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Mechanistic Aspects of Alkylchlorosilane Coupling Reactions

R. R. Rye, G. C. Nelson, and M. T. Dugger*

Sandia National Laboratories, Albuquerque, New Mexico 87185

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Toluene solutions of monochlorosilane and trichlorosilane coupling agents are shown to react differently with hydrated and dry silicon surfaces. For typical hydrated surfaces produced by piranha ($H_2O_2 + H_2SO_4$) etching, the saturation coverages of octadecyldimethylchlorosilane (ODMS) (one reactive Si−O bond) are approximately a third that of octadecyltrichlorosilane (ODTS) (three reactive Si−O bonds). In contrast, for samples vacuum baked at 400 °C, the saturation coverages of ODTS and ODMS are comparable. These data are consistent with coupling reactions limited to the surface hydroxyl groups. The ODTS saturation coverage on vacuum-fired silicon samples can be increased by soaking in water followed by a second ODTS exposure. From X-ray photoelectron spectra (XPS) and secondary ion mass spectra (SIMS) obtained as a function of solution exposure time, saturation coverage is shown to take at least 2 h and to be limited by the concentration of surface hydroxyl groups; a direct correlation is seen in SIMS between the exposure dependent gain in the surface alkyl signal and the loss of the SiOH signal. The coefficient of friction of silicon (piranha etched) is reduced by an order of magnitude by saturation coverages of ODTS, but continued rubbing for over 50 cycles at a normal loading of 245 mN results in decay of the friction coefficient to the value appropriate for uncoated silicon. These results as well as others from the literature are discussed in this paper in terms of a mechanism for the reaction of alkylchlorosilanes with silicon.

I. Introduction

Micromachined devices, such as micromotors, produced by removing sacrificial silicon oxide layers in concentrated HF are characterized by two major problems:[1] adhesion of the released parts from surface tension forces involved in the final liquid rinse step, and friction between the moving parts. A potential solution to both problems is to coat the surface with silane coupling agents. Such coatings have been reported to be promising in significantly improving micromotor performance.[1] Coupling agents and the coupling agent chemistry of the chlorosilanes can be complex, despite being dominated by the reaction between a Si−Cl bond and O−H groups:

$$\mathrm{Cl{-}SiR_3 + H{-}O{-}R' = R'{-}O{-}SiR_3 + HCl} \qquad (1)$$

If R′ is the silicon oxide surface and R is a normal alkane, the result is to covalently bond the molecule to the surface with the alkane pointing away from the surface, converting the normal oxide to a low-energy alkane-like surface. However, the reaction is also rapid with water ($R' = H$). This requires such coupling reactions be performed in inert environments using anhydrous solutions; this is especially true for the trichlorosilanes where water can lead to polymerization in solution. Since SiO_2 surfaces normally contain a thin water layer which can be 10−15 Å thick,[2] there will be a competition between reaction with surface hydroxyl groups (H−O−R′, above) and reaction with this thin water layer. As Allara et al.[2] have suggested, understanding reactions with this water layer is fundamental to controlling the properties of surface films produced by these coupling agents.

Such silane coupling agents have been widely used to increase adhesion to silica surfaces,[3] especially for fiber-glass-reinforced materials. Chemical bonding of the coupling agent to the oxide surface, as represented by eq 1, is the oldest and most widely known model for the action of these molecules as adhesion promoters. But as Plueddemann[3] pointed out, it is far from clear that adhesion promotion results from reactions with surface hydroxyl groups; it may also involve wetting, rheology, and other handling properties. For oxide surfaces containing only freely vibrating hydroxyl groups (i.e., water free) produced by heating to 800 °C, Hair has shown, with IR spectroscopy, a first-order reaction between trimethylchlorosilane and surface hydroxyl groups.[4] In contrast to this direct reaction with surface hydroxyl groups on a dry surface, for surfaces containing a surface water layer, Tripp and Hair[5] report that there is no direct reaction of octadecyltrichlorosilane (ODTS) with surface hydroxyl groups or with the first bound water layer, but reaction does occur with subsequent water layers. Few, if any, Si−O−Si bonds form with the surface.[6] Both Tripp et al.[7] and Allara et. al.[2] conclude that understanding and/or controlling reactions with the hydrogen-bonded water layer present at the surface of silicon oxides is the critical feature of the reactions of silane coupling agents with oxidized Si surfaces. This is particularly the case with silane coupling agents such as octadecyltrichlorosilane (ODTS). In this case, reactions with surface water and surface hydroxyl groups can control different properties; with surface water one can have ordered two-dimensional polymerization of ODTS with no strong bonds to the surface, while, with surface hydroxyls, the result is to solidly anchor the molecule to the surface by chemical bonds. Application or need determines which is most important. For example, in a paper directed toward organized layers, Allara et. al.[2] argue that one should decouple the monolayer as much as possible to allow in-plane organization, while in a paper directed toward triboelectrification, Tripp et. al.[7] point out that reaction with hydroxyls, which forms a strong

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* To whom correspondence should be addressed. Current address: Department 1832\MS-0340, Sandia National Laboratories, Albuquerque, NM 87185-0340.

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(1) Deng, K.; Collins, R. J.; Mehregany, M.; Sukenik, C. N. *J. Electrochem. Soc.* **1995**, *142*, 1278−1285.

(2) Allara, D. L.; Parikh, A. N.; Rondelez, F. *Langmuir* **1995**, *11*, 2357−2360.

(3) Plueddemann, E. P. *Silane Coupling Agents*; Plenum; New York, 1991.

(4) Hair, M. L. *J. Non-Cryst. Solids* **1975**, *19*, 299−309.

(5) Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, *8*, 1120−1126.

(6) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 1215−1219.

(7) Tripp, C. P.; Veregin, R. P. N.; McDougall, M. N. V.; Osmond, D. *Langmuir* **1995**, *11*, 1858−1859.

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covalent bond to the surface, is necessary for robust films. Since one can always expect a thin water layer at the surface of oxidized Si, properties of the resulting film result from a competition between reaction with surface water and reaction with surface hydroxyl groups.

In this paper we report on studies of the reaction of two silane coupling agents with oxidized silicon: octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCl_3$ or ODTS) and octadecyldimethylchlorosilane ($CH_3(CH_2)_{17}Si(CH_3)_2Cl$ or ODMS). From X-ray photoelectron spectroscopy (XPS) we show that the saturation coverage of ODMS is a factor of ~3 smaller than that of ODTS and is comparable to that obtained for ODTS for vacuum-fired surfaces free of water. Further, we show that saturation exposures of vacuum-fired surfaces of oxidized silicon to ODTS are capable of considerable additional adsorption of ODTS if soaked in water. XPS and SIMS studies of the coupling agent coverage as a function of solution exposure time show similar growth kinetics while SIMS shows a corresponding loss of SiOH signal consistent with consumption of reactive species as in eq 1. Standard pin-on-disk friction measurements show that the coefficient of friction is reduced by an order of magnitude for saturation coverages of ODTS on oxidized silicon. These observations are discussed in terms of a mechanism for the surface reactions of coupling agents.

II. Experimental Section

ODTS and ODMS were obtained from Gelest, Inc. Prior to use each was vacuum distilled and collected under nitrogen in a flask sealed with a rubber septum. For solution preparation aliquots were withdrawn through the rubber septum using a volumetric hypodermic for transfer to a volumetric flask where solutions were made to a final concentration of 0.001 M using Aldrich anhydrous toluene. When not in use solutions were stored in a sealed flask in a desiccator and never opened unless under an inert atmosphere. All silicon samples were cut from the same 6 in. polished wafer which was treated as a final step in Piranha etch, a mixture of sulfuric acid and hydrogen peroxide, in order to oxidize the surface. All exposures were conducted in a glovebag or glovebox under a dry nitrogen atmosphere for the desired exposure time and then transferred to pure toluene followed by an ultrasonic rinse in methanol to remove all excess material.

X-ray photoelectron spectra were obtained using a Physical Electronics model 12-255G double-pass cylindrical mirror analyzer with a VG Instruments MK II dual anode (Mg/Al) X-ray source for excitation. Spectra were normally taken using Mg X-rays and 100 V pass energy for survey spectra and 50 V pass energy for individual peaks. Computer control of the analyzer allowed multiplexing between several individual peaks.

Time-of-flight SIMS (TOF-SIMS) measurements were carried out using a PHI-TRIFT spectrometer. Surface measurements were carried out using a 15 keV *pulsed* Ga ion beam rastered over a 90 μm × 90 μm area. Collection times were 1 min. Depth profiles were obtained using a 15 keV dc Ga sputter beam rastered over a 190 μm × 190 μm area and a sputter increment of 1 s; after sputtering, some surface Ga was detected. Data collection steps for the sputter profiles were carried out for 10 s using a beam rastered over a 65 μm × 65 μm area. Dosage during data collection periods was of the order of 10^{11} ions.

Friction measurements were performed using an Implant Sciences ISC-200 pin-on-disk tribometer. Silicon samples approximately 2.5 cm × 2.5 cm were mounted on a horizontal rotating platform and brought into contact with stationary, polished Si_3N_4 balls (Hoover Precision Products, Inc.) of 0.318 cm diameter under a load of 245 mN. This results in a maximum contact pressure (at the center of the contact) of about 52 MPa, using properties for bulk silicon and silicon nitride. Both the ball and disk surfaces were either untreated or exposed to a 0.001 M ODTS solution for 2 h without preheating. The ball contacted the wafer section approximately 1 cm from its center of rotation, to create a circular wear track on the silicon surface. The lateral friction force was measured using a calibrated load cell, and sampled at 10 Hz. Sliding took place in laboratory ambient air at 22 ± 3 °C and 10−18% relative humidity, and at an interfacial velocity of 5.1 ± 0.7 cm/s. Sliding continued until a visual wear scar could be detected on the silicon surface accompanied by a steady value of the friction coefficient, typically about 200 disk rotations.

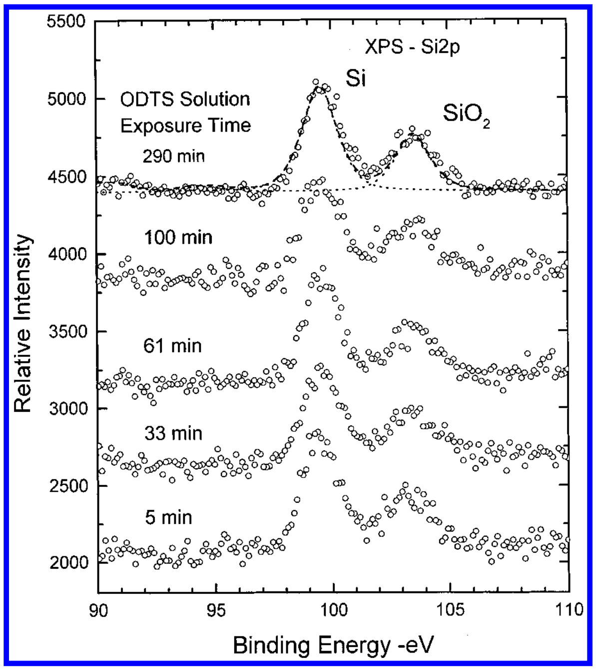

Figure 1. Si(2p) XPS spectra as a function of solution (1 mM ODTS in toluene) exposure time. All Si substrates were obtained from the same 6 in. wafer, and all spectra were obtained for the same total data accumulation time.

III. Results and Interpretation

IIIA. X-ray Photoelectron Spectroscopy. Figure 1 contains the Si(2p) XPS spectra for a series of oxidized silicon samples reacted with ODTS for the indicated solution exposure times. For each exposure in Figure 1, a number of samples were treated together through the entire exposure process. One each of these individual samples was reserved for XPS, SIMS, contact angle, and ellipsometric measurements. All silicon samples were taken from the same 6 in. oxidized silicon wafer, and all spectra have been normalized to the same total collection time for relative intensity comparisons. The spectra are characterized by uniformity; all are approximately the same total intensity, all consist of peaks at 99.5 eV due to Si and 103.5 eV due to SiO_2,[8] and all show approximately the same SiO_2/Si ratio. The spectrum for 290 min of ODTS exposure is shown decomposed into two component peaks using model peaks composed of Gaussian and Lorentzian components, the dotted curves are the individual peak components and the dashed curve is the sum of the model peaks. This relative constancy of the SiO_2 component suggests that it can be used as a reference for quantification of the coupling agent adsorption. This relative constancy of the Si spectra with increasing exposure might seem surprising given the short mean free path for characteristic XPS electrons. However, the oxidized Si surface contains a water layer, that can be 10−15 Å thick,[2] which is consumed during the coupling reaction (discussed later), and Si is added by the coupling reaction. How to include these factors is not clear and not important to our present needs, since the experimental observation is that

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(8) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muitenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer: Eden Praire, MN, 1979.

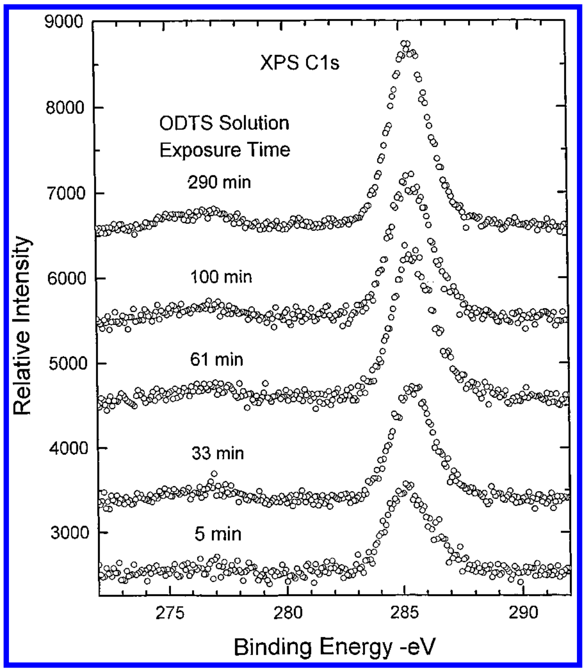

Figure 2. C(1s) XPS spectra obtained by multiplexing with those in Figure 1.

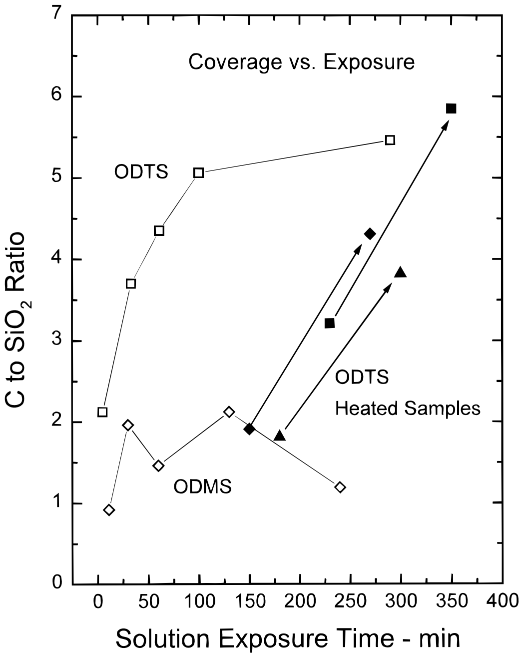

Figure 3. Carbon to Si (SiO_2) ratio from spectra as in Figures 1 and 2: open square points, ODTS; open diamond points, ODMS. Pairs of solid points are from vacuum-fired Si samples exposed to ODTS (low exposure), then water, and a second ODTS exposure (high exposure).

the spectra are relatively constant. In contrast, Figure 2 contains the C(1s) region XPS spectra obtained concurrently with the Si(2p) spectra in Figure 1 by multiplexing. Again, all spectra have been scaled to the same total collection time for relative intensity comparisons. Only a single C(1s) peak is observed consistent with only a single alkane environment in the molecule, and the intensity of this peak increases with increasing exposure.

The area under a specific XPS peak is proportional to the number of atoms sampled, and using the relative sensitivity factors reported in the XPS Handbook,[8] one can determine the relative concentration. From the Si(2p) spectra the obvious standard is the SiO_2 component which for the spectra in Figure 1 is relatively constant at between 34% and 35% of the total Si. The ratio of the area under the C peak in Figure 2 to the area under the SiO_2 component, in Figure 1, corrected for relative sensitive factors, is shown plotted as the open squares in Figure 3. The ratio is proportional to the amount of reacted ODTS, and clearly between 2 and 3 h are necessary to reach saturation. The same procedure applied to the reaction of ODMS yields the open diamonds in Figure 3. The only difference between these molecules is that ODTS has three Cl atoms attached to the Si atom while ODMS has two methyl groups and a single Cl atom. With only a single Cl atom, reaction of ODMS with surface water will not result in surface binding, but only conversion of the Si−Cl bond into Si−OH and a molecule which is capable, at most, of only hydrogen bonding. Reaction of the hydrolyzed ODMS molecule, either at the surface or in solution, is capable only of dimer formation. Only reaction with surface hydroxyl groups should lead to surface-bound coupling agent. With ODTS, coupling to surface hydroxyls can occur as well as water-catalyzed polymerization. Despite ODMS containing 11% more C atoms, the relative saturation amount of carbon is nearly a factor of 3 lower, reflecting its more limited reaction capability.

For ODTS reacting with oxidized silicon, the critical feature is a competition between reaction of the Cl atoms with surface hydroxyl groups and reaction with the thin film of adsorbed water. This competing water can be removed by using vacuum-fired samples. The three pairs of solid points in Figure 3 result from experiments in which oxidized silicon samples were vacuum-fired at 400 °C for 24 to 48 h and transferred, still hot, to the inert atmosphere glovebag. After cooling in the dry nitrogen atmosphere, two samples were immersed in the ODTS solution for the same total exposure. One of these was removed for XPS spectra and the second removed and soaked in deionized water for several hours. After drying, the water-soaked sample was returned to the glovebag for a second ODTS exposure followed by XPS. Thus, for each pair of solid points (circles, squares, and triangles) in Figure 3, the lower exposure point is the coverage of ODTS after exposure of the vacuum-fired sample to ODTS and the second point is the ODTS coverage resulting from water exposure and a second ODTS exposure; the exposure plotted for the second point is the total of both ODTS exposures. The vacuum-firing step is effective in greatly reducing the coverage of ODTS to a level comparable to that for ODMS, which is capable only of reacting with surface hydroxyls. Since this first step reaction is one between a coupling agent with three Cl atoms and surface hydroxyl groups present in a very low concentration,[2] the result should be an ODTS molecule covalently bonded to the surface, but with two active Cl atoms still capable of hydrolysis by water, allowing subsequent ODTS reaction. Thus, this two-step process is one of first maximizing the covalent bonding to the surface at isolated sites and then using water-catalyzed polymerization to fill in between.

Ellipsometry thickness measurements, made using variable angle spectroscopic ellipsometry, indicate a film thickness of nearly 26 Å. This thickness is hard to interpret, since the initial state consists of an oxidized Si layer covered with an unknown thickness of surface water which is consumed during the reaction and Si is added by the reacting molecule. However, the magnitude of the thickness is clearly consistent with the coupled molecules “standing up” and fully extended. A complete set of samples, treated concurrently with those used for XPS and ellipsometry, were used for the advancing and receding contact angle measurements for water given in Figure 4. The saturation advancing contact angle is 98° and reaches saturation at slightly lower exposure than

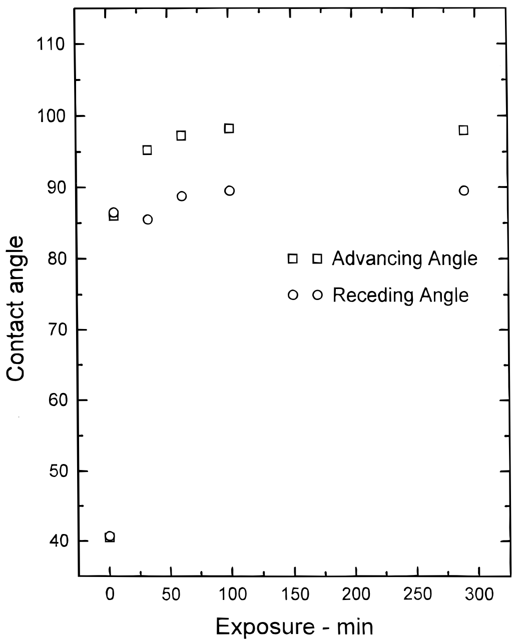

Figure 4. Contact angle as a function of exposure time for samples exposed concurrently with the samples used for the spectra in Figures 1 and 2.

the coverage. This is to be expected, since for incomplete coverages the water molecule will still see a hydrocarbon surface, but given the flexibility of the hydrocarbon chain it will simply be a less well organized layer.

IIIB. Secondary Ion Mass Spectroscopy. Figure 5 contains SIMS spectra, over a limited segment of the available mass range, that are representative of samples uncoated and coated with ODTS. In addition to its high spatial resolution (sampling area as small as 1 μm^2), SIMS is capable of high mass resolution, as seen in Figure 5. At mass 43, resolution of fragment peaks due to C_3H_7 and $SiCH_3$ is possible. C_3H_7 is a typical hydrocarbon fragment and can be used to monitor the growth of coupling agent at the surface. The SiOH peak at mass 45 reflects both true surface hydroxyl groups as well as rearrangement products from silicon and water. The sensitivity of the SiOH signal to surface water is seen in Figure 6, where the ratio of the SiOH to Si signal is shown as a function of sputter time for both a hydrated Si surface and a vacuum-fired Si surface. For the vacuum-fired sample there is a large decrease in the SiOH to Si ratio consistent with dehydration of the surface and modification of the reactivity of ODTS as seen in Figure 3. In addition to this thermal sensitivity of the SiOH signal, the examples given in Figure 5 show that the C_3H_7 signal increases and the SiOH signal decreases for reaction of ODTS.

For a set of ODTS-coated samples prepared concurrently with those for the data in Figures 1 and 2, the C_3H_7/Si and SiOH/Si normalized SIMS intensities are plotted vs the solution exposure time in Figure 7a and b, respectively. The C_3H_7 intensity grows with exposure and, as will be shown shortly, reaches a saturation level with a shape similar to the XPS data for ODTS in Figure 3. In contrast, the SiOH intensity decreases with increasing exposure, reflecting a consumption of reactive OH-containing surface species.

More correctly, the SiOH signal reflects active OH-containing species at the growing coupling agent/SiO_2 *interface*. This is shown to be the sputter profile data in Figure 8a, where the C_3H_7, SiOH, and Si intensities are shown plotted as a function of sputter time for a representative coated sample. The C_3H_7 intensity shows an immediate decrease, reflecting loss of the outermost species, while the SiOH intensity initially increases to a maximum and then decreases, reflecting loss of slightly deeper species. In Figure 8b the sputter profiles are shown for an untreated sample and samples exposed to ODTS for 5 and 33 min. By only 33 min this interface SiOH is nearly consumed, and by 60 min it is essentially completely at the base line. From both the XPS and SIMS data the coverage of ODTS is approaching saturation at this point.

Not only is the loss of SiOH signal nearly complete when saturation coverage of ODTS is reached but the exposure dependence of the consumption of OH closely parallels the gain in surface hydrocarbon. This is seen in Figure 9, where the C_3H_7 intensity (squares) is shown plotted with the inverse of the SiOH peak intensity (circles) with the latter scaled vertically to illustrate the shape similarity. Also plotted in Figure 9 are the XPS data (diamonds) from Figure 3 again scaled vertically to illustrate the shape similarity. The XPS results for vacuum-fired samples in Figure 3 show that both surface hydroxyls and surface water are involved in the coupling of ODTS to oxidized Si. This is further confirmed by the SIMS data. Moreover, this close shape similarity between the C_3H_7 and SiOH intensities would suggest that the ODTS coverage is limited by the reactive OH-containing species on the surface.

IIIC. Friction. Representative results of sliding friction experiments for untreated and ODTS-treated surfaces are shown in Figure 10. The open and solid symbols represent untreated and treated samples, respectively. The friction coefficient, given by the measured force parallel to the surface divided by the applied force perpendicular to the surface (245 mN in this case), is plotted as a function of the number of disk revolutions. Although there is considerable scatter in the data, the trends are clear; coating of the silicon surface with ODTS results in an order of magnitude decrease in the initial friction coefficient. For the untreated surfaces, the friction coefficient rapidly increases to the order of 0.4−0.5 within one disk revolution. This high value of friction coefficient is accompanied by a significant amount of scatter, caused by debris generation and stick−slip phenomena. Debris generation roughens the surfaces and causes momentarily high forces as particles become lodged at the interface and impede sliding. Upon release, the friction coefficient drops to a low value as the pin slides over a layer of debris. This is a purely mechanical effect. Stick−slip refers to momentary bonding of the sliding surfaces due to chemical interaction or asperity interlocking on the mating surfaces and thus may have both chemical and mechanical components. The surfaces remain stuck together until elastic deformation of the device exerts sufficient force to separate the surfaces. Both of these effects cause the friction coefficient to fluctuate between high and low values, with frequency dependent upon the nature of the materials and contact conditions, as well as the dynamic properties of the test equipment. These are generally complex, stochastic processes.

In contrast, the data for ODTS-treated surfaces show an initial friction coefficient of about 0.05, or nearly an order of magnitude decrease relative to that of the untreated samples. The friction coefficient for these surfaces increases gradually but remains lower than that for the untreated surfaces for 30−40 disk revolutions, at which point the behavior is similar to that of untreated surfaces. Development of a friction coefficient near 0.4 and significant noise accompanies the appearance of a visible wear scar on the treated surface. The ODTS layer initially prevents debris generation and damage accumulation on the silicon but is eventually removed or degraded. The scatter in the friction data, attributed to

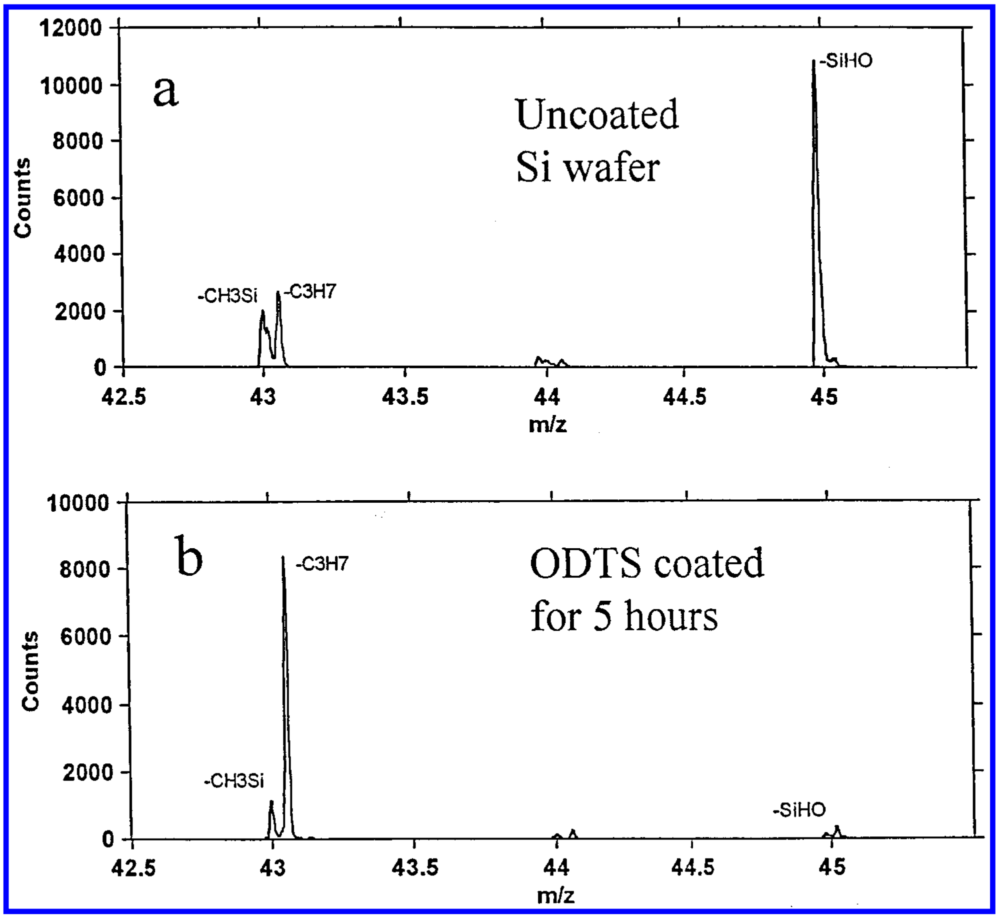

Figure 5. Representative SIMS mass spectra of uncoated Si (a) and ODTS-coated Si (b).

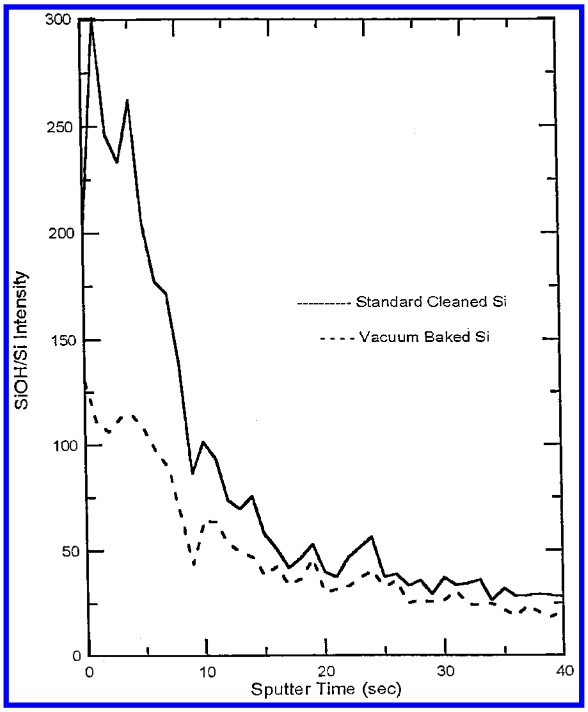

Figure 6. SiOH sputter profiles for hydrated and vacuum-fired Si. SiOH signal intensities are normalized to the Si signal.

stick−slip phenomena, is also substantially reduced in the early stages of sliding for the ODTS-treated surface.

IV. Discussion

The reaction of silicon coupling agents with oxidized silicon has been loosely described as leading to self-assembled monolayers. However, there is a major difference between the nature of the interaction of a molecule such as ODTS with silicon and that between organic thiols and gold, the classical example of organized self-assembled monolayers. The gold/thiol interaction is weak while the coupling agent chemistry is dominated by strong covalent bonds (eq 1). This difference is reflected in their formation conditions.

As recently noted by Thomas et al.,[9] Au films produced by a wide range of conditions, yielding a wide range of Au surfaces with different grain sizes, surface roughness, etc., all produce SAM films having similar macroscopic properties. Typically solution adsorption times of 1−100 h are used, but as Thomas et al.,[9] point out, there is evidence that it takes many days for self-assembly to be complete. In contrast, formation of a silicon coupling agent layer is typically much more rapid, or at least the reported exposure times are much shorter. As noted by several groups,[2,7] hydration of the surface of silica is a critical factor in its reaction with ODTS, and as we have shown above, the presence or absence of this surface water can have a dramatic influence on the surface coverage. Angst and Simmons[10] report that the coverage of ODTS on dry oxide surfaces or ODMS on both dry and hydrated surfaces is significantly less than that of ODTS on hydrated surfaces.

A model of how this surface water can be involved in the reaction of ODTS with oxidized Si is schematically illustrated in Figure 11, where an ODTS molecule is shown reacting with silica having a thin surface water layer. Allara et al.[2] suggest from the literature that this layer can be 10−15 Å thick. Due to this two-dimensional

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[9] Thomas, R. C.; Yang, H. C.; DiRubio, C. R.; Ricco, A. J.; Crooks, R. M. *Langmuir* **1996**, *12*, 2239−2246.

[10] Angst, D. L.; Simmons, G. W. *Langmuir* **1991**, *7*, 2236−2242.

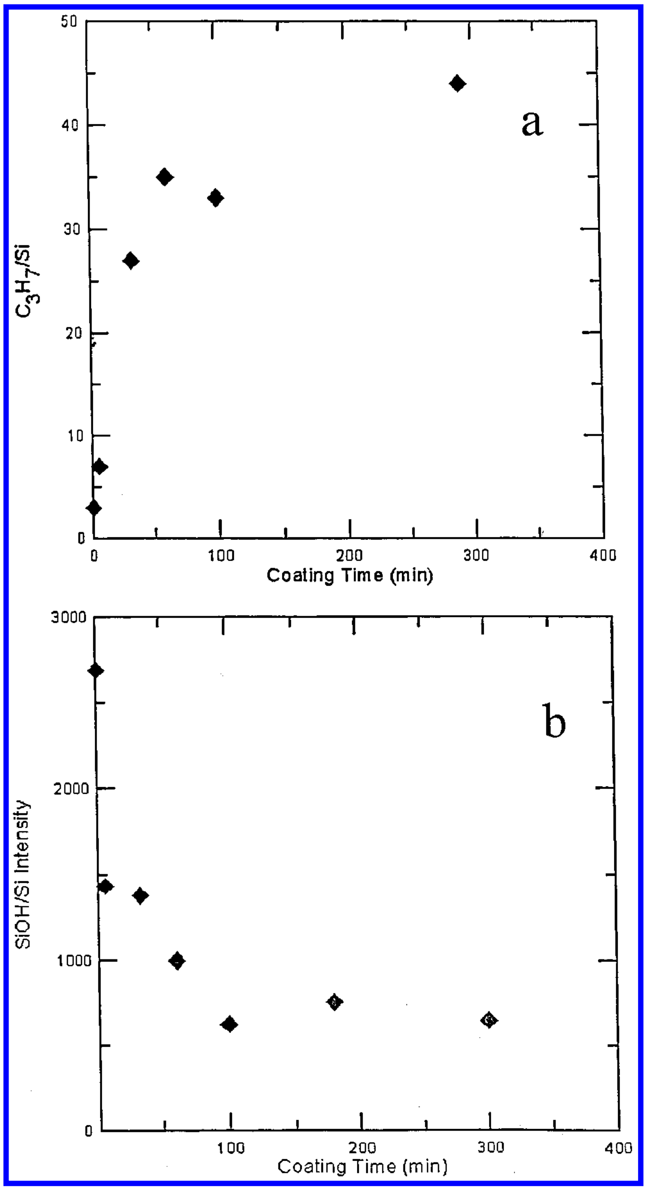

Figure 7. Individual SIMS mass intensity vs ODTS exposure for C_3H_7, (a) and SiOH (b). Samples treated concurrently with those in Figures 1, 2, and 4.

localization of reactants (water or hydroxyls), only those ODTS molecules oriented with the Si end of the molecule next to the surface can react, resulting in a layer of bound ODTS molecules with the hydrocarbon "tail" pointing away from the surface, consistent with the sputter profile data in Figure 9. In this sense the film is organized, or self-assembled, vertically by the spatial localization of the reactants.

Reaction with the surface is complicated by reactions of the type outlined by eq 1 with both surface water and surface hydroxyl groups. The water layer should be continuous, but there is only a low density of hydroxyl groups, ~5 OH/nm^2.[2] As illustrated in step 1 of Figure 11, an ODTS molecule from the solution has a good probability of arriving at an area of the surface containing no hydroxyl groups where only reaction with water is possible. This reaction, following eq 1, simply hydrolyzes the Si−Cl groups to Si−OH groups, producing a molecule ($CH_3(CH_2)Si(OH)_3$) which is, at most, hydrogen bonded to the surface. At this point the hydrolyzed ODTS has two possible courses, as illustrated on the right hand side of eq 1 in Figure 11. One, the molecule can move back into solution where reaction with solution phase ODTS will occur, forming dimers and eventually solution phase polymeric materials which can return to the surface as impurities. Two, if a subsequent ODTS molecule arrives in the immediate vicinity of the hydrolyzed ODTS before it leaves the surface, dimerization and eventually polymerization can occur on the surface. This competition between desorption of the hydrolyzed ODTS molecule and reaction with a second ODTS molecule should produce a distribution of nucleation sites in both space and time, a distribution which is clearly seen in the AFM work of Schwartz et al.[11] Two factors are important in this process: solution concentration and solution volume. Low concentration reduces the probability of the polymerization reaction at the surface by reducing the probability of multiple molecules arriving before the hydrolyzed molecule leaves the surface. Large volumes increase the probability that the hydrolyzed molecule "gets lost" in the solution and does not return as polymerized impurities.

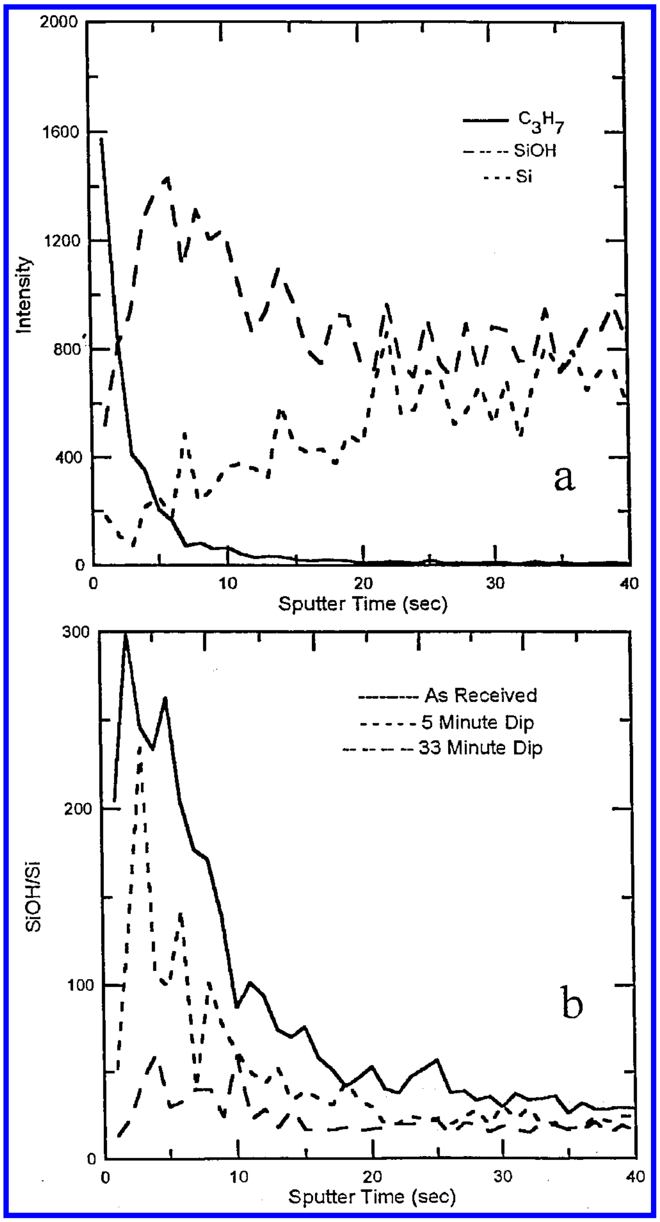

Figure 8. SIMS sputter profiles. (a) C_3H_7, SiOH, and Si intensities as a function of sputter time; (b) SiOH intensity vs sputter time for samples exposed to ODTS for different times.

If the ODTS molecule arrives at or near a surface-bound hydroxyl group, as illustrated in step 2, the basic reaction

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(11) Schwartz, K. K.; Steinberg, S.; Israelachvili, J.; Zasadzinski, J. A. N. *Phys. Rev. Lett.* **1992**, *69*, 3354−3357.

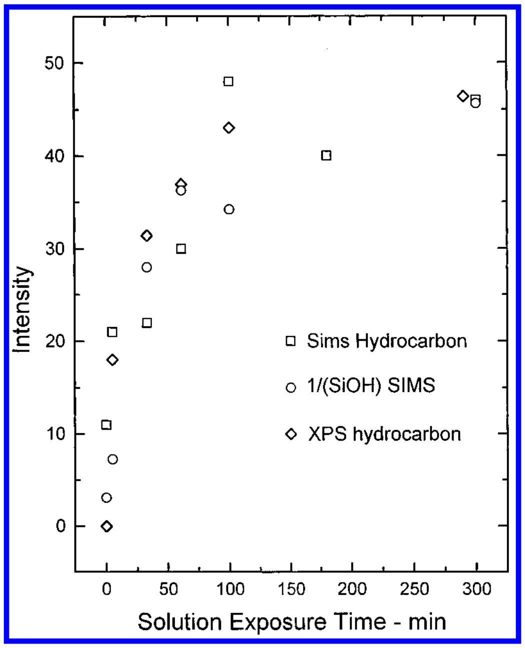

Figure 9. Data in Figure 7 replotted as the C_3H_7 (squares) intensity, the reciprocal of the SiOH (circles) intensity, and the XPS data (diamonds) from Figure 3. Data are scaled vertically to illustrate the shape similarity.

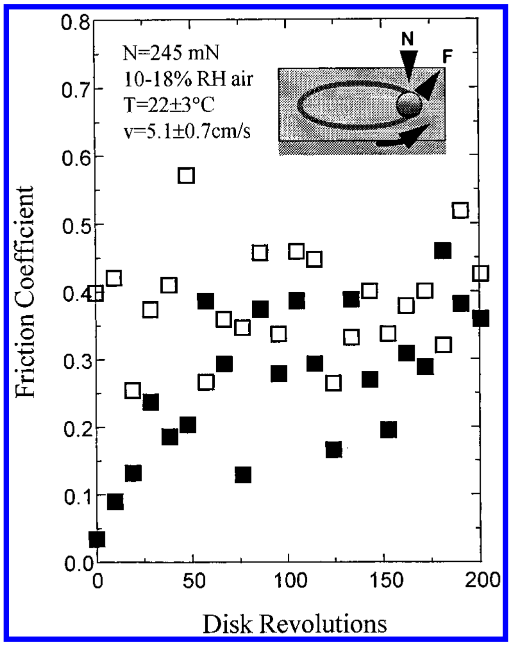

Figure 10. Friction coefficient variation with disk revolutions in a pin-on-disk test. Solid symbols result from a test on ODTS-coated silicon. Open symbols are from a test on uncoated silicon. Multiple tests were performed in each case with identical results, but only one curve for each condition is shown for clarity.

covalently couples the molecule to the surface through the surface-bound oxygen and more importantly converts the remaining two Si−Cl groups to Si−OH by reaction with water. Such molecules effectively would have infinite lifetimes and serve as nucleation sites for polymerization. Further ODTS molecules arriving in the same proximity now have the possibility of reaction with water or with the hydroxyl groups of the previously coupled ODTS molecule. This is a chain polymerization reaction in which the reaction adding each new molecule to the growing film at the same time produces new sites for subsequent reactions. Note that step 3 is illustrated as one-dimensional, but the actual polymerization is two-dimensional. In summary, this mechanism would suggest high solution concentration and/or a thick water layer for a polymerized but weakly bound layer, and low concentration for a nucleated, covalently bound layer.

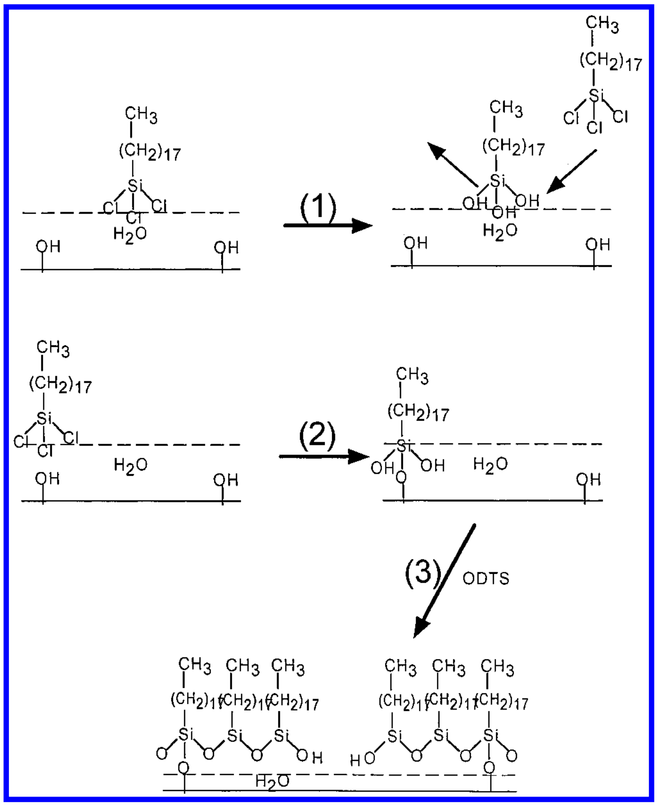

Figure 11. Reaction model. See text for details.

In a normal coupling reaction to silicon, steps 1, 2, and 3 occur simultaneously. In the experimental reactions with vacuum-fired Si samples, steps 2 and 3 were separated as distinct steps; vacuum firing removes the water layer but not the surface oxide. With no surface water, only step two is possible with a much smaller saturation coverage. In Figure 3, the saturation coverage of ODTS on vacuum-fired Si is a factor of ~3 smaller than on normal Si. With no surface water this results in binding to the surface through only one of the original three Si−Cl groups, leaving the remaining two available for subsequent hydrolysis by water, and the surface is sufficiently open as to allow such subsequent water exposure to promote step 3 as a distinct step. Since all three steps consume surface water, with step 1 being a nonproductive consumption step, the coupling reactions should be accompanied by a loss of surface water and hydroxyl groups. This is observed in the SIMS data, Figures 7b and 9, where the SiOH peak is reduced nearly to the base value by a 33 min exposure. As suggested by the gain in C_3H_7 SIMS intensity and the loss of SiOH signal, as shown in Figure 8, reaction of ODTS with the Si surface is limited by the SiOH surface concentration, whether due to true surface hydroxyl groups or to hydrolyzed ODTS molecules. A thin water layer and a low density of hydroxyl groups would favor rapid consumption of water and a low coverage of ODTS. For the same hydroxyl density, a thick water layer would lead to maximum coverages of ODTS, but with little covalent bonding to the surface; for a thick water layer the dominant reaction would be polymerization. Higher coverages might be possible with sequential water and ODTS exposure steps, but this is expected to be self defeating. With increasing coverage the hydrophobic nature of the coated surface will make it increasingly hard for the water to get to the silica/coupling agent interface, the necessary location for further polymerization.

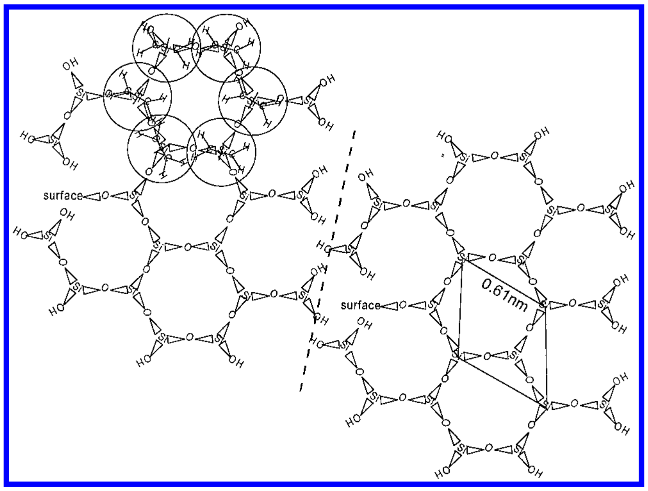

Figure 12. Model structure constructed using a Si−O distance of 1.84 Å and a Si−O−Si bond angle of 144°. The Si−O−Si layer is drawn in the plane of the paper, with, for simplicity, an all-trans octadecane chain depicted as normal to the surface.

This view of the coupling reaction proceeding by polymerization laterally from nucleation sites, either in the water layer or from bonding to hydroxyl groups, results in a polycrystalline film with grain boundaries. In Figure 12, we schematically illustrate two such crystallites. The models have been drawn to scale using a Si−O bond distance of 1.84 Å and a Si−O−Si bond angle of 144°. For the right hand crystallite, only the Si−O−Si base structure is shown. For the left hand crystallite, the alkane chain has been included for illustration as a chain normal to the surface using projected distances appropriate to covalent radii and a tetrahedral structure. The superimposed circles reflect the 2 Å cylindrical van der Waals radius appropriate for normal alkanes.[12] Although the case for crystallites nucleated and grown from initial molecules coupling to the surface is illustrated in Figure 12, the case for reaction with the water layer is essentially the same. Several points follow from consideration of this model. One, multiple nucleation sites necessarily require grain boundaries unless the highly improbable situation exists of nucleation sites being in exact registry with the growing structure. Two, the alkane chains will be forced into serious crowding by the covalent bonded Si−O framework. Such crowding, or course, could be reduced by tilting relative to the surface normal. Such tilting is in fact necessary if the first carbon has a tetrahedral structure and an all-trans alkane configuration is maintained.

What is clear is that reaction of the coupling agent with the oxidized silicon surface produces a surface film terminated by a dense array of linear alkanes; the extent to which this film is covalently bound to the Si surface is not known. The friction coefficient between silicon surfaces is known to be governed by the presence of adsorbates. Sliding between polycrystalline silicon surfaces in ultrahigh vacuum produced friction coefficients near 0.8,[13] while friction coefficients between silicon surfaces in controlled gaseous ambients can be in the range 0.2−0.8.[14−16] Ample evidence exists that these differences in friction coefficient are determined by the presence of dangling bonds on the sliding surfaces. Gardos recently showed[17] that high adhesion and friction between Si(100) surfaces is due to the linking of the two surfaces by unsaturated Si bonds. These free radicals on the sliding surfaces can be generated by wear, or by heating. Likewise, Gardos argued that friction can be substantially reduced by dissociative chemisorption of select passivating gases at low temperature or by dimerization-induced reduction of the surface energy due to reconstruction at sufficiently high temperature.[17] ODTS serves to passivate the silicon surface, preventing adhesive interaction with dangling bonds on the oxidized silicon nitride counterface. This passivation is evidently lost as sliding progresses, probably reflecting weak bonding of the film to the surface. The performance of ODTS in this regard is about as effective as possible with the use of surface passivation to reduce friction. Gardos[17] showed that friction of silicon surfaces was reduced from the range 0.4−0.7 (interaction of unsaturated bonds) to about 0.1, upon chemisorption of species to satisfy some of these dangling bonds. Dugger and co-workers[18] observed similar reduction in the friction of polycrystalline diamond upon adsorption of gaseous species to mitigate carbon bonding across the interface, which occurs after wear in vacuum.

Since all friction tests reported here were continued well after stick−slip frictional behavior was observed, surface damage visible to the naked eye was produced. Surface composition data from these worn areas would include the effects of silicon fracture and debris transfer, and hence interpretation would be questionable. We plan future examination of worn ODTS films which will include compositional analysis at various stages of wear.

V. Summary

For reaction of silicon coupling agents with oxidized silicon surfaces, the following conclusions can be drawn.

(1) Comparable saturation coverages are obtained for ODMS reacting with oxidized Si and for ODTS reacting with vacuum-fired Si, consistent with reaction limited to surface hydroxyl groups.

(2) For vacuum-fired Si, coverages are approximately threefold less than those for a comparable oxidized Si surface, but the coverage can be further increased by soaking in water followed by a second ODTS treatment. This is consistent with reaction of a single Si−Cl bond of ODTS with a surface hydroxyl, leaving the remaining two Si−Cl bonds available for subsequent hydrolysis and reaction with ODTS.

(3) A major consideration in the reaction of silane coupling agents with silicon is *competition* between reaction with surface hydroxyl groups and surface water as discussed in a model for the reaction.

(4) ODTS surface films are shown to reduce the coefficient of friction to ∼0.05, consistent with the reduction expected from bond saturation at surfaces.

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