Dissociation of H-related defect complexes in Mg-doped GaN

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Post-growth annealing and electron beam irradiation during cathodoluminescence were used to determine the chemical origin of the main optical emission lines in moderately and heavily Mg-doped GaN. The 3.27 eV donor-acceptor pair (DAP) emission line that dominates the emission spectrum in moderately Mg-doped (*p*-type) GaN was found to be strongly reduced by electron irradiation and of different chemical origin than the DAP at a similar energetic position in Si-doped (*n*-type) GaN. These results suggest that the acceptor responsible for the 3.27 eV DAP emission in Mg-doped GaN is Mg and that the donor (20–30 meV) is hydrogen-related, possibly a (V_N-H) complex. This complex is dissociated either by electron irradiation or thermal annealing in N_2 or O_2 atmosphere. We found that upon electron irradiation, a deeper emission line (centered at 3.14 eV) emerged, which was assigned to a DAP consisting of the same Mg acceptor level and a deeper donor (100–200 meV) with a similar capture cross section as the donor in the 3.27 eV emission. Moreover, two different deep donor levels at 350 ± 30 and 440 ± 40 meV were identified as being responsible for the blue band (2.8–3.0 eV) in heavily Mg-doped GaN. The donor level at 350 ± 30 meV was strongly affected by electron irradiation and attributed to a H-related defect.

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I. INTRODUCTION

Full commercialization of GaN-based devices is restricted by the poor carrier density in *p*-type GaN, which has remained low even in state-of-the-art material as a result of self-compensation with native defects[1] as well as a relatively high thermal activation energy (~200 meV) (Refs. 2 and 3) of the acceptor levels. Currently, the level of *p*-type conductivity is adequate for light emitting diodes and just sufficient for laser diodes, but is insufficient for the fabrication of high-performance heterojunction bipolar transistors or GaN-based dilute magnetic semiconductor materials. In addition, the nature of dopants, defects and residual impurities and their impact on the *p*-type carrier concentration is partly understood, at best.

Consequently, there is recent strong interest in optical investigations of Mg-doped *p*-type GaN. The main objective of these studies in the past has been to determine the chemical origin of the dominant optical emission lines (i.e., the 3.27 eV ultraviolet (UV) emission and the 2.8–3.0 eV blue band) and to eventually understand the compensation and activation processes that are vital for the fabrication of high-performance GaN-based devices. Although there have been numerous reports over the past 20 years[3,4] that attribute the main optical emission peaks in GaN to dopants, defects, and impurities, to date there is still no consensus on their chemical origin.

In this work, we present a comprehensive analysis of the luminescent emission properties of moderately and heavily Mg-doped GaN by combining post-growth annealing processes[5] and low-energy electron beam irradiation (LEEBI) techniques[6] as well as temperature- and excitation density-resolved cathodoluminescence (CL) spectroscopy. The combination of these techniques represents a powerful approach to both investigate the optical properties and facilitate an indisputable assignment of the optical emission peaks in GaN to specific radiative recombination centers.

II. EXPERIMENTAL DETAILS

The samples studied were grown by metal-organic vapor phase epitaxy (MOVPE) on a GaN buffer layer and *c*-plane sapphire substrate. Three different sets of samples were studied in this work. The first set of samples was 2 μm thick, thermally activated GaN:Mg with a Mg concentration in the low 10^{19} cm^{-3} range and a hole concentration of $1.0\times10^{17}/cm^3$, as determined by Hall measurements, while the second set was 2-μm-thick GaN:Si with an electron concentration of $1.0–6.0\times10^{18}/cm^3$. These two sets were thermally annealed in a Stanton Redcroft STA-780 furnace in controlled gaseous atmospheres of high purity[7] [N_2,O_2,H_2(5%)/N_2]. The annealing protocol consisted of a 180 s ramp from room temperature (RT) to 780 °C, a plateau of 10 s and exponential cooling for 20 min to RT. The third set was 0.5-μm-thick GaN:Mg with a Mg concentration in the 10^{20} cm^{-3} range, which was post-growth annealed but

remained semi-insulating. The H concentration in the Mg-doped GaN samples was determined by secondary ion mass spectrometry to be in the 10^{18}–10^{19} cm^{-3} range. The CL measurements were performed between 5 and 300 K using an Oxford Instruments MonoCL2 system either installed on a JEOL35C or a LEO Supra 55VP scanning electron microscope. The CL spectra were measured using a 1200 lines/mm grating blazed at 500 nm and a Hamamatsu R943-02 Peltier cooled photomultiplier tube. All CL spectra were corrected for system response. The electron beam current I_b was measured using a Faraday cup.

III. THEORETICAL CONSIDERATIONS ON ELECTRON IRRADIATION INDUCED EFFECTS IN GAN DURING CL

It is well known that high-energy electron irradiation (several hundred keV) can locally change the sample chemistry due to generation of defect centers.[8] In the following, a quantitative estimation of the impact of electron beam irradiation during CL (~10 keV) on the sample chemistry of GaN is presented.

The relativistic cross section σ relevant for the estimation of the knock-on energy T_d that is necessary to create a Frenkel (vacancy-interstitial) pair is given by the McKinley-Feshbach[9] expression

$$\sigma = \pi(Ze^2/mc^2)^2(1/\beta^4\gamma^2)[(T_m/T_d - 1) - \beta^2 \ln(T_m/T_d) + Z\beta\pi/137\{2[(T_m/T_d)^{1/2} - 1] - \ln(T_m/T_d)\}], \quad (1)$$

where $\beta = v/c$, v is the electron velocity, c the speed of light, $\gamma = (1-\beta^2)^{1/2}$, Z the nuclear charge, e the charge of the electron, m the electron rest mass, and T_m denotes the energy transfer during a head-on collision where[10]

$$T_m = (2m/M)[(E + 2mc^2)E/mc^2], \quad (2)$$

where M is the mass of the lattice atom and E is the incident electron energy in MeV. For the specific case of electron irradiation, insertion of numerical values for m, M, and c yields[11]

$$T_m = 2147.8(E + 1.0220)E/A \ \ (eV), \quad (3)$$

where A is the atomic number. The electron energy required for the creation of a Frenkel pair is $E = E_{threshold}$. If the energy transfer due to the electron irradiation is smaller than the knock-on energy ($T_m < T_d$), then no elastic collision radiation damage will occur. In order to estimate $E_{threshold}$ for Ga and N atoms, literature values for T_d(Ga) of 20.5 (Ref. 12) and 19 eV (Ref. 13) and for T_d(N) of 10.8 eV (Ref. 12) were used. The corresponding threshold energies were calculated to be 440 (Ref. 13) −460 and 70 keV for the displacement of Ga and N atoms in GaN, respectively. No experimental values for T_d are available for the displacement of a Mg atom from the Ga site but we assume that the respective $E_{threshold}$ should be of the same order of magnitude as that for Ga. Based on these calculations, irradiation damage of the GaN lattice for electron beam energies of around 10 keV during CL can be ruled out. This result is consistent with recent CL results where an increase of the minority carrier diffusion length was found after electron irradiation instead of a decrease that would be expected if the concentration of defects was enhanced.[14]

The dominant hydrogen-related defect complexes in Mg-doped *p*-type GaN, i.e., (Mg_{Ga}-H)[6,15] and (V_N-H),[16] can, in principle, be strongly affected by electron irradiation even for very low energies (<1 keV). Calculations based on density-functional theory yielded dissociation energies of 1.5 (Ref. 17) and 1.6 eV (Ref. 18) for the Mg-H complex and 1.56 eV (Ref. 16) for the (V_N-H) complex. Experimentally, an energy of 1.76 eV for the sum of the H^+ diffusion activation energy and the H^+ binding energy to ionized Mg acceptors was reported.[18] Consequently, the energy that is generated by electron-hole recombination processes in GaN is sufficient to dissociate these complexes.[19] Yet, the mere dissociation of these complexes may not produce a permanent separation of the H from the Mg or the V_N, since the H can easily be recaptured. However, that is prevented by the electric field generated by the trapped electrons during electron irradiation, which causes a separation of differently charged species within the electron beam-solid interaction volume.[20] According to the theoretical electron-insulator interaction model by Renoud *et al.*,[21] the charge distribution forms a negative semi-ellipsoidal shell whose size is directly related to the maximum penetration range, R_{KO}, of the primary electrons[22]

$$R_{KO} = 0.0276A/\rho Z^{0.889} * E_b^{1.67} \ \ (\mu m). \quad (4)$$

The negative shell surrounds a mixing zone with a weak density of positive charge[21] leading to a nonuniform electric field and electromigration of mobile ions.[20] Therefore, H is expected to be highly affected by the electric field due to its high mobility in *p*-type GaN.[23]

For completeness, the possibility of electron beam stimulated surface desorption (Knotek-Feibelman effect)[24] driven by the Auger decay of a beam-excited core hole should be considered here as well. In nitrides, low-energy electron irradiation might cause N mass loss leaving a Ga-rich surface, which reacts with residual oxygen forming Ga_2O_3. However, it will be shown later that no mass loss or surface oxidation was observed in this work.

IV. EXPERIMENTAL RESULTS

Depending on the doping level, there are two main compensation mechanisms in Mg-doped GaN: (i) passivation of Mg acceptors with donorlike hydrogen atoms[6,15] and (ii) self-compensation by point defects due to high Mg-doping.[1] In the moderate doping regime, 3×10^{18} $cm^{-3} \leq N_A \leq 2\times10^{19}$ cm^{-3}, hydrogen passivation is very effective and impurity compensation as well as self-compensation mechanisms play a minor role.[1] The recent interest in hydrogen[25] is justified since its state in GaN influences both the activation of the Mg acceptor and the optical emission characteristics. Hydrogen plays a key role in *p*-type doping since it compensates Mg acceptors, prevents the formation of charge compensating native defects and promotes the solubility of Mg.[26] The effect of a doping driven self-compensation becomes

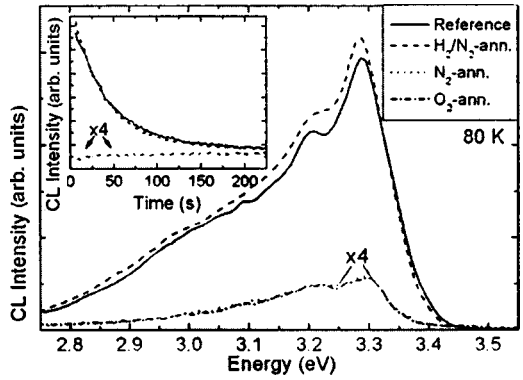

FIG. 1. 80 K CL spectra ($E_b=10$ keV, $I_b=0.25$ nA, $89\times71\ \mu m^2$) of Mg-doped *p*-type GaN after post-growth annealing (780 °C for 10 s) in controlled gaseous atmospheres (high purity N_2, O_2, and $H_2(5\%)/N_2$, respectively). For comparison a spectrum of an "as-received" reference sample is shown (solid line). The spectra for the samples annealed in N_2 and O_2 are enlarged by a factor of 4. The inset shows 80 K time-resolved CL measurements of the shallow DAP at 3.27 eV for reference and annealed samples during low-energy electron beam irradiation ($E_b=10$ keV, $I_b=20$ nA, $44\times35\ \mu m^2$).

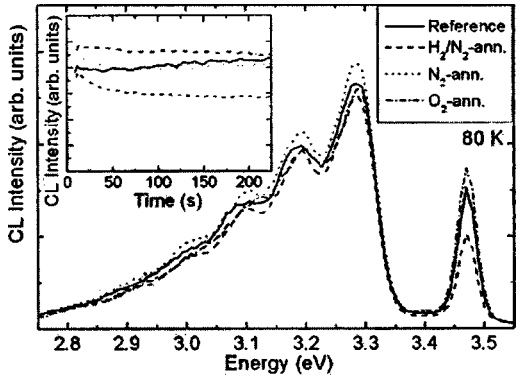

FIG. 2. 80 K CL spectra of Si-doped n-type GaN after post-growth annealing in controlled gaseous atmospheres under identical experimental conditions as in Fig. 1. The inset shows 80 K time-resolved CL measurements of the shallow DAP at 3.27 eV for reference and annealed samples during low-energy electron beam irradiation ($E_b=10$ keV, $I_b=20$ nA, $44\times35\ \mu m^2$).

significant when the magnesium concentration exceeds a value of $N_A \geq 2\times10^{19}\ cm^{-3}$.[1] Earlier photoluminescence results[27] indicated that strong Mg doping of GaN leads to the formation of three deep donor levels in addition to the shallow Mg acceptor, giving rise to a compensation mechanism that is directly related to the incorporation of Mg. In the following, experimental results for both moderately and heavily Mg-doped GaN are presented.

Moderately Mg-doped GaN

The luminescent emission of moderately Mg-doped GaN is dominated by a shallow donor-acceptor pair (DAP) emission at an energy of 3.25–3.28 eV (Refs. 28–30) at low temperatures (Fig. 1). Initially, this DAP consists of a neutral donor and a neutral acceptor, which both become ionized after the recombination process. The chemical origin of this emission line is contentious since a similar line is sometimes observed in nominally undoped or Si-doped GaN as well (Fig. 2).[30] However, it is generally believed that the number of possible candidates is limited both for the shallow acceptor and the shallow donor(s) involved in the DAP. For the shallow (delocalized) acceptor with an optical binding energy of around 225 meV,[31] Mg_{Ga},[3,32,33] C_N,[34] and intrinsic defect complexes, such as V_{Ga}-O,[35] have been proposed. Whereas possible candidates for the shallow donor (20–30 meV) are O,[36] Si,[37] Ga_i,[38] H,[39,40] and V_N-H.[16]

To determine the chemical origin of the 3.27-eV emission line, several samples from a Mg-doped (*p* type) and a Si-doped (*n*-type) GaN wafer were annealed in three different gaseous atmospheres [N_2, O_2, and $H_2(5\%)/N_2$] and subsequently investigated by CL spectroscopy. The 80 K CL spectra for three annealed and one untreated (reference) Mg-doped GaN samples are shown in Fig. 1. The differences in intensity are exclusively due to the annealing treatment since the electron beam power during CL was so low (10 keV, 0.25 nA) that electron irradiation effects can be neglected. The intensity of the dominant 3.27 eV DAP emission line in the reference sample strongly decreased after annealing in O_2 or N_2, but slightly increased after annealing in a H_2/N_2 atmosphere. The impact of electron irradiation on the 3.27 eV emission line was investigated by monitoring its CL intensity during constant electron beam irradiation with a higher beam current (20 nA) as a function of time (inset, Fig. 1). While the 3.27 eV DAP emission of the Mg-doped GaN annealed in O_2 and N_2 was not sensitive to the beam, in the reference and the H_2/N_2-annealed sample it decreased by an order of magnitude during electron beam irradiation. This quenching of the 3.27 eV emission cannot be explained by charging of the Mg acceptors as proposed by Chernyak *et al.*[14] since at room temperature the (e,Mg) emission was found to increase under identical conditions. The strong decrease of the 3.27 eV emission in the latter two samples was fitted[41] by a first order exponential decay function, expressed as

$$I_{CL}(t) = I_0 + I_1 * \exp(-t/\tau), \tag{5}$$

where $I_0=0.146\pm0.001$, $I_1=1.02\pm0.04$, and $\tau_{ref}=44.4\pm1.0$ s for the reference sample and $\tau_{H_2/N_2}=37.9\pm1.0$ s for the H_2/N_2-annealed sample. We will discuss the meaning of τ later. This exponential decrease of the intensity of the 3.27 eV emission during electron irradiation indicates that one or both partners of the original DAP are not available for this recombination process anymore. This effect was found to be permanent, i.e., after beam blanking for 1 h no further changes in the CL intensity were observed. In the electron irradiation experiments carried out in this work, no evidence for measurable Knotek-Feibelman effect[24] could be found. The surface roughness after electron beam irradiation was monitored by atomic force microscopy (AFM) and yielded two results. While no surface mass loss could be detected, a beam-induced accumulation of hydrocarbons[42] was observed, which were easily removed by O_2/Ar plasma cleaning[43] and did not affect the CL signal at all.

As shown in Fig. 2, a DAP emission line of similar energy 3.25–3.28 eV is sometimes found in nominally undoped or

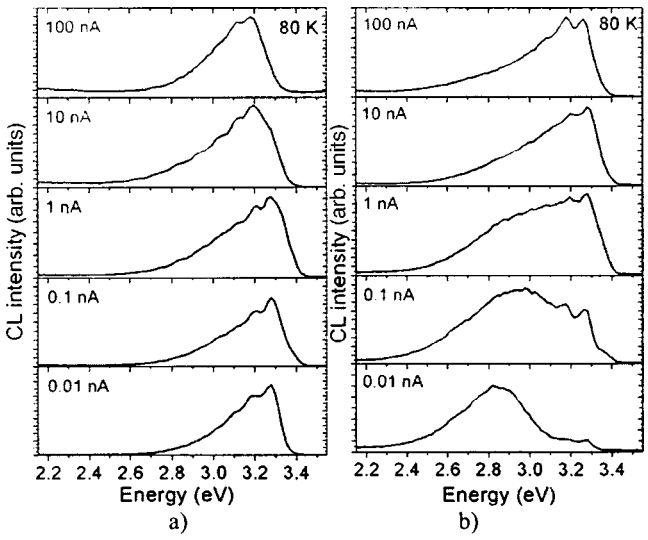

FIG. 3. Excitation density-resolved CL spectra of (a) (uncompensated) Mg-doped *p*-type GaN and (b) highly compensated Mg-doped GaN at 80 K for different electron beam excitation densities (E_b=10 keV, I_b=0.01...100 nA; probing area: 18×14 μm^2).

Si-doped (*n*-type) GaN epilayers as well. Therefore, we performed the annealing and electron irradiation experiments under identical conditions as in Fig. 1 for Si-doped GaN (Fig. 2). Annealing in both N_2, O_2 and $H_2(5\%)/N_2$ did not affect the intensity of the 3.27 eV DAP emission line at all. Moreover, the effect of electron irradiation during CL was essentially negligible (Fig. 2, inset), which is a further indication that no beam-induced defects are generated under these conditions. Based on these observations, we conclude that the chemical origin of at least one partner of the DAP emission in Si-doped GaN is different from the DAP in Mg-doped (*p*-type) GaN.

In order to analyze the observed sensitivity of the 3.27 eV DAP emission line in Mg-doped GaN to electron irradiation, both moderately and heavily Mg-doped (compensated) GaN samples were examined by excitation power density-resolved CL (Fig. 3). In this section, only the results for the moderately Mg-doped samples are discussed. While under low beam current conditions (10 pA) the 3.27 eV DAP dominates the emission spectrum, at high excitation density the 3.27 eV emission is quenched and a slightly deeper emission line centered at 3.2 eV emerges. Unlike in photoluminescence, it is not possible to attribute this result to the excitation density dependence alone, since electron irradiation-induced effects (e.g., dissociation of defect complexes) during CL have to be taken into account as well. Consequently, the time dependence of the emission lines in moderately Mg-doped GaN was monitored during continuous electron beam exposure to elucidate what mechanisms cause the CL spectrum to change with higher electron beam dose. As can be seen in Fig. 4, at a beam energy of 2.5 keV [which corresponds to a primary electron penetration depth of ~50 nm (Ref. 44)] and a current of I_b=0.14 nA, three effects were observed. First, the intensity of the 3.27 eV DAP decreased significantly with irradiation time; second, a deeper emission band centered at around 3.05 eV emerged; and

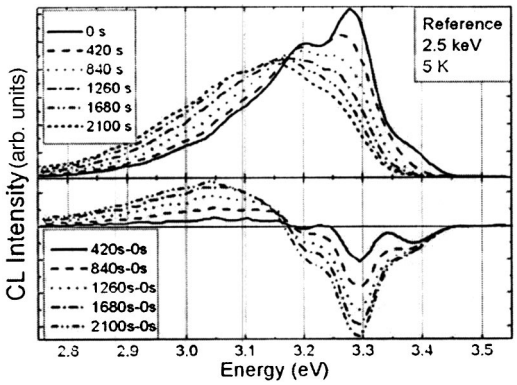

FIG. 4. Upper part: 5-K CL spectra of uncompensated Mg-doped *p*-type GaN taken repeatedly during electron beam irradiation (E_b=2.5 keV, I_b=0.14 nA; probing area: 18×14 μm^2). Time t=0 marks the end of the first CL spectrum. Lower part: Successive changes of the CL spectra, expressed as the difference between the first spectrum and each of the following spectra.

third, the weak emission line, centered at approximately 3.37 eV, and tentatively assigned to excitons deeply bound to centers located in structurally disturbed regions of GaN,[45] was completely quenched as a result of the electron exposure. These effects are illustrated in the lower part of Fig. 4, where the differences of the first (original) and each of the following spectra are illustrated. A similar result is shown in Fig. 5, where electron irradiation was carried out with a higher electron dose [E_b=20 keV and I_b=0.30 nA, the corresponding electron penetration depth is ~1.5 μm (Ref. 44)]. However, under these conditions the deeper emission line is centered at around 3.13 eV, roughly 80 meV higher than the peak under lower dose conditions. These experiments were also undertaken for a range of electron beam powers from E_b=2.5 keV and I_b=0.14 nA to E_b=30 keV and I_b=0.36 nA (not shown here). A gradual blueshift of the deeper emission line was observed, which saturated at 3.14 eV. This behavior is characteristic for a DAP transition and represents a confirmation of other recent results.[5] The origin of this deeper DAP will be discussed later.

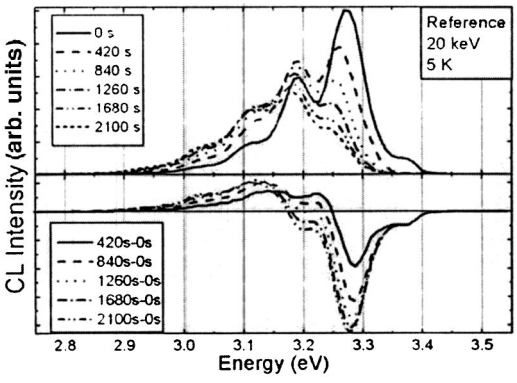

FIG. 5. Upper part: 5-K CL spectra of uncompensated Mg-doped *p*-type GaN taken repeatedly during electron beam irradiation (E_b=20 keV, I_b=0.30 nA; probing area: 18×14 μm^2). Lower part: Successive changes of the CL spectra, expressed as the difference between the first spectrum and each of the following spectra.

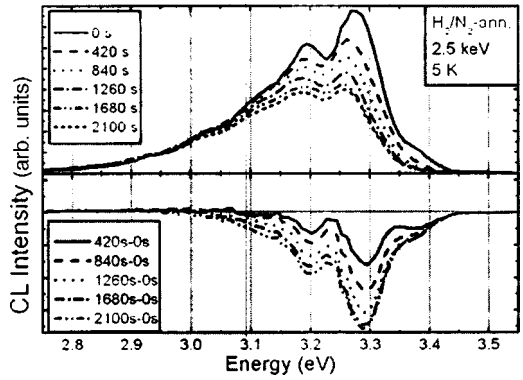

FIG. 6. Upper part: 5 K CL spectra of uncompensated Mg-doped *p*-type GaN (thermally annealed in a H_2/N_2 atmosphere) taken repeatedly during electron beam irradiation ($E_b=2.5$ keV, $I_b=0.14$ nA, probing area: $18\times14\ \mu m^2$). Lower part: Successive changes of the CL spectra, expressed as the difference between the first spectrum and each of the following spectra.

Similar experiments were carried out for the moderately Mg-doped (*p*-type) GaN annealed in H_2/N_2-atmosphere (Figs. 6 and 7). For the spectra taken during electron exposure at a beam energy of 2.5 keV (Fig. 6), the 3.27 eV DAP and the 3.37 eV emission line decreased in the same way as in the reference sample (Fig. 4) but the deeper DAP between 3.05 and 3.14 eV was not observed. However, at a higher beam energy of 20 keV [electron penetration depth $\sim1.5\ \mu$m (Ref. 44)] this emission line appeared (Fig. 7), indicating a similar behavior of the H_2/N_2-annealed and the untreated GaN:Mg at this electron penetration depth.

The results obtained from the CL measurements repeated during constant electron beam exposure were evaluated by comparing the integrated loss in CL intensity due to the quenching of the 3.27 eV DAP and the weak 3.37 eV emission line with the integrated gain in CL intensity due to the emerging deeper DAP at an energy of 3.05–3.14 eV (Fig. 8). For the reference sample, it can be seen in Fig. 8 that the integrated loss in CL intensity is counterbalanced by the integrated gain (ratio ≈1). This indicates (i) that the low-energy electron irradiation is not introducing additional (nonradiative) defects, in agreement with the aforementioned calculations and (ii) that the destruction of the 3.27 eV (and the weak 3.37 eV) recombination pathway is correlated with the opening of the deeper DAP transition pathway. Furthermore, a ratio close to 1 indicates a nearly constant radiative recombination efficiency (or internal quantum efficiency) η, which is defined as the ratio of the radiative recombination rate R_{rr} to the total recombination rate R,[46]

$$\eta=R_{rr}/R=\tau/\tau_{rr}=1/(1+\tau_{rr}/\tau_{nr}), \tag{6}$$

where τ is the carrier lifetime and τ_{rr} and τ_{nr} are the radiative and nonradiative recombination lifetimes, respectively. Since $\tau=(N\sigma V_{th})^{-1}$, η can be expressed as

$$\eta=1/(1+N_{nr}\sigma_{nr}/N_{rr}\sigma_{rr}), \tag{7}$$

where N_{rr} and N_{nr} are the densities of the radiative and nonradiative recombination centers, respectively, V_{th} is the carrier thermal velocity and σ_{rr} and σ_{nr} are the radiative and nonradiative capture cross sections, respectively. In general, both τ_{rr} and τ_{nr} result from several radiative and nonradiative recombination processes (i.e., $\tau_{rr}^{-1}=\Sigma_i\tau_{rri}^{-1}$). In the present case, the concentration of nonradiative recombination centers is not changing noticeably during electron beam irradiation. Therefore, a ratio close to 1 for the reference sample (Fig. 8) suggests similar capture cross sections for the radiative emission lines at 3.27 and 3.14 eV, respectively.

The results are different for the Mg-doped GaN annealed in a H_2/N_2 atmosphere, which strongly depend on the penetration depth of the electrons and thus on the depth where the CL signal is generated. The respective ratio is smaller than 1 for low beam energies and close to 1 for larger energies. The penetration depth of the primary electrons of ~50 nm at $E_b=2.5$ keV is much smaller than the average thickness of the sub-surface layer that is affected by gas-solid

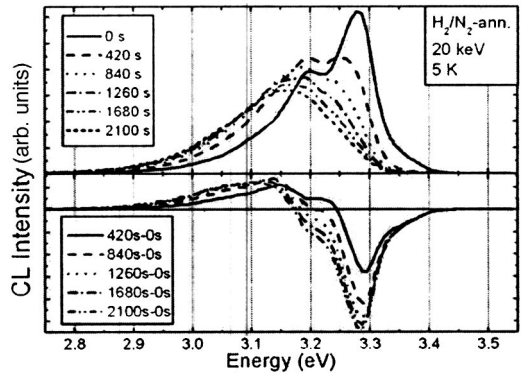

FIG. 7. Upper part: 5 K CL spectra of uncompensated Mg-doped *p*-type GaN (thermally annealed in a H_2/N_2 atmosphere) taken repeatedly during electron beam irradiation ($E_b=20$ keV, $I_b=0.30$ nA, probing area: $18\times14\ \mu m^2$). Lower part: Successive changes of the CL spectra, expressed as the difference between the first spectrum and each of the following spectra.

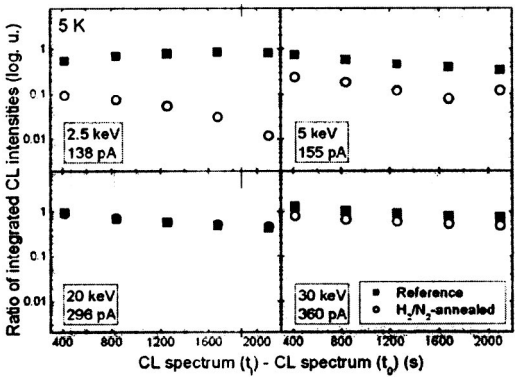

FIG. 8. Evaluation of the electron beam irradiation induced gain and loss in CL emission intensity of the uncompensated reference and the H_2/N_2-annealed Mg-doped *p*-type GaN. From the difference spectra (e.g., lower part in Figs. 4–7) both the gain and the loss in CL intensity was integrated and their ratio was calculated. The ratios are illustrated for 4 selected electron beam energies and respective beam currents (2.5, 5, 20, and 30 keV and 0.14, 0.16, 0.30, and 0.36 nA, respectively).

interactions during the annealing processes that was estimated to thickness of 200–400 nm based on depth-resolved[47] CL measurements. Therefore, it is reasonable to assume that the annealing in a H_2/N_2 atmosphere prevents the formation or the activation of the 3.14 eV DAP recombination channel, which might indicate a decrease in the concentration of other compensating defects during H_2/N_2 anneal. Before the results for the moderately Mg-doped GaN are discussed in more detail and a model for the various processes during electron irradiation is described, the results for heavily Mg-doped (compensated) GaN are presented.

Heavily Mg-doped (compensated) GaN

In the high Mg-doping regime ($N_A \geqslant 2\times10^{19}$ cm^{-3})[1] a blue band centered at 2.8–3.0 eV is generated [Fig. 3(b)]. The origin of this band is still not completely understood and recent experimental results indicate that it might consist of more than one emission line.[27,48,49] Most researchers agree that the blue band is caused by a transition between a deep localized donor and an acceptor (likely the Mg-related acceptor state).[1,27,33,50,51] Kaufmann *et al.*[1] explained the doping level dependence of the observation of the blue band by a model involving self-compensation mechanisms. Both theoretical[1,52] and experimental[1,27,53] studies concluded that the incorporation of high Mg concentrations is accompanied by a formation of additional deep donors. The formation energy of these donors rapidly decreases as the Fermi level approaches the valence band.[16] Likely candidates for deep donors in heavily Mg-doped GaN are V_N,[16] Mg-V_N,[1,54] V_N-H,[39,40] Mg_i,[49] and Mg_N.[49]

The heavily Mg-doped (compensated) GaN samples were investigated by excitation density-resolved CL spectroscopy [Fig. 3(b)] as well as temperature-resolved LEEBI experiments (Fig. 9). From Fig. 3(b) two conclusions can be drawn. First, apart from a slight shift to higher energies, the blue band saturates in intensity at higher excitation densities resulting in a domination of the shallow DAP emission at 3.27 eV for an electron beam current of 100 nA (which is well beyond PL excitation densities). This is explained by a model introduced by Eckey *et al.*:[27] At low excitation densities a small number of the initially ionized donors and acceptors are neutralized. The electrons relax to the deeper donor levels and subsequently recombine with the Mg acceptors. At higher excitation densities, the shallower donor levels will be neutralized as well and the recombination takes place between the shallow donors and the Mg acceptors resulting in the strong blueshift observed in Fig. 3. Second, potential fluctuations due to randomly distributed impurities,[55] which are sometimes observed in highly compensated Mg-doped GaN,[51] play a minor role in the investigated samples. In the potential fluctuation model, all emission lines are expected to blueshift with increasing excitation density since the potential fluctuations are screened by a larger number of generated electrons and holes. However, the 3.27 eV emission line, already present at the lowest excitation density, remains in the same energetic position for all excitation densities while the position of the blue band is shifted.

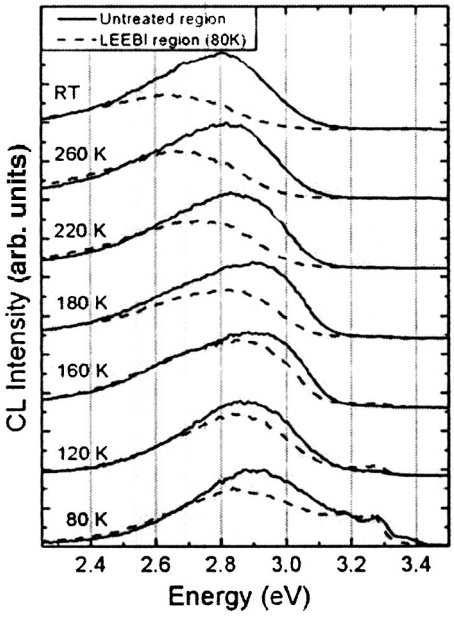

FIG. 9. Normalized CL spectra illustrated for selected temperatures of an "as-received" (solid line) and a LEEBI region (dashed line), respectively, in highly compensated Mg-doped GaN ($E_b = 10$ keV, $I_b = 0.3$ nA, scan area: 24×30 μm^2). The LEEBI region was generated at 80 K using an electron beam power of 100 μW ($E_b = 10$ keV, $I_b = 10$ nA, 180 s).

In order to investigate the impact of electron irradiation on heavily Mg-doped (compensated) GaN, temperature-dependent CL spectra were recorded both in untreated and electron irradiated (10 keV, 10 nA, 180 s) regions of the sample (Fig. 9). From these experiments it becomes evident that the blue emission band consists of at least two emission lines of different origin since the peak of higher energy (~2.95 eV at 80 K) is sensitive to electron exposure while that at lower energy (~2.86 eV at 80 K) is not affected. The thermal behavior of these emission lines indicates that the electron irradiation-sensitive emission line is dominant at 300 K but less efficient at low temperature. Furthermore, it is important to note that the electron irradiation affects both moderately and heavily Mg-doped GaN samples but not Si-doped GaN.

V. DISCUSSION

In the light of the presented results, we now discuss the properties and chemical origins of the shallow DAP at 3.27 eV, the deeper DAP at 3.14 eV and the overlapping emission lines of the blue emission band centered between 2.8 and 3.0 eV. Starting with the 3.27 eV DAP, we first concentrate on possible candidates for the shallow acceptor level. The unequivocal assignment of the respective recombination centers to specific defects or impurities is made more difficult by overlapping emission bands[49] as well as the presence of strong phonon replica. Although it has been suggested that C_N (Refs. 34 and 49) or intrinsic acceptors (e.g., V_{Ga}-O) (Ref. 35) are involved in the 3.27 eV emission, the overwhelming majority of papers favours a model with Mg_{Ga} as

the acceptor level. For example, Akasaki *et al.*[32] did not observe the 3.27 eV DAP in nominally undoped GaN, but the band appeared after doping with Mg and they consequently assigned the acceptor level to Mg. Yang *et al.*[56] observed the appearance of the 3.27 eV band after Mg in-diffusion. Based on magnetic resonance studies, Glaser *et al.*[33] identified the shallow effective-mass acceptor level in Mg-doped GaN with Mg. This is in agreement with theoretical calculations that predict a high formation energy for acceptor-like defects in Mg-doped *p*-type GaN.[16,57] The excitation density-resolved CL results presented above support this assignment since at high excitation density only the 3.27 eV emission prevails in heavily Mg-doped GaN. This indicates a high concentration of the centers responsible for this emission suggesting Mg to be the shallow acceptor level. In addition, Mg is a common contaminant in GaN. Recent secondary ion mass spectrometry (SIMS) data on hydride vapor phase epitaxy (HVPE) GaN have confirmed this situation, showing that Mg is often present in HVPE GaN with concentrations in the 10^{16} cm^{-3} range.[58]

In the following, Mg is assumed to be responsible for the shallow acceptor state and the origin of the shallow donor (20–30 meV) is discussed now. Judging from the theoretical considerations above, it is highly unlikely that Mg_{Ga} is affected by the electron irradiation, which leads to the conclusion that the shallow donor must be sensitive to electron exposure. Based on the presented annealing and electron irradiation results, some of the possible candidates for the shallow donor [O,[36] Si,[37] Ga,[38] H,[39,40] and V_N-H (Ref. 16)] can be ruled out as the donor in the 3.27 eV DAP emission. Si_{Ga}, a shallow donor with a binding energy of 29 meV,[37] is believed to have a $E_{threshold}$ for the displacement of the Si atom of the same order of magnitude as that for Ga and therefore should not be affected by the electron beam. Similar considerations apply to O_N. Additionally, annealing in O_2 atmosphere strongly decreased the 3.27 eV emission line. The Ga-interstitial was calculated[59] to have a higher formation energy than V_N or H-related complexes in *p*-type GaN and is predicted not to be present in significant amounts. Recently, H (Refs. 19, 39, and 40) and V_N-H (Ref. 16) were proposed to be the shallow donor level in MOVPE-grown Mg-doped GaN. The model involving a shallow H donor was originally introduced by Shahedipour and Wessels[39] who observed quenching of the 3.27 eV emission line in Mg-doped GaN after annealing in a N_2 atmosphere. Other recent results by our group and Koide *et al.*[40] were also interpreted by means of this model. Indeed, the decrease in the 3.27 eV emission line at low temperature due to thermal annealing[39] or low-energy electron beam irradiation (LEEBI) (Ref. 5) and the corresponding decrease in resistivity[39,6] were elegantly explained by the dissociation of hydrogen-related defect complexes (Mg-H) and the subsequent activation of the Mg acceptors.[39,40] However, this model clearly contradicts theoretical calculations by Neugebauer and van de Walle.[17,57] Isolated H exhibits a negative U behavior, meaning that the neutral state (H^0) is never stable in thermal equilibrium for all positions of the Fermi-level. Although it can be argued that this neutral state exists upon photo- or electron beam excitation,[60] a negative U behavior is characteristic for localized (deep) and not for effective-mass-like (shallow) centers. Consequently, isolated H is expected to be a deep donor. In the light of these calculations we tend to prefer the model by van de Walle,[16] who predicted that the V_N-H complex is the shallow (double) donor responsible for the 3.27 eV emission in Mg-doped GaN and present in sufficient amounts under *p*-type conditions. Hence, both the electron irradiation and the annealing experiments can be explained in terms of this model.

Comparing the intensity of the 3.27 eV emission following the annealing in H_2/N_2 and N_2 atmosphere, it is evident that H is involved in this emission line. Due to gas-solid interactions during the annealing process, some of the V_N (that are inevitably present to some extent in Mg-doped (*p*-type) GaN) might complex with H according to the equilibrium

$$H + V_N \leftrightarrow (V_N\text{-}H), \tag{8}$$

and account for a slightly higher intensity of the 3.27 eV DAP emission (Fig. 1). As a result of electron irradiation and recombination energies, the V_N-H complexes are dissociated and the 3.27 eV emission line is quenched. This is supported by a smaller time constant τ for the H_2/N_2-annealed sample ($\tau_{H2/N2} = 37.9 \pm 1.0$ s) where a larger amount of V_N-H complexes is expected than in the reference sample ($\tau_{ref} = 44.4 \pm 1.0$ s). Although no conductivity measurements were performed on the irradiated samples,[61] it is expected that the LEEBI-induced decrease of the 3.27 eV emission line is correlated with a decrease in resistivity, as shown by several other groups[6,39,62] Nevertheless, it should be noted that the presented model mainly applies to MOVPE-grown Mg-doped GaN, where H is present in large quantities.[6,15] The emission lines at similar energies, which have been observed in molecular-beam-epitaxy-grown Mg-doped GaN or Si-doped (*n*-type) GaN, do not necessarily originate from centers with the same chemical origin.

As can be seen from Figs. 4–7, the electron beam-induced quenching of the 3.27 eV emission is strongly correlated with the emergence of the 3.14 eV DAP emission. We propose the following model to account for these observations. The electron beam-induced dissociation of the V_N-H complexes generates isolated V_N and highly mobile H, which presumably forms complexes with other H or attaches to extended crystal defects.[57] Isolated V_N were found to have a binding energy of 64 ± 10 meV (according to temperature-dependent Hall measurement) or 180 meV [according to deep-level transient spectroscopy (DLTS)].[63] Therefore, V_N is a possible candidate to be the donor level in the 3.14 eV DAP. The time-dependent CL measurements of the samples annealed in a H_2/N_2 atmosphere (Fig. 6) might then be explained by a reduced concentration of nitrogen vacancies by complex formation following relation (8). Another explanation might be the removal of a specific fraction of V_N due to the excess amount of H during the annealing process since it is energetically more favourable to passivate the Mg acceptors by H than by intrinsic defects such as V_N.[17,52] The observed electron irradiation-induced quenching of the weak emission line centered at 3.37 eV, which was tentatively as-

signed to deeply bound excitons,[45] is explained by trapping of injected electrons at the respective structural defects.

The blue band between 2.8 and 3.0 eV was shown to consist of at least two different emission lines (Fig. 9). This agrees with recent intensity-resolved photoluminescence results,[48,49] where up to 4 overlapping emission bands at 2.9, 2.81, 2.7, and 2.56 eV were observed.[48] Eckey *et al.*[27] identified different deep donor levels at 240 ± 30 and 350 ± 30 meV below the conduction band, respectively, while Hacke *et al.*[53] found donor levels at 265 ± 15 and ~400 meV below the conduction band. Based on our CL results, we identified two donor levels at 350 ± 30 meV and 440 ± 40 meV. The level at 350 ± 30 meV is in excellent agreement with the findings by Eckey *et al.*[27] With respect to the low-energy electron irradiation results (Fig. 9), we postulate that this center is H-related since it exhibits a high sensitivity towards electron exposure. According to magnetic resonance studies, the acceptor was identified with the shallow Mg level,[33] which is not affected by the electron beam. The level at 440 ± 40 meV is not affected by electron exposure and might be explained Mg-V_N complexes, which are predicted to be the deep donors responsible for the self-compensation in heavily Mg-doped GaN and the generaton of the observed blue band.[1] However, we cannot rule out that the respective broad emission line at $\sim$2.86 eV consists of more than one peak, as found by intensity-resolved PL.[48] For higher excitation power densities [$>$0.1 nA, Fig. 3(b)], the 3.27 eV emission line starts to dominate the emission spectrum. Hence, a shallower donor level at around 250 meV was not observed. We attribute the discrepancy in relation to the PL results[27] to the more intense electron-excited electron-hole pair generation rates in the CL.[46] A complete band diagram of the dominant radiative recombination in moderately and heavily Mg-doped GaN discussed in this work is illustrated in Fig. 10.

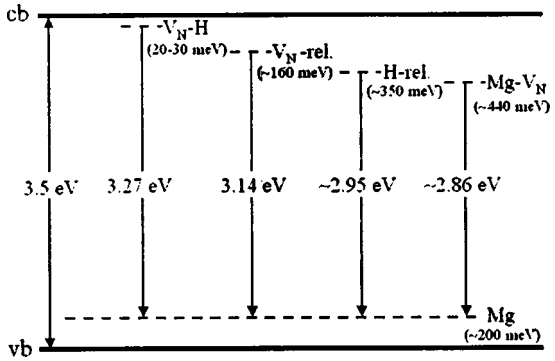

FIG. 10. Low temperature band diagram showing the dominant radiative recombination mechanisms in moderately and heavily Mg-doped GaN.

VI. SUMMARY

A combination of post-growth annealing processes and low-energy electron beam irradiation techniques during CL was used to determine the chemical origin of the main optical emission lines in moderately and heavily Mg-doped GaN. The 3.27 eV DAP emission line was found to be strongly affected by low-energy electron beam irradiation. It is suggested that the acceptor in the 3.27 eV DAP emission is Mg and that the donor (20–30 meV) is hydrogen related, presumably a V_N-H complex. This complex dissociates during electron irradiation or thermal annealing in N_2 or O_2 atmosphere. Upon electron irradiation, a deeper emission line (3.14 eV) emerged, which was assigned to a DAP consisting of the same Mg acceptor level and a deeper donor (100–200 meV) with a similar capture cross section as the donor in the 3.27 eV emission. The blue band (2.8–3.0 eV) was found to consist of at least two different deep donor levels at 350 ± 30 and 440 ± 40 meV. The emission line relating to the donor at 350 ± 30 meV was reduced during electron irradiation and attributed to a H-related defect. Finally, a comparison of the UV DAP emission lines in Mg-doped (*p*-type) and Si-doped (*n*-type) GaN indicated that the respective recombination centers are of different chemical origins.[63]

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