Optical detection of magnetic resonance in electron-irradiated GaN

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Four new optically detected magnetic resonances are observed in photoluminescence bands at $\sim$ 0.85 and $\sim$0.93 eV, which are produced in epitaxial wurtzite films of GaN by 2.5-MeV electron irradiation. One of these reveals a resolved hyperfine interaction with a single Ga nucleus, indicating a displaced Ga atom of some kind. It is tentatively identified as a complex involving interstitial Ga_i^{2+}. [S0163-1829(97)51316-6]

There is considerable current interest in the role of point defects in GaN, stimulated by the successful application of it and its alloys in blue-light emitting and laser diode devices. However, little concrete information has been obtained so far. One problem is that many of the conventional structure sensitive experimental techniques such as electron-paramagnetic resonance or local mode vibrational mode spectroscopy are difficult to apply because of the thin-layer thicknesses of the epitaxially grown material currently available.

Optical detection of magnetic resonance in photoluminescence (PL-ODMR) does not suffer from this difficulty and several workers have reported such studies of as-grown GaN layers.[1–7] Several of these studies have concentrated on an ever-present luminescence band[8] at 2.2 eV, which, in undoped n-type material, reveals a broad resonance of an unidentified deep defect plus a sharper resonance generally attributed to the dominant donor.[1–4] Unfortunately, no fine or hyperfine structure is resolved so that defect identification and structure determination have not been possible. A recent promising report of optical detection of electron-nuclear double resonance in the band has revealed weak Ga hyperfine structure in the donor resonance, but again the interpretation as to whether the Ga atom is in the core of the donor state, or just that of bulk-distant lattice atoms, could not be unambiguously established.[9] In addition, there remains a controversy as to whether the spin-dependent process being detected is the 2.2-eV irradiation itself,[8,10] or simply a feeding mechanism to a separate radiation source.[1,4]

In the present paper, we present promising results of PL-ODMR studies of GaN layers after 2.5-MeV electron irradiation. We find two overlapping luminescence bands produced in the near infrared, each of which displays ODMR signals. For one of the signals, we interpret its well-resolved structure as arising from the hyperfine interaction of a single displaced Ga atom. This resolved hyperfine structure observed for a defect in GaN, and the larger anisotropy for some of the other signals, holds promise that PL-ODMR studies of electron-irradiated materials may ultimately represent the best approach to unraveling the properties of the intrinsic vacancies and interstitials and their interactions in the nitrides.

The sample investigated was a 1-μm-thick wurtzite layer of GaN grown by metalorganic vapor phase epitaxy (MOVPE) on a sapphire substrate with a thin AlN buffer layer, as described elsewhere.[11] It was not intentionally doped, the net n-type carrier concentration being in the mid-10^{16}-cm^{-3} range. After first PL-ODMR characterization in the as-grown state, it was subsequently irradiated at room temperature by 2.5-MeV electrons from a Van de Graaff accelerator to a dose of 1×10^{18} cm^{-2}. The luminescence was excited by either the 351-nm line of an argon ion laser or the 325-nm line of a HeCd laser ($\sim$15 mW), and PL-ODMR was studied at 1.5 K in a 35-GHz spectrometer, the details of which have been described previously.[12]

Figure 1 shows a comparison of the visible luminescence under low-resolution conditions ($\sim6\,\mu$m, corresponding to $\sim$60 meV at 3.5 eV) before and after the irradiation. Before irradiation, three distinct bands that are typical of high-quality n-type GaN layers are observed. The bands at 3.47 and 3.27 eV have been assigned as exciton-related,[13] and to shallow-donor-to-shallow-acceptor recombination,[14] respectively. As described above, the origin of the 2.2-eV band is at present not established. Our ODMR studies of the 2.2-

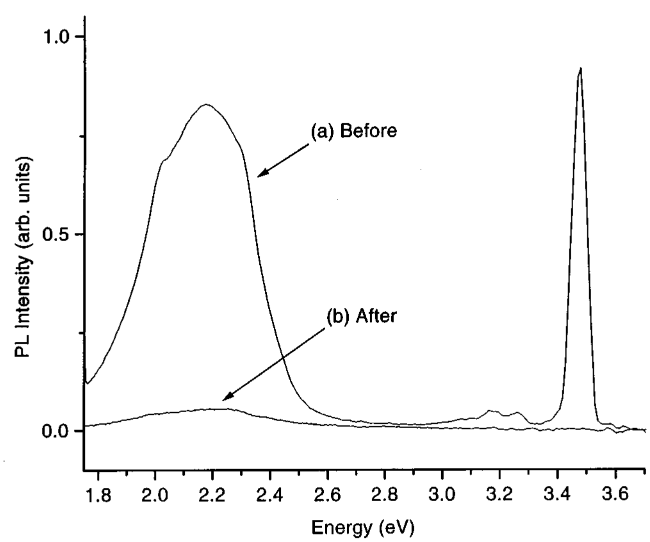

FIG. 1. Visible luminescence at 1.5 K, (a) before, (b) after, e irradiation.

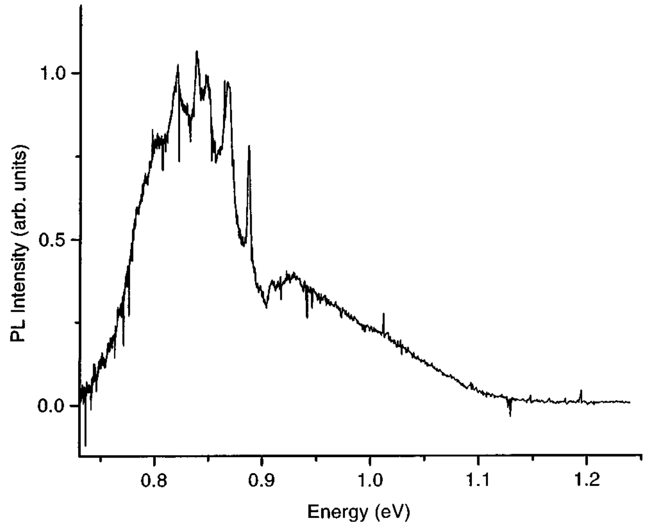

FIG. 2. Luminescence in the near infrared produced by the *e* irradiation.

eV band reveal the same two ODMR signals observed by other workers—one attributed to the shallow donor with $g_\parallel = 1.951$, $g_\perp = 1.949$—the other, unidentified, with $g_\parallel = 1.989$, $g_\perp = 1.992$.

After electron irradiation, the two higher-energy bands have vanished completely, and the 2.2-eV band has decreased by a factor of ~15. (The same two ODMR signals can still be detected weakly in the 2.2-eV band.) At the same time, a new luminescence structure has emerged in the infrared, as shown in Fig. 2, which was not present before irradiation. At least two overlapping bands are apparent, with maxima at ~0.85 and ~0.93 eV. The lower-energy one reveals sharp phonon structure. Separating the two spectral regions with low pass (<0.83 eV) and high pass (>0.88 eV) optical interference filters, different ODMR signals are observed.

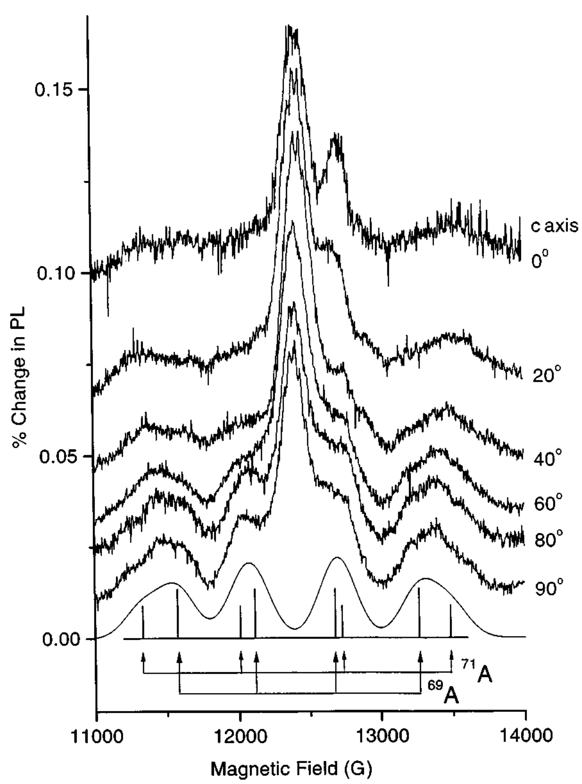

FIG. 3. ODMR spectra detected in the higher energy (>0.88 eV) luminescence band of Fig. 2 vs orientation of **B** with respect to the *c* axis. A simulated spectrum for hyperfine interaction with the naturally abundant ^{69}Ga and ^{71}Ga isotopes of a single Ga atom is compared to the **B**$\perp c$ spectrum. The recorded ODMR spectra have been displaced vertically for clarity.

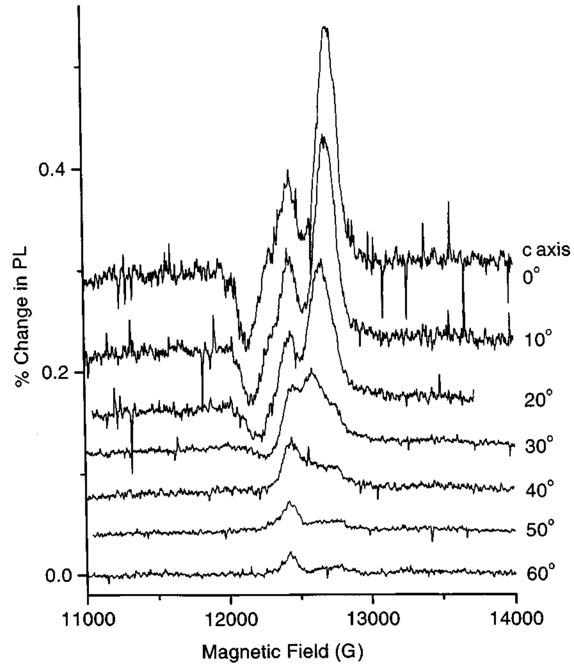

FIG. 4. ODMR spectra detected in the lower-energy (<0.83 eV) luminescence band of Fig. 2 vs orientation of **B** with respect to the *c* axis. The recorded ODMR spectra have been displaced vertically for clarity.

In Fig. 3, we show the ODMR spectra observed in the higher-energy range vs orientation of **B** with respect to the wurtzite *c* axis (epitaxial growth direction). The most prominent central line ($LE1$) is slightly anisotropic with $g_\parallel = 2.004 \pm 0.001$, $g_\perp = 2.008 \pm 0.001$. An additional weaker line is observed to emerge and sharpen up in a narrow range around $\mathbf{B} \parallel c$ at $g_\parallel = 1.960 \pm 0.002$. It appears to shift to lower field as **B** rotates away from the *c* axis becoming lost quickly under $LE1$. We label this $LE2$. Additional structure is present that sharpens up and emerges clearly as a four-line spectrum ($LE3$) when the magnetic field orientation approaches $\mathbf{B} \perp c$. This can be simulated very well, as shown also in the figure, as arising from hyperfine interaction with the two naturally abundant isotopes, ^{69}Ga (60.4%, $g_N = 1.341$) and ^{71}Ga (39.6%, $g_N = 1.703$), of a single Ga atom. For the simulation, $g_\perp = 2.002 \pm 0.005$, $^{69}A_\perp = 1580 \pm 50$ MHz, giving the positions and relative amplitudes of the sticks in the figure, which were then convoluted with a Gaussian (rms width of 125 G) to account for unresolved additional hyperfine broadening with neighbors.

Figure 4 shows the ODMR spectrum observed in the lower-energy range of the luminescence, <0.83 eV. Three lines are apparent for $\mathbf{B} \parallel c$. The line at 12 400 G is tentatively

TABLE I. Spin Hamiltonian parameters.

Defect	$\mathbf{g}\|c$	$\mathbf{g}\perp c$	A^{69}/h (MHz)	PL band
$LE1$	2.004 ± 0.001	2.008 ± 0.001		both
$LE2$	1.960 ± 0.002	~2.03		both
$LE3$		2.002 ± 0.005	1580 ± 50	>0.88 eV
$LE4$	2.050 ± 0.002	~1.97		<0.83 eV

assigned to the $LE1$ defect. There are two additional lines, one positive at $B=12\,716$ G, and one negative ($LE4$, decrease in luminescence) at $B=12\,145$ G. The positions of these lines shift and their intensities decrease as **B** is rotated away from the c axis, the lines disappearing when **B** is 60° from the c axis. Treating them as two separate $S=\frac{1}{2}$ defects, their dependencies in this angular range can be matched with $g_{\|}=2.050\pm0.002$, $g_{\perp}\sim1.97$ for $LE4$, and $g_{\|}=1.960\pm0.002$, $g_{\perp}\sim2.03$ for the positive signal. We tentatively identify the positive signal with $LE2$, seen also in the higher-energy band, Fig. 3, from their identical $g_{\|}=1.960$ values and apparent angular dependences. The results for all four ODMR signals are summarized in Table I.

We conclude that the luminescence and all of the ODMR signals arise from the GaN epitaxial layer, and not from the sapphire substrate, by the observation of little difference in their intensities between front vs back surface excitation with 325 nm light (above band gap for GaN, below for sapphire), and by their complete disappearance upon subsequent mechanical removal of the irradiated epitaxial GaN layer. Little else can be concluded about the origin of the observed ODMR signals at this stage, however, with the exception of $LE3$. For it, the resolved hyperfine interaction strongly suggests that it arises from a displaced Ga atom of some kind. This, in turn, suggests a gallium interstitial or antisite, either isolated or complexed with another defect.

The mechanism for the angular-dependent broadening of the $LE3$ hyperfine interaction is not obvious. It clearly suggests a lower symmetry than axial along the c axis, ruling out the paramagnetic Ga_i^{2+} charge state of the *isolated* gallium interstitial, which should be S like, reflecting only weakly the axial symmetry of the host wurtzite lattice. On the other hand, isolated Ga_i^{0}, or the isolated $\mathrm{Ga}_{\mathrm{As}}$ antisite in its paramagnetic $\mathrm{Ga}_{\mathrm{As}}^{-}$ charge state, would be orbitally degenerate and a lower symmetry could result from a static Jahn-Teller distortion. In these cases, however, the wave function on the central Ga atom should be p like, inconsistent, perhaps, with the large observed mostly isotropic hyperfine interaction ($\sim$20% of the free atom $4s$ value[15]). Of course, a complex of either interstitial or antisite could have reduced symmetry. But even in this case, reduced symmetry would not alone explain the breadth with $\mathbf{B}\|c$, if only anisotropy of **A** and **g** are important because the spectra from all equivalent distortions should superpose at this orientation. The presence of a quadrupole interaction comparable in magnitude to the hyperfine interaction might explain the results. In this case, additional forbidden $\Delta m\neq0$ nuclear flip transitions tend to fill in the regions between the normally allowed $\Delta m=0$ transitions when the direction of **B** departs significantly from the principal hyperfine axes of the defect. Departure of the defect axes from the crystal c axis would make them important with $\mathbf{B}\|c$.

The magnitude of the $LE3$ ^{69}Ga hyperfine interaction is similar to that observed by ODMR for a defect reported in as-grown GaP (2123 MHz),[16] and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ (1500 MHz).[17] In these cases, it was suggested that the defects were isolated interstitial Ga_i^{2+} atoms, again on the basis of the large mostly isotropic hyperfine interactions. Assuming that these reasonable interpretations are correct, we can conclude that the defect reported here is also an interstitial Ga_i^{2+} atom, but paired off with some other defect.

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