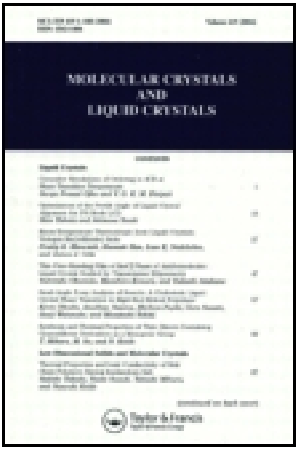

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Molecular Decomposition via Striped Phase in Self-assembled Monolayers of Alkanethiols Adsorbed on Au(111)

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Molecular Decomposition via Striped Phase in Self-assembled Monolayers of Alkanethiols Adsorbed on Au(111)

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Desorption process of octadecanethiol self-assembled monolayers (SAMs) on Au(111) was investigated by thermal desorption spectroscopy (TDS). TD spectra for several desorption species including decomposition fragments of the adsorbed molecules were observed at an elevated temperature. Scanning tunneling microscopy (STM) study shows that decomposition in SAMs is strongly related to striped phase formed via phase transition caused by desorption of molecules from densely packed monolayers.

Keywords: alkanethiol; self-assembled monolayers; striped phase; scanning tunneling microscopy; thermal desorption spectroscopy

INTRODUCTION

Alkanethiol SAMs on metal surfaces have served as a model system for fundamental studies as well as potential applications[1,2]. It is revealed that alkanthiols on gold form well-ordered and close-packed monolayers in addition to highly stable monolayers resulting from the formation of chemical bond between sulfur atoms of alkanethiols and gold substrate. For potential technical applications, it is essential to understand the thermal stability and the interactions between sulfur atoms and gold in alkanethiol SAMs. In this work, we have examined adsorptoin states and desorption process of monolayers by combining TDS with STM.

Here we discuss such problems with a molecular-scale feature as well as through the direct observation of desorption species.

EXPERIMENTAL

Au(111)/mica substrates were prepared by vacuum deposition as reported elsewhere[3]. The full-covered SAMs were obtained by exposing the gold substrates into a freshly prepared 1 mM ethanol solution of octadecanethiol ($C_{18}H_{37}SH$, ODT) for 1 day. TDS measurements were performed under high vacuum conditions of ~10^{-10} Torr with a multiple mass spectrometer at a heating rate of 1 K/s, and STM images were acquired in air using constant current mode.

RESULTS AND DISCUSSION

TDS measurements are very powerful to get information about the molecule-molecule and molecule-substrate interactions on solid interfaces. We measured TD spectra for the ODT SAMs on Au(111) to understand the interactions as well as the mechanism of molecular decomposition. Figure 1 shows TD spectra observed at various m/e of ODT SAMs. Here the m/e = 286, 287, 571, and 253 amu correspond to C18S$^+$, C18SH$^+$, $(C18S)_2^+$, and C18$^+$, respectively. TD spectrum for C18S$^+$ in Fig. 1A exhibits two desorption peaks at 115 ◫ and 182 ◫. The peak showing the most strong intensity appeared at 182 ◫ originates from desorption of molecules chemisorbed on gold surface. On the other hand, the low intensity peak at 115 ◫ is

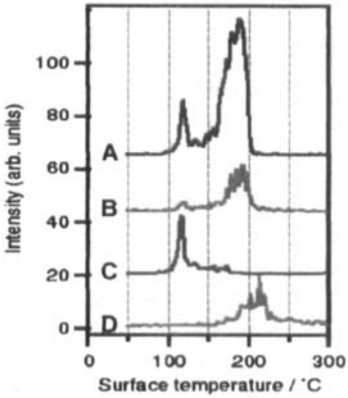

FIGURE 1 Themal desorption spectra of ODT SAMs: The m/e are (A) 286, (B) 287, (C) 571, and (D) 253, respectively.

attributed to the doubly ionization of dimer molecules ($C_{18}H_{37}SSC_{18}H_{37}$) because the peak position is the same as that of desorption of dimer molecules as shown in Fig. 1C. The position for desorption peak of C18SH$^+$ in Fig. 1B is a slightly higher temperature region compared to that of C18S$^+$. The origin and retardation of this peak can be explained by two reasons. One may be caused by hydrogen-abstraction reaction of octadecanethiolates from the walls inside chamber[5]. Another possibility can be ascribed to surface hydrogenation of octadecanethiolates. Actually, chemical reactions between alkanethiols and gold surface during the monolayer formation yield hydrogen atoms, which can be readily adsorb into the first, second, or third gold layers. Therefore octadecanethiolates can react with hydrogen atoms during desorption. This conjecture can be supported by our recent result that desortion peak for shorter alkyl chain thiols (i.e., for propanethiol SAMs) shows very broad compared to that for longer alkyl chain thiols (not shown here). This result implies the role of surface diffusion process to form alkanethiols (RSH) via reaction between alkanethiolates and hydrogen atoms on a gold surface.

The origin of dimer peak in Fig. 1C is due to associative desorption of octadecanethiolates as the case of hexanethiol SAMs[4]. Interestingly, we newly observed decomposition fragments formed after bond rupture of C18-S molecules on gold surface under UHV conditions (Fig. 1D). This decomposition process occurs ranging from 185 □ to 220 □. Previous studies have pointed out that this process depends on whether the monolayer is annealed in vacuum, or in air. It was suggested that annealing in vacuum results in desorption of adsorbed molecules, whereas annealing in air results in decomposition on the surface. In contrast to the previous suggestion, we obtained the new evidence for molecular decomposition by monitoring molecular species desorbing from the surface under UHV conditions.

To reveal decomposition pathway of the monolayer with a real-space molecular image at an elevated temperature, the heat of ODT SAM sample under UHV conditions was stopped at 200 □ when the decomposition proceeds. After cooling down to room temperature, STM imaging for this sample was performed in air. STM image in Fig. 2 shows various molecular phases on the surface. The small portion of bright areas (A region) which can be assigned to the close-packed monolayers were found. This would be expected since a number of molecules adsorbed on gold desorbed as shown in TDS spectra. The desorption of molecules gives rise to phase transition from the close-packed phase to disordered phase (region B) and striped phase (region C), followed by the complete desorption of molecules on the surface (region D). STM image shows clearly striped phase appeared as dominant structure of the monolayer. Corrugation period in the striped phase is 2.67 nm, which is nearly consistent with the length of the fully extended octadecanethiol molecule. This result suggests that molecular decomposition associated with bond cleavage between alkyl group and sulfur atom have relation to the formation of striped phase. The molecules where the molecular axes are parallel to surface in striped phase can be easily decomposed because the absorption energy per molecule is much higher than that in upright phase.

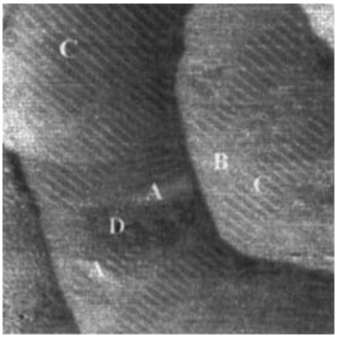

FIGURE 2 STM image exhibiting striped phase of ODT SAMs on Au(111): 100 nm × 100 nm, V_b = 0.45 V, and I_t = 0.15 nA.

In conclusion, we confirmed decomposition of the monolayer, when the monolayer was annealed under UHV conditions, contrary to the previous suggestion. In addition, it is assumed that molecular decomposition takes place primarily from molecules in striped phase.

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