

Theoretical 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. Significant binding is found for all the species considered, with binding energies up to 6.13 eV. For GaN, GaN₂, and GaN₂⁺ the lowest energy structures are those with the adsorbate forming a bridge between the Si adatom and rest atom, while for GaN⁺ it is a vertical structure connecting to Si via N. Furthermore, it is found that adsorbed GaN and GaN⁺ are essentially the same species, resembling free GaN⁻.

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1. Introduction

There is great interest in the study of chemisorption of group III metals and their nitrides at Si surfaces. Subjects of particular interest are the geometric and electronic structure of chemisorbed group III metals on Si surfaces [1,2], the surface changes associated with metal diffusion on the surface, the formation of metal-adsorbate atomic wires as well as the self-assembly of perfectly ordered nanocluster arrays [3–5]. Of particular interest is the growth of GaN films on Si surfaces [6,7], which have great potential for application in optoelectronic devices and high-power, high-temperature electronic devices [6,7]. Even though there are many experimental studies of gallium nitrides at Si(111) [4–7], to our knowledge, there have not been as many theoretical studies. For Ga deposited on Si(111), there is a theoretical study of a Ga decamer on a unit-cell model of Si(111) [8] as well as an earlier theoretical work on Ga at small Si (3–9 Si-atoms) clusters [1].

In the present study the electronic and geometric chemisorbed structures of gallium (Ga, Ga⁺) and different gallium nitrides (GaN, GaN⁺, GaN₂, GaN₂⁺) on Si(111) are

determined using density functional theory (DFT) calculations and a Si₂₆H₂₂ model of the Si(111) surface. An adequate basis set is employed and the validity of the results is examined by comparison with previous work on the free molecular systems.

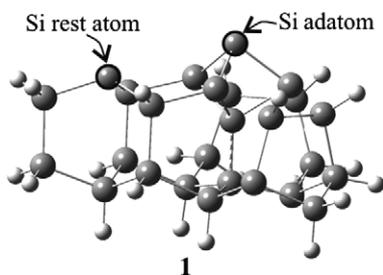
2. Computational procedure

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

Preliminary DFT calculations were carried out on diatomic and triatomic structures (GaN, GaN⁺, SiGa, SiN, GaN₂, GaN₂⁺) and on the 1R–1A Si(111) cluster so as to choose an adequate combination of functional and basis set with respect to the available experimental and theoretical data. On the basis of the above calculations, the

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B3LYP functional [12,13] and the DGDZVP basis set (double-zeta valence plus polarization, i.e., [3s2p1d_N/4s3p1d_{Si}/5s4p2d_{Ga}]) [14] were considered to be the best choice for the present calculations.

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

For all stable geometries, the binding energy (BE) of each species on the surface was calculated, where the basis set superposition error (BSSE) [15] was estimated with respect to the relevant fragments. All calculations were performed using the GAUSSIAN 03 program package [16].

3. Results

Geometries and binding energies for all the adsorbed systems calculated are given in Table 1. The lowest-energy

Table 1

Bond distances ($R_{\text{Ga-Si}}$, $R_{\text{N-Si}}$, $R_{\text{Ga-N}}$) in Å, binding energies (BE) and BSSE corrected binding energies (BE_{BSSE}) in eV of the adsorbed Ga, Ga⁺, GaN, GaN⁺, GaN₂, and GaN₂⁺ species on Si(111)

Structures	S ^a	$R_{\text{Ga-Si}}$	$R_{\text{N-Si}}$	$R_{\text{Ga-N}}$	BE (BE _{BSSE})	BE (BE _{BSSE}) ^b
2-Ga	2	2.55			2.16 (2.13)	
3	2	2.62			2.15 (2.10)	
4	2	2.58			1.72 (1.69)	
5-Ga ⁺	3	2.66			2.43 (2.39)	
6	3	2.73, 2.79			2.35 (2.27)	
7	3	2.63			1.95 (1.90)	
8-GaN	3	2.50	1.73	1.78	4.32 (4.23)	
9	3	2.47	1.73	1.77	4.10 (3.95)	
10	3		1.70	1.89	3.93 (3.84)	
11	3		1.63	1.85	3.79 (3.70)	
12-GaN ⁺	4		1.70	1.90	6.19 (6.13)	
13	2	2.45	1.71	1.78	6.12 (6.00)	
14	2	2.51	1.74	1.78	5.96 (5.81)	
15	2		1.66	1.95	5.73 (5.66)	
16-GaN ₂	2	2.61	3.34	2.89	1.96 (1.90)	2.10 (1.98)
17	2	2.59	1.93	2.74	1.64 (1.53)	1.78 (1.62)
18-GaN ₂ ⁺	3	2.67	3.75	3.54	2.19 (2.13)	2.47 (2.45)
19	3	2.56, 2.95	2.00	4.19	1.69 (1.52)	1.98 (1.78)
20	3	2.73	1.91	2.55	1.61 (1.51)	1.90 (1.74)
21	3	2.56	1.95	3.32	1.60 (1.47)	1.89 (1.71)
22	1	2.66	3.07	3.73	1.30 (1.23)	1.58 (1.55)

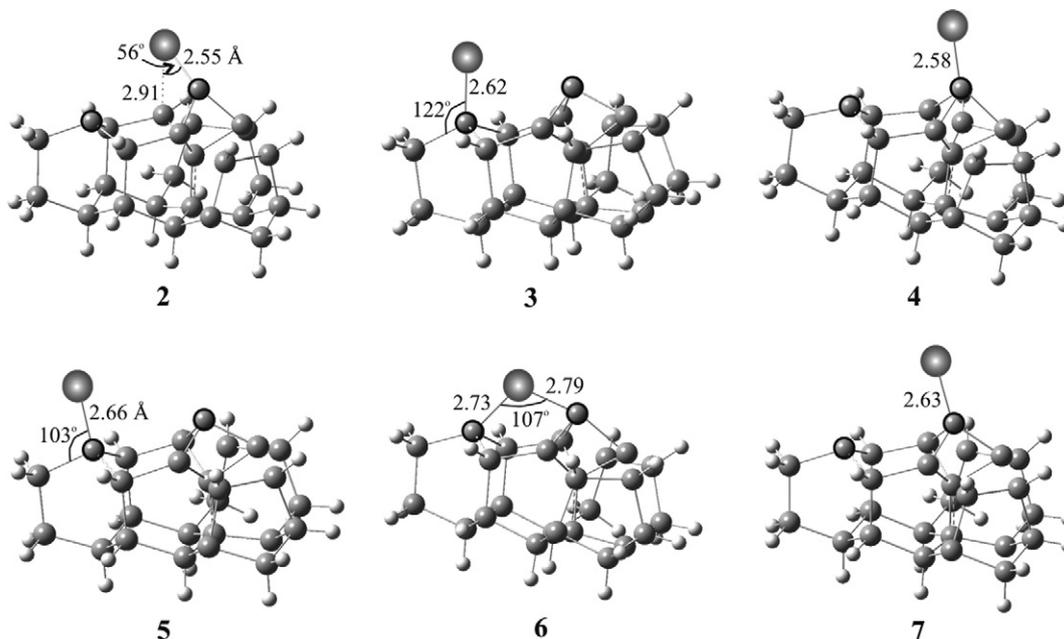
^a Spin multiplicity.

^b BE with respect to Si(111) + Ga + N₂ or Si(111) + Ga⁺ + N₂.

spin species is given in each structure calculated. Details are discussed below.

3.1. Ga-Si(111) and Ga⁺-Si(111)

Three local minima (2, 3, 4) of the potential energy surface of the chemisorbed Ga on Si(111) surface were calculated. At the lowest minimum (2) the Ga atom (large grey



spheres) is connected to Si adatom at an angle so that it is directly above a 2nd layer Si atom, adjacent to the adatom. The BSSE corrected binding energy of adsorbed Ga is $BE_{BSSE} = 2.13$ eV, with $R_{\text{Ga-Si-adatom}} = 2.55$ Å, $R_{\text{Ga-Si-adj}} = 2.91$ Å and a $\text{Si}_{\text{adatom}}\text{GaSi}_{\text{adj}}$ angle of 56° . For reasons of comparison, the dissociation energy of the ground state, $X^4\Sigma^-$, of the diatomic GaSi is calculated by B3LYP/DGDZVP at 2.24 eV and by MP4/aug-cc-pVTZ at 2.48 eV [17], showing that the B3LYP/DGDZVP method is adequate for describing the Ga–Si bond and the present value of 2.13 eV of the Ga–Si(111) bond is consistent with the result on the diatomic GaSi.

In the next two stable structures (3, 4), of BE_{BSSE} 2.10 and 1.69 eV respectively, Ga is directly above the Si rest atom in 3 and the adatom in 4. Structures 2 and 4 resemble the ‘eclipsed’ and ‘atop’ structures of Thundat et al. [1], which were calculated by HF/STO-3G using clusters of 5 and 4 Si-atoms, respectively.

Three minima (5, 6, 7) were also determined for Ga^+ adsorbed on Si(111). Minima 5 and 7 resemble the higher two structures, 3 and 4, of Ga on Si(111). Structure 5, with $\text{Ga}^+(^1S)$ connected to the Si rest atom, corresponds to the lowest minimum ($BE_{BSSE} = 2.39$ eV), while 7 with Ga^+ connected to the adatom lies 0.5 eV higher in energy. In 6 (at 0.12 eV above 5) Ga^+ occupies a bridge position, not found in the neutral, interacting with both a Si rest and a Si adatom. In the lowest energy structures (2 and 5) of adsorbed Ga and Ga^+ respectively, the partial charges on Ga are very similar, at +0.59 and +0.67, with the Si rest and adatoms withdrawing from Ga or providing to Ga^+ electron charge.

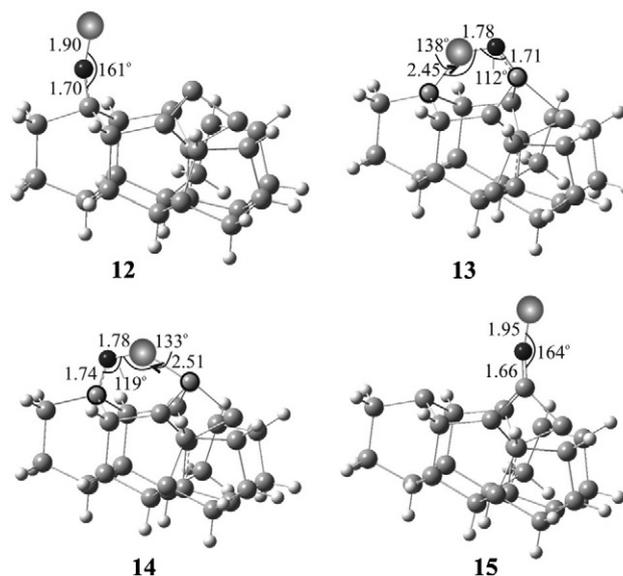
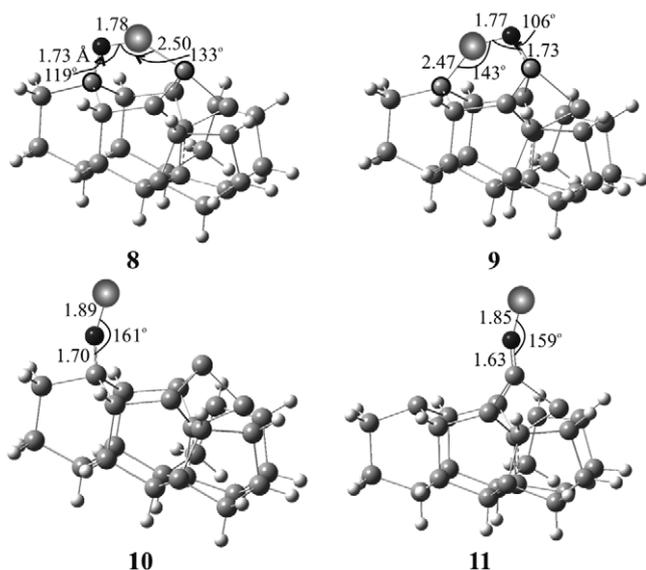
3.2. GaN–Si(111) and GaN^+ –Si(111)

Tolerable differences are found between the present B3LYP/DGDZVP results on the two lowest electronic states of the GaN molecule and previous MRCI results

[18]: For $X^3\Sigma^-(\text{GaN})$ the DFT results are $R_{\text{GaN}} = 2.046$ Å, $D_e = 2.17$ eV with corresponding MRCI values 2.021 Å, 2.08 eV. For $A^3\Pi$, DFT yields $R_{\text{GaN}} = 1.884$ Å, $D_e = 2.06$ eV, while MRCI yields 1.873 Å, 1.99 eV [18]. Similarly, the GaN–Si triatomic molecule is well described at DFT giving a dissociation energy for the GaN–Si bond and a $R_{\text{GaN-Si}}$ distance of the ground state $\tilde{X}^1\Sigma^+$ of 7.06 eV and 1.587 Å compared to 7.19 eV and 1.596 Å at RCCSD(T)/aug-cc-pVTZ level of theory.

Four local minima (8, 9, 10, 11), have been determined for adsorbed GaN (large grey spheres \equiv Ga, black spheres \equiv N), where in 8 and 9 GaN forms a bridge between the Si rest and adatom. At the lowest minimum (8) Ga is connected to Si adatom and N to the rest atom, and in 9, the GaN molecule is connected the opposite way with similar bond distances with 8. The BE_{BSSE} with respect to $\text{Si}(111) + \text{GaN}(X^3\Sigma^-)$ are calculated at 4.23 (8) and 3.95 eV (9). In 10 and 11 GaN is vertical with N atom attached to the Si-rest atom and to the Si adatom, respectively, with BE_{BSSE} of 3.84 and 3.70 eV. Structures analogous to 10 and 11 but with Ga connected to Si are local minima located at ~ 2.2 eV above 8.

Similarly, two minima (12, 15) have been found for adsorbed vertical GaN^+ with N attached to the Si rest and the Si adatom with $BE_{BSSE} = 6.13$ and 5.66 eV respectively, and two minima (13, 14) with GaN^+ forming a bridge between the Si rest and adatom. In 13, Ga^+ is connected to the rest atom and in 14 the opposite way. The BE_{BSSE} values with respect to $\text{Si}(111)$ cluster + $\text{GaN}^+(X^4\Sigma^-)$ are 6.00 (13) and 5.81 eV (14). Here too, vertical structures with Ga atom connected to Si are higher in energy by ~ 2.5 eV above 12.



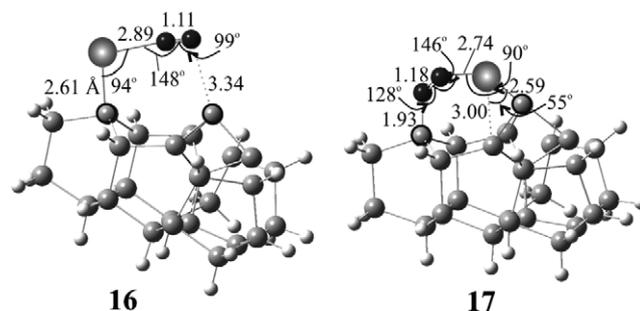
The fact that in all the structures calculated for adsorbed GaN and GaN^+ the Ga–N bond distance is significantly smaller than in the free diatomic GaN and GaN^+ systems is consistent with the transfer of electronic charge from the surface to GaN and GaN^+ , with the result that adsorbed

GaN and GaN^+ resemble free diatomic GaN^- , which was calculated to have a shorter bond than the neutral by 0.25 Å [19]. The net charges on the Ga and N atoms in these structures also suggest that essentially the same adsorbed GaN species is found for adsorbed GaN and GaN^+ : For the N atom practically the same net charge (−1.61 to −1.64) is obtained in all four bridged structures, while for Ga only a small increase is found in the Ga^+-N structures +1.31 (13) and +1.24 (14) compared to $\text{Ga}-\text{N}$ +1.18 (8) and +1.24 (9). In the vertical structures the net charges are (−1.44 to −1.71) for N and (+0.77 to +0.85) for Ga. This shows that the surface acts as a pool of charge, (cf. Section 3.1 on Ga and Ga^+) providing the required amount to give nearly the same Ga–N adsorbed species in both the neutral and the cation. Note, that there is a resemblance among the harmonic frequencies of the states of the $\text{GaN}^+ [{}^2\Delta(507 \text{ cm}^{-1}), {}^2\Pi(666)]$, $\text{GaN} [{}^3\Sigma^-(530), {}^3\Pi(635)]$ and $\text{GaN}^- [{}^2\Sigma^+(750), {}^2\Pi(676)]$ [19] which are involved in the adsorption of GaN^+ and GaN on Si(111). As the dissociation energy of free GaN^- is larger than that of GaN, this case is a counterexample to the general expectation that upon adsorption, the binding within the adsorbate is weakened [9].

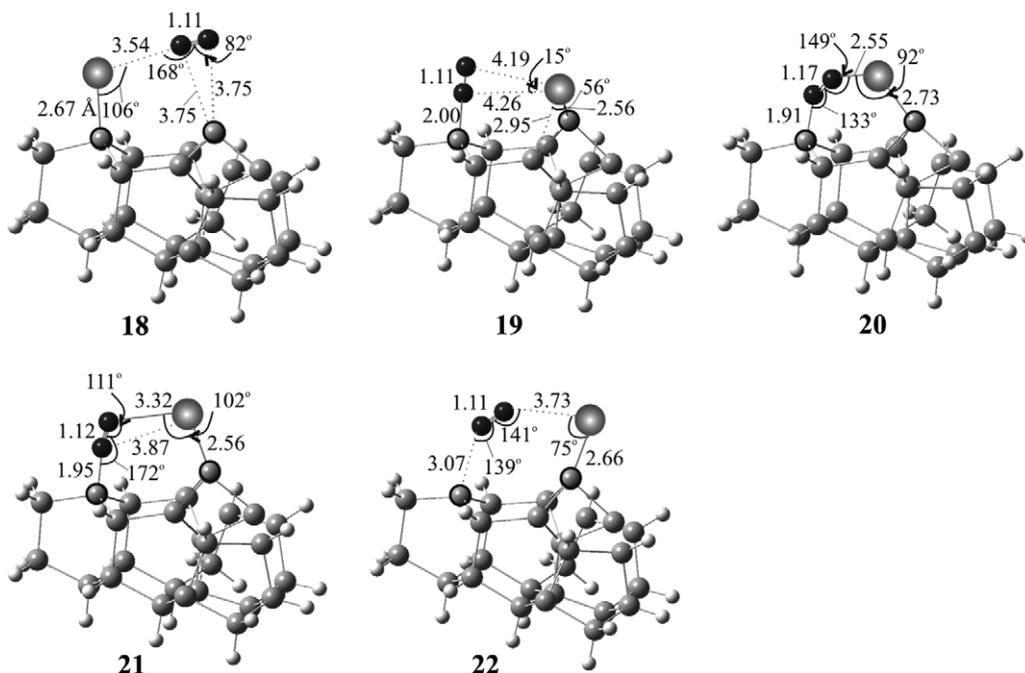
3.3. $\text{GaN}_2-\text{Si}(111)$ and $\text{GaN}_2^+-\text{Si}(111)$

Two local minima of the chemisorbed GaN_2 molecule are determined, with the adsorbate occupying bridging positions over the Si rest and adatom. The lowest minimum (16) has the outer N atom of GaN_2 just barely connected to the Si adatom, while the second minimum has the outer N atom more tightly connected to the rest atom (cf. Table 1). Moreover, Ga interacts with a lower-layer Si atom, adjacent to the adatom (as in 2). The binding energy of 16

and 17 with respect to $\text{Ga} + \text{N}_2 + \text{Si}(111)$ are 1.98 and 1.62 eV, respectively, i.e., both structures are higher in energy than the lowest adsorbed Ga atom structure (2), thus they are metastable structures.



In all of the five local minima (18–22) of chemisorbed GaN_2^+ the cation bridges over the Si adatom and rest atom. In the lowest energy structure, (18), Ga^+ is connected to the rest atom, while in the other four structures (19–22) Ga^+ is connected to the adatom. Structures 18 and 20 of $\text{GaN}_2^+-\text{Si}(111)$ resemble 16 and 17 of $\text{GaN}_2-\text{Si}(111)$, while 19, 21 and 22 are found only for the cation. In 18, the Si–N distance is long, indicating a weak interaction and $R_{\text{Ga}^+-\text{N}}$ is significantly longer than the 2.829 Å value of Ga^+-N in the free triatomic cation, which is vdW cation with $D_e = 0.24$ eV [20]. The BE_{BSE} of 18 is 2.13 eV with respect to the separated Si cluster and GaN_2^+ and 2.45 eV with respect to Si-cluster + $\text{Ga}^+ + \text{N}_2$ species, which is larger than the binding energy of adsorbed Ga^+ (structure 5). In 20, GaN_2^+ is more tightly connected to Si-rest and adatom, with $R_{\text{Ga}^+-\text{Si}} = 2.73$, $R_{\text{N}-\text{Si}} = 1.91$ Å, but it is more strained compared to the free GaN_2^+ cation, which favours a linear $\text{Ga}^+-\text{N}-\text{N}$ geometry.



The geometries and binding energies of the local minima **19**, **21** and **22** are given in the above schemes and Table 1. In **19**, the $\text{Ga}^+ \cdots \text{N}$ distances are long, thus, there is a slight interaction between Ga^+ and N_2 , but they are both stabilized through the Si surface. Moreover, the Ga atom is connected to Si adatom and it is directly above a 2nd layer Si atom. In **19** and **21** a triangular structure of chemisorbed GaN_2^+ is found, resembling the $^1\text{A}_1$ transition structure of the free triatomic cation [20].

Finally, calculations on the adsorption of N_2 on Si(111) yielded only unbound metastable structures with slight barriers to dissociation, indicating that for adsorbed GaN_2^+ the presence of Ga^+ , which forms a weak vdW bond with the N_2 , results in the stabilization of the N_2 molecule on the surface, which would not occur otherwise.

4. 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 and a five-layer 1R–1A Si cluster model of the Si(111) surface, terminated with H atoms. Three stable structures were determined for the Ga and Ga^+ adsorbed species, four for GaN and GaN^+ , two for GaN_2 and five for GaN_2^+ . For both the diatomic and the triatomic neutral and cationic nitrides, bridged structures, with the adsorbate bridging between the Si rest atom and adatom were found. For the diatomics, structures with Ga–N vertical and attached at N to a Si adatom or a Si rest atom were also calculated to be low energy minima. Furthermore, it was found that the Si cluster acts as a pool of electronic charge, as very small differences exist in the calculated net charges on adsorbed Ga between the neutral and cationic adsorbed species.

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