Origin of defect-related photoluminescence bands in doped and nominally undoped GaN

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The efficient room-temperature photoluminescence bands of wurtzite GaN, which are peaked in the red (1.8 eV), the yellow (2.2 eV), and the blue (2.8 eV) spectral range, have been studied as a function of doping (species and concentration) and excitation power density (PD). It is shown that the yellow and the blue band are induced by Si and Mg doping, respectively, while codoping with Si *and* Mg generates the red band. At high-doping levels, the yellow and the blue band reveal strong peak shifts to higher energy with increasing PD providing very strong evidence for their distant donor-acceptor (DA) pair recombination character. The deep centers involved in DA recombination having electrical activity opposite to that of the shallow level of the dopant, are suggested to arise from self-compensation and to be vacancy-dopant associates. Self-compensation is found to be weak in the case of Si doping, but significant for Mg doping. A recombination model is presented, which accounts for the essential properties of all three bands in deliberately doped GaN. These results also suggest that the yellow and the blue bands in nominally undoped GaN arise from distant DA pairs involving *residual* Si and Mg impurities, respectively, as well as their respective vacancy associates. [S0163-1829(99)06707-7]

I. INTRODUCTION

During the recent years, GaN and the related alloys $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$ have become the most useful semiconductor material system for applications in short wavelength optoelectronic devices, in particular light emitting diodes[1] (LED's) and laser diodes.[2] Green and blue GaN based LED's are commercially available and blue/violet laser diodes are currently moving out of the laboratory. This dramatic technological progress sometimes obscures the fact that certain basic material properties even of simple GaN epitaxial layers are still poorly understood. In particular, this concerns three commonly observed photoluminescence (PL) bands peaked in the red (1.8 eV), the yellow (2.2 eV), and the blue (2.8 eV) spectral range, which are efficient already at room temperature (RT). Two of these bands, the yellow and the blue one, are often found in nominally undoped material.[3,4] The impurities and deep defects giving rise to the three bands as well as the recombination type(s) are not yet well established. For instance, the yellow band has been ascribed to a shallow donor-deep acceptor transition,[5] a shallow donor-deep donor transition,[3] a deep donor-shallow acceptor transition,[6] and to extended crystalline defects.[7] So far, a consensus has not been reached. However, there is relatively early evidence that the yellow band is related to Si impurities[8] and that the blue one can be induced by high Mg doping levels.[9,10] Nothing is known about the origin of the red band, except that it can appear in Mg-doped samples.[10]

In this paper, it is shown that Si donor and Mg acceptor doping of GaN generates the yellow and the blue band, respectively, while the red band is induced by codoping with Mg *and* Si. Clear evidence for the distant donor-acceptor (DA) pair character of both the blue and the yellow band is obtained from their peak shift with excitation power density. It is suggested that these two bands are ''self-activated'' in the same sense as the famous blue emission in donor doped ZnS,[11] where a fraction of the dopant atoms is converted into deep centers of opposite electrical type by association with vacancies (self-compensation). The degree of self-compensation for GaN is found to be small in the case of Si doping, but significant for Mg doping. A simple recombination model is presented, which, apart from the shallow Si and Mg levels, contains only two deep levels, a Si related acceptor level A_d at $E_v+1.08$ eV and a Mg-related donor level D_d at $E_c-0.28$ eV. This model accounts for the properties of the blue and the yellow band in a natural way, and in particular correctly *predicts* the peak position of the red band. In analogy to ZnS it is argued that the defects A_d and D_d corresponding to the two deep levels most likely correspond to dopant-vacancy associates, namely $V_{Ga}Si$ and V_NMg, respectively.

II. EXPERIMENTAL DETAILS

All GaN layers studied in this work were grown by low-pressure metal-organic chemical-vapor deposition (MOCVD) in a horizontal flow reactor. The 0.8–2.5-μm-thick films of wurtzite structure were deposited on 2-in. *c*-plane sapphire on top of a 30-nm-thin GaN nucleation layer. They are either undoped, *n*-type Si doped, *p*-type Mg doped, or codoped with Si *and* Mg. The doping concentrations were determined by secondary ion mass spectroscopy using ion implanted standards. The Si and Mg concentrations are in the ranges 4×10^{17} to $2\times10^{19}\,cm^{-3}$ and $(1-7)\times10^{19}\,cm^{-3}$, respectively. After thermal anneal the Mg-doped layers have RT hole densities in the lower $10^{17}\,cm^{-3}$ range with mobilities near 10 $cm^2/V\,s$. In the codoped films, Mg ranges from 7×10^{17} to $3\times10^{19}\,cm^{-3}$ and Si from mid 10^{17} to $2\times10^{19}\,cm^{-3}$. The error in the doping concentrations is less than 20%. The PL setup used to study the luminescent properties of the samples comprises a He-Cd laser (325 nm, 45 mW) for excitation, a 0.5 m monochromator, a LN_2

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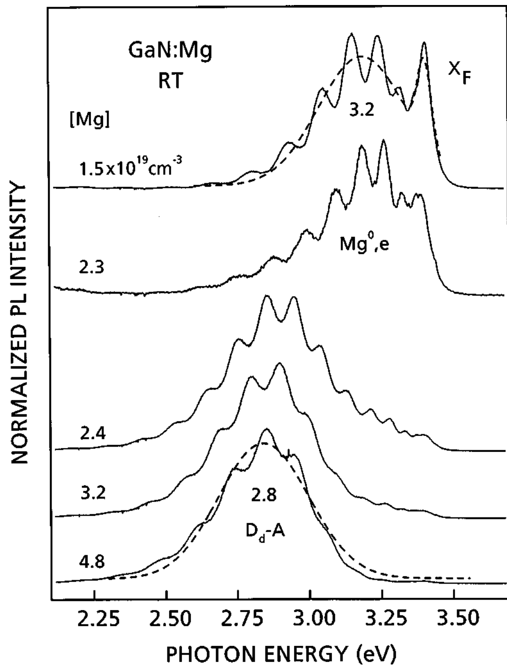

FIG. 1. PL spectra normalized to the maximum peak amplitude for different GaN:Mg layers under high PD conditions (1000 W/cm^2). The numbers attached to the spectra on the left give the Mg content in units of $10^{19}\,\mathrm{cm}^{-3}$.

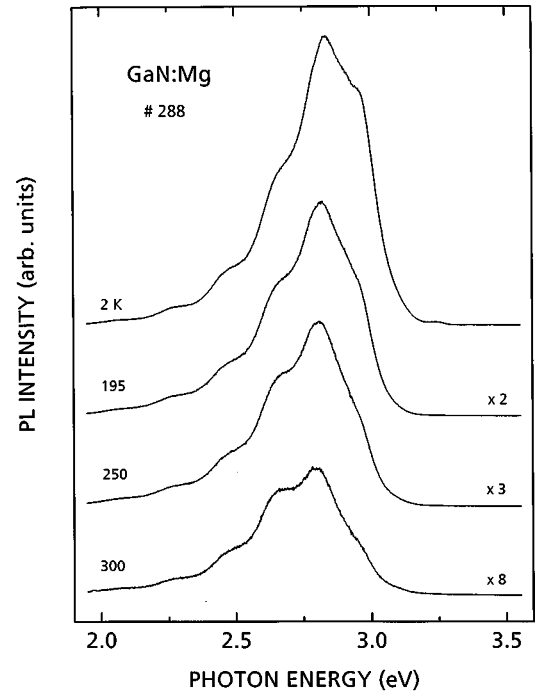

FIG. 2. PL spectra at various temperatures under moderate PD excitation conditions as observed from a GaN:Mg sample with a Mg concentration of $5.4\times10^{19}\,\mathrm{cm}^{-3}$.

cooled silicon charge coupled device detector array and a computer for measurement control and data acquisition. The setup allows reliable RT PL intensity comparisons between different samples as well as accurate measurements of changes in intensity with excitation power density (PD). This has been achieved by automating and standardizing the PD conditions (1000, 100, 10, 1, 0.1 W/cm^2) and correlating them with the detector exposure times (0.05, 0.5, 5, 50, 500 s) such that the total luminescence intensity for a *fixed number of exciting photons* is recorded in each measurement. Actually, a PL quantum efficiency (QE) is thus measured. Superimposed on all broad luminescence spectra shown in this article are oscillatory structures, which result from Fabry-Perot interferences within the GaN layers. Although these structures are sometimes perturbing to the eye, they indicate that both the surface and the interface morphology of the layers are of high quality. Using an appropriate curve fitting software one can reliably determine the essential parameters (peak position, half width) of broad bands in such cases.

III. EXPERIMENTAL RESULTS

Figure 1 displays normalized RT PL spectra, all measured under identical high PD (1000 W/cm^2) conditions, for a series of GaN:Mg films with doping levels between 1.5 and $4.8\times10^{19}\,\mathrm{cm}^{-3}$. The highest energy line most likely corresponds to the free exciton X_F. It is seen to disappear rapidly with increasing Mg content. On its low-energy side there is a broad band peaked near 3.2 eV provided the Mg content is below $2.4\times10^{19}\,\mathrm{cm}^{-3}$ under high PD conditions. This band at RT has been assigned to capture of free electrons at neutral Mg acceptors, (Mg^0,e),[12] but a minor contribution to its intensity from the corresponding shallow residual donor-Mg^0 transition cannot be excluded. A sudden change in the broad band spectra has been consistently observed for several doping series when the Mg concentration reaches a value of $\approx2.4\times10^{19}\,\mathrm{cm}^{-3}$ in the high PD case. The 3.2 eV emission is quenched and a broad blue band of approximate Gaussian shape (half width around 330 meV) dominates the spectrum. This band is peaked near 2.77 eV for the lowest PD (0.1 W/cm^2) but shifts up to 2.90 eV when the PD is increased by four orders of magnitude, see also Ref. 12. Simultaneously, its PL QE slightly decreases. For Mg concentrations in the lower $10^{19}\,\mathrm{cm}^{-3}$ range, the PL intensity is almost independent of the doping level. The GaN:Mg layers with Mg contents above $1\times10^{19}\,\mathrm{cm}^{-3}$ used for the present study never revealed a yellow band and rarely a broad red emission band with significant intensity.

The characteristics of the blue band are not significantly changed when the samples are cooled to low temperatures, as shown in Fig. 2 for a sample with a Mg content of $5.4\times10^{19}\,\mathrm{cm}^{-3}$. At 2 K the intensity is increased by about a factor of 10 and the half width is reduced by about 30 meV as compared to RT. The peak energy at 2 K and low excitation PD is about 2.85 eV.

Apart from the near band-edge emission at $\approx$3.41 eV, believed to be dominantly due to D^0,h recombination of free holes with neutral Si donors,[13] all Si-doped GaN layers studied, show a broad Gaussian-like band in the yellow centered near 2.2 eV with a half width of about 370 meV at RT, see Fig. 3. Its QE is seen to decrease with increasing PD. The exact peak position depends on the Si concentration and on PD. For Si concentrations below $5\times10^{18}\,\mathrm{cm}^{-3}$ the maximum peak shift when the PD is increased by four orders of magnitude does not exceed about 15 meV. For samples with Si in the range $(1-2)\times10^{19}\,\mathrm{cm}^{-3}$, see the inset in Fig. 3, the peak shifts are more pronounced, 32–35 meV. No peak shift is

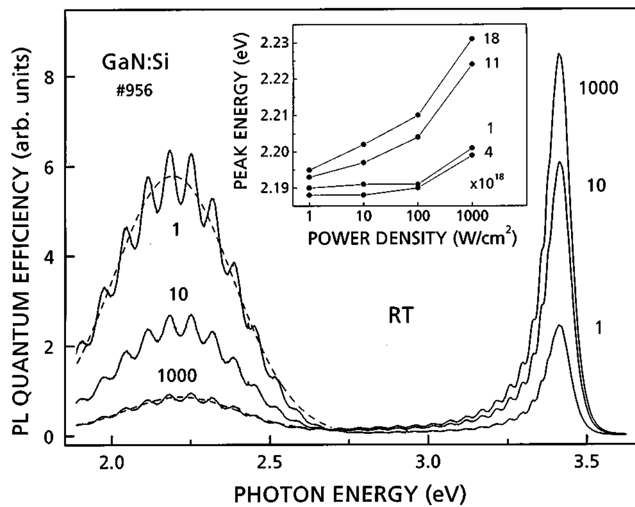

FIG. 3. PL spectra of a GaN:Si sample with a Si concentration of $1.1\times10^{19}\,\mathrm{cm}^{-3}$ for three PD levels in units of $\mathrm{W/cm}^2$. The inset shows the peak shift of the yellow band with increasing PD for four samples with Si contents between 1×10^{18} and $1.8\times10^{19}\,\mathrm{cm}^{-3}$.

observed for the near band-edge emission. For a fixed high PD the 2.2 eV band intensity is found to scale approximately linearly with the Si concentration from mid $10^{17}\,\mathrm{cm}^{-3}$ to the low $10^{19}\,\mathrm{cm}^{-3}$ range, see Fig. 4, in line with recent similar observations by another group.[14]

At high PD, GaN films codoped with Mg in the range $(1-3)\times10^{19}\,\mathrm{cm}^{-3}$ and Si in the range $8\times10^{17}-1\times10^{19}\,\mathrm{cm}^{-3}$ reveal a broad RT band peaked in the red near 1.77 eV (half width about 345 meV) in addition to the free exciton line X_F and the Mg related 3.2 eV band, see Fig. 5. For low PD, the latter two bands are seen to be strongly quenched and the red (*R*) together with the yellow (*Y*) band dominate the PL spectrum. A peak shift of the red band with PD could not be established. If present it might be masked because of overlap with the yellow band. Plotted in the inset of Fig. 5 is the PL QE of the red band at fixed PD versus the Si concentration in codoped layers. For an only weakly varying Mg concentration, $(1-3)\times10^{19}\,\mathrm{cm}^{-3}$, the red band QE is seen to increase in proportion to the Si concentration. However, the efficiency remains very small compared to that

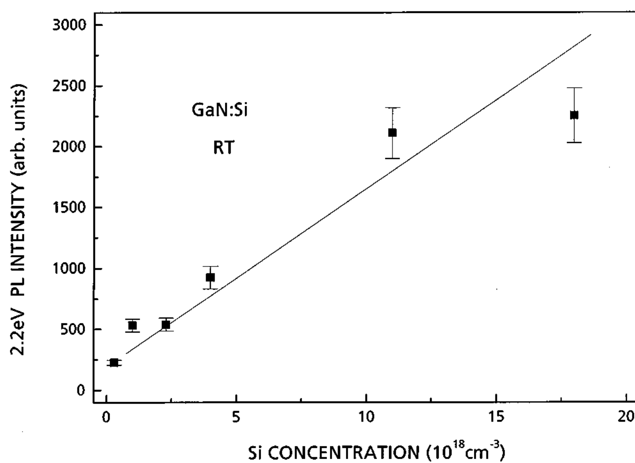

FIG. 4. Dependence of the yellow band PL intensity on Si doping concentration. The straight line is a linear fit to the data points.

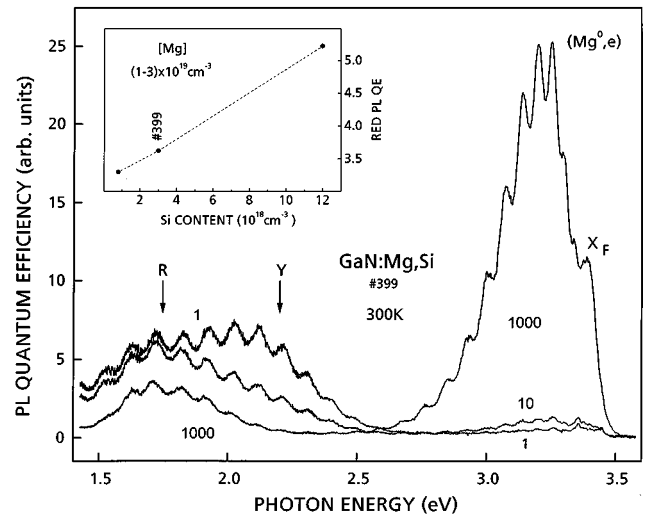

FIG. 5. PL spectra of a GaN layer codoped with Mg ($2\times10^{19}\,\mathrm{cm}^{-3}$) and Si ($3\times10^{18}\,\mathrm{cm}^{-3}$) for three PD's. Shown in the inset is the intensity of the red emission as a function of the Si content in three different layers with an almost constant Mg concentration.

of the blue or the yellow band in layers highly doped with Mg or Si. Codoped layers with Mg concentrations below $5\times10^{18}\,\mathrm{cm}^{-3}$ do not show the red band but reveal the yellow one, in particular if the Si content exceeds that of Mg.

As found before for the blue band, the characteristics of both the yellow and the red band reveal only marginal changes at low temperatures as compared to RT. This is demonstrated in Fig. 6 for the yellow band. At 2 K its peak occurs at 2.21 eV and has a half width of 315 meV for low

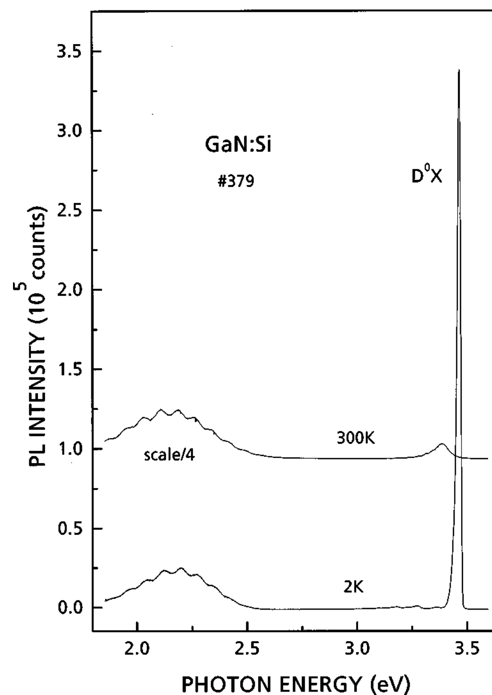

FIG. 6. RT and 2 K PL spectra of a GaN:Si sample measured under low-power density conditions. The Si concentration amounts to $4\times10^{18}\,\mathrm{cm}^{-3}$. The 300 K trace has been arbitrarily shifted vertically and blown up by a factor of 4.

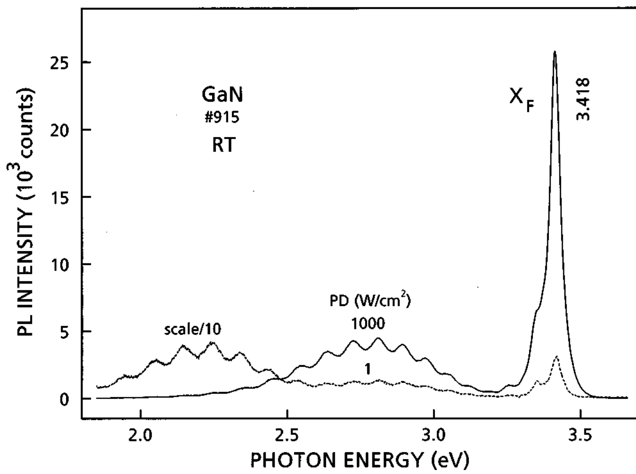

FIG. 7. PL spectra of an undoped GaN layer for high and low PD as indicated. In the latter case the spectrum is enlarged by a factor of 10, so that the absolute ordinate scale for this trace has to be reduced correspondingly.

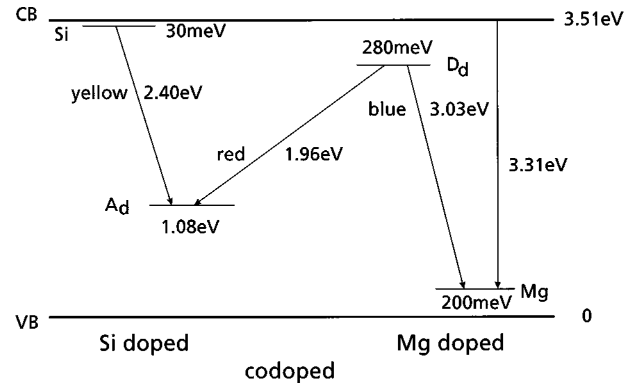

FIG. 8. DA recombination model at low temperature for the red, the yellow, and the blue band of GaN. The shallow level positions of Si and Mg are those currently accepted. The transition energies correspond to the ZP line energies of the deep bands as evaluated at the lowest PD. The deep level positions are inferred from these numbers and $E_g = 3.51$ eV at 2 K.

PD excitation. The intensity increase from RT to 2 K amounts to a factor of about 4. The peak of the red band at 2 K is at 1.81 eV and has a half width of 278 meV.

Figure 7 shows RT PL spectra of an undoped MOCVD GaN layer. For high PD, the free exciton line X_F at 3.418 eV dominates the spectrum.[15] At lower energies, there is a broad band of Gaussian shape peaked in the blue at 2.78 eV with a half width of about 420 meV. For low PD, (dotted trace) the dominating feature is a broad Gaussian band peaking in the yellow at 2.21 eV and having a half width of about 400 meV. For both bands a peak shift with PD is not detectable. A red emission around 1.77 eV has never been observed in such nominally undoped samples.

IV. DISCUSSION AND CONCLUSIONS

A. Origin of the deep PL bands

The results reported in the previous section leave virtually no doubt that the blue and the yellow emission in GaN is generated by Mg and Si doping, respectively. These two bands have very typical characteristics: Compared with the near band-gap emissions they are saturating at high PD. To a first approximation their shapes are Gaussian. Their half widths are not significantly reduced at low temperatures, less than 10% at 2 K as compared to RT. Their peak positions shift to higher energies when the temperature is reduced and the intensity increase at 2 K is moderate about a factor of 10 or less, compare Figs. 2 and 6. Their peak positions shift to higher energy with increasing PD and the PD shifts increase with increasing doping concentration, see Fig. 3 for the yellow band. The maximum peak shifts of the blue band are considerably larger, between $\approx$100 and 130 meV, for Mg contents in the lower $10^{19}\,\mathrm{cm}^{-3}$ range. Finally, the yellow band is known to have a multiexponential decay transient after pulse excitation.[16] Thus, the blue as well as the yellow band reveal the essential characteristics of *distant* DA pair recombination.[11,17] Therefore, both bands are assigned here to this type of recombination.

Since only one doping species Mg or Si is required to generate either the blue or the yellow band, the obvious question concerns the centers of opposite electrical activity in a DA pair model. These cannot be simply shallow *residual* impurities with electrical activity opposite to that of the dopant since the DA pairs expected in such a case would not be consistent with the deep character of the broad bands. Therefore, one is forced to assume that the dopant itself induces a compensating deep level in addition to the shallow one. Thus, one is facing a situation strikingly similar to that in high-gap II_B-VI compounds, in particular the well-documented cases of donor[11] and acceptor[18] doped ZnS. There it is well established that a shallow dopant also creates a deep center of opposite electrical type, leading to partial self-compensation. These deep centers have been firmly identified by electron-spin resonance as vacancy-dopant associates. It is suggested that for GaN corresponding self-compensation effects generate the deep centers D_d and A_d, which must be involved in the blue band of GaN:Mg and the yellow band of GaN:Si, respectively. The natural recombination path in a DA pair model is then a transition between the shallow dopant level and the compensating deep level. This is shown schematically in Fig. 8 for Si (left side) and Mg (right side) doping, respectively. The energetic positions of the deep levels D_d and A_d have been derived from the known positions of the shallow dopant levels, the zero phonon (ZP) energies of the yellow and the blue band at the lowest PD, and the equation describing distant DA pair recombination

$$h\nu = E_g - (E_D + E_A) + e^2/\varepsilon d,$$

where the symbols have their usual meaning. The last term represents the Coulomb attraction E_{COUL} of an ionized pair D^+A^- with an intrapair distance d. The ZP energies were derived as follows: Since the deep bands are structureless and in particular do not show a resolved ZP line there must be a moderate to strong electron phonon coupling of the electronic transition to vibrational modes. In such cases the energetic position of the ZP line can be estimated from the 2 K half width of the band, which is related to the second moment M_2.[19] Now the Franck-Condon shift d_{FC}, i.e., the separation between the peak of the broad band and its ZP line, can be calculated according to $d_{\mathrm{FC}} = M_2/\hbar\omega$, where $\hbar\omega$

is the effective phonon frequency. Assuming dominant coupling to LO phonons, $\hbar\omega = 91\,\mathrm{meV}$, gives d_{FC} values of about 180, 190, and 153 meV for the blue, the yellow, and the red band, respectively. Thus, the approximate ZP energies at low excitation PD and 2 K are 3.03, 2.40, and 1.96 eV, respectively. Neglecting the residual Coulomb interaction at the lowest PD, finally gives $E_V + 1.08\,\mathrm{eV}$ and $E_C - 0.28\,\mathrm{eV}$ for the Si and the Mg related deep level positions A_d and D_d as shown. A defect level with an activation energy close to that of A_d has also been observed by capacitance spectroscopy.[20]

The recombination type shown in Fig. 8 for the yellow emission is the same as that originally suggested.[5] However, the proportionality between the yellow band intensity and the Si concentration in Fig. 4 strongly indicates that the acceptor A_d is silicon rather than carbon related in GaN:Si layers. The model inferred here for the yellow band is in line with theoretical predictions.[21]

As far as Mg doping is concerned, the right part of Fig. 8 readily explains the switching from the 3.2 eV band to the blue band with increasing Mg concentration. As long as the Mg concentration is in the $10^{18}\,\mathrm{cm}^{-3}$ range the mean intrapair separations are large (>40 Å, estimated with the degree of self-compensation derived below) compared to the sum of the electron and hole Bohr radii, ~10 Å, of the deep donor D_d and the shallow Mg acceptor in the pair. Therefore, their wave function overlap and the recombination probability are small,[22] and recombination of free electrons with holes trapped at the Mg acceptor at RT will preferentially occur via the direct (Mg^0, e) free to bound capture mechanism. When the Mg concentration is further increased also the formation of compensating donors D_d is strongly enhanced, as discussed in more detail in Sec. IV C. Therefore the D_d-Mg intrapair distances decrease rapidly and eventually become comparable with the combined Bohr radius of the recombining particles. Thus, the indirect recombination channel for free electrons with holes on the Mg acceptor via the deep Mg-related donor level D_d is effectively unlocked. As a consequence the 3.2 eV free to bound transition is quenched and the 2.8 eV emission dominates the spectrum.

It has been emphasized that the red band in Fig. 5 is usually only observed in GaN layers codoped with Mg and Si indicating that *both* impurities are involved in this recombination process. The model in Fig. 8 provides a simple possible explanation for this band in terms of a DA pair recombination, too, now involving the deep Mg-related donor D_d and the deep Si-related acceptor A_d. The ZP line energy of the $D_d \rightarrow A_d$ transition predicted from the corresponding levels in Fig. 8 is 2.15 eV. On the other hand, the ZP line energy directly evaluated from the red band is 1.96 eV. Given the uncertainties in the level positions (≈50 meV) and the ZP line energy (≈50 meV), the agreement is good, thus supporting the model suggested. The relatively low efficiency of the red band is consistent with a small concentration of $D_d - A_d$ pairs and the deep and therefore localized character of both centers involved.

B. Self-compensation

Let us now consider self-compensation effects in more detail. This phenomenon is likely to occur only in high-gap semiconductors where intrinsic defect formation energies can be smaller than free carrier trapping energies at these defects such that the crystal minimizes its total free energy. To be specific, Si donor doping (concentration N_D) of GaN is considered first and compensation due to residual acceptor impurities is neglected. If N_A is the concentration of acceptors formed by self-compensation, i.e., acceptors which contain a donor atom D, then the degree of self-compensation, K_D, can be defined as $K_D = N_A / N_D$ with $0 \leq K_D \leq 0.5$. Note that complete compensation is reached for $K_D = 0.5$ since one half of the donors is converted into deep acceptors that compensate the other half of the donors.

The observed approximate linear increase of the yellow band PL intensity under high excitation PD with increasing Si concentration up to $2 \times 10^{19}\,\mathrm{cm}^{-3}$ is only consistent with a small or at most moderate concentration $N_A = K_D N_D$ (well below $10^{18}\,\mathrm{cm}^{-3}$) of compensating acceptors and Si-A_d pairs. The intrapair distances d, calculated from the expression for E_{COUL} and the maximum PD-induced peak shift, decrease with increasing Si concentration and reach the lowest value (≈41 Å) at the highest Si doping level $(2 \times 10^{19}\,\mathrm{cm}^{-3})$ investigated. This again indicates at most moderate pair densities (well below $10^{18}\,\mathrm{cm}^{-3}$). These d values have been used to evaluate the degree of self-compensation K_D for six GaN:Si samples assuming that d is in the vicinity of $d_{max} = (4\pi K_D N_D)^{-1/3}$, where the pair distribution function $G(d)$ is peaked.[17] In this way one obtains approximate K_D values around 0.03 and 0.07 for N_D in the low $10^{18}\,\mathrm{cm}^{-3}$ and the low $10^{19}\,\mathrm{cm}^{-3}$ range, respectively. Thus, self-compensation in the case of Si doping is weak and almost negligible for practical purposes in agreement with previous Hall effect data.[23]

For the blue band and Mg doping at levels in the lower $10^{19}\,\mathrm{cm}^{-3}$ range the situation is quite different. As mentioned, the PL intensity in this case is nearly independent of the Mg concentration. The intrapair distances, inferred from E_{COUL} (Refs. 24 and 25) and the maximum peak shifts, are small, about half as large (≈21 Å) as for comparable Si doping levels. Both results indicate that the D_d-Mg pair concentration is a significant fraction of the Mg doping concentration. Evaluating the self-compensation coefficient K_A for Mg, as outlined above for Si, one finds that K_A is around 0.3. Thus, in the case of Mg doping self-compensation is significant. This is in line with previous Hall-effect measurements on Mg-doped layers.[26]

C. Nature of the deep defects

The deep compensating defects are believed to be dopant-vacancy associates. This view is supported by theory,[27,28] the direct observation of Ga vacancies in n-GaN by positron anihilation experiments,[29] and in particular by experience with II_B-VI compounds. In several defect relevant respects, e.g., crystalline structure, ionicity, dielectric constant, and band gap, GaN resembles more closely to the high gap II-VI compounds like ZnS and ZnO, than to the conventional III-V semiconductors GaAs, GaP, and InP. In the latter case the native intrinsic defects for which sound experimental evidence exists are antisite defects.[30] On the other hand, in II_B-VI compounds, and in ZnS in particular, the dominating defects in as-grown material at RT are dopant-vacancy

associates.[11,17] Therefore, it is highly reasonable to assume that analogous associates also occur in doped GaN. According to theory the dominating lattice defects in *n*-type and *p*-type GaN at a typical MOCVD growth temperature of 1000 °C are gallium vacancies V_{Ga} and nitrogen vacancies V_N,[27] respectively. At these high temperatures, isolated vacancies are mobile[30] and positively (V_N) or negatively (V_{Ga}) charged, i.e., oppositely to the respective ionized doping species Mg or Si. Therefore, the Coulomb attraction represents a driving force for the formation of V_NMg and V_{Ga}Si associates in GaN:Mg and GaN:Si, respectively. These nearest- or next-nearest-neighbor associates are expected to act as deep donors $D_d = V_N$Mg and deep acceptors $A_d = V_{Ga}$Si, which partially compensate the isolated shallow dopants Mg and Si, respectively. The likelihood that *isolated* vacancies in doped GaN layers survive during cooldown from the growth temperature to RT is small because of the tendency to form associates with the dopant. Therefore, the involvement of isolated vacancies as the deep defects in the broad DA bands is considered unlikely.

It was mentioned before that when the Mg content is increased above $10^{19}\,\mathrm{cm}^{-3}$ one expects the concentration of compensating defects D_d to increase, too. The reason is that the V_N formation energy decreases linearly with the separation of the Fermi level E_F from the valence band.[27] This decrease becomes especially fast when E_F passes through the Mg acceptor level with increasing Mg content. In this case, also the V_N concentration grows particularly strong. This will significantly enhance the formation of compensating donors $D_d = V_N$Mg and will consequently rapidly reduce the mean D_d-Mg intrapair distances. Thus, it seems likely that the sudden switching from the 3.2 eV band to the blue band in Fig. 1 results from the enhanced generation of deep donors D_d when E_F passes through the Mg acceptor level. The same effect provides a qualitative explanation for the saturation of the RT hole density observed in the present *p*-GaN:Mg layers at a Mg concentration near $3\times10^{19}\,\mathrm{cm}^{-3}$.[31]

D. Deep PL bands in undoped GaN

In the undoped GaN layers studied, the intensities of the yellow and the blue band are comparatively weak. The peak positions agree within 20 meV with those of the corresponding bands in Si- and Mg-doped layers, respectively, under low PD conditions. The half widths are somewhat larger than those in the doped layers. It is therefore very likely that these bands in undoped GaN arise from *residual* Si (or other shallow donor impurities) and Mg impurities, respectively, leading to the yellow and the blue DA transitions shown in Fig. 8. The missing peak shifts of the bands with changes in PD in the undoped case are in line with this view. Assuming either a Si or a Mg background in the $10^{16}\,\mathrm{cm}^{-3}$ range (actually confirmed for Mg by secondary ion mass spectroscopy for the present samples) and using the degrees of self-compensation derived above one finds that the mean distances *d* in Si-V_{Ga}Si or V_NMg-Mg pairs exceed 200 Å. In this case, the expected peak shifts with PD are less than 10 meV, which is undetectable given the widths of the bands. For the yellow band in *undoped* GaN the present DA model is in conflict with the deep donor to shallow acceptor model proposed on the basis of optically detected magnetic resonance (ODMR) studies.[6] This model relies on the assignment of a nearly isotropic ODMR signal ($g_\parallel = 1.992$, $g_\perp = 1.995$) to a deep donor state. However, the evidence for the donor character of this resonance, namely, the very small negative *g* shift, is marginal, and an alternative assignment in terms of a deep acceptor state is also conceivable. This would reconcile the ODMR data in undoped GaN with the model for the yellow band suggested here for GaN:Si.

The nonobservation of the red band in nominally undoped layers is consistent with an extremly low concentration of V_NMg-V_{Ga}Si distant pairs.

V. SUMMARY

Photoluminescence studies of doped MOCVD GaN layers show that Mg *and* Si doping induces a blue and a yellow PL band, respectively. Codoping with Si and Mg generates a red PL band. The peak shift of these bands with excitation PD provides strong evidence for their distant DA pair character. The deep centers involved in DA recombination are suggested to arise from self-compensation in analogy to the situation in high-gap II_B-VI compounds. The best candidates for these deep centers are $D_d = V_N$Mg and $A_d = V_{Ga}$Si vacancy-dopant associates in Mg- and Si-doped layers, respectively. The corresponding two deep levels together with the shallow levels of Mg and Si provide a natural explanation for all three bands. Self-compensation is found to be significant in the case of Mg doping but weak in the case of Si doping. The yellow and the blue band occurring in nominally undoped GaN are suggested to arise from very distant DA pairs involving residual Si and Mg impurities, respectively, and the respective vacancy associates.

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