

Enhanced molecular patterning via microdisplacement printing

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Here we demonstrate the versatility of “microdisplacement printing,” a soft lithographic patterning technique that employs microcontact printing to replace pre-formed self-assembled monolayers (SAMs) selectively. We use molecules that are common in microcontact printing as well as low-molecular-weight molecules that cannot be patterned by traditional methods. Multiple component SAMs were fabricated by additional processing steps, extending microdisplacement printing to more complex patterns. © 2005 American Vacuum Society. [DOI: 10.1116/1.2135794]

I. INTRODUCTION

Soft lithography offers inexpensive and rapid fabrication techniques (such as microcontact printing, dip-pen nanolithography, nanoimprint lithography, and micromolding) for patterning on the nanometerscale.^{1–3} One of the most common soft lithographies is microcontact printing (μ CP)—the patterning of a substrate by contact (“stamping”) with a “molecularly inked” elastomeric stamp. It is a rapid and simple methodology that produces high spatial resolution patterns over a large printing area.^{1–3} However, it is limited in the library of applicable molecules because molecules diffuse during patterning.^{4–6} This problem can be avoided by an alternate patterning technique, “microdisplacement printing” (μ DP), which uses a preassembled monolayer that is sufficiently ordered to protect the surface, but is sufficiently labile that other molecules can displace it through competitive adsorption.⁷ Stamping on such a surface precludes the ability of the ink molecules to move anywhere but where their local concentration is highest and holds the ink molecules in place once adsorbed during the stamping procedure.

For this labile monolayer, we use 1-adamantanethiolate (AD) self-assembled monolayers (SAMs).^{7,8} Adamantane ($C_{10}H_{16}$) is comprised of a ten-carbon cage made of four fused cyclohexane rings in chair conformations. The addition of a sulfur group, creating 1-Adamantanethiol ($C_{10}H_{15}SH$), allows the carbon cage to be tethered to a gold surface while still keeping its round topology. 1-Adamantanethiolate SAMs are highly ordered and have less prominent domain boundaries than alkanethiolate SAMs, but because of their low intermolecular interaction strength, AD molecules are easily displaced by other molecules both during and after SAM formation.⁸ Solution insertion of alkanethiol molecules into AD SAMs results in the replacement of the AD molecular lattice with alkanethiolate lattices leaving two molecularly ordered phases. Given enough time, the displacement process results in a SAM composed entirely of alkanethiolate molecules.

Here, we show that the remaining AD in μ DP patterned samples can be replaced by further displacement steps, either solution immersion or contact stamping. Immersion of a patterned sample in a different thiol solution for several hours does not degrade the pattern. Additionally, three-component patterned SAMs were fabricated by the inclusion of a second displacement patterning step both on μ CP patterned samples containing AD and on μ DP samples.

II. EXPERIMENTAL METHODS

All SAMs were assembled on Au{111} via solution deposition in argon-sparged ethanol. Commercially available Au{111} on mica substrates (Molecular Imaging, Tempe, AZ) were annealed using a hydrogen flame or ultraviolet/ozone cleaned just prior to deposition. 1-Adamantanethiol (synthesized by methods previously described^{8–10}) SAMs were prepared by immersing the annealed substrates in a 10 mM ethanolic solution for 24 h. Postdeposition, each sample was rinsed in neat ethanol and blown dry with inert gas twice.

The polydimethylsiloxane (PDMS) polymer was made by combining a 10:1 ratio of PDMS Sylgard 184 Base and PDMS Sylgard 184 Cure (Dow Corning, Midland, MI) and stirring rigorously until they were thoroughly combined. Patterned stamps were formed from either diffraction grating (Optometrics LLC, Ayer, MA) or photolithographically defined silicon masters. Prior to stamp fabrication, a (heptadecafluoro-1,1,2,2-tetra-hydrodecyl) trichlorosilane (Gelest, Morrisville, PA) SAM was formed on the silicon masters to prevent PDMS adhesion to the silicon. The PDMS prepolymer was poured over the masters in empty plastic Petri dishes (VWR International, West Chester, PA) and was then deaerated in a vacuum desiccator until degassing was no longer observed. The PDMS was then cured at 90 °C for 2 h.

To remove any uncured or low-molecular-weight PDMS, once cured, the stamps were excised from the Petri dish and cleaned using a method modified from Graham *et al.*¹¹ The stamps were sonicated in hexane for 30 min, dried with inert gas, heated at 90 °C until the PDMS returned to its original size, sonicated for 5 min in 2:1 ethanol and water, and dried with inert gas three times. The whole procedure was then

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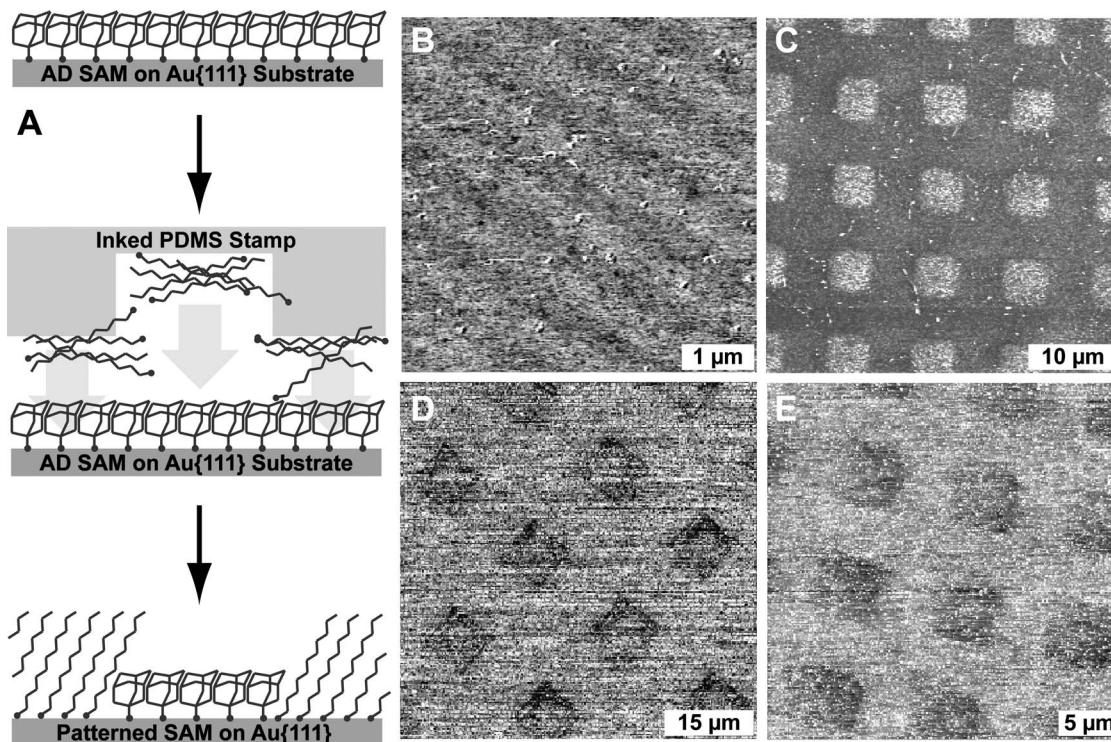


FIG. 1. (a) Schematic depicting μ DP on an AD SAM with an inked stamp of a second thiolated molecule. An AD SAM is first formed on gold by solution deposition for 24 h. Then, the molecularly inked polydimethylsiloxane stamp is contacted directly onto the AD SAM, resulting in patterned regions of both AD and the second molecule that mirror the relief pattern on the stamp. Note that the schematic is not to scale. (b)–(e) Examples of Au{111} patterned by μ DP with different molecules. (b) Lateral force microscopy micrograph of a pattern made using a 1200 lines/mm stamp inked with a 25 mM 11-mercaptoundecanoic acid solution (3 min contact time). The high-friction (shown as light) stripes are the stamped 11-mercaptoundecanoic acid and the low-friction (shown as dark) stripes are the AD SAM. The imaged area was $10\ \mu\text{m} \times 10\ \mu\text{m}$, recorded at a scan rate of 2 Hz with a force setpoint of 0.5 nN. (c) Noncontact phase micrograph of a pattern made using a stamp with $5\ \mu\text{m}$ square wells at a $10\ \mu\text{m}$ pitch that was inked with a 50 mM 1-octadecanethiol solution (3 min contact time). The high-contrast squares are the AD SAM and the low-contrast background is the stamped 1-octadecanethiolate. The imaged area was $40\ \mu\text{m} \times 40\ \mu\text{m}$, recorded at a scan rate of 1 Hz. (d) Lateral force microscopy micrograph of a pattern made using a stamp with $10\ \mu\text{m}$ square posts at a $20\ \mu\text{m}$ pitch that was inked with a 25 mM 1-decanethiol solution (5 min contact time). The low-friction squares are the stamped 1-decanethiolate and the high-friction background is the AD SAM. The imaged area was $60\ \mu\text{m} \times 60\ \mu\text{m}$, recorded at a scan rate of 2 Hz with a force setpoint of 2 nN. (e) Lateral force microscopy micrograph of a pattern made using a stamp with $5\ \mu\text{m}$ square posts at a $10\ \mu\text{m}$ pitch that was inked with a 25 mM 1-octanethiol solution (5 min contact time). The low-friction squares are the stamped 1-octanethiolate and the high-friction background is the AD SAM. The imaged area was $30\ \mu\text{m} \times 30\ \mu\text{m}$, recorded at a scan rate of 1 Hz with a force setpoint of 1 nN.

repeated three times, and finally the stamps were dried in the oven for 15 min. Between uses, each stamp was cleaned with one cycle of the previous cleaning method.

An ethanolic solution of the ink molecules was pipetted directly onto the stamp, allowed to absorb to the PDMS surface for 10 s and subsequently dried off with inert gas. 1-Octadecanethiol ($\text{C}_{18}\text{H}_{37}\text{SH}$, ODT), 1-decanethiol ($\text{C}_{10}\text{H}_{21}\text{SH}$, C10) and 1-octanethiol ($\text{C}_8\text{H}_{17}\text{SH}$, C8) were purchased from Lancaster (Pelham, NH). 11-Mercaptoundecanoic acid ($\text{CO}_2\text{HC}_{10}\text{H}_{20}\text{SH}$, MUDA) was purchased from Sigma-Aldrich (St. Louis, MO).

Microcontact printed samples were fabricated using bare, clean Au{111} on mica substrates by applying an inked stamp to the gold surface for the specified amount of time and subsequently backfilling using a 1 mM ethanolic solution of a different molecule for 5 min.^{1,12} In contrast, μ DP samples were prepared using AD SAMs on Au {111} as substrates. The inked stamp was applied to the SAM surface for the specified time and the samples were then rinsed thoroughly with ethanol (rinsing is not necessary, but removes molecules

not bound to the surface, making imaging considerably easier) and dried with inert gas. No backfill was performed.⁷

Additional solution processing steps were also performed on AD-containing μ CP and μ DP samples. In the μ CP cases, after the initial backfill with AD, the sample was rinsed with ethanol, dried with inert gas, and then immersed in another thiol solution. In the μ DP cases, after displacement patterning, the sample was immersed in another thiol solution without rinsing.

Additional patterning steps were also performed on AD-containing μ CP and μ DP samples. After the initial patterning steps, a second pattern was fabricated directly on top of the first pattern by the μ DP method.

Within minutes of preparation, each sample was imaged using either lateral force microscopy (LFM) or phase imaging. Lateral force microscopy, a contact mode measurement, uses frictional differences between molecules to map surfaces on a nanometer scale. Phase imaging (a noncontact mode that measures the difference in phase between the tip driving signal and the response signal) was used to verify the

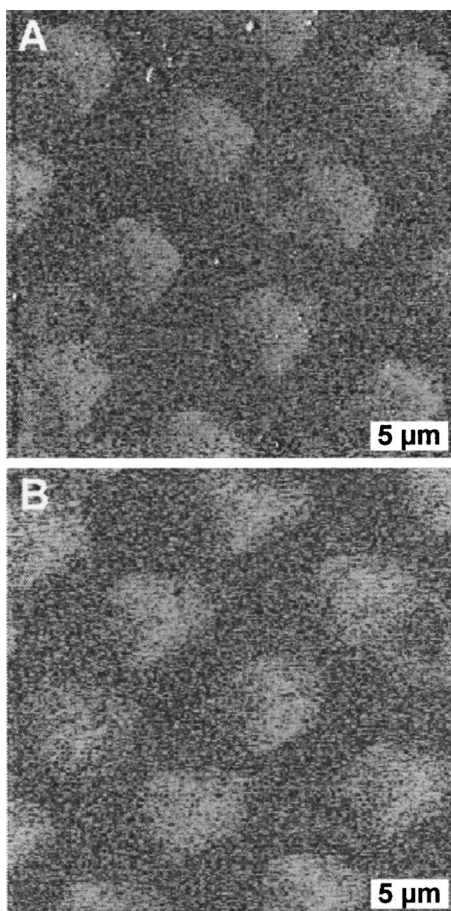


FIG. 2. Noncontact phase micrographs of Au{111} patterned by microdisplacement printing using a polydimethylsiloxane stamp with $5\ \mu\text{m}$ square posts at a $10\ \mu\text{m}$ pitch that was inked with a $50\ \text{mM}$ 11-mercaptopundecanoic acid solution (5 min contact time) before (a) and after (b) the sample was immersed in a $1\ \text{mM}$ 1-octanethiol solution for 2 h. The high-contrast squares are the stamped 11-mercaptopundecanoic acid. The imaged areas were $30\ \mu\text{m} \times 30\ \mu\text{m}$, recorded at a scan rate of 1 Hz.

existence of a pattern, however, the resulting contrast was found to give little information about the molecular species present. All atomic force microscopy (AFM) measurements were performed under ambient conditions using a Thermo Microscopes Autoprobe CP Research AFM (Veeco, Santa Barbara, CA). Silicon-nitride-coated plank-style AFM tips with a force constant of $0.03\ \text{N/m}$, or platinum-coated V-style noncontact AFM tips with a force constant of $17.2\ \text{N/m}$ were used. Both tip styles were purchased from Mikromasch (Portland, OR).

III. RESULTS AND DISCUSSION

As shown previously, it is possible to displace a labile SAM selectively using μCP methods creating a patterned SAM.⁷ Figure 1 shows the patterning procedure and demonstrates μDP patterning using a variety of molecules. As the schematic shows [Fig. 1(a)], a thiolated molecule is applied to an elastomeric stamp, which is then contacted directly to a prefabricated AD SAM. The thiolated molecules displace the AD molecules where the stamp contacts the sample, leaving

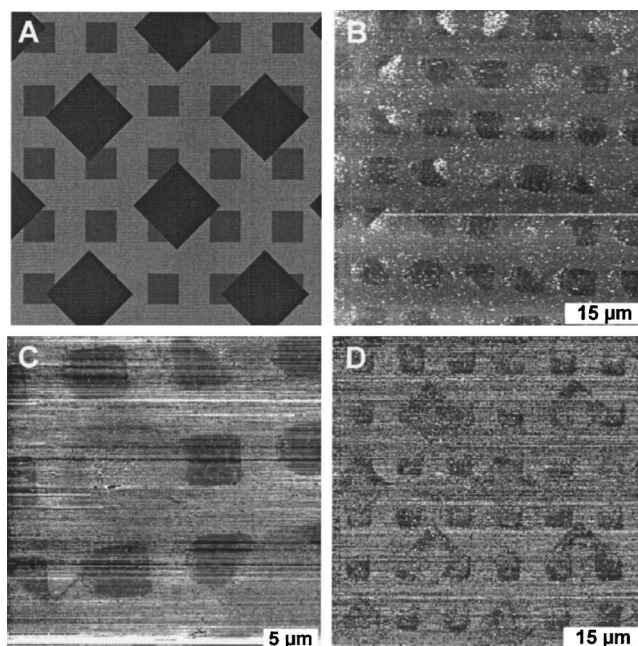


FIG. 3. (a) Schematic depicting the result of two patterning steps using a stamp with large squares first and small squares (rotated 45°) second. The light gray, black, and dark gray represent the AD monolayer, the first patterned molecule (large squares), and the second patterned molecule (small squares), respectively. (b)–(d) Examples of Au{111} patterned in two steps. (b) and (c) Noncontact phase and lateral force microscopy micrographs, respectively, of a sample patterned by microcontact printing using a PDMS stamp with $10\ \mu\text{m}$ square wells at a $20\ \mu\text{m}$ pitch that was inked with a $5\ \text{mM}$ solution of 11-mercaptopundecanoic acid (10 s contact time), back-filled with a $10\ \text{mM}$ solution of AD for 5 min, and subsequently patterned by μDP using a PDMS stamp with $5\ \mu\text{m}$ square wells at a $10\ \mu\text{m}$ pitch that was inked with a $25\ \text{mM}$ 1-octanethiol solution (5 min contact time). (b) The imaged area was $60\ \mu\text{m} \times 60\ \mu\text{m}$, recorded at a scan rate of 1 Hz. (c) The imaged area was $30\ \mu\text{m} \times 30\ \mu\text{m}$, recorded at a scan rate of 1 Hz with a force setpoint of 1 nN. Because the 1-octanethiol displaces the AD but does not displace the 11-mercaptopundecanoic acid, the result of the second pattern step is partial squares. (d) Lateral force microscopy micrograph of a sample patterned by μDP using a PDMS stamp with $10\ \mu\text{m}$ square posts at a $20\ \mu\text{m}$ pitch that was inked with a $25\ \text{mM}$ 1-decanethiol solution (5 min contact time), and subsequently patterned by microdisplacement printing using a PDMS stamp with $5\ \mu\text{m}$ square posts at a $10\ \mu\text{m}$ pitch that was inked with a $25\ \text{mM}$ solution of 1-octanethiol (5 min contact time). The imaged area was $60\ \mu\text{m} \times 60\ \mu\text{m}$, recorded at a scan rate of 2 Hz with a force setpoint of 1 nN.

regions of both AD and the second (stamped) molecule. Figures 1(b)–1(e) show the resulting patterns using MUDA, ODT, C10, and C8, respectively. Each image shows a clear pattern composed of regions of AD juxtaposed to regions of the stamped molecule. In the case of Figs. 1(d) and 1(e) the molecules used (C10 and C8, respectively) are unpatternable by conventional μCP because these low-molecular-weight molecules laterally diffuse across the Au{111} surface during the patterning procedure, before backfilling is possible.^{4–6} The presence of the AD SAM blocks diffusion *during* patterning, holding the molecules in place.

To create more complex patterns, or patterns composed of more than one low-molecular-weight molecule, it is possible to replace the AD regions via subsequent solution deposition or patterning steps.⁸

Figure 2 shows phase images of a MUDA-patterned μDP

sample before (a) and after (b) it has been immersed in a C8 solution for 2 h. Each image in Fig. 2 was taken at the same location on the sample, within a few tens of microns. Although it is not obvious from the images that the AD has been displaced, previous studies have shown that this is a sufficiently long exposure to replace the AD monolayer completely with C8.⁸ It can be seen, however, that the pattern did not degrade after 2 h in solution. Additionally, such patterns remain after exposure to a thiol solution for up to 9 h.

Further evidence that the AD in μ DP samples is labile in further processing steps is shown in Fig. 3, where a second patterning step was performed. In this case, a patterned sample containing regions of adamantanethiol is created by either μ CP or μ DP processes. This sample is then subjected to a second μ DP step during which only the adamantanethiol regions are (further) displaced. As shown schematically in Fig. 3(a), this process results in a three-component SAM made up of, in this case, large squares of one molecule, small squares of a second molecule, and the remaining AD in the background. Figure 3(b) shows a phase image of a MUDA-patterned μ CP sample (large squares) that was backfilled with AD and then patterned a second time with C8 using μ DP (small squares). The figure shows two sets of squares identified with different contrast rotated by $\sim 45^\circ$. A higher resolution LFM image of the same sample is shown in Fig. 3(c). In this image, as in the schematic, the small squares only displace the AD regions, resulting in parts of these smaller, second squares and leaving the original large square pattern intact.

By these methods, it is also possible to pattern two low-molecular-weight molecules. Figure 3(d) shows a LFM image of an AD SAM that was patterned with C10 using μ DP [large square sample shown in Fig. 1(e)], which was then further patterned with C8 using μ DP (small squares). By this method, a two-component, low-molecular-weight, separated,

patterned sample was created via a solutionless, two-step process. This complex patterning is not possible using other soft lithographic methods.

IV. CONCLUSION

We have shown that by μ DP it is possible to pattern reproducibly molecules that are not patternable by other soft lithographic methods. Additionally, we have shown that the remaining adamantanethiol regions can be displaced from μ DP samples without pattern dissolution and that with additional processing steps, we can create complex multicomponent patterns. Microdisplacement printing extends the inexpensive and simple alternatives to traditional lithographic techniques.

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