Conduction-electron spin resonance in zinc-blende GaN thin films

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We report electron-spin-resonance measurements on zinc-blende GaN. The observed resonance has an isotropic g value of 1.9533 ± 0.0008 independent of temperature, a Lorentzian line shape, and a linewidth (18 G at 10 K) which depends on temperature. The spin-lattice relaxation time at 10 K was estimated to be $T_{1e}=(6\pm2)\times10^{-5}$ sec. Using a five-band model a g value consistent with the experimental results was obtained and a conduction-electron effective mass $m^*/m_0=0.15\pm0.01$ was calculated. The observed signal, together with conductivity data, was attributed to nonlocalized electrons in a band of autodoping centers and in the conduction band.

I. INTRODUCTION

Gallium nitride is a wide-band-gap semiconductor which is anticipated to find applications for optical devices (light-emitting diodes, lasers, detectors) in the near uv region of the electromagnetic spectrum and electronic devices for high-power, high-frequency, and high-temperature applications. GaN was found to exist in two allotropic forms. The wurtzite structure is the thermodynamically stable phase and has an optical gap of 3.5 eV,[1,2] while the zinc-blende structure is a metastable phase which can be formed by epitaxial stabilization[3,4] and has an optical gap of 3.2 eV.[4] In both cases the material is found to be heavily autodoped n type, a result attributed to nitrogen vacancies.[5] In general, the electron concentration is in the range of $10^{17}-10^{20}$ cm^{-3}.

In this paper we report electron-spin-resonance (ESR) studies in autodoped n-type zinc-blende GaN thin films. The data were correlated with electrical conductivity measurements and from their analysis the nature of the resonance was determined. The measured g value was found to be in agreement with theoretical predictions based on a five-band model $\mathbf{k}\cdot\mathbf{p}$ calculation. The same calculation was also used to predict the electron effective mass.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The GaN films were grown by electron-cyclotron-resonance microwave plasma-assisted molecular-beam-epitaxy (MBE). Epitaxial stabilization of the zinc-blende structure was accomplished by using a two-temperature step process on Si(100). In this process a 200-Å GaN buffer was grown at 400 °C and the rest of the film, 4 μm thick, was grown at 600 °C. Both heavily autodoped and semi-insulating GaN films were fabricated and investigated. Transport studies in these films[6] show that the conductivity is dominated by the high-quality top layer rather than by the GaN buffer. Details on the growth are given elsewhere.[3,4] Structural studies (reflection high-energy electron diffraction, electron diffraction, and x-ray diffraction) show that the films are single crystals having the zinc-blende structure with lattice constant 4.5 Å.[3,4]

To conduct optical, transport, and spin-resonance measurements, self-standing GaN flakes were obtained by dissolving the Si substrate with a solution of HNO_3 and HF. The optical gap of the films was determined by transmission measurements and found to be 3.2 eV.[4] The electrical conductivity of one of the investigated films, determined by four probe measurements using sputtered Al contacts, is shown as a function of $1/T$ in Fig. 1. The data fit the expression

$$\sigma=\sigma_1\exp(-\varepsilon_1/kT)+\sigma_3\exp(-\varepsilon_3/kT)\ , \tag{1}$$

where the activation energies ε_1 and ε_3 are 25 and 0.5 meV, respectively.

Hall-effect measurements show that the films are n type; however, we were unable to perform accurate measurements of the carrier concentration on these self-standing GaN flakes. Based on our studies of wurtzite GaN films,[6] we anticipate that the investigated films have room-temperature carrier concentration of the order of $10^{17}-10^{18}$ cm^{-3}. The data of Fig. 1 are consistent with transport in the conduction band at temperatures higher than about 50 K and transport in a band of shallow donors at lower temperatures.[7]

The nature of these shallow donors is still controversial. They have been observed in GaN films produced by various deposition methods and attributed by early workers to nitrogen vacancies.[5] Our thin-film growth studies support this hypothesis. Since our films are grown at temperatures below the decomposition temperature of GaN, their stoichiometry can be controlled by varying the nitrogen overpressure during growth. At low active nitrogen overpressure we find that the films are n type with carrier concentration between $10^{18}-10^{20}$ cm^{-3}. Such films tend also to be decorated with gallium drop-

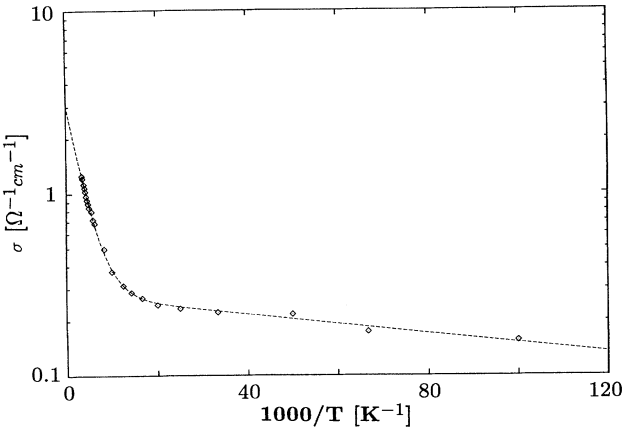

FIG. 1. Conductivity of GaN as a function of $1000/T$.

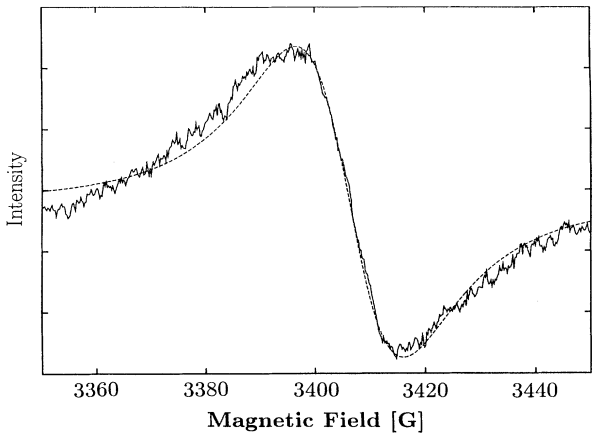

FIG. 2. First derivative absorption resonance line at 10 K and Lorentzian best fit.

lets, a result which we attribute to phase separation of excess gallium, presumably due to the narrow existence phase diagram of GaN. On the contrary, films produced under high nitrogen overpressure have carrier concentration between $10^{18}-10^{13}$ cm^{-3} and their surface is free of gallium droplets. This trend is consistent with the formation of nitrogen vacancies during growth and, if their concentration is very high, some gallium is phase separated in order for the material to maintain the stoichiometry allowed by its phase diagram. The samples investigated in this paper were free of any gallium droplets. Additionally, there is also theoretical support that the nitrogen vacancy in GaN is a shallow donor. Tight-binding calculations by Jenkins and Dow[8] have shown that the neutral unrelaxed N vacancy is a shallow donor with its singly occupied p-like level (T_2) in the conduction band and its doubly occupied s-like level (A_1) in the band gap close to the conduction-band edge. It is anticipated that lattice relaxation should shift the singly occupied level in the energy gap.

ESR measurements were performed at different temperatures in a Varian E9 spectrometer at 9.3 GHz, 100-kHz modulation frequency, and 0.5–1.0-G modulation amplitude. An α,α'-diphenyl-β-picrylhydrazyl reference was used to evaluate the g value. Figure 2 shows the ESR spectrum at 10 K of the same sample discussed in Fig. 1. This resonance has an isotropic g value of 1.9533 ± 0.0008 independent of temperature. The shape of the line is Lorentzian and the peak-to-peak linewidth ($\Delta H_{pp}=18\pm1$ G at 10 K) has a temperature dependence shown in Fig. 3. The broadening of the line with the increase in temperature prevented us from observing the resonance at temperatures higher than 110 K. The temperature dependence of the electron-paramagnetic-resonance (EPR) intensity is shown in Fig. 4.

From the saturation behavior of the resonance we estimated a spin-lattice relaxation time, at 10 K, of $(6\pm2)\times10^{-5}$ sec. No ESR signal was observed in semi-insulating GaN films.

To discuss the nature of the observed resonance we should first rule out that such a signal is not due to either plasma resonance or cyclotron resonance. Plasma resonance is ruled out based on the prediction of Dresselhaus,

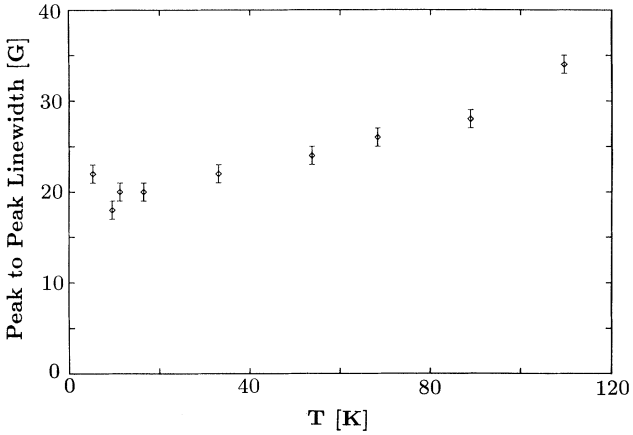

FIG. 3. Peak to peak linewidth ΔH_{pp} as a function of temperature.

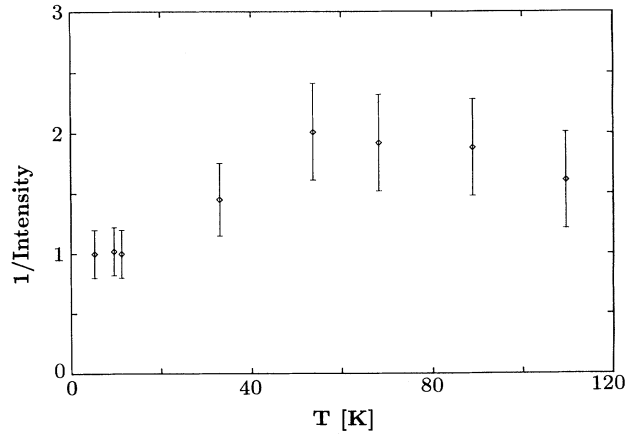

FIG. 4. Intensity of the EPR signal as a function of temperature (normalized to the value obtained at 5 K).

Kip, and Kittel[9] that the resonance moves to lower magnetic field as the frequency is increased. To test this we varied the microwave frequency in our experiment from 9.3 to 9.5 GHz and observed that the resonance moved to higher magnetic field instead. Electron cyclotron resonance also is ruled out since, assuming an effective mass similar to that of wurtzite GaN ($m^*/m_0=0.20\pm0.02$) (Ref. 10) the resonance should occur at a magnetic field ~ 5 times smaller than it was actually observed; moreover, a mobility three orders of magnitude larger than the value reported in similarly prepared GaN films[6] would be required to obtain a distinctive signal in the X band.

The observed resonance is therefore related to the ESR signal whose origin is due either to deep localized defects (intrinsic or impurities), or to delocalized electrons due to the shallow donors discussed earlier. However, the temperature dependence of the EPR intensity, shown in Fig. 4, does not follow the Curie-Weiss law suggesting that the electrons responsible for the observed resonance are not localized in deep defects. Additional arguments in favor of this conclusion are the lack of hyperfine or superhyperfine structure, expected for localized electrons in intrinsic defects of III-V semiconductors, and the lack of ESR signal in highly resistive films. The observed temperature dependence of the resonance intensity is not consistent with either a Curie or a Pauli paramagnetism. We can only speculate that the observed intermediate regime is related to the fact that the concentration of carriers in the band of the shallow donors as well as in the conduction band depend on temperature.

These findings, together with the conductivity data, suggest that the observed EPR signal at temperatures less than 50 K is due to delocalized electrons in the band of the previously discussed shallow donors and at temperatures higher than 50 K to electrons thermally activated into the conduction band. The fact that we did not observe a change in the g value as a function of temperature suggests that, to within the experimental accuracy, the g value is the same in both bands.

It is interesting to compare our experimental result of the electron g value with theoretical predictions based on the five-band model $\mathbf{k}\cdot\mathbf{p}$ calculation[11–14] and estimate the electron effective mass. According to this model the g value and the electron effective mass are given by the expressions

$$\frac{g^*}{g_e}-1=-\frac{P^2}{3}\left[\frac{\Delta_0}{E_0(E_0+\Delta_0)}+\lambda^2\frac{\Delta_0'}{(E_0'-E_0)(E_0'-E_0-\Delta_0')}\right], \tag{2}$$

$$\frac{m_0}{m^*}-1=\frac{P^2}{3}\left[\frac{3E_0+2\Delta_0}{E_0(E_0+\Delta_0)}-\lambda^2\frac{3(E_0'-E_0)-2\Delta_0'}{(E_0'-E_0)(E_0'-E_0-\Delta_0')}\right], \tag{3}$$

where $\Delta_0=\Gamma_{8v}-\Gamma_{7v}$, $\Delta_0'=\Gamma_{8c}-\Gamma_{7c}$, $E_0'=\Gamma_{8c}-\Gamma_{8v}$, and according to Chadi, Clark, and Burnham[13]

$$\lambda^2P^2=\frac{2}{m_0}|\langle\Gamma_{1c}|p_x|\Gamma_{5c,x}\rangle|^2, \tag{4}$$

$$P^2=\frac{2}{m_0}|\langle\Gamma_{1c}|p_x|\Gamma_{5v,x}\rangle|^2. \tag{5}$$

Hermann and Weisbuch[14] presented an estimate of P^2 based on simplified linear combination of atomic orbitals,

$$P^2_{\rm est}=\frac{\hbar^2\eta^2}{a^2m_0}\left[\frac{(1-\alpha_p^2)^{1/2}-S}{2(1-S^2)}\right]^2, \tag{6}$$

where α_p is the polarity and S is the overlap term[15] and η is a best-fit parameter $\eta=(1.04\pm0.07)\times10^3$.[14] From this expression, with $\alpha_p=0.62$ (Ref. 15) and $S=0.5$,[14] one obtains for GaN $P^2_{\rm est}=28\pm2$ eV. With the following values $E_0=3.2$ eV, $\Delta_0=0.009$–0.016 eV,[16] $\Delta_0'=0.06$–0.1 eV,[17] $E_0'=8.7\pm0.3$ eV,[18] $\lambda^2=0.4$,[13] we obtained $g^*=1.95\pm0.01$ in agreement with our experimental result. The electron effective-mass calculation yields a value of $m^*/m_0=0.15\pm0.01$, a value close to that measured experimentally for GaN films having the wurtzite structure [$m^*/m_0=0.20\pm0.02$ (Ref. 10)].

A brief comment on the utilized values for Δ_0, S, and λ^2 is necessary in order to put the previous calculation in the right perspective. Since the number and orientation of nearest and next-nearest neighbors are the same in the wurtzite and in the zinc-blende structures, the value of the spin-orbit splitting Δ_0 for zinc-blende GaN should not be significantly different from the value evaluated for the wurtzite structure. The latter is known[16] and used in our calculation. The overlap integral S and the parameter λ^2 depend primarily on the ionicity of the bond. GaN is the most ionic of the III-V compounds; however, its ionicity is close to the value for InP for which researchers have used $S=0.5$ (Ref. 14) and $\lambda^2=0.4$.[13]

The possible interaction mechanisms responsible for the spin-lattice relaxation rates of conduction electrons have been discussed by several authors.[19–21] As pointed out by Yafet[21] the dominant relaxation process, at least at not too low temperatures where the spin-current interaction should dominate, is the phonon modulation of the spin-orbit coupling. This mechanism gives the following spin-lattice relaxation rate:[21]

$$T_{1e}^{-1}\sim\frac{2}{\pi^{3/2}\hbar}\frac{D^2}{\rho u^2}\left[\frac{2m^*kT}{\hbar^2}\right]^{5/2}, \tag{7}$$

where ρ is the density, u the sound velocity, and, for a polar semiconductor, $D\sim Cf\delta g(\hbar^2/am^*E_0)$ with C being the deformation potential, f the relative strength of the crystal potential that is odd under inversion, δg the g shift, a a parameter of the order of the lattice constant, and E_0 the optical gap. Using values appropriate to cubic GaN [$\rho=6.1$ g cm^{-3}, $u=6.9\times10^3$ msec^{-1}, $C\sim13$ eV,[22] $f=1$ (Ref. 11)] we find $T_{1e}\sim9\times10^{-5}$ sec at 10 K in general agreement with our experimental result.

In the effort to qualitatively account for the data of Fig. 3 we need to discuss spin-spin relaxation mechanisms which determine T_{2e} and thus the magnitude of the linewidth ΔH_{pp}. The analysis of the matrix elements which contribute to T_{2e}^{-1}, for the relaxation mechanism

previously discussed, show the same **k** and **q** dependence as the matrix elements used for T_{1e}^{-1}. Therefore, T_{1e} and T_{2e} have the same temperature dependence.[21] However Eq. (7) would predict a difference in the linewidths at 10 and 100 K by a factor ≈ 300, in contrast with the experimental results of Fig. 4. We believe that this disagreement is due to the fact that additional spin-spin relaxation mechanisms set in at low temperatures. One relevant relaxation mechanism at low temperatures is the hopping of electrons from one site to another. Such a process was observed to be the dominant line-broadening mechanism at low temperatures in heavily doped n-type silicon.[23] Our conductivity data have indicated hopping conduction, in the investigated sample at temperatures below 50 K, with an activation energy $\varepsilon_3 = 0.5$ meV due to overlap of the shallow donor wave functions and the presence of compensating defects.[7] In the case of hopping motion of electrons, the linewidth is inversely proportional to the probability p of the phonon-assisted transition from one center to another, $\Delta H_{pp} \propto 1/p$. This probability depends on temperature as[7,24]

$$p \propto \left[\exp\left[\frac{\varepsilon_3}{kT} \right] - 1 \right]^{-1} . \tag{8}$$

Therefore, at low temperatures, where hopping is the dominant broadening mechanism, one should observe an increase in the linewidth as the temperature decreases, as perhaps suggested by our experimental point at 5 K.

III. CONCLUSIONS

In conclusion, we reported the observation of an electron spin resonance in zinc-blende gallium nitride thin films produced by the electron-cyclotron-resonance microwave-plasma-assisted MBE method. The EPR signal was attributed to electrons predominantly in the band of autodoping centers (N vacancies) at low temperatures and in the conduction band at higher temperatures. The electron g value was found to be 1.9533 ± 0.0008. Using a five-band model and appropriate parameters for GaN a g value $g^* = 1.95 \pm 0.01$ in agreement with the experimental value was obtained and an effective mass $m^*/m_0 = 0.15 \pm 0.01$ was calculated.

From the saturation behavior of the resonance line a spin-lattice relaxation time of the order of 10^{-5} sec at 10 K was estimated in general agreement with the theoretical value predicted considering the phonon modulation of the spin-orbit interaction as the relaxation mechanism. The temperature dependence of the resonance linewidth was semiqualitatively accounted considering, besides the phonon modulation of the spin-orbit interaction, the hopping process at low temperature as an additional spin-spin relaxation mechanism.

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