

Towards the Identification of the Dominant Donor in GaN

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We analyze optical absorption, transmission, luminescence, and Raman scattering in *n*-type GaN at hydrostatic pressures up to 30 GPa. The results show freeze-out of free electrons above ~ 20 GPa due to trapping at levels that are resonant at ambient pressure but become gap states at high pressures. *Ab initio* calculations show that both the N vacancy and the Ga interstitial undergo this transition at ~ 20 GPa, but the vacancy should be more abundant. The pressure dependence of the yellow luminescence indicates that a transition between a shallow donor and a deep acceptor is involved.

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Gallium nitride is considered to be one of the most promising materials for the construction of short-wavelength light emitting devices, such as blue diodes and lasers [1]. In spite of impressive technological achievements of the last few years (e.g., the production of the first commercially available blue diode), there are still substantial gaps in our knowledge of the basic physical properties of this material. One of them concerns the origin of *n*-type conductivity in undoped GaN crystals. Experimentally, room temperature concentrations of conduction electrons range from 10^{17} to 10^{20} cm⁻³ in bulk samples. In undoped molecular beam epitaxy (MBE) or organometallic chemical vapor deposition (OMCVD) grown epitaxial films the electron concentrations are of the order 10^{17} cm⁻³. Maruska and Tietjen [2] and Ilegems and Montgomery [3] proposed that the autodoping is due to native defects, since concentrations of contaminants are lower by a few orders of magnitude than the highest observed electron concentrations. Furthermore, the electron concentration is sensitive to the growth parameters (temperature and growth rate), which is easier to explain by a varying rate of creation of defects than by a varying incorporation of contaminants. The residual donor was tentatively identified with the nitrogen vacancy [2–5]. Technologically, it is likely that V_N appears during the growth because of the very high nitrogen equilibrium pressure at the growth temperatures; this implies that the growth occurs under Ga-rich conditions. So far, however, the dominant donor was not positively identified with the nitrogen vacancy.

Recently, *ab initio* calculations of electronic structure of native defects in GaN were performed by Bogusławski *et al.* [6] and Neugebauer and Van de Walle [7]. They have shown that V_N introduces a resonant level inside the conduction bands at about 0.8 eV above the band minimum. In the neutral charge state, the one electron that should occupy this resonance autoionizes to the

bottom of the conduction band and becomes bound by the Coulomb tail of the vacancy potential, forming a shallow level. Thus, at atmospheric pressure, the vacancy behaves like a shallow effective-mass donor. When the concentration of vacancies exceeds the critical Mott value, which is about 10^{18} cm⁻³ for GaN, the sample should become metallic.

In order to confirm the presence of a resonant level predicted by the theory we have performed experiments under high hydrostatic pressures. Our method is based on the fact that the pressure coefficient of the bottom of the conduction band is usually higher than that of the resonance. Consequently, at sufficiently high pressures a crossover should occur between the two levels, and the resonance should become a genuine gap state that may trap electrons. After the crossover, free electrons would disappear from the conduction band and would occupy the deep-defect-induced state. To induce the crossover, the conduction band minimum should rise by at least 0.8 eV, assuming that the resonance does not move. Since the pressure coefficient of the gap is about 40 meV/GPa [8], one has to apply a pressure of about 20 GPa. Such high pressures necessitate the usage of diamond anvils, which practically excludes transport measurements. In this Letter we discuss the results of four optical experiments under pressure, which both probe for the existence of the resonant-to-deep transition and shed light on the origin of the so-called yellow luminescence at about 2.3 eV [10], which acts as a lifetime killer and suppresses the important blue luminescence. The first experiment measures the absorption due to free electrons in the infrared (ir) region of the spectrum (0.9–1.6 μ m). The second, complementary experiment measures the far-infrared (2–20 μ m) transmission. The third one investigates the variation with pressure of the yellow photoluminescence. Finally, we analyze our earlier Raman experiments on bulk samples [11].

We have used two types of GaN samples. The first samples were bulk crystals grown at the nitrogen pressure of about 1.5 GPa and temperature of 1500 °C [12]. These samples are characterized by free electron concentration of about $5 \times 10^{19} \text{ cm}^{-3}$. The second type was a $2.5 \mu\text{m}$ epitaxial film grown by MBE on a sapphire substrate. The Hall concentration of electrons was $4 \times 10^{17} \text{ cm}^{-3}$. For the purpose of high pressure measurements, the substrate was thinned to about $20 \mu\text{m}$. The experiments were performed in diamond anvil cells (Mao-Bell-like [13] or Letoullec-Pinceaux [14] designs were used). We have employed a 4:1 methanol-ethanol mixture as a pressure-transmitting medium. A small piece of ruby was placed in the cell to monitor the pressure. Linear ruby scale (3.65 \AA/GPa) was used to determine the pressure from the energy of ruby luminescence.

To measure the absorption, the light beam from a 150 W halogen lamp was focused on a $100 \mu\text{m}$ pinhole, whose image was projected on the sample. The outgoing light was dispersed by a Spex 500M spectrometer and detected by a Peltier-cooled PbS detector. This experimental setup limited the available spectral range to $\lambda \leq 1.6 \mu\text{m}$. Since this represents only a very small part of the free carrier absorption, we have decided to expand the examined spectral range by measuring the transmission. In this experiment we used a Perkin-Elmer 1600 Series Fourier spectrometer equipped with an IR microscope. The microscoping system allowed us to determine very accurately the ratio of the light intensity transmitted through the sample to that passing through the pressure-transmitting medium close to the sample. We measured the total ir transmission of the sample, i.e., the ratio of intensities of the "white" light in the spectral range limited by the sensitivity of our ir detector ($2\text{--}20 \mu\text{m}$). The yellow luminescence was excited either by the 333–363 nm UV light of an argon laser or, at higher pressures, by the 325 nm line of a He-Cd laser. The Raman scattering measurements were performed with the use of a triple Dilor-XY spectrometer. The details of this experiment are given elsewhere [11].

Free carrier absorption in the near ir region was measured in a bulk single crystal with $n \approx 5 \times 10^{19} \text{ cm}^{-3}$. Figure 1 shows the absorption spectra at various pressures. For pressures lower than 15 GPa there is no substantial change in the shape of the absorption. However, between 15 and 20 GPa the intensity of the absorption decreases and practically disappears above 20 GPa.

Figure 2 shows the pressure dependence the total transmission of a thin ($15 \mu\text{m}$) bulk single crystal. The transmission is normalized to that of the pressure-transmitting medium, i.e., it is the ratio of the light intensity transmitted through the sample to that passing close to the sample. The absolute values of the intensities are given in the inset. For pressures lower than about 20 GPa, the transmission is practically constant and close to 15%. The transmission increases rapidly starting at 20 GPa. At the highest pres-

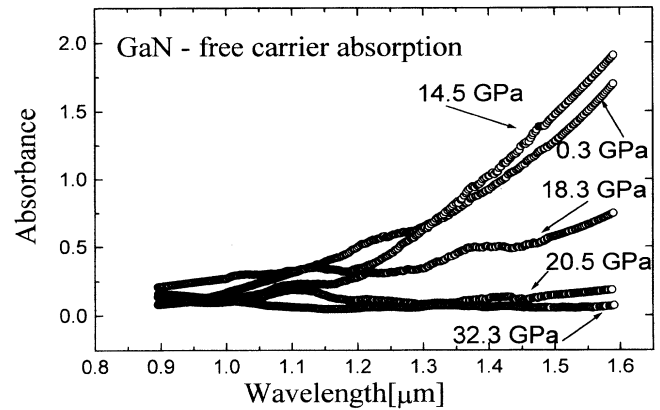


FIG. 1. Free carrier absorption spectra of single crystal bulk GaN at $T = 300 \text{ K}$ for various pressures.

ures the transmission exceeds 100%, which simply means that the absorption of the pressure-transmitting medium is higher than that of the sample.

The pressure dependence of the yellow luminescence is shown in Fig. 3. In this experiment we have used both an epitaxial film and a bulk sample. The mechanism of this luminescence will be discussed below. From Fig. 3 it follows that the energy of the luminescence band changes linearly with pressure up to about 18 GPa. (Thus, at the highest pressures, the yellow luminescence becomes blue.) Its pressure coefficient, about 30 meV/GPa , is very close to the pressure coefficient of the band gap [8]. At about 20 GPa, the slope changes and the peak position does not change with pressure.

Figure 4 compares the Raman spectra of GaN at low (2 GPa) and very high (32.2 GPa) pressures [11] for a sample with electron concentration exceeding 10^{19} cm^{-3} . It shows that new phonon peaks appear in the high pressure

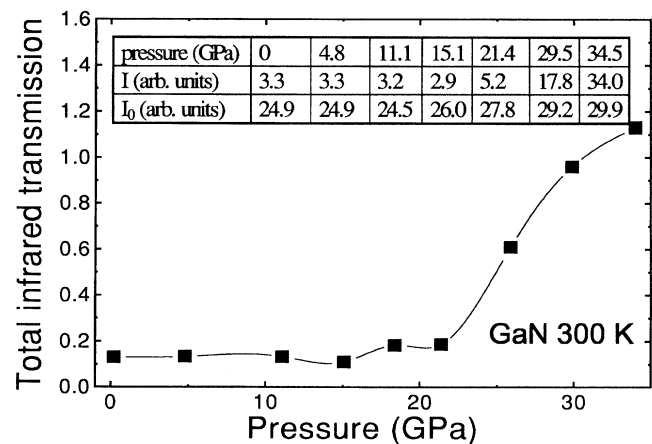


FIG. 2. Pressure dependence of the total infrared transmission of a bulk GaN single crystal at $T = 300 \text{ K}$, I , normalized to the transmission of the pressure-transmitting medium, I_0 . The inset gives absolute values of I and I_0 .

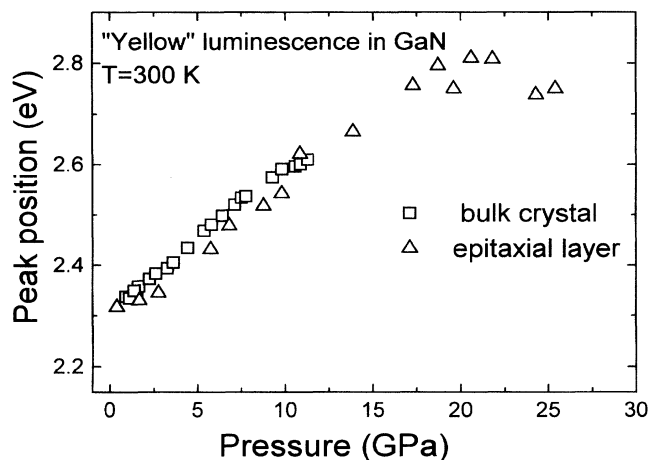


FIG. 3. Pressure dependence of the energy of the yellow luminescence for a bulk sample and an epitaxial film of GaN.

spectrum. Here we are interested in the peak labeled L_5 with wave number of about 850 cm^{-1} at 32.2 GPa. By extrapolating its position to the ambient pressure we obtain an energy of 740 cm^{-1} ; see inset. Since this energy is very close to the $738\text{--}741 \text{ cm}^{-1}$ energy of the LO phonon in GaN recently measured in epitaxial samples [15], we assign the L_5 peak to the LO phonon. The presence of this peak was detected only for pressures higher than 22 GPa, as shown in the inset of Fig. 4.

The experimental results can be consistently explained by the presence of a resonant state in the conduction band. Hydrostatic pressure induces a crossover of the resonance with the bottom of the conduction band at about 20 GPa. After the crossover, conduction electrons become trapped in the resonance-derived gap level. Consequently, since practically all electrons disappear from the conduction

band, the concentration of defects giving rise to the resonance must be equal to or higher than the concentration of dominant native donors. We propose here that it is the native donor that induces the resonance and we identify it with the nitrogen vacancy.

We will now discuss each case in more detail. Both absorption and transmission measurements show that at pressures higher than about 20 GPa the ir absorption in the $0.9\text{--}1.5 \mu\text{m}$ range abruptly decreases. There are two main mechanisms of absorption in the ir region, phonon absorption and free carrier absorption. The former mechanism is important only in the far ir region (i.e., for $\lambda \geq 0.18 \mu\text{m}$), and should not change substantially with pressure. In contrast, free carrier absorption can change considerably when the concentration of free electrons changes. Therefore, we interpret the quenching of the ir absorption as due to a freeze-out of electrons from the conduction band. More precisely, we estimate from our data that the electron concentration decreases by at least 2 orders of magnitude.

This picture explains also the Raman experiment. Our interpretation is based on the work of Mooradian and Wright [16], who observed and discussed the plasmon-phonon coupling in GaAs. They show that the plasmon-phonon coupling shifts the LO mode to higher energies and reduces its oscillator strength. This occurs at low pressures, when the concentration of free carriers is higher than 10^{18} cm^{-3} [17]. The pressure-induced freeze-out of electrons leads to a reappearance of the LO mode.

We now turn to the luminescence data. Two mechanisms of the yellow luminescence have been proposed in the literature. In the first one, the luminescence is due to a transition from the conduction band or a shallow donor state to a deep localized state [10]. The second mechanism [18] assumes a transition from a deep gap state to a

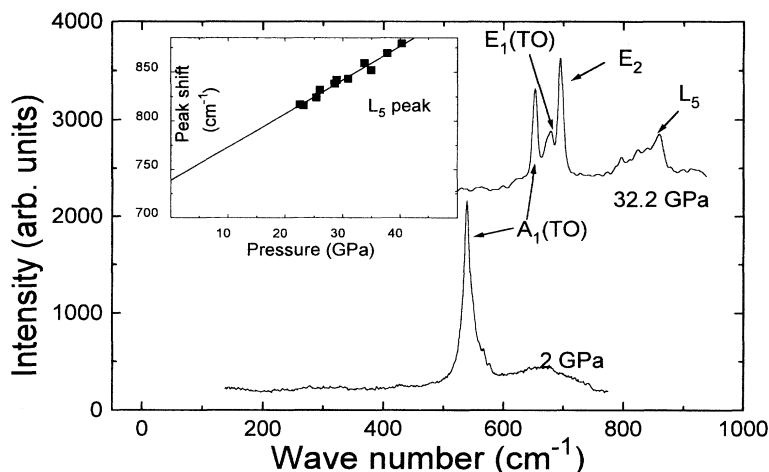


FIG. 4. Raman spectra of a bulk single crystal at low (2 GPa) and high (32.2 GPa) pressures. The peaks labeled $A_1(\text{TO})$, $E_1(\text{TO})$, and E_2 reflect the phonon modes of GaN. Their appearance results from depolarization of the laser light due to strain in the diamond anvils [11]. The peak L_5 appears above about 20 GPa. Inset: pressure dependence of the L_5 peak energy. The solid line represents a linear extrapolation of the peak energy to ambient pressure.

shallow acceptor. The agreement of the pressure coefficient of the yellow luminescence reported here with that of the band gap supports the former mechanism. Note that this interpretation implies that the pressure coefficient of the deep final state is very small, which is indeed plausible for deep states. For example, this is the case for the zinc-related luminescence in GaN [19]. In contrast, it is difficult to explain the observed pressure dependence of this luminescence in the framework of the second mechanism. Accordingly, at low pressures the pressure coefficient of the luminescence is equal to the pressure coefficient of the band gap. After the emergence of the resonance from the conduction band into the gap, the luminescence is due to a transition from the resonance-derived deep state to the same final gap state. This explains the change of slope occurring at about 20 GPa.

To confirm the proposed interpretation we have calculated the electronic structure of the nitrogen vacancy under hydrostatic pressure. The calculations were performed by quantum molecular dynamics, in large unit cells corresponding to 72 atoms in the perfect crystal. We used norm-conserving pseudopotentials, plane-wave basis, and Γ -point sampling of the Brillouin zone. The calculated pressure coefficient of the band gap is 43 meV/GPa, in good agreement with the experimental value [8]. Our results show that the vacancy-induced resonance, located at 0.8 eV above the bottom of the conduction band at zero pressure, moves down with pressure at a rate of 5 meV/GPa. The resonance crosses the bottom of the conduction band at a pressure of about 18 GPa.

We have considered two other explanations of our data. First, we have found that the interstitial Ga also introduces a resonance which crosses the bottom of the conduction band at about 20 GPa. However, the formation energy of V_N is significantly lower than that of Ga(I) [6]. At thermodynamic equilibrium, the concentration of V_N would be greater than that of Ga(I) by a few orders of magnitude [6]. Although the bulk samples and the epitaxial films contain too many structural defects to have been grown at thermodynamic equilibrium, the concentration of V_N is still likely to be higher than that of Ga(I). A second possibility is a pressure-induced crossover of the conduction band minimum at Γ with one of the secondary minima at the edge of the Brillouin zone. According to our results, this crossover occurs at about 60 GPa, which is too high.

In summary, our high pressure optical experiments show that a freeze-out of electrons from the conduction band occurs at about 20 GPa. We propose that this effect is due to an emergence of a conduction band resonance into the forbidden gap. The resonance-derived deep state captures free electrons, leading to the freeze-out of free carriers. This state was observed both in bulk samples and in the epitaxial film. *Ab initio* calculations show that two native defects, the nitrogen vacancy and the interstitial gallium, are shallow donors at ambient pressure. Each

of them introduces a resonance that crosses the bottom of the conduction band at ~ 20 GPa. The good agreement between experiment and theory shows that these are good candidates for the residual donor(s) responsible for the observed *n*-type character of bulk GaN samples. Because of its lower formation energy, the nitrogen vacancy is likely to be significantly more abundant than the interstitial Ga. Our results also show that the pressure dependence of the yellow luminescence is very similar to that of the band gap, suggesting that the yellow luminescence is due to transitions between shallow donors and deep acceptors.

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