Optimization of Silica Silanization by 3-Aminopropyltriethoxysilane

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Thin films of 3-aminopropyltriethoxysilane (APTES) are commonly used to promote adhesion between silica substrates and organic or metallic materials with applications ranging from advanced composites to biomolecular lab-on-a-chip. Unfortunately, there is confusion as to which reaction conditions will result in consistently aminated surfaces. A wide range of conflicting experimental methods are used with researchers often assuming the creation of smooth self-assembled monolayers. A range of film morphologies based on the film deposition conditions are presented here to establish an optimized method of APTES film formation. The effect of reaction temperature, solution concentration, and reaction time on the structure and morphology was studied for the system of APTES on silica. Three basic morphologies were observed: smooth thin film, smooth thick film, and roughened thick film.

Introduction

Aminated silane films are currently used in a wide variety of both industrial and research-oriented applications. Specifically, 3-aminopropyltriethoxysilane (APTES) is a commonly used coupling agent for the modification of silica surfaces to increase adhesion in fiberglass-epoxy composites.[1−4] APTES is used to promote adhesion of polymer films on glass[5,6] or is used as a coupling agent to produce temperature-[7] and photoresponsive films[8] on silica. APTES films are also used to promote protein adhesion[9−11] and cell growth[12] for biological implants and in lab-on-a-chip applications.[13−15] APTES is also used in attaching metal nanoparticles to silica substrates because of the strong interaction between the amine group and the metal particles.[16,17]

While many studies focus on the characterization of APTES[8,18−25] or other alkoxysilane[26−28] films, most are limited in scope, focusing on single reaction variables or a narrow set of deposition conditions without offering a clear, comprehensive guide to the best method of film formation. As a result, there is a wide range of reaction conditions used to deposit APTES films. There are, however, some basic mechanisms which are well established and agreed upon. Hydrolysis of silane drives the attachment of the APTES to the substrate resulting in siloxane bonds at the substrate surface.[29] Basic functional groups such as amines will self-catalyze the hydrolysis reaction leading to more aggressive monolayer formation as compared to nonaminated silanes.[18] The initial hydrolysis step can occur either in solution or at the substrate surface depending on the amount of water present in the system. An overabundance of water will result in excessive polymerization in the solvent phase, while a deficiency of water will result in the formation of an incomplete monolayer.[30]

Some of the studies surveyed claimed to be forming APTES monolayers via self-assembly. As described by Xia et al., SAMs are 2-D quasicrystalline, single molecular layer thin films which tend to be self-healing and defect-rejecting.[31] Because of the favorable head-and-tail group interactions, APTES can form zwitterions in solution and at the film surface,[24] resulting in multilayer formation as reaction time is extended.[32] APTES films are subject to disorder, even as a monolayer, as it is possible for the amines to hydrogen bond to the substrate or for the entire molecule to bend such that the head-and-tail groups are oriented

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toward the substrate surface.[18] APTES does not self-assemble as the surface reaction is neither well-ordered nor self-limiting.

Solvent, concentration, reaction time, and reaction temperature also have an effect on the attachment kinetics, but most studies only examine one or two of these parameters. Left uncontrolled, APTES deposition will proceed to form very thick, roughened layers.[18] Thick APTES layers may be useful for some applications but can be detrimental if depositing on spatially constrained regions.[33] Thus, it is often important to ensure that APTES deposits as a smooth thin film and does not experience aggregation at the surface or the deposition of multilayers. Incomplete coverage of the surface by APTES can be equally problematic. Understanding the mechanisms and kinetics of the monolayer formation is critical to creating well-controlled surfaces.

The aim of this work is to establish the optimum reaction conditions for preparing uniform thin films of APTES on silica. The ideal film in this system will have maximum surface coverage of amine functional groups and surface roughness on the order of the underlying substrate. The APTES films were characterized using X-ray photoelectron spectroscopy (XPS), ellipsometry, atomic force microscopy (AFM), and dynamic water contact angle analysis to determine ideal reaction conditions.

Experimental Methods

Materials. Anhydrous toluene, methanol, hydrogen peroxide, sulfuric acid, and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich and were used as received. Water was deionized in-house to a resistivity of 18.3 MΩ using a Barnstead Nanopure Infinity filtration system. While water concentration was not explicitly characterized,[34] control over water concentration was maintained by using silica substrates of equivalent surface area and treatment history.[35] Additionally, equal volumes of anhydrous toluene solution were used for each specimen as toluene has been shown to extract surface-adsorbed water from silica into solution, subsequently affecting silane deposition.[30]

Surface Modification. Silicon wafers were cut into 1 cm^2 slides and were cleaned by exposure to ultraviolet light in the presence of oxygen for 30 min followed by immersion in piranha solution (2:1 sulfuric acid to hydrogen peroxide) for 30 min. Slides were thoroughly rinsed in DI water and were dried under vacuum. The silicon slides were placed in individual vials which were sealed and backfilled with nitrogen through a septum. Anhydrous toluene was added to each sealed vial followed by the addition of APTES to create solution concentrations of 1%, 10%, or 33% APTES by volume (0.0345 molar, 0.345 molar, and 1.725 molar solutions, respectively). Total solution volume was consistently 2 mL for each slide. Solutions were held at temperature of either 25 °C or 75 °C. The reaction time was either 1, 24, or 72 h. Upon completion of specified reaction time, slides were removed from the APTES solution and were rinsed under flowing toluene, followed by methanol, and finally DI water. Hydrolysis of residual ethoxy functionalities was performed by immersion in DI water for 24 h at 25 °C. Slides were then dried under vacuum. Control slides were subjected to the same procedure as the other specimens but were only exposed to pure anhydrous toluene instead of an APTES solution.

Characterization Techniques. Dynamic contact angle measurements were taken using a Ramé-Hart Advanced Automated Model 500 Goniometer. Advancing and receding contact angles were measured with DI water. Reported values represented an average of at least three measurements per specimen. Film thickness measurements were taken on a Gaertner L116S Variable Angle Stokes Ellipsometer. The light source was a He−Ne laser with λ of 544 nm. The angle of incidence (from the normal to the plane) was 70°.

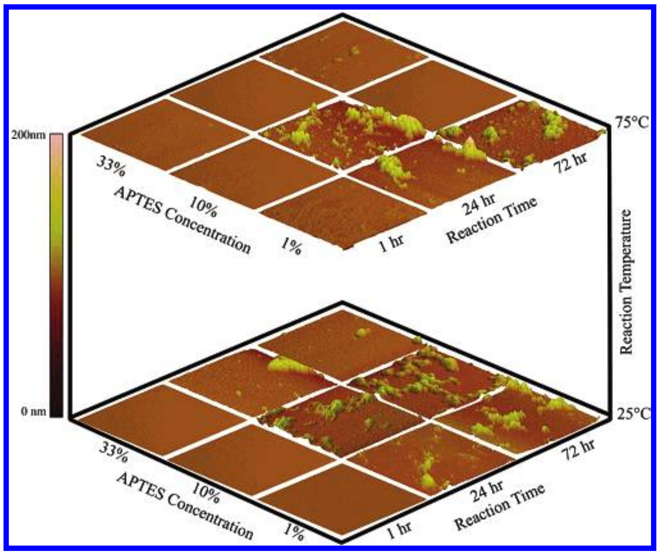

Figure 1. Three-by-three matrix of atomic force microscopy (AFM) scans of APTES films. Each individual image is 2 μm × 2 μm with a height scale of 200 nm (displayed left).

Measurements were performed for three to five different spots on each specimen. The following refractive indices were used: $n_{\text{air}} = 1.0$, $n_{\text{silica}} = 1.465$, and $n_{\text{APTES}} = 1.465$.[34] Control slides were measured to have a native silica layer of 2.5 nm. This value was subtracted from the calculated thickness as the silica and APTES were assumed to be optically identical. Atomic force microscope images were collected in tapping mode using a MultiMode Scanning Probe Microscope produced by Digital Instruments. Initially, areas of 25 μm^2 were imaged as surveys; images for publication were of a 4 μm^2 area. All images were processed with a first-order $X-Y$ plane fit; images were otherwise not altered. X-ray photoelectron spectroscopy was performed using a Kratos Axis Ultra spectrometer using monochromatized Al Kα radiation at 1486.6 eV. Survey spectra were an average of three scans acquired at pass energy of 160 eV and resolution of 1 eV/step. High-resolution spectra of N 1s, C 1s, and Si 2p were an average of five scans acquired at pass energy of 40 eV and resolution of 0.1 eV/step. Dwell time was 100 ms for survey scans, 400 ms for N 1s scans, and 300 ms for C 1s and Si 2p scans. A neutralizer gun with filament current of 0.36 A, filament bias of 0.2 V, and charge balance of 0.508 V was used to reduce charging of the samples while scanning. Binding energy corrections were made by referencing spectra to the oxygen in silica to 533 eV. Relative atomic concentrations were determined by subtracting a Shirley-type background and subsequently integrating the area under the remaining peak and dividing by the relative sensitivity. The sensitivity factors were provided by the manufacturer and are as follows: $S_{\text{O1s}} = 0.780$, $S_{\text{N1s}} = 0.477$, $S_{\text{C1s}} = 0.278$, $S_{\text{Si2p}} = 0.328$, and $S_{\text{Si1s}} = 0.324$. A transmission function correction is also made. The program used for quantification was Kratos Vision2. Spectra were taken with 30° incident beam angle to determine quantitative elemental analysis of APTES films. Because of the potential degradation of the films during the X-ray exposure, XPS was either the last or only analysis technique performed on each specimen. For this same reason, spectra were collected in the same order (survey, N 1s, C 1s, Si 2p) such that each elemental concentration for each specimen was measured after an equivalent amount of exposure to X-rays.

Results & Discussion

Atomic Force Microscopy. AFM tapping mode scans are summarized as 3 × 3 grids in Figure 1. Each plane has nine separate surfaces all with the same reaction temperature (75 °C on top and 25 °C on bottom). APTES concentration is presented along the *x*-axis, reaction time along the *y*-axis, and reaction temperature along the *z*-axis. The color scale on the individual

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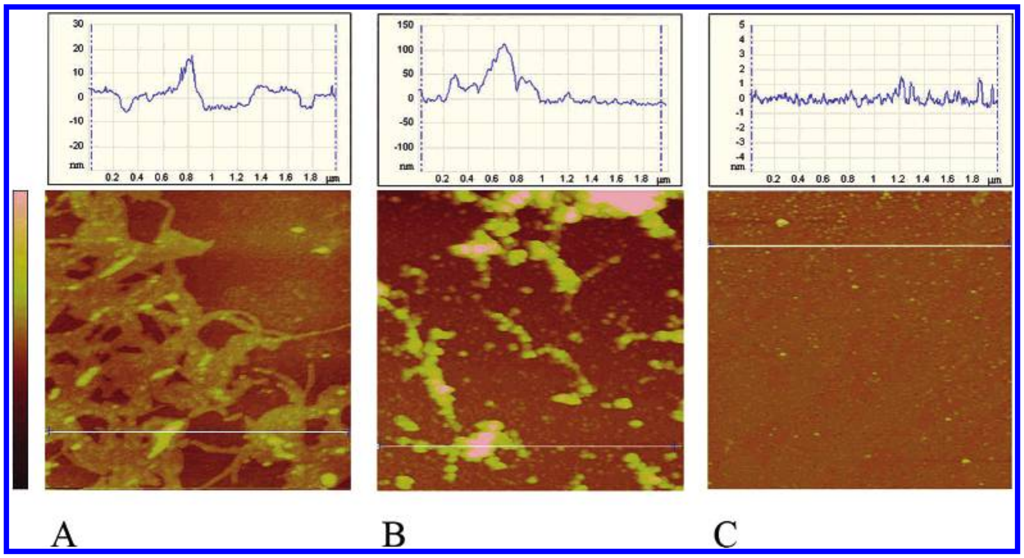

Figure 2. Representative morphologies of APTES films. (A) Multilayer-island growth on top of a complete film deposited at 1%−1 h−75 °C, height scale is 30 nm. (B) Rough APTES film deposited at 10%−24 h−75 °C, height scale is 150 nm. (C) Smooth APTES film deposited at 33%−24 h−75 °C, height scale is 10 nm. Horizontal lines indicate profile views.

Table 1. Summary of Film Quality in Terms of Roughness (AFM), Thickness (Ellipsometry), Wettability (Contact Angle), and Degree of Hydrolyzation (C:N Ratio Measured by XPS)

25 °C	RMS (nm)	Wenzel's ratio	thickness (nm)	adv./rec. angle	C:N
1 h−1%	0.53	1.01	1.5	81/29	5.5
1 h−10%	0.57	1.01	1.5	65/32	5.8
1 h−33%	0.42	1.01	1.8	83/23	6.0
24 h−1%	11.8	1.08	5.0	66/0	7.2
24 h−10%	18.1	1.16	15.7	73/0	8.9
24 h−33%	18.2	1.14	8.6	84/0	8.8
72 h−1%	19.7	1.35	11.6	51/0	8.3
72 h−10%	19.8	1.16	14.0	74/0	9.1
72 h−33%	5.50	1.05	10.8	76/0	10.2

75 °C	RMS (nm)	Wenzel's ratio	thickness (nm)	adv./rec. angle	C:N
1 h−1%	3.00	1.03	2.9	65/37	7.5
1 h−10%	1.23	1.01	2.1	78/18	7.7
1 h−33%	1.74	1.02	1.8	93/32	7.9
24 h−1%	22.1	1.20	12.3	78/0	7.7
24 h−10%	27.0	1.34	19.7	68/0	8.4
24 h−33%	1.90	1.01	17.7	68/28	8.8
72 h−1%	20.2	1.17	14.4	74/0	7.4
72 h−10%	0.34	1.01	16.3	77/21	9.7
72 h−33%	3.14	1.02	15.8	62/33	10.8

AFM scans is 200 nm, with each scan being 2 μm on each side. Representative morphologies (multilayer-island growth and smooth and rough surfaces) and sectional views with height data are presented in detail in Figure 2. Surface roughness was quantified using both root mean square (RMS) and Wenzel's roughness values which are presented in Table 1.

Upon comparison of specimens deposited under identical APTES concentration at 25 °C, increased reaction time resulted in a roughened film. Reaction time of 24 h or greater resulted in films with RMS values between 11.8 and 19.8 nm with the lone exception being 33%−72 h−25 °C films having RMS of 5.5 nm. The roughness of these films is attributed to the agglomeration of APTES molecules on the surface which is seen in detail in Figure 2B. Similar to films deposited at 25 °C, films deposited at 75 °C from 1% APTES solutions roughen as reaction time increases, having RMS values of 3.00, 22.1, and 20.2 nm for 1, 24, and 72 h reactions, respectively. Conversely, increasing the reaction time for films deposited at 75 °C from 33% APTES solutions had a negligible effect on film roughness, increasing the measured RMS from 1.74 to 1.90 to 3.14 nm for 1, 24, and 72 h reactions, respectively.

Increasing the concentration of the APTES solution for films deposited at 75 °C resulted in decreasing the RMS roughness for 24- and 72-h reactions (and it had a negligible effect for 1-h reactions). For the 24-h reaction, this effect was realized only for the 33% solution, whereas the 72-h reaction resulted in an RMS decrease for both 10% and 33% solutions compared to 1% APTES solution. These three films deposited at 75 °C were smoother than their 25 °C counterparts. The smoothing of films because of high-temperature deposition was observed only in these three sets of reaction conditions. In the other six sets of reaction conditions, increasing the temperature had minimal effect on surface roughness.

Specimens with 1 h−25 °C reaction conditions had smooth films with RMS roughness values ranging from 0.42 to 0.57 nm. Films deposited after 1 h at 75 °C had slightly higher RMS roughness values ranging from 1.23 to 3.00 nm. The roughest films of those deposited after 1-h reaction was from the 1%−1 h−75 °C reaction conditions. In this instance, the roughness is attributed to multilayer-island type growth as seen in Figure 2A, which is similar to models of SAM formation.[36] The islands as shown were multiple layers thick, as their height was much greater than the length of an APTES molecule. A notable difference, as compared to SAM formation, was that a complete film of APTES had already formed and was visible beneath the islands. Overall, APTES concentration and reaction temperature had a small effect on the roughness of films deposited after only 1 h.

Ellipsometry. The AFM data are useful in characterizing the morphology and roughness of each specimen, but taken alone, they only present a narrow picture of the actual character of the APTES films. Ellipsometry was used to determine the thickness of the APTES films; the resulting data are presented graphically in Figure 3 and are also included in Table 1. The matrix of experimental parameters is the same as in Figure 1 with APTES concentration and reaction time presented on the *x*- and *y*-axes, respectively; film thickness (nm) is presented on the *z*-axis. Film thicknesses ranging between 1.5 and 2.9 nm were observed for specimens at a reaction time of 1 h regardless of concentration

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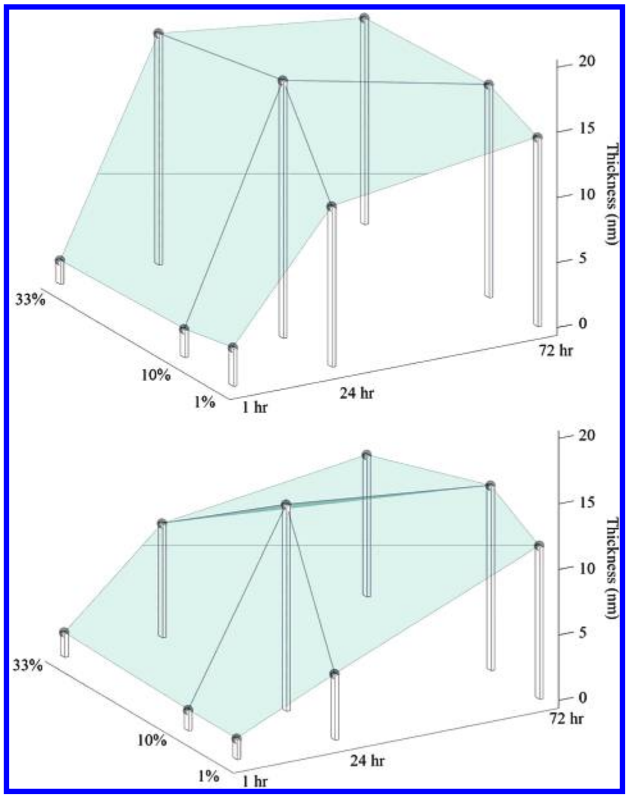

Figure 3. Ellipsometry data as a function of reaction conditions for 75 °C reaction temperature (top) and 25 °C reaction temperature (bottom).

or temperature all of which were observed to be smooth films on the basis of corresponding AFM scans. Films in this range are between two and four APTES layers thick assuming continuous layers (no agglomerates or multilayer-island growth) and APTES film thickness of ∼0.7 nm per monolayer.[18] The APTES deposition reaction is thus not limited to a monolayer but instead continues to polymerize at the surface whether the surface is exposed silica or APTES film.[32]

The films resulting from the remaining 12 sets of reaction conditions had thicknesses ranging from 5.0 to 19.7 nm. Of these specimens, films created at 10%−72 h−75 °C, 33%−24 h−75 °C, and 33%−72 h−75 °C reaction conditions had the unique combination of being thick and smooth. These three sets of films had measured thicknesses of 16.3, 17.7, and 15.8 nm, respectively, and RMS values of 0.34, 1.9, and 3.14 nm, respectively. Films created from 33%−72 h−25 °C reaction conditions had a measured thickness of 10.8 nm and were slightly rough, having an RMS of 5.50 nm.

The other sets of reaction conditions produced films with measured thicknesses on the same order of magnitude, but the films were extremely rough containing agglomerates larger than the measured film thickness. The possibility exists for two films to have nearly identical measured thicknesses but a very different surface structure such as the films deposited at 10%−24 h−75 °C compared to 33%−24 h−75 °C. The fact that the ellipsometry data represents an average thickness of a film over an area much larger than the 2 μm × 2 μm square of the AFM scans explains why a film can be measured as being ∼15 nm thick but have surface features approaching 200 nm in height. This effect is illustrated in comparing specimens with films deposited at 1%−24 h−75 °C and 10%−24 h−75 °C; both films have agglomerates of nearly identical size, but the film from the 10% solution has a greater density of agglomerates as evidenced by the higher RMS roughness and subsequently was measured as being thicker using ellipsometry.

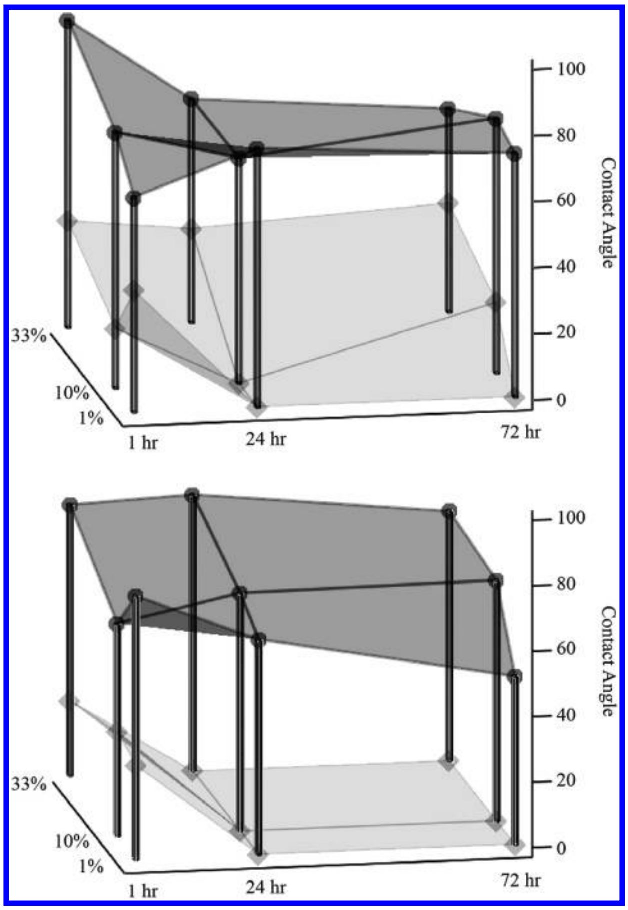

Figure 4. Advancing (circles) and receding (diamonds) water contact angles presented as a function of reaction conditions for 75 °C reaction temperature (top) and 25 °C reaction temperature (bottom).

Contact Angle. Advancing and receding water contact angles are presented in Figure 4 and in Table 1. Surfaces which had a measured RMS roughness of 5.5 nm or greater showed a zero receding water contact angle when liquid was withdrawn from a droplet on the surface, while no surface of RMS roughness less than 5.5 nm shows a zero receding water contact angle. The nine smooth surfaces had variations in advancing and receding contact angles ranging from 62° to 93°. Prior studies of APTES films have measured contact angles ranging from 26° [20,22] to 80° [8] and other values between;[15,19,23] further, some studies have observed an increase in contact angle over a matter of hours as a result of aging of the films.[22,23]

Previous reports have shown that smooth surfaces of methyl-terminated silanes have advancing water contact angles of ∼110°,[37] and smooth surfaces of amine groups will have a lower contact angle (60−68°). Our results are consistent with a chemically mixed surface with contact angles between these two values.[38]

Generally, the wetting response is a result of two factors: the exposed chemical groups at the surface and the surface roughness. Establishing how the character and quality of APTES films affect the wetting response is too complex for the scope of this study; however, the correlation between rough APTES films and zero receding angle is clearly demonstrated in the data presented here.

X-ray Photoelectron Spectroscopy. Atomic concentrations of nitrogen and carbon in the APTES films were measured using

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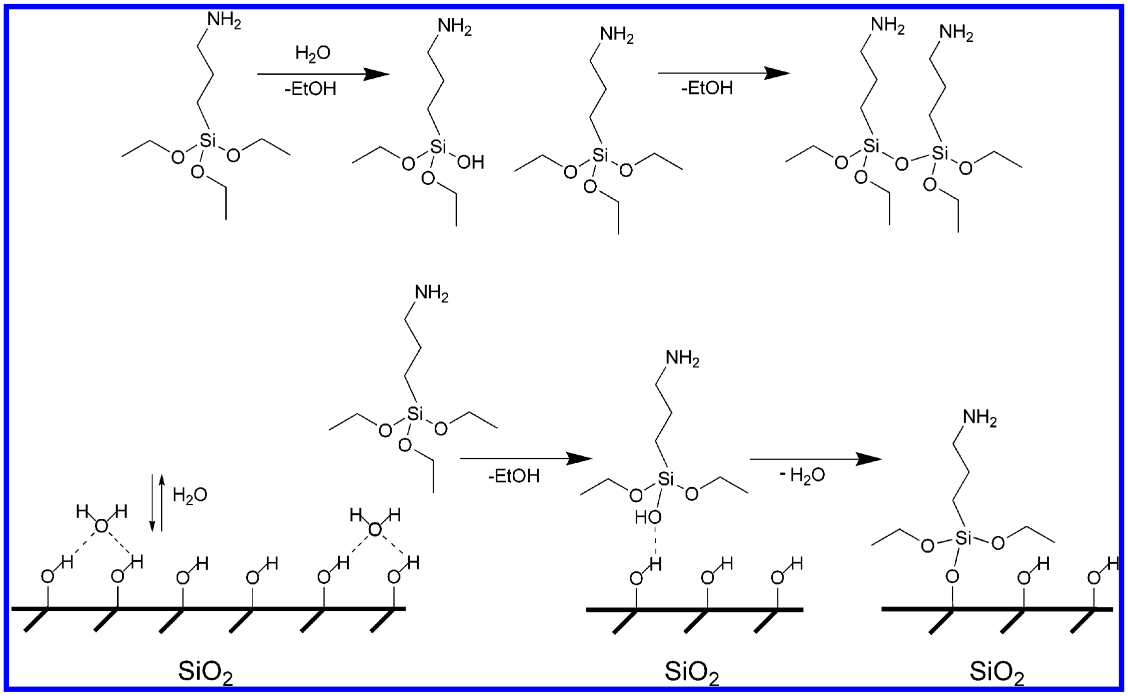
Scheme 1. Top Scheme of APTES Hydrolysis Followed by Condensation Reaction in Solution Phase. Bottom Scheme of APTES Hydrolysis Followed by Condensation at Hydrated Silica Surface



XPS. Though silicon and oxygen are also present in APTES, these atomic concentrations were not useful for characterizing the films as there was significant XPS signal from the underlying silica substrate which was not corrected for. Carbon-to-nitrogen ratios are presented in Table 1. Ideal films are best characterized by a C:N ratio of 3:1 as this measurement is indicative of perfectly hydrolyzed APTES molecules in which all three ethoxy groups have been replaced by siloxane linkages as seen in Scheme 1. Furthermore, this ratio is unaffected by variations in film thickness. APTES in its unreacted form has a C:N ratio of 9:1. The C:N ratios as measured were much higher than expected, even when accounting for the likelihood of incompletely hydrolyzed APTES films. We cannot discount the possibility that trace amounts of residual solvent or adventitious carbon is contributing to the high carbon signal. Despite the higher than expected carbon signal, C:N ratios are still useful as a relative comparison among the various reaction conditions.

The C:N ratio increased as APTES concentration increased for each trio of specimens with common reaction time and temperature. Among the six 1-h reaction conditions, an increase in reaction temperature resulted in C:N ratios increasing from between 5.5 and 6.0 to between 8.8 and 9.1. For reaction times of 24 and 72 h, changing the reaction temperature did not strongly affect the measured C:N ratio. Finally, an increase in the reaction time increased the C:N ratio for the specimens at 25 °C for all three levels of APTES concentration. This trend was not true for 1%−75 °C films in which increased time resulted in little change in the C:N ratio from 7.5 to 7.7 to 7.4 for 1-, 24-, and 72-h reactions, respectively. For 10% and 33% solutions at 75 °C, films showed a steady increase in C:N ratio between 1- and 72-h reactions.

Concentration and Time Dependence. When comparing samples at various APTES concentrations or temperatures when the APTES reaction is limited to 1 h, some important differences were apparent. Surfaces created after 1 h at 25 °C were nearly identical (roughness, thickness, chemical composition). Only the outermost layer of the APTES film contributes to the wetting character of the film; however, the C:N ratio is measured for a sampling depth much thicker than a few APTES layers. For example, a thick film such as those created at 33%−72 h−75 °C has a smooth (RMS = 3.14 nm) well-aminated surface, yet these surfaces had the highest C:N ratio measured at 10.8 indicative of residual carbon present within the film.

Generally, increasing the reaction time increased the APTES film thickness and C:N ratio.The increase of C:N ratio as deposition time increased indicates that as films thicken and roughen, complete hydrolysis of the film becomes more difficult. Increasing APTES concentration increased the C:N ratio but did not predictably affect the thickness. It is proposed that APTES hydrolysis can occur most efficiently and completely if there is sufficient surface water available for the reaction. The first monolayer of APTES reacts with a hydrated surface as shown in Scheme 1 similar to the mechanism of deposition of trichlorosilanes.[29,39] As this reaction proceeds and a continuous film is formed, water is no longer concentrated at the film surface but is primarily in solution. As APTES concentration increases, it becomes more likely that water in the system will react with an unreacted APTES molecule as opposed to further hydrolyzing APTES molecules already deposited in the film. Thus, the APTES molecules deposited from a high APTES solution concentration are quickly buried before they can fully hydrolyze. As surface water is used up, the deposited APTES can no longer attain high degrees of hydrolysis leading to an increase of C:N with reaction time.

As previously presented in Table 1, three of the reaction conditions (10%−72 h−75 °C, 33%−24 h−75 °C, and 33%−72 h−75 °C) produced films which were both thick and smooth. The mechanism of how these films develop remains unknown in light of the fact that films at 1%−72 h−75 °C and 10%−24 h−75 °C contained surface features which remained after rinsing. Surface roughness can be a result of vertical polymerization at the film surface or the attachment of agglomerates which formed in solution. Prior studies have proposed that agglomerates form in solution and are then deposited on the films[18] and that agglomerates will not form in solution above 60 °C.[22] While electrostatic interactions may be negligible at high temperature,

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

it is certainly possible for APTES to polymerize in solution.[18,25] Furthermore, conducting the reaction at high temperature does not ensure the formation of a smooth film for all reaction conditions as surface roughness was evident at 75 °C as seen in Figure 2.

Temperature Effect. At elevated temperature, the kinetics of the APTES system are accelerated by increasing the mobility of APTES in the toluene phase and increasing the reaction rate for silanization. Because of the increased reaction rate, we expect the initial film to form and increase in thickness more quickly. The films created at 1 h−75 °C were up to twice as thick as at 25 °C, which indicate a more aggressive initial deposition. Additionally, 1 h−75 °C had C:N ratios similar to thicker films created at 24 h−25 °C. The increase in C:N ratio between 1 h−25 °C and 1 h−75 °C is thought to be due to both increased reaction kinetics and the increased solubility of the surface adsorbed water at elevated temperature. The depletion of surface water resulted in the initial APTES molecules being deposited with some nonreacted ethoxy groups remaining.

The APTES reaction is highly sensitive to water concentration;[25,27,29,30,34,40] efforts here to control water content were detailed above in the experimental methods. For low temperatures, a majority of the water present in the system was adsorbed at the silica surface,[29,30] which limited the silanes to react primarily at the substrate surface. As temperature was increased, water was able to desorb from the substrate and container surfaces and enter the toluene phase.[29] While the amount of water desorbed from the surfaces of the vial and substrate was not so extreme as to completely dehydrate the surfaces,[30] film growth was likely affected. As shown in Scheme 1, water is consumed by the condensation reaction when it occurs in solution, but for the surface reaction water acts only as a catalyst.[27] At both 75 °C and 25 °C, initial film deposition occurs at a surface which has sufficient water to drive the reaction, as only one out of every five molecules needs to be bonded to the silica surface for a trifunctional silane to form a continuous film.[34] Therefore, the effect of partial surface dehydration at 75 °C is manifested as a poorly hydrolyzed thin film as opposed to an incomplete film.

As layers of APTES are built up, underlying APTES molecules which have not fully hydrolyzed become isolated and the hydrolyzation reaction becomes diffusion limited. For APTES films to hydrolyze, ethoxy groups must have access to water molecules. Thick films with a low degree of initial cross-linking between APTES molecules may prevent complete hydrolyzation by creating an impenetrable fully hydrolyzed surface film which protects the underlying APTES molecules from interaction with water. Thus, slowly developing films, which occur at low concentration or at low temperature, are more likely to be fully hydrolyzed and to have a low C:N ratio.

Summary

Characterization of roughness, thickness, wettability, and extent of hydrolyzation for thin films of APTES on silica is summarized in Table 1. Overall, the results indicate that proper control of reaction conditions was important to achieving desired results in the amination of silica by APTES. Morphology and growth kinetics of APTES films deposited from solutions were found to be affected by reaction time, solution concentration, and temperature. With these variables, film morphology and composition were controlled. Film thickness was primarily a function of time as increasing the reaction time beyond 1 h created thicker films without exception. Concentration and temperature dictated surface roughness and receding contact angle; however, concentration and temperature each had a marginal effect on film thickness. The extent of allowable hydrolyzation shows strong temperature dependence.

Systems with low APTES concentration (1%) only produced good films when the reaction was time-limited (1 h). Film quality did not show strong temperature dependence for 1-h reactions. As compared to films created at longer reaction times, the films created after 1 h were all essentially smooth, having low RMS roughness, and were less than 3-nm thick. Films created at reaction conditions of (10%−72 h−75 °C), (33%−24 h−75 °C), or (33%−72 h−75 °C) produced thick, smooth, APTES layers with a measurable receding water contact angle.

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(40) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92−98.