Interaction of H(D) Atoms with Octadecylsiloxane Self-Assembled Monolayers on the 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 interaction of H(D) atoms with alkylsiloxane self-assembled monolayers deposited on oxidized Si-(100) has been examined under ultrahigh vacuum conditions. Using high-resolution electron energy loss spectroscopy, evidence is observed for the H/D exchange reaction. The reaction is initiated by hydrogen abstraction via an Eley−Rideal type mechanism to form an alkyl radical. For low exposures to H(D) atoms, the exchange reaction occurs relatively rapidly, as indicated by the rate of increase in intensity of the C−D stretch. As exposure increases, the exchange reaction slows due to steric effects. Etching of the monolayers also occurs, as indicated by the decrease in intensity of C−H modes and the increase in intensity of the Si−O modes of the underlying substrate upon exposure to atomic hydrogen. The presence of cross-linking is suggested by the rapid decrease in water contact angle as a function of H(D) exposure.

I. Introduction

The reactions of gas phase species, such as radicals and ions, with organic films have been the subject of intense study because of their considerable importance in electronic device fabrication. One example is the interaction of atomic hydrogen, which is present in plasma-processing steps, with organic polymer films used in the microelectronics industry.[1] The interaction could take place in one of two ways: either the hydrogen atom adsorbs on the surface and then reacts with the hydrocarbon (Langmuir−Hinshelwood mechanism), or a hydrogen atom from the gas phase directly reacts with the hydrocarbon without adsorbing on the surface (Eley−Rideal mechanism). For the interaction of atomic deuterium with cyclohexane adsorbed on Cu(111),[2] it was found that cyclohexane does not react with preadsorbed deuterium. Reaction does occur, however, when deuterium atoms are exposed to cyclohexane adsorbed on Cu(111), indicating that the interaction occurs through an Eley−Rideal type mechanism. The abstraction of hydrogen results in the formation of H_2 (HD) and an alkyl radical. The alkyl radical can then react in a number of different ways; for example, dehydrogenation of the radical results in the formation of a π bond. Addition of a deuterium atom to the alkyl radical results in H/D exchange. Since the addition reaction is exothermic, dissipation of the energy may result in changes in the hydrocarbon. For example, benzene and 1,4-dimethylcyclohexane physisorbed on Pt(111) were observed to desorb upon exposure to atomic hydrogen.[3]

Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. Several different varieties of SAMs have been investigated, including alkanethiols ($CH_3(CH_2)_{n-1}SH$) on Au, Ag, and Cu and alkyltrichlorosilanes ($CH_3(CH_2)_{n-1}SiCl_3$) on SiO_2, Al_2O_3, and mica. SAMs are promising candidates for use as masks for ultrahigh-resolution lithography because

they form thin, close-packed layers. Previous results have shown that they can serve as masks not only for wet etching but also for anisotropic plasma etching.[4]

In this article the interaction of H(D) atoms with alkyltrichlorosilane-derived monolayers in ultrahigh vacuum is examined. Using high-resolution electron energy loss spectroscopy (HREELS), it is found that the alkyl chains undergo a hydrogen exchange reaction. The highly exothermic addition reaction between an H(D) atom and an alkyl radical leads to some C−C bond scission, resulting in etching of the chains. Cross-linking between chains is also possible, as suggested by the rapid decrease in water contact angle as a function of atomic H(D) exposure.

II. Experimental Section

A. Sample Preparation. Samples were cut from B-doped Si(100) wafers with resistivity in the range 1-50 Ω 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 H_2SO_4/H_2O_2) at 100 °C for 10−15 min. The sample was rinsed several times in deionized water (resistivity = 18 MΩ) and then dried using nitrogen. Monolayers were formed by placing the oxidized samples in a 2.5 mmol solution of the octadecyltrichlorosilane (OTS) 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. Silanization was carried out at room temperature. Film quality was checked by water contact angle, which was 112º, in good agreement with earlier results.[5]

B. Calibration of Hydrogen Flux. Atomic hydrogen and deuterium were generated by dissociation of the respective molecules with a spiral tungsten filament heated to 1850 K. The sample was positioned approximately 3 cm from the hot filament. To calibrate the hydrogen atom flux to the sample, a monohydride Si(100)-(2×1) sample was prepared through argon ion sputtering and annealing, followed by exposure to atomic hydrogen. Temperature-programmed desorption (TPD) was used to determine the hydrogen coverage and, thus, the hydrogen exposure that corresponded to one monolayer of hydrogen. By assuming that the adsorption probability is unity and that one monolayer of hydrogen corresponds to 6.8×10^{14} atoms/cm² (the number of Si atoms on a (100) surface), the hydrogen atom flux was determined. The atomization rate of molecular hydrogen on the hot tungsten filament is linearly dependent on the H_2 pressure for $P(H_2) \leq$

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

† Current address: Korean Institute of Chemical Technology, Taejon, Korea.

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10^{-6} Torr.[6] Typical atom fluxes were $\sim 3 \times 10^{13}$ atoms/(cm² langmuir) (1 langmuir $\equiv 10^{-6}$ Torr s) at the sample surfaces. From uncertainties in the pressure, hydrogen coverage on Si-(100), and the filament temperature, the error in the flux is estimated to be approximately 20%.

C. Experimental Procedure. Samples are 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.[7] The chamber contains low-energy electron diffraction, Auger electron spectroscopy, HREELS, and a differentially-pumped quadrupole mass spectrometer coupled to a temperature controller for TPD. The base pressure is 1×10^{-10} Torr. All samples were annealed to 520 K for 30 min prior to acquiring HREEL spectra and exposing the sample to hydrogen. This procedure leaves the chains intact, as they do not desorb until much higher temperatures,[8,9] and was found to improve sample reproducibility. All HREEL spectra were obtained in the specular mode using an incident electron energy of 6 eV and with the sample temperature held at 120 K. The resolution of the elastic peak was typically between 40 and 50 cm⁻¹ at about 10^4 counts/s. The spectra were unchanged even after several hours of exposure to the incident electron beam.

To ensure that the monolayers were not affected by the hot filament, a sample was placed in front of the filament for 45 min (typical dosing times were between 5 and 20 min) without admitting hydrogen into the chamber. The HREEL spectrum and water contact angle were unchanged following this treatment. During hydrogen dosing the sample temperature increased to about 180 K. Hydrogen doses are reported in units of langmuir of the molecular gas. To check the reproducibility of the exposure experiments, two different samples were exposed to deuterium. The C–H stretch peak area ratio, $[\equiv C-H]/[\equiv C-H]_0$, where $[\equiv C-H]_0$ refers to the peak area before deuterium exposure, was found to agree closely for both samples. Error bars are determined using the standard deviation of the two samples.

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 comparing the monohydride desorption temperature (from the sample used to calibrate the hydrogen flux) with the value of 795 K reported in the literature.[10]

HREELS measurements were complemented by contact angle analysis and ellipsometry. A Model A-100 Ramé-Hart NRL goniometer was used to measure water contact angles in room air using the sessile drop method.[11] A microsyringe delivered drops of deionized water ranging from 1 to 5 μL. The stage was backlit with a lamp covered with green acetate paper to minimize heating of the drop. Ellipsometry measurements were carried out using a Woolam M-44 ellipsometer, using an optical constant of 1.46 for the monolayers. A thickness of 20 Å and an optical constant of 1.54[12] were assumed for the oxide substrate. Because of uncertainties in the thickness of the oxide substrate, the thicknesses measured for the monolayers have an uncertainty of approximately 25%.

III. Results and Discussion

A typical HREEL spectrum for the oxidized, then OTS-coated Si(100) surface is shown in Figure 1. This sample was annealed to 520 K for 30 min prior to this measurement. The peak assignments are summarized in Table
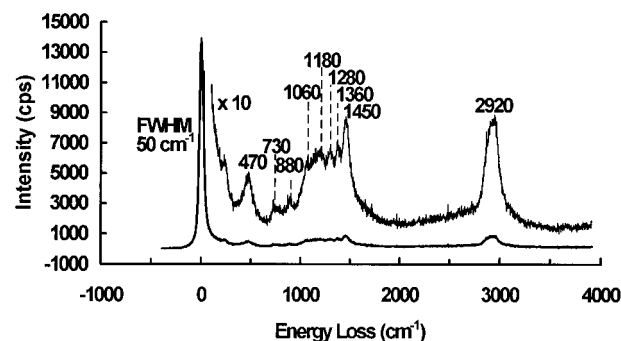
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Figure 1. HREEL spectra of octadecylsiloxane monolayer on oxidized Si(100). The sample has been annealed to 520 K for 30 min.
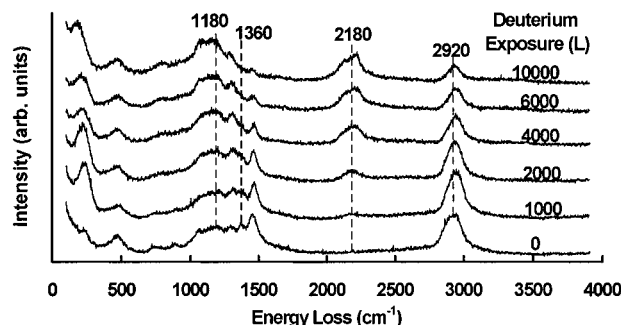

Figure 2. HREEL spectra as a function of deuterium exposure for octadecylsiloxane monolayers. All spectra were obtained from the same sample.

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

peak position (cm⁻¹)	assignment	reference
2920 (2180)	C–H (C–D) stretch	13
1450 (1090)	CH₂ (CD₂) scissor	13, 14
1360 (1000)	CH₃ (CH₃) symmetric bend	13, 14
1280	CH₂ twist-rock	14
1180	Si–O–Si asymmetric stretch (bulk oxide)	15
1060	Si–O–Si stretch (between the surface and the head group)	16
880	CH₃ rock	14
800	Si–O–Si symmetric stretch	15
730	CH₂ rock-twist	13, 14
470	Si–O–Si bend	15

1.[13–16] The presence of the monolayers is indicated by the broad C–H stretch at about 2920 cm⁻¹ and the C–H bends between 1280 and 1450 cm⁻¹. The positions of these modes are consistent with those for normal alkanes such as butane and hexane.[13] The small peaks at 730 and 880 cm⁻¹ are assigned to C–H bending modes. The region from 1000 to 1200 cm⁻¹ contains peaks due to the asymmetric stretch of bridge-bonded oxygen.[15,16] Evidence of the underlying oxide is also seen in the bending mode at 470 cm⁻¹.

A. H/D Exchange. Figure 2 shows the HREEL spectra for the octadecylsiloxane monolayer as a function of deuterium exposure. All data were obtained from the same sample. The spectra show the appearance and growth of the C–D stretch at about 2180 cm⁻¹ and in parallel a decrease in the intensity of the C–H stretch at

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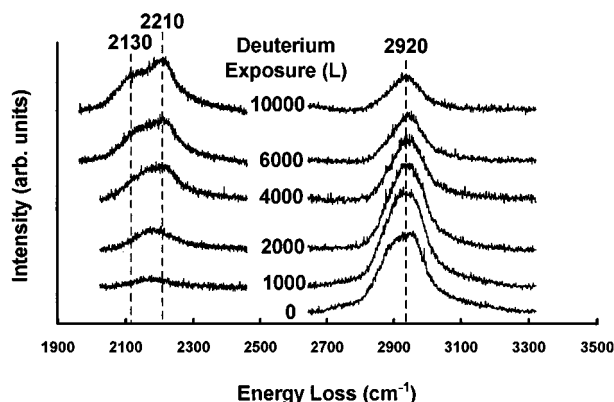(16) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

Figure 3. Close-up of the C−D and C−H stretch region as a function of deuterium exposure.

2920 cm^{-1}, indicating that H/D exchange is taking place. The intensities of the CH$_2$ bends at 1280 and 1450 cm^{-1} also decrease, and the CH$_3$ bend at 1360 cm^{-1} essentially disappears after a deuterium exposure of 4000 langmuirs. The oxide asymmetric stretch at 1180 cm^{-1} increases slightly in intensity, and the symmetric stretch at about 800 cm^{-1} becomes evident. The appearance of C−D bending modes in the range between 1000 and 1100 cm^{-1} likely contributes to the increase in the oxide asymmetric stretch. The increase may also be related to etching and cross-linking of the monolayers, as discussed below. No peak is observed in the 1550 cm^{-1} region, indicating that no Si−D groups are present.

Close-ups of the C−D and C−H stretch regions as a function of deuterium exposure are shown in Figure 3. For low deuterium exposures, the C−D stretch appears as a broad peak centered at 2180 cm^{-1}. On the basis of the expected isotopic shift of the CH$_2$ asymmetric stretch, this peak is assigned to the CD$_2$ asymmetric stretch. The peak position is in good agreement with studies on deuterated Langmuir−Blodgett films where this mode was observed at about 2195 cm^{-1}.[17,18] Partially deuterated groups may also contribute to the peak at 2180 cm^{-1}; the C−D stretch of CH$_2$D groups has been observed at 2177 cm^{-1}.[19] The initial position of the C−D stretch at 2180 cm^{-1} suggests that CH$_2$ groups have been deuterated and that the terminal CH$_3$ groups are only partially deuterated. As deuterium exposure increases to 4000 langmuirs, two peaks become evident at about 2130 and 2210 cm^{-1}. The peak at 2210 cm^{-1} is assigned to the CD$_3$ asymmetric stretch. This mode was observed at about 2215 cm^{-1} for the deuterated Langmuir−Blodgett films.[17,18] On the basis of the expected isotopic shift of CH$_2$ and CH$_3$ symmetric stretching modes, the peak at 2130 cm^{-1} is attributed to the symmetric stretching modes of CD$_2$ and CD$_3$ groups. The shift to 2210 cm^{-1} following exposures of more than 4000 langmuirs signals the presence of fully deuterated CH$_3$ groups.

As deuterium exposure increases, the C−H stretch decreases in intensity and changes shape. As seen in Figure 3, for no deuterium exposure the C−H stretch is quite broad, with a peak maximum ranging from about 2900 to 2950 cm^{-1}, due to the presence of the symmetric and asymmetric modes of CH$_2$ and CH$_3$ groups. As deuterium exposure increases, the peak narrows, such that after a deuterium exposure of about 4000 langmuirs, the peak is centered at 2920 cm^{-1}, corresponding to the
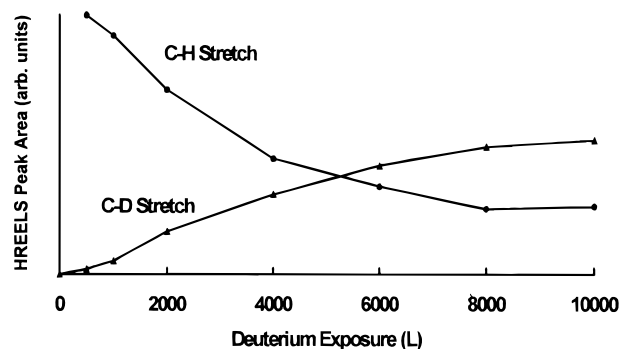
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Figure 4. HREELS peak areas for the C−H (●) and C−D (▲) stretch as a function of deuterium exposure.

position of the CH$_2$ asymmetric stretch.[13] The narrowing of the peak is attributed to the disappearance of the asymmetric CH$_3$ stretch at 2950 cm^{-1} and corresponds well with the disappearance of the CH$_3$ bend at 1360 cm^{-1}. These changes indicate the disappearance of CH$_3$ groups due to deuteration and are consistent with the behavior observed in the C−D stretching region of the spectrum.

Figure 4 shows the HREELS peak areas for the C−H and C−D stretches as a function of deuterium exposure. Deuterium exchange takes place relatively rapidly at low deuterium doses, then slows for exposures greater than 4000 langmuirs and appears to saturate by an exposure of 10^4 langmuirs. The saturation behavior is likely related to steric effects, as has been discussed for the fluorination of alkanethiols on Au(111).[20] The greater the distance from the monolayer−vacuum interface, the harder it becomes for deuterium atoms to react with the alkyl chains, until a saturation point is reached. The observed behavior may also be affected by etching and cross-linking, which are discussed in more detail in the following section.

The first step in the H/D exchange reaction has been shown to be hydrogen abstraction through an Eley−Rideal type mechanism to form HD and an alkyl radical:[2]

$$D^• + {\equiv}C{-}H \rightarrow {\equiv}C^• + HD{\uparrow} \qquad (1)$$
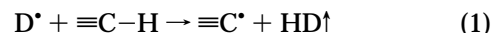
Abstraction is followed by addition of a deuterium atom to the alkyl radical

$$D^• + {\equiv}C^• \rightarrow {\equiv}C{-}D \qquad (2)$$

These steps are shown schematically in Figure 5. Because the flux of deuterium atoms is essentially constant, the overall reaction is assumed to be first order in the concentration of C−H bonds. Also, because reaction 2 is the addition of two radicals, it is assumed to occur rapidly; thus, reaction 1 is the rate-limiting step. With these assumptions, the kinetics of H/D exchange simplifies to the kinetics of hydrogen abstraction, reaction 1. The rate of disappearance of C−H bonds is described by the following equation:

$$\frac{d[{\equiv}C{-}H]}{dt} = -\sigma\,[{\equiv}C{-}H]\,J(D) \qquad (3)$$

which has the following solution

$$\ln\!\left(\frac{[{\equiv}C{-}H]}{[{\equiv}C{-}H]_0}\right) = -\sigma\,J(D)\,t \qquad (4)$$

where brackets denote concentrations, σ is the cross section for exchange, and $J(D)$ is the flux of deuterium atoms.

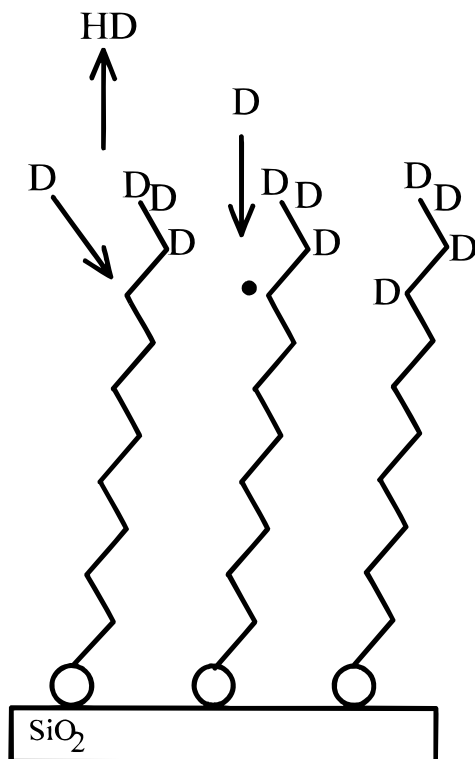(20) Robinson, G. N.; Freedman, A.; Graham, R. L. *Langmuir* **1995**, *11*, 2600.

Figure 5. Schematic view of the reaction occurring upon H(D) exposure of alkylsiloxane monolayers on oxidized Si(100). H(D) atoms abstract a hydrogen atom from the chain, leaving behind an alkyl radical. An additional H(D) atom reacts with the radical to complete the exchange reaction.
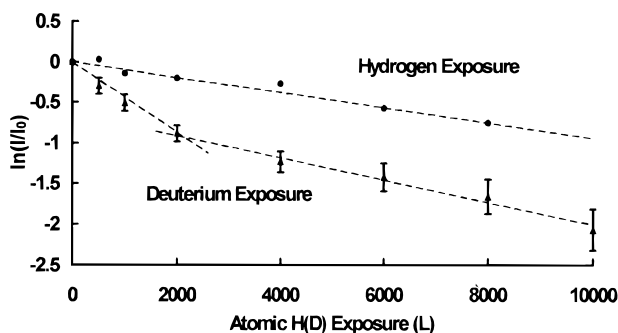

Figure 6. Plot of the ln(normalized C−H stretch peak area) as a function of hydrogen (●) and deuterium (▲) exposure. Reaction cross sections are calculated from the slopes of the best fit lines.

The cross section for exchange, σ, can then be calculated from a plot of the left hand side of eq 4 vs deuterium exposure. To obtain a qualitative indication of the magnitude of these cross-sections, HREELS peak areas normalized by the elastic peak intensity were assumed to be a measure of the concentration of C−H bonds. With this assumption, one obtains the plot in Figure 6. The initial slope is steep, indicating that the exchange reaction is occurring rapidly; this is followed by a change to a slower rate of reaction. The reaction cross section in the low-exposure region is calculated to be 0.14 Å^2. This value is in good agreement with previous results on organic films, in which observed cross sections ranged from 0.05 to 0.5 Å^2.[2,21] The small cross section for the exchange reaction supports the assumption that reaction 1 is rate limiting. In the high-exposure region, the cross section is calculated to be 0.05 Å^2. These cross section values are only order

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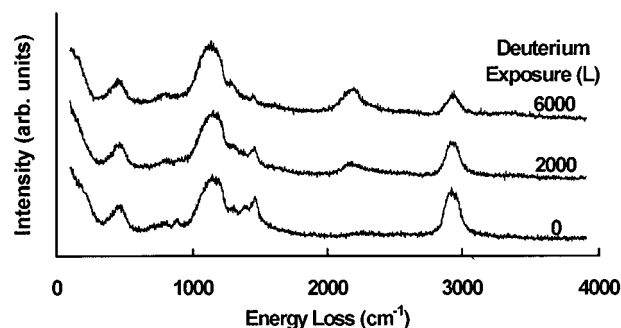

Figure 7. HREEL spectra as a function of deuterium exposure for butylsiloxane monolayers.

of magnitude estimates because of uncertainties in the deuterium flux and the HREELS peak areas. These values represent an average for the entire chain, since steric effects cause the cross section to vary with distance from the vacuum−interlayer interface. Additionally, intrinsic variations due to the chemical nature of the site and the stability of the radical may contribute to variations in the cross section.

Figure 4 shows that a saturation point is reached before the entire chain is deuterated. The observation of a saturation point suggests that only the carbon atoms closest to the vacuum−monolayer interface become deuterated. Similar behavior was suggested for exposure of alkanethiols on Au(111) to fluorine atoms, where it was inferred that fluorination did not extend beyond the top six carbon atoms.[20] To estimate the depth of deuteration of alkylsiloxane monolayers, butylsiloxane (C$_4$) monolayers were exposed to deuterium atoms. A shorter chain was chosen in order to minimize attenuation effects in HREEL spectra due to differences in depth of origin, that is, the reduction in intensity for C−H groups residing farther away from the vacuum−monolayer interface. In Figure 7, the spectrum for the undosed butylsiloxane monolayer shows that, compared to octadecylsiloxane monolayers, Si−O−Si modes are more intense relative to C−H modes, confirming that attenuation effects are reduced for the shorter chains. Figure 7 shows that butylsiloxane monolayers exposed to deuterium exhibit essentially the same behavior as the longer chains. Neglecting attenuation effects, and taking the HREEL peak areas to be proportional to the number of groups on the surface, it is estimated that after a deuterium exposure of 6000 langmuirs, approximately six of the nine hydrogen atoms on the butyl chain have been exchanged. Thus, two to three of the carbon atoms in the chain have been deuterated on average. Linearly extrapolating, the exposure of 10^4 langmuirs used for the octadecylsiloxane monolayer corresponds to deuteration of four to five carbon atoms. Because of the observed saturation behavior (Figure 4), the linear extrapolation likely overestimates the depth of deuteration. Because the butylsiloxane monolayers are not as closely packed as the octadecylsiloxane monolayers, the C−H groups may be more accessible in the former case, again resulting in an overestimate of the depth of deuteration. The presence of the etching reaction would also complicate matters. Despite the complications, the above estimate shows that the monolayers do not become completely deuterated, suggesting that deuterium is not able to penetrate to the oxide interface for the case of octadecylsiloxane monolayers.

B. Monolayer Interaction with Hydrogen. The increased intensity of the bridge-bonded oxygen peak at 1180 cm^{-1}, as well as the appearance of other oxide peaks, suggests that H/D exchange is not the only reaction

Figure 8. HREEL spectra as a function of hydrogen exposure for octadecylsiloxane monolayers.

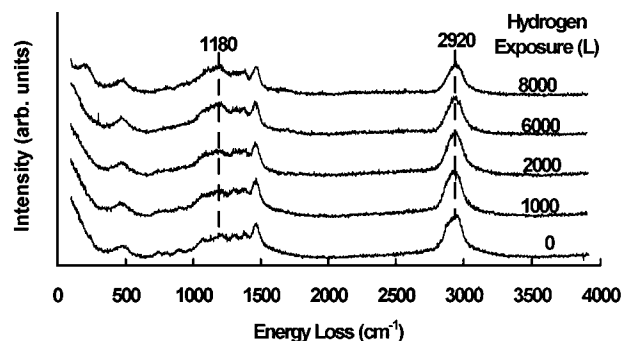**Figure 9.** Water contact angle as a function of H(D) exposure for octadecylsiloxane monolayers.

occurring as a result of atomic deuterium exposure. It is likely, however, that the change in the 1180 cm^{-1} region is partially due to the presence of C–D bending modes. Therefore, to examine the possibility of other reactions without the complication of H/D exchange, octadecylsiloxane monolayers were also exposed to atomic hydrogen. Figure 8 shows the HREEL spectra as a function of hydrogen dose. As exposure increases, the intensities of the C–H stretching and bending modes decrease slightly, while the intensity of the asymmetric oxide stretch increases. After 8000 langmuirs exposure, small peaks appear at about 1650 and 2300 cm^{-1}. These peaks have previously been assigned to overtones and combination modes of the oxide.[22] This behavior can be understood in terms of etching of the monolayers. It is also possible that cross-linking of the chains is taking place. In the following sections, these two reaction channels are discussed.

1. Etching. One possible reaction is etching of the chains through C–C bond scission. The hydrogen atom and alkyl radical association reaction is exothermic by about 100 kcal/mol. Thus, it is possible that dissipation of this energy results in scission of C–C bonds (80 kcal/mol) and a decrease in chain length. As the chain length decreases, modes due to the oxide substrate are expected to become more intense relative to the C–H modes, as evidenced by comparing the HREEL spectra for the undosed octadecylsiloxane (Figure 2) and butylsiloxane (Figure 7) monolayers. The changes observed as a function of atomic hydrogen exposure are consistent with a decrease in the thickness of the monolayer. To estimate this decrease, monolayer thickness as a function of hydrogen exposure was measured using ellipsometry. The results show essentially no change in the monolayer thickness as hydrogen exposure increases, suggesting that the etching reaction occurs quite slowly. However, uncertainties in the thickness of the oxide substrate from sample to sample lead to uncertainties in the monolayer thickness of about 25%, which prevents ellipsometry from detecting small changes in the film thickness.

A decrease of the carbon chain length through direct attack of an alkyl group by a hydrogen atom (H + CH$_3$–R → CH$_4$ + R, where R represents an alkyl group) can be ruled out because the direct etching of alkyl chains has not been observed at temperatures below 300 K.[21] More likely, the same two-step process discussed above for H/D exchange occurs. First, hydrogen abstraction produces an alkyl radical, then hydrogen atom addition to the radical releases 100 kcal/mol of energy, which breaks a C–C bond and results in a reduction in the C–H stretch intensity. The normalized logarithmic scale plot of the C–H peak area as a function of hydrogen dose is shown in Figure 6.
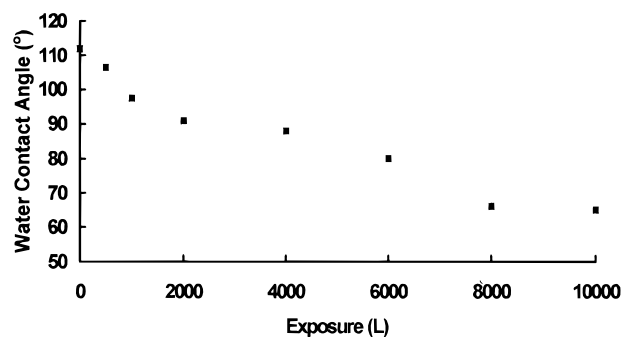
The cross section for etching, calculated from the slope of the plot, is 0.03 Å^2. The small cross section compared to that of the H/D exchange reaction indicates that C–C bond scission is not a main dissipation channel for the energy released from the addition of atomic hydrogen to the alkyl radicals. Furthermore, the cross section observed for hydrogen exposure is similar to that observed for deuterium exposures of 4000 langmuirs and greater. As suggested by the hydrogen exposure results, etching occurs throughout the entire exposure range. For the case of deuterium exposure, the exchange reaction dominates the etching for exposures less than about 2000 langmuirs. For higher exposures, the exchange reaction is slowed due to steric effects, and the etching reaction is observed more clearly.

In addition to C–C bond scission, it is also possible for energy from the hydrogen addition reaction to be dissipated through collision with gas phase hydrogen molecules or through the lattice modes of the silicon substrate. During hydrogen exposure, the chamber pressure is on the order of 10^{-6} Torr. At this pressure, an alkyl radical would be struck, on average, by about one hydrogen molecule per second. This time is significantly longer than the time for C–C bond scission; thus, collision with hydrogen molecules is not a viable mechanism for energy dissipation. HREELS data suggest that some etching of the monolayer chains occurs but that C–C bond cleavage is not a dominant channel. Therefore, energy dissipation through the lattice modes of the silicon substrate is the most likely mechanism.

The alkyl radical may also undergo dehydrogenation to form a π bond.[2] No peaks due to π bonds, such as the C=C stretch at 1700 cm^{-1} or the C–H stretch for sp^2 carbon at 3050 cm^{-1}, are observed in the HREEL spectra following hydrogen exposure, however. This observation is consistent with the fact that the cross section for hydrogen addition to the π bonds is about an order of magnitude higher than that for hydrogen abstraction.[2]

2. Cross-Linking. It is also possible for the alkyl radical to react with an adjacent alkyl radical to form a cross-link between chains. Such a reaction has been proposed to occur for the case of electron beam exposure of OTS monolayers on oxidized Si(100).[4] Such exposure resulted in a decrease in the water contact angle from 115° to 60°, although X-ray photoelectron spectroscopy indicated a reduction in carbon content of only about 25%. In the present study the water contact angle was measured as a function of atomic hydrogen exposure. The results, shown in Figure 9, indicate that the contact angle decreases rapidly at low exposure and then levels off at about 60° after exposure to 8000 langmuirs of hydrogen. The same behavior was also observed for deuterium exposure. This decrease occurs even though the HREEL spectra (Figure 8) and the monolayer thickness measured by ellipsometry show minimal change even after exposure

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to 8000 langmuirs of hydrogen. The large decrease in water contact angle after hydrogen exposure indicates an increase in the surface energy of the sample. One possible cause is the presence of polar groups on the surface. Polar groups may physisorb on the sample as it is brought into air for contact angle measurements. To examine this possibility, a sample was exposed to hydrogen, exposed to air, then reintroduced to the chamber and analyzed again with HREELS. The only change in the spectrum was a small increase in the Si−O−Si peak intensity. The observed intensity change cannot explain the substantial decrease in the water contact angle because the intensity of the Si−O−Si peak is still much smaller than that of an octylsiloxane (C_8) film on oxidized Si(100), which has a contact angle of 108°.[9] Furthermore, the HREEL spectrum does not indicate the presence of polar species such as oxygen in the monolayers. For example, no evidence is seen for O−H groups (3300 cm^{-1}) or C=O groups (1700 cm^{-1}).

A similar decrease in contact angle has been observed for alkanethiols on Au(111) exposed to fluorine atoms.[20] The decrease was attributed to the presence of CHF-type species, which are polar and thus have a higher surface energy than a methyl group. Deuteration does not result in polar groups on the surface, however.

The change in water contact angle following electron beam exposure in the previous study[4] was proposed to be due to cross-linking. The electron beam likely creates alkyl radicals; adjacent radical sites can then react with each other to form cross-link bonds. For the present case of hydrogen exposure, the same mechanism is possible. Cross-linking would result in a decrease in the number of C−H groups, as C−H bonds are replaced with C−C bonds. The thickness of the film would not be affected by cross-linking, but the order of the film would be disrupted. The increase in the number of defects would cause a decrease in the water contact angle but only a small change in the HREEL spectra and monolayer thickness. Because an alkyl radical is more likely to encounter a hydrogen atom than an adjacent alkyl radical, hydrogen addition is expected to be the dominant reaction channel. However, in view of the results presented in this section, we argue that etching and cross-linking are also taking place upon exposure of octadecylsiloxane monolayers to H(D).

IV. Summary

Exposure of octadecylsiloxane monolayers on Si(100) to atomic deuterium resulted in H/D exchange. H/D exchange occurred relatively quickly for exposures of less than 2000 langmuirs; for larger exposures the rate decreased. It was estimated that the four or five carbon atoms closest to the vacuum−monolayer interface are deuterated for an exposure of 10^4 langmuirs, the largest exposure investigated; deuterium is unable to react with hydrogen on the deeper-lying carbon atoms due to steric effects. In addition to H/D exchange, etching of the monolayer occurred through C−C bond scission, although HREELS and ellipsometry data indicate that etching is not a major reaction channel. Furthermore, cross-linking of the monolayers may occur, as suggested by the rapid decrease in water contact angle at low atomic hydrogen exposures. The etching and cross-linking of chains have important implications for the use of self- assembled monolayers in lithography. In addition, these processes are likely to play a role in the behavior of polymer films currently used in the microelectronics industry.