

Reversible Liquid–Liquid Transitions in the Early Stages of Monolayer Self-Assembly

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Time-resolved atomic force microscopy, contact angle analysis, and X-ray photoelectron spectroscopy were employed to study the effect of cyclic heating and cooling of a partial octadecyltrichlorosilane (OTS) monolayer on the oxidized Si(100) surface. A reversible structural change of the partial monolayer between high density and low density two-dimensional liquid phases was observed as a function of temperature at constant coverage. These studies show that the monolayer exists in a highly mobile hydrogen-bonded state akin to the equilibrium state of Langmuir films at the air–water interface. The lifetime of the mobile state was measured to be on the order of several minutes, after which grafting and cross-linking immobilize the monolayer. The results show that the mobile state permits large scale rearrangements of the molecules within the monolayers.

Introduction

Octadecyltrichlorosilane-based monolayer self-assembly is a prime example of silanization, a technologically important process with applications as diverse as ultrafine scale lithography, protein immobilization, and microelectromechanical systems lubrication.^{1–4} The existence of a threshold temperature for high quality silanization was discovered by Brzoska et al., who suggested that this temperature is analogous to the triple point of a Langmuir film.^{5–7} Later, it was shown that silanization occurs via three markedly different growth regimes,⁸ separated by well-defined transition temperatures. For $T < 16$ °C, the OTS-based monolayer forms by island growth, the islands consist of fully extended chains, and essentially no OTS molecules are found on the substrate between islands. For $T > 40$ °C, growth is homogeneous and no island is observed. For 16 °C $< T < 40$ °C, islands of extended chains are observed in a uniform background of chains that are presumably disordered (e.g., contain gauche defects).

These states were conjectured to correspond to three thermodynamic phases of a Langmuir film at the substrate–solvent interface,⁹ rather than to originate from kinetic effects. To prove this conjecture, we set out to induce phase transformations in a partial monolayer at constant coverage by changing the temperature and studying their reversibility. A reversible structural change between high- and low-density liquid phases⁹ was observed. These studies show that the monolayer exists in a highly mobile state akin to the equilibrium state of Langmuir films, as originally proposed in ref 7.

Experimental Details

Our experiments were carried out in a controlled environment, where we can simultaneously maintain a constant relative humidity ($\pm 2\%$) and temperature (± 1 °C). Relative humidity was kept fixed in all experiments at 40%, at which value a thin

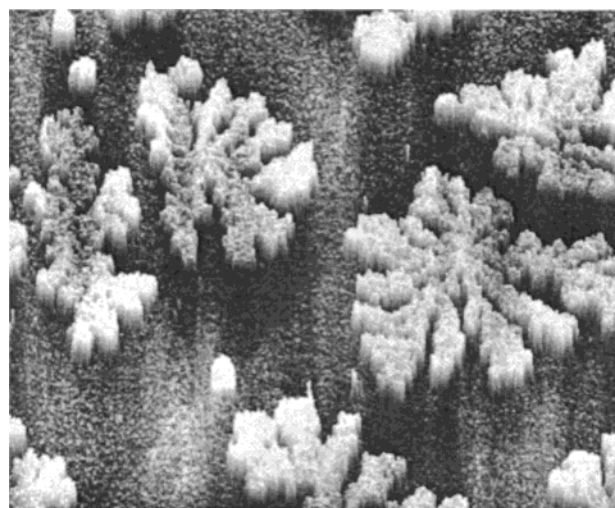


Figure 1. AFM image ($20 \times 20 \mu\text{m}^2$) of a partial octadecyltrichlorosilane monolayer grown at 10 °C for 5 s.

film of water (about three monolayers thick) is known to be present on silica.¹¹ Oxidized silicon (100) substrate was prepared by chemical oxidation of single crystalline silicon with peroxy-sulfuric 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 ± 0.4 Å rms). The samples were then introduced into the OTS solution (1 mM in carbon tetrachloride), where they were kept at given temperatures for specified amounts of time. Film growth was quenched by transferring the samples into pure carbon tetrachloride baths. Atomic force microscopy (AFM) images of the samples were obtained on a Digital Instrument Nanoscope III operating in air in tapping mode. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using the Kratos XSAM-800 system. A model A-100 Ramé-Hart NRL goniometer was used to measure water contact angles in room air using the sessile drop method.

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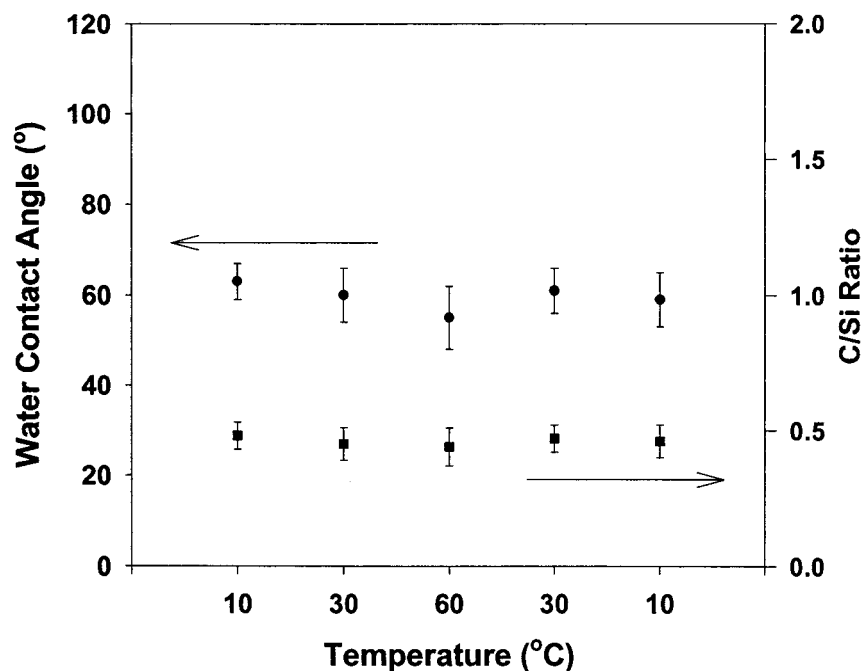


Figure 2. Water contact angles and C/Si ratios of the partial monolayer as a function of temperature.

Results and Discussion

In the first set of experiments, the oxidized silicon was placed in the OTS solution held at 10 °C. Monolayer formation was quenched by removing the sample from the solution after 5 s and rinsing it in carbon tetrachloride at 10 °C. At this point, the partial monolayer consists of islands (~ 25 Å high) of close-packed, fully extended chains, as shown by the AFM image in Figure 1. The static water contact angle is about 62° and the $^{13}\text{C}/^{29}\text{Si}$ peak area ratio measured by XPS is about 0.5. For comparison, the complete monolayer was prepared by immersing the oxidized silicon in the OTS solution for one h. It has a static water contact angle of 112° and a C/Si ratio of 1.7. These values indicate that the partial monolayer has an OTS coverage of approximately 30% of the complete monolayer.

To study the effect of thermal cycling on a partial monolayer, samples, prepared as just described, were immediately transferred into pure carbon tetrachloride baths at given temperatures and held in each bath for a specified amount of time. We studied the following sequences (all starting with an OTS deposition at 10 °C for 5 s; arrows denote transfer into a new bath): (a) \rightarrow 10 °C (600 s); (b) \rightarrow 30 °C (600 s); (c) \rightarrow 60 °C (30 s); (d) \rightarrow 60 °C (30 s) \rightarrow 30 °C (600 s); (e) \rightarrow 60 °C (30 s) \rightarrow 10 °C (600 s). To quantify the OTS coverage, contact angle and XPS measurements were performed on each sample. The static water contact angles and the C/Si ratios from XPS are qualitatively similar, as shown in Figure 2, indicating that the loss of OTS molecules from the partial monolayer to the carbon tetrachloride baths at the various annealing temperatures is minimal.

Atomic force microscopy images of the partial monolayers were obtained at the end of each sequence and are displayed in Figure 3A–E. After the partial monolayer is annealed to 30 °C, the islands are much smaller (Figure 3B). By 60 °C, no islands are present (Figure 3C), indicating the OTS molecules of the islands spread over the substrate surface. The height distribution histogram confirms that the spreading of the molecules is quite homogeneous indeed. Upon lowering the temperature after the 60 °C bath, the sequence of structural change is reversed, as shown in Figures 3 D and E: cooling back the sample causes the islands to reappear. Although the

size of recovered islands (Figure 3E) is smaller than found originally (Figure 3A), the number of islands is higher, so that the coverage of the OTS islands remains essentially the same. We have also imaged a sample subjected to the sequence \rightarrow 30 °C (30 s) \rightarrow 60 °C (30 s) \rightarrow 30 °C (60 s) \rightarrow 10 °C (60 s), and found it very similar to Figure 2E.

The above measurements suggest that OTS molecules are strongly confined to two dimensions, presumably by hydrogen bonding forces between the hydrolyzed headgroups and the thin water layer wetting the silica. However, the reversibility of the structural change of the partial monolayer as a function of temperature, with the OTS coverage intact, directly indicates that the OTS molecules are in a mobile state on oxidized silicon.

We next turn to the important issue of immobilization of the OTS molecules during the monolayer formation. The three Si–Cl bonds of the OTS molecule become hydrolyzed and form silanols. The silanol groups can interact with the silanol groups of adjacent molecules and surface hydroxyl groups, forming covalent siloxane bonds to the surface and intermolecular cross-linking.¹¹ Hence, the final structure of the monolayer is that of an amorphous two-dimensional solid.¹² The time scale for cross-linking or grafting to the substrate is an upper limit to the lifetime of the mobile state. To determine this lifetime, partial monolayer samples, made at 10 °C, were immersed into carbon tetrachloride at 60 °C for varying amounts of time. Upon lowering the temperature back to 10 °C, the samples were imaged by AFM. No islands were observed for those samples that were annealed at 60 °C for more than 10 minutes. For shorter annealing times, islands are observed, but their height above the background decays with time spent in the high temperature bath. This is because more of the chains, which are spread uniformly on the substrate (see Figure 3C), become immobilized, producing larger material accretion between fewer (and smaller) extended islands. The decay half-life was found to be about 250 s, and essentially independent of temperature in 10 to 60 °C range. This time scale is obviously long enough to allow one to observe the occurrence of temperature-induced phase transformations, such as those reported in Figure 3. Similarly, the islands on a partial monolayer kept in pure carbon

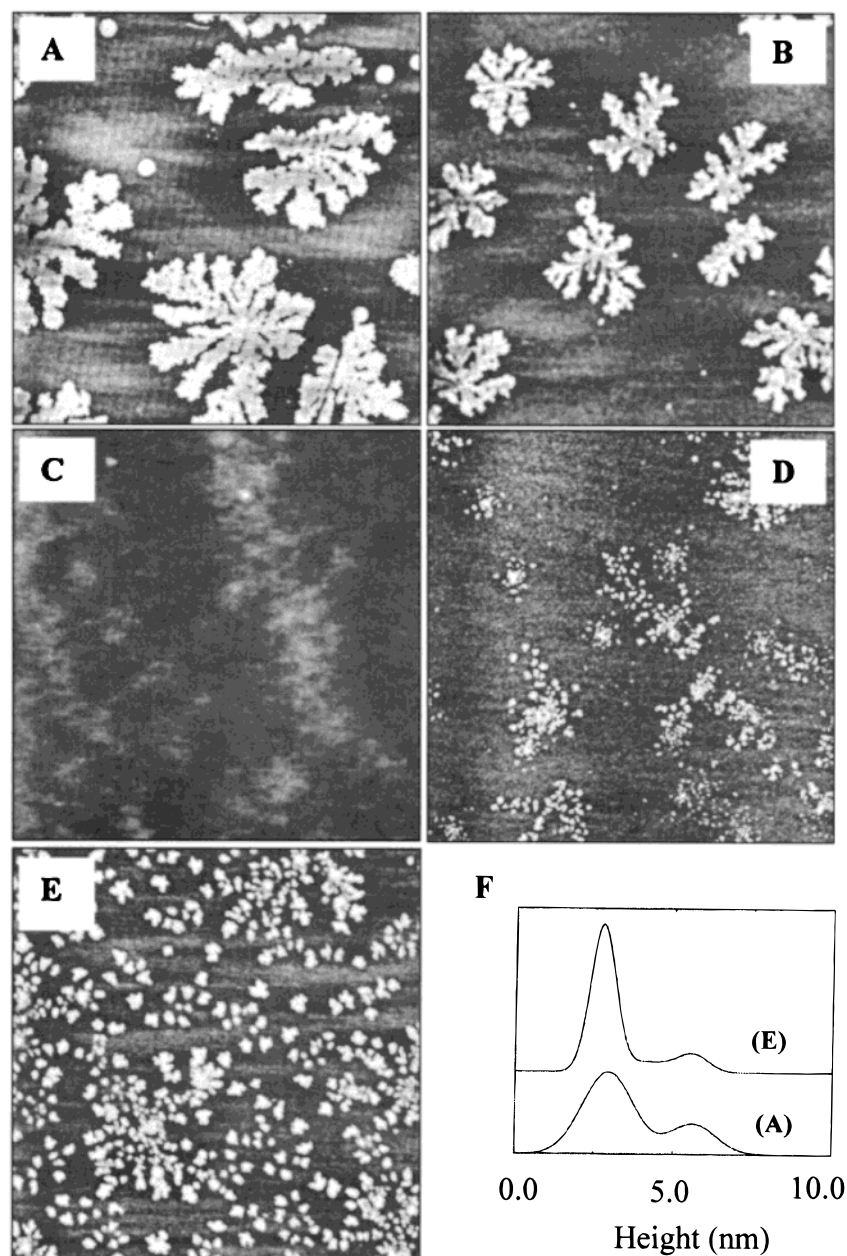


Figure 3. AFM images ($20 \times 20 \mu\text{m}^2$) of the partial monolayer as a function of temperature. Starting with an OTS deposition at 10°C for 5 s: (A) $\rightarrow 10^\circ\text{C}$ (600 s); (B) $\rightarrow 30^\circ\text{C}$ (600 s); (C) $\rightarrow 60^\circ\text{C}$ (30 s); (D) $\rightarrow 60^\circ\text{C}$ (30 s) $\rightarrow 30^\circ\text{C}$ (600 s); (E) $\rightarrow 60^\circ\text{C}$ (30 s) $\rightarrow 10^\circ\text{C}$ (600 s). Inset F shows the height distribution histograms for images A and E, which yield island coverages of 24% and 21%, respectively.

tetrachloride at 10°C for 10 min or longer could not be made to disappear when the sample was transferred into the 60°C bath.

In summary, we have directly observed a highly mobile state during the monolayer formation, and we have measured its lifetime. A similar state has been observed in monolayer formation from alkanethiols on Au(111) surface,¹³ suggesting that a mobile state is necessary for the self-assembly of well-ordered monolayers. In addition to improving our understanding of self-assembly mechanism, the highly mobile state presented here may be useful in controlling formation and properties of alkylsiloxane self-assembled monolayers. The capability of a partial monolayer to undergo large-scale structural changes during self-assembly may yield a novel method to pattern submicrometer-size features on silica, e.g., by exploiting microphase separation in mixed films, similarly to what can already be realized in Langmuir–Blodgett films. This method would be a viable alternative to monolayer transfer when the latter is

impractical, as for example, when dealing with released (free-standing) microelectromechanical devices.¹⁴

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