(64) McIntosh, T. J.; Simon, S. A. *Biochemistry* **1986**, *25*, 4058.
(65) Israelachvili, J. N.; Pashley, R. M. *Nature* **1982**, *300*, 341. Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Evans, D. F. *Science* **1985**, *229*, 1088. Claesson, P. M.; Blom, C. E.; Herder, P. C.; Ninham, B. W. *J. Colloid Interface Sci.* **1986**, *114*, 234.
(66) Marra, J.; Israelachvili, J. N. *Biochemistry* **1985**, *24*, 4608. Marra,

J. J. Colloid Interface Sci. **1985**, *107*, 446. Marra, J. *Biophys. J.* **1986**, *50*, 815.
(67) Israelachvili, J. N.; Wennerström, H. *Langmuir* **1990**, *6*, 873.
(68) Marsh, D. *Biophys. J.* **1989**, *55*, 1093.
(69) LeNeveu, D. M.; Rand, R. P.; Parsegian, V. A.; Gingell, D. *Biophys. J.* **1977**, *18*, 209.

Monomolecular Layers and Thin Films of Silane Coupling Agents by Vapor-Phase Adsorption on Oxidized Aluminum

Dirk G. Kurth and Thomas Bein*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (Received: November 25, 1991; In Final Form: April 13, 1992)

Thin films of tetraethoxysilane [TEOS], (3-bromopropyl)trimethoxysilane [BPS], trimethoxyvinylsilane [VS], and 3-(trimethoxysilyl)propyl methacrylate [TPM] on oxidized aluminum surfaces have been investigated by reflection–absorption FTIR spectroscopy, ellipsometry, contact angle, and quartz crystal microbalance (QCM) measurements. Gravimetric measurements with the QCM can reveal quantitative aspects of adsorption and film formation, even for films as thin as monolayers. Adsorption of these silane coupling agents from solution typically produces multilayer films. Vapor-phase adsorption of TEOS and TPM at room temperature results in monomolecular layers. The coupling agents VS and BPS require additional heating after the vapor-phase adsorption to initiate the hydrolysis and condensation reactions necessary for the surface attachment, which produces one to three layers. For vapor adsorbed films a packing density of 4–7 molecules/nm^2 was found. The data strongly suggest that the organic moieties in several of these films have a preferential orientation on the surface; they can be viewed as two-dimensional, oligomeric siloxane networks with oriented organic chains. Subsequent heating of TPM films results in structural rearrangements; heating of TEOS results in complete condensation to SiO$_2$ films.

Introduction

The molecular modification of surfaces is a field of current interest.[1] Applications are found in areas such as thin film optics,[2] sensors,[3] chemically modified electrodes,[4] and protective layers.[5] Methods of surface modification include the Langmuir–Blodgett technique, self-assembly of various precursor molecules, and adsorption or grafting of polymers. The Langmuir–Blodgett technique permits reproducible formation of well-ordered mono- and multilayers.[6] Self-assembly of organic monolayers includes the adsorption of alkanethiols,[7] dialkyl disulfides,[8] and dialkyl sulfides[9] on gold; fatty acids on alumina;[10] and alcohols and amines on platinum.[11]

Organosilicon compounds (silane coupling agents, SCA) on appropriate substrates provide another route to surface derivatization.[12] The structure of the resulting siloxane film is complex and depends on the functionality of the silane and the experimental conditions.[13] The covalent bond between the native oxide surface layer of the underlying substrate and the organosilicon compound makes these films particularly robust. SCAs are generally applied from solutions. Many functionalized organosilicon compounds are readily available.[14]

Our research on these systems has two objectives. First, we explore ways to generate single layers of immobilized functional groups on surfaces. Second, we investigate the experimental parameters that affect the structure of SCA thin films. Because short-chain molecules, such as the ones used here, do not self-assemble into crystalline films, the functional groups are expected to be more exposed at the solid/ambient interface, which makes these systems attractive for surface-chemistry related studies.

To gain more insight into quantitative aspects of adsorption and film formation, we have introduced the quartz crystal microbalance[15] (QCM) in our studies. The relation between the frequency change, Δf, and the mass adsorbed on one face, Δm, has been derived by Sauerbrey:[16]

$$\Delta f = -2f_0^2 \Delta m / A\sqrt{\rho\mu} \qquad \Delta m = -c_f \Delta f \qquad (1)$$

where A = piezoelectric active area, f_0 = fundamental frequency,

TABLE I: Peak Positions and Band Assignments^a of TEOS Monolayer Adsorbed on an Aluminum Surface

freq	assignments
2977	–CH$_3$, asym str r^-_a
2886	–CH$_3$, sym str r$^+$
1394	–CH$_3$, sym str $\delta(\pi)$
1167 1123 1091	–Si–O–C– asym str (doublet), –Si–O–Si– str

^{a} Literature sources are found in refs 21 and 24.

μ = shear modulus, ρ = density of quartz, and c_f = sensitivity factor.

For a 9-MHz crystal operated at its fundamental frequency the sensitivity factor c_f is 5.4 ng Hz^{-1} cm^{-2}. The QCM provides enough sensitivity even for measurements on monomolecular films.[17] A molecular layer is very thin compared to the wavelength of the shear wave in the resonator, such that the adsorbed layer should entirely exist at the antinode of the shear wave. Therefore, the adsorbed layer should experience no significant shear deformation, and its viscoelastic properties should have no influence on the measurement. If the change in frequency caused by the mass loading is less than 2% of the fundamental frequency and the mass is equally distributed over the electrode surface, eq 1 can be used, as has been demonstrated by Ward[18] and Jones and Mieure.[19]

Results and Discussion

Adsorption of Tetraethoxysilane (TEOS) on Oxidized Aluminum. TEOS films are interesting for two reasons. First, remaining ethoxy groups on the surface can react with other reagents via condensation. Second, fully condensed films of TEOS form SiO$_2$ layers, which can serve as insulating or protecting layers. The vapor-phase adsorption of TEOS provides a convenient route for the formation of extremely thin SiO$_2$ films with nanometer thickness. This approach complements the well-developed sol–gel techniques that typically result in much thicker films.[20]

Figure 1 shows the RAIR spectrum of a TEOS film, generated by vapor-phase adsorption on a water vapor-exposed substrate.

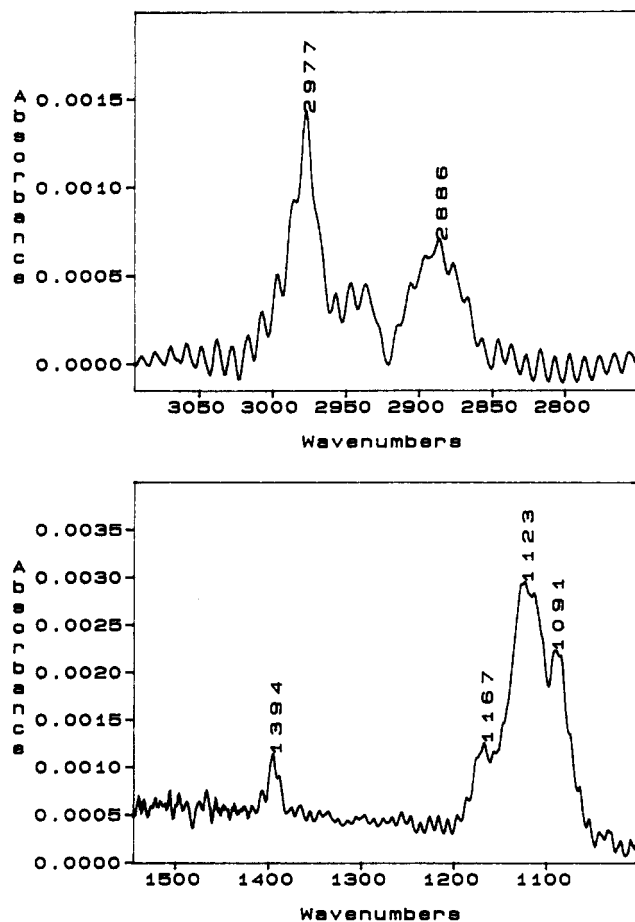**Figure 1.** RAIR spectrum of TEOS on oxidized aluminum.

Figure 2. RAIR spectrum of BPS on oxidized aluminum.

The calculated film thickness is 6 Å, as measured by optical ellipsometry. Table I summarizes the peak positions and band assignments.

The transmission FTIR spectrum of TEOS shows bands at 1091, 1123, and 1167 cm^{-1}, which are assigned to Si–O–C modes. The RAIR spectrum shows, in addition, a strong band around 1123 cm^{-1}, which is assigned to the Si–O–Si stretch. The band at 1394 cm^{-1} is assigned to the symmetric deformation of the methyl group. The CH stretching region shows the symmetric and asymmetric mode for the CH$_3$ modes at 2886 and 2977 cm^{-1}. The data indicate that TEOS vapor adsorption at room temperature results in immobilized ethoxysilane layers with a low degree of cross-linking. This is confirmed by the relatively high wettability; the advancing contact angle of water is 64°.

Heating in nitrogen atmosphere at 80 °C results in completion of cross-linking. The RAIR spectrum shows only a broad band around 1110 cm^{-1}, characteristic for SiO$_2$; no CH modes are detected. The contact angle of water is 68°; the SiO$_2$ film is polar and is expected to spread water. The calculated film thickness decreases to a nominal value of 4 Å.

Vapor-adsorbed TEOS films were successfully employed to attach zeolites in a subsequent step to the surface. The presence of the zeolites was confirmed by RAIR spectroscopy, SEM, and nitrogen sorption measurements. Zeolites, attached in this fashion, withstand ultrasonic treatment, showing a stable bond between the surface and the zeolite.

The QCM measurements indicate that chemisorption occurs only on substrates that were exposed to water vapor before the adsorption. Adsorption from a water–TEOS vapor mixture gives similar results. Adsorption of TEOS vapor in a static atmosphere produces frequency changes between 20 and 39 Hz. Assuming the attachment of Si(OEt)$_2$ species, this is equivalent to 47–92 ng cm^{-2}, or 2.4 to 4.7 molecules/nm^2; the occupied surface per molecule is 40–22 Å^2. Adsorption from a TEOS–nitrogen flow on a water-coated substrate results in average frequency changes of 40 Hz, which is equivalent to 95 ng cm^{-2}, or 4.7 molecules/nm^2. After heating for 1 h at 80 °C under nitrogen, the frequency

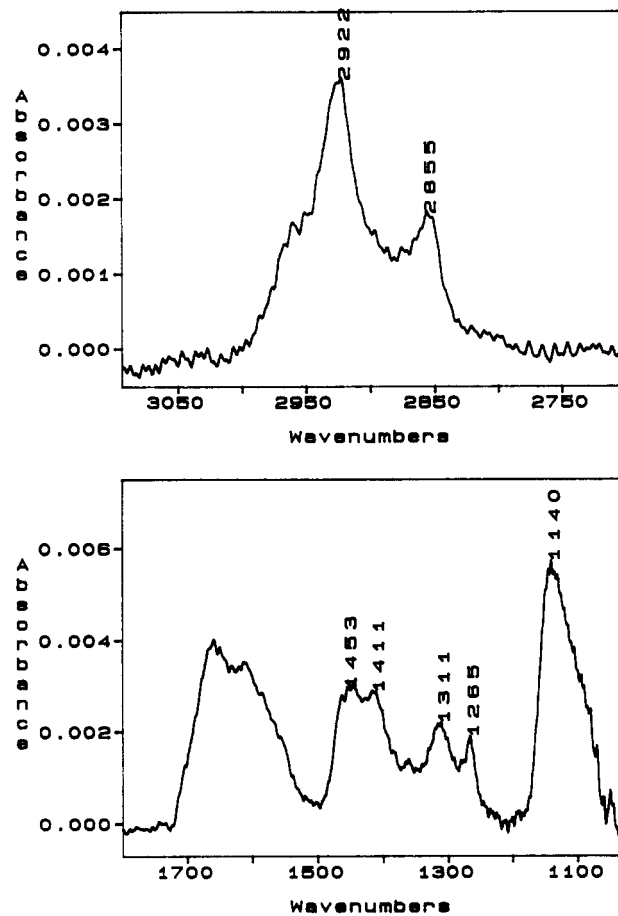**TABLE II: Peak Positions and Band Assignments[a] of BPS Monolayer Adsorbed on an Aluminum Surface[b]**

| freq	assignments
2922	–CH$_2$–, asym str d$^-(\pi)$, ip $\perp$ CCC chain
2855	–CH$_2$–, sym str d$^+(\pi)$, ip $\parallel$ CCC plane
1658	
1613	
1453	–CH$_2$–, def $\delta(\pi)$, ip $\parallel$ CCC chain
1411	–CH$_2$–, def
1311	–CH$_3$–, def (–OMe)
1265	–Si–CH$_2$–, def (wag) op $\delta(\pi)$ $\parallel$ CCC chain
1140	–Si–O–Si–, polymeric

[a] Literature sources are found in refs 21 and 24. [b] Nomenclature: $\parallel$, parallel; $\perp$, perpendicular; str, stretch; def, deformation; sym, symmetric; asym, asymmetric; wag, wagging; sci, scissoring; ip, in-plane; op, out of plane; r^-_a, asym; C–H str ip (CH$_3$); r^-_b, asym; C–H str op (CH$_3$); r$^+$, sym C–H str; d$^-(\pi)$, asym C–H str (CH$_2$); d$^+(\pi)$, sym C–H str (CH$_2$); $\delta(\pi)$, CH$_2$ def. Directions are approximated from the normal mode description.[10]

change decreases to 17 Hz, or 40 ng cm^{-2}, which is equivalent to 4 SiO$_2$ units/nm^2. These data show that heating results in condensation and only little desorption of the precursor species.

The variations in coverage are explained by changes in the amount of surface adsorbed water, which causes varying degrees of hydrolysis and cross-linking within the film.

Adsorption of (Bromopropyl)trimethoxysilane (BPS) on Oxidized Aluminum. The hydrolysis and condensation reactions of BPS are relatively slow. Thus, thin films can be prepared by adsorption from solution. The use of a catalyst in solution is advantageous. Figure 2 shows the RAIR spectrum of a 16-Å thin BPS film on aluminum prepared by adsorption from solution under acid catalysis (pH = 3–7). Table II summarizes the band assignments and positions.

The positions of the CH-stretching modes of the propyl group, d$^+(\pi)$ and d$^-(\pi)$ (2855, 2922 cm^{-1}), in the RAIR spectrum, are similar to those found in polymethylene chains. The intensity ratio of the d$^+(\pi)$ and d$^-(\pi)$ bands in the RAIR spectrum is 3.0; the
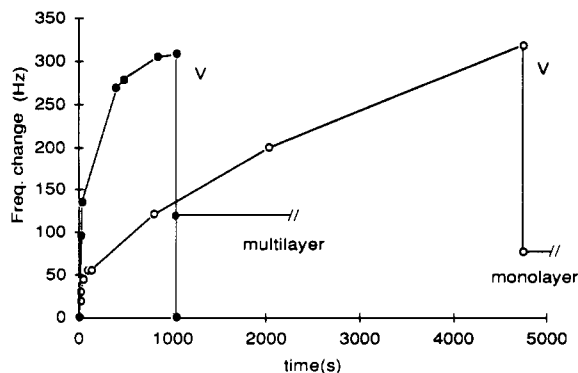
Figure 3. In situ frequency–time response upon vapor adsorption of BPS (●) and TPM (○). Evacuation (V) removes the physisorbed film of BPS completely ($\Delta f = 0$). Additional heating results in one to three layers. TPM forms a chemisorbed monomolecular layer at room temperature that is not removed by evacuation (V; $\Delta f = 77$ Hz).

ratio of the intensities in liquid hydrocarbons is 1.7.[21] On the basis of the surface selection rules, the bromopropyl groups have a preferential orientation. The broad Si–O–Si band around 1140 cm^{-1} and the absence of the methoxy vibrations in the RAIR spectrum indicate a high degree of cross-linking within the siloxane moiety. The film, therefore, consists predominantly of BPS polymer networks.

The advancing contact angle of water is 82°. The low wettability is in agreement with the chemical nature of the bromopropyl group, i.e., lack of hydrogen-bonding capability.

Figure 3 shows the in situ response of the QCM during vapor adsorption of BPS under dry nitrogen at room temperature. Evacuation (V) completely removes the BPS layer ($\Delta f = 0$), even if the adsorption is carried out in a moist atmosphere. Because the hydrolysis of the methoxy groups to silanol groups, which are necessary for surface condensation reactions, is slow at room temperature (no catalyst is present), BPS cannot chemisorb under these conditions. To initiate the surface attachment reactions, the samples were heated at 75 °C for 1 h after the adsorption in a dry nitrogen atmosphere. The frequency change thereafter varies between 70 and 120 Hz, which is equivalent to 5.4 and 9.2 BPS molecules/nm^2 (if two MeO groups are removed). The thickness measured with optical ellipsometry varies between 12 and 27 Å. The QCM and ellipsometry results suggest the formation of one to three BPS layers under these conditions. Apparently, the heat treatment accelerates the surface bonding and cross-linking reactions such that the film is not removed by desorption.

Adsorption of Trimethoxyvinylsilane (VS) on Oxidized Aluminum. The rate of hydrolysis of trimethoxyvinylsilane is smaller than for the other trialkoxysilanes in this study. The surface attachment from solution requires therefore a catalyst. Under basic catalysis the hydrolysis is fairly fast, however, the aluminum substrate can be corroded. Under acidic catalysis the adsorption is not reproducible, as demonstrated by varying contact angles and film thicknesses.

However, vapor-phase adsorption of VS and subsequent heating (under nitrogen) of the sample produces well-defined films. Figure 4 shows the RAIR spectrum of a monomolecular VS layer. The calculated film thickness is 4 Å. Table III shows the band assignments and positions. The advancing water contact angle of 81° indicates a hydrophobic interface, composed of nonpolar vinyl groups.[22]

The presence of the bands for the double bond in the RAIR spectrum demonstrates that no reaction of the vinyl groups, such as oxidation or cyclization, has occurred during the heat treatment.[14]

The RAIR spectrum of the VS monolayer is very similar to the transmission spectrum. The bands at 2958 and 2847 cm^{-1} are assigned to the asymmetric and symmetric CH stretching vibrations of the methoxy groups. The origin of the band at 2927 cm^{-1} is not clear yet, but it might be associated with the CH stretching vibrations of the vinyl group.[23] The CH$_3$ rocking (1195 cm^{-1}) and the Si–O–C stretching mode (1104 cm^{-1}) are subject to interference with the asymmetric Si–O–Si stretching band (1144
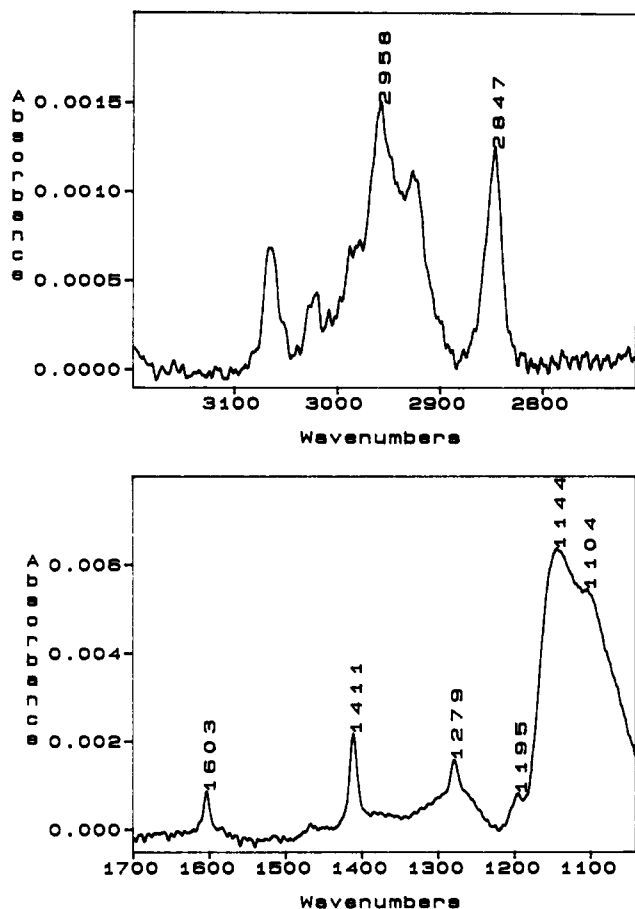
Figure 4. RAIR spectrum of a monomolecular VS film on oxidized aluminum.

TABLE III: Peak Positions and Band Assignments[a] of VS Monolayer Adsorbed on an Aluminum Surface

freq	assignment
3067	=CH$_2$, asym str, ip, ⊥ C=C bond
3028	=CH, sym str, ip HCC plane
2988	
2958	–OCH$_3$, str
2927	
2847	–OCH$_3$, sym str, ‖ O–C– bond
1603	C=C, sym str, ‖ CC bond
1411	=CH, def ip
1279	
1195	–Si–O–CH_3 (rock)
1144 1104	–Si–O–C asym str, –Si–O–Si– str (oligomeric)

[a] Literature sources are found in refs 21 and 24.

cm^{-1}).[24] The presence of Si–O–C and methoxy modes in the RAIR spectrum indicates a low degree of cross-linking within the siloxane layer, in agreement with the slow hydrolysis reaction.

The band width of 10 cm^{-1} of the deformation modes is small and indicates a high degree of homogeneity within the film. The thickness of 4 Å, determined by ellipsometry, matches very well with the projection of the molecular axis of an upright oriented VS molecule onto the surface normal.

Vapor adsorption of VS results in a physisorbed film that is completely desorbed by evacuation, as indicated by the QCM response ($\Delta f = 0$).[25] The physisorbed film requires heating to initiate the surface attachment reactions. Heating at 90 °C in a dry nitrogen atmosphere results in a frequency change, Δf, of 28 Hz, which is equivalent to 66 ng/cm^2. Subsequent evacuation does not further change the frequency of the QCM. The film thickness of approximately 4 Å agrees with the formation of a monomolecular film with approximately 4 molecules/nm^2.

Adsorption of 3-(Trimethoxysilyl)propyl Methacrylate [TPM] on Oxidized Aluminum. The formation of monomolecular TPM films was not possible by adsorption from solution.[26,27] Different
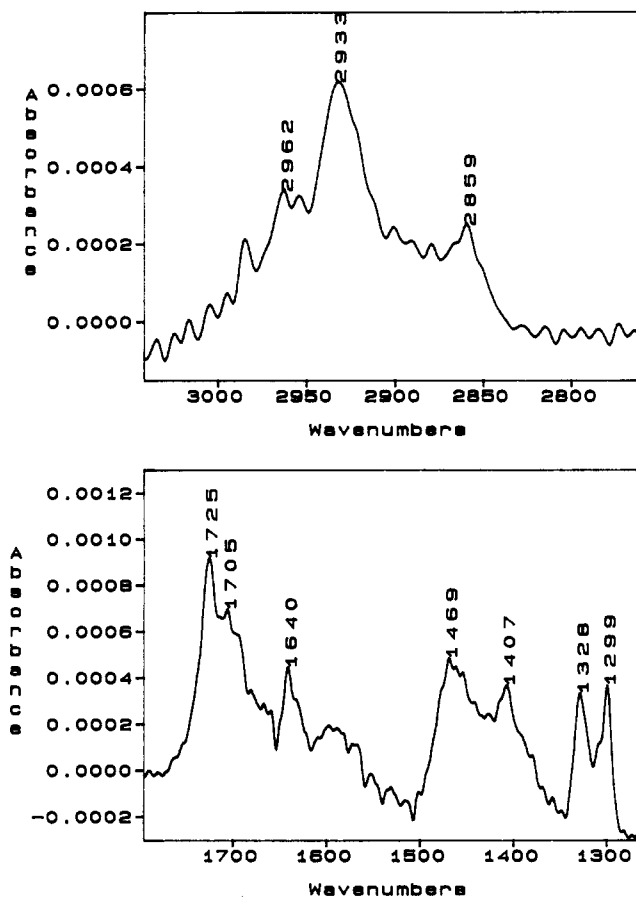
Figure 5. RAIR spectrum of a monomolecular TPM film on oxidized aluminum.

TABLE IV: Peak Positions and Band Assignments[a] of TPM Monolayer Adsorbed on an Aluminum Surface

freq	assignment
2962	—CH$_3$, asym str r^-_a (shoulder)
2933	—CH$_2$—, asym str d$^-$(π), ip $\perp$ CCC chain
2859	—CH$_2$—, sym str d$^+$(π), ip $\parallel$ CCC plane
1725 1705	C=O, str, $\parallel$ CO bond (associated, free)
1640	C=C, str, $\parallel$ CC bond
1469	—CH$_2$—, def
1407	=CH, def ip
1328	—C—O—, sym str
1299	
1260	—Si—CH$_2$—, def (wag) op δ(π) $\parallel$ CCC chain
1175	Si—O—CH$_3$ (rock)
1101	—Si—O—C asym str (broad) —Si—O—Si— str

[a] Literature sources are found in refs 21 and 24.

solvents, mixtures, and pH were explored. Films prepared by adsorption from solution show broad IR bands in the 1100-cm^{-1} region characteristic for polymeric siloxanes (Si–O–Si).[28] In addition, the bands are asymmetric, which indicates structurally disordered films. Vapor adsorption from a boiling TPM/toluene mixture generates multilayer films with a thickness of around 20 Å.[29]

In contrast, monomolecular films are readily prepared by vapor adsorption at room temperature. Figure 5 shows the RAIR spectrum of a 5-Å thin film. Table IV gives the band assignments and positions. The CH stretching vibrations of the C=C double bond are not observed in the RAIR spectrum. The positions of the CH stretching vibrations, d$^-$(π) and d$^+$(π), are similar to the positions found for polymethylene chains; the ratio of the intensities of these modes is 4.1, indicating a preferential orientation of the propyl group on the surface.

The carbonyl stretch is typically found between 1705 and 1725 cm^{-1}. The lower frequency mode is characteristic for associated
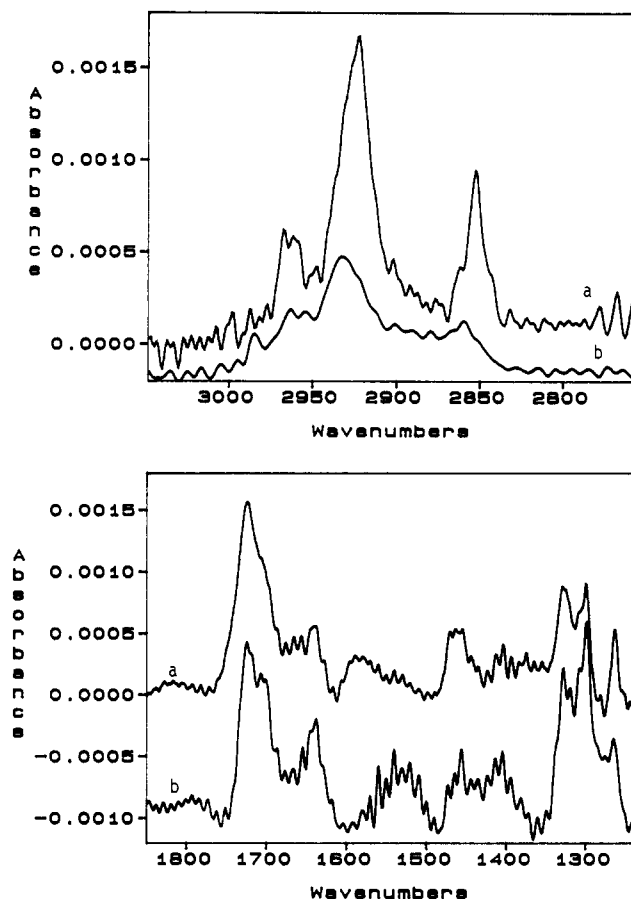

Figure 6. Change of the intensities of the CH stretching and C=O stretching modes of TPM before (b) and after (a) heating the film at 90 °C.

carbonyl groups and has been attributed to interactions of the carbonyl with the surface.[13,30] The film thickness after adsorption is 5 Å, which is smaller than the extended molecular chain (approximately 12 Å). The presence of the double bond vibration and the methyl CH stretch in the RAIR spectrum prove that no ester cleavage occurs.[31] Therefore we conclude that the propyl chain is initially tilted towards the surface.[32]

The asymmetric Si–O–Si and Si–O–C stretching modes are located around 1100 cm^{-1}. The band at 1175 cm^{-1} is assigned to the Si–O–CH$_3$ rocking vibration.

Figure 6 shows the RAIR spectra of the TPM monolayer before (b) and after heating (a) at 80 °C under nitrogen. The intensity of the associated carbonyl stretch at 1705 cm^{-1} strongly decreases and the intensity of the CH wagging mode at 1260 cm^{-1} is enhanced after heating. The transition dipole moment of this mode is parallel to the propyl backbone. The increased intensity is consistent with a more upright oriented propyl backbone. The advancing water contact angle (75°) does not change significantly upon heating, but it is higher than a previous value for polymeric TPM films on glass (50°).[13] The difference is attributed to variations in the structure and the extent of hydrolysis in TPM monolayers compared to polymeric films.

Vapor adsorption of TPM at room temperature under dry nitrogen results in a chemisorbed and a physisorbed layer, as demonstrated by the QCM measurements (Figure 3). Evacuation (V) removes the physisorbed layer; the remaining frequency change of 77 Hz is equivalent to 183 ng/cm^2, or 6 TPM molecules/nm^2. The fairly low effective area of 17 Å^2 per TPM molecule suggests formation of Si–O–Si networks, in agreement with the RAIR data. Adsorption under ambient atmospheric conditions results in thick films.

Conclusions

In this study the molecular modification of aluminum surfaces with tetraethoxysilane, (3-bromopropyl)trimethoxysilane, tri-

methoxyvinylsilane, and 3-(trimethoxysilyl)propyl methacrylate was studied with reflection–absorption FTIR spectroscopy, contact angle measurements, ellipsometry, and the quartz crystal microbalance. The covalent Si–O–Si linkages are important for the stability of these films. The amount of water that is required in order to form monomolecular layers remains, however, undefined. The adsorption of the silane coupling agents, discussed here, from solution under different experimental conditions typically results in multilayers. Adsorption from very dilute solutions containing less than 0.1% of the SCA gave films with varying film thicknesses and contact angles and ill-defined RAIR-spectra. In contrast, vapor-phase adsorption on oxidized aluminum substrates at room temperature under anhydrous conditions results in monomolecular films of TEOS and TPM. Very similar results were also found for (3-aminopropyl)triethoxysilane, as presented elsewhere.[33] Films of VS and BPS require heating after the adsorption for covalent surface attachment.

If the results for the trialkoxysilanes are compared, a relation between the functional groups present in the organic moiety and the vapor adsorption behavior can be deduced. If a polar or basic group is present, the SCA forms a chemisorbed film by vapor adsorption at room temperature. The possible catalytic activity of a functional group toward the surface attachment reactions could involve two different mechanisms, either by assisting the hydrolysis of the alkoxy groups or by proton abstraction from surface hydroxy groups. For instance, deprotonation of surface hydroxy groups, as a catalytic pathway in the silylation reaction, has been proposed for amines.[34]

In the absence of a basic group in the SCA, apparently no covalent bonding with the surface occurs at room temperature, but heating is required to initiate the surface-attachment reactions. During heating, competitive and sequential processes occur, including hydrolysis, condensation, and desorption of the SCA. In some cases this can result in the formation of one to three layers, such as BPS, or in the formation of a monolayer, as with VS.

RAIR spectroscopy of these and all other examples prepared in our laboratory suggest that the SCAs have a preferential orientation with respect to the surface in monolayer assemblies. The relative intensities of the CH stretching modes provide a qualitative measure for the degree of orientation of the organic moiety. In thick films, with a random orientation of the oscillators, the ratio of the symmetric and asymmetric CH stretching modes approaches the limiting value of bulk hydrocarbons. Films of TPM undergo a structural rearrangement upon heating as indicated by changes in the RAIR spectra.

The number of hydroxy groups on aluminum-oxide is approximately 6.5 sites/nm². The surface loading of 4–7 molecules/nm², as determined with QCM measurements, corresponds to about 100% site coverage.[35] Lateral and up–down cross-linking of the SCAs under formation of Si–O–Si bonds may cause the high effective surface coverage. It appears that the rates of the hydrolysis and cross-linking reactions affect the surface coverage. Films of VS have, therefore, lower coverages than films of TPM. On the basis of the ellipsometric measurements, TEOS, TPM, and VS form single layers. The films can be viewed as two-dimensional, monomolecular siloxane networks[36] with oriented organic chains.

The surface chemistry of these films will be addressed in subsequent articles.[37]

Experimental Part

Materials. The silane coupling agents were obtained from Aldrich or Petrarch and were used as received. All the solvents were used as received. For the water contact angle measurements, HPLC grade water from Aldrich was used. For the adsorption experiments distilled water was used. The QCMs were supplied from International Crystal Manufacturing (ICM, Oklahoma City).

All experiments were repeated at least six times and good reproducibility was found if not stated otherwise.

Preparation of Aluminum Substrates. Glass slides were immersed in a piranha solution (7:3 concentrated H_2SO_4/30% H_2O_2)

at 90 °C for 1 h, 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 (99.999%, Aldrich) was thermally or e-beam evaporated on the precleaned microscope glass slides (Fischer, 7.5 cm × 2.5 cm) at a base pressure of 5×10^{-6} Torr. After evaporation the bell jar was purged with helium. The aluminum slides were stored in plastic boxes until used in experiments, generally as soon as possible. Before adsorption of the SCA the aluminum surfaces were treated in an oxygen or nitrogen plasma[38] (Reytheon Microwave generator, McCarrol Coaxial chamber). In both cases a 30–80-Å thin oxide layer is maintained as demonstrated by ellipsometry and XPS. Surfaces prepared in such a way showed no organic contamination in the RAIR and were totally wetted by water.[39] In some cases the slides were exposed to water vapor prior to the adsorption of the SCA.[40] From SEM micrographs the average grain size on the surface was measured to be 100–150 nm. The nitrogen adsorption isotherm of an aluminum-coated quartz crystal microbalance shows that the aluminum surface has no significant porosity.[41] An analysis of the nitrogen isotherm of three different samples based on the BET-method gave a surface roughness of 1.12 cm²/cm².

Gold slides were prepared in a similar fashion. The glass slides were modified by a monolayer of (3-mercaptopropyl)trimethoxysilane [MPS] before the gold deposition. MPS was adsorbed from the vapor phase on the precleaned substrate and annealed for 1 h at 75 °C. Slides prepared in this way showed an improved adhesion of gold.[42]

Adsorption of Silane Coupling Agents. The precleaned aluminum-coated slides were immersed into the solution of the SCA (0.1–20% by volume). Ethanol, isopropyl alcohol, butanol, toluene, and mixtures with water were explored. The pH was adjusted with acetic acid. The solution was stirred and immersion times varied from several minutes to several hours.

The adsorption from a boiling mixture of the SCA and a solvent is described in detail by Haller.[29] The apparatus and the solvents used were dried before the experiment.

The vapor-phase adsorptions were carried out in specially designed glass dishes of 8.5 cm × 3.5 cm; 200–500 μL of the SCA was dropped at the bottom of the dish with an Eppendorf pipet under nitrogen (static adsorption). The slide to be modified was immediately deposited onto the dish with the aluminum side facing the SCA. Flow experiments were carried out in a flow chamber with two inlets. The QCM, connected by electric feed throughs, was placed between the inlets. Nitrogen was bubbled at 60 mL/min through an SCA solution into the chamber (dynamic adsorption). In several cases, the samples were exposed to water vapor obtained by bubbling N_2 through water.

The adsorption was carried out under dry nitrogen, in a humid environment (placing a drop of water on the blank side of the slide), or under ambient atmospheric conditions (25% relative humidity). Adsorption times varied from several minutes to several hours. The slides were evacuated (10^{-3} Torr, molecular sieve pump) and purged with nitrogen to remove an excess layer of physisorbed material. Heating was carried out under nitrogen or vacuum, if possible, at 80 °C after the adsorption of the SCA.

Reflection–Absorption FTIR Spectroscopy. Absorption spectra were obtained in the single reflection mode using a nitrogen-purged Mattson Polaris Fourier transform infrared spectrometer with a narrow-band liquid nitrogen cooled MCT detector and a Harrick versatile reflection attachment. Best results were obtained by masking the beam with a 2-mm-wide iris. The plane-polarized light was incident at 86°. After triangular apodization the spectral resolution was 4 cm⁻¹. The moving mirror velocity was 1.264 cm/s; 1000 scans were recorded. All spectra were reported in $-\log R/R_0$, where R is the reflectivity of the sample and R_0 is the reflectivity of the reference slide. Evaporated gold-on-glass slides were used as reference surfaces. The spectra were electronically corrected in the baseline. Typically two points were chosen at the outer edges of the group of bands.

Ellipsometry. All measurements were taken on a manual Rudolf research ellipsometer equipped with a HeNe laser (632.8 nm).

The complex refractive index of the substrate was measured prior to the adsorption experiment. After the film formation the samples were again analyzed. The thickness was calculated with the refractive index of the bulk material and the previously measured index for the substrate using the two-phase model with an algorithm developed at Sandia National Laboratories (Tardy, H. L. Ellipse User's Manual and Program Reference; Report No. 89-0008; Sandia National Laboratories: Albuquerque, NM, 1989). The angle of incidence was 70°. All measurements were made taking four-zone data. Several spots on the sample were measured. The transmission minimum was determined with the swing method. Several data points were taken and the Null was interpolated from an azimuth, PMT-signal curve fit. The calculated film thicknesses have typically an error of ±1 Å.

Gravimetric Adsorption Measurements. The mass change upon adsorption was measured on polished, AT-cut quartz cystal microbalances (f_0 = 9 MHz) with aluminum electrodes with self-developed oscillator circuitry and a BK precision frequency counter, Model 1803; the measurement has an error of typically ±2 Hz.

Before the adsorption the crystals were cleaned in a nitrogen or oxygen plasma. The adsorptions were carried out under the same experimental conditions as the adsorption on the aluminum slides. The QCM was mounted with a plastic disk in a small glass vial that contained 0.5 mL of the SCA. All measurements were taken under nitrogen atmosphere or vacuum.

The QCMs were calibrated by underpotential deposition (UPD) of a monolayer of copper on a gold electrode.[43] The weight of the copper film and the calculated weight from the frequency shift with the Sauerbrey equation matched within 5%.

The Sauerbrey equation was used to calculate the weight per unit area, taking into account the surface roughness (determined from nitrogen sorption measurements). From the average molecular weight of the surface attached species the number density was calculated.

Wetting Measurements. Advancing water contact angles were determined with a self-built goniometer. The temperature was not controlled and varied between 20 and 25 °C. The atmosphere in the sample chamber was saturated with water vapor by filling the well of the chamber with water. The advancing contact angle was determined by lowering the needle to the surface and injecting 1 μL of the liquid onto the surface. The drop would advance over the surface. The needle was raised. With this technique the contact angles were most reproducible. The tangent to the drop at its intersection with the surface was estimated visually. Both sides of the drop were measured and several spots on the sample were averaged. The measurement is accurate within ±1°. Angles below 20° were considered as total wetting. Typically contact angles were stable over a long period of time.

References and Notes

(1) Swalen, J. D.; Allara, D. L.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932–950.

(2) Bubeck, C.; Laschewsky, A.; Lupo, D.; Neher, D.; Ottenbreit, P.; Paulus, W.; Prass, W.; Ringsdorf, H.; Wegner, G. *Adv. Mater.* **1991**, *3*, 54 and references therein.

(3) Edmonds, T. In *Chemical Sensors*; Edmonds, T., Ed.; Chapman & Hall: New York, 1988.

(4) Murray, R. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; 1984; Vol. 13, pp 191–368.

(5) (a) Stratmann, M. *Adv. Mater.* **1990**, *2*, 191. (b) Fuchs, H.; Ohst, H.; Prass, W. *Ibid.* **1991**, *3*, 10 and references therein. (c) Chung, F. *J. Appl. Polym. Sci.* **1991**, *42*, 1319.

(6) (a) Gaines, G. *Insoluble Monolayers at the Liquid-Gas Interphase*; Interscience: New York, 1966. (b) Ulman, A. *J. Mater. Educ.* **1989**, *11*, 205.

(7) (a) Bain, C. D.; Troughton, E. B.; Tao, Y.; Evall, J.; Whitesides, G. M.; Nuzzo, R. *J. Am. Chem. Soc.* **1989**, *111*, 321. (b) Bain, C.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506. (c) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(8) Nuzzo, R. G.; Fusco, R. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358.

(9) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365.

(10) (a) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45. (b) Allara, D. L.; Nuzzo, R. G. *Ibid.* **1985**, *1*, 52.

(11) Bigelow, W. C.; Picket, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513.

(12) (a) Sagiv, J. *Isr. J. Chem.* **1979**, *18*, 346. (b) Wassermann, S.; Tao, Y.; Whitesides, G. M. *Langmuir* **1989**, *5*, 5. (c) Maoz, R.; Sagiv, J. *Langmuir* **1987**, *3*, 1045. (d) Wasserman, S.; Tao, Y.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

(13) Lee, L. H. *J. Colloid Interface Sci.* **1968**, *27*, 751.

(14) (a) Speier, J. *Adv. Organomet. Chem.* **1979**, *300*, 407. (b) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.

(15) (a) Ward, M. D. *J. Phys. Chem.* **1988**, *92*, 2049. (b) Schumacher, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 329.

(16) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.

(17) (a) Melroy, O.; Kanazawa, K.; Gordon, J. G.; Buttry, D. *Langmuir* **1986**, *2*, 697. (b) Mieure, J. P.; Jones, J. L. *Talanta* **1968**, *16*, 149.

(18) Ward, M. D.; Delawski, E. J. *Anal. Chem.* **1991**, *63*, 886.

(19) Jones, J. L.; Mieure, J. P. *Anal. Chem.* **1969**, *41*, 485.

(20) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, 1990.

(21) (a) Nakanishi, K.; Solomon, P. *Infrared Absorption Spectroscopy*, 2nd Ed.; Holden-Day: 1977. (b) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; 3rd ed.; Wiley: New York, 1975; Vols. 1 and 2.

(22) (a) Bascom, W. D. *Prepr. Div. Org. Coatings Plastics Chem.* **1967**, *27*, 27. (b) Bascom, W. D. *Adv. Chem. Ser.* **1969**, *87*, 38.

(23) If a neat sample of 0.5 mL of VS is heated in air to 75 °C to remove the methoxy groups in a condensation reaction, the bands at 2846 and 2958 cm^{-1} and the shoulder at 2988 cm^{-1} clearly loose in intensity. For this reason these bands are associated with the methoxy groups. The intensity of the band at 2927 cm^{-1} does not change during the heat treatment.

(24) (a) Anderson, D. R. In *Analysis of Silicones*; Smith, A., Ed.; Wiley: New York, 1974; Chapter 10. (b) Richards, R. E.; Thompson, H. W. *J. Chem. Soc.* **1949**, 124.

(25) Zettlemayer, A. C.; Hsing, H. H. *J. Colloid Interface Sci.* **1977**, *58*, 263.

(26) Boerio, F. J.; Cheng, S. Y. *J. Colloid Interface Sci.* **1979**, *68*, 252.

(27) Gorski, D.; Klemm, E.; Fink, P.; Hörhold, H. *J. Colloid Interface Sci.* **1988**, *126*, 445.

(28) Miller, J.; Ishida, H. *Langmuir* **1986**, *2*, 127.

(29) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050.

(30) Ishida, H.; Naviroj, S.; Koenig, J. *Physicochem. Aspects Polym. Surf. (Proc. Int. Symp.)* **1983**, *1*, 91 and references therein.

(31) Comyn, J.; Horley, C. C.; Pritchard, R. G.; Mallik, R. R. *Adhesion (London)* **1987**, *11*, 38.

(32) Miller, J.; Ishida, H. *Surf. Sci.* **1984**, *148*, 601.

(33) Kurth, D.; Bein, T. *Langmuir*, submitted for publication.

(34) (a) Kallury, K. M.; Krull, U. J.; Thompson, M. *Anal. Chem.* **1988**, *60*, 169. (b) Blitz, J. P.; Murthy, R. S.; Leyden, D. E. *J. Colloid Interface Sci.* **1988**, *126*, 387.

(35) Blum et al. find approximately 4 molecules/nm^2 by NMR studies for VS and TPM on silica (Blum, F. D.; Meesiri, W.; Kang, H. J.; Gambogi, J., in press). Miller reports 3 TPM molecules/nm^2 on lead oxide determined by DRIFT spectroscopy (Miller, D. J.; Ishida, H. *Langmuir* **1986**, *2*, 127) and Murray reports approximately 3 molecules determined by electrochemical means. Moses, P. R.; Weir, L. M.; Lennox, J. C.; Finklea, H. O.; Lenhard, S. R.; Murray, R. W. *Anal. Chem.* **1978**, *50*, 576.

(36) The term *monolayer* is understood as a level, molecular carpet which consists of *two-dimensional* networks of SCA molecules. Cross-linking in an irregular fashion within the siloxane network results in a perturbation of the structure, as there are no strong ordering forces.

(37) Kurth, D.; Bein, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 336.

(38) O'Kane, D. F.; Mittal, K. L. *J. Vac. Sci. Technol.* **1974**, *11*, 567.

(39) Schrader, M. In *Surface Contamination: Genesis, Detection, and Control* [*Proceedings of a Symposium*], Washington, DC, 1978; Mittal, K. L., Ed.; Plenum: New York, 1979; Vol. 2, p 541.

(40) (a) Vedder, W.; Vermilyea, D. A. *Trans. Faraday Soc.* **1969**, *65*, 561. (b) Thiel, P.; Madey, T. *Surf. Sci. Rep.* **1987**, *7*, 211.

(41) Lowell, S.; Shields, J. In *Powder Surface Area and Porosity*, 2nd ed.; Scarlett B., Ed.; Chapmann & Hall: New York, 1984.

(42) Wasserman, S. R.; Biebuyck, H.; Whitesides, G. M. *J. Mater. Res.* **1989**, *4*, 886.

(43) Manne, S.; Hansma, P. K.; Massie, J.; Elinds, V. B.; Gewirth, A. A. *Science* **1991**, *251*, 183.