Method for the Preparation of Hydrophilic/Hydrophobic Patterned Surfaces with Photoinitiated Hydrosilylation

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Received 14 July 2008; accepted 7 October 2008
DOI 10.1002/app.29452
Published online 23 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Recently, there has been considerable interest in hydrophilic/hydrophobic patterned surfaces because they serve as important templates for the selective deposition of various materials. We report a novel and simple method for the creation of hydrophilic/hydrophobic patterned surfaces using soft UV irradiation (365-nm wavelength). The method employs a photoinitiated hydrosilylation reaction of vinyl-terminated polydimethylsiloxane with H—Si groups catalyzed by platinum(II) acetylacetonate. In UV-irradiated regions, the photohydrosilylation reaction occurs, forming hydrophobic regions. In unirradiated regions, the remaining H—Si groups are converted into HO—Si groups in the presence of aqueous sodium hydroxide to form hydrophilic regions. The photoinitiated hydrosilylation reaction is completed within a little over 1 min, and this has been confirmed by reflection–absorption spectroscopy. The value of the water contact angle for the hydrophilic regions is about 10°, and that for the hydrophobic regions is about 103°. The success of pattern formation at the micrometer scale has been confirmed by scanning electron microscopy. The difference in the chemical structure at the surface has been confirmed by the decoration of the hydrophilic regions by a fluorescent dye and characterization with a fluorescence analyzer. Atomic force microscopy has shown that the height of the hydrophobic regions is about 20 nm. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 910–916, 2009

Key words: coatings; microstructure; photopolymerization; polysiloxanes; thin films

INTRODUCTION

Control over surface hydrophobicity or hydrophilicity has attracted substantial recent research activity. It is also desirable to control the spatial distribution or pattern of hydrophilic or hydrophobic regions on surfaces because hydrophilic/hydrophobic patterned surfaces serve as important templates for the selective deposition of metal oxides,[1] polymers,[2] organic and inorganic colloidal particles,[3–7] nanoparticles,[8–12] and biomolecules[13–16] such as DNA, proteins, peptides, and cells. Actually, current applications in microelectronics, information storage, optics, microarray/diagnostic sensors, biomedical uses, and microfluidics call for hydrophilic/hydrophobic patterned surfaces that are patterned on micrometer or submicrometer scales.

Consequently, many methodologies have been successfully developed for forming hydrophilic/hydrophobic patterned surfaces onto solid substrates such as metals, glass, and silicon. These micropatterning approaches include a soft lithographic method,[17] photolithography of self-assembled monolayers (SAMs),[18] polymer brushes,[19] physical changes in the surface morphology,[20,21] and electrochemical methods.[22] Many of these techniques are based on coating the substrates with SAMs of organosilanes (for glass and silicon substrates) and alkane thiols (for gold substrates) because they form uniform films of the appropriate thickness and can be designed to present a functional surface. Photolithography of SAMs normally requires short wavelengths (172 or 254 nm) for efficient patterning, and these harsh conditions are often associated with nonspecific photodegradation, ozone-induced damage, and a poorly defined surface. Widely used photoreleasable hydrophobic protecting groups, such as the one involving *ortho*-nitrobenzyl alcohol linkages,[23,24] can be removed by photolysis at a relatively long wavelengths (365 nm) to generate hydrophilic functionalized SAMs. However, although increasing the wavelength reduces the likelihood of undesired photodegradation, it also seems to be quite difficult to complete the 365-nm photolysis within 5 min.

In this article, we illustrate a new approach to forming hydrophilic/hydrophobic patterned surfaces. The method employs a photoinitiated hydrosilylation reaction[25,26] of vinyl-terminated polydimethylsiloxane with H—Si groups catalyzed by

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Journal of Applied Polymer Science, Vol. 112, 910–916 (2009)
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platinum(II) acetylacetonate. In UV-irradiated regions, the photohydrosilylation reaction occurs to form hydrophobic regions. In unirradiated regions, the remaining H—Si groups are converted into HO—Si groups in the presence of aqueous sodium hydroxide to form hydrophilic regions. These reactions are expected to proceed rapidly by soft UV irradiation (365-nm wavelength). In addition, polydimethylsiloxane is a representative hydrophobic polymer, and HO—Si groups possess a strongly hydrophilic character. The success of pattern formation is demonstrated by water contact angle measurements, reflection–absorption spectroscopy (RAS), scanning electron microscopy (SEM), and so forth.

EXPERIMENTAL

Materials

Vinyl-terminated polydimethylsiloxane (code DMS-V21, molecular weight = 6000) was purchased from Gelest, Inc. (Morrisville, PA). Triethoxysilane and (3-aminopropyl)triethoxysilane were purchased from Tokyo Kasei, Co., Ltd. (Tokyo, Japan). Platinum(II) acetylacetonate was purchased from Aldrich (St. Louis, MO). Ethyl alcohol, isopropyl alcohol, methyl alcohol, *N,N*-dimethylformamide (DMF), dichloromethane, acetone, 0.1 mol/L NaOH, and 0.1 mol/L HCl were purchased from Kanto Chemical Co., Inc., (Tokyo, Japan), and used as received. Distilled water was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Fluorescein-4-isothiocyanate (FITC) was purchased from Dojindo Laboratories (Kumamoto, Japan).

Hydrolytic condensation of triethoxysilane

To a stirred solution of triethoxysilane (1.0 g, 6.1 mmol) in isopropyl alcohol (100 g) was added 0.1 mol/L HCl (0.32 g, 17.7 mmol as H_2O). The solution was stirred for 12 h at room temperature.

Hydrolytic condensation of (3-aminopropyl)triethoxysilane

To a stirred solution of (3-aminopropyl)triethoxysilane (1.0 g, 4.5 mmol) in isopropyl alcohol (100 g) was added water (0.24 g, 13.3 mmol). The solution was stirred for 12 h at room temperature.

Substrate preparation

The substrates used in this study were silicon wafers, glass substrates, and aluminum substrates. Silicon wafers were purchased from Mitsubishi Materials Corp. (Tokyo, Japan). (one side was polished, and the other side was etched; both surfaces of the silicon wafer were covered with a layer of silicon dioxide with a thickness of 10–20 nm). Glass substrates were obtained form Asahi Glass Co., Ltd. (Tokyo, Japan). Aluminum substrates were prepared by the sputtering of aluminum onto glass substrates. The aluminum thickness was 200 nm. All substrates used in this study were washed ultrasonically for 30 s in ethyl alcohol and then dried with nitrogen at room temperature and cleaned by exposure to UV and ozone for 10 min. We hereafter refer to these silicon wafers as Si substrates and to these aluminum substrates as Al substrates.

Patterning solution

To stirred isopropyl alcohol (50.0 g) were added vinyl-terminated polydimethylsiloxane (0.2 g), platinum(II) acetylacetonate (7 mg), and the hydrolytic condensate of triethoxysilane mentioned previously (5 g). The solution was stirred for 1 h at room temperature.

Preparation of hydrophilic/hydrophobic patterned surfaces

The patterning solution was spin-coated onto Si substrates, glass substrates, or Al substrates at 3000 rpm for 20 s. The coated substrates were placed under an ultrahigh-pressure mercury lamp (Ushio SXUI1501HQ optical module X and Ushio USH-500SC superhigh-pressure UV lamp, Ushio Electric, Inc., Tokyo, Japan) and exposed to UV (365-nm wavelength, 100 mW/cm^2, with a chromium/quartz photomask in contact with the sample on the top in the case of patterning). The surface-irradiated substrates were washed by soaking in isopropyl alcohol for 30 s and dried with nitrogen. The hydrophilic/hydrophobic patterned surfaces were achieved by immersion into 0.1 mol/L NaOH for 30 s. The substrates with patterned surfaces were rinsed sequentially with 0.1 mol/L HCl, distilled water, and ethyl alcohol, and then the samples were dried with nitrogen.

Immobilization of FITC

A glass substrate with a hydrophilic/hydrophobic patterned surface was prepared according to the process mentioned previously. A layer of amino-terminated organosilanes was spin-coated onto the patterned surface from the hydrolytic condensate of (3-aminopropyl)triethoxysilane at 3000 rpm for 20 s. The substrate was washed by soaking in isopropyl alcohol for 30 s and dried with nitrogen. The resultant substrate was immersed in a 0.1% w/w solution of FITC in DMF at 37°C for 30 min. The sample was rinsed sequentially with DMF, dichloromethane, acetone, and methyl alcohol and was dried with nitrogen.

Static contact angle measurements

Water contact angle measurements were carried out at room temperature with a model CA-X150 (Kyowa Interface Science Co., Ltd., Saitama, Japan). The contact angles were recorded immediately after 2-μL water droplets were dispensed with a pipette onto the surface. The reported values are average values of measurements at three different locations for each sample.

RAS

RAS spectra were recorded on a Magna 760 (Thermo Fisher Scientific K.K., Waltham, MA). The samples were prepared with Al substrates.

SEM images

SEM images were obtained with an S-800 (Hitachi, Ltd., Tokyo, Japan). The analysis chamber pressure was lower than 7×10^{-3} Pa. An accelerating voltage of 5 kV was used for the imaging of the patterned surfaces. The samples were prepared with Si substrates.

Fluorescence analysis

Fluorescence imaging was carried out with a Fujifilm (Tokyo, Japan) FLA-8000 microarray scanner with a second harmonic generation laser (blue, 473 nm) as the excitation source. A fluorescence image was acquired with the following parameters: 473-nm excitation, 530-nm emission filter, 20-μm resolution, 200 mm/s scan speed, and 100% photomultiplier voltage.

Atomic force microscopy (AFM) observation

An AFM height image was obtained with an SPA400 (Seiko Instruments, Inc., Chiba, Japan). The tapping mode with silicon cantilevers with a spring constant of about 15 N/m was used.

RESULTS AND DISCUSSION

Strategy to form hydrophilic/hydrophobic patterned surfaces

The first step in our approach was to choose a reaction that takes only a few minutes to complete and is capable of forming hydrophilic or hydrophobic regions on the surface of a substrate. A rapid surface patterning technique is essential for a high-throughput production process. In the example described herein, we used a photoinitiated hydrosilylation reaction[25,26] of vinyl-terminated polydimethylsiloxane with H—Si groups catalyzed by platinum(II) acetylacetonate to form hydrophobic regions and subsequently the conversion of H—Si groups to HO—Si groups in the presence of aqueous sodium hydroxide to form hydrophilic regions. The basis of this choice is that photoinitiated

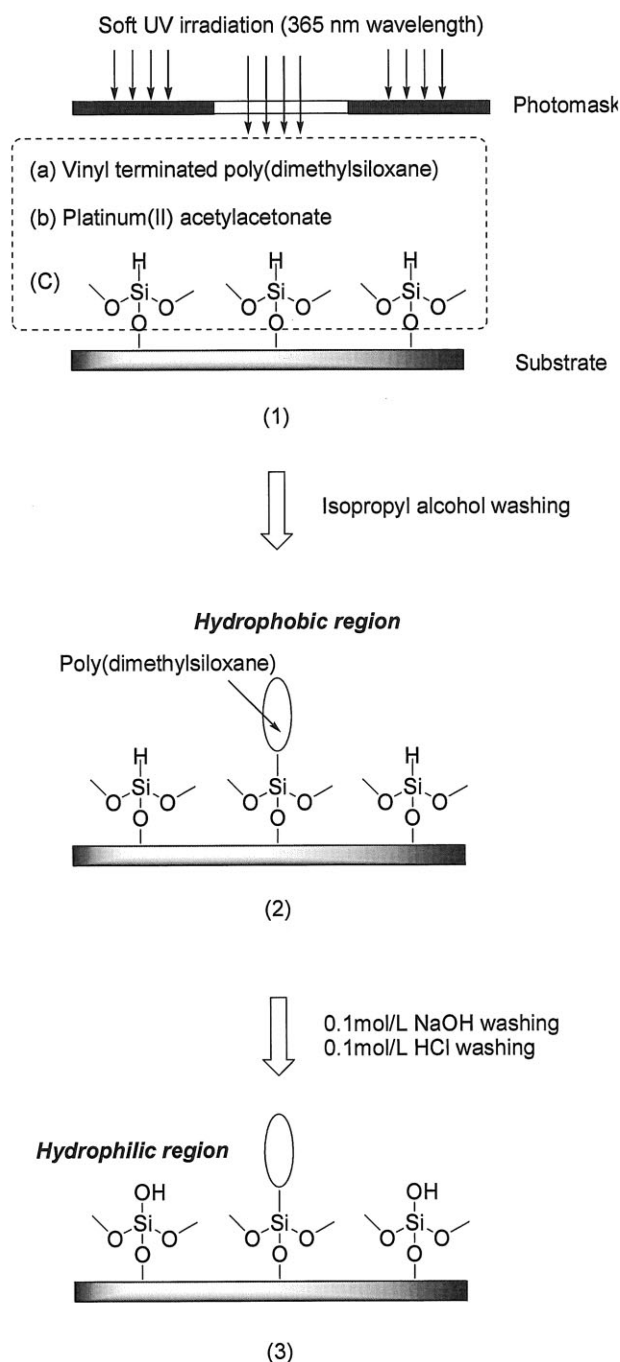


Figure 1 Strategy for the formation of hydrophilic/hydrophobic patterned surfaces on substrates. (1) After exposure to UV light through a photomask, photoinitiated hydrosilylation occurred. (2) The sample was then washed in isopropyl alcohol to yield hydrophobic regions. (3) The remaining H—Si groups were converted into HO—Si groups to yield hydrophilic regions.

hydrosilylation should proceed rapidly with soft UV irradiation (365-nm wavelength). In addition, polydimethylsiloxane is a representative hydrophobic polymer, and HO—Si groups possess strongly hydrophilic character. Our strategy for hydrophilic/hydrophobic patterning is depicted in Figure 1. The patterning agent

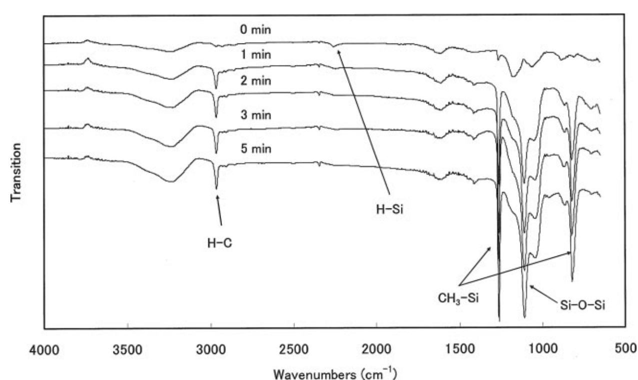


Figure 2 RAS spectra of samples prepared by changes in the UV irradiation time (365-nm wavelength, 100 mW/cm^2). The samples were prepared with Al substrates.

was composed of (1) vinyl-terminated polydimethylsiloxane, (2) platinum(II) acetylacetonate as a catalyst, and (3) a hydrolytic condensate of triethoxysilane. A layer of the patterning agent was spin-coated on top of a substrate from its solution in isopropyl alcohol. The hydrolytic condensate of triethoxysilane was expected to self-assemble at the surface of the substrate. When the resultant patterning agent/the substrate was exposed to soft UV (365-nm wavelength) with a photomask, a photoinitiated hydrosilylation reaction occurred in the UV-irradiated regions [Fig. 1(1)]. To eliminate excess vinyl-terminated polydimethylsiloxane, the sample was then washed in isopropyl alcohol to form hydrophobic regions [Fig. 1(2)]. It is well known that H—Si groups are rapidly converted into HO—Si groups in the presence of alkali catalysts. Therefore, when the sample was treated with 0.1 mol/L NaOH and then 0.1 mol/L HCl, the remaining H—Si groups were converted into HO—Si groups to form hydrophilic regions [Fig. 1(3)].

The second step was to confirm that the photoinitiated hydrosilylation reaction proceeds on a timescale of minutes (Fig. 1). The support for the progress of the photoinitiated hydrosilylation reaction was obtained from RAS measurements. The patterning agent was spin-coated onto Al substrates from its solution in isopropyl alcohol. The coated substrates were exposed to UV (365-nm wavelength) for different irradiation times. To eliminate excess vinyl-terminated polydimethylsiloxane, the surface-irradiated substrates were then washed in isopropyl alcohol and dried with nitrogen. Figure 2 shows the RAS spectra for the samples. A peak at 2150 cm^{-1}, assigned to the H—Si bond, disappeared about in 1 min, whereas new peaks associated with H—C, CH_3—Si, and Si—O—Si bonds appeared, and their intensity reached its highest value within 2 min and remained unchanged with prolonged irradiation. Thus, it was suggested that the photoinitiated hydrosilylation reaction proceeds to completion within 1 or 2 min.

The third step in our approach was to confirm that H—Si groups are converted rapidly into HO—Si groups in the presence of alkali catalysts. First, the hydrolytic condensate of triethoxysilane was spin-coated from its solution in isopropyl alcohol (1.0% w/w) on a Si substrate. The water contact angle for the surface of the sample was 91°. Then, the sample was immersed in 0.1 mol/L NaOH for 30 s and rinsed sequentially with 0.1 mol/L HCl, distilled water, and ethyl alcohol, after which the sample was dried with nitrogen. The water contact angle of the surface decreased to 5°. This result indicates that H—Si groups are converted into HO—Si groups on a timescale of seconds.

From these results for the reaction rates, we conclude that our method is effective in forming hydrophilic/hydrophobic patterned surfaces in a short time period.

Surface wettability of the patterned surfaces

Hydrophilic and hydrophobic regions need to be distinguished clearly from each other by their surface wettability. This allows various materials to be deposited to hydrophilic regions more selectively. The patterning agent was spin-coated on Si substrates from its solution in isopropyl alcohol. The coated substrates were exposed to UV (365-nm wavelength) for different irradiation times with a photomask with a 2.5/2.5 cm line/space width. To eliminate excess vinyl-terminated polydimethylsiloxane, the surface-irradiated substrates were then washed in isopropyl alcohol and dried with nitrogen. The values of the water contact angle for the hydrophilic region (UV-unirradiated region) and hydrophobic region (UV-irradiated region) of each sample are plotted against the UV irradiation time in Figure 3. The water contact angles for the hydrophobic region increased with increasing UV irradiation time, reached a limiting value of about 103° within 1 min, and remained unchanged with prolonged irradiation. On the other hand, the initial water contact angle for the hydrophilic region was about 10° and almost constant during UV irradiation. The result shows that our method offers a large contact angle difference between the hydrophilic and hydrophobic regions, distinguishing the regions clearly from each other by their surface wettability.

Surface morphology

Studies on the optical images of the hydrophilic/hydrophobic patterned surfaces were accomplished as follows. Si substrates with patterned surfaces were prepared with a photomask with a 10/10 μm line/space width or with a 50/3 μm line/space width. The UV-irradiation time was 1 min. Such

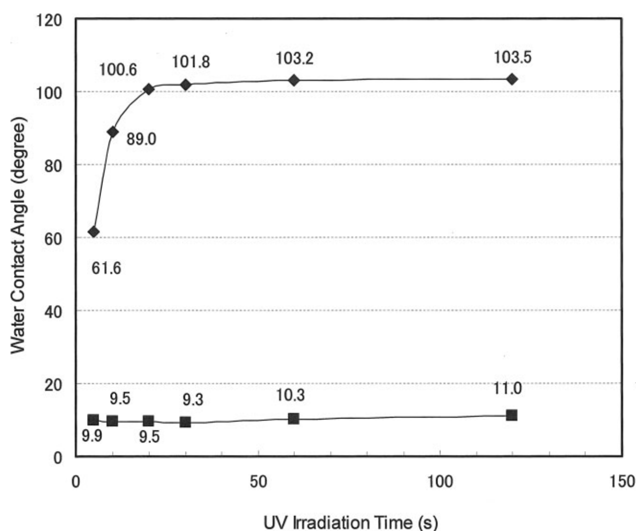
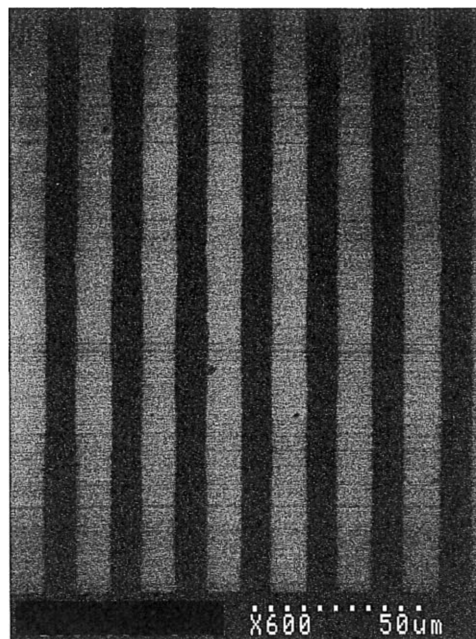


Figure 3 Plot of the water contact angles of samples prepared by changes in the UV irradiation time (365-nm wavelength, 100 mW/cm^2): (◆) hydrophobic and (■) hydrophilic regions. The values in the graph indicate the actual measurements of the water contact angle. The samples were prepared with Si substrates.

patterned surfaces can be readily imaged by SEM.[27] Figure 4(a,b) shows the images of the patterned surfaces. The UV-irradiated regions, in which the photoinitiated hydrosilylation reaction occurred, served to decrease the electron yield, and hence these regions appear darker. A period of line/space in the photomask was transcribed onto the surfaces. These SEM images demonstrate that the method can fabricate hydrophilic/hydrophobic patterned surfaces on the micrometer scale with soft UV irradiation (365-nm wavelength).

The SEM images, however, do not prove that there is any difference in the chemical structure at the surface. To clarify this, the patterned surface was decorated by a fluorescent dye as shown in Figure 5 and characterized with a microarray scanner. A glass substrate with a hydrophilic/hydrophobic patterned surface was prepared with a photomask with a 100/100 μm line/space width according to the process illustrated in Figure 1 [Fig. 5(1)]. A layer of amino-terminated organosilanes was spin-coated onto the patterned surface from the hydrolytic condensate of (3-aminopropyl)triethoxysilane in isopropyl alcohol [Fig. 5(2)]. Then, the substrate was treated with the solution of FITC, which reacted easily with the surface terminal amino groups [Fig. 5(3)]. In this case, the layer of amino-terminated organosilanes should be present only in the hydrophilic regions on the surface by direct covalent bonding to the surface silanol groups [Fig. 5(2)]. Fluorescence was therefore observed only in the hydrophilic regions on the surface. Figure 6 shows the image of the surface decorated by FITC, revealing that there is a difference in the chemical structure at the surface.



(a)

(b)

Figure 4 (a) An SEM image of the patterned surface obtained with a photomask with a 10/10 μm line/space width. The dark regions correspond to regions in which photoinitiated hydrosilylation occurred, which yielded hydrophobic surfaces. (b) An SEM image of the patterned surface obtained with a photomask with a 50/3 μm line/space width. Both samples were prepared with Si substrates.

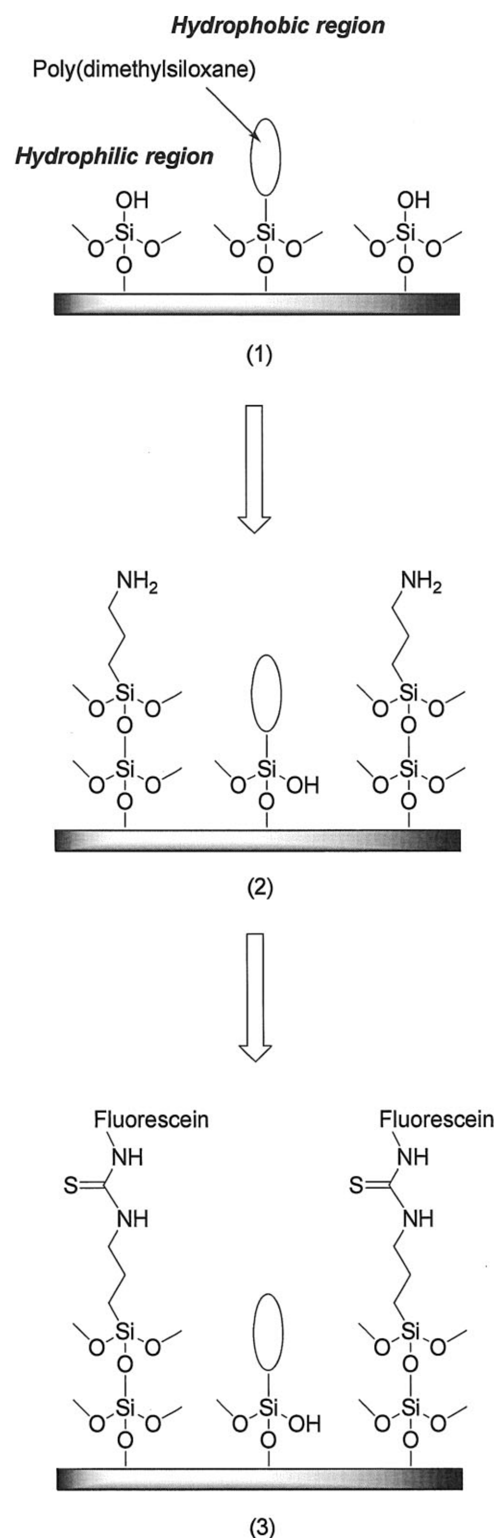


Figure 5 Schematic representation of FITC micropatterning: (1) a glass substrate with a hydrophilic/hydrophobic patterned surface, (2) covalent coupling of amino groups to the hydrophilic region, and (3) subsequent micropatterning of FITC by molecular recognition with immobilized amino groups.

The thickness of the hydrophobic region was measured by AFM observation. Figure 7 shows an AFM height image of the patterned surface. The thickness of the layer was estimated to be about 20 nm by the measurement of the height difference between the surface of the hydrophobic region and the bare surface of the Si wafer.

CONCLUSIONS

We demonstrated a novel and simple method for forming hydrophilic/hydrophobic patterned surfaces using soft UV irradiation (365-nm wavelength). The method uses a combination of a photoinitiated hydrosilylation reaction of vinyl-terminated polydimethylsiloxane with H—Si groups and subsequently a conversion of H—Si groups into HO—Si groups. The success of pattern formation was confirmed by water contact angle measurements, RAS, SEM, fluorescence analysis, and AFM. The advantages of the

Figure 6 Fluorescence micrograph illustrating how FITC could be templated onto hydrophilic/hydrophobic patterned glass substrates. The hydrophilic/hydrophobic patterned surface was prepared with a photomask with a 100/100 μm line/space width. The bar on the lower right indicates 1000 μm.

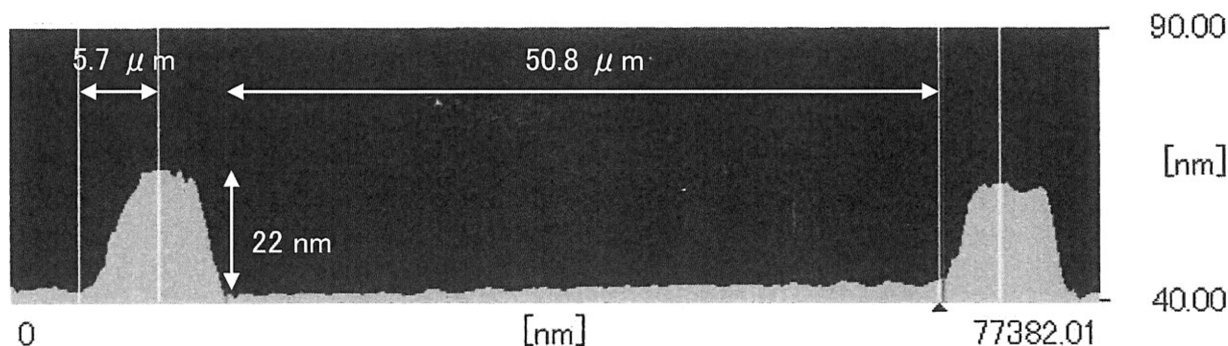


Figure 7 AFM height image of the patterned surface obtained with a photomask with a 50/10 μm line/space width. The samples were prepared with Si substrates.

method are as follows: (1) the photoinitiated hydrosilylation reaction is completed within a little over 1 min and therefore provides a mild and rapid method of forming hydrophilic/hydrophobic patterned surfaces; (2) a large contact angle difference between the hydrophilic and hydrophobic regions is attained, allowing various materials to be deposited to hydrophilic regions more selectively; and (3) the surface can be patterned on micrometer-size scales. The resultant patterned surfaces should template the deposition of various materials onto substrates.

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