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Effects of Surface Hydration on the Deposition of Silane Monolayers on Silica

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The deposition of a silane monolayer on silica depends on the chemical reactions between the silane molecules and the hydroxyl groups on the silica surface. We have studied the effects of dehydration and rehydration of flat silica substrates on the deposition of a self-assembled monolayer of octadecyltrichlorosilane by using FTIR spectroscopy and ellipsometry. The results demonstrate that monolayer coverage increases with degree of hydration of the substrate. Patches of ordered chains form on a dehydrated surface and that coverage increases with hydration. A fully hydrated surface, however, is not necessary for complete coverage of the substrate, suggesting that not every silane group is bonded to the surface.

1. Introduction

Recently, we have initiated a program to study the polymer–silica interface on optical fiber by using monolayers of silanes deposited on the silica by the technique of self-assembly. The mechanical strength of optical fiber degrades in the presence of water due to the reactivity of the silica surface with water. Static fatigue of the fiber, in which it fails under a constant applied stress after a time delay, results from the interaction of water with the stressed bonds of the silica and depends on the concentration of water in the environment. Our long term objective is to investigate possible ways of reducing fiber fatigue, by applying monolayers of various silane compounds to optical fiber and studying the fatigue behavior of that fiber in different environments.

Self-assembled monolayers are densely packed, ordered films which attach to the surface by chemical bonds.[1-4] By depositing such a monolayer on silica, we achieve full coverage of the silica surface and form a hydrophobic layer which may impede diffusion of water to the interface.[5] By changing the chemistry of the constituent molecules and studying the effects on fiber fatigue, we hope to contribute to the understanding of the underlying mechanisms of water-mediated corrosion of silica. We have chosen octadecyltrichlorosilane (OTS), shown in Figure 1, for the initial experiments because of the large amount of previous work on the deposition and characterization of monolayers of this compound.[1,2,6,7]

OTS, a long chain silane, is structurally similar to a coupling agent, such as (glycidoxypropyl)trimethoxysilane, in that both have hydrolyzable functional groups on a silicon atom which can bond to silanol groups on the silica surface. Silane coupling agents are either mixed into a polymer or applied directly to a silica substrate, in which case a cross-linked network of Si–O bonds forms between silane molecules. In the case of optical fiber, coupling agents are mixed into the coating to enhance adhesion to the silica; however, the interaction between those molecules and the silica surface after fiber draw is not well understood. At 2200 °C, the furnace temperature in the fiber draw process, all water molecules and almost all OH groups are removed from the surface. A self-assembled monolayer can be used as a model system to study the bonding of silanes to a silica surface.

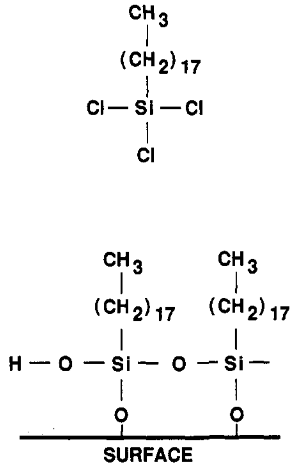

Figure 1. Structure of octadecyltrichlorosilane (OTS) and a schematic of the molecule on the surface after deposition by self-assembly.

Although there have been numerous studies of the structure of self-assembled monolayers, the structure of the silane–silica interface has not been thoroughly characterized. Water, which is either bound to the surface or present in the solution, hydrolyzes the chlorosilanes to form silanols. These silanols then form stable bonds to the silica upon reacting with the surface silanols and release water.[8,9] It is generally assumed that a fully hydrated surface, which has 5 OH groups per 100 Å^2,[10] is necessary for self-assembled monolayer formation.[6]

Results from recent experiments, however, suggest that there may not be extensive chemical bonding between the monolayer and the surface. The surface of silicon coated

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by an OTS monolayer, for example, is smoother than that of uncoated silicon, as if the monolayer covers the surface without bonding to it.[8] It has been observed by FTIR spectroscopy of high surface area silicas exposed to OTS solution, that the absorption peaks for water and OH do not change upon exposure to OTS,[11] a result that is consistent with the idea that few bonds form between the monolayer and the silica surface. In this paper, we have addressed the question of the formation of bonds to the OH groups on the surface directly by studying monolayer deposition on dehydrated and partially hydrated surfaces.

2. Dehydration, Rehydration, and Hydroxyl Groups on Silica

The surface chemistry of silica is controlled by the following reaction of water with the SiO_2 network

$$-Si-O-Si- + H_2O \rightarrow 2Si-OH$$

which produces silanols on the surface. Hydroxyl groups on silica can hydrogen bond to each other and to water molecules. Water molecules concentrate on the surface at silanol groups to which they either physisorb or chemisorb. These molecules are available to attack other Si–O linkages on the surface.[12] Surface silanols are also the sites to which other adsorbates, such as alkylsilanes, bond. The silica surface on fiber, therefore, needs to be hydroxylated enough to form bonds to the polymer, in our case the alkylsilane monolayer.

Much work has been done previously to characterize the hydroxyl groups on hydrated and dehydrated high surface area silica. In this work we are using low area silicas and, because there has been little work on the surface chemistry of bulk fused silica, we must assume that it is similar to that of the high area silicas. The kinetics of dehydration depends on the concentration of surface silanols and temperature.[10] Physisorbed water is removed from the surface by pumping at room temperature. Silanol groups are removed by heating the silica either in vacuum or under a gas flow to remove the water which evolves from the surface. At temperatures between 170 and 400 °C, silanol groups condense and eliminate water. This dehydration process is reversible because less than half the hydroxyl groups have been removed at 400 °C, and water readily reacts with the silanols remaining on the surface. Above 400–450 °C, the process starts to be less reversible as the density of silanols decreases.[13] Above 700 °C, for example, all of the silanols are unpaired, isolated OH groups occurring at a density of roughly 1 OH per 100 Å^2.[14] The silica surface becomes hydrophobic above 850 °C, and chemisorption of water is inhibited.[15] At 1000 °C, the temperature selected for our experiments, the surface is left with less than 1 OH per 100 Å^2.[10]

Rehydration of the silica surface occurs very slowly after heating the glass to temperatures above 400 °C.[16,17] The surface becomes increasingly hydrophobic with increasing temperature because water molecules concentrate locally on the surface OH groups, leaving an increasingly larger area dry as the density of OH decreases with temperature. Above 800 °C water molecules can concentrate on the isolated OH groups, but because these occur at a low density, almost all of the silica surface remains dry.[15] The more a surface is dehydrated, i.e. the more hydroxyl groups are removed, the longer rehydration takes. A silica aerogel heated at 1100 °C for 10 h has 0.06 OH per 100 Å^2 and requires 60 h in boiling water to be rehydrated. Silica dehydrated to 0.66 OH per 100 Å^2 after 10 h at 900 °C requires several years in room temperature water to be rehydrated.[10,18]

3. Experimental Methods

Monolayers of OTS were deposited by the self-assembly technique on plates of fused silica (Hereaus Amersil TO8) and on the oxide surface of silicon wafers, which were either hydrated, dehydrated, or rehydrated. The thickness and relative order of the hydrocarbon chains were determined by ellipsometry of the monolayers on oxidized silicon and transmission FTIR spectroscopy of the monolayers on silica.

All of the silica slides and silicon wafers were cleaned in an ultrasonic bath of high-purity water to remove dust and then boiled for 20 min in a mixture of water, ammonium hydroxide, and hydrogen peroxide at a ratio of 5:1:1 by volume. The slides were rinsed in an overflow rinse for a half hour and then blown off with dry nitrogen. Before use they were stored under high-purity water at room temperature for at least 24 h. We dehydrated the slides by baking them in a glass tube furnace at 1000 °C for 10 h under a constant flow of dry nitrogen. The nitrogen was the boil-off from a liquid nitrogen supply. Upon removal from the furnace the slides were either submerged immediately in the OTS solution for monolayer deposition or submerged in water for rehydration.

A 2.5×10^{-3} M solution of OTS in a mixture of 20% CCl_4/80% Isopar G[19] by volume was prepared 30 min before deposition.[7] The Isopar G was run through an alumina column, equilibrated overnight with a trace of water (2 drops per 100 mL) and decanted into the solution flask. The substrates were immersed in the solution for 30 min and then rinsed sequentially in carbon tetrachloride, ethanol, and carbon tetrachloride. Each rinse step consisted of drenching the sample with the solvent from a squeeze bottle a minimum of ten times.

OTS is deposited on the oxide layer of silicon wafers as a control to ensure that there are no problems with either the solution or deposition procedure. The thickness of the monolayer is then measured with a Gaertner L115B ellipsometer. We have assumed that the monolayer has the same index, 1.46, as the oxide layer on the silicon and, therefore, measure the change in the effective thickness of the oxide after OTS deposition. This is done by comparing the thickness of the layer on two pieces of the same wafer that have undergone all of the same processing steps prior to OTS deposition on one of the pieces. The assumption of 1.46 for the index of the silane film is a reasonable one because organic films typically have indices of refraction in the range of 1.4 to 1.5; moreover it has been shown that a variation of 0.05 in index changes the thickness obtained by only 1 Å.[6] The thickness measured for each sample is an average over roughly 10 different spots on the sample.

The degree of ordering between the hydrocarbon chains of monolayers on fused silica has been measured by FTIR spectroscopy in transmission. The spectra were obtained with a Nicolet 7199 spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector sensitive over the range of 400 to 4000 wavenumbers. All spectra were averaged over 1024 scans at a resolution of 1 or 2 cm^{-1}. Spectra of monolayers were ratioed to background spectra measured from the substrate silica. The silica plates were cut into halves prior to the cleaning and dehydration/deposition processes. The halves used for background scans were exposed to all of the same procedures as the sample halves, except for the deposition step. The peak position and width (fwhm) of the C–H stretch at 2918 cm^{-1} were studied for films deposited on substrates, which were either hydrated, dehydrated, or rehydrated, to determine the effect of surface

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Table I. Ellipsometry of OTS on Oxidized Silicon

degree of hydration	OTS film thickness (Å)
hydrated overnight	28 ± 2
dehydrated[a]	14.2 ± 5.4
dehydrated[b]	29 ± 2
rehydrated in water	28 ± 2

[a] Ambient humidity in room outside furnace estimated to be 10–30%. [b] Ambient humidity in room outside furnace estimated to be 50–60%.

Table II. FTIR Spectra of OTS on Fused Silica

degree of hydration	peak position (cm^{-1})	ABS (%)	fwhm (cm^{-1})
hydrated overnight	2918.0 ± 0.6	1.40 ± 0.35	15 ± 2
dehydrated[a]	2918.6 ± 1.1	0.84 ± 0.2	16 ± 3
rehydrated	2917.9 ± 0.5	1.36 ± 0.25	13 ± 2

[a] Ambient humidity outside furnace estimated to be 50–60%.

hydroxyl groups on OTS deposition. Baselines of the transmission spectra were corrected for excess slope and shifted to 100% transmission. Peak positions and widths were then determined using the software routines of the instrument.

4. Results and Discussion

OTS monolayers deposited on silica are characterized either by ellipsometry of monolayers on the oxide layer of silicon wafers or by FTIR spectroscopy of monolayers on fused silica. Results of these measurements for monolayers deposited on silica that is hydrated, dehydrated, or rehydrated are summarized in Tables I and II.

OTS on Hydrated Silica. OTS monolayers deposited on the fully hydrated oxide surface of pieces of silicon wafer are measured to be 28 ± 2 Å thick after subtracting the thickness of the native oxide on a reference wafer. The native oxide is 11.3 ± 1.4 Å. The measured thickness of 28 Å is an average over samples from 10 experiments and is in reasonable agreement with previous measurements which range from 23 to 26 Å.[6,7] The difference of several angstroms between this value and previously published values may be explained by a combination of factors such as the accuracy of the ellipsometric calculation for such a thin film, the estimation of the monolayer index, and the variation in the underlying oxide thickness. Given these sources of uncertainty in calculating thickness, the measured value of 28 Å is consistent with the thickness expected for a densely packed monolayer with chains oriented normal to the substrate in an all-trans configuration.

OTS monolayers on fused silica plates are characterized by FTIR spectroscopic measurements in transmission. Although the signal-to-noise ratio is smaller than that obtained by internal reflection techniques, there is enough signal from the layers on the two sides of the slide to monitor the C–H stretching modes at 2851 and 2918 cm^{-1}. The 2918-cm^{-1} peak is particularly useful as both its position and width are affected by the degree of conformational ordering in the alkyl chains. It has been shown in spectral calculations that the symmetric and antisymmetric C–H stretches shift roughly 6 cm^{-1} in going from an ordered, all trans alkyl chain to a disordered chain with gauche defects.[20] We have verified this effect by comparing the spectrum from a KBr pellet of stearic acid with that of liquid Nujol. The peak position for stearic acid, located at 2915 cm^{-1}, shifts to 2924 cm^{-1} in Nujol, a long chain hydrocarbon liquid. In addition, the peak width for Nujol of 62 wavenumbers is considerably broader than the 27 wavenumber width of that peak in the spectrum of stearic acid. The spectrum, plotted by the dotted line in Figure 2, of an OTS monolayer deposited on a fully hydrated fused silica plate, exhibits a C–H stretching peak at 2918 cm^{-1} with a peak width (fwhm) of 15 cm^{-1}. Both the position and width of the peak are in agreement with attenuated total reflection (ATR) measurements of OTS deposited on the hydrated oxide surface of silicon.[7,21]

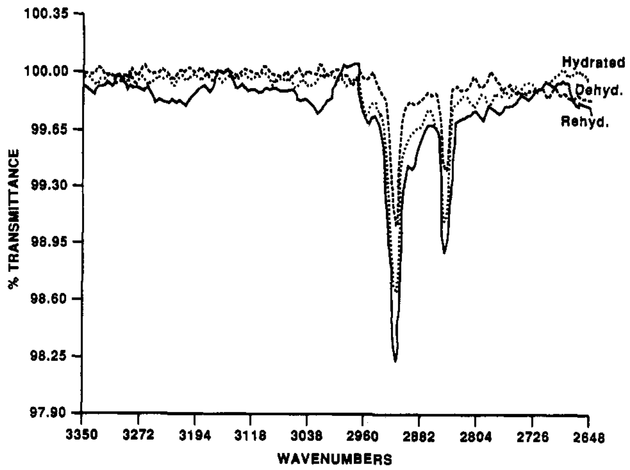

Figure 2. FTIR transmission spectra, in the region of the C–H stretching modes, of OTS monolayers on silica surfaces that are fully hydrated (dotted line), rehydrated in room temperature water (solid line), and dehydrated (dashed line) before monolayer deposition.

OTS on Dehydrated Silica. Deposition of OTS monolayers on dehydrated silica is extremely sensitive to the humidity to which the silica is exposed after removal from the furnace. Monolayers deposited on the oxidized surface of silicon following dehydration at 1000 °C in a nitrogen atmosphere ranged in thickness from 14.2 ± 5.4 Å thick in the winter to 28 ± 2 Å in the spring months. We estimate that the relative humidity in the lab varies from a low of 10% in the winter to a maximum value of 60% in the summer.

The transmission FTIR spectra of OTS monolayers on fused silica that is dehydrated, also suggest a strong dependence of deposition on relative humidity. The C–H stretching mode at 2918 cm^{-1} is broadened and less intense than in the fully hydrated case; however, none of the spectra exhibit a shift as would be expected for a monolayer of disordered chains. The intensity and peak widths are sensitive to relative humidity. The spectrum in Figure 3, for example, is from a monolayer deposited after surface dehydration in the winter. Although the signal-to-noise is too low to determine the peak position by the software of the instrument, it does not appear to be shifted from 2918 cm^{-1}. Spectra of OTS deposited on dehydrated fused silica in the spring months, as shown by the dashed line in Figure 2, exhibit a more intense C–H stretching peak which is only slightly broadened. Positions, widths, and heights of the 2918-cm^{-1} peak are tabulated in Table II; each number represents an average of ten independent samples prepared at the specified conditions. The values for monolayers on dehydrated substrates are obtained only from experiments run after April (i.e. the samples that exhibit spectra with large enough signal-to-noise to analyze).

In order to eliminate rehydration of the silica surface by high relative humidity (in the spring and summer months), we have tried transferring the slides from the furnace to the OTS solution in a glovebag inflated with

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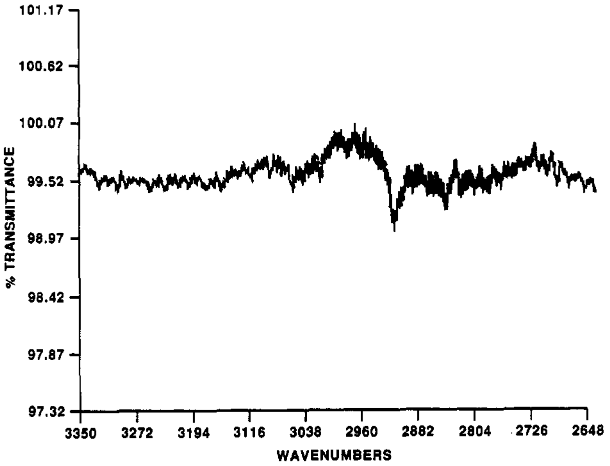

Figure 3. FTIR transmission spectrum of OTS on fused silica exposed to OTS solution at low ambient humidity (estimated to be 10–30%).

argon. The spectra of OTS monolayers on these substrates exhibit similar widths and intensities for the C–H stretch peak. The dependence of deposition on relative humidity, therefore, must be either from the amount of residual water in the dry nitrogen lines or from the concentration of water in the OTS solution. Since the dry nitrogen is from the liquid nitrogen supply, it is more likely that the dehydrated silica is picking up water from the OTS solution. The extent of this rehydration depends on relative humidity because of the variation in the concentration of water in the OTS solution and in the vapor above it. X-ray photoelectron spectra (XPS) of monolayers deposited on dehydrated surfaces, however, do not exhibit peaks for chlorine.[7,22] This indicates that even at low relative humidity there is enough water present in the solution to hydrolyze the chlorosilane groups and that the variation in deposition with relative humidity is not due to incomplete hydrolysis of the OTS. XPS spectra[22] also show low levels of carbon for the surfaces of the background substrates indicating that variations in the spectra are not due to surface contamination. This is especially true for dehydrated surfaces which have the lowest level of residual carbon. This is not surprising as any organic contaminants are vaporized in the 1000 °C furnace.

The decrease in thickness observed by ellipsometry of monolayers on oxidized wafers may be explained either by submonolayer coverage, i.e. islands of molecules with ordered chains, or by a homogeneous distribution of molecules with disordered chains. It appears, however, since the C–H stretch is not shifted in wavenumber but the intensity is still less than that of a monolayer on a hydrated surface, that the molecules are driven by strong chain–chain interactions to form dense patches on the surface. The surface coverage changes with the number of hydroxyl groups on the substrate surface, and at some critical degree of hydroxylation, monolayer coverage is achieved.

OTS on Rehydrated Silica. If dehydrated silica substrates are submerged in liquid water at room temperature for several minutes, the resulting density of hydroxyl groups on the surface is sufficient for deposition of OTS monolayers which are indistinguishable from monolayers deposited on fully hydrated surfaces. The thickness of monolayers grown on these rehydrated surfaces is 28 ± 2 Å, as measured by ellipsometry.

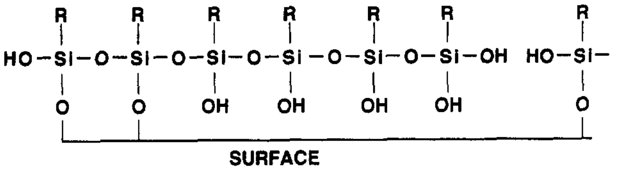

Figure 4. Proposed structure for an OTS monolayer in which roughly one in five chains forms a bond to the silica surface.

FTIR transmission spectra of OTS monolayers on rehydrated fused silica, as shown by the solid line in Figure 2, indicate that after a few minutes in water there are enough hydroxyl groups on the surface for the surface to be completely covered by a dense monolayer of ordered hydrocarbon chains. The absorption intensity, width, and position of the higher energy C–H stretching mode tabulated in Table II are indistinguishable from the values for monolayers deposited on fully hydrated surfaces within the standard deviations between different samples of the same type.

It has been observed in experiments measuring reaction rates of water with high surface area silicas that two types of strained ring defects on the surface react with water at time constants of 17 ms and 1 s at 100% RH,[23] corresponding to time constants of 170 ms and 10 s at the lower limit of 10% relative humidity in the winter. Clearly, the faster process, which occurs at $t \ll 1$ s for all conditions, is not relevant to OTS deposition. The dependence of OTS deposition on relative humidity may be explained by the interaction of the slower reacting defect with water, or by other even slower reactions occurring at larger, less strained rings. The rates of such reactions may depend on the concentration of water at the surface and, therefore, be enhanced by silanols that have formed at the highly strained defect sites. We estimate that even after the strained defects on the surface hydrolyze, the total number of OH groups on a dehydrated surface is between 1 and 2. The silica is extremely hydrophobic after dehydration and the density of available defects is low ($\leq 0.1/100$ Å^2).[23] We have shown that dense monolayers of ordered chains can form on a partially hydrated surface, suggesting that only 10 to 20% of the chains need to form bonds to the surface. The monolayer formation is primarily driven by the strong interactions between the hydrocarbon chains and the Si–O linkages forming between adjacent silanols. A schematic picture of the silane/silica interface is shown in Figure 4. The glass surface is depicted as flat. We have measured the surface roughness of the fused silica plates using surface profilometry, and have verified that the silica is flat at a resolution of several angstroms. This picture of the monolayer/silica surface is consistent with the works cited above on the smoothness of the monolayer-coated surface[8] and on the reactions between water and high surface area silica.[11]

5. Conclusions

Although there have been numerous studies on high surface area silicas, there has not been as extensive work on the surface chemistry of low area, bulk silicas, which are critical to applications such as device protection and fiber reliability. Because our main interest is in the silica/polymer interface of coated optical fiber, we have studied the effects of dehydration on the deposition of silanes on silica. We have based the interpretation of our results on prior knowledge of high surface area silicas. It is still necessary to study the surface hydration of bulk, low area

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silica and compare its surface chemistry to that of high surface area silica.

The results of our experiments demonstrate that silica plates that are dehydrated can be rehydrated within minutes in room temperature water for the deposition of a dense, well-ordered OTS monolayer, the infrared spectrum of which is indistinguishable from that of a monolayer on a fully hydrated surface. Furthermore, OTS molecules form dense patches of ordered chains on a dehydrated surface that is exposed to moisture. The coverage of the surface depends on the number of OH groups on the surface; however, a completely hydrated surface is not necessary for complete coverage of the surface. Based on what is known about the dehydrated surface of high surface area silica, we believe that only some OTS chains, on the order of one in five chains, form bonds to the surface. The density and order of the monolayer are derived from the strong chain–chain interactions and the local polymerization that occurs between chains.

The implication of this result is that it is possible to deposit a monolayer on a freshly drawn fiber to study the effects of interface structure on the mechanical behavior of the fiber. Since the fiber is drawn from a furnace at 2200 °C and not at the specific conditions used here, the deposition of the film on the fiber would still have to be verified. These results also suggest that silane coupling agents can react with a partially hydrated surface.

Many techniques have been applied in the past to the structure of organic monolayers. The experiments described here are focused on the inorganic/organic interface and underscore the need for applying other techniques to understand this interface in technologically relevant surfaces.

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