Fabrication of Three-component Micropatterned Organosilane Monolayer by a Stepwise Photolithography Process

Tomoyuki Koga, Hideyuki Otsuka, and Atsushi Takahara*
Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581

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Three-component micropatterned organosilane monolayer was successfully fabricated on Si-wafer substrate by a stepwise photolithography process. Scanning force microscopic observations revealed that three kinds of organosilane monolayers with different physicochemical properties were area-selectively immobilized on a Si wafer.

Organosilane monolayers, which have surfaces terminated by many kinds of functional groups, are useful for manipulation of physicochemical properties of solid surfaces such as wettability and nanotribology.[1,2] Micropatterned organosilane monolayers have been used as the substrate for various chemical modifications; for example, the micropatterned surfaces have been used as templates for some microfeatures. In recent years, photolithography has been developed as a novel micropatterning technique for organosilane monolayers.[3] Using photolithography, we prepared a micropatterned surface with various organosilane compounds by way of a stepwise chemical vapor adsorption (CVA).[4–7]

Figure 1 outlines the essential steps for the fabrication of three-component micropatterned organosilane monolayers. The first step was the preparation of octadecyltriethoxysilane (OTES)-grafted Si substrates by CVA method.[5] Atomic force microscopic (AFM) observation revealed that there was no large aggregate and defect on the organosilane monolayers prepared by CVA method.

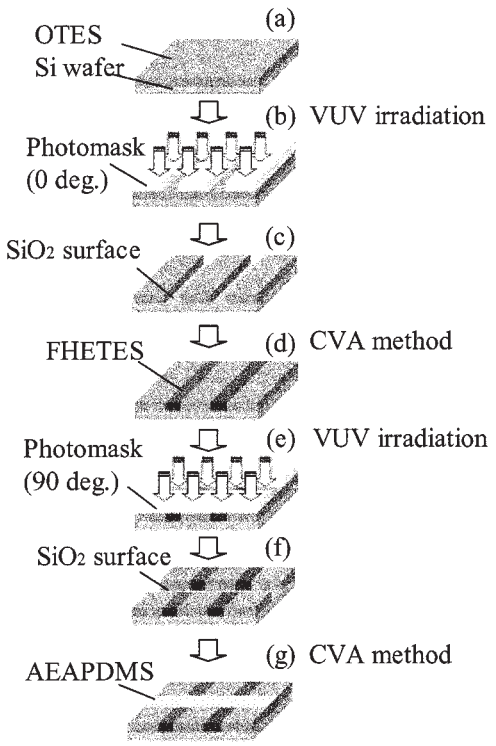

Figure 1. Outline for the fabrication of three-component micropatterned organosilane monolayers.

In photolithography, irradiation of vacuum ultraviolet-ray (VUV, $\lambda = 172$ nm) leads to excitation cleavage of C–C bonds, and formation of surface Si-OH residues.[5] The OTES grafted Si-wafer was placed in an evacuated vacuum chamber. The sample was then covered with a photomask (20 mm × 20 mm square, 4 μm Cr pattern, 2 μm slit with 20 mm line length) in preparation for irradiation (Figure 1(b)). The sample irradiated for 15 min with VUV light generated from an excimer lamp. To remove the decomposed residue of organosilane monolayers, the patterned sample was sonicated for 10 min in ethanol and dried in vacuo. The second organosilane monolayer (2-perfluorohexylethyl)-triethoxysilane (FHETES), was then introduced into the first patterned surfaces by a similar method with alkylsilane (Figure 1(d)).[8] The OTES/FHETES sample was then irradiated for 20 min with VUV, resulting in crossline micropatterns on the substrate's surfaces (Figure 1(e)). The third organosilane monolayer, [3-(2-aminoethylamino)propyl](dimethoxy)methylsilane (AEAPDMS) was finally introduced into the second-patterned substrate surfaces, again by the CVA method (Figure 1(g)).[9]

Changes in the surface chemical compositions of the micropatterned organosilane monolayers were characterized by X-ray photoelectron spectroscopy (XPS). The OTES monolayer showed C_{1s}, O_{1s}, Si_{2s}, and Si_{2p} peaks at 285, 533, 151, and 100 eV, respectively. The OTES/FHETES patterned Si substrate clearly showed additional F_{1s} peaks at 690 eV, while the OTES/FHETES/AEAPDMS grafted Si substrate showed further N_{1s} peaks at 400 eV.[8,9] These results indicated that the three kinds of organosilane molecules were subsequently grafted on the substrate surfaces.

Changes of surface functional groups by micropatterning were also reflected in the surface free energy. Table 1 shows the surface free energies of uniform or micropatterned organosilane monolayers. The surface free energy was calculated from the contact angles of water and methylene iodide based on Owens and Wendt's method.[10] The surface free energy of the OTES/FHETES micropatterned surface is smaller than that of the OTES monolayer surface; the decrease can be attributed to the fluoroalkyl groups of FHETES, which is known to decrease surface free energy. On the other hand, the surface free energy, especially the component of hydrogen bonding and dipole-dipole interaction (γ_s^h), extensively increased after the grafting of AEAPDMS; this increase was attributed to the relatively high polarity of amino groups introduced in the grafted AEAPDMS monolayer.[10] This stepwise change of surface free energy confirmed that the three-component organosilane surface has

Table 1. Surface free energies of uniform or micropatterned organosilane monolayers

Component	θ_{H_2O}/deg.	$\theta_{CH_2I_2}$/deg.	γ_s^d/mJm^{-2}	γ_s^h/mJm^{-2}	γ_s/mJm^{-2}
OTES	100.1	75.9	18.1	2.0	20.1
FHETES	106.9	86.6	13.1	1.6	14.7
AEAPDMS	61.8	39.5	34.3	13.2	47.5
OTES/FHETES	104.8	82.3	15.5	1.6	17.1
OTES/FHETES/AEAPDMS	92.4	72.1	19.7	4.1	23.8

been micropatterned with highly hydrophobic (FHETES, $\theta_{H_2O} = 106.9$ deg.), hydrophobic (OTES, $\theta_{H_2O} = 100.1$ deg.) and hydrophilic (AEAPDMS, $\theta_{H_2O} = 61.8$ deg.) area.

Successful fabrication of a micropattern with three kinds of functional groups was confirmed by scanning force microscopic observation (SFM). Cantilevers used were microfabricated from Si_3N_4 with a bending spring constant of 0.032 Nm^{-1}. The imaging force was in the range of 1–3 nN. Imaging was done in air at 300 K with 50–60% humidity. Figures 2(a) and (b) show AFM and lateral force microscopic (LFM) images of a three-component micropatterned organosilane monolayer, respectively. Together, these figures show lattice-like microstructures fabricated on the Si-wafer substrates. The widths of the fabricated FHETES and AEAPDMS lines were consistent with the widths of slits of the photomask. The height difference between the OTES and FHETES surfaces was ca. 1.4 nm. The height difference corresponds to the difference in the molecular length (ca. 1.3 nm), between OTES and FHETES. On the other hand, the height difference between the OTES and AEAPDMS surfaces was ca. 1.5 nm, corresponding to the difference in the molecular length (ca. 1.4 nm) between OTES and AEAPDMS. The origin of the contrast in the LFM image is explained by the difference in surface properties of three components, i.e., the chain rigidity, crystallinity, and the chemistry of terminal functional groups of the organosilane molecules.[2] The FHETES-grafted areas showed a higher magnitude of lateral force in comparison with the OTES-grafted ones, owing to the larger shear strength of the rigid fluoroalkyl chain of the FHETES chains.[2] AEAPDMS-grafted areas are the brightest among the three components, because the terminal amino groups gave high lateral force due to the strong interaction between hydrophilic amino group and the Si-OH group of the cantilever tip. The area ratio of the micropatterned monolayer is in accord with that of the target value, i.e. the estimated area ratio of OTES/FHETES/AEAPDMS was 4/2/3.

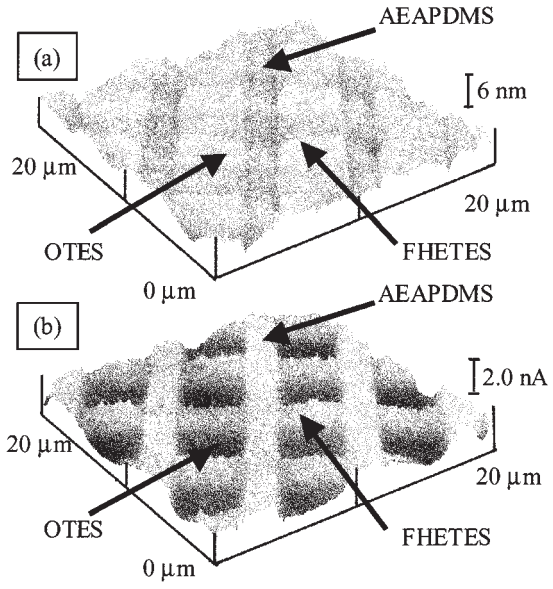

Figure 2. AFM and LFM images of three-component micropatterned organosilane monolayer. (a) AFM image; (b) LFM image.

From these results obtained above, the present method is expected to afford multi-component monolayer as a substrate of organic electronic devices, biosensors, microfluidic system and template surfaces for 2-dimensional arrangement of organic or inorganic materials.

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