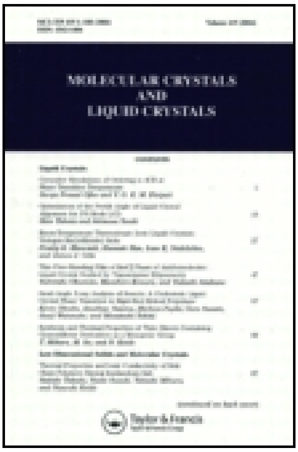

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Structural Study of Dialkyl Sulfide Self-Assembled Monolayers on Au(111)

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Dialkyl sulfide self-assembled monolayers on gold were characterized by Fourier transform infrared reflective absorption spectroscopy (FTIR-RAS) and scanning tunneling microscopy (STM). It was found that dialkyl sulfide SAMs have quite different surface characteristics compared to alkanethiol SAMs. Our STM result clearly elucidated that dialkyl sulfide SAMs are composed of the liquid-like disorder phase with many small nucleations, not the ordered phase.

Keywords: alkanethiol; dialkyl sulfide; self-assembled monolayers; scanning tunneling microscopy; Fourier transform infrared spectroscopy

INTRODUCTION

Self-assembled monolayers (SAMs) prepared by organosulfur molecules on gold have attracted considerable attention because they can provide powerful means for technical applications due to their high structural order and easy control of the surface properties[1-4]. It has been revealed that alkanethiol and dialkyl disulfide SAMs on gold have similar surface characteristics such as molecular structure and adsorption condition of sulfur headgroups. However, dialkyl sulfide SAMs showed significantly different monolayer properties such as less dense packing, order, and lower film thickness than those prepared from alkanethiols and dialkyl disulfides. It is assumed that such surface characteristics result from different adsorption processes of the mono-sulfides[5,6]. As a matter of fact, a better understanding of SAM structure enables us to examine new physical phenomena and technologies. Herein, in order to understand dialkyl sulfide SAMs in more detail, we have investigated and compared surface structure of alkanethiol and dilakyl sulfide SAMs by FTIR-RAS and STM.

EXPERIMENTAL

The Au(111) substrates were prepared by thermal deposition of gold onto freshly cleaved mica surface as reported in previous papers[5,6]. The SAMs were prepared by dipping the gold substrates in freshly prepared 1 mM ethanol solutions of octanethiol ($CH_3(CH_2)_7SH$, OT) and dioctyl sulfide ($(CH_3(CH_2)_7)_2S$, DOS) for 1 day. Infrared measurements were carried out by FTIR-RAS equipped with a mercury-cadmium telluride detector under dry N_2 atmosphere. P-polarized incident angle was 80° from the surface normal. The nominal spectral resolution was 4 cm^{-1} and several hundred scans were accumulated for acceptable signal to noise ratio. All STM images were obtained in air using constant current mode.

RESULTS AND DISCUSSION

It is well known that IR spectrum can provide useful information about chain conformation, orientation, and packing of organic monolayers on solid surfaces. Figure 1 shows the IR spectra for (a) OT SAMs and (b) DOS SAMs on gold in the CH stretching region. It is generally believed that alkanethiols form well-ordered and closely packed SAMs[1-3]. Fig. 1(a) for OT SAMs shows a typical example for IR spectra of alkanethiol SAMs with high structural degree as shown in Figs. 2(a) and (b). The band at 2964 cm^{-1} assigned to the CH_3 asymmetric in-plane CH stretching mode, $\nu_a(CH_3, ip)$, and the band at 2936 and 2878 cm^{-1} are assigned to the CH_3 symmetric CH stretching mode, $\nu_s(CH_3, FR)$, which is split due to Fermi resonance interactions with the lower frequency asymmetric CH_3 deformation mode[7]. The bands at 2922 and 2853 cm^{-1} are assigned to the CH_2 asymmetric and symmetric CH_2 stretching mode, $\nu_a(CH_2)$ and $\nu_s(CH_2)$, respectively.

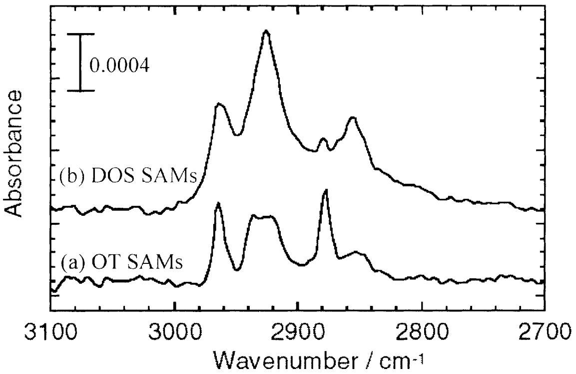

FIGURE 1 FTIR-RAS spectra of (a) OT and (b) DOS SAMs on gold.

However, IR spectra for DOS SAMs exhibit a significant difference compared to those for OT SAMs, which strongly indicates a remarkable change in molecular order. The $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands at 2926 and 2856 cm^{-1} are predominant and these band positions are typically related to a fluid or disordered structure for the monolayer[8]. The absence of $\nu_s(CH_3)$ split by Fermi resonance may be considered as an qualitative indication of structural disorder within this monolayer.

To understand the SAM characteristics from the nanoscopic viewpoint, we have examined and compared the surface structures of both OT SAMs and DOS SAMs by STM. The STM images in Figs. 2(a) and (b) show surface structure for OT SAMs on Au(111). Figure 2(a) presents uniform surface having well-ordered domains, domain boundaries, and vacancy islands with the monatomic step height of 2.5 Å. High-resolution STM image in Fig. 2(b) shows well-ordered and

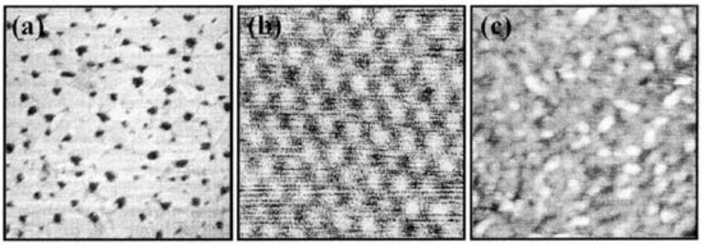

FIGURE 2 STM images of (a and b) OT and (c) DOS SAMs obtained after 1 day immersion. Scan sizes were (a) 75 nm × 75 nm, (b) 4 nm × 4 nm, and (c) 75 nm × 75 nm, respectively.

densely packed monolayer, which is described as a hexagonal (√3 × √3)R30° structure[2]. However, as shown in Fig. 2(c), the DOS SAMs have completely different surface structure. We could not observe ordered domains and vacancy islands in the SAMs, unlike the case of alkanethiol SAMs. The DOS SAMs are composed of disorder phase with many small nucleations with a size of approximately 5 nm, which are likely due to aggregation of DOS molecules on Au(111) surface. Regarding the existence of disorder structure for dialkyl sulfide SAMs, this STM result is consistent with the FTIR-RAS result. As revealed by our recent work[6], such a remarkable structural difference in both SAMs is attributed to a nondissociative adsorption without the C–S bond cleavage of dilakyl sulfide during the self-assembly process, contrary to the S–H bond cleavage of alkanethiol. A poor structural integrity in dialkyl SAMs formed via a nondissociative process may result from large steric repulsion between two alkyl groups attached to the single sulfur atom during two-dimensional ordering process of SAMs.

We have demonstrated that the SAM characteristics prepared by dialkyl sulfides on gold are quite different from those prepared by alkanethiols. Our STM result clearly revealed that the unusual SAM properties of dialkyl sulfide are mainly due to the liquid-like disorder phase with many small nucleations. We believe that this result will be helpful in fabrication and design of molecular devices based on organosulfur SAMs on metal surfaces.

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