Optically detected magnetic resonance of GaN films grown by organometallic chemical-vapor deposition

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(Received 28 November 1994; revised manuscript received 26 January 1995)

Photoluminescence (PL) and optically detected magnetic resonance (ODMR) experiments have been performed on a set of GaN epitaxial layers grown by organometallic chemical-vapor deposition. Both undoped and Mg-doped GaN films were investigated. Samples were studied from three laboratories to obtain general trends and behavior. The ODMR experiments on the undoped films reveal resonances from both effective-mass and deep-donor states. These two features appear in all of the undoped GaN films and are most likely associated with an intrinsic point defect or defects. The same two donor resonances and a Mg-related quasideep acceptor resonance are found from the ODMR experiments on the Mg-doped samples. The energy level of the deep-donor state is found from ODMR spectral studies to be ~ 1 eV below the conduction-band minimum. The PL experiments provide evidence for shallow acceptors in the undoped films and in a GaN sample lightly doped by residual Mg in the growth reactor. Models are proposed that describe the capture and recombination among these shallow- and deep-donor and acceptor states. The assignments of the magnetic resonance features are compared with the latest theoretical calculations of defect states in GaN.

I. INTRODUCTION

There has been a renewed interest in group-III nitrides due to advancements in the growth of single-crystal GaN epitaxial layers by either organometallic chemical-vapor deposition (OMCVD) or molecular-beam epitaxy (MBE).[1] Much progress has been realized in spite of the large lattice mismatch ($\sim 14\%$) between the GaN films and the sapphire (Al_2O_3) substrates typically employed. A major advantage of this III-V system for technological applications is that the bandgap of GaN (3.4 eV at room temperature) can be either lowered by alloying with InN (1.9 eV) or raised by alloying with AlN (6.2 eV).

A significant barrier which has been recently overcome is the ability to dope GaN and its associated alloys *p* type. Both Mg and Zn are now commonly employed in conjunction with post-growth electron irradiation and/or thermal anneal treatments to activate the dopants.[2–4] This has led to the fabrication of commercial blue light-emitting diodes (LED's) with the highest luminosity in this wavelength region reported to date.[5] Other optoelectronic devices based on GaN that are undergoing intense development include laser diodes[6] and ultraviolet (UV) sensors. In addition, $Al_xGa_{1-x}N$/GaN metal-semiconductor field-effect transistors (MESFET's) with high cutoff frequencies (f_{max}) for microwave and millimeter wave applications have been reported.[7,8]

The behavior of dopants in GaN must be understood and, ultimately, controlled to achieve maximum performance of electronic[9] and optoelectronic devices based on this material system. In addition to the issues associated with the intentionally introduced dopants (e.g., the role of H with regard to passivation of the impurities[10–12]), one of the long-standing problems that has not been satisfactorily answered is the origin of the *n*-type conductivity invariably observed from the recent GaN epitaxial layers grown by OMCVD or, with the exception of one group,[13] MBE. Room-temperature electron concentrations on the order of 10^{17} cm^{-3} have been reported for these films. However, this represents a reduction of two orders of magnitude compared to what was typically reported two decades ago for films grown by, for example, the vapor phase reaction[14] between GaCl and NH_3. The high electron concentration in the earlier films was attributed to N vacancies.[15] Alternate models, such as oxygen substitutionally incorporated onto N sites,[16] have also been proposed. The question arises whether *n*-type behavior found for more recent films can also be attributed to the N vacancy or can be linked to some other intrinsic defect or residual impurity.

The behavior of both intrinsic and extrinsic defects can be determined from their emission bands as revealed by photoluminescence (PL) spectroscopy. More recently, magnetic-resonance techniques such as electron-spin resonance (ESR) and optically detected magnetic-resonance (ODMR) have provided details on the electronic states of point defects in GaN. For example, a sharp resonance attributed to conduction electrons was observed from ESR studies at 9 GHz on both zinc-blende GaN films grown by electron cyclotron resonance plasma-assisted MBE (Ref. 17) and on wurtzite GaN layers grown by low-pressure OMCVD (Ref. 18). Concurrent with the ESR studies, our ODMR experiments[19,20] on emission from undoped GaN films grown by OMCVD revealed evidence of both shallow and deep donor states. In addition, another group has recently reported ODMR signals assigned to Fe from both undoped and Fe-doped GaN layers[21] and three resonances from Mg-doped GaN films.[22]

The present work expands on our earlier ODMR papers,[19,20] which focused on the magnetic resonance detected on luminescence from a single undoped GaN film. In this work, PL and ODMR studies have been performed on a set of GaN epitaxial layers grown by OMCVD. Samples were studied from three different laboratories in order to obtain general trends and behavior. In addition, both undoped and Mg-doped GaN films were investigated. The magnetic-resonance information obtained in these studies helps to reveal whether a particular state is effective-mass (EM)-like in character or is highly localized in real space, referred to as a deep state. A major emphasis of this work is on the nature of the recombination mechanisms associated with the various emission bands reported in the literature for these films.

The paper is divided into five sections. Section I is the introduction. In Sec. II, the photoluminescence and optically detected magnetic-resonance experiments are described. In addition, a table of sample parameters is provided and the results of structural characterization studies (e.g., double-crystal x-ray diffractometry) are summarized. The results of PL and ODMR experiments performed on the undoped and Mg-doped GaN epitaxial layers are given in Sec. III. Analysis of the results and models proposed for the recombination mechanisms in these layers are provided in Sec. IV. In addition, the assignments of the various magnetic-resonance features are compared with the latest theoretical calculations of defect states in GaN. Some general comments drawn from the combined results of the PL and ODMR studies on these undoped and Mg-doped GaN layers are given in Sec. V. Overall conclusions of this work are in Sec. VI.

II. EXPERIMENTAL DETAILS

The PL and ODMR experiments were performed on a set of GaN epitaxial layers grown on (0001)-oriented sapphire substrates by low-pressure organometallic chemical-vapor deposition. The films were of wurtzite structure. A thin (250–500-Å) GaN buffer layer grown at ~500 °C was deposited on the substrates prior to the growth of the GaN layers.[23] The GaN films (1.5–6 μm) were grown at substrate temperatures between 1000 °C and 1100 °C. Results for four undoped and three Mg-doped samples are discussed in this work. Of the three Mg-doped samples, one was lightly doped by residual Mg in the OMCVD reactor and the other two were heavily doped to $>10^{19}$ cm^{-3}. Some fraction of the Mg dopant species was electrically activated post-growth using a thermal annealing procedure. Further details of the growth are described elsewhere.[24–27] The layer thicknesses and the conductivity type and carrier concentration determined from room-temperature Hall-effect and capacitance-voltage (*C-V*) profiling measurements are summarized in Table I.

Most of the samples investigated in this work have been studied by one or more additional structural and optical characterization tools. These include double-crystal x-ray diffractometry, Raman spectroscopy,[26] secondary-ion mass spectroscopy (SIMS), and plan-view transmission electron microscopy (TEM).[28] Some of these results are noted below or referred to later in the paper.

The double-crystal x-ray-diffractometry full width at half maximum linewidths obtained for these samples were between 250 and 500 arc sec. These are typical linewidths reported by several laboratories[24,29,30] for GaN films ~3 μm thick grown on Al_2O_3 by OMCVD. Similar linewidths have been found for layers grown on Al_2O_3 or 6H-SiC by MBE (Ref. 31). The linewidths reflect the high misfit dislocation densities ($\sim 10^{10}$ cm^{-2}) in the films due to the large lattice mismatch with the substrates.[28]

The PL from the GaN layers was excited with above-band-gap radiation provided by an Ar^+-ion laser operating at 351.1 nm (3.53 eV) or with the 325.0-nm line (3.81 eV) from a He-Cd laser. The emission from 1.7–3.6 eV was analyzed by a 0.85-m double-grating spectrometer and detected by a UV-enhanced GaAs photomultiplier tube (PMT). A continuous-flow liquid-helium cryostat was used to carry out the PL studies at 6 K.

TABLE I. Summary of pertinent parameters of the GaN epitaxial layers investigated in this work (NRL is the Naval Research Laboratory, and APL is the Applied Physics Laboratory).

Sample Designation	Source	Thickness	Doping	Carrier concentration (300 K)
No. 1 (No. 304021)	APL	1.3 μm	None	*n*-type (highly resistive)
No. 2 (No. 30624A)	NRL	3.6 μm	None	$n \sim 3.4\times10^{16}$ cm^{-3}
No. 3 (GaN No. 1)	APA Optics	5.6 μm	None	$n \sim 3.0\times10^{16}$ cm^{-3}
No. 4 (No. 30924A)	NRL	1.6 μm	None	$n \sim 3.0\times10^{17}$ cm^{-3}
No. 5 (No. 304051)	APL	1.3 μm	Mg	*p*-type (highly resistive)
No. 6 (No. 1136)	APA Optics	2.6 μm	Mg	$p \sim 2.0\times10^{17}$ cm^{-3}
No. 7 (No. 1151)	APA Optics	0.8 μm	Mg	$p \sim 1.0\times10^{18}$ cm^{-3}

The ODMR was detected as the change in the total intensity of PL which was coherent with the on-off amplitude modulation of 50 mW of microwave power. The GaN epitaxial layers were studied in a K-band (24 GHz) spectrometer. One of the samples (No. 3) was also analyzed in a Q-band (35 GHz) spectrometer. For the ODMR, the PL was continuously excited by 3.53-eV radiation with power densities between 0.15 and 1.5 W/cm^2. The emission was detected by a UV-enhanced Si photodiode. The samples were studied under pumped-helium conditions ($T \sim 1.6$ K) in commercial optical cryostats. The dc magnetic field for the 24-GHz spectrometer was provided by a 9-in. pole-face electromagnet with a maximum field of 1.1 T. A 7-T split-coil superconducting magnet was used for the ODMR studies at 35 GHz. Calibration of the g values for the ODMR was carried out by performing ESR of diphenylpicrylhydrazyl (DPPH).

ODMR spectral studies were also performed on some of the GaN epitaxial layers. Two different methods were employed. First, with the applied dc magnetic field fixed at the peak position of a particular resonance feature, the emission was analyzed with a 0.25-m double-grating spectrometer and detected by a UV-enhanced GaAs PMT. Second a series of visible and near-infrared cutoff filters were placed in front of the Si photodiode employed for the swept-field ODMR experiments in this work. The ODMR for a certain spectral range was then obtained by the digital subtraction of the raw spectra found for the different individual filters.

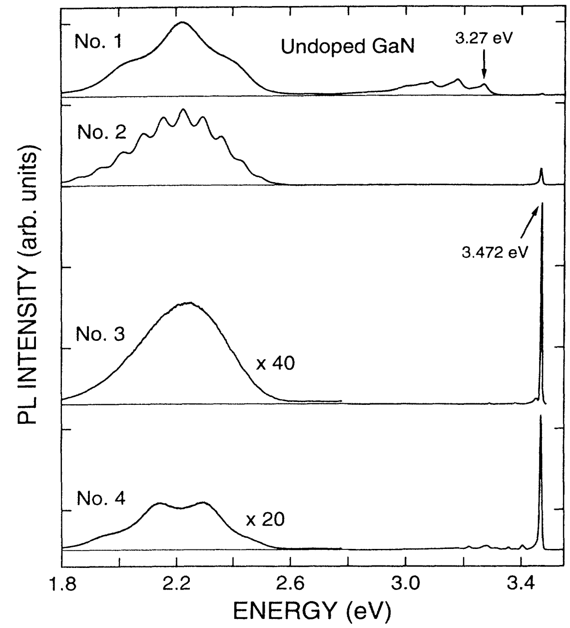

FIG. 1. Photoluminescence spectra obtained from several undoped GaN epitaxial layers at 6 K.

III. RESULTS

A. Undoped films

The layers were all found to be n type from room-temperature Hall-effect measurements, as is usually the case for undoped GaN. The photoluminescence obtained at 6 K under similar excitation power conditions from the four undoped GaN samples is shown in Fig. 1. Three PL bands were found with different strengths from the individual samples. The sharp band at 3.472 eV is the dominant emission observed for samples No. 3 and 4. This band (referred to as the I_2 line) has been assigned to excitons bound to neutral donors[32] and is considered a PL fingerprint of n-type GaN. The linewidth of this band for these samples, $\sim$2.7–3.2 meV, indicates the high quality of the films. The second band is characterized by a zero-phonon line at 3.27 eV and a series of LO-phonon replicas ($E_{\mathrm{LO}} \sim 92$ meV) at lower energies. This emission is most easily observed for sample No. 1. The band is also readily observed from the three other undoped layers at low excitation power densities. This emission has been assigned to shallow-donor–shallow-acceptor pair recombination.[33] The third band is a broad emission with peak energy near 2.2 eV. This so-called yellow band is the strongest emission observed from samples Nos. 1 and 2. With sufficient gain, the 2.2-eV band can also be detected from samples Nos. 3 and 4. Except for the periodic features due to the interference effects found for samples Nos. 1, 2, and 4, this emission is usually absent of structure. The Gaussian line shape is typical for deep emission bands in a variety of semiconductors and, hence, suggests a strong electron-lattice-coupling interaction. This band has been found to be significantly enhanced by doping with C during growth[34] or by ion implantation.[35] One group studied this band in much detail and found that the recombination was due to donor-acceptor pairs.[34] They proposed that the emission involved a shallow donor ($E_D = 25$ meV) and a C-related deep acceptor ($E_A = 860$ meV).

ODMR spectra obtained at 24 GHz on the 2.2-eV emission band from sample No. 3 are displayed in Fig. 2. ODMR could not be observed on the strong excitonic emission at 3.472 eV due to a short lifetime ($\tau \ll 1$ μs) of this band.[33] The results are shown for the applied magnetic field (**B**) aligned perpendicular and parallel to the **c** axis. Two luminescence-increasing resonances were found on the deep emission band.[19] The features are described in turn below.

The strongest signal (labeled EM in Fig. 2) is a sharp resonance with $g_{\parallel} = 1.9515 \pm 0.0002$ and $g_{\perp} = 1.9485 \pm 0.0002$. The full width at half-maximum amplitude of this resonance is $\sim$2.2 mT. The sense of g anisotropy (i.e., $g_{\parallel} > g_{\perp}$) is the same as that found for shallow donors in the wurtzite semiconductors CdS (Ref. 36) and ZnO.[37] A line with identical g values and a linewidth of 0.5 mT was previously observed by ESR studies of similar GaN samples.[18] In addition, an isotropic signal with the same average g value (i.e., $g \sim 1.95$) was reported from ESR of undoped GaN layers with zinc-blende crystal structure.[17] This line was assigned by these groups to electrons with effective-mass (EM) character from a g-value analysis, the linewidth and its temperature dependence, and the mi-

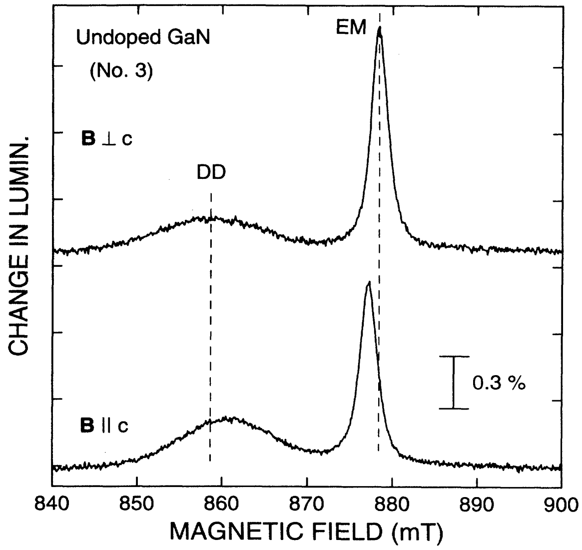

FIG. 2. ODMR spectra obtained at 24 GHz detected on the 2.2-eV PL band from undoped GaN sample No. 3. Results are shown for **B** oriented perpendicular and parallel to the crystalline **c** axis. The dashed lines indicate the positions of the broad (labeled DD) and sharp (labeled EM) features with **B**⊥**c**.

crowave power saturation.

The second signal, labeled DD (deep donor) (Ref. 38) in Fig. 2, detected on the 2.2-eV band from sample No. 3 has been revealed only by the ODMR experiments.[19,20] The full width at half-maximum of the resonance is ~13 mT with $g_{\parallel}=1.989\pm0.001$ and $g_{\perp}=1.992\pm0.001$. The line is much broader and the sense of the g anisotropy (i.e., $g_{\perp}>g_{\parallel}$) is opposite to that found for the sharp resonance described above.

As noted in Sec. II, the emission from sample No. 3 was also studied in a 35-GHz spectrometer. The resonance positions of the two ODMR signals were found to scale in proportion to the change in microwave frequency. This result demonstrates that the resonances have unique g values. In addition, the linewidth of the broad ODMR signal was the same as that found from the 24-GHz study.

ODMR detected on the 2.2-eV emission bands (see Fig. 1) from several undoped GaN epitaxial layers (including sample No. 3 discussed above) grown by three laboratories is shown in Fig. 3. Two ODMR signals (labeled EM and DD) with similar g tensors and linewidths to those described above are found for all the samples. Also, the broad ODMR signal is the dominant feature observed for samples Nos. 1, 2, and 4, in contrast to what is found for sample No. 3. The slightly different resonance field positions of the sharp and broad lines reflect small changes in microwave frequencies among the four samples.

ODMR spectra studies were also performed on sample No. 3 to determine specifically which parts of the 2.2-eV emission band contribute to the ODMR (see Fig. 4). The spectral dependences were obtained, as described in Sec. II, with the magnetic field fixed at the peak of the sharp ODMR signal (**B**=878 mT) and at the peak of the broad

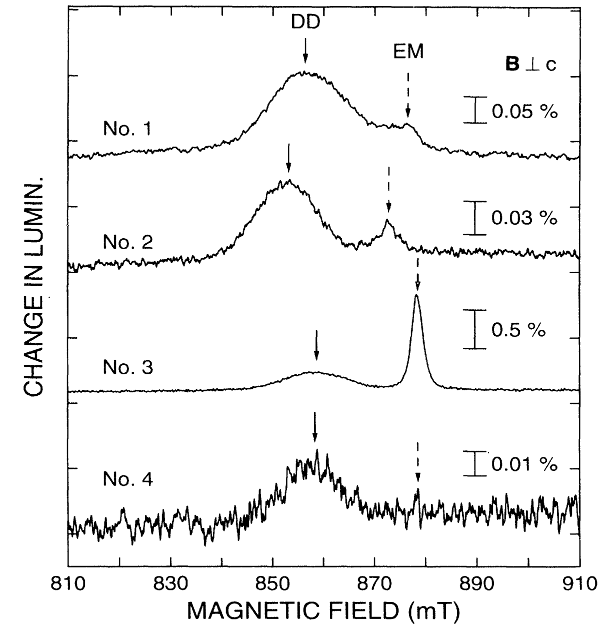

FIG. 3. ODMR spectra found on the deep emission bands from several undoped GaN films with **B**⊥**c**. Magnetic-resonance features labeled EM (solid arrows) and DD (dashed arrows) are observed in all these samples. The slightly different resonance field positions of each line reflect small changes in microwave frequency for each spectrum.

ODMR feature (**B**=858 mT). The spectral behavior is found to be identical within the signal-to-noise ratio to that observed for the 2.2-eV emission band.

B. Mg-doped films

The photoluminescence obtained at 6 K from the three Mg-doped GaN films is shown in Fig. 5. As noted in Sec.

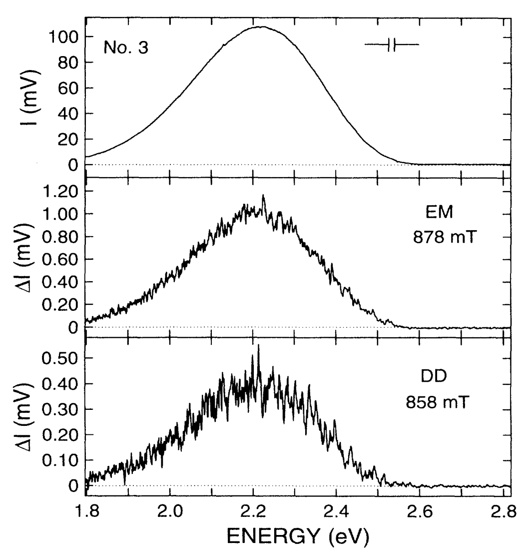

FIG. 4. The PL and spectral dependences of the ODMR of undoped GaN sample No. 3 with **B**⊥**c**. Results are shown for **B** fixed at the resonance positions of the sharp and broad features (see Fig. 2) described in the text.

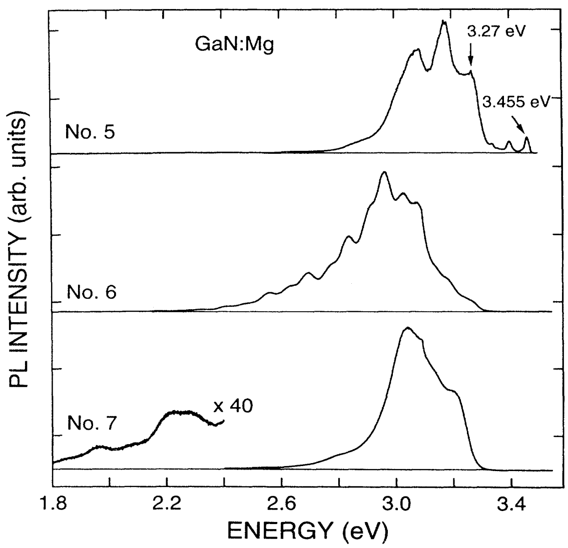

FIG. 5. Photoluminescence spectra obtained from a lightly Mg-doped GaN sample (No. 5) and from two highly Mg-doped GaN films (Nos. 6 and 7). All samples exhibit emission near 2.0 eV when the gain is sufficiently expanded.

II, one of the layers (sample No. 5) was lightly doped by residual Mg in the growth apparatus (referred to as a memory-doping effect). This sample was determined to be highly resistive from Hall-effect measurements. Samples Nos. 6 and 7 were intentionally doped with Mg to concentrations greater than 10^{19} cm^{-3}, and were found to have room-temperature hole concentrations of $\sim 2\times 10^{17}$ and 1×10^{18} cm^{-3}, respectively. A variety of emission bands were found from these samples. The dominant emission common to all three samples is donor-acceptor pair recombination and is discussed below.

A weak PL band at 3.455 eV was found for sample No. 5. This line (referred to as the I_1 line) has been previously observed from similar lightly Mg-doped GaN films, and was attributed to the decay of excitons bound at neutral acceptor sites.[32,39] This emission was not observed for the more heavily Mg-doped samples investigated in this work, nor from PL studies of similar Mg-doped films reported by several other groups.[2,22,39] The lightly doped sample also exhibits some evidence of phonon-resolved emission with a zero-phonon line at 3.27 eV and two LO-phonon replicas. This PL has been reported for similar residually Mg-doped films[39] and for Mg-doped GaN with [Mg]$=1.6\times 10^{19}$ cm^{-3} (Ref. 2). The emission was attributed to recombination between unidentified shallow donors and shallow (i.e., effective-mass-like) Mg acceptors with $E_A \sim 190$ meV (Ref. 39). Note that this same emission was found, though only under much lower excitation power conditions, from the undoped films discussed in Sec. III A. The dominant emission observed from the heavily Mg-doped samples is a broad band with peak energy near 3 eV, approximately 0.25 eV below the zero-phonon line found at 3.27 eV from sample No. 5. Most of the structure found in the spectrum from sample No. 6 is due to interference effects as described previously. This band has been observed from similar Mg-doped samples studied by several other workers.[2,22,39] Finally, weak emission at energies below ~ 2.3 eV was found, with sufficient gain, from all three Mg-doped samples (see, e.g., the bottom panel in Fig. 5).

A representative ODMR spectrum obtained on emission less than 3.0 eV from one of the highly Mg-doped GaN layers (sample No. 7) is shown in Fig. 6. Three luminescence-increasing resonances are well-resolved with the magnetic field oriented 30° from the **c** axis. The features labeled EM and DD have the same g tensors as found for the two lines detected on the 2.2-eV band from all the undoped GaN films discussed above. The linewidth of the resonance labeled EM is ~ 17 mT, almost an order of magnitude larger than the corresponding line in the undoped layers (see, e.g., Fig. 2). The third ODMR detected on this emission, labeled Mg in Fig. 6, is also described by an axial g tensor with $g_{\parallel}=2.080\pm 0.005$ and $g_{\perp}=2.000\pm 0.005$. This resonance was first reported by Kunzer *et al.* from ODMR studies of similar Mg-doped GaN films,[22] and has only been seen from such samples. Also, the line labeled DD in Fig. 6 has similar resonance parameters to the unidentified resonance labeled X observed from a similar Mg-doped GaN layer in Ref. 22.

Representative ODMR spectra obtained on PL with energy less than 3.0 eV from the three Mg-doped GaN layers discussed in this work are shown in Fig. 7. Several features are evident. First, the line labeled EM is clearly observed for the highly Mg-doped films (samples Nos. 6 and 7) but only weakly detected for the lightly doped sample (No. 5). Second, the DD signal is strong for samples Nos. 5 and 7 but only possibly observed as a weak shoulder on the low-field edge of the EM resonance for sample No. 6. Third, the Mg resonance is a strong signal for all three Mg-doped films. Finally, a fourth ODMR

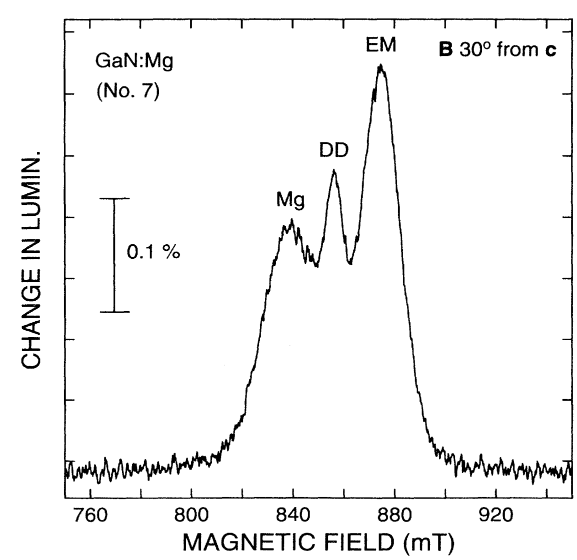

FIG. 6. ODMR spectra obtained on emission less than 3.0 eV from Mg-doped GaN film No. 7 with **B** oriented 30° from **c**. Three resonances are clearly observed. The assignments are discussed in the text.

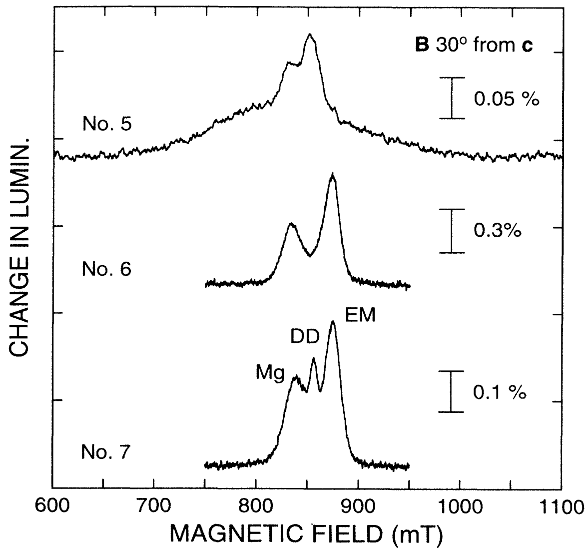

FIG. 7. ODMR spectra obtained on emission less than 3.0 eV from several Mg-doped GaN layers with **B** aligned 30° from **c**.

signal is found on the emission from sample No. 5. The line is quite broad (FWHM ~170 mT) compared to the other signals observed from these samples. The g value is ~2.09±9.02 for **B** 30° from **c**. Angular rotation studies of this sample reveal that the g value is fairly isotropic but the intensity of the line is highly anisotropic. The maximum amplitude is found with **B** oriented 30°–60° away from the **c** axis. However, the line is very weak with **B** aligned either parallel or perpendicular to the **c** axis. A compilation of the magnetic-resonance parameters of the four ODMR signals found from both the undoped and Mg-doped samples investigated in this work is shown in Table II.

ODMR spectral studies were also performed on some of the Mg-doped layers. The results obtained while analyzing the strong emission band near 3.0 eV from sample No. 7 with **B** fixed at the EM and Mg-related resonance positions are shown in Fig. 8. The spectral behaviors of the two signals are very similar. However, the peak ODMR response of both features is ~100 meV below the peak energy (~3.1 eV) of the emission band.

ODMR spectral studies were also carried out on sample No. 7 with a series of visible and near-infrared filters inserted in front of the Si photodiode due to the weak emission observed below 2.5 eV (see Fig. 5). The results are shown in Fig. 9. The EM and Mg signals are clearly detected on the strong emission near 3.0 eV, confirming the spectral studies of Fig. 8. A different spectrum is found for PL less than 2.0 eV. The DD and Mg-related features are the dominant resonances observed. Note that the Mg resonance is common to both spectral regions.

IV. DEFECT STATES AND RECOMBINATION MECHANISMS

Undoped layers

As discussed above, two luminescence-increasing resonances are observed on the 2.2-eV deep emission bands from all of the undoped GaN layers investigated in this work. Due to the identical g tensor with the resonance found from electron paramagnetic resonance (EPR) studies on similar samples,[18] the sharp ODMR feature (labeled EM in Fig. 2) is assigned to electrons bound at effective-mass donors.

The broader ODMR feature (labeled DD in Fig. 2) is described by g values slightly less than the free-electron g value of 2.00, but larger than the EM donor g values. In addition, the similar linewidth of the broad resonance found from the K- and Q-band experiments indicates that it arises from unresolved hyperfine interactions between the electronic spin and the central nuclear spin or the spin of the nuclei of nearby atoms. This interaction can be significant for deep electronic levels due to the localized nature of the wave function. Also, the resonance cannot be assigned to a shallow hole state associated with the $J_Z=\pm\frac{3}{2}$ ground-state valence band[32] which is split above the $J_Z=\pm\frac{1}{2}$ valence band by ~22 meV due to the wurtzite structure crystal field, since the expected g tensor is $g_{\parallel}\sim$, $g_{\perp}=0$ (Ref. 40). These characteristics taken together lead to an assignment of this resonance to a deep-donor (DD) state. Further evidence for this identification is revealed by the ODMR studies of the Mg-doped samples as discussed in Sec. IV B.

In the first report of ODMR (Ref. 19), the deep-donor state was tentatively assigned to the N vacancy due to the similarity of the resonance parameters with those of anion vacancies in other III-V and II-VI semiconductors such as the O vacancy in ZnO.[41] In a subsequent paper,[20] both shallow- and deep-donor states revealed from the ODMR experiments were linked with the two N-vacancy energy levels predicted by recent tight-binding calculations.[42] According to this model, the neutral N vacancy is a triple donor with two electrons in a localized (deep) state of a_1 character ~150 meV below the conduction-band edge, and one electron in a resonant state above the conduction-band minimum. This electron

TABLE II. Magnetic-resonance parameters of the defect states observed in this work.

Defect	$g\parallel c$	$g\perp c$	g 30° from **c**	ΔB (mT)
EM donor	1.9515±0.0002	1.9485±0.0002		2.2–17
Deep donor	1.989±0.001	1.992±0.001		13
Mg related	2.08±0.01	2.00±0.01		26
$S>\frac{1}{2}$ defect			2.09±0.02	170

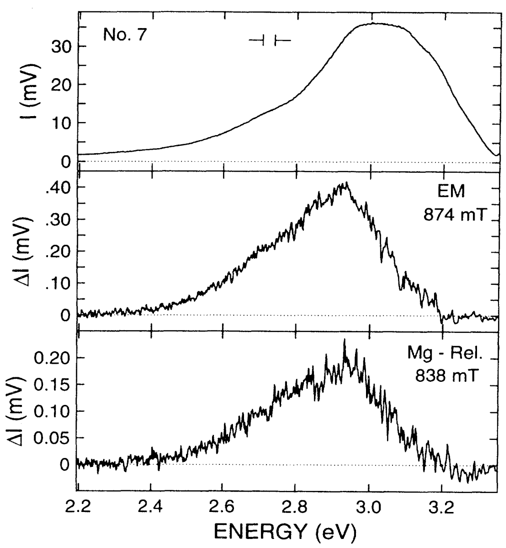

FIG. 8. The PL and spectral dependences of the ODMR of Mg-doped GaN sample No. 7 with **B** 30° from **c**. Results are shown for **B** fixed at the resonance positions of the EM- and Mg-related features (see Fig. 6) described in the text.

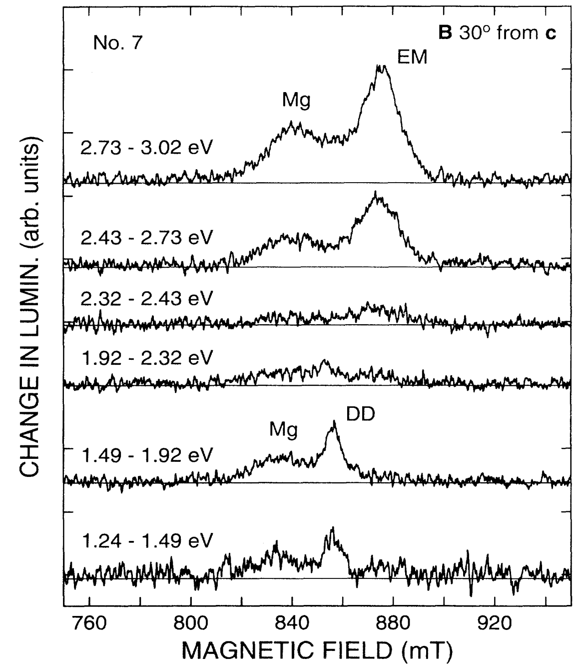

FIG. 9. The spectral dependences of the ODMR of Mg-doped GaN layer No. 7 obtained with a series of visible and near-infrared filters placed in front of the Si photodiode detector as described in the text. Subtraction of digitized data gives the spectra shown. The resonances labeled EM and DD are detected on emission near 3.0 eV. The signals labeled DD and Mg are found on emission near 2.0 eV.

will autoionize and become bound by the Coulomb potential in an effective-mass state. However, the N-vacancy model for the shallow- and deep-donor states observed in the GaN films must now be called into question in light of two very recent state-of-the-art calculations[43,44] of formation energies and electronic structure for intrinsic defects in GaN. In particular, neither theory predicts a deep state in the gap associated with the N vacancy. In fact, the a_1 state is found to be resonant in the valence band due to strong Ga-Ga interactions.[44] The electronic structure predicted for the Ga interstitial by one group[43] may correspond better with the two ODMR donor states. This needs to be explored further.

The following model is proposed to describe the PL and ODMR observations from these undoped films despite the lack of an exact knowledge at this time of the chemical identity(ies) of the shallow- and deep-donor states. The model (see Fig. 10) incorporates a two-stage process involving three distinct states: the shallow- and deep-donor states and an effective-mass acceptor state revealed from the weak, phonon-resolved 3.27-eV PL band. Note that ODMR of an acceptor was not found for the undoped samples. This nonobservation can also be understood within the model described below by assuming that the defect giving rise to the DD resonance is a double donor and that some fraction of these states are singly occupied at the start due to the high Fermi level in these n-type films. The ODMR occurs via a strong spin-dependent capture (process 1 in Fig. 10) of an electron from the neutral EM donor state to a singly ionized (thus positively charged) deep double-donor state:

$$D^0+(DD)^+ + A^0 \Longrightarrow D^+ + (DD)^0 + A^0 + E_{\text{th}} \ . \qquad (1)$$

These two donor states are singly occupied initially and, thus, are paramagnetic. This process is followed by radia-

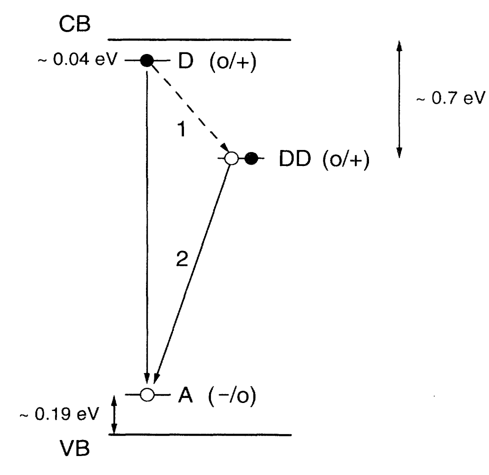

FIG. 10. The model proposed for the shallow-donor–shallow-acceptor pair recombination and deep photoluminescence band in undoped GaN epitaxial layers. Nonradiative, spin-dependent electron-capture (process 1) proceeds from a neutral, effective-mass donor state (D^0) to a singly ionized, deep double-donor state [$(\mathrm{DD})^+$]. This is followed by radiative recombination (process 2) between the deep donor state and a shallow acceptor state (A^0) with peak energy at 2.2 eV. The D^0-A^0 recombination competes weakly with the recombination through the deep donor.

tive recombination (process 2 in Fig. 10) between the neutral deep donor and effective-mass acceptor states:

$$D^{+}+(DD)^{0}+A^{0}\Longrightarrow D^{+}+(DD)^{+}+A^{-}+h\nu\ . \quad (2)$$

This part of the cycle gives rise to the 2.2-eV yellow emission band. However, no ODMR arises from this process because the neutral deep-donor state is doubly occupied with its spins paired off and, thus, not paramagnetic. Note that the 2.2-eV band is always stronger than the 3.27-eV emission band in these undoped films. This suggests that the EM donors participate much more strongly in the capture process rather than in radiative recombination with the shallow acceptors.

The binding energy of the deep donor is roughly determined if one uses the estimate for the position of the zero-phonon line associated with the yellow emission band of ~2.6 eV (Ref. 34) and a shallow acceptor binding energy of ~0.2 eV. This procedure yields a value of approximately 0.7 eV ±0.1 eV for the binding energy of the deep donor in the undoped GaN films.

It is thus proposed in this work from the above discussion that the ubiquitous 2.2-eV deep emission band involves recombination between a deep-donor state and shallow acceptor state. This contrasts with the model put forth for this PL band by previous workers.[34] It was suggested that the 2.2-eV band arose from recombination between shallow donors and deep acceptors, possibly involving C. This model was certainly logical at the time in light of the lack of evidence for additional donorlike states. However, we would also like to suggest that the shallow acceptor may be due to C. First, there is recent experimental evidence for C acting as a shallow acceptor in GaN.[13] Second, SIMS measurements of the two undoped GaN films grown at the Naval Research Laboratory discussed in this work show a positive correlation between the strength of the 2.2-eV band and the C concentration in the layers.

As noted earlier, among the undoped GaN films, the intensity of the EM shallow-donor resonance was found to be much larger than the intensity of the deep-donor resonance (feature labeled DD) only for sample No. 3. In addition, this sample exhibited the strongest excitonic recombination band at 3.472 eV relative to the strength of the 2.2-eV band. This indicates that sample No. 3 probably has the least compensation by shallow acceptor centers among the four undoped films. Similar PL and ODMR results were found for samples with approximately an order of magnitude larger electron concentrations grown by the same laboratory that provided film No. 3. Thus the relative strengths of the EM and DD resonances may be related to the degree of compensation in the undoped films. This needs to be studied further.

B. Mg-doped layers

The PL and ODMR results from the Mg-doped GaN films both indicate that heavy doping gives rise to quasideep (i.e., non-effective-mass like) acceptor states. First, evidence for shallow-donor–shallow-acceptor recombination at 3.27 eV has been observed in this work and in the work reported by several other groups only from lightly doped GaN samples or from samples with only a small fraction of the Mg dopant activated. Second, the g tensor for the Mg related state (i.e., $g_{\parallel}\sim 2.08$ and $g_{\perp}\sim 2.00$) has only a small anisotropy. This is surprising since the valence-band structure of GaN (Ref. 32) is very similar to that, for example, of 6-H SiC, a semiconductor with a similar hexagonal crystal structure.[45] For that case, highly anisotropic g tensors were observed from ODMR studies of both Ga and Al shallow acceptors.[45,46] However, a g-tensor with only a weak anisotropy ($g\sim 2$) was found for B acceptors[46] in 6-H SiC; similar to that observed for the Mg-related state in GaN. Though somewhat controversial in light of some recent work,[47,48] the ionization energy of B acceptors in 6-H SiC was found to be ~2–3 times larger than that for Ga and Al as determined from an analysis of photoluminescence spectra.[49] Thus the magnetic-resonance parameters combined with the shift of the PL band by ~250 meV below the known shallow-donor–shallow-acceptor recombination energy lead to an assignment of the Mg-related signal to a quasideep or perturbed acceptor state. The energy level of this Mg-related state was determined approximately from a combination of the PL threshold energy and the results of the ODMR spectral studies as discussed below.

As noted in Sec. III B, the same two resonances labeled EM and DD in Fig. 2 found for the undoped layers and attributed to shallow- and deep-donor states are also observed in most cases from the Mg-doped samples investigated in this work and by another group.[22] The ODMR spectral studies of the Mg-doped sample No. 7 (see Fig. 9) clearly show that the resonances labeled EM and DD can be assigned to two donor states in pair recombination with Mg-related acceptor states. These two recombination processes are depicted schematically in Fig. 11. The spectral studies (see Figs. 8 and 9) reveal that the strong emission near 3.0 eV involves recombination between the EM shallow-donor and Mg-related acceptor states while

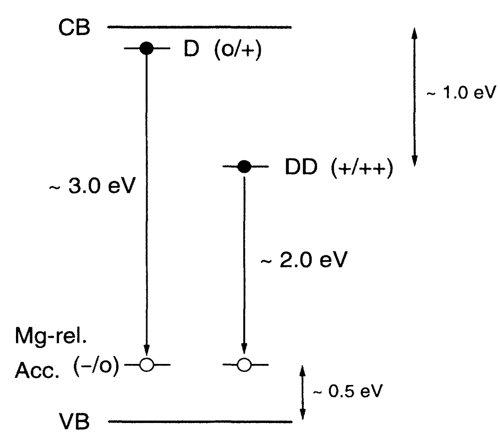

FIG. 11. The model proposed for the donor-acceptor recombination in highly Mg-doped GaN films. Two recombination pathways are revealed by the ODMR spectra studies. The emission around 3.0 eV is assigned to EM donors (D) recombining with Mg-related acceptors. The deeper emission (near 2.0 eV) is assigned to recombination between deep donors (DD) and Mg-related acceptors.

the deep-donor (resonance labeled DD) and Mg-related acceptors participate in the weak emission near 2.0 eV. Thus the binding energy of the Mg-related acceptor state is ~0.5 eV assuming the ioinization energy of the EM donor to be ~40 meV from previous work.[33] In addition, the energy level of the deep donor in the Mg-doped layers is determined to be roughly 1.0 eV ±0.1 eV below the conduction-band edge using the threshold energy (i.e., ~2.0 eV ±0.1 eV) of the emission on which the DD and Mg-related resonances are found (see Fig. 9) and the Mg-related acceptor binding energy of ~0.5 eV. Thus the energy splitting between the (0/+) and (+/++) electrical levels associated with the deep double donor is found to be 0.3 eV ±0.2 eV. Similar charge-state splittings (i.e., 0.3–0.5 eV) have been calculated recently for the Ga vacancy in GaN.[42]

The recombination that gives rise to the deep emission in the Mg-doped films is spin dependent (in contrast to the behavior observed for the undoped samples), because some fraction of the deep donors and Mg-related acceptors is singly occupied (i.e., paramagnetic). Thus the ODMR of each state can be observed. This is a consequence of the fact that the quasi-Fermi level is located below the deep-donor state for these *p*-type films.

Additional evidence that the defects responsible for the EM and DD resonances act as shallow and deep donors, respectively, in pair recombination with Mg-related acceptors in the *p*-type films comes from a comparison of the EM and DD ODMR linewidths. The narrower linewidth of the deep-donor resonance compared to that found for the EM shallow-donor resonance (see Fig. 9) indicates, as expected, that there is less overlap in real space between the wave functions of the deep donor and Mg-related acceptor state than between the wave functions of the EM shallow donors and Mg-related acceptors.

Another piece of evidence that the strong emission near 3.0 eV from the Mg-doped GaN sample No. 7 involves recombination between EM shallow donors and Mg-related quasideep acceptors is revealed from the spectral shift of the ODMR signals associated with these features (see Fig. 8). The observation that the peak in ODMR response of both features is shifted ~100 meV below the peak of the PL band partially arises from the fact that the ODMR is usually stronger for more distant donor-acceptor pairs due to the reduced exchange interaction which acts to broaden the resonances.[50] These pairs contribute on the low-energy side of the emission band. The Coulomb shift is calculated to be ~15 meV using the average separation between the donors and acceptors. This distance is determined by the larger of the two respective concentrations (i.e., the acceptor concentration of $\sim 1\times10^{18}$ cm^{-3}). While there is some evidence (top panel in Fig. 8) for shallow-donor–shallow-acceptor recombination at 3.27 eV and LO-phonon sidebands (unresolved) at lower energies, only the quasideep Mg-related acceptor states contribute to the ODMR. This accounts for most of the observed shift.

The origin of the broad resonance feature with $g \sim 2.09$ (see Fig. 7) detected on emission from the lightly Mg-doped GaN film (sample No. 5) is not clear. The highly anisotropic intensity of the signal suggests that the resonance is associated with a spin greater than $\frac{1}{2}$ center interacting with a crystal field. Possible candidates include an effective-mass acceptor with $J_Z=\frac{3}{2}$ or a triplet state.[51] The anisotropy is similar to that found from previous ODMR studies of shallow acceptors in wurtzite CdS.[36] However, the g value of the broad line is nearly isotropic and larger than the free electron g value of 2.0023. These two characteristics indicate that the resonance could be attributed to a deep acceptor. More work is required to make a definitive assignment.

V. DISCUSSION

Some further inferences can be drawn by comparing and contrasting the results from undoped and Mg-doped samples. For example, the spectral shift of the ODMR signals assigned to the EM shallow donors and Mg-related quasideep acceptors found on emission near 3.0 eV from the Mg-doped films (see Fig. 8) contrasts with the spectral dependences found for the undoped GaN layer No. 4 in which no shift was observed between the ODMR responses of the EM shallow- and deep-donor signals and the spectral behavior of the 2.2-eV PL band (see Fig. 4). This is consistent with the capture/recombination model proposed for this emission since the EM shallow donors act, in effect, as a source of electrons for capture onto the deep-donor state. No shift is found because only one of the potentially ODMR-active states (i.e., the deep donor) participates in the 2.2-eV recombination.

Some additional remarks can be made based on the observation of the shallow- and deep-donor states in the undoped and most of the Mg-doped GaN samples investigated in this work and from parallel studies by another group.[22] First, the fact that both donor states appear in most of these samples suggests that they arise from an intrinsic defect or defects. This still needs to be verified. We note that recent photoemission capacitance transient spectroscopy experiments on *n*-type GaN reveal evidence for a series of deep-level states located ~0.9–1.5 eV below the conduction-band edge.[52] Second, these donor states will act as compensation centers in the Mg-doped samples or, in general, for GaN films doped with any other *p*-type dopant species. This is one of the reasons why it is difficult to fabricate *p*-type GaN with room-temperature hole concentrations greater than 1×10^{18} cm^{-3}. Third, this work provides experimental evidence to support the notion of compensation by intrinsic donor defects that arise more easily due to reduced formation energies when impurities are introduced to make *p*-type wide-band-gap semiconductors.[53,54] For example, a native defect compensation mechanism was proposed to explain the difficulty in achieving high *p*-type conductivity in ZnSe.[53]

VI. SUMMARY

Photoluminescence and optically detected magnetic-resonance experiments have been performed on a set of GaN epitaxial layers grown by organometallic chemical

TABLE III. Summary of the defect states and their emission bands from the GaN films investigated in this work.

Defect/state	Material	PL	Character	Energy level
EM donor	All	3.472 eV, 3.0–3.27 eV, (2.2 eV)	CB	E_c-42 MeV[a]
Deep donor (DD)	All undoped, most doped	2.2 eV, 2.0 eV	Deep donor	$E_c-1.0$ eV[b]
Mg related	Lightly and heavily Mg doped	3.0 eV, 2.0 eV	Perturbed acceptor	$E_v+0.5$ eV[b]
EM acceptor	Lightly Mg doped	3.455 eV, 3.27 eV	VB	$E_v+0.19$ eV[c]

[a]Reference 33.
[b]This work.
[c]Reference 39.

vapor deposition. Samples were studied from several laboratories to obtain general trends and behavior. Undoped and Mg-doped GaN films were both investigated. The defect states inferred from these experiments are summarized in Table III. Four defect states are revealed by the PL and/or ODMR experiments. Also listed in Table III are the PL bands in which the various defect centers participate either directly or indirectly.

The ODMR experiments on the undoped GaN films reveal evidence for both an effective-mass (EM) donor state and a deeper donor state. These states are observed on the deep 2.2-eV emission band. It is proposed that the ODMR of these states is revealed through a nonradiative, spin-dependent capture process between the shallow- and deep-donor states. The capture process is followed by radiative (but not spin dependent) recombination between the deep-donor state and a shallow acceptor (possibly C on a N site).

The same two donor states and a Mg-related quasideep acceptor are found from ODMR experiments on the Mg-doped samples. ODMR spectral studies on a heavily Mg-doped GaN film show evidence that the strong emission near 3.0 eV involves recombination between the EM donor and Mg-related quasideep acceptor states while the deep donor and Mg-related deep acceptor participate in the weak emission near 2.0 eV.

An additional, unidentified broad resonance is observed from a GaN layer lightly doped with Mg. The highly anisotropic intensity of the signal suggests that the resonance is associated with a defect with spin $>\frac{1}{2}$ such as an effective-mass acceptor or a triplet state. The weak g anisotropy and the fact that the g value (~ 2.09) of the line is larger than the free-electron g value of 2.0023 suggest that the resonance could be attributed to a deep acceptor. Further work is needed to make a clear assignment.

The observation that the shallow- and deep-donor states appear in all of the undoped and most of the Mg-doped GaN films investigated in this work suggests that these states are associated with an intrinsic point defect or defects. This still needs to be verified. Also, more work is required to make definitive chemical identifications of these donors. Optically detected electron-nuclear double-resonance (ODENDOR) experiments which can, in principle, probe the local environment of defect centers have been attempted to address this issue. However, these experiments have not been successful to date, probably due to the random strain in the layers which tends to broaden the resonances to such a degree that they cannot be observed. Finally, this work provides strong evidence in the p-type films for compensation via a native defect mechanism predicted theoretically for wide-band-gap semiconductors such as GaN.

ACKNOWLEDGMENTS

We thank W. E. Carlos (NRL) and M. Kunzer (Fraunhofer Institut, Freiburg) for many helpful discussions and the exchange of results prior to publication. Thanks are also due N. M. Johnson (Xerox PARC, Palo Alto) for SIMS analyses and to S. C. Binari (NRL) and G. Kelner (NRL) for electrical transport measurements of some of the samples investigated in this work. L. B. Rowland acknowledges support from a NRC-NRL Cooperative Research Associateship.

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