Pressure Induced Deep Gap State of Oxygen in GaN

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O and Si donors in GaN are studied by Raman spectroscopy under hydrostatic pressure p. The ground state of O is found to transfer from a shallow level to a deep gap state at $p > 20$ GPa reminiscent of DX centers in GaAs. Transferred to $Al_xGa_{1-x}N$ we predict that O induces a deep gap state for $x > 0.40$. In GaN:Si no such state is induced up to the highest pressure obtained ($p = 25$ GPa) equivalent to $x = 0.56$ in $Al_xGa_{1-x}N$ and possibly higher. We attribute this distinction to the lattice sites of the dopants. O substituting for N is found to be the origin of high free electron concentration in bulk GaN crystals. [S0031-9007(97)03179-7]

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Donors in III-V compound semiconductors are of special interest because they can assume both extended or localized states, i.e., they can be metastable [1–4]. In the most thoroughly studied system, GaAs, either a high free carrier concentration n, alloying with AlAs, or application of hydrostatic pressure p can induce a transition from a shallow hydrogenic state of the dopant to a strongly localized one of the same impurity. Many different donor species, e.g., Si_{Ga} (group-IV element on group-III site) and S_{As} (group-VI on group-V site), transform into the nonhydrogenic configuration at very similar characteristic transition pressures [3,4]. In addition, metastability effects, such as a limited free electron concentration and persistent photoconductivity, have been found and interpreted with activation barriers between the different configurations of the donor. All of these effects have been associated with a so-called DX center [2].

In GaN we find that the O donor dopant shows characteristic features of a DX defect when hydrostatic pressure is applied. Si, in contrast, behaves like a hydrogenic donor. This distinction is attributed to the actual lattice site of the impurity, and this effect is extremely pronounced in this compound semiconductor system. The pressure experiments can directly be transferred from GaN to the $Al_xGa_{1-x}N$ system predicting a strongly localized gap state of O for higher Al concentrations.

Dopant impurities typically can induce both resonant and hydrogenic defect levels in the electronic band structure. In many cases only the hydrogenic level is relevant. Under certain conditions, however, a charge transfer from a quasihydrogenic state to a strongly localized neutral charge state (D^0) can occur [5]. In addition, as proposed by Chadi and Chang [1], a structural relaxation of the donor impurity in the vicinity of the transition conditions can lead to an activation barrier between the two states. This widely accepted model of a structural relaxation explains the metastability and the activation barrier between the different states of DX centers. Promoted by the transfer of electrons, this new strongly localized state (DX) can be the ground state [6]. *Ab initio* calculations reproduce the experimental observations in GaAs, including the very similar transition conditions found for all substitutional donor species in GaAs [1].

An interesting new aspect of this model is offered by the III-V compound GaN, which exhibits an extreme mass ratio of its two host lattice atom species and a very strong bond. We have studied both types of donors, namely, Si (group-IV on group-III site) and O (group-VI on group-V sites), in GaN under large hydrostatic pressures. In GaN at ambient pressure both Si [7] and O [8,9] are known to be effective donor dopants. In addition, a high background n-type conductivity found in many samples has been attributed to the N vacancy V_N. The donor-type doping behavior of all of these defects has been confirmed by theory [10,11]. Calculations of their respective formation energies, however, find that only Si_{Ga} and O_N defects are likely to form in n-type material [11]. We study the localization of donor states by monitoring n as a function of p. This is done optically by Raman spectroscopy of the free electron plasmon-optical phonon coupled mode. Decreasing the bond length in the crystal by applying hydrostatic pressure increases the band gap at a rate of about 42 ± 2 meV/GPa in GaN [12,13]. Donor states dominated by the conduction band

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minimum (typically shallow), which are described by the hydrogenic model of the effective mass theory in dilute doping, $N_D < 10^{18}$ cm^{-3} in GaN (Mott criterion), directly follow the conduction band edge when pressure is applied, neglecting the small variations of the effective Rydberg energy. Strongly localized donor levels (typically but not necessarily deep), however, are influenced by the entire Brillouin zone.

The series of highly conducting GaN samples studied consists of two highly O doped films (O1 [14] and O2 [15]) grown by hydride vapor phase epitaxy (HVPE) and a highly Si doped film (Si) grown by metal organic vapor phase epitaxy (MOVPE) [16]. For comparison we include data from a MOVPE film (ref) very weakly doped with Si and a highly conducting bulk GaN crystal (bulk) [12,17]. All epitaxial films were grown on (0001) sapphire substrates. Electron mobilities μ and carrier concentrations n were derived from Hall effect and resistivity measurements at room temperature. The doping level was obtained from calibrated secondary ion mass spectroscopy (SIMS) depth profiles using a Cs ion source. All transport and doping data are collected in Table I.

Hydrostatic pressure up to 38 GPa was applied by means of a Mao-Bell–type diamond anvil cell. Pressure was monitored by standard ruby fluorescence and subsequently by the frequency of the E_2 phonon mode of GaN. The integrated intensity of the E_2 mode serves as a reference for the scattering cross section. Nonresonant Raman spectroscopy was performed using 120 mW of the 476.5 nm line of an Ar ion laser. All data were taken at room temperature.

The A_1(LO) mode and the E_2 mode are Raman active in the $z(x,-)z$ forward scattering geometry in wurtzite GaN [18]. The scattering rate of the coupled A_1 phonon mode can be described by the complex dielectric function in an oscillator model for phonons and free electron Drude plasma. The applicability of this model to describing the line shape and position of the A_1(LO) as a function of n is well established [17,19,20].

Raman spectra of the highly conducting, O doped GaN sample O1 are presented in Fig. 1(a). All spectra are normalized to the integrated intensity of the E_2 mode and offset proportional to p for clarity. At low pressure the spectra show the E_2 mode only. This is in contrast to the lightly Si doped reference sample (ref) (see Fig. 2 in Ref. [21]), where the A_1(LO) mode appears at about 10% of the E_2 peak height. From a stimulation of the scattering cross section of the phonon-plasmon coupled mode [17] only material with $n \leq 10^{18}$ cm^{-3} will have an observable A_1(LO) coupled mode in this range. In the high mobility case $\mu \gg 100$ cm^2/V s, as in this sample, the mode broadens and vanishes in the background signal. Under these conditions the relative height of the LO mode is a measure of n. Accordingly, no A_1(LO) mode is found in the highly conducting bulk crystal (bulk) [Fig. 1(b)] or the highly Si doped film (Si) (see Fig. 4 in Ref. [21]).

For $p > 20$ GPa the situation changes drastically. In all highly conducting samples except the Si doped on, the A_1(LO) mode appears and grows significantly with increasing pressure. Assignment of the new feature observed at $\sim$800 cm^{-1} at $p > 20$ GPa to the A_1(LO) phonon was confirmed by its greatly diminished intensity relative to E_2 in (x,y) polarization. Appearance of this mode due to resonance effects is considered unlikely because the laser excitation (2.60 eV) is well above the band gap of GaN.

TABLE I. Parameters of the GaN samples studied. N_D denotes the averaged experimental impurity concentration of known donor type species from SIMS profiles.

Sample	Growth	μ_{el} (Hall) (cm^2/V s)	N_{el} (Hall) (10^{16} cm^{-3})	N_D (SIMS) (10^{16} cm^{-3})
O1	HVPE[a]	90	3500	O:2000, Si:30
O2	HVPE[b]	124	1000	O:800, Si:30
Si	MOVPE[c]	170	1000	Si:1000
ref	MOVPE[c]	410	8.9	Si:9
Bulk	HPS[d,e]	60	1000–5000	O:10 000, Si:10

[a]See Ref. [15].
[b]See Ref. [14].
[c]See Ref. [16].
[d]High pressure synthesis; see Ref. [12].
[e]See Ref. [27].

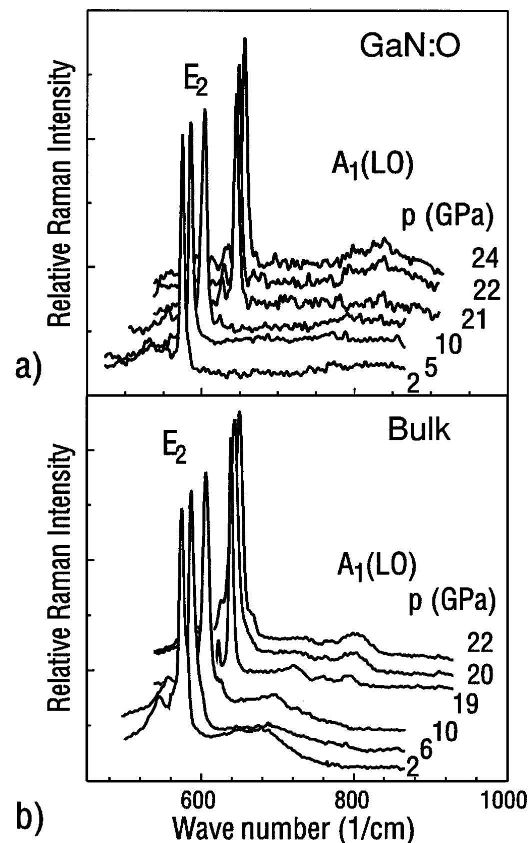

FIG. 1. Raman spectra in $z(x,-)z$ polarization of (a) 2×10^{19} cm^{-3} highly O doped O1, and (b) bulk GaN single crystal (bulk) as a function of hydrostatic pressure. The A_1(LO) mode only appears in the O doped sample for $p > 20$ GPa. Spectra are offset for clarity.

The intensity of this mode scaled to the E_2 mode is shown in Fig. 2 with typical error bars. The increase of the relative A_1(LO) mode intensity in the O doped samples is readily observed at $p = 20 \pm 2$ GPa [Fig. 2(a)]. This effect is reversible. The A_1(LO) mode vanishes when the pressure is decreased to ambient conditions. In the Si doped sample (Si) and the reference sample (ref) a constant height is found [Fig. 2(a)].

The effect is seen only in the O doped samples, and we, therefore, ascribe this feature to the behavior of the dominant O_N donor. Because of the very similar behavior of the HVPE samples (O1, O2) and the bulk crystal, we also conclude that the high carrier concentration in the bulk crystal is caused by O donors (see also Refs. [8,22,23]). The different slopes of the A_1(LO) mode intensity versus p beyond the onset at 20 GPa are attributed to the sample specific mobility and/or impurity concentration.

From this reversible appearance of the A_1(LO) mode in the O doped material at the location of the respective mode in the undoped sample (ref) we conclude that this increase in the A_1(LO) mode intensity at $p = 20 \pm 2$ GPa is due to n falling below 10^{18} cm^{-3}. We previously reported a 97% reduction of n in bulk GaN at 27 GPa [17]. A carrier freeze out has also been observed in ir absorption [20] and ir reflection [17]. Such a strong decrease of n can be explained by a $0/-$ (or higher degeneracy) donor state sinking into the band gap as the band gap increases with rising pressure.

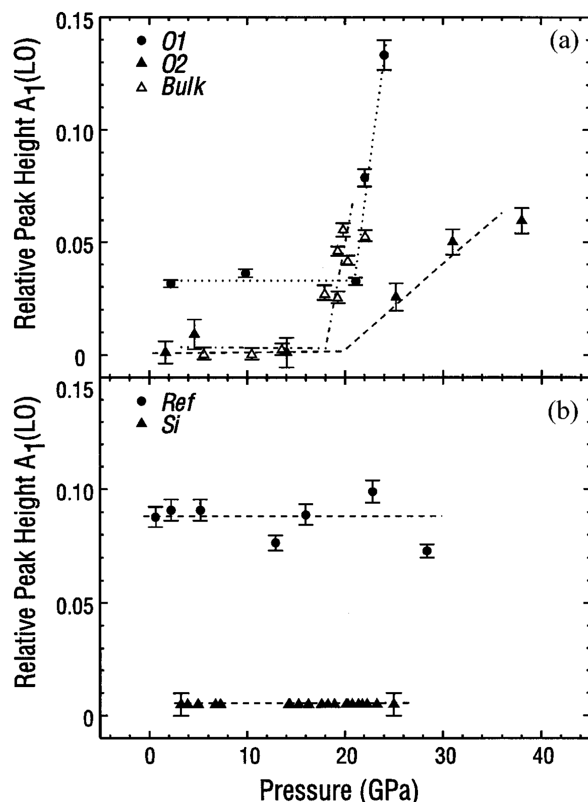

FIG. 2. Peak height of the A_1(LO) mode relative to the E_2 scattering intensity as a function of pressure. (a) In all O doped samples the LO mode occurs around 20 ± 2 GPa as the ground state of the O donor transfers from a shallow defect state to a strongly localized gap state. This behavior shows some aspects of *DX* centers in GaAs. (b) High O1 and low Si (ref) doped films mark constant levels. Si does not induce a strongly localized gap state in this pressure range. The lines serve as a guide to the eye.

The characteristic freeze out in the O doped samples, therefore, has to be attributed to a strongly localized state associated with this specific donor. No such state can be observed up to 25 GPa for the Si doped material. The high value of the critical pressure observed in the O doped samples indicates that the equivalent neutral state is in resonance with the conduction band in GaN at ambient pressure. As pointed out earlier we predicted this $0/-$ level to lie 0.40 ± 0.10 eV above the conduction band minimum [17]. Because it is in resonance with the conduction band, this state cannot be the ground state at ambient pressure. Instead, in the resonant range, i.e., for $p <$ 20 GPa, electrons will autoionize to the conduction band minimum and bind in quasihydrogenic states to the dopant atom at low temperature for dilute doping. At ambient pressure only this hydrogenic ground state would be seen. Because of the high doping level in the samples studied, these levels are degenerate with the conduction band.

Our results clearly show that the electronic ground state of O undergoes a transition from a hydrogenic level (dilute doping) or degenerate level (high doping) below the critical pressure of 20 GPa to a strongly localized gap state above it. We anticipate that similar to *DX* states in GaAs, the electron capture of the gap state is accompanied by a structural rearrangement of the defect due to the change in its charge state. This appears especially likely when comparing the bond strength of O to its nearest Ga neighbors with the strong Ga-N bond of the host. Indeed very recent calculations predict such a behavior in GaN [24] and AlGaN [25]. The present data, however, are not conclusive about any potential barrier between the two configurations, i.e., as yet we cannot make an assignment of the strongly localized state to either a D^0 or *DX* state.

The consistently different behavior for the highly Si doped film shows that Si does not induce a gap state in the pressure range considered. Within this range an increase of the Si binding energy by at least a factor of 3 would have been observed as an emerging A_1(LO) mode. We conclude that dilute Si forms a purely hydrogenic state for $p \leq 25$ GPa and possibly higher values. We tentatively relate this property to the bond strength of the dopant to the neighboring atoms. Si surrounded by four N atoms forms stronger bonds than O surrounded by four Ga atoms. This makes a bond angle relaxation for Si very unfavorable. Furthermore, Si has to be excluded as the source for the high n in all the other samples studied, namely, the bulk GaN crystals formed by high pressure synthesis, because it does not form a deep gap state at 20 GPa.

Because of the similar effects caused by hydrostatic pressure and by alloying with AlN, our results can be transferred to AlGaN alloys. The difference in band gaps

of GaN and AlN is 2.8 eV, 2.0 eV of which is the conduction band offset. If we assume, as in most III-V compounds, that pressure increases the conduction band edge much more than the valence band and that the conduction band increase is linear in pressure, 1 GPa corresponds to about 2.1% AlN. Therefore Si is expected to be a good hydrogenic donor for at least $0 \leq x \leq 0.56$. O is expected to induce a strongly localized gap state for $x \geq 0.40$. This is consistent with the observation of a significant drop of n in $Al_xGa_{1-x}N$ for $x > 0.20$ [26]. Because of the strong affinity between Al and O, unintentional O doping in $Al_xGa_{1-x}N$ is extremely difficult to suppress.

In summary, we have shown experimentally that O and Si donors in GaN behave very differently upon application of large hydrostatic pressure. While Si behaves like a standard hydrogenic donor over the pressure range from 0–25 GPa, the levels associated with O are strongly localized as a deep gap state at pressures $p > 20 \pm 2$ GPa. The behavior of O is similar to the *DX*-type behavior of donors in many other III-V compounds. In contrast to GaAs, however, a significant difference was found in regard to which sublattice the donor resides. We predict that Si should be a good hydrogenic donor over a wide range of Al concentrations in $Al_xGa_{1-x}N$, whereas O is expected to display shallow donor behavior only for small x. For $x > 0.40$ we conclude that O will be a strongly localized, deep gap state in $Al_xGa_{1-x}N$. We find that O doping can lead to a very high n-type conductivity in GaN at ambient pressure. It is likely that the unintentional incorporation of O accounts for high background conductivity in GaN and AlGaN films from many different growth techniques.

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