

oxygen and argon in the appropriate percentage before injection into the cuvette. For mechanical measurements, the samples were molded by Teflon vessels, had a thickness of 0.8–1 mm, were transparent, homogeneous and flexible (leaving aside the sample with $x=0$, which exhibited noticeable brittleness).

Mechanical measurements were performed using a dynamic mechanical thermal analyzer (DMTA) by Polymer Laboratories. The mechanical characteristics (internal friction and dynamic modulus) were carried out in the temperature range 120–460 K and at variable frequency (0.3–30 Hz), in a controlled atmosphere of nitrogen to avoid water contamination. The data were collected by using a running temperature with a rate of 2 K/min. Photophysical measurements were carried out using an Edinburgh FL900 single-photon counting spectrometer and a Perkin Elmer LS-5B spectrofluorimeter equipped with a red-sensitive Hamamatsu R 928 photomultiplier.

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- [1] *Chemical, Biochemical, and Environmental Sensors* (Eds: R. A. Lieberman, M. T. Wlodarczyk), The International Society for Optical Engineering, Bellingham, WA, 1989, Vol. 1172.
- [2] S. M. Angel, *Spectroscopy* 1989, 2, 37.
- [3] R. Dorn, D. Baums, P. Kersten, R. Regener, *Adv. Mater.* 1992, 4, 464.
- [4] E. P. Diamandis, T. K. Christopoulos, *Anal. Chem.* 1990, 62, 1149 A.
- [5] R. A. Bissel, P. de Silva, *Chem. Soc. Rev.* 1992, 21, 187.
- [6] a) A. W. Czarnik in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Eds: H. J. Schneider, H. Durr) VCH, Weinheim 1991, p. 109. b) *Fluorescent Chemosensors for Ion and Molecule Recognition* (Ed: A. W. Czarnik), ACS Symp. Ser. 538, American Chemical Society, Washington, DC 1992.
- [7] a) A. Del Bianco, F. Baldini, M. Bacci, I. Klimant, and O. S. Wolfbeis, *Sens. Actuators* 1993, B11, 347. b) C. Preininger, I. Klimant, O. S. Wolfbeis, *Anal. Chem.* 1994, 66, 1841.
- [8] J. R. Bacon, J. N. Demas, *Anal. Chem.* 1987, 59, 2780.
- [9] J. N. Demas, B. A. De Graff, *Anal. Chem.* 1991, 63, 829A.
- [10] E. R. Carraway, J. N. Demas, B. A. DeGraff, J. R. Bacon, *Anal. Chem.* 1991, 63, 337.
- [11] T. J. Meyer, *Pure Appl. Chem.* 1986, 58, 1193.
- [12] A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belsler, A. von Zelewsky, *Coord. Chem. Rev.* 1988, 84, 85.
- [13] *Comprehensive Polymer Science, Vol. 2, Polymer Properties*, Pergamon Press, 1989, p. 533.
- [14] G. D. Hager, G. A. Crosby, *J. Am. Chem. Soc.* 1975, 97, 7031.
- [15] S. R. Allsopp, A. Cox, T. J. Kemp, W. J. Reed, V. Carasiti, O. Traverso, *J. Chem. Soc. Faraday Trans. 1* 1979, 75, 353.
- [16] M. McGuire, G. McLendon, *J. Phys. Chem.* 1986, 90, 2549.
- [17] J. Wheeler, J. K. Thomas, *J. Phys. Chem.* 1982, 86, 4540.
- [18] P. Chen, E. Danielson, T. J. Meyer, *J. Phys. Chem.* 1988, 92, 3708.
- [19] A. Masschelein, A. Kirsch-De Mesmaeker, C. J. Willsher, F. Wilkinson, *J. Chem. Soc. Faraday Trans. 1* 1992, 87, 259.
- [20] S. Campagna, A. Bartolotta, G. Di Marco, *Chem. Phys. Lett.* 1993, 206, 30.

Reduction in the Size of Features of Patterned SAMs Generated by Microcontact Printing with Mechanical Compression of the Stamp**

By Younan Xia and George M. Whitesides*

Microcontact printing (μ CP) uses a relief pattern on the surface of an elastomeric stamp (usually made from polydimethylsiloxane, PDMS) to form patterns in the plane of self-assembled monolayers (SAMs).^[1–6] The required relief pattern is most easily made by casting PDMS (in the form of a prepolymer) onto a complementary relief pattern in a master (usually a thin film of polymethylmethacrylate, PMMA, supported on a silicon wafer). This relief pattern is fabricated, in turn, using photolithography.

The difficulty in forming appropriate masters increases rapidly as the feature size decreases from micrometers to less than 0.5 micrometers, because photolithography becomes challenging in this range of feature sizes.^[7–9] We are developing procedures that extend the capabilities of μ CP into the submicrometer region, and that do not require high resolution photolithography.^[9, 10]

Here we wish to describe a new method for forming patterns with submicrometer-sized features using μ CP, in which the relief pattern in the PDMS stamp is first formed with relatively large features (2–10 μ m) and then compressed mechanically by the application of lateral force. The resulting stamp can be used *while under compression* in μ CP, and is capable of forming patterns with certain of its features reduced by a factor of almost ten relative to the original, uncompressed pattern, while retaining the regularity in the original pattern.

This methodology illustrates a new strategy—mechanical compression of an elastomeric solid—for producing small feature sizes. The smallest features we have produced to date using this technique are rectangular “slots” in a supported gold film with lateral dimension of \sim 200 nm (formed from a stamp with feature sizes of \sim 2.5 μ m when not compressed). This procedure for preparing submicrometer-sized features is general, and does not require advanced photolithographic tools. It also suggests a new type of lithography, in which dimensions in selected areas of the pattern can be made larger or smaller by mechanical distortion of the template that produces the pattern.

Figure 1 outlines the procedure employed to form and use the compressed stamp in μ CP.^[3, 5] Figures 2,3 show test patterns produced using this technique. Both one- and two-dimensional compressions were possible. When used in com-

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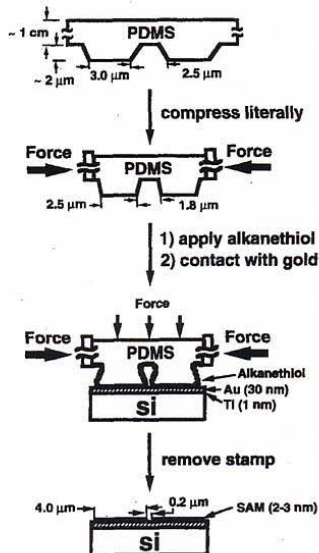


Fig. 1. Schematic outline of the procedure for microcontact printing with a mechanically compressed stamp. Only one-dimensional compression is shown here.

pressed form, a pair (or two pairs) of small plates were used to apply lateral force(s) to the stamp.

Several characteristics of the patterns in Figures 2,3 fabricated without and with mechanical compression, are relevant to understanding the micromechanics of compression and printing using this procedure. In particular, it is possible to achieve large reductions in size of some of the features of the pattern but not others: areas in which the SAM is printed—that is, areas corresponding to the raised areas of the stamp—slightly increase their lateral size on compression, while areas in which the SAM is not printed—those corresponding to the recessed areas of the stamp—decrease (sometimes substantially) in size.

The SEM photographs (Fig. 2a) of a cross section of the stamp without and with mechanical compression suggest the kind of deformations that would result in the observed characteristics of the printed patterns. It appears that under mechanical compression, the dimensions of both the recessed and the raised parts of the stamp are reduced. We speculate that when the stamp is in contact with the gold surface, the dimensions of the raised areas of the stamp again increase as a result of the vertical compression caused by pressing the stamp against the gold substrate (see Fig. 1). The dimension of the areas of the pattern in which the SAM is printed—those corresponding to the raised part of the stamp—increase slightly in lateral dimension, while the areas in which the SAM is not printed (that is, the areas of bare gold or, after etching, of exposed Si/SiO₂) decrease in lateral dimensions in this compressive μCP process.

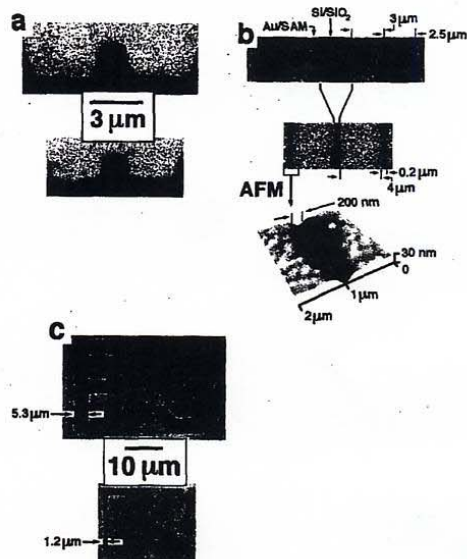


Fig. 2. a) Scanning electron micrographs of the cross-section of the stamp without and with mechanical compression obtained by stamping with this cross section on gold surface. b) Scanning electron micrographs of test patterns fabricated by microcontact printing without and with one-dimensional mechanical compression. This one-dimensional compression left the width of the gold lines approximately unchanged, but reduced the spacing between these lines from ~2.5 μm to ~0.2 μm. c) Scanning electron micrographs of patterns of alphanumeric characters generated without and with two-dimensional mechanical compression. In each, a SAM of hexadecanethiol was patterned on a gold film and the unprotected gold was then removed by etching with CN^o/O₂. The bright regions are gold covered by SAM and the dark regions are Si/SiO₂ in regions where the underivatized gold has been removed by etching.

The reproducibility of the features is currently limited by the mechanics of the system used to compress the stamp laterally using pressure applied to the plates that sandwich it; this compression is accomplished using screws, and is reasonably reproducible. The extent of compression of the features of the stamp while it is in contact with the surface is determined by vertical pressure, and is not currently well controlled, since the vertical pressure is controlled only by hand. We can obtain satisfactory reproducibility for size reductions in the range from 2 to 0.5 μm—that is, in the range that can be achieved by lateral compression; the smaller features that are achieved by vertical compression of the stamp while it is in contact with the surface would require more complex mechanical systems. A detailed model of the forces and deformations on the stamp during compression should be possible, but it is beyond the scope of the current study.

In summary, this work demonstrates a new technique based on μCP that generates features with submicrometer dimensions. This technique is based on reduction in certain dimensions of the stamp by mechanical compression. The largest reductions observed—from ~2.5 μm to ~0.2 μm—

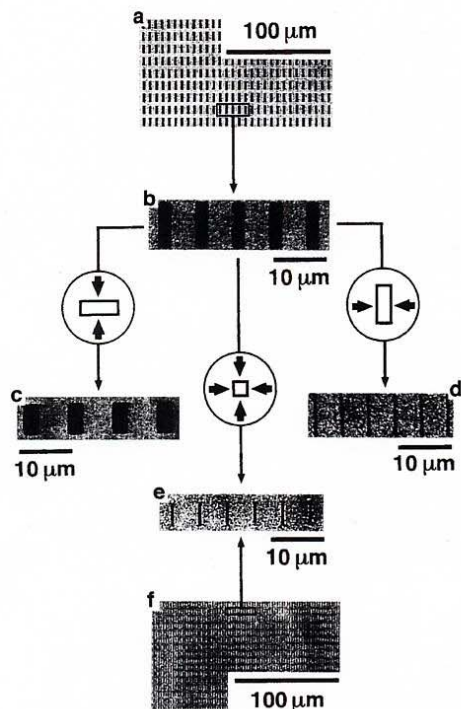


Fig. 3. Scanning electron micrographs of another test pattern fabricated by microcontact printing without and with mechanical compression. a,b) No compression; c) compressed in the vertical direction; d) compressed in the horizontal direction; e) compressed in both horizontal and vertical directions; f) lower magnification of (e) illustrates the uniformity of the microstructures fabricated using this combination of μ CP and mechanical compression. The light regions are gold covered with SAM and the dark are Si/SiO_2 . Note that the dimensions of the gold "slots" were reduced from $\sim 9 \mu\text{m} \times 2 \mu\text{m}$ ($\sim 18 \mu\text{m}^2$) to $\sim 4 \mu\text{m} \times 0.4 \mu\text{m}$ ($\sim 1.6 \mu\text{m}^2$) by two-dimensional compression; these dimensions demonstrate a decrease in area of > 10 .

are sufficient to provide access to features with sizes whose fabrication would normally require advanced photolithographic techniques. This adaptation of μ CP to the preparation of features with submicrometer-sized dimensions is not competitive with photolithography for complex patterns with rigid requirements for dimensional stability. It offers, however, a very convenient method for producing certain types of simple patterns. It also suggests a new strategy for the generation of patterns with small lateral dimensions, in which these dimensions are achieved by mechanical compression of an elastomeric template, rather than by fabrication of a rigid mask with small features.

Experimental

Fabrication of stamps and microcontact printing were conducted following our previously reported procedures^[4,5,9]. The PDMS used was a soft silicone

elastomer (PELD 15, Hüls). A 2 mM solution of hexadecanethiol (purified by chromatography through silica gel) in ethanol was used as "ink" in the printing. The lateral force was applied using a pair of small plates. The distance between the two plates, and hence the magnitude of the compressive shrinking, was adjusted by screws. Gold not protected by the SAM was removed by etching using a solution containing KOH (1 M) and KCN (0.01 M) with vigorous stirring with air (oxygen) as the oxidant. The time required to etch features larger than $0.5 \mu\text{m}$ was about 10 minutes (for a gold film 300 \AA thick) and that for the features smaller than $0.5 \mu\text{m}$ was about 15 minutes. SEM was done on a JEOL JSM-6400 scanning microscope. AFM was done on a Topometrix TMX 2010 scanning probe microscope (Mountain View, CA); the images were obtained in the lateral force mode.

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- [1] G. M. Whitesides, P. E. Laibinis, *Langmuir* **1990**, *6*, 87.
- [2] L. H. Dubois, R. G. Nuzzo, *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
- [3] A. Kumar, H. Biebuyck, N. L. Abbott, G. M. Whitesides, *J. Am. Chem. Soc.* **1992**, *114*, 9188.
- [4] A. Kumar, G. M. Whitesides, *Appl. Phys. Lett.* **1993**, *63*, 2002.
- [5] A. Kumar, H. Biebuyck, G. M. Whitesides, *Langmuir* **1994**, *10*, 1498.
- [6] J. L. Wilbur, A. Kumar, E. Kim, G. M. Whitesides, *Adv. Mater.* **1994**, *6*, 600.
- [7] W. M. Moreau, *Semiconductor Lithography: Principles and Materials*; Plenum, New York **1988**.
- [8] P. N. Dunn, *Solid State Technology* **1994**, June, 49.
- [9] Y. Xia, G. M. Whitesides, *J. Am. Chem. Soc.*, in press.
- [10] Y. Xia, G. M. Whitesides, unpublished results.

Doping of Polyaniline via Pseudoprotonation by an Ionic Salt**

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Polyaniline (PAn) can be converted into a conducting form by either protonation of the imine site or oxidative doping at the amine site. The protic acid dopants used are inorganic acids (such as HCl, H_2SO_4 , HBF_4 , etc.)^[1-3] or organic acids (such as toluene sulfonic acid);^[4] while the oxidative dopants are $(\text{NO}^+)(\text{PF}_6^-)$, FeCl_3 , H_2O_2 , SnCl_4 etc.^[5]

This paper reports a new class of dopant, ionic salts, such as LiClO_4 , LiBF_4 , $\text{Zn}(\text{ClO}_4)_2$, etc. for PAn (emeraldine base). An ionic-salt-doped PAn is obtained by mixing PAn and ionic salt solutions in 1-methyl-2-pyrrolidone (NMP) and then casting the mixed solution into film under dynamic vacuum pumping at 50°C for 48 hours. The resulting film usually contains about 15% by weight of residual NMP and, with LiBF_4 as dopant, has a conductivity of 10^{-2} S/cm . The PAn therein is doped via pseudoprotonation of the imine nitrogens by the metal cations.

The UV-vis spectra of films of LiBF_4 -doped PAn with the mole ratios of LiBF_4 to the approximate number of repeat units of PAn ($-\text{C}_6\text{H}_4\text{NH}-$), 1/9.7, 1/7.3, 1/4.8 and 1/2.9, are shown in Figure 1. It can be observed that the PAn is doped by the ionic salt as reflected in the presence of the absorption

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