

# Thermal Behavior of Alkylsiloxane Self-Assembled Monolayers on the Oxidized Si(100) Surface

G. Jonathan Kluth, Myung M. Sung, and Roya Maboudian\*

Department of Chemical Engineering, University of California, Berkeley, California 94720

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The thermal behavior of alkyltrichlorosilane ( $\text{CH}_3(\text{CH}_2)_{n-1}\text{SiCl}_3$ ) based self-assembled monolayers on the oxidized Si(100) surface has been examined under ultrahigh vacuum conditions for  $n = 4, 8$ , and  $18$ . Using high-resolution electron energy loss spectroscopy and contact angle analysis, it is found that the monolayers are stable in vacuum up to about  $740\text{ K}$  independent of chain length. Above  $740\text{ K}$  the chains begin to decompose through C–C bond cleavage, resulting in the desorption of hydrocarbon fragments. Following this initial desorption step, methyl groups attached to silicon atoms are observed. The siloxane head groups remain on the surface following decomposition of the monolayers until about  $1100\text{ K}$ .

## I. Introduction

Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. They are the subject of intense study because of their potential utility in such applications as wetting, adhesion, lubrication, and high-resolution lithography.<sup>1,2</sup> Several different varieties of SAMs have been investigated, including alkanethiols ( $\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$ ) on Au, Ag, and Cu, and alkyltrichlorosilanes ( $\text{CH}_3(\text{CH}_2)_{n-1}\text{SiCl}_3$ ) on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and mica. Each of these monolayer systems consists of three main parts. The first is the head group, which chemisorbs to the surface. Because of the strong interaction between the head group and the substrate, the molecules attempt to adsorb at all surface sites, resulting in a close-packed monolayer. The second part of the monolayer is the alkyl chain. In the simplest case this is a long chain normal alkane. van der Waals interactions between chains further contribute to the ordering of the monolayer. Alkanethiols on Au(111), for example, are tilted approximately  $30^\circ$  with respect to the surface normal in order to maximize the van der Waals interactions. The third part is the terminal group. The simplest terminal functionality is a methyl group; however, the chain may be terminated with a number of different groups (e.g.,  $\text{NH}_2$ ,  $\text{OH}$ , or  $\text{COOH}$ ), allowing SAMs to be tailored to a particular application. Functionalization of the end group also allows multiple layers to be adsorbed on top of the monolayers.<sup>1</sup>

The majority of work on SAMs has focused on the formation of the monolayers and their structure. In the case of alkanethiols on Au(111), the S–H bond is broken, and the molecule adsorbs as a thiolate.<sup>3</sup> Helium diffraction studies show that the monolayers form a  $c(4\sqrt{3} \times 2\sqrt{3})R30^\circ$  overlayer with four molecules per unit cell.<sup>4</sup> These molecules were originally thought to occupy the 3-fold hollow site on the Au(111) surface. More recent X-ray diffraction studies have found that molecules occupy different sites and suggested that the sulfur head groups

form dimers.<sup>5</sup> This picture is supported by X-ray photoelectron spectroscopy<sup>6</sup> and temperature-programmed desorption (TPD) data,<sup>7</sup> although the dimers have not been observed directly.

In the case of alkyltrichlorosilanes on  $\text{SiO}_2$ , adsorption takes place through the hydrolysis of the Si–Cl bonds to form Si–OH groups. All Si–Cl bonds become hydrolyzed, as no chlorine is detected following monolayer formation.<sup>8</sup> The OH groups interact with OH groups on the oxidized surface, forming Si–O–Si bonds to the substrate through condensation reactions. It is believed that Si–O–Si bonds are also formed between adjacent head groups, creating a cross-linked network at the surface. Water is found to play a key role in the formation step.<sup>8–10</sup> The presence of too much water causes polymerization of the precursor molecules and leads to poor monolayer formation. But a small amount of water is required for the formation of high-quality films. It has been proposed that a thin water film exists on the hydrophilic  $\text{SiO}_2$  surface and that the chains physisorb on this water film.<sup>9,10</sup> In this stage, the chains are mobile while bonded to the water layer, allowing them to pack more closely before the condensation reaction takes place, at which point they become pinned to the surface. Chain length is observed to affect the quality of the monolayers, as indicated by contact angle analysis. For  $n > 6$  the water contact angle is approximately  $110^\circ$ ; for shorter chain lengths, the contact angle decreases to about  $90^\circ$ ,<sup>8</sup> indicating that the shorter chains are not as well-packed.

Another important consideration in the application of SAMs is their thermal stability. To successfully incorporate these films into the production of low surface energy structures, it is necessary for the films to withstand the temperatures used in subsequent processing and packaging steps. A TPD study of octadecanethiol ( $n = 18$ ) adsorbed on Au(111) observed desorption of entire chains at about  $450\text{ K}$ ,<sup>7</sup> indicating that desorption takes place through cleavage of the Au–S bond. For alkyltrichlorosilane-derived monolayers, previous studies using contact angle analysis have shown that water contact angles on octadecyltrichlorosilane (OTS)-coated surfaces remain

\* To whom correspondence may be addressed: email, maboudia@uclink4.berkeley.edu; phone, (510) 643-7957; fax, (510) 642-4778.

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(1) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: Boston, MA, 1991.

(2) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932.

(3) Nuzzo, R. G.; Flusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.

(4) Camillone, N.; Chidsey, C. E. D.; Liu, G.-Y.; Scoles, G. *J. Chem. Phys.* **1993**, *98*, 3503.

(5) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216.

(6) Zuberägel, Ch.; Deuper, C.; Schneider, F.; Neumann, M.; Grunze, M.; Schertel, A.; Wöll, Ch. *Chem. Phys. Lett.* **1995**, *238*, 308.

(7) Nishida, N.; Hara, M.; Sasabe, H.; Knoll, W. *Jpn. J. Appl. Phys.* **1996**, *35*, L799.

(8) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

(9) Silberzan, P.; Léger, L.; Ausserré, D.; Benattar, J. J. *Langmuir* **1991**, *7*, 1647.

(10) Allara, D. L.; Parikh, A. N.; Rondelez, F. *Langmuir* **1995**, *11*, 2357.

the same upon annealing for 5 min to temperatures as high as 675 K in a nitrogen ambient.<sup>11</sup> Above this temperature the contact angle was observed to decrease, indicating degradation of the films. The studies do not reveal information about the mechanism by which these films degrade, however.

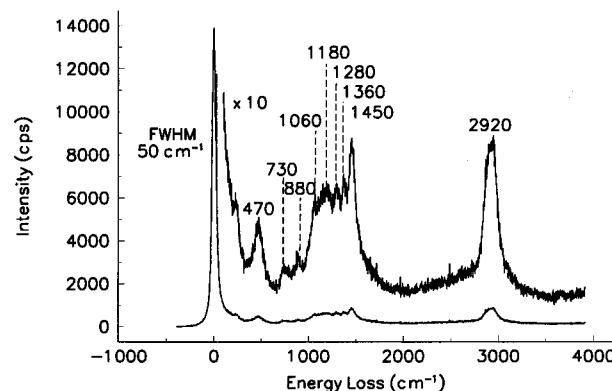
In this article the thermal behavior of alkylsiloxane monolayers in ultrahigh vacuum is examined. Using high-resolution electron energy loss spectroscopy (HREELS) and contact angle analysis, it is found that the monolayers are stable in vacuum up to about 740 K independent of chain length. Above that temperature, the monolayers decompose primarily through the cleavage of C–C bonds. Methyl groups attached to silicon atoms are observed on the surface following this initial decomposition step; these methyl groups react as the temperature is raised further. The siloxane head groups remain on the surface until about 1100 K.

## II. Experimental Section

**A. Sample Preparation.** Samples were cut from B-doped Si(100) wafers with resistivity in the range 1–50  $\Omega$  cm. The samples were first degreased ultrasonically in chloroform. A chemical oxide was grown by placing the sample in a piranha solution (4:1 mixture of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) at 100 °C for 10–15 min. The sample was rinsed several times in deionized water (resistivity = 18 M $\Omega$ ) and then dried using nitrogen. Monolayers were formed by placing the oxidized samples in a 2.5 mmol solution of the alkyltrichlorosilane precursor dissolved in 4:1 hexadecane/chloroform for 1 h. The samples were then ultrasonically washed in chloroform to remove excess reactants and dried with nitrogen. For OTS, silanization was carried out at room temperature. For butyltrichlorosilane (BTS) and octyltrichlorosilane, silanization was performed at 10 °C in order to remain below the transition temperature at which the monolayers reach their highest packing density.<sup>12</sup> Film quality was checked by water contact angle, which was 98° for the BTS-coated samples investigated here, 109° for octyltrichlorosilane-coated samples, and 112° for OTS-coated samples, in good agreement with earlier results.<sup>8</sup>

Monolayers were also produced using octadecyldimethylchlorosilane (ODMS) as a precursor. Because this molecule has only one chlorine atom attached to the silicon head group, the monolayer is expected to form few or no cross-linking bonds to adjacent chains. Hence, ODMS-coated samples were used to examine the effect of cross-linking on the thermal stability of alkylsiloxane monolayers. Silanization was performed at 10 °C for 6 h at a concentration of 5 mmol. The water contact angle for these monolayers was 80°.

**B. Experimental Procedure.** Samples were introduced into ultrahigh vacuum by means of a load lock system. Both the ultrahigh vacuum (UHV) chamber and the load lock have been described previously.<sup>13</sup> The chamber contains low-energy electron diffraction, Auger electron spectroscopy, HREELS, and a differentially-pumped quadrupole mass spectrometer (QMS) coupled to a temperature controller for TPD. The base pressure is  $1 \times 10^{-10}$  Torr. All samples were annealed to 520 K for 30 min prior to higher temperature annealing to desorb any physisorbed species. This procedure leaves the chains intact, as they do not desorb until much higher temperatures, and was found to improve sample reproducibility. The thermal behavior of the films was studied by annealing the sample to a given temperature for approximately 1 min, during which time the QMS was used to check the composition of the background gas in the range from 1 to 300 amu. Following all high-temperature treatments, the sample temperature was reduced to and then held at 520 K until the chamber pressure fell to about  $1 \times 10^{-9}$  Torr. This temperature minimized readsorption on the sample but did not



**Figure 1.** HREEL spectrum of the OTS-coated oxidized Si(100) surface after annealing to 520 K for 30 min.

result in desorption of the monolayers. After cooling the sample to 120 K, HREEL spectra were obtained in the specular mode using an incident electron energy of 6 eV. The resolution of the elastic peak was typically between 40 and 50  $\text{cm}^{-1}$  at about  $10^4$  counts/s. The spectra were unchanged even after several hours of exposure to the incident electron beam. HREEL spectra were fit using Gaussian peaks. Peak widths were fixed based on the width of the elastic peak, while peak positions were fixed based on positions reported in the literature. Peak intensities were varied to fit the experimental data.

In order to have simple sample transfer capabilities, the sample temperature cannot be measured directly. The temperature was measured by a type K thermocouple attached to a Ta plate behind the sample. The thermocouple reading was calibrated for sample temperature by preparing a clean Si(100) surface in vacuum through sputtering and annealing to 1200 K. The clean surface was then exposed to atomic hydrogen, which was subsequently desorbed in a TPD experiment. The desorption temperature of the monohydride species was then compared with the value of 795 K reported in the literature<sup>14</sup> to calibrate the sample temperature.

HREELS measurements were complemented by contact angle analysis. A Model A-100 Ramé-Hart NRL goniometer was used to measure water contact angles in room air using the sessile drop method.<sup>15</sup> A microsyringe delivered drops of deionized water ranging from 1 to 5  $\mu\text{L}$ . The stage was backlit with a lamp covered with green acetate paper to minimize heating of the drop.

## III. Results

**A. Structure of Alkylsiloxane SAMs.** A typical HREEL spectrum for the oxidized and then OTS-coated Si(100) surface is shown in Figure 1. This sample was annealed to 520 K for 30 min. To the best of our knowledge, this is the first report of the use of HREELS for the study of alkylsiloxane SAMs. The peak assignments are summarized in Table 1. The presence of the monolayers is indicated by the broad C–H stretch at about 2920  $\text{cm}^{-1}$  and the C–H bends between 1280 and 1450  $\text{cm}^{-1}$ . The positions of these modes are consistent with those for normal alkanes such as butane and hexane.<sup>16,17</sup> Small peaks are also present at 730 and 880  $\text{cm}^{-1}$ , which are assigned to C–H bending modes. The region from 1000 to 1200  $\text{cm}^{-1}$  contains peaks due to the asymmetric stretch of bridge-bonded oxygen<sup>18,19</sup> and will be discussed in more detail below. Evidence of the underlying oxide is also

(11) Houston, M. R.; Maboudian, R.; Howe, R. T. *Proceedings of Solid-State Sensor and Actuator Workshop*, Hilton Head, SC, June 2–6, 1996, p 42.

(12) Brzoska, J. B.; Azouz, I. B.; Rondelez, F. *Langmuir* **1994**, *10*, 4367.

(13) Kluth, G. J.; Maboudian, R. *J. Appl. Phys.* **1996**, *80*, 5408.

(14) Sinniah, K.; Sherman, M. G.; Lewis, L. B.; Weinberg, W. H.; Yates, J. T.; Janda, K. C. *J. Chem. Phys.* **1990**, *92*, 5700.

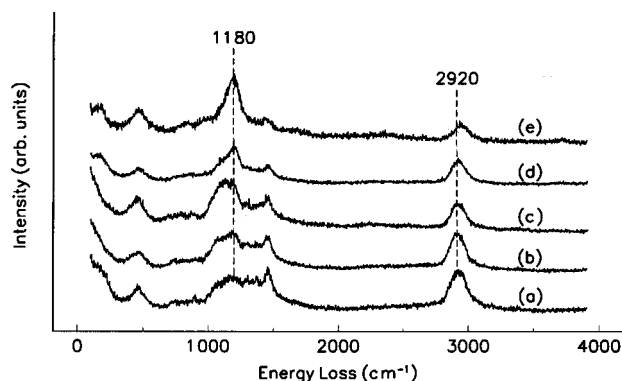
(15) Neumann, A. W.; Good, R. J. *Surface and Colloid Science Vol. II: Experimental Methods*; Plenum Press: New York, 1979.

(16) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958.

(17) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1963**, *19*, 85.

(18) Schaefer, J. A.; Göpel, W. *Surf. Sci.* **1985**, *155*, 535.

(19) Ibach, H.; Bruchmann, H. D.; Wagner, H. *Appl. Phys. A* **1982**, *29*, 113.



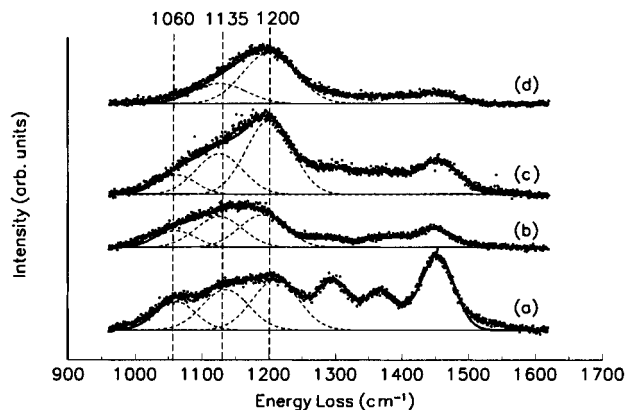
**Figure 2.** HREEL spectra as a function of chain length for oxidized Si(100) coated with (a) OTS, (b) octyltrichlorosilane, and (c) BTS. The ODMS-coated sample (d) is also shown. The oxidized sample (e) was prepared in exactly the same manner as the others, with the exception that no precursor was present in the hexadecane/chloroform solution. All samples were annealed to 520 K for 30 min. Each spectrum has been normalized by the elastic peak intensity.

**Table 1. Peak Assignments for Alkylsiloxane Self-Assembled Monolayers on Oxidized Si(100)**

peak position (cm <sup>-1</sup> )	assignment	refs
2920	C-H stretch	16
1450	CH <sub>2</sub> scissor	16, 17
1360	CH <sub>3</sub> symmetric bend	16, 17
1280	CH <sub>2</sub> twist-rock	17
1180	Si-O-Si asymmetric stretch (bulk oxide)	18, 19
1060	Si-O-Si stretch (between the surface and the head group)	20
880	CH <sub>3</sub> rock	17
800	Si-O-Si symmetric stretch	18, 19
730	CH <sub>2</sub> rock-twist	16, 17
470	Si-O-Si bend	18, 19

seen in the bending mode at 470 cm<sup>-1</sup>. It is interesting to note that the oxide is still detected by HREELS, even for the case of  $n = 18$ , corresponding to a film thickness of 2 nm.

Spectra a–c of Figure 2 show the HREEL spectra of alkyltrichlorosilane-coated oxidized Si(100) surfaces as a function of chain length. For comparison, HREEL spectra of an ODMS-coated surface and a sample that has been oxidized but not placed in a monolayer solution are also shown in spectra d and e of Figures 2, respectively. For trichlorosilane-derived monolayers, as the chain length decreases from 18 to 4 carbon atoms, the Si–O modes from the underlying SiO<sub>2</sub> substrate become more intense relative to the C–H modes. For BTS, the C–H bending modes at 730 and 880 cm<sup>-1</sup> become harder to resolve, possibly because of the appearance of the Si–O–Si symmetric stretch at 800 cm<sup>-1</sup>. There is also a small peak at about 2250 cm<sup>-1</sup> which may be an overtone of the Si–O–Si asymmetric stretch. This peak is observed only for the BTS-coated sample because the Si–O–Si asymmetric stretch is more intense for that sample than for the longer chain monolayers. For the ODMS-coated sample, the C–H and Si–O–Si intensities are similar to those of the BTS-coated sample, even though each chain consists of 18 carbon atoms. Combined with the low contact angle of 80°, this observation suggests that the ODMS-derived monolayer is not as close-packed as the trichlorosilane-derived monolayers. The spectrum for the oxidized sample indicates that carbon is also present on this surface. The position of the C–H stretch is shifted to higher energy on the oxidized sample, however, indicating that the hydrocarbon is different from the self-assembled monolayers; it is likely due to contamination.



**Figure 3.** Bridge-bonded oxygen stretch region of the HREEL spectra for (a) OTS-, (b) BTS-, and (c) ODMS-coated Si(100). Spectrum d shows the same region for an oxidized sample with no monolayer adsorbed. The dashed lines indicate fits to the experimental data for the Si–O–Si peaks.

Figure 3 shows close-up scans of the bridge-bonded oxygen region for (a) OTS-coated Si(100), (b) BTS-coated Si(100), and (c) ODMS-coated Si(100). Also shown is the same region for an oxidized sample with no monolayer adsorbed (d). The large peak at about 1180 cm<sup>-1</sup> for the oxidized sample (Figure 3d) cannot be fit using a single Gaussian peak; peaks at 1135 and 1200 cm<sup>-1</sup>, which are more readily observed on the OTS-coated sample, are used to fit this region. These peaks are present for all samples; therefore, they are assigned to the bridge-bonded oxygen stretch of the bulk, chemically prepared oxide that serves as the substrate for monolayer adsorption. For all samples on which the monolayers have been adsorbed, an additional peak is observed at 1060 cm<sup>-1</sup>; this peak is not present for the oxidized sample. On the basis of an IR study of methylsilanols on silica surfaces,<sup>20</sup> this peak at 1060 cm<sup>-1</sup> is assigned to the Si–O–Si bond between the alkylsiloxane head group and the oxidized surface.<sup>21</sup> The previous study also detected the presence of a mode at 1007 cm<sup>-1</sup> which was assigned to the cross-linking Si–O–Si bond. This mode is expected for the trichlorosilane-coated samples, but not for the ODMS-coated surface. This peak cannot be resolved in the present study, however, because of its proximity to the 1060 cm<sup>-1</sup> peak.

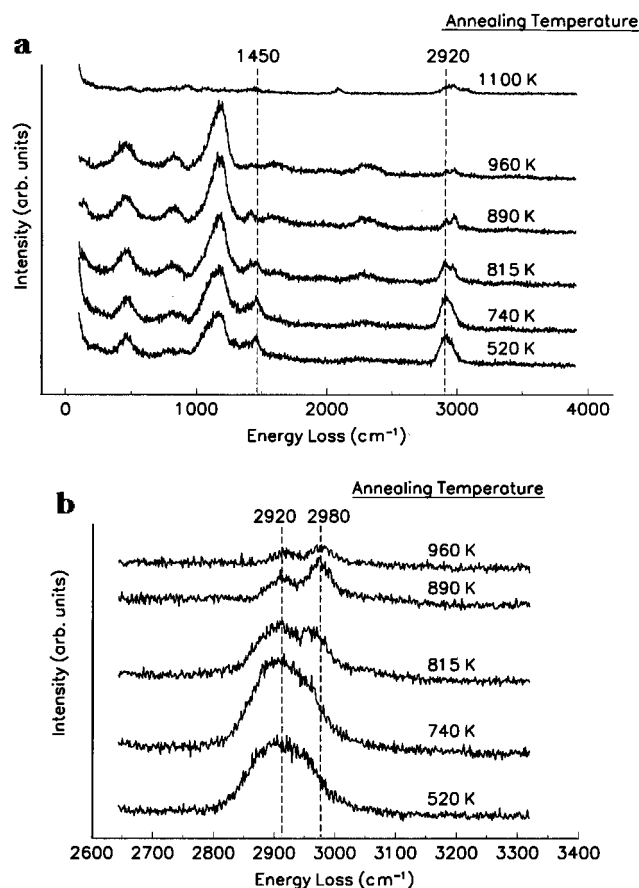
**B. Thermal Decomposition–HREELS.** HREEL spectra for a BTS-coated surface as a function of annealing temperature are shown in Figure 4a. The spectrum of the sample annealed to 520 K shows a broad C–H stretch which can be well fit using the reported positions for the symmetric and asymmetric stretches of CH<sub>2</sub> and CH<sub>3</sub> groups in normal alkanes.<sup>16</sup> The monolayers remain intact up to temperatures of about 740 K. After annealing to 815 K, the intensity of the C–H stretch decreases and its shape changes. Two peaks are resolved at about 2920 and 2980 cm<sup>-1</sup>. The C–H bending modes decrease in intensity and a new peak appears at 1400 cm<sup>-1</sup>. The intensities of the Si–O–Si modes increase, with the symmetric Si–O–Si stretch at 800 cm<sup>-1</sup> becoming more apparent. The position of the symmetric stretch may also be affected by the presence of Si–OH groups, which would give rise to a peak at 820 cm<sup>-1</sup>,<sup>22</sup> and Si–C groups, which would result in a peak at about 715 cm<sup>-1</sup>.<sup>23</sup> In addition,

(20) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

(21) The peak at 1060 cm<sup>-1</sup> could also be due to the C–C stretch. This assignment is ruled out, however, because the intensity of this peak does not scale with the intensities of the C–H stretching and bending modes.

(22) Ibach, H.; Wagner, H.; Bruchmann, D. *Solid State Commun.* **1982**, *42*, 457.

(23) Schmidt, J.; Stuhlmann, Ch.; Ibach, H. *Surf. Sci.* **1994**, *302*, 10.



**Figure 4.** HREEL spectra as a function of annealing temperature for the BTS-coated oxidized Si(100) surface. Wide scans are shown in (a); close-ups of the C–H stretch are shown in (b).

the peak at  $2250\text{ cm}^{-1}$  increases in intensity, consistent with its interpretation as an oxide overtone. These changes all indicate that the monolayer has begun to desorb. Upon annealing to 890 K, the intensities of the C–H modes further decrease, while the intensities of the Si–O–Si modes increase. The intensities of the peaks at  $1400$  and  $2980\text{ cm}^{-1}$  rise and fall with each other, suggesting that they are due to the same species. After annealing to 960 K the monolayers have almost completely desorbed as indicated by the virtual disappearance of the C–H modes, and the spectrum is dominated by Si–O–Si modes. The overtone at  $2250\text{ cm}^{-1}$  has increased in intensity and become broader. The broad peak at about  $1650\text{ cm}^{-1}$  may be a combination of Si–O–Si modes ( $470 + 1180 = 1650\text{ cm}^{-1}$ ). The oxide desorbs upon annealing to 1100 K, as indicated by the disappearance of the oxide modes at 470, 800, and  $1180\text{ cm}^{-1}$ . The C–H stretch at  $2960\text{ cm}^{-1}$  and the Si–H stretch at  $2090\text{ cm}^{-1}$  indicate the presence of a small amount of carbon and hydrogen contamination.

The C–H stretch region of the HREEL spectra for a BTS-coated surface is shown in Figure 4b as a function of annealing temperature. As stated earlier, the spectra clearly show that upon annealing to 815 K, the C–H stretch decreases in intensity, and individual peaks are resolved at  $2920$  and  $2980\text{ cm}^{-1}$ . In addition, a peak appears at  $1400\text{ cm}^{-1}$  in the C–H bending region. Infrared spectra of methylsilanols adsorbed on silica show similar peak positions,<sup>20</sup> as do HREEL and IR spectra of methyl iodide on Si(100), which dissociates to yield adsorbed iodine and methyl groups.<sup>24,25</sup> Furthermore, IR spectra of

**Table 2.** Comparison of Peaks Observed after Annealing Butylsiloxane Monolayers to  $>800\text{ K}$  with Infrared Data

system	peaks, $\text{cm}^{-1}$				ref
	$\text{CH}_3(\text{a})$ stretch	$\text{CH}_3(\text{s})$ stretch	$\text{CH}_3$ bend	$\text{CH}_3$ umbrella mode	
alkylsiloxane SAM	2980	2920	1400	<i>a</i>	<i>b</i>
annealed to $>800\text{ K}$					
methylsilanols on silica	2970	2920	1430	1275	20
$\text{CH}_3\text{I}$ on Si(100)	2990	2930	1425	1260	24
$\text{CH}_3\text{I}$ on Si(100)	2955	2890	--	--	25
tetradecamethylcyclotriheptasiloxane $[(\text{CH}_3)_2\text{SiO}]_7$	2960	2900	1410	1260	26
hexamethylcyclotrisiloxane $[(\text{CH}_3)_2\text{SiO}]_3$	2960	2900	1400	1260	26

<sup>a</sup> The  $\text{CH}_3$  bend at  $1260\text{ cm}^{-1}$  cannot be resolved because of the intensity of the adjacent Si–O–Si stretch. <sup>b</sup> This work.

methylsiloxane molecules (such as hexamethylcyclotrisiloxane)<sup>26</sup> show peaks which closely match the observed energies for the C–H stretching and bending modes. The peak positions for these systems are summarized in Table 2. On the basis of the spectra of these systems, the peaks at  $2920$  and  $2980\text{ cm}^{-1}$  are assigned to the C–H stretch of Si– $\text{CH}_3$  species, while the peak at  $1400\text{ cm}^{-1}$  is assigned to the bending mode. For Si– $\text{CH}_3$  species one would also expect an intense peak at  $1260\text{ cm}^{-1}$  due to the  $\text{CH}_3$  umbrella mode. This peak cannot be resolved in the monolayer spectra because of the presence of the strong Si–O–Si asymmetric stretch at  $1180\text{ cm}^{-1}$ .<sup>27</sup> With these assignments, the HREEL spectra show that following annealing to 815 K,  $\text{CH}_3$  groups remain on the surface. Furthermore, the spectra indicate that the methyl groups are attached to silicon and not oxygen atoms. Attachment to oxygen atoms would result in surface methoxy species. Such species would give rise to a peak at about  $2820\text{ cm}^{-1}$  due to the symmetric C–H stretch of the methoxy group, as observed in infrared studies of methyl ethers<sup>28</sup> and HREELS studies of methanol on silicon.<sup>29,30</sup> Also, the C–H bending mode of methoxy species occurs at about  $1450\text{ cm}^{-1}$ , instead of the  $1400\text{ cm}^{-1}$  observed in the present study. The absence of these modes indicates that methoxy groups are *not* present following high-temperature annealing, and thus, the carbon present following the initial desorption step must be attached directly to silicon atoms. These observations suggest that the desorption of the monolayers is primarily the result of C–C bond cleavage and that initially Si–C bonds remain intact. Upon further heating to 890 K, the intensities of the Si– $\text{CH}_3$  peaks decrease, indicating reaction of the  $\text{CH}_3$  groups.

Similar behavior as a function of annealing temperature was observed for OTS-coated surfaces and for the intermediate case of octyltrichlorosilane-coated surfaces. Figure 5a shows HREEL spectra for the OTS-coated surface as a function of annealing temperature. After the sample was annealed to 815 K, the C–H stretch decreases in intensity with two peaks becoming resolvable (shown in Figure 5b), accompanied by a shift in the C–H bends to a single peak at  $1400\text{ cm}^{-1}$ . After the surface was annealed to 850 K, the spectrum is dominated by Si–O–Si modes,

(25) Kong, M. J.; Lee, S. S.; Lyubovitsky, J.; Bent, S. F. *Chem. Phys. Lett.* **1996**, 263, 1.

(26) Craver, C. D. *The Coblenz Society Desk Book of Infrared Spectroscopy*; The Society: Kirkwood, MO, 1982.

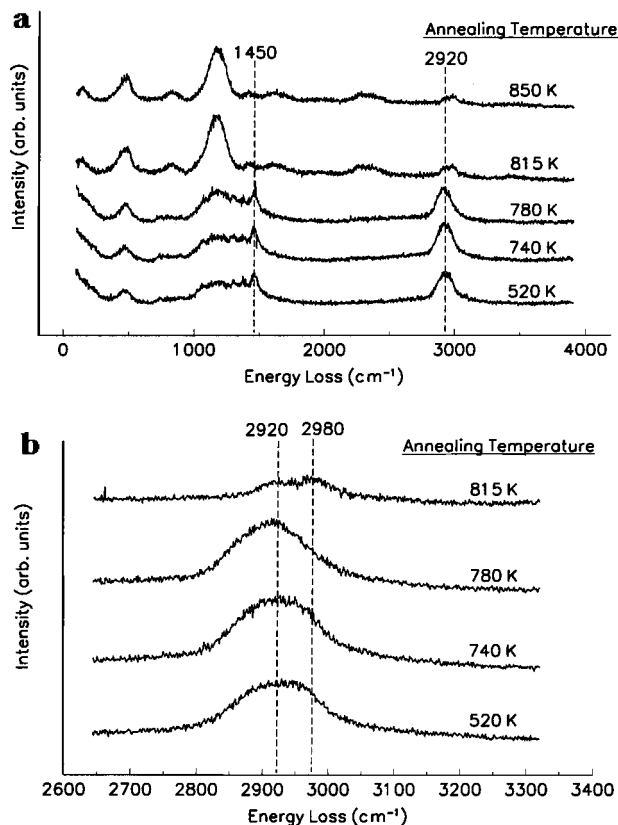
(27) We have examined monolayers formed from BTS-coated  $\text{Si}_3\text{N}_4$ . Upon annealing, these monolayers also show evidence for  $\text{CH}_3$  groups. In this case, the Si–O–Si stretch is not present, and the  $\text{CH}_3$  umbrella mode is observed at  $1260\text{ cm}^{-1}$ .

(28) Henbest, H. B.; Meakins, G. D.; Nicholls, B.; Wagland, A. A. *J. Chem. Soc.* **1957**, 1462.

(29) Strocio, J. A.; Bare, S. R.; Ho, W. *Surf. Sci.* **1985**, 154, 35.

(30) Glass, J. A.; Wovchko, E. A.; Yates, J. T. *Surf. Sci.* **1995**, 338, 125.

(24) Colaianni, M. L.; Chen, P. J.; Gutleben, H.; Yates, J. T. *Chem. Phys. Lett.* **1992**, 191, 561.

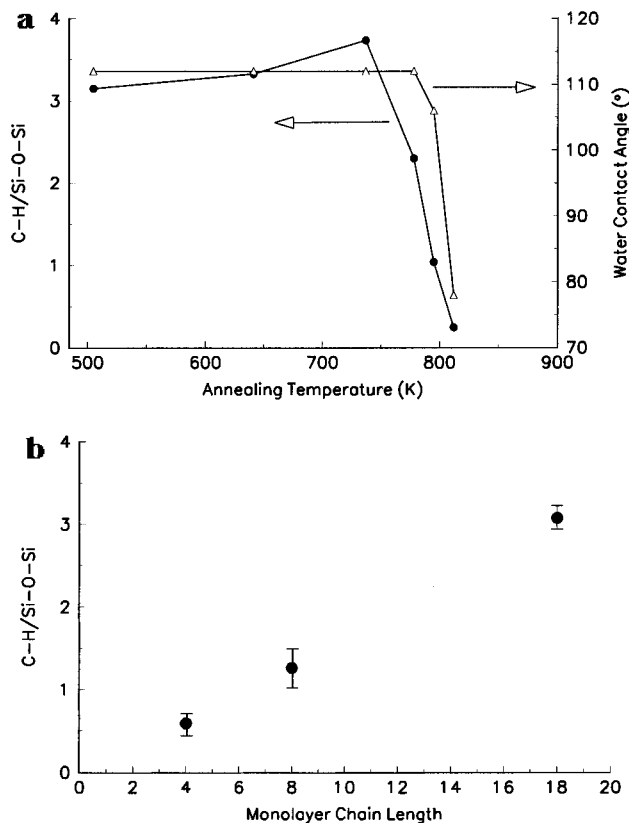


**Figure 5.** HREEL spectra as a function of annealing temperature for the OTS-coated oxidized Si(100) surface. Wide scans are shown in (a); close-ups of the C–H stretch are shown in (b).

including the combination and overtone losses at 1650 and 2350  $\text{cm}^{-1}$ , respectively.

Similar behavior was also observed for ODMS-derived monolayers. Upon annealing to 950 K, two peaks are observed in the C–H stretch region, and the single C–H bend at 1400  $\text{cm}^{-1}$  is observed. These observations suggest that the same desorption mechanism is present as the trichlorosilane-derived monolayers. Thus, *the thermal stability of these monolayers is not determined by the head group bonding configuration (e.g., cross-linking Si–O bonds) but rather by the Si–C or C–C bonds.*

**C. Thermal Decomposition—Water Contact Angle Analysis.** The contact angle for OTS-coated samples was measured as a function of annealing temperature in vacuum. This monolayer was chosen because it had the largest contact angle before annealing and, thus, the largest range in which to observe changes. Figure 6a shows that the contact angle remains constant at about 112° up to 780 K and then rapidly declines to about 80° upon annealing to 815 K. This behavior is in good agreement with a previous contact angle study carried out in a nitrogen ambient.<sup>11</sup> Before contact angle measurement, a HREEL spectrum was obtained for each of these samples. Figure 6a shows the ratio of the C–H stretch (2920  $\text{cm}^{-1}$ ) HREELS peak area to the Si–O–Si asymmetric stretch (1180  $\text{cm}^{-1}$ ) peak area. This ratio is approximately constant up to 740 K, consistent with the notion that the monolayers are stable up to this temperature. Upon annealing to 780 K, however, this ratio decreases as the monolayers begin to desorb. Upon annealing to 795 K, the peak area ratio has decreased to approximately 1, less than half the initial ratio, while the contact angle remains high at 106°. To obtain a qualitative sense of what the decreased peak area ratio implies about the annealed monolayers, we have plotted in Figure 6b the peak area ratio as a function of chain length for samples



**Figure 6.** (a) Water contact angle ( $\Delta$ ), and the ratio of the C–H stretch peak area (2920  $\text{cm}^{-1}$ ) to the Si–O–Si asymmetric stretch peak area (1180  $\text{cm}^{-1}$ ) ( $\bullet$ ) as a function of annealing temperature for the OTS-coated oxidized Si(100) surface. (b) Ratio of the C–H stretch peak area to the Si–O–Si asymmetric stretch peak area as a function of chain length. The contact angle for BTS-coated surfaces is 98°; for octyltrichlorosilane-coated surfaces it is 109°; for OTS-coated surfaces it is 112°.

that have been annealed to 520 K for 30 min. While there is some scatter in the measurements, it is clear that the C–H/Si–O–Si peak area ratio decreases as chain length decreases. The peak area ratio of 1 for the OTS-coated sample annealed to 795 K indicates a substantial reduction in chain length from the original 18 carbon atoms. However, at this point the sample still has a high contact angle value of 106° (Figure 6a), suggesting that the monolayer remains reasonably well-ordered even with the reduction in chain length.

#### IV. Discussion

In this paper, we have investigated the thermal stability of alkylsiloxane monolayers on the oxidized surface of Si(100) for different chain lengths. The thermal behavior is observed to be essentially independent of chain length. HREELS results indicate that the monolayers are stable in vacuum up to 740 K. In the analysis of the initial decomposition mechanism of the monolayers, three possibilities are considered: cleavage of the Si–O head group bond, cleavage of the Si–C bond, and cleavage of C–C bonds. Si–O–Si modes are observed in HREEL spectra up to temperatures of about 1100 K, in agreement with TPD studies of the decomposition of thin ( $\sim 2$  monolayers) oxide layers on Si(100).<sup>31</sup> The Si–O bonds of the head groups are slightly different from those of the substrate, as evidenced by their position in HREEL spectra. This difference is unlikely to result in a large decrease in desorption temperature, however. The observation of

(31) Sun, Y.-K.; Bonser, D. J.; Engel, T. J. *Vac. Sci. Technol., A* **1992**, *10*, 2314.

similar desorption behavior on OTS- and ODMS-coated surfaces suggests that the thermal behavior of the monolayers does not depend on the Si–O cross-linking of adjacent chains and, thus, that the silicon head groups remain on the surface even after the monolayer has decomposed until about 1100 K. Thus, desorption of the monolayer must be the result of Si–C or C–C bond cleavage.

As the monolayers begin to desorb, the intensity of the C–H stretch decreases and two peaks are clearly resolved in the HREEL spectra. These peaks indicate the presence of methyl groups on the surface following the initial decomposition of the monolayers. Their positions are consistent with methyl groups directly attached to silicon atoms. These methyl groups are not the result of contamination because the sample was held at 520 K after high-temperature annealing in order to minimize readorption. Furthermore, the C–H modes on the oxidized sample (Figure 2e), which are attributed to contamination, have a much different character than the C–H stretch on these annealed monolayer samples. Specifically, the C–H bending mode on the oxidized sample appears at about 1450  $\text{cm}^{-1}$ , while it appears at about 1400  $\text{cm}^{-1}$  on the annealed monolayer sample. Also, the C–H stretch for the oxidized sample is a broad peak centered at about 2950  $\text{cm}^{-1}$ , as opposed to the two peaks observed in the annealed monolayer sample. These observations suggest that *the Si–C bonds remain intact and that decomposition initially occurs primarily through C–C bond cleavage.*

Contact angle data as a function of annealing temperature further support this picture. The contact angle for OTS-coated Si(100) remains constant at 112° up to 780 K. When the surface is annealed to 795 K, the contact angle decreases to 106°. At this point, the HREEL spectra show a decrease in the C–H stretch intensity and an increase in the Si–O–Si intensity. The ratio of these two modes suggests that the chain length has significantly decreased, yet the contact angle data show that the monolayer is still reasonably well-ordered. If Si–C bond cleavage were occurring to a significant extent, leading to the desorption of entire chains, one would expect the remaining monolayer to become disordered, perhaps with some of the underlying oxide becoming exposed, resulting in a contact angle much lower than the observed 106°. Thus, the contact angle data are consistent with decomposition through C–C bond cleavage.

The thermal behavior of polyethylene also supports the picture of decomposition through C–C bond cleavage. It has been observed that upon heating polyethylene in the absence of oxygen, gaseous products are not formed until 640 K.<sup>32</sup> Decomposition occurs through the homolytic cleavage of C–C bonds. It is postulated that decomposition begins at weak links in the polymer, such as branching points.<sup>33</sup> The alkylsiloxane monolayers on oxidized silicon examined here are primarily straight chains, with few defects and branching points. The smaller number of defects compared to polyethylene may explain the slightly higher decomposition temperature observed for the monolayers.

As a result of C–C bond cleavage, an alkyl radical is left on the surface and an alkyl radical desorbs. The alkyl radical on the surface is highly reactive and likely reacts with molecules in the chamber before the sample can be analyzed with HREELS. Under annealing conditions,

there is a high partial pressure (on the order of  $10^{-8}$  Torr) of molecular hydrogen. In gas phase studies, the reaction of molecular hydrogen and methyl radicals has been observed to yield methane and a hydrogen atom.<sup>34</sup> By analogy with this reaction, the radical on the monolayer surface reacts with molecular hydrogen to yield the Si–CH<sub>3</sub> species that is observed by HREELS.

As the sample is annealed to 890 K, the intensities of the CH<sub>3</sub> HREELS peaks decrease, indicating reaction of the methyl groups. By 960 K, virtually no CH<sub>3</sub> groups are observed with HREELS. Possible reaction pathways are discussed in terms of studies of methyl groups adsorbed on clean Si(100). It has been reported that methyl groups decompose on the Si(100) surface, resulting in adsorbed hydrogen and carbon.<sup>24</sup> Unfortunately, on the oxidized samples studied here, the presence of the Si–O–Si symmetric stretch at about 800  $\text{cm}^{-1}$  makes it difficult to detect Si–C modes. The presence of adsorbed hydrogen is also difficult to detect, as the oxidized Si–H stretch would appear at 2250  $\text{cm}^{-1}$ ,<sup>35</sup> the same position as the oxide overtone. Alternatively, it has also been observed that, at high surface coverage, methyl radicals desorb from clean Si(100) at 825 K.<sup>36</sup> It was argued that because decomposition of methyl groups requires an empty site on which hydrogen can adsorb, occupation of all surface sites can serve to stabilize the methyl groups, allowing them to desorb as methyl radicals. On the basis of the present study, both reaction pathways are possible for the methyl groups.

In summary, the thermal stability of alkylsiloxane self-assembled monolayers on the oxidized surface of Si(100) has been studied using HREELS and contact angle analysis. The monolayers are stable in vacuum up to temperatures of about 740 K independent of chain length. Above 740 K the chains begin to decompose primarily through the cleavage of C–C bonds. After this initial desorption step, methyl groups attached to silicon atoms are observed; they subsequently react upon annealing to 890 K. The siloxane head groups remain on the surface until about 1100 K.

Decomposition of the alkylsiloxane monolayers on the oxidized Si(100) surface presents an interesting contrast to the thermal behavior of alkanethiols. It has been observed that octadecanethiol desorbs from the Au(111) surface at about 450 K.<sup>7</sup> Desorption occurs through Au–S bond cleavage, with the chains remaining intact. The difference in behavior results primarily from the weaker bonding of the alkanethiol head group to the surface (the Au–S bond strength is estimated at about 44 kcal/mol<sup>37</sup>) compared with the alkylsiloxane monolayers.

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(32) Wall, J. *Res. Natl. Bur. Stand.* **1948**, *41*, 315.

(33) Oakes, W. G.; Richards, R. B. *J. Chem. Soc.* **1949**, 2929.

(34) Taylor, H. S.; Rosenblum, C. *J. Chem. Phys.* **1938**, *6*, 119.

(35) Schaefer, J. A.; Frankel, D.; Stucki, F.; Göpel, W.; Lapeyre, G. *J. Surf. Sci.* **1984**, *139*, L209.

(36) Reuter M. A.; Vohs, J. M. *J. Vac. Sci. Technol., A* **1991**, *9*, 2916.

(37) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.