

Multilayer Alkoxysilane Silylation of Oxide Surfaces

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Anhydrous silylation of vinyltrimethoxysilane (VTMS) onto silica and zirconia substrates was investigated experimentally to demonstrate and quantify the effects of surface water on multilayer silylation. Silylation coverage was controlled by the availability of surface water, which is consumed in multilayer silylation reactions. Silylation coverage increased with surface water coverage, reaching a maximum at approximately two monolayers of water. The subsequent decline in silylation coverage is attributed to the formation of bulk polysilanes and the decreased accessibility of the water-bearing surface to the hydrophobic VTMS molecules. Atomic force microscopy images revealed a nanometer-scale clusterlike surface morphology consistent with the formation of bonded polysilanes. The present study suggests that multilayered silylated surfaces can be prepared reproducibly. Such surfaces could prove useful in applications that require a high concentration of surface active groups such as in ceramic membrane modification, construction of biocompatible surfaces, and adhesion enhancement in polymer composites.

Introduction

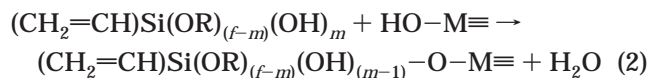
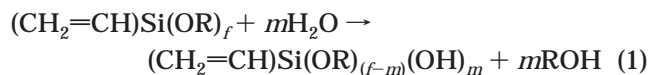
Modification of oxide surfaces (e.g., silica and zirconia) by silylation is a well-known method of altering the chemical and physical properties of ceramic substrates. For some applications, such as promotion of adhesion between polymers and ceramics, monolayer silylation coverage may be desired.¹ However, for applications where the organosilane molecules provide a specific functionality, multilayer coverage can be more appropriate. For example, in free-radical graft polymerization, vinylsilane groups can be bonded to the surface during a silylation reaction and subsequently provide vinyl anchoring sites for polymer chains.^{2–6} In this latter case, maximum chain surface density is largely controlled by the initial surface concentration of vinyl groups, which also affects the yield and distribution of grafted polymer chains on the support surface.^{7,8}

Surfaces of inorganic substrates can be modified with a variety of silane molecules using either gaseous or liquid-phase reactions.⁹ It is generally accepted that silylations performed in the vapor phase or with monofunctional silanes result in a monolayer or near-monolayer surface coverage. Multilayer silylation coverage can be achieved using a di- or trifunctional silylating agent in either aqueous or anhydrous (i.e., organic solvent) solution.

The choice of solvent in liquid silylation reactions greatly affects the resulting silylation coverage. For example, in aqueous-phase silylation, alkoxy- and chlorosilanes undergo hydrolysis and condensation into polysilane net-

works prior to deposition onto the surface. The siloxane bonds that are formed allow polymerization of multifunctional silane molecules to proceed parallel and perpendicular to the surface.⁹ However, in aqueous systems, deposition and adsorption of bulk-formed polysilanes can render portions of the surface inaccessible to further silylation and thus may result in poor silylation control as well as incomplete and nonuniform surface silylation coverage.

Anhydrous silylation of oxide surfaces, which is the focus of the present work, has been shown to be an effective method of achieving a controlled degree of surface silylation coverage. With multifunctional silanes (e.g., di- or trifunctional alkoxy- or chlorosilanes) anhydrous silylation occurs by hydrolysis of one or more of the chloro or alkoxy groups, followed by a condensation reaction between the surface hydroxyl groups and the hydrolyzed silane molecules¹⁰



where OR is an alkoxy (e.g., $-\text{OCH}_3$ or $-\text{OCH}_2\text{CH}_3$) group, $\text{M}\equiv$ is a surface molecule of either Si or Zr, and the number of hydrolyzed groups, m , is less than or equal to the maximum functionality, f , of the precursor silane. It should be noted that the general forms of eqs 1 and 2 do not preclude the possibility of silanes attached to the surface via multiple points through sequential or simultaneous reaction with closely placed surface hydroxyls. In eq 1, the reaction for a vinyl alkoxy silane has been given, but similar equations can be obtained for chlorosilane reactions by replacing the OR groups of eqs 1 and 2 with chlorine groups. During anhydrous silylation, the H_2O molecules indicated in eq 1 can be provided by water molecules adsorbed onto the support surface,^{10–14} trace

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amounts of water in the organic solvent,^{15,13} or humidity present during a postsilylation curing step.¹³ The hydrolysis reaction (eq 1) is a requirement for condensation; direct condensation between chloro- or alkoxysilanes and surface hydroxyls in the absence of water or amine catalysts is not observed.^{10,15–17}

It has been shown that silylation coverage obtained via anhydrous silylation of an inorganic oxide surface depends on the degree of hydration/hydroxylation of the surface. Lower silylation coverages are expected for surfaces that are dried at high temperatures, owing to progressive dehydration (loss of surface water at temperatures up to 180 °C) and dehydroxylation (loss of hydroxyl groups above 180 °C). For example, Kallury et al. reported a silylation coverage of 10 $\mu\text{mol}/\text{m}^2$ for octadecyltrichlorosilane on fumed silica dried under vacuum at 200 °C for 2 h vs 15.4 $\mu\text{mol}/\text{m}^2$ on fumed silica with no high-temperature pretreatment.¹⁴ Murthy and Leyden (1986) reported that 3-aminopropyltriethoxysilane (APTES) silylation coverages on silica gel varied from 0.77 to 8.5 $\mu\text{mol}/\text{m}^2$ when the silica was dried under vacuum at temperatures that varied from room temperature to 220 °C.¹¹ In another study, Caravajal et al. reported a decrease in APTES coverage on silica gel from 4.1 to 2.0 $\mu\text{mol}/\text{m}^2$ by drying the gel at 200 °C prior to anhydrous silylation.¹²

Surface hydroxyl groups available on silica and zirconia surfaces (i.e., $\text{Si}_{(\text{s})}\text{—OH}$, $\text{Zr}_{(\text{s})}\text{—OH}$) are required for the covalent bonding of chlorosilanes or alkoxysilanes to the surface. The surface concentrations of hydroxyl groups on fully hydroxylated silica and zirconia are 7.6 (4.6 molecules/ nm^2)¹⁸ and 5.6–5.9 $\mu\text{mol}/\text{m}^2$ (3.4–3.6 molecules/ nm^2),^{19,20} respectively. Thus, the maximum possible monodentate silylation coverage is limited to 7.6 $\mu\text{mol}/\text{m}^2$ for silica and 5.6–5.9 $\mu\text{mol}/\text{m}^2$ for zirconia. Multilayer coverages with yields beyond the above limit are possible by using di- or trifunctional silanes capable of multiple surface attachments and/or silane cross-linking.

The main goal of this paper is to study quantitatively the effects of adsorbed water on silylation yield for situations where these multilayers (i.e., silane networks) are formed. We demonstrate that adsorbed surface water plays a key role in determining the silylation coverage achieved by anhydrous silylation of ceramic substrates, with special focus placed on nonporous silica and zirconia surfaces. It is also shown that the anhydrous silylation technique can produce a dense surface silylation coverage, although there is some lateral distribution of the polysilane surface mass as viewed by atomic force microscopy (AFM).

Materials and Methods

Materials. The silane coupling agent used for all silylation reactions was VTMS (vinyltrimethoxysilane) (Aldrich Chemical Co., Milwaukee, WI), and the solvent was certified ACS grade

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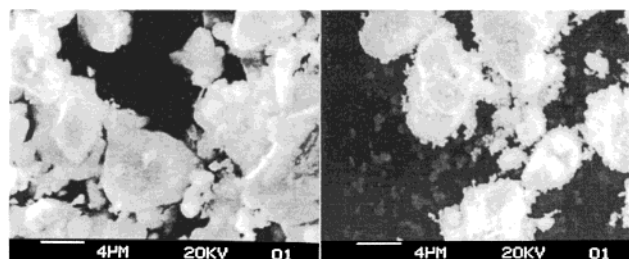


Figure 1. SEM images of unmodified Novacite silica particles (on left, specific surface area 2.2 m^2/g) and unmodified zirconia particles (on right, specific surface area 6.1 m^2/g).

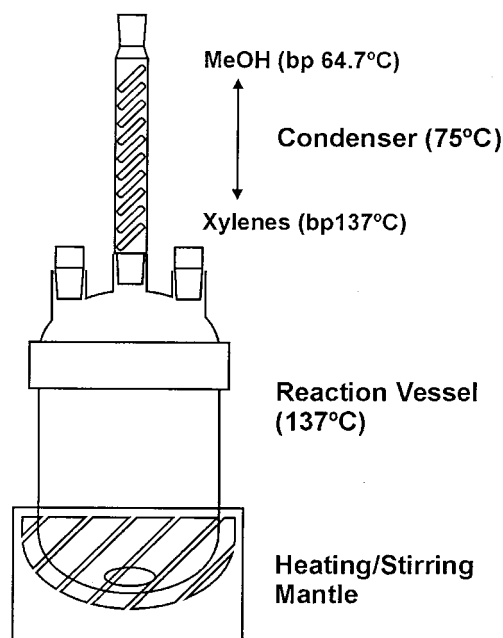


Figure 2. Silylation reaction apparatus.

isomeric xylenes (Fisher Scientific, Pittsburgh, PA). Methanol, acetone, sulfuric acid, and 30% w/w hydrogen peroxide used in wafer cleaning were all certified ACS grade (Fisher Scientific). All water used in the study was distilled and deionized.

Silylation of silica particles was conducted with nonporous Novacite silica particles with a 5 μm average diameter and a surface area of 2.2 m^2/g (Malvern Mineral Co., Hot Springs, AR). Corresponding zirconia silylation reactions were carried out using nonporous zirconia particles with a diameter of 5 μm or less and a surface area of 6.1 m^2/g (Aldrich Chemical). Nonporous particles of this size were chosen in order to facilitate their separation from solution, to avoid possible problems with surface water inhomogeneity due to microporosity, and to eliminate pore blockage effects during silylation. Particle surface areas were determined experimentally by Brunauer–Emmett–Teller nitrogen adsorption (Autosorb-1, Quantachrome, Boynton Beach, FL). Images of the native silica and zirconia particles were obtained by scanning electron microscopy (SEM) using a Cambridge Stereoscan 250 microscope. The resulting images of the particle surfaces are presented in Figure 1. SEM images revealed a marked difference in the surface morphology and shape of the zirconia and silica particles. The observed roughness of the zirconia particles is consistent with the higher zirconia surface area relative to the silica particles.

Ceramic Particle Silylation and Characterization. The silylation reactor system (Figure 2) consisted of a 500 mL glass reaction flask (Scientific Glass and Instruments, Inc., Houston, TX), which was heated and stirred using a heating/magnetic stirring mantle (Electrothermal, Ltd., Southend, England) and a magnetic stirring bar. Water for the condenser was heated using a circulating constant-temperature bath (Lauda and Co., West Germany). All glassware for the silylation reaction was dried overnight under vacuum at 110 °C to remove adsorbed

water. To control the amount of surface water, the ceramic support material was first dried overnight under vacuum at 110 °C to establish the dry weight. Just prior to reaction, the ceramic particles were resuspended in water for 30 min, and the suspension was then filtered and dried to obtain the desired water content. Silylation of the particles was carried out in a solution of 10% (v/v) VTMS in xylenes solvent. The substrate loading for both silica and zirconia particles was approximately 80 g/L solution. The reaction was carried out for a period of 5 h with the reaction temperature maintained near the boiling point of xylenes (137–140 °C). The temperature of the condenser was kept at 75 °C to reflux the solvent back to the reactor while allowing passage of the methanol byproduct (bp 65 °C) formed during the silylation reaction.⁴ The suspension of particles was then filtered, and the particles were rinsed with pure xylenes to remove unreacted silanes. Subsequently, the silylated material was dried overnight under vacuum ($T = 130$ °C, $P = 50$ Torr).

The presence of surface-bonded VTMS was confirmed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy using a Bio-Rad FTS-40 with an attached 091-0428A diffuse reflectance accessory (Bio-Rad Digilab Division, Cambridge, MA). DRIFT spectroscopy has been widely used in modified-surface studies of high surface area silica, such as Cab-o-Sil.^{21,22} The above method is preferred to transmission IR with pressed particle pellets, since hydrolysis of surface-attached silanes has been shown to occur as a consequence of the compression step.²³ DRIFT IR spectra for silylated zirconia and silica were obtained and were further processed by subtraction of the DRIFT spectra of clean unmodified samples of the corresponding native material. The resulting spectra are calculated in Kubelka–Munk (K–M) units, which for diffuse reflectance measurements have absorption values directly proportional to the concentration of absorbing species. Silylated zirconia and silica particles with coverages of approximately 16 and 27 $\mu\text{mol}/\text{m}^2$, respectively, were analyzed as representative samples.

Silylation coverages were determined by thermogravimetric analysis (TGA) (TGS-2, Perkin-Elmer Co., Norwalk, CT). Silylation coverage (n_s) was calculated as

$$n_s = 10^6 \frac{\Delta m_s}{(m_s)(S_s)(MW_{\text{silane}})} \quad (3)$$

where n_s is the silylation coverage ($\mu\text{mol}/\text{m}^2$), Δm_s is silylation weight gain for the support (g), m_s is the mass of the support material (g), S_s is the specific surface area of the support (m^2/g), and MW_{silane} is the molecular weight of the bonded silane molecule ($\text{g}/\text{g mol}^{-1}$). It is important to note that, as a silane unit hydrolyzes and/or condenses, the effective molecular weight associated with that silane unit will decrease. The average molecular weight for each VTMS unit can theoretically be as high as 125 g/mol for the case of monolayer coverage and as low as 79 g/mol for the case of complete hydrolysis and condensation in a vinyltrialkoxysilane network. For reporting simplicity, silylation coverages in this work were calculated by using the molecular weight resulting from monodentate attachment (i.e., one bond with the surface per silane unit) of the VTMS with no hydrolysis or condensation of the two remaining methoxy groups. This leads to a lower limit estimate of the actual number of vinyl groups.

Wafer Silylation and Characterization. The native oxide layer of prime-grade (100) silicon wafers (Wafernet, San Jose) were used as a surrogate surface for AFM analysis of the silylated layer. Wafers were first soaked in acetone and subsequently methanol to remove soluble organic contaminants. The wafers were then suspended in a 7:3 (v/v) solution of sulfuric acid and 30% hydrogen peroxide in water to thoroughly clean and oxidize the wafer surface (*Caution: this solution reacts violently with many organic materials and should be handled with extreme care*). Following oven-drying under vacuum at 110 °C, the wafers were wetted by immersion in deionized water and then equilibrated at approximately 50% relative humidity for 10 h prior to

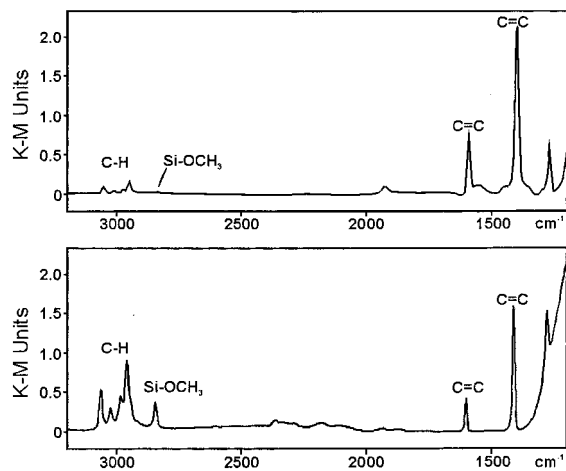


Figure 3. Diffuse reflectance IR spectra of silylated particles; top = zirconia, 16 $\mu\text{mol}/\text{m}^2$ VTMS; bottom = silica, 27 $\mu\text{mol}/\text{m}^2$ VTMS; Y-axis in Kubelka–Munk units.

silylation. The low surface area of the wafer prevented surface water determination by gravimetric methods; however, hydration obtained for particles equilibrated under similar conditions implies the presence of approximately one water monolayer on the wafer at the start of silylation. Silylation was performed in a reaction vessel with a condenser setup identical to the particle silylation reaction. The wafer was held in a stainless steel mesh basket suspended in a 1100-mL reaction solution of 10% v/v VTMS in xylenes solvent. Other silylation reaction conditions and equipment were identical to those listed above for the ceramic particles. At the end of the reaction, the wafers were triple-rinsed with xylenes and dried overnight at 130 °C under vacuum.

Elemental analysis of the silylated wafers was carried out by scanning Auger performed using a PHI 680 Auger Nanoprobe (Physical Electronics). AFM imaging of the unmodified and silylated wafers was performed at the Environmental Molecular Sciences Laboratory (Richland, WA), using a Digital Instruments (Santa Barbara, CA) multimode atomic force microscope with a Nanoscope IIIa SPM controller operating in tapping mode. Sample AFM images were taken for areas measuring 5×5 , 1×1 , and $0.2 \times 0.2 \mu\text{m}$. Root mean square (rms) surface roughness was obtained from analysis of 4–7 different $5 \times 5 \mu\text{m}$ areas on each wafer in order to obtain a representative sample.

Results and Discussion

Surface Characterization. The presence of VTMS on the surface of the silylated silica and zirconia particles is confirmed by the Fourier transform infrared spectra (Figure 3) in which the peaks at 1600 and 1410 cm^{-1} are characteristic of the C=C bond of vinylsilane. A series of four peaks that appear around 3000 cm^{-1} represent the C–H stretch resulting from VTMS vinyl and methyl groups. The single peak at 2840 cm^{-1} corresponds to absorption from the Si–OCH₃ alkoxy silane bond on the attached VTMS. Because unattached silanes will vaporize from the surface at the oven-drying conditions (vacuum, 130 °C) used in this work, the appearance of these peaks demonstrates the bonding of the silane to the silica surface.^{15,16,21}

The differences in absolute magnitude between peak areas on the two samples shown in Figure 3 are understandable, considering that the silylation coverage for the silica sample, calculated by TGA weight loss, was almost 70% higher than for the zirconia surface (27 vs 16 $\mu\text{mol}/\text{m}^2$). However, when the peaks are normalized to the vinyl peak area, it is apparent that the ratio of the Si–OCH₃ and C–H stretch absorption peak area to the vinyl peak area is much smaller for the silylated zirconia than for the silylated silica. This result suggests that the ratio of alkoxy silane group concentration to vinyl group concen-

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tration on the zirconia surface is lower than the corresponding ratio on the silica surface. A possible explanation for these results is a greater degree of postreaction hydrolysis of surface alkoxysilanes (i.e., loss of VTMS Si–OCH₃ groups to form Si–OH) for zirconia as compared to silica. In addition to greatly reducing the Si–OCH₃ peak at 2840 cm⁻¹, the loss of alkoxy groups through hydrolysis would lead to a reduction in the concentration of surface CH₃ groups and would also produce the observed decrease of the 3000 cm⁻¹ C–H stretch relative to the vinyl peak.

Accurate quantification of the number of moles of silane attached to high specific surface area (375 m²/g) silicas such as Cab-o-Sil has been performed by several researchers.^{16,21,23} However, the significantly lower surface area of silica and zirconia particles used in the present study represents a greater challenge to DRIFT analysis, since the resulting coverage in terms of gmoles of silane per gram of particles is several orders of magnitude lower than for Cab-o-Sil. Therefore, for the present choice of particles, DRIFT analysis was of insufficient resolution for accurately determining the surface silylation yield, and thus, thermogravimetric techniques were used as described in the text below.

The clean unmodified wafer possessed an almost completely flat surface (Figure 4a) with an rms surface roughness of 0.21 nm, which is in the range expected for a polished silicon wafer. The VTMS-silylated wafer surface, in comparison, had a rms roughness of 3.15 nm (for five separate, randomly chosen areas with standard deviation of 0.232 nm) and displayed a very different surface topology (Figure 4b). AFM images revealed that the silylated surface consisted of raised, roughly hemispherical clusters of material that are on the average about 10–20 nm high, separated on the average by about 50 nm. The visible structures had a mean diameter of 22 nm with a standard deviation of ± 10 nm; 90% of the clusters were smaller than 32 nm in diameter. Elemental analysis by XPS and scanning Auger confirmed that the clusters consisted primarily of carbon and silicon and did not detect any contamination on the surface.

The clusters observed in the AFM images (Figure 4b) have well-defined boundaries and are distributed on the surface without appreciable clumping. Characterization of the surface clusters using fractal dimension analysis resulted in a two-dimensional fractal dimension of 2.16, suggesting that the clusters are distributed randomly without ordered aggregation. The structures have smooth edges and do not appear to be the result of aggregation of smaller clusters. The cluster surface topology is believed to result from the formation of chemically attached polysilane networks grown on the surface during silylation and/or the attachment of solution-formed polysilanes by condensation reactions. It is noted that the hemispherical clusters resulting from VTMS silylation are similar to aggregates observed by Vandenberg et al. in the SEM of silicon wafers silylated with APTES in toluene solution.¹⁷ However, that work showed sporadic "weblike" structures on an inhomogeneous surface with a wide range of cluster densities, while AFM images of the current work show an even coverage of fairly uniform clusters.

Using a 200 × 200 nm scan (Figure 4c), the surface roughness was examined more closely to determine if modification was limited to large surface clusters. After inspection of the regions between the clusters that were visibly apparent at the 1- μ m level (i.e., 15 nm or greater diameter), it was found that the clusters vary continuously in size down to a very small scale (to the limit of tip convolution and AFM resolution). The rms roughness values resulting from these regions were about 0.6 nm,

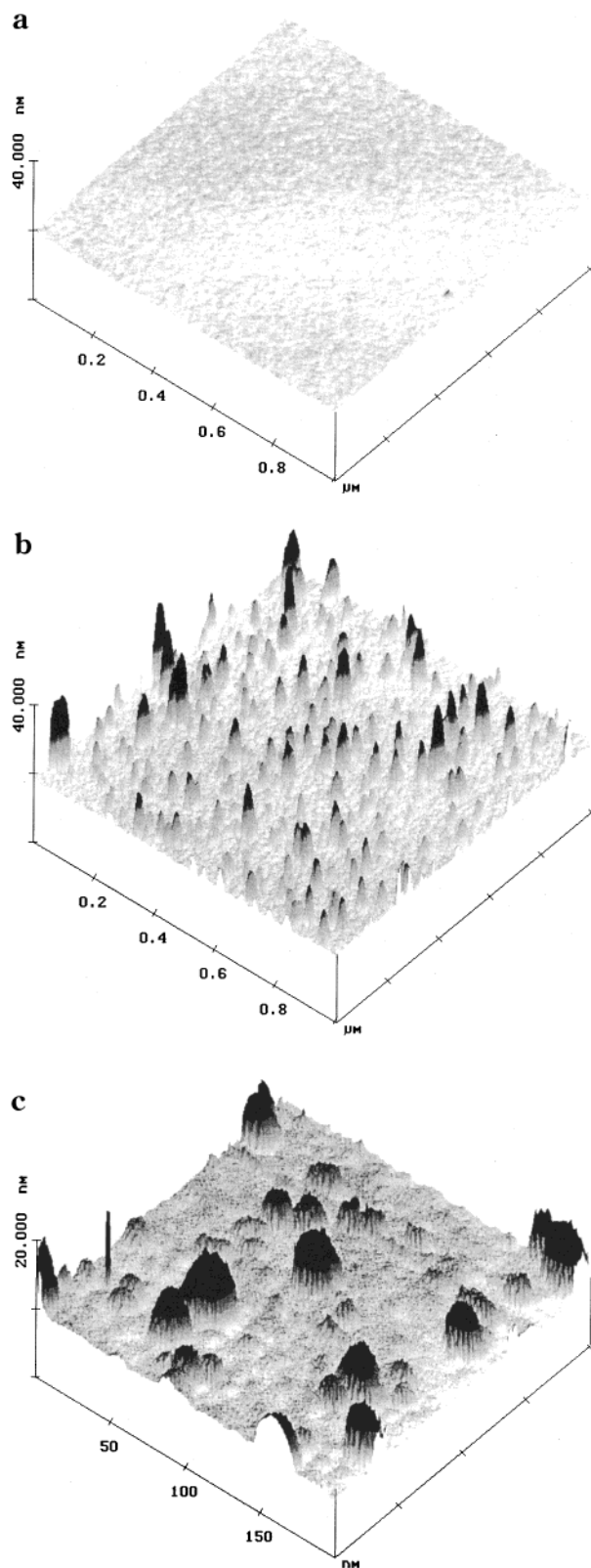


Figure 4. (a) AFM image of unmodified (clean) silicon wafer; 1 × 1 μ m region with a vertical scale of 40 nm. (b) AFM image of silylated silicon wafer; 1 × 1 μ m region with a vertical scale of 40 nm. (c) AFM image of silylated silyl "island" structures; 200 × 200 nm region with a vertical scale of 20 nm.

approximately 3 × higher than a 200 × 200 nm scan of an unmodified surface. This suggests that surface silylation was not simply limited to the elevated areas and that the majority of the surface was covered with surface-bonded VTMS clusters with a continuous size distribution. The

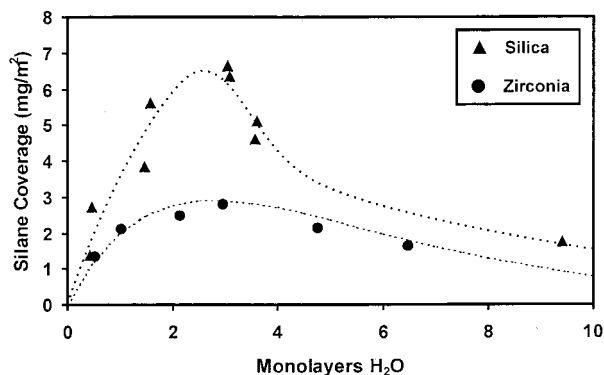


Figure 5. Effect of surface water on silylation coverage for silica and zirconia particles.

appearance of evenly distributed clusters in the AFM images shows that the surface silane coverage is heterogeneous at the nanometer scale but fairly uniform at the micrometer scale. The formation of the silane structures on the surface is affected by the presence of surface water as described in the following section.

Effects of Surface Water. Silylation experiments with both substrates confirmed that surface yield was a sensitive function of the initial amount of adsorbed water. To better illustrate the effect of surface water on the silylation process, it is instructive to express the amount of adsorbed water in terms of an equivalent number of adsorbed monolayers. For a given weight of adsorbed water, the number of equivalent monolayers (ψ) is given by

$$\psi = \frac{M_{\text{H}_2\text{O}} N_A A_{\text{H}_2\text{O}}}{MW_{\text{H}_2\text{O}} S_s} \quad (4)$$

in which $M_{\text{H}_2\text{O}}$ is the weight of adsorbed water (g), N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$), $MW_{\text{H}_2\text{O}}$ is the molecular weight of water, S_s is the support surface area (\AA^2), and $A_{\text{H}_2\text{O}}$ is the area of a water molecule, taken as 10.8 \AA^2 .²⁴

Surface silylation coverage was found to be negligible at low surface water coverage (Figure 5) but increased quickly with the number of water monolayers to a maximum at around 2–3 water monolayers, followed by a marked decline at higher initial surface water coverage. The silylation coverage on the silica particles was higher than on the zirconia particles over the range of water surface coverages investigated. The difference may be attributed, in part, to the lower initial OH concentration of about $5.6\text{--}5.9 \mu\text{mol/m}^2$ on fully hydroxylated zirconia, which is 22% lower than for silica ($7.4 \mu\text{mol/m}^2$). It is also reasonable to expect that not all of the rough zirconia surface (Figure 1) was accessible to the reacting silanes. This would result in further reduction in the zirconia silylation coverage relative to the Novacite silica particles.

The maximum and subsequent decline in silylation coverage at high surface water may be attributed to the hydrophobic nature of the vinyl group of VTMS. If the thickness of the surface water layer exceeds the size of the VTMS molecule, it would become increasingly difficult for the silanes in the reaction solution to penetrate the water layer and access the surface. We note that the thicknesses of one, two, and three monolayers of adsorbed H_2O , based on molecular modeling of a hydrogen-bonded structure of the water monolayers,¹⁸ are estimated as 1.16,

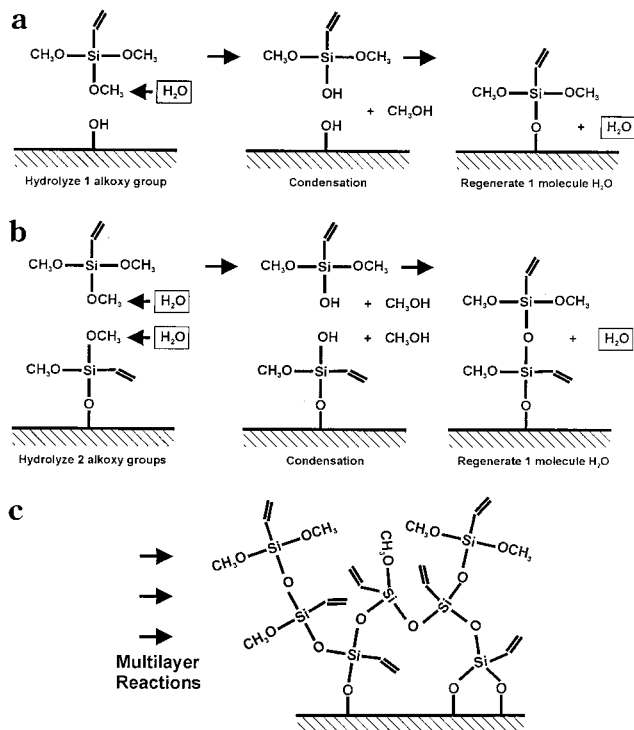


Figure 6. (a) Reaction for initial VTMS coverage (hydroxy/alkoxy). (b) Reaction for multilayer VTMS coverage (alkoxy/alkoxy). (c) Surface-bonded multilayer polysilane resulting from initial and multilayer reactions.

2.69, and 4.27 \AA , respectively. By comparison, the size of a completely hydrolyzed trialkoxysilane is about 3.02 \AA .²⁵ It is reasonable to expect that, above two monolayers of surface water, polysilanes can condense in the surface water layer without attaching to a surface hydroxyl. The above argument is consistent with the suggestion of Tripp and Hair (1992) that, when a thick surface water layer is present, silane molecules might condense in the water layer without covalent attachment to the surface.¹⁶ Unattached silanes that are formed in the water layer could be removed by the solvent or could temporarily remain on the surface, preventing accessibility and subsequent covalent attachment by other silanes. It must be noted that in the present study exhaustive postreaction washing of the silylated surfaces with xylene solvent was performed in order to remove physically deposited silanes.

A complete quantitative description of the silylation dependence on surface water is at present unavailable. However, the initial increase in silylation coverage with increasing surface water coverage (Figure 5) can be quantitatively rationalized based on a simple reaction model. In anhydrous silylation, initial surface attachments of VTMS proceed by the reaction between water molecules and alkoxy silanes to form hydrolyzed alkoxy silanes, which then condense with surface hydroxyl groups with the regeneration of water (eqs 1 and 2). Although the net reaction between the surface hydroxyls and the alkoxy silane molecules does not consume water, covalent bonding of silanes cannot proceed in the complete absence of water because water plays a catalytic role in this reaction.⁹ This behavior can be observed in Figure 5 as negligible silica and zirconia silylation coverages at surface water coverages less than approximately half of a monolayer.

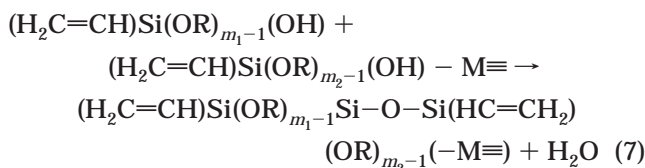
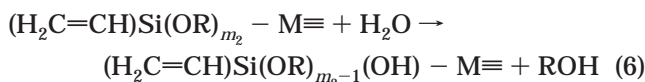
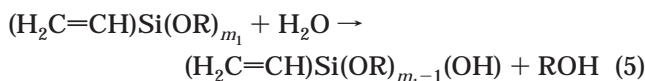
Once initial surface silylation coverage is achieved via first-layer reactions (eqs 1 and 2), subsequent growth of

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the silylated surface layer in that region of the surface will proceed by multilayer silylation reactions (Figure 6b). It is not expected (or necessary) that the entire surface will be covered with a monolayer prior to the advent of multilayer reactions, and thus first-layer and multilayer silylation reactions can proceed simultaneously in different areas of the surface. A schematic of the surface-bonded polysilane resulting from these reactions is shown in Figure 6c. It should also be noted that the schematic reactions shown in Figure 6a–c are not intended to provide a mechanistic view of the reactions (e.g., possible intermediate hydrogen-bonding steps between hydroxyl groups)¹⁵ and are only presented here to illustrate the subsequent stoichiometric analysis.

Multilayer silylation reactions proceed by hydrolysis of the alkoxy groups of a free silane (eq 5) and a surface silane (eq 6), followed by a condensation reaction (eq 7):



Unlike initial hydroxy/alkoxy condensation reactions (Figure 6a) between silica and an alkoxysilane, which do not consume water, the net reaction of two unhydrolyzed alkoxysilane molecules consumes one water molecule per siloxane bond formed, i.e., $\text{Si}-\text{OR} + \text{RO}-\text{Si} + \text{H}_2\text{O} \rightarrow \text{Si}-\text{O}-\text{Si} + 2\text{ROH}$. Because the available VTMS is greatly in excess in typical silylation reaction mixtures, the degree of multilayer silylation coverage is limited by the consumption of surface water. This was tested by increasing the initial VTMS concentration in the reaction mixture from 10 to 25% v/v for an initial surface water coverage of one monolayer. This increase in silane concentration did not result in increased silylation coverage, thereby supporting the assertion that the final coverage reached is limited by surface water coverage.

It should be noted that the above silylation mechanism (eqs 5–7) may not apply to silane molecules in which the fourth group of the silane molecule (i.e., the vinyl group for VTMS) is an active participant in the silylation reaction. For instance, studies of aminosilanes such as aminopropyltriethoxysilane have demonstrated that the amino group catalyzes the direct reaction between silane alkoxy groups and surface hydroxyl groups.^{13,14,17} However, even in the case of direct hydroxy/alkoxy condensation reactions, multilayer reactions must still follow the reaction stoichiometry outlined in Figure 6b and are thus limited to one siloxane bond formed per available surface water molecule.

For the regime where water is the limiting reagent for the silylation reaction, the stoichiometric relationships as stated by eqs 5–7 can be used to estimate the maximum possible bonded polysilane mass on the surface. As two alkoxy groups of two VTMS molecules react, one water molecule is consumed, leading to the formation of a polysilane bond (i.e., $\text{Si}-\text{O}-\text{Si}$; Figure 6b). Given the above, the number of silanes attached to the surface can

be estimated as the total number of reacted alkoxy groups divided by f_{bond} , the average number of reacted alkoxy groups per silane mer (i.e., structural unit within the surface silane network). It is apparent that in this analysis f_{bond} is a surface parameter similar to the degree of condensation c commonly used to describe bulk sol–gel processes.²⁶ The stoichiometric number of alkoxy groups that react with surface hydroxyls is simply equal to the initial surface hydroxyl concentration, N_{OH}^0 (gmol/m²), while the stoichiometric number of reacted alkoxy groups due to subsequent condensation reactions (Figure 6b) is $2\times$ the initial concentration of adsorbed surface water, $N_{\text{H}_2\text{O}}^0$ (gmol/m²). We note, however, that bonded alkoxy groups can hydrolyze and consume water without bonding to neighboring alkoxy groups, adding to residual surface hydroxyls denoted by N_{OH}^e (gmol/m²). Therefore, the expression for silane graft yield, N_{si} (gmol/m²), is given as

$$N_{\text{si}} = \frac{m_{\text{si}}}{\text{MW}_{\text{smr}}} = (1/f_{\text{bond}})(2N_{\text{H}_2\text{O}}^0 + N_{\text{OH}}^0 - N_{\text{OH}}^e) \quad (8)$$

in which m_{si} is the experimentally determined silane graft yield (g/m²), MW_{smr} is the average molecular weight of a silane mer within the attached polysilane, and f_{bond} can vary from unity (corresponding to monolayer silylation) to the maximum alkoxy functionality of the alkoxysilane precursor molecule (e.g., three for a vinyltrialkoxysilane). It is noted that, for a given initial surface water coverage, eq 8 implies that a lower f_{bond} would result in a higher number of attached silane molecules per unit surface area, since this suggests that a smaller number of surface water molecules would be required to be consumed per bonded silane. Therefore, it is suggested that when silylating with multifunctional alkoxysilanes (e.g., with $f \geq 3$) it may be possible to control the structure, surface density, and mass yield of the silane layer mixture by using a mixture of dialkoxy-, trialkoxy-, and tetraalkoxysilanes.

The f_{bond} value can be estimated from the experimental silylation mass data (Figure 5) using eq 8 and the value of MW_{smr} in the network. The average molecular weight in the network is obtained by considering a silane unit as containing one silicon atom, one or more nonhydrolyzable groups, $(f-f_{\text{bond}})$ hydrolyzable groups, and f_{bond} bridged oxygen atoms that it shares with other silane units, thus

$$\text{MW}_{\text{smr}} = (1/2)\text{MW}_{\text{O}}f_{\text{bond}} + (\text{MW}_{\text{hyd}})(f-f_{\text{bond}}) + (\text{MW}_{\text{R}}) + (\text{MW}_{\text{Si}}) \quad (9)$$

where MW_{O} is the molecular weight of an oxygen atom (16 g/gmol), MW_{hyd} is the molecular weight of a silane hydrolyzable group, MW_{R} is the combined molecular weight of nonhydrolyzable groups on the silane, and MW_{Si} is the molecular weight of a silicon atom (28 g/gmol). For VTMS, MW_{hyd} is 31 g/gmol ($-\text{OCH}_3$), MW_{R} is 27 g/gmol ($-\text{CH}=\text{CH}_2$), and f is 3; therefore, $\text{MW}_{\text{smr}} = (148 - 23f_{\text{bond}})$ and eq 8 becomes

$$m_{\text{si}} = (1/f_{\text{bond}})(148 - 23f_{\text{bond}})(2N_{\text{H}_2\text{O}}^0 + N_{\text{OH}}^0 - N_{\text{OH}}^e) \quad (10)$$

The application of eq 10 is reasonable when all of the surface is accessible to the reacting alkoxysilanes, as is expected for relatively smooth and impermeable surfaces. This condition is not fulfilled for the rough zirconia surface,

(26) Devreux, F.; Boilot, J. P.; Chaput, F.; Lecomte, A. *Phys. Rev. A* **1990**, *41* (12), 6901–6909.

where it is clear that the particle surface roughness (Figure 1) could render portions of the surface area inaccessible to the reacting alkoxy silanes as the reaction proceeds. In contrast, the surface of the impermeable silica Novacite particles is smoother; thus, in the present study, the analysis of eq 10 was applied only to the silica particles. Plotting eq 10 in the low surface water regime ($1/2$ –2 monolayers) as m_{si} vs $N_{\text{H}_2\text{O}}^p$ would then yield a straight line with a slope from which an estimate of f_{bond} can be derived. The same line would have an intercept of $(148/f_{\text{bond}} - 23)(N_{\text{OH}}^p - N_{\text{OH}}^e)$. Because initial surface hydroxyl concentration, N_{OH}^p , for a fully hydroxylated silica surface is about $7.4 \mu\text{mol}/\text{m}^2$, this provides a value for N_{OH}^e . The linear fit of eq 10 for the above region resulted in average values of $f_{\text{bond}} = 1.45$ and $N_{\text{OH}}^e = 2.0 \mu\text{mol}/\text{m}^2$. This residual hydroxyl concentration is much less than the initial concentration of surface hydroxyls. The above result is consistent with the observed hydrophobicity of the resulting modified surface and is expected, given that the silylation reaction was performed with a large stoichiometric excess of alkoxy silane. Although the values resulting from the fit are physically reasonable ($1 < f_{\text{bond}} < 3$ and $N_{\text{OH}}^e > 0$), it must be stressed that these parameter values are only estimates to illustrate the utility of the mass balance. In reality, it is plausible for f_{bond} to vary with the initial surface water coverage. Clearly, simultaneous experimental determination of the evolving surface silylation yield and network connectivity would be desirable to assess the precise effect of water over the entire range covered in the present study.

It is noted that several researchers^{12–14} have demonstrated cross-polarization/magic-angle spinning NMR analysis as a potential technique to directly determine network connectivity (and thus f_{bond}) of silica gel modified with γ -aminopropyltriethoxysilane; a similar study on anhydrous silylation of VTMS would be beneficial but is yet to be performed. DRIFT techniques that are more suitable for low specific area silica and zirconia particles could provide similar information on the structural

makeup of the silane layer and could also be used to establish a better value for f_{bond} . Finally, we note that, in the region past the maximum silylation coverage (Figure 5), the silylation efficiency is significantly reduced, which as suggested previously is attributed in part to the formation of polysilanes and thus reduced surface attachment due to steric effects. In this region, eq 10 is not applicable, and this suggests the need for a theory that accounts for bulk polysilane formation and the ensuing effect.

Conclusions

Silylation experiments performed on silica and zirconia particles show that silylation coverage with alkoxy silanes on oxide surfaces can be quantitatively controlled by varying the initial amount of adsorbed water on the support surface. AFM imaging confirmed a clusterlike surface morphology consisting of uniformly distributed polysilane structures of a 22 nm mean diameter but also suggested that VTMS clusters varied in size down to a very small scale. Low or nonexistent silylation coverages at very low surface water coverages are consistent with reports of similar behavior found in the literature. The initial increase in silylation coverage at low water coverage follows from the multilayer silylation reaction stoichiometry. In this region, the degree of network connectivity was estimated, based on the reaction stoichiometry, in terms of the average number of reacted alkoxy groups per silane mer in the network. A decline in the silylation coverage was observed past a maximum at an initial water coverage of about two water monolayers. In this regime, it is postulated that free hydrophobic VTMS molecules may condense in the surface water layer to form polysilanes that are only physically deposited on the surface. Unlike covalently bonded multilayer silanes, these physically attached polysilanes are removed by the postreaction solvent wash.

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