

# ADVANCED MATERIALS

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### Solvent-Assisted Microcontact Molding: A Convenient Method for Fabricating Three-Dimensional Structures on Surfaces of Polymers\*\*

By Enoch Kim, Younan Xia, Xiao-Mei Zhao, and  
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"Soft lithography" is the name we use for a group of non-photolithographic methods for forming high-quality micro- and nanostructures. These strategies require remarkably little in capital investment. They are becoming attractive as routes to micro- and nanostructures that cannot be made (or cannot be made as easily) by photolithography. Micromachining,<sup>[1]</sup> microcontact printing ( $\mu$ CP),<sup>[2]</sup> embossing (or imprinting),<sup>[3]</sup> micromolding in capillaries (MIMIC),<sup>[4]</sup> microtransfer molding ( $\mu$ TM),<sup>[5]</sup> and replica molding<sup>[6]</sup> are a few examples of such methods that have been used to fabricate (in some cases, to manufacture) structures on the sub-micrometer scale. More recently, embossing<sup>[7]</sup> and replica molding<sup>[8]</sup> have been extended as procedures to form patterned polymeric nanostructures as small as 25 nm in lateral dimension. These nanometer-sized structures are beyond the capability of conventional photolithography; currently they are fabricated using advanced lithographic techniques<sup>[9]</sup>—for example, deep UV photolithography, X-ray lithography, electron-beam writing, and scanning probe lithography—that are still in development.

Here we report a new method for fabricating structures and modifying surface morphologies of polymers, using a method we refer to as "solvent-assisted microcontact molding" (SAMIM, see Fig. 1). The operational principle of this technique shares characteristics with both embossing and

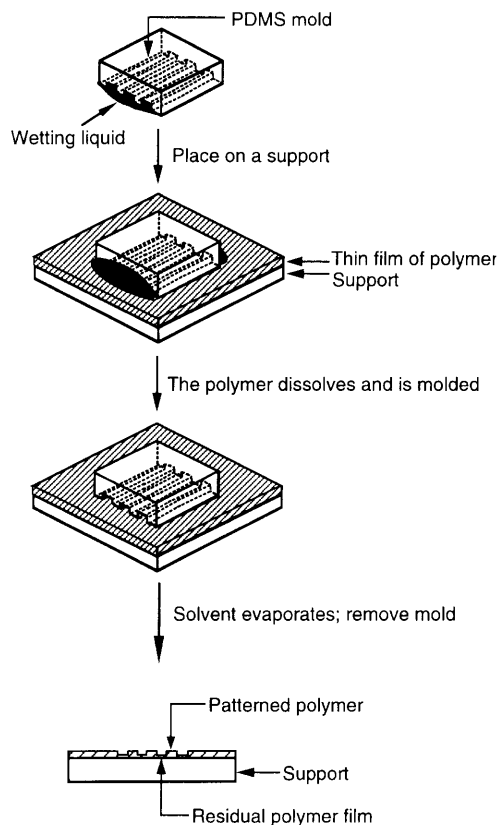


Fig. 1. Schematic procedure for SAMIM.

replica molding. SAMIM begins with a type of elastomeric mold (usually made from poly(dimethylsiloxane), PDMS) that has been used in much of our previous work.<sup>[2,4-6,8]</sup> In SAMIM, a liquid that is a good solvent for the polymeric substrate is applied to the surface of the PDMS mold using Q-tips before it is brought into contact with the polymer surface. As the mold is placed on the surface of the polymer, the solvent dissolves (or swells) a thin layer of the polymer, and the resulting (probably gel-like) fluid comprising polymer and solvent conforms to the surface topology of the mold. The polymer solidifies as the solvent dissipates,<sup>[10]</sup> while the mold maintains conformal contact with the substrate. The overall morphology of the patterned polymer represents a negative replica of the relief patterns on the PDMS mold.

The key element of this procedure is wetting of the PDMS mold by a solvent and conformal contact between the elastomer mold and the substrate (Fig. 1). The liquid solvent fills the recessed regions on the surface of the PDMS mold in order to minimize the area of the liquid/vapor interface and maximize that of the solid/liquid interface. For an illustration, we have concentrated on a commercially available photoresist (Microposit 1813, Shipley, a positive-tone novolak resin), but we have applied this procedure (with different solvents) to many other polymers, including polystyrene (PS), poly(methylmethacrylate) (PMMA), cellulose acetate (CA), and poly(acrylonitrile-butadiene-styrene) (ABS). A thin film of photoresist (PR)

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was prepared on a Si wafer by spin-coating at 5500 rpm for 30 s, and then baked for 3.5 min at 105 °C; the resulting film was ~1.2 μm thick. PDMS (Sylgard 184, Dow Corning) molds having relief patterns (~1.2 μm thick) on their surfaces were fabricated according to published procedures.<sup>[2-4,6]</sup> The PDMS mold was wetted with ethanol, which filled the recessed regions on the PDMS surface.<sup>[11]</sup> When the mold was placed on the film of PR, the elastomer made conformal contact with the PR, forming micrometer-scale channels (or cavities) between them. Because PDMS is compliant, the elastomer adhered spontaneously to the surface and squeezed out the excess ethanol from those regions of the mold that were in contact with the PR. The remaining solvent dissolved (or swelled) the PR polymer, and a pattern complementary to that on the mold was formed in the resulting polymeric fluid by a process similar to embossing (or imprinting). The mold was allowed to remain on the surface for ~5 min at room temperature until most of the solvent had dissipated. The stamp was peeled away: a patterned microstructure of PR was left behind on the surface of the substrate. We have used the same PDMS mold for several cycles (> 10) of this process without observing a decrease in performance.

Choosing the appropriate solvent for a polymeric material determines the effectiveness and success of SAMIM. The solvent should dissolve or swell the surface of the polymer; it should not, however, swell the PDMS stamp and thereby destroy the conformal contact between the polymer and the stamp. Many non-polar solvents (for example, hexane, toluene, and methylene chloride) cannot be used in SAMIM because they swell the cross-linked PDMS.<sup>[12]</sup> In general, the solvent should have a relatively high vapor pressure and a moderately high surface tension (for example, methanol, ethanol, and acetone) to ensure rapid evaporation of the excess solvent and minimal swelling of the PDMS mold. Dyes and inorganic salts can also be added into the solvents, and subsequently be incorporated into the formed polymeric microstructures. Solvents with low vapor pressures (for example, ethylene glycol and dimethyl sulfoxide) are not well suited for SAMIM. Solvents with high surface tensions (for example, water) do not work at all, because they only partially wet the PDMS surface.<sup>[13]</sup>

Figure 2 shows scanning electron micrographs (SEMs) of representative structures that were formed by SAMIM: all structures were fabricated from spin-coated films of PR with ethanol as the solvent. Figure 2A and C represent positive and negative structures of the same pattern: each was fabricated using the appropriate stamp containing a complementary pattern. Figure 2B shows an oblique view of the fractured edge of the pattern in Figure 2A; it shows well defined corners and the presence of a thin film on those regions where the PDMS mold contacted the surface of PR. Figure 2D shows a more complex pattern taken from a microelectronics circuit; it illustrates that the three-dimensional information on the surface of the PDMS mold (Fig. 2E) can be faithfully transferred to the polymer layer in a single step.

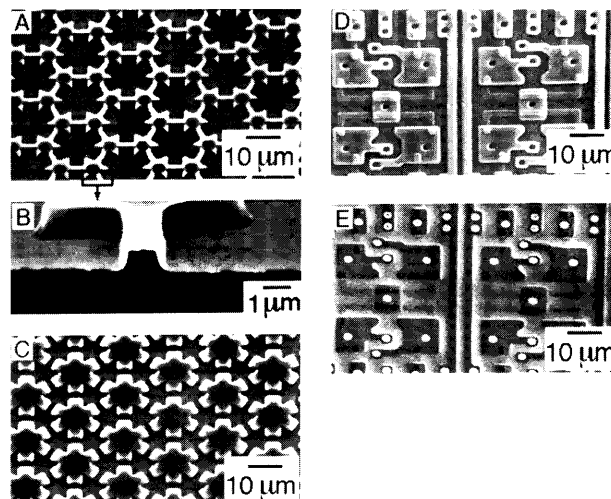


Fig. 2. A–D) SEMs of test structures formed in thin films of novolak photoresist using SAMIM, with ethanol as the solvent. E) SEM of the PDMS mold used to generate the sample shown in (D).

A common characteristic of patterned microstructures generated using SAMIM is that the resulting structures are adjoined by a thin film of polymer. For example, star-shaped structures in Figure 2C are connected to one another by a thin film of PR that is, usually, thinner than 100 nm. We have been able to remove these thin films using reactive ion etching (RIE). Figure 3A shows the

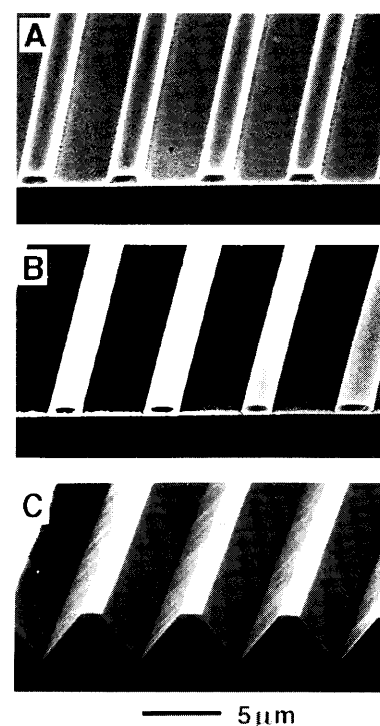


Fig. 3. A) SEM of a test pattern of PR formed using SAMIM on a silicon wafer covered by thermally formed SiO<sub>2</sub> (0.4 μm thick). B) SEM of this sample after RIE for ~5 min. C) The same sample as in (B) after further etching in aqueous HF for ~2 min, and in an aqueous KOH/2-propanol solution for ~10 min at 65 °C. The PR structures dissolved or lifted off in the KOH/2-propanol solution at this temperature. The SiO<sub>2</sub> mask has been removed after Si etching.

cross-sectional SEM of a test pattern of PR that was formed on Si/SiO<sub>2</sub> using SAMIM; Figure 3B shows the cross-sectional SEM of this sample after RIE in an oxygen plasma (180 mtorr) for ~5 min. Figure 3C shows the cross-sectional SEM of the same sample, after it had been etched in HF (~1%) for ~2 min, followed by anisotropic etching in an aqueous KOH/2-propanol solution at 65 °C for ~10 min. These SEMs clearly demonstrate that the thin films can be removed by homogeneous thinning with RIE.

Figure 4 shows atomic force microscopy (AFM) images of the smallest features that have been generated in a thin film of PR (Microposit 1805, Shipley; the thickness of the film was ~0.4 μm) using SAMIM: parallel lines that are ~60 nm in width and ~50 nm in height.

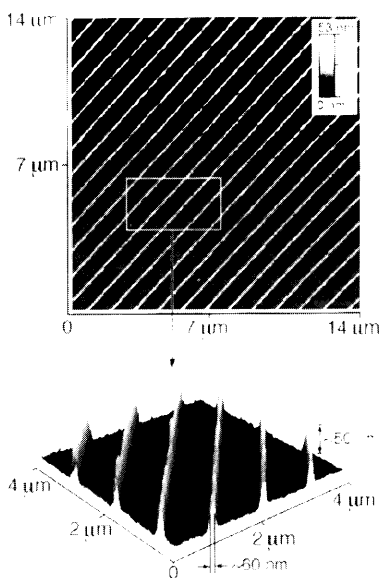


Fig. 4. AFM images of the smallest structures (in a film of PR) that have been fabricated using SAMIM.

SAMIM is an "apply and wick" process: it involves applying a solvent on the PDMS mold and wicking the solvent into the channels (or cavities) formed between the mold and the substrate. SAMIM can also be carried out using pretreatment of the surface of the polymer. If the polymeric substrate (for example, a PR film) is exposed to a solvent or the vapor of a solvent, the substrate becomes "softened". When the mold is brought into contact with the surface of this pretreated substrate, the surface morphology of the polymer changes to a relief pattern complementary to that on the surface of the mold. SAMIM can, therefore, be applied to pattern a large number of polymers whose surfaces can be modified using appropriate solvents. Figure 5A shows the SEM of a patterned surface of ABS (0.85 mm thick, Goodfellow). The surface morphology was generated via SAMIM using acetone as the solvent. The patterned features, having three different levels of height (0.8, 1.3, and 1.4 μm, respectively), show smooth surfaces and good structural integrity. Figure 5B shows a patterned

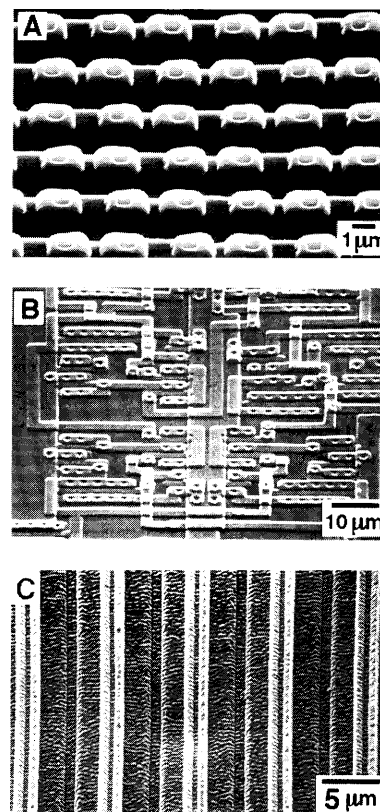


Fig. 5. SEMs of polymeric structures formed using SAMIM (with acetone as the solvent) in thin films of A) ABS, B) polystyrene, and C) cellulose acetate.

surface formed on a PS film (2.0 mm thick, Goodfellow) using SAMIM with acetone as the solvent. The features are well defined and clearly resolved. Figure 5C shows a patterned surface of CA (0.5 mm thick, Goodfellow) produced using SAMIM with acetone as the solvent. The overall morphology of the pattern shows good replication of the features on the surface of the PDMS mold, except that the surface of the patterned polymer is highly textured. Such patterned and textured surfaces may be useful in processes where a high surface/volume ratio is important, such as in adhesion and catalysis.

In summary, SAMIM is a convenient technique for single-step patterning. It can generate quasi-three-dimensional structures or morphologies on the surface of a polymer using a solvent that can soften the polymeric substrate without affecting the PDMS mold. SAMIM has important differences from other existing techniques. 1) It does not suffer from the disadvantage of slow rates of capillary filling that limits MIMIC to relatively small areas. We have used SAMIM to pattern areas of several square centimeters, and extension to even larger areas should be possible. 2) Application of SAMIM is not limited to fabrication of hydraulically connected structures; isolated structures can also be fabricated. 3) SAMIM can be used with a wide range of polymers or prepolymers: the only requirement seems to be for a solvent that dissolves the polymer of the

substrate and also wets the surface of the elastomeric mold. 4) It uses an elastomer as the component in the mold. PDMS provides a surface that is low in interfacial free energy and inert in reactivity: polymers being molded do not adhere to or react with the surface of PDMS. The elastic characteristic of PDMS also allows it to be released easily, even from complex and fragile structures. 5) The basis of SAMIM is spontaneous formation of channels or cavities when an elastomer containing three-dimensional relief structures comes in intimate contact with a substrate; it does not require external pressure in maintaining conformal contact. 6) The surface of the polymer is "softened" using a solvent (or vapor) instead of temperature; the process is rapid and does not require specialized equipment or systems for aligning mold and substrate.

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- [11] A homogeneous thin layer of solvent could be easily applied to the surface of PDMS mold using Q-tips.
- [12] See, for example, a) L. C. DeBolt, J. E. Mark, *Macromolecules* **1987**, 20, 2369. b) L. E. Pierre, H. A. Dewhurst, A. M. Bueche, *J. Polym. Sci.* **1959**, 36, 105.
- [13] We can modify the surface properties of the PDMS mold by plasma-treatment or other chemical processes to make its surface wettable by a polar solvent.

## Effect of Surface Fractality on the Permeability of Transparent Gas Barrier Coatings\*\*

By Gema García-Ayuso, Roberto Salvarezza, José M. Martínez-Duart, Olga Sánchez, and Luis Vázquez\*

In the last few decades inorganic barrier coatings on polymers have been used as protective coatings in several industrial applications, in particular in the flexible packaging industry. In this case the coating deposited on a polymer film should behave as a good barrier against moisture, oxygen, and exposure to light in order to avoid the degradation of the packed product (usually food). As the preservation requirements become increasingly more stringent, the development of coatings with better barrier properties has attracted the interest of groups in both research and industry. From the scientific point of view, different aspects of the barrier properties have been studied. In particular the diffusion of gases, such as oxygen and water vapor, through porous barriers has been investigated.<sup>[1,2]</sup>

Diffusion of gases through a porous solid is a complex process that requires, for a complete understanding, a detailed description at the micro- and nanometer level of the solid structure.<sup>[1]</sup> There are several mechanisms that explain the diffusion of gases and liquids through porous solids. In the case of solids with pore size ( $d$ ) in the 3–30 nm range so-called Knudsen diffusion is one of them.<sup>[2]</sup> This mechanism, which involves diffusion in the gas phase, allows different diffusing species to be separated, as the permeability ( $P$ ) is inversely proportional to the square root of the molecular weight of these species. The degree of the pore network irregularity is described in terms of a tortuosity factor,  $\tau_g$ , which is reflected in the Knudsen transport as  $P \propto 1/\tau_g$ .<sup>[2]</sup>

In addition to the Knudsen transport, there could be a flow of adsorbed gaseous species on the pore surface, which in a first approximation occurs parallel to and independently of the gas flow.<sup>[2]</sup> In many cases the magnitude of this mechanism of transport can be 2–3 times that of the Knudsen transport contribution.<sup>[3,4]</sup> This surface diffusion contribution should be affected by the degree of internal

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