## Stability of deep donor and acceptor centers in GaN, AlN, and BN

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We examine the atomic and electronic structure of substitutional Be, Mg, and C acceptor impurities and of Si, Ge, S, and O donor impurities in GaN, AlN, and BN through first-principles calculations. The small bond lengths in III-V nitrides are found to inhibit large lattice relaxations around impurities and, with a few exceptions, this leads to a significant stabilization of effective-mass states over deep centers despite the large band gaps of these materials. In particular, we find that Ge and S impurities do not have stable or even metastable DX centers in GaN, AlN, or BN, independent of crystal structure. Similarly, the effective-mass states of Be, Mg, and C acceptor impurities in GaN are found to be more stable than the corresponding deep AX centers. We propose that persistent photoconductivity in Mg-doped GaN arises from the bistability of a N-site vacancy that is accompanied by a charge-state change from +3e to +1e. [S0163-1829(97)00719-4]

## I. INTRODUCTION

There is currently great interest in III-V nitrides, particularly GaN and  $Al_xGa_{1-x-y}In_yN$  alloys, as a result of progress in making light-emitting diodes and lasers with emission wavelengths spanning a wide range of the visible spectrum from red to blue. The room-temperature band gap of  $Al_xGa_{1-x-y}In_yN$  varies from 1.95 eV to 6.2 eV, making even shorter wavelength light-emitting devices a possibility in the future.<sup>1,2</sup> Currently, blue-light-emitting diodes<sup>3,4</sup> with a luminous intensity of over 1 cd have been successfully fabricated. For reasons that are not yet well understood but appear to be related to their small bond lengths and strong bond strengths, III-V nitrides are more robust against defects than wide-band-gap II-VI semiconductors. These materials are also of interest for potential applications in hightemperature and high-power electronic devices.<sup>2</sup>

Control of carrier density has been a major challenge in many wide-band-gap semiconductors. The difficulties generally affect either *n*- or *p*-type doping, but not both. In the case of III-V nitrides, particularly GaN, *n*-type doping is easy but *p*-type doping has proved troublesome. Currently, Mg is the most widely used acceptor impurity in GaN and hole concentrations of about  $3 \times 10^{18}$ /cm<sup>3</sup> have been obtained.<sup>5-9</sup> A recent report on persistent photoconductivity (PPC) in *p*-type Mg-doped GaN has raised the possibility that Mg may have both effective-mass and deep acceptor states.<sup>10</sup>

As-grown GaN is generally *n*-type with an electron density of about  $5 \times 10^{19}$ /cm<sup>3</sup> resulting from unintentional impurity incorporation or native defects during growth.<sup>11–13</sup> The incorporation of donor impurities such as oxygen can perhaps be minimized by using molecular-beam epitaxy (MBE) and samples with far lower electron densities have been made.<sup>14–17</sup> It is not presently known whether such high values of electron density can be maintained in larger bandgap nitrides such as Al<sub>x</sub>Ga<sub>1-x</sub>N alloys and BN. The role of wurtzite versus cubic crystal structure on doping has not been considered in detail either. In the analogous cubic GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As alloy series, GaAs can be *n*-type doped to a maximum level of  $2 \times 10^{19}$ /cm<sup>3</sup>, but at a pressure of

20–25 kbar or when more than 22% of Ga atoms are replaced by Al, deep donor DX centers become energetically more stable than shallow donor centers and the carrier density decreases.<sup>18,19</sup> A similar decrease of carrier density in as-grown *n*-type GaN subjected to hydrostatic has been observed recently raising the possibility that  $Al_xGa_{1-x}N$  alloys are similar in their doping properties to  $Al_xGa_{1-x}As$ .<sup>11</sup> As discussed below, we find that the two systems are, however, quite different and, except for a few impurities, deep centers are far less likely in III-V nitrides than in  $Al_xGa_{1-x}As$  alloys.

The most important conclusion from our study is that the small lattice constants of III-V nitrides do not allow large lattice relaxations for many impurities and this leads to a significant decrease in the stability of deep centers. For example, we find that the effective-mass state of a Mg impurity in GaN is stable against AX center formation, indicating that PPC in Mg-doped GaN (Ref. 10) is not a manifestation of the bistability of Mg. Instead we propose that PPC is related to the bistability of a N-site vacancy. We also find that Be and C impurities should be as suitable as Mg for the *p*-type doping of GaN. In the case of *n*-type doping, we find that Ge and S impurities that readily form DX centers in  $Al_xGa_{1-x}As$  alloys (with binding energies that increase with band  $gap^{18,19}$ ) are totally immune to DX center formation in cubic or hexagonal  $Al_{x}Ga_{1-x}N$  and BN despite their much larger band gaps. This result suggests that high n-type doping levels can be obtained in these materials even for band gaps exceeding 6 eV. For oxygen, which has a small covalent bonding radius, we find that a stable DX center can form under high pressures or alloying with AlN. A comparison of our results with experimental data provides strong evidence that O is the principle unintentional impurity in highly *n*-type as-grown GaN.

The paper is organized as follows. The stability of effective-mass states relative to deep AX acceptor states of Be, Mg, and C is examined in Sec. II. The question of PPC in *p*-type GaN and its connection to the bistability of a N vacancy is discussed in Sec. III. The stabilities of shallow donor states relative to deep DX centers for various donor impurities are examined in Sec. IV. A possible application of

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III-V nitrides as a new class of photorefractive materials is briefly discussed in Sec. V and the conclusions are given in Sec. VI.

The results reported in the following sections have been obtained from first-principles pseudopotential total-energy calculations<sup>20,21</sup> based on the local-density-functional approximation.<sup>22</sup> Norm-conserving nonlocal pseudopotentials<sup>23</sup> were generated by the scheme of Troullier and Martins,<sup>24</sup> and a Kleinman-Bylander type of fully separable pseudopotentials was constructed.<sup>25</sup> Brillouin-zone summations were done with special *k*-point sets<sup>26</sup> in a three-dimensionally periodic 32-atom bcc supercell. Total-energy minimization was achieved by a Davidson-type self-consistent diagonalization method.<sup>27</sup>

## II. Mg, Be, AND C ACCEPTOR IMPURITIES

We first examine the stability of AX centers for Mg and Be in III-V nitrides such as GaN and AlN by calculating the change in energy for the self-compensation reaction<sup>28</sup>

$$2a^0 \rightarrow a^- + AX^+. \tag{1}$$

In Eq. (1) *a* represents a substitutional tetrahedrally coordinated shallow impurity, AX denotes a deep acceptor center resulting from large lattice relaxation, and the superscripts specify the charge states. If the reaction is exothermic then an  $AX^+$  center captures the hole emitted by a second impurity and this leads to compensation.

We have recently identified the lowest-energy atomic configuration for AX centers in zinc-blende crystals.<sup>28</sup> The same type of defect is possible in the wurtzite structure. An AX center arises from the rupture of *two* host bonds and the formation of a new covalent bond between two second-neighbor anions, as shown in Fig. 1. We have labeled this configuration a double-broken-bond (DBB) state. The DBB state in zinc-blende crystals is the analog of the V<sub>k</sub> center in an alkali halide such as KCl in which two Cl atoms move towards each other to create a defect that traps a hole.<sup>29</sup> In the case of the DBB AX center, the formation of the anion-anion bond leads to the capture of *two* holes making AX a positively charged center.

Because of the small size of N, the atomic relaxations needed for the formation of a N-N bonded AX center in III-V nitrides are much larger than in other III-V semiconductors. The covalent radius of N is only 0.7 Å, while the initial N-N separation in bulk GaN is nearly 3.2 Å. The formation of an AX center for a Be impurity in GaN leads to a N-N bond length of 1.50 Å, while the value for Mg is 1.52 Å. The formation energies of a DBB-type AX center in cubic and wurtzite crystal structures are found to be very similar. The DBB states of Be and Mg impurities in GaN and AlN are found to be high-energy metastable states in both crystal structures, indicating that these impurities should be effective-mass-type acceptors. In GaN, the reaction energy in Eq. (1) is calculated to be endothermic by 0.7 eV for Be and 2.0 eV for Mg. The corresponding numbers for AlN are 0.8 eV and 2.2 eV. As might be expected, the stability of the DBB state is strongly dependent on the atomic size of the impurity. For Be with a small covalent radius of 1.06 Å as compared to Mg with a covalent radius of 1.40 Å, lattice strain is more easily relaxed leading to a lower-energy struc-



FIG. 1. The ideal zinc blende lattice is shown in (a). A schematic illustration of the atomic structure of the double broken bond (DBB) state for a Be acceptor impurity that leads to the rupture of two Ga-N bonds and the formation of a N-N bond is shown in (b). The DBB state for a C acceptor impurity in GaN is shown in (c). The dotted lines denote broken bonds.

ture. We expect that the AX center for a Zn impurity should also be unfavorable because of its large covalent radius. Our results are in agreement with experimental data showing that Mg and (more recently) Be are shallow acceptors.<sup>5–9,30</sup>

We have also examined the stability of C-derived AX centers in GaN. Since the covalent radius and ionicity of C are similar to those of N, we expect that C impurities will occupy predominantly N sites. The AX state for C in GaN is found to have a DBB-type structure similar to that of N in ZnSe as shown in Fig. 1(c).<sup>28</sup> The formation of the C-induced DBB AX center is calculated to be endothermic

by 2.8 eV in GaN, suggesting that substitutional C should be an excellent acceptor impurity in GaN. We note that *p*-type conductivity has been recently observed in C-doped GaN grown by MBE.<sup>31</sup>

## III. PERSISTENT PHOTOCONDUCTIVITY IN *p*-TYPE GaN

A recent report on PPC in Mg-doped GaN has raised the possibility of structural bistability for Mg.<sup>10</sup> If PPC is related to such a bistability, then in order to explain the increased carrier density resulting from illumination it is necessary that the deep AX state of the impurity should be more stable than the effective-mass state, a result at variance with experimental data and to our finding that the AX center is metastable. To explain PPC we have considered, therefore, other alternatives.

We suggest that the PPC is caused by the bistability of nitrogen vacancies. Previous theoretical studies have identified the nitrogen vacancy as the native defect with the lowest formation energy in p-type GaN.<sup>12,32,33</sup> The nitrogen vacancy is bistable with two distinct charge states and atomic structures. The charge states are +1 (single donor) and +3 (triple donor). The +3 state occurs only after a large lattice relaxation consisting of an outward breathing mode relaxation (by 16–20 % of a bond length) of the four Ga atoms surrounding the vacancy. The +3 charge state is 0.78 eV more stable than the +1 charge state in *p*-type GaN when the Fermi level is located at the valence-band maximum (VBM). The +3 state remains more stable than the +1 state as long as the Fermi level is within 0.39 eV of the VBM. From our calculations we find that the +1 and +3 charged states are separated by a relatively small 0.14-eV energy barrier for hole capture. The +3 state, but not the +1 state, has a defect level in the gap at 0.9 eV above the VBM. Occuption of this level via optical excitation converts the +3 state into the +1 charge state thereby releasing two holes into the VBM and giving rise to PPC. We note that experimentally a hole capture barrier of 0.13 eV has been observed in Mg-doped GaN samples exhibiting PPC.<sup>10</sup>

The situation is essentially the same when the vacancy is coupled to a Mg impurity. Such a coupling reduces the formation energy of the vacancy.<sup>32</sup> We find a binding energy of 0.53 eV for the Mg-V<sub>N</sub> complex. The Mg component of the complex is an acceptor and is in a negative charge state. This complex, therefore, exhibits a bistability associated with doubly positive and neutral charge states. In the +2 charge state of the complex, an outward breathing relaxation of the three Ga atoms surrounding the vacancy takes place. The stable state of the Mg- $V_N$  complex in *p*-type GaN is the +2 charge state. In this state,  $(Mg-V)^{2+}$  has an empty deep level 0.7 eV above the VBM. Optical excitation of electrons into this deep level transforms the structure into a neutral state with the Ga atoms moving back into essentially unrelaxed positions. The transformation from the +2e state to the neutral state results in an increase in the hole concentration that also leads to PPC.

Recent photoluminescence measurements in Mg-doped GaN have revealed two emission lines at 2.43 eV and 2.87 eV (in addition to the emission line at 3.25 eV) that were attributed to deep centers associated with Mg-defect complexes.<sup>34</sup> From the results of our calculations on defect levels, we propose that triple (and double) positively charged  $V_N$  (and Mg- $V_N$ ) defects with large breathing mode relaxations are the source of these photoluminescence lines.

### **IV. DONOR IMPURITIES**

### A. DX centers in hexagonal III-V nitrides

The energetics of deep donor formation were determined by considering the following negative U reaction for DXcenters,<sup>19</sup> which is similar to that for AX centers in Eq. (1):

$$2d^0 \rightarrow DX^- + d^+. \tag{2}$$

In Eq. (2), d denotes a substitutional shallow impurity, DX represents a broken-bond (BB) state, and the superscripts specify the charge states.

The BB state occurs for donor impurities on either a cation or an anion sublattice as shown in Figs. 2 and 3. In both cases, the BB state results from the motion of a cation site atom (either the impurity itself or a nearest-neighbor atom) into an interstitial position. The BB geometry is sometimes referred to as a vacancy-interstitial-pair defect and is the analog of a Frenkel defect in alkali halides.<sup>29</sup> As discussed further below, for oxygen impurities the BB configurations are not the only types of structures to give a *DX* center.<sup>35</sup>

In a *wurtzite* structure, there are two different BB types of DX centers for every impurity. The rupture of a bond can take place either along a bond parallel to the *c* axis or along one of the three other equivalent bonds. We denote the BB structure along the *c* axis [see Fig. 3(b) by  $\gamma$ -BB and the others by  $\alpha$ -BB [Fig. 3(c)].

The  $\gamma$ -BB-type structure is found to be unstable for all impurities in  $Al_xGa_{1-x}N$  alloys in the wurtzite structure. The reason for the instability is that in the BB state, the cation atom displaced into the interstitial position experiences repulsive interactions with three host Ga or Al atoms [see Fig. 3(b)] and with a host N\* atom lying along the displacement axis. The repulsive interactions are a consequence of the small bond length of  $Al_xGa_{1-x}N$  alloys relative to cationcation separations that occur in the process of DX center formation. Consider, for example, the trigonal  $\gamma$ -BB structure of an impurity such as Ge in GaN. When the Ge atom is displaced by the "normal" 44% of a bond length into an antibonding site, the separation between it and the three nearby Ga atoms is only 2.51 Å. Considering the fact that the sum of covalent radii is 2.48 Å and that no bonds are forming, the interaction between Ge and the Ga (or Al) atoms is strongly repulsive. This makes the  $\gamma$ -BB DX center highly unstable.

The local atomic environment is different for the  $\alpha$ -BB type of *DX* center where bond rupture is not along the *c* axis. In this case a cation-site impurity displaced into the antibonding interstitial site comes within the interaction radius of four host cations. In GaN doped with Si, when the Si atom is displaced 44% of the bond length into the interstitial position, two Ga atoms [Ga<sub>1</sub> in Fig. 3(c)] are at a distance of 2.51 Å (same with  $\gamma$ -BB) and the other two atoms (labeled Ga<sub>2</sub>) are at 2.79 Å. The repulsive interactions are weaker than in the case of the trigonal  $\gamma$ -BB state and this state gives rise to a local minimum or a global minimum in the total



FIG. 2. The broken-bond (BB) type of DX center for a Si impurity in GaN is shown in (a). The BB DX state for a column VI donor impurity such as S is shown in (b). The dotted lines denote broken bonds. A different type of DX center denoted as cation-cation-bonded (CCB) is shown in (c). The CCB DX center is important for oxygen in GaN and for S in other III-V semiconductors. The oxygen donor impurity is displaced along a [001] axis and two bonds (dashed lines) around it become weak.

energy depending on alloy composition. For the somewhat larger-sized Ge impurity even the  $\alpha$ -BB-type DX center is found to be unstable. The results are discussed in more detail below.

# B. Si and Ge impurities in wurtzite and cubic structure $Al_xGa_{1-x}N$ alloys

As mentioned above, we find that Si, unlike Ge, has stable and metastable DX centers in wurtzite (w) structure  $Al_xGa_{1-x}N$  alloys. Relative to the shallow donor state, the deep donor  $\alpha$ -BB center of Si is metastable in w-GaN but



FIG. 3. The ideal wurtzite lattice is shown in (a). The brokenbond *DX* center with bond breaking along the *c* axis (i.e., the  $\gamma$ -BB *DX* center) is shown in (b). The second type of BB *DX* center (the  $\alpha$ -BB *DX* center) is illustrated in (c).

stable in *w*-AlN. The binding energy of  $\alpha$ -BB is estimated to increase from -0.43 eV (i.e., unbound) in *w*-GaN to 1.54 eV in *w*-AlN. We find a large energy barrier of 0.68 eV separating shallow from deep donor states. Structurally, the Si atom is displaced by 44% of the ideal bond length toward the antibonding interstitial position. The *DX* formation energies in GaN and AlN indicate that in hexagonal Al<sub>x</sub>Ga<sub>1-x</sub>N alloys, Si donors should become selfcompensated by  $\alpha$ -BB *DX* centers as the Al mole fraction increases. By linear interpolation, we expect a shallow-deep transition at  $x \sim 0.24$  in hexagonal Al<sub>x</sub>Ga<sub>1-x</sub>N.

In *cubic* GaN (*c*-GaN) there is only one type of DX center with a trigonally symmetric broken-bond configuration. The BB DX structure for Si is found to be unstable in *c*-GaN and *c*-AlN because of a steric hinderance effect arising from repulsive cation-cation interactions similar to that of the unstable  $\gamma$ -BB center in *w*-GaN. This indicates that Si impurities should be immune to self-compensation by DX formation in c-Al<sub>x</sub>Ga<sub>1-x</sub>N alloys and that one should be able to achieve high *n*-type conductivity for all compositions.

For Ge in GaN or AlN, we find that BB-type DX centers are *unstable* in either the hexagonal or cubic phases. The reason that Ge does not have a stable or metastable  $\alpha$ -BB-type DX center is related to the slightly larger atomic size of Ge as compared to Si. The Ge-N bond length is calculated to be 9% (0.2 Å) longer than the Si-N bond length. This amounts to more than 10% of the GaN bond length and is sufficient to change the interactions between interstitial and host atoms and to alter the energy of the deep donor center of Ge relative to Si. Our results suggest that Ge should be a much better dopant in  $Al_{x}Ga_{1-x}N$  than Si, consistent with experimental data.<sup>15–17</sup> Room-temperature freeelectron concentrations of at least as high as  $3.7 \times 10^{19}$ cm<sup>-3</sup> can be achieved for Ge-doped  $w - Al_x Ga_{1-x}N$  with a relatively high Al mole fraction of x=0.2,<sup>15</sup> while for Sidoped Al<sub>x</sub>Ga<sub>1-x</sub>N with a *smaller* Al mole fraction of only x=0.1, the maximum free-carrier concentration of  $2 \times 10^{18}$ cm<sup>-3</sup> is more than an order of magnitude smaller.<sup>16</sup> Halleffect studies on Si-doped GaN show high compensation under a doping density of the order of  $10^{19}$  cm<sup>-3</sup>.<sup>17</sup>

### C. Sulfur

We now consider the broken-bond DX center for a S impurity. The BB state for S involves the motion of either an Al or a Ga atom into an interstitial position. For w- $Al_xGa_{1-x}N$  we find no secondary local minimum in the total energy for the two types of BB states discussed above. This implies that S is immune to DX center formation, even in a metastable state, and that it should be an excellent choice as a shallow donor impurity in w-Al<sub>x</sub>Ga<sub>1-x</sub>N alloys with large band gaps. For c-Al<sub>x</sub>Ga<sub>1-x</sub>N alloys the results are similar to those for the wurtzite phase. Although a Ga nearest-neighbor atom of S undergoes a large (0.88-Å) lattice relaxation into an antibonding position, the relaxation of the S impurity along the same direction prevents a true bond-breaking type of structure from occurring. In principle, the existence of this state with a large lattice relaxation could give a deep center as the Al mole fraction increases. However, the localized DX level is found to follow the conduction-band maximum and it does not develop into a bona fide deep state.

#### D. Oxygen

Another important anion-site dopant in GaN is substitutional oxygen. It has been suggested to be the impurity primarily responsible for the unintentional heavy *n*-type doping of as-grown GaN.<sup>36,37</sup> An important question is whether oxygen is a shallow or deep donor in  $Al_xGa_{1-x}N$ . It is expected that oxygen impurities are located predominantly at N-substitutional site in III-V nitrides. In a substitutional structure, nearby Ga atoms are relaxed *outward* from O atom by 4.2% of the bond length even though oxygen has a smaller covalent bonding radius than N.

For anion-site substitutional impurities, we have recently identified a different type of DX center with orthorhombic symmetry and a very different lattice relaxation around the

impurity [see Fig. 2(c)].<sup>35</sup> Except for an interchange of cations and anions, the cation-cation-bonded (CCB) type of DX center is structurally similar to the DBB AX center discussed in Sec. II. It is characterized by covalent bond formation between initially second-nearest-neighbor cations and it occurs only for an anion site impurity with a covalent bonding radius smaller than the atom it replaces.<sup>35</sup> Like BB DX, the CCB DX center is stable only in a negatively charged state. The CCB type of DX center is important primarily for oxygen in III-V nitrides and for sulfur impurities in other III-V semiconductors with larger lattice constants.<sup>35</sup> In III-V nitrides, the CCB DX state of S is found to be unstable in either the cubic or wurtzite phases because S has a larger ionic radius than N.

For oxygen in cubic GaN and AlN, the CCB *DX* configuration is estimated to be 0.16 eV *lower* in energy than the BB *DX* state. The stability of the CCB *DX* state relative to the shallow donor state in c-Al<sub>x</sub>Ga<sub>1-x</sub>N depends on alloy composition. The reaction in Eq. (2) is estimated to be 0.34-eV endothermic in *c*-GaN, but to become 2.4 eV exothermic in *c*-AlN.

In the wurtzite structure, the CCB *DX* center for oxygen is found to transform itself into an  $\alpha$ -BB-type *DX* state. The stability of the latter relative to the shallow donor state is also composition dependent. The  $\alpha$ -BB state is metastable in *w*-GaN with an energy 0.3 eV above the shallow donor state. But in *w*-AlN, the  $\alpha$ -BB state becomes the ground state of an oxygen donor impurity and the reaction in Eq. (2) is found to become exothermic by a large 2.5 eV.

These results suggest that oxygen is a shallow donor impurity in either cubic or wurtzite structure GaN, but a deep DX center in Al-rich Al<sub>1</sub>Ga<sub>1-x</sub>N alloys.<sup>38</sup> As Ga atoms are replaced by Al, CCB or  $\alpha$ -BB types of DX centers become progressively more stable than the shallow donor state. For hexagonal Al<sub>x</sub>Ga<sub>1-x</sub>N alloys, we expect a shallow-deep transition of the oxygen donor level as the Al mole fraction *x* becomes greater than 0.2.

The results of our calculations support the idea that oxygen impurities are a primary source of unintentional doping of GaN.<sup>36,37</sup> Zhang *et al.* have shown that the free-electron concentration in unintentionally doped  $Al_xGa_{1-x}N$  is sharply reduced as the Al mole fraction increases above 0.2,<sup>15</sup> consistent with the above results for the stability of O:DX centers in  $Al_xGa_{1-x}N$ . More recently, a pressureinduced shallow-deep transition of the donor state in unintentionally doped GaN was measured at 20 GPa.<sup>11</sup> The pressure-induced shallow-deep transition is one important characteristic of DX centers. The results of our calculations show that the oxygen-derived DX center can be stabilized at a pressure of 22 GPa, which happens to be in very good agreement with the experimental data.<sup>11</sup>

### E. Boron nitride

To further test the effect of the lattice constant on the stability of deep centers we have examined BN, which has a smaller bond length than either GaN or AlN. The results of our calculations show that Si, Ge, and S impurities in BN give do not possess stable or metastable DX centers despite a large band gap of 6.4 eV. This is consistent with experimental data showing that BN can be easily *n*-type doped and that

Si is a shallow donor impurity in this material.<sup>39</sup> Similarly, we have examined Be and C acceptor impurities and find that AX centers are structurally unstable relative to effective-mass states in BN. This implies that there should be no problem in the *p*-type doping of BN either.

### V. APPLICATIONS

Finally, we would like to note that highly *n*-type-doped III-V nitrides may be suitable materials for optical applications. Recently, the phenomena of persistent photoconductivity exhibited by *DX* centers was shown to yield a different class of photorefractive materials.<sup>40</sup> Materials operating at room temperature would be optimal for practical use. The III-V nitrides should lead to higher operating temperatures because of their stronger elastic properties as compared to  $Al_xGa_{1-x}As$ :Si or II-VI semiconductors. We estimate the electron capture barrier between the shallow donor and the *DX* state for a Si impurity in *w*-Al\_xGa\_{1-x}N to be about 0.68 eV for x = 0.24, suggesting that PPC can persist to a temperature of 230 K.

### VI. SUMMARY

In summary, we have examined the electronic and structural states of several acceptor and donor impurities in III-V nitrides. We find that the stability of *AX* and *DX* centers in GaN, AIN, and BN are determined largely by the bonding radii of impurities and that the steric hindrances introduced by the small lattice constants of these materials inhibit the generation of deep centers for many impurities. From the results of our calculations we conclude that Mg, Be, and C TABLE I. The occurrence of DX centers as either stable or metastable states in  $Al_xGa_{1-x}N$  alloys is summarized. Results for both the simple broken-bond (BB) and the cation-cation-bonded (CCB) types of DX centers in cubic and wurtzite crystal structures are included. A "Yes" implies that the impurity forms a stable or metastable DX center. A "No" means that the impurity is immune to DX center formation.

Structure	С	Si	Ge	0	S
Cubic: BB	Yes	No	No	Yes	No
Cubic: CCB	No	No	No	Yes	No
Wurtzite: $\alpha$ -BB	Yes	Yes	No	Yes	No
Wurtzite: $\gamma$ -BB	Yes	No	No	No	No
Wurtzite: CCB	No	No	No	No	No

impurities should give effective-mass type states in  $Al_xGa_{1-x}N$  and BN. We propose that persistentphotoconductivity in Mg-doped GaN is not associated with the bistability of Mg but with that of a N-site vacancy. Despite their large band gaps, we find that  $Al_xGa_{1-x}N$  alloys and BN can be highly *n*-type doped. With a few exceptions, the small lattice constants of these materials prevent the formation of deep centers arising from large lattice relaxations. Substitutional oxygen with a small covalent radius is found to be a shallow donor in GaN, but a deep *DX* center in AlN. The energetics of *DX* center formation for a number of impurities including C on a Ga site in GaN and AlN are summarized in Table I. Although we did not examine largersized impurities such as Sn, Se, and Te, we expect that they should be shallow donors because of their large atomic radii.

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