Deep-center hopping conduction in GaN

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Molecular-beam-epitaxial GaN layers change from strongly conductive ($\rho \simeq 10^{-2}\ \Omega$ cm at 300 K) to semi-insulating ($\rho \simeq 10^{6}\ \Omega$ cm) as the N flux is increased. Layers grown at low fluxes show strong *n*-type conduction, with transport in the conduction band at high temperatures and in a shallow donor band at low temperatures. For layers grown at high N fluxes, the Hall coefficients become too small to measure, suggesting hopping conduction among deep centers. The temperature-dependent resistivity data are most consistent with multiphonon, rather than single-phonon, hopping. © *1996 American Institute of Physics.* [S0003-6951(96)01033-9]

I. INTRODUCTION

The successful commercialization of bright, blue GaN light-emitting diodes (LEDs) and the expected production of GaN blue diode layers in the near future have recently prompted much research on this material.[1] However, little is known about the compensation and conduction mechanisms. For example, most of the undoped material, both bulk and epitaxial, has strong *n*-type conductivity, with electron concentrations ranging from 10^{17} to 10^{20} cm^{-3}.[2,3] The dominant donor producing these larger concentrations is thought to be the N vacancy V_N,[4–6] although oxygen contamination may also be important.[7,8] It is difficult to produce *p*-type material, although doping with Mg and annealing in particular ways has proven to be successful[9,10] and, in fact, is the key to the blue (LED) production. However, besides *n*- and *p*-type layers, it is desirable to have semi-insulating (SI) material, especially for electronic applications. There are very few reports[2,3,11] and no detailed analyses of SI GaN in the literature. In this work we show that increased N flux in molecular beam epitaxial (MBE) growth changes the electrical properties from highly conductive to semi-insulating, and that the conduction in the latter is likely due to hopping.

Shallow-donor hopping conduction (or donor-band conduction) has already been observed in GaN at low temperatures,[3] but such behavior is well-known from studies of other semiconductors controlled by shallow donors or acceptors.[12,13] Deep-center hopping, on the other hand, has been reported only for a few semiconductors, such as neutron-irradiated SI GaAs,[14] and low-temperature-grown MBE GaAs.[15] It has been speculated that deep-defect hopping may explain the conduction in SI GaN,[3] but the present work is the first detailed analysis of this phenomenon.

II. ELECTRICAL AND OPTICAL MEASUREMENTS

Three of the GaN layers discussed here were grown by electron cyclotron resonance microwave plasma assisted MBE (nitrogen source) on the (0001) plane of sapphire.[1] The nitrogen fluxes ranged from 5.5×10^{15} cm^{-2} s^{-1} to 3.4×10^{16} cm^{-2} s^{-1}, and the substrate temperature was 750 °C. A fourth sample was grown at 800 °C with an ammonia source. Growth and 296-K electrical parameters are summarized in Table I. Thicknesses were measured by analyzing Fabry–Perot reflectance oscillations. It is seen that the resistivity ρ increases and the Hall mobility μ_H decreases as the N flux is raised. For samples 5175 and 5069, the Hall coefficient was too low to be measured ($\mu_H \lesssim 0.5$ cm^2/V s) over the entire temperature range.

Layer 5169 is quite representative of typical GaN samples discussed in the literature. The temperature dependencies of ρ, μ_H, and n_H are shown in Fig. 1 and are interpreted as follows: above 140 K, the dominant electrical transport mechanism results from conduction by electrons thermally excited from shallow donors into the conduction band. Below 140 K, the dominant mechanism is due to electrons ''frozen out'' in a band formed by these same shallow donors. This shallow-donor band is probably formed from the hydrogenic-type wave functions of electrons loosely bound to N vacancies. For an effective mass $m^* = 0.2m_0$, and a static dielectric constant $\kappa = 9.5$, we can calculate a Bohr radius $a_0 = 23.8$ Å for these electrons. Then, the electron motion in the donor band would become ''free'' (the Mott transition) at a critical concentration given by $N_c = (0.25/a_0)^3 \simeq 1.2 \times 10^{18}$ cm^{-3}. At a higher concentration, $N_{cb} \simeq 5N_c \simeq 6 \times 10^{18}$ cm^{-3}, the donor band would merge with the conduction band.[16] Note that sample 5169 has $n \simeq N_c$, which explains why donor-band effects are so apparent below 140 K. The chained line in Fig. 1 is a fit to the μ vs T data for $T \gtrsim 200$ K. Ionized defect scattering was in-

TABLE I. Properties of GaN layers, including 296 K values of ρ, μ, and n.

Sample	T_{sub}	N flux (cm^{-2} s^{-1})	d(μm)	ρ(Ω cm)	μ_H (cm^2/V s)	n_H (cm^{-3})
5169	750 °C	5.5×10^{15}	3.8	4.3×10^{-2}	1.3×10^{2}	1.1×10^{18}
5176	750 °C	1.6×10^{16}	5.3	1.4×10^{1}	3.5	1.3×10^{17}
5175	750 °C	3.4×10^{16}	5.3	3.1×10^{3} [a]	⋯	⋯
5069	800 °C	unknown	6.0	1.9×10^{6} [a]	⋯	⋯

[a]Hopping conduction.

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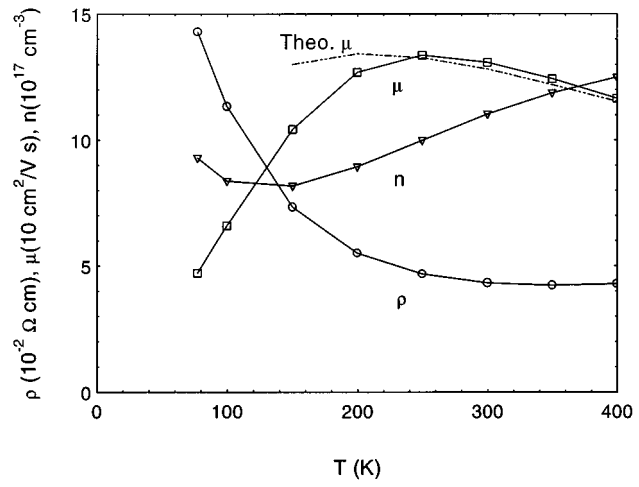

FIG. 1. Resistivity ρ, carrier concentration n, and mobility μ as a function of temperature T for sample 5169. The solid lines are added to aid the eye. The theoretical dependence of μ on T is shown as a chained line.

cluded through the usual Brooks–Herring formalism, and the Boltzmann transport equation was solved by Rode's iterative method.[17–19] The result was $N_D \simeq 6 \times 10^{18}$ and $N_A \simeq 5 \times 10^{18}\,\mathrm{cm}^{-3}$, giving $N_I \simeq N_D + N_A \simeq 1.1 \times 10^{19}\,\mathrm{cm}^{-3}$, where N_I is the ionized-defect concentration. Note that μ falls off much more rapidly below 160 K than predicted by theory. This observation suggests that μ is significantly lower in the donor band than in the conduction band.

In Fig. 2 we present ρ vs T data for sample 5169, discussed above, as well as the other samples mentioned in Table I. Sample 5176, which was grown in a N flux about 3× that of 5169, exhibited a Hall concentration of about $1 \times 10^{17}\ \mathrm{cm}^{-3}$, nearly constant with T, and a very low mobility, increasing from 0.7 to 4 cm^2/V s, as T increased from 77 to 400 K. Theoretical fitting of these data, assuming transport in the conduction band, gives $N_D \simeq N_A \simeq 1.4 \times 10^{20}\ \mathrm{cm}^{-3}$ so that $N_I \simeq 2.8 \times 10^{20}\ \mathrm{cm}^{-3}$, although it is doubtful that the Brooks–Herring theory would be accurate at such

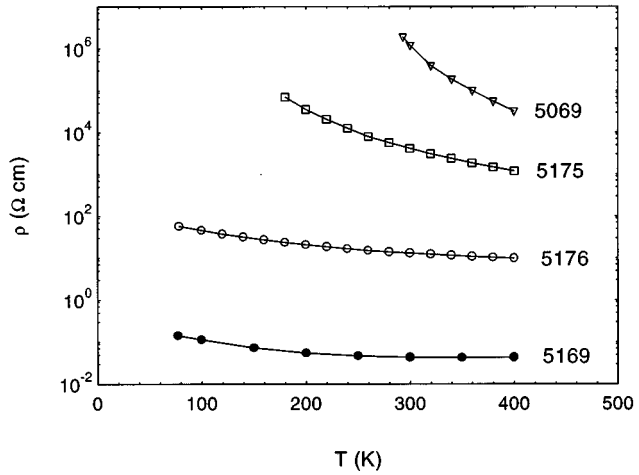

FIG. 2. Resistivity ρ vs temperature T for various GaN layers grown by MBE. The upper curves represent samples grown with higher N fluxes. The solid lines are added to aid the eye.

concentrations,[20] and the assumption of single scattering events would likewise be questionable.[21] However, there is another argument casting doubt on the possibility of such high values of N_D and N_A. The photoluminescence linewidths of the free excitons, observed at $T = 2$ K in all of the samples discussed in this paper, are subject to Stark (electric-field) broadening. An estimate of this field is given by $E = e/4\pi\kappa R^2$, where $R \simeq (3/4\pi N_D)^{2/3}$. Then, the energy spread across the exciton radius ($r_{ex} \sim a_0/2$) will be $\sim \Delta\mathscr{E} \simeq eE(a_0/2) \simeq 5 \times 10^{-15} N_D^{2/3}$, where N_D is in units of cm^{-3}. For sample 5169, we calculate $\Delta\mathscr{E} \simeq 16$ meV, which is within range of the observed value, 9 meV, especially when free-carrier screening is considered. For sample 5176, however, an N_D of $1.4 \times 10^{20}\ \mathrm{cm}^{-3}$ would predict $\Delta\mathscr{E} \simeq 135$ meV, whereas the actual linewidth is only about 6 meV. Thus, we believe that the low mobility in sample 5176 suggests transport in a defect band, rather than the conduction band. In any case, this sample must be studied further before a complete understanding will be possible.

Sample 5175, grown with an even higher N flux, exhibits a much higher resistivity than that of samples 5169 and 5176, and no measurable Hall coefficient ($\mu_H < 0.5$ cm^2/V s), even at 400 K. For conduction-band transport, such a small μ_H would require $N_I \gtrsim 5 \times 10^{20}\ \mathrm{cm}^{-3}$, and $n \ll N_D, N_A$ (to minimize free-carrier screening). Sample 5069 continues this trend, and also would require a very high ionized defect concentration to explain the low (vanishing) mobility. However, as argued above, PL data are inconsistent with a trend of higher defect concentrations along the sequence, 5169, 5176, 5175, and 5069. For example, the PL exciton linewidths become narrower along this sequence, and the deep-center emissions, such as the broad ''yellow band'' at 2.26 eV, diminish. In fact, sample 5069 shows excellent free-exciton emission (both A and B excitons are resolved, with linewidths <5 meV) and virtually no deep-center emission.[22] Thus, the PL results lead to the conclusion that the higher resistivities and vanishing Hall mobilities observed in samples 5175 and 5069 cannot be explained by strong scattering due to very large defect concentrations.

III. HOPPING CONDUCTION

A better explanation for the above phenomena is that the electrical transport in these SI samples does not consist of free-electron transport in the conduction band but, instead, phonon-assisted hopping among localized defect centers. Such hopping will often produce a very small or vanishing Hall coefficient, in agreement with observation. Basically, hopping involves two limiting factors:[12,13] (1) the energy ϵ_3 necessary to hop from an occupied defect to one which is unoccupied; and (2) wave function overlap. Consider a system of randomly placed donors of concentration N_D, among which electrons hop from occupied to unoccupied sites. The standard theory[12,13] predicts, for nearest-neighbor (nn) hopping, a conductivity

$$\sigma_{\mathrm{nn}} = C_{\mathrm{nn}} e^{-\alpha R/a_d} e^{-\epsilon_3/kT}, \tag{1}$$

where C_{nn} is a constant independent of temperature, a_d is the extent of the defect wave function, R is an average distance between neighbors [$R \simeq (3/4\pi N_D)^{1/3}$], and $\alpha \simeq 1.8$, near the

expected value of 2. From simple potential considerations, one would estimate $\epsilon_3 \simeq e^2/4\pi\kappa R$, since the empty sites to which the hop must take place should be those near charged acceptors, giving them an energy about e^2/R higher than that of filled sites. Thus, we might expect $\epsilon_3 \simeq 1.6e^2N_D^{1/3}/4\pi\kappa$, whereas a more detailed theory[13] gives $\epsilon_3 \simeq 0.99e^2N_D^{1/3}/4\pi\kappa$. We can fit the three samples (Fig. 2) exhibiting hopping conduction to Eq. (1) [$\rho_{nn} \sim \exp(\epsilon_3/kT)$] and get $\epsilon_3 \simeq 0.016$, 0.11, and 0.38 eV for samples 5176, 5175, and 5069, respectively. These values of ϵ_3 would correspond to the following magnitudes of N_D: 1.1×10^{18}, 4.4×10^{20}, and 1.6×10^{22} cm^{-3}, respectively. However, the latter two concentrations would lead to much larger PL linewidths than observed, as discussed earlier, and thus are unrealistic. Moreover, the values of ϵ_3 themselves are too high to correspond to absorption of a single, acoustic phonon, which is an implicit requirement in the standard theory.

However, at low temperatures, more distant hops to sites closer in energy will dominate. Consider a subset ΔN_D of donors all lying within $\Delta\epsilon$ of the Fermi level, and suppose $\Delta N_D \propto \Delta\epsilon$. Then, if we substitute $\Delta\epsilon$ for ϵ_3 in Eq. (1), and ΔN_D for N_D, and then maximize σ with respect to ΔN_D, we get

$$\sigma_{vr} = C_{vr}e^{-(T_0/T)^{1/4}} \tag{2}$$

where ''vr'' denotes ''variable range'' hopping, C_{vr} is a constant, and from the detailed percolation theory:

$$T_0 \simeq \frac{21.3}{kg(\epsilon_F)a_d^3}. \tag{3}$$

Here, $g(\epsilon_F)$ is the density of states at the Fermi level. Since the number of empty states in the donor band equals N_A, we can approximate $g(\epsilon_F) \simeq N_A/\epsilon_3$, so that $T_0 \propto N_D^{1/3}/N_A$. A typical compensation ratio in good quality GaN is $N_A/N_D \simeq 0.4$, and if $a_d \simeq 10$ Å, then $T_0 \simeq 9 \times 10^{18}N_D^{-2/3}$. Again, we can fit each curve to Eq. (2), giving $T_0 = 7.2 \times 10^4$ K ($N_D \simeq 1.5 \times 10^{21}$ cm^{-3}), 4.4×10^7 K ($N_D \simeq 9.7 \times 10^{16}$ cm^{-3}), and 2.4×10^9 K ($N_D = 2.4 \times 10^{14}$ cm^{-3}). Although these values of N_D are reasonable (or could be made reasonable with a different choice of a_d, which is unknown), another consideration casts doubt on the validity of such an analysis. That is, above a certain critical temperature T_c, given[13] by $T_c = e^2N_D^{2/3}a_d(N_A/N_D)^{1/3}/k(4\pi\kappa)$, the hopping process should change from variable range to nearest neighbor. For the values of N_D calculated above (which were based on $a_d = 10$ Å and $N_A/N_D = 0.4$), we get $T_c = 1.6 \times 10^4$, 26, and 0.5 K, for samples 5176, 5175, and 5069, respectively. Thus, the use of Eq. (2) for samples 5175 and 5069, at high temperatures, is internally inconsistent. In short, neither nn [Eq. (1)] or vr [Eq. (2)] hopping in these formalisms seems to give the correct picture.

Emin[23] has pointed out that the theory leading to Eqs. (1) and (2) is really valid only under the conditions of very low temperatures and single-phonon hops. In particular, the single-phonon limit requires that $3\gamma(\Delta/\hbar\omega_D)^2 \ll 1$, where Δ is a disorder energy ($\Delta \sim 2\epsilon_3$), and $\gamma \simeq E_{DP}^2/Ms^2\hbar\omega_D$. Here, E_{DP} is the acoustic deformation potential, M the atomic mass, s the speed of sound, and ω_D the Debye frequency. Using known or estimated values of these parameters for GaN, along with $\Delta \simeq 0.1$ eV, we get $3\gamma(\Delta/\hbar\omega_D)^2 \simeq 5 \times 10^2$. Even for $\Delta \simeq 0.01$ eV, which is much lower than any of our fitted activation energies, $3\gamma(\Delta/\hbar\omega_D)^2 > 1$; thus, the single-phonon theory should not apply. Interestingly enough, however, Emin has shown that a multiphonon theory gives a hopping rate in which the C_{nn} in Eq. (1) is not constant, but can vary with an $\exp(-T_0/T)^{1/4}$ dependence over a considerable temperature range. Thus, instead of *either* an $\exp(-\Delta/2kT)$ *or* an $\exp(-T_0/T)^{1/4}$ dependence, the multiphonon picture can include both factors, at least over a certain temperature range. Zuppiroli and Forro[24] have used such an analysis to explain data in a variety of disordered materials, such as ceramics, organic conductors, and polymers.

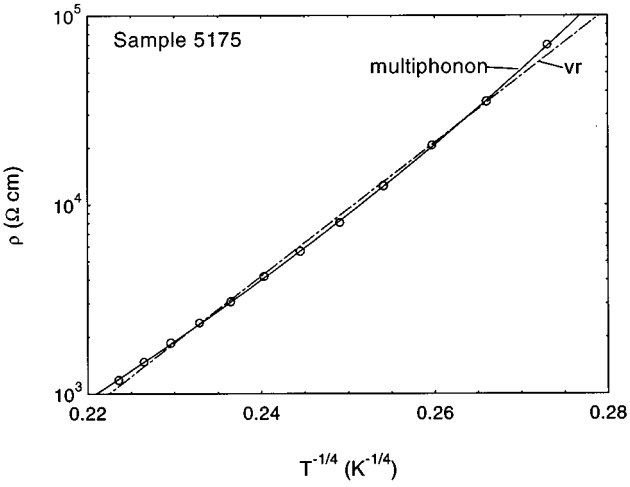

FIG. 3. A comparison of multiphonon and variable range, single phonon fits for sample 5175.

A comparison of a single-phonon, variable-range fit (giving $T_0 = 4.4 \times 10^7$ K) and a multiphonon fit (giving $T_0 = 1.8 \times 10^6$ K and $\Delta/2 = 0.063$ eV) for sample 5175 is shown in Fig. 3. Here the multiphonon fit is somewhat better, and it is also better than a single-phonon, nearest-neighbor fit (not shown). Emin[23] suggests that $T_0 \simeq 10^7 - 10^{10}$ K in typical cases, which is within range of the above T_0's. A more detailed discussion of the multiphonon hopping theory is beyond the scope of this paper, but this mechanism seems sufficient to explain our data.

The trend of the PL results, discussed earlier, suggests that the observed decrease of carrier concentration n with higher N flux during growth is due to a decrease in the donor (thought to be V_N) concentration rather than an increase in the acceptor concentration. In Ga-rich material, such as sample 5169, the Ga antisite Ga_N, with unfilled midgap states,[4,5] is probably the dominant acceptor. Then, for more N-rich conditions, both the V_N and Ga_N concentrations should decrease. However, if $[V_N]$ decreases faster than $[Ga_N]$, then eventually the condition $[V_N] < [Ga_N]$ will occur, and the sample will become semi-insulating. Another acceptor defect, V_{Ga}, will be increasing in concentration under these conditions and may also enter the compensation

picture. It would be of great help to know E_F in samples 5175 and 5069, but this knowledge is difficult to obtain, because n cannot be measured (no Hall effect). To estimate an upper limit for n in sample 5069, we note that the lack of a Hall effect is consistent with a conduction-band conductivity σ_b being much less than σ_{meas}, about $10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$. For an electron mobility $\mu \simeq 100\ \text{cm}^2/\text{V s}$, the inequality $\sigma_b \ll 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$ gives $n \ll 6 \times 10^{11}\ \text{cm}^{-3}$, or $E_C - E_F > 0.4$ eV. Thus, E_F could possible reside at the Ga_N $(0/-)$ level, which is at about $E_C - 1.5$ eV according to theoretical estimates.[5]

IV. SUMMARY

In summary, we have observed multiphonon hopping conduction in localized states for MBE GaN layers grown with high N fluxes. This conduction mechanism is in contrast to the usual conduction-band (or shallow donor band) transport observed in layers grown with lower N fluxes. Resistivities as high as $10^7\ \Omega$ cm at 300 K have been observed, but with no measurable Hall effect. The high N fluxes appear to reduce the dominant donor (V_N) concentrations and drop the Fermi level to a deeper defect level, perhaps the $(0/-)$ level of Ga_N. Hopping then takes place among these centers.

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