LOCALIZED DONORS IN GaN: SPECTROSCOPY USING LARGE PRESSURES

C. WETZEL *,***, H. AMANO *, I. AKASAKI *, T. SUSKI **, J.W. AGER ***,
E.R. WEBER ***, E.E. HALLER ***, and B.K. MEYER ****

* High Tech Research Center, Meijo University, Tempaku-ku, 468 Nagoya, Japan,
Wetzel@meijo-u.ac.jp; ** High Pressure Research Center, Warsaw, Poland; *** Materials
Science Division, Lawrence Berkeley National Laboratory and University of California,
Berkeley, CA 94720, USA; **** 1. Physics Institute, Justus-Liebig-University Giessen, 35392
Giessen, Germany.

ABSTRACT

Properties of GaN and its alloys are strongly controlled by impurities and strain. Using large hydrostatic and biaxial pressure we identify the role of donor dopants and stress induced fields. The doping of Si and O as relevant representatives of group-IV and group-VI impurities are studied in Raman spectroscopy. For pressures above 20 GPa we find that oxygen induces a strongly localized gap state while Si continues to behave as a hydrogenic donor. Such a DX-like behavior of O indicates and corresponds to doping limitations in AlGaN alloys. The site specific (O_{N} , Si_{Ga}) formation of a gap-state is attributed to bond strengths of the respective neighbors. In photoreflection of pseudomorphic GaInN we observe pronounced Franz-Keldysh oscillations corresponding to piezoelectric fields of 0.6 MV/cm. An observed redshift of the luminescence is found to originate in electric field induced tailstates. A reduced but similar effect is expected for GaN possibly explaining observations of persistent photoconductivity in a wide range of materials.

INTRODUCTION

Application of wide gap GaN and group-III nitrides requires control of the electronic band and defect structure by means of growth and doping. While for GaN a trend towards residual n-type conductivity is observed AlN is found highly resistive. A transition between both regimes is indicated by a significant drop in conductivity in ternary $\text{Al}_x\text{Ga}_{1-x}\text{N}$ for $x > 0.2$. A similar behavior in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and many other III-V compounds is well established and has been ascribed to the ability of the donor related ground state to assume both extended and localized states [1-5]. A transition of a shallow quasi-hydrogenic state of the dopant to a strongly localized state of the same impurity can be induced in GaAs by either a high carrier concentration n , by alloying with AlAs, or by application of hydrostatic pressure p . In addition, metastability effects such as persistent photoconductivity are found and have been 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 many III-V's the chemical nature of the dopants was found to play a minor role and very similar transition conditions are found for group-IV elements on group-III site (e.g. Si_{Ga}) and group-VI on group-V site (e.g. S_{As}) [2,3]. As a consequence charge transfer between the states severely limits conduction control in, e.g., $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys. Effects of persistent conductivity have also been reported in GaN, both in n-type and p-type material. We found electron freeze-out retardation of several hours in GaN:Si after a sample cool down [6]. Photocurrent decay times of hours in a wide range of temperatures have been observed [7-9]. Resembling the

properties of AlGaAs several models have been proposed including distinctively different trapping times for electrons and holes and DX-type behavior of impurities [7-9] and spatial charge separation [6].

In general orthogonalization of the dopant states and the host states induces both classes of defect states: Hydrogenic levels dominated by the wave function of the band edges due to Coulombic interaction and strongly localized states controlled by the atomic bond strength directly. The latter are represented by an average of the entire Brillouin zone. Within the vicinity of the bandgap hydrogenic levels in most cases dominate but a charge transfer into a strongly localized level may occur whenever it coincides with the Fermi level. Carriers can therefore become trapped in such strongly localized neutral charge states (D^0) [10].

In addition a structural relaxation of the donor impurity can occur in the vicinity of the electron transfer condition and may lead to an activation barrier between hydrogenic and strongly localized relaxed state. Proposed by Chadi and Chang [1] this widely accepted model of a structural relaxation explains the metastability and the activation barrier between the different states of these DX-centers.

Due to the similarities of the properties in AlGaAs and the observation in AlGaN it must be feared that the n-type doping limitations in AlGaN might not be overcome by selection of any type of donor dopant. This would significantly affect the applicability of AlGaN alloys and AlN in a wide range of devices. At present the results in AlGaN might be limited by growth technology and we therefore choose a model for alloying GaN with AlN which has proven suitable also in the case of AlGaAs alloys. In this analogy alloying with AlN should be equivalent to application of large hydrostatic pressure to the respective binary compound, i.e., GaN.

In GaN dopant impurities Si [11] and O [12,13] are found to be effective donors. In addition, the vacancy of nitrogen V_N has frequently been referred to as a possible origin of high unintentional n-type conductivity.

By applying large pressures we investigate the electronic band and impurity structure of GaN in search for possible carrier trap mechanisms. GaInN at variable InN fraction pseudomorphically grown on GaN acts as a suitable model for biaxial stress conditions in GaN, while hydrostatic pressure is applied to GaN as a model for AlGaN alloys. In GaN both major classes of donor dopants namely Si representing group-IV element on group-III site and O representing group-VI on group-V site are studied. We employ a contactless and purely optical method for monitoring the free carrier concentration by Raman spectroscopy within a diamond anvil cell. In the result we identify the major donor dopant in as-grown highly n-type GaN from high pressure synthesis and propose a promising donor species for high Al-content alloys.

EXPERIMENTAL

For the biaxial pressure experiments single $Ga_{1-x}In_xN/GaN$ heterostructures in the composition range $0 < x < 0.2$ were studied. Samples were grown in metal organic vapor phase epitaxy (MOVPE) on (0001) sapphire substrates using low temperature deposited AlN buffer layers. Ternary layers at a thickness of 40 nm were grown pseudomorphically onto 2 μm GaN. InN fraction and pseudomorphic growth was determined from high resolution x-ray diffraction measurements.

For the hydrostatic pressure experiments a set of highly conducting GaN samples consisting of two highly O doped films (O1: $[O] = 2 \times 10^{19} \text{ cm}^{-3}$, $n = 3.5 \times 10^{19}$ [14] and O2: $[O] = 8 \times 10^{18} \text{ cm}^{-3}$, $n = 1 \times 10^{19} \text{ cm}^{-3}$ [15]) grown by hydride vapor phase epitaxy (HVPE) and a highly Si doped film (Si: $[Si] = 1 \times 10^{19} \text{ cm}^{-3}$, $n = 1 \times 10^{19} \text{ cm}^{-3}$) grown by metal organic vapor phase

Figure 1 Photoreflectance ($T=300\text{K}$) of pseudomorphic 400 Å GaInN/GaN films. Franz-Keldysh oscillations due to the piezoelectric field are clearly observed marking the DOS bandgap at $i=0$.

E_2 phonon mode of GaN. Non-resonant Raman spectroscopy well below the bandgap was performed with 120 mW of the 476.5 nm line of an Ar ion laser. All data were obtained at room temperature.

In wurtzite GaN in $z(x,-)z$ forward scattering geometry $A_1(\text{LO})$ and E_2 modes are Raman active. However, while E_2 is only Raman active the LO mode couples to the plasma of the free electrons through deformation potential electron-optical-phonon interaction and electron-longitudinal-optical-phonon interaction (Fröhlich interaction). A detailed quantitative analysis of the coupled phonon plasmon lineshape for variable carrier concentration is given elsewhere [4,19].

EFFECTS OF BIAXIAL STRESS IN GaInN AND GaN

In search for the origin of persistent photoconductivity in GaN we investigate the effects of biaxial pressure typically induced by large lattice mismatch between substrate, typically sapphire and the epitaxial GaN film. The progress of group-III nitride epitaxial growth is essentially based on the beneficial effects of buffer layers to accommodate large lattice mismatch and along this development structural, electrical and optical parameters have improved significantly. As a controllable model for GaN we use biaxially strained GaInN/GaN structures.

epitaxy (MOVPE) [16]. For comparison we include data from a MOVPE film (Ref: [Si] = $9 \times 10^{16} \text{ cm}^{-3}$, $n = 9 \times 10^{16} \text{ cm}^{-3}$) very weakly doped with Si and a highly conducting bulk GaN crystal (Bulk: [O] = $1 \times 10^{20} \text{ cm}^{-3}$, $n = 1 - 5 \times 10^{19} \text{ cm}^{-3}$ [17,18]). All epitaxial films were grown on (0001) sapphire substrates. Electron densities n were derived from Hall effect and resistivity measurements. The actual doping level was obtained from calibrated secondary ion mass spectroscopy (SIMS) depth profiles using a Cs ion source.

Photoreflectance (PR) at room temperature was performed in near-to-perpendicular reflection. Periodic modulation was performed by above-bandgap photoexcitation using a 40 mW 325 nm HeCd Laser. The AC signal component was normalized to the DC signal forming $\Delta R/R$. Phase was fixed to the phase of the photoluminescence. 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

Forcing hypothetically free standing $\text{Ga}_{1-x}\text{In}_x\text{N}$ with lattice constants $c_x = c_{\text{GaN}}(1-x) + c_{\text{InN}}x = 5.184\text{\AA}(1-x) + 5.705\text{\AA}x$, $a_x = a_{\text{GaN}}(1-x) + a_{\text{InN}}x = 3.188\text{\AA}(1-x) + 3.540\text{\AA}x$ in pseudomorphic c -direction growth onto $2\text{ }\mu\text{m}$ GaN/sapphire with lattice constants $c_1 = 5.189\text{\AA}$, $a_1 = 3.182\text{\AA}$ induces strain in the ternary layer: $\epsilon_{xx} = a_1/a_x - 1 < 0$ and, as a consequence, $\epsilon_{zz} = c_1/c_x - 1 = -2 c_{13}/c_{33} \epsilon_{xx} > 0$ (elastic constants c_{11}, c_{33}) [20]. For $x = 0.2$ we therefore induce strain $\epsilon_{zz} = 0.015$, $\epsilon_{xx} = -0.023$ corresponding to pressures of $p = 16$ kbar. Depending on substrate and growth technique strain values up to $\epsilon_{zz} = 0.0012$ are obtained in epitaxial GaN films. Despite these large values and a thickness of 40 nm GaInN films are found to remain unrelaxed as observed from x-ray diffraction of both lattice constants. The InN fraction x of the films has been determined using the above model.

Photoreflectance under biaxial pressure

Photoreflectance of a selection of five samples is presented in Fig. 1 (in sequence of c lattice constant, offset for clarity). In the range of 3.4 eV remnants of the bandgap in GaN underneath the ternary film are seen. The most prominent feature centering in the range from 3.1 eV to 2.7 eV is ascribed to the density of states (DOS) bandgap in the strained GaInN layer. The width of the double structure increases, as the bandgap decreases for higher InN fraction or c -values. Oscillations are also seen on the high energy side with decreasing amplitude and period. These features are characteristic for Franz-Keldysh oscillations above the bandgap in the presence of an electric field.

The degeneracy in the center of the Brillouin zone Γ in wurtzite is not affected by the electric field, however, bands are tilted in real space. Within the coherence volume of an excitation previously non-degenerate states would therefore be forced to coincide in energy. As a consequence they repel each other forming periodic oscillations in the energy dependence of the joint density of states. In the limit of highest fields the new quantization will dominate and Stark ladders would be formed. According to Aspnes the modulation in form of Airy functions can be approximated [21] by an exponentially decaying cosine with a half-period of:

$$n\pi = \frac{4}{3} \left[\frac{E_n - E_g}{\hbar\Theta} \right]^{3/2} + \chi \quad (1)$$

Index 0 marks the dominant minimum which in the limit of vanishing damping corresponds to the DOS bandgap E_g (see ticks and labels in Fig. 1). Another important feature of the Franz-Keldysh effect is the formation of tail states below E_g . An exponentially decaying DOS with a slope parameter determined by the electro-optical energy $\hbar\Theta$ is induced by the electric field. The respective band corresponds to an enhanced reflection in the maximum labeled $i = -1$ in the PR signal (Fig. 1).

Interpretation of the extrema positions according to Eq. 1 versus index number is presented in Fig. 2. Up to six extrema could be resolved. For each sample points can be approximated by straight lines the slope of which corresponds to $(\hbar\Theta)^{3/2}$, and to the electric field $F = (\hbar\Theta)^{3/2} 2\mu/e\hbar$. Herein $\mu = 0.2$ is the joint effective DOS mass assumed to be constant at the GaN value.

Piezoelectric redshift

We identify electric field strengths in the range of $F = 0.14 - 0.65\text{ MV/cm}$. The field strength is not affected by a variation of the photo excitation power by a factor of 10 and together with

the very high value of the determined field we conclude that this field is not induced by the photoreflexion mechanism. Instead it is a constant field in the structure and we attribute it to the piezoelectric field induced by the axial stress conditions. From an interpretation of the quantum confined Stark effect in GaInN quantum wells Takeuchi *et al.* [22] recently interpreted a field of 1.3 MeV for $x = 0.1$. The field increases with strain in the layer in parallel to the increasing InN fraction. A schematic of the band structure is given in Fig. 3.

Luminescence in these sample was found to exhibit a redshift with respect to the above defined bandgap E_g from photoreflexion. The splitting closely corresponds to one half-period of the Franz-Keldysh oscillations and peaks around maximum labeled $i = -1$ (Fig. 1). This maximum corresponds to the enhanced density of states below the bandgap, i.e. the electric field induced tailstates. The redshift between luminescence gap and photoreflexion gap can be well approximated by $\Delta E = F a_r = 35 - 170$ meV where a_r is the effective Bohr radius as a characteristic dimension of the electron-hole pair. Our model might also explain previous observations of large redshifts in GaInN alloys [23].

Fields of this strength and the corresponding level splitting energies dominate over exciton binding energies and higher order multi-particle effects. Consequently for a description of the interband transition processes in perturbation theory these effects have to be considered first.

Possible charge separation

The presence of such a large internal field has severe consequences for non-equilibrium carriers, both holes and electrons. Photocarriers will be separated in the field and drift along in opposite direction (see Fig. 3). At bandoffsets to adjacent layers quasi-two-dimensional carrier gases will be formed and possibly lead to channels of high mobility. The charge separation is limited by the built-up of a diffusion field between the accumulated carriers that will compensate the piezoelectric driving force.

Figure 2 Interpretation of oscillation extrema according to Aspnes [21]. A field strength of up to 0.6 MV/cm is observed and attributed to the strain induced piezoelectric field.

Figure 3 Schematic of bandstructure in presence of strain and a piezoelectric field. The DOS is modulated by an electric field (Franz-Keldysh effect) inducing tailstates below the gap. Charge separation of photocarriers occurs in the field.

The process should be independent of the doping conditions. Accumulation of high mobility carrier gases is expected to behave as a bi-stable switch. Recombination or re-trapping of the carriers is strongly suppressed by the large spatial separation of the carriers [6]. The process is expected to be suitable for a variety of devices including memory cells for electrical or optical pulses. Performing the transfer to binary GaN we expect identical effects to occur leading to fields of ≈ 50 KV/cm in typically strained GaN/sapphire heterostructures. This field should provide sufficient charge separation to explain observed effects of persistent photoconductivity and possibly other remanence effects in the photoluminescence of GaN [24].

Metastability in GaInN/InN and strained GaN layers could therefore be well explained with wurtzite inherent piezoelectricity. In this case no effects of dopants behaving like DX centers are necessarily involved.

LOCALIZED DONORS IN GaN UNDER HYDROSTATIC PRESSURE

In our second approach we shall investigate possible doping limitations in AlGaN in the model of applying large hydrostatic pressure to GaN. The behavior of both Si and O impurities is studied by monitoring the interaction of free carriers with LO phonons in non-resonant Raman spectroscopy (for details see Ref. [4]).

Undoped GaN

For reference Raman spectra of the phonons in very weakly doped GaN (*Ref*), i.e., negligible interaction of phonon and carrier plasma, in forward scattering is shown in Fig. 4 as a function of hydrostatic pressure (normalized to the E_2 mode). Both E_2 and $A_1(\text{LO})$ modes are well resolved and increase linear with pressure up to 25 GPa. Unlike the LO mode, E_2 is not affected by the electronic susceptibility and can also be used as an internal reference for the scattering cross section.

Si doped GaN

In the highly Si doped film only the E_2 mode is found (Fig. 5). In the presence of the high carrier concentration the LO phonon couples to the plasmon of the free electrons and due to the limited mobility vanishes in the background of the Raman signal. Increasing the hydrostatic pressure in a wide pressure range up to 25 GPa this mode never occurs indicating that indeed the carrier concentration can not be reduced from $1 \times 10^{19} \text{ cm}^{-3}$ to a value that would have been expected to be observable like

Figure 4 Raman spectra of quasi-undoped GaN. Phonon modes shift in parallel. De-coupled from the free electrons the LO mode is observed throughout the pressure range.

$1 \times 10^{18} \text{ cm}^{-3}$ in this pressure range at room temperature. This minimum concentration at a fixed doping level of $1 \times 10^{19} \text{ cm}^{-3}$ corresponds to an upper limit for the binding energy of the donor of $\approx 70 \text{ meV}$. Under ambient conditions its binding energy of about $17 - 27 \text{ meV}$ [11,16] is close to the effective mass value of 35 meV . From this experimental evidence we conclude that Si is an effective mass type donor in GaN and it does not undergo a transformation to a DX-like configuration at hydrostatic pressures up to 25 GPa.

O doped GaN

Raman spectra of the highly conducting, O doped GaN sample (OI) are presented in Fig. 6. At low pressure the spectra show the E_2 mode only. Again due to the high carrier concentration the LO mode is suppressed. However, for $p > 20 \text{ GPa}$ the situation changes drastically. The $A_1(\text{LO})$ mode appears and grows significantly with increasing pressure. The E_2 mode remains unaffected. This appearance is reversible and the $A_1(\text{LO})$ mode vanishes when the pressure is decreased to ambient conditions.

Bulk GaN crystal

At low pressure we again find only the strong E_2 mode at 565 cm^{-1} but there is no evidence for the LO mode (Fig. 7). Upon increasing the pressure above 20 GPa the $A_1(\text{LO})$ mode appears and its intensity strongly increases for higher pressure.

The occurrence of the LO mode in this sample coincides with the appearance of the Reststrahlen band in infrared reflectivity for pressures $p > 20 \text{ GPa}$ [18]. On identical material Perlin *et al.* [25] had reported a significant reduction of the near infrared absorption for $p > 18 \text{ GPa}$.

Discussion

The intensity of modes appearing in the range expected for $A_1(\text{LO})$ modes scaled to the respective E_2 modes are shown in Fig. 7 with typical error bars. The relative increase in the O doped samples is readily observed at $p = 20 \pm 2 \text{ GPa}$ (Fig. 7a)). In the Si doped sample (Si) and the reference sample (Ref) a constant signal is found (Fig. 7b)). The effect of the carrier freeze-out is seen only in the O-doped samples and we therefore ascribe this feature to the behavior of the dominant O_N donor. Due to the very similar behavior of the HVPE samples (OI, O2) and

Figure 5 Raman spectra of highly Si doped GaN. With reference to the E_2 mode, no LO mode can be observed at any pressure up to 25 GPa due to strong coupling to the electron plasmon.

Figure 6 Highly O doped GaN in Raman spectroscopy. Coupling of LO-phonon to plasmon is released for pressure above 20 GPa. Due to the formation of a strongly localized level of O the carrier density has dropped below $1 \times 10^{18} \text{ cm}^{-3}$.

therefore, has to be attributed to a strongly localized DX-like state associated with this specific donor. At present we can not make an assignment of this level belonging to either a D^0 or DX state. In striking contrast no such state can be observed for the Si doped material.

Because it is in resonance with the conduction band, this state can not be the ground state at ambient pressure. Instead, within the resonant range, i.e., for $p < 20$ GPa, electrons will autoionize to the conduction band minimum and bind in quasi-hydrogenic states to the dopant atom at low temperature for dilute doping. At ambient pressure only such a quasi-hydrogenic ground state would be seen. A small positive central cell correction is expected due to a repulsive potential of the defect core because the corresponding neutral level lies above the band edge.

Our results clearly show that the electronic ground state of O undergoes a transition from a quasi hydrogenic level below the critical pressure of 20 GPa to a strongly localized gap state above this pressure. We anticipate that similarly 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. The consistently different behavior for the highly Si doped film shows that Si does not induce a gap state in the pressure range considered. 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.

the bulk crystal we also conclude that the high carrier concentration in the bulk crystal is caused by O donors (see also Ref. [12,26]). We assign the reversible appearance of the LO mode to n falling below 10^{18} cm^{-3} . We previously reported a 97 % reduction of n in bulk GaN at 27 GPa [18].

Such a strong decrease of n can be explained by a donor state sinking into the bandgap as the bandgap increases with rising pressure. The high value of the critical pressure observed indicates that the equivalent neutral state is not a shallow state that gradually sinks deeper into the gap due to a variation of the effective Rydberg energy. Instead the abrupt transition indicates the emerging of this state from the continuum of the conduction band. The freeze-out in the O doped samples,

Due to the similar effects caused by the application of hydrostatic pressure to GaN and by alloying with AlN our results can be transferred directly to AlGaN alloys. Assuming a linear shift of the bandgap energy with Al concentration, we find that 1 GPa corresponds to about 1.6 % AlN. Si is therefore expected to be a good hydrogenic donor for at least $0 \leq x \leq 0.40$. O will induce a strongly localized gap state for $x \geq 0.30$. This is in agreement with the observation of a significant drop of n in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ as the Al concentration increases beyond $x > 0.2$ [27].

Oxygen incorporation in AlN ceramics has been studied in great detail. Harris and Youngman [28]

constructed a level scheme of the O related defects with donor binding energies of 0.8 eV and 2.3 eV both of which significantly exceed the expected effective mass value. Due to the strong affinity between Al and O and similar vapor pressures of TMAI and TMOAl, unintentional doping in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ with O is extremely difficult to suppress.

NITROGEN VACANCIES VERSUS OXYGEN

The origin of the high free electron concentration found frequently in nominally undoped GaN has been controversial since the very early days of GaN studies. Thermodynamic arguments have led to the conclusion that nitrogen vacancies acting as donors should be the origin. On the contrary early elemental analysis by Pankove *et al.* [12] of red colored GaN crystals by secondary ion mass spectroscopy found very high quantities of oxygen. Correlations of lattice parameters and free carrier concentration supported the interpretation of nitrogen vacancies [29] while a purification of ammonia could reduce n supporting the interpretation of O [13].

Thereafter assignment of nitrogen vacancies became synonymous for the background donor without further clarification. Then in 1994 this assignment gained support by the interpretation of a pressure induced drop in the near infrared absorption by Perlin *et al.* [25]. Studying the pressure induced freeze-out dynamics an assignment to a strongly localized donor level (such as the V_N) was supported by infrared and Raman data by the present authors [18]. At that point a change of the donor's category from shallow to localized state however could not be excluded.

The doping behavior of impurities and native defects in GaN has then been studied extensively in first principles calculations by Neugebauer and Van de Walle [30] and

Figure 7 Highly conducting bulk GaN from high pressure synthesis in Raman scattering up to 22 GPa. Similar to the O doped sample a clear $A_1(\text{LO})$ mode appears at 20 GPa after trapping of the electrons. The background donor is therefore assigned to unintentional incorporation of oxygen.

Figure 8 $A_1(LO)$ mode intensity with respect to E_2 mode versus applied pressure. a) O doped samples undergo a DX-like transformation of the impurity state for $p > 20$ GPa. b) Si induced levels remain hydrogenic throughout the range. Bulk GaN crystals behave identical to O doped ones. The $A_1(LO)$ signal of undoped GaN serves as a reference.

could clarify the role of the respective dopants [4].

Considering O in GaN and AlN Mattila and Nieminen [34] find that O should form a shallow center in GaN and a deep center in AlN predicting a DX-like transition along the AlGaIn-alloy composition. Very recently Van de Walle, Stampfl and Neugebauer [35] have investigated the pressure dependence of both Si and O in GaN in first principles calculations. For Si they indeed observe that the shallow nature is maintained under large pressure, while O does undergo a transition into a DX-like state. Above a transition pressure of 20 GPa a strong outward relaxation of the O through the (0001) plane of the adjacent three Ga atoms is calculated. Most interestingly the transition of O does not occur in the model of cubic GaN, but appears when considering third nearest neighbors in wurtzite. These results are in ideal agreement with our experimental findings above.

SUMMARY

In summary we have performed a study of donor localization in GaN under both, axial and hydrostatic pressure. In form of axial stress in pseudomorphic GaInN/GaN single heterostructures the occurrence of piezoelectric fields of 0.6 MV/cm has been observed by

Boguslawski *et al.* [31]. Both groups confirm the single donor character of the nitrogen vacancies found in earlier tight binding calculations [32]. Both O and Si were found to form shallow donors [30,31,33], and considering the respective formation energy Van de Walle and Neugebauer [30] found that while Si and O should be incorporated most easily in p-type as well as in n-type material the V_N should only be likely to form in p-type material as a compensating defect. The nitrogen vacancy could therefore not be held responsible for high free electron concentrations in the first place.

The present results in turn find that oxygen undergoes the transition from quasi-hydrogenic to a strongly localized defect level and strongly supports the assignment to oxygen incorporation as the major unintentional donor type dopant. It was not until a study on controllably doped and SIMS verified samples in combination with the characteristic freeze-out

clearly resolved Franz-Keldysh oscillations in photoreflection spectroscopy. Photoluminescence is found to originate in electric field induced partially discrete tail states corresponding to the $i = -1$ PR maximum. An apparent redshift between luminescence and the thus determined PR bandgap is therefore well described considering the piezoelectric field. A separation of photocarriers in the piezoelectric field is proposed to lead to persistent photoconductivity effects observed in a wide range of GaN films and structures.

We have shown that O and Si donors in GaN behave very differently upon application of large hydrostatic pressure. Si behaves like a standard hydrogenic donor over a range from 0 – 25 GPa while the levels associated with O undergo a transition from quasi hydrogenic to strongly localized gap state for pressures $p > 20 \pm 2$ GPa. This 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 regards to which sublattice the donor resides. We predict that Si should be a good hydrogenic donor over a wide range of Al concentrations in $\text{Al}_x\text{Ga}_{1-x}\text{N}$, whereas O is expected to display shallow donor behavior only for small x . For $x > 0.30$ we conclude that O will be a strongly localized, deep gap state in $\text{Al}_x\text{Ga}_{1-x}\text{N}$. 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 AlGaIn films from many different growth techniques.

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