

Microcontact Printing of Palladium Colloids: Micron-Scale Patterning by Electroless Deposition of Copper

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This paper describes a new method for forming micron- and submicron-scale patterns of copper on surfaces. This method uses microcontact printing (μCP) to deposit colloids that serve as catalysts for the selective electroless deposition of copper. A patterned elastomeric stamp fabricated from poly-(dimethylsiloxane) was used to deliver the catalyst—palladium colloids stabilized with tetraalkylammonium bromides—to the substrate surface. The electroless deposition of the copper on the sample occurred only where palladium colloid was transferred to the substrate. Electroless deposition catalyzed by the colloids resulted in the formation of metal structures with features having submicron dimensions, with an edge resolution in the range of 100 nm. This technique of activating substrates for electroless metalization was successfully used to pattern glass, (Si/SiO₂), and polymers; both flat and curved substrates were used. Microcontact printing of colloids was also used to fabricate metal structures whose thicknesses were varied in different regions of the sample (multilevel metal structures). Free-standing metal structures were produced by dissolving the substrate after the metal film had reached the desired thickness.

Introduction

Electroless deposition of metals such as copper, silver, gold, nickel, rhodium, and cobalt is a process widely used for the production of fine metal patterns in printed circuits. $\hat{\mathbf{1}}^{-7}$ Electroless deposition occurs by an autocatalytic redox process, in which the cation of the metal to be deposited is reduced by a soluble reductant at the surface of the metal features being formed, or at the surface of catalysts used to initiate the deposition. This redox process generally takes place only on surfaces capable of catalyzing it: noncatalytic surfaces first have to be activated with a metal catalyst such as palladium before the metalization can occur. Selective deposition can be achieved either by the selective deactivation of a catalytic substrate or by the selective activation of a nonreactive surface by a catalyst.⁴ Several methods of producing patterned catalysts are known, most of them based on photolithographic techniques.^{5,8,9} The size of the features produced by electroless deposition of metals can be as small as 0.1 um.⁵ Another route to selective metalization is chemical vapor deposition (CVD).¹⁰⁻¹³

In this paper we report a new technique of patterning surfaces with a catalyst by microcontact printing (μCP)

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of colloids. The process is analogous to microcontact printing of alkanethiols on gold; we have described this process previously for the formation of patterned selfassembled monolayers (SAMs).^{14,15} Patterning of the surface with colloids by *u*CP enables selective metalization by electroless deposition on areas of the surface activated by the deposited colloids. The key step in this procedure is the direct transfer of the catalyst (in this case a palladium colloid) from an elastomeric stamp to the substrate to activate the surface for selective electroless metal deposition.

Palladium is important as a catalyst for the electroless metalization of dielectric substrates such as ceramics or polymers.^{7,16} The most extensively used palladium catalysts are based on the tin/palladium mixed catalysts.¹⁶ For the work reported here, we have synthesized palladium colloids stabilized with tetraalkylammonium $bromides.^{17-19}\ Palladium (II) \, acetate \, is \, reduced \, by \, ethanol$ in the presence of tetraalkylammonium bromides as stabilizers. By varying the length of the alkyl chains of the stabilizer, it is possible to adjust the solubility of the colloid. Palladium colloids stabilized with tetrabutylammonium bromide are soluble in DMF, and those stabilized with tetraoctadecylammonium bromide are soluble in toluene.

Our process demonstrates a new strategy-the combination of the direct application of the catalyst on the surface by microcontact printing and electroless metal deposition—for producing metal features with submicron dimensions. The procedure has broad generality. A wide variety of patterns can be easily transferred using μ CP of colloids. Once a catalyst is transferred onto the substrate by μ CP, it is possible to generate metallic features with submicron dimensions and thicknesses of the film greater than 1 μ m. The process is applicable to flat and curved

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Figure 1. Transmission electron micrograph and (inset) electron diffraction pattern of palladium colloids stabilized by tetraoctadecylammonium bromide. The colloids are deposited on a carbon film. The average diameter of the palladium particles is approximately 7 nm.

substrates of glass, to silicon with a native silicon dioxide layer (Si/SiO_2) , and to a variety of polymers, without requiring advanced photolithographic techniques. Although we have demonstrated it only for the electroless deposition of copper, it should be applicable to a number of other metals.

Results and Discussion

Preparation of the Palladium Colloid Suspension. Palladium colloids stabilized with tetraoctadecylammonium bromide (Pd/[C₁₈H₃₇]₄N⁺Br⁻) were synthesized from a suspension of palladium(II) acetate and tetraoctadecylammonium bromide in a 5:1 (v/v) mixture of toluene and THF. After addition of absolute ethanol, the mixture was refluxed overnight. The precipitation of the colloids was initiated at room temperature by slow addition of an excess of absolute ethanol with vigorous shaking. The lightly colored supernatant solution was decanted, and the precipitate was dried under reduced pressure. A grayblack powder containing ${\sim}79$ wt % of palladium was isolated. Figure 1 shows a transmission electron microscopy (TEM) image of a palladium colloid stabilized by tetraoctadecylammonium bromide (inset) and the corresponding electron diffraction intensities of these particles. The well-separated palladium particles are about 7 nm in diameter. The solution of colloidal palladium was prepared by dissolution of the palladium colloid powder in toluene. These suspensions were stable and active for months while in solution.²⁰ They could be handled in air.

Pretreatment of the Substrates. A pretreatment of the substrates was necessary to ensure a strong interaction between the catalyst (and subsequently a good adhesion of the deposited metal layer) and the underlying substrate. We used silicon wafers with a native oxide layer (Si/SiO₂), glass, and different polymers as substrates for the electroless metalization process. The pretreatment of the $substrates \, included \, (i) \, cleaning \, of \, the \, surface, (ii) \, oxidation$ of the surface in order to form surface hydroxyl groups (for the polymer surfaces), and (iii) silanization of the surface by immersion of the substrates in a solution of organosilanes in ethanol or heptane. For the silanization, we used organosilanes with different terminal groups $(CH_3, CN, SH, NH_2, and NHCH_2CH_2NH_2)$. The silanization step gave a high degree of control over the surface chemistry of the samples and enabled us to use the same procedure for the patterning of all the different substrate materials.²¹⁻²³

(20) We used the same solution of palladium colloids for over 3 months without detecting any significant loss in its catalytic activity.



Figure 2. Schematic outline of the procedure for microcontact printing of colloids. After the stamp was inked with the solution of palladium colloid, the stamp was placed on the substrate that had been silanized with functionalized organosilanes. The catalyst was transferred from the relief regions of the stamp to the surface of the substrate. After the stamp was removed, the substrate was immersed in the plating solution. Metalization occurred only where the substrate was activated with the palladium colloid.

Microcontact Printing of Colloids Transfers Colloids from an Elastomeric Stamp to the Substrate Surface by Contact. In a typical experimental procedure (Figure 2), we "inked" a poly(dimethylsiloxane) (PDMS) stamp¹⁵ by dipping the stamp into a solution of palladium colloids stabilized by tetraoctadecylammonium bromide in toluene. This palladium colloid was hydrophobic and "wetted" the surface of the PDMS stamp readily. After the stamp was dried under a stream of nitrogen, it was placed on the substrate by hand. If necessary, light pressure was applied to the stamp to ensure contact. The contact between stamp and substrate allowed the transfer of the colloid. After separation of the stamp from the substrate, the substrate was immersed in the plating solution. The electroless deposition of the metal on the sample occurred only where palladium colloid was transferred to the substrate. Attempts to use palladium colloids that were stabilized with tetrabutylammonium bromide, tetraoctylammonium bromide, or tetradodecylammonium bromide failed, probably because they did not wet the PDMS stamp.

Microcontact Printing of Colloids Produces Features in the Submicron Range. Figure 3A-D shows SEM pictures of representative microstructure of copper generated on (Si/SiO₂), polyimide, and glass substrates. Panels A-C illustrate the complexity of features that we

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Figure 3. Typical microstructures that can be produced by the combination of microcontact printing of colloids and electroless metalization. (A–D) SEM images of microstructures fabricated with microcontact printing of palladium colloids on (Si/SiO₂) (A, D), polyimide (B), and glass (C) followed by electroless deposition of copper (bright regions). Prior to the stamping of the colloids, the substrates were silanized with $H_2NCH_2CH_2CH_2Si(OEt)_3$. There are imperfections and defects in the structures (indicated with white arrows in panel A). Panel C suggests the minimum size of the features that can be produced by *u*CP of colloids. The copper lines with width between 1.5 and ~0.5 *µ*m are clearly resolved. (D) SEM image showing a fracture profile of a copper line. After metalization, this structure was annealed with a propane flame for ~3 s. The edge resolution is about 100 nm.

could produce routinely using μCP of colloids and electroless plating. Typically, the thickness of these metal features was between 0.5 and 1 um. Close inspection of these structures (and the others in this paper) revealed small defects in the copper structures (indicated with arrows in Figure 3A). There are several possible sources of these defects. First, the patterning of the substrates and the metal deposition was done under ambient laboratory conditions, where dust and other atmospheric contaminants can lead to defects in the structure. Second, the stamps may have contained defects. Third, contaminants from the plating solution could have deposited onto the substrate during the plating process.²⁴ Figure 3C suggests the minimum size of the features that can be reproduced: the 500 nm wide lines are clearly resolved. Figure 3D shows the fracture profile of a 400 nm thick copper line. The edge resolution of the structures formed by μ CP of colloids is about 100 nm and seems to be determined by the size of the copper grains (Figure 3D). Thus, the resolution of the colloid stamping technique is comparable to that achieved in the case of the much thinner metallic structures (100 nm or less) formed by etching of patterned SAMs that were formed by microcontact printing of alkanethiols on gold substrates.¹⁵ We have used the PDMS stamps for μ CP of colloids up to 100 times without performance loss.

The average resistivity of the copper lines²⁵ measured with the two-point method was $\sim 2.2 \ \mu\Omega$ cm. This value

is close to the resistivity reported for electroless deposited copper of $\sim 2~\mu\Omega$ cm. 26

Microcontact Printing of Colloids Can Be Carried Out on a Range of Different Substrates (Glass, (Si/ SiO₂), and Polymers). The patterning of catalysts by μ CP of colloids is an extremely general method of activating different substrates for the electroless deposition of metals. We have used uCP of colloids to pattern a number of substrates²⁷ (Figure 3). The key step in this process is the transfer of the palladium colloids from the stamp onto the substrate. Our process takes advantage of the affinity of the palladium colloids for certain organic functional groups. The formation of a thin film of functionalized organosilanes on the substrate surface as a part of the pretreatment of the substrate not only enabled the transfer of the colloid to proceed efficiently independently of the underlying material but also improved the adhesion of the deposited metal film to the substrate. The strength of adhesion of the copper structure to the different organosilane films decreased in the following order: NH₂ $\approx \mathbf{NHCH}_2\mathbf{CH}_2\mathbf{NH}_2 \approx \mathbf{SH} > \mathbf{CN} \gg \mathbf{CH}_3.$

For a test of adhesion of the copper film as a function of the substrate, the different substrates were pretreated with (3-aminopropy) triethoxysilane, patterned and metalized with electroless copper to produce a 500 nm thick metal film. On all substrates, peel tests with Scotch tape indicated "complete adhesion" ²⁸ of the metal film to the surface. Similar peel tests on thicker metal structures showed that the adhesion on the polymers was higher

⁽²⁴⁾ Although we cannot assign each defect directly to one of these three sources, we have clear indications that all three are important: First, carrying out the microcontact printing process in the clean room, thereby eliminating the influence of particulates, resulted in a decrease in the number of defects (Zhao, X.-M.; Xia, Y.; Kim, E.; Whitesides, G. M. *Chem. Mater.*, submitted); second, we could identify defects in our stamps under the microscope; third, particles formed by decomposition of the plating solution during the metalization process could easily be deposited on the sample surface since we did not filter the plating solution before or during the metal deposition.

⁽²⁵⁾ The dimension of the copper lines for the conductivity measurement were length, ~ 0.4 cm; width, ~ 15 , ~ 40 , and $\sim 80 \,\mu$ m; and thickness, $\sim 0.6 \,\mu$ m.

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⁽²⁷⁾ The materials we have used as substrates include glass, silicon with a native silicon dioxide layer, polystyrene, polyethylene, polyimide, and polyvinylidene.





5 mm

Figure 4. μ CP of colloids can be used to pattern curved substrates. Photograph of a glass bottle (r = 1.25 cm) that was patterned with palladium colloids using microcontact printing and metalized with copper by electroless deposition. The inset shows an optical micrograph of the pattern on the curved substrate taken with transmitted light. The resolution of the features on the curved substrate is similar to the the resolution achieved on planar substrates.

than on the glass or (Si/SiO_2) substrate.²⁹ The greater roughness of the polymer surfaces may be an important contributor to this stronger adhesion. μ CP of colloids worked equally well on all of the substrates that we have used. Provided that the appropriate surface modification had been carried out, the resolution of the features was independent of the underlying material.

Microcontact Printing of Colloids Can Be Used To Pattern Curved Substrates. Most microlithographic technologies are restricted to planar surfaces. It is especially difficult to extend the current photolithographic and e-beam lithographic techniques to curved substrates, because the focal plane is very thin. We have previously demonstrated microcontact printing of alkanethiols to generate a pattern on curved gold surfaces and have generated patterns on substrates with radii of curvature from 5 cm to 25 μ m.³⁰ We could use the same process to pattern curved substrates with palladium colloids (Figure 4). The curved substrate was rolled across the "inked", patterned stamp. The colloid was transferred from the raised regions of the stamp to the surface of the substrate. Figure 4 shows a photograph of a copper film deposited on a glass bottle (r = 1.25 cm). As demonstrated by the inset in Figure 4, the resolution of the features on the curved substrate is similar to that on planar substrates.

Microcontact Printing of Colloids Allows the Fabrication of Free-Standing Metal Structures. We have used two procedures to fabricate free-standing metal structures with micron-scale features using *u*CP of colloids. One takes advantage of the high internal stress of the electroless copper layer; this stress leads to delamination once the total stress of the electroless copper layer exceeds the adhesion strength.³¹ When the film delaminates, it can be floated away and redeposited on another substrate. This sequence is shown in Figure 5A–D. With increasing plating time (from A to D), the copper structure became thicker and thicker. As soon as the internal stress exceeded the adhesion, the copper film started to delaminate.



Figure 5. SEM image of copper structures on a (Si/SiO_2) substrate. The substrate was immersed in the plating bath for increasing time $(A \cup D)$. With increasing plating time, the film thickness became thicker and the internal stress in the film increased. As soon as the internal stress exceeded the adhesion forces, the copper microstructure delaminated (B, C). Finally the entire structure came off (D).



Figure 6. SEM image of a free-standing copper structure fabricated by aCP of colloids on glass followed by electroless deposition of copper. The copper film then was detached from the substrate by dissolution of the glass in a dilute aqueous solution of HF. The film was floated away and deposited on another substrate. Although the folding of the sample was accidental, it illustrates the flexibility of the structure.

nate, first only at the edges of the features (B, C), then over larger areas until the entire structure came off (D).

A second possible route to free-standing structures is the dissolution of the substrate after the film has reached the desired thickness. We demonstrated the principle using a glass as a substrate. The copper film was detached from the substrate by dissolution of the surface layer on the substrate with a dilute aqueous HF solution. Figure 6 shows a free-standing copper film of about 500 nm thickness. After the film separated from the glass substrate, it was picked up carefully with tweezers and placed on another glass slide.

Microcontact Printing of Colloids Allows the Fabrication of Multilevel Microstructures. Most

^{(28) &}quot;Complete adhesion" means that no copper residues were visibleon the Scotch tape after the tape was peeled off the sample.(29) The strength of adhesion was qualitatively determined by the

amount of metal removed by the Scotch tape test. (30) Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M. Science **1995**.

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Figure 7. μ CP of colloids allows the fabrication of multilevel microstructures by using double stamping of the substrate. The AFM picture shows a grid of 10 μ m lines that was produced by the double-stamping technique. The height difference between the two levels is about 400 nm. Areas on the metal film that were not covered with palladium colloid during the second stamping are slightly thicker and broader than are the treated regions.

electroless deposition processes produce a film of approximately uniform thickness. We have developed two different ways of fabricating metal structures whose thicknesses are varied in different regions (multilevel metal structures). The first method is based on the fact that the thickness of the metal film depends on the duration of plating. After stamping and depositing copper, the process of *uCP* of colloids and metalization can be repeated with the same substrate and can generate a copper microstructure with different thicknesses. Figure 7 shows the AFM image of a copper microstructure that was fabricated by (i) stamping one set of lines, (ii) metalization, (iii) stamping another set of lines perpendicular to the first one, and (iv) repeating metalization. The areas on the metal film that were not covered with palladium colloid during the second stamping are slightly thicker and broader than the untreated regions, because copper catalyzes the oxidation of formaldehyde more effectively than palladium.⁵ Electroless plating is an isotropic process: during the metalization process, the lines grow both thicker and broader. The deposition of a thin layer of palladium colloids during the second μ CP resulted in a slight retardation of the copper deposition in these areas in all directions.

Another way to obtain microstructures with different layer thicknesses was to use a PDMS stamp that itself had relief structures of different heights. As Figure 8 suggests, the multilevel information in the PDMS stamp could be transferred in the copper film. So far we have been unable either to control the difference in height between the different levels or to fabricate reproducibly structures like the ones shown in Figure 8, but the demonstration that these structures can be generated constitutes a proof of principle.



Figure 8. SEM images of a copper microstructure fabricated by *u*CP of colloids using a PDMS stamp that had relief structures of different heights. The height information in the PDMS stamp was transferred to the copper film resulting in a microstructure with different thicknesses.

Conclusion

This work demonstrates a new method of patterning surfaces with a catalyst for the selective deposition of metals. Microcontact printing (μ CP) of a colloidal catalyst uses a patterned elastomeric stamp to deliver the catalysts to the pretreated substrate surface. μ CP of colloids is experimentally simple and can be carried out in the open laboratory. It is capable of routinely generating metal structures with features having submicron dimensions. The technique is flexible: it allows patterning on various substrates, including glass, (Si/SiO₂), and polymers. Flat and curved surface substrates can be used without loss of resolution. μ CP of colloids can also be used to produce free-standing metal structures and metal films with different thicknesses.

Experimental Section

All solvents were of reagent quality and used without further purification. All organosilanes used in this study ((3-aminopropy))triethoxysilane (Huels), (3-mercaptopropy))triethoxysilane (Huels), (3-cyanopropy))triethoxysilane (Huels), octadecyltrichlorosilane (Aldrich), and (3-((2-aminoethyl)amino)propy))trimethoxysilane (Fluka) were used without further purification.

Substrate Pretreatment. Glass substrates (cover glass No. 2, Corning) were cleaned immediately before use by soaking in freshly prepared "piranha" solution (7:3 (v/v) mixture of concentrated H_2SO_4 and 30% H_2O_2) for at least 30 min. (**CAUTION:** "Piranha" solution reacts violently with many organic materials and should be handled with extreme care!) The cleaned substrates were rinsed thoroughly with deionized H_2O and dried under a stream of nitrogen.

Silicon substrates were n-type semiconductor grade silicon $\langle 100 \rangle$ wafers (2 in. diameter) from Silicon Sense Inc. They were immersed immediately before use in a freshly prepared "piranha" solution for 30 min. The substrates then were rinsed thoroughly with deionized H₂O and dried under a stream of nitrogen.

Polystyrene (2 mm thick sheets, crystalline), polyethylene (0.5 mm thick sheets), and polyimide (0.125 mm thick films) from

Goodfellow were oxidized by soaking in CrO_3/H_2SO_4 for 1 min.³² The oxidized substrates were rinsed thoroughly with deionized H₂O and dried under a stream of nitrogen. Polyvinylidene chloride (Saran Wrap, Dow Chemical) was treated with a lowpower, radio frequency oxygen plasma in a Harrick plasma cleaner (Model PDC-23G) for 5 min at an oxygen pressure of 30 mbar.

After this pretreatment, the substrates were immersed in a solution of organosilanes (50 mM) in heptane for 1 h. After rinsing with heptane and drying under a stream of nitrogen, the substrates were used for the stamping procedure. Only freshly prepared substrates were used.

Palladium Colloids. The tetraoctadecylammonium bromide stabilized palladium colloid $(Pd/[C_{18}H_{37}]_4N^+Br^-)$ was synthesized as follows: 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 addition of 25 mL of absolute ethanol, 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 with vigorous shaking. 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, ${\sim}88\%$ yield based on palladium) containing ${\sim}79\,\mathrm{wt}\,\%$ of palladium was isolated. The powder was readily resuspended in toluene. The TEM image showed spherical, well-separated palladium particles of 7 nm diameter. A similar procedure was used to synthesize the palladium colloids stabilized with tetrabutylammonium bromide (Pd/[C_4H_9]₄N⁺Br⁻), tetraoctylammonium bromide (Pd/[C_8H_{17}]₄N⁺Br⁻), and tetradodecylammonium bromide $(Pd/[C_{12}H_{25}]_4N^+Br^-)$. The solvents were THF for the synthesis of $(Pd/[C_4H_9]_4N^+Br^-)$ and $(Pd/[C_8H_{17}]_4N^+Br^-)$ and a 1:1 (v/v)mixture of toluene and THF for the synthesis of $(Pd/[C_{12}H_{25}]_4N^+)$ Br^{-}

The suspensions of colloidal palladium (Pd/[$C_{18}H_{37}$]₄N⁻Br⁻) were prepared by dissolution of 0.3 g of the powder in 200 mL of toluene and sonication in an ultrasound bath for 5 min. (Pd/ [C_4H_9]₄N⁺Br⁻) was soluble in DMF, (Pd/[C_8H_{17}]₄N⁻Br⁻) in THF, and (Pd/[$C_{12}H_{25}$]₄N⁺Br⁻) in toluene. The solutions were stable and active for months while in solution²⁰ and could be handled in air.

(32) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. Langmuir 1988, 4, 921-937. μ CP of the Catalyst. The elastomeric stamps used for the direct stamping process of the palladium colloids were fabricated as reported previously.¹⁵ The PDMS stamp was "inked" with the colloid by immersion of the stamp in the colloidal suspension for 2 s, removal of the stamp, and drying under a stream of nitrogen. This procedure was repeated two to three times. The stamp then was placed in contact with the pretreated substrate for 15 min. When we patterned curved substrates,³⁰ the contact time was only a few seconds, but still long enough to allow the transfer of the colloid onto the substrate.

Electroless Metal Deposition. For the electroless deposition of copper, we used the following copper plating bath:³³ Solution A contained 3 g of CuSO₄, 14 g of sodium potassium tartrate (Rochelle salt), and 4 g of NaOH in 100 mL of distilled water. Solution B was an aqueous formaldehyde solution (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 in the mixture for 30–600 s at room temperature. The plating time to achieve a certain film thickness depended on the age of the plating bath and the type of substrate. The plating process could be stopped by removal of the sample and rinsing 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). TEM was performed on a Phillips EM420 microscope. Optical microscopy was carried out using a Leica instrument.

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