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Site-Specific Arrangement of Microparticles on Organosilane Monolayer Patterned through Photolithography Process

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In this study, micropatterned fluoroalkylsilane/aminosilane monolayer was prepared as a template surface for site-specific arrangement of sulfonyl group-modified polystyrene (PS) microparticles. Micropatterned organosilane monolayer was prepared by using of chemical vapor adsorption method and photolithography process. Si wafer substrates with micropatterned organosilane monolayer were then exposed to the dispersed aqueous solution of sulfonyl group-modified PS microparticles. Atomic force microscopic (AFM) observation and field emission scanning force microscopic observation revealed that the PS microparticles were area-selectively adsorbed onto the aminosilane phase. The height of adsorbed PS microparticles is in good agreement with the diameter of PS microparticle. This result suggested that the sulfonyl group-modified PS microparticles formed a monolayer on the substrate surface. This consideration was supported by the results of adhesion force measurements. Adhesion force measurements clearly showed the specific interaction between sulfonyl groups of cantilever tip and amino groups of aminosilane patterned surface. Compared with fluoroalkylsilane phase, strong adhesion force was observed on the aminosilane phase. It is considered that the micropatterned surface prepared by the present method can be applied for novel template surface for area-selective arrangement of various kinds of microparticles.
Key words: organosilane monolayer, micropatterned surface, microparticle, adhesion force measurement, acid-base reaction

1. INTRODUCTION

Two-dimensional arrangement of microparticle, such as colloidal silica and gold nanoparticles, on the substrate surface might be a promising method to fabricate functional materials.[1-3] Organosilane monolayer with charged micropatterned surface has a bright prospect of site-selective assembling of charged materials because of their well-controlled surface physicochemical properties.[4] In this study, the micropatterned organosilane monolayers with fluoroalkylsilane/aminosilane phases were prepared as the template surface for site-specific immobilization of charged microparticles. The authors investigated the adsorption behavior of negatively charged polystyrene (PS) microparticles onto the micropatterned organosilane monolayer by scanning force microscope (SFM) and field emission-scanning electron microscope (FE-SEM) observations. Furthermore, adhesion force measurements with surface-modified cantilever tips were carried out to investigate interaction between the micropatterned surfaces and charged microparticles.

2. EXPERIMENTAL

2.1 Sample Preparation

[2-perfluorohexyl] ethyltrimethoxysilane (FHETMS) and N-[2-aminoethyl]-3-aminopropylmethyldimethoxy silane (AEAPDMS) were used as surface modifers. FHETMS / AEAPDMS micropatterned monolayer was prepared based on chemical vapor adsorption (CVA) method through photolithography process[4-6]. Figure 1 outlines the area-selective adsorption of sulfonyl group-modified PS microparticles. The AEAPDMS phase was prepared into the area-selectively decomposed FHETMS phase. The Si wafer substrate with micropatterned surface was then exposed to the 0.1 g l^{-1} pH=6 aqueous dispersed solution of sulfonyl group-modified PS microparticles (diameter is ca. 200 nm) for 30 min. The substrate was rinsed with distilled water and dried in vacuo.

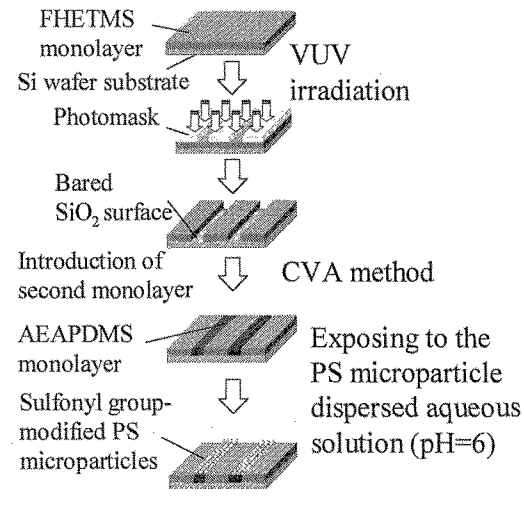

Figure 1 Schematic representation of the area-selective adsorption of PS charged microparticles.

Aqueous solutions with constant ionic strength were prepared by mixing 0.01 M mono-, di-, and tribasic sodium phosphate stock solutions in different proportion. The solutions were prepared to give a final ionic strength of 0.06 mol kg^{-1}.

2.2 Characterization of sample surfaces

The adsorbed PS microparticles onto the micropatterned surfaces were observed by SFM and FE-SEM observations. SFM observations were carried out with TMX-2100 (Vecco Inc.) at room temperature under constant force mode with a reference force under 0.1 nN. Cantilever tips used were microfabricated from Si_3N_4 with a bending spring constant of 0.032 Nm^{-1}. The adsorbed PS microparticles were also investigated using FE-SEM (S-4300SE, HITACHI High-Technologies Co.) at an acceleration voltage of 5 kV.

2.3 Adhesion force measurement

Adhesion force measurements were carried out with SPA 400 (Seiko Instruments Inc.). Cantilevers used were made of Si_3N_4 with a bending spring constant of 0.09 Nm^{-1}. The adhesive interactions between tips and samples modified with organosilane monolayer were determined by recording force versus distance curves.[7] The imaging force was in the range of 1-3 nN. The used cantilever tips with the radius of curvature were ca. 20 nm. Average adhesion force values were determined from histograms of the magnitude of adhesion force obtained from 100 individual force values. Adhesion force measurements were carried out in sodium phosphate solution and pH=6 HCl aqueous solution which is model solution for PS particle disperse solution with a reference force under 0.1 nN at room temperature. 3-Mercaptopropyltrimethoxisilane (MTS), AEAPDMS and FHETMS was adsorbed on cantilever tips by CVA method. MTS modified cantilever tips was irradiated UV-ray (λ=255 nm) for 10 h.[8] Then, the terminal mercapto group of MTS monolayer were transformed to sulfonyl group by photooxidation. Formation of sulfonyl group was identified based on X-ray photoelectron spectroscopy (XPS). XPS S_{2p} peak shifts from 163.3 eV (before irradiation) to 169.0 eV (after irradiation).

3. RESULTS AND DISCUSSION

3.1 Adsorption of the negatively charged PS microparticles onto the micropatterned surface

Figure 2 shows (a) atomic force microscope (AFM) and lateral force microscope (LFM) images of AEAPDMS/FHETMS micropatterned surface. In AFM image, height difference between FHETMS phase and AEAPDMS phase was not observed because there is almost no difference between molecular lengths of these organosilane compounds. In LFM image, bright areas and dark areas corresponded to AEAPDMS and FHETMS monolayer phases, respectively. It seems that higher frictional force in AEAPDMS phase is due to the contribution of strong adhesion force between hydrated amino groups of AEAPDMS monolayer surface and cantilever tips. [9]

Figure 3 shows (a) AFM image of the micropatterned AEAPDMS/FHETMS monolayer surface after exposure

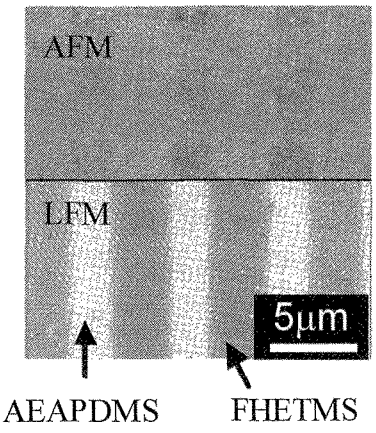

Figure 2 AFM and LFM images of AEAPDMS / FHETMS micropatterned surface.

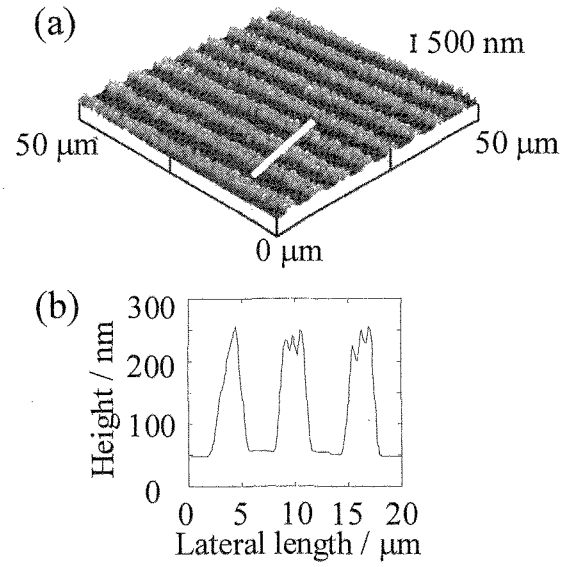

Figure 3 (a) AFM image of the AEAPDMS / FHETMS exposed to the aqueous dispersion of sulfonyl group modified PS microparticles and (b) lineprofile of white line part in (a).

to the aqueous dispersion of sulfonyl group-modified PS microparticles and (b) lineprofile of white line part in (a). Figure 4 shows the results of FE-SEM observation performed for the same sample of AFM observation. As shown in Figures 3 and 4, the site-specific immobilization of PS particles was successfully achieved on the micropatterned substrate surface. The line width of immobilized sulfonyl group-modified PS microparticles corresponded to the line width of AEAPDMS phases. The FE-SEM, AFM image, and its lineprofile give a size of layers consist of adsorbed sulfonyl group-modified PS microparticles with a height of ca. 200 nm. The height estimated from AFM image is in good agreement with the diameter of sulfonyl group-modified PS microparticles. This result suggested that the sulfonyl group-modified PS particles were

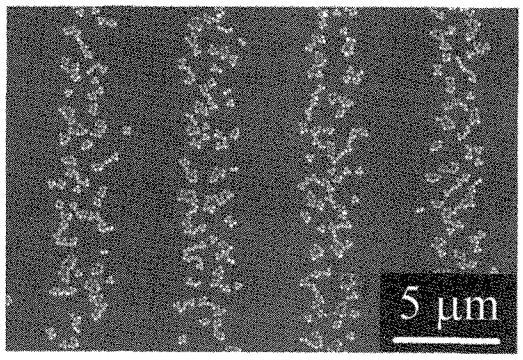

Figure 4 FE-SEM image of AEAPDMS/FHETMS micropatterned monolayer surface exposed to sulfonyl group-modified PS microparticle dispersed solution.

adsorbed on the surface as monolayer.

3.2 p*Ka* value of surface functional groups of organosilane monolayers

p*Ka* of surface functional groups of organosilane monolayer and PS microparticles was estimated by using of adhesion force measurements with organosilane modified cantilever tips. The adhesion force was defined a magnitude of observed attractive force when cantilever tip jumped from sample surface. In this study, adhesion force between tips and samples in aqueous solution were monitored by average force value versus pH of aqueous solutions. Figure 5 shows the average adhesion force values obtained at different pH values for tips and Si wafer substrate functionalized with AEAPDMS (filled circles) and oxidized MTS (filled squares) monolayer terminating with amino groups and sulfonyl groups, respectively. The oxidized MTS was used as the model surface of the sulfonyl group-modified PS microparticles surface. The data of oxidized MTS show weak adhesion force values in investigated pH regions (1.5<pH<7.9) indicating a repulsive interaction.[7] Furthermore, any remarkable change was not observed in adhesion force measurements. These results are consistent with ionization of sulfonyl groups on tip and sample surfaces. Therefore, it seems that p*Ka* value of surface sulfonyl groups exists below pH=1.5.

On the other hand, the data of AEAPDMS-modified tips and sample surface show that the adhesion force drops to almost zero below pH=4. Solid line in Figure 5 represents to solution-like titrtations: pH = p*Ka* + log (1-*f* / *f*), where *f* is the degree of protonation of surface amino groups of AEAPDMS monolayer.[6] In the case of *f*=0, it is assumed that surface amino groups are not protonated at all. In the case of *f*=1, it is presumed that surface amino groups are completely protonated. In this fitting, the fraction of unprotonated amino groups is identified with the ratio of adhesion forces, F_{adh}(pH=X : 0<*f*<1) / F_{adh}(pH>7, ca. 0.93 nN : *f*=1). The solid line was consisted with the results of adhesion force measurements when p*Ka* value was 4.2. Thus, these results apparently indicate that p*Ka* of surface amino groups exists around pH=4. The estimated p*Ka* value of surface amino groups was lower than that of free amino groups (p*Ka*=9~11). In previous study, it has been considered that the hydrophobic nature of aminosilane

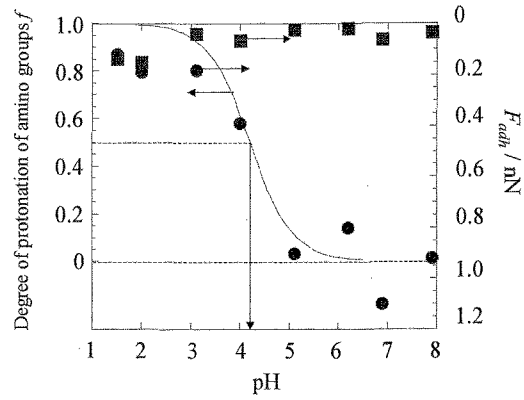

Figure 5 Adhesion force between cantilever tips and Si wafer substrate surface modified with organosilane monolayer versus pH; AEAPDMS (filled circles), and oxidized MTS (filled squares). Solid line indicates the degree of protonation of surface amino groups of AEAPDMS monolayer.

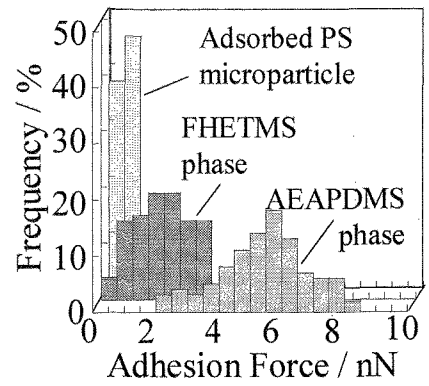

Figure 6 Histograms of adhesion force observed on the surface of adsorbed sulfonyl group-modified polystyrene (PS) microparticle, aminosilane and fluoroalkylsilane phase of micropatterned surface with oxidized MTS modified cantilever tip

monolayer likely arises from a disordered structure that exposes methylene groups at the surface.[7] Therefore, it seems that the shift of p*Ka* is ascribed to hydrophobic environment surrounding the amino groups by exposing hydrophobic methylene groups at the surface.

3.3 Adhesion force measurement of micropatterned organosilane monolayer

Adhesion force measurements were carried out between micropatterned surface, adsorbed charged microparticles, and sulfonyl group-modified AFM cantilever tip, which is a model of negatively charged microparticles in aqueous solution. The adhesion force was estimated from the maximum attractive force observed as a minimum in force-distance curve. Figure 6 shows histograms of adhesion force observed on the surface of adsorbed sulfonyl group-modified PS microparticle, aminosilane, and fluoroalkylsilane phase of micropatterned surface in pH=6 HCl aqueous

solution. The adhesion force between the AEAPDMS phase and cantilever tips is larger than that between FHETMS phase and cantilever tips. Since the surface of cantilever tip is covered with sulfonyl groups, the strong adhesion force presents between amino groups of AEAPDMS patterned phase and sulfonyl groups of cantilever tips. The above-mentioned investigation of p*Ka* value of organosilane monolayers revealed that the amino groups of AEAPDMS monolayer surface are not protonated. Thus, it seems that the interactive force between AEAPDMS phase and sulfonyl group-modified PS microparticles surface is due to the acid-base reaction between surface amino and sulfonyl groups. On the other hand, in the case of FHETMS patterned phase, the adhesion force was weak due to the lack of acid-base reaction on the surface of FHETMS micropatterned phase. This result supported the site-selective adsorption of sulfonyl group-modified PS microparticles on the AEAPDMS phase. Furthermore, the adhesion force was almost zero on the surface of sulfonyl group-modified PS microparticles. Electric repulsion force is present between both sulfonyl groups on the surface of cantilever tips and PS microparticles. This result suggested that the presence of electrostatic repulsive force between adsorbed PS microparticles and dispersed PS microparticles in aqueous solution. The sulfonyl group-modified PS microparticles thus formed monolayer on the micropatterned surface.

4. CONCLUSIONS

In conclusion, the authors succeeded in site-specific arrangement of sulfonyl group-modified PS microparticles onto the micropatterned aminosilane / fluoroalkylsilane monolayer surface. The PS microparticles area-selectively formed monolayers onto the aminosilane phase. Adhesion force measurements revealed that the origin of interaction between AEAPDMS phase and sulfonyl group-modified PS microparticles surface is due to the acid-base reaction between surface amino and sulfonyl groups.

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