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Binary Mixtures of Self-Assembled Monolayers on SrTiO₃: Experimental Evidence for Phase Segregation

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The formation of monolayers from mixed solutions of alkylsiloxane molecules on the surface of SrTiO₃ has been studied. The monolayers were formed by self-assembly from dilute *n*-hexadecane solutions of two binary mixtures of long- and short-chain alkyltrichlorosilanes. These films have been studied by atomic and lateral force microscopy and wettability measurements. One mixture showed evidence of phase segregation on the vicinal surface of a SrTiO₃ (001) crystal. The long-chain molecules are found to preferably adsorb at or migrate toward the step ledge, probably to increase their van der Waals interaction and minimize the surface free energy.

The formation of structures with dimensions well below the micrometer scale has attracted considerable attention. Most practical applications rely on lithographic methods, where a complete film is structured down to the desired patterns. A challenging alternative is to form structures from single molecules by assembling and organizing them in certain patterns. A method capable of doing so is the chemical technique of self-assembly from solution. It is now well established that self-assembled monolayers (SAMs) are highly organized films, whose surface properties can be tailored to specific needs.[1] Although the final properties of complete SAMs have extensively been characterized lately,[1,2] relatively little is known about the details of the adsorption mechanism and the microscopic properties needed to design such patterns. Despite their simple formation, a detailed description of the bonding of the molecule to the surface is lacking. Even the exact mechanism of formation of the organized structure is unknown to date.

The system of thiols on gold is the best studied one,[2] and their formation has been studied by scanning probe microscopy.[3−5] Several observations regarding the microscopic organization process have been made. First a complete layer is formed with all molecules "lying down", followed by a densification of the monolayer via a "standing up" mechanism.[4,5] Dense islands are formed by aggregation of single molecules, and growth proceeds by attachment of an ever increasing number of molecules. During adsorption, the gold surface is partly etched and pits or holes are formed.[6] A subsequent anneal, at temperatures up to 150 °C, effectively removes these holes, indicating an exchange mechanism[7,8] where molecules can fill in a previously empty site. In addition, the second important

class of SAMs of alkyltrichlorosilanes on hydrophilic and oxide materials as SiO₂ or SrTiO₃ has witnessed some progress, but even fewer details on their microscopic structure are known. From AFM and infrared spectroscopy (IRS) measurements, it is found that such monolayers form via an island formation mechanism and an analogy with Langmuir monolayers on the water−air interface is proposed.[9−12] Individual molecules are physisorbed onto the water surface covering the crystal and are mobile enough to find a lower energy position adjacent to other monomers, oligomers, and already formed islands.

Moreover, also theoretical models[13] have been applied to thiols on gold which suggest that if the system is in thermodynamic equilibrium, only one of the two components is favored on the surface. Monte Carlo simulations[14,15] and experimental results,[16] on the other hand, suggest that mixed composition monolayers show phase segregation into microscopic (<50 nm) domains. Experiments conducted by Offord et al. with binary mixtures of long- and short-chain alkyltrichlorosilanes on SiO₂ did not show evidence for macroscopic phase separation.[17]

In this paper, we show that phase segregation is possible for binary mixtures and provide additional proof supporting the Langmuir analogy used to describe the growth of siloxane SAMs on oxide substrates. We have formed SAMs from two different binary mixtures of a short- (dodecyltrichlorosilane, DTS) and a long-chain alkyltrichlorosilane (octadecyltrichlorosilane, OTS) on the vicinal surface of the (001) face of SrTiO₃. Experimental details on the preparation and characterization of SrTiO₃[18] and self-assembled monolayers on these surfaces are described elsewhere.[19] The monolayers were characterized

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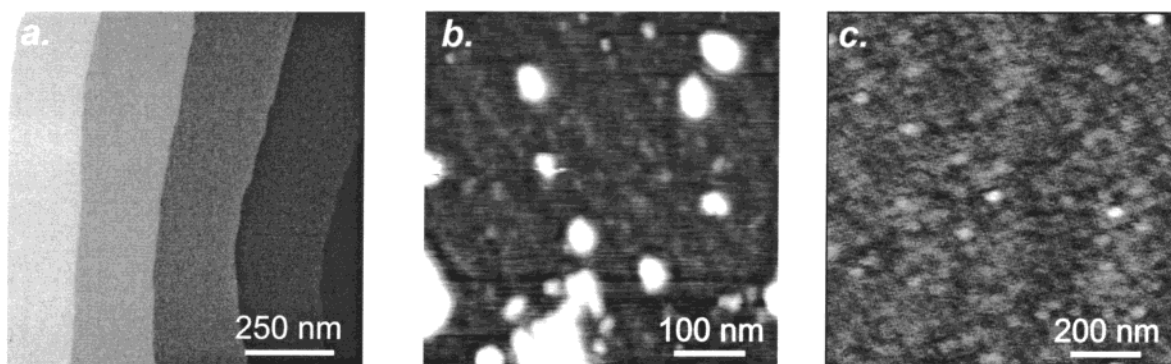(17) Offord, D. A.; Griffin, J. H. *Langmuir* **1993**, *9*, 3015.

Figure 1. Atomic force micrographs of (a) the surface of SrTiO₃ (001) prior to adsorption and after adsorption of a monolayer nominally composed of 25 mol % DTS and 75 mol % OTS, (b) after 2 h of immersion (z-range 5 nm), and (c) after rubbing with piece of lens tissue soaked in chloroform (z-range 2 nm).

by atomic and lateral force microscopy (AFM and LFM) and wettability measurements.

Before adsorption of a monolayer from the *n*-hexadecane (HD) solution, the SrTiO₃ surface shows very clear steps with a height difference of 0.39 nm (the unit cell of SrTiO₃); see Figure 1a. The morphology of a film formed from the solution S25 is shown in Figure 1b. Directly after adsorption, the morphology is quite rough with features up to 8 nm high. These films are clearly composed of more than a single molecular layer. Careful rubbing the surface with a piece of lens tissue drenched in chloroform removes most of the chemisorbed material forming the multilayers, as shown in Figure 1c.[20] The surface is left with only few remaining islands or protruding molecules. The height of the islands after rubbing is 0.5−1.0 nm. It should be noted that removal of the extra material was never possible by simply rinsing in several solvents. AFM measurements performed in the contact mode do not notably change the surface morphology at the usual contact forces in air as judged from many micrographs. Apparently, the extra material is either chemisorbed or strongly physisorbed to the original surface.

The surface morphology of a film formed from a solution composed predominantly of the short-chain molecule (S75) appears even rougher than the surface of S25; see Figure 2a. Even the lowest achievable contact force during scanning greatly modifies the surface. The scanned area is partly removed and piled up at the edges (not shown). The area that can be removed by contact mode AFM has a depth of 1.6 nm, which is approximately the length of an all-trans extended DTS molecule (estimated to be 1.8 nm[21]). To obtain a micrograph that truly represents the actual surface, tapping mode AFM must be used and an example is shown in Figure 2a. The typical range of peak-to-peak z-values is found to be ∼4 nm. After the surface was rubbed with a piece of lens tissue drenched in chloroform, the surface morphology distinctly changes

Table 1. Wettability Measurements on Simultaneously Coadsorbed Monolayers of a Long- and Short-Chain Alkylsiloxane on SrTiO₃ Substrate with Different Solution Ratios[a]

	$\theta_a^{H_2O\ b}$ (deg)	$\theta_r^{H_2O\ b}$ (deg)	θ_a^{HD} (deg)	θ_r^{HD} (deg)
S25	112.3 (3.2)	91.9 (4.5)	20.9	0−5
S25[c]	112.2 (3.2)	102.0 (3.0)		
S25[d]	111.4 (4.1)	101.5 (4.3)	∼20	0−5
S75	85.9 (2.6)	45.6 (4.8)	∼10	0

[a] The values presented here were taken after careful rubbing with a piece of lens tissue drenched in chloroform. [b] Number between parentheses is the standard deviation. [c] Anneal 100 min at 80 °C. [d] Anneal 90 min at 100 °C.

again. The remaining molecules are more strongly bound to the surface, since contact mode AFM does not modify the surface. The steps due to the surface miscut reappear, and these steps are decorated by molecules that extend 3−4 Å above the surrounding matrix (Figure 2b,c). The apparently higher areas also display lower friction;[22] see Figure 2d. After subtraction of the average plane, and fitting the histogram data to two Gaussian curves (Figure 2e), representing the two molecules, it is found that the longer chains occupy ∼29% of the surface, surprisingly close to the solution ratio.

Contact angles of water and HD on both films have been measured after rubbing and are summarized in Table 1. The initially low receding angles of the S25 film improve to over 100° after annealing these films at temperatures of 80 and 110 °C for 90−100 min. The HD contact angles, however, do not improve drastically and stay rather low, indicating significant disorder in the exposed methyl layer. The contact angles of the S75 film are significantly lower than those of the S25 film. Our wettability data are in qualitative agreement with Offord et al.,[17] and similar results have been obtained for mixtures of thiols varying in chain length on gold.[23] In general for binary systems where only the lengths of the chains differ, the contact angle at very low solution ratio of either adsorbent should be approximately equal (for methyl-terminated chains $\theta_a^{H_2O} \sim 110-115°$). A similar behavior is expected if phase segregation results in macroscopic domains. If the domains are smaller than those that can be probed by a contact angle measurement (<∼100 nm), a deviation in the middle region of solution ratios can be expected. The outer region

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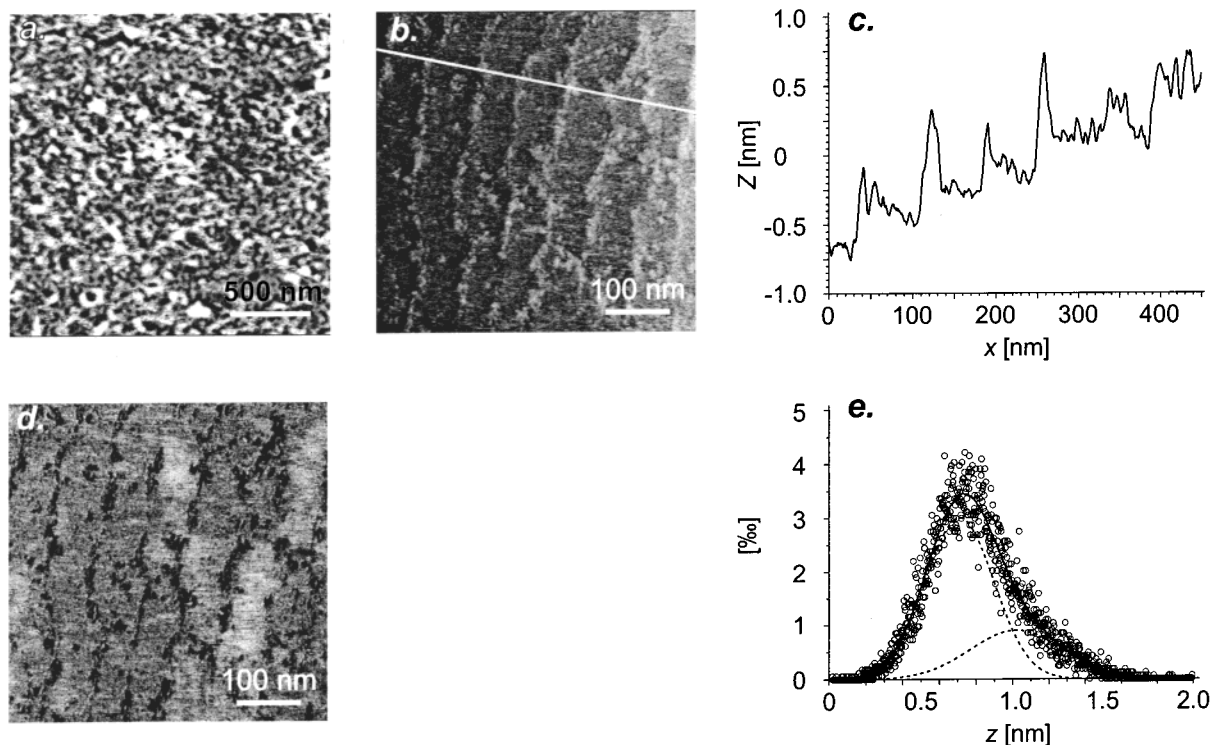
Figure 2. Atomic force micrographs: a monolayer nominally composed of 75 mol % DTS and 25 mol % OTS (a) before rubbing (recorded by tapping mode, z-range 10 nm) and (b) after rubbing (z-range 3 nm); (c) cross section along line shown in (b); (d) lateral force micrograph (z-range 0.2 V), simultaneously recorded with micrograph shown in (b); (e) histogram of the micrograph shown in (b). The dashed lines are Gaussian fits to the data, the left curve (lower z-value) represents the DTS molecules, and the higher z-value represents the OTS.
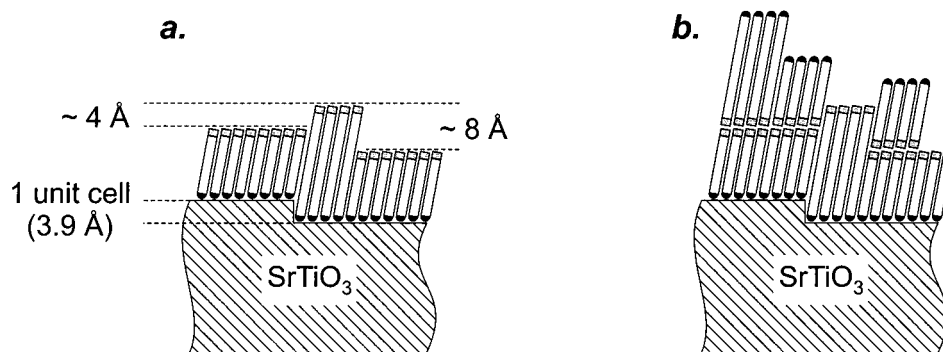

Figure 3. Possible structure of a mixed monolayer composed of 75% DTS and 25% OTS on a stepped $SrTiO_3$ surface.

of the chains near the chain terminus is disordered and therefore exposes methylene parts of the chain to the contacting liquid. This results in a decrease of the contact angle.[23,17] The films formed from solution S25, display better hydrophobicity, since the longer chain molecules are better able to shield the probe liquids. However, we have not been able to form very high quality and densely packed DTS layers,[19] as is reflected in the films formed from the solution S75. The contact angles of S25 are in agreement with the surface structure as observed by AFM. The molecules adjacent to a step ledge are more disordered near the chain terminus (Figure 2b and 3a).

The S75 monolayer clearly displays elevated domains of longer molecules of OTS in a matrix composed of DTS after rubbing. Most of the longer chains are lined up along the step ledges, thereby forming a kind of one-dimensional molecular nanowire. The reason for the preferential position of molecules is the increased stability of the longer chains if they are attached to the steps, as shown in Figure 3a, and the accompanying decrease in interfacial free energy. This explanation is also capable of accounting for

the initially rough morphology, since extra molecules are easily adsorbed on top of the first (disordered) layer because of increased van der Waals interactions of adjacent molecules as is indicated in Figure 3b.

The mechanism that is responsible for the observed phase segregation is not known. Rubbing itself does not lead to phase segregation, because the very robust chemical bond between the first layer of molecules and the substrate prevents changes in organization of the monolayers (as judged by wettability merasurements). Also we have performed measurements that show that partially formed monolayers have a tendency to adsorb preferentially along step ledges. Folkers et al. argue that if the system is in thermodynamic equilibrium, only one phase exists on the surface.[13] Equilibration is argued to take place via exchange reactions with molecules from the solution, until a single component remains.[13] However, thermodynamic equilibrium is not so easily achieved (especially not at room temperature), and in this case, the two components can coexist on the surface. Stranick et al. observed slow lateral diffusion by time-lapse STM within

single-component thiols on Au and motion of a thiol–Au complex to reduce the edge tension of high curvature domains in two-component SAMs.[16] These values are considerably smaller than lateral diffusion in Langmuir films on a water surface.[24] We propose that in the case of alkylsiloxane molecules on oxide substrates, lateral diffusion is possible prior to the final anchoring step. If the surface density of the mixture on the substrate is low enough, the longer chain molecules can find their optimal position (i.e., along the step ledges) in order to reduce the interfacial free energy. The adsorption of additional molecules leads to a higher stability of the longer chain molecules along the step ledges and to a decrease in lateral diffusion, because steric hindrance plays a major role. Such a mechanism provides additional proof of the Langmuir analogy.

The islands visible in Figure 1 are associated with an extra layer of DTS molecules on top of the first DTS molecular layer, thereby filling up the voids left by the shorter DTS inside the matrix of OTS. We conclude that DTS has no preference to adsorb along the step ledges and that they are dispersed more or less randomly in the stabilizing OTS matrix.

Having established the possibility of obtaining small domains by lateral mobility of at least one component, the next experiment would be to vary the tail group to technologically more important functional groups such as amines ($-NH_2$) and carboxylic acids ($-COOH$). Although the alkyl chain contributes a main portion of the total free energy, the terminal functionality might play an important role in the final arrangement of the molecules. Introducing polar groups or hydrogen bonding functionalities complicates the properties of the system considerably,[25,26] because such interactions may add the necessary extra amount of energy needed for more complete phase segregation. Incorporation of polar groups in a mainly nonpolar surface could be disfavored, just as the solubility of specific tail groups could be decreased. If the domains can be made small enough to bind single molecules (e.g., proteins), the properties of that molecule can be studied in detail. Such a technique would then produce much smaller scale structures than the more traditional "*top-down*" techniques are capable of. It was shown that the isolation of single molecular wires in a matrix of nonconducting molecules is a viable and promising technique and that these wires were indeed conducting.[27,28]

In conclusion, we have presented evidence for phase segregation in self-assembled monolayers comprised of binary mixtures of long- and short-chain alkyltrichlorosilanes on $SrTiO_3$. In mixtures predominantly composed of short-chain molecules, the longer chains are shown to preferentially move toward a step ledge. The other case, a mixture mainly composed of long-chain molecules, does not display phase segregation. The step ledges provide an additional lowering in interfacial energy for the longer chains. The data provide strong support for the analogy with Langmuir films at the air–water interface.

Experimental Section

Dodecyltrichlorosilane (DTS, 98%), octadecyltrichlorosilane (OTS, 95%), and *n*-hexadecane (HD, 99+%) were obtained from Aldrich and used as received. $SrTiO_3$ substrates were obtained from ESCETE (Enschede, The Netherlands), cut within 0.2° of the (001) direction, and polished. For the water contact angles, filtered and deionized Millipore water ($R = 15$ MΩ) has been used.

Before adsorption took place, the $SrTiO_3$ substrates were cleaned ultrasonically in a sequence of solvents (chloroform, acetone, and alcohol). To achieve clean and regularly stepped surface, the substrate is immersed for 10 min in Millipore water, etched in a buffered HF solution (Merck, NH_4F:HF = 87.5:12.5 with pH = 5.5) for 30 s, and finally annealed at 950 °C for 1 h in a flow of oxygen.[18] Each adsorption was carried out in a freshly prepared mixture solution of DTS and OTS in HD. The total adsorbent concentration in *n*-hexadecane (HD) amounts to 1 mM. The first mixture nominally contained 25 mol % DTS and 75 mol % OTS (referenced to as solution S25), whereas the second mixture nominally contained 75 mol % DTS and 25 mol % OTS (S75).[29] The temperature and relative humidity during deposition are controlled as well as possible; i.e., the adsorption took place in a climate room ($T \leq 20$ °C, relative humidity 20–40%). To remove physisorbed and/or complexed HD, the monolayer was sonicated several minutes in chloroform and ethanol. Immediately after adsorption, the films are characterized by their advancing contact angle with water ($\theta_{adv}^{H_2O}$), atomic force microscopy (AFM), and lateral force microscopy (LFM).

Contact angles have been measured on several locations on the sample. All results were averaged, and the accuracy obtained by this method is approximately ±3°. AFM and LFM measurements were performed in the contact mode on a Nanoscope IIIa (Digital Instruments). Standard cantilevers (supplied by DI) with different nominal force constants (k_N (k_{tors}) = 0.08, 0.18, 0.38 (80), or 0.58 (175) N/m) have been used.

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(29) The ratio of molecules on the surface does not necessarily reflect the solution ratio.[13]