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Adsorption and Dissociation of a Bicyclic Tertiary Diamine, Triethylenediamine, on a Si(100)-2 × 1 Surface

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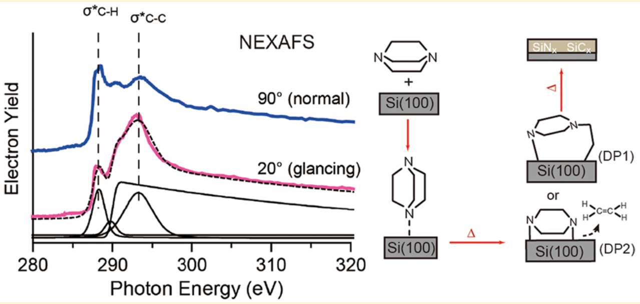
S *Supporting Information*

ABSTRACT: This study investigates the adsorption and thermal transformations of a bicyclic tertiary amine, triethylenediamine, on the clean Si(100)-2 × 1 surface. Below room temperature, triethylenediamine adsorption leads to the formation of a strong dative bond between one of the nitrogen atoms of this compound and the silicon surface. In contrast to previously studied amines, the datively adsorbed triethylenediamine features a second tertiary amine entity that is not bonded to the surface, with a lone pair orbital that is directed away from the surface and is available for further reactions. The thermal chemistry and electronic properties of triethylenediamine on silicon are studied using thermal desorption spectroscopy, infrared spectroscopy, and X-ray photoelectron spectroscopy. Near-edge X-ray absorption fine structure measurements are utilized to clarify the geometry of the adsorbates at room temperature. Density functional theory calculations are used to describe the binding geometry and electronic properties of the resulting surface species and the likely reaction paths at elevated temperatures.



I. INTRODUCTION

Interest in the organic functionalization of semiconductor surfaces has seen tremendous growth over the last several decades due to existing and potential applications in such diverse fields as microelectronics, catalysis, and biosensing.[1−8] The silicon and germanium surfaces in particular have attracted much attention due to their electronic properties and well-defined reactivity. The clean (100) surfaces of silicon and germanium are characterized by rows of asymmetrically tilted dimers, which can be used as a template to modify the surface using controlled reactions with organic molecules. Recently, in an attempt to create a robust and chemically stable organic−inorganic interface, a number of studies have focused on grafting nitrogen-containing molecules onto silicon and germanium.[9−22] The chemisorption of primary and secondary amines on Si(100) generally begins with the nitrogen atom forming a dative bond with the down-buckled atom of a silicon dimer, followed by N−H dissociation and the transfer of the hydrogen atom to a nearby up-buckled silicon atom.[18,22−26] The N−H dissociation step is governed by the properties of this datively bonded species, as the dative bond weakens the N−H bond and increases the nucleophilicity of the up-buckled silicon atom.[18] In contrast to the Si(100) surface, primary and secondary amines on the Ge(100) surface typically form stable datively bonded species without undergoing N−H dissociation at room temperature. Bent and co-workers[27] have rationalized these trends by comparing the nucleophilicity of the Si(100) and Ge(100) surfaces and finding that the up-buckled atoms on silicon have a higher proton affinity than those on germanium. Tertiary amines do not have any N−H bonds, and the kinetic barriers to N−C dissociation are much more prohibitive.[18,23] This makes tertiary amines an interesting target for investigation with high potential for creating selective surface templates based on the resulting electronic properties of the silicon surface covered with datively bonded adsorbates. For example, the coadsorption of trimethylamine and boron fluoride on the Si(100) surface leads to the formation of a novel surface-mediated donor−acceptor complex as reported by the Hamers group.[28] Such a complex would be very difficult to form using primary or secondary amines because the

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competing N−H dissociation reaction would deplete the dative adsorbate.

Among the tertiary amines, trimethylamine (TMA) adsorption on Si(100) has been studied in some detail. This includes theoretical studies into the activation energy of N−C bond dissociation,[23] XPS studies of the dissociation products at elevated temperature,[26] thermal desorption following TMA dosed at 100 K,[29] and other aspects of the adsorption process.[30,31] To summarize this work, at room temperature TMA mostly forms a stable datively bonded species, and a minor channel leads to N−C cleavage. Similar to TMA, triethylamine (TEA) is also an interesting tertiary amine capable of forming a stable datively bonded species on silicon. XPS studies of TEA adsorption on Si(100)-2 × 1 also point to the behavior that is very similar to that of TMA: the formation of a datively bonded adduct and a dissociated adduct through scission of N−C bond.[32] In addition, a scanning tunneling microscopy study confirmed that at low coverage a datively bonded TEA produces the c(4 × 2) templating of the silicon surface; at a nearly saturated coverage, datively bonded TEA molecules self-organize into c(4 × 2) domains, with an occupancy of one molecule per two dimers, and exhibit a ternary symmetry.[32] Thus, these experimental and computational studies confirm the potential implications of using tertiary amines as templates for patterning Si(100)-2 × 1 surfaces.

Of course, besides patterning and altering the properties of silicon or germanium surfaces, the amines can also serve as anchors to introduce new functionalities to these substrates. Bifunctional molecules, and amines in particular, have attracted considerable interest due to their potential to serve as a platform for further surface functionalization.[1] Toward this aim, various nitrogen-containing bifunctional molecules, including pyrimidine,[14] tetramethylethylenediamine,[33] phenylenediamine,[15] and ethylenediamine,[34] have been studied on both Ge(100) and Si(100) surfaces. For example, Yoshinobu and coworkers[33] have demonstrated that a dual tertiary amine can link between two down-buckled silicon atoms of two neighboring dimers of the Si(100)2 × 1 surface. In order to create a template that retains the well-defined patterning capabilities of TMA and at the same time provides a reactive remaining functional group available for further surface modifications, the choice of amine for such a modification has to be based on a constrained molecule that would only be expected to create a single anchored adsorbate with a fully retained additional chemical functionality. In the work presented here, these tasks are addressed by utilizing a bicyclic cage as a means for both retaining a single possibility for the formation of surface adsorbate and retaining the well-defined chemical functionality. The adsorption and stability of triethylenediamine (TEDA), also known as 1,4-diazabicyclo[2.2.2]octane (DABCO), on Si(100) was investigated in order to understand its dative bonding and to follow its thermal dissociation pathways. Triethylenediamine has not been previously studied on elemental semiconductor surfaces, but its adsorption behavior has been known on carbon matrices[35,36] and on aluminum oxides.[37−39] The initial expectation is that triethylenediamine could form a stable dative bond on Si(100)-2 × 1 and still have one remaining nitrogen available for further functionalization.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

Fourier-transform infrared (FT-IR) experiments were performed at the University of Delaware in an ultrahigh vacuum (UHV) chamber with a base pressure below 1 × 10^{-9} Torr. Attached to the chamber was an ion gun for cleaning the sample surface, and an unshielded mass spectrometer (SRS 200 RGA) was used to confirm the purity of the compounds dosed into the chamber. The chamber is equipped for Auger electron spectroscopy (AES) and coupled to an infrared spectrometer (Nicolet, Magna 560) with an external mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The spectrometer was set up in a multiple internal reflection (MIR) mode for the experiments presented here.

The silicon (100) sample used for the FT-IR experiments was a dual-side polished silicon crystal with 45° beveled edges (25 mm × 20 mm × 1 mm, Harrick Scientific Corporation). The sample was mounted on a manipulator capable of heating the sample to 1100 K and cooling to approximately 100 K with liquid nitrogen. The surface was cleaned by sputtering with argon (99.9999%, Matheson, no further purification), followed by 20 min of annealing at ∼1050 K; the cleanliness of the surface was confirmed with AES. Triethylenediamine (98%, Aldrich, CAS Number 280-57-9) is solid at room temperature, but its vapor pressure is sufficient for dosing in vacuum. The compound is very hygroscopic, but any water adsorbed during transfer can be removed with moderate heating in vacuum. The purity of the vapor was confirmed *in situ* by mass spectrometry.

The FT-IR spectra were collected using 512 scans per spectrum at a resolution of 4 cm^{-1}. The compound was introduced into the chamber via a leak valve following the acquisition of a background spectrum. After the desired exposure was reached, the chamber was evacuated to base pressure, and a sample spectrum was collected. When annealing of the surface to a higher temperature was required, the sample spectrum was taken after the crystal was allowed to cool to the temperature of the background. All exposures are reported in units of Langmuir (1 L = 10^{-6} Torr·s).

Temperature-programmed desorption (TPD) experiments were performed in a separate UHV chamber with a base pressure below 1 × 10^{-9} Torr. This chamber is equipped with a differentially pumped mass spectrometer (SRS 200 RGA) to characterize the molecular fragments that evolve from the surface during TPD. This instrument is also equipped with an ion gun for surface sputtering and an Auger spectrometer for confirming the cleanliness of the surface following the preparation procedure. After triethylenediamine was leaked into the chamber via the leak valve to achieve the desired exposure, the crystal was placed in front of the mass spectrometer, and the temperature was increased linearly at a rate of approximately 2 K/s using a Eurotherm controller.

In-situ XPS and near-edge X-ray adsorption spectroscopy (NEXAFS) experiments were performed on the soft X-ray (SXR) beamline at the Australian Synchrotron.[40] Silicon (100) samples were 0.04−0.06 Ohm·cm Sb-doped (Virginia Semiconductor Inc.) that were degassed at ∼550 °C overnight before the first use. Atomically clean and flat Si(100) surfaces were prepared by flash annealing to ∼1200 °C (10 A, 6 V direct current) for 10 s with a programmed cool down. Low-energy electron diffraction (LEED) was used to confirm the atomic reconstruction of the surface. High-resolution Si 2p spectra recorded over a period of an hour showed only a slight reduction in the intensity of the low binding energy peak associated with the up-buckled surface dimers,[41] confirming only very low levels of adsorption from contaminant species from the chamber background. Triethylenediamine preparation and deposition were performed in the same manner described

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above. Clean Si(100) surfaces were prepared via flash anneal prior to each triethylenediamine dose, with the sample being allowed to cool for 10 min between flashing and triethylenediamine exposure. The sample temperature was confirmed to be lower than 80 °C at the time of dosing by a thermocouple mounted on the sample holder (but not in direct contact with the silicon). The sample temperature during annealing was recorded indirectly by monitoring the sample heating power. We estimate temperature using a linear extrapolation from the heating power (5.2 W) where the sample exhibited a barely visible dull cherry red glow, to which we assigned a temperature of ∼525 °C.[42] Once dosed, the samples were immediately transferred under UHV to the adjacent analysis chamber for XPS or NEXAFS measurements. XPS measurements were acquired with a photon energy of 440 eV to maximize sensitivity to nitrogen and allow both carbon and nitrogen spectra to be acquired without changing the beam energy. For each carbon/nitrogen measurement a Au (4f) reference spectrum was acquired using a gold reference foil in electrical contact with the sample, which was later used for energy calibration. The CasaXPS software[43] was used for data processing and peak fitting.

Carbon and nitrogen K-edge NEXAFS spectra were recorded in a partial electron yield (PEY) mode for five angles between normal and grazing angle photon incidence (90, 70, 55, 40, and 20°). Normalization was performed using reference scans from a clean Si(100) surface together with the flux signal from a 50% transmissive gold grid placed upstream of the sample.[44]

We note that at high photon intensity the triethylenediamine-dosed Si(100) surface was susceptible to beam-induced changes in surface composition. However, we were able to strongly limit the deleterious effects of the photon beam on our sample by reducing the intensity of the beam. We used XPS monitoring of the carbon and nitrogen 1s spectra during continuous exposure to the beam to confirm that beam-induced changes were negligible at the lowered beam intensity for exposures of less than 10 min. We then ensured all individual measurements could be made in no more than 10 min and repositioned our beam on the sample between individual measurements, thus ensuring that all acquired data reflect the undamaged state of the organic functionalized surface.

XPS and NEXAFS measurements of the triethylenediamine-dosed Si(100) surface were performed as a function of substrate temperature by annealing the silicon sample via direct current annealing.

Density functional theory (DFT) calculations were conducted using the Gaussian 09 suite of programs.[45] Calculations were performed with the B3LYP functional[46] and the 6-311+G(d,p) basis set.[47] A comparison with the B97*D*/6-311+G(d,p)[48,49] approach has also been performed as discussed below, and the resulting energetics is provided in the Supporting Information section. The B3LYP/311+G(d,p) approach has been previously shown to yield reliable results to describe the adsorption chemistry of organic molecules on the Si(100)-2 × 1 surface.[50] A comparison with the B97D/6-311+G(d,p) computation demonstrates the effect of dispersion interactions. The silicon surface is represented using Si_9H_{12} and $Si_{15}H_{16}$ cluster models that describe one and two Si−Si dimers, respectively. These clusters were first optimized at the B3LYP/6-311+G(d,p) level of theory with all atoms allowed to fully relax. Then, the desired adsorbate was added to the cluster model, and the entire structure was reoptimized at the same level of theory. Vibrational frequencies were calculated at the B3LYP/6-311+G(d,p) level of theory. Predicted binding energies of XPS peaks of nitrogen and carbon were derived from these calculations using the calibration procedure based on Koopmans' theorem described in detail in ref 51.

III. RESULTS AND DISCUSSION

III.1. Thermal Desorption Investigation of the Proposed Adsorption and Decomposition Mechanisms for Triethylenediamine on a Clean Si(100)-2 × 1 Surface.

In order to understand the key steps of the adsorption and thermal chemistry of TEDA on a clean Si(100)-2 × 1 surface, thermal desorption experiments were carried out on both monolayer and multilayer samples. Figure 1 summarizes the main observations of these experiments.

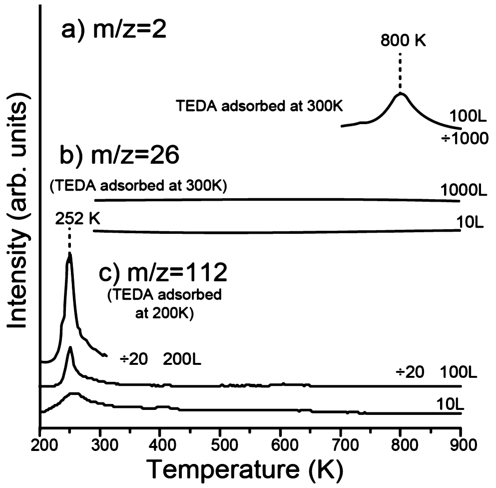


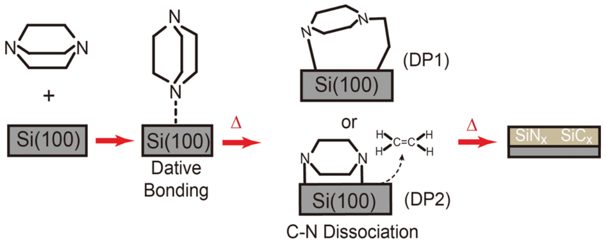
Figure 1. Summary of temperature-programmed desorption studies of triethylenediamine adsorbed on a clean Si(100)-2 × 1 surface. (a) Desorption of H_2 ($m/z = 2$) following triethylenediamine adsorption at 300 K. (b) Desorption of ethylene ($m/z = 26$) following small (10 L) and large (1000 L) exposures of triethylenediamine at 300 K showing the absence of ethylene evolution. (c) Molecular desorption profile of multilayers of triethylenediamine condensed at 200 K.

The two main thermal desorption processes observed are molecular desorption ($m/z = 112$) at approximately 250 K and desorption of molecular hydrogen ($m/z = 2$) at approximately 800 K. Molecular desorption is only observed for the multilayer samples prepared at 200 K. Hydrogen desorption presumably occurs as a result of TEDA decomposition on the surface. No evidence is found for the desorption of other signature fragments, such as ethylene ($m/z = 26$).

The enthalpy of sublimation measured for triethylenediamine by differential thermal analysis is reported to be 61.9 kJ/mol.[52] The experimental data recorded in Figure 1 for molecular desorption around 252 K yield the corresponding activation energy of 66.7 kJ/mol approximately estimated based on the first-order desorption evaluated by Redhead analysis with pre-exponential factor of 10^{13} s^{-1}.[53] This number is fully consistent with the reported enthalpy of sublimation of triethylenediamine.

Based on the thermal desorption investigation and on the previously reported chemistry of amines on silicon, it is proposed that the adsorption and thermal chemistry processes for TEDA on a clean Si(100)-2 × 1 surface proceed as outlined in Scheme 1.

Scheme 1. Reaction Pathways of Triethylenediamine Transformations on a Clean Si(100)-2 × 1 Surface[a]



[a] DP1 represents the structure yielded by dissociating a single C−N bond; DP2 represents the structure obtained following double C−N dissociation and ethylene elimination.

According to the proposed mechanism, we expect that the triethylenediamine molecule would absorb to the clean silicon surface by forming a dative bond. At elevated temperatures, this datively bonded species would undergo dissociation, as illustrated for the C−N bond in Scheme 1. Eventually, the molecule would completely break up and form carbide and nitride species on the surface. In order to test this hypothesis, we need to (1) demonstrate that the initial adsorption of the triethylenediamine molecule results in a datively bonded species, (2) that C−N dissociation is associated with the start of molecular decomposition, and (3) that at elevated temperatures no processes take place other than the formation of surface silicon carbide and nitride species and the desorption of hydrogen. Infrared spectroscopy should be the most appropriate surface analytical technique to provide the information about the mechanism of surface decomposition. A pertinent question to be addressed is whether the decomposition of the TEDA molecule leads to the formation of Si−H bonds.

III.2. Infrared Investigation of the Adsorption and Thermal Decomposition of Triethylenediamine on a Clean Si(100)-2 × 1 Surface. Adsorption and thermal transformations of triethylenediamine were followed by infrared spectroscopy, as summarized in Figure 2. Spectra a−d in this figure describe the adsorption of a small amount (0.5 L dose, submonolayer as will be demonstrated later by XPS) of triethylenediamine on a clean Si(100)-2 × 1 surface at 130 K followed by brief annealing to the temperatures indicated. With 0.5 L of triethylenediamine dosed onto the clean Si(100) at 130 K, the surface was briefly heated to different temperatures up to 200 K, and the infrared spectra after each annealing were collected after the surface cooled back to 130 K. All these spectra contain the expected absorption bands (ν_{C-H} = 2869.6 cm^{-1}, 2937.3 cm^{-1}; δ_{C-H} = 1465 cm^{-1}, 1315.4 cm^{-1}) corresponding to the molecular triethylenediamine. These assignments are fully supported by the DFT investigation with the predicted spectra of a molecular and datively bonded triethylenediamine presented underneath the experimental data. Despite some subtle differences between the two predicted spectra, as expected, they describe very similar species that cannot be distinguished based solely on this set of studies. However, it is interesting to contrast the cryogenic temperature investigation with the room-temperature adsorption shown in spectra e−g. The spectrum collected following the triethylenediamine dose at room temperature (where no multilayers can be adsorbed) looks very similar to those collected at cryogenic temperatures. Although the intensity of the absorption features drops noticeably, all the expected features are the same as those in the low-temperature spectra.

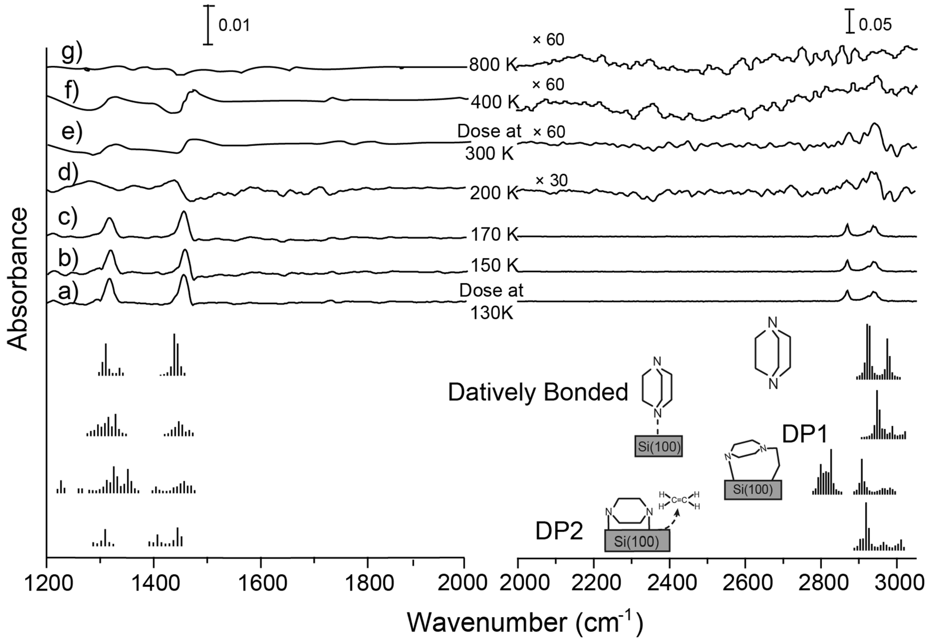


Figure 2. Summary of the infrared spectroscopy investigations of the adsorption and thermal transformations of triethylenediamine on a clean Si(100)-2 × 1 surface. (a), (b), (c), and (d) represent the spectra of the surface exposed with 0.5 L of triethylenediamine at 130 K and then consecutively annealed to 150, 170, and 200 K. The background used was the spectrum collected from a clean Si(100) surface at 130 K. (e), (f), and (g) represent the spectra of the surface exposed to 1000 L of triethylenediamine at 300 K and then consecutively annealed to between 400 and 800 K. The background used was the spectrum collected from the clean Si(100) surface at 300 K. Shown underneath the experimental spectra are the vibrational frequencies predicted by DFT of molecular triethylenediamine, the datively bonded adsorbate, and the dissociated adsorbates DP1 and DP2. These calculations were performed using the B3LYP/6-311+G(d,p) approach.

Annealing to 400 K does not affect the spectra too much; however, a noticeable absorption around 2800 cm^{-1} is now observed. According to the thermal desorption studies described above, no products desorb from the surface within this temperature range, and thus the spectral changes can only be caused by surface reactions. The absence of Si−H vibrations (that are normally of substantially higher intensity than C−H bands) demonstrates that hydrogen transfer from the molecule to the surface is not a major decomposition pathway for triethylenediamine on Si(100). The two possible surface reaction pathways suggested in Scheme 1 lead to the formation of two very different species, whose infrared spectra are also predicted using DFT and displayed in Figure 2. Only one of these species, namely, the C−N dissociation structure DP1, exhibits substantial absorption in the spectral region between 2700 and 2900 cm^{-1}. This suggests that the reaction pathway leading to structure DP1 is worth investigating further. This is also consistent with the fact that the ethylene elimination caused by a double dissociation of C−N bonds is not observed in thermal desorption. It is expected that if ethylene is formed on a clean Si(100)-2 × 1 surface it would remain bound until approximately 600 K[54,55] depending on the neighboring surface species. In fact, desorption temperatures as high as 700 K were reported for ethylene desorption from ethylene adsorbed as well as iodoethane adsorbed on Si(100) surfaces.[55,56] However, the TPD studies presented in Figure 1 do not record any ethylene desorption even at these high temperatures.

Annealing the surface to 800 K, shown in spectrum g of Figure 2, results in a featureless spectrum, consistent with elimination of hydrogen and dissociation of hydrogen-containing species, which is also consistent with the formation of poorly defined surface carbide (SiC_x) and nitride (SiN_x) species.

Thus, infrared investigations suggest that the nature of adsorbed species of triethylenediamine does not change substantially between 130 and 300 K and that thermal decomposition starts around 400 K; however, spectral similarity of several proposed adsorption species prevents a more precise identification of the decomposition products.

III.3. XPS Analysis of Thermal Chemistry of Triethylenediamine on a Clean Si(100)-2 × 1 Surface. To investigate the nature of triethylenediamine adsorbed on a clean Si(100)-2 × 1 surface, a set of XPS studies were performed as a function of surface temperature, as shown in Figure 4a and 4b corresponding to C 1s and N 1s spectral regions. As was mentioned above in the infrared spectroscopy studies, the observed spectroscopic signatures involving carbon atoms are very similar in the adsorbed species and in all the models considered. Thus, for the characterization of triethylenediamine, the N 1s spectral region is expected to be much more informative.

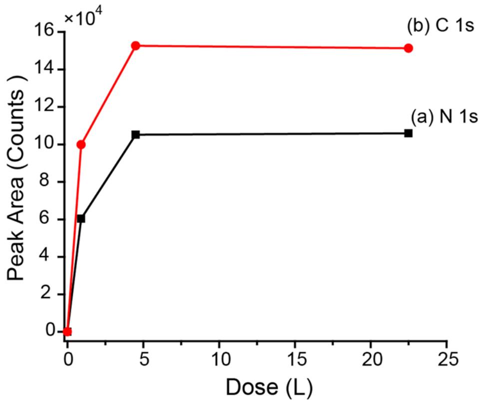


Figure 3. Surface coverage profile as determined via XPS peak areas for (a) N 1s and (b) C 1s with the exposure of 0.9, 4.5, and 22.5 L of triethylenediamine at room temperature.

Figure 4a and 4b show synchrotron-based XPS spectra collected from samples prepared in situ as described in the Experimental section. The bottom trace corresponds to the exposure of 0.9 L of triethylenediamine dosed on a silicon surface at room temperature. Following brief annealing to the temperatures indicated, all the other traces are obtained. According to the coverage profile in Figure 3, the dose of 0.9 L corresponds to approximately 60% of the monolayer, and thus this set of experiments allows for investigation of the behavior of individual triethylenediamine molecules adsorbed on a clean Si(100)-2 × 1 surface. By comparing the experimental spectra collected for room-temperature adsorption, it is clear that the spectra at different exposures are very similar. The main features observed correspond to the positions expected for free and datively bonded nitrogen atoms. These assignments are supported by the DFT modeling provided in Figure 2 and are consistent with the previous observations of multilayers of amines with N 1s features at 400.2[57] and 400.6 eV[58] and datively bonded amines with the same features at 402.2[28] and 401.2 eV.[58] The high binding energy at 401.1 eV from experimental measurements lines up well with the DFT-predicted 401.3 eV representing the nitrogen atom datively bonded with the silicon atom. The other peak standing for the free nitrogen has a 0.5 eV higher shift than the DFT predicted peak. This probably resulted from the complex environment around the free nitrogen atom. If the free nitrogen is reactive to bind with some unavoidable species in chamber, such as CO and H_2, the chemical environment may be changed. For example, it has been proved that the nitrogen in structures like tetraalkylammonium salts will have a higher binding energy shift.[26,59] Also, different basis sets, functional methods, and correction methods will influence the natural bond orbital (NBO) analysis used for the computational models.

However, one immediate question arising from these assignments is why these two features differ in intensity. It is expected that a datively bonded structure would result in one free nitrogen atom and another one on the same molecule bonded to surface silicon, thus resulting in two features of equal intensity. However, this expectation is based on the binding of an individual molecule to a perfect Si(100)-2 × 1 surface followed by the corresponding charge redistribution between two nitrogen atoms within the same adsorbate. However, if the adsorption occurs at neighboring surface sites or at surface sites near impurities present in small quantities, this charge redistribution may be very different. To illustrate this point, two additional cluster models, representing a surface-bound hydrogen atom or a hydroxyl group (expected surface impurities on silicon), were investigated. The results of this comparison are presented in Figure 4a and 4b for these models that can be briefly described as H−Si−Si−TEDA and OH−Si−Si−TEDA. It is very clear that the formation of a datively bonded species by triethylenediamine on a silicon surface that has H- or HO-neighboring species not only moves the electronic environment of the two nitrogen atoms for them to appear closer to each other in the XPS spectrum but also shifts the energy toward substantially lower binding energies, which is consistent with the results in Figure 4b. Furthermore,

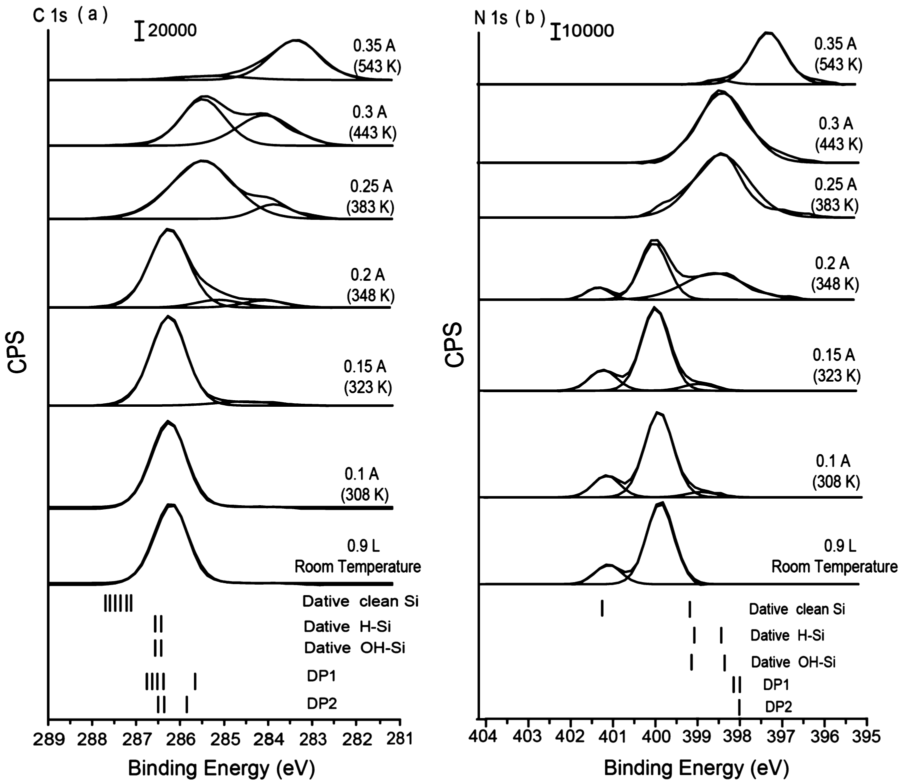


Figure 4. In situ XPS (a) C 1s spectra and (b) N 1s spectra collected with 0.9 L of triethylenediamine on the Si(100) surface at room temperature, followed by elevating the temperature with changing the current. Note that the temperatures are converted from heating power using a linear extrapolation from 5.2 W/800 K; this leads to an underestimate in the temperature that is most significant at the higher temperatures. DFT-predicted C 1s and N 1s binding energies using different reaction models are shown below the experimental data.

the C 1s spectra observed in Figure 4a gave us more consistent results in the comparison between H−Si−Si−TEDA and OH−Si−Si−TEDA modeling binding energies with experimental binding energies. Before we built up H−Si−Si−TEDA and OH−Si−Si−TEDA models, we found the experimental results had a lower shift than DFT dative bonding species on a clean Si(100) surface.

The next question that can be addressed with the help of XPS is thermal transformations of datively bonded triethylenediamine. As the surface with triethylenediamine adsorbed at room temperature is briefly annealed to the temperatures indicated in Figure 4b, the peak around 398 eV, which is barely visible at room temperature, becomes very pronounced, while the overall intensity of the N 1s features does not change. This peak corresponds to the thermal C−N dissociation process proposed above, and the XPS signature is consistent with the predicted positions for either one of the two proposed structures described in Scheme 1. This approach can also be used to interpret the C 1s spectra in Figure 4a. DFT-predicted DP1 and DP2 carbon binding energies both gave a lower peak around 285.6 eV. Similar to the N 1s observation, when the surface was heated to a certain temperature with 0.2 A current, a new peak became intense at 284.0 eV. Although the experimental peak position is not fully consistent with the DFT-predicted position for dissociation products, as we mentioned in the previous paragraph, this shift between experiments and modeling could be explained if we take surface defects and minority species such as H−Si−Si and OH−Si−Si into consideration. However, since ethylene desorption was not observed, it is most likely that the structure denoted as DP1 is dominant on a surface at this temperature. In general, given that C−N dissociation of a datively bonded triethylenediamine is expected to provide a structure of the type of DP1 as a starting point and given that this structure has the second nitrogen atom directed away from the surface, elimination of ethylene to form structure DP2 does not seem likely, unless it is a concerted process with simultaneous breaking of both C−N bonds in triethylenediamine. However, again based on the observation of the datively bonded structure and infrared and TPD studies described above, this pathway is not observed by any of the approaches reported here.

Finally, again consistent with the rest of the investigations, when the annealing temperature is increased substantially, N 1s and C 1s both shift to a much lower binding energy, which corresponds to the formation of surface silicon nitride[60] and silicon carbide.[61]

Thus, the XPS results confirm that triethylenediamine forms a datively bonded species at room temperature within a monolayer on a Si(100)-2 × 1 surface. This adsorbate undergoes C−N dissociation at elevated temperatures to yield predominantly the DP1 species. Finally, at temperatures around 800 K, surface nitride species are formed.

III.4. NEXAFS Analysis of Room-Temperature Adsorption of Triethylenediamine on a Clean Si(100)-2 × 1 Surface: Geometry of the Adsorbate. Figure 5 shows the summary of NEXAFS measurements following the dose of 0.9 L of triethylenediamine onto the Si(100) surface at room temperature. There is a clear peak present at 288.0 eV, just below the ionization potential, that can be attributed to C−H σ^* resonance states.[62] This feature shows clear dichroism with the intensity of the peak exhibiting a maximum at the normal incident beam angle, consistent with our expectation for a

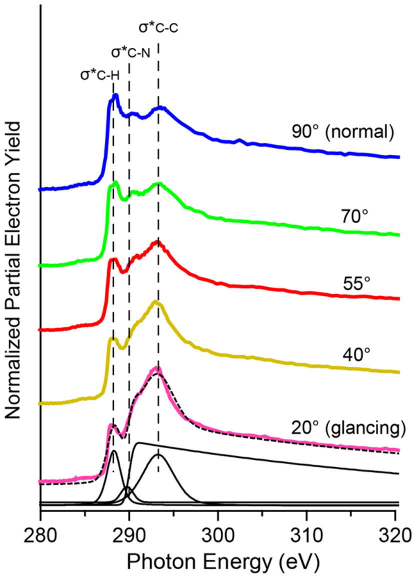


Figure 5. Angle-dependent carbon K-edge NEXAFS spectra of the Si(100) surface exposed to 0.9 L of TEDA at room temperature.

datively bonded triethylenediamine structure that the C−H bonds lie somewhat in the plane of the surface. Fitting the variation in intensity of this peak to the incident photon angle by the procedure described in detail by Stöhr[63] produces an angle of 61 ± 1° (Figure S2). There is an additional pair of peaks above the ionization potential at 290.3 and 293.9 eV. The energetic location of these peaks suggests they are associated with σ* resonances. The peak at 293.9 eV shows an increasing trend in intensity at the grazing-incident angle, consistent with a vertically orientated bond, and in this case a fit produces an angle of 21 ± 1° with respect to surface normal. This peak clearly corresponds to the C−C bond in the structure of $-CH_2-CH_2-$ of the datively bound molecule, indicating that the structure of −C−C− is orientated nearly normal to the surface. The feature at 290.3 eV corresponds to the σ*(C−N) resonance.[64,65] However, fitting the angular dependence of the intensity of this feature is unreliable since the intensity depends drastically on the fit of the ionization potential step.

It can be noted that the overall balance of the thermal process is consistent with the surface coverage recorded by AES and summarized in Table 1. These data suggest that there is no significant decrease in carbon-to-nitrogen ratio with the increasing temperature. In agreement with what was observed from TPD results, if the dissociation with temperature increase happens with the formation of ethylene, we were supposed to observe the ethylene desorption at around 600 K and the decrease in C/N ratio. According to the lack of the expected results from ethylene formation, we could assume that the dissociation pathway is likely to be accompanied by only one C−N cleavage, as shown in Scheme 1.

Table 1. Elemental Concentration Data Calculated for Silicon, Carbon, and Nitrogen from AES Spectra at Several Temperatures[a]

	C/N
300 K	3.5 ± 0.1
400 K	2.7 ± 0.2
500 K	2.9 ± 0.2
600 K	2.9 ± 0.3
700 K	2.6 ± 0.3

[a] The values for C/N were calculated and applied with sensitivity factors.

III.5. DFT Explanation of the Adsorption and Decomposition of Triethylenediamine on a Clean Si(100)-2 × 1 Surface.

In order to explore the thermodynamics of the thermal decomposition of triethylenediamine on Si(100), DFT calculations were performed for the proposed surface structures. The adsorption and decomposition of a single triethylenediamine molecule were modeled on a two dimer Si(100) cluster ($Si_{15}H_{16}$). The objective of these calculations is to compare the stability of three plausible structures as shown in Figure 6. These are (1) a stand-up dative bonding structure, (2) a structure labeled DP1 in which one C−N bond dissociation has occurred and the carbon atom binds a silicon atom in the same dimer, and (3) a structure labeled DP2 in which two C−N bond dissociations have occurred such that a separate ethylene fragment has formed that binds in a [2 + 2] fashion to an adjacent dimer. Of these three structures, DP2 is the most stable. However, it requires the datively bonded complex to either undergo some complex concerted process of ethylene elimination, which was ruled out by experimental TPD and infrared studies, or be initially structured like DP1 followed by dissociation of the bond between the second nitrogen and a carbon. However, this geometry is extremely unfavorable for such a process, as the second nitrogen atom is directed away from the surface and in fact is located at the apex of the structure that is the furthest away, making this transformation extremely unlikely despite the ultimate thermodynamic stability predicted by DFT. Therefore, the calculation results agree with our experimental data. First, at room temperature or lower, datively bonded species could be formed on a clean Si(100) surface. Second, with increasing temperature, dissociation reactions can happen, provided the energy barriers are overcome. The fact that ethylene products are not observed experimentally suggests that the surface product of the type of DP1 is formed following C−N dissociation. The expectation of the C−N dissociation is fully

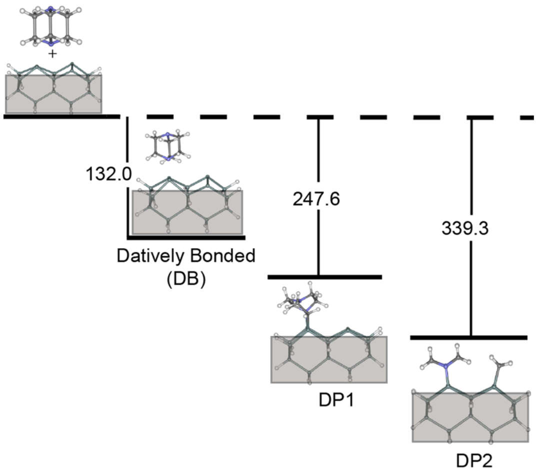


Figure 6. DFT calculations using the B3LYP functional and the 6-311+G(d,p) basis set. The datively bonded complex is −132.0 kJ/mol more stable compared to the gas-phase triethylenediamine. Dissociation product DP1 and dissociation product DP2 both have much higher stability at −247.6 kJ/mol and −339.3 kJ/mol, relative to the gas-phase species.

consistent with the observation previously reported by Hamers that a TMA molecule would form a very stable dative-bond monolayer at room temperature.[26] In fact, our own calculations for a TEDA−$Si_{15}H_{16}$ datively bonded complex suggest that compared to the analogous structure formed by TMA triethylenediamine is actually more stable on this surface (−132.0 kJ/mol for triethylenediamine compared to −120 kJ/mol for TMA).[26] Thus, triethylenediamine is able to form a stable datively bonded structure on a Si(100) surface with a nitrogen atom available for further functionalization. The Supporting Information (Figure S1) also presents the summary of the computational description of the same species at the B97*D*/6-311+G(d,p) level of theory to account for the effects of dispersion interactions. These results are fully consistent with those obtained using B3LYP/6-311+G(d,p).

IV. CONCLUSIONS

The reaction behavior of triethylenediamine on the Si(100) surface has been investigated. It is found that a datively bonded TEDA−Si−Si complex forms on the surface at room temperature as well as at cryogenic temperature with low exposure. Infrared spectroscopy and NEXAFS have confirmed the vibrational signature and orientation of triethylenediamine on this surface. Based on the XPS and IR results, heating above 400 K leads to C−N dissociation and ultimately the formation of surface nitride and carbide species; however, no other products evolve from the surface except for H_2. Thus, consistent with the DFT investigation, a stable and well-defined surface species is formed at room temperature upon triethylenediamine adsorption on a clean Si(100) surface with a nitrogen atom in the resulting structure available for further functionalization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10485.

> Computational investigation with B97D functional and intensity of selected NEXAFS features plotted against the incident beam angle and complete references 34 and 45 (PDF)

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Notes

The authors declare no competing financial interest.

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