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Defect Donor and Acceptor in GaN

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High-energy (0.7–1 MeV) electron irradiation in GaN grown on sapphire produces shallow donors and deep or shallow acceptors at equal rates, 1 ± 0.2 cm⁻¹. The data, in conjunction with theory, are consistent only with the shallow donor being the N vacancy, and the acceptor the N interstitial. The N-vacancy donor energy is 64 ± 10 meV, much larger than the value of 18 meV found for the residual donor (probably Si) in this material. The Hall-effect measurements also reveal a degenerate n-type layer at the GaN/sapphire interface which must be accounted for to get the proper donor activation energy.

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Rapid progress in the development of blue light emitters, uv detectors, and high-temperature transistors in the III-V nitride system (GaN, AlGaN, and InGaN) has led to great activity in the growth and characterization of these materials [1,2]. In the early days of GaN growth, the electrical nature was nearly always strongly n type, and it was implicitly assumed that the donor was a native defect, the N vacancy (V_N) [3,4]. However, later studies have concluded that O (Ref. [5]) and Si (Ref. [6]) may be the prime candidates for residual donors, and, indeed, Si is known to be an effective donor dopant up the 10¹⁹ cm⁻³ range [7]. Theory suggests that the V_N defect has a level in the conduction band (CB) which, when occupied, autoionizes into a hydrogenic configuration, i.e., with an energy about 30–40 meV (plus central-cell correction) below the CB edge [8,9]. High-pressure optical experiments are consistent with the residual donor in bulk GaN being V_N (Ref. [4]); however, nobody, to our knowledge, has proven that V_N is indeed a shallow donor. We have irradiated GaN layers grown on sapphire with 0.7–1 MeV electrons which are expected to produce N and/or Ga vacancies. By fitting the temperature dependences of both electron concentration (n) and mobility (µ) it is possible to determine the concentrations of donors (N_D) and acceptors (N_A) and the energy (E_D) of the donors [10]. We argue below that the data presented here and theory presented elsewhere are consistent only if the donor and acceptor are components of the N Frenkel pair, i.e., the N vacancy, and N interstitial, respectively. This model confirms the expected donor nature of V_N and demonstrates the rare appearance of an interstitial (N_I) as an acceptor.

Although high-energy electron irradiation has been used extensively in the past to study vacancy defects in such semiconductors as Si [11], GaAs [12], and ZnSe [13], no similar studies have been conducted in GaN, to our knowledge (however, see note at end). Low-energy (<30 keV) electron irradiation has been used to activate Mg acceptor impurities in GaN [14], but these energies are much too low to cause displacements. A very recent irradiation study, using x rays and ⁶⁰Co γ rays, reported nearly no change in mobility, even though the γ rays decay to 0.6 MeV electrons, which should be able to displace N atoms, and possibly Ga atoms also [15]. However, the γ-ray dose, 4.5 × 10⁶ rads, was probably too small to give an observable displacement effect.

A side result of the present study is the confirmation of a degenerate, n-type layer at the highly dislocated GaN/sapphire interface. This layer modifies the n vs T (and to a lesser extent µ vs T) data such that the main donor seems too shallow and a second, deeper donor falsely appears at high temperatures (typically ≥300 K). The presence of such a degenerate layer has been reported recently [16], but the effects on n vs T and µ vs T are shown here for the first time.

The samples chosen for this study were thick (20–60 μm), high-mobility (µ = 700–900 cm²/V s), GaN layers grown by the hydride vapor phase epitaxial (HVPE) technique on sapphire [17]. The expected range for 1 MeV electrons in GaN is about 700 μm, from the Katz-Penfold relationship [18,19]; thus, energy loss is small in 60 μm and may be neglected. Electron fluences F ≈ 1–7 × 10¹⁶ cm⁻² were generated by a Van de Graaff accelerator at a beam current of 10 μA/cm². Hall-effect measurements were carried out over a temperature range 10–400 K, using a magnetic field of 5 kG. The experimental Hall-effect data are presented in Figs. 1 and 2 for a 60-μm-thick HVPE sample, 262D. In these figures, the triangles denote an unirradiated sample, and the circles, the same sample irradiated at a fluence of 5 × 10¹⁶ 1-MeV electrons/cm². The curves at 1, 2, 3, and 4 × 10¹⁶ cm⁻² fall smoothly in between those displayed, but are not included, for purposes of clarity. In Fig. 1, the minima in the apparent carrier concentrations, n_H = 1/µR, where R is the Hall coefficient, are similar to those commonly seen in semiconductors when electrons freeze out on their parent donors, and the

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concentration changes from conduction-band transport to donor-band or hopping transport (see Ref. [10], p. 115). However, the latter explanations do not hold in this case because hopping conduction would not be temperature independent and would not exhibit a strong Hall coefficient at low temperature, as observed, and conduction in a donor band would also not be temperature independent at such a low (~10^{17} cm^{-3}) donor concentration. To illustrate this latter point, we note that, for a Bohr radius \( a_0 = 0.511 \, e/m^* = 24 \, \text{Å} \), the Mott (critical) concentration [20] is \( N_c = (0.25/a_0)^3 = 1 \times 10^{18} \, \text{cm}^{-3} \), and the concentration at which the Fermi level enters the conduction band [21] is \( N_{CB} = 1/4 \pi a_0^3 \approx 6 \times 10^{18} \, \text{cm}^{-3} \). Thus, in order to have flat (degenerate) electrical characteristics, the effective thickness of a layer with \( N_D \sim 10^{17} \, \text{cm}^{-3} \) would have to be much less than 60 \( \mu \text{m} \), and, in fact, no larger than \( 60(1 \times 10^{17}/6 \times 10^{18}) = 1 \, \mu \text{m} \). Indeed, recent etching experiments on material grown in the same reactor have demonstrated a strong, “residual” conductance within a thickness of <1.2 \( \mu \text{m} \) from the GaN/sapphire interface [16]. Transmission electron microscopy results show a highly faulted interface region of about 0.3-\( \mu \text{m} \) thickness, and our results are well explained if this region has a carrier concentration \( n = 1 \times 10^{17} \, (60/0.3) \approx 2 \times 10^{19} \, \text{cm}^{-3} \). The measured low-temperature mobility of 56 cm^{2}/Vs is realistic for such a concentration [7].

To account for this degenerate layer, we use a two-layer analysis and note that the quantities \( \sigma_\square \) and \( R_{\square} \), \( \sigma_\boxdot \) and \( R_{\boxdot} \) are additive; i.e., \( \sigma_\square = \sigma_\square + \sigma_\boxdot \), and \( R_{\square} \sigma_\boxdot = R_{\square} \sigma_\boxdot + R_{\square} \sigma_\boxdot \), where the symbol “\( \boxdot \)” denotes a sheet concentration [10]. In terms of mobility and carrier concentration, we can write \( \mu_{\text{meas}} = (n_1 \mu_1 + n_2 \mu_2)/ (n_1 \mu_1 + n_2 \mu_2) \) and \( n_{\text{meas}} = (n_1 \mu_1 + n_2 \mu_2)^2/(n_1 \mu_1 + n_2 \mu_2) \), where subscript “1” denotes the bulk of the 60-\( \mu \text{m} \) sample, and subscript “2”, the degenerate interface layer. (For plotting purposes, we normalize \( n_2 \) in the full, 60-\( \mu \text{m} \) thickness, rather than in the actual 0.3-\( \mu \text{m} \) thickness.) The bulk carrier concentration \( n_1 \) was found from the charge-balance equation for a single donor: \( n_1(T) + N_A = N_D/[1 + n_1(T)/\phi(T)] \), where \( \phi(T) = g_0/g_{1 N_c} T^{3/2} \exp(-E_D/kT) \). (For the irradiated sample, a second donor was included.) Here \( N_c \) is the effective density of states at \( T = 1 \, \text{K} \), \( g_0 \) is the unoccupied-state degeneracy, and \( g_1 \) is the occupied-state degeneracy. For an s-type state, \( g_0 = 1 \) and \( g_1 = 2 \). The bulk Hall mobility \( \mu_1 \) was accurately determined from an iterative solution of the Boltzmann transport equation [22,23]. All of the relevant lattice-scattering parameters were taken from the literature: acoustic deformation potential [24] \( E_1 = 9.2 \, \text{eV} \); piezoelectric-potential constant [25] \( \epsilon_{14} = 0.5 \, \text{C/m}^2 \); static and high-frequency dielectric constants \( \epsilon_0 \) [26] and \( \epsilon_\infty \) [27], 10.4\( \epsilon_0 \) and 5.47\( \epsilon_0 \), respectively; Debye temperature [22] \( T_D = 1044 \, \text{K} \); and effective mass [28] \( m^* = 0.22m_0 \). The only fitted parameter was the acceptor concentration \( N_A \). The values of \( n_2 \) and \( \mu_2 \) were directly determined from the degenerate, low-temperature data: \( n_2 = 1.3 \times 10^{17} \, \text{cm}^{-3} \) (normalized to 60 \( \mu \text{m} \)), and \( \mu_2 = 56 \, \text{cm}^2/\text{Vs} \). Finally, the equations for \( n_{\text{meas}} \) (\( n_1, \mu_1, n_2, \mu_2 \)) and \( \mu_{\text{meas}} \) (\( n_1, \mu_1, n_2, \mu_2 \)), given earlier, were fitted to the data of Figs. 1 and 2, respectively, to get fitting parameters \( N_D, N_A, \) and \( E_D \). The heavy solid line in Fig. 1 shows \( n_1(T) \) at \( F = 5 \times 10^{16} \, \text{cm}^{-2} \), and the heavy solid line in Fig. 2 shows \( \mu_1(T) \) at \( F = 0 \). The effect of the degenerate interface layer is clearly seen by comparison with the light solid lines in these two figures, which are the fits to \( n_{\text{meas}}(T) \) and \( \mu_{\text{meas}}(T) \), respectively.

**FIG. 1.** Apparent Hall concentration (\( n_H = 1/eR \), where \( R \) is the Hall coefficient) vs inverse temperature for an unirradiated sample (\( \triangledown \)), and a sample irradiated with \( 5 \times 10^{16} \) 1-MeV electrons/cm² (\( \circ \)). The light solid lines are theoretical fits of the raw data, and the heavy solid line is the extracted, bulk carrier concentration (\( n_1 \)) for the irradiated sample. Inset: Production rates for N and Ga Frenkel pairs vs electron energy.
A confirmation of the validity of our two-layer analysis comes from a comparison of Hall measurements with 300-K capacitance-voltage C-V measurements. The C-V results are not affected by the interface layer, so that $n_{C-V}$ should equal $n_1$ (heavy solid curve in Fig. 1). Indeed, we find $n_{C-V} = n_1$ within 10% at 300 K.

The one-donor fits to $n_{\text{meas}}$ and $\mu_{\text{meas}}$ at $F = 0$, shown as light solid lines in Figs. 1 and 2, respectively, give $N_{D1} = 12.5 \pm 0.4 \times 10^{16}$ cm$^{-3}$, $E_{D1} = 17 \pm 1$ meV, and $N_A = 3.1 \pm 0.2 \times 10^{16}$ cm$^{-3}$. There is evidence that Si is the residual donor in this material, and, indeed, the fitted value of $E_{D1}$ agrees reasonably well with the expected theoretical value: $E_{D1} = E_{D01} - \alpha N_{D1}^{1/3} = 18.1$ meV, with $E_{D01} = 29$ meV [26], and screening factor $\alpha = 2.1 \times 10^{-5}$ meV cm$^{-1}$ [29] for Si in GaN. The irradiation would not be expected to affect the Si donors so that the irradiated sample should be fitted with a two-donor charge-balance equation [10], in which $N_{D1}$ and $E_{D1}$ are held constant. The second donor, generated by the irradiation ($F = 5 \times 10^{16}$ cm$^{-2}$), has fitting parameters $N_{D2} = 5.1 \pm 0.4 \times 10^{16}$ and $E_{D2} = 64 \pm 10$ meV, and the new $N_A$ is $7.7 \pm 0.2 \times 10^{16}$ cm$^{-3}$ (see relevant light solid lines, Figs. 1 and 2). Thus, $\Delta N_{D2} = 5.1 \pm 0.4$ and $\Delta N_A = 4.6 \pm 0.3 \times 10^{16}$ cm$^{-3}$, or $\Delta N_{D2} = \Delta N_A = 4.9 \pm 0.6 \times 10^{16}$ cm$^{-3}$, and the defect production rates ($\Delta N/\Delta F$) are $\tau_A = \tau_D = 1.0 \pm 0.2$ cm$^{-1}$. As a check, a two-donor fit to 1-MeV data at $F = 3 \times 10^{16}$ cm$^{-2}$ gives the same $\tau_A$ and $\tau_D$, within 0.1 cm$^{-1}$, and the same $E_{D2}$, within 5 meV. Note that the defect donor has a screened energy $E_{D2} = 64 \pm 10$ meV, which would probably translate to an unscreened value of about 76 $\pm$ 10 meV, clearly higher than the $E_{D0}$ for Si in GaN (30 $\pm$ 5 meV). Thus, there is evidently a large, central-cell correction for this defect donor.

We now argue that the created donor and acceptor are the N vacancy $V_N$ and N interstitial $N_I$, respectively. No other model is reasonable, as demonstrated below.

(i) Production rate.—Both N and Ga atoms are expected to be displaced from the lattice by 1-MeV electrons. The relativistic cross section for atomic displacement, as a function of electron energy $E$, can be written [19], in units of cm$^2$:

$$\sigma(E) = 2.5 \times 10^{-25} \frac{Z^2 \gamma^2}{(\gamma^2 - 1)^2} \times \left[ \frac{E_m}{E_d} - 1 - \beta^2 \ln \left( \frac{E_m}{E_d} \right) + \frac{\pi \gamma}{137} (\gamma^2 - 1)^{1/2} \right]$$

$$\times \left[ 2 \left( \frac{E_m}{E_d} \right)^{1/2} - 2 - \ln \left( \frac{E_m}{E_d} \right) \right],$$

where $\gamma = E/m_0 c^2 + 1$, $\beta = (\gamma^2 - 1)^{1/2}/\gamma$, $E_m = 2E(E + 2m_0 c^2)/1823 A m_0 c^2$, $Z$ is the atomic number, $A$ the atomic weight, and $E_d$ the energy necessary to create a Frenkel (vacancy-interstitial) pair. For GaAs, the experimental value of $E_d$ is about 10 eV [12], and for Si, about 13 eV [30]. The production rate ($\Delta[N]/\Delta F$ or $\Delta[Ga]/\Delta F$) is just $\tau = N_0 \tau_1$, where $N_0 = 2.19 \times 10^{22}$ cm$^{-3}$ is the lattice density of each of the atomic species, Ga and N. To get $\tau_1 = 1$ cm$^{-1}$, we would require, from Eq. (1), $E_d(N) = 10.8$ eV, and to get $\tau_{Ga} = 1$ cm$^{-1}$, a value $E_d(Ga) = 20.5$ eV is necessary. For these values of $E_d$, the full energy dependences of $\tau_{Na}$ and $\tau_{Ga}$ are plotted in the inset of Fig. 1. Clearly, $\tau_{Ga}$ is highly energy dependent for $E = 0.5$–1.5 MeV, and $\tau_N$ is quite flat. At $E = 0.7$ MeV, the lowest practical energy for our accelerator, a two-donor fit to data taken at $F = 3 \times 10^{16}$ cm$^{-2}$ gives $\Delta N_{D2} = 3.1 \pm 0.5 \times 10^{16}$ cm$^{-3}$, and $\Delta N_A = 2.7 \pm 0.3$ cm$^{-3}$, or $\tau_A = \tau_D = 1.0 \pm 0.2$ cm$^{-1}$, thus confirming that the displacements are in the N sublattice, not the Ga sublattice. That is, for Ga displacement, $\tau_{Ga}$ should drop by a factor of 2 at 0.7 MeV. The value of $E_{D2}$ is $57 \pm 10$ meV, within error of the energy (64 meV) determined from the 1-MeV data.

(ii) Theory.—Two different first-principles total-energy calculations [8,9] have found that $V_N$ is a single, shallow donor (after autoionization), and $N_I$ is a single, deep acceptor at approximately $E_d = 1.0$ eV. Our N Frenkel-pair model is entirely consistent with this picture. For the Ga Frenkel pair, on the other hand, $Ga_I$ is a single donor, and $V_{Ga_I}$, a triple acceptor, in $n$-type material. Thus, in order to keep the high-temperature $n$ nearly constant, as observed [see $n(400)$ K, Fig. 1], we would have to produce exactly $\frac{1}{2}$ as many acceptors as donors. Clearly, this is inconsistent with Frenkel-pair production on a single sublattice, and such a constant $n$ (at high $T$) would be highly improbable if both sublattices were involved. It is possible that the singly charged $Ga_I$ and triply charged $V_{Ga_I}$, if formed, recombine immediately after displacement, a scenario which is also postulated to exist in GaAs [12]. On the other hand, $E_d(Ga)$ may simply be too high to get significant Ga displacement at 0.7–1.0 MeV.

The 47-meV difference in energy between $V_N$ and our residual donor (probably $Si_{Ga}$) represents a rather large, but not unusual, central-cell correction for “effective-mass-like” donors and acceptors. For example, group II acceptors in GaAs range from 26 meV (Be) to 58 meV (Hg). A defect potential could be expected to be even more highly perturbed than the usual substitutional case.

(iii) Annealing.—An isochronal annealing study was performed on a different HVPE layer, 289B, as shown in the inset of Fig. 2. The solid line is a theoretical fit to the mobility data at 80 K, achieved by a first-order annealing analysis [31]:

$$\mu_{i+1} = \mu_{i-1}^{-1} + (\mu_{i-1}^{-1} - \mu_{i}^{-1}) \exp \left[-\nu \tau \exp \left(-E_A/kT_i\right)\right],$$

where the subscript $i = 1, 2, \ldots, 6$ denotes the annealing step [$T_0 = 298$ K (25°C), $T_1 = 523$ K (250°C), etc.],
$t$ is the annealing time ($t = 600 \text{ s}$), $v$ is a frequency factor ($v = 10^{13} \text{ s}^{-1}$, commonly assumed), and $E_A$ is the activation energy. To fit the data precisely, as shown, $E_A$ was varied in a linear fashion from $1.67 \text{ eV}$ at $250 \degree \text{C}$ to $2.12 \text{ eV}$ at $400 \degree \text{C}$. Such a variation would be expected if the various Frenkel pairs have different separations. Note that a first-order annealing is expected if each vacancy recombines with its original interstitial, as would be expected for a Frenkel pair. If all of the pairs are greatly separated, and the recombination is random, then a second-order process is expected [31]. We have also fitted the data with second-order theory, but the fit was not as good.

To summarize the data and analysis, the N Frenkel-pair model is strongly supported by the following facts: (1) shallow donors and deep or shallow acceptors are produced at the same rate; (2) theory predicts that $V_N$ is a shallow donor, and $N_I$, a deep acceptor in $n$-type material; and (3) the annealing is well fitted with first-order theory, expected for Frenkel-pair recombination. We believe that this experiment constitutes the first proof of the donor nature of the N vacancy. An analysis of optical data under pressure by Perlin et al. [4] showed that the dominant donor in their sample had a state in the conduction band, but an absolute identification of $V_N$, as opposed to Ga$_I$, or even O impurity, could not be made. An important implication of our results is that the frequently measured donor energies in the range 25–35 meV (normalized to $N_D = 0$) could not be due to $V_N$, but are likely associated with substitutional impurities. Finally, the existence of $N_I$ as an acceptor is experimentally shown here for the first time. Total-energy calculations suggest that neither $V_N$ nor $N_I$ should exist in the large numbers in as-grown, $n$-type material [8], but various complexes, which may not change the electronic energy significantly, cannot be excluded [8]. Further theory on the electronic energy levels of such complexes would be helpful.

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Note added.—Linde et al. [32] have recently studied a 1-$\mu$m-thick GaN/Al$_2$O$_3$ layer irradiated with $1 \times 10^{18} \text{ cm}^{-2}$ of 2.5 MeV electrons. This heavy irradiation produces two broad photoluminescence bands centered at 0.85 and 0.93 eV, respectively. The latter has been tentatively identified as a Ga$_I^{2+}$ complex by analysis of optically detected magnetic resonance data. Because of the much different irradiation conditions, it is difficult to compare our results with theirs at this time.