A9.3 O, C, and other unintentional impurities in GaN and related compounds

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A INTRODUCTION

Alloys of GaN, InN and AlN provide an ideal host with a wide range of the electronic bandgap but it is due to the control of impurities that allows to form devices. The role of unintentional impurities becomes especially important when their role as dopants is not established and their incorporation remains undetected. Oxygen concentrations up to some $10^{15}$ cm$^{-3}$ are present in any high purity GaAs, Si or Ge. Due to its large binding energy, however, influence on transport properties is negligible (O deep double donor in Si and GaAs). Its role in the nitrides in contrast has become subject of detailed investigations [1-6]. Carbon on the other hand is known as an effective and shallow acceptor in GaAs (deep double donor in Si) and is expected to serve as such in GaN, too [7-10]. In order to provide control of doping it is essential to identify the levels induced by the impurities and to differentiate dopants with effective mass type, typically shallow, levels from dopants with strongly localized, typically deep, levels. For a deeper analysis of elements considered as useful dopants such as Si, Mg, and Be please also refer to the respective chapters in this book [11,12].

B IMPURITY INCORPORATION

Contaminations with C and O are very likely in the aggressive growth environment of ammonia at high growth temperatures above 1000 °C. Structural material such as quartz tubing and graphite crucibles are subject to erosion delivering O, C as well as Si. The second main path are the precursors themselves. While high purity metal sources are standard from other semiconductor processes, there is less experience in electronic grade ammonia. Traces of water vapor are frequently found and considering the typical large V/III flux ratios offered in MOVCD, i.e. 10 000, a significant amount of O can be accumulated. C is offered in vast amounts in the metal organics of the MOVPE sources. In MBE growth a typical low growth rate provides ample opportunity to incorporate O and C from the base pressure of the vacuum. Cl is a major residue from hydride VPE employing HCl as a carrier gas.

C CLASSIFICATION HYDROGENIC – STRONGLY LOCALIZED DEFECT STATE

The orthogonalization of impurity states with the bands of the host crystal induces strongly localized (in real space) dopant related levels throughout the energy range, i.e. in resonance with bands or within the bandgap. Carriers in occupied states in resonance with the conduction band auto-ionize to the bandedge and bind in delocalized effective mass states to the impurity atom in perturbation of the hosts wave functions. The ionized original state becomes important again whenever the bandgap is increased, i.e. by alloying of the host lattice, by application of hydrostatic pressure or by an increasing Fermi–energy. Application of hydrostatic pressure distinguishes both types of states along their spatial extension within the host potential that is affected by the volume change. Averaging the entire Brillouin zone in momentum space strongly localized levels experience a much weaker pressure shift than effective mass states dominated by states in the conduction band minimum. For the case of strongly localized states in the bandgap the relative binding energy will increase and carriers will be re-trapped. Or for the case of a resonant level the same will occur beyond a certain threshold alloy composition or threshold pressure. This charge transfer in the vicinity of the crossing point may be accompanied by a large lattice relaxation facilitating a second electron to form a negative charge state DX$^-$ [13]. Considerable hysterisis effects in the carrier trapping and ionization process are expected. For reviews on the extensively studied subject of DX centers see Refs. [14-16]
D EXPERIMENTAL STUDIES OF CARBON

The presence of a shallow acceptor level in GaN has been attributed to C substituting on N site by Fischer et al. [7]. In luminescence experiments of GaN from high temperature vapor phase epitaxy in a C-rich environment donor-acceptor and conduction-band-to-acceptor transitions have been distinguished in temperature dependent experiments. From the separation of both contributions an optical binding energy of 230 meV close to the value of effective mass type acceptors was obtained. Hole concentrations up 3x10^{17} cm^{-3} were achieved by C doping with CCl₄ by Abernathy et al. [10]. In addition, Ogino and Aoki [17] proposed that the frequently observed yellow luminescence band around 550 nm should be related to a deep level of a C-Ga vacancy complex. The identification of this band, however, is still very controversial.

E EXPERIMENTAL STUDIES OF OXYGEN -- AND ITS DISTINCTION FROM Si, VN

GaN

Oxygen has been proposed to be the origin of high background n-type conductivity in GaN grown by a wide range of processes [18,19,1]. O should therefore play a significantly different role than in e.g. GaAs. Another frequently cited candidate is the vacancy of nitrogen (VN). A brief summary of the controversy has been given in Ref. [20]. In contrast to other systems such as GaAs, Si, and Ge, O delivered in the form of water vapor [18,21], O₂ [22] or N₂O [23] is an effective donor dopant in GaN. Controlled O doping has been achieved by N₂O in MOCVD with free electron concentrations in the range of 4x10^{16} – 4x10^{18} cm^{-3} at RT. Concentrations in the range of 10^{19} cm^{-3} [24,1] and 10^{20} cm^{-3} [21] at RT were achieved with water vapor. Doping by implantation of elemental O achieved a low dopant activation of 4% [25] and a thermal ionization energy of 29 meV. In Hall investigations of Si doped films a secondary thermal ionization energy of 34 meV at an active concentration of 7x10^{16} cm^{-3} was observed and tentatively assigned to O [26]. These values are close to the binding energy 35.5 meV of the isolated effective mass donor determined by far-infrared absorption by Meyer et al. [27]. Based on the experimental results given below incorporation of O is proposed to be the main source of unintentional n-type doping in GaN. The rich literature on unintentionally n-type GaN must therefore be reconsidered as GaN:O.

The following are some spectroscopic results that explicitly consider the incorporation of O. In luminescence experiments an emission band centered at an apparent optical binding energy of 60-80 meV was found to correlate in its appearance with the incorporation of water during growth [21]. Experiments under large hydrostatic pressure [28] find a pressure coefficient identical to the excitonic bandgap. Therefore a shallow effective mass type nature of this level was concluded despite its large binding energy. The assignment of this level to O [21] remains controversial. Models involving incorporation of cubic inclusions [29], and locations of biaxial tensile strain inverting the valence band structure to bring up the light hole band [30] have been proposed.

GaN under hydrostatic pressure

A classification of the O donor level in GaN according to its degree of localization, i.e. hydrogenic effective mass type behavior or strongly localized defect, has been performed by Wetzel et al. [1]. In experiments under large hydrostatic pressure O is found to re-trap its electrons beyond a threshold pressure of 20±2 GPa. Studying the coupling of the free carrier plasma and the longitudinal optical phonon mode [31] the carrier density was monitored contactlessly by non-resonant Raman scattering using diamond anvil high pressure cell techniques.

Raman spectra have been obtained up to 38 GPa. An internal reference for the scattering intensity is provided by the E₂ mode. Initially the A₁(LO) mode can not be observed due to its strong coupling to the carrier plasma. The situation changes at around 20 GPa when the mode appears after the carrier density has dropped by some two orders of magnitude [32]. This observation parallels an earlier result obtained in small bulk GaN crystals from high pressure synthesis [32]. A transition to transparency in the near infrared at a pressure of 18 GPa was observed by Perlin et al. and attributed to localized donors sinking into the bandgap [33]. This effective freeze-out was also observed in infrared reflection. Only beyond 20 GPa the Reststrahlen band in the phonon region can be distinguished from the plasma reflection [32]. These results
on O doped GaN reveal that O performs a transition from a shallow effective mass state to a strongly localized gap state sinking into the bandgap for pressures increasing beyond 20 GPa. Such a behavior is a key feature of DX-centers encountered in many other III-V compounds, e.g. GaAs. For comparison undoped and highly Si doped material has been studied [43]. Si had been proposed as another candidate for unintentional background doping. Comparing the observation of the LO mode versus pressure only O doped material was found to perform this transition. Si doped material remains highly conducting up to the largest pressure applied of 25 GPa. Undoped material served as a reference for the $A_1(LO)$ mode frequency and intensity.

In contrast to other compounds where DX centers are stabilized as the ground state at very similar pressures (2.2 – 2.5 GPa) [34], here in GaN a significant difference is found depending on the species of the dopant or the lattice site it resides, i.e. the element it replaces. O substituting on N site performs this transition at 20 GPa while for Si substituting on Ga site a transformation can not be observed up to 25 GPa. All results under hydrostatic pressure can be transferred to AlGaN alloys where the bandgap increase in $\Gamma$ is performed by alloying GaN with AlN. Such a center should be suitable for an optical memory switch operating at short wavelengths.

AlN
Commercial AlN powder typically contains 1.0 to 1.5 wt.% of O which in part is dissolved in the host lattice and in part forms an oxide around each powder grain [35]. Its incorporation in AlN strongly reduces thermal conductivity, a property widely exploited in AlN in the form of a ceramic. Harris and Youngman [36] and Pastrnak et al. [37] studied the luminescence of deep centers in O doped AlN and developed a corresponding level scheme involving donor and acceptor pairs and complexes [35]. In dependence of the O concentration a dominant luminescence band is found centering around 308 nm (0.1% O) and 377 nm (0.7% O) [35]. The fact that it has not been possible to render AlN n-type may be related to oxygen generating charge states deep in the gap. The strong affinity of O to Al is a well known problem in the epitaxy of Al containing compounds and it is very difficult to reduce unintentional incorporation of O.

AlGaN
Along the composition range of unintentional n-type Al$_x$Ga$_{1-x}$N from GaN to AlN a significant reduction of the free carrier concentration from some $10^{20}$ cm$^{-3}$ was found beyond $x=0.2$ by several orders of magnitude by Yoshida et al. [38]. This contrast between the binary endpoints GaN and AlN indicates the participation of strongly localized impurity levels shifting independently from the bandgap. In a model neglecting explicit alloying effects the doping behavior of dopants may be interpolated from the results in the binary compounds. Similar to the case of GaAs and AlGaAs by application of a suitable transfer scheme the results of GaN under hydrostatic pressure can be converted to an alloy composition in Al$_x$Ga$_{1-x}$N [1,32]. This method bears the experimental advantage to avoid variations in the growth process of samples with different composition and to exclude typical alloy fluctuation effects such as line broadening. Assuming a linear variation of both the GaN bandgap with pressure and the Al$_x$Ga$_{1-x}$N bandgap with $x$ Wetzel et al. find that O should convert from a shallow effective mass level to a strongly localized gap state at $x=0.40$ [1,28]. A structural relaxation at the transition to form a DX center is likely and has been confirmed in theory. O as a difficult-to-avoid impurity in Al containing compounds may therefore severely limit the application of wide bandgap AlGaN alloys. On the other hand any activation barriers between the different configurations are expected to be significantly higher in this wide gap system than in AlGaAs and hysteresis effects may well be exploited in electro-optical memory devices. Similarly to the pressure results Si is expected not to convert to a deep center but remain an effective mass type donor to an Al fraction of at least $x=0.56$. Both critical values are expected to be slightly smaller for positive bowing parameters of the AlGaN bandgap.

F IMPURITY LOCALIZATION IN THEORY

The solubility of impurities in group-III nitrides as well as their role as shallow or strongly localized deep dopants has been studied recently in detailed first principles calculations by Boguslawski, Briggs and Bernholc [8,39], Mattila and Nieminen [3,40], Park and Chadi [4], and Stampfl and Van de Walle [5]. Considerable theoretical progress has been made considering the classification of impurity ground states into shallow and strongly localized states, especially by considering large lattice relaxations around
impurities as an indication of a strongly localized state. The range of impurities considered on both substi-
tutional lattice sites includes C, O, S, Si, Ge, Be, and Mg. Placed in supercells of either 32 or 72 atoms the
ground states for all impurities have been calculated considering large lattice relaxation around the
impurities on substitutional lattice sites. Various configurations for DX-centers are found including a
large relaxation of the impurity along the <0001> c-direction (DX$_1$, or γ-BB DX) or the <1000> a-direction
(DX$_2$, or α-BB DX) (BB: broken bond) [39,4]. Park and Chadi in addition consider a cation-cation bond
(CBB) formation of the first impurity neighbors [4]. Differences of the various models include the number
of points considered to represent the Brillouin zone and the treatment of the Ga 3d bands as either explicit
valence states, treatment in non-linear core correction or as core states. The calculations also differ in the
treatment of wurtzite and zincblende host lattices. Some values are obtained by transfer of the results
obtained in one structure, others are obtained by considering the respective structure already in the
initialization of the calculations. For details see Table 1.

Table 1: Some details of first principles calculations of impurities in III-nitrides. Columns list the treatment
of the 3d shell if specified (nlcc = non-linear core correction), size and symmetry (c=cubic,
w=wurtzite) of the super cell and the points considered in the irreducible wedge of the Brillouin
zone (BZ).

<table>
<thead>
<tr>
<th>Authors</th>
<th>3d shell</th>
<th>supercell</th>
<th>BZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boguslawski, Briggs, Bernholc [8]</td>
<td>---</td>
<td>72w</td>
<td>Γ</td>
</tr>
<tr>
<td>Mattila and Nieminen [3]</td>
<td>nlcc</td>
<td>32c,</td>
<td>2 pts</td>
</tr>
<tr>
<td>Mattila and Nieminen [40]</td>
<td>nlcc</td>
<td>32c</td>
<td>2 pts</td>
</tr>
<tr>
<td>Boguslawski and Bernholc [39]</td>
<td>---</td>
<td>72w</td>
<td>Γ</td>
</tr>
<tr>
<td>Park and Chadi [4]</td>
<td>32c</td>
<td>spec. pts</td>
<td></td>
</tr>
<tr>
<td>Stampfl and Van de Walle [5]</td>
<td>32c/72w</td>
<td>2-3 pts</td>
<td></td>
</tr>
<tr>
<td>Van de Walle [6]</td>
<td>nlcc</td>
<td>32w (72w)</td>
<td>3 spec. pts</td>
</tr>
</tbody>
</table>

Results of the calculations are represented in Table 2 for wurtzite structure and Table 3 for the zincblende
structure. Tables are divided into impurities substituting on the group-III host cations site and on the group-
V host anion site (N-site). Next impurities are grouped into their primary donor or acceptor behavior. As
the respective host nitride compounds are listed in the sequence of increasing bandgap. Hydrostatic
pressure as an external parameter to increase the bandgap is also considered for GaN. The equivalent effect
is expected for alloying GaN and AlN and results are also listed. In both cases the parameter range
(temperature or composition) for stable DX-states are given.

G RESULTS IN WURTZITE

Substitutions on cation site
On cation site C, Si and Ge are found to be effective mass type [41] donors in GaN [39] (Si is found a
shallow [41] donor [42,4]). A DX$_2$ level is found to lie close for C [39]. Self compensation and pairing of
C, Si and Ge are found to be negligible in Al$_x$Ga$_{1-x}$N for 0<x<0.4 under Ga rich conditions, but expected
otherwise [39,8]. While C shows amphoteric behavior, incorporation on N-site (acceptor behavior) is found
to dominate [8]. Under hydrostatic pressure Si is experimentally found to be a hydrogenic donor up to a
pressure of at least 25 GPa [43]. From an interpretation of data in AlN a hydrogenic behavior of Si is
expected in GaN up to 41 GPa [6].

In AlN contradicting results are found for Si and Ge. C again is found to have shallow and DX level lying
very close (±100 meV) [8]. Bernholc and Boguslawski find that Ge in AlN is stable in a DX$_1$ state [39]
under N-rich growth conditions. Here self-compensation and pairing is expected [39]. On the other hand
Park and Chadi do not find any stable DX state [4]. Both groups and Mattila and Nieminen [40] agree,
however, that Si should form a DX$_1$ state. Here Van de Walle finds a positive correlation energy U =+0.31
eV and no stable DX center.
Table 2: Impurity behavior in wurtzite group-III nitrides in experiment and theory arranged according to their substitutional lattice site in the sequence of increasing host lattice bandgap.

<table>
<thead>
<tr>
<th>Wurtzite</th>
<th>Group-III host cation site</th>
<th>Group-V host anion site (N-site)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Be</td>
<td>Mg</td>
</tr>
<tr>
<td></td>
<td>a,b</td>
<td></td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaN</td>
<td>emA</td>
<td>emA</td>
</tr>
<tr>
<td></td>
<td>BFB,</td>
<td>PC</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td></td>
</tr>
<tr>
<td>Energy of impurity level</td>
<td>(0.06 eV)&lt;sup&gt;m&lt;/sup&gt; BFB (DX U=0.7 eV PC)</td>
<td>(0.23 eV&lt;sub&gt;m&lt;/sub&gt; FBBV (DX U=2.0 eV PC))</td>
</tr>
<tr>
<td>Pressure range for DX stability</td>
<td>exp. not below 25 GPa</td>
<td></td>
</tr>
<tr>
<td>AlGaN</td>
<td>emA</td>
<td>emA</td>
</tr>
<tr>
<td>Composit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ion range for DX stability</td>
<td>no transition below 0.56 We&lt;sup&gt;a&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;, &gt;0.24 PC&lt;sup&gt;g&lt;/sup&gt;, &gt;0.6 BB&lt;sup&gt;j&lt;/sup&gt;</td>
<td>0.3 BB&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>AlN</td>
<td>emA</td>
<td>emA</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td>PC</td>
</tr>
<tr>
<td>Energy of impurity level</td>
<td>DX U=+0.3 eV&lt;sup&gt;j&lt;/sup&gt;</td>
<td>DX U=0.31 eV VdW</td>
</tr>
<tr>
<td>BN</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>no DX</td>
<td>no DX</td>
</tr>
</tbody>
</table>

exp... experimental result  
em... effective mass ...  
s... shallow, d... deep ...  
...D ... donor, ...A ... acceptor  
...X with large lattice relaxation, as considered  
BB Boguslawski, Bernholc, Ref. [39].  
BBB Boguslawski, Briggs, Bernholc, Ref. [8].  
BFB Bernardini, Fiorentini, Bosin, Ref. [45].  
FBBV Fiorentini et al., Ref. [44].  
Fi Fischer, Wetzel, Meyer, Ref. [7].  
MN Mattila and Nieminen, Ref. [3].  
MNB Mattila and Nieminen, Ref. [40].  
NW Neugebauer and Van de Walle, Ref. [42].  
PC Park and Chadi, Ref. [4].  
SW Stampfl and Van de Walle, Ref. [5].  
VdW Van de Walle, Ref. [6].  
We Wetzel et al., Ref. [1].

a Self compensation and pairing negligible in AlGaN for 0<x<0.4 (Ga rich composition), but expected otherwise (BB, BBB).  
b Incorporation on anion site dominates (BBB).  
c Levels lie close ±0.1 eV and metastability is possible (BB, BBB).  
d Interpolating U in GaN and AlN.  
e Assumed bowing parameter b = 0 eV.  
f Under N-rich growth conditions.
For SiAl or Ga in AlGaN 0<x<0.6 no self-compensation nor N-N pairs expected. For x>0.6 DX-like stable in wurtzite (BB).

For Ge in AlGaN on cation site selfcompensation and pairing expected (BB).

For C_{Al} in the negative charge state the DX-like configuration is likely to be stable (BB).

Interpolating U in GaN and AlN by the bandgap increase.

Assumed gap bowing parameter b = 0.53 eV.

Interpolated with \( V/V_0 = 0.84 \) (=41 GPa):

\[ U = -0.62 \text{eV (VdW)} \]

Thermal ionization energy (typ. error ±0.1V).

Contribution of cation vacancies proposed (SW).

Calculation in zincblende structure proposed to hold in wurtzite (MNb).

Consequently transitions between both results are expected in Al_{x}Ga_{1-x}N for Si and Ge. Transferring experimental results from GaN under pressure assuming a linearized increase of the bandgap with pressure and alloy composition Si is expected to behave as a hydrogenic donor for at least x<0.56. This is in excellent agreement with the prediction that Si is no DX center in AlN by Van de Walle. In turn Bernholc and Boguslawski [39] predict Si to transfer into a DX state for x>0.6 while Park and Chadi find x>0.24 [4].

In BN no DX state can be found for Si and Ge donors [4].

Be and Mg on cation side are found to behave as effective mass type acceptors in GaN (Be: Ref. [45], a typical error margin of ±0.1 eV should be considered) AlGaN and AlN [4]. The same is predicted for Be in BN [4].

Substitutes on N-site

On the N anion site Fischer et al. [7] experimentally find C as a shallow acceptor in GaN. Theory agrees and finds identical results throughout the AlGaN composition range from GaN to AlN and in BN [39,4]. Boguslawski, Briggs and Bernholc [8,39] point out that the amphoteric nature of C is expected to lead to partial selfcompensation and pairing of C in AlGaN for x>0.4. Otherwise incorporation as acceptor on the N site dominates. Ga of Si and Ge are predicted to be deep acceptors in GaN and AlN [39]. O is known experimentally [18,21] to incorporate as a donor and S is expected to behave similarly. From a perturbation of large hydrostatic pressure O is found to behave as a hydrogenic donor for pressure below 20±2 GPa [1].

As shown by Wetzel et al. [1] O above 20±2 GPa behaves as a strongly localized donor exhibiting DX-type behavior. Within the framework of the different approaches (see Table 1) theory very well agrees with these findings predicting a shallow donor behavior in GaN under normal conditions [3,4,6]. Van de Walle [6] performed calculations for equilibrium and a reduced crystal volume corresponding to a pressure of 41 GPa and finds a DX behavior with a large relaxation of the O impurity towards the third nearest Ga neighbor. The correlation energy for the DX'-state is found to decrease from \( U = +0.48 \) eV (ambient pressure) to \( U = -0.62 \) eV (41 GPa). This pressure result is found exclusively for wurtzite GaN, but not for the zincblende polytype. Park and Chadi calculated a transition pressure of 22 GPa [4].

In AlN Youngman and Harris [35] and Pastnak [37] found O to induce deep gap states in luminescence. Recent theory indeed finds a DX behavior in wurtzite AlN (\( U = -2.5 \) eV [4], -0.57 eV [6]). Similar to the pressure results Van de Walle predicts this to be unique to the wurtzite phase [6]. Accordingly transitions between shallow donor and DX-behavior are expected in AlGaN. Dependent on the assumed interpolation schemes used by the different groups different critical compositions are found. Based on a linear variation of the bandgap in GaN with pressure and AlGaN with composition Wetzel et al. [1] expect O to convert into a deep state at x=0.40 while Van de Walle predicts x=0.46 [6]. Based on a bowing parameter in AlGaN of b=-0.53 eV a value of x=0.30 is found [6]. Mattila and Nieminen [3] as well as Park and Chadi [4] predict x=0.2.

S in GaN and AlN behaves as a shallow donor and no DX center is found for S in BN [4]. For AlGaN a behavior of Si, Ge and S identical to the GaN or AlN host may be assumed.
Table 3: Impurity behavior in zincblende group-III nitrides in experiment and theory arranged according to their substitutional lattice site in the sequence of increasing host lattice bandgap.

<table>
<thead>
<tr>
<th>Zincblende</th>
<th>Group-III host cation site</th>
<th>Group-V host anion site (N-site)</th>
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<tbody>
<tr>
<td></td>
<td>Be</td>
<td>Mg</td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>Acceptor</td>
<td>Donor</td>
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<tr>
<td><em>InN</em></td>
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<tr>
<td>GaN</td>
<td>emA</td>
<td>PC</td>
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<tr>
<td></td>
<td>(DX U=0.7 eV)</td>
<td>(DX U=2.0 eV)</td>
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<tr>
<td>Pressure range for DX stability</td>
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<tr>
<td>AlGaN</td>
<td>emA</td>
<td>PC</td>
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<tr>
<td></td>
<td>(DX U=0.8 eV)</td>
<td>(DX U=2.2 eV)</td>
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<tr>
<td>Composi-</td>
<td>tion range for DX stability</td>
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<tr>
<td>AlN</td>
<td>emA</td>
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<tr>
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<td>(DX U=0.8 eV)</td>
<td>(DX U=2.2 eV)</td>
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<tr>
<td>Energy of impurity level</td>
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<tr>
<td>BN</td>
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</tbody>
</table>

em... effective mass... a Considering trigonal broken bond type DX center (PC).
...D donor, ...A acceptor b Considering cation-cation bonded DX center (PC).
...X shallow, deep... c Large relaxation without bond breaking expected (PC).
MN Mattila and Nieminen, Ref. [3]. d Contribution of cation vacancies proposed (MN).
MNB Mattila and Nieminen, Ref. [40].
PC Park and Chadi, Ref. [4].
VdW Van de Walle, Ref. [6].

H RESULTS IN ZINCBLENDE

Substitutions on cation site
For C Park and Chadi [4] find a trigonal broken bond type DX center in GaN, AlN and AlGaN. The same center was not found to be stable for Si [40,4] and Ge [4] on cation site. Also Van de Walle finds no DX center for Si in zincblende AlN. This is in contrast to the wurtzite case where a DX behavior is expected by
Mattila and Nieminen [40] and Park and Chadi [4], but negated by Van de Walle [6]. Mg and Be are expected to be effective mass type acceptors in GaN, AlN, and AlGaN [4].

Substitutes on N-site

O donors have been studied in zincblende and a shallow donor behavior is expected in GaN [3,4,6]. Mattila and Nieminen [3] find that O should be a DX state in AlN and a transition to occur at x=0.4 in AlGaN. Its energy should be fixed at 4.0 eV above the valence band in GaN, AlGaN and AlN. Park and Chadi agree and expect the correlation energy to decrease from U=+0.34 eV (GaN) to U=-2.4 eV (AlN) [4]. In contrast Van de Walle expects no DX center to occur in AlN nor AlGaN [6].

I CONCLUSION

The wide range of electronic bandgap covered by the group-III nitrides provides a wide window for strongly localized states to occur in the bandgap. Dopants and unintentional impurities are found to exhibit shallow effective mass type behavior and strongly localized states with DX-type behavior. O as a common impurity is found to play an important role as shallow donor in GaN and DX center in AlN. In contrast to other III-V's Si is found to still be a good shallow donor under conditions where O has converted to a DX state, e.g. in AlGaN. The hysteresis effects associated with DX centers are expected to be large enough to be used in optoelectronic memory cells. Observed distinctions in the theoretical results should encourage experimental investigations.

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REFERENCES

We use expressions as given in the original references distinguishing shallow and effective mass type states.