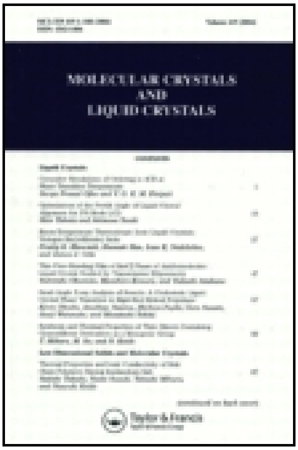

Molecular Crystals and Liquid Crystals

Temporal Stability of Thiophene Self-Assembled Monolayers on Au(111)

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Temporal Stability of Thiophene Self-Assembled Monolayers on Au(111)

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Temporal stability of close-packed thiophene (TP) self-assembled monolayers (SAMs) on Au(111) was investigated by scanning tunneling microscopy (STM). Molecular-scale STM imaging reveals that the structural transitions of TP SAMs in the structure and size of ordered domains and the distribution of vacancy islands (VIs) occurs after long-term storage for 1 year. During this time period, the ordered domain sizes were remarkably increased and the fraction of the areas of the VIs to the total surface area was steeply decreased from 6.5% to 1.7%. We demonstrate that the temporal factor strongly affects two-dimensional SAM structures and our results will be very useful in designing a molecular template for SAM-based further applications.

Keywords: scanning tunneling microscopy; self-assembled monolayers; surface structure; temporal stability; thiophene

INTRODUCTION

Organic thin films formed by π-conjugated thiophene (TP) and its oligomers on metal surfaces have drawn much attention because they can be used for the fabrication of electronic devices due to high molecular conductivity [1]. It has been generally accepted that self-assembly techniques is very powerful method for making monomolecular films with well-controlled two-dimension structures [2–4]. As a result, the surface characteristics of self-assembled monolayers (SAMs) such as

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electrical and chemical properties can be much easier to control than any other techniques. SAMs potentially have a wide range of applications, including corrosion inhibition, molecular recognition, sensors, nanolithography, and molecular electronic devices [2,5]. TP SAMs on Au(111) were examined by several surface sensitive techniques to understand the binding conditions, molecular orientations, and adlayer structures [6–11]. Scanning tunneling observation (STM) revealed that TP SAMs on Au(111) have well-ordered structures [6–9]. X-ray photoelectron spectroscopy and thermal desorption spectroscopy measurements elucidated that the sulfur atom of TP would chemically interact with the gold surface [6,8,9]. Molecular orientation of TP SAMs depending on surface coverage was monitored by Fourier-transform infrared reflection absorption spectroscopy [11].

For further application of SAMs, it is essential to understand the temporal stability of TP SAMs on the gold surfaces. In this study, we found from a nanoscopic viewpoint that the dynamic phase transition of TP SAMs on Au(111) occurs after long-term storage at room temperature.

EXPERIMENTAL

Thiophene (TP) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification. The Au(111) substrates with an atomically flat, large, single-crystal terrace were obtained by the vacuum evaporation of gold onto freshly cleaved mica sheets as described previously [12]. Pre-covered SAM samples were prepared by dipping the gold substrates in a 1 mM ethanol solution of TP for 1 day. To examine temporal stability of TP SAMs on Au(111), pre-covered SAM samples were immediately put in a Petri Dish, and then it was tightly sealed under a vacuum of ~400 Torr with a vinyl bag to prevent oxidation and contamination of the monolayer at room temperature for 1 year.

STM measurements were performed using a NanoScope E (Veeco, Santa Barbara, CA) with a commercial Pt/Ir (80/20) tip. All STM images were obtained using the constant current mode in air at room temperature.

RESULTS AND DISCUSSION

STM images in Figure 1 show surface structures of TP SAMs on Au(111) formed after immersion of the Au(111) substrates into 1 mM ethanol solution for 1 day. A large-scan STM image in Figure 1(a) shows many vacancy islands (VIs) with the depth of 0.25 nm, which

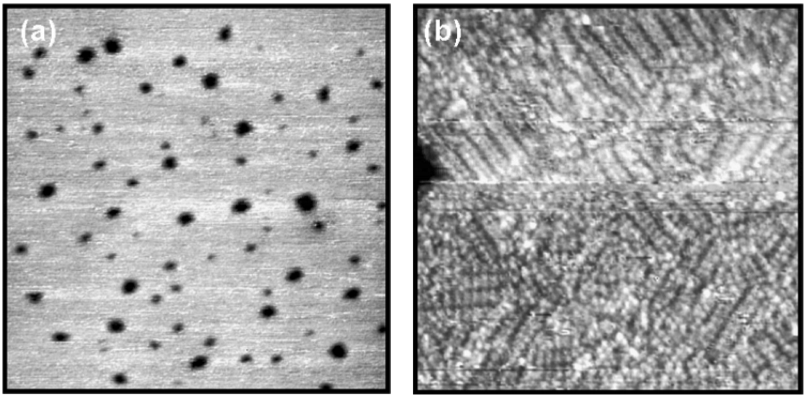

FIGURE 1 Surface structures of TP SAMs on Au(111) formed after immersion of the Au(111) substrates in 1 mM solution for 1 day. STM images showing (a) distribution of vacancy islands (120 nm × 120 nm, $V_b = 0.40$ V, and $I_t = 0.25$ nA) and (b) randomly adsorbed molecular domain and paired-row ordered domains (18 nm × 18 nm, $V_b = 0.41$ V, and $I_t = 0.28$ nA).

is close to the monatomic step height of the Au(111) surface. The fraction of the areas of the VIs to the total surface area was measured to be approximately 6.5%, which is slightly smaller than that observed in alkanethiol SAMs [13]. High-resolution STM image in Figure 1(b) revealed that the spontaneous adsorption of TP on Au(111) leads to the formation of ordered SAMs. Interestingly, TP SAMs have two molecular domains: one is short-range ordered domains with paired-rows separated from each other by 4.35 Å, and the other is randomly adsorbed molecular domains. The detailed structural model of TP SAMs was reported in our previous report [6]. From STM results, a cofacial interaction between TP molecules is one of very important factors for the formation of TP SAMs, however the existence of domains consisting randomly adsorbed molecules in the monolayer implies that the interactions between the sulfur atom and the gold surface is also a critical parameter for SAM formation.

Figure 2 shows the surface structures of TP SAMs after long-term storage for 1 year at room temperature. A large STM image in Figure 2(a) reveals that the remarkable structural transitions of TP SAMs on Au(111) surface occur depending on time. In particular, the total number and the fraction of the areas of the VIs to the total surface area (~1.7%) were steeply decreased compared with those observed from as-deposited TH SAMs. In addition, the size of ordered domains with three domain orientations (as indicated by white arrows) increased.

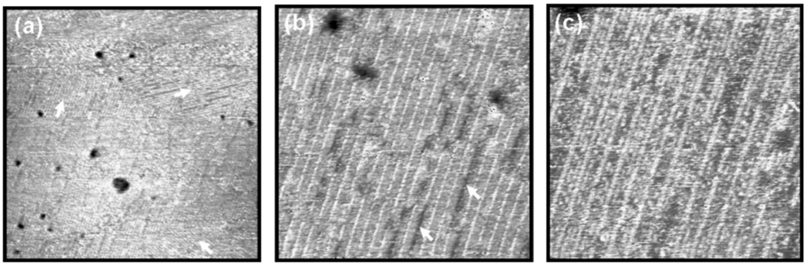

FIGURE 2 Surface structures of TP SAMs on Au(111) formed after long-term storage of as-deposited SAM samples for 1 year. STM images showing (a) distribution of vacancy islands (120 nm × 120 nm, $V_b = 0.50\,V$, and $I_t = 0.17\,nA$), (b) structural defects in the ordered domains (30 nm × 30 nm, $V_b = 0.41\,V$, and $I_t = 0.17\,nA$), and (c) ordered molecular rows (18 nm × 18 nm, $V_b = 0.45\,V$, and $I_t = 0.15\,nA$).

We often observed the domains with the larger than 50 nm size. Our previous STM study demonstrated the time-dependant structural transition of octanethiol SAMs from the $c(4 \times 2)$ superlattice to the $(6 \times \sqrt{3})$ superlattice resulting from structural rearrangement caused by both the dynamic movement of the adsorbed sulfur atoms on several adsorption sites of the Au(111) surface and the change of molecular orientation in the ordered layer [14]. Similar to alkanethiol SAMs on the gold surface, TP SAMs also showed structural dynamics with temporal function even though it has been generally considered that organosulfur SAMs forms quite stable two-dimensional monolayers after 1 day immersion.

High-resolution STM images in Figure 2(b) and 2(c) clearly show ordered molecular rows. Spacing between two bright rows is measured to be 1.3 nm (see Fig. 2(b)). It was also visualized that there exist two molecular rows inside two bright rows (see Fig. 2(c)). On the basis of this observation, real spacing between two rows is approximately 4.3 nm, which is nearly identical with that between the paired rows observed from as-deposited TP SAMs. This result implies that molecular packing density of TP SAMs would not significantly change after long-term storage. It can be considered that the dark molecular rows indicated by white arrows in Figure 2(b) may be due to the desorption of several molecules. Interestingly, the line defects were formed not randomly but one-directionally, reflecting that the adsorption energy of molecules are nearly the same in a row. Therefore, if the desorption of a molecule initiates, desorption process proceeds successively in a row. In addition, the randomly adsorbed molecular domains were completely disappeared after long-term storage, this result indicates that the long-term rearrangement process of molecules in SAMs can enhance remarkably two-dimensional order of TP SAMs on Au(111) surface. We assumed that the main driving force for such a structural transition is due to the increase of lateral interaction between molecules resulting from the enhancement of structural order.

CONCLUSION

High-resolution STM study revealed that structural characteristics of TP SAMs, such as the structure and size of domains and the number and fraction of VIs, on Au(111) were remarkably changed after long-term storage. It can be considered that the main driving force for this phase transition is to maximize van der Waals interactions between TP molecules. Our results will be very useful in designing SAM-based molecular templates for technical applications.

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