Use of Controlled Reactive Spreading of Liquid Alkanethiol on the Surface of Gold To Modify the Size of Features Produced by Microcontact Printing

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This paper describes a procedure that uses the controlled reactive spreading[1,2] of a liquid on a solid surface to reduce the size of features produced by microcontact printing (μCP).[3] It suggests a strategy for generating small features (100−500 nm) in patterns on surfaces that relies on a physical process occurring on a surface—lateral reactive spreading of a liquid—rather than on exposure to short-wavelength radiation or electrons.

μCP prints the patterned self-assembled monolayer (SAM)[4] on the surface of gold, using an elastomeric stamp whose surface has itself been patterned in an appropriate relief structure. The stamp is wetted with an alkanethiol (typically hexadecanethiol, $CH_3(CH_2)_{15}SH$) and brought into contact with the gold in air for 10−20 s. It is a very convenient technique for forming patterned SAMs with features having dimensions of ~2 μm or larger. The photolithography required to make the masters used to mold the elastomeric stamps is straightforward at this scale,[5] and the edge resolution that can be obtained presently using this method (about 50 nm)[2] does not limit the resolution of the overall pattern. It is more difficult to make features smaller than 2 μm by μCP, primarily because fabricating the required stamps requires more complex photolithography. Features as small as 200 nm have, however, been made using masters prepared (with difficulty) by X-ray lithography.[5-7]

We are developing procedures that extend the capabilities of μCP into the submicrometer range and that do not require high-resolution photolithography.[8,9] In particular, we wish to find methods that start with an elastomeric stamp having features with dimensions of ~2 μm or larger (that is, in the range that is easily prepared by routine photolithographic methods) and

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(10) The PDMS stamps were made according to published procedures.[7] The "ink" solutions were hexadecanethiol (purified by chromatography through silica gel) in ethanol with concentrations from 0.01 to 6.5 mM. The gold films were prepared by e-beam sputtering. For μCP under water, a piece of gold substrate was put in a polystyrene Petri dish that was half-filled with deionized water, and the inked stamp was then brought into contact with the gold surface (avoiding trapping air bubbles between the stamp and gold surface). Separating the stamp from the surface without smearing the pattern required care: we used two methods to accomplish this separation. In the first, the stamp and the gold substrate were taken out from the water together while still in contact, carefully dried in a stream of nitrogen, and then separated. In the second, the stamp was separated from the gold substrate while under water, the water was replaced with several volumes of clean water to remove alkanethiol floating on its surface, and the gold substrate was then removed from the water and dried in a stream of nitrogen. Each time the stamp was used again, it was rinsed with excess ethanol to remove alkanethiol left on the stamp from the previous uses. After applying alkanethiol, the stamp was dried in a stream of nitrogen for ~1 min. Gold was removed by using a cyanide solution (KCN, 0.1 M; KOH, 1 M) with vigorous stirring using air (oxygen) as oxidant.[7]
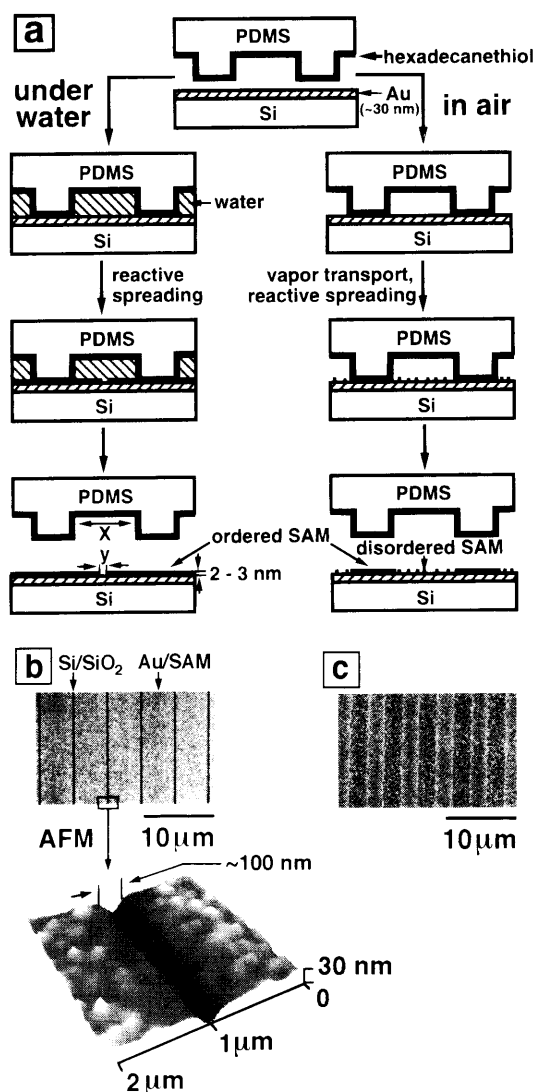

Figure 1. (a) Illustration of microcontact printing under water and in air, respectively. By conducting the printing under water, the transport of hexadecanethiol to the surface through the vapor phase is completely suppressed. The uniform reactive spreading of hexadecanethiol from the edge of the SAM could be used to control the dimensions of features. (b,c) Scanning electron micrographs of test patterns produced by μCP under water and in air using a solution of 2 mM hexadecanethiol in ethanol, with a time of contact of the stamp with the gold of 5 min. The inset is the AFM picture to show the detail of a trench etched in the gold. In this example, $x \approx 3$ μm, $y \approx 0.1$ μm.

to find nonlithographic methods of generating patterned SAMs with features *smaller* than the features of the stamps used in their preparation. We have reported one such method, in which the stamp is compressed mechanically before printing the SAM onto the gold.[8] Here we report a second method, in which reactive spreading of hexadecanethiol under controlled conditions extends the edge of the patterned SAM beyond the area of the stamp in contact with the surface.

This process is illustrated in Figure 1a.[10] The most significant feature is that the reactive spreading of the hexadecanethiol reduces the lateral dimensions of the *bare* gold surface after μCP to dimensions *smaller* than the corresponding recessed features on the surface of the stamp (and of course makes the dimensions of the regions covered by the SAM larger than the raised regions on the stamp). The key to this process is to carry out the microcontact printing step *under water*, using an alkanethiol that is insoluble in water. If printing was carried out in air, a sharp pattern was not formed: SAM also formed in the regions not in contact with the stamp (Figure 1c) by

Communications to the Editor

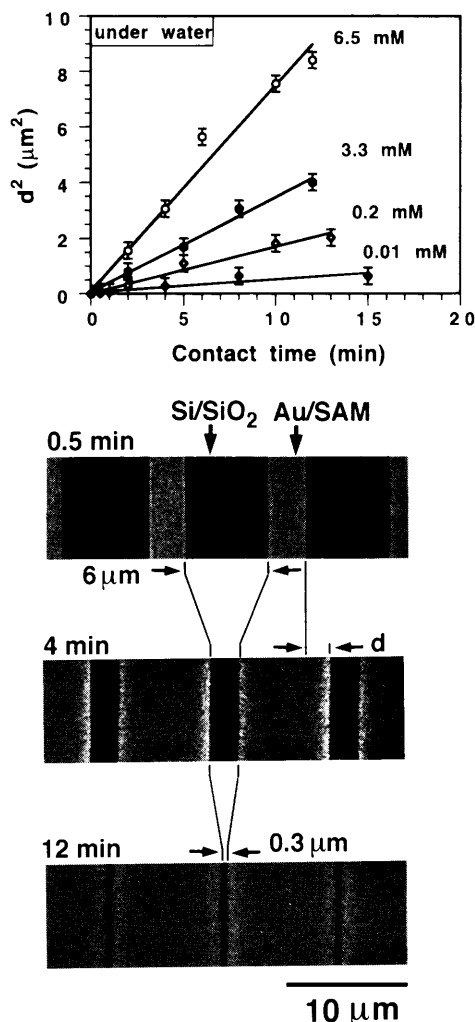J. Am. Chem. Soc., Vol. 117, No. 11, 1995 3275

Figure 2. Scanning electron micrographs of a test pattern produced by μCP under water for different times. A 6.5 mM solution of hexadecanethiol in ethanol was used. These submicrometer-sized features produced in this way are uniform over the whole area of the stamp we used (usually ~1 cm²). The graph relates the distance over which the edge of the SAM advances to the concentration of hexadecanethiol originally used to wet the stamp and the contact time used in printing.[13]

processes that include, we presume, reactive spreading and the diffusion of hexadecanethiol to the surface through the vapor phase.[11,12]

Figure 2 shows the evolution of a test pattern of parallel lines as a function of the time in which the stamp is in contact with the surface of the gold when the μCP was carried out under water. The high edge resolution of the system under water and the progressive advance of the drop edge are clearly evident in these images. The growth of the SAM occurs predominantly by uniform spreading from its edge. The distance d (μm) over which the edge advances is related to the concentration of alkanethiol [C] (mM) and time t (min) by the empirical equation[13] $d^2 \approx (0.16[C]^{1/2})t$.

(11) We expect the vapor diffusion to be a relatively rapid process since the cavity formed between the gold substrate and the stamp is only ~2 μm, a value close to the mean-free-path (λ) of hexadecanethiol, ~0.03 μm. The mean-free-path of hexadecanethiol was estimated as follows: $\lambda = (^1/_2{}^{1/2}\sigma)kT/P$; here σ is the collision section (~10⁻¹⁸ m²), and P is the pressure (~1.01 × 10⁵ Pa).

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(13) Interpretation of the "concentration dependence" in this relation in terms of the factors determining the rate of reactive spreading is not straightforward since the ethanol in which the hexadecanethiol is dissolved will dissolve rapidly on contact with water. The "concentration" of hexadecanethiol in ethanol is probably important primarily in determining the *quantity* of hexadecanethiol delivered to the surface of the gold during μCP.
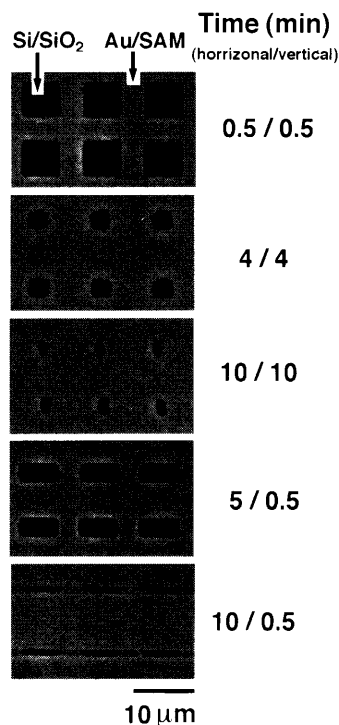

Figure 3. Scanning electron micrographs of gold grids with different dimensions produced by "cross-stamping" under water, followed by chemical etching in cyanide solution (see the text for detail).

Figure 3 shows a second set of test patterns formed by μCP under water. In this series, the same stamp used in Figure 2 was first contacted with the surface for an interval of time. It was then removed, cleaned with ethanol, rewetted with hexadecanethiol ink, and recontacted with the surface with the orientation of the pattern rotated by ~90° from the first impression. By using different intervals of times for these two steps, we produced a variety of approximately rectangular shapes (the resolution of the 90° corners was lost relatively rapidly in these experiments).

In summary, microcontact printing *under water*, using a long interval of contact between the stamp and the surface of the gold, can produce patterned SAMs with uncovered areas having dimensions as small as ~100 nm (Figure 1b), that is, smaller than could be formed conveniently using conventional μCP (in air, with short contact times) or by the usual techniques of photolithography. It is a technique that expands the regions covered by the SAM and shrinks the bare regions. Using this technique, it is straightforward to fabricate structures such as arrays of gold microelectrodes with submicrometer dimensions.[14] Combination of printing (using this technique) and removal of both the bare gold (by etching in cyanide solution) and the unprotected silicon (by etching in aqueous base) produces arrays of submicrometer-sized cavities;[15] we believe that these cavities will be useful in templated crystallization and in carrying out synthetic and analytical reactions on a micro scale.

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