free electrons and the concentration of electrons bound to the nonradiative centers, recombination is redirected from the main radiative channel to the nonradiative channel, and all PL bands (that involve transitions of electrons from the conduction band) are quenched abruptly on the temperature scale.

The characteristic temperature at which the abrupt quenching of PL occurs depends on the binding energy of the acceptor and on the PL excitation intensity. Therefore, the binding energy of the acceptor causing the dominant PL band can be determined from the dependence of T_0 on the excitation intensity, whereas the slope of the temperature dependence in the region of the abrupt quenching has no relation to any binding or activation energy. [Figure 5](#) shows dependences of the inverse of T_0 on the logarithm of the excitation intensity for three ZnO samples. For convenience, the excitation intensity is expressed as laser excitation power density P_{exc} (top scale) and as electron-hole generation rate G (bottom scale). In the simplest model of light absorption, which is used in this work, $G = \alpha P_{exc}/\hbar\omega$, where $\alpha \approx 10^5 \text{ cm}^{-1}$ for GaN and $\hbar\omega = 3.81 \text{ eV}$ for a HeCd laser [26,34].

Fig. 5. Dependence of the characteristic quenching temperature T_0 on excitation intensity for the OL and exciton bands in three ZnO samples. The lines are calculated using Eq. (3) with $E_A = 0.65$ eV and $B = 3 \times 10^{33} \text{ cm}^{-3} \text{ s}^{-1}$ (solid line), $E_A = 0.55$ eV and $B = 8 \times 10^{31} \text{ cm}^{-3} \text{ s}^{-1}$ (dashed line), and $E_A = 0.75$ eV and $B = 8 \times 10^{34} \text{ cm}^{-3} \text{ s}^{-1}$ (dotted line).

The dependence of the characteristic quenching temperature T_0 on excitation intensity can be fit with the following expression [26]:

$$T_0 = \frac{E_A}{k \ln(B/G)}, \quad (3)$$

where E_A is the binding energy of the radiative acceptor and B is a sample-dependent constant:

$$B = C_{pA} \left(\frac{1}{\eta_0} - 1 \right) (N_A - N_D) \frac{N_v}{g}. \quad (4)$$

Here, η_0 is the quantum efficiency of PL via this acceptor at temperatures below the quenching, N_v is the effective density of states in the valence band, and g is the degeneracy of the acceptor level. Other parameters of the model, such as the concentration of nonradiative centers (N_S) and the hole-

capture coefficient for the nonradiative center (C_{ps}), also affect T_0 , but they are included into the experimentally determined value of η_0 [26].

From the fit of five dependences for the OL and exciton bands in ZnO samples, we determined that $E_A = 0.65 \pm 0.10$ eV and the coefficient B is in the range between 10^{32} and 10^{35} $\text{cm}^{-3}\text{s}^{-1}$. While E_A governs the slope of the dependence, the parameter B shifts the dependence in the vertical direction. From the value of $B = 3 \times 10^{33} \text{ cm}^{-3}\text{s}^{-1}$ (corresponding to $E_A = 0.65$ eV) and the experimentally found value of η_0 (0.08), we can estimate that $C_{pA}(N_A - N_D) \approx 4 \times 10^{13} \text{ s}^{-1}$. This agrees with reasonable values of $C_{pA} \approx 10^{-5} \text{ cm}^3/\text{s}$ and $(N_A - N_D) \approx 10^{18} \text{ cm}^{-3}$. It is doubtful that the parameters C_{pA} and $(N_A - N_D)$ (and therefore, the parameter B) can be higher. Thus, the values of E_A exceeding 0.65 eV are unlikely because they require unreasonably high values of B , even though from the slope of the dependence the values of E_A up to 0.75 eV appear to be acceptable.

We used numerical calculations to solve rate equations from [26] for the model of three types of defects (where the nonradiative center S is a deep donor) and to fit the temperature dependences of the OL quantum efficiency at different excitation intensities. The best fits are shown in Fig. 2 only for the highest and lowest excitation intensities for clarity. The parameters of the fit are shown in the figure caption (where C_{DA} is the effective capture coefficient for transitions from shallow donors to the acceptor, while other parameters were defined above). Note that excessive constraint of model parameters makes it difficult to obtain a better fit with experimental data, because there are many characteristic features in the experimental dependences. The largest disagreement between the calculated curves and experimental dependences is observed at $T > T_0$ for the lowest excitation intensity, where the experimental dependence is less steep than the simulated one (Fig. 2). Among the reasons for such disagreement may be the temperature dependence of the

capture coefficients or the thermal emission of charge carriers from the nonradiative center, which were not accounted for in the model. Note that we consider only one (dominant) type of nonradiative center, while in reality there are several sources of nonradiative recombination. Indeed, if the recombination efficiency of the nonradiative channel gradually decreases with increasing temperature, the intensities of all PL bands will proportionally increase with temperature. Then, the slope of the thermal quenching of PL bands will decrease. This assumption is supported by the temperature behavior of the exciton emission (Fig. 3). The calculated slope in the temperature dependence of η for the exciton emission at $T > T_0$ corresponds to the dissociation of free excitons with binding energy of 60 meV (the lowest solid line in Fig. 3). However, in experiment we observe nearly temperature independent η between 270 and 320 K.

4.2. About the binding energy of the Li_{Zn} acceptor

Finally, the binding energies for the Li_{Zn} acceptor reported in other experimental works are considered. The value of 800 meV was first reported in [7,8], where it was found from the shape of the OL band, with the assumption that the high-energy side of this band ends at 2.5 eV. The thermoluminescence spectrum was analyzed in these works, and the maximum of the OL band appeared at 1.96 eV for temperatures between 36.5 and 40 K (Fig. 3 in [8]). The shape of the OL band in [8] is nearly identical to the shape of the OL band previously measured with our PL setup and reported in [31]. It can be fit with a Gaussian curve:

$$I^{PL}(\hbar\omega) = I_{\text{max}}^{PL} \exp\left(-\frac{(\hbar\omega - \hbar\omega_{\text{max}})^2}{2\sigma^2}\right), \quad (5)$$

where I_{max}^{PL} and $\hbar\omega_{\text{max}}$ are the PL intensity and photon energy corresponding to the OL band maximum, and $\sigma \approx 0.22$ eV. The full width at half maximum for the OL band is 0.50 eV and $\hbar\omega_{\text{max}}$

= 1.96 eV at low temperature and low excitation intensity. Note that in some other works, the position of the Li-related PL band maximum is slightly different, and it is sometimes called the yellow band. For example, Schirmer and Zwingel in an earlier work mention the Li-related yellow luminescence with a maximum near 2.2 eV studied by thermoluminescence, yet no luminescence spectrum was shown [7]. Meyer *et al.* [14,35] describe the Li-related band with a Gaussian shape and a maximum at 2.05-2.10 eV. McCluskey *et al.* [13] analyze the Li-related PL band and refer to it as the yellow band with a maximum at 2.25 eV. Note that the OL band is rarely observed as an isolated PL band, and the contribution of the green luminescence at its high energy side effectively shifts the maximum of the observed broad band (as in our Fig. 1, in Fig. 2 of Ref. [35], and in Fig. 5 of Ref. [13]). In addition, very careful calibration of a PL setup is needed to account correctly for its spectral response and to avoid distortion of a very broad band. All these reasons make it very difficult to analyze the high-energy side of the PL band with the intention of estimating the position of the acceptor energy level.

Useful information can be obtained from the analysis of a PL excitation (PLE) spectrum. According to McClusky *et al.* [13], the PLE spectrum (taken for PL at 2.25 eV) shows an onset at ~3.1 eV. Using this value, the authors of Ref. [13] have constructed a configuration coordinate diagram, in which the resonant excitation occurs at photon energy 3.1 eV. However, the onset in the PLE spectrum corresponds not to the excitation band maximum but only the low-energy side of this band, which may be close to the zero-phonon transitions (as in the case of the YL band in GaN [36]) or far from it (as in the case of the GL2 band in GaN [37]). Thus, the PLE data in Ref. [13] provide insufficient information, and it can be concluded from these data only that the binding energy of the Li_{Zn} acceptor is larger than ~0.4 eV. Further, the temperature dependence of electrical resistivity in Li-doped ZnO reveals an activation energy of 0.86 eV [13]. However, this value may correspond to the thermal emission of electrons from a deep compensating donor to the conduction

band, since the sign of free carriers was not determined in this experiment. Based on the analysis of the results in Sec. 4.1, we conclude that the binding energy of the Li_{Zn} acceptor is about 0.65 eV, and that values close to or higher than 0.75 eV are unlikely.

5. Conclusions

In this work, abrupt and tunable thermal quenching has been reported for the first time for high-resistivity ZnO, and the activation energy of the Li_{Zn} acceptor has been calculated to be $E_A = 0.65 \pm 0.10$ eV. Abrupt and tunable thermal quenching has only been reported for a few systems including high-resistivity GaN. This study shows that this phenomenon may be more generally applied to other semiconductor systems. Additionally, this work provides more evidence to settle the dispute concerning the energy position of the Li_{Zn} acceptor in ZnO.

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Figure captions

Fig. 1. PL spectra from undoped ZnO (sample M27) where $P_{exc} = 0.023 \text{ W/cm}^2$ for select temperatures. The defect-related OL and GL bands (the shapes are indicated with dashed lines) contribute to a broad band at low temperatures. With increasing temperatures, the GL band quenches and disappears by 200 K, after which the quenching of the OL band begins.

Fig. 2. Temperature dependence of the PL quantum efficiency, η , for the OL band in ZnO (sample M6) at several excitation intensities. The solid lines are numerical solutions of rate equations [26] using the following parameters: $N_s = 2 \times 10^{17} \text{ cm}^{-3}$, $N_A = 2.3 \times 10^{17} \text{ cm}^{-3}$, $N_D = 0.9 \times 10^{17} \text{ cm}^{-3}$, $C_{nD} = 10^{-10} \text{ cm}^3/\text{s}$, $C_{ns} = 3 \times 10^{-10} \text{ cm}^3/\text{s}$, $C_{pS} = 4 \times 10^{-5} \text{ cm}^3/\text{s}$, $C_{pA} = 7 \times 10^{-6} \text{ cm}^3/\text{s}$, $C_{nA} = C_{DA} = 10^{-14} \text{ cm}^3/\text{s}$, $E_D = 50 \text{ meV}$, $E_A = 600 \text{ meV}$, $G = 1.6 \times 10^{23} \times P_{exc} \text{ cm}^{-3}\text{s}^{-1}$. Vertical arrows indicate positions of T_0 for $P_{exc} = 1.9 \times 10^{-4}$ and 0.19 W/cm^2 .

Fig. 3. Temperature dependence of the PL quantum efficiency, η , for the exciton luminescence band in ZnO (sample M6) at several excitation intensities. The solid lines are calculated using Eq. (1) with $E_{exc} = 60 \text{ meV}$ and $C = 36$. The dashed lines are calculated using Eq. (2) with $E^* = 350 \text{ meV}$. PL quenching occurs with two slopes: the first part corresponding to the dissociation energy of the excitons in ZnO, and the second resulting from the abrupt thermal quenching of the OL band and the relative drop in intensity of all channels. A vertical arrow indicates the position of T_0 for $P_{exc} = 0.19 \text{ W/cm}^2$.

Fig. 4. PL quantum efficiency as a function of excitation power density for the OL and exciton emission bands in ZnO (sample M27).

Fig. 5. Dependence of the characteristic quenching temperature T_0 on excitation intensity for the OL and exciton bands in three ZnO samples. The lines are calculated using Eq. 4 with $E_A = 0.65 \text{ eV}$ and $B = 3 \times 10^{33} \text{ cm}^{-3}\text{s}^{-1}$ (solid line), $E_A = 0.55 \text{ eV}$ and $B = 8 \times 10^{31} \text{ cm}^{-3}\text{s}^{-1}$ (dashed line), and $E_A = 0.75 \text{ eV}$ and $B = 8 \times 10^{34} \text{ cm}^{-3}\text{s}^{-1}$ (dotted line).