

A DFT Study of Adsorption of Gallium and Gallium Nitrides on Si(111)

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Abstract Adsorption of gallium (Ga, Ga⁺) and gallium nitrides (GaN, GaN⁺, GaN₂, GaN₂⁺) on a model Si(111) surface was studied by density functional theory calculations. In total 30 structures were determined. The binding energies (corrected for basis set superposition error) of the lowest structures were found to be 2.13 for Ga, 2.39 for Ga⁺, 4.23 for GaN, 6.13 for GaN⁺, 1.90 for GaN₂, and 2.13 eV for GaN₂⁺. Low-lying bridged structures, with the adsorbate bridging the Si rest atom and adatom were found for the diatomic and the triatomic neutral and cationic nitrides. Moreover, for the diatomics, structures with Ga-N vertical, attached to a Si adatom or a Si rest atom were also found. From electron charge distribution analysis it is confirmed that the Si cluster acts as a pool of electronic charge resulting in the adsorbed Ga and Ga⁺ to have similar net charges.

Keywords: DFT calculations, gallium nitrides, Si(111), adsorption

1 Introduction

There is great interest in the study of chemisorption of group III metals and their nitrides at Si surfaces, especially in the geometric and electronic structure of the interface [1–3], in the change of the surface associated with metal diffusion on the surface and in the formation of metal-adsorbate atomic wires as well as the self-assembly of perfectly ordered nanocluster arrays [4, 5]. Moreover, the growth of GaN films on Si surfaces [6, 7] has great potential for application in optoelectronic devices and high-power, high-temperature electronic devices [6–8]. Although there are many experimental studies of gallium nitrides at Si(111) [4–8], as far as we know, there have not been as many theoretical studies, and most of them are on Ga at Si [1, 3].

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The present work is a continuation of our previous study of chemisorbed structures of gallium (Ga, Ga⁺) and gallium nitrides (GaN, GaN⁺, GaN₂, GaN₂⁺) on Si(111) using density functional theory (DFT) calculations and a Si₂₆H₂₂ model of the Si(111) surface [9]. In the present work more structures are presented and the distribution of the electron charges is analyzed confirming that the Si cluster acts as a pool of electronic charge resulting in the adsorbed Ga and Ga⁺ to have similar net charges for all three neutral or charged adsorbates.

2 Computational Approach

Chemisorbed structures of Ga, Ga⁺, GaN, GaN⁺, GaN₂, and GaN₂⁺, at Si(111) are calculated at a 5-layer one-rest one-atom (1R-1A) cluster model of Si(111) (see Fig. 1) constructed as before [9, 10] using the dimer-atom-stacking fault (DAS) structure [11] and the LEED data of Tong et al. [12] for the Si(111) reconstructed surface. Hydrogen atoms (white spheres in Fig. 1) have been added to terminate the 26-Si atom cluster (grey spheres ≡ Si) at the sides as well as below the lowest Si level, while the adatom and rest atom are left with one dangling bond each, i.e., one unpaired electron.

Preliminary calculations were carried out on parts of the structures of interest in order to determine an adequate combination of functional and basis set. The diatomic GaN, GaN⁺, SiGa, and SiN and triatomic GaNSi, GaN₂ and GaN₂⁺ molecules were investigated using different kinds of basis sets such as LANL2DZ, 6-31+, 6-31(d), 6-311+G(2df), DGDZVP and functionals such as B3LYP, UB3PW91, UPBEPBE and LSDA. The results were compared with available experimental values and existing medium or high quality calculations in the literature. In the case of the GaSi and GaNSi molecules, where there is no theoretical or experimental work in the literature, calculations were carried out employing the second and fourth order perturbation theory (MP2, MP2(full), MP4) and the coupled cluster technique CCSD(T), combined with the augmented correlation-consistent basis aug-cc-pVTZ [9]. Calculations on the Si(111) cluster were done using the LANL2DZ, 6-31+, 6-31(d), and DGDZVP basis sets and the B3LYP functional.

Thus, we concluded that the best and computationally tolerable (since the systems studied have about 50 atoms) combination of functional and basis set for

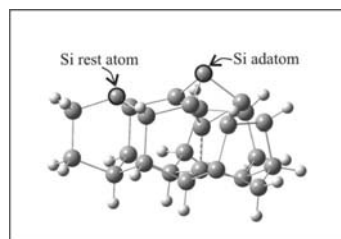


Fig. 1 5-layer one-rest one-atom (1R-1A) cluster model of Si(111)

diatomics and triatomics and consequently for the chemisorbed gallium nitrides on Si(111) is the B3LYP/DGDZVP. B3LYP is a DFT functional using Becke's three parameter gradient corrected functional [13] with the gradient corrected correlation of Lee et al. [14]. The DGDZVP basis set is a double-zeta valence plus polarization, i.e., [3s2p1d_N/4s3p1d_{Si}/5s4p2d_{Ga}] [15].

Employing the B3LYP/DGDZVP technique the electronic and geometric structures of chemisorbed gallium (Ga, Ga⁺) and gallium nitrides (GaN, GaN⁺, GaN₂, GaN₂⁺) on the 5-layer 1R-1A cluster (cf. Fig. 1) were investigated. Three chemisorbed structures for each of Ga-Si(111); four for Ga⁺-Si(111); eight for GaN-Si(111); six for GaN⁺-Si(111); two for GaN₂-Si(111); and seven for GaN₂⁺-Si(111) were determined by energy optimization with respect to the coordinates of the Si rest and Si adatom as well as those of the adsorbed species. The remaining cluster was kept fixed in order to retain the Si(111) surface structure.

For all stable geometries, binding energy (BE) and the corrected values with respect to the basis set superposition error (BE_{BSSSE}) [16] of each species on the surface were calculated. All calculations were done using the Gaussian 03 program package [17].

3 Results and Discussion

The structures which were calculated for Ga- and Ga⁺-Si(111) are given in Fig. 2, for GaN- and GaN⁺-Si(111) in Fig. 3, and for GaN₂- and GaN₂⁺-Si(111) in Fig. 4. The minima which have been determined are labeled by 2 characters followed by the name of the adsorbed species. The first character refers to the spin multiplicity, and the second to the geometric structure. E.g., **2a-Ga**, means that the minimum

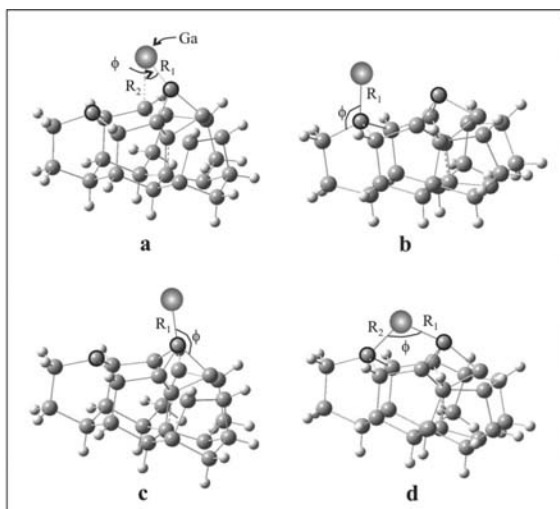


Fig. 2 Four structures of Ga-Si(111) and Ga⁺-Si(111)

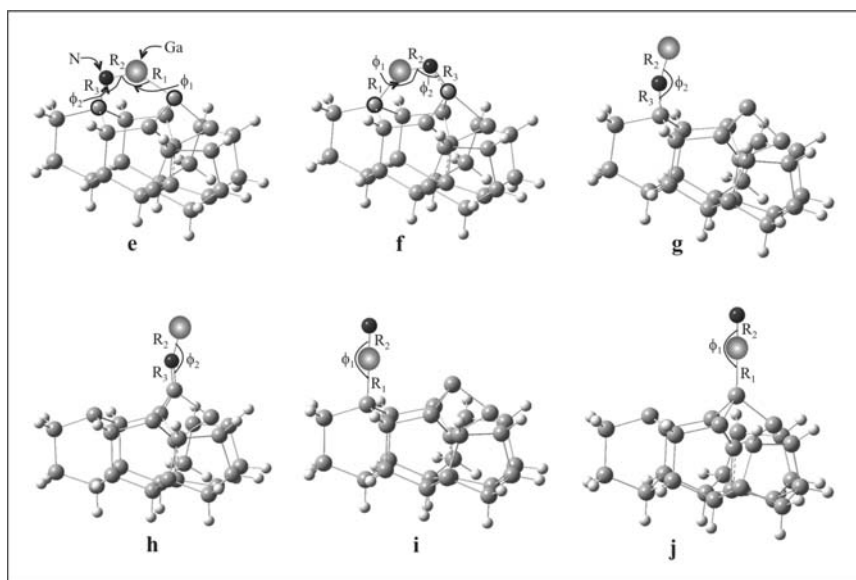


Fig. 3 Six structures of GaN-Si(111) and GaN⁺-Si(111)

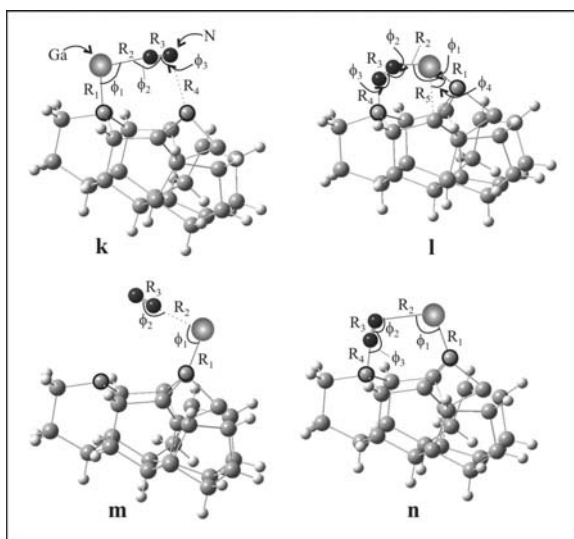


Fig. 4 Four structures of GaN₂-Si(111) and GaN₂⁺-Si(111)

is a doublet corresponding to the **a** structure shown in Fig. 2 of the Ga-Si(111) cluster. The geometry, the binding energy and the natural population analysis of the structures determined are given in Table 1 for Ga- and Ga⁺-Si(111), in Table 2 for GaN- and GaN⁺-Si(111), and in Tables 3 and 4 for GaN₂- and GaN₂⁺-Si(111).

Table 1 Geometry (bond distance R in Å, angle ϕ in degrees), binding energies BE and corrected values for BSSE BE_{BSSE} in eV and net charges of the Ga-Si(111) and Ga^+ -Si(111) structures

Structures	R ₁	R ₂	ϕ	BE(BE_{BSSE})	Si-rest	Si-adat	Ga
Si(111)					+0.08	+0.22	
2a-Ga	2.55	2.91	56	2.16(2.13)	+0.06	-0.21	+0.59
2b-Ga	2.62		122	2.15(2.10)	-0.57	+0.20	+0.63
2c-Ga	2.58		141	1.72(1.69)	+0.06	-0.42	+0.65
3b-Ga ⁺	2.66		103	2.43(2.39)	-0.59	+0.30	+0.67
3d-Ga ⁺	2.79	2.73	107	2.35(2.27)	-0.33	-0.04	+0.79
3c-Ga ⁺	2.63		140	1.95(1.90)	+0.06	-0.35	+0.83
1d-Ga ⁺	2.65	1.69	111	1.88(1.81)	-0.27	-0.08	+0.84

Table 2 Geometry (bond distance R in Å, angle ϕ in degrees), binding energies BE and corrected values for BSSE BE_{BSSE} in eV and net charges of the GaN-Si(111) and GaN^+ -Si(111) structures

Structures	R ₁	R ₂	R ₃	ϕ_1	ϕ_2	BE(BE_{BSSE})	Si-rest	Si-adat	Ga	N
Si(111)							+0.08	+0.22		
GaN($X^3\Sigma^-$)		2.046							+0.66	-0.66
GaN($A^3\Pi$)		1.884							+0.75	-0.75
3e-GaN	2.50	1.78	1.73	133	119	4.32(4.23)	+0.75	-0.16	+1.14	-1.65
3f-GaN	2.47	1.77	1.73	143	106	4.10(3.95)	-0.30	+0.86	+1.27	-1.63
1e-GaN	2.48	1.78	1.74	137	117	3.98(3.89)	+0.74	-0.16	+1.18	-1.64
3g-GaN		1.89	1.70		161	3.93(3.84)	+0.73	+0.22	+0.77	-1.46
3h-GaN		1.85	1.63		159	3.79(3.70)	+0.09	+0.96	+0.78	-1.71
1f-GaN	2.47	1.77	1.73	143	107	3.78(3.64)	-0.30	+0.86	+1.27	-1.62
3i-GaN	2.40	1.78		179		1.72(1.62)	-0.39	+0.18	+1.10	-0.89
3j-GaN	2.41	1.78		179		1.50(1.41)	+0.09	-0.21	+0.97	-1.68
GaN ⁺ ($X^4\Sigma^-$)		2.740							+0.99	+0.01
GaN ⁺ ($^2\Pi$)		1.872							+1.39	-0.39
4g-GaN ⁺		1.90	1.70		161	6.19(6.13)	+0.69	+0.32	+0.84	-1.46
2f-GaN ⁺	2.45	1.78	1.71	138	112	6.12(6.00)	-0.29	+0.89	+1.31	-1.62
2e-GaN ⁺	2.51	1.78	1.74	133	119	5.96(5.81)	+0.73	-0.14	+1.24	-1.61
2h-GaN ⁺		1.95	1.66		164	5.73(5.66)	+0.10	+0.84	+0.85	-1.44
4i-GaN ⁺		metastable								
4j-GaN ⁺		metastable								

3.1 Ga-Si(111) and Ga^+ -Si(111)

Four geometric structures, **a**, **b**, **c** and **d** (see Fig. 2), were examined with doublet and quartet spin symmetry for the Ga-Si(111) cluster and singlet and triplet spin symmetry for the Ga^+ -Si(111) cluster. The geometry, the binding energy and the natural population analysis of only the lowest lying structures are given in Table 1.

The lowest minimum of Ga-Si(111), (**2a-Ga**), has the Ga atom connected to Si adatom. Moreover, Ga is directly above a 2nd layer Si atom, adjacent to the adatom. The BSSE corrected binding energy of adsorbed Ga is $BE_{BSSE} = 2.13$ (**2a-Ga**), 2.10 (**2b-Ga**) and 1.69 (**2c-Ga**) eV. The natural population analysis shows that the Si surface pulls electron charge from the Ga atom, leaving Ga with a positive partial

charge of +0.59 to +0.65 electrons, in the different structures. In all cases the Si atom connected to the Ga atom has a negative charge and the most negative charge, -0.57 electrons, is found on the Si rest atom of the **2b-Ga** structure.

The lowest **3b-Ga⁺** structure of Ga⁺-Si(111) has Ga⁺ connected to the Si rest atom. The BSSE corrected binding energy of adsorbed Ga⁺ is BE_{BSSE} = 2.39 (**3b-Ga⁺**), 2.27 (**3d-Ga⁺**), 1.90 (**3c-Ga⁺**) and 1.81 (**1d-Ga⁺**) eV. Minima **3d-Ga⁺** and **1d-Ga⁺** have the same structure but different spin multiplicity with the triplet being lower by 0.5 eV, see Table 1. The natural population analysis shows that the Si surface transfers electron charge to Ga⁺, and as a result the adsorbed Ga⁺ has a positive partial charge of +0.67 to +0.84, rather than +1. In all cases the Si atom connected to Ga⁺ cation has a negative charge and the most negative charge is found on the Si rest atom of the **3b-Ga⁺** structure, -0.59 as in the case of the **2b-Ga** of the Ga-Si(111). Hence, the partial charges on Ga and Ga⁺ are very similar, with the surface withdrawing from Ga or providing to Ga⁺ electron charge, while the Si rest and Si adatoms have negative charges -0.21 to -0.59 .

3.2 GaN-Si(111) and GaN⁺-Si(111)

Six geometric structures, **e**, **f**, **g**, **h**, **i**, and **j** (see Fig. 3), were calculated with singlet and triplet spin symmetry for GaN-Si(111) and doublet and quartet spin symmetry for GaN⁺-Si(111). The geometry, the binding energy and the natural population analysis of the lowest lying structures are given in Table 2.

Eight local minima (**3e-GaN**, **3f-GaN**, **1e-GaN**, **3g-GaN**, **3h-GaN**, **1f-GaN**, **3i-GaN**, and **3j-GaN**) have been determined for adsorbed GaN. In the lowest minimum (**3e-GaN**) Ga is connected to Si adatom and N to the rest atom, and in **3f-GaN**, the GaN molecule is connected the opposite way. The BE_{BSSE} with respect to Si(111) + GaN($X^3\Sigma^-$) are calculated at 4.23 (**3e-GaN**) and 3.95 eV (**3f-GaN**). Structures **1e-GaN** and **1f-GaN** have a BE_{BSSE} about 0.3 eV smaller than the corresponding triplet structures. The geometries of **3e-GaN**, **3f-GaN**, **1e-GaN**, and **1f-GaN** minima are similar (cf. Table 2). In the remaining four structures GaN is nearly perpendicular to the surface with the N atom attached to either the Si-rest atom or to the Si adatom in **3g-GaN** and **3h-GaN**, respectively, while in **3i-GaN** and **3j-GaN** the Ga atom is attached to the Si-rest atom or to the Si adatom, respectively. The BE_{BSSE} of **3g-GaN** is 3.84 and of **3h-GaN** 3.70 eV larger about 2 eV than the BE_{BSSE} value of **3i-GaN** and **3j-GaN**.

The lowest minimum of the GaN⁺-Si(111) cluster, **4g-GaN⁺**, has the adsorbed GaN⁺ with N attached to the Si rest atom with BE_{BSSE} = 6.13 eV with respect to Si(111) cluster + GaN⁺($X^4\Sigma^-$); while in the second minimum **2f-GaN⁺**, the GaN⁺ forms a bridge between the Si rest and adatom with a BE_{BSSE} = 6.00 eV. These two minima lie very closely. The next two minima have a BE_{BSSE} value of 5.81 (**2e-GaN⁺**) and 5.66 (**2h-GaN⁺**) eV. The vertical structures with Ga atom connected to Si (**4i-GaN⁺** and **4j-GaN⁺**) are higher in energy by ~ 2.5 eV above **4g-GaN⁺** but they are not stable because they can easily changeover to a bridged structure.

In all 14 species calculated for adsorbed GaN and GaN⁺, the Ga-N bond distance is significantly smaller than in the free diatomic GaN and GaN⁺ systems. This is consistent with the transfer of electronic charge from the surface to GaN and GaN⁺ with the result that adsorbed GaN and GaN⁺ resemble free diatomic GaN⁻, which was calculated to have a shorter bond than the neutral by 0.25 Å [18]. It appears that the same adsorbed GaN species is found in all the adsorbed structures calculated. This is consistent with the net charges on the Ga and N atoms in these structures, where N atom practically the same net charge obtains in all structures about -1.6 with the exception of **3i-GaN** while for Ga and Ga⁺ the net charge ranges from +0.8 (when the Ga is not attached to Si(111)) to between +1.0 and +1.3 (when the Ga is attached to Si(111)). The above results show that the surface acts as a pool of electronic charge, (as in the case of adsorbed Ga and Ga⁺ cf. Sect. 3.1 and Table 1) providing the required electronic charge to give nearly the same Ga-N adsorbed species in both cases, see Table 2. Furthermore, the significant shortening of the internuclear distance in adsorbed GaN and GaN⁺ at Si(111), as compared to the free diatomic systems, makes this case a counter example to the general expectation that upon adsorption, the binding within the adsorbate is weakened, as, for example, is the case of adsorption of halobenzenes at Si(111) [10], where the C-X bond weakens and breaks.

3.3 GaN₂-Si(111) and GaN₂⁺-Si(111)

Four geometric structures, **k**, **l**, **m** and **n** (see Fig. 4), were calculated with doublet and quartet spin symmetry for the GaN₂-Si(111) cluster and singlet and triplet spin symmetry for the GaN₂⁺-Si(111) cluster. The geometry of the lowest energy structures is given in Table 3 while their binding energy and the natural population analysis are given in Table 4.

Two local minima of the chemisorbed GaN₂ molecule are found, with the adsorbate occupying bridging positions over the Si rest and Si adatom. Structure **2k-GaN₂**, has the outer N atom of GaN₂ just barely connected to the Si adatom, while structure **2l-GaN₂**, has the outer N atom tightly connected to the rest atom and its Ga interacts with a lower-layer Si atom, adjacent to the adatom (as in **2a-Ga**), see Tables 1 and 3. The BE_{BSSSE} of **2k-GaN₂** and **2l-GaN₂** with respect to Ga+N₂+Si(111) are 1.98 and 1.62 eV, respectively. It should be noted that both structures are higher in energy than the lowest adsorbed Ga atom structure (**2a-Ga**), thus they are metastable structures (with respect to adsorbed Ga at Si plus free N₂) [9].

In all local minima (**3k-GaN₂⁺**, **3l-GaN₂⁺**, **3l'-GaN₂⁺**, **3n-GaN₂⁺**, **1l-GaN₂⁺**, and **1n-GaN₂⁺**) of chemisorbed GaN₂⁺ with the exception of **3m-GaN₂⁺** the cation bridges over the Si adatom and Si rest atom. In the lowest energy structure, **3k-GaN₂⁺**, Ga⁺ is connected to the rest atom, while in the other six structures Ga⁺ is connected to the adatom. The BE_{BSSSE} of **3k-GaN₂⁺** is 2.13 eV with respect to the separated Si cluster and GaN₂⁺ and 2.45 eV with respect to Si cluster + Ga⁺ + N₂

Table 3 Geometry (bond distance R in Å, angle ϕ in degrees) of the GaN₂-Si(111) and GaN₂⁺-Si(111) structures

Structures	R ₁	R ₂	R ₃	R ₄	R ₅	ϕ_1	ϕ_2	ϕ_3	ϕ_4
GaN ₂ (X ² Π)		2.447							
2k-GaN ₂	2.61	2.89	1.11	3.34		94	148	99	
2l-GaN ₂	2.59	2.74	1.18	1.93	3.00	90	146	128	55
GaN ₂ ⁺ (X ⁴ Σ ⁻)		2.798							
3k-GaN ₂ ⁺	2.67	3.54	1.11	3.75		106	168	82	
3m-GaN ₂ ⁺	2.65	3.04	1.11			92	175		
3l-GaN ₂ ⁺	2.56	4.19	1.11	2.00	2.95	79	86	179	56
3l'-GaN ₂ ⁺	2.73	2.55	1.17	1.91	3.36	92	149	133	47
3n-GaN ₂ ⁺	2.56	3.32	1.12	1.95		102	111	172	
1l-GaN ₂ ⁺	2.56	4.74	1.11	2.00	3.19	102	107	174	52
1n-GaN ₂ ⁺	2.66	3.73	1.11	3.07		75	141	139	

Table 4 Binding energies BE and corrected values for BSSE BE_{BSSE} in eV [BE(BE_{BSSE})] with respect to GaN₂- or GaN₂⁺-Si(111) and BE1(BE1_{BSSE}) with respect to Ga or Ga⁺ + N₂-Si(111)] and net charges of the GaN₂-Si(111) and GaN₂⁺-Si(111) structures

Structures	BE(BE _{BSSE})	BE1(BE1 _{BSSE})	Si-rest	Si-adat	Ga	N	N
Si(111)			+0.08	+0.22			
GaN ₂ (X ² Π)					+0.18	-0.21	+0.03
2k-GaN ₂	1.96(1.90)	2.10(1.98)	-0.56	+0.19	+0.60	-0.02	+0.05
2l-GaN ₂	1.64(1.53)	1.78(1.62)	+0.42	-0.19	+0.58	-0.10	-0.37
GaN ₂ ⁺ (X ⁴ Σ ⁻)					+0.98	-0.14	+0.16
3k-GaN ₂ ⁺	2.19(2.13)	2.47(2.45)	-0.60	+0.27	+0.68	-0.01	+0.04
3m-GaN ₂ ⁺	1.94(1.91)	2.23(2.20)	+0.07	-0.37	+0.76	-0.06	+0.08
3l-GaN ₂ ⁺	1.69(1.52)	1.98(1.78)	+0.35	-0.22	+0.63	-0.10	+0.24
3l'-GaN ₂ ⁺	1.61(1.51)	1.90(1.74)	+0.40	-0.16	+0.72	-0.07	-0.26
3n-GaN ₂ ⁺	1.60(1.47)	1.89(1.71)	+0.36	-0.40	+0.66	+0.17	-0.13
1l-GaN ₂ ⁺	1.35(1.23)	1.64(1.50)	+0.36	-0.30	+0.69	+0.24	-0.09
1n-GaN ₂ ⁺	1.30(1.23)	1.58(1.55)	+0.28	-0.42	+0.73	+0.04	+0.01

species, which is larger than the binding energy of adsorbed Ga⁺ (structure **3b-GaN₂**). Structures **3k-GaN₂**⁺ and **3l'-GaN₂**⁺ of GaN₂⁺-Si(111) resemble **2k-GaN₂** and **2l-GaN₂** of GaN₂-Si(111), while the rest five minima are found only for the cation. In **3l'-GaN₂**⁺, GaN₂⁺ is more tightly connected to Si-rest and Si adatom, but it is more strained compared to the free GaN₂⁺ cation, which favours a linear Ga⁺-N-N geometry.

Structure **3m-GaN₂**⁺ is an open structure where a GaN₂⁺ molecule is connected to the Si adatom with a BE_{BSSE} = 1.91 eV and a BE_{BSSE} = 2.20 eV with respect to Ga⁺ + N₂ + Si(111).

In some minima such as **3l-GaN₂**⁺ the Ga⁺...N distances are long, thus, there is only a slight interaction between Ga⁺ and N₂, but they are both stabilized through the Si surface. Moreover, in all **1l-GaN₂**⁺ (**3l**, **3l'**, and **1l**) structures the Ga atom is connected to the Si adatom and it is directly above a 2nd layer Si atom.

As in the case of adsorbed Ga and Ga^+ (cf. Table 1) or GaN and GaN^+ (cf. Table 2), the Ga and Ga^+ of the triatomic adsorbed species have similar net charge (+0.58 to +0.76) showing that the surface acts as a pool of electron charge (see Table 4).

Finally, it should be noted that the Ga^+ of the adsorbed GaN_2^+ , which forms a weak bond with the N_2 , results in the stabilization of the N_2 molecule on the surface, which would not occur otherwise. This is consistent with our calculations on the adsorption of N_2 on Si(111) which yielded only unbound metastable structures with slight barriers to dissociation [9].

4 Remarks and Conclusions

The electronic and geometric structures of gallium (Ga, Ga^+) and gallium nitrides (GaN , GaN^+ , GaN_2 , GaN_2^+) adsorbed on Si(111) were studied by DFT calculations. A 5-layer 1R-1A Si cluster model of the Si(111) surface, terminated with H atoms was used. Three stable structures were determined for adsorbed Ga, four for Ga^+ , eight for GaN, six for GaN^+ , two for GaN_2 and seven for GaN_2^+ . The binding energies to the Si surface (corrected for basis set superposition error) of the lowest structures were found to be 2.13 for Ga, 2.39 for Ga^+ , 4.23 for GaN, 6.13 for GaN^+ , 1.90 for GaN_2 , and 2.13 eV for GaN_2^+ . The diatomic neutral and cationic nitrides form low lying bridged structures, with the adsorbate bridging between the Si rest atom and Si adatom, as well as structures with only one bond with the surface and the molecular axis nearly perpendicular to the surface. The triatomic adsorbates form mostly bridged structures. The geometry as well as the electron population analysis of the adsorbed species and of the Si rest atom and Si adatom demonstrate the equivalence of bonding in the neutral and charged structures indicating that the charge can be drawn from or delivered to the surface as required to make the adsorbates studied have similar charges. Of course, there exist differences in the corresponding binding energies of the adsorbed neutral and cationic species, since the zero of the energy (i.e. the dissociation products) are quite different.

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