

## Imaging of Charged Micropatterned Surface on the Organosilane Monolayer Using Chemical Force Microscope

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Chemical force microscopy (CFM) was applied for the lateral force microscopic (LFM) imaging of micropatterned organosilane monolayer surfaces with oppositely charged phases using chemically modified cantilever tips. The cantilever tips modified with oxidized mercaptosilane and aminosilane were employed as a tip for CFM. LFM imaging of the micropatterned surface with opposite charge was achieved by controlling the pH of the aqueous solution in consideration with the electrostatic condition of functional groups on the cantilever tip and substrate surface.

Key words: chemical force microscope, lateral force microscope, organosilane monolayer, electrostatic interaction

### INTRODUCTION

In recent years, in order to investigate the physicochemical properties of materials surface, chemical force microscopy (CFM) with chemically modified cantilever tip has been attracted much attention as an excellent technique for the determination of chemically interaction, such as hydrophobic interaction and the interactive force due to hydrogen bonds.[1,2] Few studies have also reported about the sensing and imaging of electrostatic interaction between the cantilever tip and substrate surface.[3] However, in order to distinguish the pH dependent contribution of the tip functionality to the tip-substrate attractive force, it is necessary to detect electrostatic attractive force among the cantilever tip and ionized surface. In the present paper, we report the imaging of negatively and positively charged phases in the same micropatterned surface by CFM through detection of the lateral force value using the cantilever tip with negatively and positively chargeable surface modifiers.

### EXPERIMENTAL SECTION

Butyltrimethoxysilane [ $\text{CH}_3(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ , BTMS], [3-(2-aminoethylamino)propyl]-(dimethoxy)-methylsilane [ $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$ , AEAPDMS], 3-mercaptopropyltrimethoxysilane [ $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ , MTS], and octadecyltrichlorosilane [ $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ , OTS] were used as organosilane compounds. The Si-wafers (thickness; 0.5 mm) were cleaned by piranha solution and irradiation of vacuum ultraviolet-ray (VUV,  $\lambda=172$  nm) for 10 min under 15 mmHg in order to remove an organic contaminant. Water for the preparation of samples was purified with the NanoPure Water system (Millipore, Inc.). HCl aq. was used to adjust the pH of aqueous solution using CFM measurements. BTMS, AEAPDMS, and MTS monolayers were prepared by the chemical vapor adsorption (CVA) method.[4,5] The MTS monolayer surface was irradiated with UV-ray

( $\lambda=254$  nm) for 10 h in air.[3] Then, the terminal mercapto groups of MTS monolayer were transformed to sulfonic acid groups by photooxidation. Formation of sulfonyl group was identified by X-ray photoelectron spectroscopy (XPS). The XPS  $\text{S}_{2p}$  peak shifts from 163.3 eV (before irradiation) to 169.0 eV (after irradiation).[4] The OTS monolayer was prepared onto the Si-wafer substrate from a 5 mM OTS bicyclohexyl solution using a chemisorption method.[5] Micropatterned samples for the CFM observation were prepared using the photolithography method by area-selective irradiation of VUV-ray.[4,5]

The CFM observation was carried out based on the electrostatic interaction between charged monolayer surface and cantilever tip surface. Fig. 1 illustrates a schematic drawing of electrostatic interaction between

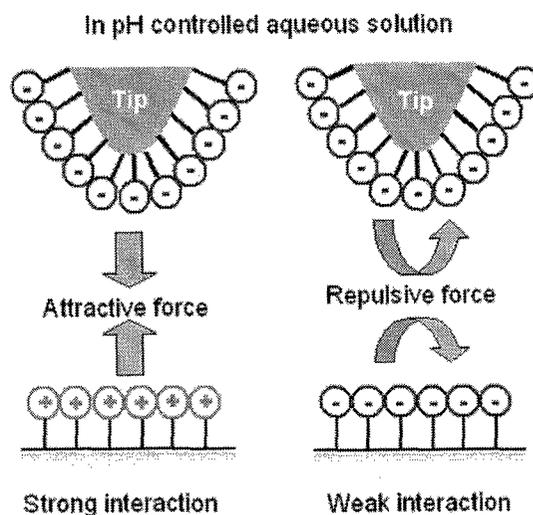


Fig. 1 Schematic drawing of electrostatic interaction between ionizable monolayer surface and chemically modified cantilever tip. This is a case that the cantilever tip surface is covered with negatively charged functional groups.

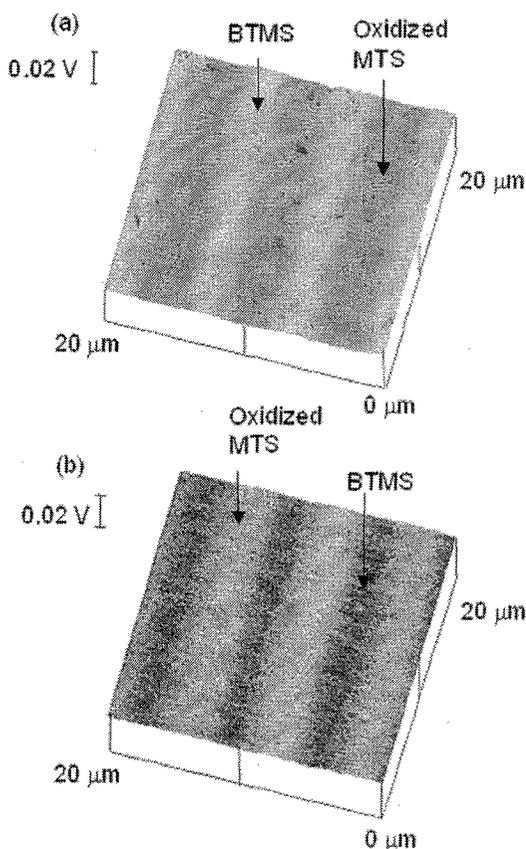


Fig. 2 LFM images observed on the (BTMS / oxidized MTS) micropatterned surface in pH = 7.3 water. [(a) with the cantilever tip modified with oxidized MTS, (b) with the cantilever tip modified with AEAPDMS.]

ionizable monolayer surface and the chemically modified cantilever tip. Both surfaces of monolayer and cantilever tip were modified with sulfonic acid groups of the oxidized MTS or amino groups of AEAPDMS. A  $100 \mu\text{m} \times 100 \mu\text{m}$  scanner and a  $\text{Si}_3\text{N}_4$  cantilever tip with a spring constant of  $0.09 \text{ N m}^{-1}$  were used. The surface  $\text{SiO}_2$  layer of  $\text{Si}_3\text{N}_4$  cantilever tip was chemically modified with either oxidized MTS or AEAPDMS by the CVA method.[4,5] The advantage of the CVA method is that it reduces a damage on the cantilever tips due to the capillary force during handling because CVA method is a dry-process. In the case of the chemisorption method from solution phase, the cantilever tip is often damaged by the capillary force. The cantilevers surface can be uniformly modified with the organosilane monolayer because the organosilane monolayer prepared by CVA method has little aggregations and defects on their surface.[5] The cantilever tips were cleaned by irradiation of VUV-ray before modification. The scan rate of lateral force microscopic (LFM) measurement was  $10.0 \mu\text{m s}^{-1}$ , and tip load was 1.0 nN.

## RESULTS AND DISCUSSION

In order to investigate the recognition of the attractive and repulsive force, the lateral force between the cantilevers modified with AEAPDMS or oxidized MTS and (BTMS/oxidized MTS) micropatterned surface was estimated. There is no difference between the BTMS

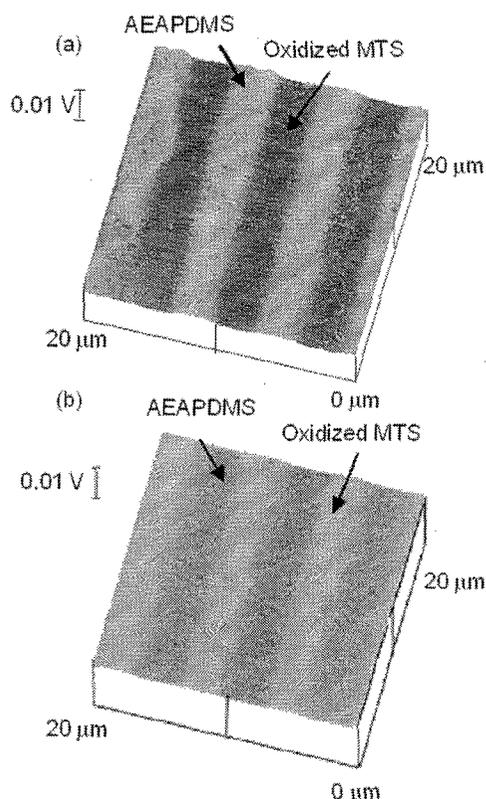


Fig. 3 LFM images of the (oxidized MTS/AEAPDMS) micropatterned surface in pH = 2.9 HCl solution. [(a) with the cantilever tip modified with oxidized MTS, (b) with the cantilever tip modified with AEAPDMS.]

monolayer and the oxidized MTS monolayer from the view point of chemical structure except for the terminal functional groups. Therefore, it is considered that the influence of the difference in terminal functional groups can be investigated. Fig. 2 shows LFM images observed on the (BTMS/oxidized MTS) micropatterned surface in pH = 7.3 water [(a) with the cantilever tip modified with oxidized MTS, (b) with the cantilever tip modified with AEAPDMS]. In the LFM images in Fig. 2(a), clear difference of magnitude of the lateral force was observed. The bright and dark areas corresponded to the BTMS and the oxidized MTS monolayer phases, respectively. The authors reported that the sulfonic acid groups on oxidized MTS monolayer surface are negatively charged above  $\text{pH}=1.5$ . [4] Conversely, the sulfonic acid groups on the substrate and the cantilever tip surface were negatively charged at  $\text{pH} = 7.3$ . Therefore, it is considered that the observed difference of lateral force on the (BTMS/oxidized MTS) patterned surface is derived from repulsive force between the cantilever tip and the micropatterned phases modified with sulfonic acid groups. On the other hand, in Fig. 2(b), a contrast in the LFM image was reversed by using the cantilever tip modified with AEAPDMS. The  $\text{p}K_a$  of amino groups on the AEAPDMS monolayer surface has been reported to be approximately  $\text{pH} = 4.0$ . [3] Thus, amino groups of AEAPDMS monolayer are not protonated at  $\text{pH}=7.3$ . The observed difference of lateral

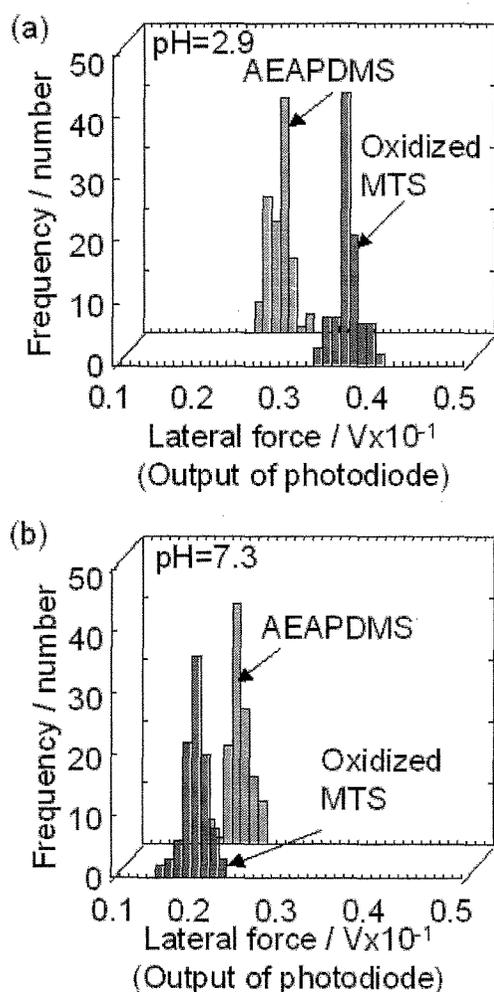


Fig. 4 Histograms of observed lateral force on the (oxidized MTS / AEAPDMS) micropatterned surface with cantilever tip modified with AEAPDMS in (a) pH=2.9 HCl aqueous solution, (b) pH = 7.3 water.

force on the (BTMS / oxidized MTS) surface is derived from attractive force being originated from the acid-base interaction between the unprotonated amino groups on the cantilever tip and the negatively charged sulfonic acid groups on Si-wafer surface.

Fig. 3 shows the LFM images of (oxidized MTS/AEAPDMS) micropatterned monolayer surface in pH = 2.9 HCl aq. [(a); with the cantilever tip modified with oxidized MTS, (b); with the cantilever tip modified with AEAPDMS]. In Fig. 3(a) and (b), clear difference of the lateral force between oxidized MTS phase and AEAPDMS one was observed on the (oxidized MTS / AEAPDMS) micropatterned surface. In pH = 2.9 HCl aq., the sulfonic acid groups of oxidized MTS and the amino groups of AEAPDMS were negatively and positively charged, respectively. Therefore, this result apparently indicated that clear contrast in the LFM image of the (oxidized MTS / AEAPDMS) micropatterned surface is due to the contribution of (1) electrostatic attractive force among the oppositely charged functional groups on the Si-wafer substrate and the cantilever tip surface; and (2) electrostatic repulsive force among the ionized functional groups with same

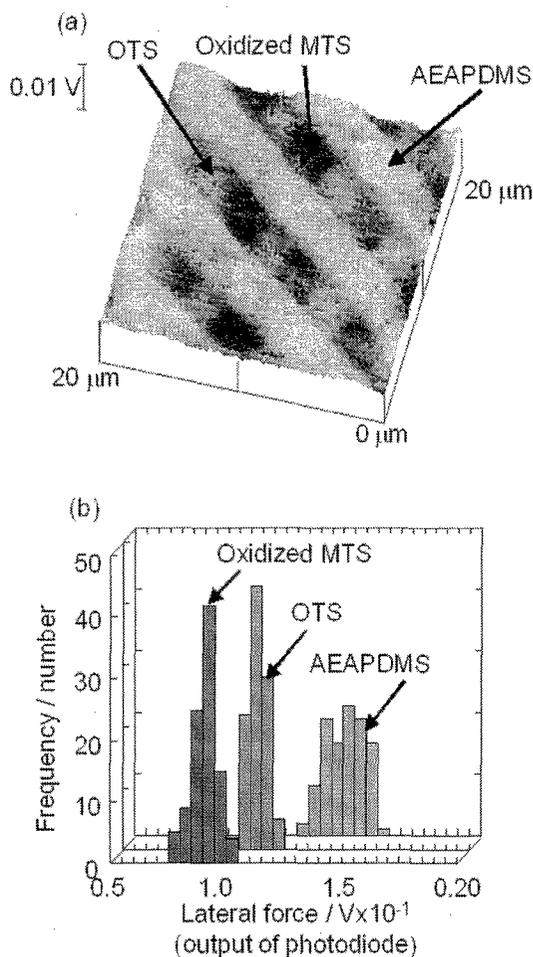


Fig. 5 (a) LFM image and (b) histograms of observed lateral force on the (OTS / oxidized MTS / AEAPDMS) micropatterned monolayer surface with the cantilever tip modified with oxidized MTS at pH = 7.3.

charge on the Si-wafer substrate and the cantilever tip surface.

By using the cantilever tip modified with ionizable functional groups, relative differences in lateral force can be changed by controlling the pH of aqueous media. Fig. 4 shows histograms of the lateral force observed on the (oxidized MTS/AEAPDMS) monolayer surface by using the cantilever tip modified with AEAPDMS in (a) pH = 2.9 HCl aq. and (b) pH = 7.3 water. The data in Fig. 4(a) correspond to the LFM image of Fig. 3(b). In the case of the cantilever tip modified with AEAPDMS, there were no large difference in the histograms of lateral force at pH = 7.3 [Fig. 4(b)]. In pH = 7.3 water, almost all amino groups of AEAPDMS monolayer were not protonated. Thus, the attractive interaction due to the hydrogen bonds between cantilever tip and micropatterned phase modified with AEAPDMS at pH = 7.3 was observed. However, attractive force due to the acid-base behavior was also observed between cantilever tip modified with unprotonated amino groups and micropatterned phases modified with negatively charged sulfonic acid groups as described previously. Thus, the difference of lateral force between oxidized MTS phase

and AEAPDMS one was not observed.

Multi-component micropatterned surface with opposite charge can also be imaged using CFM. Fig. 5 shows (a) the LFM image and (b) the histograms of the observed lateral force on the (OTS/oxidized MTS/AEAPDMS) monolayer surface, which has three phases with different surface chemistry, in pH=7.3 water by the cantilever tip modified with oxidized MTS. As shown in Fig. 5, three different monolayer phases were clearly identified. The AEAPDMS phases are the brightest among three monolayer phases due to the acid-base interaction between AEAPDMS monolayer and cantilever surface modified with oxidized MTS. The origin of difference of lateral force value among OTS phase and oxidized MTS phase was explainable by the following two reasons. First reason is the electrostatic repulsive force among negatively charged cantilever tip modified with oxidized MTS and negatively charged sulfonic acid groups on the oxidized MTS phase. Second reason is the difference of the aggregation state of organosilane monolayers. We have reported that observed lateral force on the organosilane monolayers with long alkyl chains depends on their molecular packing density and thermal molecular motion.[6] Thus, large lateral force was observed on the crystalline organosilane monolayer with long alkyl chains, such as OTS monolayer prepared by chemisorption method from solution phase, because of the large shear strength due to their tightly packed alkyl chains and decrease of thermal molecular motion.[5,6] Taking into account the high molecular packing density and less active thermal molecular motion of alkyl chains of OTS phase, the difference in lateral force between the OTS phases and the oxidized MTS phases is originated from the electrostatic repulsive force between the oxidized MTS phases and the cantilever tip surface modified with oxidized MTS, and the difference in the shear strength of long alkyl chains in OTS phase due to the tightly packed molecular density and small thermal molecular motion of octadecyl groups.

## CONCLUSION

The imaging of micropatterned charged monolayer surfaces was successfully achieved by using lateral force measurement with the cantilever tip modified with oxidized MTS or AEAPDMS. This technique is based on the detection of electrostatic attractive or repulsive force between terminal functional groups of monolayer surface and those of cantilever surface. The magnitude of lateral force could be control by optimizing the electrostatic condition of terminal functional groups.

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