

Inkless Microcontact Printing on SAMs of Boc- and TBS-Protected Thiols

Alexander A. Shestopalov,[†] Robert L. Clark,^{*,†} and Eric J. Toone^{*,†}

[†]Department of Chemistry, Duke University, Durham, North Carolina 27708, and [†]Hajim School of Engineering and Applied Sciences, University of Rochester, Rochester, New York 14627

ABSTRACT We report a new inkless catalytic μ CP technique that achieves accurate, fast, and complete pattern reproduction on SAMs of Boc- and TBS-protected thiols immobilized on gold using a polyurethane-acrylate stamp functionalized with covalently bound sulfonic acids. Pattern transfer is complete at room temperature just after one minute of contact and renders sub-200 nm size structures of chemically differentiated SAMs.

KEYWORDS Microcontact printing, soft lithography, catalytic lithography

Microcontact printing (μ CP) was first introduced by Whitesides and co-workers in 1993 as a new flexographic technique for patterning self-assembled monolayers (SAMs) on metal surfaces.^{1–9} It represents the prototypical embodiment of a family of related patterning techniques, collectively termed soft lithography, that make use of conformal contact between a substrate and a flexible stamp as a means of pattern reproduction.^{5,8,10} Since its inception, μ CP has become a highly successful low-cost printing method that efficiently reproduces high-resolution patterns over large surface areas. During the past 20 years μ CP has been successfully utilized to pattern small organic compounds, inorganic substances, biomolecules, and even living cells on a variety of hard materials. Recently, μ CP has been used for the fabrication of organic thin film transistors, where it is utilized as an inkjet printing alternative to pattern conductive organic polymers on both hard and flexible substrates.^{11–15}

Although traditional μ CP is capable of reproducing features with reasonably high spatial resolution, structures smaller than 300 nm significantly limit the number of possible ink-substrate systems and demand precise control over stamping time, the amount of ink applied, the printing force, and the shape and definition of the stamp pattern.^{6,14} In routine applications, several shortcomings of traditional μ CP, especially distortion and deformation of the elastomeric stamp,^{15,16} and more importantly, spreading of molecular inks by both gas diffusion and diffusive wetting,¹⁷ preclude accurate replication of submicrometer features. Several approaches to minimize ink spreading have recently been developed, through substitution of liquid inks by various solid analogues, such as polymers and metal thin films,^{18–22} or by avoiding the use of chemical inks com-

pletely and utilizing instead a catalytic reaction between the elastomeric stamp and substrate.^{23–26} The first example of catalytic microcontact printing was reported in 2003 by Reinhoudt et al., who used an oxidized PDMS stamp to deprotect TMS- and TBS-modified SAMs on gold. The method clearly demonstrated the ability of an acidic stamp to deprotect immobilized silyl ethers and reproduce micrometer-size features with sub-100 nm edge resolution, although the approach achieved only partial cleavage and required a new stamp for each pattern transfer.²³

Recently, we reported two inkless μ CP methods that employ catalysts bound to polymeric stamps to reproduce patterns on functionalized SAMs. In the first protocol a stamp-immobilized biocatalyst is used to transfer pattern on a substrate monolayer. More specifically, an acrylamide stamp bearing immobilized exonuclease I (ExoI) achieved catalytic ablation of single-stranded DNA immobilized on both glass and gold surfaces. Although the technique completely obviates the diffusive limitation of traditional μ CP, its resolution was constrained by deformation and distortion of the acrylamide stamp, which lacked the mechanical integrity necessary to support and transfer submicrometer features.²⁵ The second approach renders complete transfer of submicrometer features with sub-50 nm edge resolution using a chemical catalyst bound to a rigid polymeric stamp capable of supporting very accurate high-resolution patterns.^{27,28} In this variation, a polyurethane-acrylate stamp bearing 2-aminomethyl piperidine was used to promote catalytic deprotection of an Fmoc-protected SAM. The technique achieves 100% cleavage of Fmoc-groups in regions of stamp-substrate contact and allows subsequent functionalization of printed surfaces. The approach, however, requires prolonged reaction times at elevated temperatures.²⁶

Here we report a new inkless catalytic μ CP technique that achieves accurate, fast, and complete pattern reproduction on SAMs of Boc- and TBS-protected thiols immobilized on gold using a polyurethane-acrylate stamp functionalized with

*To whom correspondence should be addressed. E-mail: eric.toone@duke.edu (E.J.T.) and rclark@rochester.edu (R.L.C.).

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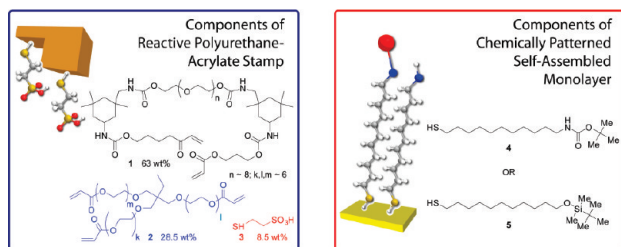


FIGURE 1. Components of the catalytic stamp and functionalized self-assembled monolayers.

covalently bound sulfonic acid moieties. The protocol achieves complete ablation at room temperature just after one minute of contact and renders sub-200 nm size structures of chemically discriminated SAMs. The strategy permits direct functionalization of the printed surfaces,^{29–31} providing a convenient method for chemical and biochemical modifications of surfaces in a spatially controlled fashion.

Our approach utilizes an elastomeric stamp comprising monomers **1** and **2**, and 2-mercaptoethanesulfonic acid (**3**) as a reactive element to promote catalytic pattern-specific cleavage of Boc- and TBS-protection groups from SAMs of *tert*-butyl 11-mercaptoundecylcarbamate (**4**) and 11-(2,3,3-trimethylbutan-2-yloxy)undecane-1-thiol (**5**) chemisorbed on gold (Figure 1).

To moderate the deformation and distortion associated with many stamp materials used in μ CP, we employed a rigid polyurethane-acrylate polymer as the stamp support. This polymer has previously been utilized for both submicrometer μ CP and replica molding and can be easily functionalized prior to polymerization through covalent incorporation of nucleophiles to the acrylate monomer.^{26–28} To produce stamps bearing acidic moieties, polyurethane-acrylate monomer **1** was first mixed with triacrylate **2** and a photoinitiator and allowed to react at 50 °C in the presence of thiolated sulfonic acid **3**. The resulting mixture was deoxygenated under vacuum, cooled to room temperature, and polymerized between two glass plates or between a glass plate and a patterned master to produce flat or patterned acidic stamps, respectively. Figure 2 shows scanning electron microscopy (SEM) images of stamps, prepared with 6.5 μ m size dots and with various submicrometer features (down to \sim 170 nm lines).

Boc- and TBS-protected SAMs were formed by immersing freshly prepared or oxygen plasma cleaned gold chips in 1 mM solutions of **4** or **5** in EtOH at room temperature for at least 20 h. Contact angle measurements of the resulting monolayers (**4** $\theta_A = 89^\circ$, $\theta_R = 65^\circ$; **5** $\theta_A = 108^\circ$, $\theta_R = 95^\circ$) showed significant hysteresis indicating formation of loosely ordered low-density hydrophobic SAMs, presumably due to the presence of bulky protection groups, and were consistent with the previous reports.²⁴ XPS spectra also confirm monolayer formation and indicate the presence of the thiolated hydrocarbons on the gold surface (Supporting Information).

A featureless acidic polyurethane-acrylate stamp was used to deprotect Boc- and TBS-modified monolayers. Freshly

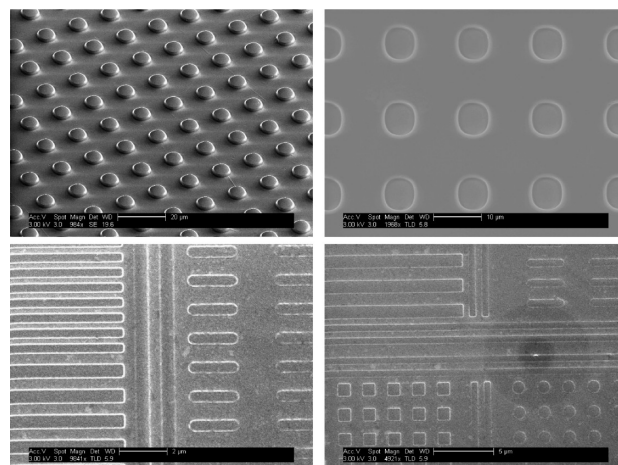
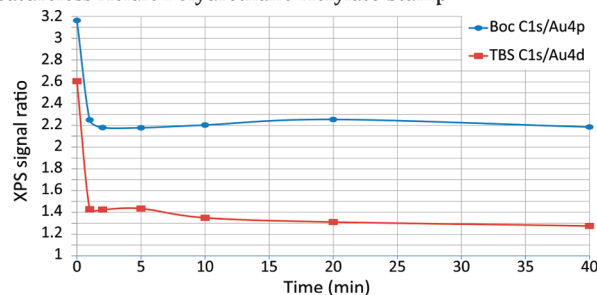


FIGURE 2. SEM images of patterned acid-functionalized stamps.

TABLE 1. Deprotection of Boc- and TBS-Modified SAMs with the Featureless Acidic Polyurethane-Acrylate Stamp



| Time (min) | Boc SAMs (C _{1s} /Au _{4p}) | Boc SAMs (O _{1s} /Au _{4p}) | TBS SAMs (C _{1s} /Au _{4d}) |
|-------------------------|---|---|---|
| 0 | 3.164 | 0.458 | 2.606 |
| 1 | 2.25 | 0.313 | 1.429 |
| 2 | 2.18 | 0.284 | 1.427 |
| 5 | 2.178 | 0.299 | 1.435 |
| 10 | 2.203 | 0.278 | 1.35 |
| 20 | 2.254 | 0.335 | 1.311 |
| 40 | 2.185 | 0.296 | 1.275 |
| Depr(TFA) ¹ | 1.054 | 0.148 | 0.6 |
| Depr(calc) ² | 2.175 | — | 1.686 |

¹ Deprotection with a TFA/CH₂Cl₂ solution

² Calculated for 100% deprotected substrates

prepared SAMs of **4** and **5** were brought into conformal contact with the flat acidic stamps at room temperature for intervals ranging from 1 to 40 min. The treated gold substrates were rinsed with ethanol and water and analyzed by XPS to determine deprotection efficiencies. Table 1 shows C_{1s}/Au_{4p} and O_{1s}/Au_{4p} XPS signal ratios of Boc-protected SAMs and C_{1s}/Au_{4d} signal ratios of TBS-protected SAMs before and after stamping. On the basis of these data, it is apparent that the acidic polyurethane-acrylate stamp effects complete deprotection of both Boc- and TBS-modified SAMs after 1 min, and no significant change in signal ratios occur beyond this time for either monolayer. The carbon concentration (C_{1s}/Au_{4p} and C_{1s}/Au_{4d} ratios) in the stamped

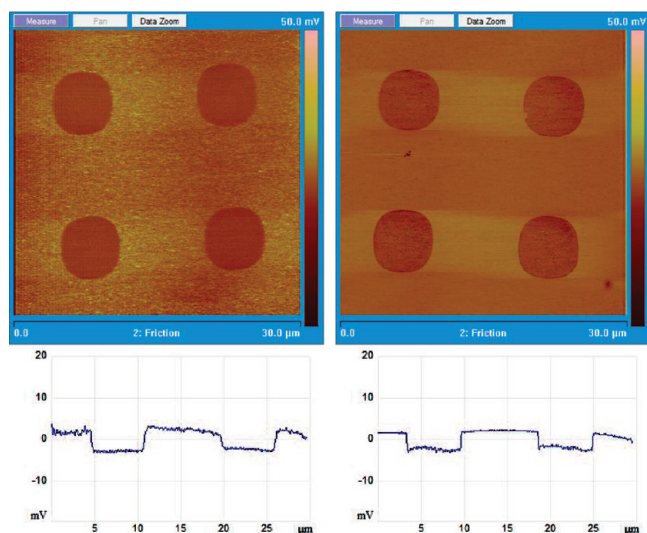


FIGURE 3. AFM friction images of the patterned Boc- (left) and TBS- (right) modified substrates.

substrates correlates with calculated XPS carbon signals for 100% deprotected samples (Table 1), suggesting a high degree of deprotection for both Boc- and TBS-functionalized SAMs. Boc- and TBS-protected substrates were also treated with 1:1 TFA/CH₂Cl₂ for 1 h at room temperature to produce fully deprotected reference surfaces. These substrates show a significantly lower carbon signal than predicted for fully deprotected surfaces, presumably the result of trifluoroacetic acid mediated desorption through oxidative degradation of the loosely ordered Boc- and TBS-protected monolayers.

To evaluate the ability of the acidic stamp transfer patterns to functionalized SAMs we prepared a reactive polyurethane-acrylate stamp containing ~6.5 μm dots. The stamp was placed in conformal contact with Boc- or TBS-protected SAMs for 4 min at room temperature only under the weight of the stamp. Following reaction, substrates were rinsed with ethanol and water, dried under a stream of nitrogen, and analyzed by contact mode lateral AFM to determine tribological and topological properties. Figure 3 clearly demonstrates the effectiveness of the protocol for the fabrication of uniform patterns on both surfaces. The patterns produced on both Boc- and TBS-functionalized SAMs are consistent across the entire substrate area and showed friction differences of ~6 and ~4.5 mV, respectively, with very small height differences between protected and deprotected regions (Supporting Information), indicating formation of chemically distinctive features.^{24,26} As predicted, given the catalytic nature of pattern transfer, a single patterned stamp produced identical features during multiple applications.

The efficiency of our patterning technique was also analyzed by SEM.^{32,33} Following atomic force microscopy (AFM) experiments, the same patterned stamp (6.5 μm dots) was placed on top of functionalized SAMs and held in contact for intervals ranging from 2 to 40 min with no external load. Following reaction, the substrates were rinsed with ethanol

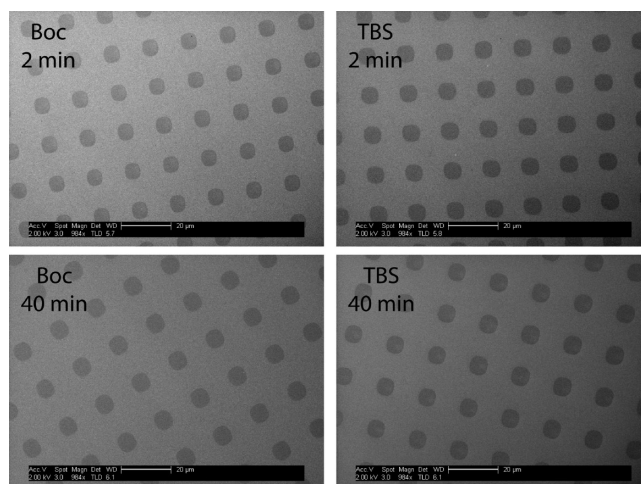


FIGURE 4. SEM images of the patterned (6.5 μm dots) Boc- (left) and TBS- (right) modified substrates.

and water and analyzed by SEM. Figure 4 again demonstrates that the acidic polyurethane-acrylate stamp successfully deprotected SAMs of thiols **4** and **5** in the areas of conformal contact. The patterns produced on all substrates were identical regardless of protection group or stamping time, suggesting a truly catalytic pattern transfer free of diffusive spreading and the resulting degradation of feature contrast. Notably, a single catalytic stamp was used to transfer patterns on all TBS- and Boc-functionalized substrates, again confirming the catalytic nature of pattern transfer. The patterned acidic stamp retained identical catalytic efficiency even after two months and showed no evidence of polymer degradation. Control stamps bearing no sulfonic acid moiety failed to produce any detectable change in surface character or morphology.

To further demonstrate the extent to which catalytic printing protocols eliminate the diffusive limitations of conventional μCP, a TBS-protected substrate was reacted for 4 min with the acidic polyurethane-acrylate stamp containing a series of low aspect ratio features ranging in sizes from 170 to 3000 nm. SEM images of the resulting surfaces demonstrate the accuracy and precision of the transfer of small densely populated structures, as well as large deprotected areas and micrometer size features, a task that remains one of the most challenging for traditional μCP (Figure 5).⁶ The transferred pattern contains 3000 × 600 nm rods separated by 2000 nm and were produced from stamp structures with 0.042 aspect ratio; these features were accurately and uniformly reproduced over the entire stamped region, indicating the absence of gas diffusion and suggesting an exceptionally low deformation in the patterned acidic stamp. In traditional μCP diffusive wetting results in at least 50 nm ink spreading, even under optimal conditions.⁶ Here, a patterned acidic stamp transferred 240 nm lines separated by 170 nm on TBS-protected substrate. Figure 5 clearly show that the printed lines and other features have dimensions identical to those of the corresponding Si-PMMA master

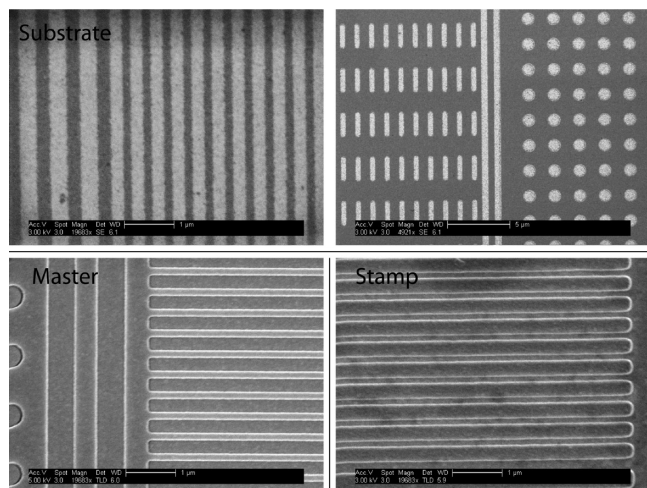


FIGURE 5. SEM images of the patterned TBS-protected substrate, Si-PMMA master, and corresponding catalytic stamp.

demonstrating the powerful capabilities of pattern transfer by nondiffusive means. The edge resolution of the printed features was in a sub-50 nm region (Supporting Information), suggesting that the ultimate resolution of this method is limited only by the structure of the underlying substrate (in this case polycrystalline granular gold (111)).

In conclusion, we have demonstrated that catalytic μ CP with functionalized polyurethane stamps effectively transfer patterns on both Boc- and TBS-functionalized SAMs on gold. In this inkless variant of μ CP, an acidic polyurethane-acrylate stamp catalytically deprotects acid-labile functional groups with complete conversion after just one minute of contact. The approach limits the edge resolution to the size of gold grains (15–30 nm) and allows fast and accurate reproduction of small features completely obviating the limitations of both gas diffusion and diffusive wetting inherent to traditional μ CP. Our method also permits defect-free replication of features with very low aspect ratio (to 0.042) eliminating the deformation behavior of many PDMS-based techniques. We continue to explore and expand catalytic μ CP and will report our results in due course.

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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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