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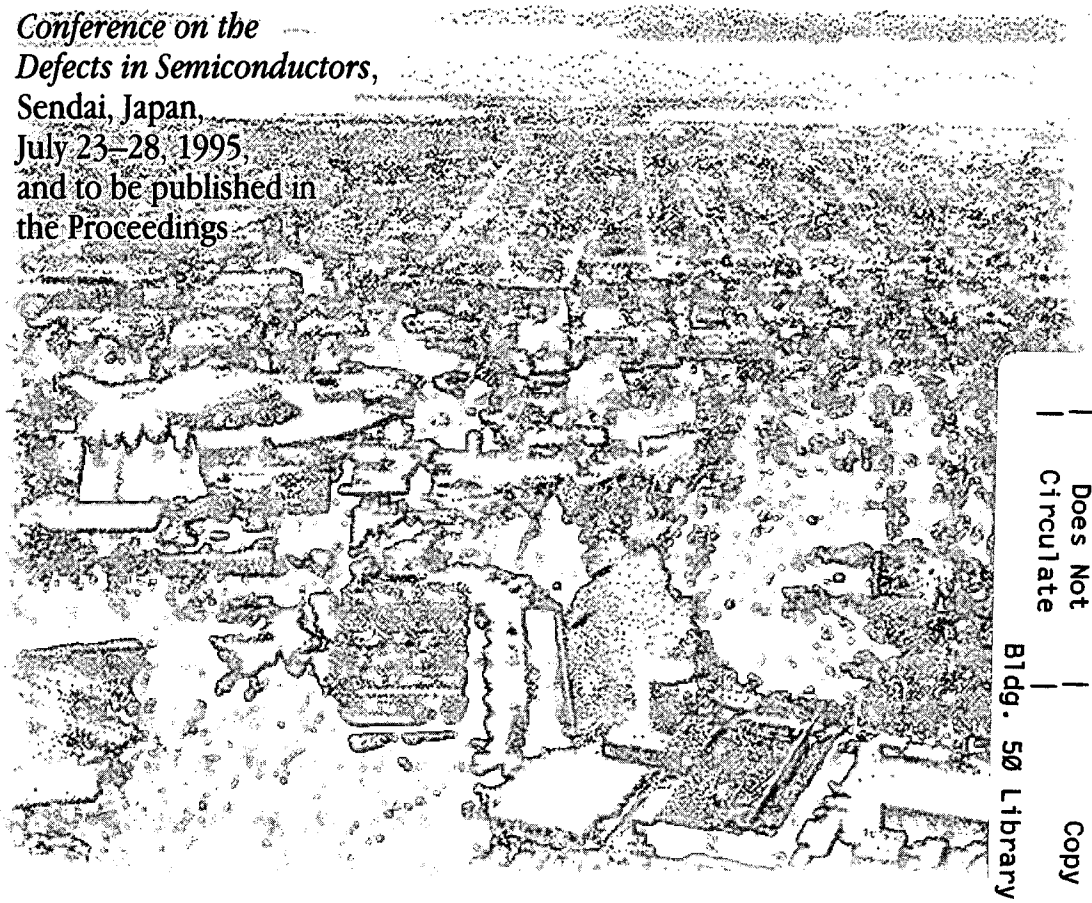

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# CARRIER LOCALIZATION IN GALLIUM NITRIDE

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Key words; GaN, donor, hydrostatic pressure, infrared, Raman

**Abstract.** In wide bandgap GaN a large number of interesting and important scientific questions remain to be answered. For example, the large free electron concentration reaching $10^{19}$ to $10^{20}$ $cm^{-3}$ in nominally undoped material are ascribed to intrinsic defects because no chemical impurity has been found at such high concentrations. According to theoretical models a nitrogen vacancy acts as a donor but its formation energy is very large in n-type materials making this suggestion controversial. We have investigated the nature of this yet unidentified donor at large hydrostatic pressure. Results obtained by infrared reflection and Raman scattering indicate strong evidence for localization of free carriers by large pressures. The carrier density is drastically decreased by two orders of magnitude between 20 and 30 GPa. Using several techniques we provide independent evidence for results contained in earlier reports and present the first quantitative analysis. A possible interpretation of this effect in terms of the resonant donor level is presented.

## Introduction

Group-III nitrides have regained considerable interest through the successful implementation of bright blue and blue-green light emitting diodes [1,2,3]. However, the development of advanced opto-electronic devices such as laser diodes require a better understanding of the defect formation and doping processes in GaN. As-grown GaN can display very high n-type conductivity with carrier densities N in the $10^{20}$ $cm^{-3}$ range [4]. Si is known to be an effective donor in GaN and O is also a likely candidate. So far, however, no impurities could be identified at sufficiently high concentrations as to account for the high electron concentration. Consequently high concentrations of structural or intrinsic defects like vacancies, interstitials and antisites have to be considered. Carrier concentrations in the $10^{16}$ $cm^{-3}$ have been reported, however, the question of the dopant has not been solved. The doping behavior and the binding energies of various defects have been calculated by several authors [5,6,7]. Among these the nitrogen vacancy, $V_N$, is the most likely one to act as a donor [5,6] though its formation energy seems to be large.

The interpretation of a strongly localized defect is supported by a comparison of GaN with AlN which is an excellent insulator. It was found that the carrier concentration decreases monotonically with $x$ in the ternary system $Al_xGa_{1-x}N$ [8]. This can be explained by a level emerging from the conduction band (CB) into the energy gap as the bandgap widens with the Al concentration. In analogy to the $Al_xGa_{1-x}As$ system, the effects of alloying with Al should be equivalent to the effect of hydrostatic pressure [9]. Recently Perlin *et al.* [10] found a decrease in the near infrared absorbance at pressures of 18 to 20 GPa. This was interpreted in terms of a reduced Drude

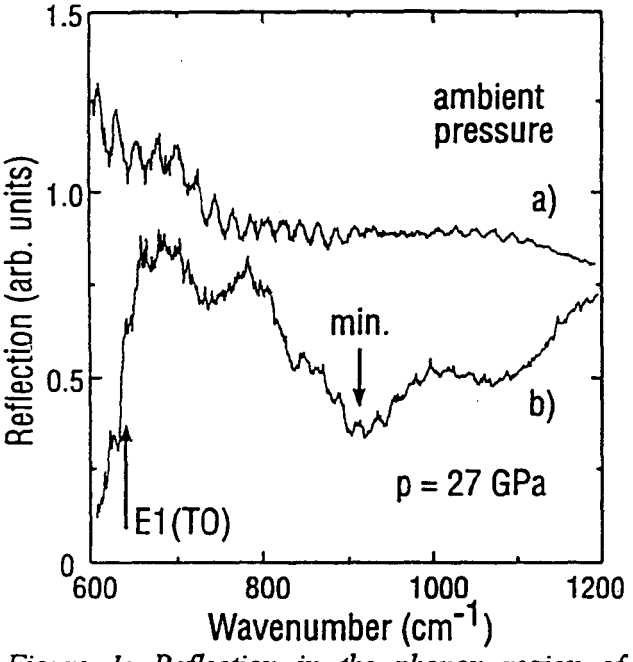


*Figure 1: Reflection in the phonon region of highly conducting GaN at ambient pressure a) and after carrier localization at 27 GPa b).*

absorption as carriers freeze out to a localized donor state emerging from the CB into the bandgap under pressure. In contrast to this qualitative results we have measured the free carrier concentration under pressure and determined the position of the localized state with respect to the band edge.

**Experimental**

We have investigated bulk GaN crystals grown by high pressure synthesis [11]. The typical size of these platelets are 500 x 300 x 20 $\mu m^3$ with the c-axis normal to the larger dimensions. Hall measurements show electron concentrations of $1x10^{19}$ $cm^{-3}$. Infrared reflection was measured using a Bruker spectrometer and a microscope. 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 both backward and forward scattering. Hydrostatic pressure was applied by a diamond anvil cell (DAC) using nitrogen as a pressure medium. All data were taken at room temperature.

The concentration of free carriers can be determined from their strong interaction with optical phonons. Using an oscillator model, this can be expressed by the dielectric function $\varepsilon(\nu)$. The susceptibility of the free carriers is dominated by the plasma frequency $\omega_p^2 = Ne^2/(\varepsilon_0 \varepsilon_{stat} m^*)$ with a singularity at $\nu = 0$ within the complex wavenumber plane $\nu$ ($m^*$ electron effective mass). Optical phonon contribution to $\varepsilon(\nu)$ can be approximated by a harmonic oscillator at the transverse optical (TO) phonon frequency.

In the case of a small carrier concentration and vanishing $\omega_p$ reflection is strong in the reststrahlen band extending from the TO to the longitudinal optical phonon (LO) frequency with a characteristic minimum at $\nu$ slightly higher than the LO phonon. At higher carrier concentration the LO mode couples to the plasmon and 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 [4]. From a fit to the model we find a relation between the minimum position and the carrier concentration. Reflection data on a very thick GaN layer with low N were presented elsewhere [12].

Besides reflection experiments in the infrared the phonon-plasmon coupled mode can be studied by Raman scattering where the position and the shape of the phonon-plasmon is sensitive to N [13]. 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. This was shown recently for GaN by Kozawa *et al.* [14] who correlated Raman spectra with Hall data and found good agreement. Using their model and parameters one can relate the frequency of the phonon-plasmon peak to the free electron concentration for $N \leq 1 \times 10^{19}$ $cm^{-3}$

$$N = 1.1x10^{17}\ cm^{-3}\ (\upsilon_{max}/cm^{-1} - 736)^{0.764}. \qquad (1)$$

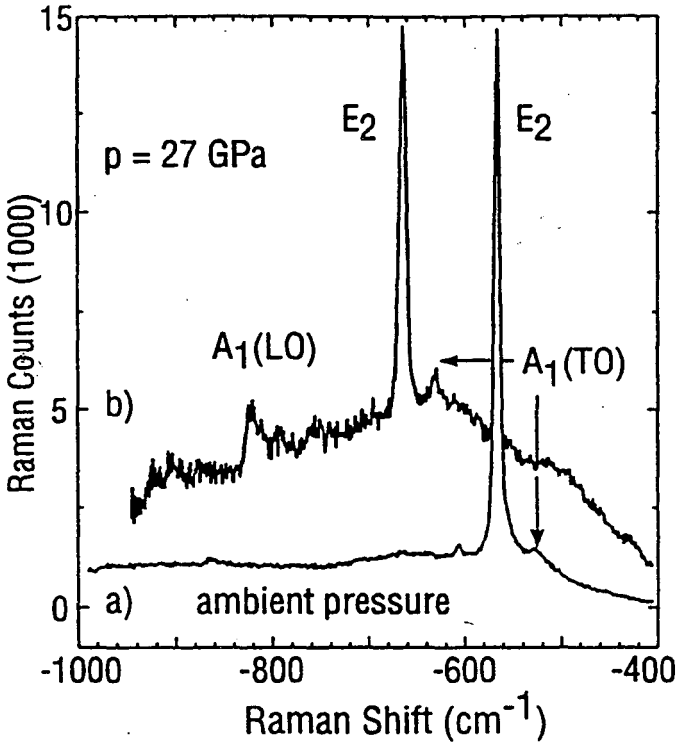


*Figure 2: Raman scattering at ambient pressure (backward scattering) a) and at 27 GPa (forward scattering) b). Note the appearance of the distorted $A_1$(LO)-plasmon coupled mode at 825 $cm^{-1}$ in curve b).*

An expression for the line shape is given in Ref. [14].

**Results**

The reflection of the highly conducting sample at ambient pressure is shown in Fig. 1, spectrum a). The reststrahlenband is smeared out over a wide range due to the interaction of the LO phonons with the overdamped plasmons. At a large hydrostatic pressure of 27 GPa, however, the reflection changes quite significantly (spectrum b). A clear reststrahlen band stretches from 600 to 900 $cm^{-1}$. The $E_1$(TO) phonon mode is found at ~635 $cm^{-1}$ and the $E_1$(LO)-plasmon mode is assigned to the falling edge of this band. The adjacent minimum is located at ~910 $cm^{-1}$. Here phonons are decoupled from the plasmons after N is strongly reduced.

In addition this effect can be observed 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 $cm^{-1}$) (Fig. 2a). These modes do not couple to the plasmon and they are observed at high N whereas there is no evidence for a LO mode. At 27 GPa again the situation has changed (Fig. 2b). The $E_2$(high) mode is shifted by ~100 $cm^{-1}$ similar to the $E_1$(TO) mode observed in reflection. The $A_1$(TO) mode has moved by a similar amount. But in addition the coupled $A_1$(LO)-plasmon mode appears at 825 $cm^{-1}$ with a rather broad line. From an analysis of the line shape of the coupled mode as described by Kozawa *et al.* [14] we find $N \approx 3 \times 10^{17}$ $cm^{-3}$.

**Discussion**

Due to the wurtzite structure of GaN TO and LO modes are split into $A_1$ and $E_1$ modes. In the adopted geometries the $A_1$ modes are Raman active and the $E_1$ modes show up in the infrared. For all observed modes we find a similar pressure coefficient $d\upsilon/dp = 3.6 - 3.8$ $cm^{-1}$/GPa, which is consistent with earlier reports [15]. We, therefore, can expect a similar shift of the unperturbed LO modes. Using these values in the interpretation of the reflection minimum located at 910 $cm^{-1}$ we find $N \leq 1 \times 10^{18}$ $cm^{-3}$ from the reflection measurement and N to be in the range of 0 to $3 \times 10^{17}$ $cm^{-3}$ from the Raman experiment. As mentioned above, an interpretation of the Raman line leads to $N \approx 3 \times 10^{17}$ $cm^{-3}$ which in good agreement with the other results.

We, therefore, conclude that at a pressure of 27 GPa the carrier concentration has dropped by about two orders of magnitude. From this reduction down to 3 % we can determine the location of

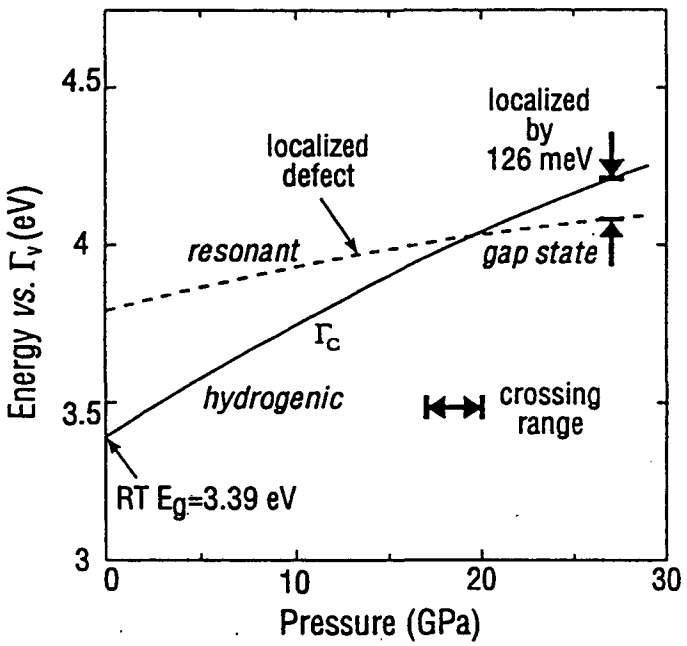


*Figure 3: Model of the energy levels. Experimental results are represented by thick lines and arrows, calculation results by thin lines. The neutral donor level is predicted at $E_C$ + 0.40 ± 0.10 eV at ambient pressure.*

the localized neutral donor level. The donor concentration $N_d$ = $1x10^{19}$ $cm^{-3}$ is given by the Hall data at room temperature. At 27 GPa only $N_{di}$ = $3x10^{17}$ $cm^{-3}$ are ionized. This corresponds to a Fermi energy at 56 meV below the CB edge $\Gamma_c$. At this point it should be mentioned that these findings are independent of any assumption of a distribution of donor levels.

In a next step we can assume that one level dominates the defect distribution and we can determine its position. Ionizing 3 % of the twofold spin degenerate donors corresponds to a binding energy of 126 +20/-5 meV at 27 GPa.

The localization of carriers has to be considered with respect to the band edges. From band structure calculations [16] the fundamental bandgap $\Gamma_c$ - $\Gamma_v$ is predict to shift by 820 meV at 27 GPa (thin solid line in Fig. 3). Experimental data are available only for low pressures p ≤ 5.5 GPa and can not be extrapolated to 27 GPa [11].

Donor type states of strongly localized defects require the full Brillouin zone of the first CB for an accurate description and their pressure dependence is typically given by the average of those bands [17]. To determine the pressure variation of the localized state we average the pressure dependent shifts of the points c ∈ {Γ, K, M, A, L, H} using a normalized weighing function $d_i$. In this function we include the degeneracy, the number of equivalent points and the density of states as given by the bandstructure calculation [16]. We find a strong contribution of d = 38 % of the M-minimum, which results from the slowly varying dispersion in its vicinity and a high density of states. We therefore obtain the predicted pressure dependence (dashed line in Fig. 3)

$$\Delta E_{avg}/\text{meV} = 15.4\ (\text{p/GPa}) - 0.17\,(\text{p/GPa})^2 . \qquad (2)$$

The absolute value is given by the experimental value $E_C$ - 126 meV at 27 GPa (*gap state* in Fig. 3). From this dependence we expect this neutral donor level to lie about 0.40 ± 0.10 eV above the Γ band edge at ambient pressure (*resonant* state). 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 infrared transmission experiments [10].

**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 net donor concentration as high as $1x10^{19}$ $cm^{-3}$. This donor is strongly localized and has its main bandgap 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 donor state at 0.40 ± 0.10 eV above the conduction band edge at ambient pressure. Our findings support the model of strongly localized defects, e.g., the nitrogen vacancy as discussed by several authors [5,6,7].

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