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Donor-related recombination processes in hydride-vapor-phase epitaxial GaN

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High-resolution, variable-temperature photoluminescence studies of recombination processes associated with excitons bound to donors in hydride-vapor-phase epitaxial GaN are presented. Detailed analyses of the two-electron satellite (2ES) region identify transitions associated with ground and excited states of both the donor-bound exciton complexes and of the donor itself. All of the 2ES transitions observed in this work can be accounted for by the recombination of excitons bound to Si and O substitutional impurities and the line positions are in excellent agreement with the energies of donor intraimpurity transitions measured previously by infrared absorption. Conflicting aspects of donor identification and the binding energies of impurities and excitons are clarified.

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III-V nitrides exhibit a unique combination of physical and chemical properties that allows the formation of alloys and heterostructures that are necessary for the fabrication of optical devices for the visible-UV spectral range and electronic devices capable of operating at high power and high frequency, and/or under extreme environmental conditions. Recent significant improvements in the control of the optical and electronic properties of GaN-based heteroepitaxial films have resulted in several breakthroughs in optoelectronic device performance, enabling the commercialization of a variety of optical devices. Despite this outstanding technological progress, our basic understanding of the electronic properties of nitride-based materials remains limited. Heteroepitaxial layers are commonly characterized by large background donor concentrations and large biaxial strains that lead to substantial inhomogeneous broadening of spectral features.[1] As the material quality has improved, it has become possible to use optical spectroscopy as a probe of impurity identification and impurity concentrations. In this paper, we take a significant step in this direction by providing a detailed explanation of the complex near band-edge photoluminescence (PL) spectrum in high-quality freestanding GaN templates. This rich spectrum is dominated by transitions of donor-bound excitons in both their ground and rotational excited states that may leave the neutral donor's bound electron in either its ground ($1s$) or excited ($2s$, $3s$, $4s$, $2p$, $3p$) states.

PL spectral lines that arise from the recombination of neutral donor-bound excitons can provide important information about the chemical identity of donor impurities in semiconductors. This follows because recombination of the exciton localized at the donor can leave the donor in its ground or excited state and, due to central-cell interactions, these energies occur at different spectral locations, thus providing a fingerprint for each donor impurity. However, previous studies have not taken advantage of the full power of the PL technique because these spectra can be quite complex. This complexity arises from the presence of multiple donors in the sample, the appearance of rotational excited states of the bound exciton complexes, and numerous possible final states of the donor ($1s$, $2s$, $2p$, $3s$, $3p$, etc). PL lines generated by radiative recombination of an exciton bound to a donor, leaving the donor in an excited state, are referred to as two-electron satellite (2ES) transitions. Their correct assignments are very important because they provide a simple way to measure the donor binding energies and catalog the different donor species present in the material. Early experiments on 2ES's in GaN were performed by Jayapalan *et al.*[2] However, at the time of those measurements, material quality was not as high as it is today and unique identifications of the transitions were not possible. More recently, high-quality optical spectroscopy has been performed on homoepitaxial layers deposited by organic-metallic vapor-phase epitaxy on high-pressure-high-temperature bulk GaN substrates.[3,4] Rotational excited states of donor-bound excitons have been observed and analyzed.[4] However, the chemical nature of the background donors was not determined. To date, there is rather poor agreement between recently reported 2ES line assignments[2,5,6] and those determined from Fourier-transform infrared (FTIR) transmission.[7–9] In high-purity semiconductors such as GaAs, for example, there is excellent agreement between intraimpurity transitions measured by 2ES's in PL and FTIR transmission. In order to clarify these conflicting results of donor properties in GaN, we report high-resolution photoluminescence experiments on the same set of hydride-vapor-phase epitaxial (HVPE) samples previously used in our FTIR-secondary-ion mass spectroscopy[9] (SIMS) and FTIR-Zeeman[10] studies in the spectral regions associated with the free excitons, bound excitons (BX), and 2ES's.

Recently, we detected[9] three shallow donors in infrared studies of thick, high-quality, unintentionally doped (UID), freestanding GaN films fabricated by HVPE.[11] Comparison of high-resolution FTIR transmission with high-sensitivity SIMS allowed identification of two of the donors: $\mathrm{Si}_{\mathrm{Ga}}$ and O_{N} with binding energies of 30.18 ± 0.1 and 33.20 ± 0.1 meV, respectively. The third donor, with a binding energy of 31.23 ± 0.1 meV, is still unidentified. FTIR-Zeeman spectroscopy of these samples[10] showed clear transitions from the ground state to $2p_{\pm}$ and $3p_{\pm}$ excited states, and the separation rates for the $2p_{+}$ and $2p_{-}$ excited states yielded an electron effective mass of $0.22m_0$.[8,10] The experimental results reported in this paper allow us to identify most of the strong lines present in the complex 2ES spectra through their excellent agreement with the FTIR and FTIR-Zeeman data.

UID freestanding HVPE GaN samples with final thicknesses between 140 and 170 μm, with a typical carrier concentration of $\sim 2 \times 10^{16}$ e/cm^3, and with dislocation density $\leqslant 10^7$ cm^2, were used in the present experiment.[11] Double-crystal x-ray-diffraction studies carried out with various beam diameters show an over tenfold reduction of the full width at half maximum (FWHM) with decreasing x-ray beam width. Measurements performed with a 100-μm beam width gave symmetric sharp lines with a of FWHM ~ 55 arcsec.[11] These results, in combination with Raman-scattering studies,[11] indicate that our wurtzite templates have large preferentially oriented grains and low biaxial strain. Therefore, these samples are adequate substrates for homoepitaxial growth.

The PL measurements were carried out with the samples placed in a continuous flow cryostat with temperatures ranging from 1.6 to 320 K. The luminescence was excited with the 325-nm HeCd laser line and calibrated neutral density filters were employed to vary the excitation intensity. The samples were aligned to the spectrometer optical axis using a laser diode beam through the spectrometer to define the optical path. Narrow spectrometer slits were used to achieve the required spectral resolution for this experiment, and a spectral band pass between 70 and 100 μeV was commonly employed. The reproducibility of the measurements was ± 25 μeV. Bound excitons with full width at half maximum between 315 and 375 μeV have been observed in our samples. Because of the high resolution required for this study, instrumental vibrations and laser spot size were minimized to reduce the effects of sample inhomogeneities that promote inhomogeneous line broadening.[1] The spectrometer calibration was verified with standard lines from a mercury calibration lamp.

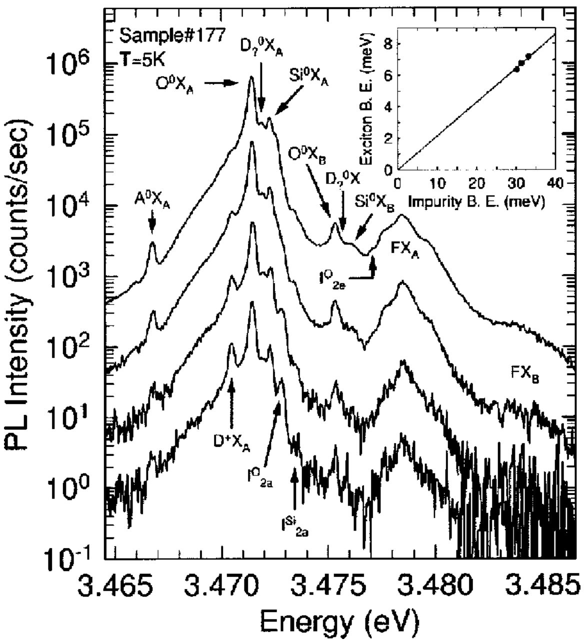

FIG. 1. 5-K PL spectra measured with four laser excitation power densities, from top to bottom, 61.1, 8.4, 0.80, and 0.08 $\mathrm{W/cm}^2$. The assignment of the emission peaks is represented. The inset represents the linear dependence of the excitons' binding energy with the neutral-donor binding energy.

Figure 1 presents a collection of spectra recorded with high resolution (band pass <100 μeV) at 5 K under several laser excitation intensities. The dominant features in all spectra are emissions associated with the recombination of ground-state excitons bound to neutral donors (often designated I_2^0) centered around 3.4714(2) eV (all energy values are corrected for the index of refraction of air) and weaker features assigned to the excited states of the donor-bound excitons. The dominant peak is, in fact, composed of three peaks at 3.4714(4), 3.4718(9), and 3.4722(8) eV (average values obtained from a number of measurements) which we assign to A excitons bound to neutral O donors on the nitrogen site ($\mathrm{O}_{\mathrm{N}}^0 X_A$), neutral unknown donors ($D_?^0 X_A$), and neutral Si donors on the Ga site ($\mathrm{Si}_{\mathrm{Ga}}^0 X_A$), respectively. These assignments were determined by comparing the current work to our previous FTIR and SIMS study[9] and the dependence of PL spectra on Si doping of homoepitaxial layers, not discussed in the present work. A plot of the binding energies of the three donor-bound excitons, as determined from PL, versus the neutral donor binding energies, as measured by FTIR transmission,[10] is presented in the inset of Fig. 1. The observed linear dependence between these two energies follows the empirical Haynes rule[12] with a linear coefficient of 0.214. This value is close to the previously reported 0.2 ± 0.01.[13]

Due to the complexity of the spectra, we have found the usual notation for emission line identification to be limited in its application to the 2ES region. Therefore, we generalize the notation to specify the nature of the bound exciton complex, its excitation condition, and the excitation state of the donor after the recombination process. For example, an A exciton bound to neutral Si on the Ga site, with the BX in its ground state, will be designated $\mathrm{Si}_{\mathrm{Ga}}^0 X_A(0)$. We also must indicate the final state of the donor (or acceptor) after the exciton recombination. For example, the recombination of the above Si BX, while in the a excited state, leaving the donor in its $1s$ ground state, will be designated $\mathrm{Si}_{\mathrm{Ga}}^0 X_A(a){:}1s$. Similarly, the 2ES transition leaving the donor in the $2p$ excited state will be designated $\mathrm{Si}_{\mathrm{Ga}}^0 X_A(a){:}2p$. This notation casts normal BX recombination and 2ES recombination in the same form.

In this new notation the dominant peak in our PL spectra, Fig. 1, is composed of $\mathrm{O}_{\mathrm{N}}^0 X_A(0){:}1s$, $\mathrm{Si}_{\mathrm{Ga}}^0 X_A(0){:}1s$, and the

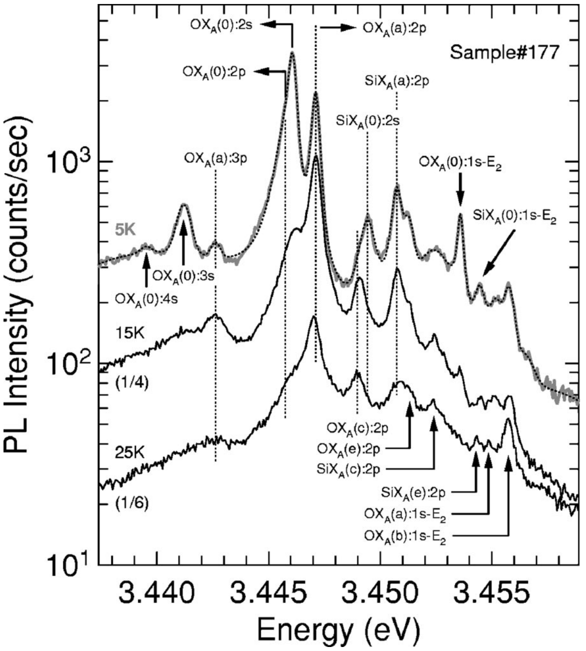

FIG. 2. Spectra taken at 5, 15, and 25 K in the 2ES region. The dotted line overlapping the 5-K spectrum (gray line) represents our best fit. Emission-peak assignments apply to the indicated spectrum only except for emission peaks connected by a dotted line. The spectrum intensities measured at 15 and 25 K were divided by 4 and 6, respectively, to minimize overlapping.

weaker unidentified donor transition $D_?^0X_A(0){:}1s$. This notation is relaxed in Fig. 1, in which all donors are left in their $1s$ state. Weaker, but easily observed, are recombinations involving the free exciton associated with holes from valence band *A* around 3.4784 eV, the free exciton involving holes from valence band *B* at 3.4843 eV, the exciton *B* bound to the O donors on the N site $\mathrm{O_N^0}X_B(0){:}1s$ at 3.4753 eV, the exciton *B* bound to Si donors on the Ga site $\mathrm{Si_{Ga}^0}X_B(0){:}1s$ at 3.4758 eV, and the *A*-valence band exciton bound to a neutral unknown acceptor, $A^0X_A(0){:}1s$, at 3.4668 eV. These assignments are based upon the shift between valence bands *A* and *B*.

Also observed in the spectra of all studied samples are the very weak peaks at 3.4704, 3.4727, 3.4735, and 3.4770 eV (average values), and represented in Fig. 1 by D^+X_A and the traditional designations I_{2a}^{O}, I_{2a}^{Si}, and I_{2e}^{O}, respectively. Note that the intensity of the D^+X_A relative to the intensity of $\mathrm{Si_{Ga}^0}X_A(0){:}1s$ increases with decreasing excitation intensity, indicating that the photoneutralization reduces the concentration of centers associated with D^+X_A. This suggests that D^+X_A results from the annihilation of excitons bound to a charged center. Since Si is the shallowest neutral impurity and, therefore, expected to be partially compensated,[10] we are tempted to assign D^+X_A to recombination process associated with the annihilation of excitons bound to Si^+. However, this assignment must be verified by additional experiments.

The weak peaks $\mathrm{O_N^0}X_A(a){:}1s$ and $\mathrm{O_N^0}X_A(e){:}1s$, designated I_{2a}^{O} and I_{2e}^{O}, are separated from the $\mathrm{O_N^0}X_A(0){:}1s$ recombination by 1.255 and 5.593 meV (average of several measurements on same sample), respectively. In addition, the weak peak $\mathrm{Si_{Ga}^0}X_B(a){:}1s$, designated I_{2a}^{Si}, is shifted 1.244 meV (averaged) from $\mathrm{Si_{Ga}^0}X_B(0){:}1s$. Because these energy separations are very close to the energy differences reported by Neu and co-workers[14] between the ground state *a* and *e* rotational excited states of the neutral BX recombinations, we have adopted the same assignments and nomenclature. Two additional peaks, $\mathrm{O_N^0}X_A(c){:}1s$ and $\mathrm{O_N^0}X_A(d){:}1s$ (or I_{2c}^0 and I_{2d}^0), may also be present, but they lie beneath the intense $\mathrm{O_N^0}X_B(0){:}1s$ and $\mathrm{Si_{Ga}^0}X_B(0){:}1s$ peaks.

TABLE I. Identifications of major features in the PL 2ES spectra.

Position at 5 K (eV)	Identification	Position at 25 K (eV)	Identification
3.439 68	$\mathrm{O_N^0}X_A(0){:}4s$	3.442 66	$\mathrm{O_N^0}X_A(a){:}3p$
3.441 21	$\mathrm{O_N^0}X_A(0){:}3s$	3.447 04	$\mathrm{O_N^0}X_A(a){:}2p$
3.442 63	$\mathrm{O_N^0}X_A(a){:}3p$	3.448 98	$\mathrm{O_N^0}X_A(c){:}2p$
3.445 74	$\mathrm{O_N^0}X_A(0){:}2p$	3.450 72	$\mathrm{Si_{Ga}^0}X_A(a){:}2p$
3.446 07	$\mathrm{O_N^0}X_A(0){:}2s$	3.451 29	$\mathrm{O_N^0}X_A(e){:}2p$
3.447 11	$\mathrm{O_N^0}X_A(a){:}2p$	3.452 40	$\mathrm{Si_{Ga}^0}X_A(c){:}2p$
3.449 43	$\mathrm{Si_{Ga}^0}X_A(0){:}2s$	3.454 96	$\mathrm{Si_{Ga}^0}X_A(e){:}2p$
3.450 74	$\mathrm{Si_{Ga}^0}X_A(a){:}2p$	3.455 74	$\mathrm{O_N^0}X_A(b){:}1s\text{-}E_2$ phonon(?)
3.453 59	$\mathrm{O_N^0}X_A(0){:}1s\text{-}E_2$ phonon		

PL results for the 2ES region are given in Fig. 2 for an HVPE sample at three representative temperatures: 5, 15, and 25 K. The peak energies were determined by fitting 16 Gaussian-Lorentzian lines, including broad background features. All the major features observed in Fig. 2 have been assigned; identities of the donor excited states have been determined by comparison of the 2ES features with donor excitation spectra from infrared (IR) transmission. Agreement between the intraimpurity transition energies of the donors determined by the two techniques is found to be better than 250 μeV. The dominant feature in the 5-K spectrum is clearly asymmetric and is consistently resolved by the fitting program into two lines; the lower-energy component is identified as $\mathrm{O_N^0}X_A(0){:}2p$ and the higher-energy one as $\mathrm{O_N^0}X_A(0){:}2s$. The inferred $2s$-$2p$ splitting is 0.33 meV. This is in reasonable agreement with calculation of the O $2s$ core shift using the $1/n^3$ rule (0.51 meV) that has been found to be well approximated in semiconductors[15] and with a previously unidentified feature on the low-energy side of the oxygen $1s$-$2p$ absorption in IR transmission.[9] We now identify that feature as a weakly allowed $1s$-$2s$ transition. Identification of the major features observed at 5 and 25 K are given in Table I.

Assignments given in Table I at 5 K differ from those proposed in a recent paper describing PL at 15 K on the same type of HVPE GaN.[5] In order to understand our interpretation, consider the temperature dependence of the 2ES features in Fig. 2. At 5 K the line labeled $\mathrm{O}X_A(0){:}2s$ is dominant followed by $\mathrm{O}X_A(a){:}2p$. When the temperature reaches

25 K, $OX_A(0){:}2s$ is unobservable and $OX_A(a){:}2p$ is dominant; in fact, $OX_A(a){:}2p$ is dominant at 15 K and higher. The same is true of the corresponding Si transitions. This indicates that the 2ES spectra are dominated by recombinations from the *a*-excited donor-bound excitons at 15 K and above, not by recombinations from the unexcited donor-bound excitons. If one wishes to calculate the donor ground-to-excited-state transition energy using data taken at 15 K or above one must subtract the energy of the 2ES transition leaving the donor in its $2p$ state from the excited exciton transition leaving the donor in its $1s$ state. For example, subtract $OX_A(a){:}2p$ from $OX_A(a){:}1s$.

The authors of Ref. 5 performed their experiment at 15 K but assumed the 2ES spectra arise from recombinations of unexcited donor-bound excitons. Consequently, they subtracted $OX_A(a){:}2p$ from $OX_A(0){:}1s$ to determine the oxygen donor $1s$-$2p$ energy separation. This produces an error that is equal to the difference between $OX_A(0){:}1s$ and $OX_A(a){:}1s$ [or $SiX_A(0){:}1s$ and $SiX_A(a){:}1s$]. That difference is approximately 1.3 meV (Ref. 14) for both O and Si; consequently, Ref. 5 proposes $1s$-$2p$ energy differences that are approximately 1.3-meV too small, translating into an approximately 1.7-meV error in the Si donor binding energy. Thus their data, when the transitions are appropriately assigned, actually indicate an Si binding energy of approximately 30.1 meV rather than the 28.8 meV they state in Ref. 5. This value is in excellent agreement with our 30.18 meV from magneto-optical measurements.[10] Their value for the O binding energy contains a second, compensating error since they assumed that a simple effective-mass calculation applies to O. O has a significant core shift; its binding energy cannot be found simply by multiplying the $1s$-$2p$ transition energy by $\frac{4}{3}$. Rather, one should add the $2p$ binding energy, one-quarter times the effective-mass binding energy, to the $1s$-$2p$ transition energy. But, since their two errors partially compensate one another, the value they found for O, 32.6 meV, is near the correct value 33.20 meV.[10]

We find that 2ES recombinations from unexcited donor BX leave the donor preferentially in *s*-like final states while recombinations from excited donor BX leave the donor preferentially in *p*-like excited states (see Table I). This is consistent with theoretical models that find the excited BX to be *p*-like[16] and with experiments on donors in ZnTe.[17] The parity-conserving PL recombination transitions at excited BX would be expected, other parameters constant, to leave the neutral donor preferentially in *p*-like states. The observed weakness of excited donor BX recombination, e.g., $O_N^0X_A(a){:}1s$, compared with unexcited donor BX recombination, e.g., $O_N^0X_A(0){:}1s$, and the temperature dependence of donor-bound excited exciton recombination have been documented.[14] These results are consistent with *p*-like character of the excited BX. Finally, we note that the PL peak at 3.455 74 eV, most intense at 25 K, is consistent with the expected position of the lower-energy E_2 optical-phonon replica of $O_N^0X_A(b){:}1s$, i.e., $O_N^0X_A(b){:}1s$-E_2. However, the emission peak at the same position at 5 K cannot be ascribed to this mechanism. That peak diminishes on warming above 5 K and is replaced by another peak at the same position that increases with temperature above 15 K.

Our findings are consistent with the observations of Wysmolek *et al.*[6] They observed PL spectra in the 2ES region of homoepitaxial GaN that are dominated by transitions to $2p$ excited states of the donor. They also find a small discrepancy in the $1s$-$2p$ transition energy of the donor compared with IR measurements of Si donors. Both these unexpected findings can be understood using the model we present here if we assume that the sample temperature was sufficiently high to allow *a*-excited exciton recombination to dominate in the 2ES region. In this case *p*-like final donor states are expected and the donor $1s$-$2p$ transition energy from their data is near the expected value for Si donors.

The present work has clarified conflicting aspects of the optical properties of GaN associated with bound exciton transitions in GaN. This includes the spectral identification of excitons bound to neutral Si and O donors in GaN films. These measurements and their interpretation provide a unified picture that describes both the photoluminescence and FTIR/FTIR-Zeeman properties of the dominant shallow donors in high-quality GaN, provide a catalog of PL signatures, and clarify the signature's complex relationship to the chemical identification of donor impurities. The long-standing discrepancy between donor binding energies measured by IR transmission and those measured by PL is resolved by the excellent agreement found here.

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