Formation and Structure of Cyclopentanethiol Self-Assembled Monolayers on Au(111)

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Organic self-assembled monolayers (SAMs) prepared by the spontaneous adsorption of organosulfur compounds on gold have drawn much attention because they provide an excellent means to tailor the physical and chemical properties of surfaces for various technological applications in biosensing, nanopatterning, corrosion inhibition, and molecular electronic devices.[1-7] To date, alkanethiol SAMs on gold surfaces have been the most thoroughly studied for understanding self-assembly phenomena of organic molecules.[8-12] In addition, many studies have reported the structures and properties of aromatic thiol SAMs on gold surfaces, which are desirable due to their high electronic conductivity.[10,13-16] It has been generally considered that the structures of the SAMs are determined by a balance of the chemical interactions between the sulfur headgroups and gold as well as van der Waals interactions between alkyl chains or aromatic groups. The contribution of van der Waals interactions plays a major role in determining the final SAM structure, and such interactions would be easily controlled by changing the alkyl groups or aromatic groups.

As one of new classes in the SAM system, SAMs formed by thiols with spherical hydrocarbon cage or bulky alkyl groups on gold were prepared and characterized.[17-19] Scanning tunneling microscopy (STM) studies reveals that sulfur compounds with bulky bicyclo[2.2.2]octane moieties can form unique ordered SAMs having a nearest neighbor spacing of 5.9 Å, which is larger than that the ($\sqrt{3}$ × $\sqrt{3}$)R30° hexagonal structure for alkanethiol SAMs.[17] From these STM studies, it is considered that van der Waals interactions between bulky alkyl groups is a dominant factor

in the formation of ordered SAMs because alkanethiols with similar molecular lengths are rather difficult to form two-dimensional (2D) ordered SAMs. The high-resolution STM study also revealed that cyclohexanethiol (CHT) containing a flexible six-membered aliphatic ring on Au(111) can form long-range 2D ordered SAMs, which can be described as a ($5 \times 2\sqrt{10}$)R48° superstructure.[20] This unique superstructure can be ascribed to two geometrical isomers of the CHT molecule, the equatorial and axial chair isomers.

In this study, the effect of the size of aliphatic cyclic ring on the structure of the SAMs formed by cyclopentanethiol (C_5H_9SH, CPT) with a five-membered aliphatic ring on the Au(111) surface was examined. To the best of my knowledge, there has been no study on the adsorption behavior of CPT molecules on gold surfaces thus far. To extend SAM-based applications, it is very important to understand the nature of the self-assembly processes of the molecules and the structure of SAMs. In this paper, the first molecularly resolved STM results of CPT SAMs with a ($\sqrt{3.5}$ × $\sqrt{5}$)R25° structure are reported.

Experimental Section

Au(111) substrates with atomically flat terraces of 100-300 nm sizes on mica were prepared by vacuum deposition as reported in an earlier paper.[21] CPT SAMs were prepared by dipping Au(111) substrates into freshly prepared 1 mM ethanolic solutions of CPT at room temperature for 1 day. STM measurements were performed using a NanoScope E (Veeco, Santa Barbara, CA) with a Pt/Ir tip (80 : 20). All
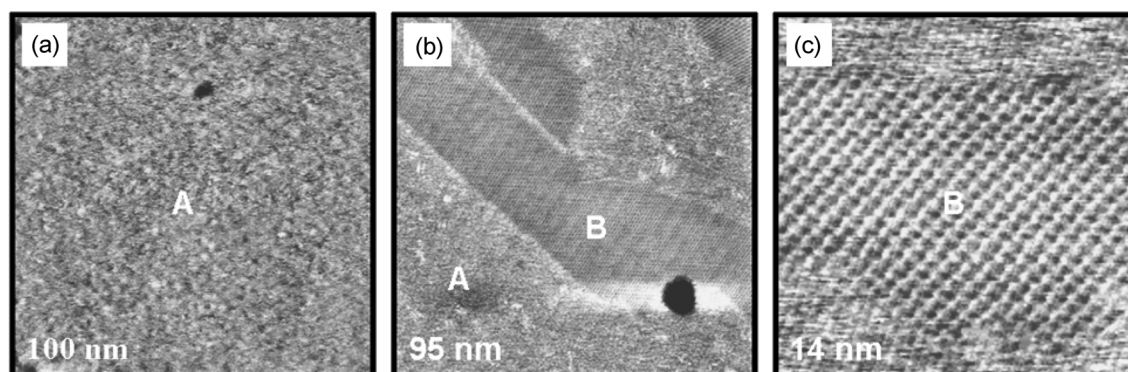

Figure 1. STM image of CPT SAMs on Au(111). (a) The STM image shows the disordered phases of the CPT SAMs formed after a 1-day deposition (as-deposited SAMs). (b) Large and (c) small scan-size of STM images showing the new ordered phase that appeared after incubating the as-deposited SAMs for 1 month.

STM images were obtained under ambient conditions in the constant current mode using tunneling currents between 0.3 and 0.5 nA and a sample bias between 400 and 500 mV. The STM images presented in this paper were raw data without filtering.

Results and Discussion

The STM image of Figure 1a shows the disordered phases (indicated by A) of the CPT SAMs on Au(111) formed after the immersion of the gold substrates in a 1 mM solution for 1 day. The structural behavior of the CPT SAMs was completely different from that of the CHT SAMs with highly ordered 2D domains.[20] Considering this result, the CHT molecule with a six-membered cyclic ring can easily form 2D ordered SAMs compared with the CPT molecule with a five-membered cyclic ring. Therefore, it is suggested that the van der Waals interactions between the six-membered cyclic rings contribute much more to the formation of the 2D crystallized ordered phases than those between the five-membered cyclic rings. The structural behavior of the CPT was nearly similar to that of *n*-alkanethiols with short alkyl chains ($HS(CH_2)_nCH_3$, $n \leq 5$) because they often form liquid-like disordered phases due to week lateral interactions.[1,22]

On the other hand, the previous study revealed that the disordered phases can crystallize to 2D ordered phases as a result of the structural rearrangements of molecules in the SAMs after a long-term incubation of the disordered SAMs.[5] In order to obtain the 2D ordered phase of the CPT SAMs, the CPT SAMs were kept at room temperature for 1 month after sealing them completely in a vinyl bag under a vacuum at 400 Torr at ambient conditions to prevent any contamination or side reactions.[23,24] After this time period, two mixed phases were found: disordered and ordered phases (indicated by A and B) as shown in the STM image of Figure 1b. It was considered that the formation of the new ordered phase resulted from the formation of a crystallized phase due to the long-term rearrangements of the CPT molecules in the SAMs, which implies that thermodynamic factor is more important than kinetic factor, contrary to the case of CHT SAMs. After scanning a small area of the B phases, as shown in Figure 1c (14 nm × 14 nm STM image), well-ordered CPT SAMs were observed.

The molecularly resolved STM image in Figure 2a clearly shows the molecular arrangements with a high degree of structural order in the CPT SAMs on Au(111). In particular, a 2-D filtered STM image (3 nm × 3 nm) inserted on the STM image shows a high degree of structural order in the CPT SAMs with uniform molecular features. The cross-sectional profiles in Figures 2b and 2c taken along lines a' and b', corresponding to the oblique unit cell in the Figure 2a, show the superperiodicities of the CPT molecules in SAMs. The lattice constants extracted from the high-resolution image are: a = 5.4 ± 0.1 Å = $\sqrt{3.5}$, b = 6.4 ± 0.1 Å = $\sqrt{5}$, α = 25°, and γ = 80° (See Figure 3).

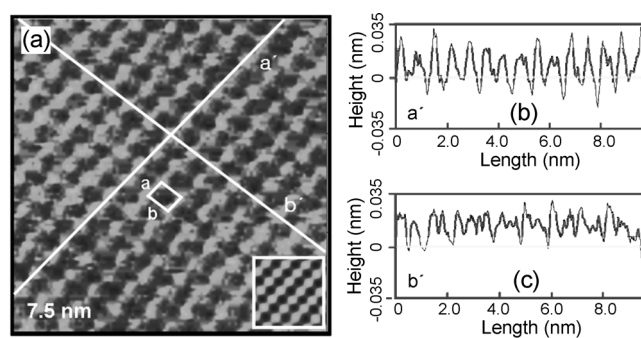Figure 3 shows proposed structural models for the CPT SAMs adsorbed on Au(111). From the model of Figure 3a, it

Figure 2. (a) Molecularly resolved STM image of CPT SAMs on Au(111). The inset shows a 2-D filtered STM image (3 nm × 3 nm) that presents high-structural order. (b, c) Height profiles along lines a and b on the image show the superperiodicities of the adsorbed molecules.
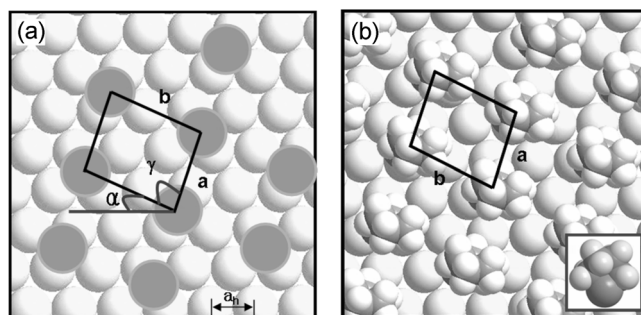

Figure 3. (a) Schematic structural model and (b) space-fill drawing model of the proposed structure for CPT SAMs on Au(111). Note that bright balls and dark circles represent gold atoms and CPT molecules, respectively. The lattice constants extracted from the high-resolution image are: a = 5.4 ± 0.1 Å, b = 6.4 ± 0.1 Å, α = 25°, and γ = 80°, where a_h = 2.88 Å and represents the interatomic distance of the Au(111) lattice. The inset in Figure 3b shows the side view of adsorbed CPT molecules.

was found that all sulfur atoms in the CPT SAMs preferentially sat on the bridge sites of the Au(111) lattice. Recent studies have reported that the most stable adsorption site for simple alkanethiols is not the threefold hollow sites, but bridge sites of the Au(111) lattice.[25,26] These results for CPT SAMs on Au(111) also support this bridge-site adsorption model. Based on the structural model of Figure 3a, the structure of the CPT SAMs can be assigned as the ($\sqrt{3.5}$ × $\sqrt{5}$)R25° overlayer structure. The average areal density for the adsorbed molecule was calculated to be about 34.6 Å²/molecule. The CPT SAMs have a molecular density that is 2.6 times higher than the CHT SAMs with an average areal density of 88.3 Å²/molecule.[20] This is because the CPT molecule with a five-membered aliphatic rings have a more rigid geometric structure than the CHT molecule with a six-membered aliphatic ring, which provides two isomers with a large molecular volume, *i.e.*, equatorial and axial isomers in the CHT SAMs. However, the CPT SAMs have a molecular density that is 1.6 times lower than *n*-alkanethiol SAMs with an average areal density of 21.6 Å²/molecule (($\sqrt{3}$ × $\sqrt{3}$)R30° packing structure).[1,5,23] This resulted from a larger molecular volume of the CPT due to their ring structure. In

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Notes

addition, a space-fill drawing model in Figure 3b shows that, even if cyclopentane ring is supposed to have torsional strain and nonplanar envelope like structure, the top and side views of each CPT molecule are the same. As a result, STM imaging for CPT SAMs showed a uniform molecular feature, unlike the case of CHT SAMs. This result is an indirect evidence for the fact that the two different molecular features observed from the unit cell of CHT SAMs originated from the two stable isomers.[20]

In summary, we have demonstrated at the molecular level that CPT molecules on Au(111) can form ordered SAMs, which are described as a ($\sqrt{3.5} \times \sqrt{5}$)R25° structure. In addition, the structural rigidity and size of the aliphatic cyclic ring of molecules play a very important role in determining the final SAM structure and the self-assembly processes of the molecules.

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