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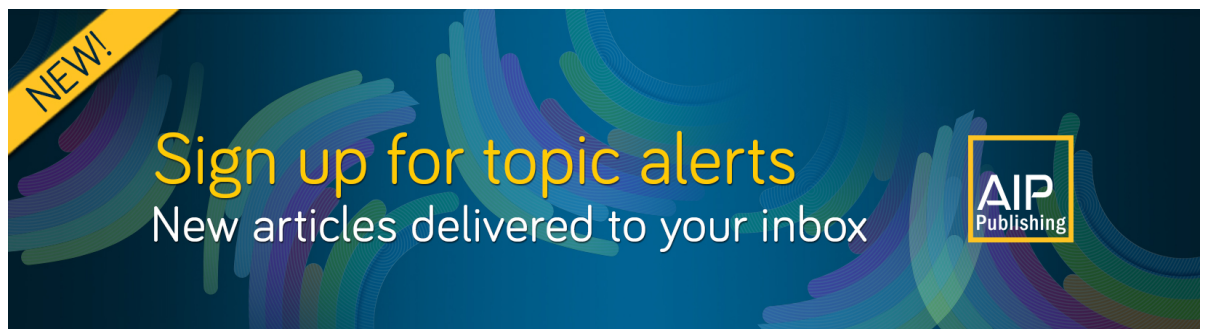
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## Photoluminescence lineshape of ZnO

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The merger of the absorption coefficient dispersion, retrieved from transmission by the modified Urbach rule introduced by Ullrich and Bouchenaki [Jpn. J. Appl. Phys. **30**, L1285, 1991], with the extended Roosbroeck-Shockley relation reveals that the optical absorption in ZnO distinctively determines the photoluminescence lineshape. Additionally, the *ab initio* principles employed enable the accurate determination of the carrier lifetime without further specific probing techniques. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4897383>]

Comprehensive knowledge of the optical properties, particularly of the room temperature (RT) photoluminescence (PL), of ZnO is essential for the future employment of this wide-band gap (~3.3 eV at 300 K) II-VI compound semiconductor in photonic and optoelectronic device structures.<sup>1</sup> Hence, vigorous research activities on ZnO thin films, epilayers, and crystals took place during the last two decades, encompassing a vast variety of effects and phenomena such as birefringence,<sup>2</sup> photocurrent,<sup>1</sup> PL<sup>1,3,4</sup> including sub-band gap emission,<sup>5</sup> reflectance,<sup>1,4</sup> transmittance,<sup>1,6</sup> excitonic properties,<sup>7</sup> Raman modes,<sup>8</sup> and absorption edge steepness.<sup>9</sup> However, despite that large body of knowledge and its essential importance for light emitting processes, a discussion of the ZnO PL lineshape and its relation to the fundamental absorption is not found in the literature. This work is closing the void: Employing the model of Ullrich and Bouchenaki,<sup>10</sup> the absorption dispersion of bulk ZnO is deduced from transmission measurements and, by use of this information, we demonstrate via the extended Roosbroeck–Shockley relation (RSR)<sup>11–13</sup> the intrinsic relationship between absorption and PL lineshape.

The ZnO crystal investigated with dimensions and electron concentration of 10 mm × 10 mm × 0.5 mm and  $\sim 4 \times 10^{13}$  cm<sup>-3</sup>, respectively, is provided by Semiconductor Wafer Inc. (Lot no. SWI-7930, typically 99.99% pure). The <0001> oriented crystal is two-side polished with the optical *c*-axis perpendicular to the surface. The quality and orientation of the sample was confirmed by surface backscatter Raman spectroscopy showing the E<sub>1</sub> (high) and A<sub>1</sub> modes,<sup>3</sup> which are typical for oriented crystalline ZnO.<sup>8</sup> Transmittance (*T<sub>r</sub>*) and reflectance (*R<sub>e</sub>*) measurements were carried out with a spectrophotometer manufactured by Perkin Elmer (model: LAMBDA 950 UV/Vis/NIR). The PL was excited using a vertically polarized pulsed laser (11 ns, 22 kHz) emitting at 266 nm from Laserglow Inc. (model: LQS-0266-NSW-P0010-10 FDA-Compliant Laser system), i.e., the geometry of our PL experiments refers to  $E \perp c$ , where *E* is the vector of the electric field. In order to keep the excitation in a moderate regime, the sample was exposed over an area of 0.5 cm<sup>2</sup> to an impinging continuous wave (cw) laser intensity of 60 mW/cm<sup>2</sup> corresponding to 250 W/cm<sup>2</sup> per pulse. The PL was recorded in reflection geometry with a StellarNet fiber spectrometer (model:

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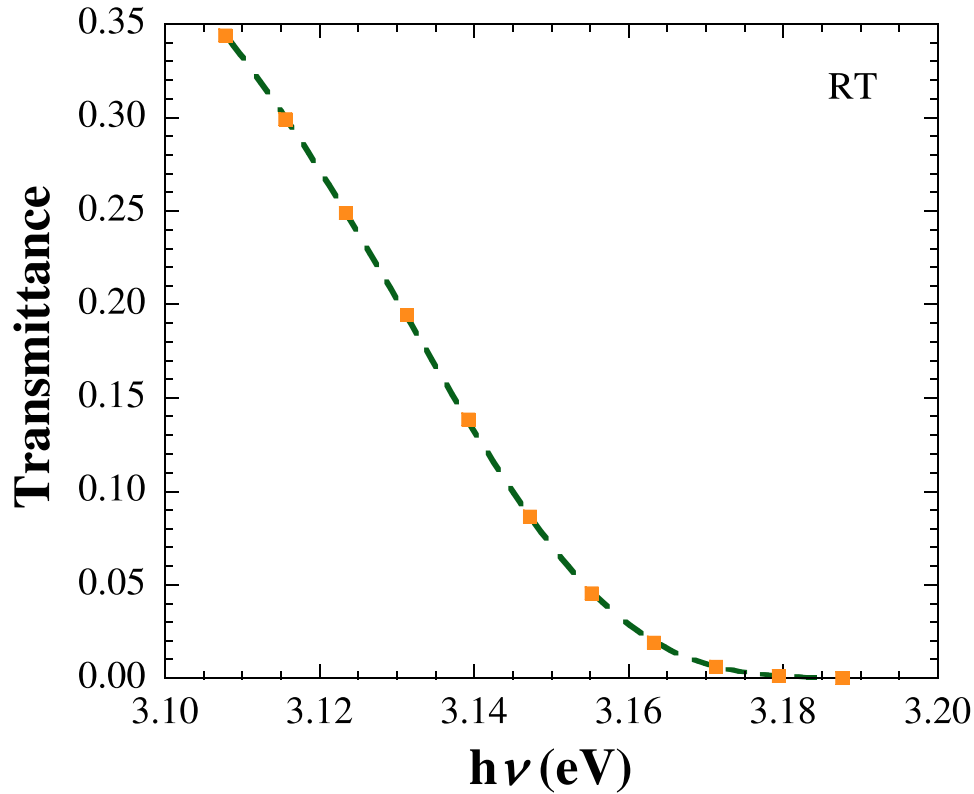


FIG. 1.  $Tr$  spectrum of the ZnO crystal: Symbols and broken line represent measurements and fit, which was accomplished with Eqs. (1) and (2). The error bars do not exceed the symbol size.

C-SR-200). We varied the impinging cw power in the range of 19 mW/cm<sup>2</sup> to 342 mW/cm<sup>2</sup> without noticing a shift of the PL peak. Hence, under the experimental conditions applied the PL was not altered due to photo-thermal effects.

The symbols in Fig. 1 show the  $Tr$  of the ZnO crystal and the broken line represents the data fit carried out with the well known relation,

$$Tr(h\nu) = (1-Re)^2 \exp[-\alpha(h\nu)d], \quad (1)$$

where  $h\nu$  is the photon energy ( $Re$  is assumed to be constant because it hardly varies within the energy range displayed in Fig. 1),  $d$  is the thickness of the sample (=0.5 mm) and  $\alpha$  is the absorption coefficient whose dispersion is expressed by the modified Urbach rule,<sup>10</sup>

$$\alpha(h\nu) = A(kT/2\sigma)^{1/2} \exp[\sigma(h\nu-h\nu_{cr})/kT], \quad (2)$$

where,  $A$  is a constant depending on the  $\alpha$  saturation,  $kT$  is the ambient thermal lattice energy (=0.025 eV),  $\sigma$  is a dimensionless parameter defining the steepness of the absorption edge, and  $h\nu_{cr}$  is the cross-over energy beyond which the Urbach tail absorption ends and band-to-band transitions (basically ruled by the density of states) start to govern the absorption events.<sup>10,12,13</sup> The essential fit parameters in Fig. 1 are:  $A = 2.32 \times 10^5 \pm 1.66 \times 10^5 \text{ cm}^{-1} (\text{eV})^{-1/2}$ ,  $\sigma = 0.94 \pm 0.03$ ,  $h\nu_{cr} = 3.323 \pm 0.013 \text{ eV}$ . We should stress the outstanding match between theory and experiment found with the chi-square test, i.e.,  $\chi^2 > 0.999$ , where  $\chi^2$  equal unity represents the perfect fit.<sup>14</sup> The notable point is that the fit with Eq. (2) delivers the parameters necessary to prolong  $\alpha(h\nu)$  for  $h\nu > h\nu_{cr}$  by means of the adapted density of states formula,<sup>10</sup>

$$\alpha(h\nu) = A[h\nu-h\nu_{cr} + kT/(2\sigma)]^{1/2}. \quad (3)$$

Figure 2 shows the PL intensity spectrum ( $I_{PL}$ ) of the ZnO crystal. Maintaining the fit parameters used in Fig. 1, the solid line, which matches the measured symbols very well ( $\chi^2 > 0.996$ ),<sup>15</sup>

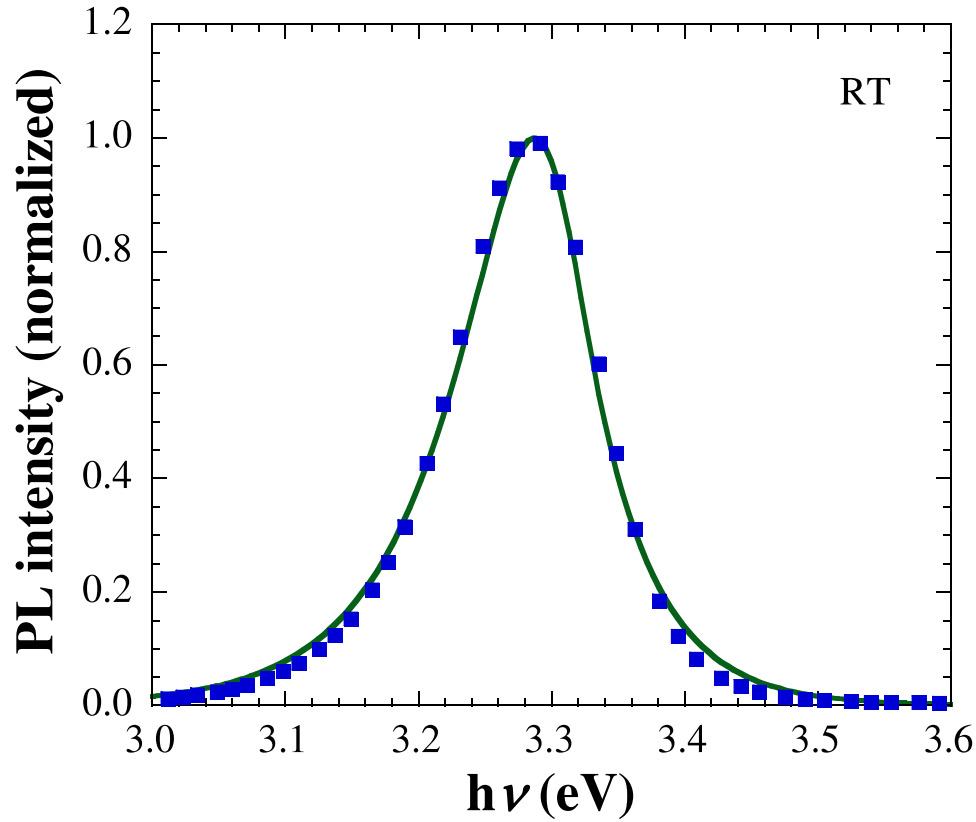


FIG. 2. PL spectrum of the ZnO crystal. The symbols are the measured data and the solid line is the fit carried out with Eqs. (2)-(4) using the unchanged parameters established with the fit in Fig. 1. The symbol size matches the error bars.

was achieved with the extended RSR,<sup>12,13</sup>

$$I_{\text{PL}}(h\nu) \propto [h\nu]^2 \times (1 - \exp[-\alpha(h\nu)d_{\text{eff}}]) \times \{\exp(h\nu/kT_c) - 1\}^{-1}, \quad (4)$$

by expressing  $\alpha(h\nu)$  with Eqs. (2) and (3) in the respective energy ranges. Hence, the effective sample thickness  $d_{\text{eff}}$ , which defines the depth of the volume contributing to the PL,<sup>12</sup> and the carrier energy  $kT_c$ , - found to be  $1.48 \pm 0.09 \mu\text{m}$  and  $0.045 \pm 0.003 \text{ eV}$  - are the only fit parameters in Fig. 2. While in the literature PL was used to study the electronic properties of semiconductor surfaces,<sup>16-19</sup> we demonstrate here how the PL fit parameters reflect the lifetime of the excited electrons. The value of  $d_{\text{eff}}$  coincides with the electron diffusion length<sup>13</sup> and can be employed to calculate the electron lifetime ( $\tau_n$ ) by using  $\tau_n = d_{\text{eff}}^2/D_n$ , with  $D_n = \mu_e kT_c/|e|$  being the electron diffusion constant, where  $\mu_e = 200 \text{ cm}^2/\text{Vs}$ <sup>20</sup> is the ZnO electron mobility and  $e$  is the elementary charge. The calculation results in  $\tau_n = 2.4 \text{ ns}$ . The value represents a fairly intrinsic number because we do not expect strong band bending in the surface region of a sample with such a low electron concentration.<sup>16</sup> We further emphasize that the lifetime is in very good agreement with the reported value of  $2.8 \pm 0.6 \text{ ns}$  pointed out with z-scan technique probing 1 mm thick ZnO bulk samples<sup>21</sup> - and the fit parameters used in Fig. 2 are in harmony with  $d_{\text{eff}} = 0.73 \mu\text{m}$  and  $kT_c = 0.067 \text{ eV}$  reported in Ref. 12 for thin-film (1.58  $\mu\text{m}$ ) CdS PL spectra excited with a YAG laser (355 nm, 6 ns, 10 Hz) at RT, reflecting the longer lifetime and reduced mobility in thin CdS films with respect to ZnO crystals.

The energy parameter  $h\nu_{\text{cr}}$  in Eq. (3) deserves closer attention because by its definition given above it can be interpreted as the optical ZnO band gap energy  $h\nu_g$ , i.e. the lowest intrinsic exciton peak. Indeed, the value of 3.323 eV precisely coincides with the reported lowest free exciton energy at  $3.323 \pm 0.002 \text{ eV}$  by Tomm *et al.*<sup>1</sup>

In conclusion, by combining the data from transmission spectroscopy with the extended RSR, we find an excellent PL line fit for crystalline bulk ZnO. The result explains the observed asymmetry of the PL spectrum by the two different absorption regions forming the emission spectrum, i.e., on the low energy side the modified Urbach tail and on the high energy side density of states. The satisfactory applicability of the latter reveals that exciton absorption does not essentially contribute to the overall PL lineshape of ZnO at ambient temperatures. The work also stresses the capability of the RSR to determine the carrier lifetime of semiconductors without employing time resolved spectroscopy.

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