Detection of Interstitial Ga in GaN

K. H. Chow* and G. D. Watkins
Department of Physics, Lehigh University, 16 Memorial Drive East, Bethlehem, Pennsylvania 18015

Akira Usui and M. Mizuta
Systems Devices and Fundamental Research, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan
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We report the direct detection of interstitial Ga by optical detection of electron paramagnetic resonance (ODEPR) in the photoluminescence of *n*-type GaN after irradiation *in situ* at 4.2 K with 2.5 MeV electrons. It is stable upon annealing until room temperature, where it becomes mobile and trapped to form a new defect which is observed to emerge as the interstitial disappears. The time constant of the process at room temperature is ~200 min. The emergence of another ODEPR center beginning at ~135 K suggests even easier migration of one of the other intrinsic defects in the GaN lattice.

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There is growing interest in the role of the intrinsic point defects, i.e., lattice vacancies, self-interstitials, and antisites, in GaN and its alloys [1]. This interest is motivated to a large extent by the recent successful application of GaN and its alloys in blue-light emitting and laser diodes, and also by its recognized potential for high temperature, high power, electronic devices. In order to understand the various diffusion, ion-implant, annealing, etc., process steps involved in modern device fabrication, as well as possible degradation processes, it is essential to determine the properties of the intrinsic defects which control them. In addition, unraveling and understanding the electronic and lattice structures of such defects in this new class of wide band gap semiconductors provide an important new fundamental scientific challenge, as yet not successfully accomplished. Although there have been several theoretical studies of intrinsic defects in GaN [2–5], at present no direct experimental information exists. In this Letter, we report the direct observation and identification of interstitial Ga in GaN, and characterize some of its important properties. We believe that this is the first unambiguous identification and characterization of an intrinsic lattice defect in this important new class of semiconducting materials.

Our method for studying these defects involves first irradiating the sample with MeV energy electrons to produce the interstitials and vacancies, and subsequently probing the sample by optically detected electron paramagnetic resonance (ODEPR) in the photoluminescence (PL). In a previous study, we reported the results of such a study after 2.5 MeV electron irradiation to a fluence of $\sim 10^{18}$ cm^{-2} at *room temperature* [6,7]. There it was found that the prominent visible and near band gap ultraviolet PL originally present in the material was greatly reduced by the irradiation, and two new infrared PL bands emerged. The higher energy of these bands was broad and centered at $\approx$0.95 eV, while the lower energy band displayed a zero phonon line (ZPL) at 0.88 eV with associated phonon-assisted structure. Four new EPR centers, labeled $L1$ to $L4$, were observed via ODEPR in these bands. $L1$, $L3$, and $L4$ were $S = 1/2$ centers, detected in the 0.95 eV PL band, while $L2$ was an $S = 1$ center that accompanies the 0.88 eV PL band. These defects were found to be stable at room temperature, annealing in separate stages between 400 to 600 °C. It was not possible to establish the identity of $L1$ and $L2$. However, strong well-resolved hyperfine interaction with a single Ga nucleus was observed for both $L3$ and $L4$. These centers were suggested to be a Ga interstitial atom, either isolated in two different configurations in the lattice or trapped by impurities or other defects originally present in the samples, presumably in that case the consequence of long range migration of the interstitial.

In such a robust high temperature semiconductor as GaN, one might expect the intrinsic defects to be relatively immobile and therefore stable at room temperature. Therefore, to test whether the two Ga-related centers, $L3$ and $L4$, or, in fact, any of the four $L1$–$L4$ centers seen in this previous study could be related directly to the initially produced intrinsic defects, frozen into the lattice before they have had a chance to migrate, we have initiated new ODEPR studies of GaN irradiated by 2.5 MeV electrons *in situ* at 4.2 K. Here we report on these results.

The sample studied was a high quality $\approx$500 μm thick freestanding GaN single crystal platelet grown at NEC by hydride vapor phase epitaxy using a facet-initiated epitaxial lateral overgrowth technique on a GaN-nucleated sapphire substrate which was subsequently removed. The details are described in Ref. [8]. The sample was not intentionally doped, but was *n* type, with $n < 10^{17}$ cm^{-3}, and with low dislocation content ($\sim 10^{7}$ cm^{-2}). The *c* axis of the crystal was perpendicular to its platelet surfaces. Prior to the electron irradiation, its PL revealed several prominent overlapping bands in the visible, plus sharp luminescence structure in the near-IR identified with trace concentrations of V^{3+} [9] and, more weakly, Fe^{3+} [10].

The setup for the ODEPR experiments was similar to that of earlier work in II-VI semiconductors [11–13]. Briefly, a 20 GHz EPR spectrometer, capable of *in situ* 4.2 K electron irradiation, was modified for ODEPR by

inserting into the TE_{011} microwave cavity a fused quartz capillary tube. This tube served as a light pipe to extract the photoluminescence, and within it was threaded an optical fiber through which the sample could be photoexcited with ultraviolet light. To monitor the ODEPR signals, the luminescence was detected with either a silicon (EG&G 250UV) or cooled germanium (North Coast EO-817S) diode detector, and excitation ($\leq$3 mW) was supplied by the 364 nm line of an argon ion laser. This wavelength is just below the band gap of GaN and allowed for bulk penetration of the thick samples, which were immersed in pumped liquid helium ($\sim$1.5 K). Microwave power from a 300 mW Gunn diode was on-off modulated at $\approx$200 Hz, and synchronous changes in the luminescence were detected via lock-in detection. The platelet sample was indium-soldered onto a post cut at 45° in order to provide equal surface area for the horizontal electron irradiation and subsequent vertical photoexcitation. (The magnetic field could be rotated in the horizontal plane and therefore only directions between $\mathbf{B} \perp c$ axis and 45° to the c axis were accessible.)

Irradiation with 2.5 MeV electrons *in situ* at 4.2 K to a dose of only $\sim 5 \times 10^{16}$ cm^{-2} is found to reduce the visible PL significantly ($\sim$40% remaining), while a broad IR PL band emerges (integrated intensity comparable to that from V^{3+} before irradiation), which appears identical to the broad 0.95 eV band observed previously in the room-temperature irradiation studies. The structured PL with ZPL at 0.88 eV is absent, however. The ODEPR observed in the IR luminescence is shown in Fig. 1. *None of the signals seen previously in the room-temperature irradiation studies are present.* Instead, two negative signals are seen, one associated with the shallow effective mass (EM) donor [14], as indicated, the other a set, not previously observed, which we label $L5$. The positions of the $L5$ lines can be accurately fit by the following spin Hamiltonian:

$$\mathcal{H} = \mu_B g \mathbf{S} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{A}_j \cdot \mathbf{I}_j , \qquad (1)$$

where μ_B is the Bohr magneton, $\mathbf{B}$ is the external magnetic field, and $\mathbf{A}_j$ is a hyperfine tensor which couples the electronic spin $\mathbf{S}$ to a nuclear spin $\mathbf{I}_j$. As shown in Fig. 1, the structure is accurately reproduced by assuming that $L5$ is an $S = 1/2$ center with a strong, slightly anisotropic, hyperfine interaction from a single Ga nucleus (isotopic abundance: 60% ^{69}Ga, 40% ^{71}Ga; $\mu^{69}/\mu^{71} = 0.787\,03$, and for both, $I = 3/2$). The fit gives $g = 2.000(1)$, $^{69}A_{\|} = 3.99(1)$ GHz, and $^{69}A_{\perp} = 3.77(1)$ GHz, where "parallel" refers to the c axis of the wurtzite crystal. The hyperfine parameters are larger than those of $L3$ and $L4$ described above, indicating that $L5$ is also a deep level and even more localized. In fact, we can compare estimates of the ^{69}Ga free neutral atom hyperfine interactions for a $4s$ ($a = 7430.4$ MHz) and $4p$ ($b = 148.2$ MHz) orbital [15] to the experimental values of $|A_{\|}| = |a + 2b|$ and $|A_{\perp}| = |a - b|$, leading to $\approx$52% $4s$ and $\approx$50% $4p$ of the spin wave function located on the Ga atom. Hence,

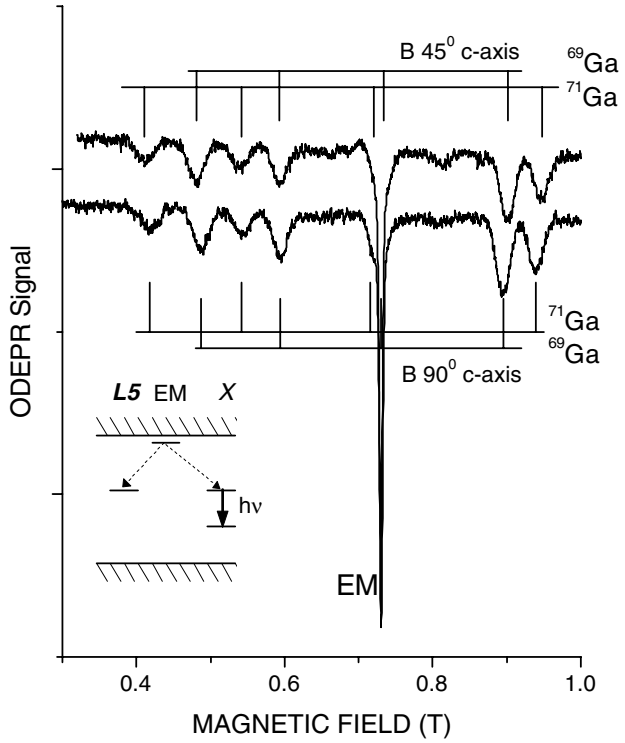

FIG. 1. ODEPR signals observed in the IR luminescence after 2.5 MeV electron irradiation *in situ* at 4.2 K to a fluence of $\sim 5 \times 10^{16}$ cm^{-2}. As shown, spectrum $L5$ reveals well-resolved hyperfine structure with a single $I = 3/2$ Ga nucleus (^{69}Ga, 60% abundant; ^{71}Ga, 40% abundant). It and the EM donor signal are negative, indicating spin-dependent recombination between the two which competes with the luminescence process, as illustrated in the inset.

as in the case of $L3$ and $L4$, the wave function is highly localized on a single Ga atom in a $4s$-$4p$ orbital pointing along the c axis of the crystal.

The simultaneous presence of the EM and $L5$ signals, both *negative*, reveals a spin-dependent electron transfer process between the two,

$$L5^n + \mathrm{EM}^0 \rightarrow L5^{n-1} + \mathrm{EM}^+ , \qquad (2)$$

which is *competing* with, but not directly related to, the radiative recombination processes giving rise to the PL being observed. Here the integer n (positive or negative) represents the charge state of the defect giving rise to the $L5$ signal. Consistent with this, the two negative signals are also seen in ODEPR of the remaining visible PL, in that case in addition to positive signals present before the irradiation.

An isochronal annealing sequence of the sample is shown in Fig. 2(a). At each temperature shown in the figure, the sample was first annealed in the dark for $\approx$30 min, followed by ODEPR characterization at 1.5 K. It was then taken again to the same temperature for $\approx$30 min while simultaneously illuminating the sample with $\approx$12 mW of 364 nm laser light, followed again by ODEPR characterization at 1.5 K. The motivation

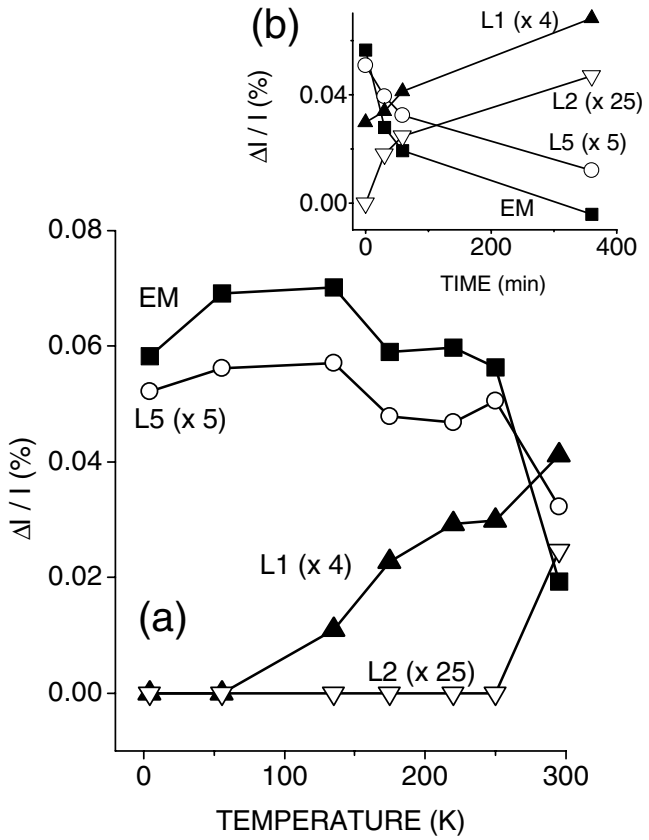

FIG. 2. (a) Result of isochronal annealing (60 min) on the amplitudes (percentage change in the luminescence $\Delta I/I$) of the various ODEPR spectra observed in the IR luminescence at 1.5 K. (For $L5$ and $L2$, which are composed of more than one line each, the plotted point is that for a selected one of their lines.) (b) Time dependence of the anneal at 295 K.

behind the illumination experiments was to investigate whether recombination-enhanced migration mechanisms—demonstrated dramatically in similar experiments for interstitial Zn in ZnSe [12,13]—might be important also in GaN. No evidence was found that the light had any significant additional effect, and the ODEPR intensities given in the figure are therefore those after the total of 1 h at each temperature. The intensities of $L5$ and EM remain essentially constant until room temperature, where they disappear together with a time constant of $\approx$200 min [Fig. 2(b)] [16]. Similar annealing is observed for the two signals in ODEPR of the visible luminescence. At the same time, $L2$ emerges in close 1:1 correspondence to the disappearance of $L5$ and EM, accompanied also by the emergence of its related 0.88 eV ZPL PL system. In addition, we note that $L1$ emerges during this annealing sequence, appearing first at $\approx$135 K, but growing in continually with subsequent anneals and with continued increase also upon prolonged annealing at room temperature [17]. The weaker $L3$ and $L4$ signals have not been detected. However, if their intensities relative to $L1$ and $L2$ were the same as observed in the room-temperature irradiations, they would have been too weak to detect at this low irradiation fluence.

From these results, we can already draw several important conclusions: (i) None of the four defects previously observed after room-temperature electron irradiation is present immediately after a 4.2 K *in situ* irradiation. They are therefore not the pristine vacancy- and interstitial-related defects produced by the irradiation. (ii) They emerge only after subsequent higher temperature annealing, revealing that they result either from local lattice rearrangements of the pristine defects or their long range migration to be trapped by other impurities or defects. A previous observation in the room-temperature irradiation study [7] that the relative intensities of the individual $L1$–$L4$ spectra varied depending upon the sample source appears inconsistent with local rearrangements as the mechanism, and argues strongly that long range migration must therefore be occurring. (iii) $L5$, present initially after the 4.2 K irradiation, must be directly related to one of the intrinsic defects, and, when it begins to migrate and be trapped at room temperature, $L2$ appears to be one of the direct products. (iv) The emergence of $L1$ at lower temperatures suggests that long range motion may also be occurring for one of the other intrinsic defects which is not being detected directly in the ODEPR [18].

Let us now consider the identity of $L5$. Having been formed at random in the lattice by Rutherford scattering recoil of a host atom at 4.2 K, it must be one of the intrinsic defects. The obvious one is interstitial gallium in its Ga_i^0 or Ga_i^{2+} paramagnetic state. However, let us first exclude one other possibility that might also account for high localization on a single Ga atom—a nitrogen vacancy for which the unpaired electron is highly localized on only one of its four Ga neighbors. (Such a configuration has been demonstrated for the negative Zn vacancy V_{Zn}^- in ZnSe, for example, where a strong trigonal Jahn-Teller distortion occurs with the paramagnetic hole localizing on a single Se neighbor [19].) We can reasonably rule this out for the V_N^0 paramagnetic state because all theoretical calculations appear to agree that it should be a shallow EM state [2–5]. In addition, none of the more recent *ab initio* calculations [3–5] predict the presence in the gap for the other paramagnetic state, V_N^{2+}. But, even if it existed [2], it should be undistorted (no Jahn-Teller instability) with one electron in an orbitally nondegenerate a_1 state. We can reasonably conclude therefore that $L5$ must arise from interstitial Ga in one of its paramagnetic states, Ga_i^0 or Ga_i^{2+}, and that it can execute long range migration through the lattice at room temperature. The spin-dependent capture process of Eq. (2) suggests that it is Ga_i^{2+}. Our results at present do not distinguish between the two possible interstitial sites (O and T) in the wurtzite lattice. (It is interesting to compare this to the theoretical predictions of Boguslawski *et al.* for interstitial Ga [4]. They predict little energy difference for the interstitial between the O and T sites, but that, for each,

the Ga_i^{2+} charge state is *metastable,* the defect displaying negative-U properties between its nonparamagnetic Ga_i^{+} and Ga_i^{3+} charge states. If that prediction actually turns out to be correct, then we must be observing the metastable Ga_i^{2+} state formed by particle capture at these cryogenic temperatures, which is, of course, possible.)

In summary, interstitial Ga has been observed for the first time in GaN by ODEPR directly after *in situ* 2.5 MeV electron irradiation at 4.2 K. In its paramagnetic Ga_i^{2+} charge state, its unpaired electron is highly localized in a $4s$-$4p$ orbital pointing along the crystal c axis, consistent with the C_{3v} symmetry of either the O or T interstitial site in the wurtzite lattice. We have presented strong evidence that its activation barrier for diffusion is sufficiently low to allow its long range migration and trapping by impurities or defects at room temperature. (Assuming a typical pre-exponential factor for the single jump rate of $\sim 10^{13}$ s^{-1} and $\sim 10^5$ jumps before trapping, the 200 min decay time at 295 K suggests an activation energy of ~ 0.7 eV.) There is no evidence that this motion is enhanced by optical excitation. One of the defects which emerges when this occurs is $L2$, a center previously observed and partially characterized in room-temperature irradiation studies. We can tentatively conclude therefore that $L2$ is a trapped Ga interstitial of some kind. (The observation by Chen *et al.* [20] that the 0.88 eV phonon structure is similar to that for substitutional oxygen in GaP suggests that oxygen, a common impurity in GaN, may be the trap involved.) A second defect, $L1$, previously observed and partially characterized also in the room-temperature irradiation studies, begins to grow in at a much lower temperature, suggesting that one of the other intrinsic defects (interstitial N, or a vacancy on either of the two sublattices) may be even more mobile. Our ongoing experiments reveal that $L1$ contains complex partially resolved hyperfine structure which was missed previously [6,7]. It is currently under study. It is clear therefore that this approach—ODEPR studies of *in situ* low temperature electron-irradiated GaN—shows great promise for providing a rather complete description of the properties of the intrinsic defects in this important new semiconducting material.

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*Present address: TRIUMF, 4004 Wesbrook Mall, Vancouver, BC, Canada, V6T2A3.

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[17] Evidence of additional recovery processes is also seen in the PL. The visible PL appears to recover partially at each annealing step, with no evidence of a discreet stage, returning to $\sim 85\%$ of its before-irradiation value by the end of the room-temperature anneal. The broad 0.95 eV PL appears to decrease in two distinct stages: to $\sim 70\%$ of its initial value at the 175 K anneal and to $\sim 10\%-20\%$ during the room-temperature anneal.
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