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DX-center formation in wurtzite and zinc-blende $Al_xGa_{1-x}N$

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The transition from shallow to deep centers as a function of pressure or alloying is investigated for oxygen and silicon donors in GaN and AlN, based on first-principles total-energy calculations. The stability of the localized deep state (*DX* center) is found to depend on interactions between the impurity and third-nearest-neighbor atoms, which occur in different positions in the zinc-blende and the wurtzite phase. *DX*-center formation is suppressed in the zinc-blende phase, as well as for silicon donors. The results strengthen the identification of oxygen as the unintentional dopant in *n*-type GaN, and shed new light on the driving force for *DX* formation. [S0163-1829(98)50404-3]

The behavior of the *n*-type conductivity in the nitride semiconductors is a subject of intense investigation. These materials often exhibit unintentional *n*-type doping, the source of which is still being debated. It is also known that $Al_xGa_{1-x}N$ alloys suffer a rapid decrease in the conductivity as $x > 0.4$.[1] Pressure experiments have proved very useful in studying the nature of the donors. In GaN a freezeout of carriers was observed at a hydrostatic pressure of about 20 GPa.[2,3] Originally the freezeout was explained by attributing the conductivity to nitrogen vacancies, which would give rise to a resonance in the conduction band; this state would emerge into the band gap under pressure, causing the decrease in conductivity. Computational studies have shown, however, that nitrogen vacancies are unlikely to form in *n*-type GaN; instead, unintentional impurities, such as oxygen, were proposed to be the source of the conductivity.[4] The presence of oxygen in unintentionally doped highly conductive samples has recently been confirmed by secondary ion mass spectroscopy (SIMS).[5,6] The issue then is whether the observed pressure and alloy dependence of the conductivity is consistent with the properties of the oxygen donor.

In this paper we show, based on first-principles calculations, that oxygen undergoes a transition from a shallow to a deep center in wurtzite (WZ) GaN under pressure, explaining the observed reduction in free-carrier concentration. This behavior is similar to Si in GaAs, which is the prototype of the so-called *DX* center.[7] The transition is accompanied by a strong relaxation of the impurity off the substitutional site.[8] We find that the transition can also be induced by alloying with AlN, which increases the band gap in a fashion similar to the application of hydrostatic pressure. Since oxygen is readily incorporated as a contaminant during nitride growth, and silicon is widely used as an *n*-type dopant, our results have direct consequences for nitride materials and device development. In addition, however, our calculations produce a number of interesting results that shed light on the fundamental mechanisms of metastability in compound semiconductors:

(1) We find that the *DX* transition does *not* occur in *zinc-blende* (ZB) AlGaN. This difference is surprising, since the local environment of the impurity is very similar (the two phases only differ at the positions of third-nearest neighbors and beyond (see Fig. 1) and no qualitative differences had been observed for any defects or impurities so far,[9,10] with the exception of the nitrogen antisite, which experiences a repulsion from the third-nearest-neighbor N atom in the WZ structure.[11] We explain the difference in *DX* behavior by analyzing the interaction between the oxygen impurity and third-nearest neighbors, showing that a Coulombic attraction provides a driving force for the large lattice relaxation.

(2) The *DX* transition does not occur for Si, neither in the WZ nor the ZB phase. This will be explained on the basis of Si occupying the Ga lattice site, where the Coulombic driving force for the lattice relaxation is absent.

The structural differences between wurtzite and zinc-blende phases are illustrated in Fig. 1, for the example of an oxygen impurity on a nitrogen site in AlN. GaN normally occurs in the WZ phase, but the ZB phase is only slightly higher in energy and can be produced by growth on suitable substrates. Previous studies of the atomic and electronic structure of native defects and impurities revealed only quantitatively small differences between WZ and ZB.[9] The similarity between WZ and ZB also applies to the oxygen and silicon impurities studied here, as long as they reside on the substitutional lattice site; this site is the only energy minimum for the positive as well as the neutral charge state of the impurity. However, we find a marked difference between the

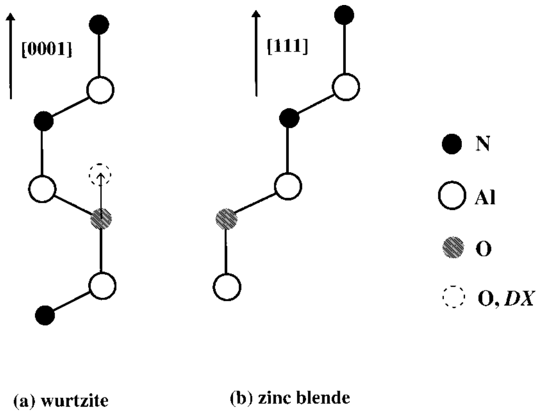

FIG. 1. Schematic illustration of the local environment of an oxygen impurity in (a) wurtzite and (b) zinc-blende AlN. The dotted lines indicate the oxygen position in the *DX* configuration.

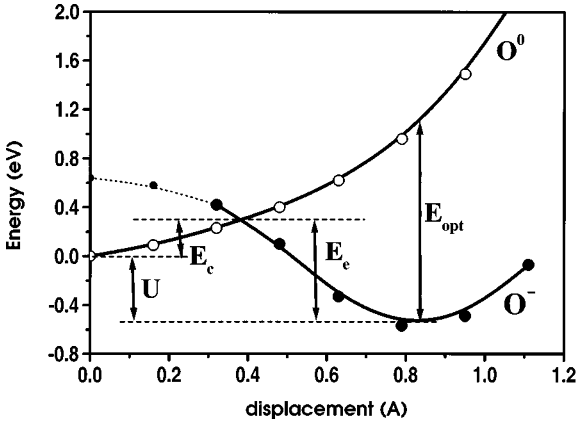

FIG. 2. Configuration coordinate diagram for oxygen displacements in wurtzite AlN, showing calculated formation energies for oxygen in the neutral (open circles) and negative (closed circles) charge states as a function of displacement along [0001]. The Fermi level is assumed to be located at the bottom of the conduction band, and the zero of energy corresponds to the formation energy of O^0 at the substitutional site. The lines are a guide to the eye. U is the energy gain due to DX-center formation. E_{opt} is the optical ionization energy. E_c and E_e are capture and emission barriers for electrons.

WZ and ZB phase when exploring DX-like configurations, which occur for the negative charge state. In the ZB structure the substitutional site is by far the lowest energy structure, and the DX state is never stable. In the WZ phase, on the other hand, oxygen clearly favors the DX state.

Figure 2 shows a configuration coordinate diagram for oxygen displacements along the [0001] direction in the WZ structure (see Fig. 1). The data points were obtained from first-principles calculations as described below. The figure shows that in the WZ phase a state reflecting a large displacement of the oxygen atom becomes the global minimum. Similar calculations for the ZB structure indicate the substitutional site is the global (and in fact the only) minimum of the energy surface. We conclude that in the ZB structure the impurity has no tendency to assume a deep DX-like state.

The explanation for this remarkable difference between the behavior of the impurity in the two phases lies in the different positions of the third-nearest neighbors. In the WZ phase [Fig. 1(a)] the third-nearest neighbors of the oxygen atom along the [0001] direction are Al atoms; in the undistorted configuration the separation between oxygen and the third-nearest neighbor Al is 3.1 Å (to be compared with a bond length of 1.89 Å). In the DX state, the oxygen impurity is negatively charged, and a Coulombic attraction arises with the Al atom in the [0001] direction: in the final DX configuration the oxygen moves out by almost 0.9 Å, and the distance between O and the third-nearest-neighbor Al is reduced to 2.06 Å. This distance is only about 0.2 Å larger than the host bond length (1.89 Å) or typical Al-O bond lengths (1.86 Å), indicating that a significant interaction develops between the O and Al atoms. One indication of this interaction is a 0.14 Å relaxation of the Al atom in the direction of the oxygen. Further evidence comes from an investigation of the electronic structure, as discussed below. In the process of moving the O atom, the bond length to its first Al neighbor along the c axis increases to 2.76 Å, indicating that this bond is effectively broken. The distances to the other Al neighbors decrease to 1.80 Å.

An attractive interaction between the O atom and the third-nearest-neighbor Al atom stabilizes the DX state for O in WZ AlN. In the ZB phase [Fig. 1(b)] the nearest Al atom along the [111] direction is 5.68 Å away from the oxygen atom, too far for any interaction to develop. DX center formation will therefore be less favorable in ZB AlN.

The importance of interactions with the third-nearest neighbors also helps us understand the behavior of Si. In contrast to oxygen, the silicon atom substitutes on the cation site. A negatively charged $\mathrm{Si}_{\mathrm{Al}}$ atom moving in the [0001] direction will experience repulsion from the *nitrogen* atom that is now the third-nearest neighbor, and a DX configuration is unfavorable. All of these qualitative conclusions will be confirmed by our explicit first-principles calculations, to be discussed next.

We now quantify the stability of the DX state. Following Chadi and Chang[8] we use the labels d^0 for the neutral and d^+ for the positively charged donors on the substitutional site; and DX^- for the localized, relaxed configuration in the negative charge state. The formation of DX centers leads to self-compensation according to the reaction:[8]

$$2d^0 \rightarrow d^+ + DX^- . \tag{1}$$

The energy difference between the left and right sides of Eq. (1) is given by the effective correlation energy U:

$$U = E^+ + E^- - 2E^0 , \tag{2}$$

where E^q is the formation energy of the impurity in charge state q. The quantity U can be thought of as the binding energy of the DX configuration, as illustrated in Fig. 2. $U<0$ indicates that the DX center is stable.

The formation energies were calculated based on density-functional theory in the local-density approximation (LDA), using *ab initio* pseudopotentials, the nonlinear core correction to include effects of Ga 3d states, and a supercell geometry. Hellmann-Feynman forces were used in the structural optimization. References and details of the computational approach are given in Refs. 9 and 10. Most of our calculations for the wurtzite structure were carried out in 32-atom supercells. Selected configurations were also studied in 72-atom supercells, confirming the results obtained with the 32-atom cells. In the 72-atom cells we found it essential to use a Brillouin-zone sampling with three special points in the irreducible part of the zone; using only the Γ point produces erroneous results. All our calculations are performed at the theoretical lattice constants, to ensure that relaxations are calculated correctly. Finally we note that the formation energy of the neutral charge state is obtained by equating it to the formation energy of the positive charge state when the Fermi level is at the bottom of the conduction band, for reasons explained in Ref. 12.

We have explored a wide variety of geometries. In addition to the above-mentioned impurity displacements along [111] or [0001], we have considered orthorombic-symmetry broken-bond models;[13] large displacements of one of the host atoms neighboring the impurity; and other low-symmetry configurations. None of these produced stable DX states. In the WZ structure the impurity atom can also be

TABLE I. Calculated effective correlation energy U [Eq. (2)] for DX transitions of oxygen and Si in various environments; WZ (wurtzite) and ZB (zinc blende) indicate the phase and V/V_0 is the volume compression. The entry ''no DX'' indicates that the on-site substitutional position is the only minimum in the energy surface.

Host:impurity	Structure	V/V_0	U (eV)
GaN:O	WZ	1	0.48
GaN:O	WZ	0.84	-0.62
GaN:O	ZB	0.84	no DX
AlN:O	WZ	1	-0.57
AlN:O	ZB	1	no DX
AlN:Si	WZ	1	0.31
AlN:Si	ZB	1	no DX

displaced along a bond direction other than [0001]. Displacements along such a direction move the impurity towards an interstitial site that is more similar in character to that in the ZB structure. Our calculations for Si showed that a metastable minimum occurs along this direction (in contrast to the [0001] direction), but the state is unstable with respect to the substitutional configuration (i.e., $U>0$). For oxygen the metastable minimum along this direction is higher in energy than the [0001]-oriented configuration. This result provides additional evidence for our thesis that interaction between the impurity and the Al atom along [0001] lowers the formation energy of the DX configuration.

Table I summarizes the results for all the configurations we have investigated. Our most detailed calculations were for oxygen in WZ AlN, where we not only determined the value of U but mapped out a complete configuration coordinate diagram as shown in Fig. 2. In the positive and neutral charge state, the minimum-energy location is at (or near) the substitutional site, and no additional metastable minima are found. The negative charge state is most stable for a large displacement of the oxygen impurity. The calculations indicated with dotted lines for O^- near the substitutional site suffer from uncertainties related to the occupation of conduction-band states. These uncertainties do not affect any of our conclusions. A contour plot of the defect wave function for the DX state is shown in Fig. 3. Notice the high concentration of electron charge on the oxygen atom, and the lobe in the charge density extending towards the Al atom; these features are indicative of the attractive interaction between oxygen and Al.

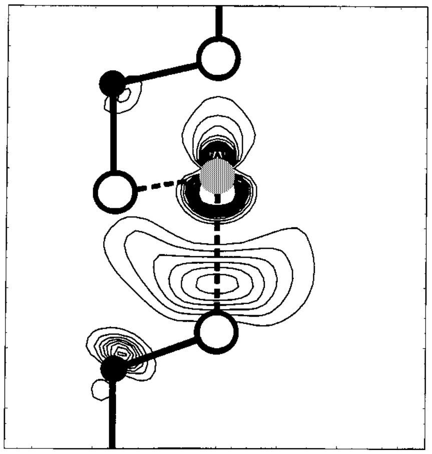

FIG. 3. Contour plot of the charge density corresponding to the defect state for the DX configuration of oxygen in wurtzite AlN. Atomic positions and symbols denoting atoms are as in Fig. 1(a).

We obtained $U=-0.57$ eV for the oxygen DX state in WZ AlN. In WZ GaN the oxygen DX configuration is unstable, with $U=0.48$ eV. Linear interpolation between GaN and AlN indicates that the DX center would be stabilized at $x=0.46$ in $Al_xGa_{1-x}N$. At the point where $U=0$ the theoretical band gap is 0.73 eV larger than that of GaN. Using the actual experimental gaps and assuming a bowing parameter equal to 0.53 eV, an increase in the band gap by 0.73 eV occurs for an alloy composition $x=0.30$. These estimates based on linear interpolation do not take into account the explicit alloying effects, with the oxygen being surrounded by varying numbers of Ga and Al atoms. Still, our estimates are in reasonable agreement with the observation that $Al_xGa_{1-x}N$ becomes highly resistive at $x\approx 0.4$.[1]

The oxygen DX configuration is unstable in WZ GaN at equilibrium volume, but application of pressure stabilizes the DX center. We carried out calculations for a volume compression of 16% (i.e., $V/V_0=0.84$ where V_0 is the equilibrium volume), finding that $U=-0.62$ eV. By interpolation we find that the DX configuration is stabilized at a volume $V/V_0=0.93$. Using Murnaghan's equation of state[14] and our calculated bulk modulus and derivative we find this corresponds to a pressure of 18 GPa. This value is in good agreement with the results of Wetzel and co-workers,[3] who studied the pressure dependence of oxygen in GaN using Raman spectroscopy of the free-electron plasmon-optical phonon coupled mode; they observed a transition to a deep state at 20 GPa.

Turning now to Si, we do not find any evidence of DX-center formation for Si in ZB AlN; the entry in Table I indicates that the on-site substitutional position was the only minimum in the energy surface. For Si in WZ AlN we found a metastable minimum, but $U>0$, i.e., the deep state is unstable. As described above, this metastable minimum is not oriented along the [0001] direction (due to repulsion from the third-nearest-neighbor N atom), but along one of the other bond directions. We did not perform calculations for Si in GaN under pressure; however, the absence of DX formation in AlN allows us to predict that Si will not form a DX center in GaN under pressure, either. Once again, this is consistent with the results of Wetzel and co-workers,[3] who reported that for Si donors no transition was observed up to a pressure of 25 GPa. The absence of the DX state for Si in $Al_xGa_{1-x}N$ (as opposed to, e.g., $Al_xGa_{1-x}As$) is probably related to the small lattice constants and large elastic constants of the nitrides, which raise the energy cost of a state that involves large relaxations. The smaller size of the oxygen atom makes it more suitable for large displacements.

Table I shows that neither Si nor O forms a DX state in ZB material. The suppression of DX formation in ZB nitrides could be a technological advantage for growth of these materials in the cubic phase. The absence of oxygen DX formation in ZB AlN is consistent with the results of Mattila and co-workers,[15] although those authors initially gave a different interpretation to their results. Using a computational approach very similar to the one in the present work, they[15] reported that the levels for the $+/0$ and $0/-$ transitions were deep in the band gap. Additional work,[16] including calculations on 64-atom supercells, now also indicates that substitutional oxygen behaves as a shallow, not a deep, donor in ZB AlN—in agreement with our conclusions.

After completion of our work we learnt about recent calculations by Park and Chadi[17] for various donor impurities in GaN and AlN. While agreeing with their conclusion that oxygen forms DX centers in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ and GaN under pressure, we disagree on a number of key points, including the tendency of Si to assume the DX state, and the stability of the localized centers in the ZB phase. In the absence of information in Ref. 17 about important calculational aspects such as treatment of the Ga $3d$ states or which lattice constants were used, the source of the discrepancies remains unclear.

In summary, we have performed first-principles calculations to examine the transition between extended and localized states for Si and O donors in GaN and AlN in the WZ and ZB phase. We found that an attractive interaction between the displaced impurity and third-nearest-neighbor atoms in the WZ structure stabilizes the DX formation. The small lattice constant of the nitrides enhances the importance of this third-nearest-neighbor interaction. The first-principles results are summarized in Table I. We conclude that DX centers do not form in GaN at equilibrium pressure. We also find that Si does not form DX centers. Oxygen forms a DX center in GaN under hydrostatic pressure and in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloys with sufficiently high Al content. These results lend additional support to the identification of oxygen as the unintentional donor in n-type GaN and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$. Finally, we find no evidence of DX formation in the ZB phase, a prediction that can be experimentally tested. It would be interesting to investigate whether similar differences between ZB and WZ occur for DX formation in semiconductors other than the nitrides, for instance in II-VI compounds.

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