

# Doping of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys

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## Abstract

We have investigated the doping of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys on the basis of density–functional–pseudopotential calculations for native point defects and dopant impurities. We have identified two possible causes for the experimentally observed decrease in n-type conductivity for  $x > 0.4$ : (1) in the case of doping with oxygen, a  $DX$  transition that converts the shallow donor into a deep level; and (2) compensation by cation vacancies. For p-type doping, the reduction in doping efficiency with increasing  $x$  is attributed to (1) compensation by nitrogen vacancies; and (2) an increase in the Mg acceptor ionization energy. We also investigated a number of alternative acceptor impurities; none, however, exhibit overall characteristics superior to those of Mg. Only beryllium emerged as a possible candidate, though it may be hampered by compensation due to Be interstitial donors. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Doping; First-principles calculations; AlGa<sub>N</sub>; Acceptors; Oxygen

## 1. Introduction

Successful doping of AlGa<sub>N</sub> alloys is a major requirement for the development of wide-band-gap devices such as laser diodes, ultraviolet detectors and high-temperature/high-power transistors.  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys, however, are known to suffer a decrease in the conductivity with increasing Al content  $x$  [1–5]. For unintentionally n-type doped  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , Lee et al. [2] reported a rapid decrease in conductivity for  $x > 0.4$ . Similar results were reported by McCluskey et al. [3], who were able to attribute the unintentional conductivity to oxygen. Bremser et al. [5] achieved intentional n-type doping with silicon for  $0.12 \leq x \leq 0.42$ , but for  $x > 0.42$  the addition of Si resulted in highly resistive films.

The efficiency of p-type doping is also known to decrease with increasing  $x$ . While p-type doping of Ga<sub>N</sub> was originally a problem, difficulties have largely been overcome due to the use of the Mg acceptor and the understanding of the role of hydrogen [6,7]. For  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , however, Bremser et al. [5] reported a failure to achieve p-type conductivity with Mg doping for  $x > 0.13$ . Other studies have also found a decrease

in achievable hole concentration when the Al content of the AlGa<sub>N</sub> alloy is increased [8,9].

We have addressed these doping issues by performing a comprehensive first-principles study of native defects and impurities in AlN. Together with previous calculations for Ga<sub>N</sub>, we are able to obtain an understanding of the dependence of the conductivity on alloy composition in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  [10]. We have identified two mechanisms that can reduce the n-type doping efficiency: (1) in the case of doping with oxygen (the most common unintentional donor), a  $DX$  transition occurs which converts the shallow donor into a negatively charged deep level [11]; and (2) cation vacancies ( $V_{\text{Ga}}$  or  $V_{\text{Al}}$ ) act as triple acceptors and increase in concentration with alloy composition  $x$ . For p-type doping, we find that (1) nitrogen vacancies act as compensating centers and are more easily formed in AlN than in Ga<sub>N</sub>; and (2) the ionization energy of the Mg acceptor increases with alloy composition  $x$ .

It would therefore be desirable to identify other p-type dopants that do not suffer from the limitations imposed by Mg. We performed extensive investigations for a wide range of candidate acceptor species, addressing criteria such as solubility, ionization energy, and potential compensation due to interstitial configurations of the acceptor impurity; we did not, however, find any of the candidates to exhibit better characteris-

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tics than Mg in all respects. Beryllium has comparable solubility and may have a shallower acceptor level, but it likely suffers from compensation by Be interstitials.

## 2. Methods

The density–functional calculations were performed within the local density approximation (LDA) and by using the pseudopotential-plane-wave method [12,13]. We employ a supercell approach and use a tight-binding initialization scheme for the electronic wave functions [14]. The 32-atom zinc-blende and 72-atom wurtzite supercells were used with an energy cut-off of 40 Ry and two and three special  $k$ -points in the irreducible part of the Brillouin zone, respectively. The pseudo-potentials were created using the scheme of Troullier and Martins [15].

The formation energy of a defect in charge state  $q$  is expressed as

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

where  $E_{\text{defect}}^{\text{tot}}(q)$  is the total energy of the defect 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. In evaluating the chemical potentials, which depend on the experimental growth conditions, we assume thermal equilibrium:  $\mu_{\text{Al(Ga)}} + \mu_{\text{N}} = \mu_{\text{Al(Ga)N}}$ . We consider either Al(Ga)- or N-rich conditions: in metal-rich conditions  $\mu_{\text{Al(Ga)}}$  is put equal to the energy of bulk Al(Ga) and in N-rich conditions, the chemical potential is determined by the energy of an  $\text{N}_2$  molecule. The atomic chemical potentials for the impurity species (O, Si, and Mg) were determined by equilibrium with  $\text{Al}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$ , and  $\text{Mg}_3\text{N}_2$  [16]. For Li, Na, K, Be, Zn, and Ca, the chemical potentials of  $\text{Li}_3\text{N}$ , Na, K,  $\text{Be}_3\text{N}_2$ ,  $\text{Zn}_3\text{N}_2$ , and  $\text{Ca}_3\text{N}_2$  were used.

## 3. Results for n-type doping

Recent first-principles studies have shown that the formation energy of the nitrogen vacancy in n-type GaN [17–21] and AlN [10,20,21] is too large for this defect to occur in any appreciable concentrations. This indicates that the nitrogen vacancy is not the dominant center responsible for the n-type conductivity of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ . Nitrogen vacancies were traditionally thought to be responsible for the large background n-type conductivity in GaN. Neugebauer and Van de Walle proposed [17] that oxygen and silicon impurities and not the nitrogen vacancy [18] are responsible for unintentional n-type conductivity in GaN. In support of this, recent experiments have shown that uninten-

tionally doped GaN contains concentrations of oxygen, determined by secondary ion mass spectrometry (SIMS), approximately equal to the measured electron concentrations [22,23].

The cause and behavior of n-type conductivity in GaN have been studied by hydrostatic pressure experiments [24,25]. Freeze-out of carriers was reported under the application of hydrostatic pressure greater than 20 GPa. These findings can be explained by the behavior of oxygen, which undergoes a transition from a shallow to a deep  $DX$  center in wurtzite GaN under pressure [11,25]. The stable shallow center at the equilibrium volume of GaN corresponds to oxygen at the substitutional nitrogen site. The  $DX$  geometry corresponds to an oxygen atom moving off the substitutional position along the [0001] direction (Fig. 1(a)). This geometry becomes stable under hydrostatic pressure. The associated 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. The stability of the localized deep  $DX$  state is attributed to interactions between the negatively charged oxygen impurity and a third-nearest-neighbor cation along the  $c$  axis: a Coulombic attraction has been proposed to be the driving force for the large lattice relaxation that stabilizes the  $DX$  geometry [11]. These third-nearest-neighbor atoms are in different positions in the zinc-blende structure (Fig. 1(b)), rendering the  $DX$  configuration less favorable there.

Alloying with AlN increases the band gap of GaN in a similar way to hydrostatic pressure.  $DX$  center formation should therefore also occur in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ . Indeed, computational studies showed that the  $DX$  configuration is the stable state for the oxygen impurity in wurtzite (but not zinc-blende) AlN [11]. Recent studies based on Hall effect, persistent photoconductivity, and optical threshold measurements have confirmed that oxygen exhibits a metastability and acts as a  $DX$  center in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  for  $x > 0.27$  [3].

The calculations of [11] indicated that silicon, a donor substituting on the cation site [18], does not exhibit the  $DX$  transition. This is consistent with the pressure studies of [25], where it was found that Si remains a shallow donor in GaN up to a pressure of 25 GPa. The suppression of  $DX$  behavior should render silicon more suitable as a donor for  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  at high  $x$ . Indeed, McCluskey et al. found that  $\text{Al}_{0.44}\text{Ga}_{0.56}\text{N}$  intentionally doped with silicon exhibited a free-electron concentration close to the silicon concentration. It was also found, however, that even in the intentionally Si-doped sample a background of oxygen was present. Those oxygen atoms can still undergo the  $DX$  transition, effectively becoming compensating centers. It is important, therefore, to suppress oxygen incorporation when growing Si-doped  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  with high  $x$ .

Donors in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  with high  $x$  may also experience some degree of compensation due to cation vacancies [10]. In Fig. 2(a), we show the calculated defect formation energies for the Al vacancy and for Si and O donors as a function of the Fermi energy,  $E_F$ , for Al-rich conditions in AlN. For each defect, we only show the line segment corresponding to the charge state that gives rise to the lowest energy at a particular value of  $E_F$ . The change in slope of the lines therefore represents a change in the charge state of the defect (Eq. (1)). Fig. 2(a) applies to the zinc-blende phase and shows  $E_F$  spanning the theoretical (GW) band gap for zinc-blende AlN (5.0 eV) [26] which is larger than the LDA band gap in the calculations (3.15 eV). Results for the wurtzite phase are similar. For n-type conditions ( $E_F$  high in the gap), silicon donors will suffer from some degree of compensation by  $V_{\text{Al}}^{3-}$ . The behavior of  $V_{\text{Al}}$  is similar to  $V_{\text{Ga}}$  in GaN [17], however, due to the larger band gap of AlN, the formation energy of  $V_{\text{Al}}^{3-}$  in AlN becomes

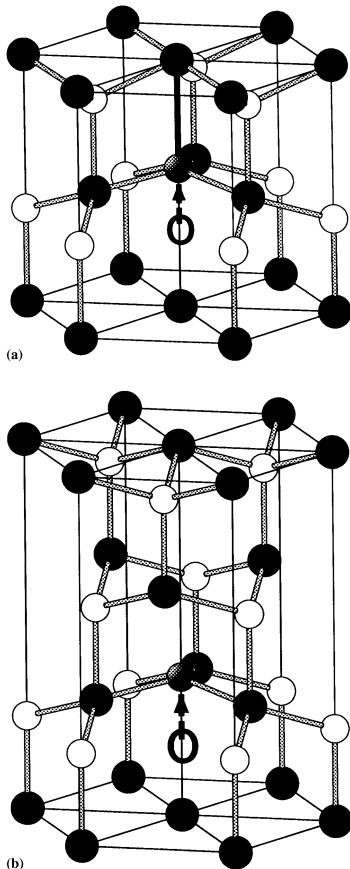


Fig. 1. Schematic diagram of (a) wurtzite and (b) zinc-blende structures indicating a  $DX$  geometry for an oxygen atom on a nitrogen site. Filled and open circles represent cations and anions, respectively. The substitutional position of the oxygen impurity is indicated by the thick-line open circle, and the arrow indicates movement from the substitutional position to that of a  $DX$  geometry. In the wurtzite structure, an interaction occurs with a cation third-nearest-neighbor along the  $c$ -axis (thick black line). In the zinc-blende structure no cation atom occurs in that position, and the absence of that attractive interaction suppresses the  $DX$  state.

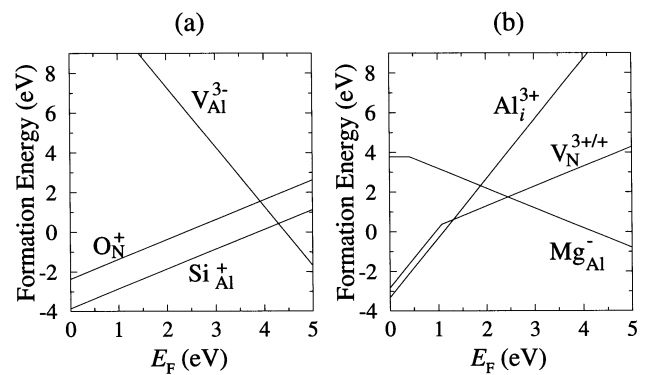


Fig. 2. Defect formation energies as a function of the Fermi level for native defects and impurities in zinc-blende AlN under Al-rich conditions: (a) Donor impurities (O and Si) and the Al vacancy (relevant for n-type doping); (b) Mg acceptor, N vacancy, and Al interstitial (relevant for p-type doping).  $E_F = 0$  corresponds to the valence band maximum. We note that the formation energy of Al is significantly higher in wurtzite AlN than the value for zinc-blende shown here.

significantly lower than that of  $V_{\text{Ga}}^{3-}$  in GaN for Fermi-level positions high in the gap. Cation vacancies thus become an increasingly important source of donor compensation as the Al content  $x$  is increased in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ .

Both mechanisms discussed here, i.e. unintentional incorporation of oxygen acting as a compensating  $DX$  center, and compensation by cation vacancies, may explain the decrease in n-type conductivity in Si-doped  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  for  $x > 0.42$  observed in [5].

#### 4. Results for p-type doping

We now address the cause(s) for the observed decrease in p-type doping efficiency of Mg-doped  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  with increasing  $x$ . In both GaN and AlN, the Mg acceptor assumes the cation substitutional position. Park and Chadi [27] have shown that the Mg impurity has no tendency to form deep levels (so called  $AX$  levels, analogous to  $DX$  for donors), indicating that a shallow–deep transition cannot explain the decrease in hole concentrations. 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). An increase in the ionization energy will lead to a decrease in doping efficiency.

Compensation by native defects is another important mechanism that could contribute to a decline in hole concentrations. We discovered that two defects with low formation energies may inhibit successful p-type doping of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ , namely the nitrogen vacancy and the cation interstitial. In Fig. 2(b), we show the calculated formation energies in zinc-blende AlN as a function of Fermi level and charge state. We also include our calculated formation energies for substitu-

tional Mg on an Al site. The nitrogen vacancy ( $V_N$ ) behaves as a donor which can donate one, two, or three electrons. Only the  $V_N^+$  and  $V_N^{3+}$  charge states are found to be stable; the  $V_N^{2+}$  state is unstable, presenting a negative- $U$  effect. The aluminum interstitial ( $Al_i$ ) in the zinc-blende structure also behaves as a triple donor. Fig. 2(b) shows that  $V_N^{3+}$  and  $Al_i^{3+}$  have particularly low formation energies in p-type material, especially for Al-rich conditions. Both  $V_N^{3+}$  and  $Al_i^{3+}$  will thus compensate the Mg acceptors.

For all of the native defects studied here, we observed very similar behavior in zinc-blende and wurtzite material. The only exception is for self-interstitials: The characteristics of the aluminum interstitial in zinc-blende are qualitatively very different from wurtzite, due to the different local atomic geometries of the interstitial sites [10]. 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 that the Al interstitial will act as a compensating center.

For magnesium in GaN, we concluded that achievable doping levels are mainly limited by the solubility of Mg in GaN [28]. We have also investigated other candidate acceptor impurities. Important properties for a successful acceptor are the solubility (equilibrium concentration, as determined by the formation energy), the depth of the acceptor level, and the stability with respect to other atomic configurations of the acceptor dopant (e.g. interstitials). Preliminary results were reported in [29]. These investigations have now been extended to Li, Na, K, Be, Zn, and Ca in GaN. None of the candidate impurities exhibit characteristics exceeding those of Mg in all respects. The only acceptor with a slightly higher solubility (and potentially slightly lower ionization energy) than Mg is Be. We find, however, that doping with Be may be complicated due to the fact that the small Be atom easily incorporates on interstitial sites, where it acts as a donor, thus causing self-compensation.

## 5. Conclusions

We have reported a comprehensive study of impurities and defects in AlN and GaN, from which we have drawn conclusions about the limitations on doping in  $Al_xGa_{1-x}N$  alloys. Our first principles calculations indicate that the  $DX$  behavior of oxygen and compensation by the cation vacancy are responsible for the decrease in n-type conductivity in  $Al_xGa_{1-x}N$  with increasing  $x$ . With respect to p-type doping of  $Al_xGa_{1-x}N$ , our results show that the nitrogen vacancy becomes an increasingly dominant compensating center as  $x$  increases. We also observe an increase in the Mg ionization energy with increasing Al content. Investiga-

tions of a wide range of potential alternative acceptors show that none emerge as being superior to Mg; Be may be a possibility, but could suffer from compensation by Be interstitials.

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