

Adsorption and Thermal Chemistry of Nitroethane on Si(100)-2 × 1

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Surface chemistry of nitroethane on Si(100)-2 × 1 has been investigated using multiple internal reflection Fourier transform infrared spectroscopy (MIR–FTIR), Auger electron spectroscopy (AES), and thermal desorption mass spectrometry. Molecular adsorption of nitroethane at submonolayer coverages dominates at cryogenic temperatures (95 K). As the surface temperature is increased to 140 K, chemical reaction involving nitro group occurs, whereas the ethyl entity remains intact. Similar behavior is observed for nitromethane. Thus, a barrier of approximately 36 kJ/mol is established for the interaction of nitroalkane molecules with the Si(100)-2 × 1 surface in contrast to the essentially barrierless transformation predicted previously theoretically for nitromethane. Further annealing of the silicon surface leads to the decomposition of nitroethane. The concentration of nitrogen and oxygen remains constant on a surface within the temperature interval studied here, whereas approximately half of the ethyl groups undergo hydrogen elimination, which releases ethylene and produces surface hydrogen. The rest of the ethyl groups decompose leading to the formation of surface carbon as confirmed by AES.

Introduction

Adsorption and chemical transformations of organic compounds on silicon surface have been a subject of rigorous scientific investigation for several decades (see, for example, reviews in refs 1–8). Interest in the chemisorption of organic molecules on semiconductor surfaces has been fueled by a variety of present and potential applications. The adsorption and subsequent reactions of organic compounds have enormous importance in the design of many devices. For example, controlled deposition of organic films on surfaces has found applications in sensor technology, optoelectronic devices, nonlinear optical materials, and microelectronics. The electronic response, readily available on well-ordered single-crystal surfaces, inherent ordering of the surface atoms, and the highly developed technology for accurate surface patterning provide unique opportunities for developing new devices on silicon.

Modification of the silicon surface using organic molecules is one of the most common methods to tune its electrical and chemical properties. For example, incorporation of nitrogen and oxygen allows the formation of the dielectric layer that is important in metal–insulator–semiconductor devices. Here, interactions of nitroethane with a Si(100)-2 × 1 are analyzed.

Although multiple studies addressed the thermal stability of the ethyl group as a suitable ligand for deposition of various materials onto silicon surfaces,^{9–12} the vibrational studies of adsorption and decomposition of ethyl-containing species are very scarce.^{13–15} Several aspects of the thermal chemistry of the surface bound ethyl group on single-crystal silicon were described in refs 9–12, 14, and 16–19 and followed by temperature-programmed reaction/desorption (TPR/D), laser-induced thermal desorption (LITD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and high-resolution electron energy loss spectroscopy (HREELS).

The reaction was shown to result in ethylene and hydrogen desorbing from the surface around 600 and 800 K, respectively. β -Hydrogen elimination was found to be the major pathway for the surface ethyl group decomposition with a minor reaction following the α -hydrogen elimination pathway.^{9–12,14,16–19} Our own previous multiple internal reflection Fourier transform infrared spectroscopy (MIR FT-IR) studies of iodoethane adsorption and decomposition on a Si(100)-2 × 1 surface provided valuable spectroscopic benchmarks for the analysis of ethyl groups on semiconductors.^{20,21}

Here we show that spectroscopic characteristics of the ethyl entity can be used to analyze the binding environment of the ethyl group and to understand the nature of chemical interaction of nitroalkane molecules with surfaces. The presence of a nitro group provides a reactive center for the interaction of nitroethane with Si(100), whereas the ethyl group remains intact until the surface temperature exceeds 500 K. Previous *theoretical* investigations of the nitroalkyl compounds on a Si(100)-2 × 1 surface²² suggested that the barrier for the initial step of this reaction, a 4 + 2 addition of a nitro group to the silicon dimer of the Si(100)-2 × 1 surface, is negligibly small. This analysis relied on an optimized trajectory for the interaction of a nitro group with a silicon dimer.

This study will take advantage of the cryogenic temperatures to estimate the energetic barriers for nitroethane and nitromethane reactions with the Si(100)-2 × 1 surface *experimentally*.

Experimental Methods

The studies presented here were performed in two ultrahigh vacuum chambers at the University of Delaware. One of the chambers is equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a setup for low energy electron diffraction (LEED), an ion gun for surface sputtering, a shielded mass spectrometer (Stanford Research Systems, 0–200 amu) differentially pumped by the chamber for thermal

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desorption studies, and an FTIR system configured to take infrared spectra in a multiple internal reflection mode. The sample (Harrick Scientific Corporation; 25 mm × 20 mm × 1 mm, 45° beveled edges) is mounted on a manipulator with capabilities for heating the sample to 1150 K and cooling it to 95 K. The sample was prepared by sputtering with 0.5 kV Ar⁺ ions at room temperature followed by annealing to 1150 K for 20 min. A clean well ordered Si(100)-2 × 1 sample was obtained, as confirmed by LEED and AES. Another ultrahigh vacuum chamber is equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES), a setup for low energy electron diffraction (LEED), an ion gun for surface sputtering, and a shielded mass spectrometer differentially pumped by the chamber for temperature-programmed reaction/desorption (TPR/D) studies. This chamber was used for thermal desorption studies presented here. The temperature ramp was 2 K/s.

Argon (99.9999%, Matheson) was used without further purification. Nitroethane and nitromethane (99%, Aldrich) were prepurified by several freeze–pump–thaw cycles before introduction into the reaction chamber. The purity of the compounds was verified in situ by mass spectrometry. All exposures are reported in Langmuirs (L), where 1 L = 10^{−6} Torr s. The pressures have not been corrected for different ion gauge sensitivities of the compounds.

A Nicolet Magna 560 FTIR spectrometer with external liquid-nitrogen-cooled MCT detector was used in our spectroscopic experiments. The IR data were collected by accumulating 2048 scans with resolution of 4 cm^{−1}.

During temperature-dependent infrared studies, the single beam spectrum of the clean and well-ordered silicon single crystal sample was collected as a background. Then nitroethane (or nitromethane) was adsorbed, and the crystal was briefly annealed to the desired temperature and then cooled to the original temperature. After that, the resulting infrared spectrum was recorded.

Results and Discussion

The investigation consists of two parts: chemistry of nitroethane adsorbed on a Si(100)-2 × 1 surface at cryogenic temperatures (95 K) and at room temperature.

(a) Monolayer Chemistry of Nitroethane Adsorbed on a Si(100)-2 × 1 Surface at 95 K. To evaluate the monolayer chemistry of nitroethane at low temperatures, TPR/D studies (Figure 1) were performed. The NO₂ fragment ($m/e^+ = 46$) was followed in these studies because the cracking fragment corresponding to the molecular mass of nitroethane ($m/e^+ = 75$) is negligibly small in its mass spectrum. Up to ~4 L dose, nitroethane predominantly decomposes on Si(100)-2 × 1. At higher exposures molecular desorption commences around 190 K. The temperature of this desorption feature and its shape suggest that it corresponds to the molecular desorption from a multilayer.

Figures 2b–g and 3 illustrate the dependence of the infrared absorption on the coverage of nitroethane adsorbed on a Si(100)-2 × 1 surface at a cryogenic temperature. The infrared spectrum of nitroethane adsorbed on this surface at room temperature is presented in Figure 2a for future comparison, vide infra. This set of studies was divided in two spectral regions for clarity because the absorbance in the NO₂ stretch region is approximately an order of magnitude more intense than in the C–H stretch region. Comparison of the coverage profiles in Figures 2b–g and 3 indicates that even at the lowest submonolayer coverages studied (less than a quarter of the monolayer based on the TPR/D studies outlined in Figure 1) the vibrational

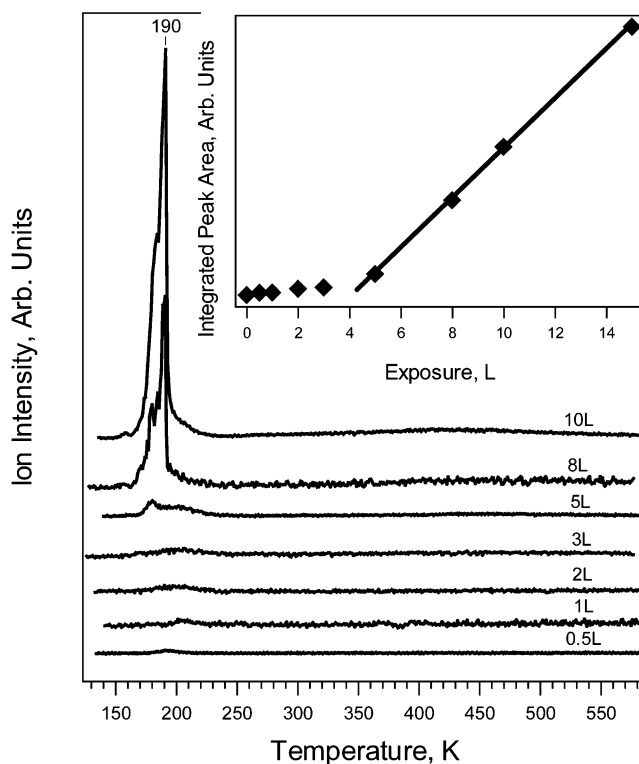


Figure 1. Temperature programmed reaction/desorption studies of nitroethane adsorbed on a Si(100)-2 × 1 surface at cryogenic temperatures (below 130 K). $m/e^+ = 46$ was followed as a function of nitroethane exposure. The inset shows the integrated peak areas as a function of the initial exposure.

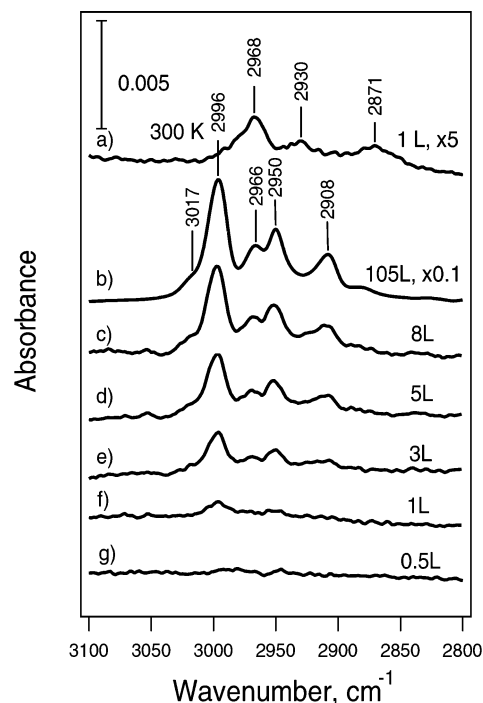


Figure 2. MIR FT-IR studies of nitroethane adsorbed on the Si(100)-2 × 1 surface at (a) 300 K and (b–g) 95 K as a function of nitroethane exposure. 2800–3100 cm^{−1} spectral region.

spectrum of the adsorbed nitroethane is practically the same as at the multilayer coverages. Specifically, all of the C–H stretch modes and all of the features corresponding to the presence of the NO₂ group are the same regardless of coverage. Thus, it can be concluded that nitroethane molecules adsorb intact on the Si(100)-2 × 1 at 95 K even at a submonolayer coverage.

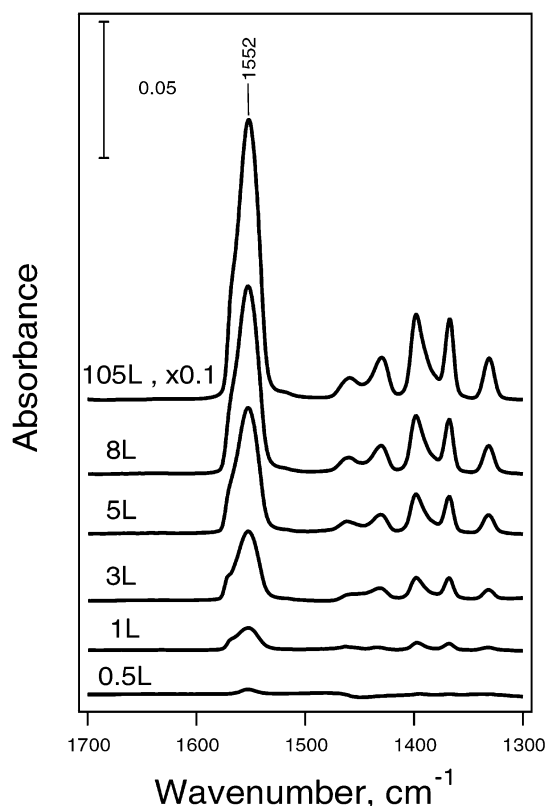


Figure 3. MIR FT-IR studies of nitroethane adsorbed on the Si(100)-2 \times 1 surface at 95 K as a function of nitroethane exposure. 1300–1700 cm^{-1} spectral region.

This is in a clear contrast with the room-temperature spectrum shown in Figure 2a (the corresponding portion of the spectrum between 1500 and 1700 cm^{-1} is featureless (not shown here) within our signal-to-noise ratio, and the absorption below 1500 cm^{-1} cannot be measured reliably in our experimental setup because silicon substrate exhibits significant absorption below this wavenumber at room temperature).

Table 1 compares vibrational signatures of the ethyl groups in ethyl-containing compounds condensed on different surfaces

and chemisorbed ethyl groups.^{13,20,23–25} The vibrational assignment of the absorption bands in the spectrum of nitroethane condensed at a multilayer coverage at 95 K in these studies is performed based on the previous assignments.²³ Both multilayer spectra of nitroethane condensed on a Si(100)-2 \times 1 surface at 95 K and the room temperature spectrum indicate clearly the presence of ethyl group. However, when nitroethane is adsorbed at room temperature, the spectral features are shifted as compared with the molecular adsorption in multilayers. In fact, the infrared spectrum of the nitroethane adsorbed on a Si(100)-2 \times 1 surface at room-temperature resembles the spectra of ethyl groups in iodoethane,^{20,24} ethyl groups adsorbed on a silicon surface,^{13,20} or ethyl groups chemisorbed on TiO₂.²⁵ Although this assignment is based on comparison with other ethyl-containing species, the important point that can be deduced from this comparison is that the ethyl groups are intact in both nitroethane condensed on a Si(100)-2 \times 1 surface at 95 K and in nitroethane chemisorbed on the same surface at room temperature. However, the chemical environment of the ethyl entity differs significantly in these two cases.

To understand the chemistry of the nitroethane interaction with the silicon surface, the annealing experiments were performed as shown in Figures 4 and 5. Two different approaches could be taken in order to follow the spectral changes in nitroethane adsorbed on a Si(100)-2 \times 1 surface at 95 K and annealed to different temperatures. First, as shown in Figure 2 and discussed above, the characteristic absorption bands corresponding to the C–H stretches in a 2800–2100 cm^{-1} spectral region look different at cryogenic temperature as compared to room-temperature experiments. Thus, the evolution of these features, for example the change in frequency of the most intense absorption feature in this region, can be followed as a function of surface annealing temperature. Figure 4 summarizes annealing studies that were conducted as follows. The clean Si(100)-2 \times 1 surface was cooled to the cryogenic temperature of 95 K, and its absorption spectrum was recorded to be used as a background. Then submonolayer coverage of nitroethane was deposited by 1 L dose and briefly annealed to the temperature indicated. After that, the surface was cooled to 95 K, and the resulting spectrum was recorded. Only one annealing

TABLE 1: IR Frequencies in the 2800–3100 cm^{-1} Region for Ethyl Groups on Various Substrates and in Molecular Analogs

system	ethyl precursor	type of vibration					ref
		2 δ_a bending	CH ₃ sym. stretch	CH ₂ sym. stretch	CH ₃ antisym. stretch	CH ₂ antisym. stretch	
C ₂ H ₅ NO ₂ /Si(100)-2 \times 1, 95 K, multilayer	C ₂ H ₅ NO ₂	2908	2950 components not resolved		3017(Sh) 2996	2966	this work ^c
C ₂ H ₅ NO ₂ in Ar matrix	C ₂ H ₅ NO ₂	2919	2954 2948	2925	3024 2999	2972 2961	23
C ₂ H ₅ I/Si(100)-2 \times 1, 95 K, multilayer	C ₂ H ₅ I	2854	2913	2953	2968	3010	20
solid C ₂ H ₅ I	C ₂ H ₅ I	2848	2908	2954	2975(ν_{13}) 2968(ν_1)	3017	24
C ₂ H ₅ NO ₂ /Si(100)-2 \times 1, 300 K	C ₂ H ₅ NO ₂	2871	2930	2968 components not resolved			this work
C ₂ H ₅ I/Si(100)-2 \times 1, 300 K	C ₂ H ₅ I	2864	2913	2953	2971		20
C ₂ H ₅ I/TiO ₂ ^a	C ₂ H ₅ I	2872	2912		2980	3026	25
(CH ₃ CH ₂) ₂ SiH ₂ on porous Si at 300 K ^b	(CH ₃ CH ₂) ₂ SiH ₂	2879	2912		components not resolved 2955 components not resolved		13

^a High pressure (6 Torr) experiments (gas phase + surface). ^b Experimental frequencies are taken from this reference without original assignment.

^c Other frequencies recorded in a 1300–1700 cm^{-1} region are 1331, 1367, 1398, 1430, 1459, 1552, and 1569 (sh).

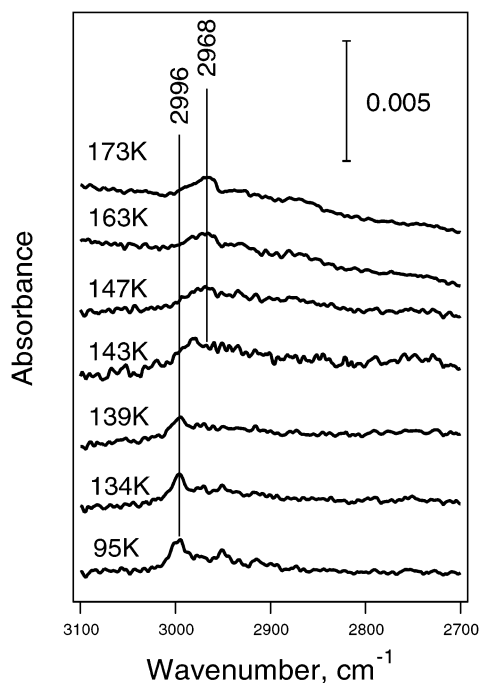


Figure 4. MIR FT-IR studies of a submonolayer coverage (1 L exposure) of nitroethane adsorbed on a Si(100)-2 × 1 surface at 95 K and subsequently briefly annealed to the temperatures indicated. 2700–3100 cm⁻¹ region. Each annealing point was obtained in a separate experiment.

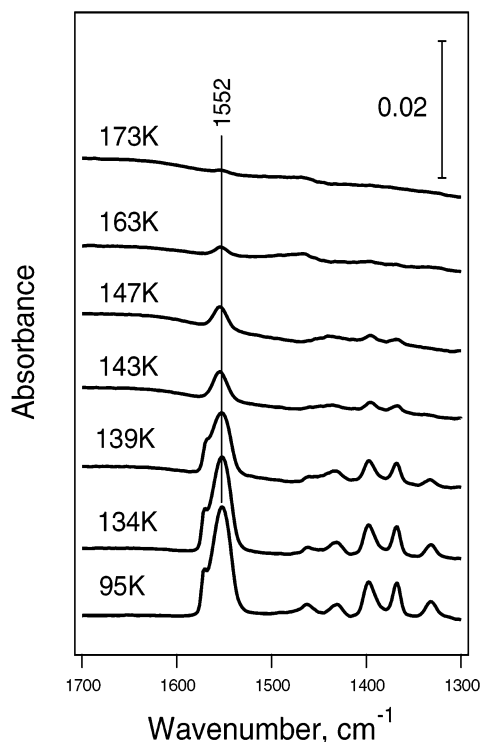


Figure 5. MIR FT-IR studies of a submonolayer coverage (1 L exposure) of nitroethane adsorbed on a Si(100)-2 × 1 surface at 95 K and subsequently annealed to the temperatures indicated. 1300–1700 cm⁻¹ region. Each annealing point was obtained in a separate experiment.

temperature was recorded per experiment. Despite a relatively low signal-to-noise in this spectral region for a small exposure of 1 L of nitroethane, it is clearly seen that approximately between 139 and 147 K the absorption band corresponding to this feature shifts from 2996 to 2968 cm⁻¹. The more quantita-

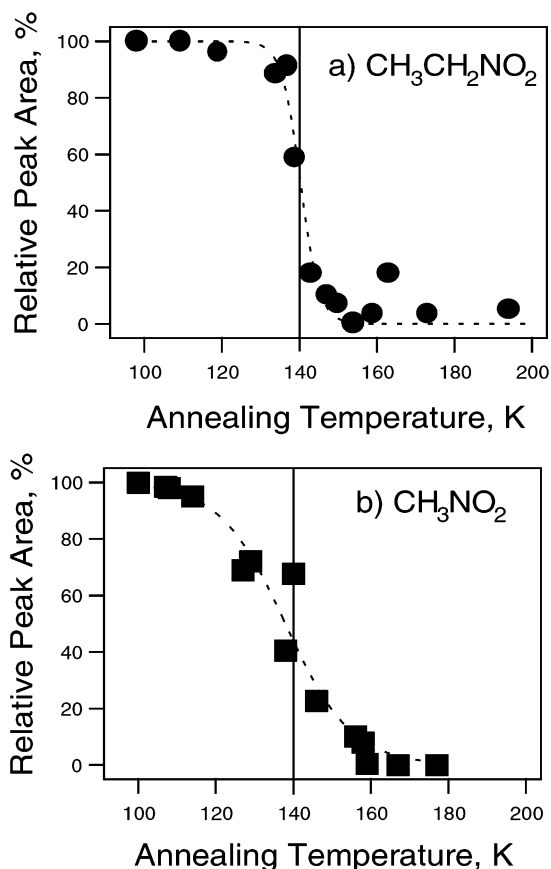


Figure 6. Integrated area of (a) the 1552 cm⁻¹ absorption band of nitroethane and (b) the 1558 cm⁻¹ absorption band of nitromethane plotted for a submonolayer exposure of either compound (1 L exposure) as a function of surface annealing temperature.

tive analysis is complicated by the low signal-to-noise level. However, in the 1300–1700 cm⁻¹ region of the nitroethane spectra, the characteristic NO₂ vibrations at 1552 cm⁻¹ provides a more reliable signature to follow. Figure 5 shows a spectral window of 1300–1700 cm⁻¹ for the same set of experiments as in Figure 4. The integrated relative peak areas for the 1552 cm⁻¹ absorption feature are plotted as a function of the annealing temperature in Figure 6a. The inflection point on the curve corresponds approximately to 140 K. At this temperature, the integrated area of the 1552 cm⁻¹ absorption feature is half of the original value. The activation energy of this process can be estimated using Redhead analysis²⁶ for a first-order reaction with the preexponential factor of 10¹³ s⁻¹ and assuming an effective heating rate of 1 K/s for annealing studies. The estimated activation energy is 36 kJ/mol. Although this number may be somewhat different from the activation energy determined by other methods, for the purposes of our discussion, it is important that it is significantly higher than zero.

In a previously published theoretical analysis,²² it was shown that nitromethane chemisorption on silicon surface is essentially barrierless. To obtain a more direct correlation with the theoretical studies, we have compared the chemistry of nitroethane and nitromethane at cryogenic temperatures. Although the decomposition pathways are different for these two nitroalkanes, they both physisorb on a Si(100)-2 × 1 surface at 95 K at submonolayer coverages and have similar vibrational characteristics that correspond to the nitro group being intact. Figure 6b summarizes the nitromethane studies of the 1558 cm⁻¹ absorption feature, whose decrease as a function of surface temperature for an exposure of the clean Si(100)-2 × 1 surface

to a submonolayer coverage of nitromethane represents a chemical reaction of the nitro group of nitromethane with the surface. Similarly to the studies of nitroethane outlined in Figure 6a, the inflection point in the integrated absorption feature corresponding to the nitro group is observed around 140 K. Thus, both nitromethane and nitroethane exhibit significant chemisorption barriers.

There may be several reasons for experimental observation of the reaction barrier for nitroalkanes reacting with a Si(100)-2 \times 1 surface. In a theoretical investigation,²² the nitromethane molecule approached the dimer of a Si(100)-2 \times 1 surface in optimized geometry. In our experiment, however, nitroethane molecules may have a variety of different ways to adsorb on the silicon surface. The energy required for these molecules to attain a configuration amenable for the reaction with the silicon surface dimer will contribute to the overall reaction barrier. The rate of such a transformation will also be affected by the entropy loss associated with ordering of nitroethane molecules randomly physisorbed on a Si(100)-2 \times 1. The energy required for the chemisorption process to occur may be quite small, but only certain pathways lead to the surface reaction. Some of these pathways may be missed in a theoretical investigation, especially if the energy barriers analyzed are small. Also, the cluster size used in the theoretical analysis of nitromethane on Si(100)-2 \times 1²² limits the possibilities of complex transformations involving multiple surface species. In addition, the size of the cluster used can sometimes affect the outcome of the calculation.²⁷

Another important factor that may contribute to the activation energy barrier observed here can be understood in terms of the precursor-mediated adsorption and desorption analysis, described in detail previously.²⁸ Once the molecules are adsorbed on a surface, the intermolecular interactions may play a significant role in their further chemical transformations. In other words, the reaction pathway considered for a single adsorbed molecule may change if several molecular entities are bound together. For example, water adsorption on semiconductor surfaces has been studied both experimentally^{29–33} and theoretically,³⁴ and one of the possible explanations of the reaction barrier observed in experimental studies was based on the fact that water molecules adsorbed on semiconductor surfaces can form agglomerates that prevent any of them from attaining a configuration needed for the reaction with a surface to occur. Only after the intermolecular interactions are broken, the reaction can take place. At the same time, agglomeration prevents single water molecules from desorbing from the surface increasing the desorption barrier. A similar situation may occur for nitroalkanes described here. In fact, because similar doses are required to produce a monolayer of nitroethane at room temperature, *vide infra*, and at cryogenic conditions, while cryogenic temperature adsorption does not lead to an immediate reaction, it is likely that the activation barrier for the chemical reaction is lower than the barrier for the desorption process. If the agglomeration takes place, it may affect both barriers, but based on our observations, the reaction barrier is still lower than the desorption barrier.

The presence of the reaction barrier for interaction of the reactive silicon surface with entities as reactive as a nitro group opens an interesting opportunity for surface self-assembly for bifunctional molecules. It is well-known that on metallic surfaces differences in activation energy of surface processes as low as 4 kJ/mol may result in over 90% selectivity for the surface process with a lower barrier if it is started at cryogenic temperatures.³⁵ Thus, for a bifunctional molecule, it should be

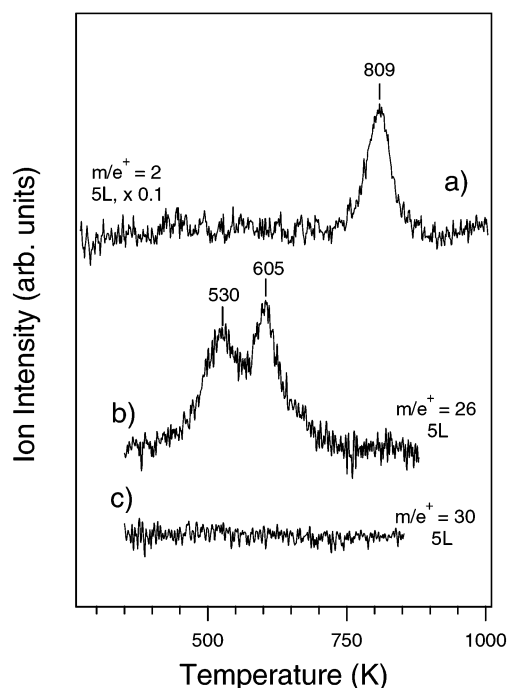


Figure 7. Temperature-programmed reaction/desorption studies of nitroethane adsorbed on a Si(100)-2 \times 1 surface at room temperature. 5 L exposure was used to produce a saturated monolayer. The evolution of (a) hydrogen ($m/e^+ = 2$), (b) ethylene ($m/e^+ = 26$), and (c) ethane or NO ($m/e^+ = 30$) are shown. $m/e^+ = 26$ was followed for ethylene evolution analysis to avoid interference from the background gases.

possible to reach a very high reaction selectivity even on a surface as reactive as Si(100)-2 \times 1, if the activation barriers for the interaction of these functional groups differ by several kJ/mol and if the reaction is started at cryogenic temperature, where both reaction pathways are extremely slow. The studies of bifunctional molecules are under way in our laboratory.

(b) Monolayer Chemistry of Nitroethane Adsorbed on a Si(100)-2 \times 1 Surface at Room Temperature. According to TPR/D studies presented in Figure 7, the only products of the reaction of nitroethane and a Si(100)-2 \times 1 surface that are released into the gas phase are ethylene and H₂, which is consistent with the hydrogen elimination reaction as the major pathway for the surface chemistry of ethyl groups. Ethylene desorption was followed by monitoring $m/e^+ = 26$ evolution as a function of surface temperature. This mass-to-charge ratio was chosen instead of $m/e^+ = 28$ (molecular ion of ethylene) to avoid interference from the background gases. Similarly to other studies of ethyl groups undergoing hydrogen elimination on silicon,⁹ ethylene is evolved between 500 and 650 K. Double desorption features have also been observed previously for this type of process.^{20,21} Hydrogen is evolved from the surface as H₂ around 800 K, which is consistent with the reaction limited recombinative desorption.^{36,37} A TPR/D trace monitoring $m/e^+ = 30$ (NO) is given in Figure 7 for reference. Neither NO nor any other possible reaction products except for ethylene and hydrogen were found to desorb from the surface within the temperature range studied.

Consistent with TPR/D studies, Auger electron spectroscopy data proved the presence of carbon, nitrogen, and oxygen on the Si surface between the temperatures of 300 and 900 K. The spectra taken at 300 K were compared to those taken after annealing to 500, 700, and 900 K. The amounts of nitrogen and oxygen remain essentially constant, and the amount of carbon decreased approximately 50% after annealing to 700 K,

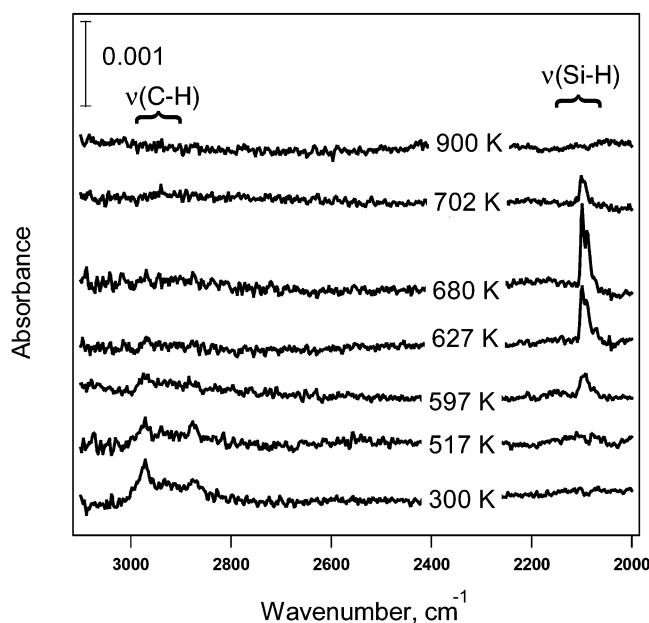


Figure 8. MIR FT-IR studies of a saturated monolayer of nitroethane produced on a Si(100)-2 × 1 surface by 100 L exposure at room temperature and annealed to the temperature indicated.

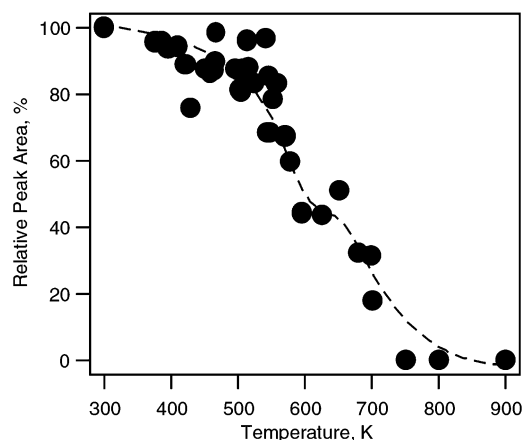


Figure 9. Integrated area of the C–H stretch absorption features (2700–3100 cm⁻¹) plotted for a saturated monolayer exposure of nitroethane onto a Si(100)-2 × 1 surface as a function of annealing temperature.

after which it remains constant. Also consistent with the TPR/D and AES studies are the infrared investigations presented in Figures 8 and 9. As shown in Figure 8, nitroethane adsorbed on a Si(100)-2 × 1 surface at room temperature gives rise to the C–H stretch region absorption bands, whereas the absorption bands below 2000 cm⁻¹ could not be observed at our signal-to-noise ratio (also silicon samples exhibit significant absorption below 1500 cm⁻¹ at room temperature). As the temperature of the surface is increased in a series of brief anneals to the temperatures indicated in the figure, the group of the C–H stretch absorption bands decreases in intensity, whereas its shape remains practically the same. As the integrated area of the C–H absorption bands decreases, the Si–H absorption bands become visible around the 2100 cm⁻¹ region. Only after the surface temperature is increased above 700 K does the intensity of these bands decrease as H₂ is desorbed from the surface. Finally, the changes in the integrated intensity of the C–H stretch absorption bands are summarized in Figure 9. The dashed line is only given to guide the reader's eye; however, it is consistent with the

presence of two desorption features in the TPR/D analysis given for ethylene in Figure 7.

Conclusions

A combination of MIR–FTIR, AES, and thermal desorption was used to understand the chemistry of nitroethane and nitromethane on Si(100)-2 × 1 with the focus on the monolayer chemistry at cryogenic temperatures. The energy barrier for both the nitroethane and nitromethane chemisorption was found to be approximately 36 kJ/mol, which is in disagreement with the theoretically predicted barrierless chemisorption. The explanation of such a discrepancy was proposed based on several factors that can play a role in our experimental studies.

It was also found that upon further surface reactions following the chemisorption of nitroethane on a Si(100)-2 × 1 surface all nitrogen and oxygen and ~50% of carbon remain on the surface even after annealing as high as 900 K. The rest of the carbon atoms are released from the surface as ethylene during the course of hydrogen elimination by ethyl groups. Hydrogen resulting from this process desorbs around 800 K.

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References and Notes

- (1) Waltenburg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 1589–1673.
- (2) Hamers, R. J.; Wang, Y. *Chem. Rev.* **1996**, *96*, 1261–1290.
- (3) Hovis, J. S.; Liu, H.; Hamers, R. J. *Surf. Sci.* **1998**, *402–404*, 1–7.
- (4) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N., Jr. *Acc. Chem. Rev.* **2000**, *33*, 617–624.
- (5) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413–41.
- (6) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879–903.
- (7) Bent, S. F. *J. Phys. Chem. B* **2002**, *106*, 2830–2842.
- (8) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271–1308.
- (9) Klug, D.-A.; Greenlief, C. M. *J. Vac. Sci. Technol. A* **1996**, *14*, 1826–1831.
- (10) Keeling, L. A.; Chen, L.; Greenlief, C. M.; Mahajan, A.; Bonser, D. *Chem. Phys. Lett.* **1994**, *217*, 136–141.
- (11) Sampson, G. M.; White, J. M.; Ekerdt, J. G. *Surf. Sci.* **1998**, *411*, 163–175.
- (12) Du, W.; Keeling, L. A.; Greenlief, C. M. *J. Vac. Sci. Technol. A* **1994**, *12*, 2281–2286.
- (13) Dillon, A. C.; Robinson, M. B.; Han, M. Y.; George, S. M. *J. Electrochem. Soc.* **1992**, *139*, 537–542.
- (14) Coon, P. A.; Wise, M. L.; Dillon, A. C.; Robinson, M. B.; George, S. M. *J. Vac. Sci. Technol. B* **1992**, *10*, 221–227.
- (15) Dillon, A. C.; Robinson, M. B.; George, S. M.; Roberts, D. A. *Surf. Sci.* **1993**, *286*, L535–L541.
- (16) Coon, P. A.; Wise, M. L.; Walker, Z. H.; George, S. M. *Surf. Sci.* **1993**, *291*, 337–348.
- (17) Colaiaanni, M. L.; Chen, P. J.; Gutleben, H.; Yates, J. T. *Chem. Phys. Lett.* **1992**, *191*, 561–568.
- (18) Darlington, B.; Foster, M.; Campion, A. *Surf. Sci. Lett.* **1994**, *304*, L407–L412.
- (19) Foster, M.; Darlington, B.; Scharff, J.; Campion, A. *Surf. Sci.* **1997**, *375*, 35–44.
- (20) Bulanin, K.; Shah, A. G.; Teplyakov, A. V. *J. Chem. Phys.* **2001**, *115*, 7178–7195.
- (21) Bulanin, K. M.; Shah, A. G.; Fitzgerald, D. R.; Doren, D. J.; Teplyakov, A. V. *J. Phys. Chem. B* **2002**, *106*, 7286–7289.
- (22) Barriocanal, J. A.; Doren, D. J. *J. Phys. Chem. B* **2000**, *104*, 12269–12274.
- (23) Groner, P.; Meyer, R.; Günthard, H. H. *Chem. Phys.* **1975**, *11*, 63–85.
- (24) Durig, J. R.; Thompson, J. W.; Thyagesan, V. W.; Witt, J. D. *J. Mol. Struct.* **1975**, *24*, 41–58.
- (25) Wu, W.-C.; Liao, L.-F.; Shiu, J.-S.; Lin, J.-L. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4441–4446.
- (26) Redhead, P. A. *Vacuum* **1962**, *12*, 203–211.
- (27) Widjaja, Y.; Mysinger, M. M.; Musgrave, C. B. *J. Phys. Chem. B* **2000**, *104*, 2527–2533.
- (28) Doren, D. J.; Tully, J. C. *Langmuir* **1988**, *4*, 256–268.

- (29) Kuhr, H. J.; Ranke, W. *Surf. Sci.* **1987**, *187*, 98–111.
- (30) Papagno, L.; Caputi, L. S.; Frankel, D.; Chen, Y.; Lapeyre, G. J. *Surf. Sci.* **1987**, *189/190*, 199–203.
- (31) Papagno, L.; Frankel, D.; Chen, Y.; Caputi, L. S.; Anderson, J.; Lapeyre, G. J. *Surf. Sci.* **1991**, *248*, 343–348.
- (32) Larsson, C. U. S.; Flödstroem, A. S.; Karlsson, U. O.; Yang, Y. J. *Vac. Sci. Technol. A* **1989**, *7*, 2044–2048.
- (33) Larsson, C. U. S.; Flödstroem, A. S. *Vacuum* **1991**, *42*, 297–300.
- (34) Föraker, A.; Doren, D. J. *J. Phys. Chem. B* submitted.
- (35) Kash, P. W.; Yang, M. X.; Teplyakov, A. V.; Flynn, G. W.; Bent, B. E. *J. Phys. Chem. B* **1997**, *101*, 7908–7918.
- (36) Ning, B. M. H.; Crowell, J. E. *Surf. Sci.* **1993**, *295*, 79–98.
- (37) Flowers, M. C.; Jonathan, B. H.; Liu, Y.; Morris, A. J. *Chem. Phys.* **1993**, *99*, 7038–7048.