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First-principles study of the dissociative adsorption of NH_3 on the Si(100) surface

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We have studied the energetics and bonding geometry of the ammonia adsorbed Si(100) surface by performing density-functional total-energy calculations within generalized gradient approximation. Ammonia molecules are found to adsorb on the down atoms of buckled Si dimers with an adsorption energy of 1.2 eV, but there exists a low-energy (of about 0.6 eV) activation pathway to the more stable dissociative chemisorption where NH_2 (H) bonds to the down (up) Si atom. This energy diagram implies that the molecular physisorption may survive at sufficiently low temperature, but thermal activation at higher temperatures possibly carries the system into the dissociated state over the energy barrier. Especially, the calculated adsorption energy (of 2.0 eV) and bonding geometry for the dissociated state is in good agreement with the measurements in recent desorption and photoelectron diffraction experiments. [S0163-1829(98)02932-4]

I. INTRODUCTION

Adsorption of molecules on silicon surfaces has been an active research field in surface science not only due to the technological importance in microelectronics, such as in controlled thin-film growth, but also for the fundamental interest on the interaction of molecules with the dangling bond states of semiconductor surfaces. One prototypical example for such studies is the ammonia adsorption on the dimerized Si(100) surface, which is important in connection with silicon nitride film growth.

Since Bozso and Avouris[1] suggested that ammonia molecules on the Si(100) surface dissociate at as low temperature as 90 K, a number of experimental[2–15] and theoretical[16,17] studies have been performed to identify the NH_3-derived adsorbed species. At room temperature it is generally agreed that ammonia molecules on the Si(100) surface adsorb dissociatively in the form of NH_2 and H, adsorbing on both atoms of the substrate Si dimer. This was first suggested by the electron stimulated desorption experiments of Dresser *et al.*[4] and the vibrational electron-energy-loss spectroscopy studies by Fujisawa *et al.*,[5] and is also consistent with other vibrational[6,7] and electronic[8–13] spectroscopic studies. The ammonia adsorption is saturated at the coverage of one NH_3 per Si dimer[4,13] where all the reactive surface dangling bonds are passivated by the dissociated species, NH_2 and H. Such dissociated species are found to be stable up to ~600 K, above which the amino species (NH_2) further dissociates or recombines with H.[4,5] By temperature programmed desorption (TPD) experiments, Dresser *et al.*[4] estimated the activation energy for the associative desorption of NH_3 at about 2.0 eV, and Chen *et al.*[7] found that the barrier for further dissociation of NH_2 is slightly higher than that for associative desorption.

At low temperature, however, the surface structure is not clear yet. Ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS, respectively) studies[1,8–10] indicated that below ~120 K, for sufficiently high exposures, there are condensed ammonia layers in addition to the dissociated species. Furthermore, Dufour *et al.*[13] suggested in their recent XPS study that there are two more nitrogen-containing species, each assigned as atomic nitrogen and molecular ammonia below the condensed ammonia layers. Moreover, the coverage of each species and the atomic structure are not known.

So far theoretical studies are limited to molecular orbital methods. The atomic and electronic structures of the dissociated species were studied by Zhou *et al.*[16] using the ASED-MO (atom superposition and electron delocalization-molecular orbital) and the DV-$X\alpha$ (discrete variational $X\alpha$) methods, and by Moriarty and Smith[17] using the Slab-MINDO (slab modified intermediate neglect of differential overlap) molecular orbital method.

In the present work we performed density functional theory (DFT) calculations using the generalized gradient approximation (GGA) within the pseudopotential method for the ammonia adsorbed Si(100) surfaces. The application of DFT-GGA to the molecule-surface interaction is in the beginning stage and the accuracy of the approach is still under examination, especially for the adsorption or dissociation energy of molecules on extended surfaces. Here we performed extensive tests of our approach on isolated molecules and bare Si surfaces, and then studied the energetics and the equilibrium geometries for the dissociatively (NH_2+H) adsorbed surfaces with varying surface periodicities and ammonia coverages. In order to understand the dissociation process, we also considered the molecularly (NH_3) adsorbed surfaces and carefully examined the dissociation energetics for the molecular-precursor mediated dissociation channel.

In the following section we present the details of our theoretical approach. In Sec. III we deal with (A) test calculations for the clean Si(100) surfaces and isolated molecules, (B) the optimized geometries and adsorption energies for the ammonia adsorbed Si(100) surfaces, and (C) the dissociation pathway and energetics. A summary follows in Sec. IV.

II. COMPUTATIONAL DETAILS

Our DFT calculations have been performed using the GGA of Perdew, Burke, and Ernzerhof[18] for the exchange-correlation functional. In solid-state calculations the GGA was implemented in an efficient way by the scheme of White and Bird.[19] We employed the pseudopotential formalism for the electron-ion interaction. The norm-conserving pseudopotentials of Si and H atoms were constructed by the scheme of Troullier and Martins.[20,21] The Kleinman-Bylander representation[22] was used for the nonlocal s and d components of the Si pseudopotential. For nitrogen whose $2p$ valence orbital is strongly localized, we used the Vanderbilt ultrasoft pseudopotential.[23,24] All the pseudopotentials were generated in the ground-state configuration of neutral atoms.

We modeled the Si surface by a periodic slab geometry consisting of an eight atomic layer Si slab and a vacuum region of seven such layers. Ammonia molecules were adsorbed on both sides of the slab. The electronic wave functions were expanded in a plane-wave basis set using a cutoff energy of 20 Ry. For the integration in reciprocal space we used four **k** points in the surface Brillouin zone of the (2×2) cell. The calculated adsorption geometries and energetics are sufficiently converged with these calculation parameters, as will be shown in detail in the next section. Total energies and atomic forces in our DFT calculations were determined self-consistently by employing a preconditioned conjugate gradient method[25] and an efficient density mixing scheme of Johnson.[26] The positions of all atoms, except the innermost two Si layers held at their bulk positions, were allowed to relax until all the residual force components are well within 0.1 eV/Å.

III. RESULTS

A. Clean surfaces and molecules

To begin with, we present the result of our test of the present theoretical scheme on the bulk and clean surfaces of Si and on some isolated molecules. For bulk Si in the diamond structure we get the equilibrium lattice constant of 5.475 Å, the bulk modulus of 85 GPa, and the cohesive energy of 4.55 eV. The experimental values are 5.430 Å, 98 GPa, and 4.63 eV, respectively. For the purpose of comparison we also calculated the same structural properties of bulk Si using the local density approximation (LDA),[27] which resulted in 5.390 Å, 92 GPa, and 5.31 eV, respectively. The present GGA exchange-correlation functional corrects most of the LDA overestimation of the cohesive energy, but overestimates the lattice constant and underestimates the bulk modulus, in accord with the trend demonstrated in our previous calculations for several semiconductor systems.[28]

As a reference for the clean substrate, we calculated the equilibrium structures of the Si(100) surface for three different reconstructions; i.e., the symmetric and asymmetric $p(2\times1)$ phases and the $p(2\times2)$ phase with alternating dimer bucklings. In good agreement with previous first-principles calculations,[29] the asymmetric $p(2\times1)$ phase is more stable than the symmetric one by 0.15 eV/(2×1), and the surface further lowers its energy by 0.07 eV/(2×1) through the $p(2\times2)$ reconstruction.[30] For the asymmetric $p(2\times1)$ phase the vertical separation between the top-layer dimer atoms is 0.73 Å and the tilt of the dimer is 18.2°. For the $p(2\times2)$ phase the corresponding values are 0.76 Å and 18.5°. These values agree well with the recent room-temperature LEED fits of 0.72 ± 0.05 Å and $19\pm2°$.[31]

In order to probe the accuracy of our scheme in describing the interatomic interaction between H, N, and Si atoms, we calculated the equilibrium properties of several molecules containing them using a large tetragonal supercell of size $8\times8\times12$ Å^3 within the present plane-wave basis scheme. The calculated bonding geometries for selected molecules are presented in Table I. We find that our calculations resulted in very accurate equilibrium geometries: the bond lengths are in accord with experimental values within 0.03 Å and the bond angles are within $\sim1°$. In Table II, we present the bond dissociation energies for some selected bonds. Here we included the spin-polarization effect in atomic calculation, but not in molecular calculation, and did not consider the zero-point vibration. The result is in good agreement with experimental values: the bond energies were slightly underestimated by the present GGA calculation, but its overall accuracy is in contrast with usual large overestimation of binding energy in LDA. A larger cutoff of 25 Ry for the plane-wave basis hardly changes molecular geometries (less than 0.01 Å for bond lengths and 0.3° for bond angles), but increases the bond dissociation energies by 1% for Si-Si, 4% for H-H, and 9% for N-N, resulting in better agreement with experiment. A somewhat large disagreement for Si-Si is due to the neglect of the spin polarization effect in molecular calculation since the ground state of Si_2 is spin-triplet.

TABLE I. Equilibrium geometries for selected molecules containing H, N, or Si. Bond lengths are in angstroms and bond angles are in degrees. Numbers in parentheses are experimental values taken from Ref. 32.

H_2	d(H-H) = 0.741 (0.741)	
N_2	d(N-N) = 1.115 (1.098)	
Si_2	d(Si-Si) = 2.230 (2.246)	
NH	d(N-H) = 1.066 (1.036)	
NH_2	d(N-H) = 1.049 (1.024)	∠HNH = 102.1 (103.3)
NH_3	d(N-H) = 1.030 (1.012)	∠HNH = 106.2 (106.7)
SiH	d(Si-H) = 1.552 (1.520)	
SiH_4	d(Si-H) = 1.498 (1.480)	
Si_2H_6	d(Si-H) = 1.502 (1.492)	∠HSiH = 108.6 (108.6)
	d(Si-Si) = 2.345 (2.331)	∠SiSiH = 110.3 (110.3)
SiN	d(Si-N) = 1.604 (1.572)	

B. Adsorption geometries and energetics

We have determined the equilibrium geometries of the ammonia adsorbed Si(100) surfaces by varying the adsorption coverage and periodicity, both for the molecular (NH_3) and for the dissociative (NH_2 and H) adsorption cases. In what follows, we present first the structural properties for the

TABLE II. Calculated bond dissociation energies in eV. Experimental values are taken from Ref. 32.

Bond	Theory	Expt.
H-H	4.20	4.48
N-N	9.01	9.75
Si-Si	2.83	3.35
H-N	1.15	
H-SiH_3	4.25	3.94
N-Si	4.01	4.83

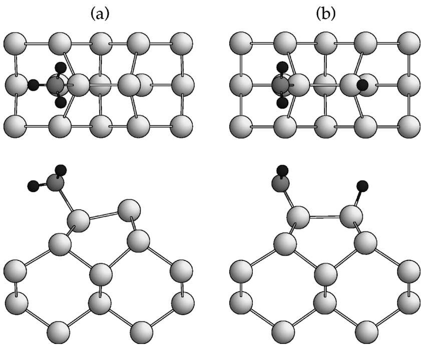

FIG. 1. Top and side views of the equilibrium atomic structures for the NH_3 adsorbed Si(100)-(2×1) surfaces: (a) the molecular adsorption and (b) the dissociative adsorption. The large, medium, and small circles represent Si, N, and H atoms, respectively.

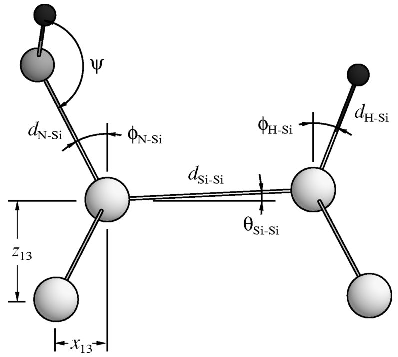

FIG. 2. Schematic side view of the atomic geometry for the dissociatively adsorbed surface with the definition of structural parameters.

(2×1) surfaces shown in Fig. 1 and then extend to other coverage and surface periodicity.

To begin with, we describe the result for the molecular adsorption for its simplicity. We took the bonding geometry of the molecular state such that the nitrogen atom points towards the down Si atom of the buckled dimer since its empty-bond state is expected to attract the lone-pair state of NH_3. In fact, this geometry turned out to be the only one for stable molecular adsorption. Other configurations like N atom pointing the up Si atom or H atom pointing the Si dimer were found to be unstable compared to the gas phase. The optimized structural parameters for the molecular adsorption are listed in Table III: the bond length between N and Si is 2.08 Å, the bond angle 31°, and the substrate Si dimer still remains asymmetric with a reduced tilt angle of 12°. We found that the adsorbed NH_3 molecule can rotate easily around the N-Si axis: the energy barrier for the molecular rotation is as low as 0.05 eV.

We move on to the dissociative adsorption. This is known as the room-temperature adsorption phase, and previous experimental and theoretical data are available. The bonding geometry of the dissociated species was taken from the mentioned molecular state by removing one H atom from the adsorbed NH_3 and attaching it on the up Si atom [see Fig. 1(b)]. This geometry was already speculated by experimental works.[4,5] The optimized structural parameters are listed in the lower part of Table III: the bond length and angle of N-Si are 1.76 Å and 28°, and the Si dimer tilt is less than 1°. This shorter N-Si bond length can be understood as a result of that the amino species forms a more strong chemical bond with silicon than the ammonia molecule does. The energy barrier for molecular rotation with respect to the N-Si axis is calculated as 0.09 eV for NH_2, i.e., the amino species is to some extent constrained to the equilibrium geometry unlike the molecular case.

While experimental data is rare for NH_3 on the Si(100) surface, key structural parameters like $d_{\text{N-Si}}$ and $\phi_{\text{N-Si}}$ (see Fig. 2) were determined by the room-temperature photodiffraction (PD) experiments by Franco *et al.*[15] Our calculated values for $d_{\text{N-Si}}$ and $\phi_{\text{N-Si}}$, 1.76 Å and 28°, agree well with the experimental values of 1.73±0.08 Å and 21±4°.[33] Franco *et al.* also emphasized that the Si dimer becomes essentially symmetric by the dissociative adsorption of ammonia, which is confirmed by our result of the dimer tilt angle of less than 1°. Actually, their conclusion was based on the measurement of the relative positions of the first- and the second-layer Si atoms on the NH_2 side (x_{13} and z_{13} in Fig. 2). The calculated $x_{13}=0.61$ and $z_{13}=1.23$ Å are also compared well with the experimental values of 0.50±0.25 and 1.12±0.06 Å.

Whereas the ASED-MO calculations by Zhou *et al.*[16] show noticeable discrepancies with our results, especially in bond lengths, the Slab-MINDO results by Moriarty and Smith[17] agree well with ours except for ψ, the angle between the NH_2 molecular plane and the N-Si bond. Though their calculation gave 168° for ψ, resulting in a nearly planar configuration for Si-NH_2, our calculation predicted 146°, closer to experimental suggestions.[4,5]

TABLE III. Calculated structural parameters for the ammonia adsorbed Si(100)-(2×1) surfaces in comparison with previous theoretical and experimental results. For the definition of the parameters, see Fig. 2.

		Si-NH_X ($X=2$ or 3)				Si-Si		Si-H	
Species		$d_{\text{N-Si}}$	$\phi_{\text{N-Si}}$	$d_{\text{N-H}}$	ψ	$d_{\text{Si-Si}}$	$\theta_{\text{Si-Si}}$	$d_{\text{H-Si}}$	$\phi_{\text{H-Si}}$
NH_3	Present theory	2.08	31°	1.04	127°	2.41	12°		
NH_2+H	Present theory	1.76	28°	1.03	146°	2.44	0°	1.51	20°
	ASED-MO [a]	2.04	25°	1.10			0°	1.38	25°
	Slab-MINDO [b]	1.71	23°	1.02	168°	2.42	−2°	1.52	20°
	PD Expt. [c]	1.73±0.08	21±4°						

[a] Reference 16 (Zhou, Cao, and Fu, 1991). Si dimers are assumed to be symmetric.

[b] Reference 17 (Moriarty and Smith, 1992).

[c] Reference 15 (Franco *et al.*, 1997).

TABLE IV. Adsorption energies for the molecular NH_3 and the dissociated NH_2+H species on the Si(100) surface. For all cases except where noted, the ammonia coverage is assumed to be one NH_3 molecule per Si dimer. $N_{\mathbf{k}}$ is the number of **k** points in the (2×2) surface Brillouin zone. N_{layer} represents the slab thickness of the Si substrate. For the calculation of adsorption energies, the clean Si(100) surface is referred to as the $p(2\times2)$ reconstructed surface.

Cell size	E_{cut} (Ry)	$N_{\mathbf{k}}$	N_{layer}	E_{ads} (eV)	
				NH_3	NH_2+H
$p(2\times1)$	20	4	8	0.69	1.97
$p(2\times1)$	25	4	8	0.71	1.95
$p(2\times1)$	20	16	8	0.70	2.01
$p(2\times1)$	20	4	12	0.69	1.95
$p(2\times1)$	20	4	8	0.69	1.97
$p(2\times2)$	20	4	8	1.07	2.02
$p(2\times2)$ [a]	20	4	8	1.21	1.99

[a] 1/2 NH_3 per Si dimer.

The local structures of the molecular and the dissociated species on the Si(100)-$p(2\times2)$ surface, at the coverage of 1/2 or 1 NH_3 per Si dimer, are nearly identical with those on the $p(2\times1)$ surface, i.e., the bond lengths and the bond angles change within 0.01 Å and 2°, respectively. One exception is the bond length of N-Si for the molecular state, which becomes slightly shorter on the $p(2\times2)$ surface, giving 2.01 Å.

Finally, we summarized the calculated adsorption energies in various adsorption geometries in Table IV. Results given in the first four rows in the table, with the $p(2\times1)$ surface periodicity, are presented to demonstrate that our calculated adsorption energies are well converged within 0.05 eV with respect to the used computational parameters, i.e., the plane-wave basis size, the number of **k** points, and the substrate slab thickness. The next three rows in the table show the dependence of the adsorption energies on the surface periodicity and the ammonia coverage. While the adsorption energy of the dissociated state shows a nearly constant value of about 2.0 eV for all the environments, the adsorption energy for the molecular state depends strongly on the coverage and the arrangement of NH_3 molecules, in the range 0.7–1.2 eV. This indicates that the interadsorbate repulsive interaction is strong for the molecular species but negligible for the dissociated species.[34] The calculated adsorption energy of 2.0 eV for the dissociated state is in good agreement with the activation energy for the associative desorption of NH_3, 2.0 eV, determined by the TPD experiment of Dresser *et al.*,[4] but, for the molecular adsorption energy, there are no experimental data to be compared.[35]

C. Molecular-precursor mediated dissociation pathway

With a much larger adsorption energy, the dissociated state is energetically more favored than the molecular state. This accords with the fact that only the dissociated species are observed in room-temperature experiments. Since the molecular state itself appears to be locally stable in total-energy calculations, however, it is also interesting to consider its stability over the dissociation into the lower-energy chemisorption state. This problem is referred to as the question on the existence of a so-called precursor state, which would play an important role in low-temperature dissociation of NH_3 on the Si(100) surface. We pursue this possibility by examining the energy diagram obtained for the most probable dissociation pathway we found for the molecular state.

We put together in Fig. 3 the calculated energy diagram and, for clarity, the atomic geometries at four representative points in the diagram. Along the path from the gas-phase NH_3 (a) to the molecularly adsorbed state (b), there is no adsorption barrier due to the energetically favored hybridization between the lone-pair state of NH_3 and the empty dangling bond state of the down atom of the Si dimer. The energy barrier for the adsorbed NH_3 (b) to dissociate into NH_2 and H (d) was found to be ~0.6 eV at the saturation coverage, with a slight increase of about 0.1 eV at lower coverages.

This energy diagram implies that the molecular physisorption may survive at sufficiently low temperature by the existence of a certain energy barrier, but thermal activation at

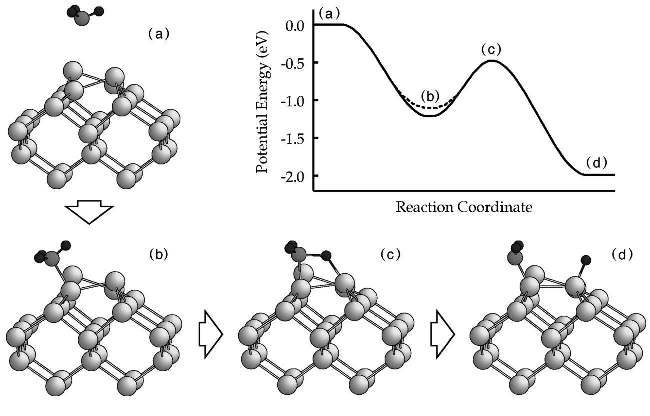

FIG. 3. Calculated energy diagram for the precursor mediated dissociation process of NH_3 on the Si(100) surface and the atomic geometries at four representative points in the diagram. At the coverage of 1/2 NH_3 per Si dimer (solid line), the molecularly adsorbed NH_3 is stable by ~1.2 eV with respect to the gas-phase NH_3 and the activation energy for dissociation is estimated to be ~0.7 eV. At the saturation coverage of one NH_3 per Si dimer (dashed line), the adsorption energy and the resulting dissociation barrier become slightly lower by ~0.1 eV. The adsorption energy of the final dissociated state is ~2.0 eV.

higher temperatures possibly carries the system into the dissociative chemisorption state over the energy barrier. In our estimation, based on the Arrhenius-type activation process with use of the attempt frequency ranging from 10^{13} to 10^{15} Hz, the barrier of 0.6 eV corresponds to 200–230 K for full dissociation. This is consistent with the experimental fact that at room temperature only one nitrogen species is found and that is the NH_2 species.

For an adsorbed molecular NH_3, there are many Si sites for an H atom detached from the NH_3 to adsorb on. But we considered only the case of the H atom adsorbing on the Si atom in the same dimer unit. This is because, in our $p(4\times1)$ unit cell calculation, the energy barrier for an H atom to hop to the neighboring dimer was found to be slightly higher ($\sim$0.2 eV) than that necessary for hopping in the same dimer.

It should be noted that the aforementioned precursor-mediated dissociation channel is not necessarily the only dissociation channel. Experimentally, it is known that the NH_2 species exists at very low adsorption temperature of about 100 K. This may be explained either by further lowering of the dissociation barrier due to the interaction of the molecularly adsorbed ammonia with the overlaying condensed ammonia layers, that are usually formed on the Si(100) surface at very low temperature, or by the existence of direct dissociation paths bypassing the molecular precursor state.

Our results should not be directly compared with the work of Zhou, Cao, and Fu,[16] where they found no dissociation barrier. The initial molecular state in their model is completely different from ours, i.e., the adsorbed ammonia molecule bridges two unbuckled dimers that lie along the dimer direction. We found that such a configuration is highly unstable compared to our molecular configuration.

IV. SUMMARY

We have presented the results of density-functional total-energy calculations for the ammonia adsorbed Si(100) surface, for the cases of both molecular and dissociative adsorption. In the dissociative adsorption, NH_2 (H) prefers to adsorb on the down (up) atoms of buckled Si dimers, and the calculated adsorption energy of 2.0 eV, bond (N-Si) length of 1.76 Å, and bond angle of $\sim$28° are in good agreement with recent experimental results. The molecular adsorption, where ammonia molecules bond to the down Si atoms, is also stable with an adsorption energy of 1.2 eV, but there exists a low-energy (of about 0.6 eV) activation pathway to the more stable dissociative adsorption. This molecular-precursor mediated dissociation channel explains well the experimental fact that most ammonia molecules exist in the dissociated form at room temperature and will be useful in understanding the adsorption process at sufficiently low temperature.

ACKNOWLEDGMENTS

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minimization of the Kohn-Sham energy functional as in the usual *direct* approach.

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[33] Our calculated bond lengths of Si-NH$_X$ for $X=3$, 2, and 1 are 2.08, 1.75, and 1.66 Å, respectively. Hence, the room-temperature PD data of $d_{\text{N-Si}}=1.73$ Å provides more evidence that the nitrogen-containing species at room temperature is NH$_2$.

[34] The substrate relaxation effect is also incorporated in the adsorption energy difference, but it would be at most about 0.1 eV for the molecular species, corresponding to the energy difference between the $p(2\times2)$ phase and the asymmetric $p(2\times1)$ phase, and would be negligible for the dissociated species regardless of the surface periodicity since the underlying Si dimer is nearly symmetric.

[35] Ammonia molecules are, however, known to adsorb molecularly on the Ge(100) surface: Ranke reported in Ref. 36 that at the coverage of one NH$_3$ per Ge dimer the surface periodicity becomes $p(2\times2)$ and the adsorption energy for the molecular NH$_3$ is 0.9–1.4 eV. Our value of 1.1 eV obtained from the same geometry on the Si(100) surface suggests that the bonding of NH$_3$ with Si is similar to that with Ge.

[36] W. Ranke, Surf. Sci. **342**, 281 (1995).