Doping of Al$_x$Ga$_{1-x}$N

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$N$-type Al$_x$Ga$_{1-x}$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 ($V_{\text{Ga}}$ or $V_{\text{Al}}$), 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 $x$.

Al$_x$Ga$_{1-x}$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$_x$Ga$_{1-x}$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$_x$Ga$_{1-x}$N films with $x>0.4$ were highly resistive. Lee et al.\(^2\) studied Al$_x$Ga$_{1-x}$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$_x$Ga$_{1-x}$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$_x$Ga$_{1-x}$N the efficiency of Mg doping has been observed to decrease rapidly with $x$; no $p$-type conductivity has been obtained for $x>0.13$.\(^6\)

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$_x$Ga$_{1-x}$N. Specifically, we find that for $n$-type doping two mechanisms are active: (i) 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

$$E_f(q) = E_{\text{def}}^\text{tot}(q) - \sum_X n_X \mu_X + q E_F,$$

where $E_{\text{def}}^\text{tot}(q)$ is the total energy of the defect as calculated using the supercell, and $n_X$ and $\mu_X$ 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$_2$O$_3$, Si$_3$N$_4$, and Mg$_5$N$_2$.\(^9\) 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.\textsuperscript{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\textsubscript{1-x}Ga\textsubscript{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\textsubscript{1-x}Ga\textsubscript{x}N.

In GaN, it was proposed that not the nitrogen vacancy, but oxygen and silicon impurities are responsible for unintentional n-type conductivity.\textsuperscript{12} This suggestion has been supported by experimental determinations of the impurity concentrations in n-type samples.\textsuperscript{16,17} Recent pressure studies reported a freeze-out of carriers in oxygen-doped samples by application of hydrostatic pressure of about 20 GPa.\textsuperscript{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 positively charged, i.e., it is a deep donor and will, therefore, trap free carriers. More details of these calculations will be published elsewhere.\textsuperscript{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\textsubscript{1-x}Ga\textsubscript{x}N. Indeed, we find that the DX configuration is the stable state for the oxygen impurity in AlN.\textsuperscript{20,21} 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\textsubscript{1-x}Ga\textsubscript{x}N alloys. The shallow–deep DX transition of O in Al\textsubscript{1-x}Ga\textsubscript{x}N, therefore, provides a very plausible explanation of the drop in carrier density a x \approx 0.4.

However, as mentioned in the introduction, the decrease of n-type conductivity in Al\textsubscript{1-x}Ga\textsubscript{x}N also occurs for silicon-doped samples. Silicon impurities in GaN substitute on Ga sites, and behave as shallow donors.\textsuperscript{12} In contrast to oxygen, we find that silicon does not undergo a DX transition, either under hydrostatic pressure or in Al\textsubscript{1-x}Ga\textsubscript{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\textsuperscript{4} in Si-doped samples for x \approx 0.42?\textsuperscript{22}

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\textsubscript{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\textsubscript{F} spanning the theoretical GW band gap for zinc-blende AlN (5.0 eV),\textsuperscript{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\textsubscript{Al}\textsuperscript{3–}.

The behavior of V\textsubscript{Al} is similar to V\textsubscript{Ga} in GaN,\textsuperscript{11} but because of the larger band gap of AlN, the formation energy of V\textsubscript{Al}\textsuperscript{3–} becomes significantly lower than V\textsubscript{Ga}\textsuperscript{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\textsubscript{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\textsubscript{1-x}Ga\textsubscript{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\textsubscript{1-x}Ga\textsubscript{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 doping of Al\textsubscript{1-x}Ga\textsubscript{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\textsuperscript{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$_x$Ga$_{1-x}$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 $V_N^{2+}$ 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. 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 additional compensating 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$_x$Ga$_{1-x}$N at $x = 0.4$. With respect to p-type doping of Al$_x$Ga$_{1-x}$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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9. The O chemical potential is obtained directly from calculations of Al$_2$O$_3$; for Si and Mg, we use the calculated energy of the elemental phase combined with experimental heats of formation of Si$_N$ and Mg$_N$.