Solvent Effect on the Structure of the Self-Assembled Monolayer of Alkanethiol

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Structures of self-assembled monolayer (SAM) of decanethiol on Au(111) surface prepared in ethanol, toluene, DMF and heptane solution were examined by scanning tunneling microscopy (STM) and electrochemical reductive desorption measurement in 0.5 M KOH aqueous solution. While no significant difference was detected in the reductive desorption measurement except for the SAM prepared in heptane, the STM observation showed that domain size and pit size were strongly affected by solvent.

Self-assembled monolayers (SAMs) of alkanethiols on gold surface have attracted many researchers because they provide an excellent way to control surface properties in molecular level. The SAMs are known to be formed as a result of the chemical bond formation between gold atoms and sulfur atoms of the molecule and the van der Waals interaction between alkylchains. The structure of the SAM of alkanethiol on Au(111) has been studied by various techniques[1] and it is known that the molecules arrange in $(\sqrt{3}\times\sqrt{3})R30^\circ$ or $c(4\sqrt{3}\times2\sqrt{3})$ structure with the tilt angle of 30° from the surface normal. The scanning tunneling microscopy (STM) investigation showed that there were pit-like defects on the SAMs of alkanethiol.[2] These pit-like defects were revealed to be vacancy islands (VIs) of gold atoms, which are considered to be formed as a result of chemical etching[3] and/or squeezing out of gold atoms initiated by adsorption of alkanethiol.[4] In addition, missing-row-defects, i. e., orientational and translational domain boundary, running between the pits were observed.

It is essential to construct a defectless SAM to use the SAM for practical applications. To obtain fundamental information, we have studied the self-assembly process of alkanethiols in solution by *in situ* STM observations.[5] These results suggest that surface diffusion of alkanethiols plays important roles in the self-assembly process. Thus, solvent is expected to affect the structure of the SAMs. In addition, if the etching process of gold occurs, the polarity of the solvent should affect the density and shape of VIs of gold surface. In most studies, however, ethanol is used as solvent in modification and the solvent effect on microscopic features of the SAMs has not been studied well while there are several reports on the macroscopic featuers.[6]

In this letter, we carried out STM examinations and electrochemical reductive desorption (RD) measurements of the SAM of decanethiol ($CH_3(CH_2)_9SH$: $C_{10}SH$) prepared in ethanol, toluene, DMF and heptane.

All chemicals were purchased from Wako Pure Chemicals and used without further purification. Gold thin films (thickness : 100 nm) prepared by vacuum evaporation onto mica which was kept at 300 °C during evaporation at 0.1 Å/s were used for STM observation. Electrochemical measurements were carried out with an Au(111) electrode made by the Clavilier's method[7] with hanging meniscus technique in a 0.5 M KOH aqueous solution. The electrode potential is referred to Ag/AgCl. Modification of the gold substrate for both STM and RD measurements was carried out by immersing the substrate into 10 μM $C_{10}SH$ solution for 1 h. The surface were rinsed with the pure liquid of the solvent used in the modification and, then, dried with Ar gas.

Figure 1a shows an STM image of a gold substrate which was modified in 10 μM $C_{10}SH$ ethanol solution. Flat regions corresponding to the SAM layer with the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure and many pits of 0.25 nm deep corresponding to VIs of gold surface were observed as reported before.[2] Figures 1b and c show STM images of the Au(111) substrate after the modification in DMF and toluene solution containing 10 μM $C_{10}SH$, respectively. The gold surface again showed the existence of the monolayer with pits of ca. 0.25 nm deep. When the modification was carried out in DMF (Figure 1b), the pits were tend to be connected each other and the density of the missing-row-defect was very low, resulting in very large domains. The area of each pit seemed to be larger and missing-row-defects running between the pits were seen when the SAM was prepared in toluene (Figure 1c). The magnified STM images of the Au(111) surface covered with SAM prepared in DMF and toluene also revealed the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure as shown in Figure 2a. The same molecular arrangement was imaged inside the pits, indicating the pits were the VIs of gold surface as was the case obtained in ethanol.

The structure of the $C_{10}SH$ SAM prepared in heptane was quite different from the ones prepared in ethanol, DMF and toluene as shown in Figure 1d. There were no clear flat regions on the gold surface while pits existed and a magnified STM image showed no ordered structure (Figure 2b). These results

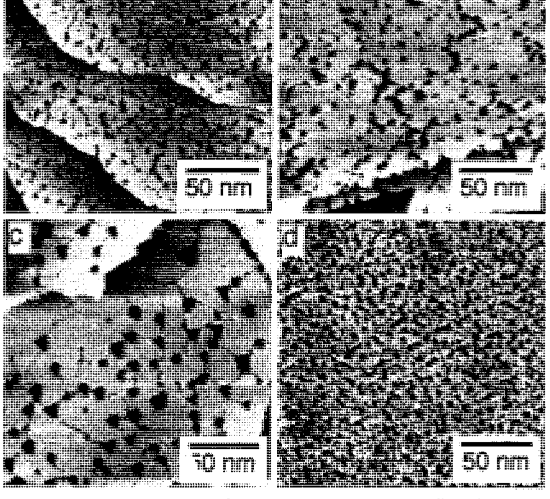

Figure 1. STM images of Au(111) surface modified in 10 μM solution in (a) ethanol , (b) DMF, (c) toluene and (d) heptane for 1 h.

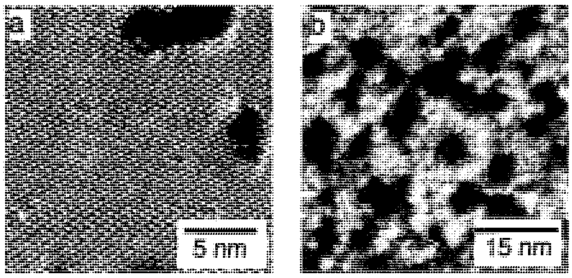

Figure 2. STM images of Au(111) surface modified in 10 μM solution in (a) toluene and (b) heptane for 1 h.

were in contrast to our recent reports of *in situ* STM observation of the formation process of the SAM in heptane where the formation of the island leading to the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure was observed.[5] The islands observed *in situ* was obscure in many cases indicating that the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure is not firmly formed in heptane. Thus, when the solvent is removed, the fragile islands were destroyed and disordered phase, which was observed in *ex situ* observation, was formed.

The quantitative analysis of the domain and pit sizes were carried out as summarized in Table 1.[8] The averaged domain size of the SAM prepared in DMF was very large as mentioned before. The domain size of the SAM prepared in toluene, where the domain boundary was clearly defined, was 7 times as large as that of the SAM prepared in ethanol. The fraction of the integrated pit area to the total surface area was, however, almost uniform regardless of the solvent, although the averaged pit size was dependent on the solvent. This result indicates that the dependence of the pit size on solvent arises from the difference in the rate of migration process of gold atoms.[9] Although Edinger et. al reported that the density and averaged size of the pits were low and small, respectively when modification was carried out in hexane for 24 h compared to the SAM prepared in ethanol,[10] we were not able to reproduce their results.[11]

Figure 3 shows cyclic voltammograms of the gold electrode covered with the C_{10}SH SAM prepared in (a) ethanol, (b) DMF, (c) toluene and (d) heptane. A sharp cathodic current peak was observed around -1.0 V at all electrodes except for the electrode modified in heptane which gave the peak at more positive potential. These peaks were attributed to the reductive desorption of C_{10}SH SAM.[12] It is interesting to note that the structural difference observed by STM does not affect the desorption behavior. It seems to be reasonable to attribute the positively shifted current peak seen in Figure 3d to the desorption of the molecules in the disordered phase which was observed in the STM examination and therefore, the results of the RD measurement are consistent with the STM examination.

In conclusion, we have shown that solvent used for modification affects the structure/order of the SAMs such as sizes of the domains and pits. The RD measurement was not sensitive to such differences. The fraction of the integrated area of pits to the surface area was uniform regardless of the solvent.

Table 1. Size of domains and pits estimated from STM images.

Solvent	Domain Size / nm^2	Pit		
		Size / nm^2	σ[a] / nm^2	Fraction[b] / %
Ethanol	250	25	26	14
DMF	> 5000	42	56	12
Toluene	1700	55	42	12
Heptane	-	25	27	15

[a] Standard deviation of the pit size.
[b] Ratio of the integrated pit area to the total surface area.

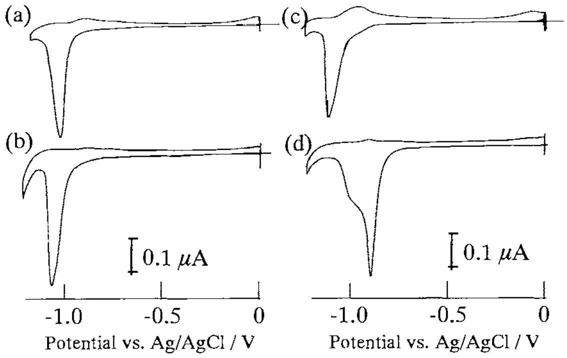

Figure 3. Cyclic voltammograms of Au(111) electrode obtained in 0.5 M KOH aqueous solution at 10 mVs^{-1}. Gold electrode was modified with C_{10}SH in (a) ethanol, (b) DMF, (c) toluene and (d) heptane solution.

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