

Printing of Au nanoparticles by VUV-exposed patterned surfaces of a poly(dimethylsiloxane) film

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This paper dealt with exposure of a nanometer-level flat cross-linked poly(dimethylsiloxane) film to vacuum ultraviolet light (VUV) at a wavelength of 172 nm and its application to printing of Au nanoparticles. FTIR and contact angle measurements allowed us to confirm the formation of a silica outermost layer on the PDMS film due to photo-oxidation of a methylsilyl group to a silanol group and condensation to a Si-O-Si moiety. It was indicated by AFM observation on a PDMS film surface patterned by imagewise VUV-exposure that the height of VUV-exposed regions was lower than that of unexposed regions by approximately 10 nm due to shrinkage by condensation among the photogenerated silanol groups. Location-selective inking of an Au-nanoparticle/toluene solution was possible on the VUV-exposed patterned PDMS surfaces. Au-nanoparticle micropatterns in about 30 μm size were successfully transcribed on a silica substrate surface from the inked PDMS film.

Key words: PDMS, pattern, printing, wettability, Au nanoparticle, VUV-exposure

1. INTRODUCTION

Since the report in 1993, microcontact printing (μCP) has proven a versatile technique for pattern fabrication of advanced materials with (sub)micrometer-sized critical dimensions.¹ In μCP , a relief-structured soft elastomer stamp with a relief height range of 0.2 – 20 μm is brought in contact with ink (a solution containing molecules, biomolecules or nanoparticles), and the ink is transferred on a solid substrate surface by subsequent contact with the elastomer stamp.² The contact regions are separated by voids of stamp relief-structure. An ethanol solution of alkanethiol is used mainly as ink to tune physicochemical surface property. In contact regions, a patterned self-assembled monolayer (SAM) is formed. A solution of metal nanoparticles has been used recently as advanced ink, and their single-layered patterns are investigated as a conductive material.^{3,4} A nickel or silicon master mold to prepare an elastomer stamp of cross-linked poly(dimethylsiloxane) (PDMS) is fabricated by photolithography with an organic resist material. Therefore, another method for patterning directly a PDMS film is desirable because mold fabrication steps are reduced.

In this article, we prepared a nanometer-level flat surface of a PDMS film and irradiated the PDMS surface with vacuum ultraviolet light (VUV) at a wavelength of 172 nm. The photoinduced events were investigated by FTIR, AFM, and contact angle measurements. We demonstrated that a PDMS stamp with hydrophobic PDMS surface regions and hydrophilic silica surface regions made by photolithographic micropatterning was available to patterning of Au nanoparticles on a silica

substrate surface.

2. EXPERIMENT

2-1. Material and Method

Liquid poly(dimethylsiloxane) (Sylgard 184A) and cross-linker (Sylgard 184B) were purchased from Dow Corning Co., Ltd. The Sylgard 184A contains siloxane base oligomers with plural vinyl groups, while the Sylgard 184B contains siloxane base polymers with hydrosilyl groups and a platinum-type catalyst to carry out hydrosilylation reactions. A hydrosilyl (Si-H) group is reacted with a vinyl group to form a -Si-CH₂-CH₂- linkage.^{5,6} A substrate surface of mica or naturally oxidized Si(100) plate was immersed in trimethylchlorosilane before use. A mixture at a weight ratio of 1 Sylgard 184B to 10 Sylgard 184A was prepared and spin-coated (3000 rpm, 20 s) on the modified mica plate or Si(100) plate subjected to FTIR measurement. After curing at 65 °C for 12 h, a PDMS film was peeled from the substrate surface, and its flat PDMS surface was irradiated with vacuum ultraviolet light at 172 nm emitting from a Xe excimer lamp (Ushio Co., Ltd.) under a reduced pressure of 1 kPa. Photopatterning was performed with a copper grid photomask. A toluene solution containing 5-wt% decanethiol-passivated gold (Au) nanoparticles having an average diameter of 2.2 nm (Tanaka Kikinzoku Group Co., Ltd) was used as ink.

2-2. Characterization

Contact angle measurements were carried out by a contact angle meter (Kyowa Interface Science, CA-X) using deionized water as probe liquid. Surface images were taken in a tapping mode by an atomic force microscope (AFM) (Nanoscope III, Veeco Instrument). Optical

microscope images were captured by an optical microscope (Olympus, BX60) with a color CCD camera (Olympus, DP70).

3. RESULTS AND DISCUSSION

3-1. Preparation of a Self-Standing Flat PDMS Film

A self-standing flat PDMS film was obtained by peeling a cross-linked PDMS film cast on a mica plate modified with trimethylchlorosilane (TMS). The TMS treatment allowed us to peel away readily the PDMS film from the mica plate. Fig. 1(a) shows a photograph of the self-standing PDMS film. The PDMS film was transparent and flexible. A PDMS surface prepared on a side of the TMS-treated mica surface was visualized by AFM. Fig. 1(b) showing the topographical image ($100 \times 100 \mu\text{m}^2$) in a tapping mode clearly supported that the PDMS surface was flat at a nanometer level. The value of root-mean-square (RMS) roughness was 1.9 nm. The flat self-standing PDMS film was successfully prepared using the TMS-modified mica surface.

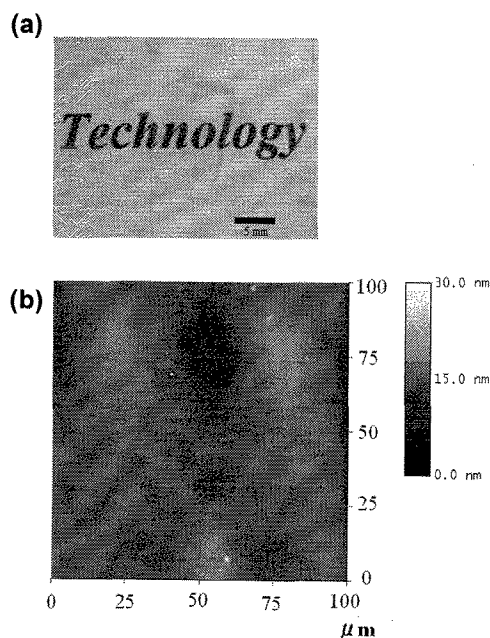


Fig. 1. (a): Photograph of a self-standing flat PDMS film peeled from a TMS-modified mica plate. (b): An AFM topographic image of the film surface prepared on a side of TMS-modified mica surface.

3-2. Chemical Change in a PDMS Surface by VUV-Exposure

Vacuum ultraviolet light (VUV) at a wavelength of 172 nm causes an oxygen molecule to alter to an oxygen atom, $\text{O}^{\text{(1D)}}$, in a singlet state. The $\text{O}^{\text{(1D)}}$ attacks a hydrocarbon moiety

and results in generation of H_2O and CO_2 species eventually by so-called photo-oxidation.⁷ We applied the photo-oxidation to the film surface of PDMS. The VUV-exposure was carried out under three different pressures of 101 (an atmosphere pressure), 1.0 and 0.1 kPa.

Contact angle measurements using water as probing liquid allowed us to follow alteration from a hydrophobic PDMS surface to a hydrophilic surface by VUV-exposure. Fig. 2 indicates changes in contact angle of the PDMS surface for water as a function of exposure time. Under 101 kPa, the contact angle of $115 \pm 3^\circ$ was decreased slightly to $110 \pm 2^\circ$ by the VUV-exposure for 60 s. In contrast, the hydrophobic PDMS surface altered completely to a hydrophilic surface exhibiting a contact angle lower than 5° by the VUV-exposure for 30 s under 0.1 and 1.0 kPa. The decreased contact angle for water implies that organic hydrocarbon moieties such as methyl groups were removed from the PDMS outermost surface by

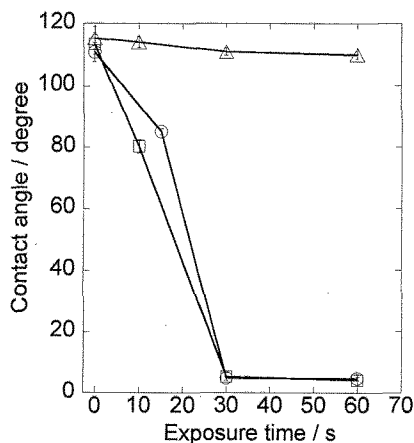


Fig. 2. Contact angle changes for water on a self-standing PDMS surface as a function of VUV-exposure time under (Δ) 101, (\circ) 1.0 and (\square) 0.1 kPa.

photo-oxidation. According to the result, we determined the VUV-exposure time for 30 s and the reduced pressure of 1 kPa as a condition of the VUV-exposure.

A PDMS spin-coated film having a thickness of about 150 nm was prepared on a Si plate to follow chemical transformation of the PDMS film by the VUV-exposure. Fig. 3 shows FTIR spectral changes of the PDMS film by VUV-exposure. The VUV-exposure caused a noticeable decrease in absorbance derived from CH_3 rocking and Si-C stretching vibration bands at 800 cm^{-1} and a symmetric $-\text{CH}_3$ deformation vibration band at 1260 cm^{-1} in Si- CH_3 moiety. Decreases in their absorbance intensities clearly supported that methyl groups in the PDMS film

disappeared by photo-oxidation. In contrast, two bands centered at 1026 and 913 cm^{-1} , attributable to an asymmetric Si-O-Si and a Si-OH stretching vibration band, respectively, grew by the VUV-exposure. This means that $\text{CH}_3\text{-Si-O}$ segments in PDMS were transformed to

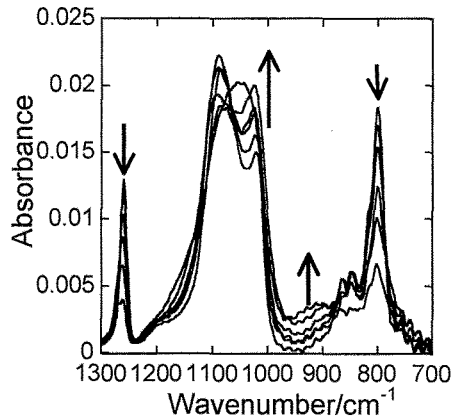


Fig. 3. FT-IR spectral changes of a PDMS film having a thickness of 150 nm on a Si(100) plate with an increase of VUV-exposure time (0, 10, 30, 60, 120, and 300 s).

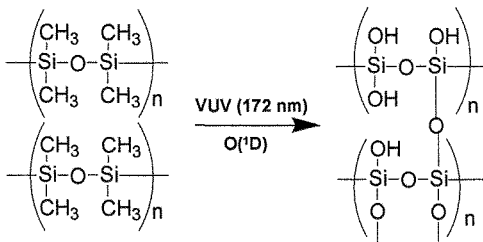


Fig. 4. Photo-oxidation and condensation of PDMS by VUV-exposure.

HO-Si-O segments, followed by condensation to O-Si-O moieties as shown in Fig. 4. The FTIR and contact angle measurements allowed us to confirm the formation of a silica outermost layer on the PDMS film due to photo-oxidation of a methylsilyl group to a silanol group and condensation to a Si-O-Si moiety.

Phely-Bobin and coworkers report that a hydrophobic PDMS surface can be changed to a hydrophilic surface by irradiation with UV-light at 185 and 254 nm emitting from a low-pressure Hg lamp. They conclude that the UV-exposed PDMS surface is like a silica surface.⁸ To obtain such a silica surface, very long UV-exposure time for 5400 s is required. It took only 30 s to carry out surface refinement of the PDMS surface in our method using VUV-exposure at 172 nm.

3-3. Morphological Change in a PDMS Surface by VUV-Exposure

We investigated whether any topological changes were brought about at the PDMS surface by VUV-exposure. A copper grid as a photomask was placed on the PDMS film surface, and VUV-exposure was carried out. A topological change of the PDMS surface was traced by AFM. Fig. 5 shows AFM images of the PDMS film surface after imagewise VUV-exposure. Fig. 5(a) and 5(b) indicate its topographic image and phase-shift image, respectively. The topographic image revealed that any changes in roughness were not caused in VUV-exposed regions. A feature to describe is

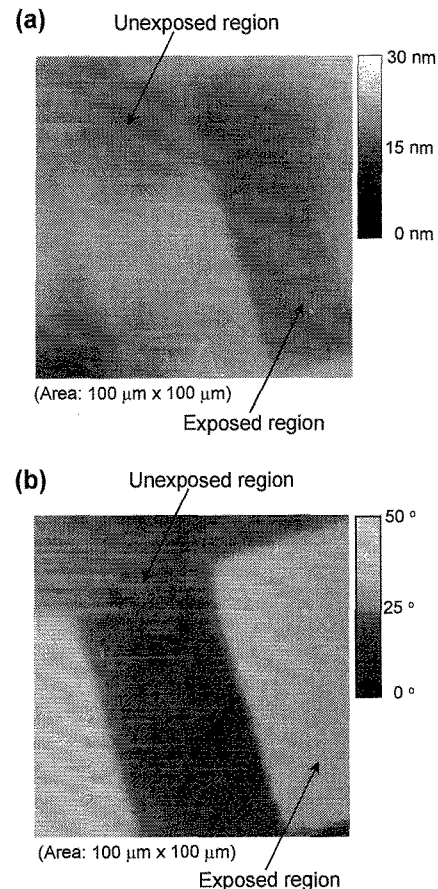


Fig. 5. (a) Topographic and (b) phase-shift AFM images of a surface of a self-standing PDMS film by imagewise VUV-exposure for 30 s.

that the height of VUV-exposed regions was lower than that of unexposed regions by approximately 10 nm. The phase-shift image clearly showed a difference between the VUV-exposed and unexposed regions. A phase delay of cantilever oscillation in the unexposed regions was significantly smaller than that in the VUV-exposed regions. The difference in phase

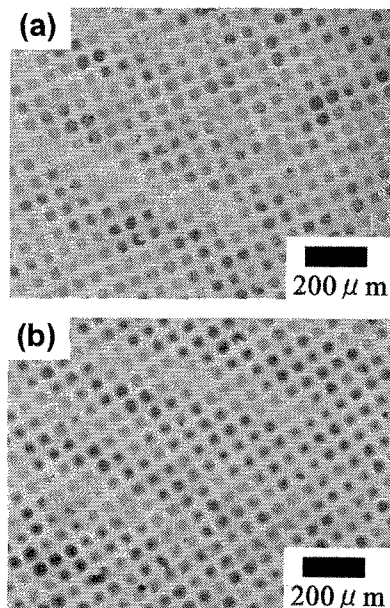


Fig. 6. Optical microscope images of (a) a VUV-exposed patterned PDMS surface coated with ink of Au nanoparticle/toluene solution and (b) a silica substrate surface transcribed from the PDMS surface with ink pattern.

delay was probably due to formation of rigid silica layer on an outmost surface of the PDMS film.

The studies on the VUV-exposed surface of the PDMS film by means of FTIR, contact angle and AFM measurements clarified next. When the PDMS film was exposed to VUV at 172 nm, methyl groups in the PDMS film was removed by photo-oxidation. The photo-oxidation caused silanol groups to be formed at an outmost layer of the PDMS films. Photogenerated silanol groups were condensed, to form Si-O-Si networks like silica in the PDMS surface. The VUV-exposed PDMS surface stepped back by the condensation reaction.

3-4. Location-Selective Inking on a VUV-Exposed Patterned PDMS Surface and Transcription of Ink Pattern on a Solid Substrate.

As mentioned in introduction, in μ CP, a relief-structured soft elastomer stamp with a relief height range of 0.2 – 20 μ m is brought in contact with ink, and the ink is transferred on a solid substrate surface.² We could prepare flat PDMS elastomer stamp by VUV-exposure which can not be categorized into μ CP in terms of the relief height range. The flat PDMS stamp consisted of VUV-exposed silica surface regions

and unexposed PDMS surface regions. The height difference between the VUV-exposed and unexposed regions was approximately 10 nm.

We chose a toluene solution of 5 wt% Au nanoparticles having an average diameter of 2.2 nm as ink. When the ink was cast on the VUV-exposed patterned PDMS film surface, interestingly the unexposed PDMS surface repelled the ink. As a result, the ink was collocated only in the VUV-exposed PDMS surface as shown in Fig. 6(a). The selective inking of the Au-nanoparticle/toluene solution on a VUV-exposed patterned surface was probably due to the photogenerated silica surface with a surface energy higher than the unexposed PDMS surface and/or topographic depression by 10 nm compared with the unexposed PDMS surface.

The inked PDMS film was contacted with a silica substrate surface. As can be seen in Fig. 6(b), the Au-nanoparticle/toluene ink was successfully transcribed on a silica substrate surface. Patterns of Au nanoparticles in about 30 μ m size could be obtained easily.

4. CONCLUSION

In this article, we demonstrated that a PDMS film exposed to vacuum ultraviolet light (VUV) at 172 nm through a photomask was available to printing of Au-nanoparticles on a silica substrate surface. VUV-exposure caused a hydrophobic PDMS surface to be transformed to a hydrophilic silica surface by photo-oxidation. The photo-oxidation was carried out effectively by using a Xe excimer lamp. To our knowledge, this article is the first report on selective inking and printing of Au nanoparticles by a PDMS stamp fabricated by means of exposure technique.

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