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Oriented Polymers, Followed by Thermal
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Langmuir[®]
The ACS Journal of Surfaces and Colloids

Reprinted from
Volume 12, Number 21, Pages 5209–5215

New Strategy for Controlling the Size and Shape of Metallic Features Formed by Electroless Deposition of Copper: Microcontact Printing of Catalysts on Oriented Polymers, Followed by Thermal Shrinkage

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Received March 13, 1996*

This paper describes a new method of reducing the size of the metal features made by electroless deposition and fabricating complex-shaped, patterned surfaces. Microcontact printing (μ CP) was used to pattern oriented glassy polymers with palladium colloids, stabilized with tetraoctadecylammonium bromide. These colloids are catalysts for the selective electroless deposition of copper. Annealing of the activated polymer at a temperature slightly above its glass transition temperature led to a shrinkage of the substrate. Immersion of the shrunken substrate in the plating bath yielded the metal features. The maximum shrinkage of the feature size achieved was on the order of a factor of ~ 4 in one direction of the oriented polymer and of ~ 7 in the perpendicular direction. Control of the extent and direction of shrinkage allowed the fabrication of metal features with sizes and shapes different from those on the polydimethylsiloxane stamp used for the patterning of the substrate and from the draw ratios. Free-standing metal structures were produced by dissolving the substrate after the metal film had reached the desired thickness. Complex-shaped, patterned surfaces could be fabricated by wrapping the activated polymer film around a scaffolding or template; during the annealing, the polymer adapted the shape of the underlying scaffolding. Metalization of the activated, shaped substrate resulted in patterned three-dimensional structures.

Introduction

In this paper we describe a new strategy to reduce the feature size of structures fabricated by electroless deposition of copper. The size reduction is achieved by shrinkage of the substrate—a biaxially oriented polystyrene film—after it has been patterned and activated with the catalyst—a palladium colloid—but before the electroless metalization with copper. Our process involves three steps: first, activation of the substrate by microcontact printing (μ CP) of palladium colloids;¹ second, shrinkage of the activated substrate to the desired size and shape; and third, electroless deposition of copper on the patterned, shaped substrate.

Electroless deposition of metals such as copper is of great technological interest because of its potential for the use as interconnects in microelectronic devices and for the formation of thin metal etch masks for deep-ultraviolet lithography.^{2–9} Electroless plating occurs by an autocatalytic redox process, in which the cation of the metal to be deposited is reduced chemically at the substrate

surface. The metalization of a substrate by electroless deposition can be directed by either selective deactivation of a catalytic substrate or selective activation of a nonreactive surface.⁵ Catalysts typically used for the deposition of copper include mixed Sn Pd colloids,^{10–16} surface-bound palladium(II) species,^{17–21} or palladium colloids.^{1,22} Most methods of patterning a substrate with the catalyst are based on photolithographic techniques.^{2,6,19,20,23} One limitation of these techniques is that the size of the metal features is determined by the size of the metal mask used in the photolithographic process. A second limitation of photolithographic technologies is that they are applicable only to planar surfaces. It is difficult to extend them to curved substrates or to more complex surface topologies, because the focal plane in photolithography is very thin.

Microcontact printing of colloids¹ is a new technique for the activation of substrates for electroless deposition. It is analogous to the processes of microcontact printing of alkanethiols on gold^{24,25} and of alkylsiloxanes on Si/SiO₂^{26,27} that we have developed for the formation of patterned

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† Abstract published in *Advance ACS Abstracts*, September 1, 1996.

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self-assembled monolayers (SAMs). μ CP of colloids uses the relief pattern on the surface of an elastomeric stamp inked with the catalyst—palladium colloids stabilized with tetraalkylammonium bromide^{1,28–30}—to pattern and activate the substrate for electroless metalization. The transfer of the catalyst from the elastomeric stamp to the substrate occurs by mechanical contact. μ CP of colloids allows the surfaces of the substrate to be patterned and activated in one step at room temperature. It can be carried out on flat and curved surfaces and on a variety of substrate materials (e.g. glass, Si/SiO₂, and polymers).

Biaxially oriented polystyrene^{31–34} is a commercial product used primarily for packaging applications.³⁵ Orientation of the polymer results in improved mechanical properties compared to those of the unoriented polymer (for example, higher resistance to crazing) and allows the fabrication of thin (25 μ m) films. The processing of this material involves heating sheets of polystyrene to a temperature that is a few degrees below the glass transition temperature³⁶ and drawing ('hot stretching') the sheet into a film. In general, the polymer is stretched between rollers in the "machine direction", and the polymer is drawn in the transverse direction by pulling the edges of the film. The maximum draw ratio in the machine direction is 3.7–4, and it is about 8.7 in the transverse direction.³⁵ The entangled polymer chains have highly extended conformations in the plane of the film after processing. As the material relaxes, the polymer chains reorganize themselves to their original unperturbed conformations. Relaxation is accelerated by heating the polymer above its glass transition temperature. The consequences of this reorganization are that the film shrinks in the plane of the film and thickens. The degree of shrinking is approximately equal to the draw ratio of the orientation process. The way the stretching of the polymer film is done in the manufacturing process determines the shape the film will adapt after annealing. If the film was stretched over a cylindrical roller, for example, then the polymer will have "shape memory" and reorganize itself during the annealing with a radius of curvature equal to the radius of curvature of the roller.

Microcontact printing of colloids¹ on oriented polymers for patterning of catalyst for the electroless deposition of copper opens a new route for the size reduction³⁷ of metal features made by electroless deposition and for the fabrication of complex-shaped surfaces that are patterned

with metals. The possibility of reducing the feature size after the substrate has been activated with the palladium colloid frees this process from some of the limitations on size imposed by the patterning technique. In the present study we demonstrate the reduction of the feature size and the fabrication of complex shaped, patterned surfaces by using copper for the metalization process and biaxially oriented polystyrene as shrinkable substrate.

Experimental Section

All solvents were reagent quality and used without further purification. 3-Aminopropyltriethoxysilane (Huels) was used without further purification. Polyimide films (0.125 mm thick) were obtained from Goodfellows. Biaxially oriented polystyrene sheets (Shrink-It) were obtained from Aleene's (Buellton, CA); these 0.25 mm thick sheets shrink almost isotropically by a factor of 2.3–2.5. Oriented thin films of polystyrene were obtained from Kama Corp. (Hazelton, PA); the shrinkage factors of the 25- μ m thick films were \sim 4 in the machine direction and \sim 7 in the transverse direction.

Pretreatment of the Polymer Substrates. The polymer sheets were oxidized by soaking in CrO₃/H₂SO₄ for 1 min at 70 °C.³⁸ The oxidized substrates were rinsed thoroughly with deionized water, dried under a stream of nitrogen, and immersed in a solution of 3-aminopropyltriethoxysilane (50 mM) in ethanol overnight. After rinsing with ethanol and drying under a stream of nitrogen, the substrates were patterned by μ CP of colloids. Only freshly prepared substrates were used.

Suspension of Palladium Colloid. The tetraoctadecylammonium bromide-stabilized palladium colloid (Pd/[C₁₈H₃₇]₄N⁺Br⁻) was synthesized as follows:¹ Palladium(II) acetate (Fluka, 4 g, 17.8 mmol) and tetraoctadecylammonium bromide (Fluka, 5 g, 4.5 mmol) were suspended in 200 mL of a 5/1 (v/v) mixture of toluene and THF at 30 °C. After 25 mL of absolute ethanol was added, the mixture was refluxed at 65 °C for 12 h. The color of the solution turned to deep brown-black. To initiate the precipitation of the colloids, an excess (100 mL) of absolute ethanol was added slowly while shaking vigorously. The solution was allowed to stand for 5 h at room temperature to complete the precipitation. The slightly colored supernatant solution was decanted, and the precipitate was dried under reduced pressure. A gray-black powder (2.1 g, \sim 79 wt % palladium, \sim 88% yield based on palladium) was isolated. The TEM image showed spherical, well separated palladium particles with a diameter of \sim 7 nm.

The suspension of colloidal palladium (Pd/[C₁₈H₃₇]₄N⁺Br⁻) was prepared by dissolution of 0.2 g of the powder in 30 mL of toluene and sonification in an ultrasound bath for 5 min. The brown solution was stable and active for months while in solution and could be handled in air.

Microcontact Printing of Colloids for Patterning the Palladium Catalyst. The elastomeric stamps used for contact printing of the Pd colloids were fabricated as reported previously.²⁵ The PDMS stamp was "inked" with the colloid by immersing the stamp in the colloidal suspension for 2 s, removing it, and drying it under a stream of nitrogen. This procedure was repeated two to three times. We then placed the stamp in contact with the polystyrene substrate (whose surface had previously been activated by oxidation and silanization) for 15 min.

Shrinkage of the Substrate. After the patterning of the substrates with the palladium colloid, the polymer sheets³⁹ were placed on a Teflon sheet and annealed in an ambient atmosphere at 110 °C for about 2 h. As the shrinking started, the substrates first began to curl up; eventually, they unfolded and flattened out. They then were removed from the oven and cooled in air. The polymer films⁴⁰ were treated in the same way; in case a special shape or only a limited amount of shrinkage was desired, they were wrapped around or fixed in a scaffolding prior to the annealing.

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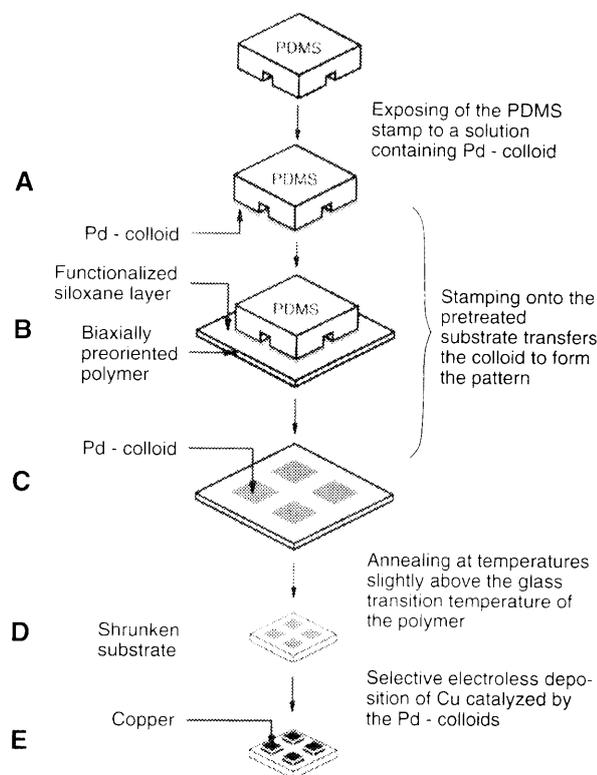


Figure 1. Schematic outline of the procedure for the size reduction of electroless deposited copper features by shrinkage of the substrate. After inking of the elastomeric stamp with the catalytic palladium colloid (A), the stamp was placed on the oriented glassy polymer substrate (B), which had been previously silanized with 3-aminopropyltriethoxysilane. The catalyst was transferred only from the relief regions of the stamp to the surface of the substrate (C). After the stamp was removed, the substrate was shrunk by annealing slightly above its glass transition temperature (D). Finally, the shrunken substrate was immersed in the plating solution. Metalization occurred only where the substrate was activated with the palladium colloid (E).

Electroless Metal Deposition. For the electroless deposition of copper, we used the following copper plating bath:⁴¹ Solution A contained 3 g of CuSO_4 , 14 g of sodium potassium tartrate (Rochelle salt), and 4 g of NaOH in 100 mL of distilled water. Solution B was an aqueous solution of formaldehyde (37.2 wt %). The two solutions A and B were mixed in a 10/1 (v/v) ratio just before the bath was used. To deposit copper, we immersed the patterned substrate into the mixture for 30–600 s at room temperature. The plating time to achieve a certain film thickness depends on the age of the plating bath and the type of the substrate. The plating process could be stopped by removing the sample and rinsing it with distilled water.

Instrumentation. Scanning electron microscopy was carried out using a JEOL JSA-6400 instrument at an acceleration voltage of 7–15 keV. Scanning probe microscopy was performed with a Topometrix TMX 2010 scanning probe microscope (Mountain View, CA).

Results and Discussion

Figure 1 shows a schematic of the procedure for the size reduction of electroless deposited features by shrinkage of the substrate after patterning it with colloid particles by μCP . A patterned elastomeric stamp made from polydimethylsiloxane (PDMS)²⁵ was “inked” with the catalyst by dipping it into a solution of palladium colloid stabilized by tetraoctadecylammonium bromide in toluene (A). The solution of hydrophobic palladium colloid “wetted” the surface of the PDMS stamp readily. After the stamp had been dried under a stream of nitrogen, it was brought into contact with the substrate (B), an oriented

polymer that had been previously silanized with 3-aminopropyltriethoxysilane to ensure a strong interaction between the catalyst and the underlying substrate.⁴² Light pressure was applied to the stamp to ensure contact. The contact between stamp and substrate allowed the transfer of the colloid (C). After separating the stamp from the substrate, the substrate was annealed at a temperature slightly above the glass transition temperature of the oriented polymer. The residual stresses in the oriented polymer relaxed, and the substrate shrank to its original size (D). The shrinking factor was determined by the draw ratio employed in the processing of the oriented polymer. After cooling, the patterned, shrunken substrate was immersed in the plating solution (E).⁴¹ The electroless deposition of the metal on the sample occurred only where palladium colloid had been transferred to the substrate.

Figure 2 shows scanning electron microscopy (SEM) pictures of representative microstructures of copper on polyimide (A) and biaxially oriented polystyrene (B–D).³⁹ We used the same elastomeric stamp to activate these substrates. After patterning the substrates with palladium colloids, the polyimide film (A) was immersed in the plating solution; the polystyrene substrate (B) was annealed at 110 °C before it was immersed in the plating solution, whereas the second polystyrene substrate (D) was first immersed in the plating solution and then annealed. The thickness of the metal structures fabricated this way was typically between 0.5 and 1 μm . Comparison of the structures A and B shows that the shape of the metal features was almost perfectly retained during the shrinkage process. The surface roughness of the metal structures deposited on the annealed polystyrene was slightly bigger than that on polyimide. Figure 2C shows the detail of the metal structures on the shrunken polystyrene substrate. The edge resolution of the features in the range of 100 nm is mainly determined by the size of the single copper grains. The process of shrinkage did not distort the features; even the corners of the triangle retained their sharp edges. This retention in shape reflects the isotropic shrinkage of the polymer. Any distortion of the edges is masked, at this level, by the significant size of the copper grains. When the copper was deposited *before* the annealing (D), the shrinkage of the substrate resulted in the destruction of the deposited metal pattern: the polystyrene substrate shrunk isotropically in the plane of the sample, whereas the copper features retained their size; the resulting stress led either to detachment of the “stars” from the substrate or to deformation of their shape.

In order to measure the electrical conductivity of the copper structures made by the combination of μCP of colloids, annealing, and electroless deposition of copper, we fabricated a series of copper lines connected to two contact pads (Figure 3).⁴³ The average resistivity of the copper lines measured with the two-point method was $\sim 2.4 \mu\Omega \text{ cm}$. This value is close to the resistivity reported for electroless deposited copper of $\sim 2 \mu\Omega \text{ cm}$. The inset shows the profile of the copper line (D) that was measured with AFM. For comparison, we have included the profile of the polymer³⁹ before (A) and after (B) annealing at 110 °C, as well as the profile of copper electroless deposited on an unshrunken polystyrene substrate (C). The shrinkage of the polymer during the annealing resulted in a

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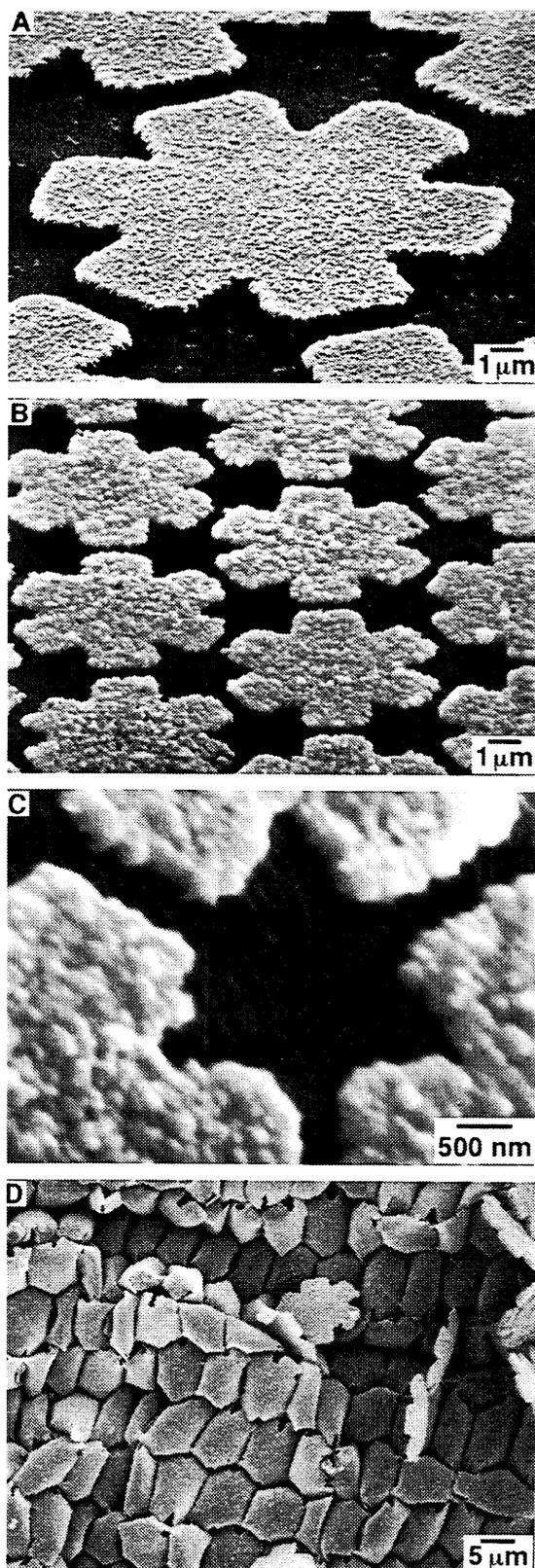


Figure 2. SEM pictures of representative copper microstructures fabricated by using the combination of microcontact printing of colloids on oriented polymers and electroless metalization. **A** and **B** demonstrate the size reduction of electroless deposited copper features that can be achieved by shrinking of the substrate³⁹ after it was activated with palladium colloids. The SEM images were taken with the same magnification; they show copper microstructures (**A**) on polyimide (original size) and (**B**) on a polystyrene substrate³⁹ that was shrunk before the metalization. (**C**) Detail from the copper structure on the shrunken polystyrene substrate shown in (**B**). The details of the pattern are well preserved after the shrinkage process. The irregularity of the edges of the features is mainly determined by the size of the copper grains. The gap between the different copper areas is in the range of 250 nm. (**D**) SEM picture of a copper structure on a polystyrene substrate³⁹ that was shrunk after the metalization.

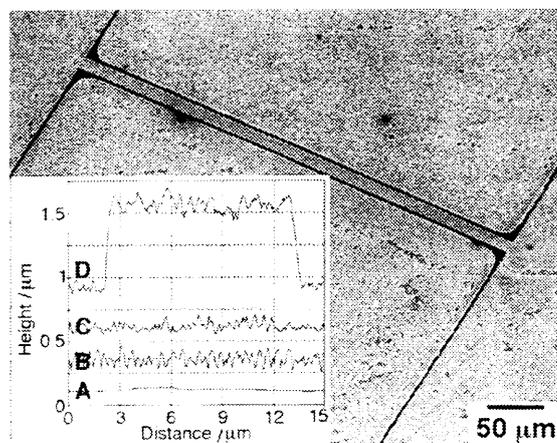


Figure 3. SEM image of a test pattern to measure the conductivity of the electroless deposited copper. The line is connected to two isolated contact pads. The inset shows the superimposed graphs of the profile of the copper line (**D**), the profile of the polymer³⁹ before (**A**) and after (**B**) annealing at 110 °C, as well as the profile of copper electroless deposited on an unannealed polymer substrate (**C**).³⁹ The y-axis shows the relative height of the features.

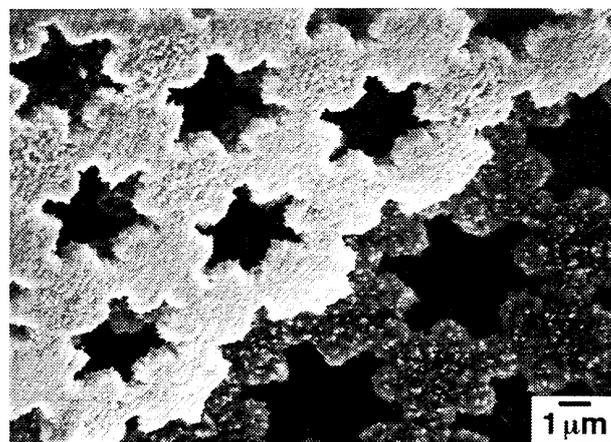


Figure 4. SEM image of a free-standing copper structure fabricated by μ CP of colloids on an oriented polystyrene sheet³⁹ followed by annealing and electroless deposition of copper. The copper structure was subsequently detached from the substrate by dissolving the polystyrene in methylene chloride. The film was floated away and deposited on a silicon wafer. The picture shows both the front (dark) and back (bright) sides of the copper film. During the annealing of the patterned polymer film, the size of the copper pattern was reduced by a factor of ~ 2.5 .

significant increase of the surface roughness that subsequently influenced the roughness of the copper film.⁴⁴

Our strategy of decreasing the feature size by shrinkage of the substrate after patterning can also be applied to reduce the feature size of freestanding metal structures. Figure 4 shows a free-standing copper structure of about 0.8 μm thickness. After metalization of the patterned, shrunken polystyrene,³⁹ the copper structure was detached by immersing the substrate in CH_2Cl_2 . The copper structure was picked up carefully with tweezers and placed on a silicon wafer. Figure 4 shows the front- (dark) and backside (bright) of the copper structure. The backside of the copper film reflects the roughness of the polymer surface after the annealing (see also Figure 3, inset B).

The samples shown in Figures 2–4 were annealed until changes in their size and shape were no longer perceptible.

(44) We used the arithmetic mean of the deviations in height from the profile mean value (R_a) as a measure for the roughness: $R_a = (1/N)\sum_i |Z_i - Z|$. Z is defined as the sum of all height values (Z_i) divided by the number of data points (N) in the profile. The R_a values for the oriented polymer were ~ 8 nm, those for the annealed polymer ~ 35 nm, and those for the copper line ~ 53 nm. For comparison: the R_a value of a copper deposited on the unannealed polymer was ~ 35 nm.

and does not require the manufacturing of different photomasks with the corresponding pattern: interruption of the shrinkage and restamping of the substrate enables the fabrication of structures with different feature sizes on the same sample using one single stamp. This technique also allows the fabrication of patterned, complex three-dimensional structures that would be difficult to realize with conventional techniques.

Although we have demonstrated our strategy for the size reduction of metal features and for the fabrication of patterned, complex-shaped surfaces only using a single example—electroless deposition of copper on oriented polystyrene as a shrinking substrate—it should also be applicable to the electroless deposit of other metals and (by extension of applications of μ CP to direct chemical vapor deposition (CVD)²⁷) to some CVD-based processes as well. Other oriented glassy polymers that should be

equally suited for this application include poly(methyl methacrylate), polycarbonate, and glycol-modified poly(ethylene terephthalate); oriented semicrystalline polymers that may be applicable include polypropylene and poly(ethylene terephthalate).

Acknowledgment. This work was supported in part by the Office of Naval Research, the Advanced Research Projects Agency, and the ARO Multidisciplinary University Research Initiative, Award Number DAAH04-95-1-0102. It used MRSEC shared Facilities supported by the NSF under Award Number DMR-9400396. P.C.H. gratefully acknowledges the Swiss National Science Foundation and the Janggen—Poehn Foundation for financial support.

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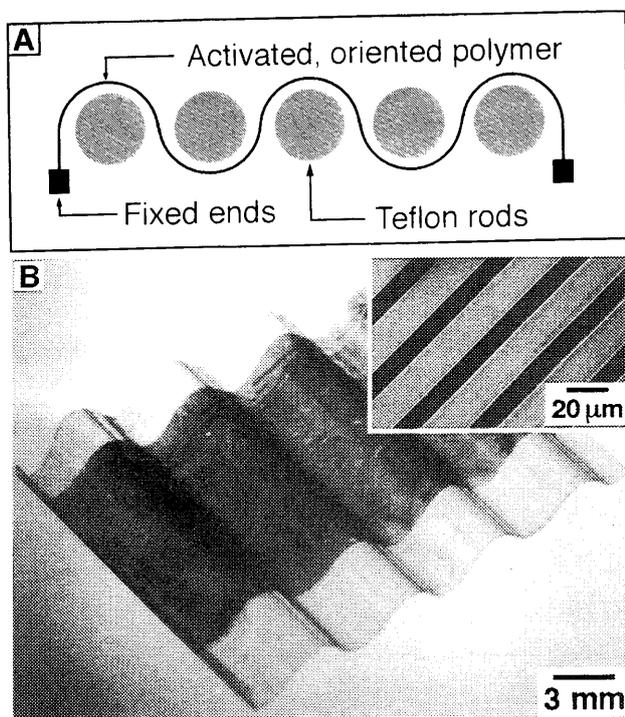


Figure 7. Photograph of a patterned, complex-shaped polymer⁴⁰ substrate. (A) The activated polymer was wrapped around Teflon rods. Both ends of the polymer were fixed in order to prevent shrinkage. During annealing, the polymer film adopted the wavelike shape. (B) The dark region in the photograph corresponds to the area metalized with copper. The inset shows a SEM picture of the copper structure and the copper pattern deposited on the polystyrene substrate.

polymer film then can be removed from the supporting scaffolding. Figures 7 and 8 show photographs of samples fabricated in this way. The patterned, activated polymer film⁴⁰ shown in Figure 7 was wrapped tightly around Teflon rods. After annealing, the scaffolding was removed and the substrate was immersed in the plating solution. By variation of the spacing between the bars and using bars with different diameters, we can fabricate patterned samples with almost any radius (or several different radii) of curvature. Pressing the activated oriented polymer against a relief surface during the annealing leads to a three-dimensional structure. The structure in Figure 8 was made by pressing the polystyrene film against an array of Teflon balls (4.7 mm in diameter). The adaptation of the shape of the balls during the annealing forced the polymer film to shrink unevenly in the different regions, resulting in a slight deformation of the pattern. This could be corrected in principle by a proper design of the PDMS stamp that considers this different shrinkage of the pattern. If desired, we can pattern the polymer film with a metal film on the underside, the top side, or both. We note that samples fabricated in this way are heat sensitive; as soon as the temperature gets near the glass transition temperature of the polymer, the interrupted shrinkage process resumes and proceeds until the polymer film has relaxed.

Conclusions

This work demonstrates a new technique based on microcontact printing of palladium colloids on oriented polymers to reduce the size of the metal features made by electroless deposition and to fabricate complex shaped, patterned surfaces. Annealing of the activated polymer at temperatures slightly above the glass transition temperature results in a shrinkage of the substrate. Immersion of the shrunken substrate in the plating bath

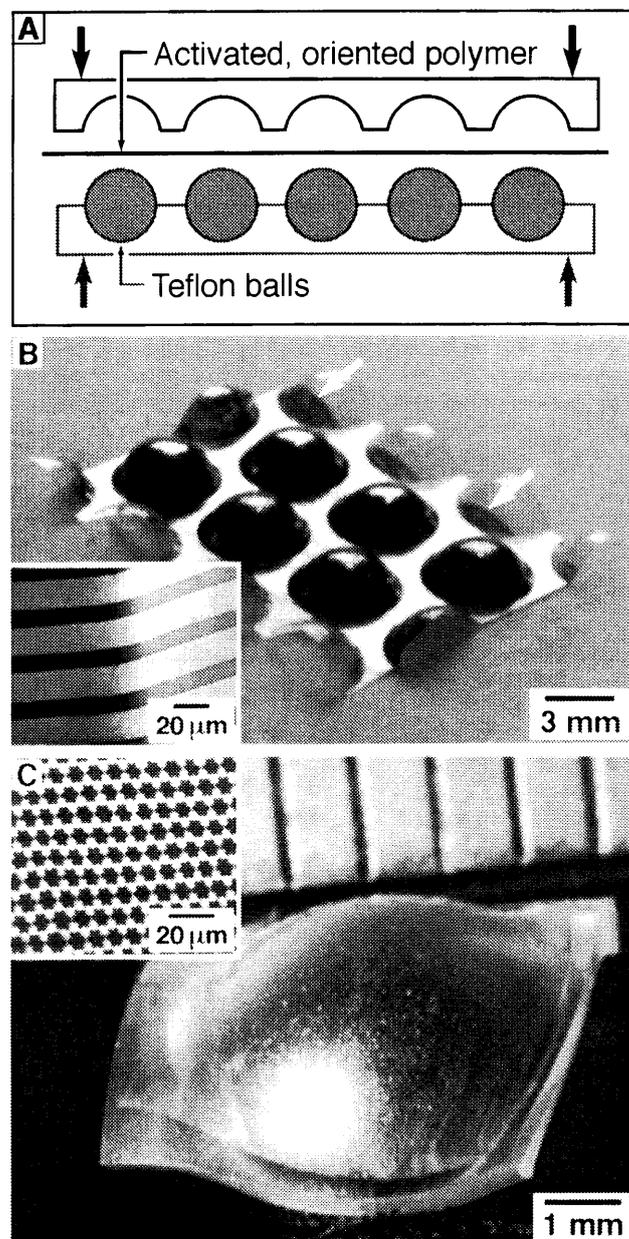


Figure 8. Array of patterned hemispheres made by gently pressing the activated polymer⁴⁰ against Teflon balls (4.7 mm in diameter) during the annealing (A). The dark region in the photograph (B) corresponds to the area metalized with copper. The border of the patterned area is indicated with arrows. The inset shows a SEM picture of the copper structure on the polystyrene substrate in a region in which the transition occurs between the flat and curved parts of the sample. The copper lines are on the underside of the polymer film. (C) Hemisphere made by shrinking of the polymer film over a steel ball. The polymer film patterned with the colloid was laid over the steel ball and annealed without applying pressure. The inset shows part of the copper structure—the “negative” pattern from the one shown in Figure 2—on the hemispherical polymer surface.

yields the metal features. The shape of the features is retained during the shrinkage process. This possibility of reducing the feature size after the activation of the substrate by μ CP provides the basis for a wide flexibility in the patterns and shapes produced. Using a stamp with relatively large features, patterns with small lateral dimensions can be produced simply by controlling the shrinkage of the substrate rather than by fabrication of a rigid mask: the control of the extent and direction of the shrinkage allows the fabrication of metal features with sizes and shapes that are different from those on the PDMS stamp. The fabrication of a range of patterns with different dimensions is now possible with one single stamp