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Adsorption of NH_3 on Ge(001)

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Using a first-principles pseudopotential method we have studied the interaction processes involved in the adsorption of ammonia on the germanium surfaces. We have found that ammonia adsorbs molecularly on the germanium surface and, in contrast to the interaction of the same species with the silicon surface, no dissociation takes place. The adsorption process is barrierless and the adsorption energy for the first NH_3 molecule is 19.6 kcal/mol. A second ammonia molecule will be adsorbed in a (2×2) periodicity, i.e. following the flip of the dimer tilt direction of every second dimer row, with an adsorption energy of 12 kcal/mol. This suggests that there is most certainly a critical coverage around $\frac{1}{4}$ ML (monolayer) after which the adsorption rate decreases, but nothing forbids the completion of $\frac{1}{2}$ ML. The most probable structure is characterized by asymmetric and elongated Ge-Ge dimers, and by an adsorbed NH_3 specie with structural characteristics very close to the free molecule. Our calculated vibrational spectra further support the molecular adsorption model for the NH_3 interaction with the germanium surface.

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I. INTRODUCTION

Studies of adsorbate covered semiconductor surfaces have attracted a great deal of attention in the past few years, in particular due to their role in device manufacture. In particular, ammonia has been extensively explored in the microelectronics industry as a precursor for thermal nitridation applications in silicon. For this reason, there has been a great deal of interest in the study of nonequilibrium methods for growth and doping, in order to bypass the thermodynamic constrains on chemical composition.[1] The importance of the use of dopants in modifying both the surface energies and morphologies of films grown by chemical vapor deposition (CVD) or gas-source molecular-beam epitaxy has increased dramatically, mainly due to its widespread use in the production of new device technologies. However, surface segregation[2] and island formations are just some examples of the undesirable effects in device production. As a result, a considerable experimental effort has been devoted to understanding the adsorption and chemisorption process of some common CVD gas source on the semiconductor surfaces, with the ultimate aim of achieving control of dopant concentration and its spatial distribution in the film. Therefore it is essential to study details of the geometry and electronic structure of the interaction of the common CVD gas sources, in particular NH_3. Ammonia is an excellent nitration agent, useful in the production of ultrathin, sharp silicon nitride (SiN_x) interfaces with potential application in future ultra large-scale integrated circuits.[3] Due to its technological importance, the nitration process of the silicon surface via NH_3 is one of the most studied system among the CVD gas fonts. However, the interaction of the same species with the germanium surface is far less explored, besides its increasing importance in device production.

One of the first experimental investigation on the chemistry of NH_3 on the germanium surface was carried out by Chen and Ranke[4] using x-ray, ultraviolet, and angle-resolved ultraviolet photoelectron spectroscopies (XPS, UPS and ARUPS), low-energy electron diffraction (LEED) and spot-profile analysis LEED (SPALEED). In contrast to the dissociative adsorption of ammonia on the silicon surface (see, for example, Ref. 5 and references therein), the experimental results obtained by Tindall and Hemminger indicate a molecular adsorption of NH_3 on the germanium surface. This was later confirmed by the same group[6] by means of the analysis of 3d core level shifts. In this latter work, the authors suggest that NH_3 adsorbs initially on the electrophilic (down) surface dimer atom, as is the case for silicon. Tindall and Hemminger[7] have used high-resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy, LEED, and thermal desorption in the investigation of the chemistry of nitrogen hydrides on Ge(001). Their results are consistent with the previous findings by Ranke and co-workers. Subsequent works by Ranke and co-workers using different techniques such as photoelectron spectroscopy and LEED (Ref. 8), ARUPS and LEED (Ref. 9) and LEED and SPALEED (Ref. 10) confirms that NH_3 adsorbs molecularly with no substrate bonds breaking with an ammonia coverage of one molecule per Ge dimer in a (2×2) reconstruction, caused by a flip of the dimer tilt direction of every second dimer row. Recent investigations of the electron-stimulated dissociation of ammonia adsorbed on the germanium surface using temperature programmed desorption, electron-stimulated desorption, and XPS (Ref. 11) and HREELS (Ref.

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12) are also consistent with previous experimental analysis.

Although all experimental works so far suggest that ammonia molecularly adsorbs on the Ge(001) surface and that no evidence of the dissociation of NH_3 into NH_2+H takes place, little is known about details of the adsorption, dissociation and local geometry resulting from the interaction of ammonia with the germanium surface. In order to contribute to a better understanding of the molecule-surface interaction process, in this work we employ the state of the art pseudopotential method, within a generalized gradient approximation to the density functional theory to investigate the adsorption process involved in the interaction of NH_3 with the germanium surface. Possible dissociation paths are also investigated and the results are compared to our previous study for the silicon based system. In addition, we have also determined local vibrational modes and compared them to experimental data available in the literature, with a view to support the proposed models.

II. METHOD

The surface was modeled in a supercell geometry, with an atomic slab of six Ge layers and a vacuum region equivalent to eight atomic layers. The theoretical bulk lattice constant of 5.74 Å for Ge was used in the surface calculations. On the top side of the slab we placed the NH_3 molecule in different configurations, and the back surface was passivated by H atoms arranged in a dihydride structure. The pseudopotentials for Ge, N, and H were derived by using the scheme of Troullier and Martins[13] and the electron-electron exchange correlation was considered by using the generalized gradient approximation.[14] The single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 30 Ry and four special **k** points were used for the Brillouin-zone summation. Increasing the energy cutoff to 35 Ry did not change the key structural parameters by more than 0.6%, while the difference between total-energy values calculated using both plane-wave expansions are smaller than 0.1%. The electronic and ionic degrees of freedom were relaxed by adopting the scheme described by Bockstedte *et al.*[15] The atoms were assumed to be in their fully relaxed positions when the forces acting on the ions were smaller than 0.005 eV/Å. The vibrational modes were calculated by using the frozen-phonon approach.[16] In our calculations for the dynamical properties only the adsorbed system (NH_3) and the Ge dimer atoms were allowed to vibrate. The most probable pathways and predicted energies from the gas-phase molecule to the adsorbed states were obtained by using a constraint dynamics scheme in which atomic movement along the pathway is a response to forces in a local region around it. The constraint is set only for the nitrogen atoms during the adsorption and dissociation processes. The energetic barriers are estimated following the phenomenological approach in the form of the Arrhenius equation[17] (for a more complete description see Ref. 18). The adsorption energy for the NH_3 molecule was calculated as $E^{ads}_{conf}=-[E_{conf}-(E_{ref}+E^{ads})]$, where E_{conf} is the total energy for the considered configuration, E_{ref} is the total energy for the free Ge(001)-(2×2) surface and $E^{ads}=aE^{\mathrm{NH_3}}_{chem}+bE^{\mathrm{NH_3}}_{free}$, where $E^{\mathrm{NH_3}}_{free}$ is the total energy for a NH_3 molecule in a box of side 25 a.u., and $E^{\mathrm{NH_3}}_{chem}$ is the chemisorption energy of a NH_3 molecule on the Ge(001) surface. The coefficients *a* and *b* are appropriately chosen for a given configuration.[18]

III. RESULTS

A. Preliminary results

For bulk germanium our first-principles calculations produced 5.74 Å for the equilibrium lattice constant (a_o), 0.80 Mbar for the bulk modulus, and 3.96 eV for the cohesive energy. These values are in very good agreement with the experimental values presented in Ref. 19. The clean Ge(001)-(2×2) surface is characterized by tilted and alternated Ge-Ge dimers, i.e., one dimer component is at a higher position than the other and neighboring dimers are tilted in opposition. The tilting of the dimer allows charge transfer from the "down" atom (which becomes more planar or sp^2 bonded) to the "up" atom (which becomes nearly pyramidal or sp^3 bonded). Thus, the "down" Ge atom dimer is electron deficient, while the up Ge atom is electron rich. Our calculations support this model: the Ge-Ge dimer is found to have a bond length of 2.47 Å and a vertical buckling of 0.81 Å, indicating a tilt angle of 20.6°, in good agreement with previous theoretical and experimental work (see, for example, Ref. 20).

To test the reliability of the nitrogen and hydrogen pseudopotentials, we performed additional calculations. We have investigated the structural parameters of a series of gas molecules involving germanium, nitrogen and hydrogen. For the N_2 molecule, for example, we calculated the N-N bond length of 1.12 Å, in very good agreement with the experimental value[21] of 1.10 Å. For the trigonal pyramidal molecule NH_3 we found 1.05 (1.01) Å for the bond length N-H and for the bond angle of 104 (107)° H-N-H , again in very good agreement with experimental values[21] given in the parentheses.

B. NH_3/Ge(2×2)-(001) surface

Although a series of experimental works carried out by Ranke and co-workers using different techniques[8–10] suggests an ammonia coverage of one molecule per Ge dimer in a (2×2) reconstruction, i.e., a $\frac{1}{2}$ monolayer (ML) coverage, we have recently shown[18] that the interaction of phosphine (PH_3) with the silicon surface is decisively affected by the dimer interaction. For low phosphorus coverages ($\frac{1}{4}$ ML) phosphine adsorbs molecularly on one side of the Si-Si dimer and, at temperatures around 140 K, fully dissociates into PH_2 and H, with each component attached to one side of the dimer. For higher phosphorus coverages ($\frac{1}{2}$ monolayers) the interaction between adjacent dimers plays a decisive role in the dissociation process. Therefore, in order to address the possible role of the dimer-dimer interaction in the ammonia dissociation process we have also determined the equilibrium geometries of the adsorbed molecule both on the (2×1) and (2×2) reconstructions of the Ge(001) surface. In order to introduce the terminology that will be used in the present paper, we will briefly describe each of the reconstructions

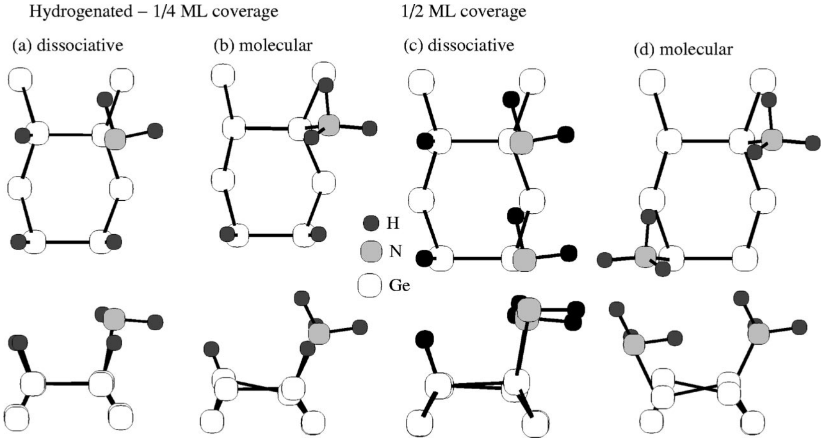

FIG. 1. Schematic views of the adsorption models of NH_3 on Ge(001)-(2×2) surface: (a) molecularly and (b) dissociated adsorption in a hydrogenate Ge(001) surface (i.e., H atoms bonded to both components of the Ge-Ge dimer), corresponding to a $\frac{1}{4}$ ML ammonia coverage; and two (a) molecularly and (b) dissociated molecules corresponding to a $\frac{1}{2}$ ML ammonia coverage. All drawings are on the $[110]$-$[1\overline{1}\overline{0}]$ plane.

considered: (a) the bridge adsorption site (i.e., NH_3 bonded to both Ge atoms on the Ge-Ge dimer); (b) the molecularly adsorption site (i.e., NH_3 molecule bonded to only one component of the dimer); (c) the dissociated adsorption site (i.e., NH_2 and H bonded to different components of the dimer); (d) hydrogenated Ge(001) surface (i.e., H atoms bonded to both components of the Ge-Ge dimer.[22]) For the (2×2) reconstruction we considered all possible combinations of the above models. However, for the (2×1) reconstruction clearly there is no possibility of combining different models. A 0.5 ML nitrogen coverage corresponds to one ammonia molecule per Ge-Ge dimer [it could be either one molecule in a (2×1) reconstruction or two molecules in a (2×2) reconstruction], while a 0.25 ML nitrogen coverage is usually associated to a (2×2) reconstruction where an ammonia molecule is bonded to one of the germanium dimers, while the other Ge-Ge dimer dangling bonds are either hydrogenated or as on a clean free surface. In the following section we are going to analyze the stability of all the proposed models considering both possible coverages.

An hypothetical 1 ML ammonia coverage would be very unlikely, as it is well established that the electron deficient (down) and electron rich (up) Ge dimer atoms tend to react as electrophile and nucleophile, respectively. In general, the dissociative adsorption of electron-rich species (Lewis bases), such as H_2O, is initiated by interaction with the electrophilic surface atom. As NH_3, and other XH_3 species ($X = \text{As}$ and P) are a Lewis bases, we expect them to initially adsorb on the electrophilic surface atom. Indeed this was already observed by us for the silicon substrate[23] and is also the case for the ammonia adsorption on the germanium surface as described below. In contrast to the case of phosphine adsorption on the silicon surface, our results suggest that the ammonia adsorption process on the germanium is not decisively affected by dimer-dimer interactions. This is because for both the (2×1) and (2×2) reconstructions the energetics of the $\frac{1}{2}$ ML nitrogen coverage are equivalent. In a similar manner, for a $\frac{1}{4}$ ML, the presence of hydrogen atoms saturating the dangling bonds of the Ge-Ge dimers not bonded to the ammonia molecule, as in Fig. 1(a), will not induce any structural or energetic changes in the picture described below. As previously observed for other XH_3 (Ref. 23) species, the bridge configuration is not found to be a stable configuration from the energetic point of view.[24] Therefore, we will refrain our discussion only to the nonhydrogenated molecularly and dissociative adsorbed structures presented in Fig 1.

For both $\frac{1}{2}$ and $\frac{1}{4}$ ML nitrogen coverages, our first-principles calculations suggest that the molecular adsorption model corresponds to the energetically more favorable structure. The molecular adsorption of the first ammonia molecule, as in Fig. 1(b), is an exothermic process with an energy gain of 19.6 kcal/mol. This is very close to isotheric heat of adsorption predicted by Ranke[8] (21 kcal/mol). The adsorption energy for the second molecule following the flip of the dimer tilt direction of every second dimer row, as in Fig. 1(d), is slightly smaller: 12 kcal/mol. However, the adsorption of a second molecule in a (2×1)-like structure, i.e., all ammonia molecules are adsorbed on the same side of the dimer row, is not found to be a stable configuration (as this second molecule does not bind to the surface), indicating that the dimer-dimer interaction is not negligible. This is consistent with the (2×2) reconstruction observed by Ranke and Platen[9,10] via LEED. Our calculations also suggest that there is most certainly a critical coverage around $\frac{1}{4}$ ML after which the adsorption rate decreases, but nothing forbids the completion of $\frac{1}{2}$ ML of adsorbed ammonia if the germanium surface is exposed to a rich NH_3 environment or if the exposure occurs for a long period of time. This is also consistent with the (2×2) reconstruction observed and with a constant sticking coefficient up to $\frac{1}{4}$ ML coverage predicted by Chen and Ranke.[4]

The dissociative adsorption structures are also found to be energetically stable systems when compared to the free ammonia molecule and the bare germanium surface. The adsorption energies for these hypothetical structures are only 20–30 % smaller than for the molecularly adsorbed systems (15.7 kcal/mol for a $\frac{1}{4}$ ML coverage and 8.3 kcal/mol for a $\frac{1}{2}$ ML coverage), suggesting that the key factor for their occurrence would be the energetics of the dissociation process. In order to investigate this possibility, we have estimated the most probable reaction pathways and predicted energetics for the adsorption and dissociation of NH_3 on the Ge(001) surface. At this point, it is worth emphasizing that it is well known that the use of pseudopotentials in nonlocal density functional theory calculations is responsible for an underestimation of the calculated activation energies. The degree of

TABLE I. Comparison of structural parameter values for the molecularly (mol) and dissociated (diss) adsorption models for ammonia on the Ge and Si(001)-(2×2) surfaces. All bond lengths are in Å, while bond angles (∠) are in °. The chemisorption energy for the $\frac{1}{4}$ ML ammonia coverage (E_{chem}) are in kcal/mol.

X	Ge		Si	
	mol	diss	mol	diss
X-X	2.58	2.57	2.35	2.39
X-X∠	17	4.5	10	2.7
X-N	2.17	1.83	1.98	1.78
X-N∠	37	43	20	12
N-H	1.03	1.03	1.03	1.06
H-N-H∠	108	109	108	103
E_{chem}	19.6	15.7	25.1	31.5

underestimation is system dependent and it was found to be around 10 kcal/mol for a Si_2H_6 model of H_2 desorption from Si(001).[25]

The adsorption of one or two NH_3 molecule on the germanium surface is found to be barrierless, i.e., we have found no energy barrier for this process. This is in agreement with our findings[23] for the adsorption of the same species on the silicon Si(001) surface. Considering the phenomenological approach in the form of the Arrhenius equation, with the choice for the A-factor between 10^{13} and 10^{15} s^{-1},[17] we have estimated that complete dissociation of the NH_3 molecule into NH_2+H after adsorption is unlikely, as it will occur only at very high temperatures (around 2400 K). This is consistent with the absence of any experimental[12] evidence for a Ge-H stretch mode that would be indicative of partial NH_3 dissociation upon adsorption as was observed on the Si(001) surface, where a much smaller energy barrier (corresponding to an activation energy around 215–250 K) was calculated by us (see, for example, Ref. 5,23). It is interesting to note that Cho and co-workers[26] have also recently observed the same pattern for water (i.e., water adsorbs dissociatively for the silicon substrate and molecularly for the germanium substrate). We would like to emphasize that the energy barrier presented here does not necessarily correspond to the experimentally observed process, as a great number of different pathways may be allowed during the adsorption or dissociation of the molecule.

Our calculations indicate that the global structural features, presented in Table I, observed for the molecularly and dissociated adsorbed models of ammonia on the Si and the Ge substrates are very similar. In both cases we have found that the Ge-Ge (Si-Si) dimers are not broken in the adsorption process. As for the silicon substrate, our structural data for the germanium substrate indicate an asymmetric dimer with a buckling of 17°, slightly larger than the 10° observed for the former. The Ge-Ge dimer gets elongated by almost 4% for the germanium substrate, but only 2% for the silicon substrate. The pronounced elongation of the Ge-Ge dimer length when compared to the Si-Si dimer indicates that there is a larger degree of charge transfer between nitrogen and germanium than between nitrogen and silicon. The Ge-N bond is characterized by a bond length of 2.17 Å and a buckling with respect to the surface normal around 37°. As is the case for the silicon substrate, in the molecularly adsorbed structure the nitrogen atom appears to be in a straight line with the Ge-Ge (Si-Si) dimer. It is interesting to note that, for the silicon substrate, only after dissociation the nitrogen atom is slightly off the Si-Si dimer line.

The NH_3 adsorbed molecule is found to retain its trigonal-pyramidal structure, in agreement with our findings for the silicon substrate. The N-H bond length (1.03 Å) and H-N-H bond angle (108°) are also very close to the calculated values obtained for the ammonia molecule. In a hypothetical dissociated structure, the bond lengths and bond angles (∠) calculated by us are as follows: Ge-Ge = 2.57 Å, Ge-Ge∠ = 4.5°, Ge-H = 1.53 Å, Ge-H∠ = 23°, Ge–N = 1.83 Å, Ge−N∠ = 43°, N–H = 1.03 Å, and H-N-H∠ = 109°. These values are consistent with our findings for the dissociate adsorption model observed for ammonia on the Si(001) surface. From our calculations, we have also inferred[27] that the work function of the Ge(001) surface decreases linearly with the ammonia coverage, in agreement with the experimental findings by Ranke and co-workers.[9]

For calculating the zone-center optical phonon frequency modes we set up a 36×36 eigenvalue problem, and only selected modes that describe a pronounced surface character. Results for our calculated zone-center vibrational modes as well as available experimental data for stretch, bend and scissors modes for the molecularly and (hypothetical) dissociatively adsorbed models of NH_3 on both the germanium and silicon surfaces are presented in Table II. In general, we find that all the surface phonon modes observed experimentally for the molecular adsorption model are reliably reproduced in our calculations. We would like to point out that our results in Table II are not corrected to reproduce experimental values. This is because we do not believe that first-principles vibrational frequencies obtained within the frozen phonon approach should be corrected at all, as these results are usually used to evaluate the quality of the schemes employed and also to predict the existence of vibrational modes to be observed experimentally.[23] The decrease of the X-N stretch mode as X changes from Si ($630\ cm^{-1}$) to Ge ($505\ cm^{-1}$) is consistent with the force constant and mass trend generally observed, i.e., $\omega\propto\sqrt{(\lambda/M)}$, which gives us confidence in our calculation scheme. As the experimental detection of vibrational modes are one of the strongest experimental indications of bond formation on adsorbed species, we believe that, based on the present calculation and the available HREELS experimental data[7,12] we can safely conclude that ammonia adsorbs molecularly on the germanium substrate and no dissociation process takes place.

It is now well established that electronic band-structure calculations for germanium using the density-functional theory (DFT) are not capable to correctly describe the germanium band gap, even when corrections as the generalized density-functional theory are applied (see, for example, Ref. 28). In fact, the majority of DFT works so far gives a zero gap for bulk germanium. This is a direct consequence of the fact that DFT is a theory developed for ground-state systems (for a complete discussion on this topic see, for example,

TABLE II. Zone-center vibrational modes, in cm^{-1}, for the molecular (mol) and dissociative (diss) adsorption models of NH_3 on Ge and Si(001)-(2×2) surfaces. Pres denotes present paper.

	Ge				Si	
	mol			diss	mol	diss
	Pres	Expt.	Expt.	Pres	Pres	Pres
$N\text{-}H^{assym}_{stretch}$	3419	$\sim$3600		3334	3447	
$N\text{-}H^{sym}_{stretch}$	3180	3270	$\sim$3400	3129		1483
$N\text{-}H_{scisors}$	1439			1339	1501	
$N\text{-}H^{assym}_{bending}$	1511	1570	1600	1690		
$N\text{-}H^{sym}_{bending}$	1093	1150	1100	835		
$N\text{-}H_{stretch}$	505			584	630	807
$N\text{-}H_{stretch}$	423			387		
$N\text{-}H_{stretch}$				1990		2083

[a] Reference 7.

[b] Reference 12.

Ref. 29). Therefore, we are not going to analyze the modifications on the electronic structure of the germanium surface upon the adsorption of an ammonia molecule. Although DFT was not developed for unoccupied states, it provides a very good description of the electronic structure for occupied states. We can make use of this feature to obtain STM (scanning tunneling microscopy) images from the calculated electronic eigensolutions, following the Tersoff-Hamann formalism, as described in Ref. 30. Figure 2 shows the theoretical STM image for the filled states of the Ge(001)-(2×2): NH_3 system. The (2×2) reconstruction is easily identified and is indicated by the dashed rectangle. It is worth pointing out that the present image is much richer than a constant-current experiment. In contrast to experimental conditions, in our simulation all tunneling currents are considered and represented by different brightness. If only the brighter regions are considered, only the adsorbate (depicted by an arrow in Fig. 2) in a (2×2) periodicity caused by a flip of the dimer tilt direction of very second dimer row can be identified. Our STM image is very similar to the experimental model proposed by Ranke and co-workers,[9,10] and indicates that the molecular adsorption model could be easily identified in a standard STM measurement.

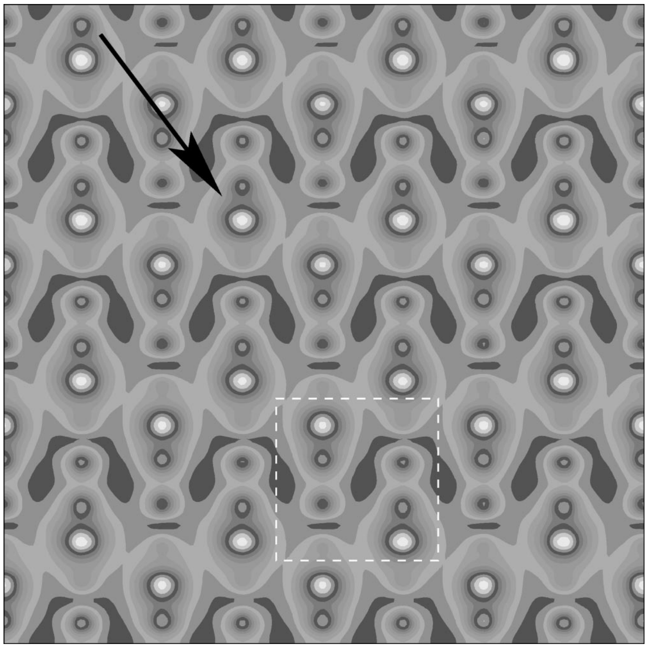

FIG. 2. Theoretical STM image obtained for a bias voltage of -2.0 V for the molecular adsorption model of the NH_3 molecule on the Ge(001)-(2×2) surface. The dashed rectangle indicates the unit cell, while the arrow indicates the adsorbed molecule features. Different brightness (contour lines) represent different tunneling current windows.

IV. SUMMARY

We have performed *first-principles* calculations for the atomic structure and the dynamical properties of the adsorption of ammonia on the germanium surfaces. We have found that, in contrast to the extensively studied system Si(001): NH_3, ammonia adsorbs molecularly on the germanium surface and no dissociation takes place. The adsorption process is barrierless and the adsorption energy for the first NH_3 molecule is 19.6 kcal/mol, very close to the isotheric heat of adsorption predicted by Ranke[8] (21 kcal/mol). A second ammonia molecule will be adsorbed in a (2×2) periodicity, i.e., following the flip of the dimer tilt direction of every second dimer row, in agreement with the experimental LEED patterns,[9,10] with an adsorption energy of 12 kcal/mol. This suggests that there is most certainly a critical coverage around $\frac{1}{4}$ ML after which the adsorption rate decreases, but nothing forbids the completion of $\frac{1}{2}$ ML. This is also consistent with the (2×2) reconstruction observed and with a constant sticking coefficient up to $\frac{1}{4}$ ML coverage predicted by Chen and Ranke.[4] We have estimated that complete dissociation of the NH_3 molecule into NH_2 + H after adsorption is unlikely, as it will occur only at very high temperatures (around 2400 K). The most probable structure is characterized by asymmetric and elongated Ge-Ge dimers, and by an adsorbed NH_3 specie with structural characteristics very close to the free molecule. Our calculated vibrational spectra further support the molecular adsorption model for the NH_3 interaction with the germanium surface.

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