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J. Am. Chem. Soc., **2007**, 129 (45), 13818-13819• DOI: 10.1021/ja076226k • Publication Date (Web): 19 October 2007

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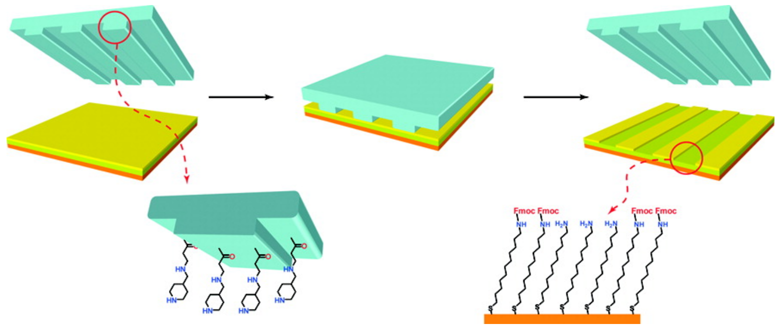

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Published on Web 10/19/2007

Inkless Microcontact Printing on Self-Assembled Monolayers of Fmoc-Protected Aminothiols

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Originally developed by Whitesides and co-workers, microcontact printing (μCP) has become the method of choice for micro- and nanoscale fabrication of surfaces and nanoparticles.[1] Despite its many advantages, several limitations remain, specifically (i) relatively high level of defects due to distortion and deformation of the elastomeric stamp,[2] (ii) a limited number of substrates and molecular inks, and (iii) practical limits to feature sizes near 100−200 nm due to diffusion of molecular inks, both diffusive wetting of surfaces and diffusion of volatile inks through the gas phase.[3] Recent efforts to circumvent these limitations include the replacement of liquid inks with solid analogues,[4] the use of reactive polymers,[5] and the subtraction of inks from flat PDMS stamps in the patterned area followed by printing of the remaining inks on a different substrate.[6]

In 2003, Reinhoudt et al. obviated the diffusive limitations of molecular inks through the use of functionalized stamps that transfer pattern through covalent modification of a preformed surface.[7] Specifically, a SAM surface displaying trimethylsilyl (TMS) ethers was converted to free alcohols during conformal contact with an oxidized PDMS stamp, although the protocol achieved only 30% cleavage. A similar study used plasma-oxidized flat PDMS to promote coupling between amino-terminated SAMs and N-protected amino acids.[8]

We recently reported a μCP method that transfers pattern through the action of a stamp-immobilized biocatalyst on a monolayer of substrate, a process that does not depend on the transfer of the molecular inks.[9] Briefly, an acrylamide stamp bearing immobilized exonuclease I (ExoI) was used to catalyze ablation of single-stranded DNA immobilized on both glass and gold surfaces. This work demonstrated that catalytic μCP can successfully transfer patterns with 14 μm features. Here, we report complete transfer of patterns with sub-micron features using a chemical catalyst bound to a rigid polymeric stamp.

The 9-fluorenylmethoxycarbonyl (Fmoc) amino protecting group is selectively cleaved under mildly basic nonhydrolytic conditions using aliphatic amines such as piperidine, morpholine, and 8-diazabicyclo[5.4.0]undec-7-ene (DBU).[10] In this embodiment of inkless μCP, a stamp bearing polymerized piperidin-4-ylmethanamine is brought into contact with a gold surface functionalized with the SAM of an Fmoc-protected aminothiol, promoting catalytic cleavage of the Fmoc groups. Fmoc-protected SAMs on gold were formed from (9*H*-fluoren-9-yl)methyl 11-mercaptoundecylcarbamate (**1**), prepared in seven steps from 11-aminoundecanoic acid (Supporting Information).[11]

A significant limitation to the resolution of catalytic μCP reported previously[9] was the use of acrylamide stamps: while these materials are easily functionalized, they lack the mechanical rigidity necessary for high fidelity transfer at short length scales. To alleviate this limitation, we utilized a polyurethane acrylate polymer, a material that has previously been used to prepare molds with densely arrayed high aspect ratio nanopatterns with sub-100 nm features for use in replica molding.[12] Monomer **2**, synthesized from isophorone diisocyanate, polyethylene glycol (av. M_w 400 g/mol), and hydroxypropyl acrylate,[13] was diluted by 30% with trimethylolpropane ethoxylate triacrylate (**2**, av. M_n 912 g/mol) to reduce viscosity. To the mixture were added photoinitiators, and the resulting prepolymeric solution was polymerized between two glass slides under UV light to produce control unfunctionalized flat stamp **I** (Figure 1). Flat (**II**) and patterned (**III**) stamps bearing reactive piperidine functionalities were prepared through Michael addition of 2-aminomethyl piperidine (**4**) (8 v/v %) to prepolymeric mixtures prior to polymerization. Preceding the printing experiments, stamps were washed with EtOH for at least 1 h, rinsed with EtOH and H_2O, and dried with filtered nitrogen. The shape and size of the stamp features were identical to those of the corresponding masters, were unaffected during storage at room temperature, and retained their integrity even after heating to 70 °C.

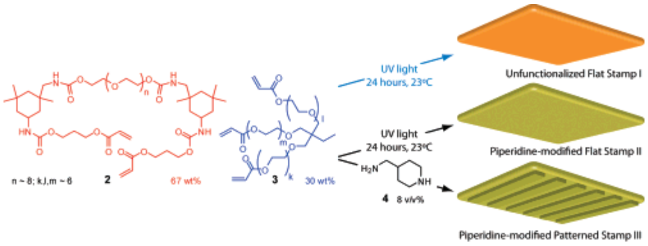

Figure 1. Preparation of polyurethane acrylate stamps.

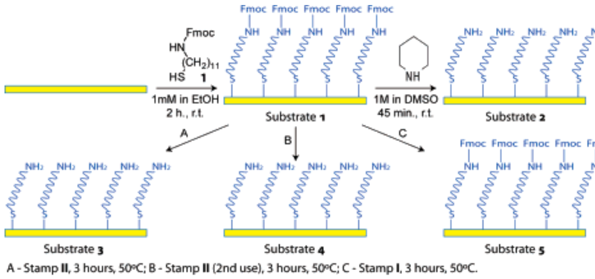

Figure 2. Experiments with unpatterned stamps.

Fmoc-protected SAMs on gold (substrate **1**) were formed by immersing clean gold substrates in 1 mM EtOH solution of **1** for at least 2 h at room temperature. Amino-terminated SAMs (substrate **2**) were prepared from these surfaces by deprotection with a 1 M piperidine solution in DMSO for 45 min at room temperature (Figure 2).[14] Unfunctionalized and reactive featureless stamps were brought into contact with Fmoc-modified SAMs on gold at 50 °C and permitted to react for 3 h (substrates **5** and **3**). Following the first application, the reactive stamp was soaked in EtOH for 1 h,

10.1021/ja076226k CCC: $37.00 © 2007 American Chemical Society

Table 1. XPS Analysis of Substrates **1**−**5**

substrate	Au4p	C1s	C1s/Au4p	Fmoc %	water contact angle
1	23934.2	10562.5	5.03	100	78°
2	32414.7	6745.6	2.37	0	65°
3	35545.4	7566.8	2.42	1.9	64°
4	33141.2	6859.7	2.38	0.4	64°
5	24534.9	10783.9	5.01	99.2	77°

rinsed with EtOH and H_2O, dried with filtered nitrogen, and applied again to fresh Fmoc-protected surfaces to ensure repeatability (substrate **4**).

The efficiency of the deprotection by piperidine-modified and blank stamps was determined by comparison of water contact angles and ratios of the C1s and Au4p signals in XPS spectra. C1s/Au4p signal ratio of unreacted surface was used as a reference for 100% Fmoc-protected sample, whereas C1s/Au4p ratio of Fmoc-protected sample treated with piperidine solution provided a completely deprotected reference. On the basis of these values, piperidine-functionalized stamps effect complete deprotection, while blank stamp produced no detectable change during the reaction. Evaluation based on O1s/Au4p ratios yielded similar results (Supporting Information). These conclusions are further supported by water contact angle measurements (Table 1).

The temperature dependence of the deprotection was examined (Supporting Information). At 60 °C, complete deprotection is achieved in 30 min, while at lower temperatures, significantly longer reaction times are required. The extent to which steric constraints of the closely packed substrates affect the rate of reaction is unclear, and awaits further study.

The goal of this work is to provide a methodology for pattern transfer that alleviates the diffusive resolution limit of conventional μCP. To evaluate this capability, stamps **III** bearing 620 nm lines separated by 380 nm with aspect ratio of 0.15 were used to selectively deprotect SAMs of (9*H*-fluoren-9-yl)methyl 11-mercaptoundecylcarbamate (**1**) on gold. An Fmoc-modified substrate was placed on top of patterned stamps preheated to 50 °C and held in contact for 3 h (substrate **6**). Following reaction, the substrate was washed with EtOH and H_2O, dried with filtered nitrogen, and analyzed by contact mode lateral AFM and SEM. Figure 3 clearly shows the efficiency of the catalytic stamp in nanoscale pattern fabrication, producing patterns consistent across the entire substrate surface and generating features identical in shape and size to those of the corresponding silicon−PMMA master. Produced pattern shows a height difference of approximately 0.65 nm between deprotected and protected regions, which correlates well with the size of the fully extended Fmoc group (∼9 Å), and a friction difference of approximately 14 mV. Printed features demonstrate edge resolution less than 50 nm, indicating diffusion-free process (Supporting Information).

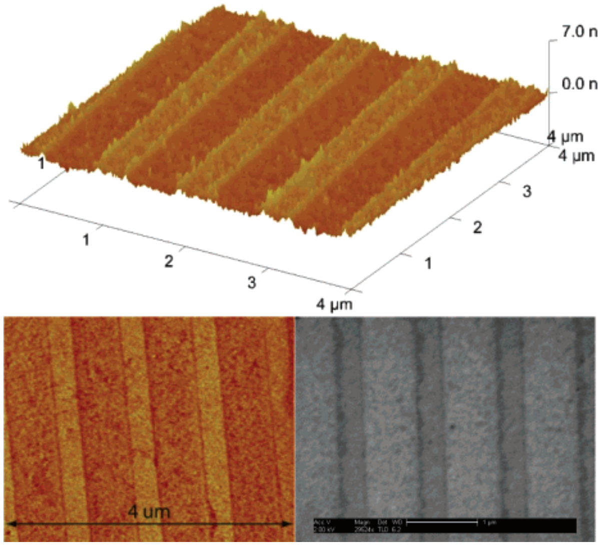

Figure 3. SEM image (bottom right), height (top), and friction (bottom left) LFM images of patterned substrate **6**.

In conclusion, we have demonstrated that piperidine-modified polyurethane acrylate stamps effectively transfer patterns in an inkless variant of μCP. The technique offers several advantages over traditional μCP. Most significantly, the approach obviates the diffusive resolution limitation of μCP and is constrained now only by the mechanical properties of the stamp material. The use of polyurethane acrylate polymer, which was recently utilized to make highly accurate patterned molds with high aspect ratios, eliminates some of the problems of traditional μCP related to deformation and collapse of the elastomeric stamps prepared from PDMS.[3] Finally, the method permits rapid subsequent functionalization of the printed surfaces, providing a route to the patterned SAMs with a range of chemical and physical properties. We continue to explore the utility of inkless μCP and will report our results in due course.

Acknowledgment. We acknowledge the financial support of the NSF (DMI-0600513) and to Matthew S. Johannes and Briana N. Vogen for technical assistance.

Supporting Information Available: Experimental details are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA076226K