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Microfabrication by Microcontact Printing of Self-Assembled Monolayers**

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1. Introduction

Microcontact printing (μCP) is a new technique for forming patterns with μm dimensions.[1,2] It offers experimental simplicity and flexibility in forming certain types of patterns. It relies on the remarkable ability of self-assembled monolayers (SAMs) of long-chain alkanethiolates on gold and other metals to act as nanometer resists by protecting the supporting metal from corrosion by appropriately formulated etchants. Patterns of SAMs having dimensions that can be less than 1 μm are formed by using the alkanethiol as an "ink", and by printing them on the metal support using an elastomeric "stamp". The stamp is fabricated by molding a silicone elastomer using a master prepared by optical or X-ray microlithography or by other techniques.

Microcontact printing of patterned SAMs brings to microfabrication a number of new capabilities. First, μCP makes it possible to form patterns that are distinguished only by their constituent functional groups; this capability permits the control of surface properties such as interfacial free energies with great precision.[3] Second, because microcontact printing relies on molecular self-assembly, it generates a system that is (at least locally) close to a thermodynamic minimum and is intrinsically defect-rejecting and self-healing. Simple procedures, with minimal protection against surface contamination by adsorbed materials or by particles, can lead to surprisingly low levels of defects in the final structures.[1,2] The procedure can be conducted at atmospheric pressure, in an unprotected laboratory atmosphere. Thus, μCP is especially useful in laboratories that do not have routine access to the equipment normally used in microfabrication, or for which the capital cost of equipment is a serious concern. Third, the patterned SAMs can be designed to act as resists with a number of wet-chemical etchants.[2] Working with liquid etchants suffers from the disadvantages of handling

solvents and disposing of wastes, but also enjoys substantial advantages: a high degree of control over contamination of surfaces; reduced damage to the substrate from energetic interactions with atoms or ions; the ability to manipulate complex and sensitive organic functionality. Because the SAMs are only 1–3 nm thick, there is little loss in edge definition due to the thickness of the resist; the major determinants of edge resolution seem to be the fidelity of the contact printing and the anisotropy of etching the underlying metal. In the current best cases, features of size 0.2 μm can be fabricated;[2] edge resolution in systems showing this resolution in feature size is less than 50 nm.

Although many other methods for the patterning of SAMs exist — for example, micromachining,[4] ion and electron beam lithographies,[5] microwriting,[6,7] and photolithography oxidative patterning with UV light — μCP seems to have the greatest opportunity for immediate and broad application.[2] This article focuses on the procedures for μCP and, in particular, describes applications aimed toward the fabrication of metallic microstructures.

2. Discussion

Self-assembled monolayers (SAMs) of organic compounds on inorganic or metal surfaces are becoming increasingly important in many areas of materials science.[11–13] Although there are many different systems of SAMs based on different organic components and supports, the best developed systems are those of alkanethiolates, $HS(CH_2)_nR$, on gold films.[14] Typically, a gold film 5–2000 nm thick is supported on a titanium-primed Si/SiO₂ wafer or glass sheet. The titanium serves as an adhesion promoter between gold and the support. The alkanethiols chemisorb on the gold surface from a solution in which the gold film is immersed, and form adsorbed alkanethiolates with loss of hydrogen. Adsorption can also occur from the vapor.[17] SAMs formed on gold from long-chain alkanethiolates of structure $X(CH_2)_n Y$-$(CH_2)_mS$ are highly ordered[18,19] and can be considered as crystalline or quasi-crystalline molecular arrays. A wide variety of organic functional groups (X,Y) can be incorporated into the surface or interior of the monolayer. SAMs

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SAMs can therefore be tailored to provide a wide variety of material properties: wettability and protection against corrosion by chemical etchants are especially relevant to μCP.

Figure 1 outlines the procedure used for μCP. An elastomeric stamp is used to transfer alkanethiol "ink" to a gold surface by contact; if the stamp is patterned, a patterned SAM forms. The stamp is fabricated by casting polydimethylsiloxane (PDMS) on a master having the desired pattern. Masters are prepared using standard photolithographic techniques, or constructed from existing materials having microscale surface features.
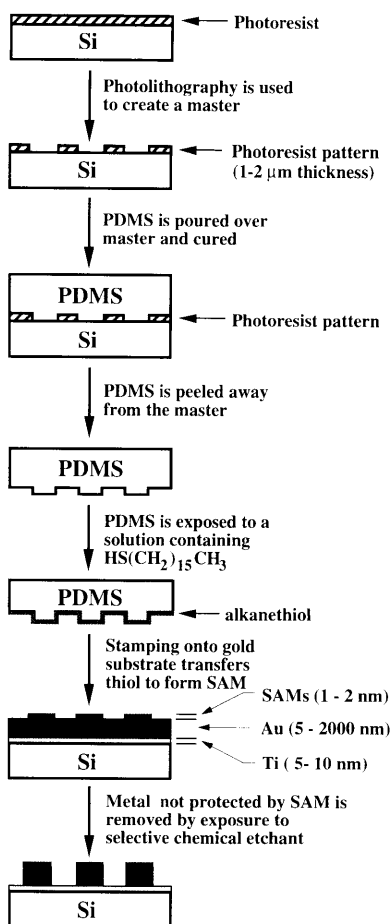

Fig. 1. Schematic of the procedure for microcontact printing (μCP) of patterned self-assembled monolayers (SAMs) of alkanethiolates on gold surfaces. Photolithography is one of several techniques that can be used to fabricate a master with the desired pattern. The stamp is fabricated by casting polydimethylsiloxane (PDMS) on the master. After curing, the PDMS is peeled from the master and "inked" with alkanethiol. The stamp is applied to the surface of a gold film (supported on a silicon wafer that is primed with an adhesion promoter, for example, titanium), and alkanethiol transfers and forms a patterned SAM. Liquid etchants remove metals not protected by the alkanethiolate layer.

In a typical experimental procedure, a photolithographically produced master is placed in a glass or plastic Petri dish, and a 10:1 ratio (w:w or v:v) mixture of SYLGARD silicone elastomer 184 and SYLGARD silicone elastomer 184 curing

agent (Dow Corning Corporation) is poured over it. The elastomer is allowed to sit for approximately 30 minutes at room temperature and pressure to degas, then cured for 1–2 hours at 60 C, and gently peeled from the master. "Inking" of the elastomeric stamp is accomplished by exposing the stamp to a 0.1 to 1.0 mM solution of alkanethiol in anhydrous ethanol, either by pouring the solution over the surface of the stamp, or by rubbing the stamp gently with a Q-tip that has been saturated with the inking solution. The stamp is allowed to dry until no liquid is visible by eye on the surface of the stamp (typically about 60 seconds), either under ambient conditions, or by exposure to a stream of nitrogen gas. Following inking, the stamp is applied (typically by hand) to a gold surface. Very light hand pressure is used to aid in complete contact between the stamp and the surface. The stamp is then gently peeled from the surface. Following removal of the stamp, the patterned gold surface can be subjected to chemical etchants (see below) that selectively remove underivatized areas of the gold surface, and if desired, the underlying support(s). Alternatively, further derivitization of unstamped areas can be accomplished, either by using a second stamp, or by washing the entire surface with a different alkanethiol.

The elastomeric character of the stamp is essential to the success of the process. Polydimethylsiloxane (PDMS), when cured, is sufficiently elastomeric to allow good conformal contact of the stamp and the surface, even for surfaces with significant relief; this contact is essential for efficient contact transfer of the alkanethiol "ink" to the gold film. The elastomeric properties of PDMS are also important when the stamp is removed from the master: if the stamp were rigid (as is the master) it would be difficult to separate the stamp and master after curing without damaging one of the two substrates. PDMS is also sufficiently rigid to retain its shape, even for features with sub-micron dimensions: we have successfully generated patterns with lines as small as 200 nm in width.[2] The surface of PDMS has a low interfacial free energy[20] ($\gamma = 22.1$ dynes cm^{-1}) and the stamp does not adhere to the gold film.[1] The stamp is durable: we have used the same stamp up to 100 times over a period of several months without significant degradation in performance. The polymeric nature of PDMS also plays a critical role in the inking procedure, by enabling the stamp to absorb the alkanethiol ink by swelling.

Microcontact printing on gold surfaces can be conducted with a variety of alkanethiol "inks". Alkanethiols that do not undergo reactive spreading[21–24] (after application to the gold film) are required for formation of small features with high resolution. For stamping in air, we use autophobic alkanethiols such as hexadecanethiol. Microcontact printing of other non-autophobic alkanethiols, for example, $HS(CH_2)_{15}COOH$, can be conducted by stamping under a liquid such as water.[25]

Patterned SAMs of alkanethiols on gold provide excellent resist character with a number of wet-chemical etchants.[1,2,6] Figures 2 and 3 show representative examples of metal mi-
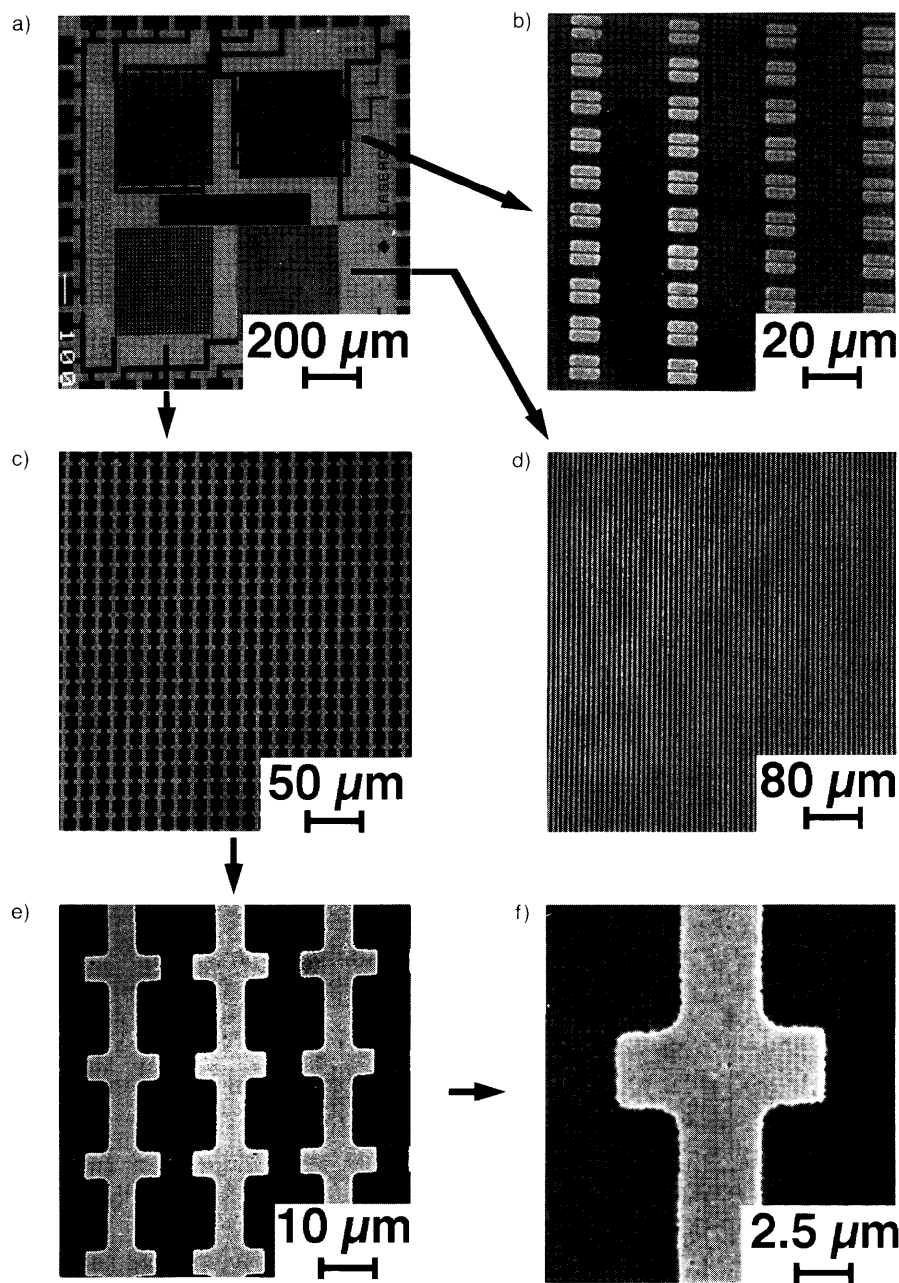
a) 200 μm

b) 20 μm

c) 50 μm

d) 80 μm

e) 10 μm

f) 2.5 μm

Fig. 2. Electron micrographs of complex patterns in gold nickel surfaces formed by a combination of microcontact printing (μCP) and wetchemical etching: a) A test pattern of the type used in microelectronics applications; b f) Subregions of (a) at higher magnifications. Dark areas represent regions where underivatized gold (and underlying nickel) was removed by the chemical etch. Contrast between micron-scale features is clearly evident. See text for experimental details.

crostructures that can be fabricated using μCP followed by chemical etching.

Figure 2 shows an etched test pattern. The PDMS stamp used to create the pattern was cast from a commercial master. Hexadecanethiol was printed on a gold surface (~ 1000 Å), which was supported on a silicon wafer with nickel (~ 250 Å) as an adhesion promoter. The substrate was submerged in a solution of KCN (0.1 mM to 1.0 M) and KOH (1 M).[26] The solution was stirred, and oxygen was continuously bubbled through the solution during etching. Underivatized areas of the gold surface were removed in approximately 15 minutes, exposing the underlying nickel. Nickel was removed by submerging the substrate in a mixture of H_2SO_4,

30% H_2O_2, H_3PO_4, and 30% $NiSO_4$ (5:5:1:4 respectively).[27]

Figure 3 shows electron micrographs[28] of patterned SAMs formed by μCP (a–c), and electron micrographs of the corresponding silicon microstructures fabricated by chemical etching of the gold and silicon layers (d f). In Figure 3a, the grid pattern was produced using a PDMS stamp consisting of parallel lines. The stamp was applied twice, with the second application oriented at 90 relative to the first. Figure 3b shows a fracture profile (at higher magnification) of a sample made with the same stamp and procedure as in Figure 3a. In Figure 3c, the pattern was created by application of a single PDMS stamp. In all cases, hexadecanethiol
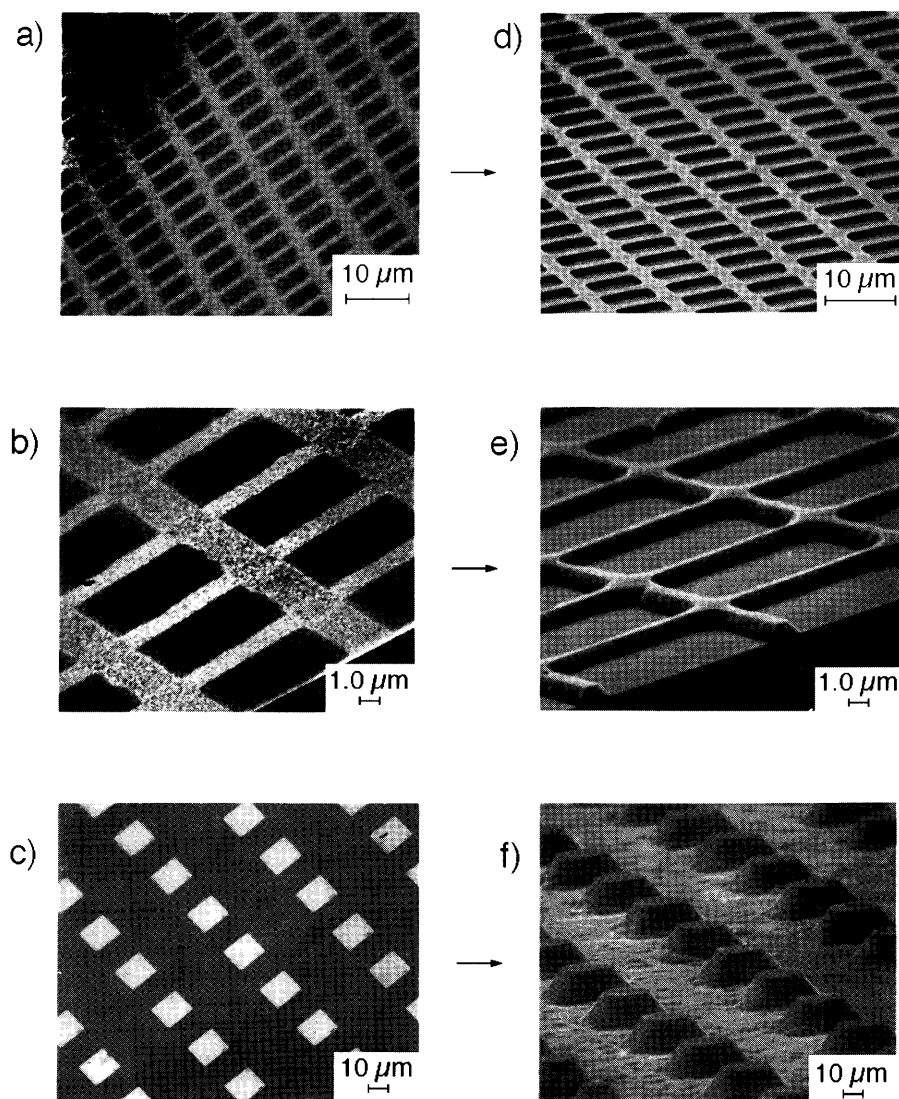
a)   10 μm

d)   10 μm

b)   1.0 μm

e)   1.0 μm

c)   10 μm

f)   10 μm

Fig. 3. Electron micrographs of patterned
SAMs formed by microcontact printing (a–c)
and, electron micrographs of silicon microstruc-
tures resulting from chemical etching of these
patterned SAMs (d–f). Anisotropic etching of
the silicon ⟨100⟩ wafer was accomplished by
submerging the substrate in a stirred solution of
KOH (2–6 M) in isopropanol (15% by vol-
ume), at 60 C, for approximately 30 minutes.
The titanium layer was removed by washing
with dilute HF. The final shapes of the resulting
silicon microstructures reflect both the original
pattern (generated by microcontact printing)
and the anisotropy of the silicon etch. Small
variations in etching times resulted in slightly
different features. Each of the images shown in
Figure 3 is from a different sample. All SEM
images in Figure 3 were obtained with the
sample tilted by approximately 70 to improve
imaging of the surface relief of the sample. The
tilt of the sample distorts the image: the rectan-
gular patterns in Figures 3a,b,e, and f would ap-
pear as squares if the sample were not tilted. See
text for additional details.

was transferred by μCP to a gold surface that was supported
on a test grade, ⟨100⟩ silicon wafer. Approximately 10 Å of
titanium was used as an adhesion promoter. Figures 3d–f
show silicon microstructures fabricated by chemical etching
of the surfaces not protected by the patterned SAMs shown
in Figures 3a–c. Underivatized gold was removed as de-
scribed previously. The titanium layer was removed by wash-
ing with dilute HF. Anisotropic etching of the silicon wafer,
in areas exposed by the removal of the gold and titanium
layers, was accomplished by submerging the substrate in a
stirred solution of KOH (4 M) in isopropanol (15% by vol-
ume) at 60 C for approximately 30 minutes.[29] After re-
moval of silicon by etching, the remaining gold layer, which
served to protect the underlying silicon (in the patterned
regions) from the chemical etch, was dissolved in aqua regia
(1:1 HNO₃/HCl). Small variations in etching times resulted
in slightly different features. Each of the images shown in
Figures 3 is from a different sample. All SEM images in
Figure 3 were obtained with the sample tilted by approxi-

mately 70 from horizontal to improve imaging of
the surface relief of the sample. The tilt of the
sample distorts the image: the rectangular patterns in
Figures 3a,b,d, and e would appear as squares if the sample
were not tilted.

The patterns and microstructures shown in Figures 2 and
3 are representative examples of the features that can be
fabricated using μCP. Complex patterns and shapes, with
dimensions ranging from < 1 μm to several hundred μm are
well resolved. Features of this size (and complexity) suggest
that the μCP technique may be useful for the fabrication of
microstructures that are normally fabricated using electron-
beam lithography and optical lithography.

3. Conclusions and Summary

Microcontact printing using an elastomeric stamp is the
most versatile method available for preparing patterned

SAMs of alkanethiolates on gold. The capacity to form patterned SAMs on gold, coupled with the ability of SAMs to act as 1–2 nm thick resists for chemical etches, provides the foundation for a new technique for microfabrication. Microcontact printing has many useful characteristics: it is experimentally simple, and can be conducted in a conventional chemical laboratory— no routine access to clean rooms or photolithographic equipment is required (although a microfabrication technique—typically photolithography—is required to make the master): the technique relies on self-assembly, and thus tends to minimize defects; with care, it is capable of producing sub-micron features, and of routinely forming micron-scale features with high fidelity; the elastomeric stamps are easily prepared and can be used hundreds of times (while stored under ambient lab conditions) without degradation in performance. At this early stage of development, the chief weakness of the method, relative to other very highly developed microlithographic methods such as photolithography, is the relatively high density of defects in the final structure. The degree of perfection that can be achieved by μCP, after careful development, remains to be established.

The simplicity and flexibility of this technique provides the opportunity for many other applications. Microcontact printing has been used for the fabrication of microstructures by methods other than chemical etching, for example, the formation of micron-scale diffraction gratings by condensation of water on hydrophilic regions,[3] for the formation of microelectrodes,[30] and for the patterned formation of microcrystals and microcrystal arrays.[2] Patterned SAMs have also been used to form patterns of adsorbed proteins and attached mammalian cells.[31] The successes of the μCP technique in these applications, and the success of the procedure for microfabrication in silicon and other materials, augers well for future applications.

[1] A. Kumar, G. M. Whitesides, Appl. Phys. Lett. 1993, 63, 2002–2004.
[2] A. Kumar, H. A. Biebuyck, G. M. Whitesides, Langmuir 1994, 10, 1498–1511.
[3] A. Kumar, G. M. Whitesides, Science 1994, 263, 60–62.
[4] N. L. Abbott, J. P. Folkers, G. M. Whitesides, Science 1992, 257, 1380.
[5] R. C. Tiberio, H. G. Craighead, M. Lercel, T. Lau, C. W. Sheen, D. L. Allara, Appl. Phys. Lett. 1993, 62, 476–478.
[6] A. Kumar, H. A. Biebuyck, N. L. Abbott, G. M. Whitesides, J. Am. Chem. Soc. 1992, 114, 9188–9189.
[7] G. P. Lopez, H. A. Biebuyck, C. D. Frisbie, G. M. Whitesides, Science 1993, 260, 647–649.
[8] C. S. Dulcey, J. H. Georger, V. Krauthamer, D. A. Stenger, T. L. Fare, J. M. Calvert, Science 1991, 252, 551–554.
[9] J. M. Calvert, J. H. Georger, M. C. Peckerar, P. E. Pehrsson, J. M. Schnur, P. E. Schoen, Thin Solid Films 1992, 211, 359–63.
[10] G. P. Lopez, H. A. Biebuyck, R. Harter, A. Kumar, G. M. Whitesides, J. Am. Chem. Soc. 1993, 115, 10774–10781; J. Huang, D. A. Dahlgren, J. I. Hemminger, Langmuir 1994.
[11] R. G. Nuzzo, D. L. Allara, J. Am. Chem. Soc. 1983, 105, 4481–4483.
[12] C. E. D. Chidsey, M. D. Porter, D. L. Allara, J. Electrochem. Soc. 1986, 133, 130.
[13] G. M. Whitesides, C. B. Gorman, in Handbook of Surface Imaging and Visualization (Ed: A. T. Hubbard), CRC Press, Boca Raton, in press.
[14] C. D. Bain, G. M. Whitesides, Adv. Mater. 1989, 1, 110.
[15] G. M. Whitesides, P. E. Laibinis, Langmuir 1990, 6, 87–96.
[16] A. Ulman, An Introduction to Ultrathin Organic Films, Academic Press, New York 1991.
[17] G. S. Ferguson, M. V. Baker, H. A. Biebuyck, M. K. Chaudhury, G. M. Whitesides, unpublished.
[18] L. Strong, G. M. Whitesides, Langmuir 1989, 4, 546–588.
[19] C. E. D. Chidsey, D. N. Loiacono, Langmuir 1990, 6, 682–691.
[20] M. K. Chaudhury, G. M. Whitesides, Langmuir 1991, 7, 1013–1025.
[21] E. F. Hare, W. A. Zisman, J. Phys. Chem. 1955, 59, 335–340.
[22] S. R. Holmes-Farley, R. H. Reamey, T. J. McCarthy, J. Deutch, G. M. Whitesides, Langmuir 1985, 1, 725–740.
[23] P.-G. deGennes, Rev. Mod. Phys. 1985, 57, 827–863.
[24] C. D. Bain, G. M. Whitesides, Langmuir 1989, 5, 1370.
[25] H. A. Biebuyck, G. M. Whitesides, unpublished.
[26] R. J. Puddephatt, The Chemistry of Gold, Elsevier, Amsterdam, 1978.
[27] See: K. Baba, Jpn. Patent 74 47, 225, 1974. The proportions of the components for the Ni etch were optimized for use in μCP: H. K. Kim, G. M. Whitesides, unpublished.
[28] G. P. Lopez, H. A. Biebuyck, G. M. Whitesides, Langmuir 1993, 9, 1513–1516.
[29] D. P. Clemens, Electrochem. Soc. Extend. Abstr. 1973, 73-2, 407.
[30] N. L. Abbott, D. R. Robson, G. M. Whitesides, Langmuir, in press.
[31] R. Singhvi, A. Kumar, G. P. Lopez, G. P. Stephanopoulos, D. I. C. Wang, G. M. Whitesides, D. E. Ingber, Science 1994, 264, 696–698.