Defect Donor and Acceptor in GaN

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(Received 12 March 1997)

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. [S0031-9007(97)04095-7]

PACS numbers: 61.72.Ji, 61.80.Fe, 71.55.Eq, 72.20.Fr

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 10^{20} 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 ^{60}Co 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, 4.5×10^6 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 $\gtrsim$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 ($\mu \simeq 700$–900 cm^2/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 of 1–7×10^{16} cm^{-2} were generated by a Van de Graaff accelerator at a beam current of 10 μA/cm^2. 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 5×10^{16} 1-MeV electrons/cm^2. The curves at 1, 2, 3, and 4×10^{16} 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, $n_H = 1/eR$, 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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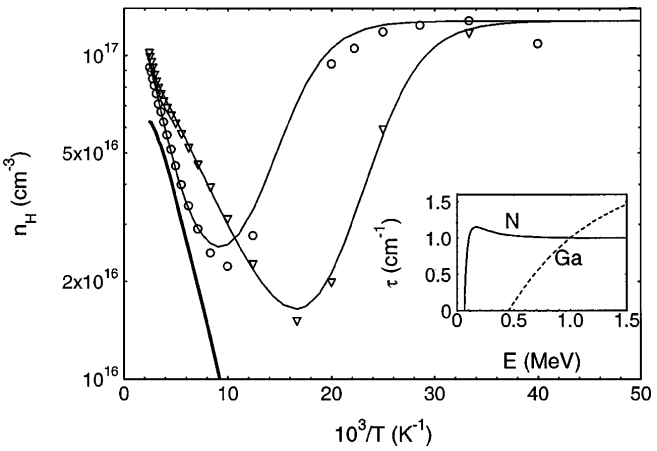

FIG. 1. Apparent Hall concentration ($n_H = 1/eR$, where R is the Hall coefficient) vs inverse temperature for an unirradiated sample ($\triangledown$), and a sample irradiated with 5×10^{16} 1-MeV electrons/cm^2 ($\bigcirc$). The light solid lines are theoretical fits of the raw data, and the heavy 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.

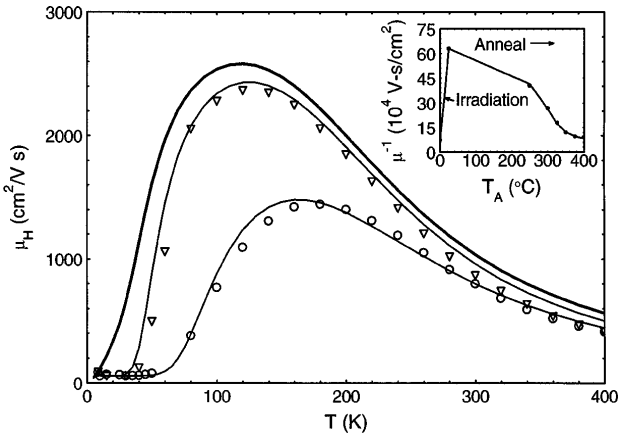

FIG. 2. Mobility vs temperature. The symbols are the same as those used in Fig. 1. The light solid lines are theoretical fits of raw data, and the heavy solid line is the extracted, bulk mobility (μ_1) for the irradiated sample. Inset: Inverse mobility (at 77 K) vs annealing temperature. The anneals were each 10 min long, and the solid line is a theoretical fit assuming first-order kinetics.

conduction 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 ($\sim 10^{17}$ cm^{-3}) donor concentration. To illustrate this latter point, we note that, for a Bohr radius $a_0 = 0.511\ \epsilon/m^* = 24$ Å, the Mott (critical) concentration [20] is $N_c = (0.25/a_0)^3 \simeq 1 \times 10^{18}$ cm^{-3}, and the concentration at which the Fermi level enters the conduction band [21] is $N_{\mathrm{CB}} = 1/4\pi a_0^3 \simeq 6 \times 10^{18}$ cm^{-3}. Thus, in order to have flat (degenerate) electrical characteristics, the effective thickness of a layer with $N_D \sim 10^{17}$ cm^{-3} would have to be much less than 60 μm, and, in fact, no larger than $60(1 \times 10^{17}/6 \times 10^{18}) \simeq 1$ μm. Indeed, recent etching experiments on material grown in the same reactor have demonstrated a strong, "residual" conductance within a thickness of <1.2 μm from the GaN/sapphire interface [16]. Transmission electron microscopy results show a highly faulted interface region of about 0.3-μm thickness, and our results are well explained if this region has a carrier concentration $n \simeq 1 \times 10^{17}\ (60/0.3) \simeq 2 \times 10^{19}$ cm^{-3}. The measured low-temperature mobility of 56 cm^2/V s is realistic for such a concentration [7].

To account for this degenerate layer, we use a two-layer analysis and note that the quantities $\sigma_{\square i}$ and $R_\square \sigma_{\square i}^2$ are additive; i.e., $\sigma_\square = \sigma_{\square 1} + \sigma_{\square 2}$, and $R_\square \sigma_\square^2 = R_{\square 1}\sigma_{\square 1}^2 + R_{\square 2}\sigma_{\square 2}^2$, where the symbol "$\square$" denotes a sheet concentration [10]. In terms of mobility and carrier concentration, we can write $\mu_{\mathrm{meas}} = (n_1\mu_1^2 + n_2\mu_2^2)/(n_1\mu_1 + n_2\mu_2)$ and $n_{\mathrm{meas}} = (n_1\mu_1 + n_2\mu_2)^2/(n_1\mu_1^2 + n_2\mu_2^2)$, where subscript "1" denotes the bulk of the 60-μm sample, and subscript "2", the degenerate interface layer. (For plotting purposes, we normalize n_2 in the full, 60-μm thickness, rather than in the actual 0.3-μm 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 $T = 1$ 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 μ_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] $E_1 = 9.2$ eV; piezoelectric-potential constant [25] $\epsilon_{14} = 0.5$ C/m^2; static and high-frequency dielectric constants ϵ_0 [26] and ϵ_∞ [27], $10.4\epsilon_0$ and $5.47\epsilon_0$, respectively; Debye temperature [22] $T_D = 1044$ K; and effective mass [28] $m^* = 0.22 m_0$. The only fitted parameter was the acceptor concentration N_A. The values of n_2 and μ_2 were directly determined from the degenerate, low-temperature data: $n_2 = 1.3 \times 10^{17}$ cm^{-3} (normalized to 60 μm), and $\mu_2 = 56$ cm^2/V s. Finally, the equations for n_{meas} (n_1, μ_1, n_2, μ_2) and μ_{meas} (n_1, μ_1, n_2, μ_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 $F = 5 \times 10^{16}$ 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 $n_{\mathrm{meas}}(T)$ and $\mu_{\mathrm{meas}}(T)$, respectively.

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 $n_{C\text{-}V}$ should equal n_1 (heavy solid curve in Fig. 1). Indeed, we find $n_{C\text{-}V} = n_1$ within 10% at 300 K.

The one-donor fits to n_{meas} and μ_{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: $E_{D1} = E_{D01} - \alpha N_{D1}^{1/3} \simeq 18.1$ meV, with $E_{D0} \simeq 29$ meV [26], and screening factor $\alpha \simeq 2.1 \times 10^{-5}$ meV cm [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 τ_A and τ_D, within 0.1 cm^{-1}, and the same E_{D2}, within 5 meV. Note that the defect donor has a screened energy $E_{D2} \simeq 64 \pm 10$ meV, which would probably translate to an unscreened value of about 76 ± 10 meV, clearly higher than the E_{D0} for Si_{Ga} (30 ± 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,

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

where $\gamma = E/m_0c^2 + 1$, $\beta = (\gamma^2 - 1)^{1/2}/\gamma$, $E_m = 2E(E + 2m_0c^2)/1823Am_0c^2$, 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 ($\Delta[\text{N}]/\Delta F$ or $\Delta[\text{Ga}]/\Delta F$) is just $\tau = N_0\sigma$, 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 $\tau_{\text{N}} = 1$ cm^{-1}, we would require, from Eq. (1), $E_d(N) = 10.8$ eV, and to get $\tau_{\text{Ga}} = 1$ cm^{-1}, a value $E_d(\text{Ga}) = 20.5$ eV is necessary. For these values of E_d, the full energy dependences of τ_{N} and τ_{Ga} are plotted in the inset of Fig. 1. Clearly, τ_{Ga} is highly energy dependent for $E \simeq 0.5$–1.5 MeV, and τ_{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, τ_{Ga} should drop by a factor of 2 at 0.7 MeV. The value of E_{D2} is 57 ± 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 $E_V + 1.0$ 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}, 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 $\frac{1}{3}$ 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}, if formed, recombine immediately after displacement, a scenario which is also postulated to exist in GaAs [12]. On the other hand, $E_d(\text{Ga})$ 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 acceptor energies 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]:

$$\mu_i^{-1} = \mu_\infty^{-1} + (\mu_{i-1}^{-1} - \mu_\infty^{-1}) \exp\{-\nu t \exp[-E_A/kT_i]\}, \quad (2)$$

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 ($t = 600$ s), ν is a frequency factor ($\nu = 10^{13}$ 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 eV at 250 °C to 2.12 eV at 400 °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.

D. C. L. and D. C. R. were supported under U.S. Air Force Contract No. F33615-95-C-1619, and R. J. M. by DARPA and Air Force contracts. Opinions, interpretations, conclusions, and recommendations are those of the authors and not necessarily endorsed by the U.S. Air Force.

Note added.—Linde *et al.* [32] have recently studied a 1-μm-thick GaN/Al_2O_3 layer irradiated with 1×10^{18} 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.

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