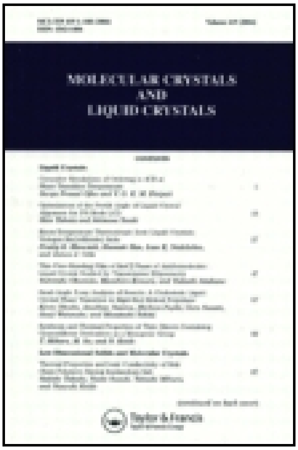

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Studies on the Adsorbed States of Alkanethiol Self-Assembled Monolayers on Au(111) by Thermal Desorption Spectroscopy

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Desorption of octadecanethiol self-assembled monolayers (SAMs) on gold was investigated by thermal desorption spectroscopy (TDS). The TDS study shows that there exist some different adsorbed states, such as monomer and dimer, and the dimerization processes also play a very important role during the SAM formation and desorption.

Keywords: self-assembled monolayer; thermal desorption spectroscopy; oxidation; dimerization; $p \times \sqrt{3}$ striped phase

INTRODUCTION

Self-assembled monolayers (SAMs) have been a subject of numerous studies for over a decade, based on interests in fundamental issues of surface science as well as in the technological significance of application such as sensor, patterning, surface reactions, and molecular recognition on the surface[1]. In particular, SAMs of thiol derivatives have been extensively studied because of their high stability, easy preparation and possibility for potential application by introducing various functional groups at the terminal positions of monolayers[2]. However, the adsorbed state of thiol molecules on gold is still under discussion although many studies have been conducted since dimer model was proposed by Fenter *et al.*[3] More recently, some people showed the existence of dimer molecules from SAMs adsorbed on gold using various spectroscopies like UV, FTIR, and thermal desorption spectroscopy (TDS),[4] though there is no crucial progress for this model for a few years. Therefore, this dimer model has turned up as an important issue again in this area.

In this study, we examined the adsorbed states of alkanethiol SAMs using TDS, and discussed the behaviors of thiol molecules on gold during the desorption process.

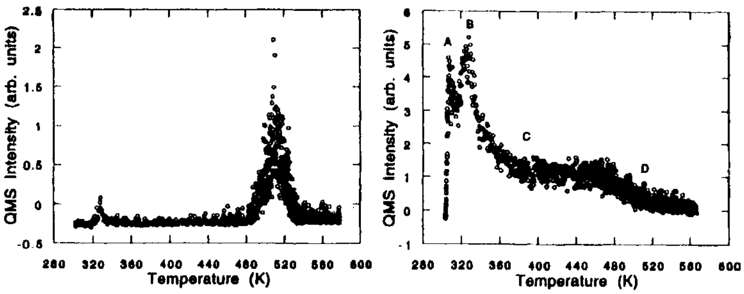
EXPERIMENTAL

The gold substrates were acquired by the thermal evaporation of gold onto freshly cleaved mica sheets as previously reported procedures[2]. Monolayers were formed by immersing the gold substrates into a 1 mM ethanol solution of octadecanethiol ($CH_3(CH_2)_{17}SH$: ODT) for 2 h immediately after the gold evaporation.

The TDS experiment was carried out in an ultrahigh vacuum chamber under 10^{-9} Torr equipped with a quadrupole mass spectrometer (QMS, Balzers QMG511). TDS spectrum was obtained from a signal of the QMS at a fixed mass to charge ratio (m/e) during the linear heating of gold surface.

RESULTS AND DISCUSSION

Fig. 1 shows the thermal desorption spectra of ODT SAMs, which were prepared by dipping the gold substrates into a freshly prepared 1 mM ODT solution for 2 h. The thermal desorption spectrum shown in Fig. 1A was recorded at an m/e of 570 corresponding to a singly ionized dioctadecyl disulfide (dimer), and it exhibits two thermal desorption peaks showing different intensity ratio of two peaks when compared to the previous report[5] at 327 K (D_{low}) and 510 K (D_{high}). Firstly, the plausible explanation for the origin of peak D_{low} is due to the insertion of dimer molecules of very few amounts existing as impurities from the 1 mM ODT solution, or that of dimers formed by oxidation of thiol monomers into SAMs during SAM



(A) (B)

FIGURE 1 Thermal desorption spectra of an octadecanethiol SAMs: (A) at a m/e of 570, (B) at a m/e of 286.

formation because the thiol molecules can be dimerized from thiol monomers by oxidation in air or thiol solution even if careful purification is performed and the purity is confirmed by mass spectrometer associatively. Secondly, the peak D_{high} can be assigned to the dimerized desorption of chemisorbed alkanethiolate molecules in alkanethiol SAMs. The dimerization of chemisorbed alkanethiolate molecules should be strongly related to the $p \times \sqrt{3}$ striped phase of SAMs because this structure was usually observed in the low coverage region formed after the thermal desorption of thiol molecules at high temperature, and also shown in the arrangements of head to head (sulfur-sulfur) like dimers[6]. A reason for relation between dimerization and the SAM structure is to have a critical energy point (482 K in Fig. 1A) for the dimer desorption. This implies that there formed a very stable SAM structure which is $p \times \sqrt{3}$ striped phase during the thermal desorption. However it is still not clear whether this striped phase is composed of monomers or dimers.

The very interesting thermal desorption spectrum as shown in Fig. 1B was obtained at an m/e of 286 corresponding to a dehydrogenated singlely ionized octadecyl sulfide, $CH_3(CH_2)_{17}S^+$. This spectrum indicates that there are several different adsorbed states in the monolayer on gold. The peak A at 315 K can be assigned to the thermal desorption peak derived from C18SH species which consist in as multilayer or insertion in the monolayer, because we could find a sharp thermal desorption peak of these molecules at around 318 K (not reported here). The peak B corresponds to the doubly ionized peak of dimer molecules (dimer^{++}). In our previous TDS study, the origin of this peak was well explained[5]. As the surface temperature increased, the chemisorbed thiol molecules in close-packed regions were desorbed from gold surface until the surface was fully covered by $p \times \sqrt{3}$ striped phase indicated as C region. Surface behaviors in this similar temperature region were easily inferred on the basis of STM result,[6] which also shows a very good agreement with our TDS results. In the D region, the peak intensity steeply decreased with increasing of surface temperature. This is mainly due to a sudden decrease of the total number of desorbing molecules by the desorption of dimer molecules through dimerization from gold surface.

Conclusively, the TDS study showed the behaviors of thiol molecules on gold during desorption process, and the dimerization was also strongly related to the SAM formation and desorption process.

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