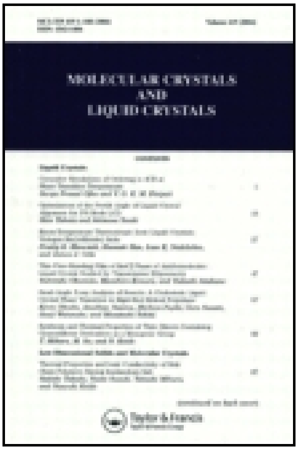

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Surface Morphology of Alkanethiol Self-Assembled Monolayers on Au(111) after Desorption Studied by Scanning Tunneling Microscopy

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Surface Morphology of Alkanethiol Self-Assembled Monolayers on Au(111) after Desorption Studied by Scanning Tunneling Microscopy

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Desorption of hexanethiol self-assembled monolayers on Au(111) in diethyl ether initiates from domain boundaries and around depressions having weaker lateral interaction than that of densely packed regions. The c(4 × 2) superlattice was observed as domain structure from SAM films formed after desorption, and also some missing-rows were exhibited, indicating the desorption of molecules in these densely packed domains.

Keywords: self-assembled monolayer; scanning tunneling microscopy; thermal desorption spectroscopy; desorption; dimerization

INTRODUCTION

Self-assembled monolayers (SAMs) have been extensively studied because their well-defined structural character provides molecular surfaces of great promise for scientific studies and technical exploration fields such as biosensing, photoresist, nonlinear optics, molecular electronic circuit fabrication, and even drug delivery system[1,2]. Even if alkanethiol SAMs on Au(111) have been widely worked as model compounds, the identification of the actual molecular species bound to the gold has been questioned recently[3].

A grazing incidence X-ray diffraction study revealed the adsorbed thiol molecules form dimer-like arrangements of sulfur atoms at the SAMs-Au(111) interface[4]. On the other hand, though the ($\sqrt{3} \times \sqrt{3}$)R30° structure and c(4 × 2) superlattice in the densely packed region were observed by a numerous STM studies[5], the origin of two domain structures has not been clear as yet. In addition, there are few reports related desorption process of SAMs compared with the adsorption process of alkanethol SAMs on gold.

In this work, we used the mild desorption process of hexanethiol SAMs in diethyl ether to investigate the correlation between structures and adsorbed states of SAMs. We will address desorption process of alkanethiol SAMs through results obtained from STM studies.

EXPERIMENTAL

Epitaxial Au(111) films were prepared by thermal evaporation of approximately 100 nm gold film onto freshly cleaved mica sheets pre-heated to 420 ℃ for 3 h under a vacuum pressure of 10^{-7}–10^{-8} Torr. After deposition, the substrates were annealed to make a flat single crystal surface of 100-300 nm size at 450 ℃ in a vacuum chamber for 2 h.

Monolayers were formed by immersing the gold substrates into a 1 mM ethanol solution of hexanethiol (HT) immediately after the gold evaporation for 1 day. Desorbed monolayers were then obtained by dipping the pre-covered HT SAMs into diethyl ether for various desorption times.

All STM images were acquired at room temperature with a Pt/Ir tip using constant current mode in air. Bias voltages (V_b) between 150 and 550 mV (sample positive) and tunneling currents (I_t) from 0.15 to 0.3 nA were applied between the tip and sample.

RESULTS AND DISCUSSION

Our previous study by thermal desorption spectroscopy (TDS) showed that there exist two thermal desorption spectra at low and high temperature regions, corresponding to the desorption of weakly adsorbed dimer molecules and dimerized desorption of chemisorbed alkanethiolate molecules in alkanethiol SAMs, respectively[6]. We assume that the domain structure for chemisorbed molecules would remain on the Au(111) due to the removal of weakly adsorbed dimer after mild desorption in solvent.

STM image in FIGURE 1 shows the coexistence of two domain structures, (√3 × √3)R30° and c(4 × 2), and the domains of c(4 × 2) superlattice having three domain directions were also observed, on the basis of hexagonal lattice of Au(111). The (√3 × √3)R30° overlayer structure with the underlying Au(111) surface was usually found during the initial SAMs from STM study[7]. Our STM study shows the c(4 × 2) superlattice could be observed from SAM films formed by a longer deposition or desorption times more than 1 day. Two possible explanations for transformation of domain structure from (√3 × √3)R30° to c(4 × 2) superlattice are the dimerization of adsorbed thiol during SAM growth or the stabilization of SAMs by some changes (tilt angle and direction of chain) to arrive a maximal van der Waals force between alkylchains. It is more likely to be the latter explanation for transfomation of domain structure because our recent TDS study reveals that desorption peak of monomer shifts from a low temperature region to a high one depending on deposition time.

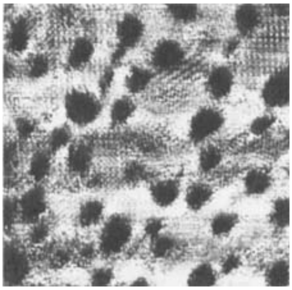

FIGURE 1 STM image of hexanethiol SAMs on Au(111): 1day deposition, scan size is 50 nm × 50 nm.

STM images shown in FIGURE 2 are the surface morphology of hexanethiol SAMs on Au(111) after desorption of thiol molecules in diethyl ether. Desorption of hexanethiol SAMs initiates from domain boundaries and around depressions having weaker lateral interaction than that of densely packed regions, and also some missing-rows were exhibited in domains, which are the meaning of starting point of desorption in close packed domains as shown in STM image of FIGURE 2A. STM image in

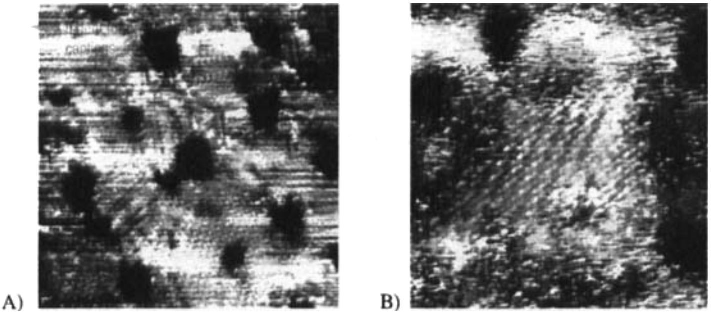

FIGURE 2 STM image of hexanethiol SAMs on Au(111): (A) 5 days desorption, scan size is 40 nm × 40 nm. (B) 7 days desorption, scan size is 17 nm × 17 nm.

FIGURE 2B shows the disordered liquid-like state formed after desorption of molecules and a highly odered new c(4 × 2) superlattice which exhibits three different height modulation having a hexagonal packed structure. The detail description of this structure will be reported elsewhere. The desorbed area of thiol molecules increased with desorption time.

In conclusion, we propose that the c(4 × 2) superlattice is more stable domain structure than hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° domain structure on a Au(111). The desorption of hexanethiol SAMs on Au(111) in diethyl ether starts from domain boundaries and around depressions, and forms missing-rows in densely packed domains.

Acknowledgments

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References

[1] R. F. Service, *Science*, **265**, 316 (1994).
[2] G. E. Poirier, *Langmuir*, **13**, 2019 (1997).
[3] N. Mohri, S. Matsushita and M. Inoue, *Langmuir*, **14**, 2343 (1998).
[4] P. Fenter, A. Eberhardt and P. Eisenberger, *Science*, **265**, 1216 (1994).
[5] I. Touzov and C. B. Gorman, *J. Phys. Chem. B*, **101**, 5263 (1997).
[6] N. Nishida, M. Hara, H. Sasabe and W. Knoll, *Jpn. J. Appl. Phys.*, **36**, 2379 (1997).
[7] R. Yamada and K. Uosaki, *Langmuir* **13**, 5218 (1997).