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Silanization of Solid Substrates: A Step toward Reproducibility

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Evidence is given for a transition temperature T_c which controls the formation of grafted alkylsilane monolayers on hydrophilic substrates. When the silanization reaction is performed below T_c, layers of high surface quality are obtained. They are characterized by an extremely low surface tension $\gamma_c = 20.5 \pm 0.5$ mN/m and low contact angle hysteresis (less than 1°) between the advancing and receding contact angles of sessile drops of test liquids. This temperature T_c is an intrinsic property of the silane molecules: it depends on their chain length but is independent of the nature of the solvents used for the grafting reaction. We have related T_c to the triple point observed in the phase diagram of amphiphilic molecules spread at the air–water interface. On the basis of this correspondence, we suggest the existence, in the early stages of the adsorption process, of large in-plane inhomogeneities of the molecular surface density, which should be observable by fluorescence microscopy. Upon further adsorption, close-packed monolayers are reached if the reaction is performed at low enough temperatures. The presence of a film of water on the bare substrate, which has been suggested earlier and is confirmed by our experiments, supports the analogy with Langmuir monolayers. Preliminary experiments on fluorinated trichlorosilanes seem to show the same trend for optimum grafting. A γ_c value of 6 ± 1.2 mN/m, together with low hysteresis, has been reached by proceeding at low temperatures.

Introduction

Modification of solid substrates by deposition of organic monolayers with controlled architecture, such as thiols on gold[1] or carboxylic acids on aluminum,[2] is a subject of growing interest. Such systems provide ideal archetypes of two-dimensional structures for fundamental studies on phase transitions on the one hand, and they can be useful in a host of technology applications on the other hand.

One of the most successful approaches so far has been the chemical grafting of long hydrocarbon chains on hydrated surfaces via a trichlorosilane ($-SiCl_3$) head group. This reaction of silanization was devised more than 40 years ago for chromatographic applications,[3] but it is only recently that detailed descriptions of the principal steps of the process have been proposed, leading to compact monolayers of low wettability.[2,4–8] The average structure of these layers has been studied by such diverse means as ATR,[2,4–6] X-ray diffraction,[7] and ellipsometry,[9] evidencing that the best monolayers are composed of close-packed, generally vertical chains, most of them being *all-trans* extended. However, despite these extensive efforts, the silanization reaction has continued to be plagued by a high level of irreproducibility in the macroscopic properties (i.e. wettability and contact angle hysteresis) of the deposited monolayers. It was therefore clear that important controlling parameters had been left out. A recent study on octadecyltrichlorosilane, performed by Silberzan *et al.*,[10] has given a first clue by pointing out the importance of water traces and of the temperature of reaction. In particular, they have observed a monotonous increase in the quality of the layer as the temperature of reaction was decreased from 35 to 18 °C. This temperature dependence was tentatively interpreted by these authors as due to a solubility decrease of the silane solutes in the hexadecane solvent, which in turn favors their physisorption on the solid substrate.

In this paper, we systematically study the influence of the temperature of reaction during the silanization process over an extended range of temperature (−1 to 60 °C), and for *n*-alkyltrichlorosilanes of different lengths. We give a step-by-step foolproof procedure which reproducibly leads to high-quality layers. We demonstrate that it is essential to maintain the temperature of the reaction bath below a well-defined temperature T_c, characteristic of the grafted molecules and independent of the solvent used. A brief account of these results has already been published.[11] We develop here a qualitative model, based on an analogy with the Langmuir monolayers of insoluble surfactants spread at the air/water interface, which allows us to explain the observed behavior; for instance, the temperature T_c appears to correlate with the triple point T_0 of the corresponding Langmuir monolayers. We also report preliminary grafting experiments, using trichlorosilanes with fluorohydrocarbon chains, which open perspectives for solids with extremely low critical surface tension and small contact angle hysteresis.

Process of Silanization

Long-chain *n*-alkyltrichlorosilanes have been deposited onto oxidized silicon wafers by using the general procedure described by Sagiv,[4] itself derived from the deposition from solution method of Zisman.[3] We have, however, intro-

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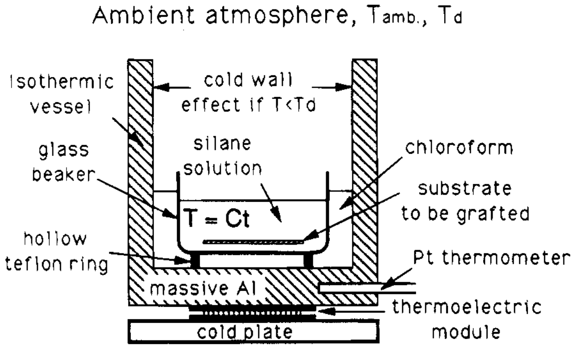

Figure 1. Thermoregulated bath used for silanization of silicon wafers. The deep aluminum vessel allows the natural accumulation of cold dry air close to the air/solution interface. For low-temperature graftings, this minimizes the change of contact between the reactive solution and humid air.

duced several modifications in the cleaning of substrates, control and localization of water traces, purity of the silanes, and control of the reaction temperature, which are reported in full detail below.

The solvents used for the silanization reaction were a series of *n*-alkanes, from decane to hexadecane, in order to adjust the chain length of the solvent to the *n*-alkyl chain of the trichlorosilane. Their freezing points were always below the chosen temperature of reaction. As suggested in earlier reports,[4,10,12] a significant quantity of a co-solvent like carbon tetrachloride (anhydrous, <0.01% water) was systematically added to help in solubilizing the polar $-SiCl_3$ head groups and in avoiding the formation of micelles, which presumably are unable to react with the substrate.

The reagents, *n*-alkyltrichlorosilanes, were purchased from Petrarch. The lower homologues (C_{10}, C_{12}, C_{16}), which had a purity better than 98%, were used as received, whereas the higher homologues (C_{18}, C_{22}), with listed purity <95%, were systematically distilled under reduced atmosphere (10^{-2} mbar) prior to use.

The reactive solution was composed of ~70% alkane, ~30% carbon tetrachloride, and $\sim 10^{-3}$ M of *n*-alkyltrichlorosilane. The silanes were always incorporated at the last moment to avoid prolonged contact with atmospheric humidity, which can induce volumetric and surface polymerization of the reagent.[13] Indeed, flakes inside the solution or haze at the air/liquid interface could sometimes be observed. For the same reason, the temperature of the solution was regulated by immersion of the container in a thermoregulated organic oil, rather than by a water bath, with an absolute accuracy of ±0.5 °C. Figure 1 shows the experimental device; note especially the thick high walls of the aluminum beaker containing the oil which allows the uptake of ambient humidity by the silane solution to be minimized. When a low grafting temperature is desired, the cold walls condense a part of the neighboring humidity, and dry cold air accumulates by gravity at the bottom of the beaker, near the silane solution. The lower temperature limit was imposed by the dewpoint of the atmosphere surrounding the bath. In the humidity conditions of our laboratory, this sets an approximate limit of −5 °C. The upper limit was imposed by the boiling point of the solvents mixture; we select a maximum temperature of 60 °C, since carbon tetrachloride boils at 76 °C.

The substrates were 2 in. (100) silicon wafers, purchased from Siltronix (France); they were covered by a natural layer (~14 Å thick) of amorphous SiO_2 with silanol surface groups onto which the trichlorosilane head groups can chemically react.

The silicon wafers were extensively cleaned in six successive steps: (1) Degreasing by sonication in chloroform to remove gross organic contamination. (2) Photochemical precleaning, front and backside, by UV radiation (λ = 185 and 254 nm) in an oxygen atmosphere at room pressure and temperature. This powerful photochemical oxidation technique[14] transforms organic compounds, like hydrocarbons and oils, into gases or water-soluble species such as fatty acids. It was continued until the surface became fully wettable by water. This condition is necessary to facilitate the next acid attack in aqueous solution. (3) "Wet" chemical oxidation for ~10 min by immersion of the silicon wafers into a freshly prepared mixture of 70% sulfuric acid−30% aqueous solution of hydrogen peroxide (at 30% H_2O_2) at 150 °C. This mixture has been preferred to the more classical sulfochromic acid solution in order to avoid metallic contamination by chromium atoms. (4) Thorough rinsing (three times) with running tap water, distilled water, and Millipore water, respectively. During this step it is important to check that total wetting is achieved on every part of the water and that there are no remaining hydrophobic patches, which could later spread surfactant contaminants over the water surface. (5) Drying in an oven at 100 °C at atmospheric pressure; it can be noted that this moderate baking preserves the naturally adsorbed layer of water.[15] (6) The final stage was again a dry photochemical $UV-O_3$ oxidation for ~1 h to remove the last traces of contaminants. It is always preferable to end the cleaning process this way since any solvent, even in its purest grade, is always susceptible to surface-active contaminants.

Immediately after the final cleaning, the substrates were dipped into the reaction bath, in which they were allowed to react between 10 min and 1 h. As they were withdrawn from the silane solution, one could observe spontaneous dewetting over the whole surface. This evidenced that the treated silicon wafers were covered with a dense monolayer of long alkyl chains. This layer acts as a protective cover and made the wafers impervious to contamination. They can then be stored in air without damage.

Contact Angle Measurements

In order to determine the critical surface tension γ_c of the modified wafers, contact angle measurements were performed on sessile drops (a few microliters) of *n*-alkanes deposited on the horizontal substrates. Rather than using the classical goniometer method, we have used an optical technique[16] in which the droplet acts like a convex mirror for a parallel light beam from a He−Ne laser, incident perpendicularly to the solid substrate. The divergence of the reflected beam is proportional to the contact angle θ at the triple contact line and is calculated by measuring the beam diameter at a known distance *h* from the droplet. This method has the advantage of an excellent accuracy of ±0.5° even for small contact angles; moreover, it can be easily extended to the determination of contact angle hysteresis. Simultaneous measurements of advancing (θ_a) and receding (θ_r) contact angles were performed by tilting the substrate until the drop started to move by gravity.

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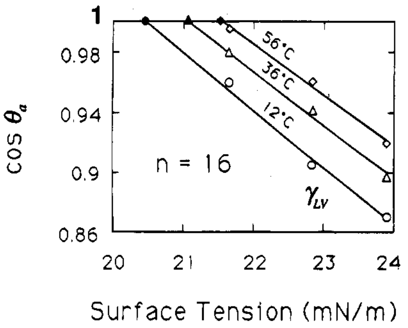

Figure 2. Zisman plot of n-hexadecyltrichlorosilane ($n = 16$) monolayers prepared at three different temperatures (12, 36, and 56 °C). The data points correspond to three different n-alkane test liquids (octane, nonane, decane). Extrapolation of the solid line to $\cos \theta_a = 1$ gives the critical surface energy of the silanized wafers γ_c.

The onset of the downward motion was detected by monitoring the displacement of dust particles deposited from air at the liquid/vapor interface, which appeared to the naked eye as bright moving dots under the laser illumination. At this point, the forward front contact angle is θ_a and the rear front angle is θ_r. If the velocity is small enough, (typically, less than .5 mm/s for a 5 mm diameter drop) the profile is quasistatic,[17] and these dynamic contact angles are identical to their static counterparts. We have checked that the θ_r values obtained by this dynamic technique agreed to within ±.5° with measurements onto static droplets submitted to partial evaporation.

Characterization of the Surfaces

The critical surface tensions γ_c of the modified substrates were derived from the contact angle data by using the extrapolation method devised by Zisman.[18] In this method, the cosine of the contact angle θ for a series of homologous apolar liquids is plotted as a function of their liquid−vapor surface tensions γ_{LV}. The data points are generally found to follow a straight line variation, and the extrapolation of this line to $\cos \theta = 1$ yields γ_c.

Figure 2 shows the results obtained for a wafer reacted with a solution of n-hexadecyltrichlorosilane ($C_{16}H_{33}SiCl_3$, HTS for short) in tetradecane at three different temperatures. At every temperature, the linear relationship between the cosine of the advancing contact angle θ_a and the surface tensions γ_{LV} of the test liquid alkanes (octane to decane, and hexadecane) is obeyed and the γ_c value can be extracted with an accuracy of ±0.5 mN/m. It should be noted that the test liquids chosen are close to complete wetting, which allows the "tangent approximation" (the Zisman's linear extrapolation of γ_c) to be performed near $\cos \theta = 1$, where γ_c is defined. We observe that the γ_c value increases with increasing T: $\gamma_c = 20.5$, 21, and 21.6 mN/m at 12, 36, and 56 °C, respectively.

Similar plots have been made for the different trichlorosilanes, and all the results are summarized in Figure 3, where γ_c is plotted as a function of the reaction temperature T. For each compound, one observes a typical "S" curve, with a low-temperature region, where γ_c takes a small and constant value of the order of 20.5 ± .5 mN/m, and a high-temperature region where γ_c is significantly larger and is a function of the alkyl chain length n. The "S" curve is especially apparent for the $n = 10$ and 12 silanes, for which the transition between the two regimes is completed over a temperature range of ≈20 °C. In these two cases, the high-temperature value for γ_c is 22.5 ± 0.7 mN/m.

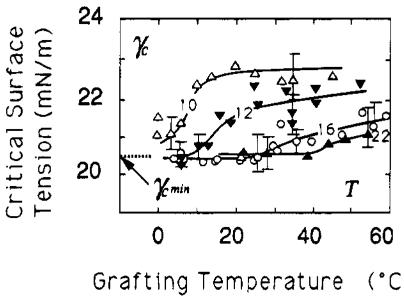

Figure 3. Variation of the critical surface tension γ_c of silicon wafers covered by n-alkyltrichlorosilane monolayers as a function of the temperature of the silanization reaction. The different symbols correspond to alkylsilanes with different chain lengths ($n = 10, 12, 16, 22$ from top to bottom). At low enough temperatures, a constant γ_c value of 20.5 ± .5 mN/m is reached, independent of n. Note the systematic shift, with increasing n, of the transition temperature T_c separating the high-temperature from the low-temperature behaviors.

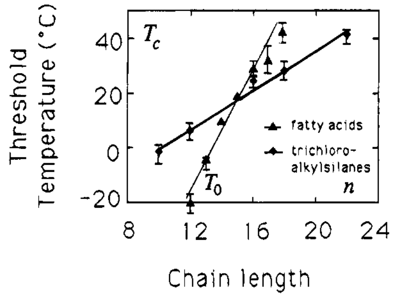

Figure 4. Dependence of the threshold temperature T_c versus the chain length n for the n-alkyltrichlorosilanes (◆) deposited on oxidized silicon wafers. Silanization reactions performed below T_c yield compact monolayers of low wettability. A linear variation of T_c is observed with a slope of ~3.5 °C per additional methylene group. On the same plot, we have superimposed the variation of the triple point T_0 with chain length for monolayers of long-chain fatty acids (▲) spread at the air/water interface (data taken from ref 29). See the discussion part.

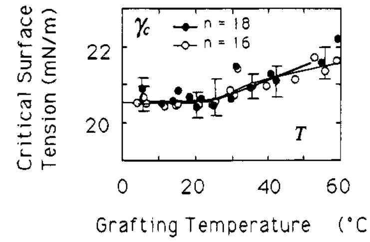

Figure 5. Variation of the critical surface tension γ_c for silicon wafers covered by OTS ($n = 18$, thick line) and HTS ($n = 16$, thin line) as a function of the grafting temperature T. The two curves are almost indistinguishable; this comes from the low degree of purity of the OTS used for this experiment.

We can empirically define a transition temperature T_c by taking the intersection of the lower asymptote (low γ_c region) with the tangent to the γ_c vs T curve passing through the inflexion point. The evolution of T_c vs n is plotted in Figure 4. It ranges from 0 °C for $n = 10$ to 38 °C for $n = 22$. It is striking that the points align on a straight line, indicating a T_c shift of 3.5 ± 0.5 °C per additional methylene group in the grafted chain. The results concerning octadecyltrichlorosilane (OTS for short, $n = 18$) are plotted separately in Figure 5 together with the data values for $n = 16$. The fact that the points for $n = 18$ are almost indistinguishable with the ones for $n = 16$ suggests the presence of chemical impurities in the OTS sample used; we will see in the following that contact angle hysteresis measurements are also anomalous for $n = 18$.

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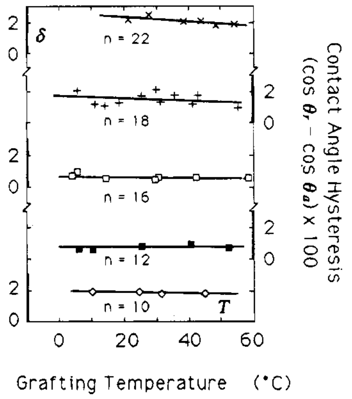

Figure 6. Contact angle hysteresis δ as a function of the grafting temperature T for n-alkyltrichlorosilanes of various chain length n. For each compound, a scale between 0 and 2 $\times 10^{-2}$ has been used. The scattered values for $n = 18$ suggest impurity problems for OTS.

Contact Angle Hysteresis

Our technique of measuring the advancing θ_a and receding θ_r contact angles simultaneously allows an easy determination of the contact angle hysteresis $\delta = \cos\theta_r - \cos\theta_a$. The results for δ as a function of the temperature of the grafting reaction are plotted in Figure 6. For pure enough n-alkyltrichlorosilanes, δ values are found to be independent of the chain length, probe liquids, and grafting temperature. Typically, we obtain $\delta \sim 10^{-2}$, which corresponds to $\theta_a - \theta_r \sim 1°$ for $\theta_a = 30°$. This value, however, can be drastically affected by the presence of impurities. For instance, the δ value obtained for the $n = 18$ compound purchased from three different commercial sources can differ by as much as a factor of 3. Similarly, the δ values for the OTS sample seem systematically high, and Figure 5 has already shown the anomalous exponential behavior of this compound.

In an attempt to quantify the effect of impurities, we have voluntarily mixed silanes of different chain lengths: a mixture of $C_{18}H_{37}SiCl_3$ and $C_{12}H_{25}SiCl_3$ (80/20% by weight) gives a δ value greater than 5×10^{-2}. A slow regular decrease of δ with temperature is also observed in that case: $\Delta\delta \sim 2 \times 10^{-2}$ for $\Delta T = 50$ °C. This observation of higher hysteresis at low temperature suggests the possibility of an in-plane demixing between the silane chains of different lengths, which would lead to a higher chemical heterogeneity of the grafted surface,[19] and then a higher hysteresis.[20]

We have observed a strong correlation between low hysteresis, monolayer robustness, and resistance to chemical attack. For instance, monolayers with a hysteresis value δ less than 10^{-2} have been repeatedly found to be unaffected by a prolonged immersion (2–24 h) in boiling water. It thus appears that highly compact and homogeneous monolayers of long hydrocarbon chains are quite effective in preventing water penetration and subsequent hydrolysis. We suspect that the detrimental role of water recently reported by Wei et al.[21] on the stability of silane-treated glass, quartz, and fused-silica slides is due to incomplete coverage, loose packing, or desorption of weakly adsorbed molecules. These arguments were already present in an earlier paper by Menawat et al.,[22] which also points out that water molecules can penetrate even a dense layer if the hydrophobic chains are too short. From these two papers, it is obvious that an increase in the contact angle hysteresis is a strong signature of a degraded organic layer.

Existence of a Transition Temperature for Optimum Grafting of Long-Chain Alkyltrichlorosilanes

Good quality layers with minimal surface energy are only achieved if the temperature of the reaction is maintained below T_c. The low γ_c value measured in this case is 20.5 mN/m, independent of n. It is in excellent agreement with the most recent results obtained by other groups using either the same deposition method of retraction from solution[4,9,10,23] or the vapor phase deposition.[24] It should be pointed out that the latter method is, however, less reproducible and gives higher hysteresis. On the other hand, it has the advantage of providing an easy way for deposition of organic coatings with wettability gradients.[25]

The value of $\gamma_c = 20.5$ mN/m is characteristic of a dense packing of methyl-terminated hydrocarbon chains. The wafers silanized at low temperatures thus appear as almost ideal hydrophobic surfaces. It is therefore tempting to compare our result with the calculated solid surface free energy using the equation of state proposed by Li and Neumann[26]

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_c}{\gamma_{LV}}}\, e^{-\alpha(\gamma_{LV} - \gamma_c)^2}$$

where α is a numerical constant equal to 0.1247×10^{-3}.

For sufficiently low contact angles ($\theta < 30°$), this equation simplifies to $\gamma_c = \gamma_{LV}/4(1 + \cos\theta)^2$ since the exponential term is then almost unity.

If we take the literature values of γ_{LV} for the three test liquids used in our experiments (namely 21.65, 22.85, and 23.90 mN/m at 20 °C for n-octane, nonane, and decane, respectively) and inject the advancing contact angle values $\cos\theta_a = 0.956$, 0.899, and 0.866, respectively (averaged over many experiments and several substrates), we obtained in each case the same γ_c value of 20.7 mN/m (to within 0.1 mN/m). Our results thus fully support Li and Neumann's claim that a single contact angle determination suffices to obtain the free energy of a solid. Moreover, the value derived from their improved equation of state is in very good agreement with our experimental value of 20.5 $\pm$ 0.5 mN/m.

Another theoretical approach worth considering is the one by Van Oss, Chandhury, and Good,[27] which allows one to calculate the Lifshitz–van der Waals and the polar, electron-acceptor and electron-donor components of the surface free energy. Their equation writes

$$(1 + \cos\theta)\,\gamma_{LV} = 2\left(\sqrt{\gamma_c^{LW}\gamma_{LV}^{LW}} + \sqrt{\gamma_c^{AB}\gamma_{LV}^{AB}}\right)$$

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[23] Some authors prefer to define the quality of their layers by the advancing contact angle of sessile drops of hexadecane. Sagiv[2] and Whitesides[7] have obtained $\theta_a = 45 \pm 1°$, in full agreement with our own value of 45°.

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where LW is the Lifshitz–van der Waals interaction parameter and the AB superscript refers to the generalized Lewis acid–base interaction parameter, a sum of electron-acceptor and electron-donor components, respectively. Experiments with hexadecane allow a direct determination of the LW component of γ_c since in that case the γ_{LV} value is entirely due to apolar L–W interactions. Using the measured contact angle value of $\theta = 45°$ and taking $\gamma_{LV}^{LW} = \gamma_{LV} = 27.76$ mN/m, we obtain $\gamma_S^{LW} = 20.22$ mN/m. Experiments with water as the probe liquid give access to the AB component of γ_c. Using $\theta \approx 110°$, we obtain $\gamma_S^{AB} = 0.0076$ mN/m, considerably smaller than γ_S^{LW}. This confirms the strong apolar character of the silanized substrates. It is also worth noticing that the γ_S^{LW} value obtained is equal to our measured critical surface tension γ_c to within 1.5%. This confirms that the use of nonpolar liquids in the Zisman method of determination of critical surface tension effectively yields the LW component of the solid surface free energy.

All the above discussion refers to the surface tension of silanized silicon wafers prepared at temperatures less than the critical temperature T_c. Above T_c, the γ_c values markedly increase. We take this as an indication that the monolayer structure becomes disorganized and contains a mixture of methylene and methyl groups at the air–monolayer interface. Indeed, the γ_c of a monolayer of pure methylene groups is ~31 mN/m.[18] The influence of the temperature of reaction on the final quality of the monolayer has already been mentioned by Silberzan *et al.*[10] However, it was interpreted as due to solubility changes of the trichlorosilanes in the reactive mixture. This explanation does not seen to apply here, since we have found no significant change in γ_c when the nature of the aliphatic solvent used for a given silane is charged. For instance, for *n*-decyltrichlorosilane, we have used decane, dodecane, and even isooctane (a ramified chain) as reaction solvents, and the measured variations in γ_c were always less than 1 mN/m. Moreover, the temperature threshold T_c was found to be independent of the solvent used and thus appears to be an intrinsic property of the selected silane.

We would therefore like to suggest here a totally different mechanism, based on our novel observation of a systematic variation of T_c with the alkyl chain length *n*.

Analogy with Langmuir Monolayers

Our argument is based on an analogy with monolayers of insoluble fatty acids spread at the air/water interface. Indeed, it has been established long ago[28] that the phase diagram in these two-dimensional systems is strongly temperature-dependent. Figure 7 shows a schematic surface pressure versus area per molecule diagram which allows the various thermodynamic states of the monolayer to be distinguished. At high temperature, the monolayer state can change from 2d gas (G) to liquid expanded (LE) and finally to liquid condensed (LC) physical states as the monolayer density is increased, whereas at low temperature the G phase is directly followed by the LC phase. These states have been listed here by rank of increasing order for the long aliphatic tails. In the LC state, they are fully stretched in their *all*-trans conformation, whereas in the LE and G states, they contain a large number of "gauche" defects. There is a well-defined temperature T_0, called the triple point, which separates the high-temperature and low-temperature behaviors. Careful measurements by Kellner *et al.*[29] have established that T_0 is a function of alkyl chain length *n* and that it increases linearly by roughly 10 °C for each additional methylene group. In the context of our discussion, it is also important to note that for an arbitrary surface density the monolayer is generally not in one of these homogeneous states. Most of the phase diagram is actually occupied by coexistence regions which can be G/LE, LC/LE, or LC/G, depending on temperature and surface density. For instance, at room temperature, the LE/LC coexistence region of pentadecanoic acid (corresponding to $n = 15$) extends between $A_{LC} = 23$ and $A_{LE} = 37$ Å²/molecule and the LE/G coexistence region extends between $A_{LE'} = 42$ and $A_G = 1500$ Å²/molecule.[30] Below 17 °C, the LC/G coexistence region goes from $A_{LC} = 23$ to $A_G = 2000$ Å²/molecule.[31]

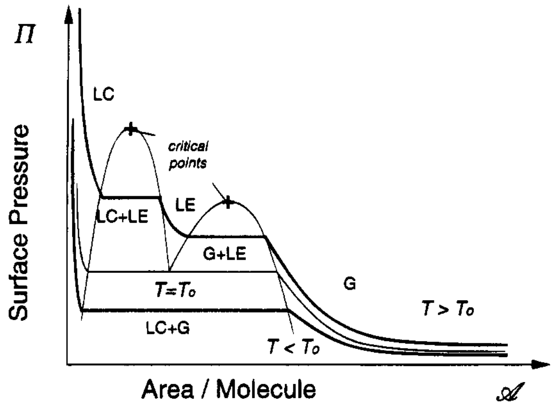

Figure 7. Typical phase diagram of a Langmuir monolayer of insoluble surfactants spread at the air–water interface. Thick lines denote the isotherms, and the coexistence curves are denoted by the thin lines. The monolayer triple point corresponds to the isotherm $T = T_0$. Above T_0, one observes two successive coexistence regions G/LE and LE/LC upon increasing the surface density (i.e. decreasing the area per molecule *A*). Below T_0, one observes only one, LC/G, coexistence region in the phase diagram.

Observations by fluorescence microscopy[32] and by ellipsometric imaging[33] of Langmuir monolayers spread at the air–water interface have given evidence of strong phase separation in these coexistence regions: for instance, isolated circular domains of LC phase are observed in a continuous background of LE phase. The fraction of the monolayer surface occupied by these patches is given by the "lever rule".[34] If *A* is the average area per molecule (obtained by dividing the total available surface by the total number of molecules), one has $\chi_c = A_{LC}(A - A_{exp})/A(A_{LC} - A_{exp})$, where χ_c is the surface fraction of the LC phase and A_{exp} is the surface density of the more expanded phase (LE or G) in the coexistence region under consideration. It then appears that, *for the same A*, χ_c will be considerably larger in the LC/G case than in the LC/LE case. Taking $A = 25$ Å²/molecule as an example, one obtains $\chi_c = 4/5$ and $\chi_c = 3/5$, respectively. The advantage of performing the silanization reaction below T_c then becomes obvious, since the percentage of the surface occupied by well-ordered LC regions is 33% higher although the average monolayer density is the same. This

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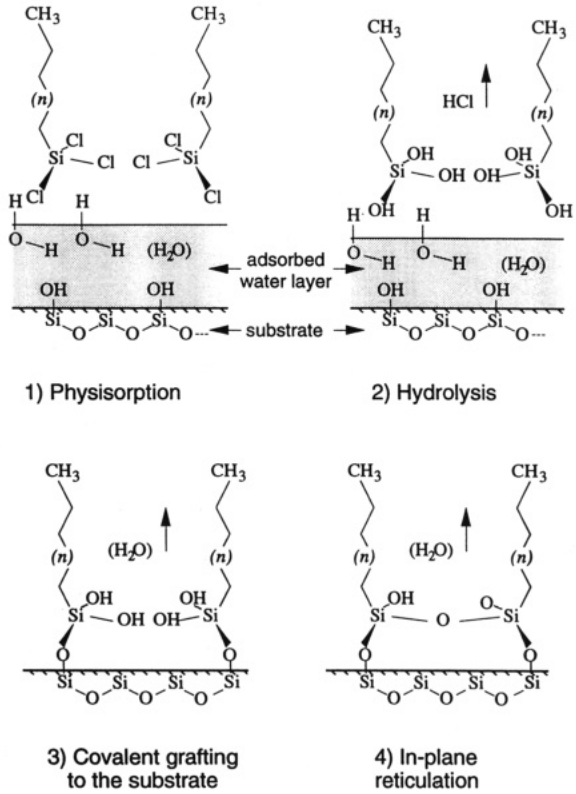
will guarantee a higher percentage of methyl groups to be in the topmost layer and therefore a lower macroscopic γ_c.

The above argument would suffice in itself to explain our observations. However, we have to deal with the fact that the final surface density cannot be defined *a priori*: the monolayer will always tend to reach its maximum surface density, since the reactive bath constitutes an infinitely large reservoir of molecules and the adsorption is supported to be irreversible. The trichlorosilane head groups arriving close to the substrate hydrolyze into highly polar trihydroxysilane $-Si(OH)_3$ which is strongly attracted to the substrate and will then prevent the n-alkyl chain molecules from leaving the interface. Upon first contact, only a few molecules will adsorb and the monolayer will definitely be in its gaseous state. At longer times, the surface coverage eventually reaches the point where a coexistence phase is entered. At low temperature, the coexistence is between the LC and the G phases, and liquid condensed domains of close-packed chains are formed. Further adsorption can still take place into the gaseous portion of the monolayer, and the process repeats itself until the whole monolayer is in the LC state. On the contrary, at high temperature (above T_0), the coexistence is first between the LE and the G phase, and the monolayer goes through a homogeneous liquid expanded (LE) state. This state, made of still disorganized aliphatic chains but at the same time considerably denser than the gaseous phase, opposes a strong barrier to further adsorption. It is then quite possible that the monolayer is unable to reach its densest LC state, at least within the time frame of our silanization reaction (10 min to 1 h), resulting in poor layer quality.

This interpretation is supported by recent experiments from three different groups. Ellipsometric measurements by Parikh et al.[35] indicate a surface coverage lower by 20% when the temperature of the reaction bath is maintained above T_c. X-ray grazing incidence diffraction data by Tidswell et al.[7] give evidence of inhomogeneous surface coverages in the case of incomplete monolayers (obtained by voluntarily limiting the immersion time in the reaction bath). The fact that the peak positions are comparable to those of complete monolayers could also be taken as a proof of liquid-condensed islands into a gaseous background; however, this possibility seems to have been rejected by these authors. Atomic force miroscopy observations by Schwartz et al.[36] on self-assembled monolayers of octadecyltrichlorosilane onto mica have revealed the presence of microscopic domains of different packing density which gradually aggregate as complete coverage is approached. To complete these observations, it would be interesting to perform in situ observations by fluorescence microscopy on the substrates at regular intervals during the adsorption process. The feasability of such experiments has already been demonstrated in the closely related case of soluble surfactants like sodium octanoate[33] or sodium dodecyl sulfate,[37] adsorbing from solution onto the air−water interface. In ref 33, the final state corresponds to the LE phase and the LC phase is apparently not reached; in ref 37, the observation of hexagonal domains suggests a LC/G coexistence region.

Presence of Adsorbed Water



1) Physisorption

2) Hydrolysis

3) Covalent grafting to the substrate

4) In-plane reticulation

Figure 8. General scheme proposed for the silanization reaction. Note the presence of a thin adsorbed water layer over the "bare" silica surface.

The analogy between Langmuir and grafted monolayers on solid substrates relies on the existence of a thin water layer between the substrate and the organic layer. Tripp and Hair have performed detailed infrared spectroscopic studies of the reaction of alkylchlorosilanes on silica surfaces covered with various quantities of adsorbed water.[38] They found that a minimum amount of water was necessary for optimum monolayer deposition. In the case of octadecyltrichlorosilane (OTS) no reaction occurs either with the silanol groups of the bare surface or with a single water layer. The rationale was that this tightly bound water is not reactive enough to participate in the hydrolysis of the chlorosilane head group. Similar conclusions had been reached earlier by other groups. For instance, Carson and Granick[39] have observed that an optimum level of physisorbed water was necessary to form robust films of OTS on mica. Angst and Simmons[40] have also reported a change in the γ_c values from 20.3 ± 1.0 to 24.3 mN/m for OTS on silica between hydrated and dry thermal oxide conditions. This was taken as an indication of a loosely packed monolayer containing disorderd alkyl chains. The proposed mechanism of silanization is summarized in Figure 8; there is an initial water layer present on the substrate onto which the organic molecules contained in the reactive solution can gradually adsorb (stage 1). Following physisorption, the trichlorosilane head groups hydrolyze and form trisilanols (stage 2). Moreover, the presence of a thin film of fluid permits the in-plane lateral mobility of the long-chain silanes by Brownian motion. This leads to important in-plane reorganizations, in a manner analogous to Langmuir monolayers of short-chain surfactants submitted to lateral compression. Under the proper thermodynamic conditions (e.g. control of the temperature of the reaction), a uniform densely packed monolayer of vertical chains in their *all-trans* ordered conformation is formed. At later times,

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[39] Carson, G. A.; Granick, S. *J. Mater. Res.* **1990**, *5*, 1745.

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covalent siloxane bonds can take place at the head group–substrate interface (stage 3). The layer becomes grafted to the solid surface. In addition, intermolecular cross-linking by the trisilanol head group can occur, provided the distance and orientation between the groups are favorable. The end result is a 2d network of polysiloxane (stage 4). Stages 3 and 4 will obviously be facilitated by a moderate baking of the substrate, which will help to remove the water layer. Reference 40 reports that the density of surface and silanol groups is substantially reduced by a 100 °C cure, as expected if covalent bonds are formed by grafting or cross-linking. To date, however, the exact fraction of grafted chains is still a matter of controversy. Our suspicion is that only a small amount of the chains needs to chemically react to form a sturdy layer. The presence of the water layer during silanization and its subsequent removal could explain some of our side observations performed on monolayers deposited on aluminum substrates.[41] Immediately after deposition, the silane layer is easily removed by fuming nitric acid, whereas it becomes impervious to chemical attack after being cured at 120 °C for a few hours or being aged in air for a few days. This behavior is consistent with the removal of the water film and with the subsequent formation of permanent covalent bonds between the alkylsilane hydrolyzed head groups and the silanol surface groups of fused silica, as observed by NMR.[42]

Silanization with Fluorohydrotrichlorosilanes

Silanization with long fluorocarbon chain silanes, $-(CF_2)_n-CF_3$, should lead to extremely low values of surface tension. For instance, Zisman has observed a critical surface tension as low as $\gamma_c = 6$ mN/m for a monolayer of perfluorolauric acid deposited onto platinum.[18] Moreover, the chemical inertness of a grafted perfluorinated monolayer should be similar to that of poly(tetrafluoroethylene) (PTFE for short). To the best of our knowledge, however, we are not aware of recent reports on homogeneous fluorocarbon coatings with reproducible γ_c values and low hysteresis. Our own previous attempts to graft such compounds had failed, giving unacceptably high δ values of the order of 0.1. Therefore, we have attempted to graft *at low temperature* two trichlorofluorosilanes at our disposal, $C_8F_{17}(CH_2)_2SiCl_3$ (Petrach) and $C_{10}F_{21}(CH_2)_2SiCl_3$ (Elf-Atochem). As an example, Figure 9 shows the Zisman plot of a monolayer of the first molecule grafted onto a naturally oxidized silicon wafer at $T = 0$ °C. The ambient temperature ($T_{ext} = -8$ °C) was selected to ensure an extremely low dewpoint ($T_d = -14$ °C). Such particular conditions of hygrometry are necessary to avoid the self-polymerization of the silane, since we have observed that the fluorinated compounds are much more reactive to water than their hydrogenated homologues. We have used a mixture of dry isooctane and carbon tetrachloride as the organic solvent. Apart from this point, the grafting procedure was exactly the same as previously described. With alkanes and PDMS oils as test liquids, the critical surface tension γ_c was measured to be 12 ± 0.7 mN/m. This is still higher than the 6 mN/m observed for a perfluorinated monolayer but significantly less than the 18 mN/m of PTFE.[18] The hysteresis was a low $\delta = 2 \times 10^{-2}$, comparable to our values for hydrogenated compounds. The combination of these two results, low γ_c value and low hysteresis, is consistent with the formation of a dense, homogeneous layer with mostly CF_3 terminal groups. Even more spectacular was the result obtained with the $C_{10}F_{21}(CH_2)_2SiCl_3$ compound. When the reaction was performed at 5 °C, a value of 6 ± 1 mN/m was reached, the lowest γ_c value ever reported for silanized wafers. Increasing the reaction temperature to 15 and 20 °C resulted in both cases in a much higher value of 12 mN/m, indicative of a layer of poorer quality. It thus appears that good grafting with fluorinated silanes also requires low temperatures of reaction as is the case for hydrogenated silanes. That there is a threshold in temperature remains to be checked in future experiments. There are, however, reasons to believe that the analogy with Langmuir monolayer holds with perfluorinated chains as well as with flexible hydrocarbon chains. For instance, recent fluorescence microscopy observations of Langmuir monolayers of a fluorinated fatty acid $C_8F_{17}(CH_2)_2COOH$ spread onto water at 20 °C have revealed the existence of at least three different states, gas, liquid-expanded, and liquid-condensed, upon increasing the surface density.[42]

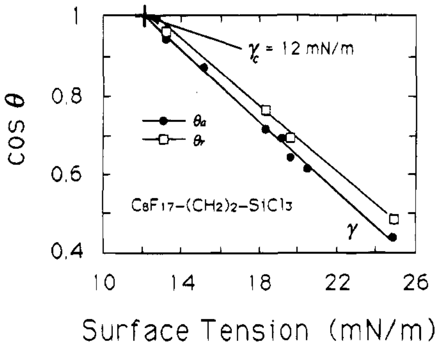

Figure 9. Zisman plot for a silicon wafer grafted with a fluorinated silane, $C_8F_{17}(CH_2)_2SiCl_3$, at $T = 0$ °C in a dry atmosphere. The test liquids were *n*-alkanes and PDMS oils. The γ_c value of the modified surface is found to be 12 ± .7 mN/m. Hysteresis δ is shown on the graph; it is of the order of 2×10^{-2}, comparable to the best values obtained with the long hydrocarbon chain silanes.

Conclusion

We have studied the influence of the temperature of silanization on the quality of grafted monolayers in the case of several *n*-alkyltrichlorosilanes ($n = 10-22$) deposited from solution onto fused silica. Clear evidence for a threshold temperature T_c has been obtained. This threshold is an intrinsic property of the molecules to be grafted and gives the condition for the optimized grafting of short-chain silanes. This condition seems also to extend to fluorinated compounds. If silanization is performed below T_c, the monolayer then reaches its highest packing density. The lowest surface energy of the modified substrate is $\gamma_c = 20.5 \pm .5$ mN/m for hydrocarbon chains and 6 ± 1 mN/m for fluorocarbon chains. The monolayer homogeneity is demonstrated by the low contact angle hysteresis.

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(41) The silanization procedure for aluminum plates is quite similar to that of silicon wafers except for the "wet" chemical cleaning step, in which the H_2SO_4 oxidizing solution is replaced by a 10 nm dip into fuming nitric acid at room temperature.

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