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Ab initio study of oxygen point defects in GaAs, GaN, and AlN

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We have studied oxygen point defects with the plane-wave pseudopotential method in GaAs, GaN, and AlN. The calculations demonstrate a qualitatively different behavior of oxygen impurities in these materials. O_{As} in GaAs acts as a deep center with an off-center displacement and negative-U behavior, in agreement with the experimental data. O_N in GaN is found to be a shallow donor with a low formation energy, and is suggested to act as a partial source for the unintentional n-type conductivity commonly observed in GaN. O in AlN is also found to easily substitute for N, which is consistent with the experimentally observed large oxygen concentrations in AlN. However, O_N in AlN is shown to be a deep center due to the wide band gap, in contrast with O_N in GaN. Our calculations thus predict that isolated oxygen acts as a DX-type center in $Al_xGa_{1-x}N$ alloys. Results for other oxygen point defect configurations and for the dominant native defects are also presented. [S0163-1829(96)01047-8]

I. INTRODUCTION

Oxygen is a common impurity in many semiconductor materials and has provided a longstanding challenge for investigators in trying to capture the relevant details of its versatile role. The extent of the oxygen incorporation depends strongly on the growth method and the material in question. Czhochralski-grown GaAs is generally known to contain 10^{15} $1/\mathrm{cm}^3$ oxygen.[1] The degree of oxygen content in GaN is not yet well documented, but recent secondary ion-mass spectroscopy (SIMS) measurements indicate that GaN can contain oxygen at least in the range 10^{16}–10^{17} $1/\mathrm{cm}^3$.[2] Finally, AlN seems to present an extreme case in this respect, because of the possibility of several percent oxygen incorporation.[3]

The theoretical modeling of oxygen in semiconductor materials has remained a challenge for the computational field. This is due to the chemical character of oxygen (e.g., bonding properties, large electronegativity), which is difficult to describe truthfully with conventional empirical or semiempirical methods. *Ab initio* studies have been rare due to the sharp character of the oxygen electronic wave functions, which are computationally costly to expand properly, especially with the plane-wave basis. However, continuous progress in the computer capacity as well as development in computational methods[4] have recently enabled the modeling of oxygen with realistic first-principles simulations.

Whereas literature for *ab initio* studies of O in GaAs remains rather limited, the experimental characterization of oxygen in GaAs is well established. For instance, local vibrational mode (LVM) measurements[5,6] have given unambiguous information even about the local atomic structure of oxygen point defects in GaAs. Similar studies have not been reported, to the best of our knowledge, for oxygen in GaN or AlN.

Our aim in this paper is to study the atomic and electronic structures of oxygen point defects in a systematic way with *ab initio* simulations in three III-V compounds: GaAs, GaN, and AlN. We start with O_{As} and O_i in GaAs, and use the extensive experimental data to verify that our method indeed provides a realistic description of the oxygen behavior. This being established, we proceed to study oxygen in GaN and AlN. Our calculations demonstrate clearly that oxygen behaves as a shallow donor in GaN, which is qualitatively different from the oxygen behavior in GaAs. This difference can be largely explained in simple terms concerning basic physical properties such as the small difference between the ionic radius of O and N compared with the case between O and As. The same argument can be applied to the behavior of O in AlN, but in this case the very wide band gap is shown to induce a deep-center character of the substitutional oxygen. More importantly, a comparison of results in GaN and AlN reveals that oxygen should act as a DX center in $Al_xGa_{1-x}N$ alloys.

The formation energy analysis shows that oxygen should be easily incorporated in both GaN and AlN into the substitutional position. In addition, $V_{Ga}{}^{3-}$ in GaN and $V_{Al}{}^{3-}$ in AlN are found to be energetically very favorable defects, suggesting that positively charged substitutional oxygen can bind to these negatively charged vacancies, as proposed earlier for AlN.[3]

II. METHODS

Our calculations are performed using the plane-wave pseudopotential method. The Kohn-Sham equations, based on density-functional theory (DFT), are solved self-consistently using the local-density approximation (LDA) for the exchange-correlation term.[7] For Ga, As, and Al, we use standard norm-conserving pseudopotentials[8] with the nonlinear core valence exchange-correlation scheme.[9] The s component is used as the local one for the Ga, As, and Al pseudopotentials. Also using these pseudopotentials for N and O would necessitate a huge number of plane waves in properly converged calculations. The reason for this is the sharp character of the nitrogen and oxygen $2p$ electronic wave functions. Therefore, we employ Vanderbilt-type non-norm-conserving pseudopotentials[4] for N and O. We expand our plane-wave basis up to a 25-Ry kinetic-energy cutoff. Tests indicate that our results are very well converged with this basis set. This clearly demonstrates the advantages of using the Vanderbilt pseudopotentials for the first-row elements; usually with the norm-conserving pseudopotentials a comparable convergence can be achieved only with at least a 60-Ry basis. For the electronic structure minimization we employ damped second-order dynamics[10] combined with the Williams-Soler[11] algorithm.

For the defect calculations we used 32-atom supercells, which are found to give a good convergence with respect to the system size provided that a proper k-point set is used in the calculations.[12,13] In our case, a $2\times2\times2$ k-point mesh[14] is found adequate. When calculating the elemental bulk energies (see below), proper special-k-point sets are also used in each case. Full atomic relaxations without symmetry constraints are allowed. The defect calculations are performed in the cubic (zinc-blende) phase for all three compounds: GaAs, GaN, and AlN. The two nitride materials also exist in the hexagonal wurtzite structure.[15] However, the zinc-blende and wurtzite structures are both tedrahedrally coordinated, which means that the nearest-neighbor shells are equivalent in both cases. Therefore, we believe that our results for O in the cubic phase also describe the situation well in the hexagonal case. This is further corroborated by earlier *ab initio* studies,[16,17] which show that, e.g., the formation energies and electronic structures for native point defects are very similar in both cases.

The defect formation energies and ionization levels were estimated using the conventional method.[18,19] For clarity, below we illustrate the method only in the case of GaN, but the analysis can be simply applied for GaAs by replacing N by As, and similarly for AlN by replacing Ga with Al. The formation energy of a defect in charge state q is defined as

$$E_f(q)=E_{\mathrm{tot}}(q)-n_{\mathrm{Ga}}\mu_{\mathrm{Ga}}-n_{\mathrm{N}}\mu_{\mathrm{N}}-n_{\mathrm{O}}\mu_{\mathrm{O}}-q(\mu_e+E_v), \tag{1}$$

where E_{tot} is the total energy of the defect supercell. $n_{\mathrm{Ga,N,O}}$ denotes the number of each atom type involved in the calculation, and $\mu_{\mathrm{Ga,N,O}}$ is the atomic chemical potential for each species. μ_e corresponds to the electron chemical potential (the Fermi-level position in the gap relative to the valence band). E_v denotes the valence-band maximum.

The atomic chemical potentials of the major constituent species are constrained by the equation

$$\mu_{\mathrm{Ga}}+\mu_{\mathrm{N}}=\mu_{\mathrm{GaN}}^{\mathrm{bulk}}. \tag{2}$$

The effect of growth conditions is taken into account by calculating the chemical potentials of the elemental reservoirs, which are considered to be orthorhombic-Ga, fcc-Al, rhombohedral-As, and N_2-dimer.[20] For instance, if μ_{Ga} is fixed to the calculated elemental value, and μ_{N} is derived from Eq. (2), this gives an estimate of nonstoichiometric growth occuring in Ga-rich conditions. In principle, μ_{O} could be associated with the elemental value (O_2 dimer). However, our calculations show that a more strict criterion for the oxygen chemical potential is set by the formation of the oxides with the group-III elements, i.e., Ga_2O_3 and Al_2O_3. Therefore μ_{O}, for the maximum oxygen concentration, has to be determined in the example case of GaN from the relation

$$2\mu_{\mathrm{Ga}}+3\mu_{\mathrm{O}}=\mu_{\mathrm{Ga_2O_3}}. \tag{3}$$

We present all our results in Ga-rich (Al-rich for AlN) conditions, which are typical of the growth of the two nitrides. Thus we fix μ_{Ga} (μ_{Al} in the case of AlN) to the calculated elemental value, and derive μ_{N} (μ_{As} in the case of GaAs) and μ_{O} from Eqs. (2) and (3).

The electron chemical potential (the Fermi-level position in the gap) affects the formation energy for the charged defects. This effect becomes extremely important in the case of wide-band-gap materials, such as GaN and AlN. We use the experimental band-gap values in calculating the formation energies and ionization levels,[23] because of the well-known tendency for gap underestimation in DFT/LDA calculations. The experimental band-gap value for GaAs is 1.5 eV.[24] For zinc-blende GaN the experimental gap is about 3.3 eV.[25] However, for zinc-blende AlN the gap is indirect, and the experimental value is not well established. Therefore we use an approximate value of 5.0 eV based on *GW* calculations[26,27]. We emphasize that we use the band-gap values reported for zinc-blende structures for consistency, and that if the experimental gap values for the wurtzite phase [w-GaN 3.4 eV and w-AlN 6.2 eV (Ref. 25)] were used in our defect charging analysis, the results would remain essentially unaltered.

Due to the finite size of the supercell, the spurious defect-defect interactions shift the reference effective potential level. This fact has been accounted for by comparing the average potential at the atom site farthest from the defect center with the corresponding site in the bulk calculation.[21,19,22] The difference in the two average potential values is then taken into account in the formation energy analysis.

III. RESULTS AND DISCUSSION

A. Oxygen in GaAs

Oxygen in GaAs is experimentally known to exist in several point defect configurations.[5] Most experimental interest has been directed toward O substituting for As (O_{As}) and isolated O interstitials (O_i).[5,6] LVM experiments have clearly revealed that O_{As} can exist in three charge states, of which the middle one is not stable. The atomic structure of the defect is characterized by O bonding to two Ga neighbors. This means that O substituting for As occupies an off-center position in the [100] direction, and therefore can be alternatively described as a $V_{\mathrm{As}}+O_i$ complex. Figure 1 illustrates this off-center atomic configuration and the notation used in describing the oxygen position with respect to the four nearest-neighbor Ga atoms.

The calculated relaxed atomic positions for each charge state of O_{As} are collected in Table I.[28] The results are in good agreement with experiment, as well as earlier cluster calculations,[29] and reveal that ${O_{\mathrm{As}}}^{-}$, ${O_{\mathrm{As}}}^{2-}$, and ${O_{\mathrm{As}}}^{3-}$ move to an off-center position along the [100] direction due to a symmetry-lowering relaxation. The displacement from the substitutional site is seen to increase slightly as a function of the number of excess electrons. The neutral and singly positive charge states are found to stay on-site accompanied with over 10% inward relaxation of the neighbouring Ga atoms. In agreement with the study by Jones and Öberg,[29] we also

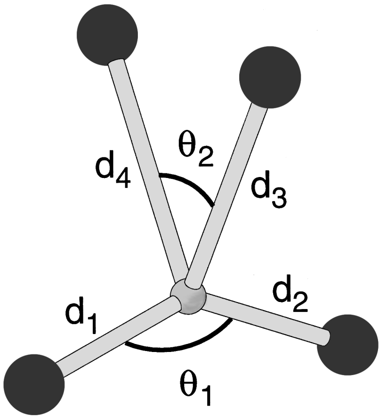

FIG. 1. The O_{As} defect in the off-center position in GaAs. The dark spheres denote Ga atoms, and the lighter one the O atom. The bond lengths and angles for different charge states of the defect are listed in Table I.

find a metastable position for the singly negative charge state at the substitutional site, which lies about 0.2 eV higher in energy than the off-center configuration. The only apparent discrepancy with respect to the cluster calculations[29] is the behavior of the Ga-O-Ga bond angle (θ_1). In our study the bond angle is seen to increase in the off-center configuration with increasing charge state, while Jones and Öberg[29] found the opposite behavior.

Figure 2 shows the formation energies and ionization levels obtained for O_{As} from our calculations. The ionization levels clearly demonstrate the deep-level character of O_{As} in GaAs, consistent with the experiments. $O_{As}{}^-$ is seen to be the most favorable charge states for a wide range of Fermi-level positions around the midgap. Two negative-U effects are seen which cause the neutral and doubly negative charge states to be unstable. This effect can be associated with the electron pairing effect: the uppermost electron level of the neutral doubly negative charge states is singly occupied (paramagnetic). When another electron is added to this level (turning the charge state to singly or triply negative, respectively) the gain in electronic pairing energy causes the doubly occupied state to be lower in energy.

Because experimentally the off-center behavior is seen to characterize substitutional oxygen in all three charge states, we associate these charge states with $O_{As}{}^-$, $O_{As}{}^{2-}$, and $O_{As}{}^{3-}$ in our calculations. $O_{As}{}^{2-}$ fulfills the experimental observation of instability of the middle one of the three charge states. Furthermore, the assignment is in nice agreement with a recent experiment,[30] in which the unstable state is found to be paramagnetic, which indeed is the case for $O_{As}{}^{2-}$.

TABLE I. Details of the atomic configuration of O_{As} in GaAs for different charge states. d_i denotes the bond length between the oxygen atom and the nearest-neighbor Ga atoms, and θ_i the corresponding bond angles, illustrated in Fig. 1. The bond-length values are given in units of the nearest-neighbor distance of the perfect lattice.

Defect	d_1	d_2	d_3	d_4	θ_1	θ_2
$O_{As}{}^+$	0.88	0.88	0.88	0.88	109.5	109.5
O_{As}	0.87	0.87	0.87	0.87	109.5	109.5
$O_{As}{}^-$	0.76	0.76	1.07	1.06	131.5	61.3
$O_{As}{}^{2-}$	0.75	0.75	1.09	1.07	136.3	60.7
$O_{As}{}^{3-}$	0.75	0.75	1.09	1.08	141.0	60.5

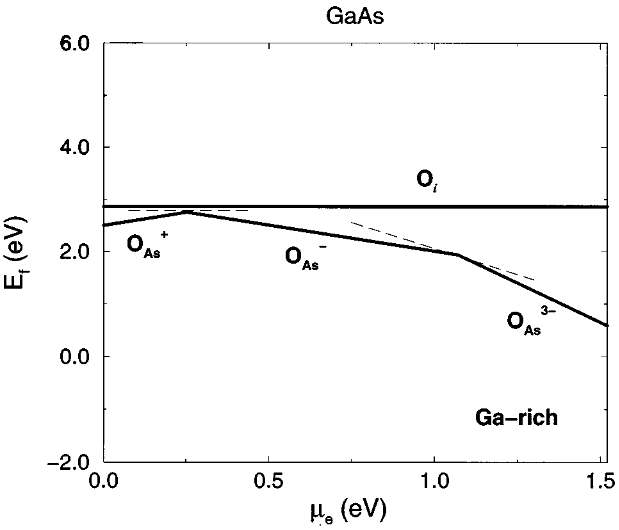

FIG. 2. The formation energies for O_{As} and O_i in GaAs in different charge states as a function of the electron chemical potential in the band gap. The situation corresponds to the Ga-rich case, and the experimental band-gap value (1.5 eV) is used to give the upper limit for the electron chemical potential. The dashed lines correspond to the unstable neutral and doubly negative charge states of the O_{As} defect.

Isolated O_i has been experimentally found to bond to a Ga and an As atom.[5] Our calculations are again in good agreement with this observation. The bond length between O and the nearest Ga (As) atom was found to be 0.73 (0.73) in units of the bond length of ideal GaAs. The Ga-O-As bond angle was 134°. There are two inequivalent interstitial sites in the zinc-blende lattice, in which O occupies a bridge position bonding to Ga and As atoms. These were found to be energetically nearly degenerate (within 0.01 eV) in our calculations. This can be motivated by the fact that the nearest neighbors are identical in both cases, and that bonding with these two atoms dominates in the total energy, and therefore the differences in the second-nearest-neighbor shell should not lead to large differences in energy. The formation energy for O_i is plotted in Fig. 2, and the defect is found to exist only in the neutral charge state for all Fermi-level positions, which suggests that O_i should be electrically inactive. This observation is in perfect agreement with the experiment.[5] The formation energy is comparable with O_{As}, in accordance with the common experimental detection of both oxygen defect types in GaAs.[5]

B. Oxygen in GaN

At present there exist few experimental studies of oxygen in GaN. Chung and Gershenzon[31] demonstrated that the amount of oxygen in the growth process has a strong influence on the carrier concentration, suggesting that oxygen should act as a shallow donor in GaN. Figure 3 presents the results of our calculations for O_N in GaN. The immediate observation is that O substituting for N is singly positively

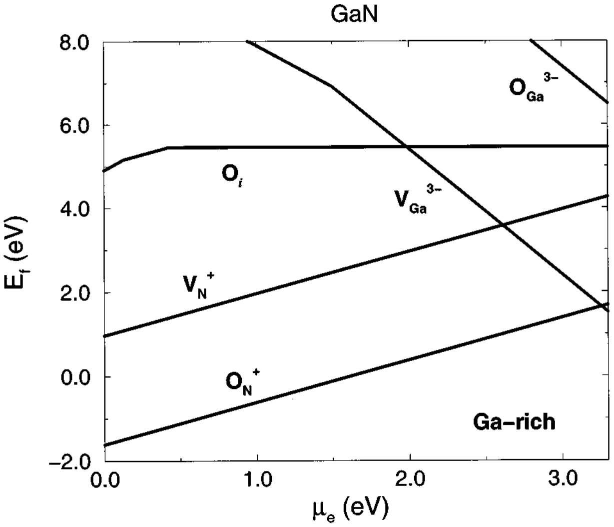

FIG. 3. The formation energies and ionization levels for the studied defects in GaN for the Ga-rich case. The experimental band-gap value (3.3 eV) is used to give the upper limit for the electron chemical potential.

charged for nearly all positions of the Fermi level in the band gap. The transition to the neutral charge state occurs close to the conduction-band minimum: experimentally the ionization energy is found to be about 30 meV.[32,2] However, the delocalized nature of the uppermost electronic state of the neutral charge state makes an accurate computational estimate of this ionization level impossible with the supercell calculations employed here.

Thus our calculation indeed shows that O_N acts as a shallow donor in GaN, which is in clear contrast with the case above, where O_{As} in GaAs was found to be a deep off-site center. The formation energy for O_N^+ is very low, as a matter of fact about 2 eV lower than for V_N^+, also depicted in Fig. 3. This suggests that large oxygen concentrations are likely to occur in GaN, which is in agreement with the recent SIMS measurements revealing large O (as well as Si) contamination.[2] Our results are fully consistent with the *ab initio* calculations by Neugebauer and Van de Walle,[33] which also predict O_N^+ to be energetically clearly favorable compared with V_N^+. We therefore support the suggestion by Neugebauer and Van de Walle[33] that O_N is likely to act as one of the dominant donors in GaN, causing the unintentional n-type conductivity in as-grown samples, in agreement with the experimental observations.[31,2,32]

The singly positively charged O is isoelectronic with N, and this provides a simple explanation of why O is easily incorporated into the N site. The ionic radius of O is much smaller than that of As, which explains the qualitative difference with GaAs, together with the larger lattice constant of GaAs (5.5 Å) compared with GaN (4.5 Å). This argument is in agreement with the observed relaxed atomic positions in our calculations: O_N^+ in GaN is found to stay on-site, with about a 3% outward relaxation of the neighboring Ga atoms, while the Ga atoms around O_{As}^+ and O_{As} in GaAs (see Table I) are found to relax considerably inwards to adjust themselves to the ''too small'' oxygen atom occupying the As site.

Figure 3 also presents the formation energy for O_i in GaN, which can be seen to be several eV higher than for O_N, thus excluding its presence in large concentrations in near-equilibrium growth conditions. In our calculations the neutral charge state of O_i is seen to dominate a wide range of Fermi-level positions in the gap, showing that the oxygen in the interstitial configuration is not electrically very active. Zolper *et al.*[32] found a very low activation efficiency for implanted oxygen to be ionized, and proposed as one explanation that the implanted oxygen as a light element is unable to substitute for the nitrogen, i.e., to create first empty nitrogen sites to be occupied. Therefore, if a significant portion of the implanted oxygen remains in the interstitial position, it should remain electrically inactive based on our results, and this could explain the low activation efficiency. On the other hand, as pointed out by Zolper *et al.*,[32] oxygen defect complexes cannot be ruled out as a source of the inactivation. Indeed, as shown in Fig. 3 the formation energy for the triply negative Ga vacancy in n-type conditions is found to be very low. Thus V_{Ga}^{3-} and O_N^+ in GaN are likely to form defect clusters in a similar way as proposed in AlN.[3]

We also investigated the possibility of O_{Ga} defects in GaN, as speculated in our earlier study.[13] Our calculations indeed show that the negatively charged oxygen defects at the gallium site experience large spontaneous atomic displacements from the substitutional site due to the Jahn-Teller effect, in close agreement with the behavior of the negatively charged nitrogen antisites.[13,17] However, the formation energy of the O_{Ga} in all charge states is found to be several eV higher than for O_N. The lowest formation energy is reached for O_{Ga}^{3-} in n-type conditions, but even then this defect type remains clearly unfavorable, as can be seen from Fig. 3. Our calculations thus predict that nearly all isolated oxygen should occupy nitrogen sites in a growth process close to thermal equilibrium.

C. Oxygen in AlN

AlN differs from GaN by the fact that generally it is found to be insulating. This has been related to defect levels which reside deep in the band gap.[15] Figure 4 shows the formation energy and ionization levels for O_N and O_i based on our calculations for AlN. O_N is again found to be energetically a very favorable defect, similarly to the case for GaN. Figure 4 also reveals a clear distinction between O_N in AlN and GaN: two ionization levels appear well below the conduction-band edge in AlN. The calculations predict two negative-U effects: the first one between the singly positive and singly negative and the second one between the singly negative and triply negative charge states. Thus the neutral and doubly negative charge states are predicted to be unstable.

The low formation energy for O_N is in agreement with the experimental observation of an easy oxygen contamination of AlN.[3] Furthermore, the deep character of O_N in AlN explains the fact that even a large oxygen concentration does not lead to n-type conductivity, and that AlN remains insulating with a high activation energy (over 2.0 eV) necessary for electrical conductivity.[34]

The positive and neutral charge states of O_N in AlN are found to stay on site, as shown in Table II. The negative charge states move to off-center position, similarly to the

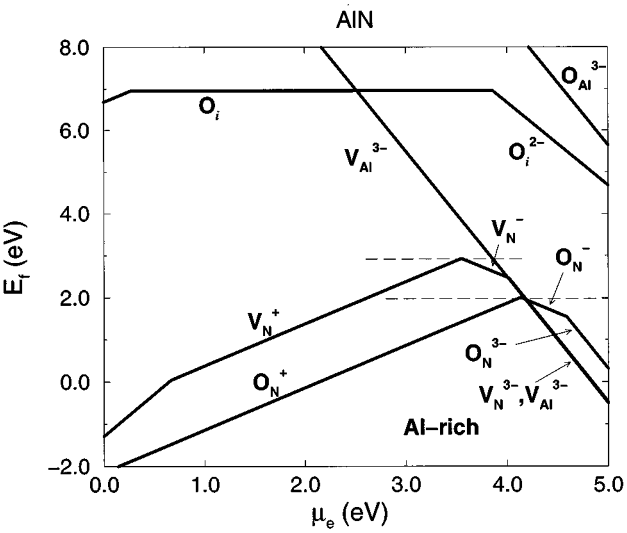

FIG. 4. The formation energies and ionization levels for the studied defects in AlN. The situation corresponds to the Al-rich case, and an estimated experimental band gap value (5.0 eV) is used to give the limit for the electron chemical potential. Dashed lines correspond to unstable charge states. For clarity, the dashed lines for the unstable O_N^{2-} and V_N^{2-} are omitted.

case for GaAs (see Table I). However, for the triply negative charge state an additional symmetry-lowering relaxation is observed, which distorts the pairing symmetry observed in GaAs. For negative charge states the magnitude of the off-center displacement is smaller in AlN than in GaAs, as a comparison between Tables I and II reveals. Similarly to GaAs, we find a metastable on-site configuration for the singly negative charge state in AlN (with about 4% symmetric outward relaxation of the nearest-neighbour Al atoms) which has 0.16 eV higher total energy than the displaced configuration. The energy barrier separating these two relaxed atomic positions is found to be very small.

The formation energies for O_i and O_{Al} in AlN are found to be clearly higher than for O_N, suggesting that oxygen should prefer the substitutional nitrogen site to all other configurations, very similarly to the case in GaN. Furthermore, Fig. 4 shows that the formation of O_N is energetically clearly favored over V_N, as was the case in GaN. In contrast to the case in GaN, V_N in AlN exhibits ionization levels well below the conduction-band edge. This resembles the observed behavior for O_N, and agrees with the experimental observation of the high activation energies needed for electrical conductivity.[34] The triply negative Al vacancy is seen to be easily created when the Fermi level is around midgap or higher. Thus V_{Al}^{3-} and O_N^+ are seen to be the most favorable oppositely charged defects to be formed when the Fermi level is somewhat above the midgap. This clearly indicates the possibility for formation of $V_{Al}^{3-}-3\times O_N^+$ defect complexes as suggested by Youngman and Harris.[3]

TABLE II. Details of the atomic configuration of O_N in AlN for different charge states. d_i denotes the bond length between the oxygen atom and the nearest-neighbor Al atoms, and θ_i the corresponding bond angles, similarly to GaAs illustrated in Fig. 1. The bond-length values are given in units of the nearest-neighbor distance of the perfect lattice.

Defect	d_1	d_2	d_3	d_4	θ_1	θ_2
O_N^+	1.03	1.03	1.03	1.03	109.5	109.5
O_N	1.03	1.03	1.03	1.03	109.5	109.5
O_N^-	0.99	0.99	1.07	1.07	118.6	86.1
O_N^{2-}	0.99	0.99	1.07	1.07	120.0	86.5
O_N^{3-}	1.03	0.94	1.11	1.03	124.2	86.2

D. *DX*-type behavior of oxygen in $Al_xGa_{1-x}N$

The point defect formation energies found in our calculations share many common features in GaN and AlN. This can be principally explained by the similar lattice constant and bonding character in these materials. However, the clear distinction between the two materials is the value of the band gap, which directly influences the formation energies of charged defects. As was seen above, while O_N in GaN is found to be a shallow donor, in AlN the same defect is a deep center with ionization levels well below the conduction band edge.

With an increasing Al concentration in the $Al_xGa_{1-x}N$ alloy, the band gap opens and can be tuned between the GaN value (3.4 eV for *w*-GaN) and the AlN value (6.2 eV for *w*-AlN). However, as our calculations demonstrate, the oxygen electronic levels simultaneuously reside deeper in the gap, and the singly positive substitutional oxygen can capture two more electrons and change from a shallow donor to a deep electron trap. Thus the situation is very similar to the well-known *DX* centers in $Al_xGa_{1-x}As$.[35] When the Al concentration exceeds 22% in $Al_xGa_{1-x}As$, the shallow Si donors are known to transform to deep donors, resulting in freeze-out in the *n*-type carriers. This is explained in a model by Chadi and Chang,[36] where the Si donor moves from the substitutional site along the [111] direction to a displaced position, accompanied by a change in the charge state to the singly negative one. On the other hand, *DX* behavior is reported also to exist with column-VI dopants, as demonstrated for S in $Al_xGa_{1-x}As$ by the same authors.[36] However, in that case the large atomic relaxation is associated with the displacement of a nearest-neighbor Ga atom.

Our results thus clearly predict that a *DX*-type behavior should also characterize oxygen in $Al_xGa_{1-x}N$. As can be seen from Table II, the oxygen atom can find an off-center equilibrium position in negative charge states in AlN. We have also investigated the possibility for the displacement of the nearest-neighbor Al, with O remaining at the substitutional site. Our calculations verify that this kind of configuration in the singly negative charge state is indeed (meta)-stable. The nearest-neighbor Al in the [111] direction finds an equilibrium position with a 30% increase in the bond length to the oxygen atom. The remaining three Al atoms relax slightly (1%) outwards. This configuration is found to lie 0.1 eV higher in energy than the case where the oxygen atom is displaced along the [100] direction. On the other hand, when compared with the on-site configuration with all four Al atoms symmetrically surrounding the O atom (see the discussion in Sec. III), the total energy is found to be 0.06 eV lower. Again, a very small energy barrier is found to separate these two atomic configurations. However, these small energy differences between the different configurations approach the accuracy of our calculations, and therefore we are not willing to make a definite conclusion regarding the stablemost oxygen position.

In our calculations the position of an observed ionization level from the singly positive to singly negative charge state (negative U) is approximately 4.0 eV above the valence-band maximum, which means that DX-type behavior should not be present in pure GaN of either zinc-blende or wurtzite structure. When the band gap exceeds a value of about 4.0 eV, the singly negative charge state of the O_N defect becomes stable. Thus if we make an approximation that the band gap increases linearly as a function of the Al concentration, DX-type centers due to oxygen should begin to appear at roughly $x=0.4$ Al concentration in the zinc-blende structure, well below the estimated direct-indirect gap transition occurring at over $x=0.5$.[37] If we extrapolate our results for wurtzite $Al_xGa_{1-x}N$, the critical Al-concentration estimate decreases to approximately $x=0.2$.

V. CONCLUSIONS

With our first-principles calculations, we investigated the behavior of oxygen point defects in GaAs, GaN, and AlN. We demonstrated a clear qualitative difference in the behavior of substitutional oxygen in these materials.

O_{As} in GaAs acts as a deep-level defect with an off-center atomic configuration and negative-U behavior in the negative charge states, while O_i in GaAs is found to be electrically inactive. The results for both defect types are in good agreement with the wide experimental data, thus verifying the reliability of our theoretical method.

Our calculations show that O_N in GaN acts as a dominant shallow donor, in clear contrast to the deep center character in GaAs. This gives support to recent suggestions that oxygen in GaN contributes as one of the dominant sources to the unintentional n-type carrier concentration in as-grown samples. When compared with O_N, other investigated oxygen point defect configurations (O_i and O_{Ga}) are found to be energetically clearly unfavorable in GaN.

When applied to O_N in AlN, our calculations reveal that although the positive and neutral defects behave nearly identically in GaN and AlN, the wide band gap of AlN allows the formation of ionization levels deep in the gap below the conduction-band minimum. As a consequence, the same phenomenon is likely to occur in $Al_xGa_{1-x}N$ alloys with sufficient Al concentrations. The transition from singly positive to singly negative charge states involves a negative-U effect, and in the negative charge state the oxygen atom is displaced into the off-center position in the [100] direction, similarly to the case of O_{As} in GaAs. However, the competing structural relaxation, in which one of the neighboring cations moves to a displaced position along the [111] direction, was found to be energetically comparable with the oxygen displacement in the [100] direction. To summarize, these observations clearly demonstrate that oxygen should act as a DX center in $Al_xGa_{1-x}N$.

$Al_xGa_{1-x}N$ alloys are potential materials for blue-UV-emitting applications. Therefore, the appearance of oxygen-induced deep levels in the band gap with increasing Al concentration should be kept carefully in mind. The deep levels reduce the n-type carrier concentration as well as serve as parasitic gap levels disturbing the optical performance.

The negatively charged cation vacancies (${V_{Ga}}^{3-}$ in GaN and ${V_{Al}}^{3-}$ in AlN) were found to be energetically very favorable compensating defects. Thus the formation of oxygen-cation vacancy complexes is suggested to occur in both GaN and AlN. Further investigation of these defect complexes is underway.

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[1] G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986).

[2] W. Götz *et al.*, Appl. Phys. Lett. **68**, 3144 (1996).

[3] R. A. Youngman and J. H. Harris, J. Am. Ceram. Soc. **73**, 3238 (1990).

[4] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); K. Laasonen *et al.*, *ibid.* **47**, 10 142 (1993).

[5] M. Skowronski, Mater. Sci. Forum **83-87**, 377 (1992); Phys. Rev. B **46**, 9476 (1992).

[6] H. Ch. Alt, Phys. Rev. Lett. **65**, 3421 (1990).

[7] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[8] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982); D. R. Hamann, Bull. Am. Phys. Soc. **33**, 803 (1988). Our pseudopotentials are verified to be ghost-free using the method by X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).

[9] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[10] F. Tassone, F. Mauri, and R. Car, Phys. Rev. B **50**, 10 561 (1994).

[11] A. Williams and J. Soler, Bull. Am. Phys. Soc. **32**, 409 (1952).

[12] S. Pöykkö, M. J. Puska, M. Alatalo, and R. M. Nieminen, Phys. Rev. B **54**, 7909 (1996).

[13] T. Mattila, A. P. Seitsonen, and R. M. Nieminen, Phys. Rev. B **54**, 1474 (1996).

[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[15] H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).

[16] J. Neugebauer and C. G. Van de Walle, in *Diamond, SiC and Nitride Wide Bandgap Semiconductors*, edited by C.H. Carter, Jr., G. Gildenblat, S. Nakamura, and R. J. Nemanich, MRS Symposia Proceedings No. 339 (Materials Research Society, Pittsburgh 1994), p. 687.

[17] T. Mattila, A. P. Seitsonen, and R. M. Nieminen, in *III-V Nitride Materials and Processes*, edited by T. D. Moustakas, J. P. Dismukes, and S. J. Pearton (Electrochemical Society, Pennington, 1996), p. 205.

[18] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).

[19] S. Pöykkö, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **53**, 3813 (1996).

[20] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1948).

[21] A. Garcia and J. E. Northrup, Phys. Rev. Lett. **74**, 1131 (1995).

[22] K. W. Kwak, D. Vanderbilt, and R. D. King-Smith, Phys. Rev. B **52**, 11 912 (1995).

[23] The experimental band-gap values are used only to extend the range of chemical potential in Eq. (1) in the formation energy analysis, and do not enter the self-consistent procedure of the LDA/DFT total-energy calculations.

[24] H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 1991).

[25] S. Strite, M. E. Lin, and H. Morkoç, Thin Solid Films **231**, 197 (1993).

[26] W. R. L. Lambrecht and B. Segall, Phys. Rev. B **43**, 7070 (1991).

[27] A. Rubio, J. L. Corkill, M. L. Cohen, E. L. Shirley, and S. G. Louie, Phys. Rev. B **48**, 11 810 (1993).

[28] The precision of the presented results is chosen to reveal the trends, e.g., in bond angles, mentioned in the text, and does not reflect the actual estimated accuracy of our calculations. For instance, we repeated all the calculations concerning O in GaAs, using *d* as the local component in the pseudopotentials, and a few percent differences were seen in the relaxed atomic positions. However, a perfect qualitative agreement remained with the results obtained with *s* as the local component. An investigation of the origin of these differences related to the choice of the local component is in progress.

[29] R. Jones and S. Öberg, Phys. Rev. Lett. **69**, 136 (1992).

[30] M. Linde, J.-M. Spaeth, and H. Ch. Alt, Appl. Phys. Lett. **67**, 662 (1995).

[31] B.-C. Chung and M. Gershenzon, J. Appl. Phys. **72**, 651 (1992).

[32] J. C. Zolper *et al.*, Appl. Phys. Lett. **68**, 1945 (1996).

[33] J. Neugebauer and C. G. Van de Walle, in *Proceedings of the 22nd International Conference on the Physics of Semiconductors*, edited by D. J. Lockwood (World Scientific, Singapore, 1994), Vol. III, p. 2327.

[34] W. A. Groen, J. G. van Lierop, and A. Roosen, J. Mater. Sci. Lett. **12**, 1224 (1993).

[35] *Physics of DX Centers in GaAs Alloys*, edited by J. C. Bourgoin (Sci-Tech, Lake Isabella, CA, 1990).

[36] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988); Phys. Rev. B **39**, 10 063 (1989).

[37] W. J. Fan, J. Appl. Phys. **79**, 188 (1996).