

Thin Films of (3-Aminopropyl)triethoxysilane on Aluminum Oxide and Gold Substrates

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The formation of thin films and monolayers of (3-aminopropyl)triethoxysilane (APS) on aluminum and gold substrates was studied with reflection–absorption FTIR spectroscopy (RAIR), ellipsometry, contact-angle, and quartz-crystal microbalance (QCM) measurements. The structure of the APS films is strongly dependent on the experimental conditions, such as substrate pretreatment, mode of adsorption, and post-treatment. APS was adsorbed on the substrates from aqueous solution, from refluxing solvent, and from the gas phase. Adsorption from solution yields multilayers. APS films of about molecular thickness are obtained by vapor adsorption on the precleaned substrate. The presence of water has a strong effect on the film formation. Depending on the experimental conditions, the final surface loading varies between about 5.3 and 8 molecules per nm², and the film thickness varies between 5 and 11 Å.

Introduction

Organic surface chemistry has become a central theme in the more general area of surface science. We can distinguish three classes of organic surfaces: layers that rely on surface coordination, e.g., mercaptans adsorbed on gold, Langmuir–Blodgett films on miscellaneous surfaces, and existing surfaces of organic solids, such as polymer interfaces.¹

Silane coupling agents (SCA) rely on surface coordination, similar to their mercaptan analogs. SCAs have found many applications in surface modifications, especially in combination with hydroxylated surfaces, such as metal oxides or ceramics.^{2,3} The final structure of the adsorbate is a sensitive function of the head–substrate, head–head, and chain–chain interactions. Long-chain silanes of the formula CH₃(CH₂)_nSiCl₃ form densely packed, highly ordered, monomolecular assemblies with solid-state-like properties.⁴ Commonly, these films are termed self-assembled monolayers. It is generally accepted that SCAs with short chains may constitute films of molecular thickness that are not crystalline but may have some preferred orientation;⁵ we name these types of films monolayers. The absence of dense packing within these films relaxes steric constraints at the interface. Reduced steric constraints make short-chain SCAs interesting precursors for multistep surface modifications employing surface-confined reactions. The formation of (3-aminopropyl)triethoxysilane (APS) thin films on smooth metallic substrates has been studied.⁶ We have recently shown that the amine functionality permits a variety of subsequent chemical modifications.⁷

The amine in the 3-position of APS has a strong effect on its chemistry in aqueous solution, compared to silanes

that lack the amine or have the amine in a different position. Experiments indicate that the alkoxy groups are immediately hydrolyzed and that no monomeric species are present in aqueous solution, even in very dilute solutions.⁸ Ishida and co-workers have attributed the rapid hydrolysis to the catalytic effect of the amino group and proposed the formation of six-membered hydrogen-bonded rings in solution.⁹ Amines also catalyze surface attachment reactions with surface hydroxyl groups.

The hydrolysis and condensation reactions of the siloxane moiety and the possible presence of several species complicate the characterization of these materials in solution. A single, continuous layer is sufficient for most applications and often represents an optimum for surface modification. The chemical constitution of the precursors in solution is of importance when considering the structure of the adsorbed silane layer on a surface.⁹ Combined with the possible presence of several species, this may result in structurally and chemically undefined films that exceed monolayer coverage.¹⁰ Ethoxy or hydroxy groups of the precursors that are not engaged in surface coordination can bind via hydrogen bonds with silanols or amines or form covalent linkages; lateral (covalent) binding is expected to cross-link the film, whereas vertical binding results in multilayer formation. Furthermore, water is essential for the surface anchoring of SCAs, but it is difficult to determine the amount of water required to form a specific layer structure. The deposition of well-defined APS films requires a detailed knowledge of the factors discussed above.

Our study has therefore two objectives: (i) to explore the effects of condensation reactions on film formation and (ii) to develop an experimental procedure that generates APS layers of molecular thickness. The characterization of the films includes RAIR spectroscopy, ellipsometry, and gravimetric measurements with the piezoelectric quartz crystal microbalance (QCM).

Experimental Section

Materials. (3-Aminopropyl)triethoxysilane (APS) was obtained from Aldrich and was used as received. All manipulations were performed under inert atmosphere (boil-off nitrogen). All

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solvents were used as received, unless stated otherwise. For the water contact angle measurements, HPLC grade water from Aldrich was used. For the adsorption experiments, deionized, distilled water was used.

Preparation of Substrates. Silicon wafers (75 mm) or glass slides (Fischer, 7.5 cm \times 2.5 cm) were immersed in a piranha solution (7:3 concentrated H_2SO_4 /30% H_2O_2) at 90 °C for 30 min, rinsed with distilled water, and blown dry with a strong flow of nitrogen. (**Caution:** "piranha" solution reacts violently with many organic materials and should be handled with extreme care.) Aluminum and gold films of 2000 Å thickness were prepared by physical vapor deposition of the pure metal (99.999%, Aldrich) on precleaned substrates (thermal evaporator/oil diffusion pump or e-beam evaporator, cryo pump, thickness monitor). To improve the gold adhesion, substrates were either precoated with a 200-Å evaporated Ti layer or by adsorbing a monolayer of (3-mercaptopropyl)trimethoxysilane (MPS). MPS was adsorbed from the vapor phase on the precleaned substrate and annealed for 1 h at 75 °C.¹¹ After evaporation the bell jar was purged with helium. The surfaces were treated in an oxygen or nitrogen plasma prior to adsorption¹² (Reytheon or OPHTOS Microwave generator, McCarroll Coaxial chamber, 10 Torr, 80–100 W, 2–5 min, short-term storage under Ar until use). With Al films, in either case a 30–80 Å thin aluminum oxide layer is maintained as demonstrated by ellipsometry and XPS. Surfaces prepared with this procedure showed no organic contamination in RAIR spectra and were totally wetted by water. Investigation with electron microscopy reveals a surface topology of shallow, rolling hills (several hundred angstroms). The optical constants of the metal films were determined immediately before exposure to APS.

Adsorption of APS. APS was adsorbed from solution (method I), from refluxing vapors (method II), and from the vapor phase above the neat liquid (method III).¹³ We also distinguish substrates that were exposed to water vapor prior to APS exposure (method III/w) and those that were not (method III/d). For deposition on QCMs we also employed a flow cell (method IV).

Adsorption from Solution, Method I. The precleaned substrates were immersed into aqueous solutions of APS at room temperature (0.1% to 20% by volume); ethanol, 2-propanol, butanol, and toluene solutions were also explored, but only aqueous solutions will be discussed in detail. The pH of a 1% aqueous solution of APS is 10.4; the pH was adjusted with acetic acid up to about pH 5 to prevent corrosion of the Al substrate. The solution was stirred and immersion times varied from several minutes to several hours. The slides were removed with Teflon tweezers, rinsed with distilled water and 2-propanol, and blown dry with a strong stream of nitrogen.

Alternatively, a known amount of APS dissolved in dry methanol was applied directly to the precleaned surface. In a typical experiment, 200 μL of APS was dissolved in 30 mL of methanol; 1 mL of this solution was diluted with 30–100 mL of methanol; 30–100 μL of this solution was applied with a GC microsyringe to the precleaned substrate and directly transferred into the spectrometer for *in situ* experiments.

Adsorption from Reflux, Method II. The adsorption from a boiling mixture of the SCA and a solvent (here: toluene) was performed as described in detail by Haller.¹⁴ The apparatus and the solvents used were dried before the experiment.

Adsorption from Vapor Phase, Method III. The cleaned substrate was placed in a glass dish that supported the substrate at the corners approximately 5 mm above the surface of the liquid. Under nitrogen, 200 μL of APS was dropped at the bottom of the dish with an Eppendorf pipet. The slide to be modified was immediately deposited onto the dish with the metallic side facing the solution, and the dish was covered with a lid. Two sets of conditions were employed, either the freshly plasma cleaned substrate was exposed immediately to APS (method III/d) or the substrate was previously exposed to a stream of water vapor in nitrogen (method III/w). In the latter case we expect a bulk

water interface rather than a hydroxylated surface.¹⁵ Although we investigated these surfaces, we have no reliable information about the resulting water layer at this point. Adsorption times were varied from several minutes to several hours. After deposition of APS, the slides were removed from the dish and evacuated (10^{-3} Torr, molecular sieve pump) and purged with nitrogen to remove an excess layer of physisorbed material. Heating was either carried out in the RAIR spectrometer sample chamber or under vacuum in an oven at 90 °C.

Gravimetric Adsorption Measurements and Method IV, Dynamic Sorption. Before adsorption of APS, the QCM crystals (International Crystal Manufacturing Co., Oklahoma, bonded electrodes, 1500 Å Au on 135 Å Cr, or 2000 Å Al, polished crystals, OD 13.7 mm, electrode diameter 10 mm) were cleaned in a nitrogen or oxygen plasma. The adsorption was carried out under the same experimental conditions as described above. For static vapor adsorption, the QCM was mounted with a plastic disk in a small glass vial that contained 0.5 mL of APS. Frequency measurements were recorded *in situ* during sorption and subsequent treatments.

Method IV, Dynamic Sorption (Gas Flow). Vapor flow experiments were carried out in a glass flow chamber with several inlets and a vacuum connection. The QCM electrodes, connected by electric feed-throughs, were positioned facing the inlets. Nitrogen was bubbled through the APS solution and fed into the chamber. The reported values from QCM measurements are corrected for flat surfaces, by taking into account the surface roughness that was determined from nitrogen adsorption isotherms (ca. 15% additional surface area).

Wetting Measurements. Advancing water contact angles at room temperature were determined with a self-built goniometer, according to the procedure described in ref 7b.

Ellipsometry. The film thickness was determined with a photometric ellipsometer with a rotating analyzer (Rudolph) at 633 nm. Linear polarized light with an azimuth of 25° was incident at 70°. These are optimum parameters for a nonabsorbing film with a thickness smaller than 250 Å on a conducting substrate.¹⁶ The surface was investigated at several spots by translating the sample with an x,y translation stage, and the individual measurements were averaged. The azimuth-intensity raw data were transferred to a computer and Fourier analyzed. We calculated the dark current from the zeroth harmonic and the ellipsometric data from the second harmonic. We evaluated the other harmonics up to the ninth for instrumental performance. Coefficients larger than 0.005 were considered significant and were suggestive of a departure from ideal instrument behavior.

The ellipticity coefficient was measured in two steps. The optical elements in the input beam were adjusted, and the input polarization was measured with the instrument in the straight-through mode (no sample). After data collection, the sample was mounted in the instrument, the angle of incidence was adjusted, and the output polarization was measured. From the complex ratio of the input and output polarization, the complex refractive index of the substrate was calculated. The importance of this method lies in a significant improvement of the accuracy of the instrument.¹⁷ The uncertainties in ψ and Δ are 0.06°; the detection limit of the change in the film thickness that can be determined with 95% confidence is 0.4 Å.

The samples were measured again after surface modifications. For thin film measurements, the refractive index of 1.421 for liquid APS was used (see Results and Discussion). We employed a three-layer model, consisting of the substrate, the film, and the ambient (air), and calculated the complex film thickness with the previously determined optical constants. We interpret the residual imaginary part of the complex film thickness, d_{fi} , as a

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(16) The sensitivity and the uncertainty of the ellipsometric parameters Δ and ψ are polarization dependent. The optimum experimental parameters were determined by maximizing the sensitivity and minimizing the uncertainty functions that are effective for the rotating analyzer ellipsometer (e.g., Aspens, D. E. *J. Opt. Soc. Am.* **1974**, *64*, 639).

(17) The input polarization is typically calculated from the settings of the optical elements in the optical wave train of the incident beam. If monolayers are under consideration, the error in this procedure can be substantial, due to errors in the calibration of each optical element, especially if a compensator is used.

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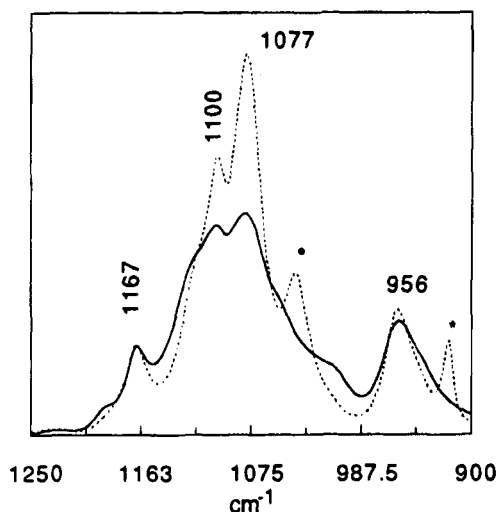


Figure 1. Normalized transmission spectra of neat APS (solid line) and APS dissolved in acetonitrile (dashed line). Dilution results in motional narrowing of the band contour. Marked bands (*) are from acetonitrile.

manifestation of errors, including experimental and model errors. The film thickness is real only in the absence of errors.¹⁸ The residual imaginary part of the total film thickness was generally less than 10%.

Reflection–Absorption Fourier Transform Infrared Spectroscopy. RAIR spectra were taken on a Mattson RS1 FTIR spectrometer, equipped with a liquid-nitrogen-cooled MCT detector. We employed *f*/20 custom-built optics to collect RAIR spectra; 100 scans at a resolution of 4 cm^{−1} were averaged. Samples could be heated in the sample chamber. The sample compartment was evacuated and the interferometer was purged with boil-off nitrogen. Gold slides were used as reference surfaces because of their optical stability. If the sample substrate has different optical properties, for example, in the case of aluminum/aluminum oxide, the baseline will be tilted; this effect can be compensated with a linear baseline correction. This method is advantageous because the oxide thickness varies for different aluminum films.

Transmission spectra were recorded with the same instrument and the internal DTGS detector; four scans were recorded at a resolution of 2 or 4 cm^{−1}; the sample compartment was purged with boil-off nitrogen.

Results and Discussion

Transmission Spectra of APS. Silanes show distinct patterns in their vibrational spectra which provide valuable information about the molecular environment. This property originates from the effective vibrational insulation by the relatively high mass of the silicon and from the presence of permanent dipole moments in the silicon–oxygen and silicon–carbon bonds.¹⁹

In condensed phase, interactions such as inter- and intramolecular hydrogen bonding between the amine and siloxane moieties become effective, leading to broad spectral envelopes. Dilution reduces the molecular interactions, resulting in narrow spectral envelopes; it is commonly accepted that the narrowing originates in the more rapid molecular motion (translation/rotation) in dilute solution.²⁰ Figure 1 shows normalized transmission spectra of neat APS and APS diluted in acetonitrile.

Table 1. Mode Assignments and Band Positions of APS Transmission Spectra (Literature Values in Brackets)^a

wavenumber (cm ^{−1})	assignment
2975	CH ₃ , asym str (−OCH ₂ CH ₃)
2926–2930	CH ₂ , asym str (CH ₂ CH ₂ CH ₂)
2890–2855	CH ₂ , sym str (CH ₂ CH ₂ CH ₂), CH ₃ , sym str (−OCH ₂ CH ₃)
Liquid	
1167, 1100, 1077, 956	Si–O–C
1605	NH, def (bending)
1500–1400	CH ₂ propyl [1470]; CH ₂ adjacent to Si (scissor) [1420–1400]; CH ₃ asym def [1460]
1390	CH ₃ , sym def
1295	(C–N)
1250	SiCH ₂
Solid (Polymerized)	
1135/1035	Si–O–Si (very broad)
1580	NH, def (bending)
1480	CH ₂ , scissoring

^a From: (a) Smith, A. L. *Spectrochim. Acta* **1960**, *16*, 87. (b) Anderson, D. R. In *Analysis of Silicones*; Smith, L. A., Ed.; Wiley: New York, 1974; Chapter 10. (c) Bellamy, L. J. In *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: New York, 1975, Vol. 1 and Vol. 2. (d) Wright, N.; Hunter, M. J. *J. Am. Chem. Soc.* **1947**, *69*, 803.

The band positions and assignments of APS transmission spectra are summarized in Table 1. The intensity contour of APS strongly depends on the conditions under which the transmission spectrum is recorded, e.g., dilution, degree of condensation, etc. The positions of the N–H deformation modes shift, depending on association, hydrogen bonding, or protonation. The C–H modes of the backbone partially overlap with the modes of the alkoxy groups. Ethoxy silanes generally show a doublet for the Si–O–C stretching mode at about 1100 and 1075 cm^{−1} and two bands at 1175–1160 cm^{−1} and 970–940 cm^{−1} (liquid APS: 1167, 1100, 1077, 956 cm^{−1}). Modes of Si–O–Si and Si–O–C can overlap. The Si–O modes of condensed silanes can occupy the entire spectral region from 1000 to 1200 cm^{−1}. The Si–O–Si stretching modes are stronger than the Si–O–C modes. The Si–O–Si modes for alkyl-substituted disiloxanes fall between 1070 and 1040 cm^{−1}, and as the siloxane chain length increases, the band splits into two peaks; for chain polymers the band covers the entire region and has two or more maxima (for example, 1135 and 1035 cm^{−1} in solid, polymerized APS).

Solution Adsorption of APS, Method I. Adsorption from aqueous solution containing 0.1–20 vol % of APS on the precleaned aluminum substrate results in films at least several molecular layers thick as indicated by ellipsometry and RAIR spectroscopy, in agreement with previous studies.⁸ Although the band contours in RAIR spectra vary slightly for different preparation methods, we can identify the following characteristics (Figure 2 and Table 2): The CH stretching region shows strong bands at 2857 and 2928 cm^{−1} that are assigned to the propyl backbone and a weak band at 2966 cm^{−1} from nonhydrolyzed ethoxy groups. The Si–O modes show very broad bands around 1100 cm^{−1} with a shoulder at about 1200 cm^{−1} (bandwidth at half height ca. 200 cm^{−1}). The self-catalyzing effect of the amino group causes rapid hydrolysis of the ethoxy groups in aqueous solution. The silanol groups are very reactive and condense to form siloxane oligomers in solution. The adsorption of siloxane oligomers on the substrate would account for the film thickness and for the reduced intensity of ethoxy modes

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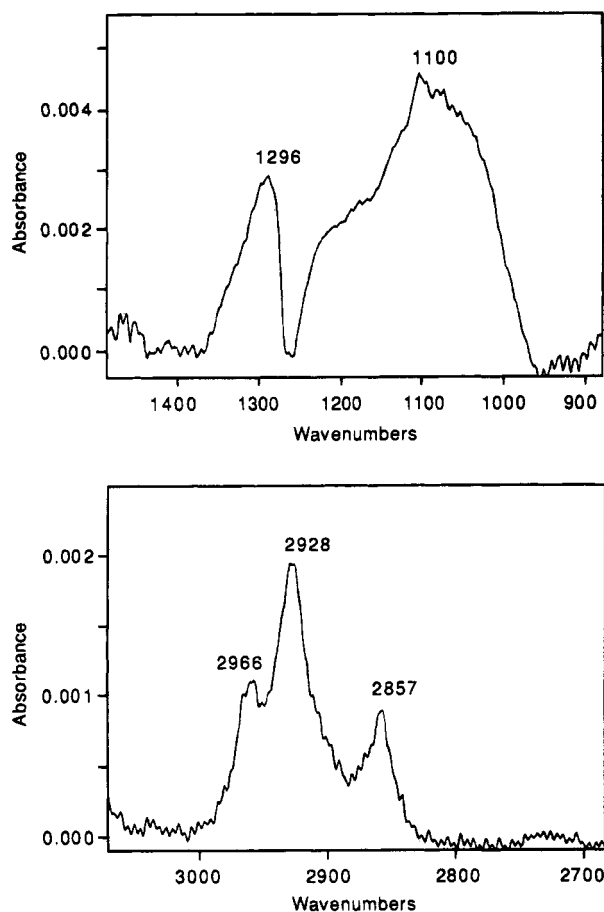


Figure 2. RAIR spectrum of APS adsorbed on aluminum from aqueous/ethanol solution at 25 °C (method I). Solution composition was 50 mL of water, 0.81 mL of ethanol, and 0.56 mL of APS; sorption time was 30 min.

Table 2. Summary of Results for Different Methods of Preparation of APS Films on Aluminum^a

	aqueous solution method I	reflux method II	vapor phase	
			method III/d	method III/w
SiO (cm ⁻¹)	1200 sh/1100	1100	1130/1090 sh	1105
fwvh (cm ⁻¹)	200 (±20)	100 (±10)	100 (±10)	100 (±10)
SiOEt	—	nr	1390/1170	nr
NH (cm ⁻¹)	—	1650 br	1600/1520 br	1510 br
CH (cm ⁻¹)	2928/2857	2924/2853	2927/2860	2926/2860
		2890 sh	2975 sh/2890 sh	
<i>d</i> (Å)	>20	21 ± 4	5 ± 1	11 ± 1
CAN (deg)	—	65 ± 5	50 ± 5	65 ± 5

^a Nomenclature: *d*, thickness; sh, shoulder; br, broad; nr, not resolved; —, inconsistent results.

in the RAIR spectra. Adsorption from dried organic solvents at room temperature afforded inconsistent results, apparently because trace amounts of water lead to various degrees of hydrolysis and condensation of the APS.

We obtained consistent results by directly applying a known amount of APS in dry methanol to the surface and drying the sample. With this technique one can establish conditions independent of the colloid chemistry in solution and control the surface loading; the resulting films are one to three layers in thickness. Figure 3 shows the Si—O and CH stretching regions of APS adsorbed on gold and the spectral development when the sample is heated in the RAIR spectrometer sample chamber (at ca. 0.01 Torr). Freshly deposited APS (spectrum 1) shows Si—O modes with maxima at 1126 and 1091 cm⁻¹ and bands at 1390, 1163, and 963 cm⁻¹ from ethoxy groups (compare Table 1). The amine bending mode is observed at 1580

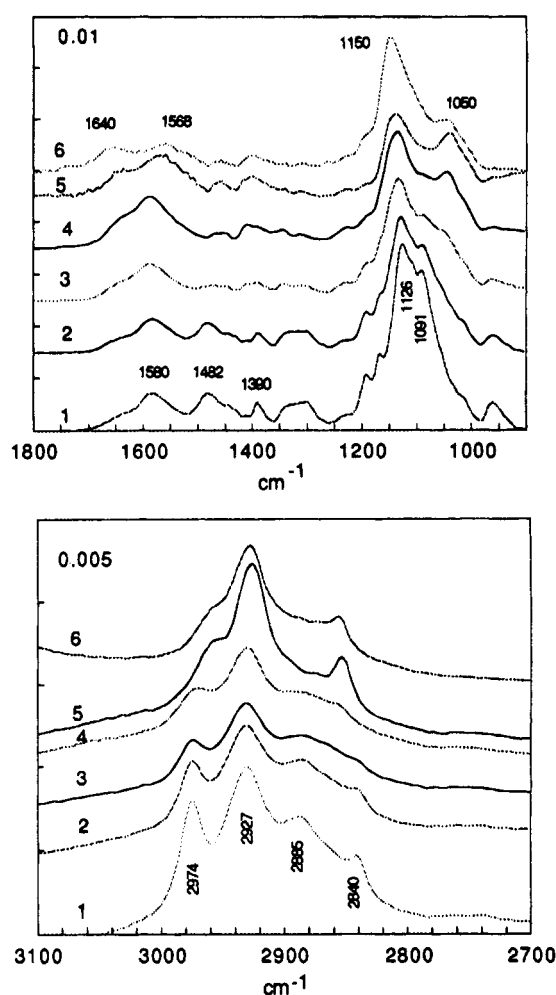


Figure 3. RAIR spectra of APS adsorbed on gold from methanol solution, as a function of hydrolysis and condensation reactions (1, first spectrum, freshly deposited APS at room temperature; 2, plus 4 min at 75 °C; 3, plus 6 min; 4, plus 6 min; 5, plus 20 min; 6, after heating for 12 h at 75 °C).

cm⁻¹. The Si—O modes broaden and develop several maxima as the adsorbate cross-links (spectrum 5); at the same time the ethoxy modes decrease in intensity (see also the C—H stretching region). For spectrum 6 the sample was removed from the spectrometer and heated for 6 h in air at 90 °C. The film is extensively cross-linked; the Si—O region shows one major peak at 1150 cm⁻¹ and a shoulder at 1050 cm⁻¹. As pointed out above, the Si—O modes reflect the particular environment of the molecules. The distinctive Si—O pattern in Figure 3 is characteristic for low-dimensional siloxane networks with reduced intermolecular interactions.²¹ One would expect mutual attractions to be diminished in a thin film where the siloxane moieties are located at the interface. The two bands around 1568 and 1640 cm⁻¹ are assigned to ammonium bicarbonate formation as the sample was exposed to the atmosphere.

Transport via Reflux (Method II). The undesired adsorption of APS aggregates that exist in solution can be prevented by adsorption from the gas phase. Vapor adsorption of amino functionalized silanes from boiling aprotic solvents was first reported by Haller (on silicon wafers).¹⁴ We employed the method described by Haller for the adsorption of APS on aluminum substrates from boiling toluene. Analysis by RAIR spectroscopy shows intensities exceeding those of molecular films; diminished intensities of the ethoxy modes (2975, 1390, and 1167

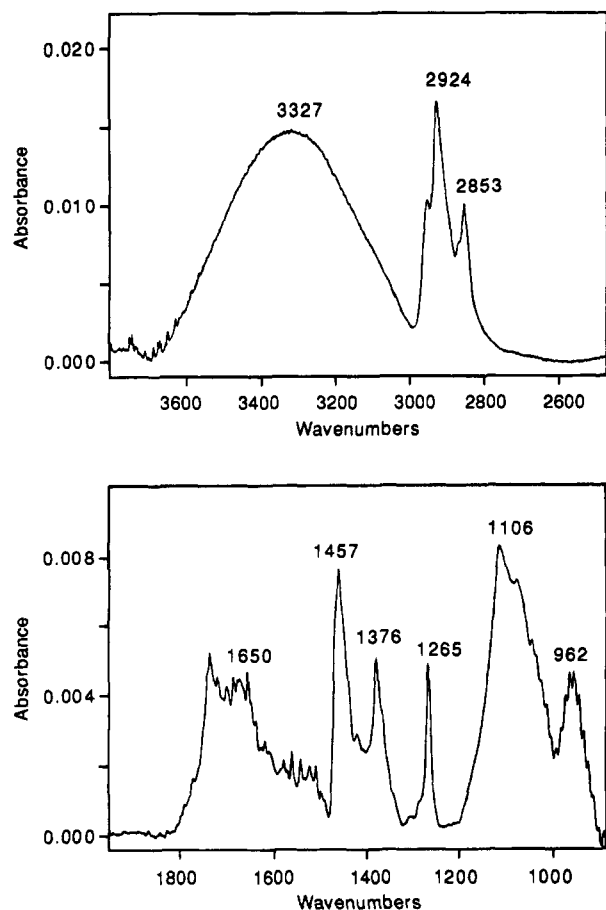


Figure 4. RAIR spectrum of APS adsorbed on aluminum from refluxing toluene solution (method II). Solution composition was 15 mL of toluene and 1.0 mL of APS; reflux time was 16 h.

cm^{-1}), and the Si—O band pattern around 1100 cm^{-1} (bandwidth at half height approximately 100 cm^{-1}) are characteristic for polymerized siloxanes (Figure 4, Table 2). We measured an advancing water contact angle of 65° . Bascom has reported contact angles for various APS films ranging from 38° to 53° .¹⁰ The wetting behavior of APS thin films is the result of several contributions, including amino, ethoxy, and silanol groups in the film, and a high contact angle is attributed to a high degree of cross-linking.

We observed variations in the film thickness; the average thickness is $21 \pm 4\text{ \AA}$ (imaginary residue 0.4). The imaginary part of the complex thickness, d_{A} , is within the uncertainty of the measurement, indicating good agreement of model and experiment. If an extended APS molecule is approximately 10 \AA in length, these films comprise two to three molecular layers. For a liquid-like APS film of molecular thickness (10 \AA), we can expect a surface loading of approximately 94 ng/cm^2 (density of APS 0.942 g/cm^3). With the QCM we measured a surface loading of 215 ng/cm^2 which corresponds to two to three molecular layers, taking into account loss of ethoxy groups as a result of hydrolysis and cross-linking. Since the adsorption is carried out at elevated temperature, this method may be particularly sensitive to trace amounts of water that efficiently cross-link APS on the surface. In summary, we found that transport via solvent reflux produced APS films with a thickness of several molecular layers.

Vapor Phase Adsorption, Method III. It was previously demonstrated for several functionalized silanes that monolayer coverage can be achieved if the reagent

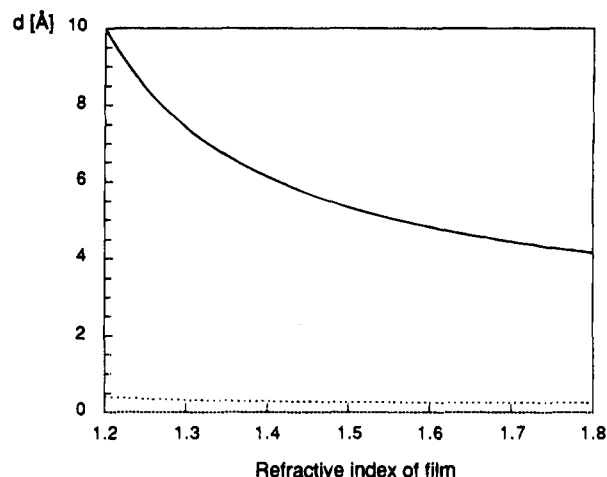


Figure 5. Real (solid line) and imaginary (dashed line) film thickness in angstroms as a function of the film refractive index for vapor-adsorbed APS on aluminum oxide (angle of incidence, 70° ; λ , 6328 \AA ; N_s , $0.873-i5.099$).

is adsorbed from the vapor phase.²² Presumably the oligomers that form in solution have a sufficiently low vapor pressure at room temperature to prevent transport to the substrate. We thus investigated APS vapor adsorption on aluminum oxide and gold surfaces from the neat liquid at room temperature. As shown below, ellipsometry, RA spectroscopy, and QCM measurements all indicate the presence of molecular APS films. We explored two methods of vapor phase adsorption: method III/d, the plasma-cleaned substrate is directly exposed to the silane vapors; and method III/w, the plasma-cleaned substrate is first exposed to a stream of water-saturated nitrogen, then to silane vapors.

The average film thickness on aluminum for method III/d is $5 \pm 1\text{ \AA}$ (imaginary residue 0.4), and for method III/w it is $11 \pm 1\text{ \AA}$ (imaginary residue 2.4). The small scatter in the real part of the film thickness indicates good reproducibility of both methods. Surface heterogeneity and surface roughness are minimal. For thin films we cannot determine the refractive index of the adsorbate from ellipsometry. Furthermore, the refractive index is a function of the degree of hydrolysis and condensation. However, variations in the refractive index have only a small effect on the calculated film thickness as shown in Figure 5. The variation of the film thickness is small and it seems justified to use the bulk refractive index for all samples.

The water contact angles of 50° for method III/d and 65° for method III/w indicate varying amounts of ethoxy groups present in the film (see discussion of RAIR spectra below). Condensation of silanes in the film increases the water contact angle and, furthermore, might increase the surface loading.

The surface loading, averaged over several QCM experiments, is 112 ng/cm^2 for method III/d (δf : $48 \pm 2\text{ Hz}$, $5.3\text{ molecules/nm}^2$) and 138 ng/cm^2 for method III/w (δf : $58 \pm 2\text{ Hz}$).²³ The number density in the former case is consistent with that of a crystalline hydrocarbon monolayer (ca. 21 \AA^2 per molecule, or $4.8\text{ molecules/nm}^2$).²⁴ The surface loading in the prewetted case III/w is somewhat larger than for dry adsorption conditions. In the extreme case of complete hydrolysis on the prewetted surface, one would expect surface loading due to the species

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(23) The silanes may have one, two or three alkoxy residues. We calculated the average surface loading for species with one remaining alkoxy group, i.e., $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})$.

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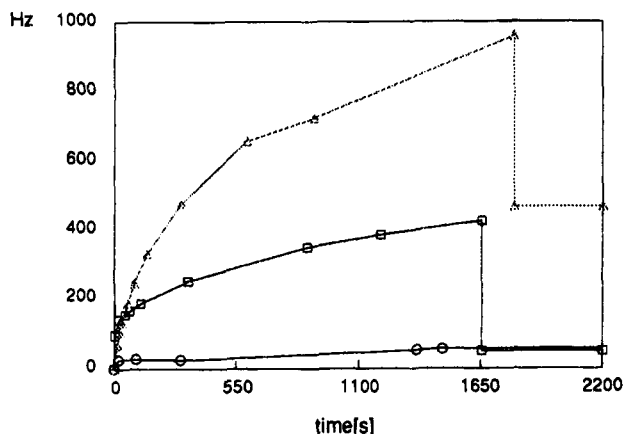


Figure 6. Real time QCM measurements of APS adsorption on aluminum electrodes: squares, static adsorption under dry conditions, δf 48 Hz (a); circles, dynamic adsorption in nitrogen/APS stream, δf 55 Hz (b); triangles, adsorption under ambient conditions, δf 465 Hz (c).

$\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}$ (one oxygen bridge supplied by the surface, the other two from water or ethoxy groups). The loading of 138 ng/cm^2 in the prewetted case now corresponds to $7.8 \text{ molecules/nm}^2$ and suggests that slightly more than a monolayer was deposited.

The real time QCM response for the adsorption of APS on aluminum-coated QCMs is shown in Figure 6. Curve a was obtained by static adsorption of APS (method III/d). Evacuation removes the physisorbed layer; the resulting frequency change corresponds to a single layer (δf : 48 Hz, Figure 6a). *Dynamic adsorption (method IV)* in a nitrogen/APS stream results also in monolayer formation (δf : 55 Hz, Figure 6b); however, no physisorbed film is formed. This effect may be related to a smaller partial pressure of APS in the nitrogen stream. Apparently, once all surface sites are consumed, no additional chemisorption takes place. The chemisorption sites are presumably the surface hydroxyl groups on Al/Al oxide. Under ambient conditions (25% relative humidity) the persistent frequency change after evacuation was much larger (δf : 465 Hz, Figure 6c). In this case, the final surface loading was a function of exposure time. This is attributed to the presence of water vapor combined with the ability of the amine to catalyze hydrolysis and condensation reactions, thus adding continuously to the siloxane film.

Representative RAIR spectra of APS films on aluminum substrates prepared with methods III/d and III/w are shown in Figure 7.²⁵ As expected, the RAIR spectra display different degrees of condensation for the two methods. Most indicative of the progress of condensation is the intensity of the ethoxy modes at 2975 and $2890 \text{ (sh)} \text{ cm}^{-1}$ (not shown), and at 1390 and 1170 cm^{-1} , that are still observed for films prepared with method III/d. We also note two resolved bands at 1130 and 1090 cm^{-1} (Figure 7A). The latter RAIR band profile is identified with low-dimensional Si-O networks with reduced intermolecular interactions (see above discussion). The film most likely consists of loosely connected APS oligomers of low molecular weight. The N-H bending modes are observed in the region around 1600 cm^{-1} , indicating both free (ca. 1520 cm^{-1}) and associated (1600 cm^{-1}) amino groups.²⁶ The presence of associated amino groups could suggest hydrogen bonding in the film, causing the APS molecule

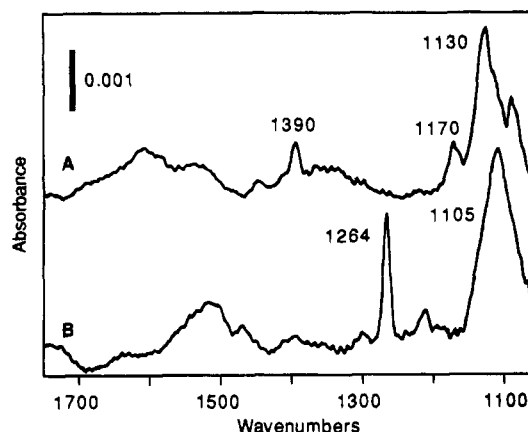


Figure 7. RAIR spectra of APS adsorbed on aluminum from the vapor phase: (A) method III/d, 0.5 mL of liquid APS equilibrated with substrate in nitrogen atmosphere, at a distance of ca. 2 cm, followed by evacuation (10^{-3} Torr); (B) method III/w, substrate was pretreated with water-saturated nitrogen at 25°C , then treated with APS as in method III/d.

to bend back to the surface, and causing the propyl group to assume a mostly horizontal orientation. Association and hydrogen bonding in APS have been proposed previously.²⁷

RAIR spectra of samples prepared with method III/w are characterized by one broad band at 1105 cm^{-1} in the Si-O-Si region (Figure 7B). The intensity of the ethoxy modes is significantly reduced. The silane head groups are now highly cross-linked. A band at 1264 cm^{-1} is associated with the methylene wagging vibration of the propyl chain. The transition dipole moment of this mode is parallel to the propyl chain, suggesting a more upright position of the propyl backbone in this sample. This is consistent with the absence of NH bending modes at 1600 cm^{-1} for associated amino groups.

A compilation of key results for different preparation methods on aluminum substrates is given in Table 2.

Heating thin films of APS (prepared according to method III/d) under nitrogen or vacuum up to 90°C results in condensation as indicated by the disappearance of the bands due to ethoxy groups and corresponding changes in the Si-O pattern (see foregoing discussion and Figure 8). Furthermore, the intensity of the methylene wag at 1264 cm^{-1} shows increased intensity, again indicating a more upright backbone orientation after heating.

On heating, the contact angle on aluminum substrates increased to as much as 75° as a result of the extensive cross-linking. Ellipsometry indicated changes in Δ and ψ which were too large to be explained by changes of APS alone; if we include the underlying oxide layer in the model, we find an increase in the aluminum oxide layer thickness, by typically 5 \AA . These changes make it difficult to extract the thickness of the organic layer. The refractive index of blank aluminum slides remains unchanged upon heating in air at 90°C . A possible explanation for the changes observed when APS is present could be its corrosive nature.

In contrast to aluminum, vapor phase adsorption of APS on gold substrates is characterized by the absence of surface coordination chemistry. QCM measurements, RAIR spectra, and ellipsometry indicate that preadsorbed water on the gold surface is essential for adsorption of APS (method III/w). The immobilized APS layer could not be washed off. Overall, the films on gold surfaces are

(25) The band intensities correspond to monomolecular coverage as isotropic simulations of RAIR spectra demonstrate (ref 21).

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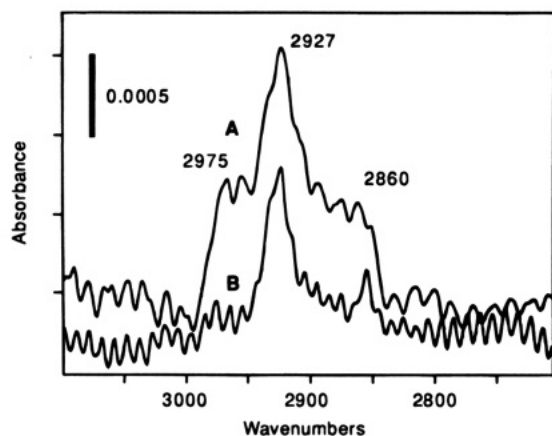


Figure 8. RAIR spectra of APS adsorbed on aluminum from the vapor phase according to method III/d: (A) spectrum taken after deposition at 25 °C; (B) spectrum taken after heating at 90 °C for 45 min in vacuum (10^{-3} Torr).

similar in terms of film thickness, RAIR band contour, and surface coverage to aluminum substrates modified with method III/w. The surface attachment is suggested to result from surface polymerization of APS; however, the exact binding mechanism remains unknown.²⁸

Conclusions

Utilizing reflection-absorption FTIR spectroscopy, ellipsometry, contact-angle measurements, and the quartz-crystal microbalance, we have investigated the adsorption of (3-aminopropyl)triethoxysilane on oxidized aluminum and gold surfaces. The specific surface properties and the final film structure strongly depend on the particular experimental conditions. The assembly process is a sensitive function of substrate conditioning, adsorption conditions, and post-treatment.

Adsorption of APS from aqueous solution probably results in adsorption of oligomeric particles; the thickness of the final film is greater than that of monolayers. Adsorption from boiling vapors results in thin films of approximately two to three layers in thickness. Vapor

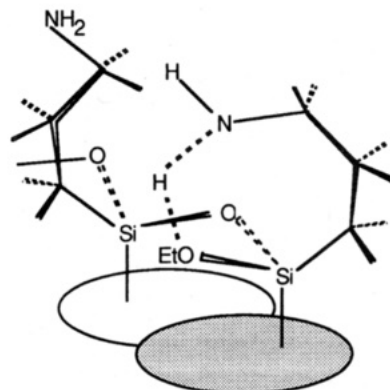


Figure 9. Graphical representation of APS adsorbed on a hydroxylated surface. The shaded area represents the projection of the molecule on the surface.

phase adsorption of neat APS at room temperature is a convenient method to prepare thin films. Water is an important factor in the surface attachment of APS. We can make a qualitative correlation: in a humid atmosphere the film thickness increases steadily with exposure time; in a dry atmosphere films of molecular thickness form. If the substrate is exposed to water vapor prior to adsorption, the final film is composed of a two-dimensional, cross-linked siloxane network; in contrast, on unexposed substrates the film still contains ethoxy silane groups. These subtleties of surface structure are reflected in the wetting behavior; films still containing ethoxysilane groups are more hydrophilic. A schematic representation is given in Figure 9; surface bonding, siloxane cross-linking, and amine association of APS are shown. In contrast to aluminum, preadsorbed water is essential for adhesion of APS on gold. Most probably, APS adheres by surface polymerization.

In the cases of molecular coverage with two-dimensionally cross-linked siloxane networks, the films are probably best viewed as "molecular carpets" with preferred orientation of the reactive amino groups toward the top surface of the film.

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