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M. A. Reshchikov

Virginia Commonwealth University, mreshchikov@vcu.edu

J. Q. Xie

SVT Associates, Inc.

B. Hertog

SVT Associates, Inc.

A. Osinsky

SVT Associates, Inc.

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Yellow luminescence in ZnO layers grown on sapphire

M. A. Reshchikov,^{1,a)} J. Q. Xie,² B. Hertog,² and A. Osinsky²

¹Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284, USA

²SVT Associates, Inc., Eden Prairie, Minnesota 55344, USA

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We conducted a detailed study of the yellow luminescence (YL) band that has a maximum of 2.19 eV at 10 K in undoped and N-doped ZnO layers grown on sapphire substrates. Important characteristics of this band and the related defect are established. The YL band is attributed to a transition between a shallow donor and an acceptor with an energy level ~ 0.4 eV above the valence band. Quenching of the YL intensity with activation energies of 85 meV and 0.4 eV is observed at temperatures above 100 and 320 K, respectively. The YL band is possibly due to a defect complex that may include a Zn vacancy. © 2008 American Institute of Physics. [DOI: 10.1063/1.2924437]

I. INTRODUCTION

Due to its unique optical properties, ZnO is regarded as an attractive alternative to GaN for solid-state emitters in the blue to ultraviolet range.¹ While structural quality of bulk and epitaxial ZnO is generally very good, the presence of point defects can significantly affect the electrical and optical properties of the material, as well as degrade the performance and reliability of ZnO devices. First-principles calculations predict that the Zn vacancy (V_{Zn}) with a $2-/-$ level near 0.8 eV above the valence band is likely to be the dominant point defect in ZnO.² Tuomisto *et al.*³ confirmed by positron annihilation spectroscopy that the concentration of V_{Zn} or V_{Zn} -related complexes is sufficiently high ($\approx 2 \times 10^{15} \text{ cm}^{-3}$) to explain the total acceptor density in high-quality ZnO. Other acceptorlike native defects, O_{Zn} and O_i , are predicted to have energy levels of ~ 1 eV above the valence band, but are expected to be less abundant due to the higher formation energy.² Among the donorlike native defects, oxygen vacancies (V_{O}) with $+/0$ and $2+/+$ levels ~ 1.9 and 2.9 eV above the valence band, respectively, are expected to be the dominant defects in *p*-type ZnO samples, while formation of these defects in *n*-type ZnO is unlikely.⁴ However, V_{O} can be produced in ZnO by electron irradiation⁵⁻⁸ and remain stable up to 400 °C (Ref. 7) or even 550 °C.⁸ V_{O} is a defect with a negative- U behavior,⁴ and its metastable $1+$ state can be observed only after optical excitation. The V_{O}^+ defect was identified in early electron paramagnetic resonance (EPR) studies,^{5,6} and later Vlasenko and Watkins⁷ established from optically detected EPR (ODEPR) that V_{O}^+ is responsible for a broad luminescence band with a peak near 600 nm. This is in contrast to the widespread belief that the green luminescence (GL) band with a maximum near 2.43 eV (510 nm) in undoped ZnO results from transitions between the $V_{\text{O}}^{2+/+}$ level and the valence band.^{9,10} This commonly held opinion is largely based on the fact that the GL band is often observed in Zn-rich ZnO (Ref. 11) as well as on an erroneous identification of the $g=1.956$ EPR signal with V_{O}^+ .^{9,10,12} In fact, the $g=1.956$ sig-

nal is due to the effective-mass shallow donors^{7,13} while an isolated V_{O}^+ is observed in EPR as a signal with $g_{\parallel}=1.9945$ and $g_{\perp}=1.9960$.⁵⁻⁷ It is also worth noting that Leiter *et al.*¹⁴ observed an ODEPR signal with $g_{\parallel}=1.984$ and $g_{\perp}=2.025$ from the GL band with a peak at 2.45 eV and attributed it to an internal transition from an excited 3T_2 state of the neutral V_{O}^0 to the 1A_1 ground state.

In addition to the GL band with a maximum at 510 nm, numerous other bands have been observed in the photoluminescence (PL) spectrum of undoped ZnO,¹ including bands with peaks at 1.94–1.97 eV,^{15,16} 2.00–2.05 eV,¹⁷⁻²⁰ 2.17–2.21 eV,^{18,19} and 2.25–2.35 eV.^{21,22} All these bands are typically attributed to native defects such as V_{Zn} and O_i .^{17,19,22} In most investigations, however, only room temperature PL spectra were analyzed leaving the most important characteristics of the related defects unknown. Moreover, PL bands resulting from several defects often overlap, and the position of the overall band maximum is misleading. Common practice is to deconvolute such broad bands into several bands with a Gaussian fitting procedure,^{20,21} which is not always justified and can lead to the creation of artificial peaks since the PL band from a single defect is often asymmetric by nature.²³ The appearance of a large number of bands in the PL spectrum of undoped ZnO indicates the presence of unintentionally introduced impurities and defect complexes, which can be formed by an interaction between native defects and dopants. These together with native defects should also be considered as possible sources of the dominant point defects. Since different defects may cause broad PL bands with similar peak positions and, possibly, similar shapes, a detailed study is required to distinguish the various defects and identify their salient features.

In this work, we present an analysis of the yellow luminescence (YL) band with a low-temperature maximum at ~ 2.2 eV in undoped and N-doped ZnO layers grown on sapphire substrates at SVT Associates. A comprehensive study of this band at different temperatures and excitation intensities, using continuous and pulse excitation, allowed us to determine characteristic properties of the related defect, which may be useful for the future development of ZnO.

^{a)}Author to whom correspondence should be addressed. Tel. 804-828-1613. FAX: 804-828-7073. Electronic mail: mreshchi@vcu.edu.

TABLE I. Characteristics of the ZnO samples.

Sample number	Thickness (μm)	Doping	Annealing T (K)	n_0 at 300 K (cm^{-3})	External QE (%) at 10 K	
					Exciton band	YL band
102	1	...	600	2.2×10^{17}	0.2	2.7
110	0.6	...	750	4.5×10^{16}	1.1	0.8
111	0.6	...	750	4.5×10^{16}	0.7	2.4
227	1	N	600	1.1×10^{17}	0.01	0.5
226	1	...	600	6.5×10^{16}	0.1	0.3
212	0.97	...	650	4.1×10^{16}	0.4	2.0

II. EXPERIMENT

Five undoped and one N-doped ZnO layers, each $\sim 1 \mu\text{m}$ thick, were epitaxially grown on *c*-plane sapphire substrates at SVT Associates using rf-plasma molecular beam epitaxy (MBE). The samples were annealed in vacuum for 5 min at temperatures between 600 and 750 °C (see Table I). Electron concentration in all the layers determined from Hall effect measurement at room temperature was $\sim 10^{17} \text{ cm}^{-3}$. There was no clear correlation between the carrier concentration and the annealing temperature or details of the growth conditions. In the Raman spectrum of the six samples, we observed two modes from ZnO: the E_2^L line at $100.4 \pm 0.4 \text{ cm}^{-1}$ and the E_2^H line at $439.3 \pm 0.4 \text{ cm}^{-1}$. These are very close to the values measured in a large number of bulk ZnO crystals (100.6 ± 0.2 and $438.8 \pm 0.2 \text{ cm}^{-1}$, respectively), indicating that there is no significant stress in the studied layers.

Steady-state PL (SSPL) and time-resolved PL (TRPL) were excited with a cw He–Cd laser (50 mW, photon energy 3.81 eV) and a pulsed nitrogen laser (1 ns pulses with repetition frequency 6 Hz and a photon energy of 3.68 eV), respectively. The PL signal was dispersed by a 1200 rules/mm grating in a 0.3 m monochromator and detected by a cooled photomultiplier tube. Calibrated neutral-density filters were used to attenuate the excitation power density (P_{exc}) in the range of 10^{-6} – 300 W/cm^2 in the SSPL experiments. Closed-cycle and high-temperature optical cryostats were used for measurements in the temperature ranges of 10–320 K and 295–640 K, respectively. The PL spectra were corrected to account for the response of the optical system. The absolute external quantum efficiency (QE) of a PL band was estimated by integrating the PL intensity over a particular band and comparing the value with those obtained from reference GaN and ZnO samples previously calibrated²⁴ and measured using the same equipment under identical conditions.

III. RESULTS

A. Low-temperature PL spectrum

Figure 1 shows the PL spectra of the ZnO layers at 10 K. The PL spectrum in the excitonic range (between ~ 3.0 and 3.45 eV) contains a set of sharp lines with the strongest peaks at ~ 3.359 and 3.363 eV. These peaks can be attributed to excitons bound to neutral shallow donors (DBE lines). A shoulder at higher energies is due to contribution from the

free exciton (FE) emission which becomes the dominant exciton peak at temperatures above 50 K. The peak at 3.331 eV labeled *Y* in Fig. 1(a) is presumably an exciton bound to structural defects.²⁵ LO phonon replicas of the main peaks can be seen at lower energies. In the N-doped ZnO layer, the DBE line is broad and very weak, while the donor-acceptor pair (DAP) band with the zero-phonon line at 3.234 eV obviously involves the shallow N acceptor.²⁵ A slightly asymmetrical broad band, called hereafter the YL band, was ob-

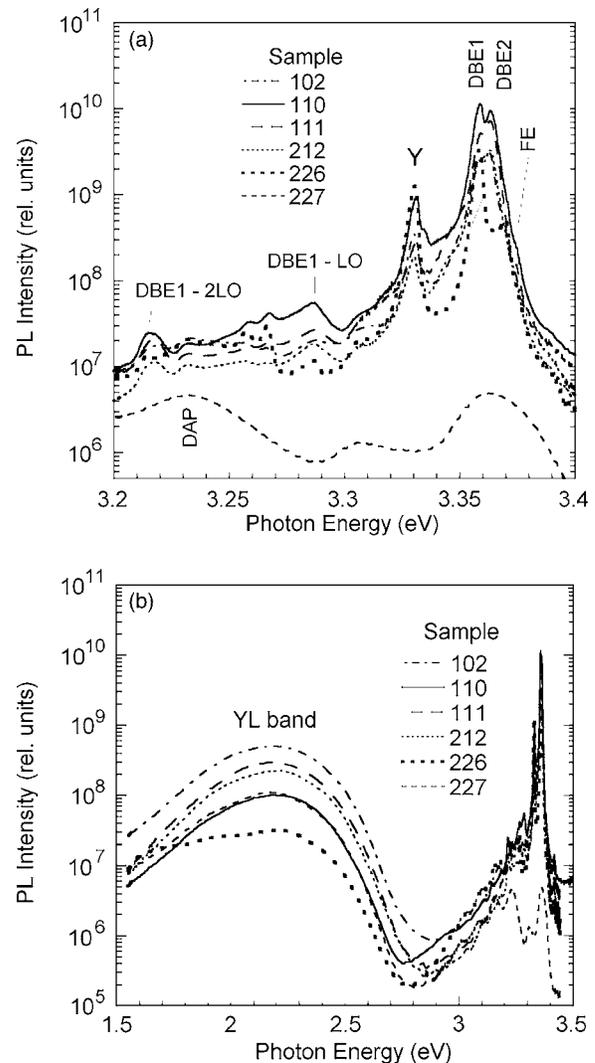


FIG. 1. PL spectrum from ZnO layers at 10 K. (a) Excitonic part. $P_{\text{exc}} = 0.3 \text{ W/cm}^2$ (b) Complete spectrum. $P_{\text{exc}} = 3 \text{ mW/cm}^2$.

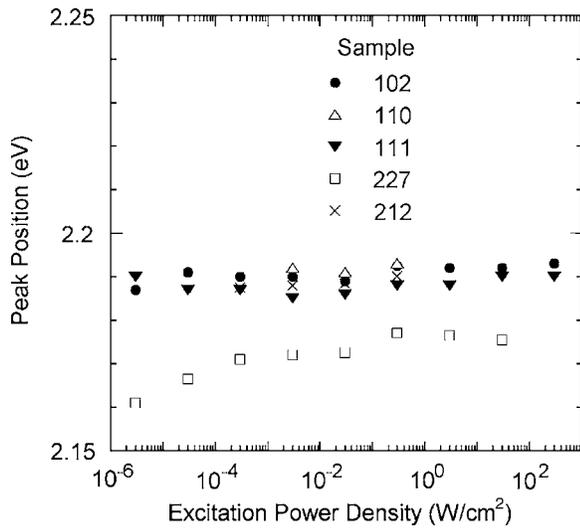


FIG. 2. Peak position of the YL band at different excitation intensities and $T=10$ K.

served at about 2.2 eV in all the samples [Fig. 1(b)]. A weak blue band with a peak at 2.9 eV could also be resolved in sample 110. One of the samples (226) was excluded from further analysis because of the presence of a red luminescence (RL) band, which appeared as a shoulder at about 1.8 eV and interfered with analysis of the YL band.

The YL band has a maximum at $E_m=2.19 \pm 0.01$ eV at 10 K in all the undoped samples and at about 2.17 eV in the N-doped sample. For a wide range of excitation intensities the YL band remained at nearly the same position and shape. The peak position of the YL band shifted by 5 ± 5 meV to higher energies in the undoped samples and by about 15 meV in the N-doped sample with increasing excitation intensity at 10 K (Fig. 2). Moreover, the peak position of the shallow DAP band increased by 7 meV as P_{exc} was increased from 3×10^{-4} – 300 W/cm². The intensity of the YL band almost linearly increased with increasing excitation power density up to about 0.1 W/cm², above which an incomplete saturation was observed. Intensity of the DBE line increased linearly with P_{exc} in the undoped samples and superlinearly ($\sim P_{exc}^{3/2}$) in the N-doped sample.

B. Effect of temperature

The evolution of the PL spectrum as the temperature increased from 10 to 320 K was studied in five samples. All five samples showed similar results. The PL spectra for an undoped and the N-doped samples are shown in Figs. 3(a) and 3(b), respectively. The shift of the YL band maximum, $E_m(T)$, and variation of the full width at half maximum (FWHM), $W(T)$, are shown in Figs. 4(a) and 4(b), respectively. Notably, the large width and asymmetric shape of the YL band together with moderate interference effects (barely visible oscillations with peak separation of ~ 0.3 eV) and contribution from the RL band at $T > 260$ K in sample 227 did not allow the determination of $E_m(T)$ and $W(T)$ with a high degree of accuracy. The band maximum shifted to higher energies [Fig. 4(a)], which is typical for defects with

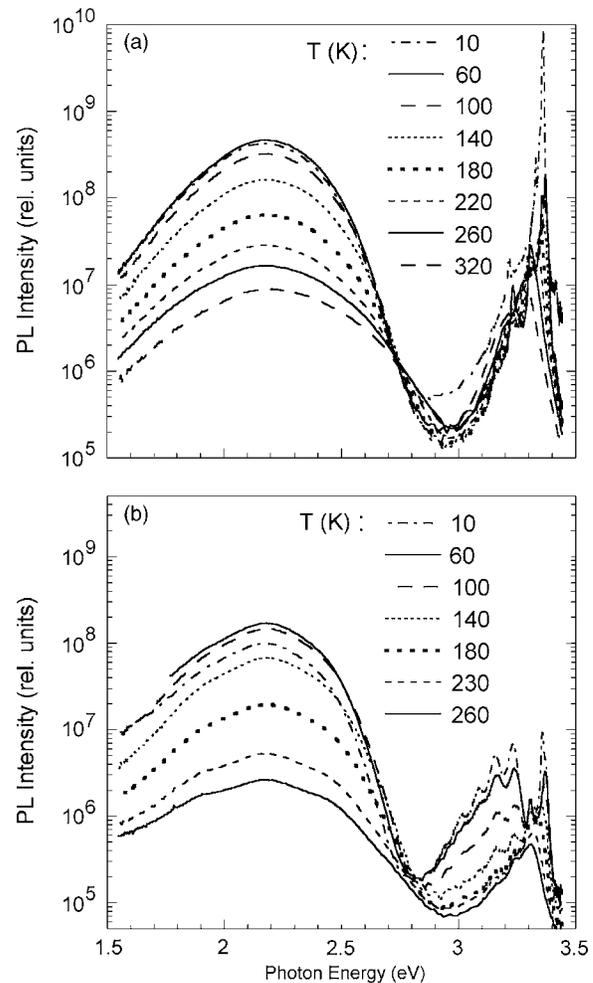


FIG. 3. Evolution of the PL spectrum with temperature. (a) Undoped ZnO, sample 111, (b) N-doped ZnO, sample 227. $P_{exc}=3$ mW/cm². Barely visible oscillations with a period of 0.25 eV in (b) are due to interference effect in a layer with a thickness of 1 μ m.

strong electron-phonon coupling. The temperature dependence of the band FWHM could be fitted [Fig. 4(b)] to the expression²³

$$W(T) = W(0) \sqrt{\coth\left(\frac{\hbar\omega_0}{2kT}\right)}, \quad (1)$$

where the band FWHM at zero temperature $W(0)$ and the effective local phonon energy $\hbar\omega_0$ are fitting parameters. The bandwidth depends on the average number of phonons emitted in each recombination. The value of $\hbar\omega_0$ can be formally related to the phonon energy corresponding to the dominant local or pseudolocal vibrational mode of the defect.

After increasing the temperature from 10 to 80 K, the integrated intensity of the YL band increased by 1.2–1.5 times. At temperatures above 100 K, a quenching of the YL was observed in all the samples [Fig. 5(a)]. The temperature dependence of the integrated intensity for the YL band in this region could be described by the well-known formula

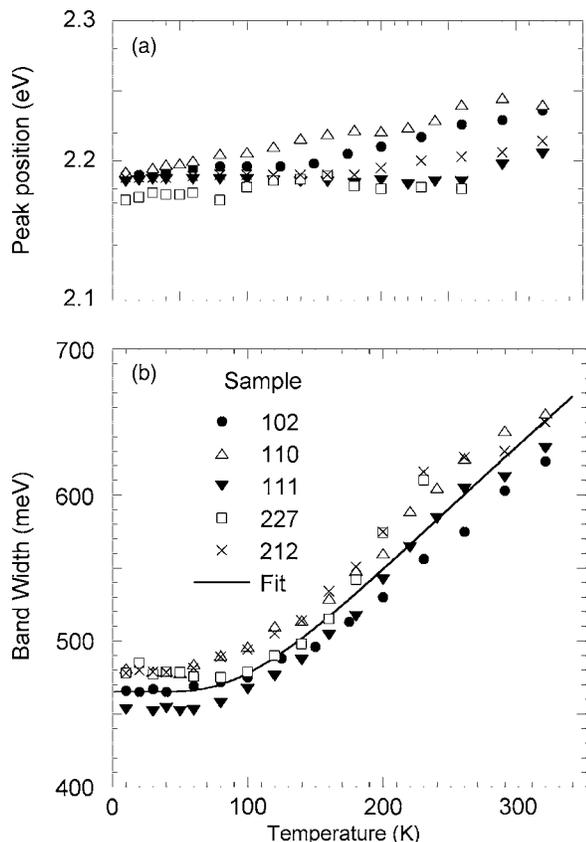


FIG. 4. Peak position (a) and FWHM (b) of the YL band in ZnO layers as a function of temperature. Solid line in (b) is calculated by using Eq. (1) with $W(0)=465$ meV and $\hbar\omega_0^e=31$ meV. $P_{\text{exc}}=30$ mW/cm².

$$I(T) = \frac{I(0)}{1 + C \exp\left(-\frac{E_a}{kT}\right)}, \quad (2)$$

where $I(0)$ is the PL intensity at temperatures before quenching and C is a constant or a variable slowly changing with temperature.²³ The activation energy E_a was estimated to be 85 ± 15 meV.

For one of the undoped samples, the PL spectrum was also studied in the temperature range of 295–640 K. The activation energy of the YL quenching in this range increased to 0.40 eV [Fig. 5(b)]. Interestingly, the integrated exciton emission intensity decreased with increasing temperature faster than the quenching with activation energy of 60 meV expected from dissociation of FEs [Fig. 5(b)]. If this discrepancy were caused by an increase of nonradiative recombination efficiency at temperatures above 320 K and this increase affected alike the exciton and YL bands, the activation energy of the YL band quenching should be corrected to become about 0.35 eV. However, the $I(T)$ dependencies for increasing and decreasing temperature coincided in the case of the YL band, while they slightly diverged in the case of the exciton emission [Fig. 5(b)]. Thus, we accept the original value of 0.40 eV as the activation energy of the YL band, rather than the corrected value of 0.35 eV. Remarkably, at 640 K the YL band peaked at 2.25 eV and its FWHM reached 0.9 eV, in good agreement with parameter $\hbar\omega_0$ found from Eq. (1).

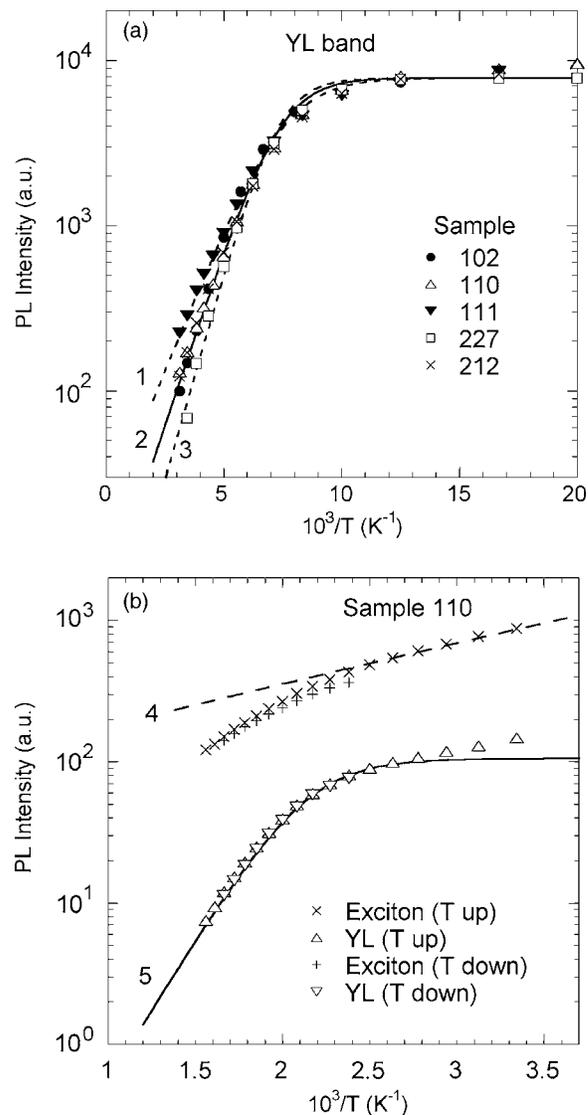


FIG. 5. Variation of the integrated PL intensity with inverse temperature. (a) $T=50$ –320 K (the YL band), (b) $T=295$ –640 K (exciton and the YL bands for sample 110). Points, experiment. $P_{\text{exc}}=30$ mW/cm². Curves are calculated by using Eq. (2) with $E_a=70$ meV (1), 85 meV (2), 100 meV (3), 60 meV (4), and 400 meV (5).

C. Time-resolved photoluminescence

TRPL is often useful for determining what type of optical transition occurs. We studied TRPL at different temperatures in two undoped samples (111 and 212) and the N-doped sample. For all three the results were similar. Figures 6(a) and 6(b) show evolution of the YL band over time at 10 K. Within an accuracy of ± 20 meV we did not observe a significant shift of the YL band over time. However, for sample 111 the YL band appears to redshift by ~ 10 meV after pulse excitation [Fig. 6(a)]. A contribution from the RL band to the PL spectrum of the N-doped layer prevented analysis of the band shift with time for that sample [Fig. 6(b)].

The PL decay at 10 K reveals two nearly exponential regions with the characteristic times of 0.1 and 300 μs (Fig. 7). Both regions appear to be related to the same YL band and not two separate overlapping bands (see evolution of the PL spectrum in Fig. 6). The effective lifetime τ^* of the fast

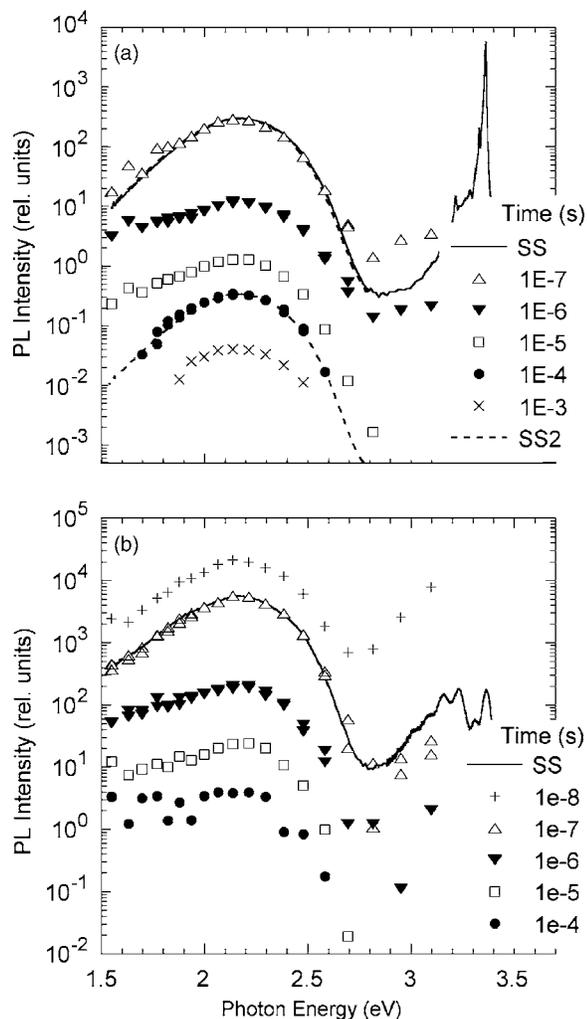


FIG. 6. Evolution of PL spectrum with time after excitation with a pulse laser at 10 K. (a) Undoped ZnO, sample 111, (b) N-doped ZnO, sample 227. Solid lines show a steady-state PL spectrum. Dashed lines show the same SSPL spectrum shifted to lower energy by 10 meV and arbitrary shifted vertically for better comparison.

and slow components was defined as the time at which the product of PL intensity on time has a maximum.²⁶ τ^* for the fast component remained constant in the temperature range 10–60 K, while τ^* of the slow component decreased exponentially as $\tau^* = \tau^*(0)[1 + C' \exp(-E_a/kT)]$ with an activation energy E_a of about 8 meV (Fig. 8). At higher temperatures, the fast and slow components merged, and above ~ 150 K the decay of YL band showed nearly a t^{-1} dependence (Fig. 7). While the shape of the PL decay showed little change between 100 and 300 K, the intensity of the YL band after pulse excitation (measured at 10^{-7} s) decreased in this temperature range, and the decrease was very similar to the observed quenching of the YL band when excited with a cw laser (Fig. 8).

IV. DISCUSSION

After comparing position, shape, and behavior of the YL band in the different samples, we conclude that the YL band originates from the same defect. The large width and slightly asymmetrical shape of the YL band indicate that the related

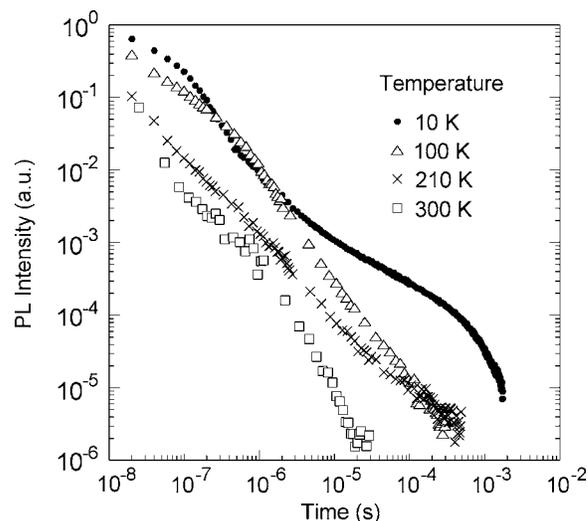


FIG. 7. Decay of PL intensity at 2.15 eV with time after excitation with a pulse laser at different temperatures in undoped ZnO (sample 111). The decay curve at each temperature is a superposition of three (at 10 K) or two (100–300 K) decays measured at different scales of an oscilloscope and plotted with overlap. Every 100th point is shown.

defect exhibits a relatively strong electron-phonon coupling, and several phonons are emitted in each recombination. The broadening and blueshift of the YL band with increasing temperature are also typical of PL bands arising from defects with strong electron-phonon coupling.^{23,27} Without PL excitation spectrum, it is difficult to determine reliably the energy of the optical transition taking place without phonon emission, E_0 . From steep decrease of the YL band intensity in the photon range of 2.5–2.7 eV at low temperature [Fig. 1(b)] it appears that E_0 is about 2.7 eV or slightly higher.

A. Type of transition responsible for the YL band

In n -type wide-band-gap semiconductors, we expect to observe transitions from shallow donors to various acceptors

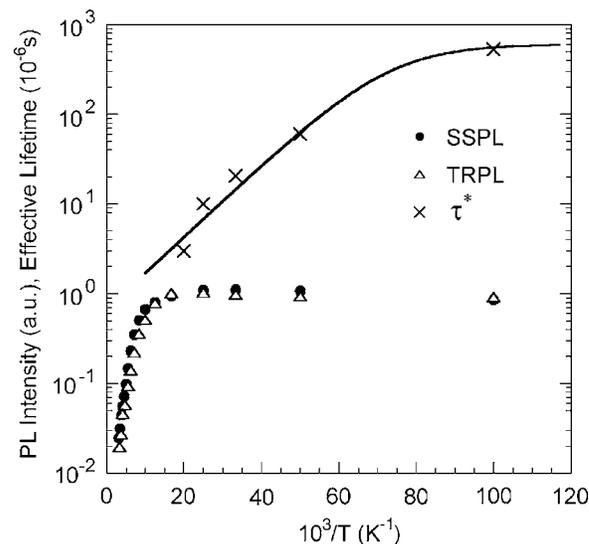


FIG. 8. Variation of the PL intensity integrated over the YL band (SSPL), PL intensity taken 0.1 μ s after pulse excitation (TRPL), and effective lifetime (long-time component) of the YL decay with inverse temperature. Points, experiment for sample 111. Solid curve is calculated by using Eq. (2) with $E_a=8$ meV.

at low temperature, which may give way to transitions from the conduction band to the same acceptor levels at elevated temperatures when the concentration of free electrons increases.²³ The DAP transitions involving shallow donors are typically dominant over any other type of transitions in the low-temperature PL spectrum because photogenerated electrons and holes are very quickly captured by positively charged shallow donors and negatively charged acceptors, respectively. Moreover, the wavefunction of electrons at shallow donors is much larger than that of electrons at deep donors. Only when the concentration of deep donors is very large and significantly exceeds the concentration of the shallow donors, such as in the case of Mg-doped GaN, can the DAP transitions involving deep donors dominate in the PL spectrum.²³ The characteristic feature of the DAP transitions is a shift of a band maximum to a higher energy resulting from an increased excitation intensity for continuous excitation or an increased time delay for pulse excitation. In both cases the shift is explained by faster recombination in nearby pairs, which contributes to the high-energy side of the band due to a stronger Coulomb interaction. Note that DAP with shallow donors cause small shifts (few meV) while DAP with deep donors may cause shifts up to 0.2 eV.²³ In this work, we observed very small shifts of the YL band with variation of the excitation intensity (Fig. 2), and no shift could be detected (within an accuracy of 20 meV) by using different time delays for pulse excitation (Fig. 6). Therefore, we conclude that, at least at low temperatures, the YL band is caused by DAP transitions involving shallow donors. The markedly larger shift of the YL band in the N-doped as compared to that in the undoped samples can be explained by the following reasoning. Although the Hall effect measurement showed a relatively high concentration of free electrons in the N-doped sample, we assume that most of the layer is highly resistive or even *p*-type while *n*-type conductivity originates either from the interface or the surface.^{28,29} This assumption is supported by the fact that only in the N-doped sample does the exciton emission intensity increase as $P_{\text{exc}}^{3/2}$, which is very similar to the dependence observed in high-resistivity GaN doped with Zn.²³ In high-resistivity semiconductors several donor levels would contribute to the DAP transitions as opposed to the low-resistivity semiconductors where the shallowest donor level filled with electrons in equilibrium contributes greater. This would cause larger shift of the PL band with increasing excitation intensity, the effect previously observed in Zn-doped GaN.³⁰ Alternatively, potential fluctuations are possible in the highly resistive N-doped ZnO sample, which may also explain the shift.²³

We assume that the ionization energy of the dominant shallow donor is ~ 60 meV,³¹ which is consistent with the position of the strongest observed exciton peak in our samples, i.e., 3.359 eV. Even at room temperature most of the shallow donors are not ionized, and DAP-type transitions may dominate over the eA transitions (from the conduction band to the same acceptor). Therefore, observation of non-exponential decay of the YL in wide range of temperatures (Fig. 7) does not contradict to the above assignment of the YL band to the DAP transitions. Note also that the broadening and blue shift of the YL band with temperature would be

nearly the same for the DAP and eA transitions since the shape and position of the broad PL bands are dictated mostly by vibrational characteristics of the acceptor (strength of the electron-phonon coupling and energies of phonon modes).

B. On the YL band quenching with temperature

The quenching of PL bands caused by transitions from shallow donors or the conduction band to acceptor levels in *n*-type semiconductors is commonly attributed to the escape of holes from the acceptor levels to the valence band.²³ However, the activation energy of the $I(T^{-1})$ dependence for the YL band in the temperature range of 120–300 K (~ 85 meV) is too small to assign it to the acceptor ionization energy. This activation energy cannot be related to the ionization of shallow donors as well. This is because the PL intensity in *n*-type semiconductors solely depends on the ability of acceptors to capture photogenerated holes since the capture rate of holes is much smaller than PL lifetimes,²³ and since the concentration of neutral donors is high in our undoped samples below the room temperature. Sometimes an unusually small activation energy for PL quenching is attributed to the interchange of the radiative mechanism of recombination with a nonradiative one above some critical temperature. According to this model, a defect in the excited state is thermally excited up to the crossing point of the adiabatic potentials for the ground and excited states, after which it relaxes to the equilibrium position of the ground state with the emission of many phonons.^{23,32} Alternatively, there may be a transition from the stable excited state to a metastable excited state over a barrier with the consequent nonradiative recombination to the ground state. In both cases the decay of the luminescence after pulse excitation should become exponential in the temperature region of PL quenching, and the PL lifetime should decrease with the same activation energy as the PL intensity at continuous excitation.²³ However, in TRPL experiment we saw nonexponential decay of PL with nearly unchanged “slope” at temperatures above 100 K (Fig. 7). Moreover, the quenching of the YL band with the activation energy of 85 meV cannot be explained by the exponential change in the hole-capture cross section of the acceptor or any other defect. Indeed, the capture cross section may exponentially increase with increasing temperature, but not decrease.³³ The decrease of the YL band intensity by two orders of magnitude observed at temperatures between 100 and 300 K cannot be caused by an exponential increase of cross section for some other (nonradiative) defect because in this case all radiative channels would quench with this activation energy. At this time we are unable to explain unambiguously neither the quenching of the YL band with the activation energy of 85 meV [Fig. 5(a)] nor the slow component of the YL decay exhibiting activation energy of 8 meV (see Figs. 7 and 8). As for the apparent “fast” component in the YL transients, it may be just a part of the usual DAP-type decay of PL.³⁴ Further studies are needed to elucidate the reason of the YL quenching with the activation energy of ~ 85 meV and unusual transformation of the YL transients with temperature.

As for the quenching of the YL band at temperatures above 320 K, it is most probably caused by escape to the valence band of holes from the acceptor level located at ~ 0.40 eV above the valence band maximum.

C. Identification of the YL band

In spite of numerous reports on the PL spectra in ZnO, no comparable investigation regarding PL bands with peaks in the yellow part of the spectrum could be found. Only a few reports of temperature-dependent PL or TRPL (but not both) are available. Egelhaaf and Oelkrug³⁵ observed enormous shift of the yellow band (from ~ 2.3 to ~ 2.05 eV) with increasing time delay after pulse excitation from 0 to 600 ns. Greene *et al.*¹⁷ observed a broad band that quenched with activation energy of 71 meV. However, the position of this band (2.05 eV) differs from the position of the YL band in our samples. Gaspar *et al.*¹⁸ observed a slow decay of the PL intensity of a broad band with a peak near 2.2 eV. They also reported a decrease in the intensity of the 2.28 eV band for temperatures above 80 K with an activation energy of 74 meV. From Fig. 4 of this work, however, the intensity of the PL band whose peak is at 2.28 eV *increases* as the temperature goes from 100 to 200 K. Chang *et al.*³⁶ observed a band (controversially named the “green band”) with a peak shifting from ~ 2.09 to 2.24 eV as temperature increased from 40 to 295 K. The intensity decreased by about ten times in this temperature range (the activation energy of the PL quenching can be roughly estimated as 60 meV from Fig. 4 in Ref. 36). A yellow band with a peak in the range of 2.13–2.17 eV, which shifted and broadened with temperature similar to the YL band reported here was observed in melt-grown bulk ZnO crystals.³⁷ However, that band quenched above 230 K with an activation energy of 0.45–0.50 eV, which contradicts the behavior of the YL band reported here. It is also worth noting that the orange luminescence (OL) band studied in detail in Ref. 37 can be easily confused with the yellow band if only at room temperature PL is considered. The maximum of the OL band shifts from 1.95 eV at 10 K to 2.10 eV at 300 K.³⁷ Zwingel and Gärtner,³⁸ Meyer *et al.*,³⁹ and Leiter⁴⁰ studied the YL band peaking at 2.18 eV in Na-doped ZnO. These authors established that, similar to the deep Li_{Zn} acceptor, a hole trapped on Na_{Zn} acceptor is localized at one of the neighboring oxygen ions, which results in nonequivalent configurations of the Na_{Zn} acceptor: axial (an oxygen ion in *c*-direction from Na_{Zn}) and nonaxial. The nonaxial configuration is energetically favored by 35 meV.³⁹ Although the YL band in our samples has the same position and nearly the same width as the Na-related YL band (at least at low temperatures), it is highly unlikely that the YL band studied in this work is related to Na. Indeed, while Li and Na may present in significant amount in undoped bulk ZnO, especially in ZnO grown by hydrothermal method, these impurities are not expected in high-purity MBE grown ZnO. Note that high absolute QE of the YL band in our undoped ZnO samples (up to $\sim 3\%$) and relatively low hole-capture cross section of the YL-band acceptor⁴¹ imply that concentration of acceptors responsible for the YL band in the studied

samples is high. We assume that these acceptors are rather native defects or complexes.

Positron annihilation experiments³ indicate that Zn vacancy (isolated or as a part of a complex defect) is probably the main native defect with a concentration of at least 10^{15} cm^{-3} in undoped *n*-type ZnO. Note, however, that V_{Zn} -related defect, studied by positron annihilation in Ref. 3, could be excited by light with photon energy of 2.3 eV, which contradicts the expected value of the zero-phonon transition of the YL band estimated in this work as 2.7 eV or higher. First-principles calculations also predict that V_{Zn} is the dominant native defect in *n*-type and especially O-rich ZnO with the $-1/2-$ energy level either at 0.8 eV (Ref. 2) or 0 eV (Ref. 42) above the valence band. It is therefore tempting to assign the activation energy of ~ 0.4 eV observed for the YL band to the V_{Zn} -related acceptor. Such an assumption appears to be in agreement with our studies of a set of Ga-doped ZnO layers. In PL spectra of these samples a dramatic decrease of the YL band intensity with Ga doping was observed.⁴³ Ga substitutes for Zn in ZnO, and we expect that it may reduce concentration of V_{Zn} . It is likely that, as in case of GaN ,²³ different complexes formed by unintentionally introduced impurities and native defects may be responsible for PL bands in the visible part of the ZnO PL spectrum and the YL band, in particular. Similar to the Ga vacancy and V_{Ga} -related complexes in GaN ,²³ in particular, V_{Zn} is likely to form stable complexes with shallow donors in ZnO. These complexes would be simple acceptors with activation energy not much different from the activation energy of the isolated V_{Zn} . Unfortunately, first-principles calculations of such complexes are unavailable.

V. CONCLUSIONS

We studied the YL band in undoped and N-doped ZnO layers grown on sapphire by MBE. The YL band, with a low-temperature peak at 2.19 eV, is attributed to transitions from a shallow donor to a deep acceptor having an ionization energy of about 0.4 eV. The deep acceptor is tentatively assigned to a V_{Zn} -related complex. With increasing temperature, the YL band shifts to higher energies, broadens, and quenches with an activation energy of 85 meV in the temperature range of 120–300 K and with an activation energy of ~ 0.40 eV at higher temperatures. DAP transitions, involving an ~ 60 meV deep shallow donor and a 0.4 eV deep acceptor, dominate in the YL band up to room temperature. Characteristics of the YL band were reliably established, which can be useful for identification of point defects in ZnO.

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