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# First principle study of nitrogen vacancy in aluminium nitride*

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In the framework of density functional theory, using the plane-wave pseudopotential method, the nitrogen vacancy ($V_{\rm N}$) in both wurtzite and zinc-blende AlN is studied by the supercell approach. The atom configuration, density of states, and formation energies of various charge states are calculated. Two defect states are introduced by the defect, which are a doubly occupied single state above the valance band maximum (VBM) and a singly occupied triple state below the conduction band minimum (CBM) for wurtzite AlN and above the CBM for zinc-blende AlN. So $V_{\rm N}$ acts as a deep donor in wurtzite AlN and a shallow donor in zinc-blende AlN. A thermodynamic transition level $E(3+/+)$ with very low formation energy appears at 0.7 and 0.6eV above the VBM in wurtzite and zinc-blende structure respectively, which may have a wide shift to the low energy side if atoms surrounding the defect are not fully relaxed. Several other transition levels appear in the upper part of the bandgap. The number of these levels decreases with the structure relaxation. However, these levels are unimportant to AlN properties because of their high formation energy.

**Keywords:** aluminium nitride, density of states, defect state, formation energy
**PACC:** 7115J, 7155G, 7120H

## 1. Introduction

Now III-nitrides have established themselves as a key materials system for high frequency and high power optoelectronics.[1] AlN is one of them with the largest bandgap and having wide applications.[2,3] However, a central problem in this area is doping, both n- and p-type AlN is difficult to obtain, which has attracted much attentions. Besides experimental studies,[4,5] much theoretical works have also been done to investigate the doping problems. Native defects are the most focused and earliest studied targets. Mattila and Nieminem [6] reported formation energies of various charge states of the N and Al vacancies and O impurity in zinc-blende AlN by performing plan wave pseudopotential (PWPP) calculation in the local density approximation (LDA). Gorezyca *et al*[7,8] used both the Green's function (GF) and the LDA linear muffin-tin orbital (LMTO) basis to examine the structure, electronic properties and influence of applied pressure of native defects and dopant impurities in a number of zinc-blende group III nitrides, while Fara *et al*[9] reported LDA PWPP studies of defects in wurtzite AlN. Stampfl and Van de Walle [10] presented a comparative study of the properties of zinc-blende and wurtzite AlN defects. More recently, Hung *et al*[11] paid special attention to vacancy defects in wurtzite AlN, using generalized gradient approximation (GGA) and hybrid function methods within both PWPP and linear combination of atomic orbital basis representations.

In the present work, we investigate specifically the nitrogen vacancy ($V_{\rm N}$) of various charge states in both wurtzite and zinc-blende AlN using the density functional theory (DFT) based GGA PWPP computational method. The structure, density of states, formation energy and thermodynamic transition level are calculated. In the previous reported works, most of them investigated only the neutral and positive charge states of $V_{\rm N}$ in AlN, all the possible charge state, form 3- to 3+, are included in this work. To get more accurate result, 96-atom supercell for wurtzite and 64-atom supercell for zinc-blende structure are used in this work, which are larger than the usually used 32-atom supercell. All the previous reported works, except Ref. [7], treated only fully relaxed structure. The atom configuration dependence of transition levels is investigated in this work by comparing the results of fully relaxed and unrelaxed structures, which can be used to compare with experimental phe-

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nomenon where both annealed and unannealed samples are used.

## 2. Calculation details

The calculations are performed with the method of GGA and PWPP basis set, specifically the three gradient-corrected functional[12] is used for the exchange correlation functional. Standard norm-conserving pseudopotential[13] for Al and N atoms is used. The plan wave cut-off energy is set at 700eV. The $k$-space integrations are performed by using the Monkhorst-Pack sampling scheme[14] with a $2 \times 2 \times 2$ $k$-point mesh. The supercell approach is used to simulate isolated point defect, with a 96-atom supercell for wurtzite AlN and a 64-atom supercell for zinc-blende AlN. Cell and geometry optimizations were performed by using a BFGS (Broyden–Fletcher–Goldfarb–Shanno) scheme.[15]

The AlN primitive cell is firstly optimized. The obtained lattice constants are $a = 3.075$ Å, $c = 4.944$ Å and an internal coordinate $u = 0.382$ for wurtzite structure, and $a = 4.380$ Å for zinc-blende structure, which are well consistent with the previous reports.[16−18] Then 96- and 64-atom supercells are created with the above lattice constants respectively, and the isolated point $V_{\rm N}$ defect models are obtained by removing one N atom from each supercell. When performing geometry optimization calculations, all atoms in supercells are allowed to move, but the lattice constants of supercells are fixed.

The concentration of a defect in thermodynamic equilibrium is absolutely determined by its formation energy. The formation energy of an isolated point defect $V_{\rm N}$ in charge state $q$ is defined as Eq.(1),[19]

$$E_{\rm F}(q) = E_{\rm tot}(q) - E_{bulk} + \mu_{\rm N} + q(E_{\rm v} + \Delta V + \mu_{\rm e}), \quad (1)$$

where $E_{\rm tot}(q)$ is the total energy of the defect supercell in charge state $q$, $E_{\rm bulk}$ is the total energy of responding bulk cell, $\mu_{\rm N}$ is the chemical potential of N in AlN, $E_{\rm v}$ is the valance band maximum (VBM) of bulk AlN, and $\mu_{\rm e}$ is the electron chemical potential, namely the Fermi level, which is set zero at the VBM. $\Delta$V is a VBM correction to the defect supercell, which is obtained from the average electrostatic potential difference between bulk and defect supercells. The chemical potential $\mu_{\rm N}$ is calculated by using the relationship

$$\mu_{\rm N} = \mu_{\rm N(N_2)} - (1 - \lambda)\Delta H. \quad (2)$$

Where $\mu_{\rm N(N_2)}$ is the N chemical potential in $N_2$ gas, $\Delta H$ is the formation enthalpy of AlN, and $\lambda$ specifies the stoichiometric condition, where $\lambda = 1$ for N-rich condition and $\lambda$=0 for Al-rich condition. The value of $\Delta H$ is determined from the computed total energies of wurtzite (or zinc-blende) AlN, face-centre cubic Al and molecular $N_2$.

The Kohn–Sham levels in the semiconductor bandgap or near the band edges introduced by defects or impurities can be obtained from a band structure calculation. But the experimental relevance levels always involve transitions between different charge states of the centre. This means that the Kohn–Sham levels of a band structure calculation cannot directly be identified with any levels that are relevant for experiment. The thermodynamic transition level $E(q_1/q_2)$ is defined as the Fermi level position where charge states $q_1$ and $q_2$ have equal formation energy. These levels can be observed in deep level transient spectroscopy (DLTS) experiment.

## 3. Results and discussion

### 3.1. Geometry optimization

The geometry optimization calculation results of defect supercells are shown in Table 1.

**Table 1.** Defect geometries as a function of charge state for $V_{\rm N}$ in both wurtzite and zinc-blende AlN. Displacements of nearest-neighbour atoms are expressed as a percentage of the ideal bulk bond length (c-direction bond for wurtzite structure). Positive values represent displacement away from the defect centre, and the negative values toward it.

| Charge state | Wurtzite | Zinc-blende |
|---|---|---|
| 3+ | 23.87 | 20.59 |
| 2+ | 12.02 | 9.76 |
| 1+ | 3.25 | 3.47 |
| 0 | 0.08 | 0.16 |
| 1– | –4.20 | –2.51 |
| 2– | –6.53 | –5.12 |
| 3– | –9.57 | –7.31 |

When $V_{\rm N}$ is positively charged, the atoms surrounding the defect center displace away from it; when negatively charged, they displace toward it, and the neutral $V_{\rm N}$ also show a slightly outward displacement. The above results are suitable to both wurtzite and zinc-blende AlN. The results of neutral and positive charge state qualitatively agree with the report of

Stampfl and Van de Walle.[10] Little work for the negatively charged $V_N$ has been reported. That is because the calculation based on DFT usually underestimates the semiconductor bandgap and the upper defect state. For negatively charged defect, the upper defect state or conduction band will be occupied by electrons. The calculated total energy is thus lower than the real. However, the geometry optimization is based on Newtonian mechanics, no matter the total energy is rightly estimated or not, the relaxed atom configuration is credible.

## 3.2. Density of states

The densities of states of $V_N$ in fully relaxed structures are shown in Fig.1, which are very similar to that of unrelaxed structures because of the negligibly small atom displacements introduced by neutrally charged $V_N$. As shown in Fig.1(a), $V_N$ in wurtzite AlN introduces two defect states in the bandgap, a doubly occupied single state lying slightly above the VBM and a single occupied triple state lying obviously below the conduction band minimum (CBM). Thus $V_N$ acts as a single deep donor. This is a doubtless conclusion, which is consistent with all previous reports.[9−11]

For $V_N$ in zinc-blende AlN, the defect induced states are analogical to wurtzite AlN, a single and a triple state, which is shown in Fig.1(b). The difference of defect states between wurtzite and zinc-blende AlN is that the triple state in zinc-blende AlN is above the CBM. This is disobedient with the result of Gorezyca *et al* by GF-LMTO method,[7] but consistent with the results in Ref.[6,8,10]. The reason of this difference can be attributed to that the wurtzite AlN is direct bandgap semiconductor and the zinc-blende AlN is indirect bandgap semiconductor. The CBM of zinc-blende AlN is at the X point, which is a very deep energy valley and makes a long tail to the density of states. That is obviously shown in Fig.1(b), from –0.5 to 0.7eV. The upper defect state superposes the tail. So $V_N$ in zinc-blende AlN is a single shallow donor.

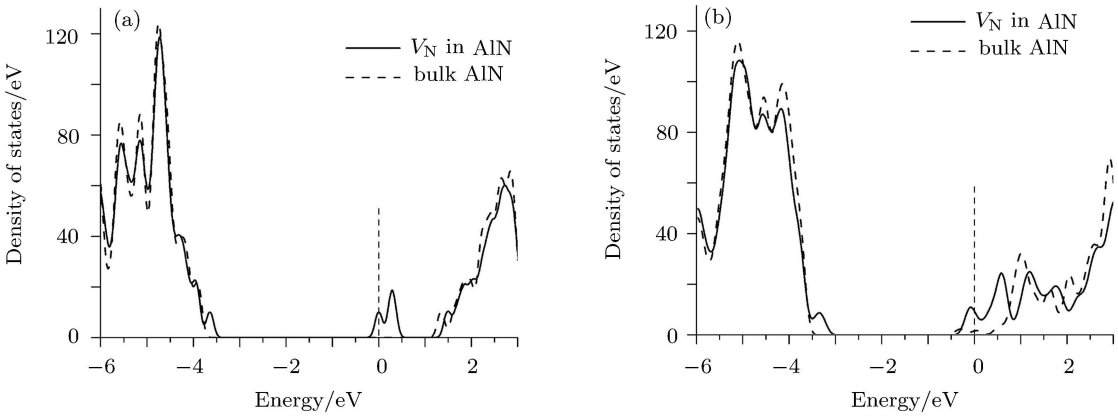



**Fig.1.** Density of states for (a) wurtzite and (b) zinc-blende AlN supercell. The solid line is the density of states of defect supercell and the dashed line is that of ideal bulk supercell. The vertical dashed line at zero is the Fermi-level of defect supercell.

## 3.3. Defect formation energy

The defect formation energy as a function of the Fermi-level, under nitrogen-rich condition, is shown in Fig.2(a) for wurtzite AlN and in Fig.3(a) for zinc-blende AlN. The solid and dashed lines respond to the fully relaxed and unrelaxed structures respectively. Only the line segment of each charge state (from 3– to 3+) that gives rise to the overall lowest energy is shown. Thus, a change in slope of the lines represents a change in the charge state of defect and the knee point is the transition level position of the responding two charge states. The Fermi-level is set to move from a little below the VBM to CBM. The bandgap value here is neither the result of direct band structure calculation nor the experimental value. We proceed to evaluate the bandgap in analogy to transition levels, specifically as shown in Eq.(3), which is the energy distance between the transition level $E(0/-)$ and $E(+/0)$ of the defect less AlN supercell.[20]

$$E_g = E(0/-) - E(+/0). \tag{3}$$

This way of proceeding is technically consistent with the transition levels, and the final result is affected by essentially the same systematic errors. The bandgaps obtained by this way are 5.1eV for wurtzite AlN and

4.3eV for zinc-blende AlN. The direct band structure calculation results are 4.2eV for wurtzite AlN and 3.3eV for zinc-blende AlN. The former are more close to the experimental values than the latter.

It can be seen from Fig.2(a) that under p-type condition (low Fermi level value) $V_{\rm N}$ in triply positively charged state, $V_{\rm N}^{3+}$, has very low formation energy. $V_{\rm N}$ in the doubly positively charged state $V_{\rm N}^{2+}$ is unstable, thus presenting a negative-$U$ effect between triply and singly positive charge states, which has also been found in GaN.[21] Under n-type condition, the formation energy of $V_{\rm N}$ is high, indicating that this defect will not occur in high concentration. Comparing the formation energy of $V_{\rm N}$ in relaxed and unrelaxed structure. That of the unrelaxed structure is naturally overall higher than the fully relaxed structure. Another difference of them is that $V_{\rm N}$ in neutral charge state exists in the unrelaxed structure, and can not exist in the fully relaxed structure, which means that transition levels of neutral charge states can appear in not fully relaxed structure and disappear in fully relaxed structure. Comparing the above results with previous reports, we find that the pattern of the dashed line is similar to the result in Ref.[9], so it may be from a not fully relaxed structure.

A clearer schematic graph of the transition levels are shown in figure 2(b). In the fully relaxed structure, transition level $E(3+/+)$ appears at 0.7 eV above the VBM, which agrees with the widely reported result. In the unrelaxed structure, this level moves down to 0.2 eV below the VBM. It means that the position of this level greatly depends on the relaxation of atoms surrounding the defect centre, it may shift in a wide range with the structure relaxation. There are another three transition levels (0.7, 1.0 and 1.5 eV below the CBM) in the upper part of the bandgap of unrelaxed structure, which come down to two levels (1.4 and 1.7 eV below the CBM) when the structure is fully relaxed. That is because of the disappearance of $V_{\rm N}$ in neutrally charged state in the fully relaxed structure.

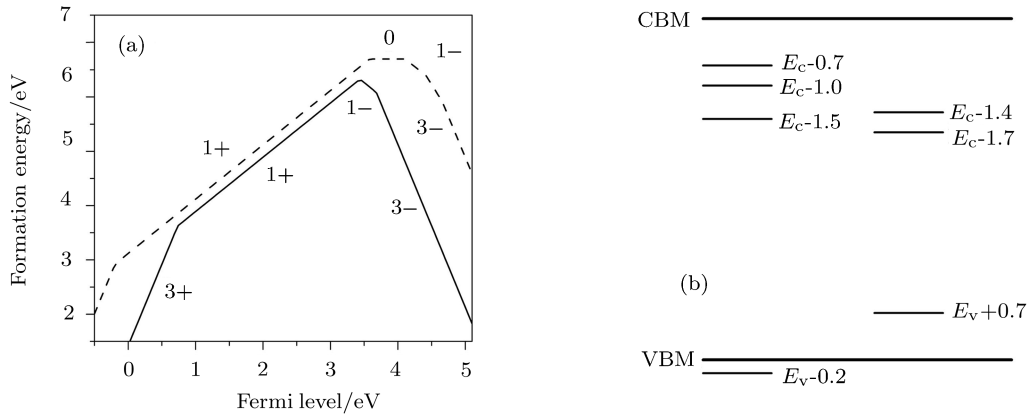



**Fig.2.** (a) Formation energy of nitrogen vacancy in wurtzite AlN as a function of the Fermi level under nitrogen-rich condition; (b) schematic graph of the transition levels, $E_{\rm c}$ and $E_{\rm v}$ are the energy of CBM and VBM.

The formation energy of $V_{\rm N}$ in various charged state of zinc-blende AlN is shown in Fig.3(a). Under p-type condition, it is analogical to that of wurtzite AlN. The doubly positively charged $V_{\rm N}$ is still unstable and presenting a negative-$U$ effect between triply and singly positive charge states. Under n-type condition, $V_{\rm N}$ in neutrally and singly negatively charged states exists in unrelaxed structure and can not exist in fully relaxed structure. A clearer schematic graph of transition levels are shown in Fig.3(b). The transition level $E(3+/+)$ may have a wide shift form 0.3 eV below to 0.6 eV above the VBM with the structure relaxation. The result of fully relaxed structure is close to Mattila *et al*'s result of 0.7 eV above the VBM,[6] but lower than Stampfl and Van de Walle's result of 1.0 eV above the VBM.[10] In the upper part of the bandgap, three transition levels (0.8, 0.9 and 1.1 eV below the CBM) of unrelaxed structure come down to one level (1.0 eV below the CBM) when the structure is fully relaxed. That is because of the disappearance of $V_{\rm N}$ in neutrally and singly negatively charged states in the fully relaxed structure.

The transition levels in the upper part of the bandgap of both wurtzite and zinc-blende AlN are little reported. There are two possible reasons. One is that the calculation based on DFT usually underestimates the semiconductor bandgap, so the total energy and formation energy of negatively charged defect are incredible. However, the bandgap values used in this work are not the direct results of band structure cal-

culation, which is processed as Eq.(3). So the relative positions of these levels are creditable. Another reason is that the formation energies of these levels are very high, which are obviously shown in Figs.2(a) and 3(a). So they will not occur in high concentration. Thus, these levels are unimportant to AlN properties. However, the formation energy of transition level $E(3+/+)$ is very low in both wurtzite and zinc-blende AlN. So it is important to AlN properties. Its wide shift with the structure relaxation may be seen in the DLTS experiment with the sample annealing.

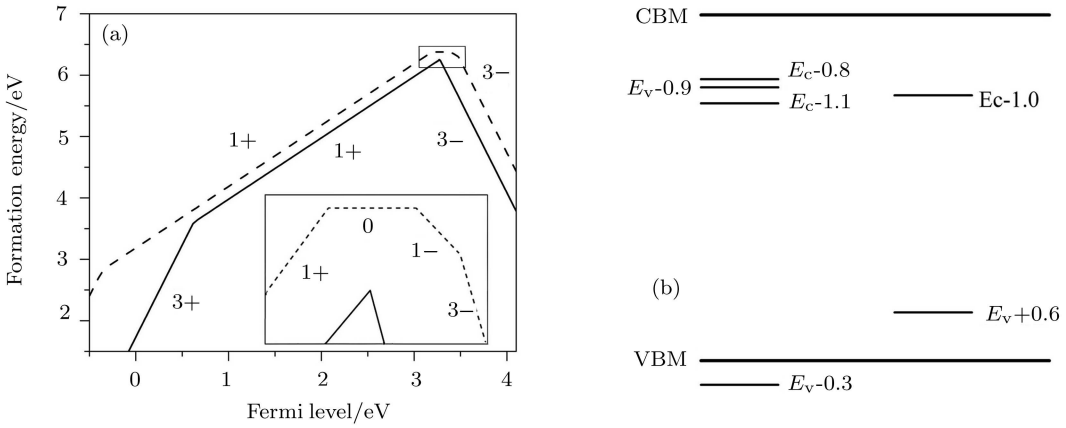



**Fig.3.** (a) Formation energy of nitrogen vacancy in zinc-blende AlN as a function of the Fermi level under nitrogen-rich condition, the inset is a megascopic graph of the rectangle area; (b) schematic graph of the transition levels, $E_c$ and $E_v$ are the energy of CBM and VBM.

# 4. Conclusion

The density of states calculation shows that the $V_N$ in both wurtzite and zinc-blende AlN introduces two defect states, which are a doubly occupied single state above the VBM and a singly occupied triple state obviously below the CBM for wurtzite AlN and above the CBM for zinc-blende AlN. So $V_N$ acts as a deep donor in wurtzite AlN and a shallow donor in zinc-blende AlN. Further formation energy calculations show that the formation energy of $V_N$ is low under p-type condition and high under n-type condition. So it will compensate the p-type doping and will not have high concentration in equilibrium n-type sample.

A thermodynamic transition level $E(3+/+)$ with very low formation energy appears at 0.7 and 0.6 eV above the VBM in wurtzite and zinc-blende AlN respectively, which may have a wide shift to the low energy side if atoms surrounding the defect centre are not fully relaxed. Several other transition levels appear in the upper part of the bandgap. The number of these levels decreases with the structure relaxation. That is because $V_N$ in several charged state can not exist in fully relaxed structure. However, these levels are unimportant to AlN properties because of their high formation energy.

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