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Effects of Solvent on the Structure of Octanethiol Self-Assembled Monolayers on Au(111) at a High Solution Temperature

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Self-assembled monolayers (SAMs) derived from the spontaneous adsorption of organic thiols on metal surfaces have drawn considerable attention because of their scientific importance and technological applications in nano and biotechnologies.[1-5] In particular, the formation and structure of alkanethiol SAMs on gold surfaces have been extensively studied using various surface characterization techniques.[6-9] Experimental conditions, such as solvent, temperature, concentration, immersion time, and substrate cleanliness significantly affect the formation and structure of alkanethiol SAMs.[1,6-9] Among them, solvent choice is a very important factor for determining the structural quality and formation kinetics of SAMs.[10-18] Ellipsometry measurements have shown that the solvent, including ethanol, *N*,*N*′-dimethylformamide (DMF), toluene, hexadecane, and cyclooctane, had no effect on the thickness of hexadecanethiol SAMs.[9] On the other hand, it has been suggested that formation kinetics of alkanethiol SAMs in certain nonpolar solvents (hexane, heptane) increased compared to when a polar protic solvent (ethanol) was used.[10,11] The first molecular-scale observation by scanning tunneling microscopy (STM) revealed that the surface structures of decanethiol SAMs on Au(111) formed at room temperature are strongly dependent on solvents.[12] In addition, the differential effects depended on the molecular system assembled on the gold surface. Therefore, the appropriate solvent should be selected to obtain SAMs with a high degree of order.[13,14]

Although it has been reported that solution temperature is one of crucial factors in determining final SAM structures,[8] studies on the effect of solvents on SAM formation have been focused only on SAMs formed at room temperature so far. To understand the effect of solvent at high solution temperature, we examined the surface structures of octanethiol (OT) SAMs on Au(111) surfaces formed with various solvents at 50 °C for 12 h using STM. Herein, we report the first STM results presenting the formation of a closely packed c($4\sqrt{3} \times 2\sqrt{3}$) phase structure (expressed as a c(4×2) superlattice) and a $5 \times \sqrt{3}$ striped phase depending on the solvent used. Our results from a molecular-scale viewpoint will provide new insight into the effect of solvent on the formation and structure of SAMs at a high solution temperature.

Au(111) substrates were prepared by thermal evaporation of gold onto mica as described previously.[3] OT SAMs were prepared by dipping the Au(111) substrate in 1 mM ethanol, DMF, toluene, or decane solutions of OT at 50 °C for 12 h. STM measurements were carried out using a NanoScope E (Veeco, Santa Barbara, CA) with a commercial Pt/Ir (80:20) tip under ambient conditions.

STM images (60 nm × 60nm) in Figure 1 show surface structures of OT SAMs on Au(111) formed from various solvents at 50 °C for 12 h. We found the large differences in the structure of OT SAMs depending on the solvents used. OT molecules in ethanol generated closely packed and ordered SAMs, which can be described as a c(4×2) superlattice with respect to the Au(111) lattice (Figure 1a). This packing structure was observed for various alkanethiol SAMs at saturation coverage. Larger, ordered domains with lateral dimensions ranging from 35 to 60 nm were observed at 50 °C, compared to OT SAMs containing small domains of ranging from 15 to 30 nm formed at room temperature.[18] The dark pits had a depth of 0.24 nm corresponding to the monatomic step height of the Au(111) surfaces, which

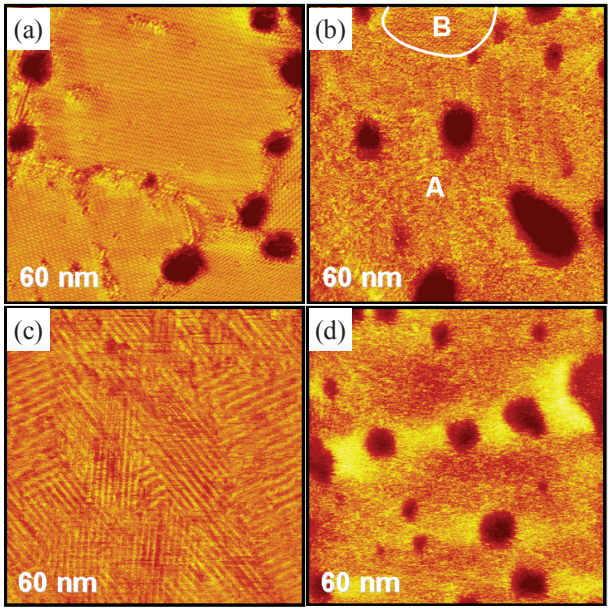


Figure 1. STM images of OT SAMs on Au(111) formed after immersion for 12 h in 1 mM (a) ethanol, (b) DMF, (c) toluene, and (d) decane OT solutions at 50 °C.

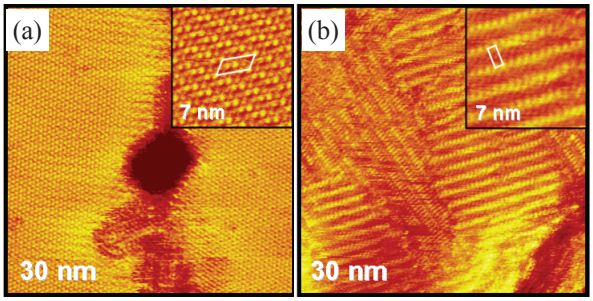


Figure 2. (a) High-resolution STM image of OT SAMs showing the closely packed c(4 × 2) superlattice on Au(111) formed in ethanol at 50 °C. (b) High-resolution STM image of OT SAMs showing the 5 × √3 striped phase formed in toluene at 50 °C. The inset STM images (7 nm × 7 nm) clearly show different packing structures.

are often referred to as vacancy islands (VIs) in the gold substrate. The VIs appeared as a result of the chemisorption of the sulfur atoms on the Au(111) surfaces during thiol self-assembly.[1,8] In contrast to the formation of OT SAMs in ethanol, OT SAMs in DMF were mainly composed of a disordered phase (Region A) containing a small fraction of the areas of the ordered phase (Region B) relative to the total surface area, as shown in Figure 1b. The ordered phase can be described as a hexagonally packed $(\sqrt{3} \times \sqrt{3})R30^{o}$ structure.[2]

Interestingly, the adsorption of OT molecules in toluene yielded ordered and striped phases in which the molecular backbone was oriented parallel to the Au(111) substrate (Figure 1c). The striped phase with a lower packing density can be appeared during the initial stage of SAM growth,[18] after thermal desorption of the closely packed SAMs in air, or under ultrahigh vacuum conditions.[16] However, contrary to other SAM samples having ordered structure, OT molecules in decane only led to the formation of disordered phases, as shown in the STM image of Figure 1d. Although toluene and decane can both be classified as nonpolar solvents, the formation and final structure of the SAMs were quite different in these solvents. We suggest that the interactions between decane and OT are relatively stronger than those between toluene and OT because decane and OT have a similar alkyl backbone structure. We suggest that these strong interactions reduced the lateral interactions of OT molecules in the SAMs by incorporating solvent molecules into the monolayers, resulting in the formation of a sole disordered phase.[1,9] However, full understanding of the solvent effect is very complex because solvent properties, including polarity, solubility, molecular diameter, and viscosity, can affect solvent-gold substrate interactions and solvent-adsorbate interactions during SAM formation.[15]

Decanethiol SAMs of good quality was formed in DMF and toluene at room temperature in the previous work,[12] whereas the closely packed, well-ordered OT SAMs with long-range ordered structure were formed in ethanol at high temperature. This one step process in ethanol at high solution temperature provides a useful methodology for obtaining alkanethiol SAMs with a high degree of structural order with few VIs. From the STM observations, we found that the solvent effect on SAM structure is strongly influenced by solution temperature.

The STM images (30 nm × 30 nm) in Figure 2 show the different ordered structures of OT SAMs on Au(111) prepared in ethanol and toluene. The inset STM images (7 nm × 7 nm) show individual OT molecules with different packing arrangements. The packing structures of OT SAMs in ethanol are assigned as the c(4 × 2) superlattice observed at saturation coverage with an "upright adsorption orientation" on the gold surface (Figure 2a).[2,6,8,16,17] The unit cell contains four alkanethiolate, and the area occupied by a single molecule was calculated to be 21.6 $Å^2$. Unlike this closely packed structure, OT SAMs in toluene yielded the formation of a low coverage striped phase with a "lying down adsorption orientation" on the gold surface (Figure 2b). The molecular distance in the ordered row was 5.0 ± 0.2 Å, and the distance between the rows was 15 ± 0.3 Å. The observed structure was assigned as a (5 × √3) striped phase containing one molecule in the unit cell. The average areal molecular density for the striped phase was calculated to be 75 $Å^2$/molecule, which was 3.5 times lower than that observed for the c(4 × 2) structure. At present, it is difficult to determine why the OT molecules in toluene would prefer the striped rather than the upright phase.

In summary, we demonstrate that solvent has an effect on the domain formation and structure of OT SAMs, and that this effect is influenced by solution temperature. STM imaging clearly reveals that the closely packed c(4 × 2) phase was formed in ethanol, whereas the 5 × √3 striped phase was formed in toluene.

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