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Theoretical study of adsorption of gallium and gallium nitrides on Si(1 1 1)

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Abstract

Adsorption of gallium (Ga, Ga^+) and gallium nitrides (GaN, GaN^+, GaN_2, GaN_2^+) on a model Si(1 1 1) 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, GaN_2, and GaN_2^+ 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^-.

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(1 1 1) [4–7], to our knowledge, there have not been as many theoretical studies. For Ga deposited on Si(1 1 1), there is a theoretical study of a Ga decamer on a unit-cell model of Si(1 1 1) [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^+, GaN_2, GaN_2^+) on Si(1 1 1) are determined using density functional theory (DFT) calculations and a $Si_{26}H_{22}$ model of the Si(1 1 1) 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^+, GaN_2, and GaN_2^+, at Si (1 1 1) are calculated at a five-layer one-rest one-adatom (1R–1A) cluster model of Si(1 1 1), (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(1 1 1) 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, GaN_2, GaN_2^+) and on the 1R–1A Si(1 1 1) 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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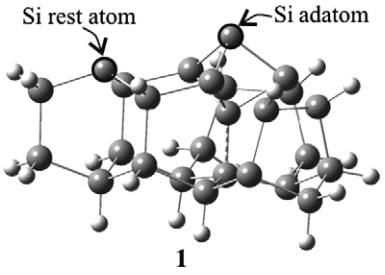

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B3LYP functional [12,13] and the DGDZVP basis set (double-zeta valence plus polarization, i.e., [3s2p1d$_N$/4s3p1d$_{Si}$/5s4p2d$_{Ga}$]) [14] were considered to be the best choice for the present calculations.

Employing the B3LYP/DGDZVP technique the electronic and geometric structures of chemisorbed gallium (Ga, Ga^+) and gallium nitrides (GaN, GaN^+, GaN_2, GaN_2^+) on the five-layer 1R–1A cluster(**1**), were investigated. Three chemisorbed structures for each of Ga- and Ga^+–Si(1 1 1); four for GaN– and GaN^+–Si(1 1 1); two for GaN_2–Si(1 1 1); and five for GaN_2^+–Si(1 1 1) 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(1 1 1) 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 spin species is given in each structure calculated. Details are discussed below.

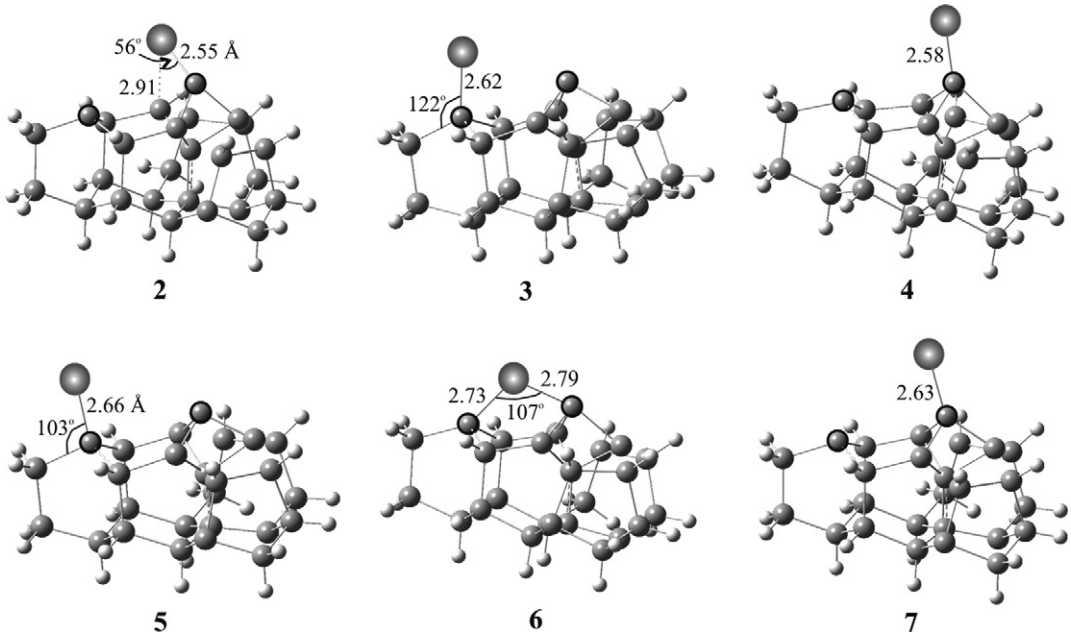
Table 1
Bond distances ($R_{Ga–Si}$, $R_{N–Si}$, $R_{Ga–N}$) in Å, binding energies (BE) and BSSE corrected binding energies (BE_{BSSE}) in eV of the adsorbed Ga, Ga^+, GaN, GaN^+, GaN_2, and GaN_2^+ species on Si(1 1 1)

Structures	S[a]	$R_{Ga–Si}$	$R_{N–Si}$	$R_{Ga–N}$	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(1 1 1) + Ga + N_2 or Si(1 1 1) + Ga^+ + N_2.

3.1. Ga–Si(1 1 1) and Ga^+–Si(1 1 1)

Three local minima (**2**, **3**, **4**) of the potential energy surface of the chemisorbed Ga on Si(1 1 1) surface were calculated. At the lowest minimum (**2**) the Ga atom (large grey



2 3 4

5 6 7