Supplementary Information for "Computational study of native defects and defect migration in wurtzite AlN: an atomistic approach"

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S.1 Technical details of the QM/MM calculation

In the main article, we employ the hybrid QM/MM embedded cluster approach to calculate the third electron affinity of nitrogen. The QM/MM technique has unambiguous definition of the vacuum level, so that a more precise ionization process can be modelled. There are three levels of theory employed in the hybrid QM/MM embedded cluster technique. At the central region, where the N^{3-} ion is positioned, QM theory is applied. The choice of our QM method is DFT, with the usage of the PBE0 hybrid functional[1,2] and def2-TZVP[3] basis set. The outer most diffuse as well as high angular moment basis functions are removed (f function for N), as they contribute very little to the results while contributing to unwanted electron spillage to the environment and waste computational time. Outside of the QM region, the surrounding environment is treated with MM theory, which includes the interatomic potentials and polarisable shell model. The interatomic potential model is the same two-body interatomic potential that is developed in this work. The thickness of both MM regions is about 15Å (containing atoms at the order of 10000 for both regions). At the interface between QM and MM theory, some of the cations are treated with semi-local pseudopotentials (effective core potentials, ECP) to compensate for the mismatch in the QM and MM environment for the outermost QM atoms. The outer layer of the

environment includes a frozen MM region. And at last, at the rim of the whole QM/MM system, there are intentionally put point charges to reproduce the Madelung potential of the infinite crystal around the defect site. A more detailed discussion of the technique can be found in the original publication of the method[4].

At the interface region, the ECPs need to be adjusted to work with the force field implemented in the technique. A semi-local ECP is fitted separately in the *FIT_MY_ECP* software (https://www.github.com/logsdail/fit_my_ecp) for the Al atoms at the interface region, minimising: (i) the gradients on the atoms in the QM, interface and active MM region; (ii) energy scatter of innermost localised states on anions[5]. The form of the pseudopotential is a linear combination of three Gaussian functions:

$$r^2 U_p(r) = A_1 r \, exp(-Z_1 r^2) + A_2 r^2 exp(-Z_2 r^2) + A_3 r^2 exp(-Z_3 r^2) \quad,$$

where the best A and Z parameters are found by using a global search for achieving the two criteria above. The resultant pseudopotential for the cations has the form:

$$r^2 U_p(r) = -36r \, exp(-25r^2) + 42.6r^2 exp(-3.4r^2) + 0.45r^2 exp(-0.55r^2) \quad.$$

The hybrid QM/MM method is realised in the Chemshell software (TCL version[6,7] and Python version[8]). The QM software is NWChem[9] (main production calculations) and GAMESS-UK[10] (for ECP fitting). The MM software for pre-optimisation and the hybrid technique is GULP[11]. A number of reports have been published using the same method for GaN[12–14] and for other ionic materials[15–19].

S.2 3-body potential model correction

As mentioned in the main article, we found that the Mott-Littleton defect energy cannot converge for all four intrinsic defects by using our 3-body interatomic potential model. The 3-body potential acts as a pure attractive force, so we employ a form of the Buckingham repulsive force between the Al core and the N core:

$$V_{3-body,\, corr.} = De^{-r/\rho_D} \quad,$$

where constants D and ρ_D are first determined analytically and then fitted empirically. ρ_D needs to be smaller than $1/2\rho_{3B}$. And D must be big enough to counteract the 3-body potential, so we have the formular by equating the correction term to the 3-body potential and we get:

$$D \geq (m-1)K\rho_{3B}\rho_D e^{\left(2\rho_{3B}\left(R_0^{12} - R_D\right) + \frac{R_D}{\rho_D}\right)} ,$$

where m is the maximum coordination number of the defect (6 for the interstitial defect), R_D is the shortest bond length of the defective cluster (~1.7 Å), and the rest of the parameters are from the 3-body potential. We further adjust the D and ρ_D value to reduce the deviation of the observing physical properties while the Mott-Littleton calculation can still converge. The best parameters are determined ($B = 5.6 \times 10^{14}$ and $\rho_B = 0.05$) to gain the closest prediction of all physical properties, but it is still far from the results in previous reports (**Table A**).

Table A Calculated properties of wurtzite AlN obtained using the corrected three-body potentials.

Property	
Lattice constant, a (Å)	3.14
Lattice constant, c (Å)	5.02
Special position, u (Å)	0.380
C_{11} (GPa)	442.6
C_{12} (GPa)	206.9
C_{13} (GPa)	190.9
C_{33} (GPa)	514.2
C_{44} (GPa)	135.4
C_{66} (GPa)	117.9
ϵ_{11}^{0}	7.82
ϵ_{33}^{0}	8.40
ϵ_{11}^{∞}	4.47
ϵ_{33}^{∞}	4.59
e_{33} (C/m²)	2.69
e_{31} (C/m²)	-1.68

Bulk modulus, B_0	285.58
Lattice energy (eV)	-90.00

S.3 Defect energy of N interstitial defect

To investigate the reason why our defect energy of N interstitial is substantially lower than the one previously reported using the interatomic potential model[20], a detail comparison is demonstrated in this section.

The N_i''' defect is obtained in GULP using the potential model in that report[20]. The interstitial defect is initially put at the centre of the octahedral chamber as the starting configuration of the geometry optimization. The Mott-Littleton radius is set to be the same as ours, i.e., 21 Å for region I and 36 Å for region IIa. The cut-off of each potential is set to be from 0 to 10 Å. Thus, the physical properties and the defect energy of the N interstitial defect are calculated. The physical properties such as lattice constants and dielectric constants are close to the reported value[20]. The defect energy of N interstitial is calculated to be -15.73 eV, about 3 eV lower than the reported value. The discrepancy can be attributed to the different potential cut-offs, larger Mott-Littleton radius, and different calculation environment (e.g., the software). Such value is still over 15 eV higher than our defect energy. We found that the higher defect energy could be attributed to the higher short-range energy between the N-N interaction. **Table B** shows the comparison of the short-range energies between nitrogen interstitial defect and the closest neighbouring on-site N ions. The overall longer N-N distances and higher positive energies from the previous potential indicate the defect induce substantial repulsive forces to the neighbouring N ions, which consequently makes the defect energy much higher than ours.

Table B Short-range energies of the interaction between the nitrogen interstitial ($N_i^{'''}$) and the closest neighbouring on-site nitrogen ions ($N_N^{\times}$). Only the energies at the longest and shortest distances are presented in the table.

$N_i^{'''}$- $N_N^{\times}$ Distance (Å)	N-N Short-range energy (eV)
Present work 2.41	0.002
2.75	< 0.001
Cormack[20] 2.51	3.826
2.67	2.111

S.4 Benchmarking of GULP and VASP

Table A presents the benchmarking comparison between the Mott Littleton method in GULP and the DFT in VASP for $V_{Al}^{'''}$ defect calculation. In GULP, the radii of Mott Littleton clusters are set to be the same as specified in the main article. The same Mott Littleton calculations were conducted 3 times and the shortest simulation time is recorded in **Table A**. In VASP, the calculation is conducted using the density functional theory (DFT) with the hybrid functional HSE06[21]. A plane-wave basis set with a cut-off energy of 600 eV has been employed to describe the valence electronic states along with the projector augmented wave (PAW) method to describe interactions between the core and valence electrons. The Al(3s, 3p) and N(2s, 2p) states were treated as valence states. The energies are calculated using $3 \times 3 \times 3$ supercell of AlN with an Al vacancy (107 atoms in total) and $3 \times 3 \times 2$ Monkhorst-Pack k-point meshes, with SCF convergence at 10^{-6}eV for both restricted (RHF) and unrestricted (UHF) Hartree Fock calculations. The criterion for ionic structural optimization convergence is set to be all the forces are smaller than 0.02eV/Å.

All the calculations were conducted on MMM Hub Thomas HPC platform, where each node has 2×12 core Intel Broadwell processors, 128GB RAM, and 120GB SSD.

Table C The time (in minute) for Al vacancy defect calculation to finish by employing Mott Littleton method in GULP and DFT method in VASP, versus the number of computer nodes used in the HPC machine.

Node count	Mott Littleton in GULP	DFT in VASP

		RHF	UHF
2	103	18655	45600
4	82	9843	24060
6	73	6628	16200
8	69	5204	12720
10	69	4320	10560

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