

FEATURE ARTICLE

Transport Mechanisms of Alkanethiols during Microcontact Printing on Gold

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Microcontact printing (μ CP) with elastomeric stamps is a versatile method to modify the chemistry of surfaces. We explore this patterning process here, examining the origin and character of its limits and demonstrating how best to use μ CP and alkanethiols for lithography on gold at submicron scales. We find that, ultimately, this type of lithography is constrained by the need to carry the monolayer-forming reaction to completion, with significant degradation of the accuracy of prints at sub-500-nm scales due to molecular diffusion. Printing monolayers of eicosanethiol on gold proved to be the best practical compromise between self-assembly of the resist and its transport along the stamp and substrate interfaces as well as through the gas phase. Results for this system were particularly sensitive to the geometry of the stamp and how eicosanethiol was placed on, and transferred from, its surface to the gold. Our experiments, and simulations that corroborate them, show the relative importance of the various paths in controlling the chemical contrast on the substrate. We demonstrate the fabrication of high-density arrays of ≈ 90 -nm gold dots using these criteria.

1. Introduction

Applying molecules to surfaces by means of printing processes is a topic of significant interest for the convenient formation of chemical patterns.^{1–10} The most extensively explored variant of this approach is microcontact printing (μ CP) of alkanethiols on gold: An elastomeric stamp having surface reliefs that are a negative of the desired pattern provides the conveyance for selective placement of the thiol on the gold surface.^{1,11} A reaction between gold and thiol supplied by the stamp causes the covalent assembly of a monolayer of thiols on the metallic substrate.^{12,13} The presence of this monolayer confers and controls many characteristics of the resultant interface between the solid film and adjacent phases, such as its wettability,^{14–17} its control of adhesion,^{18,19} its susceptibility to chemical reaction,^{20,21} and the physical barriers that control electrical conduction^{22–25} or influence mass transport of ions or neutral molecules to the underlying metal.^{26,27} The latter property of the interface is particularly relevant in lithographic applications where differential dissolution of the substrate is sought by the localized formation of a self-assembling monolayer (SAM), the monolayer that serves as a sort of ultimate resist^{28–31} because of its thinness (1–2 nm) and its tendency toward high definition and order.^{32–35}

We wanted to examine what happens when μ CP is used to assess its applicability to nanoscale patterning and fabrication. The placement of molecules on surfaces by microcontact printing avoids the most common limitation of optical lithography, the diffraction of light,^{36,37} while retaining one of its

principal attributes: the ability to effect pattern formation over a large area ($> 1 \text{ cm}^2$) at once.^{1,20} There are several limitations to the chemical contrast achievable with μ CP, however. A master is needed to template stamp formation, its features defining the ultimate bound on what is directly achievable with μ CP. Masters fabricated by electron beam (e-beam) lithography in such materials as silicon can attain resolutions of $< 20 \text{ nm}$ and feature sizes of 100 nm over large areas so that a range of features much smaller than the foreseeable needs of technology can be tested.³⁸

The process of duplication (forming the stamp) necessarily compromises the quality of the replica, the degree and type of loss given by the structure-forming properties of the material used to form the stamp, itself constrained by the requirements of the process of contact printing. Some flexibility of the stamp is sought to allow sufficient contact between the stamp and the substrate it patterns. This intimate contact between the two is ultimately the goal, so that transfer of material occurs only in the areas where they conform. Typical materials for the formation of stamps are based on elastomeric siloxanes;³⁹ poly(dimethylsiloxane) (PDMS) with a Young's modulus of $\approx 1 \text{ MPa}$ is currently the most widely employed material for this purpose. We explored some issues of master duplication in this material in a previous publication⁴⁰ and recently found siloxane-based materials capable of useful duplication of e-beam-fabricated silicon masters with features down to 50 nm .⁴¹

A third set of limitations to the resolution and accuracy attainable with the process of μ CP are those associated with the ink and, where lithography is the target, its properties as a resist. This paper focuses on the origins of these limitations, arguing that the ultimate limits of microcontact printing are

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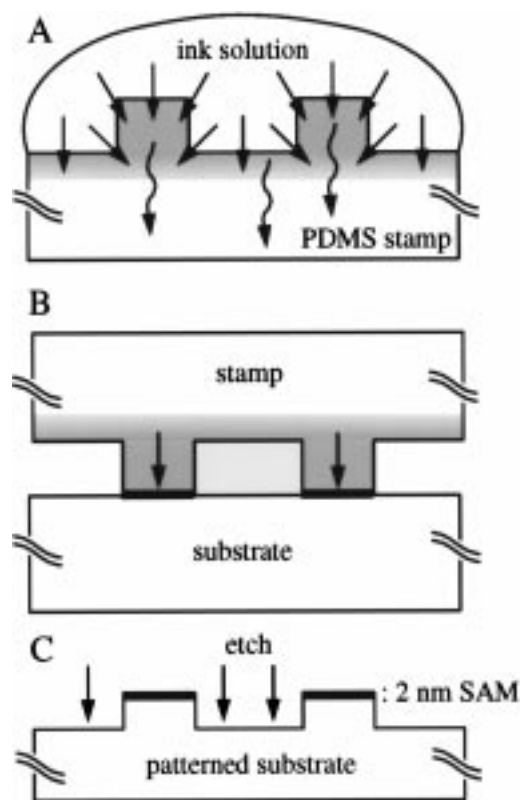


Figure 1. Fabrication of gold structures using microcontact printing of alkanethiols requires three steps. (A) The stamp is inked with a dilute solution of alkanethiol and thiols from the ink partition between the surface and the bulk of the stamp. (B) Printing a monolayer pattern onto a gold substrate is critical because diffusion of ink through liquid- or gas-phase transport outside the regions of contact diminishes the accuracy of the print. (C) A CN^-/O_2 wet-etch transfers the printed pattern into the substrate where selectivity results from regions comprising complete monolayer and regions of “bare” gold. The selectivity can be compromised by submonolayer coatings of the gold and, ultimately, by the characteristics of the substrate and the etch.

constrained only by the range and type of diffusive phenomena that occur on surfaces and in air when molecules are transferred to a surface.

2. Inking and Printing

Figure 1 outlines some of the steps of forming the contact print of alkanethiols on gold. A drop of the alkanethiol, typically diluted in a solvent such as ethanol, contacts the structured side of the stamp for some seconds before its removal under a stream of nitrogen. The surface of the stamp is left “dry”, thus avoiding the confounding effects on printing of excess liquid between the stamp and surface during their contact. Ethanol and alkanethiol nevertheless remain present on the surface and in the stamp, where they adsorb into the bulk part of the siloxane matrix in small amounts that reflect, at least in part, the composition of the inking solution and the permeability of the PDMS.⁴²

Ethanol is an excellent carrier for alkanethiol. PDMS is only slightly swollen by ethanol, by 2.5% at equilibrium for siloxanes with a Young’s modulus of 1 MPa, so that even in the worst case molded features on its surface are only fractionally distorted. Millimolar solutions of many thiols in ethanol are readily achieved.⁴³ The volatility of this solvent allows its rapid loss from the PDMS after inking, concentrating the thiol into the elastomeric matrix but also complicating an exact determination of its amount, particularly in the region of the stamp

relevant to printing (Figure 1B). The level of dilution of the alkanethiol in the stamp is a determining factor of the outcome of printing alkanethiols. We showed previously that the degree and type of order in a SAM formed by μCP is extremely sensitive to the apparent mole fraction of thiol present in the stamp.¹³ Variation of this fraction in a model system of dodecanethiol printed on epitaxially grown Au(111) substrates caused concordant but not linear changes in the appearance of the SAM at nanometer scales as well as in the macroscopic wettability of the monolayer. These results are particularly relevant where a complete SAM is required to provide good etching resistance for lithographic applications (Figure 1C).

SAMs on gold provide no out-of-plane averaging of their protective character, in contrast to thicker resists such as poly-(methyl methacrylate) (PMMA), and are thus susceptible to etch processes in which only a few molecular or conformational defects in the monolayer nucleate dissolution of the substrate.³⁰ The logical result of this sensitivity to defects and order is a strong dependence on monolayer coverage over the degree of protection of the gold. The appearance of gradients in the rate of etching of the substrate follows the presence of gradients in the molecular composition and density of its surface. Mass transport of alkanethiol from the gas phase, 2D diffusion of molecules from the periphery of points of contact of the stamp, and spreading of the bulk liquid can each contribute to these gradients after pattern formation, the first two providing the reason hexadecanethiol (HDT) is not the optimal choice of ink to provide high-resolution, accurate pattern transfer by μCP . We will illustrate this fact and provide some alternatives in the remainder of the paper.

3. System Chosen for Study

The use of HDT for μCP on gold is reported in a large body of literature.^{1,2,15–19,44–46} We suspected that uncontrolled mass transport of this thiol was a common problem in these studies because it remained largely uncharacterized owing to the small length scale of its manifestation. We consequently designed a master with submicron features anticipating that mass transport of this ink, and several others, around features in the print would be detectable as an increase in their dimensions after a cyanide-based etch, thus providing a model system for examining the transport characteristics of thiols printed by μCP at small scales.

The master, $70 \times 70 \text{ mm}^2$ and 0.4 mm thick, had fields of arrays comprising 18×36 rows and columns of depressions (raised features on the stamp) with dimensions of $3.0 \times 0.6 \mu\text{m}^2$. PDMS stamps formed from siloxane with a 1 MPa modulus had sufficient mechanical strength to replicate faithfully this master (Figure 2A), although its features are close to the minimum achievable in elastomers of this strength. Below this scale, replicated structures in the stamp lose definition due to surface tension and the relative softness of the polymer (see below).⁴⁰ Stamping was performed with no additional pressure on the stamp: The weight of the stamp, its elastic modulus, and the adhesive forces between the inked PDMS and the gold surface were, all together, sufficient to ensure intimate contact during the print. Care was taken to prevent shear forces from acting on the stamp during its application or removal from the gold substrate that might otherwise have blurred the pattern. Similarly, no in-plane deformation of the stamp was exerted before or during printing that would have modified the dimensions or geometry of its pattern.^{47,48} Contact between the gold surface and the bottom of cavities did not occur in our experiments because the structures in the stamps used here provided sufficient stability to prevent their collapse during the printing step.

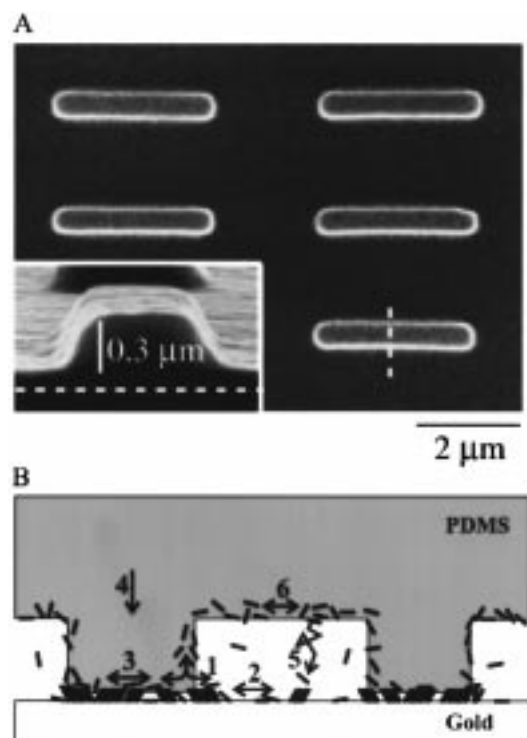


Figure 2. (A) Scanning electron micrograph of the type of PDMS stamp used in our initial survey of printing conditions. The test pattern had arrays of features each $3 \times 0.6 \mu\text{m}^2$ in area and 300 nm thick. The inset shows a cross section through a typical feature of the stamp. (B) The scheme identifies various pathways for dispersal of ink through the stamp and along its surface and that of the substrate. The numbers identify different paths and are referred to throughout the text.

One set of criteria useful for selecting the parameters for forming a print with alkanethiols is based on the observation of the local degree of protection conferred by the resulting monolayer against the cyanide etchant. The chemical composition, the thickness, and the order of the molecules in the monolayer all account for the high selectivity of this etch: SAMs on gold act as diffusion barriers against cyanide and dioxygen that complex and oxidize Au(0) .⁴⁹ Examination of the size and state of printed features is a simple and rigorous measure of monolayer quality. Etched gold crystallites in the zones of print represent defects in the degree of monolayer protection (and also in its level of completion) and are easily detected with a scanning electron microscope at the $<0.05\%$ level. The presence of crystallites outside an explicitly printed structure represents the degree of uncontrolled spreading of the ink, observable at levels down to area fractions of 1 part per million on the substrate. Etching the substrate to determine the presence of a monolayer is an indirect measure of its characteristics and distribution, of course, but finally proved the only one we found useful at submicron scales. Scanning probe techniques, or other spectroscopies (e.g., SEM, scanning Auger, microspot IR, scanning mass spectroscopy) all proved unequal to this task. As one possible application of μCP is the formation of microscopic—and possibly nanoscopic—structures, etch-based assays for the detection of defects in the monolayer also make sense as an ultimate test of the utility of μCP for one type of lithography.

We use the word “etch” throughout this paper to describe the dissolution of “bare” gold by its exposure to a solution of CN^-/O_2 in pH 12 buffer for times sufficient to result in less than 10 gold crystallites (with diameters between 20 and 30 nm) per 1 mm^2 on the Si/SiO_2 substrate. We found that 6 min

proved sufficient to etch 15-nm-thick gold when it was fresh (<1 week) from our e-beam evaporator. The use of a buffered etch solution suppressed the appearance of silicate particles reprecipitated onto the wafer by attack and dissolution of the silicon substrate at higher levels of pH.

4. Results and Discussion

The inset of Figure 2 reveals a striking fact about μCP at small dimensions: small cavities form during the contact between the stamp and the surface that place the walls and bottoms of these cavities close to the surface of the substrate, on average just 100 times the monolayer thickness in the given example. This proximity occurs because of the limited aspect ratio (depth to width) of stamps having useful submicron features. Structures with larger aspect ratios, in excess of 2, are not possible in conventional elastomeric materials.^{40,41} Thus at small feature scales ($<200 \text{ nm}$), gold exposed in cavities is very close to the ink-bearing polymer. The distribution of ink into gold exposed in these openings obviously contradicts the purpose of printing, that of delivering molecules and forming a chemical pattern. It is important, for this reason, to understand which factors limit the spread of the ink in μCP and on what scale.

Several pathways for dispersal of ink are identifiable (Figure 2B). First, the ink, if liquid, might simply spread across the surface on contact between the stamp and substrate (paths 1 and 2 in Figure 2B).⁵⁰ The stamp might be considered a type of sponge impregnated with a liquid that, in the worst case, is readily displaced and spreads across the surface (paths 1, 2, 3, and 4; Figure 2B). Stamps are generally not used wet, however. Ideal practice requires that the surface of a stamp be observably “dry”⁵¹ prior to its application. Microscopically, the state of the ink in the stamp is more difficult to assume and characteristically hard to measure, as we have discussed before.¹³ Liquid present in an ostensibly dry stamp is probably somewhat more difficult to expel as it has to work against the capillarity of a slightly swollen, but not saturated, siloxane network. Liquid inks such as those based on alkanethiols terminated by methyl groups, form low-energy monolayers on gold that, in certain circumstances, also resist spreading of the liquid by autophobic pinning.⁵² Autophobic pinning of a liquid happens when its reaction with a substrate to form a low-energy surface that is not wet by the liquid occurs faster than its spread. The description of the leading edge of contact between the liquid and surface—the three-phase contact line—includes thermal fluctuations mediated by the various interfacial tensions, heterogeneity of the interface, and the presence of precursor films.^{53–55} The latter reflect the finite time scale on which reaction takes place as well as other phenomena associated with the physicoorganic behavior of liquids on surfaces at very small scales. Observations and measurements on drops of neat HDT larger than 100 nL suggest that autophobic pinning is the most important phenomenon in controlling the spread of these “macroscopic” liquid reservoirs.⁵² Conversely, these arguments also imply that the role of autophobic pinning of inks should become less important, and probably irrelevant, as the effective surface-to-volume ratio of the liquid “drop” delivered by the stamp increases, as precursor films consume an increasingly large percentage of the whole volume of liquid applied to the surface. Thus we might reasonably expect that autophobic pinning alone will not suffice and is probably not important, to suppress the spreading of the ink at the scale of, and below, the features in Figure 2. This reasoning also provides a first clue

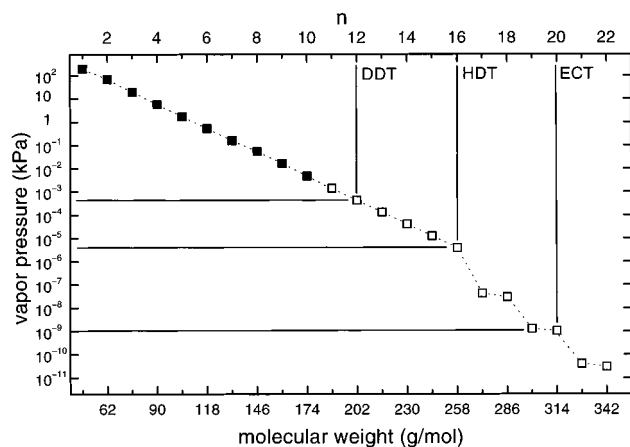


Figure 3. Vapor pressure of linear alkanethiols ($\text{HS}-(\text{CH}_2)_n-\text{CH}_3$) at 25 °C and 1 atm obtained from the literature (black squares) or extrapolated from values in the literature under different conditions (open squares).

that limiting the total quantity of ink available for printing plays a controlling role in μCP of thiols at submicron scales.

5. Molecular Weight of the Ink and Its Influence on Transport

The second and third pathways for transport of inks into nonprinted regions of a substrate, whether the ink is liquid or solid, involve gas diffusion mechanisms mediated by the surface (path 2, Figure 2B) or through the ambient (paths 5, Figure 2B), respectively. The degree of significance of transport through the ambient is proportional to the vapor pressure of the ink and its sticking probability on the surface. The former is straightforward to measure or estimate. We show a compilation of the vapor pressures for the series of homologous alkanethiols $\text{HS}(\text{CH}_2)_n\text{CH}_3$ in Figure 3.^{56,57} These data show the expected trend toward lower vapor pressure with increasing molecular weight. Estimating the sticking probability of these molecules with the surfaces is more difficult. Measurements suggest that the interaction with the surface should increase in proportion to the decrease in their vapor pressure.^{33,58} We find that, on balance, during μCP of alkanethiols on gold, effects due to vapor-phase transport dominate changes in the sticking probability for mediating surface coverage.

The final mechanism for mass transport of inks from stamps is diffusion of molecules along the surface from their point of placement (paths 1, 2, and 3; Figure 2B). If the sticking probability above is difficult to reckon, the role of transport along the surface is even more difficult to predict because the monolayer-forming reaction itself has a profound influence on the surface energy of the substrate, and thus the barriers to transport, as the SAM forms. Below we present experiments that provide an understanding of the importance of surface transport of thiols in controlling their spread on gold, providing the limits to what is ultimately achievable by μCP of these molecules on gold.

Figure 4 summarizes what happens when alkanethiols with different molecular weights are the ink in high-resolution μCP . These data provide a set of useful observations for distinguishing between the aforementioned paths (gas-phase and substrate-mediated transport) for the spread of the printed thiol. A relatively low molecular weight (MW 202 g mol^{-1}) species, DDT, showed no evidence of pattern formation, even after prolonged etching of the substrate when a stamp like that in Figure 2 was used with this ink. The complete coverage of the

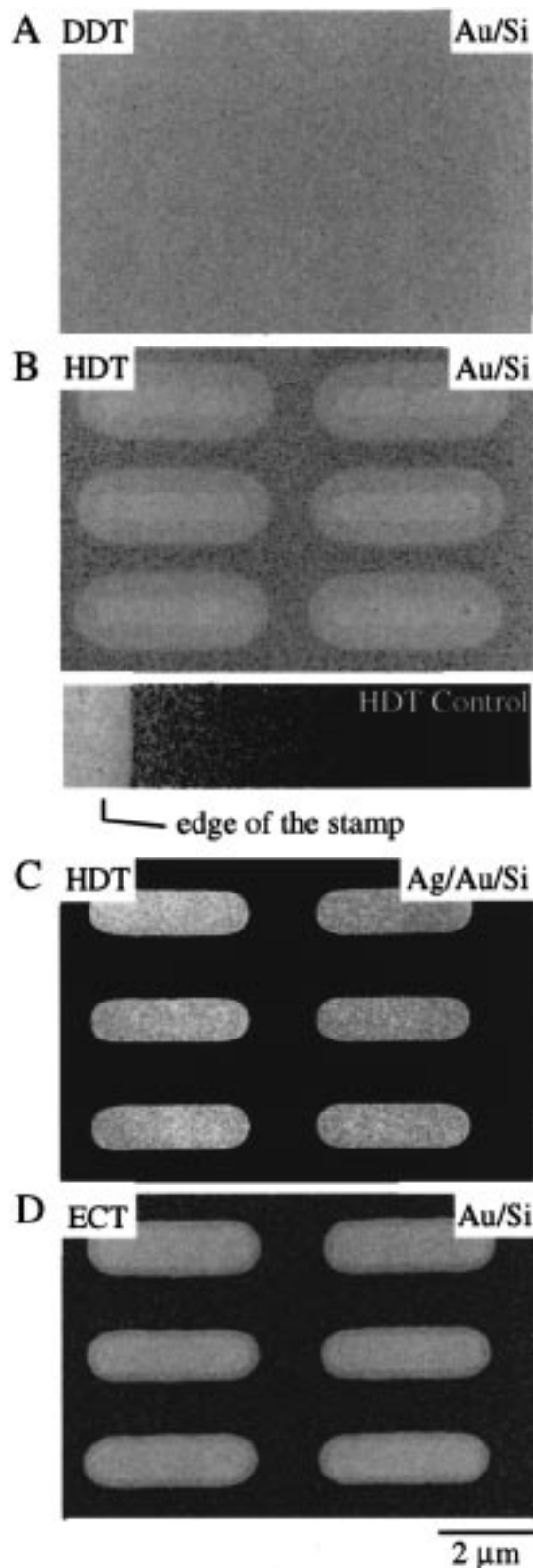


Figure 4. Increasing the molecular weight of alkanethiols used in a printing step reproduced features on the stamp more accurately. These scanning electron micrographs show the result of etching metallic substrates printed for 20 s with a stamp, as shown in Figure 2A, and inked with 0.5 mM solutions of (A) dodecanethiol, (B, C) hexadecanethiol, and (D) eicosanethiol in ethanol. The substrate was a 15-nm layer of Au on Si in all cases except (C), where an additional layer of silver, 5 nm thick, covered the Au.

gold changed to an increasingly defective, but once again nonselective, coverage of the substrate as the concentration of

thiol used to ink the stamp dropped below 0.1 mM. These observations supported the formation of incomplete SAMs as we reported previously in STM studies of the monolayers of this printed thiol on epitaxial gold.¹³ Key in these data is their support for the importance of vapor-phase transport of alkanethiols during μ CP (path 5 in Figure 2B).⁵⁹

Printing HDT proved almost as problematic as DDT at the submicron scales that characterized our survey. The failure to form accurate replicas of the pattern in the stamp provided several additional clues for our investigation. First, vapor-phase transport was still a problem even though the vapor pressure of HDT was significantly lower than that of DDT (Figure 3). Here, the increased sticking probability of DDT compared to that of HDT offsets the benefit of its lower vapor pressure. Explicit effects due to gas-phase diffusion of HDT were evident at the boundaries of the macroscopic area of the stamp, confirming its role in nonselective protection of the substrate with this ink (Figure 4B). Second, the surface-to-volume ratio of cavities in the stamp was clearly crucial in mediating the importance of gas-phase transport to the surface. When stamps having features 5 μ m wide and 3 μ m deep in the elastomer were printed using HDT under conditions identical to those in Figure 4, defect-free patterns resulted that closely approximated their dimensions in the stamp (data not shown). We return to this observation in simulations of the print discussed later in this paper. Third, a role for transport of HDT along the surface (paths 1 and 2) became plain on inspection of the patterns that did form. Two features were obvious: a diffuse background of unetched gold and regions of better protected gold in the form of the targeted pattern but having enlarged dimensions with respect to their size in the stamp. The former was, once again, the result of gas-phase diffusion. The latter apparently occurred by mass transport of HDT along the surface radiating away from its contact points of the stamp with the surface, forming progressively larger areas of a virtually complete SAM.

Transport of the thiol along the surface suggested that autophobic pinning of the liquid was insufficient, at submicron scales, to stop its spread. This refocused our attention on the role of precursor films (a liquid or gas of diffusing molecules) in μ CP. We performed a series of experiments that helped us identify more clearly the various phenomena at work in μ CP of HDT using a heterogeneous metallic substrate. Contact printing of HDT on silver was reported previously as a particularly "clean" route to the formation of metallic patterns at submicron scales.^{4,48,60,61} This observation is, at first glance, surprising. Thiols formed on silver are particularly sensitive to the state of the silver, which oxidizes quickly upon exposure to the ambient. SAMs evidently assemble on these substrates by first consuming the oxide through a redox interaction with the surface⁴⁹ and finally forming reasonably intact (but still inferior to their counterparts on gold) monolayers as inferred from macroscopic measurements of their surface properties.^{62–66} The intermediate stages of this formation involve weakly bound alkyl sulfonates that, though somewhat ordered, are readily removed from the surface by rinsing with solvent.

We speculated from our observations above that microcontact printing of HDT on silver was therefore useful because of the diminished role of vapor-phase transport on this metal. Here diffusion of thiol through the gas phase (path 5 in Figure 2B) would be sufficient to form a surface with a reasonably low surface energy (based on alkyl sulfonates) that alters subsequent mass transport by this mechanism but alone is insufficient to withstand its placement in the aqueous etch. The higher density, more liquidlike environment of thiols in contact (path 3) with

the surface at printing regions of the stamp might, on the other hand, allow sufficient turnover of molecules on the surface to provide the observed etch resistance of the surface in these areas. Figure 4C supports this contention. Features in the print were broader than expected from the master, but the patterns remained observably unaffected by vapor-phase transport of the ink. A thin film of Ag on Au thus provides the means for accurate μ CP with HDT at half-micron scales. This system introduces new limitations in its application to sub-half-micron scales, however, as the heterogeneity and morphology of the Ag coat becomes the controlling parameter. Underpotential deposition to form a monolayer of Ag and Au may plausibly circumvent these limitations.⁶⁷

Another way of limiting the effects of vapor-phase transport in contact printing was to use inks that were still further down the vapor-pressure curve in Figure 3. Eicosanethiol (ECT), though a solid at room temperature, proved the best compromise among the higher molecular-weight alkanethiols examined in this study. Printed SAMs of still heavier and less volatile thiols, such as docosanethiol, became increasingly defect-ridden (as are their monolayers formed from solution), perhaps owing to intrinsic limitations in their self-assembly at room temperature.^{32,68,69} Octadecanethiol, also a solid at room temperature, proved a reasonable candidate ink, although the effects of surface transport and a marginal influence of vapor-phase transport were observably more pronounced than where ECT was used. We tested systems based on the printing of linear alkyl disulfides or ω -terminated alkanethiols ($-\text{COOH}$, $-\text{OH}$, $-\text{CN}$, $-\text{NHCOR}$) and generally found an unacceptable degree of protection against the etch assay.

The temperature throughout the process of μ CP is clearly an important parameter, held constant at 23 °C in our experiments for practical reasons. The benefits of a much lower temperature during the printing step to reduce vapor-phase transport and diffusion of the thiols is not obvious, however, as it may interfere with the process of self-assembly. This question remains open for additional study.

6. Microcontact Printing ECT

The preceding section showed that ECT was the ink of choice for the formation of accurately printed complete SAMs on gold. We decided to construct a more elaborate characterization of the conditions, and consequential properties, of printed monolayers of this thiol. We used a procedure similar to that we found successful for characterizing SAMs of printed DDT:¹³ flat stamps without any pattern were inked with solutions of ECT in ethanol of various concentrations and printed for various durations (Figure 5). We found that prints of ECT, like those of DDT in our previous study, were very sensitive to these conditions. The degree of monolayer completion and the hysteresis in the wettability of its surface each followed progressively, but not linearly, changes in the concentration of the thiol. The measurements showed that a complete SAM of ECT was printed only by stamps inked with concentrations >1 mM when the stamp contacted the gold for 3 s. The duration of this contact also influenced the degree of completion of the monolayer, however. Combined, the graphs in Figure 5 underscore the role of the PDMS stamp as a reservoir of molecules: drawing from its contents to form a monolayer depends, quite reasonably, on what is there initially and for how long the "drain" remains open. Conformal contact, and the need to minimize temporal errors, each necessary for real lithographic processes based on μ CP, clearly benefit from longer times of contact (>1 s). Long printing times allow the use of submil-

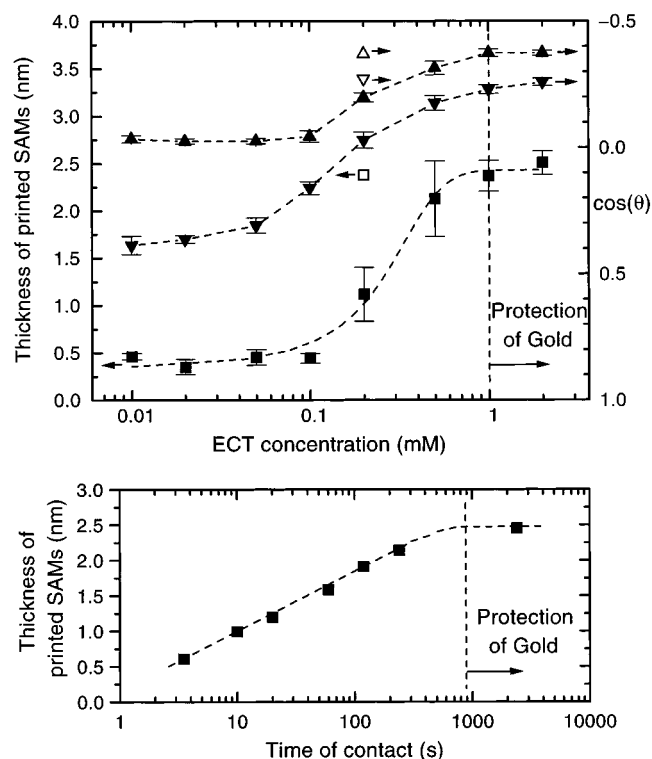


Figure 5. Printing ECT on gold is sensitive to the concentration (upper graph) of the thiol in the ink and the time of contact (lower graph) between the stamp and the substrate. The resulting monolayers were characterized by ellipsometry (squares) and their advancing (triangles) and receding (inverted triangles) contact angles with water. Featureless stamps of 50 mm² were used in these experiments to form the prints. Open symbols correspond to a monolayer of ECT adsorbed on gold from its equilibration in a 0.2 mM solution of this thiol in ethanol for 10 min. Filled symbols correspond to monolayers formed by printing for 3 s stamps inked at the indicated concentration of ECT. In the lower graph, a stamp inked with a 0.2 mM solution of ECT in ethanol was left on the gold substrate for varying durations prior to the measurement of the thickness of the resulting monolayer.

limolar inking concentrations and thereby avoid the presence of excess reactants available for diffusion of molecules and for spreading the pattern on the surface.

Figure 6 shows a range of patterns that developed after etching printed monolayers of ECT under different inking and printing conditions with patterned stamps, as in Figure 5. The extremes evident in the behavior of the system show the limiting constraint to forming patterns: achieving defect-free protection of the substrate without favoring transport of the excess thiol reactant. Printing ECT with stamps inked with a 0.01-mM drop of its solution did not result in highly protective monolayers (as expected from Figure 5) but did favorably limit the spread of this reactant on the surface. Printed transfers done at this concentration were the most accurate we observed, as no broadening of the pattern was detectable (<50 nm). We infer that the reaction between thiol and gold exhausted the number of molecules in this case, thus preventing any noticeable spread of thiol from its points of contact. A 20-fold increase of the concentration of the ink solution was sufficient to bring about a complete and protective monolayer but also led to a time-dependent broadening of the pattern. The formation of any sort of printed features at these still low concentrations of thiol was somewhat surprising given the data in Figure 5: unstructured stamps inked with a similar concentration yielded only a 30% monolayer after their contact with gold for 3 s. These data point to a geometry-dependent enhancement in the flux of molecules to printed parts of the surface, an observation we will return to

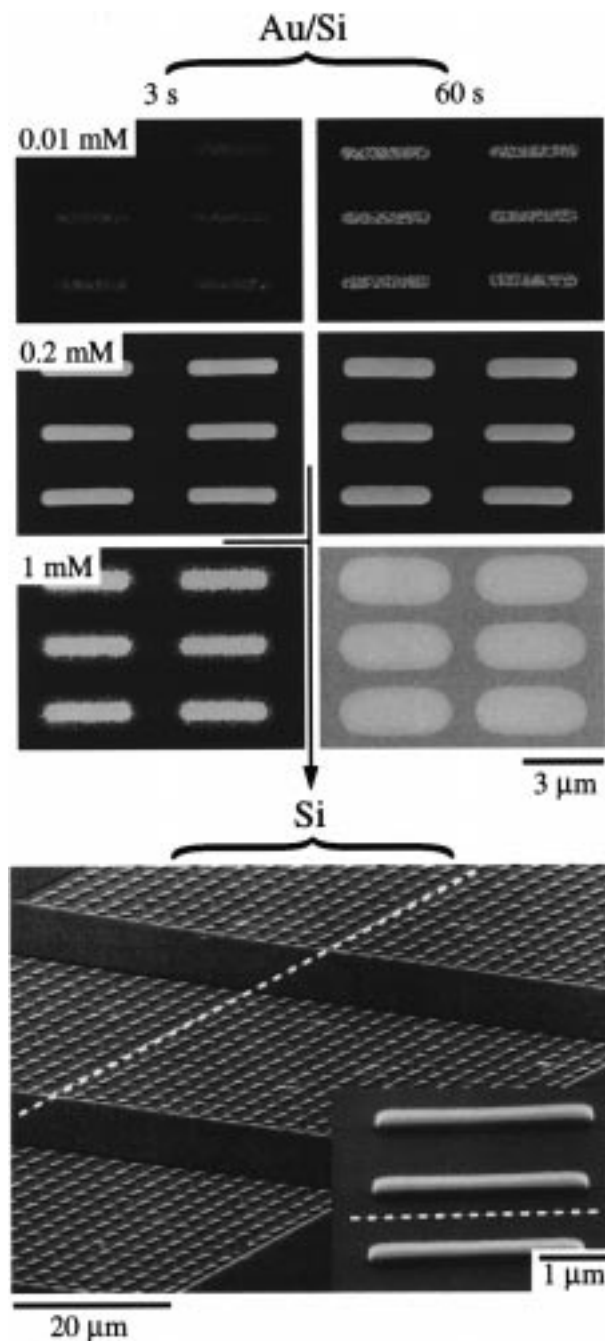


Figure 6. We judged the best printing conditions of our test stamp to be 0.2 mM of ECT and a contact time of 3 s based on the appearance (scanning electron micrographs shown here) of the patterns etched in gold. Samples prepared under these conditions could be transferred into the underlying Si substrate by reactive ion etching without evidence of spurious defects on small or large scales (bottom figure).

presently. The data also support a decreasing rate of reaction of thiol with the gold surface as its coverage increases, providing additional opportunity for molecules to diffuse away from targeted areas of the print. This case was particularly clear for more concentrated solutions of ECT that caused proportionally more severe broadening, even for short durations. The conflict inherent in using μ CP of thiols directly for lithography therefore lies in the need to form a good resist layer without interfering with its self-assembly, narrowing—and perhaps eliminating—the useful window of process conditions as the targeted scale shrinks.

We found empirically that 3-s prints of stamps inked with 0.2 mM of ECT provided the highest accuracy in the targeted

structures for the system under consideration (Figure 2). The dimensions of the pattern increased by $0.1 \pm 0.05 \mu\text{m}$ in all directions in this case. Uncontrolled diffusion over the substrate might, alternatively, be minimized by stamps having an excess of ECT molecules but used in a very fast printing step. This solution is not practically possible with planar stamps with an area greater than a few square micrometers because conformal contact between the stamp and the substrate takes seconds. Curved or cylindrical stamps may offer a solution to this problem,⁷⁰ although it is likely that effects from uncontrollable transport of thiols will remain in this case as well.⁷¹ Accurate μCP on gold with planar stamps is thus constrained to reducing the amount of ECT on the stamp close to that necessary to form complete monolayers in the zones of print.

7. Printing Small- and Large-Area Patterns Simultaneously

One fact about the inking approaches used to charge stamps for printing is that molecules are left distributed everywhere over (and inside of) the stamp. Ink in the zones of contact is supplemented by its additional supply from the walls defining cavities and from bulk parts of the PDMS (paths 4 and 6 in Figure 2B), suggesting that the geometry of the pattern itself influences the flux of molecules available to some regions of the print (as we inferred above). Figure 7 directly illustrates this case by showing what happens when structures in a stamp like those in Figure 2 are surrounded by larger regions that are also printed. Once again, we used ECT under conditions we found best for the development of accurate patterns at the 500-nm scale on gold substrates. Features much larger than these scales did not evidently form a protective monolayer under these conditions, however, except at the periphery of their zones of contact on the substrate. The observation that coverage of the surface by a printed SAM depended on the size of the features points to an additional truth about μCP of thiols: molecules are also free to diffuse over (and through) the elastomeric rubber. The flux of molecules arriving in the contact zones between the stamp and substrate is then influenced by the free surface-to-contact area ratio around objects defined as features of the stamp. The image in the figure also demonstrates that thiols much prefer the stamp environment compared to their movement outward into unprinted parts of the gold surface (path 3 vs 1). We draw this conclusion from the observation of the zones of protected gold in Figure 7. The leading edges and corners of the printed pattern remained sharp ($<200 \text{ nm}$ broadening along path 1), whereas the interiors of these printed areas showed significant coverage of the substrate up to $4 \mu\text{m}$ from their edges (the source of diffusive molecules, path 3). How these data reflect the relative changes in the barriers against the spreading of thiols, differences in their effective diffusion constants over the various surfaces, or other factors, is not immediately obvious except that transport on the stamp clearly dominates the spread of thiols into noncontacted areas of the gold substrate.

We provide support for a mechanism of concentration-dependent spreading of thiols by tracing their transport from a patterned stamp in contact with a flat substrate using computer simulations (Figure 7). The simulation began with molecules equally distributed on the surface layer of the stamp at a density corresponding to that necessary to obtain 50% of a monolayer on the gold substrate. We assumed that molecules in the zones of contact chemisorbed immediately on touching the substrate ($t = 0$ in the simulation). Molecules outside these zones on the stamp were free to diffuse along its surface until they reached uncoordinated gold. The simulation revealed a macroscopic

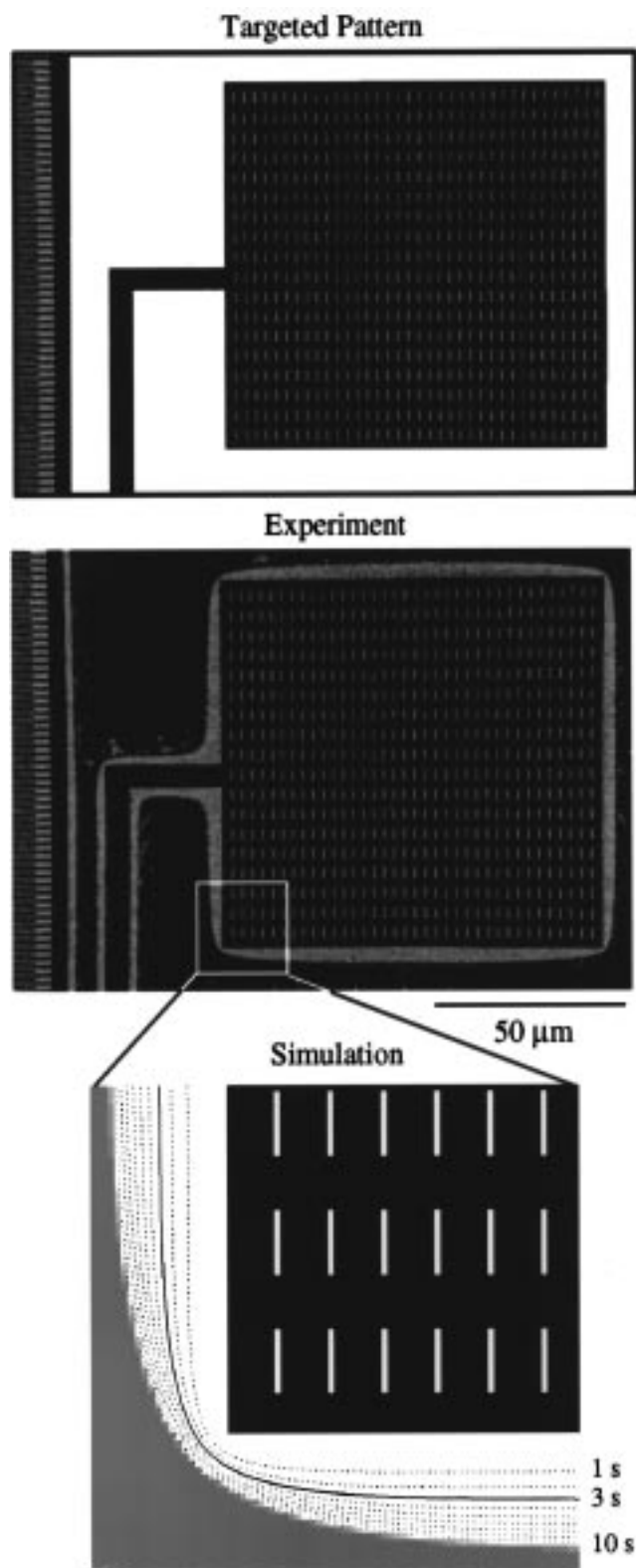


Figure 7. The pattern on the stamp alters the degree of completion of printed SAMs owing to a geometrically mediated change in the supply of ECT from the surface of the PDMS. Large regions in the targeted pattern (shown in white in the topmost image) were not protected from etching under printing conditions at which much smaller structures formed accurately (center image). These prints used inking conditions of 0.2 mM of ECT in ethanol and 3 s of contact (Figure 6). The simulation predicts the degree of monolayer completion (white = 100%, light gray = 50% and black = 0%) on a Au substrate as a function of the duration of contact of the stamp, where mass transport of ECT on the surface of the polymer creates a diffusive front of protection inside large zones of contact (paths 3 and 6, Figure 2B; see text).

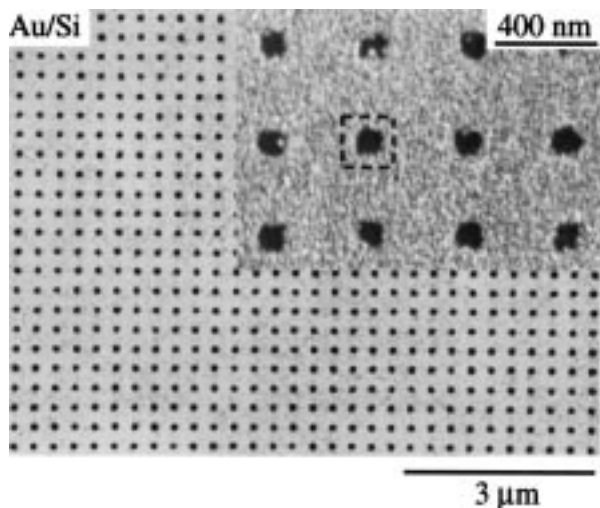


Figure 8. Surface diffusion of ECT (paths 1 and 2 in Figure 2B) during microcontact printing in air on Au allowed a coherent reduction in the dimensions of the printed, etched pattern. The stamp was inked with a 0.2 mM solution of ECT in ethanol and printed for ≈ 30 s.

front of complete monolayer starting at the periphery of zones of the large printed areas of the stamp and advancing into these zones of contact. A sufficient number of molecules arrived in areas containing patterns with small features to fill completely the expected areas of contact. The appearance of the evolving pattern of molecules on the substrate in the simulation was in good agreement with experiments. Interestingly, diffusion of thiols out of the bulk part of the stamp (path 4 in Figure 2) was neither sufficient nor necessary to explain the phenomena in the experiment shown in Figure 7, consistent with earlier data showing that the supply of molecules by this path was comparatively slow (Figure 5). Our experiments support the role of pattern geometry in controlling the flux of molecules to the substrate, particularly where their total number on the stamp is less than that needed for complete formation of a SAM. No obvious condition exists, consequently, for printing alkanethiols to form both small and large features at the same time while maintaining the accuracy of the former. A practical solution to this problem might be found by separating the pattern into several sets of related geometries for subsequent overlay, although this procedure is clearly compromising to the overall aim of μ CP, one of simplicity and simultaneity.

8. Ultimate Limits in Microcontact Printing of Alkanethiols on Gold

The previous section identified several limits to the formation of accurate patterns by μ CP of alkanethiols on gold. This understanding also provides a set of design rules for generally achieving targeted features within a given range of sizes. Lateral diffusion of the ink during the printing step of a μ CP experiment (path 3 in Figure 2) can also be used as part of the design, of course. In the study by Xia et al.⁵⁰ low-density patterns with features in the 100–200 nm sizes were produced by allowing HDT to spread across gold. This operation used a third phase, water, to inhibit mass transport of HDT through its vapor, thus preventing contact of HDT with the gold prior to arrival of the diffusive front of the molecules on the substrate. The suppression of vapor-phase transport when ECT is the ink suggests the applicability of using diffusive narrowing of features to achieve sub-100 nm features in air. We verified the idea on a small scale and for a high density of features in the experiment shown in Figure 8. A stamp having square pillars 200×200

nm² in dimension inked with ECT as above and printed for 30 s formed, after etching, ≈ 80 nm holes on a 400 nm pitch in the otherwise continuous gold film. The process window for achieving this pattern was, in practice, very narrow: several prints were attempted before achieving the result shown. Interestingly, the gold morphology began to appear and affect the resolution of the process at these scales. Gold films formed by resistive evaporation have typical grain sizes of ≈ 20 nm for a thickness of 15 nm. We found that the characteristic grain size on our silver samples was much larger and, in addition, diffusion was more extensive on this substrate, probably owing to the influence of the oxide film at sub-200-nm scales. Achieving high-density patterns by μ CP with controlled spreading of thiols on gold or silver substrates thus seems constrained by the convolution of grain-mediated and diffusive phenomena. These data nevertheless support a role for μ CP of alkanethiols on gold in the formation of large, dense arrays of nanoscale features, perhaps suitable for research applications.

How small a feature can be achieved *directly* by μ CP of alkanethiols on gold using the concepts developed in this paper? In the Introduction we assumed that neither the substrate nor the stamp prevented the formation of accurate, printed features. Our investigations showed that the first limit was the behavior of the ink, an issue we addressed in the preceding sections to arrive at conditions of inking that allowed accurate μ CP at 250 nm scales. Below this dimension our initial assumptions became less adequate and our results showed an increasing convolution between the effects of stamp formation, substrate preparation, and ink localization. We designed a master having large arrays of features with sizes ranging from 1 μ m down to 50 nm with varying densities of its structures. Replication of this master was not possible in a commercially available siloxane (Sylgard 184),⁴⁰ so we formulated higher strength siloxane polymers (Young's modulus of 15 MPa) that had acceptable mechanical stability during the steps of replicating the master and inking and printing the pattern.^{41,72} This material could provide a faithful (within ± 10 nm) reproduction of this master (Figure 9).⁷³ The structures in the gold corresponding to a print with these stamps inked with ECT reproduced most of their patterns, although with noticeable distortions: etching produced high-contrast patterns but revealed broadened structures. Gold dots in the figure have a mean diameter of 90 ± 10 nm, i.e., ≈ 40 nm larger on average than their counterparts on the stamp. Most of the structures have irregular shapes, and some contact their neighbors. We think that the structures in Figure 9 represent the limit of what is achievable in terms of the size and density of "accurately" printed patterns of alkanethiols on gold.

9. Outlook

What is the probable role of microcontact printing in chemical patterning at submicron scales? Our experiences described above suggest that using alkanethiols on gold directly as resists is not likely to work for sensible implementations at scales below 100 nm: Diffusion of linear alkanethiols and morphology of the substrates used here ultimately prove too compromising to allow highly deterministic processes. The fragility of monolayer systems also restricts their direct use in etching to limited, specific cases. Simple lithography as described here is but one, perhaps extreme, possible implementation of μ CP, however. Clearly its utility extends to more general cases that exploit molecular patterning without the very stringent requirements of near perfection in the degree of surface coverage selectively conferred by the print. Figure 6 reinforces this point, showing that stamps with very low concentrations of simple thiols do

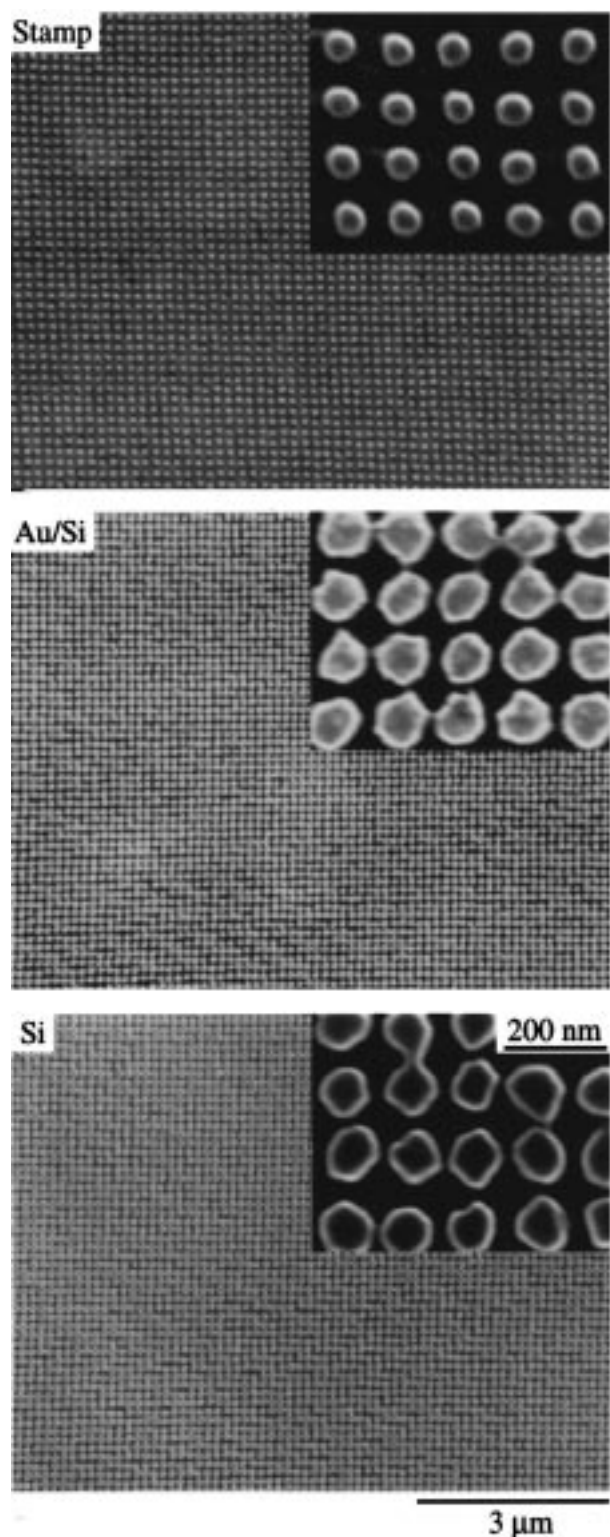


Figure 9. The ultimate accuracy of contact printing on gold is a convolution between the dimensions achievable in the stamp, the characteristics of the ink and substrate, and the type of transfer into the substrate. The stamp was formed in a "hard" siloxane polymer (Young's modulus ≈ 15 MPa) and used as in Figure 6. The gold pattern was made using cyanide-based dissolution and transferred 250 nm deep into the silicon substrate by reactive ion etching.

produce accurate, largely complete (we estimate approximately 95%) printed SAMs that are nevertheless insufficient for etching purposes. Thus other types of resist layers and ways of using the available contrast in the surface chemistry should prove fruitful. We can make stamps with stable features in high-

density arrays having 50 nm dimensions that remain capable of conformable contact with substrates such as silicon or glass. Use of these stamps in a printing step to effect placement of a chemical catalyst,⁷ modifiers of interfacial reaction or adhesion,²¹ or more generally, other systems of chemical amplification is a next line of investigation in the assessment and exploitation of printing processes below 100 nm feature sizes. We have shown that microcontact printing allows the direct placement of biological macromolecules on surfaces while preserving a large part of their structure and adherent function, for example.¹⁰ Transfer of these molecules to a variety of substrates occurred with extreme resolution with no observable diffusion on scales >10 nm. Our observations point toward opportunities in simultaneous molecular manipulations over large patterned areas on a surface, a stepping stone toward controlling chemistry on heterogeneous substrates at the nanoscale.

10. Experimental Section

10.1. Materials and Substrates. All chemicals were of reagent grade or better and used as received unless indicated otherwise. Ethanol from Fluka was of puriss. p.a. quality; water was produced with a Milli-Q Millipore purification unit and had a resistivity of $\approx 18.2 \Omega \text{ cm}^{-1}$. Dodecanethiol, hexadecanethiol, and eicosanethiol were each first passed directly through a short plug of silica (Fluka, 1 g of silica/mL of thiol with no other solvent) column, purified by column chromatography using silica gel (Silica Gel 60, Fluka, $\approx 200 \text{ g}/0.5 \text{ mL}$ of thiol) and 20:1 hexane:ethyl acetate (Merck) as the eluant, and subjected to successive cycles of freeze-pump-thaw at a pressure <100 mTorr over 24 h. Purified thiols were stored at 4 °C, away from ambient light.

One silicon master with large arrays of $3 \times 0.6 \mu\text{m}^2$ features, each $0.3 \mu\text{m}$ deep, was used to form the PDMS stamps in the first part of the study. This master was protected by a monolayer of (1,1,2,2-tetrahydroperfluorodecyl)trichlorosilane (ABCRCR) by its exposure to the vapor of the silane at pressures <1 Torr for 1 h, resulting in a fluorinated layer ≈ 1 nm thick everywhere on the silicon surface. A second master was formed by e-beam lithography on a Si/SiO₂ substrate. Its features were 70 nm deep and ranged in dimensions from 50 to 250 nm at varying pitch. This master was otherwise handled as above. Stamps in the first part of the study were made from poly-(dimethyl)siloxane (Sylgard 184, Dow Corning, Midland, MI) using the prepolymer components according to the recommendations of the manufacturer. An automatic mixer/dispenser (DOPAG MICRO-MIX E, Cham, Switzerland) provided a homogeneous and bubble-free blend of the polymer. Stamps were formed by curing the PDMS mixture on the master for at least 24 h at 60 °C. Stiffer stamps (Young's modulus > 3 MPa) were made using commercially available copolymers (ABCRCR, Karlsruhe, Germany).⁷²

The gold substrates were made by evaporating 1 nm of Ti (99.99%, Johnson Matthey) and 15 nm of Au (99.999%, Goodfellow) onto Si/SiO₂ wafers (Silitronix, Neuchâtel, Switzerland) using an Edwards FL400 e-beam evaporator operating at a base pressure of $<1 \times 10^{-7}$ Torr at an evaporation rate of 0.25 nm s^{-1} . Ag surfaces were prepared by evaporating 5 nm of Ag (99.999%, Goodfellow) onto Au substrates prepared as described above within the same set of evaporations at an evaporation rate of 0.07 nm s^{-1} and were used within 1 day of their preparation. Gold freshly evaporated and exposed to the ambient becomes contaminated by an ≈ 1 nm thick layer of adsorbates within 1 day. This contamination layer is readily displaced by alkanethiols, however, thus forming a monolayer from solution or using μCP .

10.2. Instrumentation. Stamps and printed patterns were examined using a Hitachi S-4000 scanning microscope. Cross sections through the sample were made by initiating a split on the backside of the stamp and fracturing the bulk in two. Sputtering 5 nm of Au onto the PDMS stamp with a Balzers SCD sputtering system prevented charging of the stamp during imaging. We expect that the processes of preparing and imaging the stamp led to some stress-induced distortions of its "true" appearance. Additional characterization of the gold substrates and of the monolayers adsorbed on their surfaces was done with a Dimension 3000 AFM (Digital Instruments, Santa Barbara) operated in a "tapping" mode. These measurements were particularly useful for understanding and assessing the etching of the bold as well as its rate and characteristics. AFM cantilevers (TESP, Digital Instruments) had resonance frequencies between 150 and 400 kHz and were coated with a monolayer of decyltrichlorosilane formed from the vapor phase of the silane at a reduced pressure (3 h, <10 mTorr) to provide a chemically well-defined, low surface-energy tip.

10.3. Microcontact Printing. Thiol solutions were prepared in 4-mL glass vials using ethanol freshly purged with Ar. Solutions of ECT were sonicated for 5 min to help dissolve this thiol. All solutions were stored in the dark to prevent oxidation of the thiols and were prepared fresh each week. Typically a small section ($8 \times 5 \text{ mm}^2$) of PDMS was cut from the large stamp and used for only one print.

Inking the stamp followed a consistent procedure:¹³ a drop ($1 \mu\text{L}/\text{mm}^2$ of stamp) of the thiol solution (ink) was placed on the structured or flat side of the stamp using a Wheaton pipet. The macroscopic bulk of the drop was removed after 30 s under a stream of N_2 that was continued for ≈ 10 s more. The stamp was used for μCP within 15 s of inking, placed by hand on the substrate, and left there under its own weight. Macroscopic contact between the stamp and substrate was confirmed by visual inspection using changes in the reflections of light from the surfaces as an indicator of their proximity. Its time of contact with the surface was carefully monitored and controlled to within ≈ 1 s. The ambient temperature was fixed at 23°C and held constant, within 1°C , throughout the study.

The print was transferred to gold using CN^-/O_2 (0.1 M KCN in NaOH/KCl at pH 12). We used a buffered solution of KCN at pH 12 to minimize the attack of the Si substrate, resulting in reprecipitation of silica crystallites on the samples that might be confused for defects in the gold. We note that using cyanide solutions under these conditions is somewhat more dangerous than under fully basic conditions typically employed because of the greater possibility of forming HCN gas over its surface. The etch rate of "bare" gold was $\approx 0.05 \text{ nm s}^{-1}$ at room temperature under our conditions. Etching times were kept constant for similar experiments, and the complete etch of the gold outside of the stamped region provided an internal control to signal the end of the etch.

Transfer of the gold pattern into its silicon substrate used a reactive ion etcher (STS, Bristol, UK) operating with an inductively coupled plasma at a base pressure of 6×10^{-6} Torr and using a SF_6 -based chemistry. Transfer lasted for 10–40 s at an etch rate of $\approx 0.4 \mu\text{m min}^{-1}$.

10.4. Thickness Measurements. Ellipsometry was used to measure the change in monolayer coverage of the gold samples. For this we used a Rudolph AutoEL automatic thin-film ellipsometer equipped with a 632.9 nm He–Ne laser and operating at an angle of incidence of 70° . The polarizer angle was 45° . The complex refractive index of the gold substrate, $N_s = n_s + k_s i$, was measured first. The thickness of the SAMs

was measured at precise locations ($\Delta < 0.5 \text{ mm}$), where n_s and k_s were recorded. The instrument was calibrated by measuring a series of SAMs of alkanethiols ($\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$, $n = 2, 4, 6, 8, 12, 14, 16, 18, 20$) on Au having known thicknesses. We used $n_f = 1.45$ for the refractive index of this series of thiols. The accuracy of the measurements was $\pm 0.1 \text{ nm}$ using this method.

10.5. Numerical Simulation. The simulations were based on the equation of diffusion for two dimensions $\partial c/\partial t = D(\partial^2 c/\partial x^2 + \partial^2 c/\partial y^2)$, where c is the concentration on the surface of the stamp, t is the time, and x and y correspond to the lateral coordinates of the stamp surface. This equation was discretized and transferred into a routine executable by MATLAB (MathWorks Inc.). The surface was divided into a rectangular grid with a $0.3\text{-}\mu\text{m}$ mesh; time steps of 1 ms were used to follow the evolution in the distribution of thiols on the stamp and substrate (the diffusion scale per time step was small compared to the mesh size, i.e., $2D\Delta t < \Delta x^2$). Initial conditions in the simulation used a constant concentration of thiols on the surface of the stamp, equivalent to half a monolayer if transferred entirely to the simulated substrate. The interaction between the substrate and the thiols here was considered irreversible, i.e., diffusing molecules that encountered a "free" site on the substrate were fixed there. Molecules were allowed to diffuse over noncontacting surfaces of the stamp and interfaces having a completed monolayer, where their diffusion constant was the only fitting parameter in the simulation. We found that a value of $D = 7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ provided the good fit to the data in Figure 7.

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