

LETTERS

Observation of Three Growth Mechanisms in Self-Assembled Monolayers

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Time-resolved atomic force microscopy and contact angle measurements reveal that the self-assembly of octadecyltrichlorosilane-based monolayers on the oxidized Si(100) surface can be initiated by three distinct mechanisms: island growth at low temperatures ($T < 16$ °C), homogeneous growth at high temperatures ($T \geq 40$ °C), and a mixed regime at intermediate temperatures. These results support the notion of a transient Langmuir film at the substrate–solution interface: the observed growth patterns are consistent with nucleation of liquid-condensed domains coexisting with a two-dimensional gas at low temperature, or with a liquid-expanded phase at intermediate temperatures.

Introduction

Amphiphilic self-assembly has long been exploited to produce monolayer molecular films at the air–water interface (Langmuir films)¹ and, more recently, on solid substrates (self-assembled monolayers, SAMs).² The assembly process basically entails the loss of surfactant translational entropy in favor of a lower surface energy. However, since surfactants are typically long molecules with polar end groups, conformational entropy and long-range electrostatic forces also play an important role, which is manifest, e.g., in the rich equilibrium phase diagram of Langmuir films.¹ One might expect that the kinetics of SAMs formation are similarly rich, provided that the time scales for attaining local equilibrium are shorter than those characterizing irreversible chemical reactions that may take place during SAM formation.

A class of widely used SAMs is based on *n*-alkyltrichlorosilane precursor molecules, which, through hydrolysis and polymerization, produce self-assembled alkylsiloxane films on many hydrophilic substrates. The existence of a single growth

mechanism for these SAMs, as well as the nature of the mechanism itself, has been the subject of debate. Evidence of homogeneous growth was provided by X-ray reflectivity measurements,³ suggesting that the structure of the incomplete monolayers is best described by disordered molecules that are distributed uniformly over the substrate. Backfilling experiments were interpreted in a manner consistent with this picture.⁴ A conflicting picture was inferred from FTIR⁵ and from AFM measurements,^{6–8} suggesting that alkylsiloxane monolayers self-assembled by island growth, with partial monolayers consisting of islands of close-packed, fully extended, untilted chains. A possible cause for such a discrepancy is the notorious sensitivity of the SAM formation process to external conditions, such as temperature and relative humidity. Measurements of the surface energy of fully assembled SAMs on silicon oxide surfaces provided new insight.⁹ Evidence was found of an intrinsic relation between the structure of *fully assembled* alkylsiloxane monolayers and deposition temperature. The existence of *two different growth regimes* was postulated, according to whether temperature is above or below a “critical” temperature, which correlates well with the triple point T_t of a Langmuir film. This hypothesis has prompted our investigation.

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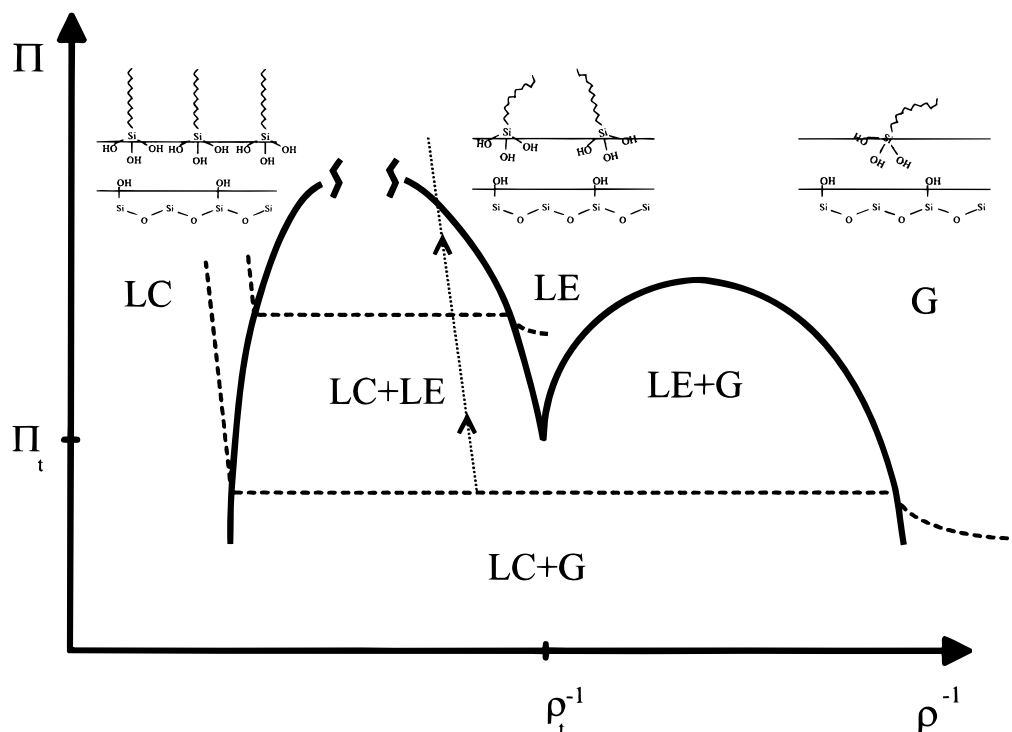


Figure 1. Schematic phase diagram of a Langmuir film in the spreading pressure-specific area plane. The solid curves delimit the coexistence regions between liquid-condensed, liquid-expanded, and gas phases. Also drawn schematically is the structure of an alkylsilanol monolayer, physisorbed on the water layer wetting the silica, in each of the three phases. The dashed lines represent two isotherms, one below the triple-point temperature and one above. The dotted line is discussed in the text.

Our results prove for the first time the existence of *three* distinct growth regimes for octadecyltrichlorosilane (OTS)-based SAMs as a function of temperature, with all other parameters constant. Our findings support the notion of a transient Langmuir film during SAM formation from octadecyltrichlorosilane. We show that the (hydrolyzed) precursor molecules retain their mobility for sufficiently long times to allow us to observe transformations between different condensed two-dimensional phases of the film. This mobility is promoted by the existence of a thin water layer on the oxidized silicon substrate. We have determined the existence of *two* characteristic temperatures, T_0 and T_c . For $T < T_0$, self-assembly proceeds initially by island growth only, the substrate between islands remaining essentially unfilled; such a growth pattern is expected if a Langmuir film nucleates liquid-condensed (LC) domains coexisting with the gas phase below the triple point (see Figure 1). Thus, T_0 can be identified with T_t . For $T > T_0$, island growth is observed to occur more slowly, while the substrate between islands is gradually filled in with OTS molecules. This growth regime (which has been observed by other authors^{7,8}) is attributed to nucleation of LC domains coexisting with a liquid-expanded (LE) phase. We find that this mechanism operates only up to a characteristic temperature T_c , above which we observe no island nucleation but homogeneous growth instead.

Experimental Section

Our experiments were carried out in an environmental chamber, where we can simultaneously control relative humidity ($\pm 2\%$) and temperature ($\pm 1^\circ\text{C}$). Relative humidity was kept fixed in all experiments at 50%, at which value a thin film of water (about three monolayers thick) is known to be present on silica.¹⁰ OTS solutions were prepared in various concentra-

tions in a solvent mixture of 7:3 volume hexadecane/carbon tetrachloride. Oxidized silicon (100) samples were prepared by cleaning samples cut from polished single crystalline wafers in peroxysulfuric acid, followed by etching in concentrated hydrogen fluoride, and finally by reoxidation in a peroxysulfuric acid solution. This treatment results in a clean, oxidized surface possessing the same topography as the original wafer ($2.2 \pm 0.4 \text{ \AA rms}$). The oxidized samples are left to equilibrate at the desired temperature and humidity inside the environmental chamber, prior to introduction into the OTS solution, where they were kept for specified amounts of time. Film growth was quenched by rinsing the samples in carbon tetrachloride. AFM images of the samples were obtained on a Digital Instrument Nanoscope III operating in tapping mode.

Results and Discussion

We first investigated SAM growth from solutions of fixed concentration (2 mM) at $T = 10, 16, 23, 25, 35, 40,$ and 45°C for various amounts of time. Figure 2 shows AFM images of SAMs grown at 10, 25 and 40°C for 30 s. The static water contact angles for the three samples were $89^\circ, 90^\circ,$ and 89° , respectively. These values indicate that the OTS coverage is incomplete, but it is qualitatively similar for the three temperatures. However, the patterns of OTS molecules on the surface are strikingly different. At low temperature, large islands have developed (note the larger scan area). Islands are much smaller at $T = 25^\circ\text{C}$ and are not present at $T = 40^\circ\text{C}$. Also shown in Figure 2 are the histograms of the profile distributions of each image, measured as depth below an arbitrary reference plane. For $T = 10^\circ\text{C}$ and $T = 25^\circ\text{C}$, the distributions possess bimodal character, with two well-resolved Gaussian peaks (the peak at shallower depth is due to the islands). The separation between

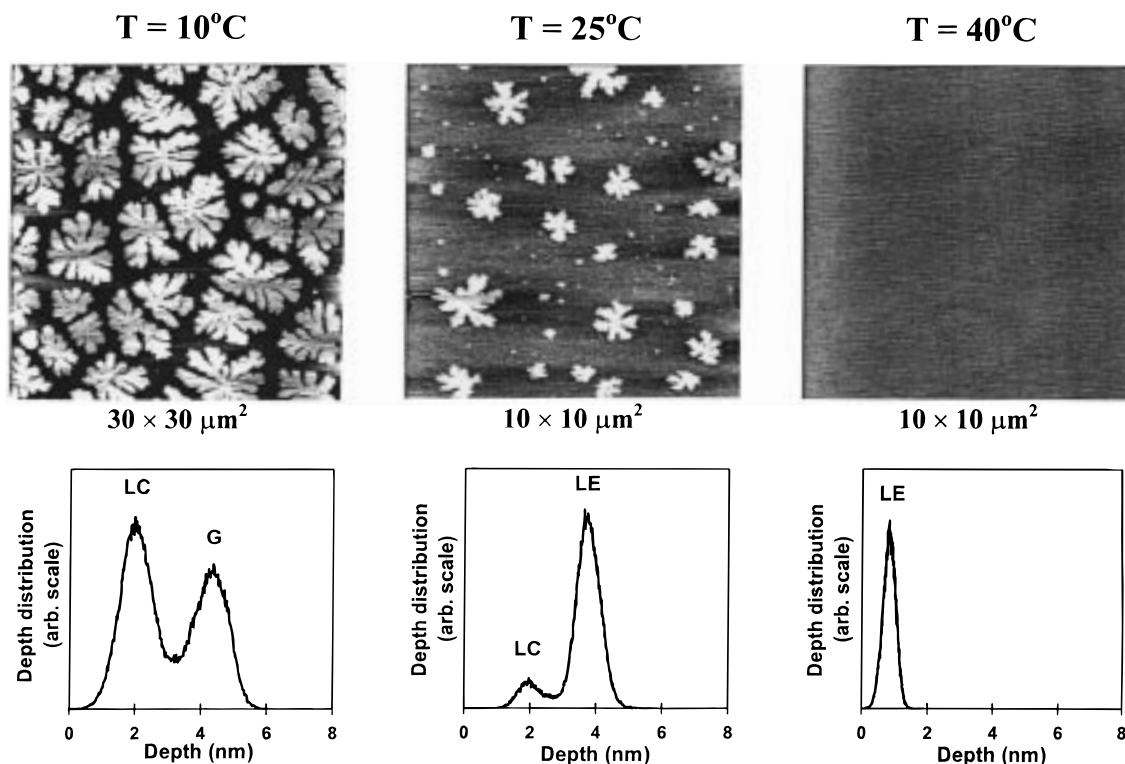


Figure 2. Top: AFM images of partial SAMs grown at 10, 25, and 40 °C for 30 s (left to right). Bottom: Depth distribution histograms for the three images above.

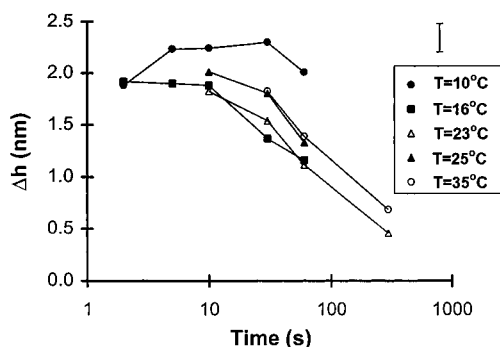


Figure 3. Peak separation of the bimodal depth distributions as a function of time. Δh represents the average measured height difference between phases of the monolayer. The error bar above the symbol inset is indicative of the run-to-run reproducibility.

the two peaks indicates the *average* height difference, Δh , between islands and “substrate.” This difference is smaller for $T = 25$ °C than for $T = 10$ °C, indicating larger material accretion between islands at higher temperatures (cf. Figure 3 below). For $T = 40$ °C, the height distribution is unimodal. Two distinct factors contribute to the width of the Gaussian peaks. One is the roughness of the underlying silicon wafer, which accounts for most of the measured width in the uniform growth mode ($T \geq 40$ °C). The second factor is density variations in the film; these appear to contribute primarily to the width of the peaks at low temperature. Large fluctuations (i.e., large compressibility) point to the metastable character of the film, as it is undergoing phase separation into two thermodynamically stable phases, before cross-linking and grafting to the substrate.

Quantitative information can be obtained from the time evolution of the depth distribution probabilities as a function of temperature. The evolution of the peak separation, Δh , of the bimodal distribution is plotted in Figure 3 for all samples

grown at $T < 40$ °C. At $T = 10$ °C, the peak separation remains *approximately constant* for as long as two peaks can be resolved, indicating that the exposed substrate between islands remains essentially free of OTS molecules. On the clean substrate, island growth is unimpeded and is observed to continue until the island edges touch, corresponding to the last data point in Figure 3 and as shown by the sequence of AFM images in Figure 4.¹¹ We attribute this low-temperature growth pattern to nucleation of LC domains coexisting with a low-density gas phase on the water layer wetting the silica.

The growth pattern is remarkably different at room temperature: the distance between islands and “substrate” peaks now *decreases with time*, signifying that growth is occurring between islands. We attribute this growth pattern to nucleation of liquid-condensed domains coexisting with a liquid-expanded phase, which is filling in the space between islands. Thus, island growth is observed to stop well before the island edges can touch, as shown by the sequence of AFM images in Figure 5. Finally, at temperatures of 40 °C and higher, growth occurs *homogeneously*, and no islands are detected: the depth profile distribution is now unimodal for all immersion times. The absence of domain nucleation is attributed to the temperature being above the LC–LE coexistence region.

Our results strongly support the analogy with Langmuir films at the air–water interface, proposed by Parikh et al.⁹ Langmuir monolayers of OTS at the air–water interface have been studied by Fang and Knobler.¹² An isotherm at $T = 18.6$ °C provided experimental evidence of coexistence between a LE and a LC phase (cf. the upper dashed line drawn schematically in Figure 1). The height of the LC islands was determined by those authors to be compatible with the length of fully extended octadecane chains. Our measurements of the height of the LC island edges above the substrate at the early stage of SAM formation are consistent with this observation, as are similar

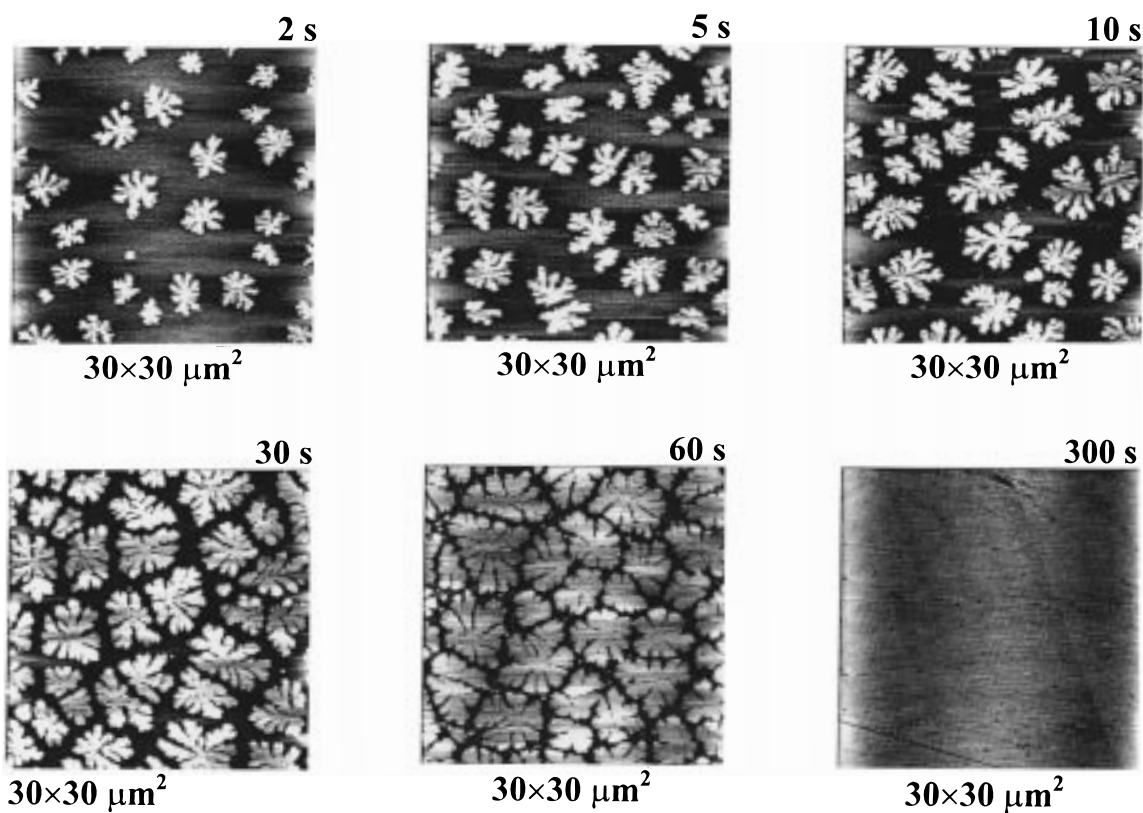
T=10°C

Figure 4. AFM images of the time-resolved sequence of partial SAMs growth at 10 °C.

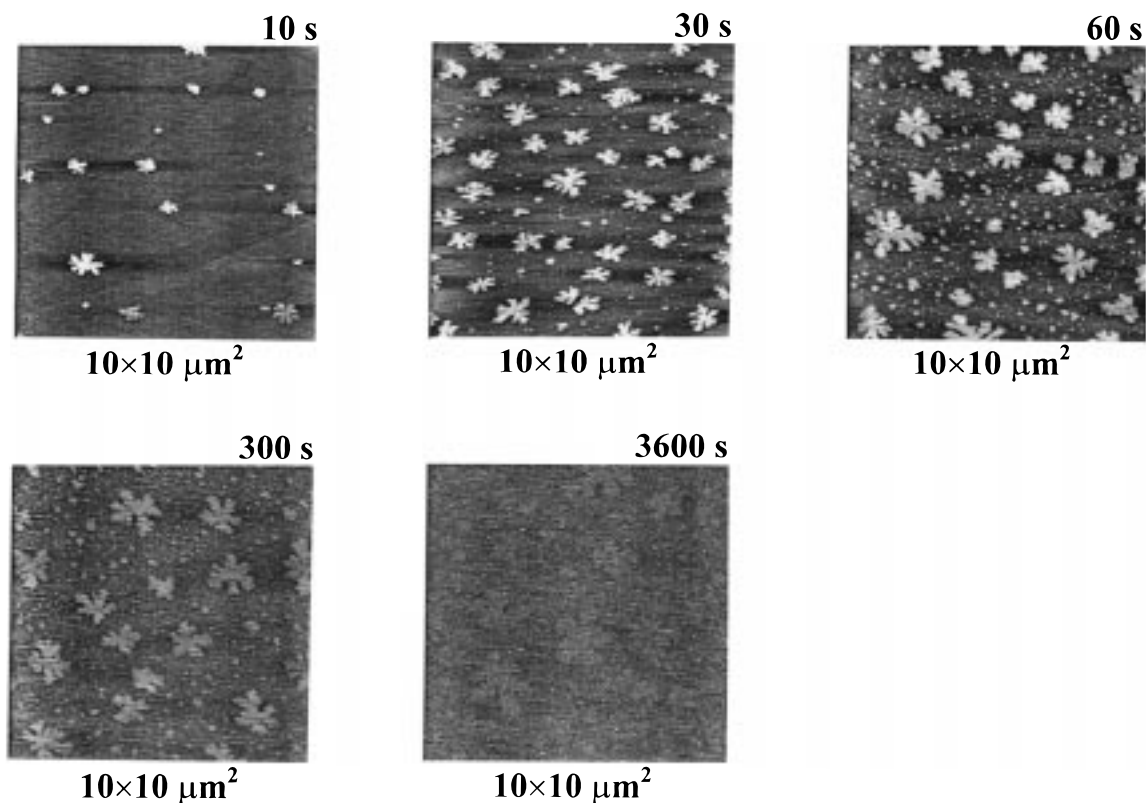
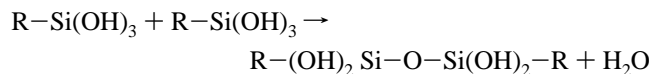
T=23°C

Figure 5. AFM images of the time-resolved sequence of partial SAMs growth at 23 °C.

measurements reported in ref 6. This suggests that the molecules in the LC phase are straight and very likely untitled.

We next turn to the important issue of irreversibility during SAM formation. The silanol groups that result from hydrolysis

of the three Si–Cl bonds of the OTS molecule are highly reactive. A polymerization reaction or similar reactions with



surface hydroxyl groups ultimately results in the irreversible cross-linking of OTS molecules to one another and/or to the silica substrate. Thus, the analogy with Langmuir monolayers is useful and justified only for times shorter than the time it takes the film to cross-link. Complete cross-linking of the film and bonding to the substrate can take tens of minutes and up to an hour at room temperature.¹³ This time scale is long enough to allow one to observe the occurrence of temperature-induced phase transformations during self-assembly.

Thus, we have studied the effect of heating a partial OTS monolayer, which is phase separating into the gas phase and the LC phase, to temperatures above the LC–LE coexistence region, following the path indicated schematically in Figure 1 by the dotted line. One expects that the height distribution function, bimodal at low T , will revert to unimodal character upon heating, unless extensive cross-linking has taken place. This expectation was borne out by experiment. Samples were immersed in an OTS solution at $T = 10^\circ\text{C}$ for 10 s and then quickly transferred into an OTS solution at $T = 65^\circ\text{C}$ for 20 s or for 40 s. The height distribution was found to be unimodal even after 20 s of heating, demonstrating that the LC phase has disappeared. If the LC domains that are observed after 10 s of cold immersion were irreversibly polymerized or grafted to the substrate, one would expect the hot immersion to result simply in the homogeneous filling of the substrate between LC islands, producing patterns quite similar to those observed for $T_0 < T < T_c$, and a bimodal height distribution.

In summary, our investigations of the growth of OTS-based

SAMs on silica reveal the presence of three different self-assembly mechanisms and provide experimental proof of the hypothesis that these monolayers can exist in a near-equilibrium physisorbed state akin to the equilibrium state of Langmuir films at the air–water interface. The existence of a Langmuir film (albeit in nonequilibrium conditions) on a hydrated solid substrate could be exploited both for practical applications, such as patterning of substrates, and for fundamental studies of the physics of solid–membrane interfaces.

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References and Notes

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- (11) After island growth stops, film growth continues, albeit at a slower rate. In this second stage, growth is homogeneous at all temperatures and results in fully assembled and cross-linked films of higher coverage, as evidenced by the higher contact angle of $\sim 110^\circ$.
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- (13) A crude estimate of this time scale is obtained from the following observation: wiping of the samples immediately after removal from the OTS solution results in a significant loss of OTS coverage and a drop in the water contact angle by as much as 25° . However, wiping a sample after 45 min of removal from solution results in a decrease of water contact angle of only a few degrees, and no loss of coverage can be detected by AFM.