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How to Prevent the Loss of Surface Functionality Derived from Aminosilanes

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Abstract

Aminosilanes are common coupling agents used to functionalize silica surfaces. A major problem in applications of 3-aminopropylsilane-functionalized silica surfaces in aqueous media was encountered: the loss of covalently attached silane layers upon exposure to water at 40 °C. This is attributed to siloxane bond hydrolysis catalyzed by the amine functionality. To address the issue of loss of surface functionality and to find conditions where hydrolytically stable amine-functionalized surfaces can be prepared, silanization with different types of aminosilanes was carried out. Hydrolytic stability of the resulting silane-derived layers was examined as a function of reaction conditions and the structural features of the aminosilanes. Silane layers prepared in anhydrous toluene at elevated temperature are denser and exhibit greater hydrolytic stability than those prepared in the vapor phase at elevated temperature or in toluene at room temperature. Extensive loss of surface functionality was observed in all 3-aminopropylalkoxysilane-derived layers, independent of the number and the nature of the alkoxy groups. The hydrolytic stability of aminosilane monolayers derived from N-(6-aminohexyl)aminomethyltriethoxysilane (AHAMTES) indicates that the amine-catalyzed detachment can be minimized by controlling the length of the alkyl linker in aminosilanes.

INTRODUCTION

Aminopropylalkoxysilanes are widely used as coupling agents^{1,2} due to their bifunctional nature. Their applications in aqueous media have been developed at a rapid pace because of the increasing relevance of surface chemistry to life and environmental sciences.³⁻⁹ The presence of the amine functionality offers aminosilanes unique properties. The amine groups can catalyze, inter- or intra-molecularly, the reaction between silane molecules and surface silanol groups to form siloxane bonds.¹⁰ For the same reason, aminoalkoxysilanes are more reactive than alkylalkoxysilanes towards water, which can cause uncontrolled polymerization/oligomerization of aminosilanes in solution. Additionally, amine groups can hydrogen bond with surface silanol groups. Thus, covalently attached aminosilane layers typically have low grafting densities due to the presence of vertically (Figure 1a) as well as horizontally (Figure 1b) positioned silane molecules.¹⁰ Hydrogen bonding interactions with surface silanols alone result in weakly attached silane molecules on silica surfaces (Figures 1c-e).

3-aminopropyltriethoxysilane (APTES) and 3-aminopropyldimethylethoxysilane (APDMES) are two commonly used aminosilanes. Chemical structures and abbreviations of the silanes discussed in this report are shown in Figure 2. Due to the presence of a single ethoxy moiety in each APDMES molecule, its reaction with silica is easier to control and should result in amine-functionalized monolayers. APTES is more commonly used because of its lower cost. Fadeev and McCarthy pointed out the complexity of silane layer structures resulting from silane molecules containing multiple reactive sites.¹¹ APTES has three ethoxy groups per molecule

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and is capable of polymerizing in the presence of water, which can give rise to a number of possible surface structures: covalent attachment, two-dimensional self-assembly (horizontal polymerization), and multilayers (vertical polymerization). It is necessary, however, to have some water at the interface to form APTES multilayers in organic solvents¹² and the number of protonated amine and hydrolyzed ethoxy groups in the silane layers depends on the amount of surface water present.¹³ A significant amount of effort has been expended on correlating reaction conditions, i.e. solvent, amount of water, reaction temperature and time, and silane concentration, to silane layer structures in terms of thickness, surface roughness, and the nature of bonding.¹⁴⁻²¹ In general, anhydrous solvents with a trace amount of water and low silane concentrations are desirable for the preparation of smooth APTES-derived silane layers.¹⁶ Vapor phase silanization has also been reported to produce smooth APTES monolayers.²⁰ Solvent rinsing procedures and drying methods are also critical to the quality of aminosilane layers. Due to the presence of hydrogen bonds in silane layers, rinsing with water can completely displace weakly bonded aminosilanes.¹⁷ Drying procedures have been used to ensure that covalent bond formation proceeds through condensation of hydrogen-bonded silanol groups and have been carried out under a nitrogen stream,²¹ under vacuum,¹⁴ or in an oven.^{15-17, 19}

While most of the literature on aminosilanes has focused on the reaction conditions for the preparation of covalently attached silane layers with controlled thickness and topography, the hydrolytic stability of the attached aminosilane layers is vital to the applications and further derivatizations of the functionalized substrates in aqueous media. The importance of hydrolytic stability of attached silanes in their applications has been realized since the early days.^{1,2} Fiberglass – reinforced polymer composites have been subjected to static immersion tests in hot water to assess the strength of the adhesive joints and silane coupling agents at the interfaces have been shown to improve the mechanical properties of the composites.¹ The equilibrium constants of hydrolysis and formation of siloxane bonds at substrate – water interfaces have been quantified.¹ Even though the consensus has been that chemical bonding between silane molecules and silica surfaces is necessary to ensure hydrolytic stability of attached silane layers, hydrolysis of the Si-O-Si linkages can occur under certain conditions. For example, siloxane bonds in polydimethylsiloxane are stable to hydrolysis only within the pH range of 2 and 12.² Fadeev et al. recently proposed that acid/base-catalyzed hydrolysis of siloxane bonds is responsible for the displacement of covalently attached monolayers of $R(CH_3)_2Si-$ by other silanes of the type of $R'(CH_3)_2SiX$, where $-X$ is either $-Cl$ or $-N(CH_3)_2$.²² Other studies point out that the amine functionality of APTES catalyzes the hydrolysis of Si-O-Si bonds in the covalently attached silane layers intra-molecularly via the formation a five-membered cyclic intermediate.^{23,24}

In this report, hydrolytic stability of aminosilane-derived layers was examined as a function of silanization conditions and the nature of the silanes. Stability concern was limited to in pure water since the effect of pH on the hydrolysis of siloxane bonds has been reported earlier.^{2, 22,23} Silane layers prepared in anhydrous toluene at elevated temperature are higher in packing density and exhibit greater hydrolytic stability than those prepared in the vapor phase or at room temperature. That all of the 3-aminopropylsilane-derived layers examined in this study underwent extensive hydrolytic degradation is attributed to the inherent structural feature of the silanes, i.e. the primary amine can coordinate to the silicon center and catalyze hydrolysis via the formation of a stable five-membered ring. The preparation of hydrolytically stable aminosilane monolayers using N-(6-aminohexyl)aminomethyltriethoxysilane, a commercially available aminosilane, is also reported and this illustrates that amine-catalyzed detachment can be minimized by controlling the length of the alkyl linker to discourage the intra-molecular catalysis.

EXPERIMENTAL

General

Silicon wafers were obtained from International Wafer Service (100 orientation, P/B doped, resistivity 1-10 Ωcm , thickness 450-575 μm). 3-aminopropyldimethylethoxysilane (APDMES), 3-aminopropyltriethoxysilane (APTES), 3-aminopropyltrimethoxysilane (APTMS), propyldimethylmethoxysilane (PDMMS), and N-(6-aminohexyl) aminomethyltriethoxysilane (AHAMTES) were purchased from Gelest, Inc. and stored in Schlenk flasks under nitrogen. House purified water (reverse osmosis) was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange and filtration steps (18.2 M Ωcm). Toluene (HPLC grade, Fisher) was dried and deoxygenated through a solvent purification system (Pure Solv, Innovative Technology Inc.). Other reagents were used as received from Fisher. All glassware was cleaned in a base bath (potassium hydroxide in 2-propanol and water), rinsed with distilled water (3x), and stored in a clean oven at 110 °C until use.

Instrumentation

Thickness measurements were carried out with an LSE Stokes Ellipsometer. The light source is a He-Ne laser with wavelength of 632.8 nm and a 70° angle of incidence (from the normal to the plane). Thickness was calculated using the following parameters: air, $n_o = 1$; silicon oxide and silane-derived layers, $n_1 = 1.46$,^{11,14,17} silicon substrate, $n_s = 3.85$ and $k_s = -0.02$. Measurement error is within 1 Å as specified by the manufacturer. The standard deviation of reported thickness values – averages of three measurements on each of at least four samples prepared in at least three separate batches – is within the instrument error unless it is specified otherwise. Contact angle was measured with a Rame-Hart telescopic goniometer with a Gilmont syringe and a 24-gauge flat-tipped needle. The probe fluid was Milli-Q water. Dynamic advancing (θ_A) and receding (θ_R) angles were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The standard deviation of reported contact angle values – averages of four measurements on each of at least three samples prepared in separate batches – is less than 2°. Atomic force microscopy images were obtained with a Veeco Metrology Dimension 3100 atomic force microscope with a silicon tip operated in tapping mode. Roughness of surface features was determined using the Nanoscope software.

Functionalization of Silicon Wafers

Silicon wafers were cut into 1.3 x 1.5 cm pieces and cleaned by submerging in a freshly prepared piranha solution containing 7 parts concentrated sulfuric acid and 3 parts 30% hydrogen peroxide for 1 h (*caution: piranha solution reacts violently with organic matter*). Wafers were then removed from the solution, rinsed with copious amounts of water, and dried in a clean oven at 110 °C for 30 min. Vapor phase silanization was carried out by suspending freshly cleaned wafers in a closed Schlenk flask containing ~0.5 mL of silane at 70 °C for a desired amount of time. There was no contact between the samples and the liquid silane. Solution phase silanization was carried out in 25 mL of anhydrous toluene containing 0.5 mL of silane under nitrogen at either 20 °C or 70 °C for a desired amount of time. The wafers were then rinsed individually with toluene (2x), ethanol (2x), and water (2x), and dried at 110 °C for 15 min in a clean oven. Characterization was carried out immediately upon cooling.

Hydrolytic Stability of Silane-Derived Layers

Freshly silanized samples were immersed in Milli-Q water at 40 °C for up to 48 h. Samples were then rinsed with water and dried in an oven at 110 °C for 15 min before characterization.

RESULTS AND DISCUSSION

Silanization using APDMES was carried out under different reaction conditions as described in the experimental section with reaction time maintained at 24 h to ensure the completion of reactions. As part of the post silanization treatment, rinsing with toluene, ethanol, and water was carried out to remove physisorbed silanes and to hydrolyze any residual ethoxy groups in the attached silane layers. Drying under a nitrogen stream, under vacuum, and in an oven at 110 °C were also evaluated in order to effectively drive condensation to form stable siloxane bonds. Results (not shown) indicate that oven drying is necessary to promote condensation and siloxane bond formation, which is consistent with literature reports.¹⁶

Stability of the attached APDMES layers was examined by immersing silanized samples in water at 40 °C for 24 h and 48 h. 40 °C was chosen to simulate (in a slightly accelerated manner) biological media where amine-functionalized surfaces with or without attached agents are often applicable. Thicknesses of the silane-derived layers and water contact angle data of the silanized samples before and after immersion are shown in Table 1. The standard deviation of all reported thickness values is within the instrument error of 1 Å unless it is specified otherwise. The standard deviation of reported contact angle values is less than 2°. All reaction conditions resulted in APDMES monolayers with very similar water contact angles, which are consistent with the reported contact angle values of 68.4°/45.2° and 62.5°/38.7° (θ_A/θ_R) on APDMES monolayers prepared in the vapor phase with and without pre-adsorbed ethylenediamine, respectively.¹⁰ The slightly lower thicknesses of the silane layers obtained from reactions in toluene at 20 °C and in the vapor phase are attributed to the presence of horizontally positioned silanes as shown in Figure 1b. On the other hand, higher molecular mobility is attained at higher temperature and in solution to overcome hydrogen bonding interactions between amine groups and surface silanols. This results in more vertically positioned silanes present in the monolayer prepared in toluene at 70 °C, as shown in Figure 1a. It is not unreasonable to expect slight differences in monolayer structures as a function of preparation conditions. What is noteworthy is the loss of APDMES silane layers upon exposure to water at 40 °C – those prepared at 20 °C in toluene are completely detached after 24 h and those prepared at 70 °C in toluene and in the vapor phase exhibited close to 50% decrease in thickness after 48 h. Water contact angles of silanized samples decrease drastically upon water exposure also indicating loss of silane molecules from the sample surfaces. The observed value of 11°/0° on the APDMES sample prepared at 20 °C in toluene after 48 h exposure to water are very close to those of clean silicon wafers, 6°/0°, which confirms the complete detachment of the APDEMS silane layer. Due to the multiple anchoring modes of the silane to the substrate as shown in Figure 1, the partial loss of the silane layers can be attributed to those silanes which are attached by only hydrogen bonding interactions between the surface silanols and ethoxy, silanol, or amine moieties of the silane molecules. The complete loss of the silane layers in aqueous media has to be attributed to the hydrolysis of the siloxane bonds between APDMES and the silica substrate, which is consistent with the hydrolysis of covalently attached APTES layers reported in literature.^{23, 24} The degradation in these attached aminosilane layers is catalyzed by the amine functionality, either intra-molecularly via the formation of a five-membered cyclic intermediate or inter-molecularly. The hypothesis is further supported by the fact that the extent of silane loss depends on the APDMES monolayer thickness (as the result of silane attachment density): the loss is the most drastic when the silane grafting density is the lowest and there is more space for the amine group to coordinate with the siloxane moiety.

We have made attempts to prepare stable amine-functionalized silane layers on silicon oxide substrates. Attention was first turned to the triethoxy analogue, APTES. Even though the amine functionality was expected to catalyze hydrolysis of siloxane bonds, it was speculated that the multiple siloxane bonds formed per molecule – with surface silanols and neighboring APTES molecules – could provide enough resistance to hydrolysis. The difficulties in working with

APTES lie in the potential hydrogen bonding interactions between the amine functionality and surface silanol groups¹⁰ as well as the three ethoxy groups giving rise to multiple reaction modes and difficulty in controlling silane layer structures¹¹ as discussed earlier.

Kinetics studies of APTES were carried out in anhydrous toluene at 70 °C, under which condition the highest density of APDMES layer was prepared (Table 1). Silanized samples were then immersed in Milli-Q water at 40 °C for up to 48 h, dried, and re-characterized. As shown in Table 2, the thickness of the silane layers is readily controllable by reaction time indicating that the trace amount of water present in anhydrous solvent and on glassware is sufficient for the preparation of APTES layers. The APTES layer prepared at 3 h silanization time is 10 Å thick, which corresponds to the reported thickness of 9 ± 1 Å for an APTES monolayer.²¹ APTES layers prepared at longer silanization times are thicker due to the formation of multilayers, e.g. silanization time of 19 h resulted in layer thickness of 57 ± 15 Å. The high standard deviation of the multilayer thickness is a direct result of the sensitivity of multilayer formation to water content in the system (humidity and the dryness of solvent and glassware). The water contact angles of the prepared APTES monolayer and multilayer are within the same small range, 38-43°/15-22° (θ_A/θ_R). The lower contact angle values indicate the hydrophilic nature of the APTES surfaces with exposed amine functionality. Water contact angles of APTES layers reported in literature vary widely – with advancing angles in the range of 51° to 93° in one study¹⁴ and from 23° to 70° in another study²¹ – depending on silanization conditions, aging of the samples, and measurement conditions.²⁰ All of the APTES functionalized substrates, however, exhibited complete loss of attached silane layers upon water immersion based on thickness data (Table 2). Other attempts to form hydrolytically stable 3-aminopropylsilane-derived layers also failed (data not shown here), including silanization with APTES in the vapor phase at 70 °C and in toluene at room temperature, using preformed APTES oligomers/polymers by incorporating controlled amount of water to the reaction media, and with 3-aminopropyltrimethoxysilane (APTMS).

In order to confirm the detachment mechanism of 3-aminopropylsilane layers in aqueous media, control experiments were carried out with n-propyldimethylmethoxysilane (PDMMS) in toluene at 70 °C for various amounts of time. The results are shown in Figure 3. The prepared PDMMS monolayers with different densities experience negligible loss (within the thickness measurement error) in water at 40 °C for up to 48 h. Another interesting feature is that the rate of silanization with PDMMS is significantly slower than that with aminosilanes (Tables 1 and 2), which indicates the role of amine functionality in catalyzing aminosilane attachment. The contact angles of the PDMMS-derived layers prepared at 2 h, 24 h, 72 h silanization time are 35°/21°, 53°/40°, 70°/60°, respectively, which are consistent with the thickness increase of the silane layers. Furthermore, that these contact angle values are not higher than those of the APDMES- and APTES-derived layers indicates that water can penetrate the PDMMS layers to similar extent. The hydrolytic stability of the PDMMS-derived layers thus points to the catalytic role of the amine functionality in aminosilane attachment as well as detachment mechanisms.

The remainder of this study involved selecting alternate aminosilanes to allow the preparation of hydrolytically stable silane layers. Since the formation of a stable five-membered cyclic intermediate is the suspected mode of amine catalysis, we turned our attention to those aminosilanes that have different length of alkyl linkers so that the formation of ring structures in the catalytic step is not favorable. N-(6-aminoethyl)aminomethyltriethoxysilane (AHAMTES), a commercially available and economical silane, fits this criterion. Kinetics studies of silanization with AHAMTES were carried out and the hydrolytic stability of the silanized samples was examined as shown in Figure 4 and Table 3. The silanization kinetics of AHAMTES is similar to that of APTES indicating that the contribution from inter-molecularly catalyzed attachment by amine groups is significant since the intra-molecular

mechanism is not likely in AHAMTES. The large standard deviation in the initial thickness of the AHAMTES multilayers (24 h) is attributed to humidity variation on the summer days when three different batches were prepared; there is little variation among samples prepared in the same batch. The most striking feature in Figure 4 is that silane layers of ~ 10 Å thick – which correspond to a close packed monolayer of AHAMTES considering the molecular size of the silane – remain on the substrates upon water immersion regardless of the initial thicknesses of the silane layers prepared. The residual silane layers are stable since all the degradation occurs within the first 24 h of immersion and no additional loss is observed between 24 h and 48 h immersion time (Table 3). AFM images of AHAMTES layers prepared at 1 h and 24 h silanization time and the samples from the same batch after immersion in water for 24 h are shown in Figure 5. The silane layer thickness and root-mean-square (rms) roughness of each sample are also shown. To provide contrast to the monolayer prepared at 1 h silanization time, a sample from a batch with large thickness was chosen for the 24 h silanization condition. 1 h silanization results in a relatively smooth monolayer, which experiences negligible change in thickness and surface features upon immersion in water indicating the absence of hydrolytic degradation of the silane layer. On the other hand, rough features with “islands” were observed on the multilayer samples prepared at 24 h silanization time. Upon water immersion, the thickness of the silane layer decreases dramatically to that of a monolayer but the surface features of the remaining layer have resemblance to those of the initial multilayer. Although the residual silane layers are comparable in thickness thus amine content, the monolayer prepared at 1 h silanization time is preferable to the multilayers prepared at longer silanization time for aqueous applications: leaching of degraded silane molecules to the aqueous environment is avoided and the monolayer has more uniform amine density across the surface.

Advancing and receding water contact angles of the four samples are within a small range of $45\text{--}54^\circ/18\text{--}21^\circ$ (θ_A/θ_R). The multilayer sample has a noticeably higher advancing contact angle and a slightly lower receding contact angle and thus larger hysteresis ($\theta_A - \theta_R$) than the other three samples, which is in agreement with the effect of roughness on contact angles. In general, water contact angles of these AHAMTES layers are low indicating that amine groups are exposed to surfaces to render the silane layers hydrophilic. This suggests that attachment of other reagents to the exposed amine groups is feasible.

SUMMARY

All surfaces prepared from all 3-aminopropylsilanes under all conditions studied exhibit hydrolysis, suggesting that the γ -aminopropylsiloxane structure is inherently more reactive than other aminoalkylsiloxanes, due largely to their ability to form stable cyclic intermediates. The hydrolytic stability of AHAMTES monolayers, either directly prepared or resulting from degraded multilayers, is special with respect to the rest of the aminosilane-derived surfaces described here. The degradation of AHAMTES multilayers to monolayers that do not degrade further is also noteworthy.

AHAMTES-derived monolayers appear to be resistant to hydrolysis indicating that neither intra- nor inter-molecular amine-catalysis is attainable. The arrested hydrolysis of the AHAMTES multilayers suggests that the density of these layers is lower (with more defects) allowing for inter-molecular amine-catalyzed hydrolysis. Other aminosilanes that have either shorter or longer alkyl linkers than propyl may be good candidates for aqueous applications as well.

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Figure 1.
Different types of bonding/interaction between aminopropylethoxysilane molecules and silicon oxide substrates.

Figure 2.
Chemical structures and abbreviations of the silanes studied in this report.

Figure 3. Thickness of PDMMS-derived silane layers as a function of silanization time in toluene at 70 °C (●) and after water exposure at 40 °C for 24 h (Δ) and 48 h (□).

Figure 4. Thickness of AHAMTES-derived silane layers as a function of silanization time in toluene at 70 °C (●) and after water exposure at 40 °C for 24 h (Δ) and 48 h (□).

Figure 5.

AFM images ($2 \times 2 \text{ }\mu\text{m}$, height scale is 20 nm) of covalently attached AHAMTES layers prepared in toluene at 70 °C for 1 h (top left) and 24 h (bottom left) and the corresponding samples after immersion in water at 40 °C for 24 h (right).

Table 1

Thickness and water contact angle (θ_A/θ_R) data of attached APDMES monolayers before and after exposure to water at 40 °C.

	Initial		After 24 h exposure		After 48 h exposure	
	T (Å)	C. A. (°)	T (Å)	C. A. (°)	T (Å)	C. A. (°)
APDMES (toluene, 70°C)	4.7	66/41	3.3	25/12	2.8	28/17
APDMES (vapor, 70°C)	3.6	67/42	1.8	20/12	2.0	21/14
APDMES (toluene, 20°C)	3.5	65/42	0.2	17/10	0.1	11/0

Table 2

Thickness of APTES-derived silane layers as a function of silanization time in toluene at 70 °C and after exposure to water at 40 °C.

Silanization time (h)	Initial (Å)	After 24 h (Å)	After 48 h (Å)
1	4	<1	<1
1.5	4	<1	<1
3	10	1	1
19	57 ± 15	2	1

Table 3

Thickness and water contact angle (θ_A/θ_R) data of AHAMTES-derived silane layers as a function of silanization time in toluene at 70 °C and after exposure to water at 40 °C.

Silanization time (h)	Initial		After 24 h exposure		After 48 h exposure	
	T (Å)	C. A. (°)	T (Å)	C. A. (°)	T (Å)	C. A. (°)
1	11 ± 1	49/21	9 ± 1	45/19	10 ± 1	43/20
2	14 ± 2	51/17	10 ± 3	43/16	10 ± 2	45/16
4	22 ± 2	50/19	9 ± 3	44/18	10 ± 1	43/20
8	27 ± 3	50/22	9 ± 1	44/18	13 ± 1	48/17
16	30 ± 3	55/23	11 ± 1	45/20	12 ± 1	44/19
24	39 ± 26	54/18	12 ± 1	48/20	14 ± 1	48/22