PHYSICAL REVIEW B **68**, 045205 (2003)

Blue emission band in compensated GaN:Mg codoped with Si

B. Han, J. M. Gregie, and B. W. Wessels*
Department of Materials Science and Engineering and Materials Research Center, Northwestern University, Evanston, Illinois 60208, USA

(Received 17 June 2002; revised manuscript received 3 February 2003; published 30 July 2003)

Codoping of *p*-type GaN with Mg and Si was investigated to determine its effect on deep level luminescence. By codoping with Si, the absolute intensity of the 2.8-eV blue luminescence band, previously tentatively attributed to deep donor-acceptor-pair (DAP) emission, decreased by more than an order of magnitude. The observed decrease is attributed to the reduction of the concentration of deep donor nitrogen vacancy complexes. The dependence of the emission peak position on hole concentration was investigated. A blueshift was observed with increasing carrier concentration. The shift of the blue band with carrier concentration and excitation intensity is explained semiquantitatively by a potential fluctuation model indicating its importance in DAP recombination.

DOI: 10.1103/PhysRevB.68.045205 PACS number(s): 61.72.Ji, 71.55.Eq, 78.55.Cr

I. INTRODUCTION

Bipolar doping in wide-band-gap semiconductors such as GaN is difficult because of compensation by native defects or impurities.[1,2] Although high-conductivity *n*-type GaN is readily achieved, *p*-type material is much more difficult to attain.[3] It has been shown that in *p*-type GaN, compensation by hydrogen donors and by nitrogen vacancy donors is a factor that leads to highly resistive material.[4] While hydrogen donors can be eliminated either by low-energy electron-beam irradiation[3] or by a N_2-ambient thermal annealing above 900 K,[5] elimination of native donors, such as the nitrogen vacancy (V_N) and its complexes, remains a more serious problem and represents the "*doping limit*" of *p*-type GaN.[6,7]

To minimize the formation of deep donor defects in GaN, codoping with shallow donors has been proposed.[4,8] Theory predicts that the formation energy of charged defects and impurities, which determines their equilibrium concentration, depends on the Fermi level.[4] The level in turn can be controlled through codoping with appropriately charged impurities. An example of the effect of codoping is that of hydrogen in *p*-type GaN.[4,9,10] Incorporation of hydrogen during growth suppresses the formation of nitrogen vacancy donors.[4] The hydrogen can be subsequently removed by annealing at high temperatures in nitrogen, thus activating acceptors.[4] Nevertheless, compensation by native defects still limits the hole conductivity in GaN:Mg layers even after hydrogen codoping and removal.[7,11] Meanwhile, only under certain restrictive conditions (e.g., low formation energy of the hydrogen defect, low activation barriers to dissociate the H-impurity complex, and high diffusivity of the H atom) can hydrogen passivation be applied to suppress native defect compensation and increase free-carrier concentration in wide-gap semiconductors.[4]

Yamamoto and Katayama-Yoshida proposed that highly conductive *p*-type GaN can be achieved by deliberate, simultaneous incorporation of *p*-type dopants and controlled amounts of *n*-type dopants.[12] Several studies have confirmed these predictions.[8,13–16] Korotkov, Gregie, and Wessels[15] and Kipshidze *et al.*[16] observed improved *p*-type conductivity upon oxygen donor codoping through a decrease of the acceptor (Mg) activation energy in GaN and AlGaN, respectively. However, the different mechanisms by which the codoping method leads to high conductivity are not well established and remain controversial. Indeed, using first-principles total-energy calculations, Zhang, Wei, and Yan predicted that under thermal equilibrium neither higher solubility of desired (*p*-type) dopants nor shallower acceptor levels in semiconductors can be achieved by codoping.[17]

In this work Mg-doped GaN has been codoped with the shallow donor Si to suppress the formation of native donors. Photoluminescence (PL) measurements were carried out on deliberately codoped material to determine the effect of shallow donor incorporation on deep donor-acceptor-pair (DAP) luminescence associated with nitrogen vacancy complexes. Upon Si codoping, the intensity of the blue DAP band in *p*-type GaN decreased by more than an order of magnitude. For heavily Si-doped, *n*-type films, the band is completely quenched. These results indicate that native defect formation can be efficiently suppressed by means of codoping the films with *n*-type dopants. This approach to defect control is generally applicable to wide-band-gap semiconductors.

II. EXPERIMENTAL DETAILS

Mg-doped and Mg-Si codoped GaN films were grown by atmospheric pressure metal-organic vapor phase epitaxy (MOVPE) on *c*-plane sapphire substrates. Ammonia (NH_3) and trimethylgallium (TMGa) were used as reactants, and hydrogen was the carrier gas. The source materials for Mg and Si are bis(cyclopentadienyl)magnesium (Cp_2Mg) and a 100-ppm silane (SiH_4) mixture in H_2, respectively. For these studies a multilayer structure was used. Film growth was initiated with a low-temperature GaN buffer layer, followed by a 500-nm insulating, Mg-doped layer. The Mg-Si codoped layer, 0.5–1-μm thick, was subsequently grown at 1030 °C. The codoped films were annealed for 15 min in N_2 at 850 °C to eliminate hydrogen.

Photoluminescence measurements were made between 17 and 350 K using a closed-cycle He cryostat. The sample temperature was measured with a carbon temperature sensor and stabilized by a temperature controller at temperatures between 17 and 350 K. A He-Cd laser (photon energy 3.81

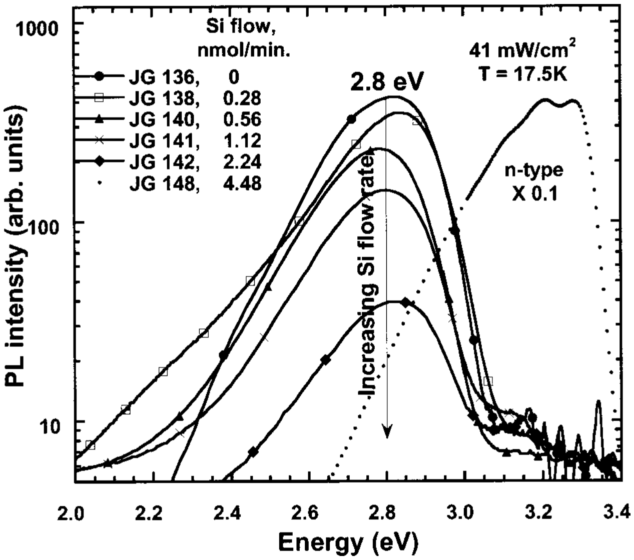

FIG. 1. PL spectra for heavily Mg-doped and Si-codoped samples taken at 17.5 K and 41 mW/cm^2. The absolute intensity of the blue band in *p*-type GaN decreased steadily with increasing Si flow rate. The dotted line shows that the band is completely quenched in *n*-type material with over codoping of Si.

eV) was used as an excitation source in the reflection configuration. The PL signal was dispersed by a 0.75-m SPEX grating monochromator and detected by a Hamamatsu photomultiplier tube R928 and a photon counting system. The excitation intensity was varied over the range $10^{-5}-3.2$ W/cm^2 using calibrated neutral density filters.

Van der Pauw measurements were conducted at room temperature. Either In or Ni/Au were used as contacts. The magnetic field was 3200 G. The applied currents were between 0.01 and 0.1 mA.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Effect of codoping on PL intensity of the blue band

PL spectra for Mg-doped and Mg-Si-codoped films were measured at 17.5 K. At a high Mg concentration, a broad blue band peaked around 2.8 eV is observed in the Mg-doped GaN as shown in Fig. 1. The origin of the blue band remains controversial. It was previously attributed to electron transitions from the conduction band (or a shallow donor) to a deep acceptor level,[9,18] a Mg complex,[19,20] or a DAP emission involving a $\mathrm{Mg_{Ga}}$ acceptor and a deep donor.[21–23] Nevertheless, previous work of our group as well as of others' supported the DAP model in which the deep donor was attributed to a nitrogen vacancy or related complex.[11,21–24]

As shown in Fig. 1, band-edge emission is quenched in the heavily doped films,[25] which is consistent with previous PL results of heavily Mg-doped GaN,[21,22,26–28] e.g., when the Mg-doping concentration is larger than 2.5×10^{19} cm^{-3}.[21,22] A band-edge emission band is not typically observed when the blue band dominants in *p*-type GaN:Mg.[11,18,24,29] The quenching of the band-edge emission presumably results from the increase of other competitive radiative recombination channels (e.g., blue emission band) and nonradiative centers by heavy Mg doping or Mg-Si codoping.

To determine the effect of Si codoping on the blue band emission intensity in *p*-type GaN, a series of Mg-Si-codoped films were grown at a constant Mg flow rate, while the flow rate of Si was varied. The growth conditions and the electrical characteristics for this series of films are summarized in Table I.

Figure 1 shows the PL spectra for this series of codoped samples at a constant excitation level. Since the maximum peak position of the blue band depends on temperature and excitation intensity, all the PL spectra in Fig. 1 were measured with an excitation density of 41 mW/cm^2. The excitation power was kept at a relatively low level to avoid saturation of the PL emission. However, the intensities of the blue band are high enough to allow comparison of the PL intensity among different samples.

The dominant emission band in the *p*-type Mg-Si-codoped samples was also around 2.8 eV at 17.5 K. As shown in Fig. 1, the measured intensity of the blue band in *p*-type GaN decreased with increasing Si doping. Compared to a Mg-doped film grown under similar conditions, but without Si, the absolute intensity of the blue band for *p*-type, Si-codoped, GaN decreased by more than an order of magnitude. When the Si-dopant concentration was very high, the film converted to *n*-type. In that case, no blue band can be observed (as shown with a dotted line in Fig. 1), and an emission band with a zero phonon line peaked at 3.28 eV dominates the spectrum.

The quenching of the blue band is attributed to suppression of the deep native donor formation by incorporation of the shallow donor—Si, which is discussed later. To deter-

TABLE I. Electrical characteristics of Mg-doped and Si-codoped samples.

Sample number	Mg (μmol/min)	Si (nmol/min)	p ($\times10^{17}$ cm^{-3})	ρ (Ω cm)	Activation energy of donor (eV)	Γ (eV)
JG 136	0.18	0	2.5	2.6	0.25	0.087
JG 138	0.18	0.28	3	1.8	N/A	0.072
JG 140	0.18	0.56	1.5	3.9	0.24	0.141
JG 141	0.18	1.12	2	3.2	0.25	0.107
JG 142	0.18	2.24	3	2.2		0.072
JG 148	0.18	4.48	55[a]	0.09		

[a] Indicates *n*-type material.

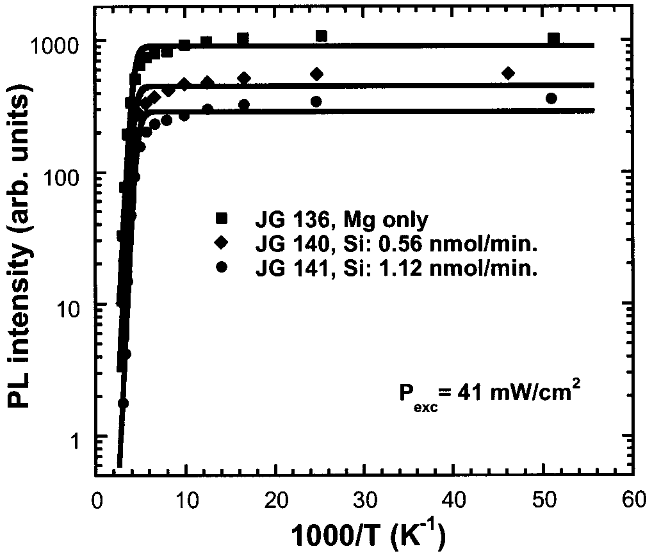

FIG. 2. Temperature dependence of the blue band emission intensity in Mg-doped and Si-codoped samples. Solid lines are fits based on Eq. (1). The calculated activation energy for donors in different samples is 245 ± 5 meV.

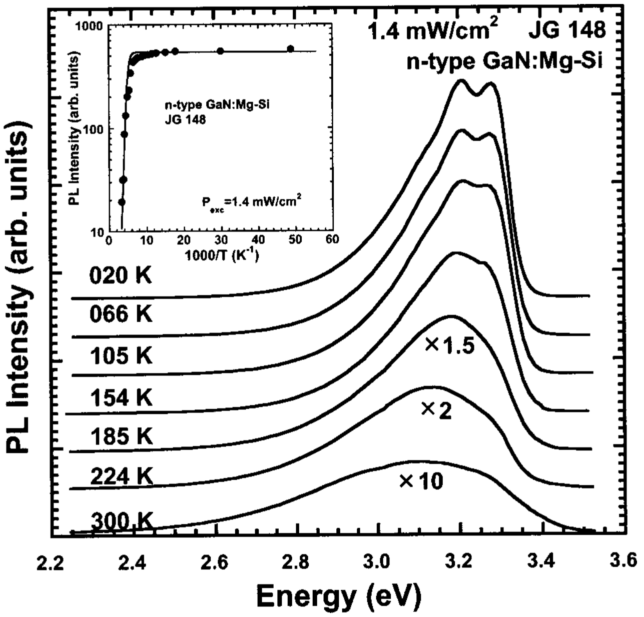

FIG. 3. PL spectra for the *n*-type Mg-Si-codoped GaN at different temperatures (20–300 K) under a low excitation density of 1.4 mW/cm^{-2}. The inset shows the temperature dependence of the 3.2-eV luminescence band intensity.

mine the nature of the defects involved in the blue band observed in codoped samples, the temperature dependence of the emission intensity was measured. The quenching of the PL intensity with increasing temperature for Mg-doped and Mg-Si-codoped *p*-type films is shown in Fig. 2. The blue band quenches in all three samples at temperatures above 150 K. The quenching is attributed to the thermal release of trapped electrons from a deep donor state.[24,30] The temperature dependence of the blue band intensity can be analyzed using the equation

$$I(T)=I_0/[1+A\exp(-E_D/kT)], \tag{1}$$

where E_D is activation energy of the donor and A is taken to be a temperature-independent constant. The measured activation energies for the samples are summarized in Table I. The quenching curves indicate that the thermal depth of the donor is 245 ± 5 meV for all the epilayers studied. Consequently, the donors involved in the DAP emission band remain unchanged with and without Si codoping. This leads to the conclusion that the donor responsible for the blue DAP emission is identical in the Mg-doped and *p*-type Mg-Si-codoped samples. Since the PL intensity decreases with increasing Si flow rate and the blue band dominates the low-temperature PL spectrum for solely Mg-doped GaN, the donor cannot be attributed to the shallow donor $\mathrm{Si_{Ga}}$ or a Si-related complex. Otherwise an increase of the blue band intensity, rather than a decrease, should be observed with increasing Si flow rate. The luminescence quenching is attributed to a decrease in the deep donor concentration.

Nonetheless, it is expected that there is a concurrent increase in the shallow donor (Si) concentration, as ultimately indicated by the conversion of the films to *n* type at a high Si-codoping level. This explains why a monotonic change of hole density with increasing Si flow rate was not observed in Table I (see Ref. 31 for details). The observed dependence is consistent with other codoping studies [for Mg-O-codoped GaN or AlGaN,[16] for Mg-Si-codoped GaN,[32] and for Mg-Zn-codoped GaN (Ref. 33)], in which no monotonic change of hole concentration was observed with increasing codopant density.

It should be noted that similar concentration quenching of the blue DAP emission was previously observed for codoping with shallow oxygen donors in GaN:Mg by Korotkov, Gregie and Wessels.[8] In that work, the absolute intensity of the blue band was also found to decrease with increasing oxygen incorporation. It was concluded that the oxygen donor was not involved in the blue DAP band.

The quenching of the blue band with Si codoping may also result from an increase of other competitive radiative or nonradiative channels, instead of a decrease of one of the centers involved. To confirm that the quenching of the blue band indeed results from a decrease of the deep donor concentration, it's important to determine whether the blue band is observed in the *n*-type codoped sample, under different temperatures and low excitation densities.

The PL spectra of the *n*-type codoped film were measured at different temperatures (20–300 K) and excitation densities (0.0014–3.2 W/cm^2). No evidence of the blue band is observed. Figure 3 shows the temperature dependence of the PL spectra of the *n*-type codoped GaN at a low excitation density of 1.4 mW/cm^2. A 3.2-eV emission band dominates the PL spectra over the entire temperature range. The 3.2-eV band is attributed to electron transition from the conduction band or a shallow donor to a Mg acceptor.[18,24,34] The PL intensity of the 3.2-eV band increased linearly with the excitation power up to 3.2 W/cm^2. The shape of this band was almost invariant over the entire power range and no blue band was observed. The 3.2-eV band redshifts by more than 100 meV between 20 and 300 K at an excitation density of

1.4 mW/cm^2. This band is thermally quenched above 130 K but no other band emerges. The quenching is attributed to thermal release of trapped holes from a deep acceptor state in an *n*-type film.[30] As shown in the inset of Fig. 3, the quenching is well described by $I(T)=I_0/[1+A\exp(-E_A/kT)]$, where E_A is the activation energy of the acceptor for thermal quenching in the *n*-type film. The resulting value of E_A is 210 meV. This value is consistent with the ionization energy of $\mathrm{Mg_{Ga}}$ determined from optical measurements, which was reported to be about 200 meV.[21,24,34] The acceptor activation energy determined in the *n*-type codoped film is very close to those in *p*-type codoped films, which is calculated in the next section to be 225 ± 5 meV. This indicates that the same acceptors ($\mathrm{Mg_{Ga}}$) are present in both *n*- and *p*-type codoped films. The fact that the blue band was only observed in *p*-type but not in *n*-type films is a consequence of the suppression of deep donor formation in the *n*-type films.

The observed quenching of the blue band with addition of shallow donors is consistent with calculations for the dependence of native defect formation energy on Fermi energy reported by Van de Walle.[35] In these calculations, the formation energy of the compensating native donor increases with Fermi energy E_F, which in turn depends on the shallow donor concentration. This deliberate shallow donor addition leads to the decrease of the concentration of native donors. Consequently, a decrease of the absolute intensity of the blue DAP band would be expected.[8,11] In the extreme case in which the film is converted to *n* type by heavy Si codoping, no blue band is observed, even at a low excitation density in the entire temperature range studied. This is consistent with a high formation energy of the native donors in *n*-type samples, as predicted by Van de Walle.[35]

Si is not highly diffusive in *p*-type GaN and cannot be eliminated as easily as hydrogen by postgrowth treatment.[4] Therefore, in order to decrease the total concentration of donors in *p*-type GaN by codoping with Si, the reduction of the native donor (nitrogen vacancy or its complexes) concentrations must be larger than the increase of Si concentration.

To determine quantitatively the effect of addition of Si on the reduction of deep donors, the dependence of deep donor formation on Fermi level needs to be considered. The equilibrium concentration of the native defect $N_{D(V_N)}$ and its dependence on formation energy is given by $N_{D(V_N)}=N_{\mathrm{sites}}\exp(-E^f/kT)$. The formation energy E^f, in turn, is a function of the Fermi level:[35]

$$E^f(\mathrm{GaN}{:}V_N)=E_{\mathrm{tot}}(\mathrm{GaN}{:}V_N)+\mu_N+qE_F, \tag{2}$$

where E_{tot} is the formation energy of the neutral defect, E_F is the Fermi level, μ_N is the chemical potential, and q is the charge state of the defect. Following the argument by Kaufmann *et al.*,[7] in the Mg-doping range $5\times10^{18}\leqslant N_A\leqslant1\times10^{20}\ \mathrm{cm}^{-3}$, the V_N^{2+}/V_N^{3+} donor level is higher than the Fermi energy. V_N^{3+} is the stable charge state of V_N and q in Eq. (2) is restricted to 3.

On the other hand, the Fermi level can be increased by adding shallow donors. In highly compensated *p*-type GaN, the dependence of Fermi energy on Si donor incorporation is[36]

$$dE_F=kT\frac{N_A}{(N_A-N_D)N_D}dN_{D(\mathrm{Si})}, \tag{3}$$

where N_A the concentration of acceptors, N_D the total concentration of donors, and $N_{D(\mathrm{Si})}$ the concentration of Si in the GaN layer. When present, Si is the dominant compensating defect in *p*-type GaN at 1300 K,[4] $N_D\approx N_{D(\mathrm{Si})}$. When $N_A>N_D$, Eq. (3) reduces to $dE_F=kTd\ln(|N_{d(\mathrm{Si})}|)$. Combining Eqs. (2) and (3), it follows that $N_{D(V_N)}$ decreases with E_F in the following:

$$\begin{aligned}dN_{D(V_N)}&=\frac{1}{kT}[N_{\mathrm{sites}}\exp(-E^f/kT)](-3dE_F)\\&=-N_{D(V_N)}[3d|N_{D(\mathrm{Si})}|].\end{aligned} \tag{4}$$

Equation (4) shows that $d\ln|N_{D(V_N)}|=-3d\ln|N_{D(\mathrm{Si})}|$. Consequently, when Si is incorporated into *p*-type GaN, the Fermi level increases and the reduction of $N_{d(V_N)}$ is more than the increase of $N_{d(\mathrm{Si})}$ because of the differences in charge states of the nitrogen vacancy and Si in *p*-type GaN. Although Si cannot be removed as hydrogen after growth, codoping *p*-type GaN with Si can still improve electrical properties of the *p*-type material by reduction of deep donors, as well as optical properties by removal of optically active donor centers.

A similar process can circumvent the problem of self-compensation by native defect centers in other wide-band-gap semiconductors as long as the dopant impurity (e.g., Si) is the dominating compensation defect at growth conditions and the charge state of native defects is larger than that of the impurity codopants.

B. Properties of the blue emission band in compensated *p*-type GaN

The dependence of emission energy on excitation power of the blue band was studied to determine the role of potential fluctuations in heavily compensated *p*-type GaN. Figure 4 shows the PL peak position of the blue band for Mg-doped and Mg-Si-codoped *p*-type samples at room temperature as a function of excitation power. A blueshift of the blue band with increasing excitation intensity has been consistently observed for all the *p*-type samples.

The reason for the variation in emission-peak energy for different samples remains controversial. The shift can be explained by the DAP nature of this transition,[24] or alternatively a model involving potential fluctuations.[18] Colton and Yu suggested that the peak energy of the blue band marks the transition from localized to delocalized states within an Urbach-type band tail.[37] All these explanations are qualitative. In this investigation, a quantitative model based on potential fluctuations is given to explain the shift of the blue emission-peak energy.

In compensated and highly doped semiconductors, potential fluctuations are expected to strongly affect the optical properties due to the inhomogeneous distribution of charged defects.[18,24,38] Diagonal radiative transitions between holes localized in the ‘‘hills’’ of the valence band and electrons

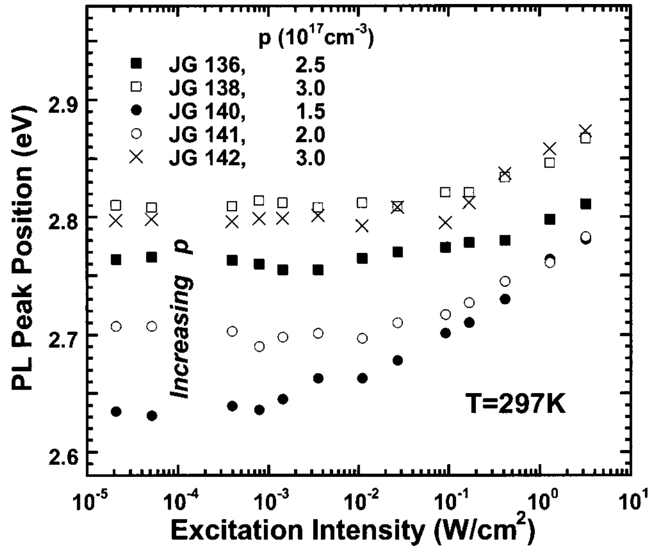

FIG. 4. Dependence of the blue band peak position on excitation intensity at room temperature for the Mg-doped and Si-codoped samples. The peak shifts saturate at the low excitation limit. Note that the peak positions of sample JG 138 and JG 142 are close at low excitation intensity.

localized in the "valleys" of the conduction band reduce the recombination energy and lead to a redshift of the PL band.[24,38] Furthermore, the wide range of photon emission energies made possible by these potential fluctuations broadens the PL band.[24,38] According to the model developed by Shklovskii and Efros,[38] when the impurities are randomly distributed, the average amplitude Γ of potential fluctuations for a compensated p-type semiconductor depends on the total concentration of charged impurities ($N_T = N_A^- + N_D^+$) and the hole concentration p:

$$\Gamma = \frac{e^2}{4\pi\varepsilon\varepsilon_0}\cdot\frac{N_T^{2/3}}{p^{1/3}}. \tag{5}$$

Note that although potential fluctuations are due to charged rather than neutral centers, large amounts of $\mathrm{Mg_{Ga}}$ acceptors remain neutral in the p-type GaN films due to their large activation energy.[36] However, the neutral impurities do not contribute significantly to the potential fluctuations and could be considered as "inert" in compensated films.[38]

The total concentration of charged impurities can be determined from the hole concentration p and the acceptor concentration N_A.[36,38,39] Upon inclusion of potential fluctuations, the DAP emission energy is given by[39]

$$E(\hbar\omega) = E_g - (E_D + E_A) - 2\Gamma = E_g - E_A - E_D - 2\cdot\frac{e^2}{4\pi\varepsilon\varepsilon_0}\cdot\frac{\left(\dfrac{2N_AK}{K+p} - p\right)^{2/3}}{p^{1/3}}, \tag{6}$$

where E_g represents the band-gap energy of this material.

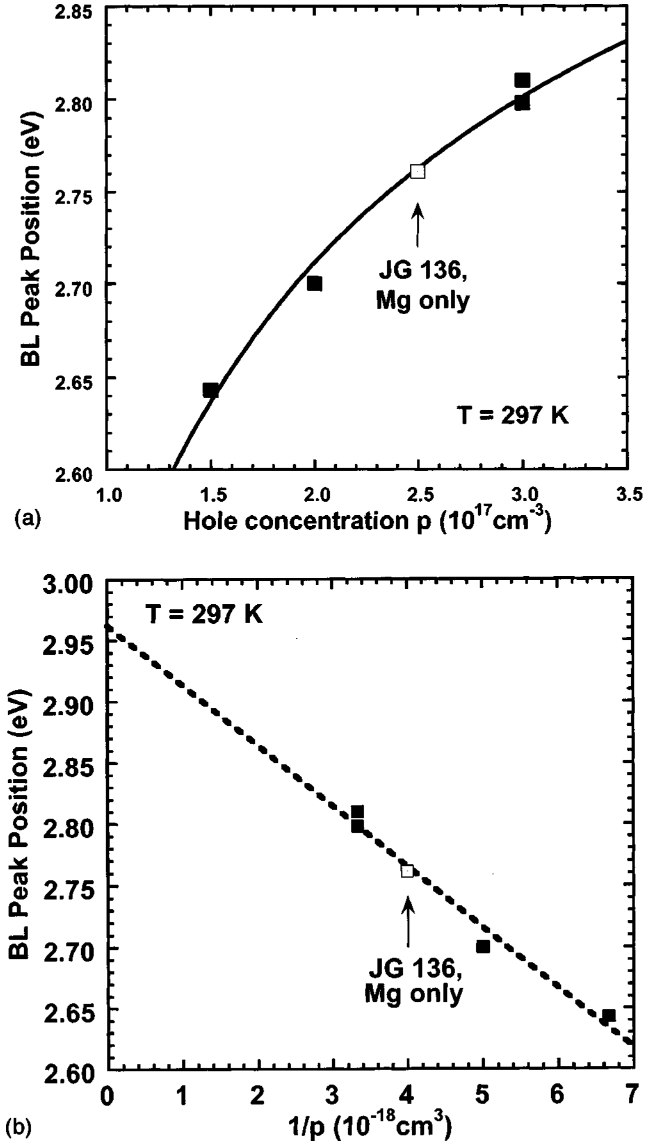

FIG. 5. (a) Dependence of the peak energy of the blue band with the cube root of the free-carrier concentration. The solid curve is the fit using Eq. (3). The fitting parameter N_A is obtained as 4.8×10^{19} cm^{-3}. (b) A linear dependence of the peak position of the blue band on the reciprocal of the hole concentration can also be used to describe the observed room-temperature dependence. From a simple linear extrapolation of the data the peak position blueshifts to 2.96 eV when the potential fluctuation $\Gamma = S \times p^{-1}$ decreases to zero at $p^{-1} = 0$. The dashed line is calculated using Eq. (7) and $S = 2.3 \times 10^{16}$ eV cm^{-3}.

In the presence of potential fluctuations, the emission band blueshifts with increasing excitation intensity because of increased screening of the potential fluctuations by photogenerated carriers,[18,24,38] as shown in Fig. 4. At the low excitation limit, no shift is observed. This can be explained by the fact that at low excitation intensity, photogenerated nonequilibrium carrier concentration is very low compared to equilibrium carrier concentration generated by thermal ionization. In this case, the hole concentration in the films is essentially identical to that obtained by Hall-effect measurements in the dark. The small change in carrier concentrations upon low-level photoexcitation leads to a negligible change of the potential fluctuation magnitude and no shift is observed.

The peak positions for two films (JG 138 and JG 142) at the low excitation limit are close, indicating similar potential fluctuation amplitudes [see Eq. (6)]. Since the hole concentration of both films is around 3×10^{17} cm^{-3}, Eq. (6) indicates that the Mg-doping density N_A is nearly the same for these samples even though the Si-doping level is different.

To determine the amplitude Γ of the potential fluctuations, the energy of the main peak at the low excitation limit is plotted versus the cube root of the measured hole concentration in the epilayers at room temperature, as shown in Fig. 5(a). The solid curve is calculated using Eq. (6) after assuming N_A is independent of Si-dopant concentration. For these calculations, N_A is used as a fitting parameter and obtained by least-squares regression. The estimated value of N_A from the fit is 4.8×10^{19} cm^{-3}. From the Mg-doping density N_A and measured hole concentration p, Γ can be calculated (Ref. 39). The potential fluctuations for the different samples range from 0.072 to 0.141 eV as listed in Table I. Using Eq. (6) the peak position of the blue band without any potential fluctuations is thus calculated to be 2.95 eV.

After taking into account the effect of potential fluctuations, the activation energy of the acceptor involved in the blue band can be determined from Eq. (6) and is given as $E_A=E_g-\hbar\omega-E_D$, where the band gap E_g is taken as 3.42 eV at room temperature, and $\hbar\omega$ (2.95 eV) is the emission energy without potential fluctuations. The activation energy of the donor (E_D) was previously determined from thermal quenching as 245 ± 5 meV (see Sec. III A). Using these values the activation energy of the acceptor (E_A) is calculated to be 225 ± 5 meV. This value is in good agreement with the $\mathrm{Mg_{Ga}}$ acceptor activation energy of 210 meV previously determined from the quenching curve in n-type codoped GaN.

While the relationship between peak position and hole concentration is well described by Eq. (6), alternatively a linear dependence of the peak position of the blue band on the reciprocal of the hole concentration can also be used to describe the observed room-temperature dependence, as indicated by Fig. 5(b). For a constant N_A, the magnitude of the potential fluctuation can be simplified to $\Gamma=S\times p^{-1}$, where $S=(2N_AK)^{2/3}e^2/4\pi\varepsilon\varepsilon_0=2.3\times10^{16}$ eV cm^{-3}.[40] Consequently, the peak energy of the blue band in p-type GaN films depends linearly on the reciprocal of the hole concentration at room temperature shown in the following:

$$E(\hbar\omega)=E_g-(E_D+E_A)-2S\times p^{-1}. \tag{7}$$

From a simple linear extrapolation of the data the peak position blueshifts to 2.96 eV when the potential fluctuation $\Gamma=S\times p^{-1}$ decreases to zero at $p^{-1}=0$. This result is consistent with the fitting result of 2.95 eV previously obtained using Eq. (6). The dashed line in Fig. 5(b) is calculated using Eq. (7) and $S=2.3\times10^{16}$ eV cm^{-3}.[40]

IV. CONCLUSIONS

Codoping of p-type GaN with Mg and Si was investigated to determine its effect on deep level luminescence. The absolute intensity of the blue luminescence band for Mg-doped p-type GaN is reduced by more than an order of magnitude with Si codoping. The blue band is attributed to deep donor-acceptor-pair recombination between $\mathrm{Mg_{Ga}}$ and a nitrogen vacancy complex. The intensity decrease is attributed to a decrease in the compensating nitrogen vacancy complex in Mg-doped p-type GaN upon codoping of n-type dopants. Our result is consistent with density-functional theory calculations for the native defect formation and the influence of Fermi energy on defect stability in GaN. The blueshift of the blue DAP band was studied for the codoped films. The shift is explained semiquantitatively by a potential fluctuation model. Potential fluctuations as large as 0.14 eV are observed in the compensated films.

ACKNOWLEDGMENTS

This work was supported by an ONR grant under Contract No. N00014-01-1-0012 (C. Wood, monitor) and by the National Defense Science and Engineering Graduate Fellowship (J.M.G.) awarded by the Air Force and the Department of Defense.

---

*Email address: b-wessels@northwestern.edu

[1] G. Mandel, Phys. Rev. **134**, A1073 (1964).

[2] J. A. Van Vechten, *Handbook on Semiconductors*, edited by S. P. Keller (North-Holland, Amsterdam, 1980), Vol. 3, Chap. 1.

[3] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **28**, L2112 (1989).

[4] J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **68**, 1829 (1998).

[5] S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, Jpn. J. Appl. Phys., Part 2 **31**, L139 (1992).

[6] S. B. Zhang, S.-H. Wei, and A. Zunger, Physica B **273–274**, 976 (1999).

[7] U. Kaufmann, P. Schlotter, H. Obloh, K. Köhler, and M. Maier, Phys. Rev. B **62**, 10867 (2000).

[8] R. K. Korotkov, J. M. Gregie, and B. W. Wessels, Mater. Res. Soc. Symp. Proc. **639**, G6.39.1 (2001).

[9] S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys., Part 1 **31**, 1258 (1992).

[10] J. A. Van Vechten, J. D. Zook, R. D. Horning, and B. Goldenberg, Jpn. J. Appl. Phys., Part 1 **31**, 3662 (1992).

[11] F. Shahedipour and B. W. Wessels, Appl. Phys. Lett. **76**, 3011 (2000).

[12] T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys., Part 2 **36**, L180 (1997).

[13] O. Brandt, H. Yang, H. Kostial, and K. H. Ploog, Appl. Phys. Lett. **69**, 2707 (1996).

[14] S. Nakamura, Japanese patents No. H10-144960 (1998) and H10-154829 (1998).

[15] R. Y. Korotkov, J. M. Gregie, and B. W. Wessels, Appl. Phys. Lett. **78**, 222 (2001).

[16] G. Kipshidze, V. Kuryatkov, B. Borisov, Y. Kudryavtsev, R. Asomoza, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **80**, 2910 (2002).

[17] S. B. Zhang, S.-H. Wei, and Yanfa Yan, Physica B **302–303**, 135 (2001).

[18] E. Oh, H. Park, and Y. Park, Appl. Phys. Lett. **72**, 70 (1998).

[19] M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang, A. Salvador, B. N. Sverdlov, A. Botchkarev, H. Morkoc, and B. Goldenberg, Appl. Phys. Lett. **68**, 1883 (1996).

[20] J. M. Myoung, K. H. Shim, C. Kim, O. Gluschenkov, K. Kim, S. Kim, D. A. Turnbull, and S. G. Bishop, Appl. Phys. Lett. **69**, 2722 (1996).

[21] U. Kaufmann, M. Kunzer, M. Maier, H. Obloh, A. Ramakrishnan, B. Santic, and P. Schlotter, Appl. Phys. Lett. **72**, 1326 (1998).

[22] U. Kaufmann, M. Kunzer, H. Obloh, M. Maier, Ch. Manz, A. Ramakrishnan, and B. Santic, Phys. Rev. B **59**, 5561 (1999).

[23] Y. H. Kwon, S. K. Shee, G. H. Gainer, G. H. Park, S. J. Hwang, and J. J. Song, Appl. Phys. Lett. **76**, 840 (2000).

[24] M. A. Reshchikov, G.-C. Yi, and B. W. Wessels, Phys. Rev. B **59**, 13176 (1999).

[25] Our *p*-type GaN is heavily doped since the PL study reveals a Mg-doping concentration around 4.8×10^{19} cm^{-3} for these Mg-doped and Mg-Si-codoped films. Detailed calculations of the Mg concentration are discussed in Sec. III B.

[26] L. Eckey, U. Von Gfug, J. Holst, A. Hoffmann, A. Kaschner, H. Siegle, C. Thomsen, B. Schineller, K. Heime, M. Heuken, O. Schön, and R. Beccard, J. Appl. Phys. **84**, 5828 (1998).

[27] M. Lachab, D.-H. Youn, R. S. Qhalid Fareed, T. Wang, and S. Sakai, Solid-State Electron. **44**, 1669 (2000).

[28] P. Vennéguès, M. Benaissa, S. Dalmasso, M. Leroux, E. Feltin, P. De Mierry, B. Beaumont, B. Damilano, N. Grandjean, and P. Gibart, Mater. Sci. Eng., B **93**, 224 (2002).

[29] J. K. Sheu, Y. K. Su, G. C. Chi, B. J. Pong, C. Y. Chen, C. N. Huang, and W. C. Chen, J. Appl. Phys. **84**, 4590 (1998).

[30] M. Leroux, N. Grandjean, B. Beaumont, G. Nataf, F. Semond, J. Massies, and P. Gibart, J. Appl. Phys. **86**, 3721 (1999).

[31] As seen from Table I, the hole concentration varies between 1.5 and 3×10^{17} cm^{-3} with the codoping of Si. Considering the complexity of MOVPE growth, the hole concentration can be regarded as nearly constant with Si codoping under these conditions. Its variation is attributed to fluctuations of dopant incorporation during film deposition (e.g., fluctuation of the gas flow rates or susceptor temperature). However, as shown in Sec. III B, noticeable changes of the PL spectrum (e.g., peak positions) are expected with the hole concentration variation.

[32] K. S. Kim, G. M. Yang, and H. J. Lee, Solid-State Electron. **43**, 1807 (1999).

[33] K. S. Kim, M. S. Han, G. M. Yang, C. J. Youn, H. J. Lee, H. K. Cho, and J. Y. Lee, Appl. Phys. Lett. **77**, 1123 (2000).

[34] M. Ilegems and R. Dingle, J. Appl. Phys. **44**, 4234 (1973).

[35] C. G. Van de Walle, Mater. Sci. Forum **338–342**, 1561 (2000).

[36] J. S. Blakemore, *Semiconductor Statistics* (Dover, New York, 1987).

[37] J. S. Colton and P. Y. Yu, Appl. Phys. Lett. **78**, 2500 (2001).

[38] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984).

[39] For *p*-type GaN, where the acceptors are incompletely ionized at room temperature and are compensated by native donors and *n*-type impurities, the relationship between total donor concentration N_D, Mg-doping concentration N_A, and equilibrium hole concentration p_0 is (Ref. 38) $\{[p_0(p_0+N_D)]/(N_A-N_D-p_0)\}=(N_v/\beta)\exp(-E_a/kT)$, where E_a is the thermal ionization energy, β is the spin degeneracy of the acceptors, and N_v is the effective density of states in the valence band. The Fermi level in the *p*-type samples is well below the energy level of potential donor impurities. Therefore, virtually all the donors are ionized. Following the argument by Kaufmann (Ref. 7), at room temperature, $\beta=3.6$ and $K=(N_v/\beta)\exp(-E_a/kT)=1.8\times10^{16}$ cm^{-3}. This leads to $N_D^+=N_D=[N_AK/(K+p)]-p$, where N_D^+ is the density of ionized donors. The electrical neutrality condition is $N_A^-=N_D^++p$ for *p*-type material. Therefore, the total concentration of charged impurities is in the following form: $N_T=N_A^-+N_D^+=[2N_AK/(K+p)]-p$, and the average potential depth can be rewritten as $\Gamma=(e^2/4\pi\varepsilon\varepsilon_0)\cdot\{\{[2N_AK/(K+p)]-p\}^{2/3}/p^{1/3}\}$. Consequently, the blue band emission energy is given by $E(\hbar\omega)=E_g-(E_D+E_A)-2\Gamma=E_g-E_D-E_A-2\cdot(e^2/4\pi\varepsilon\varepsilon_0)\cdot\{\{[2N_AK/(K+p)]-p\}^{2/3}/p^{1/3}\}$.

[40] Since the value of $2N_AK/(K+p)$ is more than an order-of-magnitude larger than p in the films and $p\gg K$, Γ can be simplified as $\Gamma=(e^2/4\pi\varepsilon\varepsilon_0)\cdot\{[(2N_AK/p)^{2/3}]/p^{1/3}\}=S\times p^{-1}$, where $S=(e^2/4\pi\varepsilon\varepsilon_0)\cdot(2N_AK)^{2/3}=2.3\times10^{16}$ eV cm^{-3} is a constant.