Large-Ordered Striped Phase of Didodecyl Sulfide Self-Assembled Monolayers on Au(111)

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Alkanethiol self-assembled monolayers (SAMs) on metal surfaces are key elements for the fabrication of functional organic layers and devices in the broad fields of nanotechnology and biotechnology.¹⁻⁷ However, it was found that alkanethiol SAMs were usually composed of structural defects such as domain boundaries and vacancy islands (VIs), which make them more amenable to oxidation.¹ Compared to alkanethiols, thioethers (RSR') are more robust to oxidation, and their chemical structures with various alkyl chains can be modified readily by a simple synthetic method.⁸ Therefore, SAMs prepared using thioethers provide a very useful means for tuning the characteristics of metal surfaces. Despite these advantages, there have only been a limited number of papers involving the formation and structure of thioether SAMs on gold surfaces.⁹⁻¹⁵ It has been revealed that dioctadecyl sulfides (DODS, CH₃(CH₂)₁₇S(CH₂)₁₇CH₃) at the initial growth stage form SAMs with striped phases in which the molecular backbones are oriented parallel to the surface,9 whereas DODS SAMs formed after long immersion have two mixed phases containing closely packed and loosely packed standing-up phases where the molecular backbones are oriented perpendicular to the surface.¹⁰ High-resolution scanning tunneling microscopy (STM) observation revealed that the SAMs of dimethyl sulfides (DMS, CH₃SCH₃) with the shortest alkyl chains on Cu(111) have a herringbone-like packing structure,¹³ whereas dibutyl sulfides (DBS, CH₃(CH₂)₃S(CH₂)₃CH₃) with slightly larger alkyl chains form striped phases.¹⁴ From these results, we assumed that the formation of dialkyl sulfide SAMs strongly depends on van der Waals interactions between alkyl chains.

So far, there no data has been reported on the formation and structure of didodecyl sulfides (DDS, $CH_3(CH_2)_{11}S(CH_2)_{11}CH_3$) with medium alkyl chains from a molecular-scale perspective. In this paper, we report the first STM results showing that the adsorption of DDS molecules at 70 °C generating long-range ordered SAMs with a 7.5 × $\sqrt{3}$ striped phase with VIs-free surfaces.

Dodecanethiol (DDT, $CH_3(CH_2)_{11}SH$) and DDS were purchased from Tokyo Chemical Industry (Tokyo, Japan). DDT and DDS SAMs were prepared by dipping the Au(111) substrate in 1 mM ethanol solutions of corresponding compounds at room temperature for 24 h. To understand the effect of solution temperature on the formation of DDS SAMs, the SAMs were prepared at 70 °C for 1 h. STM images were obtained using a NanoScope E (Veeco, Santa Barbara, CA, USA) with a commercial Pt/Ir (80:20) tip under ambient conditions.

The STM images in Figure 1 show remarkable structural differences in the formation of ordered domains and VIs (dark holes) for DDT and DDS SAMs on Au(111) formed after 24 h immersion at room temperature. Figure 1(a) shows a typical packing structure of DDT SAMs with a $c(4 \times 2)$ superlattice formed at saturation coverage. DDT SAMs were mainly composed of ordered phases with three domain orientations (Regions A, B, and C) separated by domain boundaries. The proportion of the VI areas to the total surface area was measured to be approximately 8%-12%, values which are similar to those observed from other alkanethiol SAMs.⁷ Unlike DDT SAMs, Figure 1(b) shows that the DDS SAMs have two mixed phases: the ordered phase with three domain orientations (Regions A, B, and C) and the disordered phase (Region D). The existence of three domain orientations for DDS SAMs on Au(111) means that the formation of SAMs was influenced by interactions between the sulfide atoms and gold surfaces. On the other hand, DDS SAMs contained few VIs comprising a small (2-3%) area fraction of the total surface area. The presence of disordered phases and a smaller VI fraction for DDS SAMs can be attributed to the weaker interactions between the sulfide atoms and gold surfaces compared to those between the sulfur atoms of thiols and gold surfaces for DDT SAMs. This finding is consistent with a previous result for the SAMs of DODS with long alkyl chains of 18 carbon units.¹⁰ The ordered domains have a row structure with an inter-row distance of 1.59 ± 0.03 nm, which is nearly half of the entire



Figure 1. STM images of (a) DDT and (b) DDS SAMs on Au(111) formed after 24 h immersion of the Au(111) substrates in a 1 mM ethanol solution at room temperature.

molecular length of DDS, which is 3.18 nm. It has been demonstrated that dialkyl sulfide SAMs on Au(111) were formed through the intact adsorption of molecules without S-C bond cleavage.⁹⁻¹² In general, the adsorption of dialkyl sulfides on gold surfaces often led to the formation of a striped phase in which the two alkyl chains attached to the sulfur are lying flat on the surface such that the observed periodicity of the striped phase is almost identical to an entire molecular length.^{11,13,14} Therefore, from the observation of the striped phases with a half molecular length of 1.59 nm for DDS SAMs, we assumed that one of the two alkyl chains attached to the sulfur atom in a bright row switches positions with one of the two alkyl chains bound to the sulfur atom in a neighboring bright row. As a result, the inter-row spacing could be half of the entire molecular length. We designated this structure as a $5.5 \times \sqrt{3}$ striped phase. Interestingly, a missing striped row in the ordered domains was clearly observed, as indicated by the white arrows on the STM image in Figure 1(b). This is the first STM observation showing the formation of missing striped rows in DDS SAMs on Au(111) even though missing rows in the closely packed domains of alkanethiol SAMs are often observed.¹⁵

To examine the formation and surface structure of DDS SAMs at a high solution temperature, we examined DDT and DDS SAMs on Au(111) formed at 70 °C for 1 h. STM images in Figure 2 show remarkable differences in the domain formation and structure of DDT and DDS SAMs. The sizes of ordered domains and VIs for DDT SAMs were greatly increased, but the packing structure of the $c(4 \times 2)$ superlattice was not altered at 70 °C, as shown in Figures 2(a) and (b). This result is consistent with octanethiol or decanthiol SAMs.^{6,7} The formation of large ordered domains at high solution temperature or after annealing is mainly driven by optimizing *van der Waals* interactions between alkyl chains, which results from the diminishing mismatch



Figure 2. STM images showing the structural difference between (a and b) DDT and (c and d) DDS SAMs on Au(111) formed after immersing the Au(111) substrates in a 1 mM ethanol solution at 70 $^{\circ}$ C for 1 h.

of alkyl chains at domain boundaries and around VIs. On the other hand, the surface structure of DDS SAMs drastically changed from the mixed phases consisting of the ordered striped phase and disordered phase (Figure 1(b)) to the uniform striped phase (Figure 2(c)). Interestingly, the disordered phase and VIs almost disappeared, suggesting that VI-free DDS SAMs with a high degree of structural order can be obtained at a solution temperature of 70 °C. The distance between the two striped rows was measured to be 2.18 ± 0.03 nm, which can be assigned as a $7.5 \times \sqrt{3}$ striped phase. We assume that the main driving force for the structural change of DDS SAMs at 70 °C from the $5.5 \times \sqrt{3}$ to 7.5×3 striped phase is the formation of long-range ordered striped phases formed over the entire gold surface. Therefore, the total surface energy can be decreased by an increasing the van der Waals interactions between alkyl chains.

In summary, we demonstrated that the adsorption of DDS molecules on Au(111) at room temperature or 70 °C led to the formation of ordered SAMs with $p \times \sqrt{3}$ striped phases. More specifically, DDS SAMs at 70 °C were composed of long-range ordered striped phases with a VI-free structure. The obtained results will be very useful for understanding the self-assembly phenomena and controlling the SAM structure of DDS molecules on gold surfaces.

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