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Microcontact-Printing Chemical Patterns with Flat Stamps

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We describe a strategy for microcontact printing (μCP)[1−3] that uses planar, elastomeric stamps to print chemical patterns onto substrates. This strategy relies on forming a chemical pattern on a flat poly(dimethylsiloxane) (PDMS) stamp by contact inking it with a micropatterned inker pad or by other micropatterning methods such as microfluidic networks (μFNs). The stability of the pattern of ink on the stamp largely defines the accuracy of prints achievable here. Highly diffusive ink molecules on PDMS, such as alkanethiols, strongly compromise the results, whereas less mobile molecules such as Pd complexes or proteins preserve the accuracy of the pattern, leading to well-defined prints. Planar, chemically patterned stamps can provide the pattern necessary for μCP and should simplify the fabrication of and the requirements placed on stamps used in this technique.

Microcontact printing is a "soft lithographic" method for which a micropatterned, elastomeric stamp is first inked, then dried, and finally placed onto a substrate to localize a chemical reaction between molecules from the ink and the substrate.[3,4] This technique is applicable to several types of inks and substrates, such as chemisorbing molecules onto metals or oxides,[1,5] reactants printed onto organic layers,[6] and proteins transferred to silicon or glass.[7] The printed patterns can protect the underlying substrates against etchants,[8] can nucleate metallization or crystal growth,[9−15]

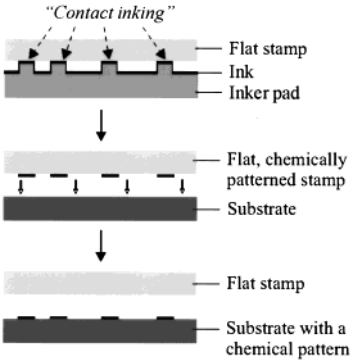

Figure 1. A patterned inker pad can direct the inking of planar stamps for μCP.

or can modify the wetting[16] or adhesion properties[17] of substrates, for example. All demonstrations and applications of μCP so far have used patterned stamps that were prepared by curing the liquid prepolymer of PDMS on a mold. Patterned stamps should (i) be peeled off their mold without being damaged, (ii) bear an accurate replica pattern of their mold, (iii) be soft enough to provide conformal contact with substrates, yet (iv) have patterns that are mechanically stable during inking and printing.[18] Planar, chemically patterned stamps should prove valuable to μCP because they fulfill these criteria and, in addition, weaken the contradiction between being an elastomer providing conformal contact with substrates and having mechanically stable patterns.

Figure 1 illustrates one example of how to use planar stamps for μCP. First, a patterned inker pad localizes the inking of a planar stamp during contact.[19] Second, printing the chemical pattern from the stamp onto a substrate completes this strategy. In addition to providing the pattern, the inker pad has to incorporate molecules from the ink in all regions of contact with the stamp. The properties of the ink itself are also important: its diffusion characteristics on the surface and through the bulk of the stamp will determine the practical limit in resolution and contrast of the patterns to be printed.[20]

Microcontact-printing alkanethiols onto gold is probably the best-explored variant of this technique. In addition to its potentially high resolution (<100 nm),[20,21] this ink−substrate system represents a scientifically rich and technologically convenient model system. For this reason, we first inspected the outcome of printing thiols on gold with a planar stamp, Figure 2. Here, eicosanethiol (ECT, MW = 314.62 g mol^{-1}) was selected because of its excellent resist-forming capability on Au and because it diffuses less on PDMS (and on gold) than its shorter analogues.[20] Printing ECT on gold with a flat PDMS stamp followed by etching the Au not protected by thiols resulted in a low-quality pattern, Figure 2A. Here, the high surface diffusion of ECT on PDMS ($D \approx 7 \times 10^{-8}$ cm^2 s^{-1})[20] compromises the use of planar stamps for μCP. Reducing the amount of ECT on

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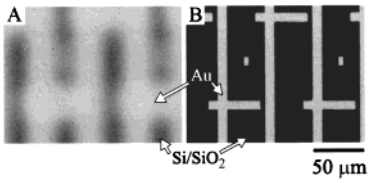

Figure 2. Scanning electron microscope (SEM) images of gold patterns on Si/SiO_2 produced by combining μCP of ECT on gold and subsequently etching the unprotected regions with a CN^-/O_2 etch bath. (A) The high diffusion of ECT on the planar stamp prevented printing an accurate pattern. (B) In contrast, a patterned stamp inked on a flat inker pad leads to a faithful Au pattern. In both cases, the inker pads were loaded with ink by exposure to a 0.2 mM solution of ECT in ethanol for 60 s and dried before use.

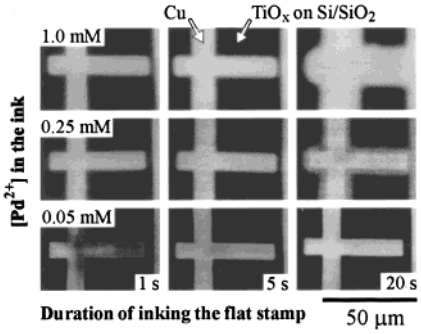

Figure 3. SEM images of Cu deposited onto catalytic Pd patterns printed with a flat stamp on Ti coated Si/SiO_2 wafers. The samples were plated for 45 s in an alkaline Cu tartrate bath containing formaldehyde as the reducing agent. O_2 plasma hydrophilized patterned and planar PDMS layers were used as the inker pad and the stamp, respectively.

the inker pad did not improve the accuracy of the printed pattern, but keeping the time of inking and the delay before printing short ($<$2 s, overall) proved helpful. Using a patterned PDMS stamp as it is usually done in contact inking[19] resulted in an accurate pattern, Figure 2B.

Microcontact-printing with planar stamps should benefit from inks having a high molecular weight or a strong affinity for PDMS surfaces, or both. We verified this possibility and used a Pd complex ($[(CH_3(CH_2)_{16}CN)_2PdCl_2]$, MW = 708.29 g mol^{-1}) dissolved in ethanol as the ink and printed it with a planar stamp onto a Ti-evaporated Si wafer. The printed Pd pattern initiated electroless deposition of Cu to provide, in addition to being a valuable method of metallization, a sensitive and direct diagnostic of the prints.[9,11] Figure 3 reveals how the concentration of Pd in the ink and the time taken to contact-ink the stamp influenced the accuracy and the contrast of the Cu patterns. Diffusion of Pd on the stamp was strong when its concentration was the highest on the inker pad in this series. Reducing it to 0.25 mM led to an optimal density of the catalyst on the stamp (and thus yielded high-quality Cu deposits) but could still not prevent the patterns from broadening, even with brief inking durations. Further reduction of the amount of Pd inked onto the planar stamp enables the formation of accurate Cu patterns independently of the inking duration. In this case, the density of the Cu patterns becomes optimal only when the inking duration was long enough, i.e., 20 s in this example. Figure 3 shows that the concentration of Pd in ethanol to ink the inker pad and the duration of contact-inking were the key parameters to manipulate to obtain accurate prints. The time elapsed between inking and printing and the printing time itself proved unimportant. These results suggest that once the amount of Pd transferred from the inker pad to the stamp had been optimized, the low mobility of the Pd complex on the hydrophilic PDMS and its high reactivity with the Ti-coated substrates prevented its diffusion.

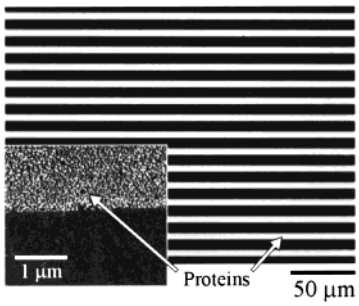

Figure 4. Fluorescence microscope and AFM images of TRITC labeled IgGs (anti-guinea pig) printed onto glass with a flat stamp selectively inked with a Si μFN. The 5-μm-wide channels of the μFN were first hydrophilized and then used to guide 200 μg ml^{-1} solutions of IgGs in PBS over the PDMS stamp. After 2 min of deposition of the proteins onto the stamp, the μFN was removed from the stamp while immersed in 50 mL of PBS. The stamp was rinsed with deionized water, dried, and directly printed for 5 s onto freshly cleaned glass.

Proteins can constitute an upper limit of the molecular weight of inks for PDMS stamps and define a different paradigm for μCP.[7] Inking these molecules on the flat stamp relied on their localized deposition from solution using μFNs.[22,23] The fluorescence image in Figure 4 directly reveals a pattern of TRITC labeled IgGs (MW $\approx$ 150 kD) printed with a planar stamp onto a glass substrate. This pattern has high contrast and resolution, which appeared to be independent of the amount of proteins present on the stamp or of the durations of inking and printing. The high molecular weight of these molecules and their affinity for surfaces prevented any noticeable diffusion on the stamp and the glass substrate, as revealed by the atomic force microscopy (AFM) inset in Figure 4. The combination of inking a planar stamp by a μFN and using it to transfer a pattern is advantageous: here, conformal contact between the glass substrate and the Si μFN was not possible to effect directly a precise derivatization of the substrate with the proteins. The planar, elastomeric stamp as an intermediate vehicle solved this problem.

In summary, μCP with planar stamps inked with spatial control enables the printing of patterns with high contrast and accuracy. This strategy is versatile but might be constrained by the diffusion characteristics of the ink on the planar stamp. Possibly, the localized positioning of molecules onto a flat stamp could, in addition to its contribution to microcontact printing, prove valuable to study the diffusion of molecules on surfaces.

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