Transient photoluminescence of shallow donor bound excitons in GaN

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We present a detailed study of photoluminescence transients for neutral donor bound excitons (DBEs) in GaN, notably the O_N donor DBE at 3.4714 eV and the Si_{Ga} DBE at 3.4723 eV. The studied samples are thick strain free nominally undoped bulk GaN samples, with a spectroscopic linewidth <0.5 meV at 2 K. The photoluminescence (PL) decay curves for these no-phonon (NP) lines are strongly nonexponential, and do not allow a proper assessment of the characteristic BE decay time. The decay of the LO-phonon replicas as well as the so-called two-electron transitions (TETs) at lower energies show a nicely exponential behavior, and allow extraction of DBE decay times of about 1.1 ns for the Si DBE and 1.8 ns for the O DBE, respectively. The initial nonexponential decay behavior of the NP lines has been studied in both the common front surface excitation-detection mode and with detection in transmission through the sample. This initial decay is explained as related to scattering processes in the near surface region, involving the DBEs and free excitons (FEs). Light scattering processes may also contribute to this complex decay shape. The DBE-LO-phonon decay does not discriminate between the O and Si DBEs because of spectral overlap involving different LO modes. The TET decays at 2 K are very different for transitions related to the DBE ground state and DBE excited states (going to *p*-like donor final states), for $T>10$ K thermalization between the DBE ground state and DBE excited states produces a common decay time. Thermalization between free and bound excitons appears to occur above about 20 K, when the DBE decay follows the FE decay. A simple two-level modeling of exciton capture and recombination for the PL decay curves of the FE and the DBEs, as commonly used in the literature, is shown to be generally inadequate. A broad PL background in the TET spectral region is suggested to be related to a radiative Auger process, where the DBEs recombine while leaving the donors ionized.

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I. INTRODUCTION

Bound exciton (BE) spectra are very important optical signatures for dopants and other impurities in semiconductors.[1–3] The sharp line BE spectrum characteristic for each impurity (defect) can be used for optical determination of the presence of the corresponding defects, and in some cases also their concentration.[4] Detailed studies of the BE photoluminescence (PL) lines under external perturbations (such as magnetic fields or strain fields) give additional information about the electronic structure of the defect.[1] Satellite spectra also occur in addition to the no-phonon (NP) PL lines, including phonon replicas and the so-called two-electron transitions (TETs) for donors.[5] The time-resolved PL (TRPL) behavior gives information on transient processes such as exciton capture, exciton transfer, and exciton recombination related to BEs.

Detailed studies of BE spectra for dopants in wide band-gap semiconductors require reasonably low doping concentrations (on the order of 10^{16} cm^{-3} or lower), in order to get a suitable linewidth for good spectral resolution and discrimination of the BE lines. This is especially important for TRPL experiments, since the decay processes related to BEs are very sensitive to additional nonradiative recombination channels, as well as to excitation transfer processes at higher doping levels.[6,7] In the case of GaN the number of relevant studies of BE spectra has so far been rather limited, due to the lack of high-quality bulk material. Most studies to date have been done on thin heteroepitaxial GaN layers grown on substrates like sapphire or SiC, with the consequence that strain and a high dislocation density have a strong influence on the quality of PL spectra. During recent years rather high-quality free-standing thick (several hundred micrometers) bulk GaN layers grown by halide vapor phase epitaxy (HVPE) have become available, as well as thin epitaxial layers grown on such bulk substrates. Such material if undoped often has the low residual doping required for high-resolution PL spectroscopy at low temperatures, i.e., with a PL linewidth of a fraction of a millielectron volt.

The main shallow donors of interest in GaN are Si_{Ga} and O_N, the former typically used for *n*-type doping in devices, the latter being a most common contaminant. Previous work on low doped strain-free bulk GaN layers has demonstrated the energies of the principal donor BE (DBE) lines for these two donors, at ~3.4714 eV for the O donor and ~3.4723 eV for the Si donor.[8] (In the literature two com-

mon short notations for donor bound excitons are found: DBE and D^oX. Both are used in this paper). Excited DBE states have also been observed experimentally,[9] and explained theoretically in terms of rotator states of the hole in the DBE.[10,11] Excited states of the neutral donors have recently been studied in TET spectra by several authors, with some discrepancy in the interpretations.[8,12–15] Our recent studies of high resolution TET spectra for O and Si donors in GaN (Ref. 16) give results for the energies of the excited donor states very similar to Ref. 8. We conclude a binding energy for the O donor as 33.2 ± 0.4 meV and for the Si donor 30.4 ± 0.4 meV, accounting for the anisotropy of the electron effective mass and the dielectric constant.[16]

This paper is focused on the transient behavior of DBEs and related PL transitions in GaN. TRPL data for bound and free excitons (FEs) in GaN have been reported in a large number of papers over the last decades, with quite a large variation in the results.[17–20] The low-temperature DBE decay times reported in thin GaN layers grown on foreign substrates are typically very short (<300 ps), related to the large defect concentrations in these samples.[17] The corresponding FE decay times are then invariably very short as well (<100 ps). In some cases when homoepitaxial layers of better quality were studied a longer DBE decay time (on the order 1 ns) was deduced at 2 K (Ref. 20) but the decay was found to be nonexponential with a shorter initial decay (<300 ps).[20] This initial part of the decay was in Ref. 20 interpreted as due to fast capture of FEs. In another recent work on high-quality HVPE GaN different decay times were reported for the O and Si donors, the O donor had a longer initial decay as 530 ps at 5 K.[21] It was recently pointed out that the TRPL decay of the LO replicas as well as the TETs was longer (>1 ns) and nicely exponential, i.e., quite different from the decay of the NP DBE line.[22] As will be demonstrated in this paper, a similar large discrepancy exists between the no-phonon BE decay and the TET decay.

There is no consistent physical explanation in the recent literature for the variety of TRPL behavior of the DBEs observed in GaN. In this work we attempt to improve on this situation. We present a comprehensive study of TRPL of the Si and O donor DBEs in GaN, for different doping densities and measurement temperatures using high-quality thick HVPE GaN layers. A consistent model for the observed variety of TRPL behavior for the NP DBEs as well as the LO replicas and the TET lines is presented, involving time-dependent spatial distributions of the active DBE states, a nonradiative surface recombination and an exciton-donor scattering process in the vicinity of the no-phonon BE lines as major ingredients.

II. SAMPLES AND EXPERIMENTAL PROCEDURE

In this paper we concentrate on two HVPE grown GaN samples. Sample no. 1 was grown at Lumilog, SA on a two-step epitaxial lateral overgrowth template,[23] and removed from the sapphire substrate at Linköping University by a laser lift-off technique, as described separately.[24] It had a thickness of about 300 μm and a residual donor concentration in the mid 10^{16} cm^{-3} range. Sample no. 2 was a 1-mm-thick free-standing layer grown at Furukawa Co. The total residual donor concentration in this sample was about 8×10^{15} cm^{-3}. The samples were measured on the Ga face in the as-grown condition, i.e., no surface etching was applied.

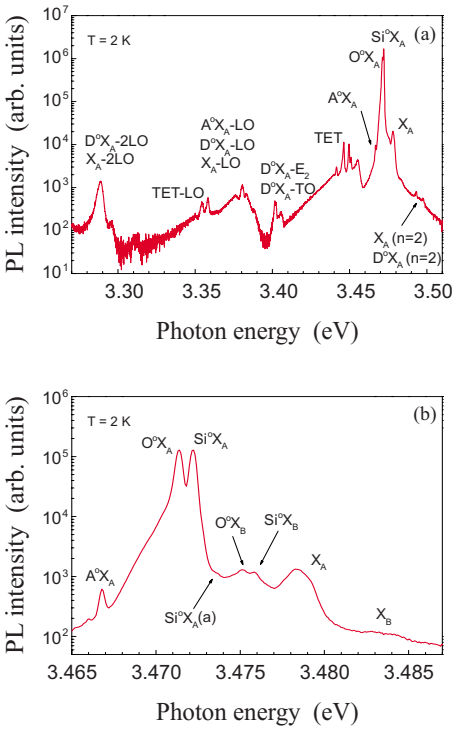

FIG. 1. (Color online) (a) Near band-gap PL spectrum at $T=2$ K for sample no. 2. The spectrum shows the FE and BE no-phonon lines, the two electron transition lines, and the corresponding phonon replicas. (b) High-resolution spectrum in the region of the no-phonon exciton lines. The excited states of DBEs are labeled (a), (b), etc.

Stationary PL spectra were measured with the fourth harmonic ($\lambda=266$ nm) of a continues wave Nd:V laser as excitation. The PL signal was dispersed by a 0.55 m monochromator and detected by a UV enhanced liquid-nitrogen-cooled charge coupled device camera. For the transient PL measurements the third harmonic ($\lambda_{exc}=266$ nm) from a Ti: sapphire femtosecond pulsed laser (pulse length 150 fs) was employed. The PL transients were detected by a UV sensitive Hamamatsu streak camera system with a temporal resolution better than 20 ps. The samples were placed in a variable-temperature cryostat for measurements in the temperature range 2–300 K.

III. EXPERIMENTAL RESULTS

A. Stationary PL spectra

A stationary PL spectrum at 2 K of sample no. 2, over a broad spectral region where all the different PL lines discussed below are shown, is displayed in Fig. 1(a). The most important lines are labeled, in some cases labels refer to groups of lines. The near band-gap region is shown in high resolution in Fig. 1(b). The main free exciton peaks are labeled X_A and X_B as related to holes from the A and B va-

lence bands, respectively. The main DBE peaks are the O $^{o}X_A$ and Si $^{o}X_A$ peaks at 3.4714 eV and 3.4723 eV respectively, with a bound hole related to the A valence band. Two weaker corresponding peaks O $^{o}X_B$ and Si $^{o}X_B$ are observed around 3.475 eV, where the bound hole is related to the B valence band.[25] Lower intensity excited state DBE lines are present in the spectral region 3.472–3.478 eV, not all resolved in Fig. 1(b). At lower energies a weak acceptor bound exciton (ABE) peak is observed at 3.466 eV (labeled A $^{o}X_A$), in the literature often ascribed to a residual acceptor of unknown origin,[26] but most probably related to Mg.[27] This peak is riding on a broad background emission related to the DBE principal lines, suggested to be due to FE-DBE scattering.[20]

At still lower energies the PL peaks are all related to satellite emissions or phonon replicas.[22] The strongest lines are the so-called TETs in the region around 3.44–3.45 eV, where the DBE recombines leaving the neutral donor in an excited final state.[5] Details of these spectra with accurate evaluations of the excited states and binding energies of the O and Si donors in this sample are reported separately.[16] There is a broad background emission present in the region 3.40–3.45 eV [Fig. 1(a)]. This emission is suggested to mainly originate from inelastic scattering of FEs at donors, where the final-state donor electron is ionized, i.e., a radiative Auger process (see further discussion below). In the range 3.38–3.41 eV there are several prominent phonon replicas of the excitons, mainly the BEs. Around 3.40 eV there are DBE phonon replicas with E_2 and TO phonons. At lower energies LO-phonon replicas of the DBEs and the ABE are present, as reported in detail separately.[28] The TET spectra are replicated with LO phonons around 3.35 eV, and finally there are two-LO-phonon replicas of the FE and the DBEs, the latter being surprisingly strong.[22,29,30]

The spectra shown for sample no. 2 in Fig. 1 are representative for nominally undoped bulk GaN samples. The other sample no. 1 has a slightly higher doping level, and consequently somewhat larger spectral linewidth but the overall PL spectrum in the range covered by Fig. 1 is very similar. The nominally undoped HVPE samples are always *n*-type, and the extrinsic (bound exciton) part of the PL spectrum is dominated by the residual O and Si donors inadvertently incorporated during growth.

B. PL transients for the no-phonon FE and DBE lines

In Fig. 2 is shown a set of TRPL spectra for sample no. 2 in the NP DBE region at 2 K. The data show the two major O- and Si-related DBE lines developing against the time delay after the excitation pulse in the presence of a broad background. It is clear that the lower energy O $^{o}X_A$ line has a somewhat longer decay time than the Si $^{o}X_A$. This is also clear from the decay curves for each line, which were shown in Fig. 3 together with the decay of the A FE line. While the X_A decay can be approximated by a single exponential at this temperature with a decay time about 90 ps, the decay of the NP DBE lines is more complex. The initial decay can be described as nearly exponential with a decay time <300 ps, and then there is a much slower nonexponential tail toward

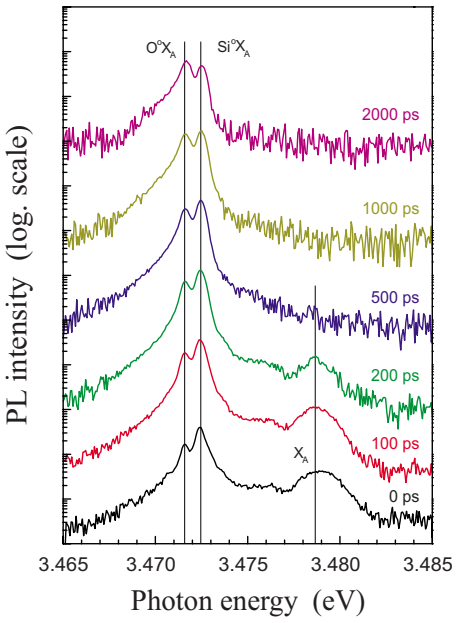

FIG. 2. (Color online) Time-resolved PL spectra at 2 K for sample no. 2 in the energy region of the no-phonon DBE emission lines. The spectra are normalized and vertically shifted for clarity. The vertical lines mark the emission lines for which PL transients are shown in Fig. 3.

longer times. The corresponding data for sample no. 1 shows a similar picture. The numbers for the decay times shown in the figure are extracted by biexponential fitting and should be regarded as a guide for the eyes.

Modeling of these data for the FE and DBE transients in terms of rate equations involving capture of the FE population to the DBE and subsequent radiative recombination cannot reproduce the experimental data without additional assumptions.[31] The major problem here is that the FEs and the BEs have different spatial distributions developing over time. From the observed properties of the FE-related transients under our low excitation conditions we are bound to conclude that the fast FE PL transient observed at 2 K is due to a dominant nonradiative recombination of FEs at the front

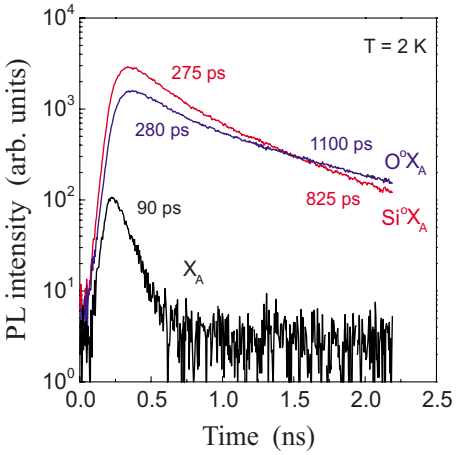

FIG. 3. (Color online) PL transients for the A free exciton and O and Si DBE no-phonon lines at 2 K.

surface of the sample.[3] In analogy with the situation in other wide band-gap semiconductors where more detailed studies have been made,[32] we further assume that there is a diffusion of FEs over a distance on the order of 1 μm beyond the shallow excitation profile (only about 50 nm in this case) at 2 K. It seems probable that a major part of the FE population at 2 K does not participate in the no-phonon FE PL emission, due to strong reabsorption of the FE-related recombination radiation before reaching the surface. The fast transient for the X_A line in Fig. 3 then originates exclusively from near surface FE recombination (which will be mainly nonradiative). The influence of the surface properties on the PL transients is further discussed below under Sec. IV.

This situation for the FE recombination complicates the discussion of the no-phonon DBE transients. Previous studies of PL excitation spectra of DBEs in GaN have showed that the DBEs are not mainly created by capture from the FE ground state, as often assumed in modeling of the FE-BE transient kinetics. Instead efficient capture into DBE states occurs mainly from FEs during their slow relaxation via acoustic phonons before reaching the FE ground state.[33] In addition capture most likely occurs via the excited states of the DBE complex. A simple modeling in a two state system for the FE-BE transient kinetics is therefore of limited value. In any case in the TRPL we should consider one separate contribution from the near surface DBEs and another from the population of DBEs further inside the sample, which will have a longer, mainly radiative decay. The near surface contribution might be affected by the fast decay of the corresponding near surface FE population. In addition even with front surface excitation, there is a light scattering process with a resonance at the NP BE lines, which will affect the initial shape of the DBE transient.[34] Also, the broadening process due to FE-DBE scattering is present in the DBE spectral region,[20] and might affect the transient behavior of the DBE NP line. The spatial origin of the FE and DBE PL will be different; the latter will on the average originate from a region deeper into the sample (for further discussion see Sec. IV). This also means that in the present experiments with front surface excitation and detection and using the data from the NP lines it is not possible to establish thermal equilibrium between the detected FE and DBE populations at 2 K,[35] as typically assumed in the rate-equation modeling of TRPL data.[36,37] Since we conclude that the observed initial BE decay is influenced by several processes from the near surface BE population, it is clear that we cannot conclude a value of the radiative decay time for the DBEs from these data for the NP transitions, although unfortunately this is the standard (but generally incorrect) procedure in the literature for DBEs in semiconductors.

At elevated temperatures the decay curve shapes for the DBEs are changed, and they gradually approach the (nonexponential) shape of the FE decay. It appears that already at about 30 K the FE and DBE populations are close to thermal equilibrium, so that a simple two level model could approximately describe the traffic of excitons between the FE and each DBE, provided the same spatial volumes are monitored for the FEs and the DBEs in the transient data. Apart from the different initial cusp in the FE and BE decay curves, mainly representing the capture of excitons to the BE states, the shape then becomes identical for the FE and the DBEs (see Fig. 4 in Ref. 22), as expected.[36,37] The decay is then governed mainly by the properties of the FEs, which are expected to have a radiative decay time that is increasing with temperature.[3,38] While the initial fast part of the FE decay is still dominated by the nonradiative surface recombination, the slower later part of the transient related to the bulk transitions further inside the sample gains in importance with temperature, due to the expected longer free exciton decay time as well as diffusion length at elevated temperatures.[32] We note that the expected temperature independent radiative lifetime of a localized transition like the DBE (Ref. 38) is completely masked by the thermalization with the FE states in these data on the NP lines.

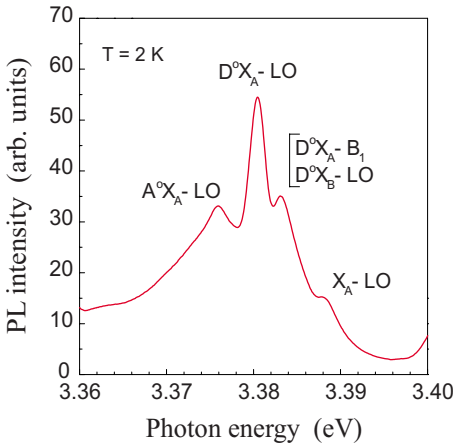

FIG. 4. (Color online) Low-temperature PL spectrum (2 K) in the region of the first LO-phonon replicas of free and bound excitons.

C. Decay characteristics of the LO replicas of FE and DBE states

The one-LO replicas of the two principal DBE lines are broadened, meaning that they have merged into one peak where the individual contributions from each replica cannot be clearly distinguished (Fig. 4). The main reason for this situation is the combination of two NP DBE lines related to O and Si, and two LO-phonon modes [A_1(LO) and E_1(LO)], giving four DBE LO replicas within about 1 meV.[28] The measured transient behavior is therefore an average of the Si- and O-related DBE LO replicas (labeled as D ^oX_A-LO). Figure 5 shows the decays of the X_A-LO and the D ^oX_A-LO at 2 K. We note the striking difference in the shape of the decays for the one-LO replica of the FE as well as for the DBE, as compared with the corresponding NP lines discussed above. The difference in the X_A decay compared to the NP line is interpreted in the following way: the initial peak is the replica of the near surface FEs that suffer from nonradiative surface recombination, the fast decay of this part is similar to the 90 ps observed for the NP X_A line. The nicely exponential decay of about 1400 ps observed at later times is interpreted as involving the radiative decay at 2 K of the FE population residing well inside the sample. (The value of the radiative lifetime cannot directly be deduced from these data

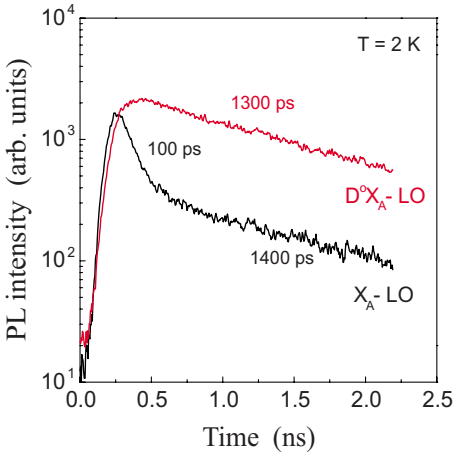

FIG. 5. (Color online) PL transients for one-LO-phonon replicas of the A free exciton and DBE at 2 K.

since the bulk nonradiative rates are not known). As mentioned above, this process is strongly affected by reabsorption of the FEs in the case of the NP FE decay, in a similar way as observed for other materials.[39] In the case of the DBE LO replica a nicely exponential decay is also observed at 2 K, in contrast to the nonexponential behavior of the DBE NP lines discussed above. A natural interpretation of this longer decay time is then that it is related to the radiative recombination time of the DBE, modified by the capture from the hot FE population, which however is expected to mainly occur during the rise time of the transient. The decay rates of the FEs and the DBE LO replicas are very similar, about 1300 ps for the D $^{o}X_{A}$-LO vs 1400 ps for the X_{A}-LO. We note again that the capture to the BEs occurs mainly from the excited (dark) FE states, at higher energies than the FE population detected in the PL experiment.[33] Also, in this case the decay time is an average value for the Si- and O-related DBEs since these are not separately resolved in the one-LO replicas. (It should be noted that measurements over a longer time range would be needed for a more accurate evaluation of characteristic decay times.) The excitation intensities used in these experiments are on the order of $<10^{15}$ cm^{-3} s^{-1}, far from saturation of the DBE population, i.e., most neutral donors in the excited part of the sample are not occupied with excitons. For the two-LO DBE replica the decays are quite similar to the one-LO replica at each temperature, as expected.

D. Decay characteristics of the two-electron transitions

The TET spectra vary strongly with temperature (see Fig. 2 in Ref. 16) as well as with delay time in TRPL spectra, as shown in Fig. 6 for time delays up to 2 ns at 2 K. As mentioned before, the temperature dependence of stationary spectra is mainly due to the corresponding temperature dependence of the occupancy of the excited DBE states, which preferentially connect to the *p*-like excited neutral donor states in the final state of the TET transition, while the DBE ground state has allowed transitions to the *s*-like neutral donor excited states.[11] The transient occupancy of the excited DBE states is reflected in the TRPL spectra, as shown previ-

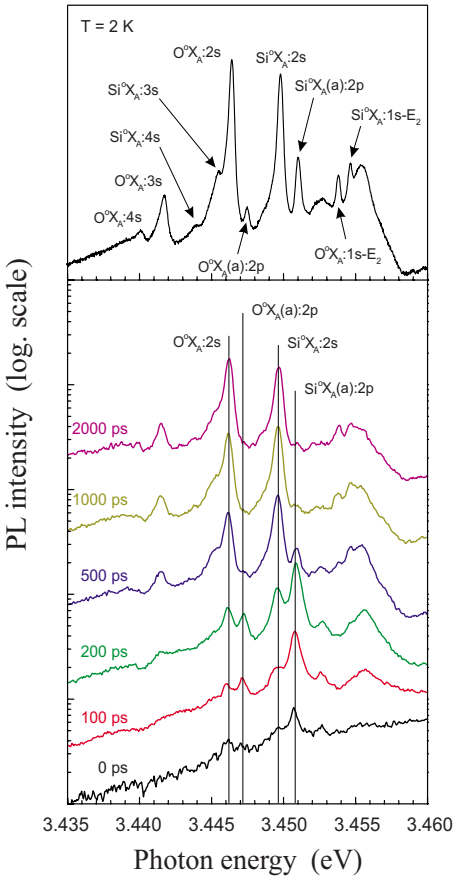

FIG. 6. (Color online) Time-resolved PL spectra at 2 K in the energy region of the two-electron transitions. All spectra are normalized and vertically shifted for clarity. The vertical lines mark the most intense emission lines for which PL transients are extracted. At the top continuous-wave PL spectrum is shown. The TETs are labeled with the initial state DBE (shown only for excited states) and the final state of the donor (1*s*, 2*s*, 2*p*, etc.).

ously in Ref. 3. It is clear that during the first nanoseconds there are strong changes in the occupancy of the excited DBE states, which at the lowest temperatures are not in thermal equilibrium with the ground state.[35] In Fig. 7(a) are shown the PL transients at 2 K for the Si-related TET lines involving 2*s* and 2*p* donor states, illustrating the drastic difference in the population of the corresponding initial states of the transitions. At higher temperatures the excited DBE states thermalize with the ground-state population, and all lines acquire the same transient behavior above about 10 K [see Fig. 16(b) of Ref. 3].

An interesting observation from these data is that the transients for the 2*s* TET lines at 2 K (and for all lines above 10 K) exhibit a well defined singly exponential decay. The decay times at 2 K (about 1100 ps for the Si $^{o}X_{A}$:2*s* line and 1800 ps for the O $^{o}X_{A}$:2*s* lines are consistent with the decay of the DBE-LO transition, where the two DBE replicas are not separately resolved but again quite different from the NP-DBE decay. Clearly the donors responsible for the TET transition seem to be in equilibrium with the population responsible for the DBE one-LO transition. This supports the idea that this decay is related to the real radiative decay time

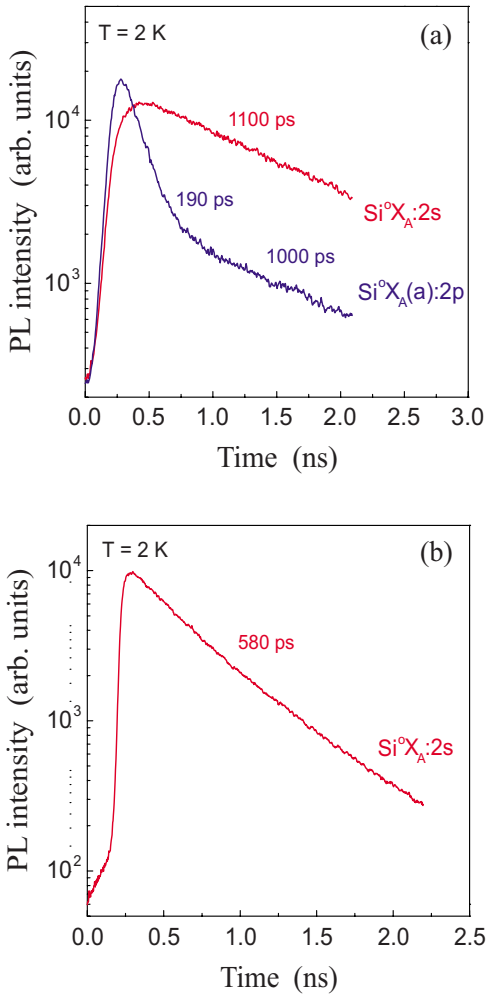

FIG. 7. (Color online) (a) PL transients of the 2*s* and 2*p* TETs related to the Si donor. (b) PL transient of the 2*s* TET related to the Si donor in sample no. 1. The shorter decay time in comparison with the sample no. 2 is presumably due to the larger background doping concentration.

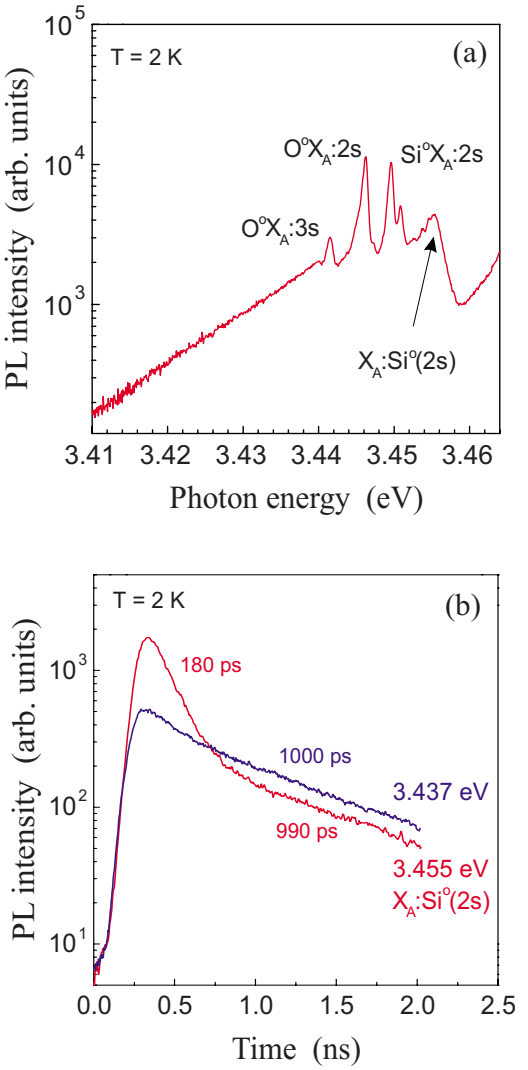

FIG. 8. (Color online) (a) Enlarged PL spectrum in the energy range of TETs showing the broad continuum background. (b) PL transients for the emission at 3.455 eV (recombination of A exciton scattered by Si donors) and 3.437 eV (continuum of TETs).

of the DBEs, possibly modified by DBE exciton transfer processes. The processes involved in the initial faster decay of the near surface population taking part in the NP DBE decay are obviously not active for the TET lines, as discussed further below.

The decay times for the TETs seem to depend on the doping level. In sample no. 1 the decay is appreciably faster, about 600 ps [Fig. 7(b)], indicating a stronger exciton transfer from the DBE states to faster recombination channels. This process competes with the radiative process, so the decay becomes slightly nonexponential. A similar decay time is found for the DBE-one-LO process in that sample. This illustrates the necessity to have samples of low donor concentrations for studies of the radiative lifetimes of the DBEs in GaN, in order to avoid transfer of the BEs to nonradiative sites. As we already pointed out above, it is possible that the longer lifetimes observed for the O and Si DBEs in sample no. 2 are still affected by interdonor exciton transfer before recombination. The radiative lifetimes of the DBEs are expected to approximately follow an $(E_{BE})^{3/2}$ power law, where E_{BE} is the DBE binding energy.[40]

E. Broad background in the 3.40–3.46 eV region

It is clear from Fig. 1 that there is a broad continuum background present in the PL spectra in the range 3.40–3.46 eV at 2 K. This background spectrum is essentially separate from the tail of the DBE NP transitions, which suffer some broadening, as previously discussed, e.g., in Ref. 20. This continuous background starts at the rather broad peak at about 3.455 eV [Fig. 8(a)], which corresponds to inelastic scattering of the X_A excitons at Si donors which are left in a 2*s* state.[41] The main evidence for this is a fast decay time [Fig. 8(b)], reminiscent of the free X_A exciton decay. After some delay time two additional PL peaks appear at about 3.4536 and 3.4545 eV (Fig. 6), assigned to phonon replicas of the principal Si- and O-related BEs with the E_2(low) phonon [17.8 meV (Ref. 42)]. At lower energies in addition to all the TET lines discussed above, there is a continuous background present, extending smoothly down to about 3.40 eV. The decay for this background is slightly nonexponential, the

initial faster decay is presumably related to the tail of the broadened FE-DBE scattering process for the main NP DBE lines. At longer times it is similar as for the discrete TET lines, i.e., on the order of 1 ns [see Fig. 8(b)]. This decay time is close to the decay of the Si DBE. This is an argument that this background is of a similar origin as the TET lines, but instead of transitions to the excited donor states continuum states in the conduction band are the final states in a radiative Auger process. Following earlier work on direct band gap materials we assume that nonradiative Auger recombination at the DBEs correspond to a longer lifetime, and may therefore be disregarded.[43] The nonradiative process is known to be dominant in indirect band-gap semiconductors, however.[1]

IV. DISCUSSION

A. Influence of the surface states and the surface depletion field on exciton recombination

A problem not often discussed for excitons is the possible influence of a near surface electric field, such as a depletion field, on the PL spectra.[44,45] In the case of GaN there are recent reports on the presence of a surface potential on the order of 1 eV on the *n*-GaN surface, independent of the growth technique.[46–48] This potential is induced by surface states, uncompensated polarization charges, intrinsic oxide-interface states and/or adsorbed impurities that can create deep levels in the band gap. Theoretically there are empty surface states about 0.6 eV below the conduction band edge on a clean *c*-plane Ga-face GaN surface.[49] In practice the surface is oxidized with an oxide film about 1–3 nm thick, the thin oxide layer is reported to have a deleterious effect on surface recombination for GaN.[49,50] Then there is a depletion field present at the surface, the strength and extension of this field is directly related to the net donor doping density.[51,52] The consequences of this for the interpretation of FE and DBE properties were discussed in Ref. 3, and we shall here summarize some important predictions for the TRPL data of DBEs: (i) there is a depletion region at the surface of Ga-face *n*-GaN, with a maximum field of 10^4–10^5 V/cm for the doping range 10^{16}–10^{18} cm^{-3} in the dark; this is smaller than the breakdown field for FEs and also much reduced under illumination, (ii) both FEs and DBEs exist in the depletion region, but their (spatially different) distribution extends well beyond that in the bulk of the material, (iii) a charge dipole is created across the depletion region due to the action of free carriers under illumination, in our case quasiequilibrium conditions were established before each transient event, (iv) there is a strong surface recombination for the FEs, dominating the TRPL of FEs for the moderate excitation conditions employed in this work, (v) the DBE population under these excitation conditions is essentially concentrated beyond the depletion range, and the TRPL data detected in the transparent energy range below the band gap should allow proper measurements of the intrinsic DBE decay times, (vi) there is an additional near surface process acting on the no-phonon DBE transitions, dominating the initial part of DBE TRPL decays.

In spite of a rather strong primary excitation in the depletion region only a fraction of the donors are expected to be neutral in that region, while just beyond this region inside the sample a larger fraction of the donors are expected to be neutral, due to the transport of photoelectrons across the depletion region. There is then expected to be a much larger concentration of BEs in this inner region of the sample, which will be reflected in the decay of the DBE-LO and the TET spectra in the transparent spectral region, as discussed above. The FEs as well as the DBEs inside the depletion region are expected to be impact ionized to some extent by the electrons created by the photoexcitation and via Auger processes during the decay. It has been established that impact ionization by electrons in bulk GaN is effective already at quite low fields (<100 V/cm).[53] This impact ionization is a contribution to the near surface nonradiative recombination for both FEs and BEs but less important for the latter. The reabsorption of the NP DBE radiation by neutral donors in the depletion region is likely to be a quite weak process, due to rather weak resonant absorption coefficient at the NP DBE lines. This absorption of the DBEs is estimated to be about two orders of magnitude weaker than for the FEs, based on the strength of the DBE reflectance feature in previously studied samples of similar quality.[54] Since the reabsorption of the FE radiation in the depletion region is significant, the impact ionization process might be a more significant contribution to the nonradiative recombination for the NP FE PL.

B. A tentative model for the faster initial decay of the bound exciton no-phonon line

The origin of the faster initial decay process for the DBEs when detected in the NP line warrants some discussion. Processes mentioned above are related to the near surface scattering effects,[20,34] and possible effects of recombination inside the depletion region. The experimental data demonstrated above give the clear indication that there is a separate process acting around the energy position of the DBE NP line, a process seemingly unrelated to the radiative recombination process of the DBEs. One important characteristic of this process is that the LO-phonon coupling seems to be absent or very weak, since there is no trace of the fast initial transient in the LO replicas of the NP PL (Fig. 5). So we suggest there is a separate process that spectrally overlaps the DBE NP PL, and that has a fast temporal behavior. Scattering processes are typical candidates, they may give important contributions, and they may not give strong LO-phonon replicas. One such process is the FE-DBE scattering discussed in Ref. 20, another is the photon scattering processes discussed in Ref. 34. An indication that there is such a process acting separately from DBE recombination is shown in Fig. 9, where the decay curves in the spectral region just below the NP DBE line recorded in transmission through the 1-mm-thick sample no. 2 are compared with conventional TRPL data with front surface detection. We note that at the peak of the DBE line the decay is exponential with a similar decay time as in Fig. 5, i.e., the initial fast decay is absent

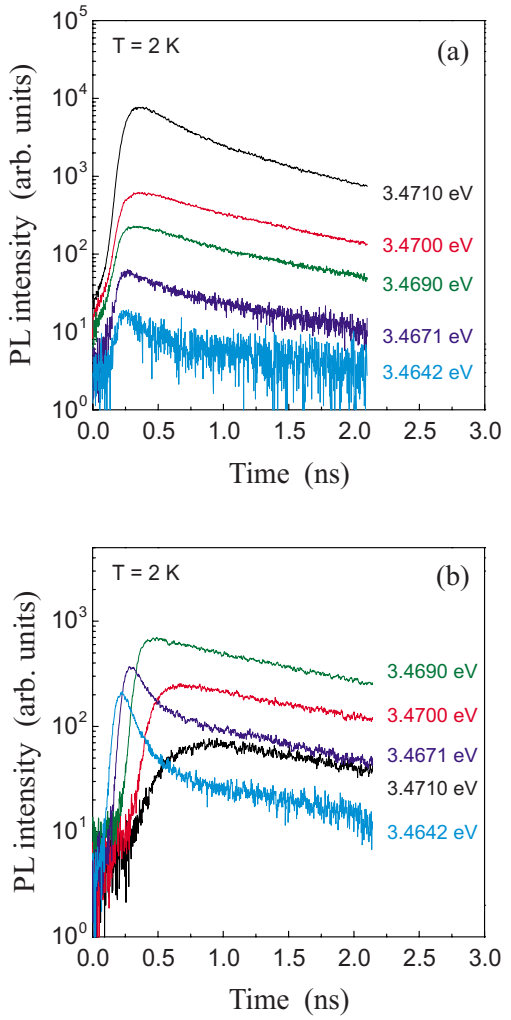

FIG. 9. (Color online) Decay curves for the emission just below NP DBE lines recorded in (a) conventional (reflection) mode and (b) transmission mode.

due to reabsorption as it passes through the sample. At slightly lower photon energies, where the reabsorption is weak, the initial fast transient is recovered. We note that this is in the energy range where the FE-DBE scattering process is suggested to be important.[20] In Ref. 20 such a process was discussed that contributes to the luminescence background around the NP DBE peak. A corresponding process involving light scattering may exist. Other contributions from light scattering have been discussed in Ref. 34. One could argue that tunneling of BEs across the thin depletion region (quite thin during optical excitation) could be a nonradiative recombination channel for the DBEs (as well as for the FEs). Such a process would reduce the decay rate of the near surface BEs, producing a faster initial part of the transient. This contribution would have the phonon coupling strength of the DBE though, and a similar fast initial transient part would then be observed for the LO replicas. Since this is not observed, we disregard near surface DBE tunneling as responsible for the anomalous shape of the NP DBE decay at low temperature.

C. Comparison with previous data for DBEs in GaN and other materials

The above data for the DBE transients in GaN together with previous work[17–21] demonstrate that an evaluation of the no-phonon DBE PL transient with above band-gap excitation does not in general give relevant data for the radiative lifetime τ_r of these processes. Obviously the obtained transients fail to demonstrate a purely exponential decay, and the initial part of this decay corresponds to a much faster process than the radiative DBE decay in the bulk of the material. In most cases the decay time in previous work has been evaluated either as an exponential fit to the initial part of the NP DBE decay, or an average over the part of the NP transient that has been measured.[12,17–21] To get a reliable value of the τ_r parameter the real bulk recombination has to be monitored. This can be done as in this work if various replicas like TETs occurring in the transparent region of the spectrum are monitored. An alternative technique might be to use below band gap excitation, in which case the bulk properties dominate. This has been demonstrated for free excitons in GaN (Ref. 55) as well as for ZnSe (Ref. 56) but was not specifically applied to the study of bound excitons.

Previous studies of DBEs in other materials also seem to suffer from the inaccuracy imposed by the study of the transient of the no-phonon line, which is a problem independent of the technique used for the registration of the decay. Reports on the recombination dynamics of DBEs in direct band-gap materials such as GaAs,[57] CdTe,[58] and CdS (Ref. 59) using above band gap or resonant excitation all suffer from this problem, and the values reported for the radiative lifetime should be revisited.

The values obtained here for the radiative recombination time for DBEs in GaN is about 1.1 ns for the Si DBE and 1.8 ns for the O DBE. These values are the lower limits, since they might be affected by excitation transfer. This can only be tested when samples of considerably higher purity become available. Theoretically values about two orders of magnitude smaller are predicted.[60] If the theoretical values are adjusted for the presence of strong degeneracy of the DBE states, i.e., the presence of numerous excited DBE states,[60] the agreement with theory is much improved.

V. SUMMARY

In this work a realistic description of optical data for the transient decay of neutral donor bound excitons in GaN is attempted, for the case of low excitation conditions. It is pointed out that the observed decay of the no-phonon DBE line is generally nonexponential in the common case where front surface excitation and detection is used, and cannot be used for evaluation of the proper decay time. Instead DBE-related recombination processes in the transparent part of the spectrum, like LO replicas or TET peaks provide accurate exponential decays for evaluation of, e.g., the radiative decay time. In addition the commonly used practice to model the FE and DBE transients via a simple rate equation coupling the two radiative channels is shown to be generally incorrect, and should be avoided. At donor doping levels above 10^{16} cm^{-3} the observed decay times for DBEs shorten due to

competition with exciton transfer processes from the neutral donors. The initial faster decay of the DBE NP line is suggested to be related to FE-DBE light scattering. Future work at higher excitation densities as well as lower donor doping is needed to understand the details of this process.

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