Theoretical evidence for the semi-insulating character of AlN

Antonella Fara, Fabio Bernardini and Vincenzo Fiorentini

(1) Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Italy
(2) Walter Schottky Institut, Technische Universität München, 85748 Garching, Germany

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We present ab initio density-functional calculations for acceptors, donors, and native defects in aluminum nitride, showing that acceptors are deeper (Be ~ 0.25 eV, Mg ~ 0.45 eV) and less soluble than in GaN; at further variance with GaN, both the extrinsic donors SiAl and CAl, and the native donor VN (the anion vacancy) are found to be deep (about 1 to 3 eV below the conduction). We thus predict that doped AlN will generally turn out to be semi-insulating in the normally achieved Al-rich conditions, in agreement with the known doping difficulties of high-x AlxGa1-x N alloys.

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III-V nitrides have by now established themselves as a key materials system for high-frequency optoelectronics. Doping is still a central problem in this area, especially as recent developments tend to focus on heterojunction systems, and hence on alloys with large In and Al content. Doping of either kind has been shown to be increasingly difficult as the AlN fraction increases in AlxGa1-x N alloys [1]. On the other hand, theoretical studies of doping have been much less detailed for AlN [2–4] than for GaN [5,6], and practically null for InN. Here we contribute to the discussion the results of accurate first principles density functional theory calculations for acceptors, donors, and vacancies in wurtzite AlN. We find that typical candidate acceptors, namely cation-substituting Be and Mg, are moderately but sizably deeper than in GaN. More interestingly, donors known to be shallow in GaN (Si, C, and the nitrogen vacancy) are in fact deep in AlN in their substitutional configuration. Our results are in general agreement with previous results, when comparable. An exception is the behavior of donors, which is at partial variance with previous studies [6], but seems to agree with experimental data [7] indicating serious n-type doping difficulties for AlN and high-x AlxGa1-x N alloys.

Method – We use local-density-functional-theory (LDA) ultrasoft-pseudopotential plane-wave calculations of total energies and forces in doped AlN wurtzite supercells typically encompassing 32 atoms, and with plane wave cutoff of 25 Ry (for further technical details see Refs. [8,9,10]), to predict from first principles the formation energies and thermal ionization energies of cation-substituting Be, Mg, Si, and C, and of the N and Al vacancies in AlN. The carrier concentrations at temperature T due to an impurity or defect with thermal equilibrium at a growth temperature of Tg, and with Ns=2.44×10^22 cm^{-3} available cation or anion site (i.e. half the theoretical atomic density of AlN). Thus, the largest the formation and ionization energies, the less efficient the doping. A non-zero formation entropy (neglected here) will of course enhance the dopant concentration. The formation energy for an impurity in charge state Q is

\[ E_{\text{form}}(Q) = E_{\text{tot}}(Q) - \sum_X n_X \mu_X + Q\mu_e + E_v^Q, \]

with \( \mu_e \) the electron chemical potential (synonymous with the Fermi energy \( E_F \) in our T=0 calculations), \( E_{\text{tot}}(Q) \) the total energy of the fully-relaxed defect supercell in charge state \( Q \), \( E_v^Q \) its top valence band energy, \( n_X \) and \( \mu_X \) the number of atoms of the involved species (X=Al, N, impurity) and their chemical potentials. The latter potentials are determined by the equilibrium conditions with AlN and the compounds (if any) of the specific impurity with Al or N. The structures and formation enthalpies of the solubility limiting compounds (Al2O3, Si3N4, Be3N2, Mg3N2, and d–C) are calculated ab initio. We generally assume the highest \( \mu^{\text{impurity}} \) compatible with the relevant solubility limit. Then, only only one independent chemical potential is left (e.g. \( \mu^N \)), and its value is determined by the imposed (N-rich ↔ Al-rich) growth conditions.

The thermal ionization energy \( \epsilon[0]/-\epsilon[0] \) of a single acceptor is by definition the formation-energy difference of the two charge states \( Q=0 \) and \( Q=-1 \) at \( \mu_e=0 \), and it corresponds to hole release from (i.e., electron promotion into) the acceptor extrinsic state with concurrent geometric relaxation. For a single donor, the analogous quantity is \( \epsilon[+]/-\epsilon[+0] \), the formation-energy difference of the charge states \( Q=+1 \) and \( Q=0 \) at \( \mu_e=0 \). This quantity is the distance of the energy level from the valence band. The thermal ionization energy of the donor electron into the conduction band is \( E_{\text{gap}} - \epsilon[+0] \). Thus, the theoretical evaluation of donor ionization energies with respect to the conduction edge requires a decent estimate of the fundamental gap. The DFT-LDA eigenvalue gap is inappropriate for two reasons: first, it is notoriously inaccurate in general [1]; second, it seems inconsistent to
compare the DFT-LDA eigenvalue-difference gap at fixed number of electrons, with our ionization levels extracted from total energy differences of variable-electron-number systems.

We thus proceed to evaluate the gap in analogy to impurity levels, specifically as the ionization energy $\epsilon[0/-]$ of a defectless cell, i.e. the difference in total energy between bulk supercells with $N$ and $N+1$ electrons respectively. This way of proceeding is technically consistent with the treatment of the defects, and the final result is affected by essentially the same systematic errors: our result of 5.6 eV for the gap, within about 10% of the experimental value of 6.2 eV, indicates that the correct theoretical gap to be compared to donor levels is indeed somewhere near the experimental value. Yet another, conceptually more satisfactory estimate would be that dictated by $\Delta$SCF theory (see e.g. Ref. [12]), whereby the gap is the difference $\epsilon[0/-] - \epsilon[+/-]$ for the defectless cell. Using this expression, we get 6.0 eV, even closer to the experimental value.

Results – The results of our calculation are summarized in Figure 1, for both Al-rich (upper panel) and N-rich (lower panel) growth conditions. The thermal levels of acceptors, referred to the valence band top, are 0.25 eV for Be$_{Al}$ and 0.45 eV for Mg$_{Al}$. Thus, these candidate acceptors are both appreciably deeper than in GaN, where the levels of Be$_{Ga}$ and Mg$_{Ga}$ are at about 0.1 and 0.2 eV, respectively [6,7].

As for the vacancies, V$_{Al}$ is a multiple acceptor with a formation energy diving to zero and below in n-type conditions. This relatively unsurprising results parallels closely that for the Ga vacancy in GaN [5], and the previous results on AIN by Mattila and Nieminen [6]. The nitrogen vacancy is a donor in p-type conditions, as in GaN: however, its first thermal level is very deep, indeed close to midgap. Negative states of V$_{N}$ are realized up to –3, in agreement with previous results [6]. We did not investigate the +2 and +3 states of V$_{N}$ found in Ref. [5], but their existence does not affect our conclusions. The realization of high charge states is not uncommon in insulators and wide gap semiconductors, a known example being oxygen vacancies in quartz-glass [6].

The implications of these results for doping are easily analyzed using the theoretical framework by van de Walle et al. [7]. For our present purposes we just need to recall that in the final analysis, in the presence of competing donor and acceptor species, the Fermi level turns out to be pinned at about the intersection of the lowest donor and acceptor formation energy curves. The Fermi levels obtained respectively via $n$ and $p$ doping for typical realistic conditions ($T_g \sim 1200$ K, $T_{oper} \sim 300$ K) are denoted by arrows in Figure 1. Doping is clearly very inefficient in all cases; let us examine the reasons for that.

As for $p$-doping, it is clear that in Al-rich conditions the N vacancy compensates the acceptors, pinning the Fermi level at about 2-2.5 eV above the valence band. In the more favorable N-rich conditions, this compensation is not effective (even if the 3+ state of Ref. [5] is accounted for). However, the formation and ionization energies of the acceptors are sizably larger than in GaN, and both the dopant and the carrier concentration will be substantially lower than in GaN, making $p$-doping of AIN even less efficient than in GaN. The shallowest acceptor will produce in the most favorable case a Fermi level at $\sim 0.5$ – 0.6 eV above the valence (Be$_{Al}$ in N-rich conditions at a MOCVD-like growth temperature $T_g \sim 1000$ – 1200 K). The co-incorporation mechanisms...
involving H or O found to be effective in GaN remain to be investigated in AlN.

As for n-doping the situation is even worse. Firstly, the shallowest level found here, that of Si Al (the natural choice, as SiGa is the standard shallow donor in GaN), is about 1 eV below the conduction band (C has a huge formation energy and is always unfavorable). Secondly, vacancy compensation is always in action. The nitrogen vacancy will compensate Si in Al-rich conditions, and the Al vacancy will in N-rich conditions. Thus, in no event will the Fermi level be higher than about 2 eV below the conduction band, in both N-rich and Al-rich growth conditions. n-doping of AlN will therefore be especially difficult, if at all possible.

In summary, ab initio calculations predict that acceptors and donors in use for GaN are not suitable for AlN and high-x AlxGaxN alloys. The acceptors Be and Mg have high formation energies and fairly high ionization energies, and suffer from nitrogen vacancy compensation in Al-rich conditions. The donors Si and C are deeper than ~ 1 eV below the conduction band, and therefore unusable for doping of AlN. In addition, in N- and Al-rich growth conditions, respectively, the Al vacancy and the N vacancy will act to compensate the donors. While the acceptor behavior of the Al vacancy is unsurprising, the deep donor character of the N vacancy is at variance with the results for GaN. In this respect our findings support the previous results by Mattila and Nieminen over those of Stampfl and van de Walle. While moderate p-type doping might be obtained in N-rich conditions, in Al-rich conditions AlN will be always semi-insulating.

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