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Positive Microcontact Printing

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We describe a novel approach for microcontact printing (μCP) in which the printed regions of a substrate are etched rather than being protected. This approach employs pentaerythritol-tetrakis(3-mercaptopropionate) (PTMP) as an ink for μCP, an oligothiol being compatible with the requirements of μCP: it is sufficiently soluble in ethanol to be inked onto poly(dimethylsiloxane) (PDMS) stamps, forms self-assembled monolayers (SAMs) on coinage metals, and exhibits low diffusion characteristics so that it can be printed with submicrometer accuracy. A SAM of PTMP printed on Au or Cu blocks the adsorption of eicosanethiol (ECT) from solution, but less the etching of the substrate. Etching those regions of the substrate that have initially been microcontact printed then becomes possible. This process, which we call positive (+) μCP, reverts the polarity of the lithography from negative to positive by analogy to photolithography.

μCP utilizes an inked, micropatterned stamp to print chemicals or biomolecules onto a substrate.[1] The most widespread application of μCP is the printing of alkanethiols onto Au,[1a] Ag,[2] Cu[3], or Pd[4] or of silanes onto Si/SiO_2[5] to form a patterned SAM. The printed monolayer can protect its substrate from dissolution in an etch bath.[1−6] μCP is also versatile to tailor surface properties such as wetting,[7] protein repellency,[8] growth of crystals,[9] and adhesion.[10] μCP resembles a negative-type lithography because it protects the substrate in the printed areas, Figure 1. Stamps are fabricated by replica molding of PDMS on a micropatterned Si wafer. PDMS is used because it is elastomeric and provides conformal contact between the stamp and the substrate, which ensures a homogeneous transfer of ink to the substrate during printing. Thus, not all patterns on a stamp are stable during unmolding, inking of the stamp, and printing.[11] Inverting the pattern on the stamp solves these problems because large recessed areas of a stamp designed for $(-)\mu$CP are inverted into large contacting zones on a stamp used for $(+)\mu$CP. In $(-)\mu$CP, printing an optimum resist-forming SAM is another challenge.[12] Chemists may feel frustrated by the constraints of reaction conditions in $(-)\mu$CP: the printing duration defines the time available for the reaction to occur in the print areas, there is in principle no solvent present, it is difficult to estimate the concentration of the ink on or in the stamp before and after printing, and microcontact printed SAMs are imperfect resists.[13] This suggests that forming the etch-protective SAM from solution using $(+)\mu$CP provides more flexibility than using $(-)\mu$CP does.

We selected PTMP on the hypothesis that this molecule (i) adsorbs on Au and forms stable SAMs owing to its numerous thiol moieties,[14] (ii) is soluble in ethanol and hence provides a stamp-compatible ink, (iii) does not form etch-blocking SAMs, and (iv) has low diffusion characteristics during printing because of its relatively high molecular weight of 488.66 g mol^{-1}.[15] The stability of PTMP on Au against exchange by ECT from solution becomes apparent in the following experiment. Immersing a 20-nm-thick layer of Au (evaporated on a Si wafer) in a 0.2 mM solution of PTMP in ethanol for 1 min results in a hydrophilic surface, Figure 2A. Immersing another Au substrate in a 0.3 mM solution of ECT in ethanol for at least 3 s results in a hydrophobic surface, Figure 2B. Exposing the Au sample with the adsorbed PTMP to a solution of ECT for 4 min does not change the PTMP/Au surface in terms of its wettability by water, Figure 2C. Ellipsometry and X-ray photoelectron spectroscopy (XPS) confirmed this observation in a quantitative manner. A SAM of PTMP formed under the same conditions as for Figure 2A is 1.1 ± 0.1 nm thick, and has a chemical composition that is consistent with the chemical structure of PTMP. SAMs of PTMP formed with longer adsorption times (>12 h) have similar thickness and contact angles. This suggests that the monolayer of PTMP adsorbed on the sample shown in Figure 2A is largely complete. After exposure of this sample to

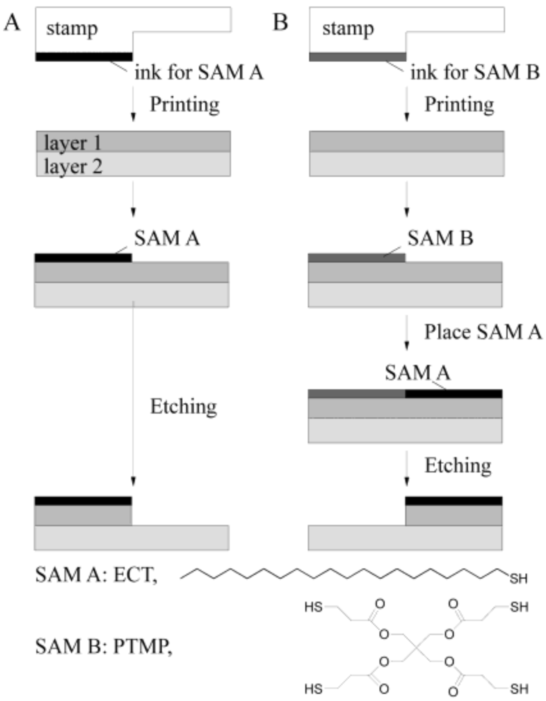

Figure 1. Strategies for $(-)\mu$CP (A) and $(+)\mu$CP (B).

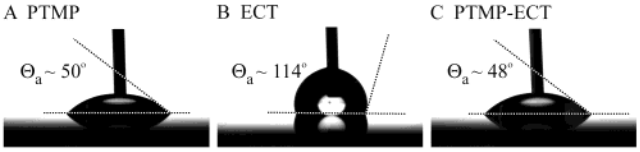

Figure 2. Images illustrating how a droplet of deionized water wets a Au surface covered with a SAM of (A) PTMP, (B) ECT, and (C) PTMP exposed to a solution of ECT. The similarity between the advancing contact angles in parts A and C suggests that no or only few ECT molecules can adsorb on the Au substrate already covered with PTMP.

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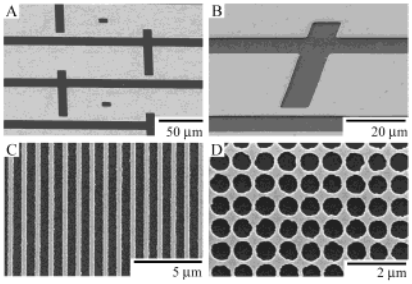

Figure 3. SEM images of structures made in Au and Cu with $(+)\mu$CP. (A) This Au surface was microcontact printed with PTMP, immersed in a 0.6 mM solution of ECT in ethanol for 15 s, and selectively etched. (B) This pattern was formed by microcontact printing PTMP on a Cu substrate, which was then exposed to a 0.3 mM solution of ECT in ethanol for 4 min and etched for 2 min 30 s in a 0.07 M aqueous solution of ammonium peroxodisulfate. (C and D) These high-resolution Cu structures result from microcontact printing Cu substrates with PTMP, immersing them into a 0.6 mM solution of ECT in ethanol for 2 min, and etching them for 3 min with ammonium peroxodisulfate. Stamps were inked for 1 min with a 0.2 mM [images A and B] or a 0.1 mM [images C and D] solution of PTMP in ethanol. Print duration was 30 s in all cases.

the solution of ECT for 4 min, the thickness of the monolayer covering the Au substrate increased to 1.2 ± 0.1 nm, suggesting a replacement of ∼2.5% of the PTMP molecules by twice as many ECT molecules. The XPS experiments on samples prepared as those shown in Figure 2 corroborate this finding and indicated an exchange of ∼2%. We used the diminution of the O 1s signal (at 532 eV) and the C 1s signal (at 289.5 eV) of PTMP to quantify this exchange (data not shown). The advantage of using PTMP is well illustrated by the following observations: Dodecanethiol (DDT) forms 1.5-nm-thick and well-ordered monolayers on Au. Immersing a complete SAM of DDT on Au into a 0.3 mM solution of ECT in ethanol for 4 min results in the replacement of one-third of the DDT molecules in the SAM by ECT molecules. This shows that DDT molecules in a monolayer are prone to desorb and/or exchange with ECT molecules dissolved in ethanol.[16] Two other disadvantages of using simple alkanethiols, such as DDT, for $(+)\mu$CP are their tendency to diffuse and evaporate from the surface of a stamp during printing and the relatively high etch resistance they can confer to a Au substrate.[12]

The exchange between PTMP and ECT found in the previous experiments is very small but, provided that μCP forms less complete SAMs of PTMP than adsorption from solution does, the number of ECT molecules exchanged with printed PTMP and/or added to the printed areas would be significantly higher. Indeed, a SAM of PTMP microcontact printed using a flat PDMS stamp inked with a 0.2 mM solution of PTMP in ethanol for 1 min and printed on Au for 30 s only resulted in a 0.4-nm-thick SAM. The limiting factor for the formation of a more complete, printed monolayer is the affinity of PTMP for PDMS (Sylgard 184) rather than the inking and printing conditions used. Exposing Au microcontact printed with PTMP to a 0.3 mM solution of ECT in ethanol for 4 min added the equivalent of ∼40% of a complete monolayer of ECT. A ∼50% complete SAM of ECT on Au provides little protection against a CN^-/O_2 etch, but will retard the etch.[12] The presence of an incomplete monolayer of ECT may not prevent the selective etching of a substrate but may necessitate adjusting the etch chemistry more stringently.[3]

The scanning electron microscopy (SEM) image in Figure 3A shows a 20-nm-thick Au pattern fabricated using $(+)\mu$CP and the conditions mentioned above. The Au was then etched selectively for 25 min using a 0.1 M solution of KCN in deionized water (buffered at pH 12.0 with KCl/NaOH) at room temperature. Contrast and resolution of these patterns are high; there are no apparent defects in the protected regions of the Au, and the etch dissolved the printed areas without leaving any background. The isotropic etch helps suppress any residual background, especially in regions where ECT might have formed islands. We also applied $(+)\mu$CP to the patterning of Cu substrates although forming SAMs of high quality is more difficult on Cu than on Au.[3] Numerous etch chemistries exist for dissolving Cu, some of them being very fast. We can consequently expect to find an etch system that is relatively insensitive to the presence of a partial SAM of PTMP or ECT in the printed regions of Cu. The result shown in Figure 3B validates this expectation. There, $(+)\mu$CP was useful to structure a 100-nm-thick Cu substrate using ammonium peroxodisulfate as the etchant. In previous experiments on $(-)\mu$CP we never observed that ammonium peroxodisulfate was a selective etch for substrates microcontact printed with ECT. Forming a SAM of ECT from solution rather than microcontact printing it to block the etch may account for this improvement. Remarkably, the high-resolution structures formed in a 50-nm-thick Cu substrate, Figure 3C,D, indicate that the diffusion characteristics of PTMP are sufficiently low to achieve microcontact printing at length scales better than 200 nm. Hence, $(+)\mu$CP complements "standard" μCP ideally, and both techniques share similar attributes in terms of achievable contrast and resolution for patterning a metal layer by printing and etching it selectively.

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