Doping of $Al_xGa_{1-x}N$

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N-type $Al_xGa_{1-x}N$ exhibits a dramatic decrease in the free-carrier concentration for $x \geqslant 0.40$. Based on first-principles calculations, we propose that two effects are responsible for this behavior: (i) in the case of doping with oxygen (the most common unintentional donor), a *DX* transition occurs, which converts the shallow donor into a deep level; and (ii) compensation by the cation vacancy (V_{Ga} or V_{Al}), a triple acceptor, increases with alloy composition x. For p-type doping, the calculations indicate that the doping efficiency decreases due to compensation by the nitrogen vacancy. In addition, an increase in the acceptor ionization energy is found with increasing x. [S0003-6951(98)03504-9]

$Al_xGa_{1-x}N$ is an important material in nitride-based optoelectronic devices; indeed, the cladding layers that surround the active region of a laser diode typically consist of $Al_xGa_{1-x}N$, for which both n- and p-type doping must be achieved. For n-type doping, a decrease in the electron concentration for unintentionally doped samples has been reported with increasing Al content x.[1–4] In particular, Khan *et al.*[1] found that $Al_xGa_{1-x}N$ films with $x > 0.4$ were highly resistive. Lee *et al.*[2] studied $Al_xGa_{1-x}N$ for x between 0 and 0.75 and found that there was an abrupt decrease (by five orders of magnitude) in bulk electron concentration and mobility for x in the range 0.4–0.6, beyond which the crystal became semi-insulating. Similarly, Bremser *et al.*[4] observed a rapid decrease in the net ionized donor concentration with increasing Al content. Bremser *et al.*[4] also achieved intentional n-type doping with silicon for $0.12 \leqslant x \leqslant 0.42$, but for $x > 0.42$, addition of Si still resulted in highly resistive films.

An even more dramatic decrease in doping efficiency with increasing x is observed for p-type doping of $Al_xGa_{1-x}N$. In GaN, the traditional difficulty in achieving p-type conductivity was overcome due to the use of the Mg acceptor and the understanding of the role of hydrogen.[5] In $Al_xGa_{1-x}N$ the efficiency of Mg doping has been observed to decrease rapidly with x; no p-type conductivity has been obtained for $x > 0.13$.[4]

Three general mechanisms can potentially give rise to these puzzling changes in conductivity with x: (i) a decrease in the density of dopants, (ii) an increase in the ionization energy of the dopants, and (iii) incorporation of a compensating native defect. Each of these mechanisms can be addressed by performing first-principles calculations for the relevant native defects and dopant impurities. In this letter, we report results of such calculations for AlN which, combined with previous results for GaN, allow us to draw clear conclusions about the dependence of the conductivity on alloy composition in $Al_xGa_{1-x}N$. Specifically, we find that for n-type doping two mechanisms are active: In the case of oxygen doping, a decrease in the density of donors occurs because at $x \approx 0.4$ the oxygen shallow donor undergoes a *DX* transition and is converted to a negatively charged deep level. Silicon donors, however, do *not* undergo this transition. The second mechanism affecting the conductivity is compensation by cation vacancies, which occur in increasingly larger concentrations as x increases. For p-type doping, we find that the ionization energy of a Mg acceptor increases slightly with alloy composition x. In addition, we find compensation by native defects, in particular, by the nitrogen vacancy.

Our first-principles calculations are performed using the density-functional–pseudopotential method in the local density approximation (LDA),[6] employing a supercell approach and a tight-binding initialization scheme for the electronic wave functions. We used 32-atom zinc-blende and 72-atom wurtzite supercells, and an energy cutoff of 40 Ry with two and three special **k** points in the irreducible part of the Brillouin zone. The pseudopotentials were created using the scheme of Troullier and Martins.[7]

The *formation energy* of a defect in charge state q is obtained as

$$E^f(q) = E^{\text{tot}}_{\text{defect}}(q) - \sum_X n_X \mu_X + qE_F, \qquad (1)$$

where $E^{\text{tot}}_{\text{defect}}(q)$ is the total energy of the defect as calculated using the supercell, and n_X and μ_X are the number and chemical potential of atoms of species X, respectively. E_F is the Fermi energy, which is set to zero at the valence-band maximum. A low value of the formation energy indicates a high equilibrium concentration of the defect under consideration, while a high value of the formation energy implies that the defect is unlikely to form. Consistent with previous work for GaN,[8] we find the formation energies for vacancies and substitutional impurities to be very similar in zinc-blende and wurtzite phases. An important difference is observed, however, for the cation interstitial as discussed below.

The chemical potentials depend on the experimental growth conditions; we assume thermal equilibrium, requiring $\mu_{\text{Al(Ga)}} + \mu_N = \mu_{\text{Al(Ga)}N}$. In the following, we consider either Al(Ga)- or N-rich conditions. In metal-rich conditions we set $\mu_{\text{Al(Ga)}}$ equal to the energy of bulk Al(Ga); in N-rich conditions the chemical potential is determined by the energy of an N_2 molecule. The atomic chemical potentials for the impurity species (O, Si, and Mg) are assumed to be determined by equilibrium with Al_2O_3, Si_3N_4, and Mg_3N_2.[9] Formation

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energies for other conditions (chemical potentials) can easily be obtained using Eq. (1).

We first consider n-type doping. Jenkins *et al.*,[10] using a tight-binding approach, proposed that a shallow–deep transition of the nitrogen vacancy was responsible for the striking change to semi-insulating behavior of $Al_xGa_{1-x}N$ with increasing x. More recent first-principles studies, however, have shown that the formation energy of the nitrogen vacancy in n-type GaN (Refs. 11–14) and AlN (Refs. 14 and 15) is too large for this defect to occur in any appreciable concentrations. In addition, we find that the nitrogen vacancy behaves as a shallow donor, not as a deep level, in both GaN and AlN. Both these arguments indicate that the nitrogen vacancy is not involved in the n-type conductivity of $Al_xGa_{1-x}N$.

In GaN, it was proposed that not the nitrogen vacancy, but oxygen and silicon impurities are responsible for unintentional n-type conductivity.[12] This suggestion has been supported by experimental determinations of the impurity concentrations in n-type samples.[16,17] Recent pressure studies reported a freeze-out of carriers in oxygen-doped samples by application of hydrostatic pressure of about 20 GPa.[18,19] Consistent with the latter experiments, we find that oxygen undergoes a transition from a shallow to a deep DX center in wurtzite GaN under pressure. The stable shallow center at the *equilibrium* volume of GaN corresponds to O on the substitutional N site. The DX geometry corresponds to an oxygen atom assuming an off-substitutional position by movement along the [0001] direction, and becomes stable under hydrostatic pressure; the induced electronic state is a highly localized deep level. In the DX configuration the defect is negatively charged, i.e., it is a deep acceptor and will, therefore, trap free carriers. More details of these calculations will be published elsewhere.[20]

Alloying with AlN increases the band gap of GaN in much the same way as hydrostatic pressure. DX center formation should, therefore, also occur in $Al_xGa_{1-x}N$. Indeed, we find that the DX configuration is the stable state for the oxygen impurity in AlN.[20] Linear interpolation between GaN and AlN suggests that the DX center would be stabilized for $x > \approx 0.4$. Given the theoretical and experimental evidence supporting the assignment of oxygen as the source of the unintentional n-type conductivity in GaN, it seems very likely that the same is true in $Al_xGa_{1-x}N$ alloys. The shallow–deep DX transition of O in $Al_xGa_{1-x}N$, therefore, provides a very plausible explanation of the drop in carrier density a $x > 0.4$.

However, as mentioned in the introduction, the decrease of n-type conductivity in $Al_xGa_{1-x}N$ also occurs for *silicon-doped* samples. Silicon impurities in GaN substitute on Ga sites, and behave as shallow donors.[12] In contrast to oxygen, we find that silicon does *not* undergo a DX transition, either under hydrostatic pressure or in $Al_xGa_{1-x}N$; this is consistent with the pressure studies of Ref. 19, where it was found that Si remains a shallow donor in GaN up to a pressure of 25 GPa (i.e., much higher than the pressure where oxygen becomes a deep level). How, then, to explain the observed high resistivity reported[4] in Si-doped samples for $x \geqslant 0.42$?

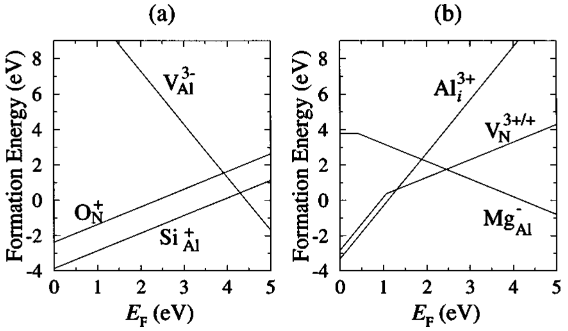

FIG. 1. Defect formation energies as a function of the Fermi level for defects and impurities in AlN under Al-rich conditions. (a) Donor impurities (O and Si) and the al vacancy, relevant for n-type doping. (b) Mg acceptor, N vacancy, and Al interstitial, relevant for p-type doping. $E_F = 0$ corresponds to the valence-band maximum. Note the formation energy of Al_i is significantly higher in wurtzite AlN.

To investigate the possibility of compensation, we performed a comprehensive study of all native point defects in AlN. For the present purposes, the main finding is the low formation energy of the Al vacancy in the triply negative charge state, consistent with the results reported in Ref. 14. In Fig. 1(a), we show the calculated defect formation energies for the Al vacancy and for Si and O donors as a function of E_F for Al-rich conditions. For each charge state of each defect we show only the line segment that gives rise to the overall lowest energy. Thus, the change in slope of the lines represents a change in the charge state of the defect [cf. Eq. (1)]. Figure 1 applies to the zinc-blende phase and shows E_F spanning the theoretical GW band gap for zinc-blende AlN (5.0 eV),[21] which is larger than the LDA band gap in the calculations (3.15 eV). Results for the wurtzite phase are very similar. It is clear that for n-type conditions, both O and Si donors will be compensated by V_{Al}^{3-}.

The behavior of V_{Al} is similar to V_{Ga} in GaN,[11] but because of the larger band gap of AlN, the formation energy of V_{Al}^{3-} becomes significantly lower than V_{Ga}^{3-} for Fermi-level positions high in the gap. When alloying GaN with AlN, the band gap is increased and the formation energy of the cation vacancy becomes lower for E_F high in the gap. At an Al concentration of $x = 0.4$, using the experimental band gaps and assuming a bowing parameter equal to 1 eV, we find that both cation vacancies have very low formation energies in n-type material. Our results, therefore, suggest that due to the particularly low formation energy of the cation vacancy, and the fact that it is a triple acceptor, this defect will increasingly compensate the n-type conductivity in $Al_xGa_{1-x}N$ with increasing x, and that the effect will be largest for N-rich conditions.

We have thus identified two mechanisms to which we attribute the observed plunge in conductivity of $Al_xGa_{1-x}N$ with increasing Al concentration: first, the transformation of oxygen into a DX center, and second, compensation by the cation vacancy.

We turn now to p-type dopoing of $Al_xGa_{1-x}N$, specifically, to the decrease in the doping efficiency of Mg. In both GaN and AlN, Mg assumes the Al substitutional position. Park and Chadi[22] have shown that the Mg impurity has no tendency to form deep levels (so-called AX levels, analogous to DX for donors), thus ruling out a shallow–deep transition as the source of the drop in hole concentration. Our calculations of the Mg acceptor indicate that its ionization energy is higher in AlN (0.4 eV) than it is in GaN (0.2 eV). This increase in the ionization energy leads to a decrease in doping efficiency. Compensation by native defects is another important mechanism contributing to the decline in hole concentrations. We discovered that two defects with low formation energies may inhibit successful p-type doping of $Al_xGa_{1-x}N$, namely, the nitrogen vacancy and the cation interstitial.

In Fig. 1(b) we show the calculated formation energies of these native defects in zinc-blende AlN as a function of E_F. We also include our calculated formation energies for substitutional Mg on an Al site. The nitrogen vacancy (V_N) behaves as a donor, which can donate one, two, or three electrons; it turns out that only the V_N^+ and V_N^{3+} charge states are stable. The V_N^{2+} state is unstable, presenting a negative-U effect. The aluminum interstitial (Al_i) in the zinc-blende structure introduces a triplet state close to the conduction-band edge, occupied by three electrons; it thus behaves as a triple donor. Figure 1(b) shows that V_N^{3+} and Al_i^{3+} have particularly low formation energies in p-type material, especially under Al-rich conditions. Both V_N^{3+} and Al_i^{3+} will thus compensate Mg acceptors.

In wurtzite material, we find a very similar behavior for the nitrogen vacancy. The aluminum interstitial (Al_i), however, exhibits quite different characteristics due to the different local atomic geometries of the interstitial sites.[15] We find that the formation energy of Al_i^{3+} in the wurtzite structure is more than 2 eV higher than in the zinc-blende structure. Therefore, only in cubic material do we expect the Al interstitial to act as an important compensation center.

In summary, our theoretical investigations indicate that the DX behavior of oxygen and compensation by the cation vacancy are responsible for the decrease in free-electron carriers in $Al_xGa_{1-x}N$ at $x \approx 0.4$. With respect to p-type doping of $Al_xGa_{1-x}N$, our results indicate that in wurtzite material the nitrogen vacancy becomes an increasingly dominant compensating center as x increases. In cubic material, the Al interstitial can act as an additional compensating center. We also observe an increase in the Mg ionization energy with increasing Al content. We hope that the predictions of the present work will stimulate experimental work aimed at observing the DX states and native defects discussed here.

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