

# Micromolding in Capillaries: Applications in Materials Science

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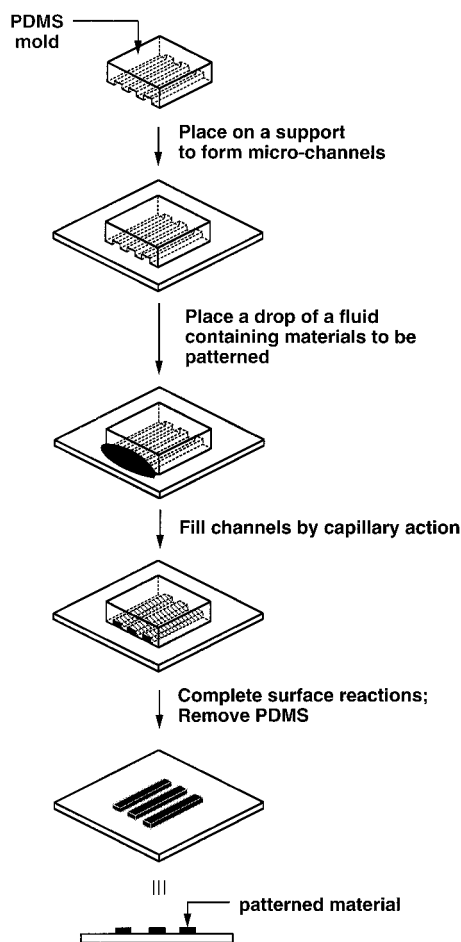
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**Abstract:** Procedures based on micromolding in capillaries (MIMIC) were used to pattern a surface of a substrate with micrometer- and submicrometer-scale structures. An elastomeric stamp made of poly(dimethylsiloxane) and having relief features in its surface was placed on a substrate; contact between the elastomeric stamp and the substrate formed a network of interconnected channels. A fluid—a precursor to a polymer, a solution, or a suspension of the material to be patterned—filled these channels by capillary action. After the material in the fluid had cross-linked, crystallized, cured, adhered, or deposited onto the surface of the substrate, the elastomeric component was removed. The microstructures remained on the surface in the pattern complementary to that present in the mold. MIMIC was used to fabricate microstructures of organic polymers, inorganic and organic salts, ceramics, metals, and crystalline microparticles.

## Introduction

This paper describes a versatile process for forming microstructures of polymers, ceramics, and metals; we refer to this procedure as MIMIC (micromolding in capillaries).<sup>1</sup> It is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact, at least one of which has a recessed relief structure, by a fluid. The fluid may be a liquid prepolymer, a solution or suspension of the materials to be formed, or precursors of these materials. This work is part of a project whose purpose is to develop new methods<sup>2–11</sup> of fabricating micrometer- and submicrometer-scale structures of organic, inorganic, and biological materials, to complement those that can be made in silicon by micromachining. We are using these structures to study mesoscale phenomena involving light and biological cells, and believe that they will be useful in other areas: MEMS, fracture mechanics, microanalytical and microchemical devices, sensors, and others.

The central problem in MIMIC is to form appropriate networks of micrometer-scale channels having surface properties that promote capillary filling. In order to expose the microstructures, after forming, we require a methodology for as-



**Figure 1.** Schematic of the procedure used in MIMIC.

sembling and disassembling a network of capillaries non-destructively. We have developed a procedure in which the capillary channels are formed between a support and an elastomeric mold made of poly(dimethylsiloxane) (PDMS) that contains recessed patterns (Figure 1). The compliant nature of PDMS allows conformal contact between the mold and the support, while its low reactivity allows easy separation from the patterned microstructures on the support. After an organic or inorganic material in the fluid has crystallized, cured/

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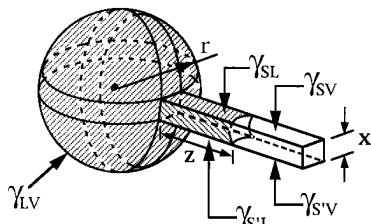
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**Figure 2.** A diagram representing a model for micromolding in capillaries. A fluid is assumed to move from a spherical drop (radius  $r$ ) into a square channel (width  $x$ ) with three surfaces identical (the PDMS) and one different (the support). The terms  $\gamma_{sv}$ ,  $\gamma_{sl}$ , and  $\gamma_{lv}$  correspond to interfacial free energies of solid–vapor, solid–liquid, and liquid–vapor interfaces;  $\theta$  and  $\theta'$  are the contact angles of the liquid prepolymer on the surface of PDMS and the support.

polymerized, adsorbed/adhered, or reacted with the surface of a substrate, the elastomeric component is removed, and a pattern of the material remains on the substrate. The pattern in the master is thus replicated in a structure supported on the surface of the substrate.

Once formed, the microstructures can be freed from the support to obtain free-standing structures. One procedure involves physically or chemically treating the support, using conditions that do not affect the patterned structures, to allow the patterned structures to separate from the surface. For example, glass and  $\text{SiO}_2$  substrates can be dissolved in HF, polymer films in appropriate solvents, and inorganic salt plates in water; silicon substrates can be oxidized in KOH; paraffin films can be melted. Another procedure involves performing MIMIC in a network of channels that has formed between two elastomeric masters, instead of a solid support and an elastomeric master. For example, after a precursor of a polymer fills and cross-links in the channels, the patterned polymeric structure can be removed (using Scotch tape or tweezers) from both elastomeric masters to generate free-standing structures that contain two layers with independent structures.

MIMIC is a process whose characteristics are determined by interfacial free energies; we analyze it quantitatively below, but an initial qualitative summary is useful. In most applications of MIMIC, three surfaces (the PDMS) of the channels have the same interfacial free energy and one (the support) a different free energy (Figure 2). Since the interfacial free energy of the mold ( $\gamma_{sv}(\text{PDMS}) = 21.6 \text{ dyn/cm}$ )<sup>12</sup> is much lower, in most cases, than that of the surface of the support ( $\gamma_{sv}(\text{Si/SiO}_2) > \sim 72 \text{ dyn/cm}$ ),<sup>13</sup> the material being molded spreads across and preferentially adheres to the support, rather than to the PDMS. Liquids (e.g., organic solvents and prepolymers) also preferentially wet the surface of the support. In general, the dominant contribution to the interfacial free energy of wetting the capillary is that from the wetting of the support. When all four surfaces of the rectangular capillary are PDMS (such as when using two face-to-face PDMS molds), the rate of capillary filling is decreased because most liquids wet PDMS only partially; this wettability may still be sufficient to fill the capillary with liquids.

A fluid with low enough surface tension to wet partially either the surface of PDMS or the support can fill the channels in MIMIC. Because filling occurs as a direct result of capillary forces, fluids having low surface tension (for example, organic solvents such as methanol and ethanol) are most useful in MIMIC; even liquids with high surface tension (e.g., water) can, however, fill the channels if the surface tension of the liquid is lowered by adding surfactants or organic solvents. Fluids having low viscosity ( $< 300 \text{ cP}$ ) are most useful in MIMIC, because

the rate of filling the capillaries is inversely proportional to viscosity. Since viscosities of most solvents are low ( $\sim 1 \text{ cP}$ ), they can act as “carriers” in MIMIC, where the solvent transports materials through the channels and onto the specific regions on the support. The viscosities of many polymeric precursors and of solutions containing materials to be patterned are low enough to be used in MIMIC.

In this paper, we describe the use of MIMIC to fabricate microstructures of organic and inorganic materials with dimensions from  $< 1 \mu\text{m}$  to  $> 100 \mu\text{m}$ . A range of other procedures that fabricate microstructures by capillary or pressure filling of molds have been described. Injection and/or compression molding<sup>14</sup> can produce structures with millimeter dimensions, but fabricating intricate structures having micrometer-scale dimension is not straightforward. Pressurized filling of the recessed regions of a photolithographically fabricated master has produced ceramic microstructures.<sup>15,16</sup> Procedures based on capillary filling are common in industrial processes such as fabrication of compact disks<sup>17</sup> and encapsulation of electronic devices<sup>18</sup> where accurate microfeatures are important. Micromolding based on capillarity has been used to replicate nanometer-scale features in semiconductors,<sup>19</sup> where relief patterns in semiconductor were filled with a monomer and cross-linked to fabricate “negative” structures. The characteristics of MIMIC that differentiate it from these prior procedures are the use of an elastomeric stamp as a key component of the mold, its ability to pattern a very wide range of types of materials, and the ease with which it can be used. Here we demonstrate that MIMIC can be used to fabricate patterned microstructures of organic polymers, inorganic and organic solids (or crystals), ceramics, metals, and microparticles on the surfaces of various substrates.

## Results and Discussion

Figure 1 sketches the process followed in MIMIC: the key elements are the formation of a mold consisting of a network of interconnected, micrometer-scale capillaries and the fabrication of microstructures on a support. The elastomeric mold was fabricated from poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) using procedures described for making stamps used in microcontact printing<sup>2</sup> ( $\mu\text{CP}$ ) of self-assembled monolayers (SAMs) of alkanethiolates on gold, by casting PDMS against a master (usually prepared using photolithography) that contained a pattern complementary to that to be reproduced. The master was used a number of times to reproduce multiple copies of the mold. A typical area of the network of channels formed between the mold and the support varied from  $\sim 0.5$  to  $4 \text{ cm}^2$ , and the length of the channels varied from  $\sim 0.4$  to  $1.5 \text{ cm}$ .

The ends of the channels in the mold were cut open to allow a liquid to enter and air to escape. Opening both ends of the capillary was not necessary: even when one end was closed, a liquid could fill the capillary. The trapped air seemed to escape by diffusion through the elastomer. When we filled channels that had been evacuated by applying vacuum, the rate of capillary filling was comparable to that of the system using two open ends: the capillary forces were the dominant factor behind

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the filling of the capillaries. When vacuum was applied at one end while filling with a fluid from the opposite end, the initial rate (the rate of filling the first 2 mm of the capillary) of capillary filling was increased by more than 2-fold, but the channels were also filled with bubbles of air.

When the elastomeric mold was placed on the surface (usually Si/SiO<sub>2</sub>), the compliant nature of PDMS allowed conformal contact between the mold and the surface,<sup>2</sup> and a network of channels formed. A fluid containing the materials to be patterned filled the channels in the mold by capillary action. It did not spread to the regions of the surface contacted by the PDMS mold.<sup>20</sup> We discuss the thermodynamics of this process below, but qualitatively the rate at which a fluid filled the capillaries varied with the viscosity and the surface free energy of the support: for example, ethanol filled a channel with cross-sectional dimensions of 3.0 by 1.5 μm over Si/SiO<sub>2</sub> at ~1–2 cm/min; a prepolymer of polyurethane (J-91, Summers) filled the same channel at ~0.5 mm/min. After the channel filled and the material crystallized, cross-linked, adsorbed, or deposited onto a support, the PDMS mold was removed from the support, and the patterned material remained on the surface.

We have used a number of liquid prepolymers successfully, including UV-curable poly(methyl acrylates), UV-curable epoxies, heat-curable epoxies, UV-curable polyurethanes, and heat-curable polyurethanes. Organic and inorganic liquids containing materials other than polymers were also used to fill the channels. We have successfully used and patterned materials onto supports using aqueous solutions (with a small amount of ethanol—5% by volume—added to lower the surface tension of the solution) containing ionic salts, organic solutions containing organic compounds, and latex solutions containing a suspension of microparticles.

We have also used solutions of monomers in MIMIC. After an aqueous solution containing acrylamide (5% by w/v), bisacrylamide (0.5% by w/v), and a catalytic amount of ammonium persulfate had filled the channels, a catalytic amount of *N,N,N',N'*-tetramethylethylenediamine (TEMED) was allowed to diffuse into and through the aqueous solution by placing a drop of TEMED at one end of the capillary. The monomer was allowed to cross-link thermally at 60 °C. Other monomers such as styrene and methyl methacrylate could not, however, be used in MIMIC when a PDMS mold was used. When these monomers filled the channels, they swelled the PDMS, and the conformal contact with the support was lost.

We have used a number of different supports: Si/SiO<sub>2</sub> (both native and thermally grown), glass, Au, Au/SAM, Ag/AgO, Pt, Cu/CuO, Ti/TiO<sub>2</sub>, polymeric films (polystyrene, polyimide, poly(methyl methacrylate), and poly(vinylidene chloride)). Curved supports could also be used, since the elastomeric mold could be brought into contact with certain types of curved support; with the relatively thick molds and simple procedures we used, the radii of curvature had to be greater than ~5 mm to give good conformal contact and filling.

**Thermodynamics and Kinetics of MIMIC.** MIMIC is a thermodynamically driven process: the liquid fills the capillaries to minimize the free energies of the solid–vapor and solid–liquid interfaces. The changes in interfacial free energies for a liquid filling (distance Δz) from a spherical drop (radius *r*) into a capillary with a square cross-section (width *x*) can be expressed as eqs 1 and 2 and approximated by eqs 3 and 4 (Figure 2), assuming that the change in interfacial free energy due to the decrease in the surface area of the spherical drop is small compared to the other terms (i.e., *r* ≫ *x*);<sup>1,21</sup> γ<sub>SV</sub>, γ<sub>SL</sub>, and γ<sub>LV</sub>

correspond to solid–vapor, solid–liquid, and liquid–vapor interfacial free energies, respectively; θ and θ' are the contact angles of the liquid prepolymer on the surface of PDMS and the support.

$$\Delta G = \gamma_{LV} \Delta A^{\text{sphere}} - f(\gamma_{SL}, \gamma_{SV}) \Delta A^{\text{channel}} \quad (1)$$

$$= \frac{x^2 \Delta z \gamma_{LV}}{r} - [3x \Delta z (\gamma_{SV} - \gamma_{SL}) + x \Delta z (\gamma_{SV} - \gamma_{SL})] \quad (2)$$

$$\cong - [3x \Delta z (\gamma_{SV} - \gamma_{SL}) + x \Delta z (\gamma_{SV} - \gamma_{SL})] \quad (3)$$

$$\cong -x \Delta z \gamma_{LV} (3 \cos \theta + \cos \theta') \quad (4)$$

These equations show that the process is driven by the free energies of solid–vapor and solid–liquid interfaces. When the sum of 3(γ<sub>SV</sub> – γ<sub>SL</sub>) and (γ<sub>SV</sub> – γ<sub>SL</sub>) is positive, the liquid spontaneously fills the capillary. For any value of θ and θ' between 0 and 90° (the condition at which the liquid at least partially wets the inside of the capillary), the liquid fills the capillary. When the sum of 3(γ<sub>SV</sub> – γ<sub>SL</sub>) and (γ<sub>SV</sub> – γ<sub>SL</sub>) is negative, the capillary does not fill. An example of this case is water using the PDMS mold and a hydrophobic SAM (–CH<sub>3</sub> terminated) on gold (θ = 105°; θ' = 112°): water does not fill the capillaries in this system. Like water, other liquids with high surface tension (e.g., hydrazine and mercury) and high values of γ<sub>SL</sub> and γ<sub>SV</sub> (θ > 90° and θ' > 90°) do not fill the capillary. When a liquid preferentially wets PDMS or the support (θ > 90° and θ' < 90°, or θ < 90° and θ' > 90°), the extent of capillary filling is ambiguous. An example of this last case is water when the mold is PDMS, and the support is a partially hydrophilic SAM (–COOCH<sub>3</sub> terminated) on gold (θ = 105°; θ' = 60°). To allow flow through the capillary, it is necessary to add surfactant or an organic solvent such as ethanol (~5% is sufficient) to the water.

The rate of liquid flow<sup>1,21</sup> in the capillary is determined by the surface tension and viscosity of the liquid, the cross-sectional dimension of the capillary, and the length of the channel (eq 5), where *R* is the hydraulic radius (the ratio between the volume

$$\frac{dz}{dt} = \frac{R \gamma_{LV} \cos \theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z} \quad (5)$$

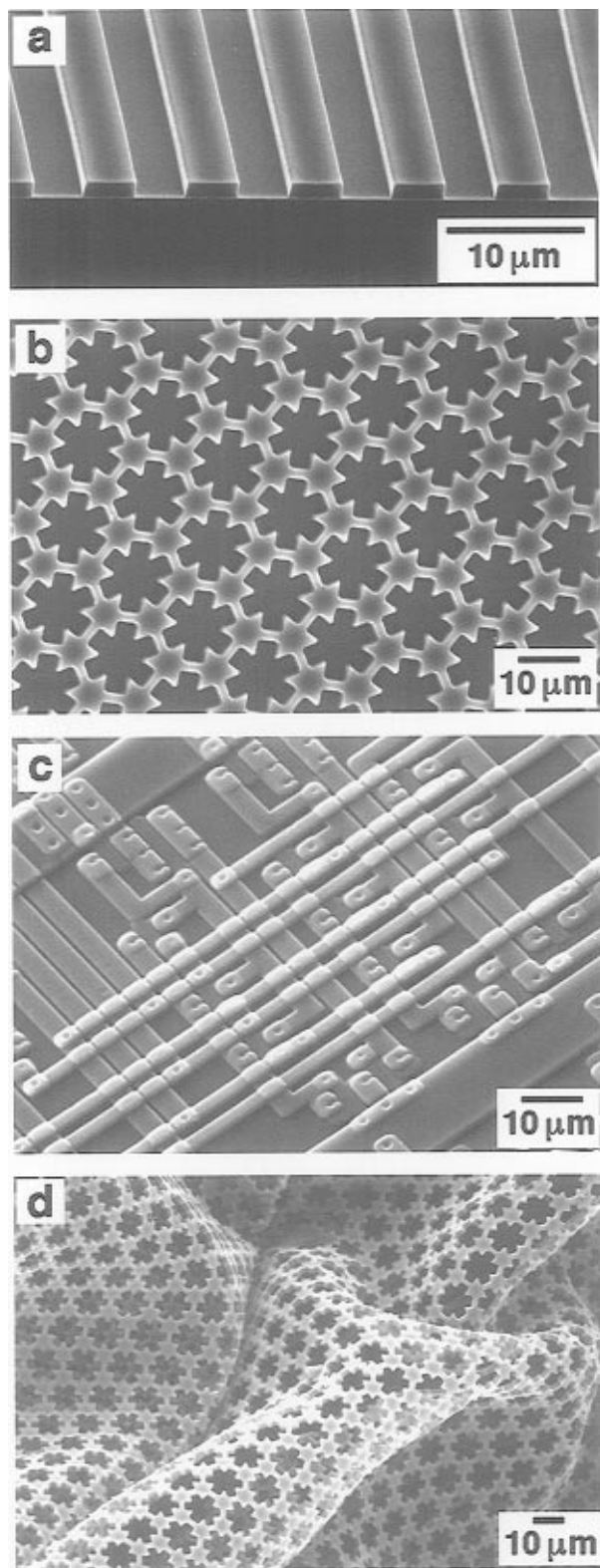
of the liquid in the capillary section and the area of the solid and liquid interface), η the viscosity of the liquid, and *z* the length of the column of liquid (Figure 2). This equation assumes that the insides of the capillary have the homogeneous interfacial free energies. Liquids with low liquid/vapor interfacial free energies (e.g., ethanol and methanol) fill the capillaries rapidly. Liquids with intermediate surface tension (i.e., with contact angle 0 < θ < 90°) fill the capillaries more slowly. Liquids with high surface tension (i.e., with contact angle θ ≥ 90°) do not fill the capillaries. With all fluids, the rate of filling is inversely proportional to the length of capillary that is filling: the rate of filling decreases as the capillary fills.

## Applications

**Fabrication of Patterned Polymeric Microstructures.** Figure 3 shows representative patterns of polymeric structures formed by MIMIC on Si/SiO<sub>2</sub>. A liquid prepolymer of poly(methyl methacrylate), polyurethane, or epoxy filled the capillaries formed between the PDMS mold and the substrate. After the prepolymer had cross-linked (either thermally or photo-

(20) When the material in the fluid could absorb into the PDMS mold, a thin film of material deposited on the region of the substrate contacted by the mold.

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**Figure 3.** Scanning electron micrographs (SEM) of patterned polymeric structures formed using liquid precursors to the polymers. (a) Polyurethane (J-91, Summer Optical) on Si/SiO<sub>2</sub> using an elastomeric mold with rectangular recessed pattern. (b) Polyurethane (J-91) pattern on Si/SiO<sub>2</sub> made using a mold containing a more complex pattern. (c) Polyurethane (NOA73, Norland) structures on Si/SiO<sub>2</sub> made using a mold containing a test pattern; it shows MIMIC can be used to pattern films with multiple thicknesses (0.5, 1.0, and 1.2  $\mu\text{m}$ ) in a single step. (d) SEM of a free-standing film formed using the structure in (b), by removing the film from its support. The film was removed from the support (Si/SiO<sub>2</sub>) by dissolving the support in HF.

chemically<sup>22</sup>), the elastomeric mold was peeled away from the patterned microstructures; the patterned polymer adhered to the

surface of the substrate. The polymers that we used adhered strongly and preferentially to the substrate rather than to the PDMS; when a clean Si/SiO<sub>2</sub> wafer was used, no polymer delaminated from the substrate when the PDMS mold was removed. This process generated polymeric structures that were negative replicas of the patterns in the mold, with an end result analogous to that in which a negative photoresist is developed in photolithography.<sup>23</sup> Features with flat edges and acute angles, as well as complex patterns, can be fabricated (Figure 3a,b); these polymeric patterns can be used as resists for subsequent additive or subtractive processes.<sup>24</sup> Typically, MIMIC was successful at patterning >95–99% of the desired area, when patterning an area of 1–2 cm<sup>2</sup>. With MIMIC, a quasi-three-dimensional processing is possible in a single step (Figure 3c); a test pattern shows complex arrays of microstructures interconnected through channels. This example demonstrates that any complex pattern may be used in MIMIC, as long as the pattern consists of a network of interconnected channels. Figure 3d shows that these planar structure may provide an entry into the fabrication of free-standing films, by a lift-off process.

Some types of structures that can be formed by conventional photolithography could also be formed by MIMIC, and it may complement photolithography in these applications. MIMIC has, however, a number of advantages over conventional photolithography as a method of forming polymeric microstructures. Photolithography requires multiple steps: forming photoresist films by spin coating, pattern-transferring by UV or e-beam exposure, and developing the pattern by removing exposed or unexposed regions; MIMIC requires one step: the pattern transfer from the PDMS master to the support occurs in a single step. Photolithography must use one exposure for each pattern; the master in MIMIC can be used many times, and photolithography is used only once (if at all) to make multiple copies of the master. The application of photolithography is limited to special classes of photoresists and photosensitizers; most polymers with low viscosity can be used in MIMIC. Photolithography is a two-dimensional process: a patterned film has a uniform thickness. MIMIC allows quasi-three-dimensional processing: patterning layers with different thicknesses and independent patterns is possible in a single step.

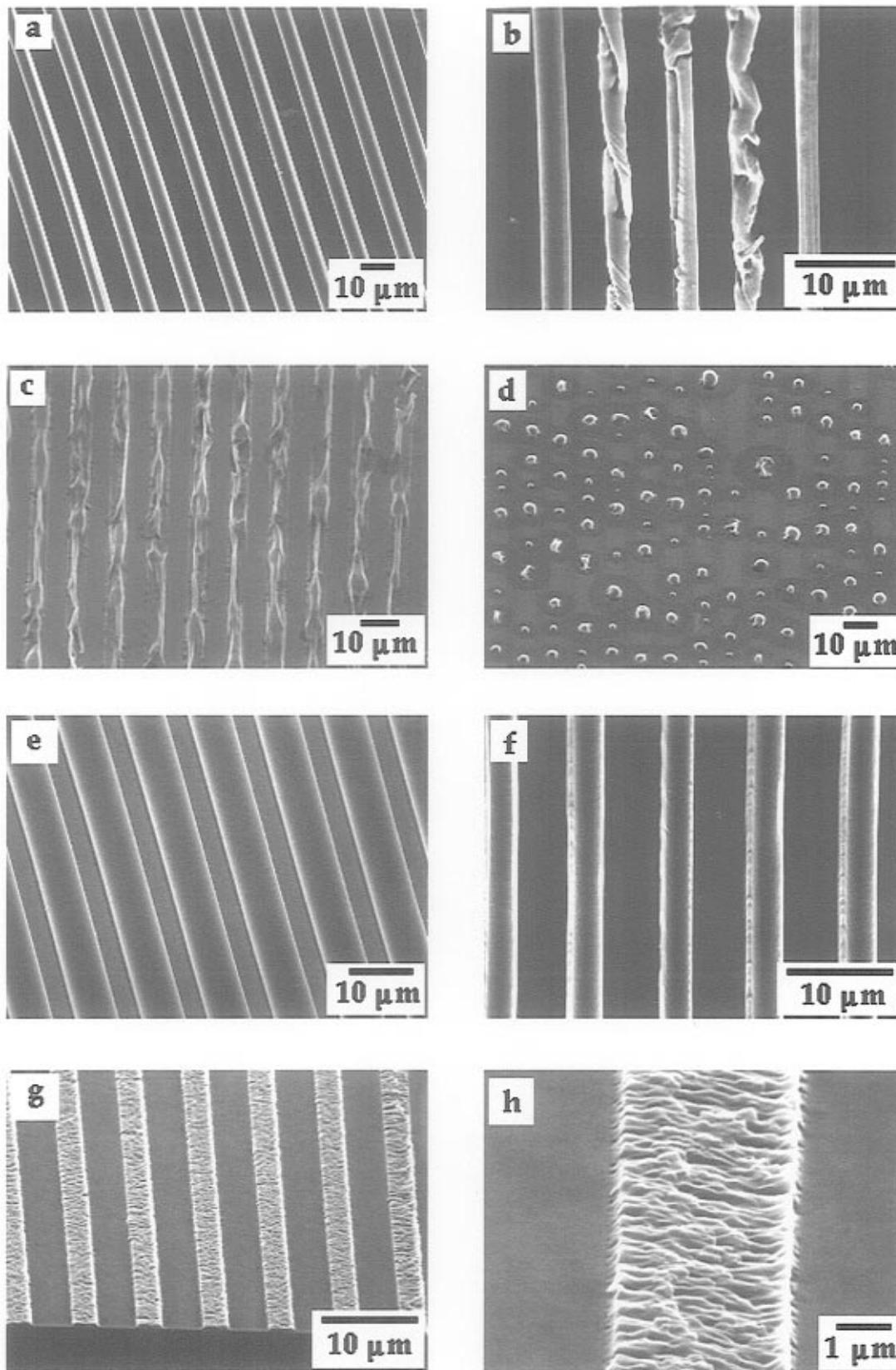
The application of MIMIC is limited by the viscosity of the liquid precursors with which the length of the capillary must be filled by capillary forces. As the liquid fills the capillary, the rate of capillary filling decreases. Filling channels having 1–2 cm length with a polymeric precursor is practical with the current procedure used in MIMIC; however, filling longer channels is experimentally impractical. MIMIC also requires a special geometrical constraint in the channels: each channel in the mold must be hydraulically continuous. The interfacial free energies of the polymer and the components of the mold must satisfy eqs 3 and 4. MIMIC, at the current stage of development, is not well-suited in fabrications that require large areas of microstructures or several layers of independent structures.

**Patterned Crystallization/Solidification.** Using channels in MIMIC to confine (or localize) solutions that contained organic or inorganic salts, we formed patterns of crystals (or solids) on the surface of supports. A fluid containing an organic or inorganic material to be patterned filled the channels, and the liquid was allowed to evaporate slowly through the openings and to cause the material to solidify (in some cases, crystallize)

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**Figure 4.** SEM showing inorganic and organic microstructures patterned by MIMIC. (a)  $\text{KH}_2\text{PO}_4$  (KDP) structures on Si/SiO<sub>2</sub>. KDP was crystallized from a 1 M aqueous solution (5% ethanol) at 4 °C over 2 days. The rod-like structures were approximately 2–3  $\mu\text{m}$  in diameter. (b) Solidification of KDP at 24 °C. (c)  $\text{Cu}(\text{NO}_3)_2$  structures on Si/SiO<sub>2</sub> solidified from a 1 M aqueous solution (5% ethanol) at 24 °C. (d) The same as (c), except the concentration was 0.05 M. (e)  $\text{CuSO}_4$  structures ( $\sim 0.8 \mu\text{m}$  in height) on glass formed from a 1 M aqueous solution. The size of the crystals was small, and they solidified to conform to the shape of the mold. (f)  $\text{K}_3\text{Fe}(\text{CN})_6$  structures ( $\sim 1 \mu\text{m}$  in height) on Si/SiO<sub>2</sub> formed from a 1 M aqueous solution containing 5% ethanol. (g) An oblique view of a fractured sample of amaranth on glass, formed from 0.1 M amaranth in ethanol. The structures are approximately 0.4  $\mu\text{m}$  in height. (h) A section of (g) at high magnification, showing the texture of solidified amaranth.

within the confinement of the channels, while the elastomeric mold remained on the support. Figure 4 shows examples of inorganic and organic microstructures formed and patterned by

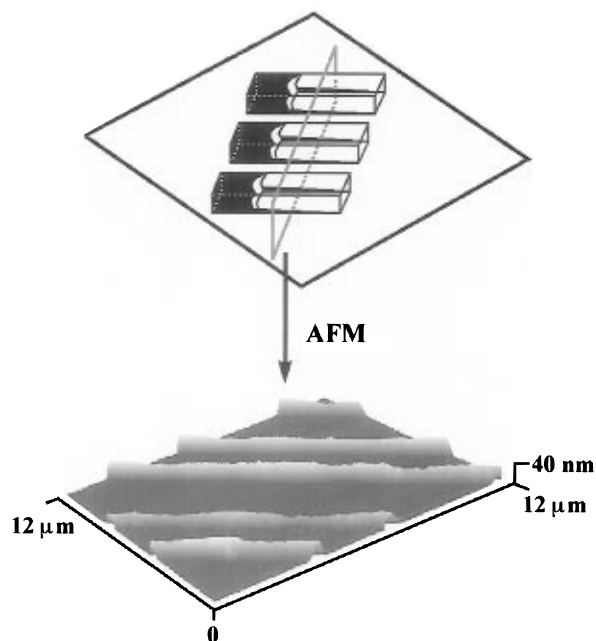
MIMIC. Though these microstructures adhered preferentially to the substrate, some structures were removed from the substrate when the PDMS mold was peeled off. Figure 4a

shows the crystallization of  $\text{KH}_2\text{PO}_4$  from a 1 M aqueous solution containing 5% (v:v) ethanol, using an elastomeric mold having rectangular, cross-sectional dimension of  $4 \times 1.2 \mu\text{m}$  and 1 cm length; a small amount of ethanol was added to lower the surface tension of the solution and to increase the rate of capillary filling. Potassium diphosphate (KDP) was crystallized at  $4^\circ\text{C}$  over 2 days. Under these conditions, these crystals of KDP had extremely high aspect ratio (some cases over 1000). Some rod-like crystals having approximately  $2\text{-}\mu\text{m}$  diameter were as long as 2–3 mm. KDP crystals have shown nonlinear electrooptical properties,<sup>25</sup> and the crystals such as these with very high aspect ratios may be useful in electrooptics as wave-guiding structures or in frequency multiplication.

The morphology and shape of the crystals formed in MIMIC could be controlled by adjusting the conditions of crystallization (e.g., concentration and temperature). The crystals of KDP in Figure 4b were crystallized using the same conditions as Figure 4a, except that the temperature was  $24^\circ\text{C}$ : the growth of crystals were still constrained by the channels, but the shapes observed for the solid KDP were different. When the liquid was allowed to evaporate more slowly, the crystals were more uniform.

Patterns of crystallization changed when the concentration of salt was varied. Figures 4c and 4d show the solidification of  $\text{Cu}(\text{NO}_3)_2$  from different concentrations in aqueous solutions: 4c shows the solidification from a 1 M aqueous solution containing 5% (by volume) ethanol and 4d from a 0.05 M aqueous solution containing 5% (by volume) ethanol. The solidified microstructures formed from a high concentration of salt in the starting solution were interconnected; the structures were disjointed when formed starting from a solution with lower concentration. Figure 4e shows the solidification of  $\text{CuSO}_4$  from a 1 M aqueous solution containing 5% (by volume) ethanol; the ionic structures were a replica of the mold (minus the volume loss due to solvent). Figure 4f shows microstructures of  $\text{K}_3\text{Fe}(\text{CN})_6$  (from a 1 M aqueous solution containing 5% ethanol). MIMIC can also be used for patterned solidification of organic salts. As an example, amaranth (the trisodium salt of 1-(4-sulfo-1-naphthyl)azo)-2-naphthol-3,6-disulfonic acid) was solidified via MIMIC, from a 0.1 M solution in ethanol (Figure 4g). Microstructures of amaranth, which can exhibit liquid-crystalline characteristics,<sup>26</sup> showed textured surfaces (Figure 4f). Using MIMIC, other liquid crystals as well as those with nonlinear optical and electrical properties can be patterned on a given substrate.

Crystallization (or solidification) via MIMIC can be used to obtain patterns of crystals (or solids) that have dimensions much smaller than that determined by the mold. When a fluid fills noncircular capillaries, it preferentially wets the corners,<sup>27</sup> and the flow of the wetting liquid occurs through the corner regions. In MIMIC, we observed that the fluid wetted corners first and the initial flow of the fluid occurred through the corners, followed by the bulk flow. If a fluid fills the capillaries only partially, some segments of the capillaries have the wetting liquid present only at the corner regions. When the solvent evaporated from these corner regions, the microstructures can be crystallized onto the surface, with the dimension much smaller than that of the capillary. Figure 5 shows a diagram illustrating such microstructures from a section of the capillary and the corresponding atomic force micrograph (AFM). The AFM shows microstructures of  $\text{CuSO}_4$  patterned on  $\text{Si}/\text{SiO}_2$  that were solidified from a 1 M aqueous solution containing



**Figure 5.** Small structures observed in patterned crystallization of  $\text{CuSO}_4$  on a  $\text{Si}/\text{SiO}_2$  substrate. A diagram shows the area that was viewed by atomic force microscopy. Small  $\text{CuSO}_4$  structures were crystallized in the region where the solution (1 M aqueous solution containing 5% ethanol) wetted only the corners of the capillaries having the cross-sectional dimension of  $1.2 \times 3 \mu\text{m}$ . The structures were approximately 20–40 nm high and 200 nm wide at the half-height.

5% ethanol. The average dimensions of these structures were 200 nm wide at the half-height and 20–30 nm high. Similar structures can also be generated using other materials such as precursors to polymers.

**Formation of Patterned Ceramics.** MIMIC can be a part of processes to pattern ceramic materials on supports. For an illustration, we chose silica as the ceramic material. Commercially available precursors to glass (Accuglass 105, 108, and 208, Allied Signal) were used to fill capillaries; these compositions are solutions of poly(ethoxymethylsiloxane) with low viscosity (0.8 cP). When the precursor is annealed at  $\sim 100\text{--}150^\circ\text{C}$ , the solvents (mostly low molecular weight ketones and alcohols) evaporate, and the precursor converts to a cross-linked silica/siloxane structure. When the polymer is subjected to temperatures above  $400^\circ\text{C}$  in air, it converts completely to silica; the organic components of the polymer vaporize or burn. Once these polymeric precursors have been converted to silica, they have shown good dielectric characteristics in VLSI interlayer applications<sup>28</sup> and useful planarizing effects.<sup>29</sup>

To form silica microstructures on a support, the channels (formed on silicon wafers or glass) in MIMIC were filled with a solution of the polymeric silicate precursor. After the capillaries had filled completely, the solvents were evaporated by heating at  $\sim 100\text{--}150^\circ\text{C}$ , while the PDMS mold remained on the support. After this initial annealing, the mold was removed from the support. Even at this stage, the patterns of microstructures adhered strongly to the support; they could not be removed from the support mechanically using Scotch tape. The precursor was then converted completely to silica by heating at  $425^\circ\text{C}$  for 1 h under nitrogen. Figure 6a shows an electron micrograph of patterned microstructures on a glass support, after the initial annealing. When the precursor was heated only to  $\sim 100\text{--}150^\circ\text{C}$ , the structures retained their sharp edges and

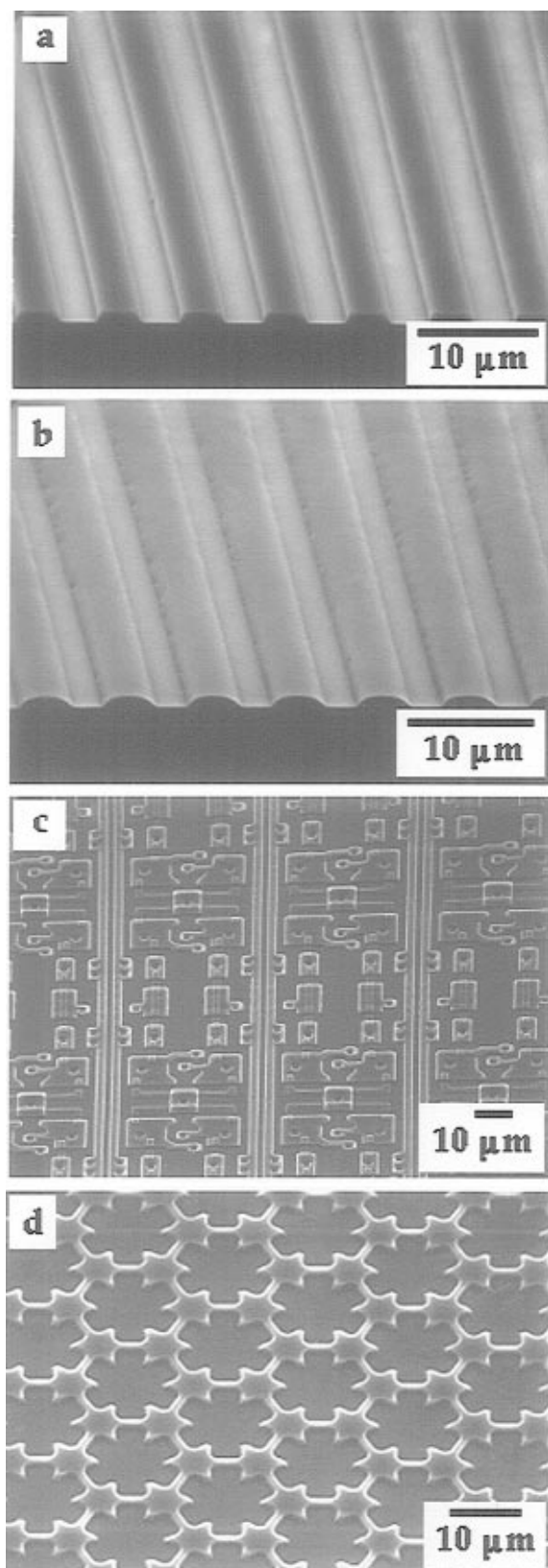
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**Figure 6.** SEM showing patterned ceramic structures. The ceramic was silica from a polymeric precursor (Accuglass 105, Allied Signal). (a) Patterns of silica/siloxane on glass. The precursor was partially converted to silica by heating at 100 °C for 20 min. The edges remained sharp. (b) The same structures in (a) were converted completely to silica by heating at 425 °C for 1 h. The edges of the structures became smooth. (c) A complex pattern of silica/siloxane on Si/SiO<sub>2</sub>. It was partially converted to silica by heating at 100 °C. (d) A pattern of silica on glass. The precursor film was converted to silica by heating at 425 °C for 1 h.

corners. When heated above 400 °C, the shapes of the microstructures changed due to the change in volume and the minimization of interfacial free energies (Figure 6b). Figure 6c illustrates that a complex pattern of silica on Si/SiO<sub>2</sub> can be fabricated. The test pattern shows three-dimensional relief of the structure, before it was converted completely to silica. These patterned layers of silica could be used as resists for further patterning of the support, such as anisotropic etching of silicon. Figure 6d shows an array of complex structures of silica on glass, fabricated by heating the structure in Figure 6b at 425 °C for 1 h under nitrogen. When they were illuminated using a point source of light, they acted as microlens arrays.<sup>30</sup> Figure 7 shows the diffraction and focusing<sup>31</sup> of light transmitted through these structures. The uniformity of these optical patterns gives some indication of the good reproducibility of these structures.

**Electroless Deposition.** Electroless deposition is an autocatalytic process in which a metal ion is reduced and deposited on a catalytic surface.<sup>32</sup> It is particularly useful in processes that involve substrates containing pits, holes, and recessed regions. MIMIC can be used to pattern surfaces by electroless deposition, taking two approaches. A direct approach is to fill the capillaries with an electroless plating solution and let the surface react with it. The surfaces of the substrate exposed in the capillaries are plated, but the areas contacted by the elastomeric mold are not. In order for this direct approach to work, the surface of the substrate must be catalytically active so that the reduction of metal ions can occur. Figure 8a shows an electron micrograph of copper microstructures formed on gold. The plating bath was a basic aqueous solution containing copper sulfate and sodium potassium tartrate, and used formaldehyde as reducing agent.<sup>33</sup> Where the plating solution for copper contacted gold, the electroless deposition occurred.

It is also possible to use MIMIC indirectly to deposit metals by electroless deposition. The basis of this method is to activate a surface, otherwise inactive toward electroless deposition, by depositing catalysts.<sup>34–37</sup> After forming channels on a substrate by contacting the mold and the substrate, the capillaries are filled with a solution containing catalytic colloids. As the solvent evaporated, the colloids remained on the surface and rendered the surface catalytic for electroless deposition of metal. Figure 8b shows an electron micrograph of copper structures formed on Si/SiO<sub>2</sub> using this indirect approach. A PDMS mold was placed on Si/SiO<sub>2</sub> whose surface had been treated with (CH<sub>3</sub>-CH<sub>2</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub><sup>38,39</sup> to form self-assembled monolayers (SAMs) of amino-terminated siloxanes.<sup>40</sup> The channels in the mold were filled with a dimethylformamide (DMF) solution containing palladium colloids stabilized with (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr.<sup>41</sup> After allowing the DMF to evaporate at 60 °C and the colloids

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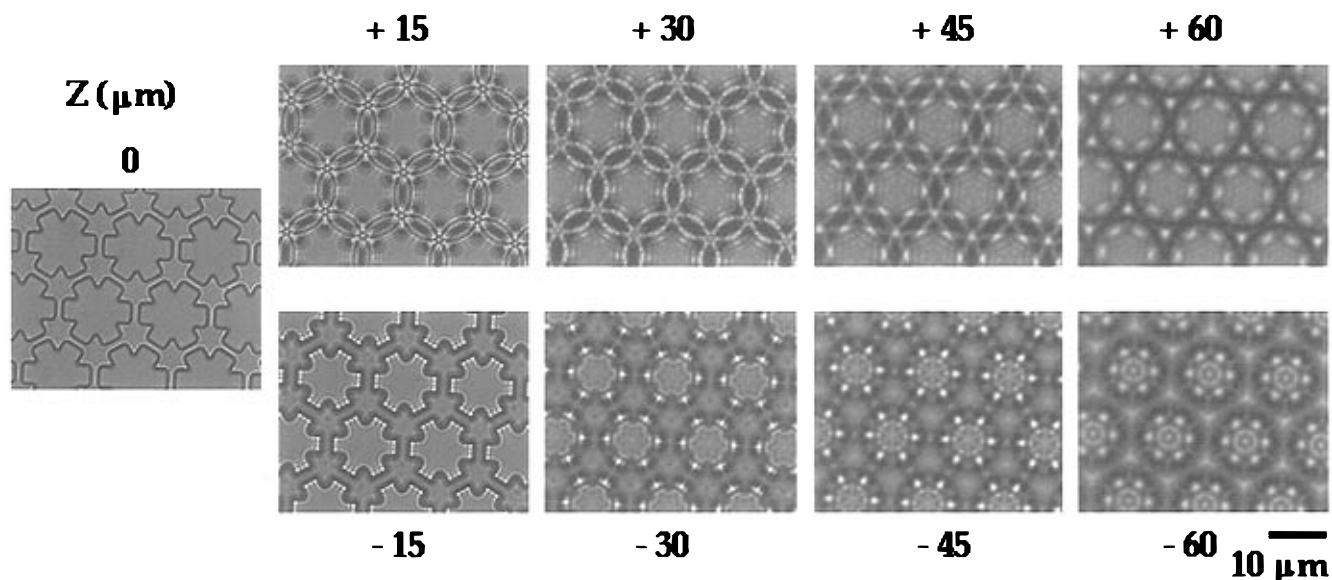
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**Figure 7.** Silica structures on glass. The structure in Figure 6d behaved as lens arrays. The array was illuminated from a point source and observed from heights ( $Z$ ) above (the top row), at (the first picture on the left), and below (the bottom row) the focal plane.

to adsorb onto the SAMs, the PDMS mold was peeled away from the support; the surface of the support was, at this point of the process, patterned with catalytically active palladium colloids.<sup>42,43</sup> When the substrate was immersed in the plating bath for copper, electroless deposition occurred on the activated regions on the surface. The copper microstructures (up to  $\sim 500$  nm in thickness) adhered strongly to the surface; they could not be removed with Scotch tape. When this indirect approach was used, we observed two distinct regions on the surface of substrate. As DMF wicked into the channels, it first preferentially wetted the corners of the channels; the bulk fluid filled the channels in a distinct, later stage. As DMF evaporated from the capillary “fronts” where only the corners of the capillaries were wetted, the palladium colloids remained on these regions; consequently, electroless deposition occurred only on them (Figure 8c): the resulting structure of copper had dimensions ( $\sim 200$  nm) much smaller than the width of the capillary ( $> 2$   $\mu\text{m}$ ). We have used this indirect approach—activation of the surface by an initial front of liquid wicking into the highest energy—successfully to deposit copper on insulators (such as glass), semiconductors (such as silicon), and polymers (such as polystyrene and poly(methyl methacrylates)), and this process demonstrates the ability of MIMIC to generate conducting patterns on semiconductors, which is potentially useful in the field of microcircuit fabrication.

**Hierarchical Self-Assembly: Two- and Three-Dimensional Crystallization of Microspheres.** Well-ordered two- and three-dimensional (2-D and 3-D) arrays of hexagonally packed microspheres form when a solvent evaporates from a suspension containing these particles. This formation usually involves two stages: nucleation and growth.<sup>44,45</sup> The nucleation is attributed to the attractive lateral capillary forces among the microspheres; the growth of the array is promoted by a laminar flow of liquid to the crystalline arrays, which is caused by evaporation of the solvent. Crystalline arrays of microparticles are interesting for potential applications in optical devices, data storage, and microelectronics and as models for protein crystallization.

Though the current methods<sup>46–50</sup> of crystallizing microspheres can fabricate 2-D and 3-D arrays reproducibly and reliably, it is difficult or impossible to pattern these arrays in a controllable way. MIMIC, however, can be used for the patterned crystallization of microspheres: it allows the crystallization of microspheres in a pattern determined by the elastomeric mold.<sup>51</sup> For an illustration, we used a latex solution containing polystyrene microspheres to fill capillaries formed between a PDMS mold and a glass surface; the microspheres were allowed to assemble and crystallized within the confinement of the capillaries.

A network of rectangular channels (cross-sectional dimension  $4 \times 1.2$   $\mu\text{m}$ ) was filled with an aqueous suspension (2.5% by weight) of microspheres, and water was allowed to evaporate through the openings of the channels at room temperature. When the elastomeric master was removed from the substrate, crystalline arrays of microspheres remained on the surface. Figure 9a shows an example of polystyrene microspheres (diameter =  $0.48$   $\mu\text{m}$ , Polybeads, Polyscience) crystallized in a linear pattern; the crystalline arrays were hexagonally close-packed but showed some defects. Some regions of the array showed a perfectly ordered array of hexagonally packed microspheres (Figure 9b). Various sizes (diameters from  $0.1$  to  $1.0$   $\mu\text{m}$ ) of microspheres have been used. Figure 9c shows an example of assembly of microspheres with diameter  $0.1$   $\mu\text{m}$ ; the arrays were not as crystalline as those obtained using larger microspheres.

When water evaporated completely while the elastomeric mold remained on the surface, only  $\sim 20$ – $40\%$  of the channels showed close-packed arrays of microspheres. In a typical experiment, approximately  $10$ – $40$   $\text{mm}^2$  of crystalline arrays of microspheres were observed. The crystalline arrays remained on the surface when the PDMS mold was removed, while some microspheres from the noncrystalline arrays were delaminated. The exit regions of the capillary showed the best crystallinity, while the packing near the entrance regions was disordered. After filling the channels with the latex solution, the capillaries

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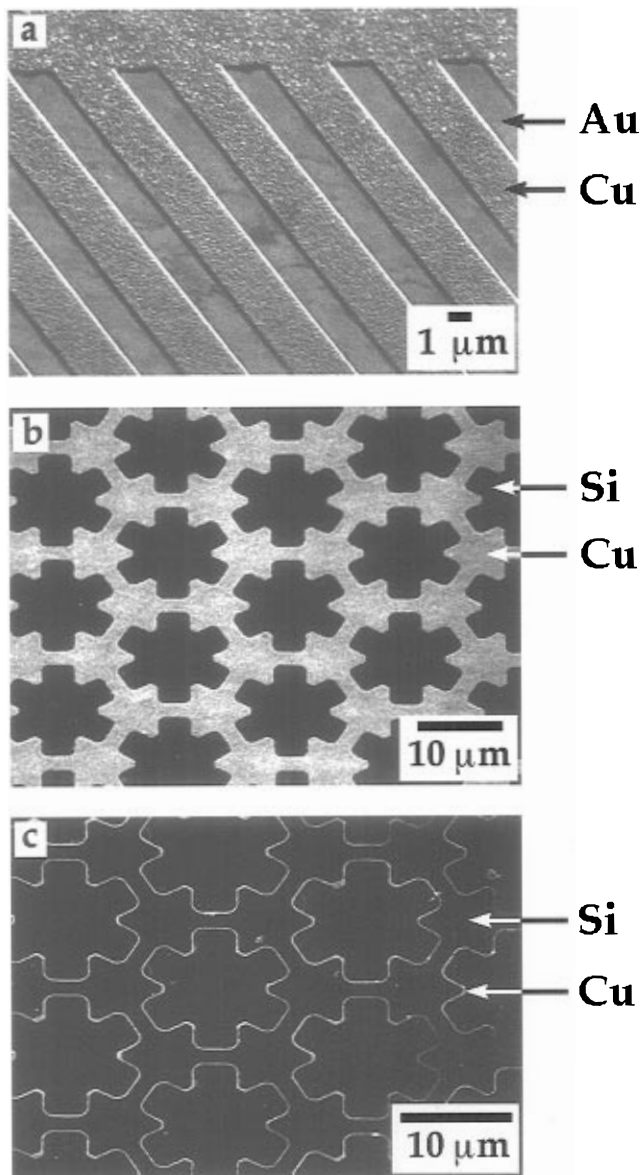
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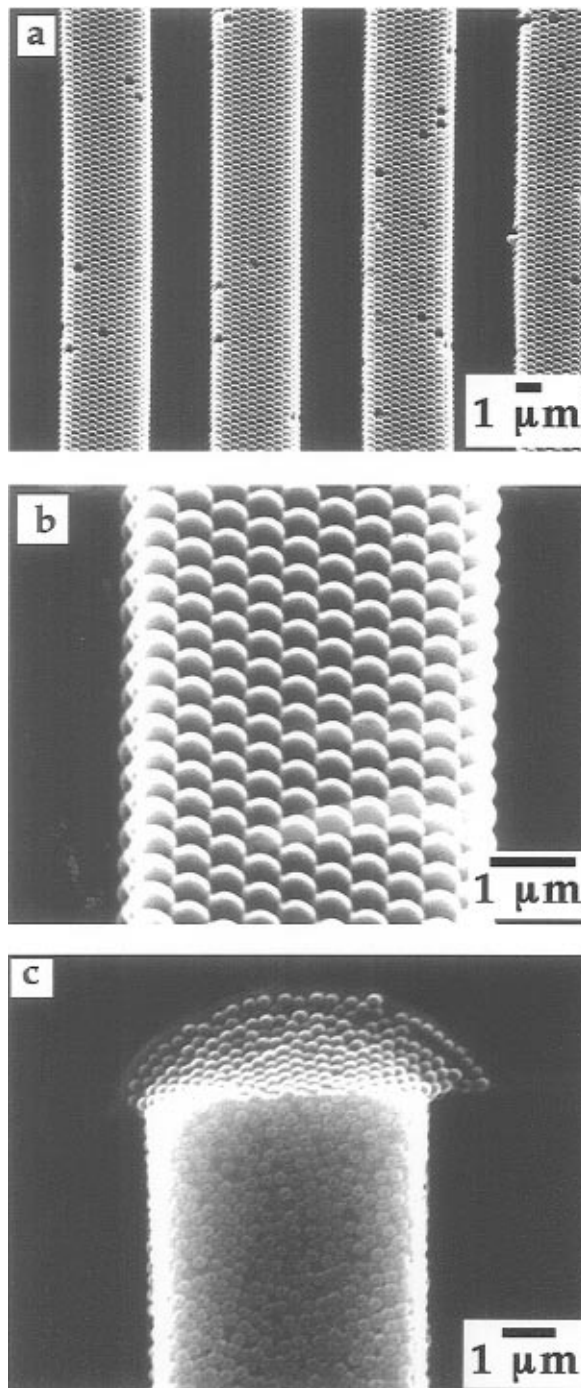




**Figure 8.** Electroless deposition. (a) Copper structures formed on gold using the direct approach. MIMIC was carried out on gold by filling the channels with the plating bath for electroless deposition of copper. (b) Copper structures formed using the indirect approach. MIMIC was carried out on a Si/SiO<sub>2</sub> substrate that has been derivatized with (3-aminopropyl)triethoxysilane, using a DMF solution containing palladium colloids to activate the surface, followed by electroless deposition of copper. (c) Copper structures formed using the indirect approach. It shows a region where the DMF solution wetted only the corners of the capillaries, and the palladium colloids activated only the edge of the pattern.

were ultrasonicated to aid packing. Ultrasonication improved the yield of crystallized arrays slightly. Even without ultrasonication, however, microspheres were crystallized in the capillaries.

The mechanism we believe to be responsible for crystallization of microspheres into ordered lattices involves two stages: nucleation and growth. At the exit end of the channel, the combination of attractive forces between microspheres and evaporation of water causes the microspheres to assemble and aggregate into nucleation sites for crystallization. The ordered lattice grows by the fluid influx toward the nucleation site in compensation of the water lost by evaporation, since this influx causes convective transport of microspheres from the bulk fluid to the lattice. A large reservoir of fluid at one end (where the latex suspension is placed) forces this flux to be unidirectional.



**Figure 9.** SEM of patterned arrays of polystyrene microspheres. (a) Three-dimensional assembly of microspheres (mean diameter = 500 nm). (b) A section of (a) that shows nearly perfect close-packing of microspheres. (c) Crystallization of smaller microspheres (mean diameter = 100 nm).

This proposal of the growth mechanism is consistent with our observations: when the unidirectional flow of fluid caused by evaporation was not possible (as in filling the channels from both ends), no ordered arrays were observed.

## Conclusion

MIMIC is a method of fabricating patterned microstructures of polymeric, inorganic, and organic materials by molding in enclosed, continuous channels formed between a substrate and an elastomeric master whose surface has been patterned with recessed regions. This method is based on spontaneous filling of these channels with a fluid by capillary action, in which the rate and the extent of filling are determined by the balance between interfacial thermodynamics and viscosity drag.

Unlike many molding processes, the fabrication of a mold in MIMIC is very simple; it requires only the conformal contact of the substrate and the elastomeric mold. MIMIC requires only limited (and in some cases no) access to facilities for lithography; it is therefore particularly convenient for use in chemical laboratories. Multiple copies of the elastomeric component can be easily fabricated from a single lithographic master, and they can be reused many times. The compliant nature of the elastomer allows fabrication on various substrates (e.g., insulators, semiconductors, metals, and polymers) and even on nonplanar surfaces. Because of the accuracy with which capillarity fills the channels, the pattern in the mold is accurately transferred to the patterned layer; in some case, a quasi-three-dimensional processing (i.e., patterning structures having multiple thicknesses) is possible in a single step. While photolithographic techniques are applicable to only certain classes of polymers (namely, photoresists), MIMIC allows the use of many different polymers, including those with useful structural and functional properties; it also offers access to free-standing films that have substantial structural rigidity. With MIMIC, the edge resolution of a final feature is not affected by backscattering and interference.

MIMIC is intrinsically limited by its ability to form recessed patterns on a surface and the accurate replication of these patterns onto the surface of an elastomeric mold. At the current stage of development, MIMIC requires a network of interconnected capillaries. Capillary filling over a short distance (up to  $\sim 1$  cm) can be achieved quickly and efficiently; over a large distance, the rate of filling decreases significantly due to the viscous drag of the fluid in the capillary and the distance over which the fluid has to be transported.

MIMIC is a simple, convenient procedure of crystallizing (or solidifying) organic and inorganic materials onto a substrate. The growth of crystals via MIMIC can be directionally constrained; conditions of solidification could be controlled to determine microstructures of solids. The microchannels involved in MIMIC may be useful in studying microreactions that involve a small volume of a liquid confined in a small area on the surface and delivering reactants (organic, inorganic, or biological) to the geometrically specific region on the surface. MIMIC may be useful in patterning the surface of a support with a ceramic material using a polymeric precursor; this process may certainly be extended to pattern surfaces with ceramic materials using sol-gel and other processes. MIMIC can provide a model for hierarchical self-assembly: the filling of the capillaries occurring as a result of a self-assembly templated by the structure of the capillaries and another self-assembly templated by the structure, shape, and function of the material (or particle) in the fluid.

## Experimental Section

**Materials and Substrates.** All solvents and chemicals were of reagent quality and used without further purification. PDMS (Sylgard 184) was obtained from Dow Corning. Commercially available precursors to polymers were used: SK-9 (poly(methyl acrylate), Summers), UV-15 and UV-15-7 (epoxy, Master Bond), F113 and F114 (epoxy, Tra-Con), J-91 (polyurethane, Summers), and NOA 60, 71, 72, 73, 88, and 113 (Norland). Precursors to silica were obtained from Allied Signal (Accuglass105, 108, and 208), and polystyrene microspheres from Polyscience (Polybeads). A thin film of gold was prepared by e-beam evaporation onto silicon wafers using titanium as an adhesion promoter. Silicon (polished single-crystal silicon wafers (test grade, n-doped), Silicon Sense, Nashua, NH) and glass substrates (cover glass, VWR Scientific) were cleaned in a freshly prepared solution of concentrated  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  (7:3 by volume), rinsed with deionized water, and dried in a stream of nitrogen. **Caution:** This solution of peroxysulfuric acid reacts violently with many materials and should be handled with care.

**Instrumentation.** Scanning electron microscopy was carried out on a JEOL JSM-6400. Scanning probe microscopy was performed using a Topometrix TMX-2010 (Mountain View, CA). Optical images were captured using a Leica microscope.

**MIMIC.** PDMS molds were fabricated according to the published procedure.<sup>2</sup> Ends of the PDMS mold were cut with a razor blade. The mold was placed on the surface of a precleaned substrate; the elastomer made conformal contact with the substrate, and a network of channels formed. This network was accessible to a fluid from the end that had been cut. A drop ( $\sim 0.2$ – $1.0$  mL) of a fluid (a precursor to a polymer, solution, or suspension containing materials to be patterned) was placed at the end of the mold, and the channels were allowed to fill by capillary action. While the mold remained on the surface, the components in the fluid were allowed to cross-link, crystallize, solidify, adsorb, or deposit onto the surface of the substrate; the mold was peeled away, and the patterned microstructures remained on the surface of the substrate.

**Fabrication of Patterned Polymeric Microstructures.** The channels were formed on silicon wafers and filled with polymeric precursors. After filling, they were cross-linked thermally at  $60$  °C or photochemically using a mercury vapor lamp (450 W medium pressure). When cross-linked photochemically, a thin ( $\sim 0.2$ – $0.5$  mm) PDMS mold was used, with the UV source 1–2 cm away from the top surface of the mold.

**Patterned Crystallization/Solidification.** A PDMS mold was placed on either glass or silicon wafers to form channels. Ionic salts were dissolved in water to appropriate concentrations, and ethanol (5% by volume) was added to lower the surface tension of the solution. Amaranth was dissolved in ethanol. After filling the channels, the solute was allowed to crystallize (or solidify) at room temperature, while the PDMS mold remained on the substrate. The mold was removed from the substrate when all liquid evaporated from the capillary channels.

**Formation of Patterned Ceramics.** Channels were filled with a commercially available precursor to glass (Accuglass, Allied Signal). After filling, the precursor was partially cured at  $100$ – $150$  °C for 20 min in an oven, while the mold remained on the substrate. Then the mold was removed, and the substrate patterned with partially converted silica was placed in an oven maintained at  $425$  °C for 1 h under nitrogen. The precursor converted completely to glass.

**Electroless Deposition.** The plating bath<sup>33</sup> used for electroless deposition of copper was freshly prepared by mixing two solutions: 10 mL of a solution containing 0.3 g of  $\text{CuSO}_4$ , 1.4 g of sodium potassium tartrate, and 0.4 g of NaOH and 1 mL of an aqueous formaldehyde solution (37.2% w/v). For the direct approach, MIMIC was carried out on a gold surface; channels were filled with the plating solution. Electroless deposition was allowed to occur at room temperature while the mold remained on the substrate. For the indirect approach, MIMIC was carried out on a Si/SiO<sub>2</sub> substrate that had been derivatized with (3-aminopropyl)triethoxysiloxane.<sup>40</sup> After filling the channels with a solution ( $\sim 1\%$  w/v) of DMF containing palladium colloids stabilized with tetrabutylammonium bromide,<sup>41</sup> the solvent was allowed to evaporate at  $60$  °C while the PDMS mold remained on the substrate. Then the PDMS mold was removed, and the substrate was immersed in the plating bath. Copper was deposited only on the activated regions on the surface of the substrate.

**Two- and Three-Dimensional Self-Assembly of Microspheres.** MIMIC was carried out on glass substrates. Channels were filled with an aqueous suspension of microspheres (Polybeads, Polyscience, diameter  $0.1$ – $1.0$   $\mu\text{m}$ ). While the PDMS mold remained on the surface, the substrate was ultrasonicated for 1 min (ultrasonication increased the extent of crystallization but was not the driving force of the crystallization), and water was allowed to evaporate at room temperature. After the complete evaporation of the solvent ( $\sim 6$  h), the PDMS mold was removed; the crystalline arrays of microspheres remained on the surface of the substrate.

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