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Novel Microcontact Printing Technique for Multipatterning of Self-Assembled Monolayers

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In this article, we focus on the development of a laminated patterning technique for various types of self-assembled monolayer (SAM) by microcontact printing (μCP). Using this technique, three types of functional SAM with hydrophobic and hydrophilic surface properties are patterned selectively on a silicon wafer. After the line shape of hexadecanethiol ($CH_3(CH_2)_{15}SH(CH_3)$, HDT) is patterned on a Au substrate by μCP, the cross line pattern of 11-mercaptoundecanoic acid ($HS(CH_2)_{10}COOH$, 11-MUA) is transferred to the laminated Au substrate. Finally, the external area of the transferred SAM pattern on the sample is coated with dodecyltrichlorosilane ($C_{12}H_{25}Cl_3Si$, DTS). The surface property of each SAM is measured by lateral force microscopy (LFM). This laminated patterning technique enables the fabrication of bio-micro-electro-mechanical system (bio-MEMS) devices by μCP.

1. Introduction

Since it was introduced for the first time,[1] microcontact printing of a self-assembled monolayer (SAM) has gained great interest in micro- or nano-patterning technology as an alternative technique to conventional photolithography. Its high throughput and low cost by the master & replication system shows the possibility of mass production in practical industry. Moreover, using individual molecules of SAM as a mask enables the transfer of a pattern on the micrometer or even submicrometer scale, which is the limitation of photolithography due to the diffraction of light.[2] As well as basic soft lithography, μCP has a high potential in recent bio-MEMS technology because of the ability to pattern the

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surface of a functional SAM that selectively binds organic materials such as proteins, DNA, and biocells.[3,4]

However, despite these advantages, there are some difficulties in the practical application of μCP to bio-MEMS devices. The patterning technique for SAMs is based on the bottom-up approach method due to the covalent bond between SAM molecules and the substrate. This method enables the transfer of a pattern directly in a wide range, rapidly and in a low-cost way. However, SAM molecules are combined with particular substrates such as thiols on Au, siloxanes on Si and silanes on SiO_2, and this limitation of the substrate restricts the extension of μCP to lithography. For this reason, μCP is not yet suitable for the multilayer processes involved in most complex systems. Some approaches have been devised to fabricate multilayer SAMs.[5,6] In our previous study, we proposed the mix-and-match patterning method of shadow-mask patterning and μCP for the development of multilayer processing.[7]

In this paper, we present a laminated patterning technique in order to fabricate multilayer patterns of various SAMs which have different functionalities. Three types of SAMs with hydrophobic and hydrophilic surface properties are transferred to laminated substrates as follows: HDT (hexadecanethiol) on a Au layer, 11-MUA (11-mercaptoundecanoic acid) on a Au layer and DTS (dodecyltrichlorosilane) on a SiO_2 layer. These various SAM patterns are confirmed by lateral force microscopy (LFM). Finally, the possibility of fabricating biodevices by μCP will be shown through this novel technique for multipatterning of various SAMs.

2. Experimental Section

2.1 *Preparation of substrate*

A silicon wafer was prepared for multipatterning of SAMs. The wafer was oxidized in an oxidation furnace in order to fabricate a 200-nm-thick SiO_2 layer for transferring the DTS pattern. On this SiO_2 layer, a Au layer for the μCP of HDT was prepared by evaporating 10-nm-thick Cr, followed by 50-nm-thick Au. After the first μCP, a 50-nm-thick Au layer was deposited again on the sample for the second μCP of 11-MUA.

2.2 *Preparation of SAM solutions*

For μCP, 10 mM HDT solution and 1 mM 11-MUA solution in 100 mL ethanol (99.5%) are prepared. A SAM used in immersion was prepared from a solution of DTS in toluene (99.5%) with 5% volume fraction in a glove box filled with nitrogen gas.

2.3 *Master fabrication*

To prepare a master of the stamp in μCP, a negative pattern of 5-μm-wide lines was transferred to a 200-nm-thick SiO_2 layer on a silicon wafer by photolithography. Using the photoresist as a mask, the SiO_2 layer was removed by wet etching in BHF solution for 3 min. After removing the photoresist layer from the sample with acetone, anisotropic KOH etching was performed on the wafer so that a 5-μm-wide V-groove silicon mold was fabricated (Fig. 1). Finally, the extra SiO_2 layer was completely removed in BHF solution.

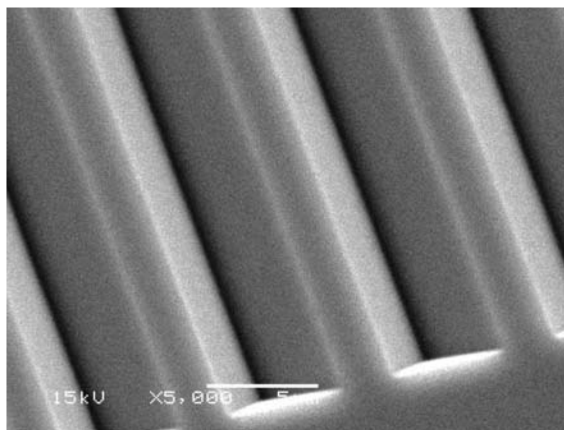


Fig. 1. SEM image of stamp mold (Si) with V-groove (5 μm width).

2.4 *Preparation of stamp*

The polydimethylsiloxane (PDMS) stamp was made from the master with the V-groove. To prepare the PDMS stamps, elastomer (Sylgard 184, Dow Corning) and curing agent (Dow Corning, more curing agent makes stamps stiffer) were mixed thoroughly in a weight ratio of 9:1. When the mixture became viscous, the solution was poured onto the master. The PDMS was kept standing in a vacuum box until all the small bubbles disappeared. Then, the material was put on a hot plate at 60°C for one hour. The stamp was removed from the master and heated again on the hot plate for approximately 4 h at 85°C. The PDMS stamp had a 5-μm-wide line structure pattern with a sharp edge (Fig. 2).

Usually, rectangular block-type PDMS stamps are used in μCP. This means that nanometer-scale PDMS is necessary for nanopatterning in μCP. In our experiments, the sharp edge of the fabricated PDMS stamp is used for nanopatterning of SAMs without special nanopatterning equipment such as that used in EB lithography. However, the sharp tip of the stamp can be distorted due to the deformation of elastomeric stamp during printing, and it is still not easy to achieve a resolution of sub-100 nm or better.

2.5 *Microcontact printing (μCP)*

During the process, μCP was performed twice. Each μCP was carried out in the same way. A cotton stick was used for inking the stamp with SAM solution: 10 mM HDT solution and 1 mM 11-MUA solution. Instead of immersing the stamp in the ink, inking in this way can minimize the diffusion of each SAM by eliminating the undesirable area contact due to stamp collapse during printing. The stamp was dried for 30 s in an air stream after inking. Stamp was put in contact with the Au surface for 10 s and bubbles between the stamp and Au were removed by pressing gently by hand.

2.6 *Au etching*

A Au-etching solution was prepared by dissolving 0.001 M $K_4Fe(CN)_6 \cdot 3H_2O$ (Wako, 99.5+%), 0.01 M $K_3Fe(CN)_6$ (Wako, 99+%), 0.1 M $Na_2S_2O_3 \cdot 5H_2O$ (Wako, 99+%) and 1 M KOH (Wako, 85+%) to a volume of 250 ml. The temperature of the etchant was

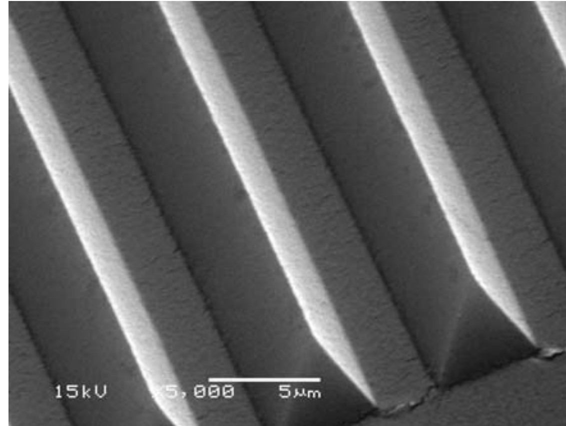


Fig. 2. SEM image of PDMS stamp with sharp edge (5 µm width).

maintained at 42°C using a hotplate with stirring of 400 rpm during etching. To determine the etching rate, the normal substrate without any SAM pattern was immersed in the etchant. After 3 min, the 50-nm-thick Au layer was completely etched. The experimental etching ratio of Au in this solution was found to be approximately 17 nm per minute. After the first and second µCPs, each sample was immersed in the same etchant for 3 min. The printed SAM on Au can be used as a resist in subsequent etching processes against etchants such as cyanide. The etching ratio is dependant on temperature. In both experiments, the 50-nm-thick Au layer except the SAM/Au pattern was completely etched.

2.7 *Laminated patterning process*

Figure 3 shows the schematic of the laminated patterning process. First, we make an HDT line pattern on a previously prepared Au/Cr/SiO_2 substrate by µCP. By using the transferred HDT pattern as a mask, the Au layer is completely etched except for the printed HDT region. In the following, an additional Au layer is deposited on the surface of the sample to prepare it for the substrate of the second µCP of 11-MUA. Another PDMS stamp of the same structure as that of the previous one is inked with 11-MUA solution and visually aligned in the cross direction of the HDT pattern. After printing, the remaining Au/Cr layer on the wafer is etched completely using the transferred 11-MUA pattern as a mask. Finally, the sample is immersed in DTS solution and coated with DTS on a SiO_2 layer. Through this process, we can produce multilayer SAM patterns.

2.8 *Surface measurements*

Each SAM pattern was characterized by two modes of topology and an LFM image obtained by AFM (JSPM-5200, JEOL Company). The surface scanning process was performed in the contact mode and the clock speed was 500 µs, the frequency of the feedback filter was 1.00 Hz, and the loop gain value was 8.

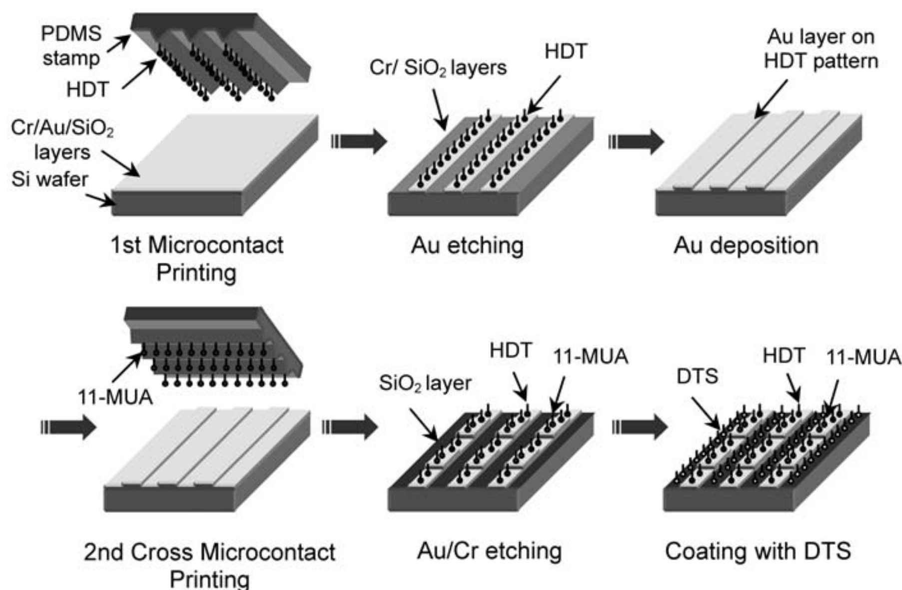


Fig. 3. Schematic view of laminated patterning process.

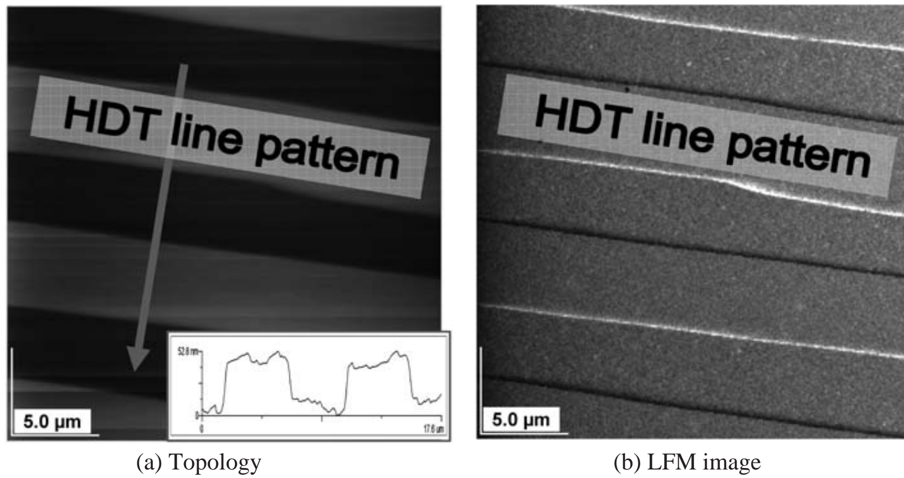
3. Results and Discussion

After the first μCP of the HDT pattern, the surface of the sample was observed by AFM to make sure that the line pattern was transferred well. Figure 4 shows the topology and LFM image of the result. A 4-μm-wide line pattern was transferred to a Au substrate. Because the external Au layer was etched completely, the height of the HDT line pattern was measured as 50 nm.

The topology of the surface transferred by the laminated patterning process is shown in Fig. 5(a). After the entire Au layer was etched, the 11-MUA dot pattern appeared 100 nm from the bottom and the HDT line pattern appeared at a height of 50 nm. At the bottom of the sample, the DTS was patterned on the SiO_2 surface. From the profile of the surface and the wettability of each area, each multilayer can be characterized.

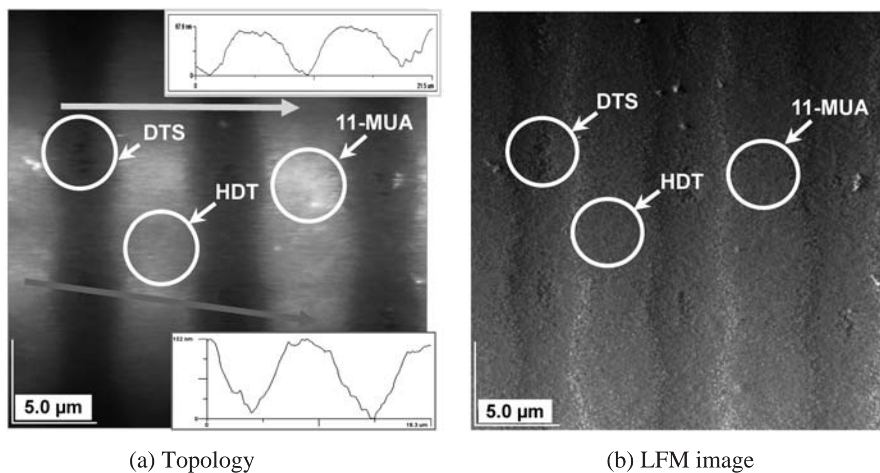
Figure 5(b) shows the LFM image of the multilayer pattern obtained by the laminated patterning process. Although the DTS pattern was not completely transferred to the surface because of the residual Cr layer, the surface property of each SAM can be clearly observed.

However, the lateral pattern size is not on the nanometer scale yet. This is mainly due to the deformation of the PDMS stamp, the diffusion of the SAM, and the etching rate. In addition, the physical and chemical properties of the SAM, such as viscosity, density, and pH, seem to be related to the size of the pattern. During μCP, SAM molecules on the side of the stamp can diffuse to the substrate gradually and these enlarge the pattern. This effect usually depends on the stamping duration. Etching rate can also have an effect on the pattern due to side-etching. In our research, we focused on decreasing the deformation of the PDMS stamp. The effects of the diffusion of SAM molecules and etching rate were not



(a) Topology (b) LFM image

Fig. 4. AFM images of HDT lines pattern obtained by mCP.

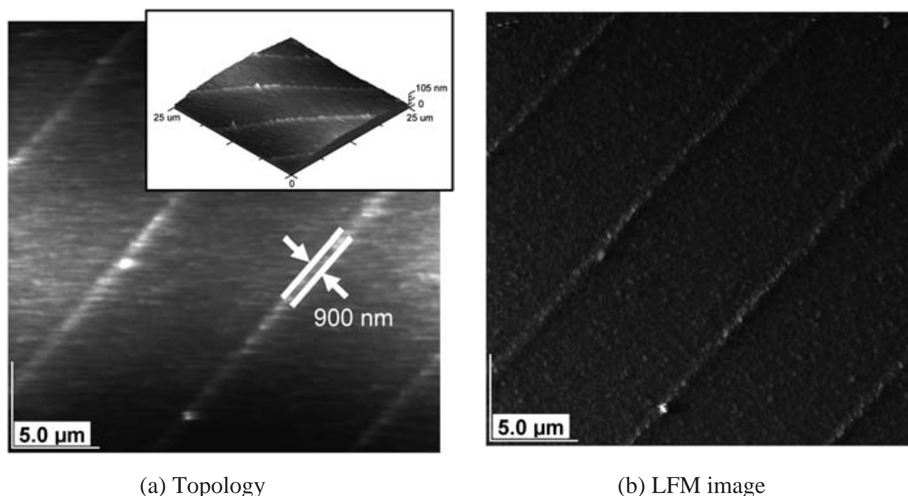


(a) Topology (b) LFM image

Fig. 5. AFM images of multilayer pattern obtained by laminated patterning process.

considered in the experiments under the same conditions. Through controlling the stamping force precisely, the pattern can be transferred with nanometer resolution. In our previous study, a sub-µm scale dot pattern of HDT was fabricated using the sharp tip of a pyramidal PDMS stamp.(8)

Figure 6 shows the possibility of patterning SAMs with nanometer resolution using the sharp edge of the PDMS stamp. In this experiment, stamping force was controlled more carefully using airflow and approximately 1/10 the pressure of the previous hand-pushing method was applied to the stamp. As a result, a 900-nm-wide line pattern of HDT was transferred onto the Au substrate.



(a) Topology (b) LFM image

Fig. 6. AFM images of HDT line pattern obtained by µCP controlling stamping force.

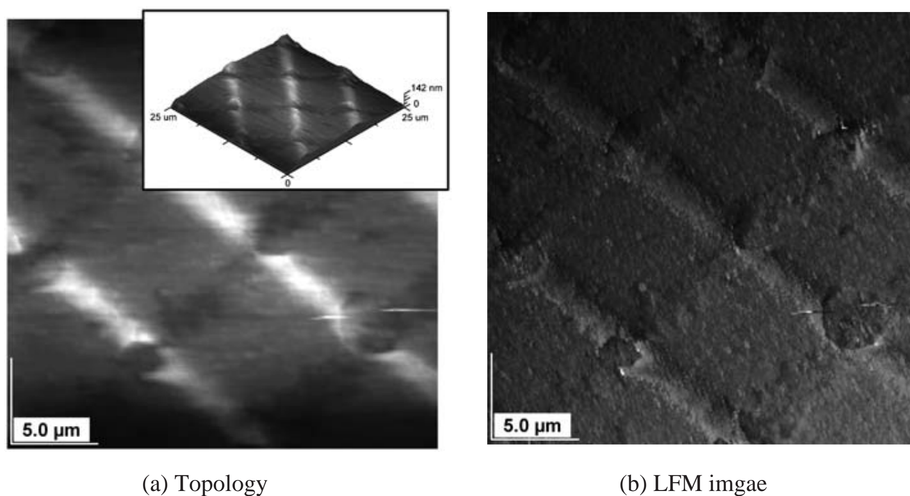
Another result of the laminated patterning process is shown in Fig. 7. A cross pattern of a 1.8-µm-wide HDT line and a 7-µm-wide 11-MUA line was transferred to laminated Au layers. Although the pattern size is not on the nanometer scale, we can confirm the possibility of fabricating a smaller multilayer cross-line SAM.

4. Conclusion

The present results indicate the possibility of multipatterning of various types of SAMs by microcontact printing. Because our study for the development of the laminated patterning technique is still in the early stage of the feasibility test, there is much room for improvement. Through a more precisely controlled process, the multipatterning of various SAMs with nanometer resolution can be accomplished. In fact, controlling the factors of µCP related to pattern size such as stamping force still remains an important problem. However, through all these experimental results, we know that nanometer-scale patterning of SAMs by the laminated patterning technique will be possible using a proper controlling device of stamping force. In addition, this novel method for the multilayer patterning of SAMs will be applied for practical industrial applications to achieve high throughput and low cost due to the use of a micrometer-scale PDMS.

The laminated patterning technique has a high potential in MEMS technology for the surface modification of various types of functional SAMs with hydrophobic and hydrophilic surface properties as well as the multipatterning technique of soft lithography by low-cost µCP.

As further study, controlling factors related to the fabrication of precise patterns, such as stamping force, diffusion of SAM and etching rate, will be investigated to realize nanometer-scale multipatterning of various SAMs. Three types of SAMs were selected to



(a) Topology (b) LFM imgae

Fig. 7. AFM images of multilayer pattern obtained by laminated patterning process controlling stamping force.

verify each SAM pattern by measuring their surface property. When this technique is used in practical applications, another type of functional SAM combined with biomaterials such as proteins and DNA, will be used. Finally, using each discriminated property of functional multilayer SAMs transferred by this laminated patterning technique, the fabrication of a biosensing device will be realized.

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