

Coexistence of Closely Packed $c(4 \times 2)$ and Striped Phases in Self-Assembled Monolayers of Decylthiocyanates on Au(111)

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Decylthiocyanate (DTC) self-assembled monolayers (SAMs) on Au(111) were prepared by solution and vapor phase deposition methods at 50 °C for 24 h. The formation and surface structure of DTC SAMs were examined using scanning tunneling microscopy (STM). STM imaging revealed that DTC SAMs formed in 1 mM ethanol solution at 50 °C were composed of small ordered domains with lateral dimensions of a few nanometers and disordered phases, whereas DTC SAMs formed in the vapor phase at 50 °C contained two ordered phases: a closely packed $c(4 \times 2)$ superlattice and a striped phase with an interstripe spacing of 2.6–2.8 nm. It was also found that the ordered domain and vacancy island formation for DTC SAMs on Au(111) differs significantly from that of decanethiol SAMs, suggesting that adsorption mechanism is different from each other. From this study, it was confirmed that DTC SAMs with a high degree of structural order can be obtained by vapor phase deposition.

Key Words: Decylthiocyanate, Self-assembled monolayers, Scanning tunneling microscopy, Structural order, Vapor deposition

Introduction

The spontaneous adsorption of organosulfur compounds onto gold surfaces yields organic self-assembled monolayers (SAMs), which provide some of the best model systems for understanding molecular self-assembly phenomena and for many practical applications in chemical sensing, biointerfacing, nanopatterning, and molecular electronics.^{1–12} Although organic thiols have been the most popular precursors for the preparation of SAMs, they tend to oxidize to disulfides and/or other compounds, which can hamper the formation of two-dimensional (2D) ordered SAMs in solution.¹³ To avoid this problem, other precursors with better chemical stability to oxidation have been developed including acetyl protected thiols,^{13–16} organic thio-sulfates,¹⁷ isocyanides,¹⁸ and sulfides.¹⁹ However, the SAMs formed by these alternative sulfur sources on gold surfaces have poor structural order and many structural defects, and surface cleanliness and SAM preparation conditions also strongly affect the 2D SAM formation and structural order. For instance, octylthioacetate SAMs (OTA) on Au(111) formed in ethanol solution were mainly composed of disordered phases, whereas OTA molecules under the same conditions formed well-ordered SAMs with a $c(4\sqrt{3} \times 2\sqrt{3})R30^\circ$ superstructure, which often refers to a $c(4 \times 2)$ superlattice. However, the density, distribution, and shape of vacancy islands (VIs) for OTA SAMs are quite different from those for octanethiol SAMs.¹⁶ Thus, the protecting group and the deposition medium may cause problems during SAM formation, resulting in the formation of a unique surface structure.

Recently, Ciszek *et al.* demonstrated that organic thiocyanates can be assembled on gold surfaces *via* a surface-mediated cleavage of the S-CN bond, and they serve as good alternative

precursors for SAM preparation that remedy the oxidative limitation of thiols.^{20,21} However, comparative studies of thiocyanate and thiol SAMs on Au(111) revealed that thiocyanate SAMs have a less ordered structure and lower packing density compared to thiol SAMs.^{20–23} Scanning tunneling microscopy (STM) experiments have shown that decyl thiocyanate (DTC) SAMs on gold and platinum surfaces contain disordered structures, which is consistent with the results obtained using other macroscopic tools.^{22,23} Contrary to this STM result, octyl thiocyanate (OTC) molecules can form ordered SAMs with a $(\sqrt{3} \times \sqrt{19})R5^\circ$ packing structure by vapor deposition at elevated temperature.²⁴ It was found that the adsorption of dodecyl thiocyanates (DDTC) on Au(111) in a purified and aged solution led to the formation of closely packed ordered SAMs having the $c(4 \times 2)$ superlattice. Based on previous results, we considered the formation and structure of organic thiocyanate SAMs on metal surfaces to be significantly influenced by experimental conditions and by the purity of the reactants. So far, there have been only a few STM studies on SAM formation of organic thiocyanates on metal surfaces. Further molecular-scale STM studies are necessary to understand the self-assembly phenomena and structures of these molecules on gold.

We found that vapor phase deposition is a more effective method for obtaining high quality OTC SAMs compared to liquid phase desposition.²⁴ In order to confirm this result and to understand the alkyl chain effect of alkyl thiocyanate molecules on SAM formation, we expanded our studies to DTC molecules ($\text{CH}_3(\text{CH}_2)_9\text{-S-CN}$), with a longer alkyl chain than that of OTC ($\text{CH}_3(\text{CH}_2)_7\text{-S-CN}$), and examined the surface structure of DTC SAMs on Au(111) prepared by solution and vapor phase deposition methods using STM. To the best of our knowledge, there have been no STM reports showing molecular-scale features

of SAMs formed by DTC. In this paper, we report that vapor deposition of DTC molecules on Au(111) formed ordered SAMs containing a closely packed $c(4 \times 2)$ phase and a low density striped phase, which have never been observed so far. Contrary to the formation of uniform closely packed SAMs by alkanethiols, the coexistence of two different packing structures in DTC SAMs strongly suggests that the adsorption mechanism of organic thiocyanates is quite different from that of alkanethiols on gold surfaces.

Experimental

DTC was synthesized according to a previously described method.⁴ The product was purified by column chromatography and confirmed by ¹H NMR analysis. The Au(111) substrates were prepared by the thermal evaporation of gold onto freshly cleaved mica sheets prebaked at 330 °C with a base pressure of $\sim 10^{-7}$ - 10^{-8} Torr. The substrates were then annealed at 350 °C in the same vacuum chamber for 2 h to obtain a large terrace in the range of 100 - 300 nm.

To elucidate the effects of alkyl chain length and deposition method on the formation of DTC SAMs on Au(111), SAM samples were prepared by solution and ambient-pressure vapor depositions. To compare the surface structures of SAMs formed by decanethiol (DT) and DTC, which have identical alkyl chains, both SAMs were prepared by immersing the gold substrates in a 1 mM ethanol solution of the corresponding compounds at room temperature or 50 °C for 24 h (solution deposition). DTC SAMs were also prepared by ambient-pressure vapor deposition. The gold substrates were placed in a 3 mL V-vial containing 3 μ L of neat DTC liquid, and the V-vial was then sealed by capping and wrapped with Parafilm. The vial was heated to 50 °C in a drying oven and kept for 24 h. Next, the SAM samples were cooled to room temperature and rinsed with pure ethanol to remove weakly adsorbed molecules from the SAM surface.

STM observation was carried out using a NanoScope E (Veeco, Santa Barbara, CA) with a commercially available Pt/Ir tip (80:20). All STM images were obtained in the constant current mode under ambient conditions. Imaging parameters were in the range of 300 - 500 mV for bias voltage and in the range of 0.30 - 0.60 nA for tunneling current.

Results and Discussion

Figure 1 shows a typical STM image of DT SAMs on Au(111) formed after immersion of the Au(111) substrates in a 1 mM ethanol solution at room temperature for 24 h. The DT SAMs consisted of well-ordered domains separated by domain boundaries and a number of VIs (dark pits). STM imaging clearly revealed that DT molecules formed closely packed domains with a $c(4 \times 2)$ superlattice. It is generally believed that the $c(4 \times 2)$ structure is thermodynamically more stable than the hexagonally packed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.²⁷ Lateral dimensions of ordered domains were in the range of 10 - 20 nm. The VIs appeared as a result of chemisorption of thiols onto gold surfaces with a 0.25 nm depth, which corresponds to the monatomic step height of the Au(111) surface. The surface structure of DT SAMs observed here is quite consistent with a number of previous STM studies for alkanethiol SAMs.^{5,11,24,26,27} This result strongly supports the idea that DT SAMs are able to reach saturated monolayer coverage with these preparation conditions.

In contrast to solution deposition forming ordered DT SAMs, as reported in a previous STM study, the same preparation conditions gave DTC SAMs that were mainly composed of dis-

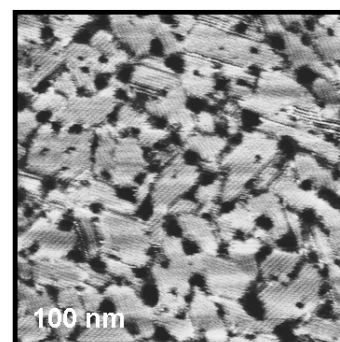


Figure 1. A typical STM image showing a well-ordered $c(4 \times 2)$ packing structure and vacancy islands of DT SAMs on Au(111) formed after immersion of Au(111) substrates in a 1 mM ethanol solution at room temperature for 24 h.

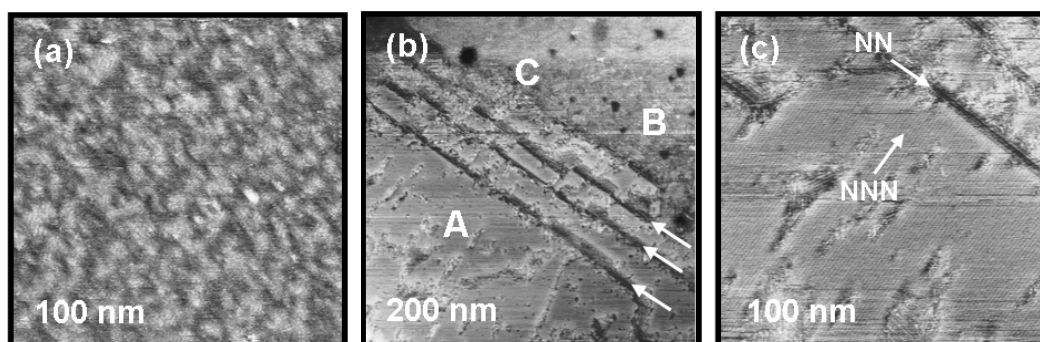


Figure 2. (a) STM image of DTC SAMs on Au(111) prepared by solution deposition at 50 °C for 24 h. (b) and (c) STM images showing the coexistence of closely packed $c(4 \times 2)$ phase (region A) and striped phase (regions B) of DTC SAMs on Au(111) prepared by vapor phase deposition at 50 °C for 24 h.

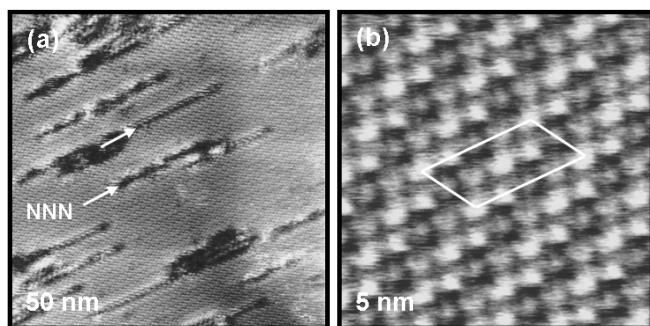


Figure 3. High-resolution STM images of the closely packed $c(4 \times 2)$ phase obtained from region A of DTC SAMs on Au(111). (a) Large ordered domains containing molecular row defects. (b) Molecularly resolved $c(4 \times 2)$ superlattice.

ordered phases.²² Recently, it was observed that the structural order of organic thiocyanate SAMs can be greatly enhanced using an elevated deposition temperature^{24,25} and vapor deposition.²⁴ The STM images in Figure 2 show the large differences in the surface structures of DTC SAMs on Au(111) formed by solution and vapor depositions. Figure 2a shows the STM image of DTC SAMs obtained from solution deposition. These SAMs contained very small ordered domains (bright regions) with lateral dimensions of a few nanometers and disordered phases (dark regions). The ordered domains appeared to be striped phases with an inter-row distance of 2.3 - 2.6 nm; such striped phases, in which the alkyl chain was lying flat on the gold surface, often appear at the initial stage of SAM growth^{28,29} or from SAMs formed after thermal annealing.²⁶ We found the surface structure of DTC SAMs to be quite similar to those of OTC SAMs,²⁴ which implies that OTC and DTC molecules have a nearly identical adsorption behavior in solution. The inferior quality of thiocyanate SAMs compared to thiol SAMs may be due to the lower sticking coefficient of thiocyanates, the high activation barrier for S-CN bond cleavage, or the lower adsorption activity of a sulfur joined to an electron withdrawing CN group.^{24,25}

On the other hand, the structural order of DTC SAMs formed by vapor phase deposition was greatly enhanced, as shown in Figures 2b and 2c. Interestingly, DTC SAMs were composed of a closely packed domain (region A), a striped phase (region B), a disordered domain (region C), and long-range row defects of a few hundred nanometers length limited by the size of gold terraces (white arrow). Until now, this type of surface structure has never been observed from any SAM systems including thiol SAMs. An ordered domain with a unidirectional orientation of approximately 120 nm was observed, which is significantly larger than domains observed with alkanethiol SAMs (see Figure 1). Long-range row defects tended to form along the nearest-neighbor (NN) direction, as shown in Figure 2c. Similar row defects in hexanethiol SAMs were formed as a result of 1-D collapse by desorption of molecules adsorbed onto the gold surface. The 1-D collapse occurs along the NN direction because the molecules are tilted approximately 14° from the NN direction.³⁰ Thus, the row defects observed in DTC SAMs on Au(111) strongly reflect the tilted adsorption geometry of the adsorbed

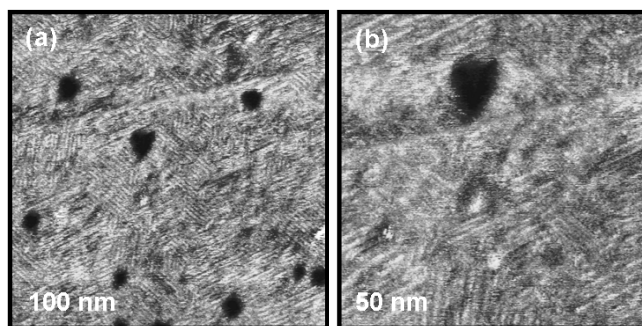


Figure 4. STM images of the striped phase obtained from region B of DTC SAMs on Au(111).

molecules. In addition, we observed very few VIs and an extremely low fraction of VIs to total surface area from DTC SAMs. A rationale for the unusual formation of VIs is unclear at present, and additional systematic studies to understand the mechanism of VI formation are required.

The STM image in Figure 3a shows the adsorption of DTC molecules on Au(111) yielding closely packed ordered domains with short-range row defects along the next-nearest-neighbor (NNN) direction. DDTC SAMs prepared under different conditions also contained such row defects in their ordered domains,²⁵ which can be considered an intrinsic property that develops during the self-assembly of organic thiocyanates on gold surfaces. The high-resolution STM image in Figure 3b clearly reveals the well-known $c(4 \times 2)$ superstructure of the basic $(\sqrt{3} \times \sqrt{3})R30^\circ$ hexagonal packing structure observed from the ordered domains of DTC SAMs. The molecular density corresponded to 21.6 \AA^2 per molecule. A previous STM study revealed that OTC molecules form ordered SAMs with a low density $(\sqrt{3} \times \sqrt{19})R5^\circ$ structure, whereas DTC molecules with a longer alkyl chain form closely packed $c(4 \times 2)$ structures, analogous to alkanethiol SAMs. This result suggests that van der Waals interactions between alkyl chains may be a dominant factor in the formation of 2D thiocyanate SAMs formed by vapor deposition. However, the contribution of lateral interactions may be minimal for solution deposition due to an unknown side-effect of solvent molecules that hinder the diffusion rate of thiocyanates or extrusion of the CN group after S-CN bond cleavage.

As shown in Figure 3b, the long-range ordered striped phase was separated by closely packed domains (regions A and B). The STM images in Figure 4 clearly show the striped phases formed by DTC molecules. Three-directional striped phases in Figure 4 were observed, suggesting that the formation of this structure was influenced by the three-fold lattice structure of the Au(111) surface. The interstripe spacing was measured to be 2.6 - 2.8 nm, which is nearly twice the molecular length of decanethiolates formed from S-CN bond cleavage. It has been previously demonstrated that the distance between stripes depends on the molecular packing density and the alkyl chain length.²⁶ Therefore, our results suggest that the formation of these striped phases can be ascribed to a head-to-head orientation of sulfur atoms on the Au(111) surface.

Conclusion

Molecular-scale STM observations clearly revealed that the mechanism of DTC SAM formation on Au(111) is significantly different from that of DT SAMs. DTC SAMs formed in a 1 mM ethanol solution at 50 °C consisted of small ordered domains with lateral dimensions of a few nanometers, along with disordered phases, whereas DTC SAMs formed from vapor phase deposition were composed of two ordered phases: a closely packed $c(4 \times 2)$ phase and a striped phase with an interstripe spacing of 2.6 - 2.8 nm. Interestingly, DTC SAMs also contained long-range row defects a few hundred nanometers long prone to form along the NN direction and short-range row defects in the ordered domains. It was found that OTC molecules form ordered SAMs with a low density ($\sqrt{3} \times \sqrt{19}$)R5° structure, whereas DTC molecules with a longer alkyl chain form a closely packed $c(4 \times 2)$ structure. From these results, we suggest that van der Waals interactions between alkyl chains may be a dominant factor in the formation of 2D thiocyanate SAMs formed by vapor deposition.

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