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Native and radiation induced point defects in AlN and Sc-doped AlN

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Abstract

We have performed first-principles calculations to investigate the electronic structure, configurations, formation, and binding energies of native and radiation induced point defects in pristine and Sc-doped wurtzite AlN. For the native defects, the nitrogen vacancy has the lowest formation energy in *p*-type material while the aluminum vacancy has the lowest formation energy in *n*-type material which is consistent with the previous studies. Several interstitial defect structures were modeled for Al, N, and Sc atoms for the first time. The effects of charge state on their relative stability were investigated. The binding energy of Sc with point defects was calculated and found to be dependent strongly on the defect type and charge state. The results obtained are discussed in light of the possible Sc effects on the radiation damage evolution in AlN. Thus the attraction of Sc atom to N vacancy and both Al and N interstitials reduces their mobility and increases Frenkel pair recombination distance.

Keywords: wurtzite AlN, first-principles calculations, point defects, radiation effects, Sc-doping

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1. Introduction

AlN is one of the group-III nitride materials with a wide bandgap that are being intensively studied because of their outstanding properties in many applications. Thus, wurtzite AlN is extensively used in optoelectronic, photonic, and piezoelectric devices [1-4]. It was recently shown that it exhibits amazing properties in forming solid state qubits [4,5]. Because of its good radiation damage tolerance [6], it has a very promising potential as a functional material for sensors in nuclear devices subjected to harsh environments. Previous studies showed that AlN provides very good radiation tolerance for piezoelectric properties and high temperature stability [6-8]. It was shown that the piezoelectric properties of AlN are unaffected by gamma radiation up to 26.8 MGy and by fast neutron fluence of 1.85×10^{18} n/cm² and thermal neutron fluence 5.8×10^{18} n/cm² [9]. Additionally, it has been shown [10,11] that AlN-based transducers maintain their piezoelectric response during the entire irradiation (neutron fluence 8.65×10^{20} n/cm² and gamma fluence 7.23×10^{21} gamma/cm² at 420°C) and perform better than other candidate ceramics such as ZnO and BiTiO₃ [11]. The ability to retain its piezoelectric response during irradiation, in combination with the overall good radiation response of AlN, makes it a candidate material for piezoelectric sensing technologies for advanced nuclear reactors [12]. However, the piezoelectric coefficient of AlN is low (about 5 pm/V) compared to the coefficients of some other ceramics (such as 10 pm/V for zinc oxide and 18 pm/V for bismuth titanate [12]). Recent studies have shown that alloying AlN with metals, such as scandium (Sc), improves the piezoelectric response by up to 40% [13-18] making these materials very attractive for practical usage.

Properties of pure and doped AlN, relevant to its unique applications, are defined mostly by their band structure thus, first-principle approaches have been intensively applied. Pristine AlN and AlN containing dopant impurities, including gases and elements from groups II, IVA-B, were investigated using the density functional theory (DFT) based calculations for example in [4, 5, 19, 20]. However, very limited information can be found on doping with Sc. Moreover, previous studies were focused mainly on optoelectronic and magnetic applications whereas piezoelectric applications under irradiation conditions have not been considered so far. Recent applications of AlN as sensors in nuclear devices demand knowledge of radiation damage mechanisms for predicting their lifetime. Neutron and ion irradiation experiments have provided important insights into the radiation response of AlN. A number of radiation effects are reported such as swelling

[21-23], loss of thermal conductivity [24-27], and growth of interstitial loops [23, 28, 29]. Thus, swelling associated with introduced gas i.e. oxygen or helium was observed in [21, 22]. The high density of small interstitial-type dislocation loops, $\leq 5\text{nm}$ in diameter, was reported after neutron irradiation [23, 28, 29]. Loops are preferentially formed in the basal plane and cause a macroscopic volume change due to corresponding elastic strain (not associated with vacancy voids). AlN has been observed to exhibit good resistance to radiation induced disordering compared to GaN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ [30]. In general, AlN ceramics demonstrate significant resistance against radiation damage although a clear understanding of the governing mechanisms is not yet achieved.

There are very few reported attempts in describing the fundamentals of high radiation tolerance of AlN. Some radiation damage effects in ceramic materials are discussed in a recent review [29]. Among the discussed effects, one key contribution might be that the onset of interstitial migration in AlN apparently occurs at $T < 80\text{ K}$ on both the anion and cation sublattice [28, 31]; this underlines the importance of understanding interstitial properties. Recent work on low-energy primary radiation damage in wurtzite AlN was studied by *ab-initio* molecular dynamic (AIMD) modeling of Frenkel pairs (FPs) formation [32]. High orientational anisotropy in threshold displacement energy was observed i.e. Frenkel pair creation is easier for primary knocked-on atoms (PKAs) displaced along the direction parallel to the basal planes. The minimum threshold energy was determined along with the directions as 19 eV for Ni-type FP (N-FP) and 55 eV for Al-type FP (Al-FP). The corresponding energies for the PKAs displaced along the [0001] direction were determined as $>39\text{ eV}$ and $>94\text{ eV}$ respectively. It was reported that the FPs formed in these recoil events modify the electronic structure forming new localized states within the bandgap. **As far as doping with Sc is concerned, no information on Sc effects on defects in AlN and its contributions to radiation effects is available.**

In the present paper, we address this gap. We studied the formation energy of native defects in pure AlN and compared them with the previous results. A detailed investigation was performed for interstitial defect, their atomic structure, and interaction with the Sc dopant atom. Last, we discuss the next approaches toward the understanding of radiation damage of these materials.

2. Methods

2.1 Modeling approach

Electronic structures and energies have been calculated within the density-functional theory [33] using the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) [34] parametrization of the electronic exchange-correlation functional. Total energies and electronic structure were calculated using the plane-wave basis projector augmented-wave approach [35] as implemented in the Vienna Ab-initio Simulation Package (VASP) [36]. A plane-wave energy cutoff of 350 eV and $2 \times 2 \times 2$ k-mesh were used to obtain defects formation energy in $3 \times 5 \times 3$ supercell containing 360 lattice sites, where the repeating unit corresponds to a minimal possible rectangular cell of wurtzite-type AlN structure. Initially, in the perfect system c/a ratio, shape, volume, and atomic positions were relaxed until the total pressure dropped below 0.1 kBar and forces acting on atoms don't exceed 10^{-5} eV/Å. As a result, we have obtained a perfect wurtzite lattice with parameters $a=3.128\text{\AA}$ and $c=5.015\text{\AA}$, $c/a=1.603$ ratio (see Fig.1). This is in good agreement with calculated and experimental data [37-41] that include bond lengths between atoms in c-plane, $(\text{Al-N})_{\text{in}}$, and normal to it, $(\text{Al-N})_{\text{out}}$, and angles between the corresponding bonds such as $\alpha_{\text{in-in}}$ between two $(\text{Al-N})_{\text{in}}$ bonds and $\alpha_{\text{in-out}}$ between $(\text{Al-N})_{\text{in}}$ and $(\text{Al-N})_{\text{out}}$ bonds as seen in Table 1. We also calculated the heat of formation of AlN and ScN that was equal to $\Delta H_{\text{AlN}} = -3.203$ eV and $\Delta H_{\text{ScN}} = -4.224$ eV per the corresponding molecule, which are quite similar to the experimentally derived energies -3.28 eV [42] and -4.56 eV [43] correspondingly. This ensures the realistic stability of the corresponding phases modeled here. During the further modeling of defects, the shape and volume of the supercell were kept constant and atomic positions were optimized until the maximum force on atoms dropped < 0.01 eV/Å.

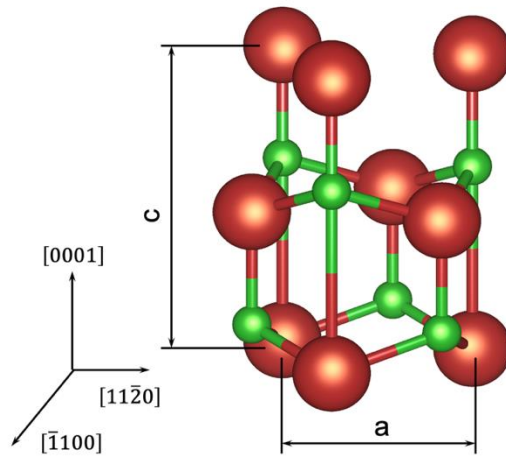


Fig.1 Atomic structure of wurtzite AlN crystal (Al – red, N – green).

Table 1. Properties of the wurtzite crystal modelled here, derived experimentally [37-39] and calculations reported in ^a [32], ^b [40] and ^c [41]. Units are Angstroms for length and degrees for angles.

	a	c	c/a	(Al-N) _{in}	(Al-N) _{out}	α_{in-out}	α_{in-in}
This work	3.128	5.015	1.603	1.901	1.914	108.2	110.7
Other calculations	3.174 ^a	5.107 ^a	1.609 ^a				
	3.118 ^b	5.041 ^b	1.616 ^b				
	3.130 ^c	5.020 ^c	1.604 ^c				
Experiment	3.110	4.980	1.601	1.889	1.903	110.8	108.9

2.2 Defects formation and binding energies

Within supercell defect formalism, the formation energy, $E_D^f(q)$, of a defect D is expressed as:

$$E_D^f(q) = E_{defect}^{tot}(q) - E^{tot}(bulk) - n_{Al}\mu_{Al} - n_N\mu_N + q(E_v - E_F) + E_{corr}, \quad (1)$$

where $E_D^{tot}(q)$ is the total energy of the supercell containing the defect in the charge state q , $E^{tot}(bulk)$ is the total energy of a perfect supercell, n_{Al} and n_N are the numbers of Al and N atoms added to or taken from the bulk crystal in order to create the considered defect, and μ_{Al} and μ_N are the corresponding chemical potentials. E_v represents the energy at the valence-band maximum of the defect free system. E_F is the Fermi energy relative to E_v . Finally, $E_{corr} = \Delta E_{MP} + \Delta E_{bf} + \Delta E_{pa}$ contains the set of finite modeling cell size corrections, i.e. the image charge corrections, ΔE_{MP} , [42-44] and the Moss-Burstein-type band-filling corrections, ΔE_{bf} , [45-46], and the potential-alignment energy correction for the supercell with a net charge, ΔE_{pa} , [43, 44]. The image charge correction for the $3 \times 5 \times 3$ supercell, obtained using the calculated value of static dielectric constant, ϵ_0 , 8.709, is $0.1q^2$ eV. The sum of band-filling and potential-alignment

corrections, $\Delta E_{bf} + \Delta E_{pa}$, is found to be dependent on the defect type and its charge state. For example, for Al-vacancy, V_{Al} , it varies from -0.14eV to -0.07 when charge varies from -3 to 0 considered here for this defect (see Table.3). For the Al interstitial atom, II_{Al} i.e. $\langle 11\bar{2}1 \rangle$ d-b, this varies from 0.06eV to 0.13eV for the considered charges from 0 to +3. This correction is quite small at the neutral state and has its maximum value at the maximal considered charge states. Sc substitution in Al site is the only defect having a significant correction at the neutral state: $\Delta E_{bf} + \Delta E_{pa} = -0.15$ eV. These are extreme cases, where the band-filling and potential-alignment corrections are maximal. In general, band-filling and potential-alignment corrections contribute at the lowest charge states, whereas ΔE_{MP} , following the charge square dependence, dominates at charged states above ± 1 . In general, E_{corr} described here is important for native defects because of their relatively low formation energies small deviations affect their equilibrium concentrations. Radiation-induced defects are not formed thermodynamically but due to ballistic interactions. Microstructure evolution under irradiation is mainly affected by defect interaction and binding which energies are less affected by the above corrections.

Calculations were also performed to evaluate defect property changes due to Sc-dopant. The binding energy of a defect D and Sc atom, $E_{D-Sc}^b(D-Sc)$, can be defined as:

$$E_{D-Sc}^b = E_D^f + E_{ScAl}^f - E_{D-Sc}^f, \quad (2)$$

where E_D^f and E_{D-Sc}^f are the minimum values of the corresponding defect formation energies in pure and Sc-doped AlN calculated via Eq. (1) for the same charge conditions. Each individual energy in Eq. (2) accounts for the finite modeling cell size corrections and, therefore, the resulting $D - Sc$ binding energy also includes these effects explicitly. It is important that E_{D-Sc}^b is charge dependent and, in general, can be related to the different defect's configurations following their relative stability.

Estimation of chemical potential values in compounds is an issue affecting the accuracy of the estimated defect formation energies. This is especially important in semiconductors, where the conditions for phase stability of matrix, its constituent elements, and doping atoms should be taken into account. Here we consider equilibrium conditions for the AlN crystal growth from free Al and N_2 . Chemical potentials for Al, N, and Sc in the AlN compound were determined following the assumptions and procedure described recently in [47]. The following constraints were applied to ensure the stability of AlN and Sc-doped AlN phases: $\mu_{Al} + \mu_N = \mu_{AlN}$ and $\mu_{Sc} + \mu_N \leq \mu_{ScN}$.

Here μ_{AlN} and μ_{ScN} are enthalpies of formation of AlN and ScN estimated by modeling the corresponding perfect crystals. The first constraint provides Al and N in thermal equilibrium with AlN , whereas the second one prevents the formation of the ScN phase in AlN . Furthermore, the chemical potentials must satisfy the boundary conditions: $\mu_N \leq 1/2\mu_{N_2}$ and $\mu_{Al} \leq \mu_{Al(bulk)}$ (if this is not the case, then AlN would be thermodynamically unstable with respect to the formation of N_2 molecules or bulk Al). In the application to the AlN matrix, one may consider nitrogen-rich (N-rich) or aluminum-rich (Al-rich) conditions. Then, at N-rich conditions $\mu_N = 1/2\mu_{N_2}$, $\mu_{Al} = \mu_{AlN} - \mu_N$, and $\mu_{Sc} = \mu_{ScN} - \mu_N$ whereas at Al-rich conditions $\mu_{Al} = \mu_{Al(bulk)}$ and $\mu_N = \mu_{AlN} - \mu_{Al}$, and $\mu_{Sc} = \mu_{ScN} - \mu_N$. The values of all chemical potentials used here for estimating defect formation energies are listed in Table 2.

Table 2. Chemical potentials (in eV) used for calculation defect formation energies under N-and Al- rich conditions.

	μ_{Al}	μ_N	μ_{Sc}
N-rich	-6.947	-7.955	-10.555
Al-rich	-3.744	-11.158	-7.325

3. Results

3.1. Electronic structure

The densities-of-states (DOS) for the perfect AlN supercell and that with relaxed N- and Al-vacancies and Sc in Al substitution are presented in Fig.2. As seen here, the calculated bandgap is 4.1 eV, which is underestimated compared to the measured value of 6.12 eV [48]. It can be seen that defects affect the DOS. The Al vacancy shifts the whole density of states slightly towards lower values of the Fermi energy, whereas the DOS shifts significantly, by the whole bandwidth, in the case of the N-vacancy. Sc substituting for Al atom provides a negligible modification to the DOS. Similar to previously published results [19], we found that a vacancy in Al site leads to the formation of triplet states at the bottom of the gap occupied by three electrons, while, the nitrogen vacancy forms two states occupied by two electrons right above the valence-band and a triplet state

at the top of the gap close to conduction band containing one electron. Substitution of Al by one isoelectronic Sc atom does not result in information of any new states. The observed underestimation of the bandgap is typically observed in the traditional density functional approach [20]. This challenge can be addressed by utilizing either the GW [49] or the hybrid functional (HF) [5, 50] approaches to accurately incorporate exchange-correlation effects. A comparison of different techniques for the bandgap estimations was presented in [51] and it was concluded that more complicated techniques, such as GW, are likely to provide better results on the electronic structure than DFT-based methods. However, the defect formation energies are not significantly different. The latter properties are of main importance in the current work addressing the Sc-doping

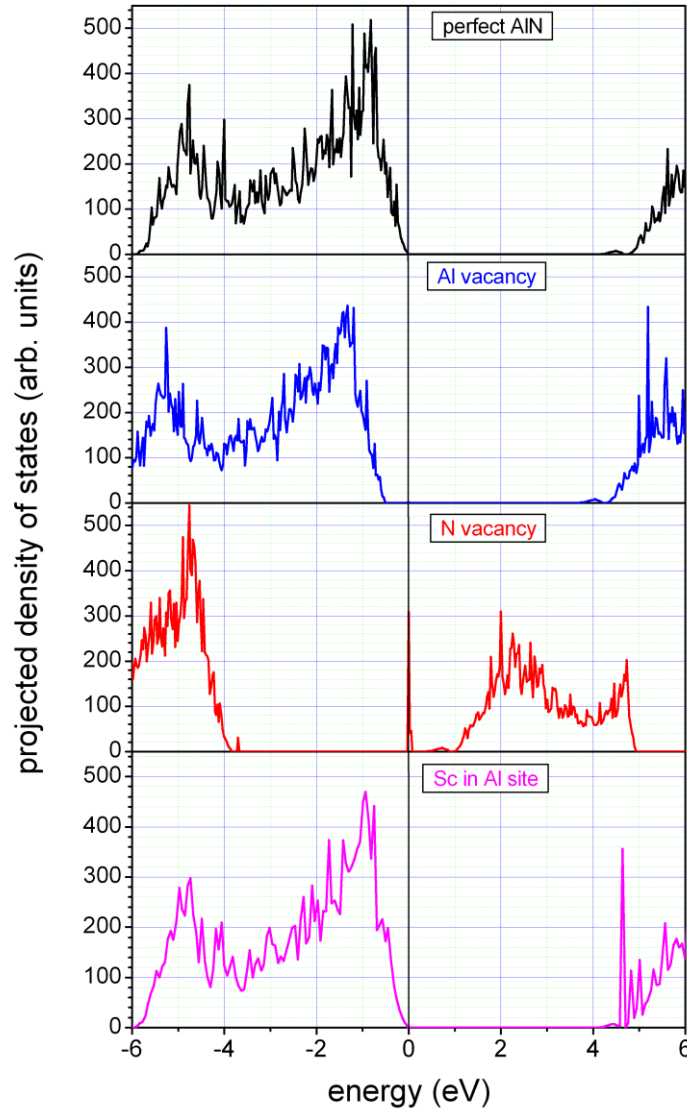


Fig. 2. Density of states for the perfect AlN supercell and including some native defects.

effects to defects energetics. Moreover, the complexity of the GW and HF calculations makes them hardly applicable to large supercell calculations while calculation of defect properties in small supercells results in errors that exceed the errors from an underestimated bandgap value. This effect is important for interstitial defects that, in general, need larger supercells than vacancy and substitution defects. The modeling approach used here allows us to model supercells larger than previously reported studies that we consider preferable for radiation defects study.

3.2. Point defects in the pristine and Sc-doped AlN

Defects in materials can be formed in different ways, such as temperature, deformation, and irradiation by energetic particles. Defects formed due to permanent ambient conditions such as temperature, are native and coexist at thermodynamic equilibrium. These defects are important for understanding properties and evolution under equilibrium or relaxation towards equilibrium conditions such as diffusion, segregation, and phase transformations. As native defects we consider here vacancies in both Al and N sites (noted as V_{Al} and V_N respectively), antistites that are Al in N sites (noted as Al_N), and N in Al sites (noted as N_{Al}), and Sc substitution in Al and N sites (noted as Sc_{Al} and Sc_N). Native defects are expected to be formed during material fabrication and their concentration depends on the equilibrium conditions considered. To estimate these correctly, defect energies need to be calculated for the applicable charge states and their minima should be used for thermodynamic equilibrium estimations. The possible charge states for the native defects in AlN were discussed in [19] and are used here for formation energy calculations. Doping by Sc-atoms in Al sites does not introduce new gap states and thus we have considered only the neutral charge state for Sc_{Al} .

Under irradiation conditions defects are formed due to ballistic effects and their evolution does not follow thermodynamic equilibrium conditions. Moreover, the charge states of primary damage defects, such as vacancy and interstitial atoms and their small clusters, are unidentified, and probably depend on the irradiation conditions for ions, electrons, and neutrons, combined with bulk and local composition. Interstitial atoms are typical examples of radiation induced defects and were not considered previously among the native defects for equilibrium conditions because of their high formation energy. Very limited information on interstitial atoms in AlN has been reported so far: the considered N interstitial atom configurations are octahedral and tetrahedral in [19, 20, 32] and a tilted $\langle 11\bar{2}0 \rangle$ -dumbbell in [32]. Like other hexagonal lattices, wurtzite

produces several structurally stable configurations for both Al (I_{Al}) and Ni (I_N) interstitial atoms that may play a role in their mobility under irradiation conditions and thus should be investigated. For example, in hcp Zr interstitial atom migration mechanism involves multiple transitions between different configurations [52, 53]. Interstitial defects were studied here, and several configurations of N, Al, and Sc interstitials and their structure are described below.

Not much information is known on the real defect charge states in AlN at irradiation conditions. Limited information is available on the vacancy-type defects in [54], where annealing of the optical absorption and electron spin resonance was studied after neutron irradiation. F and F+ center, i.e. N-vacancies that may trap one or two electrons, were observed. In our calculations, we considered charge states for different defects depending on their ability to capture or give electrons as discussed in [19]. Table 3 contains defect acronyms and short descriptions, considered charge states, and energy of neutral defects presented for general information and qualitative comparison of different configurations. Some details on the structure and energy properties are presented in the following sections: the structure of point defects in Section 3.2.1, charge dependence of the formation energy of substitution, vacancy and interstitial defects in AlN in Section 3.2.2, the effect of Sc-doping on the defect energy properties in Section 3.2.3, and Sc-doping effect to structure and energy of Frenkel pairs in Section 3.2.4.

Table 3. Abbreviation, charge state of all the defects considered and their formation energy obtained after relaxation at a neutral charge state. For complexes of two defects, “in” and “out” mean that defects are at the nearest neighbors in the same or different (0001) planes respectively.

Abbreviation	Charge states considered	Defect description		Formation energy, eV	
				Al-rich	N-rich
V_{Al}	-3 -2 -1 0	Vacancy in Al site		9.79	6.59
V_N	+1 +2 +3	Vacancy in N site		3.29	6.49
Al_N	-1 0 +1 +2 +3	Al substitution in N site		14.73	8.61
N_{Al}	-1 0 +1 +2	N substitution in Al site		6.59	12.70
I_{Al}	0 +1 +2 +3	Al interstitial atom	$I1_{Al}:\langle 11\bar{1}21 \rangle$ d-b	12.61	9.70
			$I2_{Al}:\langle 11\bar{1}20 \rangle$ d-b	14.02	11.11
			$I3_{Al}:\langle 10\bar{1}10 \rangle$ d-b	14.15	11.24
			$I4_{Al}:$ O	12.90	9.99
			$I1_N:\langle 11\bar{1}21 \rangle$ d-b	7.71	4.51

I_N	-1 0 +1	N	I_{2N} : T	8.50	5.30
Sc_{Al}	0	Sc atom substitution in Al site		1.03	1.95
Sc_N	-1 0 +1 +2 +3	Sc atom substitution in N site		16.53	22.96
Sc+Sc	0	2 Sc atoms in Al sites	in	2.26	2.32
			out	2.14	2.19
Sc+vacancy	-3 -2 -1 0	$Sc_{Al}+V_{Al}$	in	11.26	8.08
			out	10.94	7.76
	0 +1 +2 +3	Sc+ V_N	in	2.488	
			out	2.236	
Sc+interstitial atom	0 +1 +2 +3	Sc+ I_{Al}	$I_{Sc} : I_{Sc-oct}$	9.985	
			$I_{2Sc} : Sc_{Al}+I_{4Al}$	9.112	
	-1 0 +1	Sc+ I_N	$Sc_{Al}+I_{1N}$	7.258	0.851
			$Sc_{Al}+I_{2N}$	8.411	2.005

3.2.1. Structure of point defects in the pristine and Sc-doped AlN

Native defects such as vacancies and antistites usually relaxed into structurally stable configurations with a weak relaxation of surrounding atoms, except, maybe the Al in N site substitution that provoked significant atomic distortions, being nevertheless structurally stable. This configuration has quite a high formation energy $E^f = 14.73$ eV (herein and after, for brevity, we compare only Al-rich conditions; values for N-rich conditions can be found in Table 3).

Interstitial atoms are more complicated defects because of the variety of their configurations and their highly asymmetric character. Four structurally stable Al interstitial atom configurations are presented in Fig.3. Fig.3a shows the configuration that can be described as a dumb-bell along close to $[11\bar{2}1]$ direction, denoted as I_{1Al} in Table 3. The distance between dumb-bell atoms $d = 2.21$ Å and the formation energy at the neutral charge state $E^f = 12.605$ eV. One can see the left Al atom has three Al-N bonds whereas the right atom has only two Al-N bonds. Another dumb-bell configuration in the $(\bar{1}100)$ plane split along the $\langle 11\bar{2}0 \rangle$ direction is shown in Fig.3b (I_{2Al} in Table A). In this dumb-bell Al atoms are closer to each other: $d = 2.18$ Å, but the neutral charge formation energy is higher: $E^f = 14.02$ eV, while Al-N bonds are distributed in the same way as for the above I_{1Al} configuration. A symmetric dumb-bell in (0001) plane along $\langle 10\bar{1}0 \rangle$ direction is shown on Fig.3c (I_{3Al} in Table 3). This configuration is characterized with $d = 2.24$ Å, $E^f = 14.15$

eV and both dumb-bell atoms have three Al-N bonds each. The most stable orientation, at neutral charge state, was found to be a slightly asymmetric octahedral configuration shown in Fig.3d ($I4_{Al}$ in Table A). Interstitial Al atom relaxed at the distance 1.35 Å N-plane and 1.41 Å from Al-plane with formation energy $E^f = 9.70$ eV and three equal length Al-N bonds: $d_{Al-N} = 1.87$ Å. Note that $d_{Al-N} = 1.94$ Å in the perfect AlN crystal. The globally stable configuration of a neutral charged Al interstitial depends on the conditions: at Al-rich conditions it is an octahedral interstitial, whereas the most stable configuration at N-rich conditions is $[11\bar{2}1]$ dumbbell as seen in Table 3.

Two structurally stable configurations were found for N interstitial atoms. They were relaxed from initial tetrahedral or octahedral positions, but their final configurations are neither of these two as can be seen in Figs. 4. N interstitial atom initially inserted into octahedral or $\langle 11\bar{2}0 \rangle$ -dumbbell position has relaxed into N-N dumb-bell oriented along the $\langle 11\bar{2}1 \rangle$ direction with distance between N-atoms is $d_{N-N} = 1.40$ Å (see Fig.4a). Initially created N interstitial in tetrahedral position has relaxed into N-N dumb-bell oriented exactly along the $[0001]$ direction with a

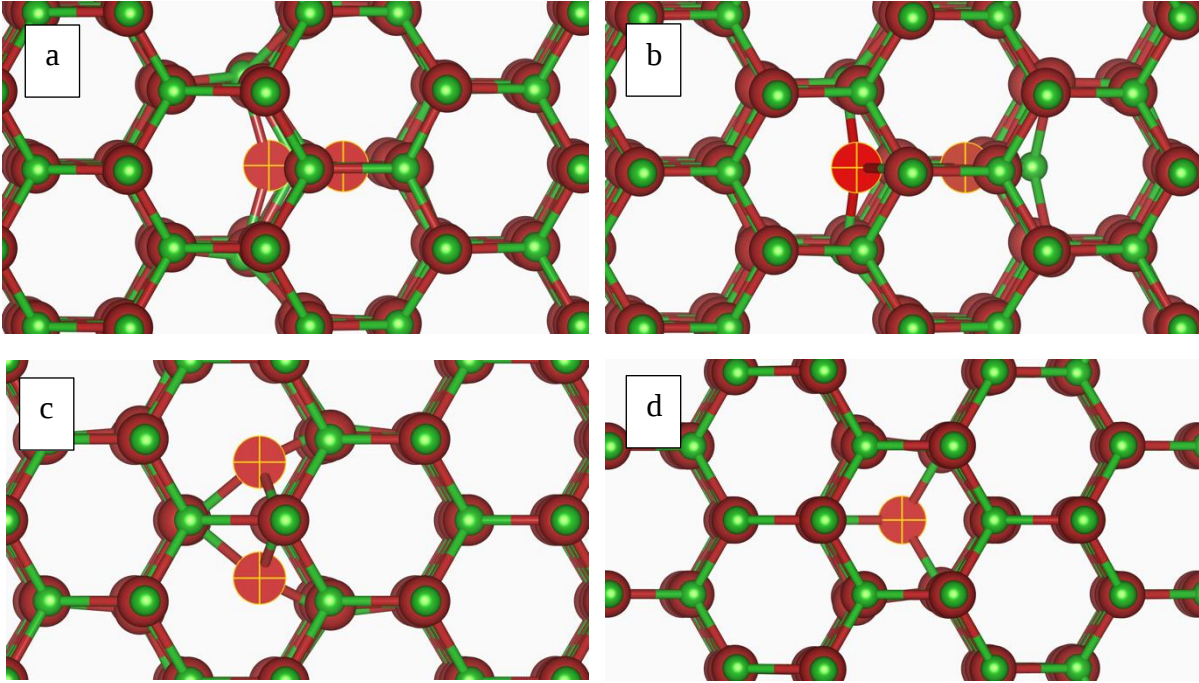


Fig.3. Neutral charge state configurations of Al interstitial atom (crossed) projected onto (0001) plane:

- a - dumb-bell in $(\bar{1}100)$ plane along close to $\langle 11\bar{2}1 \rangle$ direction;
- b - dumb-bell in $(\bar{1}100)$ plane along $\langle 11\bar{2}0 \rangle$ direction;
- c - dumb-bell in (0001) plane along $\langle 10\bar{1}0 \rangle$ direction;
- d - octahedral configuration with a slight asymmetry.

distance between N-atoms of $d_{N-N} = 1.38 \text{ \AA}$ (see Fig.4b). The main difference of this configuration from the regular tetrahedral interstitial is preferential relaxation of atoms along the $[0001]$ direction, whereas the tetrahedral configuration assumes three-dimensional relaxation of all the surrounding atoms. The $\langle 11\bar{2}0 \rangle$ dumbbell is more stable than the tetrahedral configuration for both Al- and N- rich conditions as seen in Table 3.

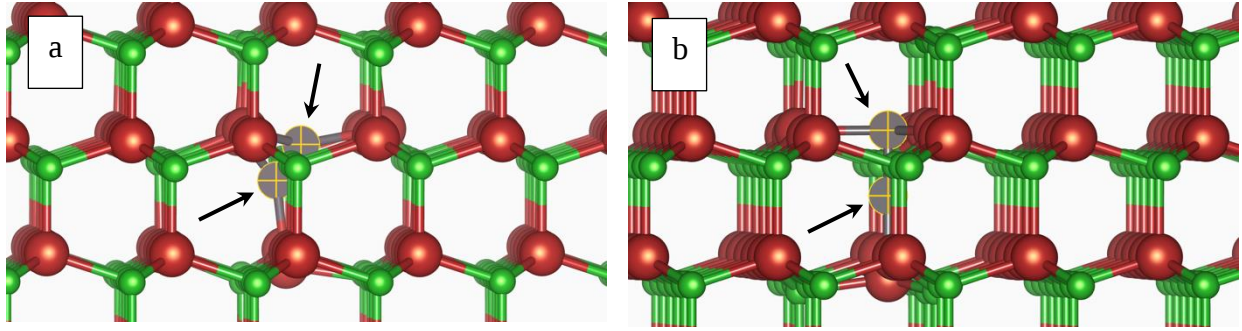


Fig.4. Neutral charge configurations of N interstitial atom (gray crosses indicated by arrows) projected onto $(11\bar{2}0)$ plane initially inserted into (a) octahedral or $\langle 11\bar{2}0 \rangle$ -dumbbell, and (b) tetrahedral configuration and relaxed at the neutral charge states.

When doping, the simplest defect is Sc replacement of Al atom: it is structurally stable and has a low formation energy. Two neighboring Sc replacements of Al atoms can form two configurations either in the same or different (0001) planes. Both are stable defects with very similar energies as can be seen in Table 3. On the contrary, Sc replacement of N atoms leads to a significant relaxation when two atoms, Sc inserted into N position and the closest Al, move significantly from their initial positions as shown in Fig.5. The distance between the marked Sc and Al atoms is $d_{Sc-Al} = 2.25 \text{ \AA}$, compared with the equivalent distance in perfect crystal $d_{N-Al} = 1.91$

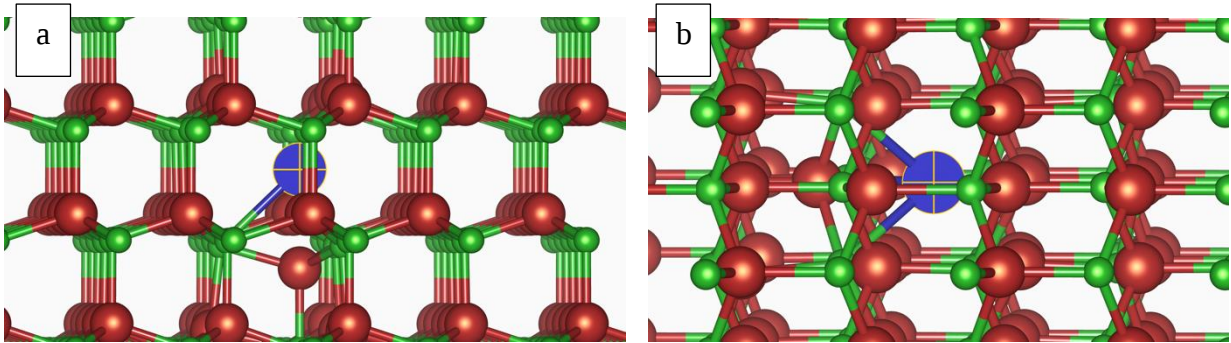


Fig.5. Relaxed neutral charge configuration of Sc atom (blue cross) substituting N projected onto (a) $(\bar{1}100)$ and (b) $(11\bar{2}0)$ planes.

Å (see Table.3). For the Sc interstitial, we have observed only two stable symmetric configurations. Sc in the octahedral position has formation energy: $E^f = 9.99$ eV ($I1_{Sc}$ in Table 3) whereas a configuration where Sc replaces an Al atom that is pushed out to the octahedral configuration has a lower neutral state energy $E^f = 9.11$ eV ($I2_{Sc}$ in Table 3). Both configurations are similar to that shown in Fig.3d with the only difference being the $I1_{Sc}$ Sc atom is in the octahedral position atoms whereas for $I2_{Sc}$ one of the closest to octahedral atom Al sites is occupied by Sc.

3.2.2 Energy of charged defects in AlN

The formation energies of native defects as functions of Fermi energy, E_F , are presented in Fig.6, for N- and Al- rich conditions. The Fermi energy was varied within a range slightly wider than the bandgap width, i.e. 5 eV instead of 4.1 eV, to show their behavior near the bandgap maximum. For each defect, we present only the segment of the whole charge state dependence related to the minimum energy among the other states at the current E_F level. Due to its relatively

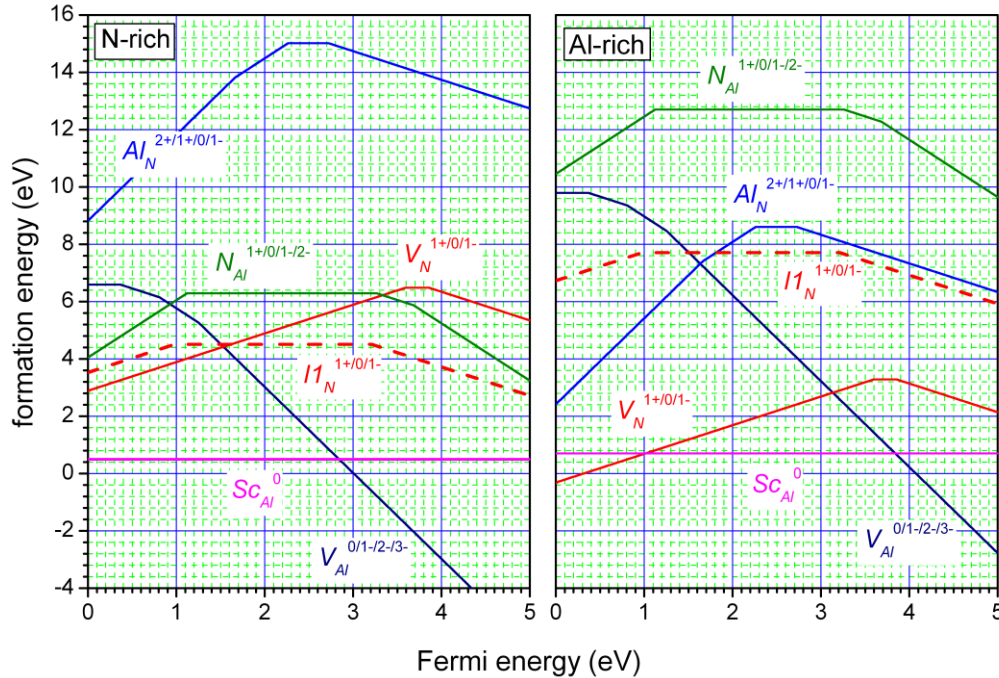


Fig.6 Formation energy of native defects in AlN as function of Fermi energy under N- and Al-rich conditions. Only the lowest energy segments are indicated for a particular charge state. Defect abbreviations and considered charges are explained in the Table 3.

low formation energy and previous studies [19,20], we also included an N-interstitial in configuration II_N among the native defects.

Radiation may induce interstitial defects and, therefore, here we considered two N-interstitials and four Al-interstitials whose structures are shown in Figs. 3 and 4 for the neutral state. Since each defect may have different charge states the total picture looks quite complicated and the relative stability of different defects depends strongly on E_F . Moreover, defect stability is quite different for the N- and Al- rich conditions considered here. The most stable defects are vacancies, thus V_{Al} may have very low formation energy when negatively charged. The structure of vacancies does not depend on their charge state; the charge state only slightly affects the length of local bonds. Another relatively stable defect is the N interstitial atom in configuration denoted as II_N in Table 3. However, the detailed structure of this defect depends on its charge state as can be seen in Fig. 7. Thus, at $q=+1$ (Fig. 7c) its structure is similar to that at the neutral state (compare with that in Fig.4a). At $q=-1$ it changes from the $\langle 11\bar{2}1 \rangle$ -dumbbell to the $\langle 10\bar{1}0 \rangle$ -dumbbell, which now lies exactly in the (0001) plane as seen in Fig. 7a-b. As a result, II_N can be quite stable near

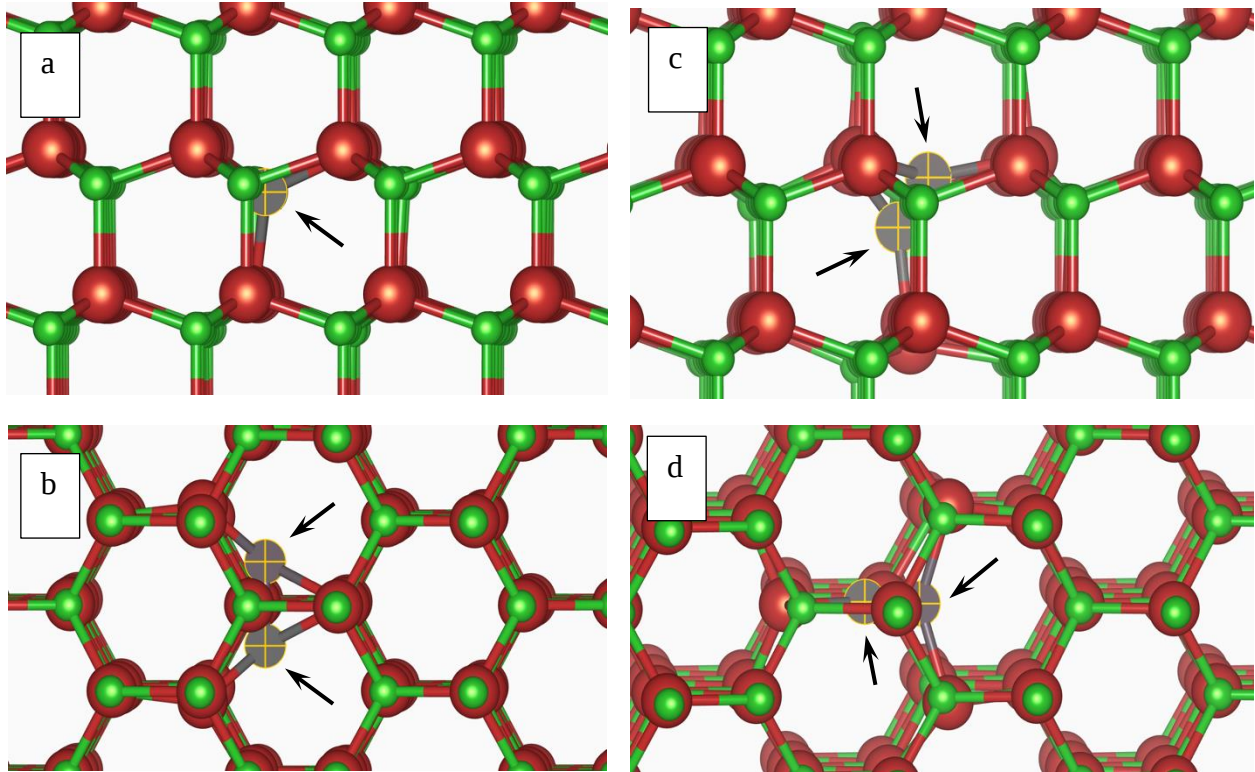


Fig.7 Structure of N-interstitial atom (gray crossed spheres indicated by arrows) in configuration II_N , at different charge states: (a, b) $q=-1$; (c, d) $q=+1$, projected onto different planes: (a, c) - $(11\bar{2}0)$ plane; (b, d) - (0001) plane.

both valence band maximum (VBM) and conduction band minimum (CBM), especially at Al-rich conditions.

Additional interstitial atom configurations in AlN were investigated at different conditions and the results on their formation energy are presented in Fig.8. Positively charged Al-interstitial can be stable near the VBM, whereas all of them have very high formation energy near the CBM. Importantly, the difference in formation energy of different interstitial defects of the same type is insignificant and sometimes their relative stability changes depending on the Fermi energy.

Assuming the variety of particular conditions between Al-rich and N-rich limiting cases, one can suggest that the defects shown in Fig.8, except antisites Al_N and N_{Al} , can be present in AlN system under certain thermodynamically equilibrium and charge conditions and, thus, could be considered as native defects.

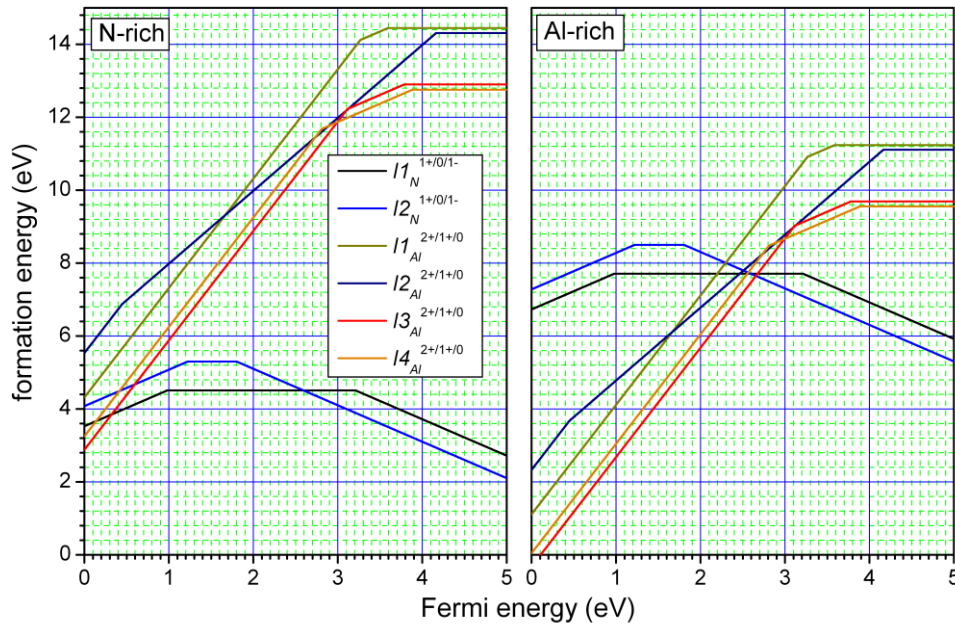


Fig.8 Formation energy of interstitial point defects in AlN as function of Fermi energy under N- and Al- rich conditions.

3.2.3 Energy of defects in Sc-doped AlN

Formation energies of the most stable interstitial defects in the pristine and Sc-doped AlN crystals as a function of Fermi energy are presented in Fig. 9. Data for the pristine AlN, solid lines, are presented for a visual demonstration of how the defect's relative stability can be changed depending on the charge state and fabrication conditions (i.e. N-rich or Al-rich): Sc-doping, shown

by dashed lines, can either increase or decrease the defect formation energy, introducing a quite overall complicated effect.

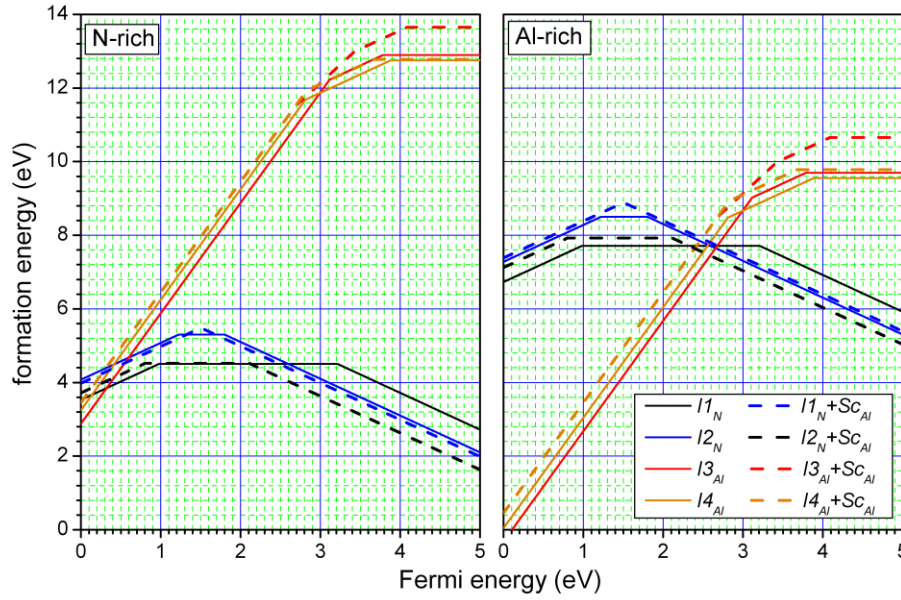


Fig.9 Formation energy of interstitial defects in the pristine and Sc-doped AlN as function of Fermi energy under N- and Al- rich conditions. Defect's abbreviations are explained in the Table 3.

Among all energy properties, the most accurate calculations are for binding energies because according to eq. 2 all chemical potentials can be eliminated and the binding energy value can be expressed as a combination of the relaxed energies of the corresponding configurations. In calculating Sc-dopant binding energy with the particular configuration, we always considered Sc substitution of the Al atom closest to the defect. The Sc-defect binding energy was calculated using the formation energies of the separate defect (E_D^f) and Sc atom ($E_{Sc_{Al}}^f$) and Sc-defect complex (E_{D-Sc}^f) taken from Figs. 8 and 9 and Table 3, according to Eq.(2). The resulting behavior of $E_{D-Sc}^b(F_F)$ varies for different defects as seen in Fig.9. Thus Sc-Sc interactions demonstrate charge-independent weak repulsion, -0.09 eV (two Sc atoms in the same (0001) plane, i.e. Sc+Sc in) and -0.22 eV (two Sc atoms are in different (0001) planes, i.e. Sc+Sc out), that should lead to a low probability of their precipitation. The Al vacancy repels an Sc atom and its initially negative binding energy decreases more towards the CBM level. Nitrogen vacancy has a weak attraction with Sc-dopant $E_{V_N-Sc}^b \sim 0.1\text{eV}$ and $\sim 0.3\text{ eV}$ when they are in different and the same (0001) planes respectively, with a narrow strong binding $E_{V_N-Sc}^b \sim 1.0$ near the VBM. Interstitials have attractive

interaction with Sc with the different effects of the Fermi level. Binding energy with N interstitials increases at higher Fermi levels up to >1 eV, whereas that for Al-interstitials increases only up to $\sim 0.3-0.5$ eV. We have found that Sc-dopant may change the interstitial configuration structure. For example, as discussed above $I1_N$ may change configuration depending on the charge state, and the most stable is the $\langle 10\bar{1}0 \rangle$ -dumbbell charged with $q = -1$ (see Fig.10a). However, in the presence of a Sc atom at the same charge state changes the configuration back to the $\langle 11\bar{2}1 \rangle$ -dumbbell (see Fig.10b), similar to that observed at the neutral state (see Fig.3a).

3.2.4 Frenkel pairs in Sc-doped AlN

The Frenkel pair (FP) is a basic radiation induced defect formed at the primary damage stage due to collision effects. In the AlN system two types of FPs can be considered: Al-FP consists of a vacancy at an Al site and an Al interstitial atom, and N-FP that consists of an N vacancy and an interstitial atom. Interstitial configurations considered were $I4_{Al}$ (octahedral) for Al-FP and $I1_N$ ($\langle 11\bar{2}1 \rangle$ -dumbbell) for N-FP. Depending on the irradiation conditions, FPs with different separation, d_{FP} , between the constituent defects are formed and those with a short d_{FP} usually recombine within a short time after the collision event. Widely separated FPs behave isolated vacancies and interstitials and the Sc-dopant effect can be estimated correspondingly, e.g. using data from Fig.10. We observed that defects in the first two coordination spheres were unstable and recombined during relaxation. The closest stable Al- and N- FPs modelled here have $d_{FP} \approx 3.7-3.8$ Å whereas the widest investigated separation, $d_{FP} \approx 11.0-11.5$ Å, was limited by the supercell size used here. The effect of doping with Sc was estimated for the maximally separated FP of each

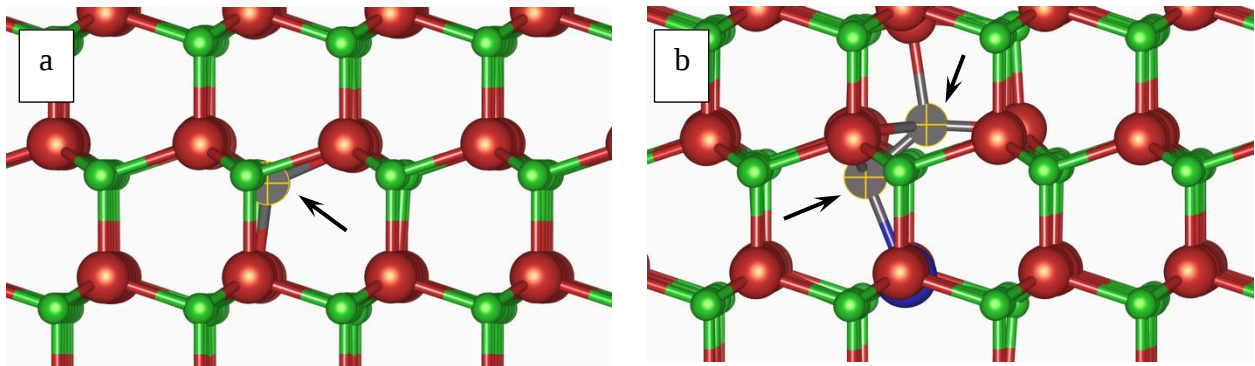


Fig.10. Configurations of N interstitial atom $I1_N$ (crossed gray spheres indicated by arrows) charged with $q = -1$ and projected onto $(11\bar{2}0)$ plane: (a) in pure AlN; (b) with Sc substitution in the nearest Al site (blue sphere).

type by substituting an Al atom, close to the center of the line between FP defects, by a Sc atom. The Sc-FP binding energy calculated via eq. (2) was found to be negative for Al-FP, $E_{FP-Sc}^b(FP+Sc)=-0.246$ eV, and positive for N-FP, $E_{FP-Sc}^b(FP+Sc)=+0.105$ eV. The repulsion from the Al-FP and attraction to the N-FP can be qualitatively understood if one takes into account the results for Sc binding with different defects presented in Fig.10 above. While more configurations need to be modelled for a complete understanding of the Sc effect on FPs stability the results presented here indicate clearly that Sc may affect the stability of FPs during irradiation.

4. Discussion

Formation energies of native defects reported in the literature were studied using different approaches. Thus, plane wave based approach with exchange-correlation considered in local density approximation (LDA) was used to model vacancies in [56]. Both LDA and GGA for the exchange-correlation functional were used in [19, 57]. FPLAPW method implemented in WIEN2K package was applied in [20] and HSE06 screened hybrid functional was used to model N-vacancy in [5]. The supercell size varied from 32 atoms in [19, 56] and 72-atoms in [20] to 96-atoms in [5, 57]. Overall, all the above approaches resulted in similar native defect formation energies and their charge state dependence and the results obtained here are within the range reported in the literature for different techniques. For example, this can be seen by comparing data in Fig.86 with the corresponding states presented in Fig. 4 or ref. [19], Fig. 1 in ref. [20] and Fig. 1 in ref. [5]. The energies obtained here are slightly higher than some published values, see e.g. N-vacancy data in Fig. 3 here and Fig. 1 in ref. [5]. The significantly larger supercell used here, i.e. 360-atoms, should provide a larger relaxation thus reducing the formation energy however this is compensated by the positive correction term E_{corr} in eq. (1). Overall, previously published results and results obtained here has demonstrated similar accuracy of the applied approaches in calculating defect formation energies. Applying a large supercell should result in more accurate configurations and energies for interstitial and Frenkel-pair defects modelled here.

A number of new interstitial configurations were observed in pure AlN are N- and Al-interstitial configurations and Sc as shown in Table 3 and Figs. 3, 4, 7 and 11. The most stable neutral Al- and N- interstitials were found to be $[11\bar{2}1]$ dumbbell, I_{Al} and I_N respectively. However, the relative stability of different interstitial configurations depends on the manufacturing conditions and charge state as seen in Fig.8. We have found only one description of interstitial

atom configuration in AlN observed in [32] after relaxing small energy collision events at the neutral state using SIESTA code. It was reported that N-FPs always include N-interstitial in configuration $\langle 11\bar{2}1 \rangle$ like the one considered here, I_{1N} at the neutral state (see Table 3 and Fig.3a), whereas Al primary knock-on atoms always produce Al-interstitials in the octahedral configuration as observed here for Al-rich conditions (see Table 3 and Fig.4d). These, the most stable, interstitial configurations were used to model Al- and N- Frenkel pairs in this work.

Sc substitution in Al sites was found to be rather stable, see Table 3 and Fig. 6, and does not strongly affect the DOS as seen in Fig. 2. The interaction between two Sc atoms is weak and negative, implying impediment of the nucleation of Sc-precipitates and thus predicting no clustering, at least, at dilute concentrations. However, Sc atoms affect the stability of different point defects. Thus Sc substituting for Al is far more stable than substituting N, as seen in Table 3. Moreover, Sc substituting for Al does not affect the charge state. Irradiation conditions assume that defects are formed due to collision events and defect evolution under irradiation is not governed by thermodynamic conditions defined by defect formation energies. Instead, this is a result of kinetic processes due to interactions between mobile defects and existing microstructures and the defect binding energy is the main driving force of microstructure evolution under irradiation conditions. The binding energies considered here are among the basic necessary parameters for evaluating radiation effects in Sc-doped AlN. All binding energies calculated here at different charge conditions are presented in Fig. 10. Al-vacancy repels Sc atom, suggesting a weak effect of Sc to vacancy evolution and a weak vacancy contribution to Sc transport. N-vacancy has positive binding energy with Sc, $\sim 0.1\text{-}0.9$ eV, which suggests a reduction of vacancy mobility and possible preferable nucleation of vacancy clusters near Sc dopants. Also, Sc can tightly bind both N and Al interstitials thus reducing their mobility. Especially strong binding is observed with N-interstitials near CBM. Taking into account that N transport under irradiation is likely to occur by interstitial migration, this suggests preferential nucleation of N-interstitial clusters around Sc dopants. This effect should be more profound at negative charge conditions.

Currently, there are no robust models that allow to consideration of local states of defects, i.e. their Fermi energy and charge, and their effect on defect evolution under irradiation. In practice some additional assumptions are made to simplify the picture presented in Fig.7. For example, in [58, 59] for modeling defect evolution in UO_2 the defect Fermi levels were assumed to be at mid-bandgap. Applying the same approach here, this is around $E_F \sim 2$ eV. According to the data in

Fig.10, at this energy the main Sc effects are a) repulsion with Al vacancy; b) weak repulsion between Sc atoms; and c) significant attraction to both N and Al interstitials.

5. Conclusions

In this work, we performed extended DFT modeling for different vacancy, substitution, and interstitial defects including small defect clusters (Frenkel pairs) that cover native and primary radiation induced defects in the wurtzite pristine AlN and Sc-doped AlN, materials relevant to sensor applications in nuclear reactor environments. Large supercell size and accounting for finite modeling cell size correction guaranteed accurate results on configurations and formation and binding energy estimations that is particularly important for interstitial and Frenkel-pair defects. We presented a detailed description of the possible aluminum, nitrogen, and scandium interstitial atom configurations, and the charge effect to their configurations, formation and binding energies is demonstrated. It was found that the most stable defects are neutral N and positively charged Al interstitial defects.

We estimated the binding energies of Sc dopant atom with point defects, which are relevant for radiation damage processes, with the following main conclusions of the Sc-doping effects in defect energetics:

- Al vacancy repels the Sc atom suggesting a generally weak effect of Sc to vacancy evolution and Sc transport by vacancy mechanism;
- N vacancy and both Al and N interstitials have attractive interaction with Sc atom that reduces their mobility;
- Strong positive N interstitial interaction with Sc suggests preferential nucleation of N-interstitial clusters associated with Sc substitutions.
- Sc-doping stabilizes the Frenkel pairs by reducing their formation energy and increasing recombination radius.
- Weak repulsion between two Sc atoms preserves the formation of Sc precipitates.

Sc-doped AlN is a promising material for sensors in nuclear reactor environments that subjected to high radiation. For predicting modeling of radiation response in this material at higher scale, further investigation of the defect properties, such as diffusion barriers, elastic properties, and their sensitivity to charge states is necessary.

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