

## Adsorption of Cationic Surfactants on Hydrogen-Terminated Si(111) Surfaces Studied by In-situ Atomic Force Microscopy

A. Imanishi<sup>1</sup>, M. Suzuki<sup>1</sup>, and Y. Nakato<sup>\*1,2</sup>

<sup>1</sup> Division of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, 560-8531, Japan

<sup>2</sup> Core Research for Evolutional Science and Technology (CREST), JST  
Fax: +81-6-6850-6236 e-mail: nakato@chem.es.osaka-u.ac.jp

The adsorption of cationic surfactants dissolved in aqueous solutions on atomically-flat H-terminated Si(111) surfaces with a hydrophobic property was investigated by in-situ atomic force microscopy (AFM). The AFM inspection showed that dodecyltrimethylammonium chloride ( $C_{12}TAC$ ) formed the most smooth and flat adsorption layer on the Si surface, most probably with the alkyl chain assembled nearly normal to the Si surface. For  $1.0 \times 10^{-6}$  M octadecyltrimethylammonium chloride ( $C_{18}TAC$ ) and dioctadecyldimethylammonium chloride (2- $C_{18}DAC$ ), troughs were formed in the adsorption layer along crystal steps of the Si surface, suggesting that surfactants were not adsorbed at the Si steps.

Key words: hydrogen-terminated, Si, surfactant, hydrophobic, in-situ AFM

### INTRODUCTION

Surfactant molecules adsorbed on solid surfaces in aqueous solutions have attracted much attention in the field of colloid and surface chemistry because of their interesting physical and chemical properties. Especially, self assembled monolayers (SAMs) have a dense and stable structure and have potential applications to corrosion prevention, wear protection, etc. In addition, biomimetic or biocompatible nature of the SAMs is of great interest in view of application to chemical and biochemical sensors.

Surfactants adsorbed at solid/liquid interfaces have been widely studied. For most studies, cleaved surfaces of layered materials such as mica [1-8] and graphite [2,9-13] were used in addition to silica surfaces [1,2,5,13]. Recently, it has been established that etching with hydrogen fluoride (HF) and 40 % aqueous ammonium fluoride ( $NH_4F$ ) produce a nearly atomically flat and H-terminated Si(111) surface with a well-defined step and terrace structure [14-22]. The surface is stable in aqueous solutions and has a hydrophobic property. Thus, this surface is also quite appropriate for study of adsorption behavior and surface morphology of surfactants. The Si surface has an advantage in that we can see the effect of surface crystal steps on the structure of adsorption layers. We can also change the geometrical structure and hydrophobic property of the Si surface by modification with chemically attached alkyl groups.

In the present paper, we report the structure of adsorption layers of cationic surfactants with various alkyl chains, formed on the H-terminated Si(111) surfaces. In-situ atomic force microscopy (AFM) was successfully applied to the structural investigations of the adsorption layers.

### EXPERIMENTAL

Single crystal wafers of n-type Si(111) of a resistivity of 10-15  $\Omega$ cm with a vicinal surface tilting in the

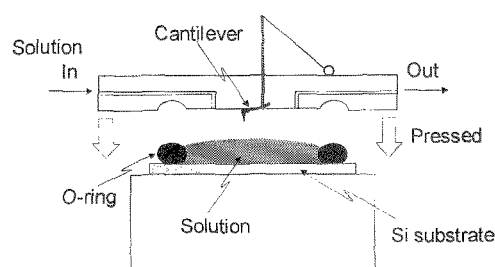


Fig. 1 Schematic illustration of a cell for in-situ AFM measurements. The seal for the liquid was provided by a Teflon O-ring and a circular groove of the pressed part of the cell. A surfactant solution was injected into the cell via in- and out-ports.

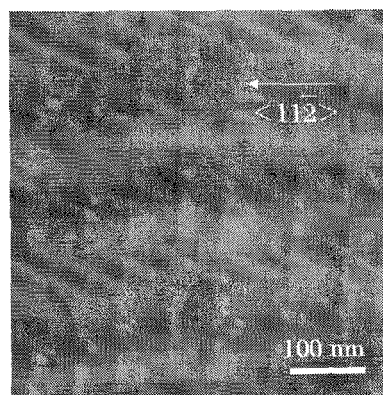


Fig. 2 In-situ AFM image of a vicinal H-Si(111) surface tilting in the  $\langle 11\bar{2} \rangle$  direction at an angle of  $0.36 \pm 0.1^\circ$ , located in pure water.

$\langle 11\bar{2} \rangle$  direction at about  $0.36 \pm 0.1^\circ$  were obtained from Osaka Tokushu Gokin Co. Ltd., Japan. They were

cut into a square shape with a dimension of  $10 \times 10 \text{ mm}^2$ , and then cleaned by the conventional RCA cleaning method, consisting of successive immersion in 98 %  $\text{H}_2\text{SO}_4 + 30 \text{ % } \text{H}_2\text{O}_2$  (4:1 in volume) for 10 min, 5 % HF for 5 min, 25 %  $\text{NH}_4\text{OH} + 30 \text{ % } \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  (1:1:5 in volume) for 10 min, and 36 % HCl + 30 %  $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$  (1:1:6 in volume) for 10 min. The wafers were then etched with 5% HF for 5 min and 40%  $\text{NH}_4\text{F}$  for 15 min to obtain atomically-flat, H-terminated Si(111) surfaces. Cationic surfactants used were dodecyltrimethylammonium chloride ( $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Cl}$ ), hereafter abbreviated as  $\text{C}_{12}\text{TAC}$ , octadecyltrimethylammonium chloride ( $\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3\text{Cl}$ ), abbreviated as  $\text{C}_{18}\text{TAC}$ , and dioctadecyldimethylammonium chloride ( $(\text{CH}_3(\text{CH}_2)_{17})_2\text{N}(\text{CH}_3)_2\text{Cl}$ ), abbreviated as 2- $\text{C}_{18}\text{DAC}$ . They were obtained from Kao Co. Ltd.

In situ observation of surface morphology was made with an atomic force microscope (NanoScope IIIa, Digital Instruments, USA) at room temperature. A sharpened silicon nitride tip (Digital Instruments, USA) and a cantilever having a spring constant 0.06 N/m, coupled with a  $10 \mu\text{m}$  scanner, were used. All AFM images were taken in a tapping mode with a tapping frequency of about 8 kHz at a scan rate of 1~2 Hz. The force between the tip and sample was 0.026 nN, which was probably small enough for observation of physisorbed surfactants in aqueous solution without affecting their structures. An in-situ AFM cell used is schematically shown in Figure 1. Adsorbed layers of surfactants were formed on the Si surface in the AFM cell, by introducing surfactant solutions into the cell through in- and out ports. Before the surfactant solution was introduced, pure water was first injected in the cell and the H-Si(111) surface with no adsorption layer was inspected. Special-grade chemicals were used without further purification. Pure water was obtained by purifying deionized water with a Milli-Q water purification system.

## RESULTS & DISCUSSION

Figure 2 shows an in-situ AFM image of an HF- and  $\text{NH}_4\text{F}$ -etched Si(111) surface located in pure water. Parallel lines seen in the image represent a step structure of the Si(111) surface, indicating that a nearly atomically-flat and H-terminated Si(111) surface was produced by the etching. This conclusion was confirmed also by the fact that the FTIR spectrum of the Si(111) surface, obtained by the multiple internal reflection method, showed a strong sharp peak at  $2083.6 \text{ cm}^{-1}$ , assigned to the stretching mode of Si-H bonds at a terrace, together with some weak peaks assigned to SiH or  $\text{SiH}_2$  bonds at steps, as reported in previous papers [23,24].

Figure 3 shows in-situ AFM images of the H-Si(111) surfaces immersed in aqueous solutions of (a)  $1.0 \times 10^{-6} \text{ M}$  and (b)  $1.0 \times 10^{-4} \text{ M}$   $\text{C}_{12}\text{TAC}$  for 120 min. Note that both solutions contained isopropanol, included as a contamination in  $\text{C}_{12}\text{TAC}$  itself. The concentration of isopropanol was  $4.0 \times 10^{-6} \text{ M}$  for (a) and  $4.0 \times 10^{-4} \text{ M}$  for (b). For the  $1.0 \times 10^{-6} \text{ M}$   $\text{C}_{12}\text{TAC}$  solution (a), the surfactant adsorption was not uniform. The average thickness of the surface unevenness was 2.0 nm and comparable to the alkyl chain length of  $\text{C}_{12}\text{TAC}$ , which might suggest that the alkyl chains of adsorbed

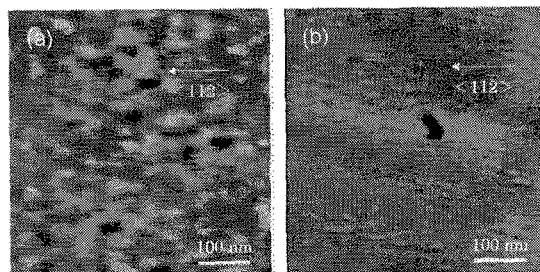


Fig. 3 In-situ AFM image of an H-Si(111) surface in contact with an aqueous solution that contains in (a)  $1.0 \times 10^{-6} \text{ M}$  and (b)  $1.0 \times 10^{-4} \text{ M}$   $\text{C}_{12}\text{TAC}$ . The solution also contains isopropanol at the concentration of  $4.0 \times 10^{-6} \text{ M}$  in (a) and  $4.0 \times 10^{-4} \text{ M}$  of (b).

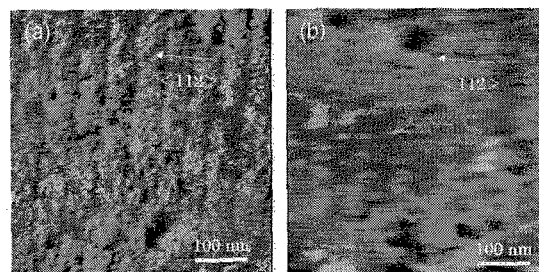


Fig. 4 In-situ AFM image of an H-Si(111) surface in contact with an aqueous solution that contains (a)  $1.0 \times 10^{-6} \text{ M}$  and (b)  $1.0 \times 10^{-4} \text{ M}$   $\text{C}_{18}\text{TAC}$ .

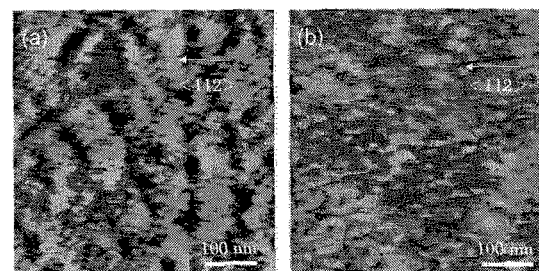


Fig. 5 In-situ AFM image of an H-Si(111) surface in contact with an aqueous solution that contains (a)  $1.0 \times 10^{-6} \text{ M}$  and (b)  $1.0 \times 10^{-4} \text{ M}$  2- $\text{C}_{18}\text{DAC}$ . The solution also contains isopropanol at the concentration of  $2.0 \times 10^{-6} \text{ M}$  in (a) and  $2.0 \times 10^{-4} \text{ M}$  of (b).

surfactant assembled fairly normal to the Si surface, with the cation headgroup pointed away from the surface. For the  $1.0 \times 10^{-4} \text{ M}$   $\text{C}_{12}\text{TAC}$  solution (b), on the contrary, a very flat adsorption layer was obtained. We can see that the topography of the surfactant covered surface in (b) resembles that of the naked H-Si(111) surface in Fig. 2. It is evident that straight lines normal to the  $\langle 11\bar{2} \rangle$  direction observed in (b) are originating from the step structure of the underlying Si surface. Additionally, the thickness of the surfactant layer, estimated from the depth of a pit accidentally formed in Fig. 3(b), was nearly the same as the alkyl chain length of  $\text{C}_{12}\text{TAC}$ . These results lead to conclude that a fairly ideal SAM was formed on the Si surface in this case, though further detailed studies are needed, including those by use of other methods, to get a definite conclusion.

Figure 4 shows in-situ AFM images of the H-Si(111) surface immersed in aqueous solutions of (a)

$1.0 \times 10^{-6}$  M and (b)  $1.0 \times 10^{-4}$  M  $C_{18}$ TAC for 120 min. For both solutions, the surface was rather uneven. The depth of pits observed for  $1.0 \times 10^{-6}$  M  $C_{18}$ TAC (a) was about 3.0 nm, which was nearly the same as the alkyl chain length for  $C_{18}$ TAC. The depth of straight troughs observed in (a) was about 2.5–3.0 nm, which was also nearly the same as the alkyl chain length. For  $1.0 \times 10^{-4}$  M  $C_{18}$ TAC, the troughs disappeared, though pits were observed here and there.

Figure 5 shows AFM images of the H-Si(111) surface immersed in aqueous solutions of (a)  $1.0 \times 10^{-6}$  M and (b)  $1.0 \times 10^{-4}$  M 2- $C_{18}$ DAC for 120 min. Both solutions contained isopropanol, included as a contamination in 2- $C_{18}$ DAC itself. The concentration of isopropanol was  $2.0 \times 10^{-6}$  M for (a) and  $2.0 \times 10^{-4}$  M for (b). The adsorption layers for these solutions were also not even, similar to the case of  $C_{18}$ TAC in Fig. 4. The thickness of the unevenness in (a) was comparable with the alkyl chain length for 2- $C_{18}$ DAC, suggesting that surfactant molecules were assembling fairly normal to the Si surface. However, the troughs observed in (a) were not straight in shape, contrary to the case of Fig. 4(a) and their width was larger than the case of Fig. 4(a). For the  $1.0 \times 10^{-4}$  M 2- $C_{18}$ DAC solution, the troughs disappeared, similarly to the case of Fig. 4.

How can these results be explained?  $C_{18}$ TAC and 2- $C_{18}$ DAC have alkyl chains of the same length, though the number of the alkyl chains is different from each other.  $C_{12}$ TAC has an alkyl chain much shorter than  $C_{18}$ TAC and 2- $C_{18}$ DAC. Accordingly, we can expect from the reported behavior of surfactants in homogeneous solutions such as micelle and vesicle formation that the best organized adsorption layer is formed for 2- $C_{18}$ DAC and the second best is formed for  $C_{18}$ TAC. However, the present experimental results are inverse to this expectation. The best organized adsorption layer is formed for  $C_{12}$ TAC. This result may be explained by taking into account that the degree of freedom for the movement of the alkyl chain at the adsorption layer on the Si surface is largest for  $C_{12}$ TAC owing to the shortest length of the alkyl chain. We should note also that the  $C_{12}$ TAC solution contains isopropanol. Isopropanol may be dissolved in the adsorption layer of  $C_{12}$ TAC on the Si surface, and play a role in softening of the layer. This induces an increase in the degree of freedom for the movement of surfactants, resulting in a smooth and flat surfactant layer. A few studies in the effect of alcohol on the surfactant layer are reported in the past [6,9]. Wanless *et al.* investigated the adsorption of sodium dodecyl sulfate (SDS) on a graphite surface in aqueous solution. They reported that in a solution of pure SDS, SDS molecules are associated into the form of long, parallel hemicylindrical aggregates, resulting in a hemi-micelle on the graphite surface. On the other hand, when 0.05–0.5 mM dodecanol was added to the solution, the curvature of the hemi-micelles decreased and the area of flat surfaces increased. The effect of addition of alcohols to surfactant solutions is an interesting subject in the future.

## CONCLUSION

The formation of SAMs of cationic surfactants on atomically flat H-terminated Si(111) surfaces of a

hydrophobic property in aqueous solutions was investigated by in-situ AFM inspection. It was revealed that all surfactants formed an adsorption monolayer on the Si surface, most probably with the alkyl chains assembled fairly normal to the surface. Troughs, arising from Si steps, were observed in the case of  $1.0 \times 10^{-6}$  M  $C_{18}$ TAC and 2- $C_{18}$ DAC, indicating that the surfactants were not adsorbed at the Si steps.  $C_{12}$ TAC formed the most smooth and flat SAM layer in aqueous solutions, which may be explained by taking into account the large degree of freedom for the movement of the alkyl chain.

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