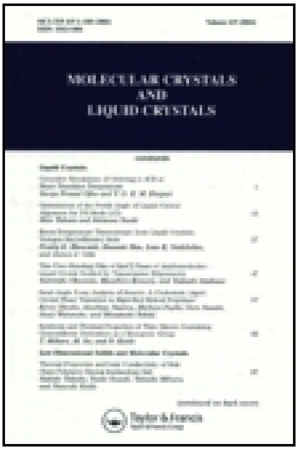

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Surface Structures in Spatio-Temporal Ordering of Alkanethiol Self-Assembled Monolayers on Au(111)

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Surface Structures in Spatio-Temporal Ordering of Alkanethiol Self-Assembled Monolayers on Au(111)

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Growth process of hexanethiol self-assembled monolayers (SAMs) on Au(111) was investigated by scanning tunneling microscopy (STM). STM imaging clearly exhibited intermediate structures in a molecular level showing phase transition from disordered phase to close-packed monolayers for the first time. It is assumed that these structures are due to the rearrangement of alkyl chains to optimize the van der Waals interaction between alkyl chains in SAMs.

Keywords: alkanethiol; self-assembled monolayer; scanning tunneling microscopy; mesh-like structure; phase transition; intermediate structure

INTRODUCTION

Alkanethiols spontaneously chemisorbed on gold surface form densely packed and highly ordered self-assembled monolayers (SAMs)[1]. In particular, such SAMs on gold can provide a powerful means of technical applications due to their high stability, easy preparation, and controllable structures[2]. To understand fundamental aspects of SAMs in more detail, the structure of SAMs has been extensively investigated by using various techniques.

Quite recently, growth mechanism in the process of self-assembly of monolayers was well studied by *ex situ* and *in situ* measurements, and several phases formed during SAM formation were newly observed[3]. However, there still exist unknown phases due to the complicated factors that influence SAM formation including the intrinsic properties of the substrate, mobility of adsorbed molecules on the surface, molecular conformation energy, heat of condensation, and edge energy.

In this work, we have examined surface structures of hexanethiol (HT) SAMs depending on surface coverage by scanning tunneling microscopy (STM). From this study, we found new phases formed during the SAM growth. We will discuss these phases and growth process of alkanethiol SAMs on gold.

EXPERIMENTAL

Au(111) substrates with domain sizes of 100-300 nm were prepared by vacuum deposition as reported in previous papers[4]. Monolayers were formed by dipping the gold substrates into a freshly prepared 5 μM ethanol solution of hexanethiol (HT) for various deposition times.

STM measurements were performed with a Digital Instruments NanoScope II and a commercial Pt/Ir (80:20) tip. All STM images were acquired in constant current mode in air.

RESULTS AND DISCUSSION

STM image in Fig. 1(a) displays striped phase (A) and disordered phase (B) from the HT SAM sample obtained after deposition for 2 min. It is well known that the striped phases where the molecules are aligned along the gold surface were usually found in the low surface coverage region. The corrugation period of this striped phase is 2.3 nm, which is nearly consistent with twice the molecular length of hexanethiol. The similar striped phase was also observed in the growth stage of decanethiol SAMs[3].

STM image in Fig. 1(b) clearly shows intermediate phase (I1) and close-packed domain (C) from the SAM sample prepared after deposition for 10 min. As with increasing the surface coverage after the longer time dipping, molecules lying flat on the surface gradually grow up two-dimensionally to the standing-up phase. Though this intermediate phase was not clearly imaged, domain-like structure (bright

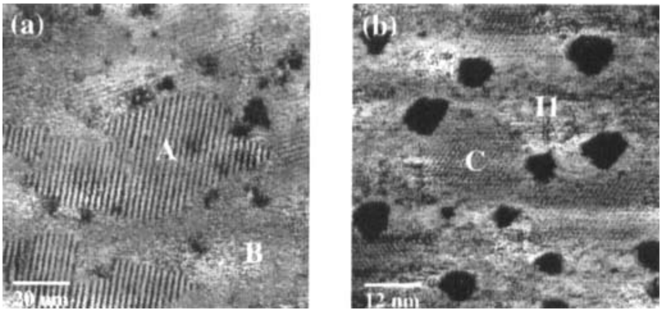

FIGURE 1. STM images of hexanethiol SAMs on Au(111): (a) 2 min deposition, imaging conditions: 0.14 nA, 0.45 V, (b) 10 min deposition, imaging conditions: 0.12 nA, 0.37 V.

spots in the I1 phase) was observed, suggesting that ordered molecular arrangements were gradually proceeded not randomly but locally forming ordered structure. Finding of I1 phase in this image strongly supports phase transition from disordered phase to highly ordered phase.

Mesh-like structure (intermediate phase 2: I2) and c(4 × 2) superlattice, on the other hand, were clearly observed from SAM sample after deposition for 1h as shown in Fig. 2. Molecularly resolved mesh-like structure was observed for the first time in this study. New findings of I1 and I2 phases can be considered as clear evidence of intermediate structures formed prior to highly ordered SAMs because these structures disappeared after 1 day deposition. Length of one mesh domain consisting of 4 molecular rows is about 3.0-4.5 nm. These mesh domains were separated by one bright row with the inter-molecular spacing of 0.5 nm (Fig 2(b)). Distance between this bright row and mesh domains is 0.87 nm, which is consistent with the next-nearest spacing in the standard model[5]. Though it should be found one molecular row in the dark row, we have not confirmed such a row yet. It seems to be a kind of missing row, but it is most likely due to low contrast imaging derived from the different orientations of terminal methyl groups rather than missing-row. If there are missing-rows in the dark row, it is rather difficult to form highly ordered molecular rows between two dark rows. However the origin of this mesh-like structure is still unclear at present,

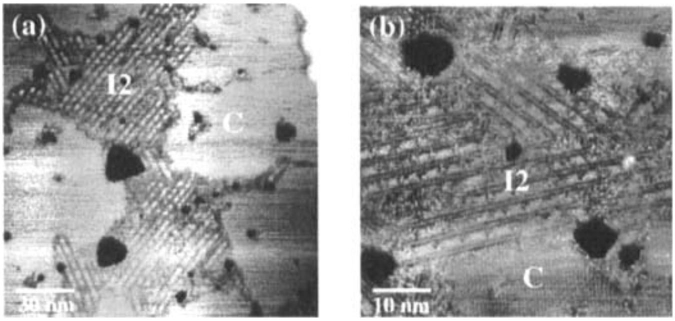

FIGURE 2. Mesh-like structure of hexanethiol SAMs on Au(111) obtained after 1 h deposition. Imaging conditions are (a) 0.28 nA, 0.31 V and (b) 0.28 nA, 0.33 V.

and we speculate that one of the possible origins is due to the rearrangement of herringbone structure of gold surface during the SAM formation[6].

CONCLUSION

The present results provided a coverage-dependant, spatio-temporal pictures of several phases formed in the growth process of alkanethiol SAMs on Au(111). We believe that these results can be helpful in understanding essential features of organic molecules on the metal surface as well as fabrication of geometrically controlled organic thin films in molecular and atomic scales.

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