Attachment of 3-(Aminopropyl)triethoxysilane on Silicon Oxide Surfaces: Dependence on Solution Temperature

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Parameters important to the self-assembly of 3-(aminopropyl)triethoxysilane (APTES) on chemically grown silicon oxide (SiO_2) to form an aminopropyl silane (APS) film have been investigated using in situ infrared (IR) absorption spectroscopy. Preannealing to ~70 °C produces significant improvements in the quality of the film: the APS film is denser, and the Si−O−Si bonds between the molecules and the SiO_2 surface are more structured and ordered with only a limited number of remaining unreacted ethoxy groups. In contrast, post-annealing the functionalized SiO_2 samples after room temperature reaction with APTES (i.e., *ex situ annealing*) does not lead to any spectral change, suggesting that post-annealing has no strong effect on the horizontal polymerization as suggested earlier. Both IR and ellipsometry data show that the higher the solution temperature, the denser and thinner the APS layer is for a given immersion time. Finally, the APS layer obtained by preannealing the solution at 70 °C exhibits a better stability in deionized water than the APS layer prepared at room temperature.

Introduction

A variety of developing technologies in biosensing, semiconductor fabrication, heterogeneous catalysis, and other high-technology applications are driving the need for high-quality, reproducibly functionalized semiconductor surfaces. The ability to control surface functionalization expands the functionality of standard bulk materials for a host of different devices. Among several organic molecules that can self-assemble on silicon surfaces and modify their intrinsic properties, silane molecules have been widely used[1] as an initial step to covalently attach adhesion promoters and cross-linkers on glass.[1−3]

Silanes are attached through the formation of a Si−O−Si bond between the surface and the silanol groups. In addition to this covalent attachment, a broad range of available chemical functionalities at the other functional end of the silane molecules allows flexible adaptation of the surface for various applications. In particular, 3-(aminopropyl)triethoxysilane (APTES) has been widely used because of its amino terminal group,[4−7] which makes APTES especially attractive for biotechnology purposes such as DNA microarrays,[8,9] protein arrays,[10] and sol−gels.[11]

APTES can form a covalently attached self-assembled monolayer (SAM) on a wide variety of substrates,[12−15] including hydroxyl-terminated silicon oxide substrates.[13−15] The reaction of the bond formation between the silicon oxide surface and the APTES molecules proceeds with the hydrolysis of the alkoxy groups (first step) followed by the covalent adsorption of the hydroxysilane product (second step), resulting in the formation of an aminopropyl silane (APS) film.[16] The presence of water at the surface of the silicon surface is therefore necessary to catalyze the reaction, as it is responsible for the first step of the reaction, and control of the moisture (physisorbed water layer) is key for the reproducible quality of the interface.[17]

Previous studies have used elevated temperatures to strengthen and densify APS layers, on the basis of the assumption that horizontal polymerization (i.e., the formation of Si−O−Si bonds between adjacent surface APS molecules) is enhanced upon heating after the SAM is attached. For this postdeposition treatment, temperatures ranging from 90 to 120 °C and reaction times from 10 min to up to 1 h have been used.[14,18−21] Very few studies have made use of elevated incubation temperatures to promote APS attachment *during* the silanization reaction,[22,23] and little analysis on the nature or quality of that Si−O−Si

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attachment has been performed. On the other hand, a similar study of the effect of temperature on silanization of a hydrophilic silicon oxide surface with chlorosilane-based molecules has indicated that the attachment is improved with decreasing temperatures, in direct contradiction with the above APTES studies.[24] To resolve these issues, it is necessary to perform comparative studies of silanization reactions performed at room temperature with subsequent ex situ heating and silanization reactions performed for a variety of solution temperatures.

In this paper, we therefore investigate with Fourier transform infrared (FTIR) absorption spectroscopy the chemical nature of surfaces prepared using both in situ annealing (varying starting solution temperatures) and ex situ post-annealing and use ellipsometry to characterize the thicknesses of the films produced. We specifically explore the influence of in situ annealing during the reaction of APTES molecules with silicon oxide surfaces. We combine elevated incubation temperatures with the established anhydrous deposition techniques to promote binding of APTES molecules to the surface and increase the molecular density at the silicon oxide surface, without harming the film surface characteristic. The method of incubation, from in situ heating to post-deposition annealing is examined. We also compare the effects of the temperature on the stability of the APS film in the presence of water, an important "solvent" used in the attachment of biological molecules such as DNA. Both the film growth and film stability are studied as a function of immersion time in APTES to determine the film formation kinetics and saturation, a critical aspect of the process that was not explored in previous studies.[23]

Materials and Methods

Slightly N-doped double-side polished silicon (Si) (100) wafers ($\rho \sim 15\ \Omega \cdot$cm) are cut into ($1.5 \times 3.8$ cm) rectangular pieces. They are treated with 1:1 HF/H_2O solution to remove the native oxide and then a standard SC1/SC2 RCA cleaning method to remove organic and metallic contaminants and to chemically reoxidize the sample surface.[25,26] The resulting chemical oxide is 15 ± 1 Å thick as measured with FTIR calibrated with oxide samples of known thicknesses.

Anhydrous APTES (98%) and anhydrous toluene (99.8%, $<0.001\%$ water) purchased from Sigma-Aldrich are used without further purification for all experiments. All products are opened in a dry nitrogen-purged glovebox with low humidity (water concentration <2 ppm) and all APTES functionalization experiments are conducted inside a dry nitrogen-purged glovebox, ensuring that excess moisture does not contaminate the reaction causing APS to polymerize during deposition.[12,27]

APTES deposition is performed as follows: after introducing a freshly cleaned Si(100) sample in the glovebox, it is then immersed in a 0.1% (v/v) solution of APTES in anhydrous toluene and incubated in the glovebox for time periods ranging from 2 min to 48 h. After the reaction, the functionalized Si sample is removed from the APS solution, rinsed with fresh anhydrous toluene and sonicated for 5 min in fresh anhydrous toluene.

Room-temperature depositions are conducted inside the glovebox without any particular thermal insulation. For high-temperature processing, Si samples are immersed in preheated APTES solutions, ensuring that the desired temperatures are reached *before* the functionalization reaction begins. A homemade sealable chamber, equipped with a thermocouple and a heating tape controlled by a feedback mechanism, is used to heat the APTES solution for these silanization reactions. Samples processed with ex situ annealing are not sonicated prior to the annealing.

To test the stability of the APS layers in water, functionalized Si samples are immersed in deionized water at room temperature for time periods ranging from 1 min to 6 h, using a test tube precleaned with an SC-1 treatment. After immersion in the open laboratory environment, the samples are removed from the test tubes, and the water is discarded. Samples are then thoroughly dried by blowing dry nitrogen gas at room temperature.

All samples are investigated using FTIR spectroscopy in transmission (74° incidence), with 4 cm^{-1} resolution. Five sets of 1000 scans each are typically recorded at a mirror velocity of 1.89 cm/second. Dry nitrogen gas is used to purge the spectrometer chamber during scans. Spectra are recorded with a (mercury−cadmium−telluride)-A (MCT-A) detector to cover the 650−4000 cm^{-1} spectral range. All spectra shown in this study are absorbance spectra that display changes in chemical features of the silicon sample due to the functionalization process, i.e., using the initial oxide surface as reference. Spectra of Si samples are recorded immediately before and after the RCA clean, and immediately after the APS deposition. For the stability studies of the APS layer in deionized water, spectra are taken at various time intervals over a 6 h period. After each time interval, the tube is rinsed with clean deionized water and reimmersed in fresh deionized water.

Ellipsometry measurements are performed with a UVISEL (HORIBA Jobin Yvon, Inc.) phase modulated spectroscopic ellipsometer on APTES films prepared at room temperature, 50 °C, and 70 °C for various incubation times as described. Only the shorter wavelength range 1.5−6.5 eV (830−190 nm) is used in order to eliminate contributions from backside reflections. The incident angle is set at 70°, and the light spot is 1 mm in diameter (the largest offered). At least three points on the surface are randomly chosen to assess the thickness uniformity of the APS layer. To model the ellipsometry data, both APS film thickness and index of refraction (using dispersion functions) are fit for all film incubation temperatures and times. Because SiO_2 and APS films have comparable indices and thicknesses, an overall independent fit is difficult. Therefore, using independent IR data (shown below), the SiO_2 thickness was fixed at 18, 19, and 21 Å to model room temperature, 50 °C, and 70 °C depositions, respectively. These thicknesses were chosen on the basis of measured values of initial chemically grown SiO_2 thickness (15 ± 1 Å), and the measured increase (from IR spectroscopy) that results from the functionalization process via the formation of dense Si−O−Si bonds as incubation temperature is increased. The calibration for the integrated area of the combined longitudinal optical (LO) and transverse optical (TO) SiO_2 absorption has been established at 0.07 ± 0.01 cm^{-1}/Å SiO_2 for thin oxides (5−50 Å) measured at 74° incidence using a combination of transmission electron microscopy (TEM), X-ray photoelectron spectrometry (XPS), and ellipsometry.

Atomic force microscopy (AFM) was performed on APTES films prepared at room temperature, 50 °C, and 70 °C for various incubation times as described in the tapping mode using a Digital Instrument Nanoscope, taking 512 points in a 500 nm × 500 nm area with a 1.5 Hz scan rate in atmosphere at room temperature.

Results

A. Silanization of Silicon Oxide (100) Surfaces with APTES Molecules. Figure 1 shows the spectra characteristic of Si surfaces functionalized with APTES molecules when the chemical reaction with SiO_2 is complete (after 48 h of incubation) and performed at room temperature (Figure 1a), 50 °C (Figure 1b), and 70 °C (Figure 1c). The most prominent features for all spectra are located between 950 and 1250 cm^{-1} (herein referred to as the SiO−X region), where Si−O−Si and Si−O−C modes have been reported.[28,29] This broad feature is dominated by two bands centered at $\sim$1035 and $\sim$1150 cm^{-1}, which are assigned to SiO_2 TO and LO stretching modes, respectively.[29] Interestingly, the intensity of the SiO_2 LO mode (1149 cm^{-1}) increases with

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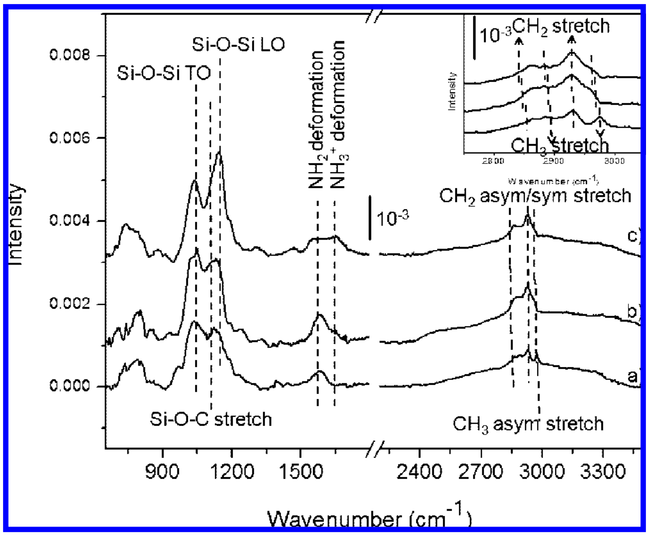

Figure 1. Transmission IR spectra for the APS film prepared at (a) room temperature, (b) 50 °C in situ, and (c) 70 °C in situ displayed on a common scale. The spectrum is referenced to the SiO_2 surface. The inset shows a zoom in the CH_x region (2750−3050 cm^{-1}), keeping the same a, b, c ordering.

increasing incubation temperature while the SiO_2 TO mode (1033 cm^{-1}) intensity remains essentially unchanged (Figure 1). In addition, the modes also appear to sharpen with increased incubation temperature. These two observations suggest that the binding mechanism between APTES chains and SiO_2 is more complex than expected. Additionally, they suggest that the incubation temperature affects the spectral shape of this region and therefore may play a key role in the attachment of the molecules onto the surface. Finally the subtle but clear change in shape of both components suggests the existence of other features in the (950−1250) cm^{-1} spectral range in addition to the TO/LO modes, as further discussed in Section B.

CH_x stretching modes are present between 2850 and 2990 cm^{-1} for all incubation temperatures. More specifically, at room temperature, the CH_2 asymmetric and symmetric stretching modes are observed at 2932 and 2864 cm^{-1}, respectively, confirming the presence of the propyl chain of the APTES molecule. Also present is the CH_3 asymmetric mode at 2975 cm^{-1} best seen for the surface prepared at room temperature (Figure 1);[29,30] the symmetric CH_3 stretching mode is not always fully apparent. The observation of the CH_3 mode suggests that some ethoxy groups have not been completely hydrolyzed as previously suggested[1] and, consequently, that the APTES molecules are not fully bonded either with the SiO_2 surface or/and with a neighboring APTES molecule (horizontal polymerization). Interestingly, the area of the CH_3 stretching mode drops significantly, i.e., by a factor of 70%, when the sample is prepared in a solution at 70 °C. In addition, the positions of the CH_2 asymmetric and symmetric stretching modes clearly red-shift from 2932 to 2928 cm^{-1} and from 2864 to 2859 cm^{-1}, respectively, as the solution temperature is increased (Figure 2), suggesting that the APS layer formed at higher temperatures exhibits denser packing of the propyl chains i.e., solid packing (crystalline-like), as observed in other SAM systems.[31]

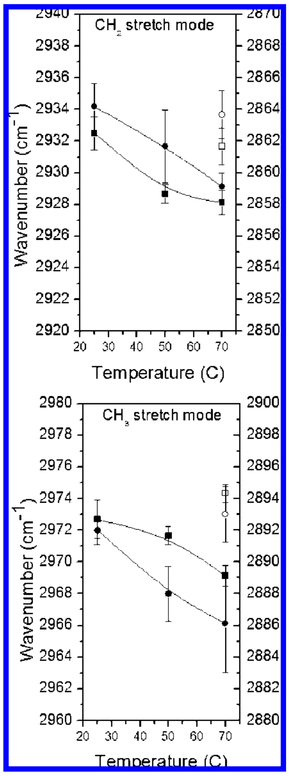

Figure 2. Evolution of the peak position of CH_2 (top panel) and CH_3 (bottom panel): asymmetric (a) (filled squares, left scale), and symmetric (b) (filled circles, right scale) stretching modes with incubation temperature. Data in upper right of panels (unfilled data points) are the wavenumbers observed for CH_2 and CH_3 when the heat is applied after the reaction has taken place (ex situ). Solid lines are the calculated exponential fits.

The remaining spectral features include an absorbance feature at 1570 cm^{-1}, corresponding to the NH_2 scissor vibration and confirming the presence of the NH_2 terminal group of APTES molecules.[29] The corresponding N−H stretching vibration at 3300 cm^{-1} is more difficult to observe because of its weak dipole moment, making its detection almost impossible for a monolayer coverage. In addition to the NH_2 scissor mode, another feature at 1610 cm^{-1}, corresponding to the asymmetric $-NH_3^+$ deformation mode, is sometimes present (see Figure 1c for example). The weak feature at 1490 cm^{-1} is also assigned to the symmetric $-NH_3^+$ deformation mode.[29] The latter increases in intensity with temperature; as evidenced by the behavior of the broad absorption feature on the low frequency side of the $-NH_2$ bending mode at 1610 cm^{-1}. The presence of these modes suggests that when the samples are exposed to air after synthesis, water molecules are weakly bonded to the NH_2 groups, thereby allowing for the protonation of the amine. The broad feature in the 2500−3500 cm^{-1} (on which the CH_x stretching modes are superposed) is evidence that water molecules undergo hydrogen bonding, most likely with the amino groups of the APS film.[32] The formation of a $-NH_3^+$ termination (as indicated by the growth of the mode at 1610 cm^{-1}) at higher incubation temperatures implies increasing stability of the ionized form of the amino group with increasing temperature, possibly influencing the mechanism though which the APS film may interact with its surrounding environment or subsequent chemical treatment. Finally, Figure 3 shows the comparison between absorbance

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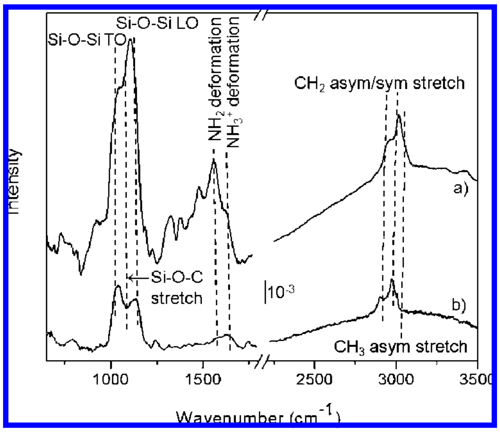

Figure 3. IR absorption spectra of APS films prepared at room temperature (24 h deposition) under (a) non-anhydrous and (b) anhydrous conditions. The reference spectrum is the SiO_2 surface.

spectra obtained for APS films grown under (a) non-anhydrous conditions and (b) anhydrous conditions for identical reaction times, i.e., 24 h. The intensity of the spectral Si−O−Si region is several times higher for an APS film grown in presence of water molecules than in an anhydrous environment. This result confirms previous studies[12,27] showing that APS films grown under non-anhydrous conditions are thicker because of extensive vertical polymerization, i.e., formation of Si−O−Si bonds in the solution among neighboring molecules that are loosely bound to the surface. Water molecules present in the solution hydrolyze the APTES molecules, allowing polymerization of the molecules before and after the attachment of APTES molecules to the surface.

B. Analysis of the Bonding Region (950−1250 cm^{-1}) Using Gaussian Fitting. The 950−1250 cm^{-1} spectral region is complex, involving at least four different vibrational modes. In addition to the SiO_2 TO and LO stretching modes at ∼1040 and ∼1140 cm^{-1}, respectively, this spectral region also contains SiO−C stretching and $SiO-CH_2CH_3$ rocking modes, both due to the presence of *unreacted* ethoxy groups.[29,30] Peak fitting is therefore necessary to analyze this 950−1250 cm^{-1} region. To this end, Gaussian functionals are most appropriate to fit the three spectra in Figure 1, using the following equation:

$$G(x) = A\exp[-(x-\mu)^2/(2\sigma^2)] \tag{1}$$

where *A* is the amplitude of the mode, μ is its wavenumber, and σ is its half-width at half-maximum.

The results of the Gaussian fitting are shown in Figure 4 for SiO_2 functionalization at room temperature (Figure 4a), 50 °C (Figure 4b), and 70 °C (Figure 4c). Peak areas determined by Gaussian fitting are normalized to the entire area of the region and are given in Table 1.

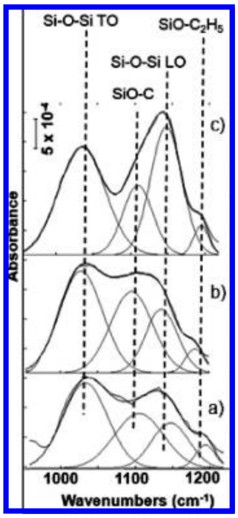

Figure 4. Gaussian peak fitting of Si−O−X regions between 950 and 1250 cm^{-1} for data taken on samples prepared at (a) room temperature, (b) 50 °C, and (c) 70 °C.

Table 1. Normalized Integrated Peak Areas (in cm^{-1}) for the SiO−X Region

	vibration			
temperature (°C)	SiO_2 TO	SiO_2 LO	SiO−C stretch	$SiO-CH_2CH_3$ rock
room	0.49	0.16	0.29	0.06
50	0.47	0.26	0.26	0.06
70	0.45	0.31	0.20	0.04

The peak positions observed for the four modes do not change significantly within the error bar when the incubation temperature is changed. The modes at 1033 cm^{-1} and 1149 cm^{-1} are attributed to the SiO_2 TO and LO stretching modes, respectively, confirming that the APTES molecules are covalently attached to the SiO_2 surface, thus increasing its effective thickness. Only a tight Si−O−Si bonding with the surface (i.e., the formation of Si−O−Si bonds that are part of the underlying SiO_2 layer) can produce this effect. The mode at 1107 cm^{-1} has been previously attributed to the SiO−C stretching mode,[29,30] while the less intense mode at 1194 cm^{-1} has been correlated to the rocking mode of $SiO-CH_2CH_3$. The latter two modes confirm that unreacted ethoxy groups are still present, consistent with the presence of CH_3 discussed above. In addition, the full width at half-maximum (fwhm) of the modes do not significantly vary with in situ incubation temperature at saturation. These four modes are present at all incubation temperatures, but the areas of the SiO−C and SiO_2 LO modes vary considerably with in situ heating (Figure 5). In order to compare the data of SiO_2 LO, TO, and SiO−C modes for the three different incubation temperatures, the area of each component is normalized to the total area of the (950−1250) cm^{-1} feature. At saturation, the normalized area for the SiO_2 TO mode corresponds to approximately 40% of the broad 950−1250 cm^{-1} band and remains almost constant for all incubation temperatures. This is not the case for the normalized area of the SiO_2 LO mode, where the normalized area steadily increases with incubation temperature, almost doubling in intensity from room temperature to 70 °C. In contrast, the normalized area of the SiO−C stretching mode decreases for treatment at 70 °C to a third of its room temperature area. The

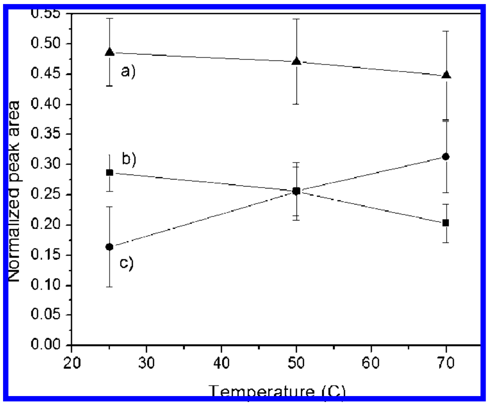

Figure 5. Normalized areas of (a) SiO_2 TO, (b) SiO−C and (c) SiO_2 LO stretch modes as a function of incubation temperature.

Table 2. Absolute Area of SiO−X Region at Saturation (in cm^{-1}) and Increase in SiO_2 Thickness (Derived from TO and LO Band Intensity)

temperature (°C)	total area (950−1250 cm^{-1})	standard deviation	additional oxide thickness (Å)
room	0.19	0.03	2
50	0.28	0.05	3
70	0.25	0.05	4

constant intensity of the TO mode suggests that the number of Si−O−Si bonds at the interface remains roughly the same. However, while the number of attached APTES chains does not depend on the temperature of the treatment, there is more covalent bond formation between the APTES molecules (i.e., horizontal cross-linking) for treatment at 70 °C with fewer ethoxy groups present at the surface, than for room temperature processing. Although it is also possible that unreacted silanol groups are still present on the APS molecules, their contribution to the spectrum in the ~3700 cm^{-1} range is below our detection limit. Finally, the absolute area of the SiO−X region at saturation (48 h reaction time) increases moderately at increased incubation temperature (50 and 70 °C) as compared with room temperature (Table 2), despite the decrease of the SiO−C mode, consistent with the fact that more Si−O−Si bonds are formed when ethoxy groups are hydrolyzed, and suggesting some additional attachment of APS molecules. At this point, we use the integrated areas of the SiO_2 LO and TO modes to estimate the slight thickness increase of the existing SiO_2 layer resulting from siloxy bond formation from APTES attachment and summarize the results in the last column of Table 2. These measured increases confirm the expectation that the oxide thickness increases over the initial amount slightly for all APS depositions, particularly for the higher temperature preparations, and justifies the addition of these thicknesses to the measured chemical oxide thickness of the samples prior to APTES deposition for the ellipsometric analysis.

C. Dependence of APS Attachment on Processing Time and Temperature. In order to understand the effect of the temperature during the growth of APS films, we have studied the change in the (950−1250) cm^{-1} and (2800−3000) cm^{-1} spectral regions as a function of reaction time. All the vibrational features increase in intensity with the reaction time until saturation is reached, after which the band areas remain constant (Figure 6). In particular, the SiO_2 TO and LO as well as SiO−C stretching modes areas follow an exponential progression of the form

$$y = C(1 - \exp(-kt)) \qquad (2)$$

where $C > 0$ is a constant related to the normalized peak area at saturation (i.e., maximum intensity), and $k > 0$ is the time constant. We have previously found that, at room temperature, saturation is reached after ~33 h. Specifically, the SiO_2 TO and LO mode absorptions remain constant after 33 h of reaction, while the area of the SiO−C stretching mode exhibits a plateau after 15 h. This behavior suggests that equilibrium has been reached between the number of APS chains bonded to the surface and the number of hydrolyzed ethoxy groups. For film growth performed at higher incubation temperatures, the formation of a complete film is reached faster (Figure 6). The areas of the SiO_2 TO and LO modes reach their maxima after 10 h, and the SiO−C stretch mode reaches a maximum after 7 h for deposition temperatures ~50 °C. At 70 °C, the reaction time needed to reach saturation is further decreased. The areas of the SiO_2 TO and LO modes reach their maxima after only 7.5 h, and the area of the SiO−C vibration is constant after 6 h. Performing least-squares fitting of the entire Si−O−X region with an exponential function (eq 2), the time constant is found to vary from 5.5 h at room temperature to only 49 min at 70 °C as shown in Figure 6. The decrease in time constant with increasing temperature suggests that the reaction is going faster at higher temperatures, and the use of the same fit (eq 2) indicates that similar mechanisms are involved at all temperatures.[27]

Noteworthy changes also occur in the CH_x stretching mode region (2800−3000 cm^{-1}) with respect to the incubation time (Figure 7). There are no frequency shifts of the asymmetric and symmetric CH_2 stretching modes as a function of reaction times at room temperature, but a distinct red shift at higher reaction temperatures (50 and 70 °C). This result suggests that, before reaching saturation coverage, the propyl chains can freely move behaving as liquid-like structures, and become more constrained (i.e., behave more like solid structures with collective motions) as saturation coverage is reached. This progressive change is faster at higher processing temperatures.

D. Surface Thickness, Refraction Index, and Morphology of the APS Layer. Ellipsometry can be used to characterize the APS layers using physical constraints for the SiO_2 thickness described in the experimental section. As a check, the thickness of the initial oxide (produced by SC1 and SC2 treatment and using the model described in the experimental section) is measured by ellipsometry to be 16 ± 1 Å, in excellent agreement with the FTIR thickness measurement (15 ± 1 Å). This result demonstrates that the model used for the ellipsometry data is appropriate for the system under consideration and should therefore give reasonably accurate APS film thicknesses. Figure 8 shows the dependence of (1) the APS film thickness and (2) the APS film refraction index as a function of time for samples processed at different temperatures. Samples prepared at room temperature show a slower and continuous increase in thickness over the time range, while samples prepared at 70 °C show a much more rapid increase in thickness over the first several hours followed by a plateau thereafter. Samples prepared at 50 °C exhibit growth in between these two extremes. The index of refraction for room temperature samples is lower than those observed for 70 °C preparations while the film prepared at 50 °C increases over time between these two extremes. The 20−30% increase in film thickness for samples prepared at 70 °C compared to those prepared at room temperature and the trends in the film refraction index are consistent with the FTIR presented in the previous section. The range of maximum thickness varies from 1.5 nm (room temperature, 48 h) to 1.8 nm (70 °C, 48 h), corresponding to 2−2.5 monolayers on the surface assuming an average thickness of 0.7 nm per APS monolayer.[33] These thicknesses are substantially smaller than those of films grown in non-anhydrous conditions, for which thicknesses ranging from 7.2 to 11.0 nm are observed after 48 h incubation, corresponding to 10 to 16 monolayers. The fact that the surfaces prepared at 70 °C do not correspond to a single APS monolayer (with ideal Si−O−Si cross-linking among all neighboring molecule and at least one Si−O−Si bond with the surface) and yet display a complete self-terminating growth is significant and will be addressed in the Discussion section.

AFM images taken after treatments at room temperature and 70 °C in situ preparations are shown in Figure 9, where the initial oxide surface is also shown as a reference. The presence of an organic layer is clearly visible, characterized by a larger root-mean-square (rms) roughness (~0.3 nm compared to ~0.15 nm for SiO_2), although little difference is found between the two preparation temperatures (0.30 nm for 70 °C vs 0.32 nm for room temperature). However, since the layer prepared at 70 °C is thicker than the room temperature-prepared film according to

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[33] Howarter, J. A.; Youngblood, J. P. *Langmuir* **2006**, *22*, 11142–11147.

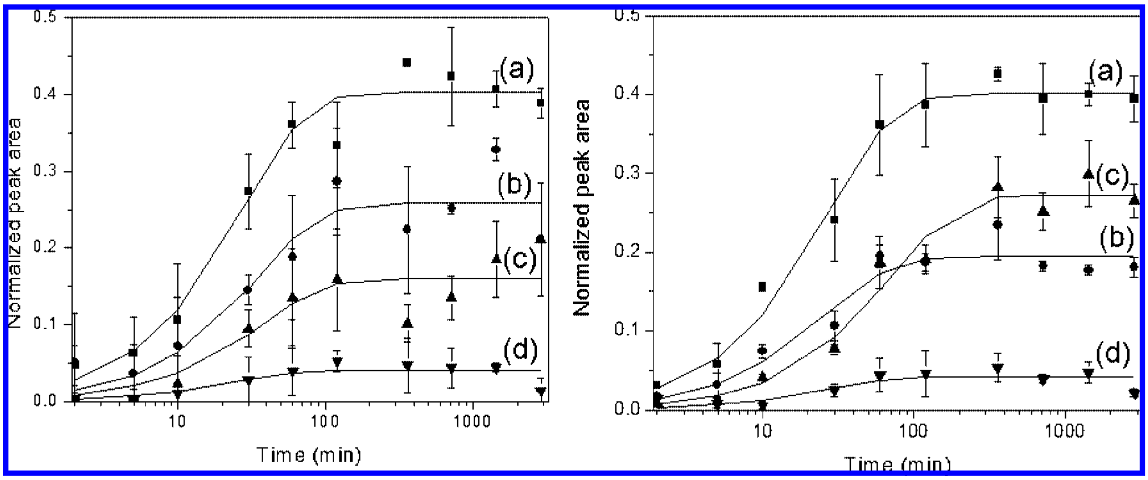

Figure 6. IR absorption intensity of (a) SiO_2 TO, (b) SiO−C, (c) SiO_2 LO, and (d) $SiO-C_2H_5$ modes as a function of reaction time. Solid lines are the calculated exponential fits. The left and right panels correspond to the results obtained at 50 °C in situ and 70 °C in situ annealing, respectively.

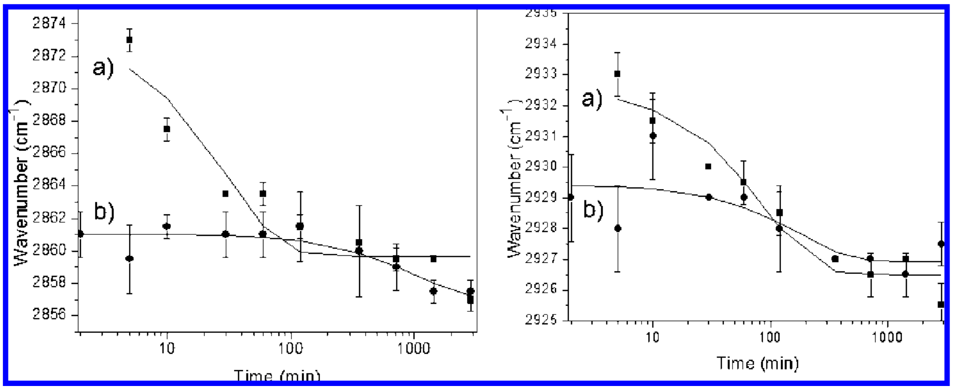

Figure 7. Stretch mode frequencies of CH_2 for APS films prepared at (a) 50 °C in situ and (b) 70 °C in situ. The left panel corresponds to the symmetric CH_2 stretching mode, and the right one corresponds to the asymmetric CH_2 stretching mode. Solid lines are the calculated exponential fits.

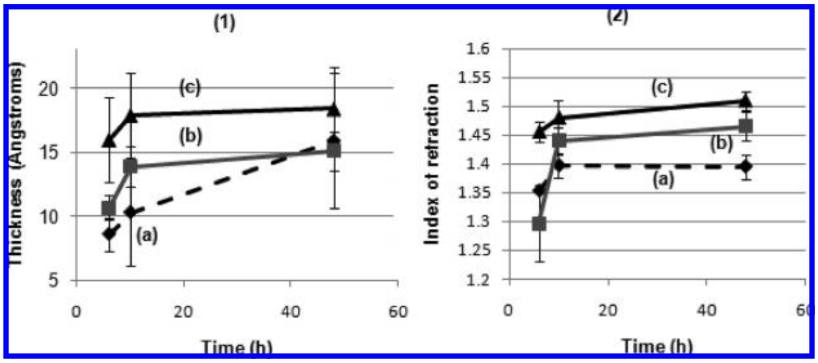

Figure 8. APS film thickness (1) and refraction index (2) as a function of preparation time derived from ellipsometry measurements for films prepared at (a) room temperature, (b) 50 °C, and (c) 70 °C.

the ellipsometry data, the fact that the former does not exhibit larger roughness is consistent with the formation of a denser, well-organized layer.

E. In Situ versus Ex Situ Heating. Heating has been used for the APTES reaction on SiO_2, but primarily as a curing method, i.e., silanized Si samples obtained after a reaction performed at room temperature are annealed for few minutes at 120 °C in air.[14,18−21] We have therefore compared the FTIR spectra obtained for an APS film cured at 70 °C (ex situ post annealing) with one observed for an APS film obtained with a 70 °C incubation (in situ heating) (Figure 10). In both cases, 70 °C has been chosen for consistency, but curing the functionalized Si sample at 70 °C or 120 °C leads to the same results (results not shown). Figure 10 shows the IR spectra of an APS film obtained after a 48 h deposition 48 h at room temperature immediately before (Figure 10 a) and after (Figure 10b) annealing at 70 °C for 24 h (ex situ post annealing); sonication is performed in both cases after the heating is complete. Figure 10c shows the IR spectrum of an APS film obtained after 6 h at 70 °C (*in situ* heating) for comparison. In contrast to the behavior of the in situ 70 °C processing, post-annealing leads to no detectable change in either the SiO−X region or the CH_x region. Especially notable are the positions of the CH_2 asymmetric (2934 cm^{-1}) and symmetric (2864 cm^{-1}) stretch modes. The lack of any red-shift at higher

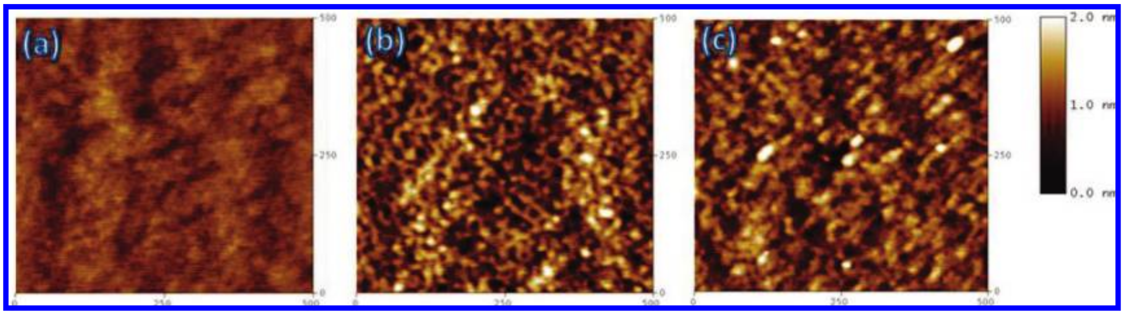

Figure 9. AFM pictures of (a) oxidized Si surface prior to functionalization, (b) room temperature preparation, and (c) 70 °C preparation. The rms roughness is (a) 0.15 nm, (b) 0.32 nm, and (c) 0.30 nm.

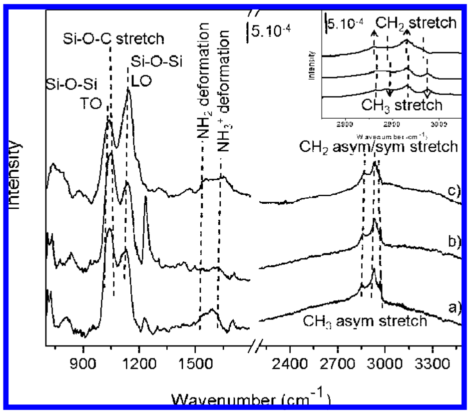

Figure 10. Infrared absorption spectra of an APS film prepared at room temperature immediately (a) before and (b) after annealing at 70 °C for 24 h. Spectrum (c) corresponds to the APS film obtained at 70 °C in situ. All spectra are referenced to the silicon oxide surface. The inset shows a zoom in the CH$_x$ region (2750−3050 cm^{-1}), where the same a, b, c ordering has been kept.

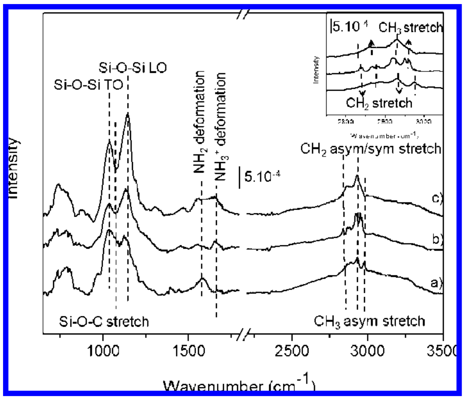

Figure 11. Infrared absorption spectra of an APS film prepared at (a) room temperature, and (b) after an additional temperature ramp (from room temperature to 70 °C), compared to (c) an APS layer obtained at 70 °C in situ. The spectra are referenced to the silicon oxide surface. The inset shows a zoom in the CH$_x$ region (2750−3050 cm^{-1}), where the same a, b, c ordering has been kept.

coverage indicates that the layers are not tightly packed. There is a significant contribution, however, at 1232 cm^{-1} (SiO$_2$ LO mode), which is attributed to oxidation of the substrate in air and not the film itself as in ref 34.

The insensitivity of the CH$_x$ stretching and Si−O−Si/SiO−C modes on ex situ heating suggests that, in contrast to what has been proposed,[35] curing the functionalized Si sample has little to no effect on the degree of attachment or density of the APS film. Curing therefore does not seem to promote horizontal polymerization or cross-linking of the APS chains on the surface. The clear presence of an asymmetric CH$_3$ stretching mode indicates that curing does not reduce the number of nonhydrolyzed ethoxy groups. In addition, the peak positions of the CH$_2$ stretching modes remain unchanged, and the fitting of the binding region (950−1250) cm^{-1} yields no significant change in peak intensities or positions.

Finally, the dependence on the time evolution of solution temperature is investigated by introducing the sample in an APTES solution at room temperature, then increasing the temperature to the desired one, and finally letting the sample incubate for 24 h at 70 °C. The time required to reach 70 °C from room temperature is ∼30 min. Figure 11b shows that the spectra resulting from this temperature ramp are very close to those prepared at room temperature (Figure 11a), suggesting that *preheating* the solution is an important step in order to ensure a better organized and attached film. Specifically, the CH$_3$ asymmetric stretching mode is much more intense, and the bimodal shape of the (950−1250) cm^{-1} spectral region is decreased when the solution is not preheated or is heated slowly during the reaction. Analysis of the bonding region shows that many changes that occur with in situ heating are absent (Figures 3 and 11). This result clearly indicates that the temperature during the first few minutes of processing, and therefore the *initial* attachment, is critical to the final quality of the APS film.

F. Stability in Water. Immersion of the saturated APS film prepared at room temperature in deionized water (pH ∼ 6) results in the degradation of the films within 1−2 h.[1] IR spectra indicate that the APS chains deposited at room temperature are removed from the SiO$_2$ surface as the SiO$_2$ surface itself is slowly etched (data not shown). Saturated APS films prepared in situ at 70 °C also exhibit the same trend in water, but the process is much slower. Figure 12 shows the normalized peak areas of the SiO$_2$ TO and LO and SiO−C stretching modes as a function of time; the sample is immersed in deionized water for an APS film prepared in situ at 70 °C. The areas of the Si−O−Si and SiO−C modes remain essentially unchanged for the first 10 min. Then, the area of all the modes decreases following an exponential decay. After 6 h in deionized water, approximately 50% of the spectral SiO−X region area has been removed. In comparison, the APS film obtained at room temperature is almost completely removed from the Si surface after the same time (i.e., 6 h) in deionized water (data not shown). In addition, for surfaces prepared in situ at 70 °C, we observe that the SiO$_2$ LO mode decreases somewhat faster than SiO$_2$ TO and SiO−C modes. This phenomenon points toward a possible mechanism of degradation: unreacted ethoxy groups constitute defect sites that

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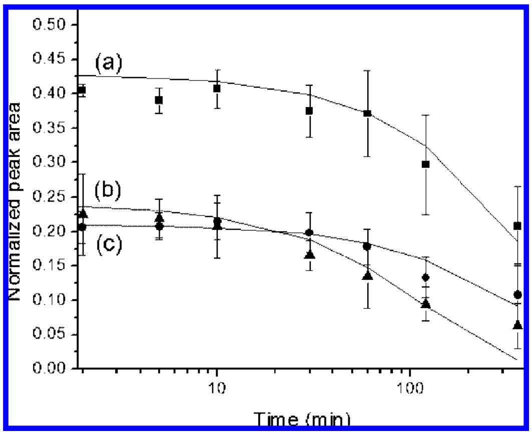

Figure 12. Normalized absorption band areas of (a) SiO_2 TO, (b) SiO_2 LO, and (c) SiO−C stretch modes as a function of time in deionized water.

can be first attacked by water, thus breaking the order of the film that is produced by in situ heating at 70 °C, and eventually removing the APS chains. The slower degradation of the layer in water further supports the assumption that the APS layer is attached more densely at the surface (i.e., less defects are present in the film) when prepared at 70 °C in situ than at room temperature, and that the breakage of the Si−O−Si bond by water molecules is sterically hindered by the close proximity and horizontal polymerization of neighboring chains. The relatively lower concentration of unreacted ethoxy groups for the APS films formed at 70 °C prevents the presence of a space that would favor the penetration of water molecules to break the Si−O−Si bond, slowing down the degradation of the film.

SiO_2 etching is eventually observed for samples prepared at 70 °C in situ after 60 min, but because of the better stability of the APS layer, such etching is less pronounced and slower than in the case of the film prepared at room temperature.

G. Discussion. The combined use of ellisometry and FTIR is helpful to provide both physical (thickness, refraction index) and chemical information for the APS films. Using the IR-derived oxide thickness increases makes it possible to model the ellipsometric data in a meaningful way. The IR spectroscopy results confirm the importance of in situ heating (preheating the APTES solution) as a way to improve the attachment and quality of APS films. In all cases, saturation is achieved, confirming the self-termination nature of the process (Figure 6), except for films grown in hydrous conditions (Figure 3), but the organization and orientation of the APS films strongly depend on how the heat is applied, when it is applied in the process, and which temperature is used, even for in situ heating. The quality of the APS films strongly depends on the first few minutes of deposition, as suggested by the results obtained after a temperature ramp (Figure 10). Most significantly, post-curing of an APS film obtained after a reaction at room temperature has little or no short-term effect on the attachment of the APS molecules to the silicon oxide surface, as evidenced by an absence of spectral changes either in the area of the Si−O−Si, SiO−C, or of the CH_3 stretching modes. IR spectroscopy data suggest that processing performed at higher temperatures leads to denser, stronger, and better-oriented APS films. Under these conditions, more Si−O−Si bonds are formed between the Si surface and the APS chains and between two APS chains (horizontal polymerization). In addition, a clear decrease in the amount of unreacted ethoxy groups is observed (decrease in the SiO−C and CH_3 stretching modes, Figures 2 and 5), suggesting that more ethoxy groups are hydrolyzed and thus susceptible to react with hydroxyl groups, either at the SiO_2 surface or with a neighboring APS molecule. Consequently, the low concentration of ethoxy groups after in situ reaction at 70 °C allows the APS chains to be closer to each other with a better packing, as evidenced by a ∼7 wavenumber red-shift in the position of the CH_2 asymmetric and symmetric stretching modes. The behavior of the SiO_2 TO and LO modes as a function of incubation temperature is also consistent with a tighter packing of the APS films prepared by higher temperature processing. Previous studies of ultrathin SiO_2 film growth and characterization have shown that the intensity of the SiO_2 TO mode depends on the amount of Si−O−Si bonding (i.e., coverage) and that of the LO mode on the long-range environment of Si−O−Si bonds.[36] The stability of the SiO_2 TO mode and the growth of the SiO_2 LO mode with increasing incubation temperature suggest that the number of chains present on the silicon oxide surface remains unchanged, but the long-range interaction and density of the bonds is increased. This result corroborates the observed increase in stability in deionized water for the APS film prepared in situ at 70 °C, for which half of the chains are still fully present on the surface after 6 h. This is strong evidence that the film is denser, making the diffusion of water molecules to the APS/SiO_2 interface more difficult. Water diffusion most likely occurs via the few defects (remaining ethoxy groups) present on these surfaces by hydrolization (lowering the steric barrier to accessing the SiO_2 surface). In short, the higher the concentration of unreacted ethoxy groups, the faster the APS film degrades.

From the IR spectroscopy results, a mechanism for the chemical reactions involved in APTES attachment at the surface can be proposed. In anhydrous conditions, physisorbed water near the silicon oxide surface is the only significant source of water in the system. The presence of this water layer is known to be crucial to the reaction, as it hydrolyses the APTES ethoxy groups from the molecule, allowing the resulting hydroxysilane to attach on the silicon oxide surface.[27] Because the availability of water is limited to the immediate vicinity of the surface (the experiment is run in a controlled atmosphere using an anhydrous solvent), there is limited temporal and steric opportunity for hydrolysis to occur. Therefore, at room temperature, significant quantities of APTES will not hydrolyze completely, leaving many ethoxy groups present. When the molecules attach, they form a disorganized and ill-defined film with many ethoxy groups and little long-range organization. As the incubation temperature is increased, increased Brownian motion of both the free and attached APS molecules promotes hydrolysis. Therefore, the ethoxy groups from the APTES reaching the surface are more fully hydrolyzed, and the APS layer formed is not as cluttered and disorganized but more ordered and denser, with stronger long-range interactions. Spectroscopically, this is supported by the red-shift of the CH_2 asymmetric and symmetric stretch modes, by the increase of the SiO_2 LO mode intensity, and by the decrease of the SiO−C mode intensity observed for higher in situ incubation temperatures. The higher stability in water of films prepared in situ at 70 °C is also consistent with these observations.

The increase of the $-NH_3^+$ mode at 1650 cm^{-1} with increasing incubation temperature suggests that the high-temperature treated surface exhibits more centers that can sustain proton transfer from other species (likely from the water molecules trapped near the APS layer). These new moieties would favor ionic interactions (stronger) with its environment rather than hydrogen bonding interactions (weaker), increasing the effectiveness of interacting with anionic or electronegative species. It is possible that both

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(36) Queeney, K. T.; Chabal, Y. J.; Weldon, M. K.; Raghavachari, K *Phys. Status Solidi* **1999**, *(a) 175*(1), 77–88.

the $-NH_2$ and $-NH_3^+$ moieties can interact with the silanol groups remaining at the surface or those on incompletely bonded APS. This proposed behavior is consistent with previous studies;[37] however, this behavior is likely limited at the exterior surface of the layer at higher temperatures by the observation that increased incubation temperatures yield a denser and thicker film, making it more difficult for amine groups to interact with the SiO_2 surface. The NH_3^+ signature could also be due to water molecules interacting with the NH_2 groups while removed from the glovebox; water in the atmosphere can enhance this if the NH_2 groups are exposed to the atmosphere. At 70 °C processing, the strong NH_3^+ signature suggests that more NH_2 groups are exposed to the atmosphere at the exterior surface than in the other cases. The amine groups are then free to interact with the outside environment or with further chemical treatments.

The increased thickness of the APS film at higher temperatures observed by ellipsometry can be rationalized as follows. Higher temperatures increase the Brownian motion of the physisorbed water, making it easier for these molecules to move and hydrolyze SiO−C, i.e., to form Si−O−Si bonds. As the layer grows, new Si−O−Si bonds are formed, creating a more hydrophilic environment for the water in this regime, further allowing for the diffusion of water within the local environment. The increased kinetic energy of the water molecules therefore not only drives the reaction faster kinetically, but increases the spatial regime in which the reaction is possible as well. The reaction terminates after a certain thickness is reached because there is insufficient water left. However, under non-anhydrous conditions, water is present in the bulk of the solution at all times during the reactions, and so the APTES molecules are free to both polymerize in the bulk or adsorb to the surface. Uncontrolled APS film growth is therefore likely a result of the adsorption of APS polymer "clumps" as well as monomers in an environment in which water is not localized near the hydrophilic surface, whereas controlled APS film growth is likely the result of monomer-only addition to the film in which water is localized. The moderate increase in film thickness with increasing incubation temperature is consistent with the commensurate increase in the Si−O−Si signal and CH_x signal for samples incubated at higher temperatures as well.

These data also show that ex situ heating does not bring the same benefits as in situ annealing. There is no spectroscopic evidence for chemical reactions within the APS film itself during annealing, although oxidation of the Si substrate takes place after a 24 h anneal in air (Figure 9). Clearly, preheating (or rapid heating) of the solution upon sample immersion is critical because the increased Brownian motion due to the increased temperature promotes the relevant reactions. Once attached and polymerized, the chains cannot easily react, even when heat is applied.

Conclusions

The effect of incubation temperature on the silanization of silicon oxide substrates with APTES has been investigated. The results have shown that in situ incubation at elevated temperatures (~70 °C) increases surface organization without compromising the self-termination of the deposition. In contrast, post-processing curing of APS films prepared at room temperature has little or no effect on the film itself. The data show that the attachment of the APS chains to the Si surface is more complete with fewer unreacted ethoxy groups. Finally the degradation in deionized water of APS-terminated Si surfaces also occurs, but the formation of a denser APS film with fewer defects at 70 °C substantially retards degradation. Application of this improved deposition method to microarray technology, organic semiconductors, and many other biotechnology and physics applications will help improve device performance in which a reliable surface attachment is desirable.

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