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Carrier localization of as-grown *n*-type gallium nitride under large hydrostatic pressure

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A quantitative study of the carrier localization in GaN under large hydrostatic pressure is presented using infrared reflection and Raman spectroscopy. The free-carrier concentration in as-grown *n*-type GaN crystals is determined optically from the phonon-plasmon–coupled mode and an analysis of the dielectric function. A strong decrease from $1\times10^{19}\,\mathrm{cm}^{-3}$ at ambient pressure to only $3\times10^{17}\,\mathrm{cm}^{-3}$ at a pressure of 27 GPa is observed. This free-carrier reduction is attributed to a strongly localized donor present at a concentration of $1\times10^{19}\,\mathrm{cm}^{-3}$ and it is in agreement with previous qualitative results. From our quantitative data we determine the position of the neutral-donor level to be 126^{+20}_{-5} meV below the conduction band at 27 GPa. We present a model for the pressure dependence of the localized defect and predict its neutral level at 0.40 ± 0.10 eV above the conduction-band edge at ambient pressure.

I. INTRODUCTION

Group-III nitrides have regained considerable interest as a wide direct band-gap semiconductor system for optoelectronic and high power devices.[1–3] GaN is currently the most widely studied member of the nitrides family. Despite that, there is still very little known about its defects and impurities; early device performance looks very promising. As-grown GaN can display very high *n*-type conductivity with carrier densities (N) in the $10^{20}\,\mathrm{cm}^{-3}$ range.[4] This can cause serious problems for certain device applications, e.g., *pn* junctions in light-emitting devices because of difficulties in forming *p*-type material. Si is known to be an effective donor in GaN (Ref. 5) and O is suspected to act as a donor, too.[6,7] However, secondary-ion mass spectroscopy yields impurity concentrations too low ($10^{16}\,\mathrm{cm}^{-3}$) to account for the observed carrier concentrations.[8–10] Therefore, high concentrations of intrinsic defects like vacancies, interstitials, and antisite defects or clusters thereof have to be considered. Structural defects like dislocations are unlikely to be electrically active and their concentration should be small in stress-reduced bulk material. Several authors have calculated the doping behavior and the binding energies of various native defects.[11–13] Among the defects considered, the nitrogen vacancy V_N is the most likely one to act as a shallow donor.[14,15,11,12,16]

It is instructive to compare different compounds of the group-III nitrides. While nominally undoped GaN displays very high electron conductivity, AlN is an excellent insulator. In the ternary alloy system $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$, N decreases monotonically when moving from GaN to AlN.[17] This behavior was explained with a deep level emerging from the conduction band (CB) into the band gap as the band gap widens with the Al concentration x. Jenkins, Dow, and Tsai[11] calculated the electronic levels of intrinsic defects in a tight-binding approach and found that the V_N should have levels close to the CB and act as a donor. In GaN they predicted a doubly occupied A_1 state approximately 0.11 eV below the CB and a T_2 level about 0.61 eV above the CB edge associated with a third electron. With increasing x the band gap would open almost linearly up to 6.2 eV in AlN.

The wave function of strongly localized defects like the V_N are built up from contributions of the whole Brillouin zone and show only a small variation with alloy composition relative to the vacuum level. In AlN these levels are predicted to lie 1.60 eV (A_1) and 0.68 eV (T_2) below the CB.[11] In a more recent first-principles calculation by Neugebauer and Van de Walle[13] for GaN these predictions of the T_2 level are confirmed. The lower A_1 bonding state, however, is calculated to lie within the valence band instead. In AlN the antibonding state of V_N should lie within the band gap and should be singly occupied.[11] Far below the CB edge this electron cannot participate in current transport, making AlN highly resistive. In GaN, however, this level should be resonant with the CB and the electron could relax to the band edge and participate in transport. The localized level should cross the CB edge at $x\simeq55\%$. The effect of a very high electron concentration in as-grown material is especially pronounced in bulk material grown by high-pressure and high-temperature synthesis.[18,19]

In analogy to the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ system, the effects of alloying with Al should be equivalent to the effects of hydrostatic pressure.[20] In a recent experiment Perlin *et al.*[21,22] found a decrease of the near-infrared absorbance at pressures of 18–20 GPa. This was interpreted in terms of a reduced Drude absorption as free carriers freeze out to a localized donor state emerging from the CB into the band gap under large pressure. This experiment could only provide qualitative results since it was not possible to determine the free-carrier concentration.

In this paper we attempt to determine the position of the localized state with respect to the band edge. We present infrared reflection and Raman spectroscopy results under large hydrostatic pressure. An independent observation of carrier localization by different experimental techniques is

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reported here, and we obtain more detailed information on the localized defect and the free-carrier concentration. A model for a donor-type localized defect is presented.

II. EXPERIMENT

Bulk GaN crystals with dimensions of 500×300×20 μm^3 were grown by high-pressure synthesis.[23] The platelets are oriented within a plane perpendicular to the c axis. Electron concentrations determined by Hall effect are $1\times10^{19}\,\mathrm{cm}^{-3}$. Infrared reflection was measured using a Bruker (IFS 66V) spectrometer and microscope mirror optics. The optical axis was aligned with the c axis of the crystals. Raman spectroscopy was performed using 5 mW of the 488-nm line of an Ar$^+$ laser in backward and forward scattering. Hydrostatic pressure was applied by a Mao-Bell–type diamond anvil cell (DAC) using nitrogen as a pressure medium. Pressure was monitored by standard ruby fluorescence. All data were taken at room temperature.

Several techniques can be used to determine the carrier concentration under large hydrostatic pressure within a DAC. Electrical measurements have been reported; however, they seem feasible only for easy-to-handle materials such as Pb and Si.[24] On the other hand, optical spectroscopy is very convenient and can provide accurate numbers for N in the high-concentration range.

The plasma of free carriers interacts strongly with optical phonons. This is expressed by the dielectric function in the oscillator model,

$$\epsilon(\bar{\nu})=\epsilon_\infty\left(1+\frac{\bar{\nu}_L^2-\bar{\nu}_T^2}{\bar{\nu}_T^2-\bar{\nu}^2+i\bar{\nu}\Gamma}-\frac{\bar{\nu}_p^2}{\bar{\nu}(\bar{\nu}-i\gamma)}\right). \qquad (1)$$

The susceptibility of the free carriers is described by the plasma frequency ω_p, $\omega_p^2=Ne^2/(\epsilon_0\epsilon_{\mathrm{stat}}m^*)$ with a scattering rate γ and a singularity at $\bar{\nu}=0$ (third term) within the complex wave-number plane $\bar{\nu}$ [$\bar{\nu}=\omega/(2\pi c)$ and m^* effective electron mass]. Optical phonons have an electric dipole moment and contribute to $\epsilon(\bar{\nu})$ by a harmonic oscillator at frequency $\bar{\nu}_T$, which is identified with the transverse-optical (TO) phonon mode and a damping coefficient Γ (second term) [$\bar{\nu}_L$ corresponds to the longitudinal (LO) mode]. ϵ_∞ is given by the high-frequency limit of $\epsilon(\bar{\nu})$, while ϵ_{stat} corresponds to $\bar{\nu}=0$. Reflection is given by $R=(1-\sqrt{\epsilon})^2/(1+\sqrt{\epsilon})^2$.

In the case of a vanishing N ($\bar{\nu}_p\rightarrow 0$) reflection is very strong in the reststrahlen band that extends from the TO to the LO frequency. A characteristic minimum is located at slightly higher wave numbers. With increasing carrier concentration the LO mode couples to the plasmon. The high-frequency edge of the reststrahlen band broadens and shifts to higher energies. Consequently, the minimum in reflectivity shifts and its position is sensitive to N. The agreement with data from Hall measurements has been demonstrated by Barker and Ilegems.[4] Within the interesting range $N\leqslant1\times10^{19}\,\mathrm{cm}^{-3}$ the dependence of the concentration on the energy of the minimum in reflection can be well approximated by a three-parameter fit for GaN:

$$\begin{aligned} N&=N_0(\bar{\nu}_{\min}-\bar{\nu}_0)^r\\ &=5.3\times10^{16}\ \mathrm{cm}^{-3}\left(\frac{\bar{\nu}_{\min}}{\mathrm{cm}^{-1}}-774\right)^{0.876}. \end{aligned} \qquad (2)$$

Here we used the following parameters: $m^*=0.236$,[25] $\epsilon_\infty=5.35$, $\bar{\nu}_{E1\mathrm{LO}}=743\,\mathrm{cm}^{-1}$, $\bar{\nu}_{E1\mathrm{TO}}=561\,\mathrm{cm}^{-1}$, $\gamma=400\,\mathrm{cm}^{-1}$, and $\Gamma=11\,\mathrm{cm}^{-1}$.[26] In the applied geometry E_1 modes are infrared active.[27] In addition to these bulklike effects, an influence of the interface has to be considered as well. Surface roughness can reduce the maximum signal, but fortunately the strong effect of the reststrahlen band and the reflectivity minimum are very little affected by an interface with any transparent medium like N_2 or air.[4] However, care must be taken for thin GaN films on sapphire or SiC substrates as they are not transparent in the GaN phonon region. In this study we use bulk material and therefore such effects can be neglected. Reflection data on a very thick GaN layer (300 μm) with low N were presented elsewhere.[28]

Besides reflection experiments, the phonon-plasmon–coupled mode can be studied by Raman scattering. In this case the position and the shape of the phonon-plasmon–coupled mode is sensitive to N.[29] From similar considerations one can obtain a relationship between N and the position and line shape of the phonon-plasmon peak in the Raman experiment. Kozawa *et al.*[26] correlated the concentration obtained by this technique with Hall data on Si-doped GaN layers and found good agreement. Here we use the identical parameters except for m^*, which has been replaced by a more recent value.[25] Similar to the case of the reflectivity spectra, as shown in Eq. (2), one can relate the frequency of the phonon-plasmon peak to the free-electron concentration in GaN using the A_1 phonons $\bar{\nu}_{A1\mathrm{LO}}=734\,\mathrm{cm}^{-1}$ (Raman active) and $\bar{\nu}_{A1\mathrm{TO}}=532\,\mathrm{cm}^{-1}$ (Raman forbidden):

$$N=1.1\times10^{17}\ \mathrm{cm}^{-3}\left(\frac{\bar{\nu}_{\max}}{\mathrm{cm}^{-1}}-736\right)^{0.764}. \qquad (3)$$

This expression is valid for $N\leqslant1\times10^{19}\,\mathrm{cm}^{-3}$. An expression for the line shape is given in Ref. 26.

III. RESULTS

Reflection at ambient pressure measured on the highly conducting sample is represented by curve (a) in Fig. 1. A high reflection is observed at low energies. It gradually decreases at higher energy without any detectable minimum. At this high N the LO mode is strongly distorted by the plasmon. As the mobility is low, approximately 200 cm^2/V s, the coupled mode is overdamped and all expected characteristic features are smeared out. Some interference fringes are observed due to terracelike steps on the front surface of the small bulk crystal.

After application of large hydrostatic pressure of 27 GPa the reflection of the sample changes quite significantly [curve (b) in Fig. 1]. A clear reststrahlen band stretches from $\sim$600 to 900 cm^{-1}. The A_1(TO) phonon mode is found at $\sim$635 cm^{-1} and the A_1(LO) plasmon mode is assigned to the falling edge of this band. The minimum is located at $\sim$910 cm^{-1}. Apparently N is strongly reduced and the LO phonon is to a great extent decoupled from the electron-plasmon motion.

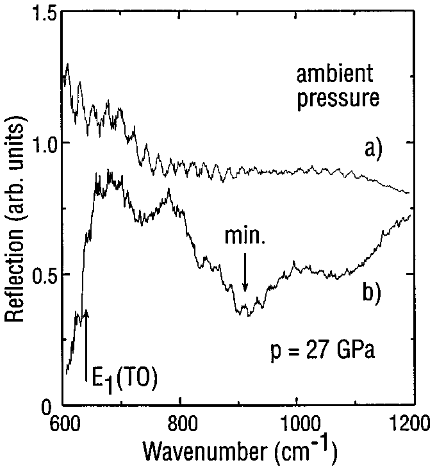

FIG. 1. Infrared reflection in the phonon region of single-crystal GaN at ambient pressure (a) and at 27 GPa (b). Note the appearance of the minimum at 910 cm^{-1} in curve (b).

Additional information is obtained by Raman scattering (Fig. 2). At ambient pressure we find a strong E_2(high) mode at 565 cm^{-1} in $z(x,-)\bar{z}$ backscattering and a weak indication of the forbidden A_1(TO) mode (529 cm^{-1}) [spectrum (a)]. As they do not couple to the carrier plasma they are readily observed at high N, whereas there is no evidence for a LO mode. Again, due to the low electron mobility in GaN, the coupled mode is overdamped and vanishes within the background signal. Beyond the transition at 27 GPa the situation changes [spectrum (b) in Fig. 2]. The E_2(high) mode (664 cm^{-1}) is shifted by $\sim$100 cm^{-1} similar to the TO mode observed in reflection. The A_1(TO) mode has moved to 631 cm^{-1}. In addition, on the high-energy side the coupled E_1(LO) phonon-plasmon mode appears at 825 cm^{-1} with a somewhat distorted line shape compared to the other resonances. The high background signal in this measurement is a consequence of our forward-scattering geometry. From an analysis of the line shape of the phonon-plasmon mode as described by Kozawa *et al.*[26] we find $N \simeq 3\times10^{17}$ cm^{-3}.

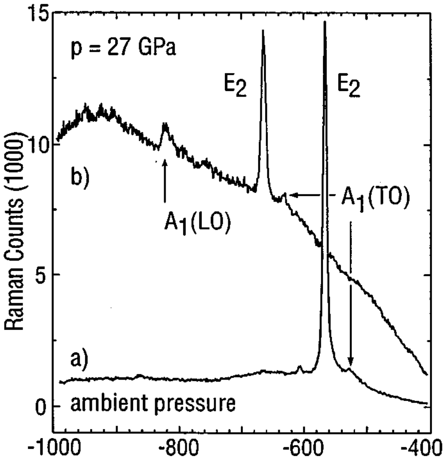

FIG. 2. Raman scattering at ambient pressure (backward scattering) (a) and at 27 GPa (forward scattering) (b). Note the appearance of the distorted A_1(LO)-plasmon–coupled mode at 825 cm^{-1} in curve (b).

IV. DISCUSSION

Selection rules in wurtzite GaN allow Raman observation of A_1(LO), E_2(high), and E_2(low) in $z(x,-)\bar{z}$ backward and $z(x,-)z$ forward scattering.[27] E_1(LO) and E_1(TO) can be observed in the infrared. In Raman the forbidden A_1(TO) mode shifts by 102 cm^{-1} from 529 cm^{-1} (ambient pressure) to 631 cm^{-1} (27 GPa) equivalent to a pressure derivative $d\bar{\nu}/dp = 3.78$ cm^{-1}/GPa in a linear model. The E_1(TO) value from reflection is very close to 635 cm^{-1} (27 GPa). This is in good agreement with experimental results[30] and corresponds to a Grüneisen parameter $G = B_0 d\bar{\nu}/(\bar{\nu} dp) = 1.74$, assuming a bulk modulus $B_0 = 245$ GPa.[30] The strong Raman mode E_2(high) shifts by about the same amount from 565 cm^{-1} to 664 cm^{-1} resulting in $d\bar{\nu}/dp = 3.67$ cm^{-1}/GPa and $G = 1.59$. For the bare A_1(LO) and E_1(LO) modes in GaN, which lie very close at ambient pressure, we may therefore assume a similar shift of $\sim$100 cm^{-1} at the pressure of 27 GPa. It is known from several III-V compounds (GaAs, GaSb, GaP and AlSb) that the same $d\bar{\nu}/dp$ is observed for LO and TO modes.[31] In a highly resistive sample the A_1(LO) mode lies at 734 cm^{-1} (ambient pressure) and compared to its expected value at 27 GPa the observed Raman mode at 825 cm^{-1} can have only a very small additional shift due to plasmon interaction.

Using these parameters in the interpretation of the reflection minimum located at 910 cm^{-1} we find from Eqs. (1) and (2) that $N \leq 1\times10^{18}$ cm^{-3} from the reflection measurement. Providing that a maximum error in the Raman peak position is ± 5 cm^{-1} we find from Eqs. (1) and (3) that N is in the range of 0–3×10^{17} cm^{-3} from the Raman experiment. As mentioned above, an interpretation of the Raman line shape results in $N \simeq 3\times10^{17}$ cm^{-3} in good agreement with the other results. This value will be used in the further interpretation.

From the pronounced reststrahlen band and the constant Raman linewidth of the E_2(high) mode we conclude that no irreversible lattice damage and disorder were introduced to the sample. We find that at a pressure of 27 GPa the carrier concentration has dropped by about two orders of magnitude. In contrast to the previous absorbance result[21,22] we have been able to measure the actual carrier concentration.

From the reduction of the free-carrier concentration down to 3% we can determine the location of the localized neutral-donor level. Dealing with such high concentrations we can neglect small defect concentrations in the range of, e.g., 1×10^{16} cm^{-3} or less, on the one hand, and even if we were to deal with a case of a broad energy distribution of defect levels, carrier statistics will be dominated by the average value discussed here. The donor concentration is given by the number of free carriers at ambient pressure, $N_d = 1\times10^{19}$ cm^{-3}. At 27 GPa and at room temperature only $N_{\mathrm{di}} = 3\times10^{17}$ cm^{-3} are ionized, which corresponds to a Fermi energy at 56 meV below the CB edge Γ_c ($\Gamma_c - 56$ meV). Ionizing 3% of the donors ($N_{\mathrm{di}}/N_d = 0.03$) from a sixfold degenerate T_2 state requires a binding energy of 100 meV. However, as pointed out by Neugebauer and Van de Walle,[13] this donor level should split due to the

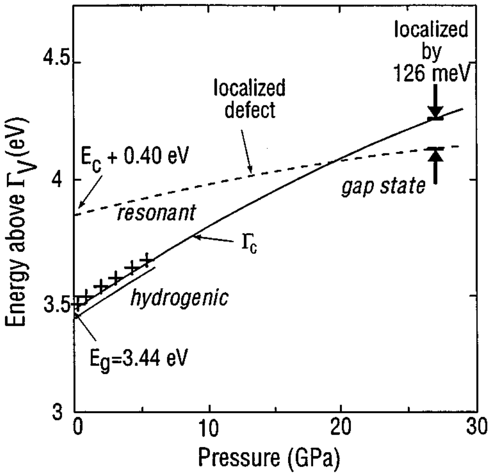

FIG. 3. Model of the energy levels. Experimental results are represented by thick crosses and arrows, calculation results by thin lines. We find the neutral-donor level at $E_c + 0.40 \pm 0.10$ eV at ambient pressure. Other models estimate $E_c + 0.8$ eV (Ref. 21) and $E_c + 0.61$ eV (Ref. 11).

wurtzite symmetry and the level in question should only be twofold spin degenerate, which then corresponds to a binding energy of 126^{+20}_{-5} meV.

The localization of carriers has to be considered with respect to the band edges. Christensen and Gorczyca[32] performed a band-structure calculation for wurtzite GaN including hydrostatic pressure. The pressure dependencies of the high-symmetry points are obtained by a local-density approximation. For the fundamental band gap $\Gamma_c - \Gamma_v$ they predict a shift of $\Delta E_\Gamma/\text{meV} = 39\, p/\text{GPa} - 0.32(p/\text{GPa})^2$ equivalent to 820 meV at 27 GPa (thin solid line in Fig. 3). Experimental data on bulk GaN crystals are available in the low-pressure range $p \leq 5.5$ GPa (thick crosses).[23] We cannot compare with data obtained from photoluminescence experiments in thin films on sapphire substrates. In these films biaxial stress induced by the lattice mismatch and the different pressure coefficients of substrate and film has to be considered in the interpretation.[33] The room-temperature band-gap value is adopted in the calculation to be 3.44 eV.[34]

Delocalized hydrogenic defect states consist of the wave function of the closest band extremum only. Assuming a constant effective mass and dielectric constant their donor levels follow the CB when the band gap increases under pressure. This is not limited to the Γ minimum since in many instances the hydrogenic donor level becomes associated with other minima as they move below the Γ minimum at large hydrostatic pressures. According to band-structure calculations[32] this is not expected to happen in GaN before the phase transition to the rocksalt structure [$\gtrsim 37$ GPa (Ref. 35), 47 GPa (Ref. 30)]. This is in contrast to the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and the $\text{GaAs}_{1-x}\text{P}_x$ systems where the X band "crosses" the Γ band under pressure and shallow bound electrons in hydrogenic levels are transferred to the X band.

The energy levels of strongly localized defects are not only dependent on the band extrema. They can actually lie inside the band or in the band gap. Donor-type states are mainly built up from the whole Brillouin zone of the first CB and their pressure dependence is typically given by the average of those bands.[36,37] To determine the pressure variation of the localized state we average the pressure dependent shifts of the points $c \in \{\Gamma, K, M, A, L, H\}$ using a normalized weight function d_i. In this weight function we include the degeneracy and the number of equivalent points and their direction-dependent effective mass $m^{*3/2}$ according to the given band-structure calculation.[32] We find $d = 7.1\%$ (Γ), 19% (K), 38% (M), 8.7% (A), 19% (L), and 7.9% (H). The dominance of the M-point results from the slowly varying dispersion in the vicinity of M, which corresponds to a high density of states. Using these relative weights we obtain the pressure dependence

$$\Delta E_{\text{av}}(p) = \sum_{i=c} d_i [E_i(p) - E_i(0)] \tag{4}$$

$$= 15.4 \text{ meV} \frac{p}{\text{GPa}} - 0.17 \text{ meV} \left(\frac{p}{\text{GPa}} \right)^2. \tag{5}$$

In this model Eq. (5) describes the pressure dependence of the localized donor state (dashed line in Fig. 3) and the absolute value is given by our experimental value $E_c - 126$ meV at 27 GPa (*gap state* in Fig. 3). From this pressure dependence we expect at ambient pressure this neutral donor level to lie about 0.40 ± 0.10 eV above the Γ band edge (*resonant* state). The accuracy of this level prediction can easily be improved as soon as experimental data for the band gap at large pressures are available. The crossing of the level with the Γ band edge is observed at about 19 GPa, which is in good agreement with the previously reported results of the infrared transmission experiments.[21]

On the other hand, neglecting any pressure dependence of the localized level with respect to the valence-band edge would result in a level location $E_c + 0.68$ eV at ambient pressure. Such a model has been used in Ref. 21. There a linear increase of the band gap was assumed at a rate of 47 meV/GPa and an energy level of $E_c + 0.8$ eV was predicted at ambient pressure. Although these values are closer to the theoretical predictions of Ref. 11, $E_c + 0.61$ eV, this agreement could be fortuitous as there is considerable uncertainty in the absolute energy calculation of localized defects. Our approach described above makes use of relative energy shifts only and the result $E_c + 0.40 \pm 0.10$ eV is much more reliable.

V. SUMMARY

From the observed strong reduction of the free carrier concentration to 3% at 27 GPa with respect to the concentration at ambient pressure we conclude a defect concentration as high as $1 \times 10^{19}\ \text{cm}^{-3}$. This defect is strongly localized and has a band-gap state 126^{+20}_{-5} meV below the conduction band at 27 GPa. It is responsible for both the high free-electron concentration at ambient pressure and for the capture and the localization at 27 GPa. We predict a resonant level of the neutral localized defect state at 0.40 ± 0.10 eV above the conduction-band edge at ambient pressure. Our findings can be explained by the model of strongly localized native defects. One candidate is the nitrogen vacancy as proposed by several authors;[11–13] however others have to be considered as well.

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