Role of Interdimer Interactions in NH_3 Dissociation on Si(100)-(2 × 1)

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The dissociation of NH_3 on Si(100)-(2 × 1) is investigated by a combination of infrared absorption spectroscopy and density functional cluster calculations, revealing that this reaction is governed by a complex set of interdimer interactions involving both bare and adsorbate-covered Si dimers. We propose that such adsorbate-induced changes in the electronic structure of neighboring dimers may have general implications for controlling the two-dimensional ordering of reactions on the dimerized Si(100) surface.

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Molecular-level control of semiconductor surface reactions is crucial to the growth of well-defined surface structures that may find use, for example, in molecular electronic devices [1,2] or biological sensors [3]. Recently Lopinski *et al.* demonstrated the ability to generate self-assembled rows of organic molecules on Si(100)-(2 × 1), offering the tantalizing potential for chemically controlled deposition of molecular wires on a semiconducting substrate [4]. The authors suggest that interaction of incoming molecules with dimers on the Si(100) surface may be significantly affected by the presence of adsorbates on neighboring sites, thereby dictating the geometry of structures obtained. While it is reasonable to expect that such interactions will play a critical role in the nanoscale growth of low-dimensional structures, to date there is, to our knowledge, no study that identifies such an interaction and provides evidence for its origin [5]. In this Letter we show that the adsorption and dissociation of ammonia (NH_3) on Si(100)-(2 × 1) is, in fact, governed by a complex set of such interdimer interactions, and that these effects ultimately determine the two-dimensional distribution of nitrogen in the initial overlayer. While NH_3 dissociation on Si(100) does not in this case form organized nanostructures, we propose that the interactions identified and elucidated herein will play a role in the spatial control of more complex reactions on this technologically critical surface.

As the most common nitriding agent for growing ultrathin Si_3N_4 films, NH_3 and its reactions with silicon surfaces have been the subject of numerous studies over the past decade. Despite the wealth of attention paid to this system, however, previous experimental studies of the adsorption of NH_3 on Si(100)-(2 × 1) have largely been limited to the identification of the dissociation products Si-NH_2 and Si-H and the description of their structure [6–10]. Two factors limit the ability of such studies to provide complete mechanistic understanding of this reaction: (1) insufficient spectral resolution to describe adsorbate bonding (including adsorbate/adsorbate interactions) with the requisite detail and/or (2) insufficient sensitivity and selectivity to identify minority adsorbate species that may play an important mechanistic role. In contrast, this Letter demonstrates that the combination of Fourier-transform infrared spectroscopy (FTIR) and density functional cluster calculations circumvents both these potential limitations to yield a full understanding of the initial reaction of NH_3 on Si(100)-(2 × 1).

To probe the full mid-IR spectral region, we have employed a single-pass transmission geometry for the FTIR experiments, as described previously [11]. All spectra were acquired with a Nicolet 860 spectrometer, using a broadband MCT-B detector at 4 cm^{-1} resolution, with the incident infrared beam 60° from the surface normal.

The infrared spectrum of a saturated overlayer of NH_3 adsorbed on Si(100)-(2 × 1) at 200 K [Fig. 1, (*d*) and inset] is consistent with dissociation of NH_3 to form Si-NH_2 [ν(Si-NH_2) = 817 cm^{-1}, δ(Si-NH_2) = 844 cm^{-1}, δ(NH_2) = 1534 cm^{-1}] and Si-H [δ(Si-H) = 624 cm^{-1}, ν(Si-H) = 2055 cm^{-1}]. The absence of any peak attributable to δ(N-H) [observed at ~1100 cm^{-1} in high-resolution electron-energy-loss spectroscopy of NH_3 on Si(111)-(7 × 7) [12]] confirms that further dissociation to NH does not take place at this temperature.

While this spectral assignment is fairly straightforward, one aspect of the spectrum in Fig. 1(*d*) defies simple explanation: specifically, the central ν(Si-H) frequency of 2055 cm^{-1} is anomalously low, at least 30 cm^{-1} lower

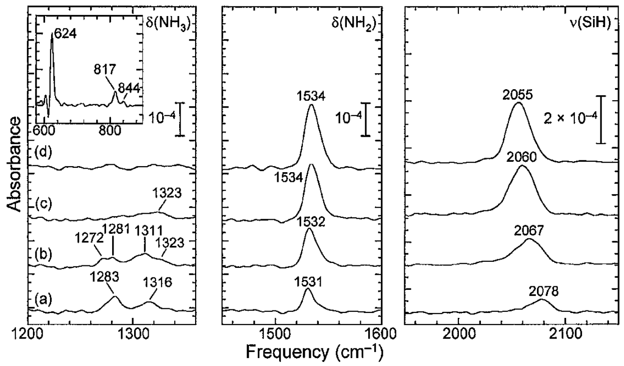

FIG. 1. Infrared spectra of NH_3 adsorbed on Si(100)-(2 × 1) at 220 K as a function of exposure, with coverages of the dissociated product estimated [from integrated ν(Si-H) intensity] at (*a*) 0.1, (*b*) 0.25, (*c*) 0.4, and (*d*) 0.5 ML. The inset shows the low-frequency region of the spectrum in (*d*). All spectra are referenced to the clean surface.

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than expected. For example, the Si-H stretching frequencies for coupled monohydride (H-Si-Si-H) are ν_a(Si-H) = 2088 cm^{-1} and ν_s(Si-H) = 2099 cm^{-1} [13]; dissociation of H_2O to form H-Si-Si-OH yields ν(Si-H) at 2085 cm^{-1} [14]. By simple electronegativity arguments, ν(Si-H) for H-Si-Si-NH_2 should fall between the frequencies for H-Si-Si-OH and H-Si-Si-H, in sharp contrast to the behavior described above.

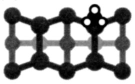
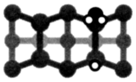
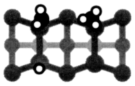
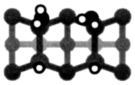
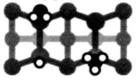
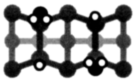
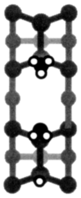
To further investigate this phenomenon we examined NH_3 dissociation as a function of exposure. Spectra acquired after a series of subsaturation NH_3 exposures [Fig. 1(*a*)–(*c*)] reveal that ν(Si-H) undergoes a continuous redshift from an initial frequency of 2078 cm^{-1} at 0.1 ML (monolayer) [Fig. 1(*a*)] to its final value of 2055 cm^{-1} for the saturated overlayer. This coverage-dependent shift is in the opposite direction than expected for dipole-dipole interactions at high coverage, and therefore the shift cannot be explained by simple coverage effects.

The coverage-dependent spectra in Fig. 1(*a*)–(*c*) also reveal two families of peaks at about 1300 cm^{-1} [e.g., at 1283 and 1316 cm^{-1} in Fig. 1(*a*)]. Since vibrational modes in this region can generally be attributed to the deformation modes of adsorbed, undissociated NH_3 species [15], we can tentatively assign this family of modes to Si-NH_3 moieties. While the presence of Si-NH_3 is in agreement with both theoretical predictions [16] and previous experimental observations at 90–120 K [10,17], the exact origin of the two distinct sets of symmetric deformation modes is not apparent by simple inspection. As will be shown below, both the explanation for the anomalous ν(Si-H) frequency and the identification of the specific Si-NH_3 species giving rise to these δ(NH_3) features are linked to a complex set of interdimer interactions that control the two-dimensional arrangement of NH_3 dissociation products on this surface.

To investigate the origin of the observed spectral features we performed first-principles theoretical calculations using the gradient-corrected B3LYP density functional method [18–20]. As in previous studies, a model cluster containing 9 Si atoms can represent a single dimer in its local environment. Clusters containing 15 and 20 Si atoms were used to represent the interaction of two dimers in the same row and in adjacent rows, respectively. In all cases, the dangling bonds resulting from truncation of Si-Si bonds were terminated with H atoms. In determining optimized structures and vibrational frequencies, the first two layers of atoms along with the adsorbate atoms were allowed to relax, whereas the remaining atoms were constrained in ideal crystalline positions. The polarized 6-31G** basis set was used for the relaxing atoms, while a 6-31G basis was used for the interior frozen atoms [21].

We begin by considering dissociation of NH_3 on a single dimer via formation of a metastable Si-NH_3 species [16] resulting from interaction of the NH_3 lone pair with the electrophilic (down-buckled) side of a buckled dimer [22]. This species (structure 1, isolated NH_3, Table I) exhibits a calculated δ_s(NH_3) frequency of 1265 cm^{-1} (see footnote in Table I for an explanation of scaling factors) and a Si-NH_3 bond strength of 28 kcal/mol, consistent with previous *ab initio* studies which found potential wells of 33 kcal/mol [16] and 29 kcal/mol [22] for NH_3 adsorbed on a single dimer [23]. Dissociation of Si-NH_3 to yield NH_2-Si-Si-H (structure 2, isolated NH_2 + H) yields ν(Si-H) at 2078 cm^{-1}, in agreement with the starting value of 2078 cm^{-1} for ν(Si-H) at low NH_3 exposure [Fig. 1(*a*)]. These two isolated structures can account for the spectral features observed at the lowest coverage, with the exception of the higher-frequency

TABLE I. Summary of the experimental and theoretical frequencies for structures considered in the Letter. Structures shown are schematic representations of the geometries calculated for each two-dimer cluster, viewed from above the dimer row.

Structure	Mode	Theory[a] (cm^{-1})	Experiment (cm^{-1})
(1) Isolated NH_3 	δ_s(NH_3)	1265	1272–1283
(2) Isolated NH_2 + H 	δ(NH_2) ν(SiH)	1522 2078	1531 2078
(3) H-bonded NH_3 + NH_2 	δ_s(NH_3) δ(NH_2) ν(SiH)	1320 1530 2059	
(4) H-bonded NH_2 + H 	δ(NH_2) ν(SiH)	1532 2073, 2077	
(5) Opposed NH_3 + NH_2 	δ_s(NH_3) δ(NH_2) ν(SiH)	1249 1514 2016	
(6) Opposed NH_2 + H 	δ(NH_2) ν(SiH)	1523 2057, 2059	1532–1534 2055
(7) Inter-row NH_3 + NH_2 	δ_s(NH_3) δ(NH_2) ν(SiH)	1300 1532 2079	1311–1323 1531–1534 2078

[a] Calculated frequencies for ν(Si-H) modes are corrected for systematic deficiencies due to anharmonic effects, etc., by -102 cm^{-1}, a value determined empirically in previous studies [11,33]. Both the NH_3 and NH_2 deformation modes are corrected by -67 cm^{-1}, a factor derived by comparing the theoretical δ_s(NH_3) frequency for gas-phase NH_3 with its experimental value.

$\delta_s(NH_3)$ mode at 1311–1323 cm^{-1}. In addition, these one-dimer models do not address the shift of ν(Si-H) to 2055 cm^{-1} as coverage is increased.

To explain these effects we now consider the interdimer interactions that emerge with increasing coverage. Once the surface is saturated [Fig. 1(*d*)], each H_2N-Si-Si-H unit resides next to another H_2N-Si-Si-H unit in the same dimer row. When the Si-NH_2 moieties of two such units are located on the same ends of their respective dimers, our calculations show that the NH_2 groups orient themselves to allow a hydrogen-bonding interaction (structure 4, H-bonded NH_2 + H). The resultant ν(Si-H) frequency is lowered only slightly from the isolated case, to 2077 cm^{-1}. In contrast, orientation of two adjacent Si-NH_2 moieties on *opposite* ends of their respective dimers (structure 6, opposed NH_2 + H) results in a dramatic redshift of ν(Si-H) to a calculated value of 2059 cm^{-1}. This opposed configuration is therefore assigned as the dominant one in the saturated overlayer of Fig. 1, by comparison with the experimental ν(Si-H) frequency centered at 2055 cm^{-1} [24]. It is interesting to note that structure 6 does not appear to be the thermodynamically preferred one, since H bonding between the NH_2 groups in structure 4 stabilizes that configuration by ~1 kcal/mol relative to opposed NH_2 + H. While longer-range interactions must be considered to evaluate the true relative stabilities of these configurations, it seems likely that kinetic control of the dissociation process dictates the distribution of NH_2 groups on the final surface, as discussed in more detail below.

The origin of the redshifted ν(Si-H) frequency lies in a charge polarization induced by NH_2 + H in adjacent dimers. A slight accumulation of positive charge on the Si atom bound to NH_2 induces an analogous polarization, oriented in the opposite direction, on the adjacent dimer. A Si-H bond located adjacent to a Si-NH_2 group on the next dimer in the row, as in structure 6, is therefore weakened by the negative polarization of its constituent Si atom, giving rise to the observed perturbation of ν(Si-H). The opposed NH_2 + H configuration, structure 6, exhibits an *enhanced* effect because of the cooperative interaction of the two opposed NH_2 groups, hence the redshift (20 cm^{-1} theoretical, 23 cm^{-1} experimental) in ν(Si-H).

This effect of adsorbate-induced charge polarization in neighboring dimers is similar in origin to the arrangement of buckled dimers on clean Si(100)-(2 × 1), with adjacent dimers within the rows buckled in opposition at low temperatures [25]. From the above discussion it follows that adsorbate-induced effects should enhance this phenomenon, with the presence of an H_2N-Si-Si-H unit inducing charge polarization in neighboring *bare* dimers such that the electrophilic (down-buckled) side of the adjacent dimer will be oriented opposed to the Si-NH_2 moiety. This prediction is in fact borne out by our calculations, which show that the presence of H_2N-Si-Si-H on one dimer of a two-dimer cluster stabilizes opposed buckling in an adjacent dimer by ~1 kcal/mol. The barrier for flipping the bare dimer to the opposite configuration is calculated to be 2 kcal/mol higher than with no adsorbate on the neighboring dimer.

The adsorbate-induced dimer buckling that occurs as a result of NH_3 dissociation has a profound effect not only on the observed adsorbate vibrational modes but also on the reactivity of subsequently impinging NH_3 molecules on this surface. As mentioned above, NH_3 interacts preferentially with the down-buckled (electrophilic) side of a bare dimer; stabilization of the specific buckled configuration of bare dimers next to H_2N-Si-Si-H units thus favors preferential adsorption of NH_3 on the side of the dimer *opposed* to any adjacent, predissociated Si-NH_2 species. Dissociation of this Si-NH_3 moiety results in the formation of opposed NH_2 + H (structure 6), thereby creating the predominant surface configuration identified above.

The second $\delta_s(NH_3)$ mode, blueshifted by ~40 cm^{-1} to 1311–1323 cm^{-1} from the isolated mode at 1272–1281 cm^{-1}, results from H-bonding interactions between NH_3 and NH_2 groups. While H bonding between adjacent Si-NH_3 and Si-NH_2 moieties in the *same* dimer row (structure 3, H-bonded NH_3 + NH_2) is predicted to produce $\delta_s(NH_3)$ ~ 60 cm^{-1} higher than the isolated mode, the presence of a significant population of such a species is inconsistent with the mechanistic picture presented above. Furthermore, such an H-bonding scheme requires reorientation of the NH_2 lone pair from its preferred position (compare structure 3 to structure 2).

In contrast, H bonding between Si-NH_3 and Si-NH_2 species in *adjacent* dimer rows (structure 7, inter-row NH_3 + NH_2) not only retains the most stable configuration for the Si-NH_2 moiety, but also is consistent with the mechanism outlined above, since such a configuration is dictated by the $c(4 \times 2)$ surface ordering that arises from the most stable long-range configuration of buckled dimers. The additional stabilization from this inter-row hydrogen bond (~1–2 kcal/mol relative to isolated NH_3) is consistent with the persistence of the higher frequency $\delta_s(NH_3)$ mode after no more isolated species are detected [Fig. 1(*c*)]. Finally, the 35 cm^{-1} blueshift predicted for $\delta_s(NH_3)$ of such species (Table I) is in excellent agreement with the experimentally observed shift of ~40 cm^{-1} [26]. We therefore assign the two distinct sets of $\delta_s(NH_3)$ modes to isolated NH_3 and inter-row NH_3 + NH_2. Note that, although the precursor to structure 6—structure 5, opposed NH_3 + NH_2—also contains an effectively "isolated" NH_3, such a structure would induce dramatic buckling in its neighboring dimer, resulting in ν(Si-H) lower than any of the intensity observed experimentally [calculated ν(Si-H) = 2016 cm^{-1}].

Through this combination of experimental and theoretical analyses, we derive the mechanistic picture of NH_3 dissociation on Si(100)-(2 × 1): in the initial stages of adsorption, NH_3 molecules are statistically more likely to impinge on isolated dimers (adjacent to clean dimers), and therefore the low-coverage spectra are dominated by isolated H_2N-Si-Si-H units. Some portion of adsorbed NH_3

molecules is transiently trapped as intact Si-NH_3 species, predominantly the isolated ones [27]. As the surface becomes populated with H_2N-Si-Si-H units, subsequent NH_3 absorption is more likely to occur on dimers adjacent to H_2N-Si-Si-H, where adsorbate-induced buckling favors formation of opposed NH_2 + H in the same dimer row, and inter-row NH_3 + NH_2 in neighboring rows. Thus the final (completely dissociated) surface is dominated by structure 6, opposed NH_2 + H [28].

We propose that this effect of adsorbate-induced changes in the electronic structure of neighboring bare dimers will apply in general to the adsorption and reaction of molecular precursors on the dimerized Si(100) surface [29]. This effect may have particularly strong implications for processes designed to achieve some degree of two-dimensional ordering, as in the growth of extended wirelike structures. The identification and understanding of such mechanisms, a crucial first step to controlling their effects, should thus be a principal aim of both experimental and theoretical efforts in this arena.

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[23] Our calculated chemisorption energies are useful only qualitatively since previous work [22] has shown that such calculated energies with small cluster models can have errors of 5 kcal/mol or more. However, our calculated vibrational frequencies (e.g., Si-H stretch) are expected to be accurate since the scaling factors used to correct them for systematic errors (see footnote, Table I) are also derived from similar small cluster models.

[24] Our assignment of opposed NH_2 + H as the dominant surface configuration agrees with the recent interpretation, via density functional slab calculations [32], of previously published N 1*s* core-level shifts as unique to the opposed configuration.

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[26] While we do not expect the absolute frequencies for our calculated $\delta(NH_x)$ modes to correspond as closely with the experimental values as do the calculated ν(Si-H) frequencies, due to a difference in the method of deriving scaling factors (see Table I), we do expect our calculations to be reasonably accurate in reproducing the *shifts* in $\delta(NH_x)$ arising from H-bonding interactions.

[27] Dissociation of trapped species occurs on the time scale of minutes—hence the complete disappearance of Si-NH_3 after sequential exposures to achieve the saturated overlayer in Fig. 1(d).

[28] The presence of a minority amount of structure 4, H-bonded NH_2 + H, is supported by a higher-frequency component to ν(Si-H) in the infrared spectrum of the saturated overlayer [Fig. 1(*d*)]. However, since dipole coupling interactions between surface Si-H moieties would favor intensity in the higher-frequency (H-bonded) modes, the dominant central frequency of 2055 cm^{-1} indicates a distinct majority of the opposed NH_2 + H configuration.

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