Comment on "Recombination of excitons bound to oxygen and silicon donors in freestanding GaN"

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(Received 27 March 2003; published 15 April 2004)

In a recent report, Wysmolek *et al.* [Phys. Rev. B **66**, 245317 (2002)] presented results of a photoluminescence study of donors in GaN. Time-resolved data were used to correlate spectral features associated with recombination processes leaving donors in the ground state and those leaving donors in excited states. The authors quoted donor $1s$-$2s$ and $1s$-$2p$ transition energies different from values recently reported and impurity state chemical shifts inconsistent with expectation. We recently reported [Freitas *et al.*, Phys. Rev. B **66**, 233311 (2002)] a different identification of donor-bound exciton features and an analysis of two-electron satellite features that integrated the effects of excited donor-bound excitons into the analysis. Differences in the two papers are discussed.

DOI: 10.1103/PhysRevB.69.157301 PACS number(s): 78.55.Cr, 71.35.Ji, 71.55.−i

In a recently published paper, Wysmolek *et al.*[1] (WEA) reported data obtained by photoluminescence (PL) studies of recombination processes involving free and donor-bound excitons (DBE) in freestanding hydride-vapor-phase epitaxial GaN. They proposed that there are three donors in their material, D_1, D_2, and D_3, with exciton-donor binding energies of 7.9 meV, 6.9 meV, and 6.0 meV, respectively. Similarities in the decay time, measured by time-resolved photoluminescence, were employed to correlate DBE recombination features leaving the donor in its ground state (BX features) with recombination features leaving the donor in an excited state [two-electron satellite (TES or 2ES) features].

Similar PL studies of similar samples have recently been published by Freitas *et al.*[2] (FEA). The samples used in both studies were produced by the same laboratory (Samsung Advanced Institute of Technology) and the PL spectra are essentially identical. Therefore, we believe the materials are very similar. However, the PL feature identifications and inferred donor $1s$-$2s$ and $1s$-$2p$ transition energies are different. The donor identifications and transition energies quoted by WEA differ from IR results by an amount substantially greater than expected experimental error. In contrast, the identifications and transition energies of the 2ES features determined by FEA agree within about 0.3 meV with IR transmission studies of the same samples.

The major difference in the two analyses is the assignments of the BX features. WEA assigned the features denoted D_1X_A, D_2X_A, and D_3X_A to excitons bound to O, Si, and unknown donors, respectively. FEA assigned these features to excitons bound to an ionized donor, O, and Si, respectively. FEA introduced a notation in which these features were denoted D^+X_A, $O_N^0X_A(0):1s$, and $Si_{Ga}^0X_A(0):1s$, and a relaxed notation where confusion was unlikely.

Similarities in the decay characteristics of the BX features and the 2ES features were used by WEA as the primary experimental identification of the BX features. Their strong 2ES features $L1$ and $L2$, assigned to O [FEA: $OX_A(0):2s$ and $OX_A(a):2p$] were shown to have a slow decay that was similar to a long-lived tail of the decay of D_2X_A and argue (bottom of first column of p. 3) that ''Such a slow recombination rate can be compared with the long-lived tail of the D_2X_A line that is probably connected with the decay of the D_1X_A line.'' On this basis, WEA assigned D_1X_A to the O BX recombination.

In contrast, FEA assigned WEA's D_1X_A feature to an ionized donor, D^+X_A, WEA's D_2X_A to O, and WEA's D_3X_A to Si. These assignments in FEA were based on six experimental observations, five of which are significant even if D_1X_A is a neutral donor.

(1) The strength of the D^+X_A feature diminishes as PL excitation intensity increases, as expected for ionized centers.

(2) Infrared studies[3,4] have shown that the shallowest neutral donor in this material is Si. Therefore, the Si BX should be the most weakly bound BX, D_3X_A.

(3) Secondary-ion-mass-spectroscopy studies of the FEA sample indicated that O and Si were the dominant donors with the O concentration exceeding the Si concentration by a factor of about 5. Therefore, we expect the O BX recombination feature to have an intensity that is significantly greater than that of the Si BX recombination feature. The BX feature assigned by WEA to O is approximately ten times weaker than the feature assigned by them to Si.

(4) FEA expect the most intense 2ES recombination features to be associated with the most intense BX recombination features. Consequently, we associate the 2ES features $L1$ and $L2$ with O^0X_A of FEA (WEA: D_2X_A). WEA have associated the strongest 2ES features with their weakest BX feature.

(5) FEA find that the intensity of the BX feature denoted Si^0X_A [WEA: D_3X_A] increases in homoepitaxial samples if they are doped with Si.[5]

(6) FEA find that their assignments of BX features give good agreement between $1s$-$2p$ transition energies for the O and Si donors determined from PL studies and those determined from IR transmission studies on the same sample. The assignments of WEA do not give good agreement (see Table I).

We believe WEA's discussion of the $1s$-$2p$ transition energies and their discussion of chemical shifts of the $2s$ states

TABLE I. Donor intrasite transitions determined as described in the text.

Transition	WEA PL (meV)	WEA PL modified (meV)	FEA PL (meV)	Ref. 3 IR (meV)
O:$1s$-$2s$	24.3	24.3	25.4	
O:$1s$-$2p$	23.3	24.6	25.7	25.9
Si:$1s$-$2s$	21.9	21.9	22.8[a]	
Si:$1s$-$2p$	20.6	21.9	22.8[a]	22.8

[a]Since the separation between $2s$ and $2p$ states of Si is only about 0.125 meV, we are not able to distinguish them experimentally.

for O and Si are misleading. Plots of the $2p$ ''transition energy'' ''with respect to the $1s$ ground state'' in Figs. 7, 8, and 10 are raw data measured with respect to the unexcited BX recombination feature with no correction for the fact that the $2p$ transitions originate in the first excited state of the parent DBE ($2p_0'$ in Fig. 10 is correctly plotted; it originates in the unexcited DBE). Therefore, except for $2p_0'$, the plotted $1s$-$2p$ transition energies are approximately 1.3 meV too small. All $1s$-$2p$ transition energies quoted in the text are also quoted without correcting for the excited DBE initial state of the $2p$ PL transition. Therefore, those $1s$-$2p$ transition energies are not correct. All discussions of lowering of $2p$ states with respect to $2s$ states also fail to take into account the excited initial state of the parent DBE of the $2p$ PL transition. In fact, after correction the $2p$ states are not lowered with respect to $2s$ states; rather the $2s$ of O is lowered approximately 0.3 meV below its $2p$ state and the $2s$ and $2p$ states of Si are essentially degenerate. Therefore, all mention in WEA of chemical shifts of $2s$ states toward the conduction band are unnecessary and misleading, since the data do not support these statements, as can be seen in columns 3 and 4 of Table I. When WEA speak of positive chemical shifts they refer to a movement of an s state toward the conduction band; the usual terminology has a positive chemical shift move the s state away from the conduction band. Correct statements of magnitude and direction of chemical shift were not given in WEA; even in the Conclusions section an incorrect statement from the earlier text was repeated. Clearly, an alert reader can correct a misleading presentation but we believe these difficulties are significant and should be brought to the readers' attention.

We have compiled $1s$-$2s$ and $1s$-$2p$ transition energies for O and Si with various assumptions in Table I. The second column gives the values quoted in the text by WEA without correcting for the excited DBE initial state of the $2p$ features in the PL 2ES spectrum. WEA do not quote a value for the $1s$-$2p$ transition of O so we have used the value plotted by them in Fig. 7. The third column represents the values we believe they would find after correcting for the excited DBE initial state of the $2p$ 2ES transitions (no corrected values were plotted or quoted by WEA). The fourth column contains the values implied by the positions for the 2ES transitions given in Table I of FEA. The unexcited BX recombinations are at 3.4714 meV and 3.4722 eV for O and Si, respectively; they are the initial states for strong 2ES recombination to $2s$ donor states at low temperature. The first excited BX recombinations in FEA are at 3.4727 eV and 3.4735 eV; they are the initial states for strong 2ES recombination to $2p$ donor states. The fifth column gives IR results for $1s$-$2p$ transitions.[3]

The assignments of FEA give very good agreement between PL and IR results, as is expected based on experience with other semiconductors such as GaAs, InP, SiC, ZnSe, and ZnTe. Consequently, statements in the Discussion section of WEA speculating that ''the $1s$ and $2s$ states, due to different extensions of their wave functions, may be coupled to lattice vibrations in a different way'' are unnecessary since no significant difference between PL and IR values for the O binding energy is found.

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