Use of Electroless Silver as the Substrate in Microcontact Printing of Alkanethiols and Its Application in Microfabrication

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We have employed electroless deposition to prepare smooth films (mirrors) of silver that could be used as substrates in microcontact printing (μCP) of alkanethiols. Good-quality SAMs of hexadecanethiolate were formed on thin films of electroless silver by printing with an elastomeric stamp; these SAMs were effective resists in protecting the underlying silver from etching in an aqueous ferricyanide solution. Thin films of silver prepared by electroless deposition show a granular morphology (the grain sizes are ∼30−60 nm) and have a rougher surface than those prepared using e-beam or thermal evaporation. As a result, hexadecanethiol liquid spreads more rapidly on electroless silver than on evaporated silver when μCP is carried out in air. This process of reactive spreading limits the resolution and fidelity of pattern transfer to electroless silver films by μCP, but could also be used as a convenient method for reducing the sizes of features of SAMs generated using μCP. The smallest features that we have fabricated using this method were trenches etched in electroless silver (∼40 nm thick) with lateral dimensions of ∼200 nm. The procedure demonstrated here allows us to form micropatterns and microstructures without the metal evaporation usually used to prepare the substrates for μCP, and thus opens μCP and related techniques of microfabrication to those who do not have access to the equipment required for evaporation or sputtering of silver. It also makes it possible to carry out micropatterning on hidden surfaces that could not be silvered by evaporation (for example, the *inside* surface of a glass tube or flask).

Introduction

This paper describes the use of electroless deposition (a typical example is the Tollens' process) to prepare thin films of silver for use as substrates in microcontact printing (μCP)[1] to form patterns of self-assembled monolayers (SAMs)[2] of alkanethiolates. Subsequent etching of SAM-patterned silver in an aqueous ferricyanide solution produced microstructures of silver that could be further used as masks in the etching of the underlying layer such as glass or SiO_2.

Microcontact printing using SAMs is a cost-effective strategy for forming small, high-quality structures that requires very little in capital investment. This procedure is remarkable for its simplicity and speed. Combining with selective etching and deposition, this procedure is immediately applicable to a variety of tasks in microfabrication that do not require multiple superimposed patterns with accurate registration between them, for example, preparation of sensors, microelectrode arrays, optical components, microanalytical systems, consumer electronic systems, and supports for cell culture.[3] Currently, microcontact printing is capable of routinely generating patterns of SAMs with feature sizes of ∼500 nm; it can also produce features as small as ∼100 nm, albeit less reproducibly.[4] We and other groups have applied μCP to a number of systems of SAMs,[3] with the

Table 1. Comparison between SAMs of Hexadecanethiolate Formed on Thin Films of Silver Prepared Using Different Methods

method	prepn[a]	SAM thickness (Å)	contact angle of H_2O (deg)		
			θ_a	θ_r	$\cos\theta_r - \cos\theta_a$
e-beam	(a)	∼25	111	100	0.185
	(b)	∼24	111	99	0.202
	(c)	∼22	108	97	0.187
electroless (solution)	(a)	∼24	112	96	0.254
	(b)	∼22	111	95	0.271
	(c)	∼17−21	110	95	0.254
electroless (spray)	(a)	∼24	111	95	0.271
	(b)	∼23	111	95	0.271
	(c)	∼17−22	109	94	0.255

[a] (a) The samples were prepared by immersing the substrates in a 2 mM solution of HDT in ethanol for 2 min; (b) the samples were prepared by μCP and the stamp was in contact with Ag for ∼20 s; (c) the samples were prepared by μCP, and the stamp was in contact with Ag for ∼5 s.

best-established ones being SAMs of alkanethiolates on evaporated thin films of gold and silver.[5,6] Microcontact printing of alkanethiols on silver surfaces seems to be particularly interesting and useful for applications in microfabrication because etching protocols for silver are more convenient to use than those for gold, and patterns of silver fabricated using the combination of μCP and selective etching in an aqueous ferricyanide solution have higher edge resolution and far fewer defects than those of gold fabricated using a similar procedure.[6]

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(1) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002.

(2) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(3) For a recent review, see: Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Microelectron. Eng.* **1996**, *32*, 255.

(4) (a) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274. (b) Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 471.

(5) Kumar, A.; Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.

(6) Xia, Y.; Kim, E.; Whitesides, G. M. *J. Electrochem. Soc.* **1996**, *143*, 1070.

(A) Silver by e-beam evaporation
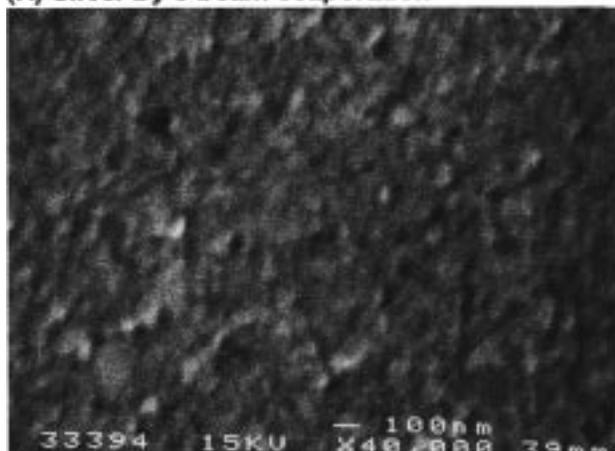
(B) Silver by electroless deposition (solution)
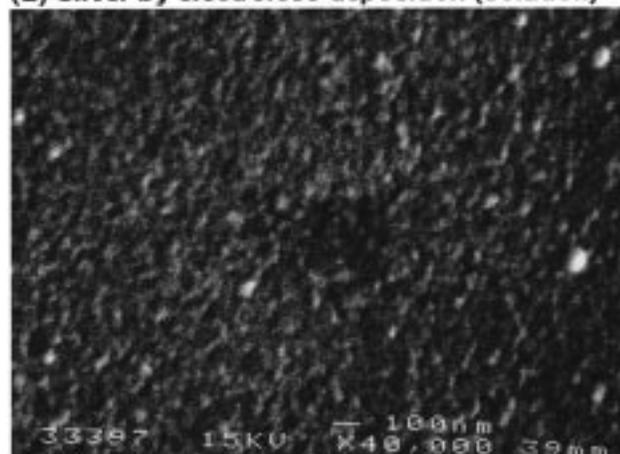
(C) Silver by electroless depostion (spray)

― 100 nm
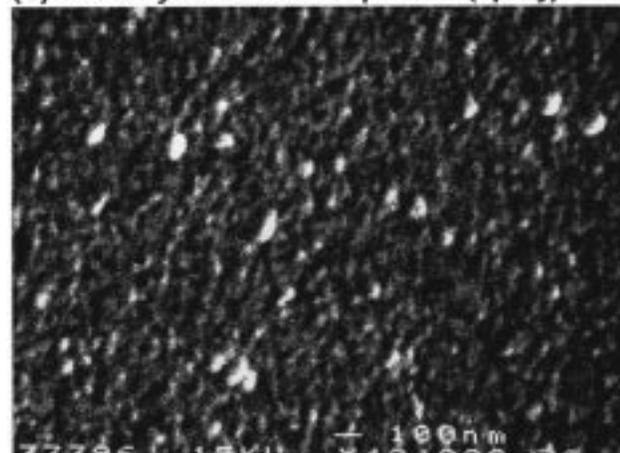
Figure 1. SEM images of thin films of silver prepared on Si-(100) wafers by (A) e-beam evaporation (40 nm thick) and (B, C) electroless deposition (~40 nm thick), respectively. The samples were tilted 45° when taking SEM images.

Figure 2. SEMs of test patterns of silver that were fabricated using μCP with HDT, followed by selective etching in an aqueous ferricyanide solution for ~14 s. The PDMS stamp was in contact with the surface of the substrate for ~20 s. The thin films of silver were prepared by (A) e-beam evaporation (40 nm thick) and (B) electroless deposition (~40 nm thick) from the spray of the silvering bath, respectively. The bright regions are silver protected by the SAM; the dark regions are bare Si/SiO$_2$ where underivatized silver has dissolved.

One of the most significant advantages of μCP over conventional photolithography is that μCP has the capability to form patterns on nonplanar surfaces.[7] This application is, however, limited by the evaporation methods (for example, thermal or e-beam evaporation)

that are currently used to prepare thin films of metals. Because metal evaporation is a line-of-sight deposition technique, shadowing precludes the formation of uniform coatings of metals on nonplanar surfaces with steep edges, on inside surfaces of hollow tubes, or on other hidden surfaces. Here we report an alternative method for forming thin films of silver that can be used as substrates to form patterns of SAMs of alkanethiolates using μCP. This method is based on electroless deposition, in which an aqueous silvering bath is used to form smooth coatings of silver on surfaces with a wide range of topologies.

(7) Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M. *Science* **1995**, *269*, 664.
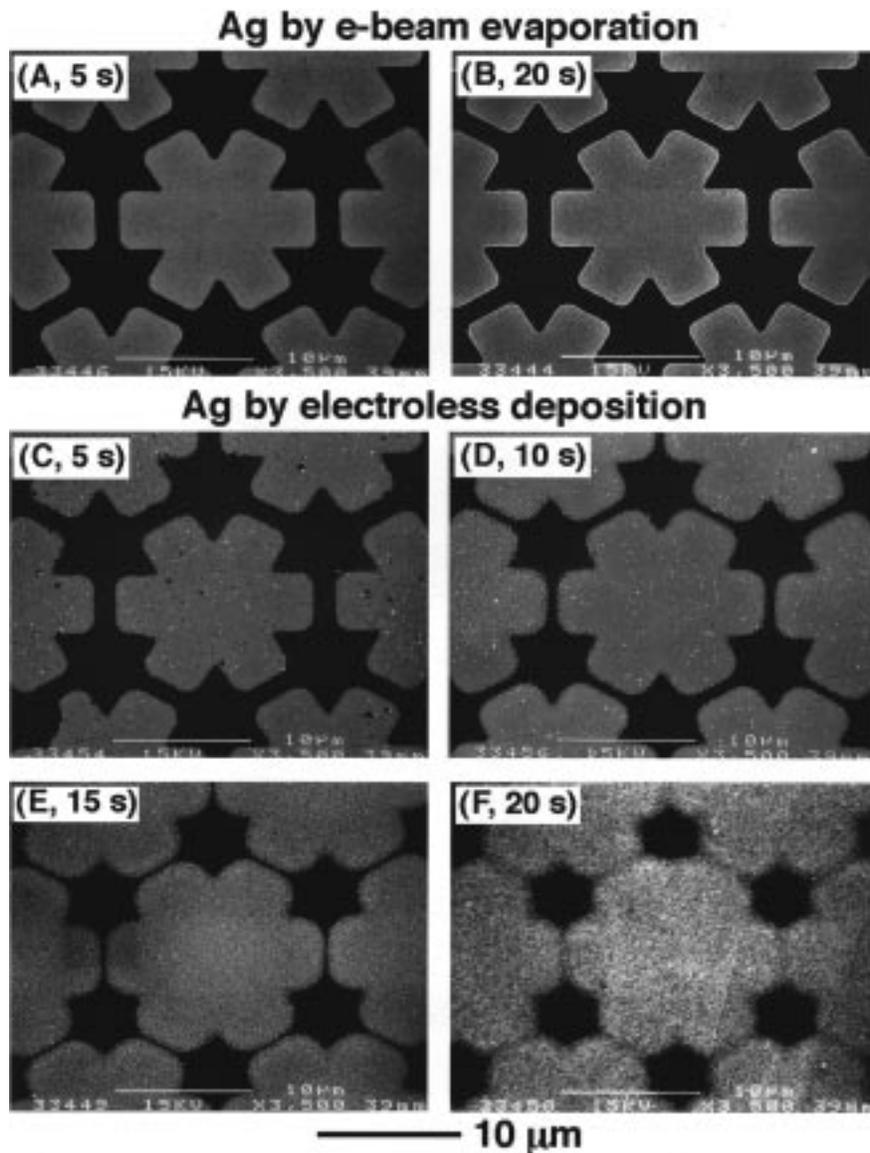
Figure 3. SEM images of test patterns of silver fabricated using μCP with HDT, followed by selective etching for ~14 s. The PDMS stamp was in contact with the surface of the substrate for different intervals of time. The thin films of silver were prepared by (A, B) e-beam evaporation (40 nm thick) and (C–F) electroless deposition (~40 nm thick) from the spray of the silvering bath, respectively. The bright regions are silver protected by the SAM; the dark regions are bare Si/SiO$_2$ where underivatized silver has dissolved.

Because electroless deposition usually produces thin films of silver with grain structures and surface morphologies different from those prepared by e-beam or thermal evaporation, and because the chemistry of the surfaces prepared by e-beam and electroless deposition may also be different, it was not clear that μCP of alkanethiols would be as successful on thin films prepared by electroless deposition as on those prepared by metal evaporation. In fact, the patterns prepared this way appear to be equivalent to those prepared by conventional procedures, except that hexadecanethiol spreads more rapidly on electroless silver than on evaporated silver. This equivalence makes it possible to prepare patterned microstructures of silver on a variety of substrates without access to a metal evaporator, and on hidden surfaces that cannot be coated by metal evaporation.

Experimental Section

Substrates and Materials. Ag (99.999%), Ti (>99.99%), K$_2$S$_2$O$_3$, K$_3$Fe(CN)$_6$, K$_4$Fe(CN)$_6$, and CH$_3$(CH$_2$)$_{15}$SH were obtained from Aldrich. The elastomeric poly(dimethylsiloxane) (PDMS) was obtained from Dow Corning (Sylgard 184, Midland, MI). Si(100) wafers (Cz, N/Phosphorous-doped, test grade, SEMI Std. flats.) were obtained from Silicon Sense (Nashua, NH) and were covered by thin layers of either native oxide or thermally formed oxide (~2 μm thick). Hexadecanethiol (HDT) was purified under nitrogen by chromatography through silica gel. Evaporated films of silver (40 nm thick) were prepared by e-beam sputtering silver onto Si wafers primed with thin layers of Ti (2–3 nm thick).

Electroless Deposition of Silver on Si and Glass. Electroless deposition is similar to electrolytic plating except that no external electrodes are needed.[8] In electroless deposition, metal ions are directly reduced into metals by the introduction of a reducing agent. Although a variety of procedures and/or reagents have been demonstrated for electroless deposition of silver,[9] their fundamental mechanisms are similar to that of Tollens'

(8) Mallory, G. O.; Hajdu, J. B. *Electroless Plating: Fundamentals and Applications*; AESF: Orlando, FL, 1990.

(9) See, for example: (a) Ingalls, A. G. *Amateur Telescope Making, Book One*, Scientific American, Inc.: New York, 1981, Part VI. (b) Warrier, S. G.; Lin, R. Y. *J. Mater. Sci.* **1993**, *28*, 4868. (c) Chang, H.; Pitt, C. H.; Alexander, G. B. *J. Mater. Sci.* **1993**, *28*, 5207.
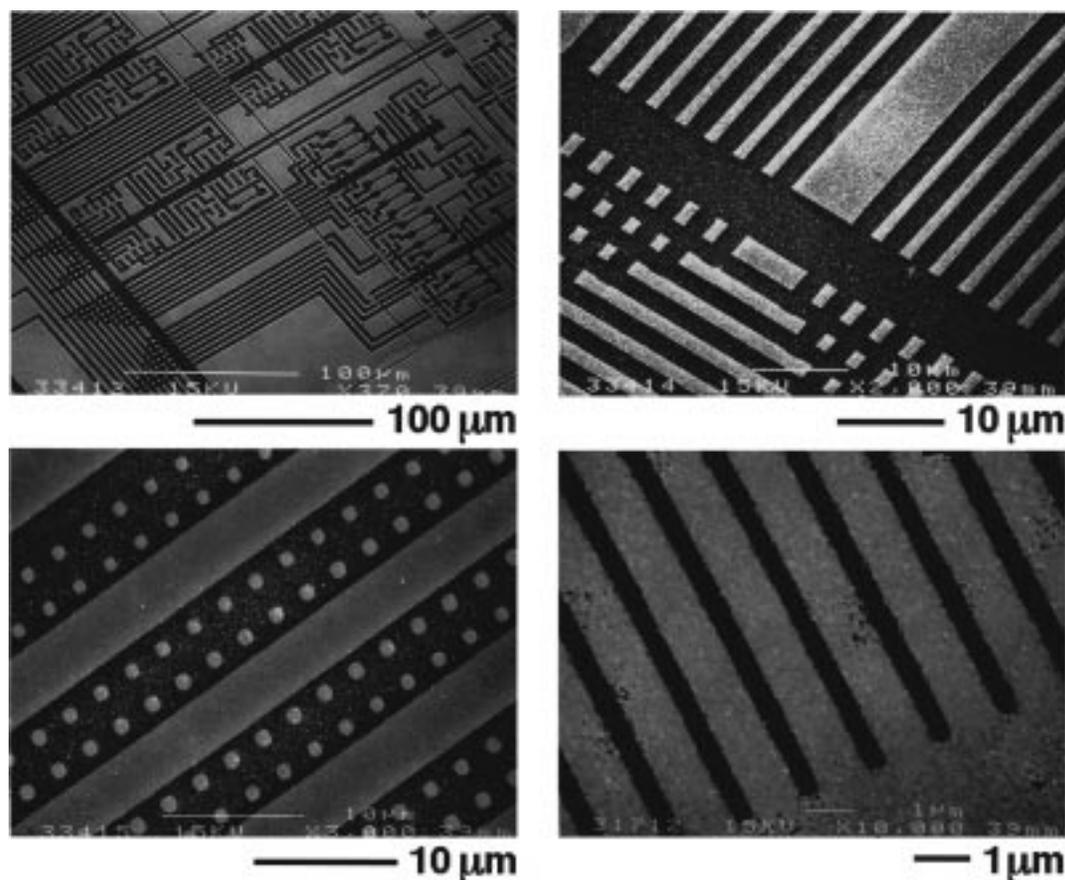
Figure 4. SEM images of test patterns of silver generated using μCP with HDT, followed by selective wet etching in an aqueous ferricyanide solution for ~14 s. The thin films of silver [~40 nm thick, supported on Si(100) wafers] were prepared using electroless deposition from the solution of the silvering bath.

process:[10]

$$RCHO(aq) + Ag^+(aq) \rightarrow RCOO^-(aq) + Ag(s)$$
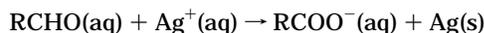
We have tried homemade Tollens' reagents to form silver coatings on glass and have successfully carried out μCP on these surfaces, but better results were obtained using a commercial silvering bath (HE-300, Peacock Laboratories, Philadelphia, PA).[11] This silvering bath is a three-part set consisting of the following concentrated solutions: (a) silver solution, (b) activator solution, and (c) reducer solution.[12] These solutions are sold separately and are mixed by users to give the silvering bath. Thin films of electroless silver used in the present work were prepared at Peacock Laboratories. The substrate was rinsed thoroughly with deionized water and washed with a solution of sensitizer (such as stannous chloride) that acted as a binding agent. Silver was then deposited onto the surface of the substrate while it remained wet using two different procedures: (1) silver was deposited directly from the silvering bath and (2) silver was deposited from a spray of the silvering bath. In silvering from the solution, the substrate was immersed in a diluted solution containing components a, b, and c for a period of time and then taken out. In silvering from the spray, two diluted solutions (one containing components a and b; the other, c itself) were simultaneously sprayed onto the substrate by the use of a two-nozzle air gun. A cross-spray technique was used: the surface was first sprayed horizontally from bottom to top, and then top to bottom, followed by spraying vertically in a similar way. The number of passes, concentrations of solutions, and overlap were

(10) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon, Inc.: Boston, 1987; p. 777.

(11) The chemicals and equipment for electroless deposition of silver are available from Peacock Laboratories, Inc., 54th St. and Paschall Ave., Philadelphia, PA 19143; (215) 729−4400.

(12) *Instructions: Resilvering and Silvering New Glass−Spray Method*; Peacock Laboratories: Philadelphia, PA, 1991.

optimized by trial and error to obtain silver coatings with desired thicknesses, and suggestions for use are usually available from the vendor of the silvering bath. The deposited silver appeared in a dark blue color, and then quickly developed a bright, shiny color in the form of a silver mirror. Following the deposition of silver, the substrate was thoroughly rinsed with deionized water and dried under a stream of air.

Microcontact Printing (μCP). PDMS stamps were fabricated according to the published procedure.[1] A solution of HDT in ethanol (~2 mM) was used as the "ink" for μCP. After applying the "ink" (by cotton Q-tip), the PDMS stamp was dried in a stream of nitrogen gas for ~1 min and then brought it into contact with the surface of the substrate. The stamp was in contact with the surface of silver for an interval of ~2 s, unless otherwise mentioned in the text.

Etchings of Ag and SiO$_2$. The etchant used for SAM-patterned films of silver was an aqueous solution containing $K_2S_2O_3$ (0.1 M), $K_3Fe(CN)_6$ (0.01 M), and $K_4Fe(CN)_6$ (0.001 M).[6] Silicon dioxide was etched in an unbuffered aqueous HF solution (~1%, w/w).

Instrumentation. SEM images were taken using a JEOL JSM-6400 scanning electron microscope. The accelerating voltage was 15 kV.

Results and Discussion

Surface Morphologies of Thin Films of Silver Prepared by Different Methods. Figure 1 shows high-resolution SEM images of thin films (~40 nm thick) of silver prepared using e-beam evaporation and electroless deposition, respectively. The evaporated silver formed continuous films with a relatively flat surface morphology: the grain sizes of these films were ~100−200 nm. Electroless silver formed granular films. The thin films of electroless silver deposited from the solution and the spray of the silvering bath were essentially the same; they

Figure 5. SEM images of test patterns of silver generated using μCP with HDT, followed by selective wet etching in an aqueous ferricyanide solution for ~12 s. The thin films of silver (~40 nm thick, supported on glass substrates) were prepared using electroless deposition from the spray of the silvering bath.

were made of small particles of silver with diameters in the range of ~30–60 nm. They have a rougher surface morphology than those prepared using evaporation.

HDT SAMs on Thin Films of Silver Prepared by Different Methods. The morphology of a surface usually affects the wetting and spreading of a liquid on this surface.[13–15] For example, DiMilla et. al. found that the morphology of a solid surface significantly affected the hysteresis in the forwarding and receding contact angles of liquids.[16] They measured contact angles of water and hexadecane on HDT SAMs formed on thin films of gold with different thicknesses and found that the hysteresis became more significant as the thickness of gold increased. They attributed this influence to the surface roughness since evaporated films of gold become rougher as the thickness increases. Table 1 compares the properties of SAMs of hexadecanethiolate formed on thin films of silver prepared by e-beam evaporation and electroless deposition, respectively. The thicknesses of SAMs formed on silver films prepared using these two methods were approximately the same when prepared under a similar condition. The hysteresis in the contact angles was smaller on evaporated silver than on electroless silver, an observation that is consistent with the previous study by DiMilla and co-workers.[16]

Reactive Spreading of HDT on Thin Films of Silver Prepared by Different Methods. Microcontact printing

relies its success on the rapid reaction of alkanethiols on the surface with formation of SAMs and on the "autophobicity" of the resulting SAMs.[17] Biebuyck et. al. demonstrated that the morphology of a gold surface influenced the spreading of HDT liquid on this surface and thus determined the resolution of patterning by μCP.[17] On the basis of lateral force microscopy (LFM) studies, they also suggested that the spreading of HDT liquid on a polycrystalline film of gold seemed to be trapped in the "valleys" approximately 20 nm across between the "hillsides" of gold crystallites approximately 100 nm across.[17] This suggestion implies that HDT liquid spreads more rapidly on those surfaces without the presence of "valleys", that is, granular films such as electroless silver. The crevices in a rough surface may also facilitate the spreading of a liquid on this surface.

Figure 2 compares μCP of HDT on thin films of silver prepared by e-beam evaporation and electroless deposition, respectively. The PDMS stamp used here had ~2-μm lines separated by ~2 μm. The SAM-patterned surfaces of silver were etched in an aqueous ferricyanide solution for ~14 s to dissolve the bare regions underivatized by HDT SAMs. When μCP was conducted in air, the spreading of HDT on the evaporated silver was extremely slow and could be neglected in the interval of time (~20 s) during which the stamp was usually in contact with the surface of the substrate. The spreading of HDT on electroless silver was much more rapid than on evaporated silver. The lateral spreading of HDT reduced the dimensions of the bare regions: in this case, the width of bare regions was reduced from ~2 μm to ~200 nm over a period

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(14) Noda, I. *Chem. Ind.* **1991**, October, 749.

(15) Borgs, C.; De Coninck, J.; Kotecky, R.; Zinque, M. *Phys. Rev. Lett.* **1995**, *74*, 2292.

(16) DiMilla, P. A.; Folkers, J. P.; Biebuyck, H. A.; Härter, R.; López, G. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2225.

(17) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 4581.
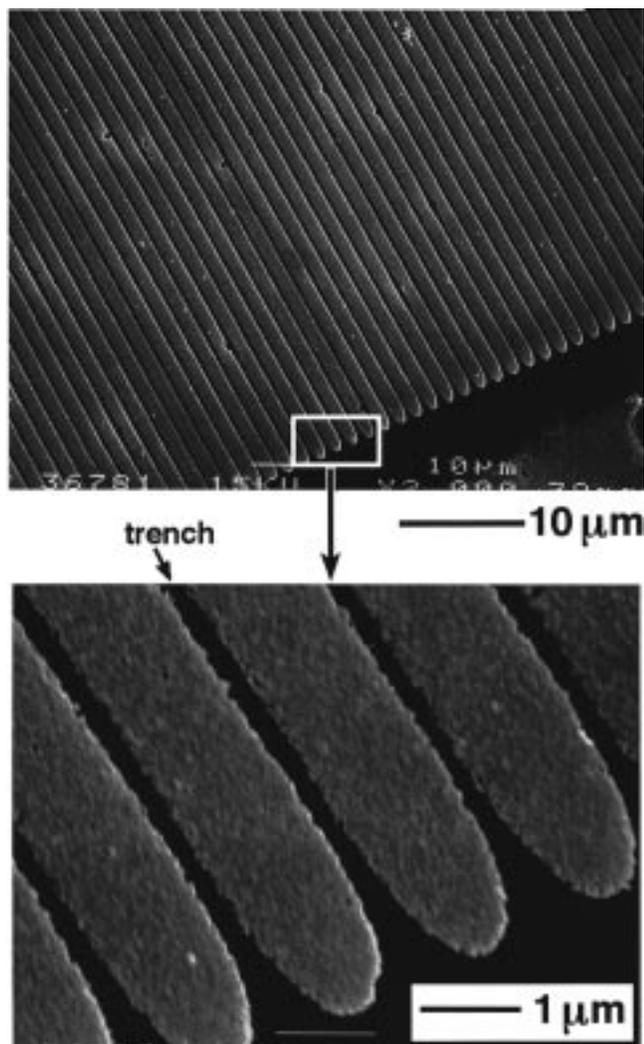
Figure 6. SEM images of submicron trenches etched in SiO_2 using an aqueous HF solution (~30 s). The mask was a pattern of electroless silver fabricated using μCP with HDT, followed by selective etching in an aqueous ferricyanide solution for ~14 s. The dark regions are trenches (~200 nm deep) etched in 2-μm-thick SiO_2 formed thermally on Si. After etching of SiO_2, the silver mask was removed by immersion in the ferricyanide etching solution for ~2 min.

of ~20 s; the edge of the patterned SAM advanced at an average rate of ~40−50 nm/s for an ~2 mM solution of HDT in ethanol.

Figure 3 illustrates the spreading of HDT liquid on electroless silver when a complex test pattern was used. The advancement of the edges of SAM-covered regions can be clearly seen from these SEM images. The spreading of HDT on electroless silver seemed to occur predominately from the edge of the patterned SAM beyond the area of the stamp in contact with the substrate and advanced at approximately the same rate from each point on the edge of the pattern. The rapid spreading of HDT liquid on electroless silver limits the use of this system for certain types of applications in which accurate transfer of patterns is the prerequisite. This process, however, can be employed to reduce the size of certain features of a pattern and provides a simple and potentially useful route to nanometer-sized features (see, Figures 2B and 3E) without using advanced lithographic techniques.[4]

Selective Chemical Etching of Electroless Silver with Printed SAMs as Masks. Patterned SAMs of hexadecanethiolate on electroless silver served as na-
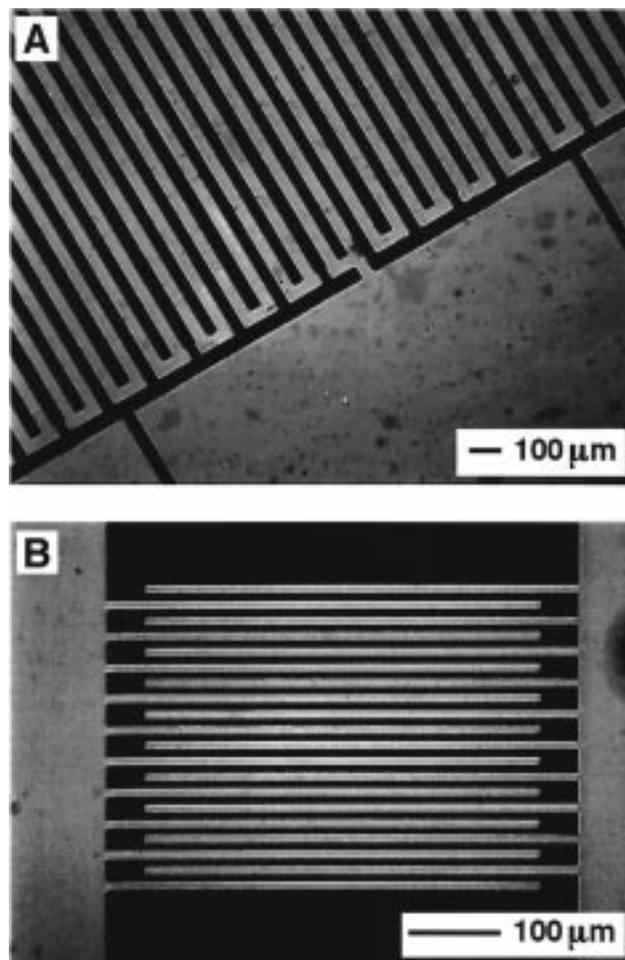
Figure 7. SEM images of test patterns of silver used for conductivity (A) and isolation (B) measurements. The patterns were generated using μCP with HDT, followed by selective etching in an aqueous ferricyanide solution for ~15 s. The thin films of silver [~40 nm thick, supported on Si(100) wafers covered with 2-μm-thick SiO_2] were prepared using electroless deposition from the spray of the silvering bath.

nometer-thick resists that effectively protected the underlying silver from certain etchants. The one that worked best in the present work was an aqueous solution containing $K_2S_2O_3$, $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$.[6] The relatively rapid spreading of HDT on electroless silver ultimately limits the resolution and accuracy of patterning based on this system. One way to reduce the extent of spreading is to shorten the time during which the stamp is in contact with the surface of the substrate. We found a contact time of ~2 s was long enough to form patterned SAMs with high enough coverage and good enough quality that could withstand the attack from the ferricyanide etchant. This short contact time allowed us to produce and transfer submicron patterns and structures of silver with relatively good accuracy and edge resolution. Figure 4 shows SEM images of test patterns of silver on Si/SiO_2 that were fabricated using μCP with HDT, followed by selective etching. Figure 5 shows SEM images of silver on glass substrates that were generated using a similar procedure. The contact time between the stamp and the silver surface was ~2 s. These SEM images represent the level of complexity, perfection, and scale that can be produced routinely using μCP of HDT on electroless silver. The ability to generate arrays of microstructures of silver with controlled shapes and dimensions is directly useful in fabricating optical components such as optical diffrac-
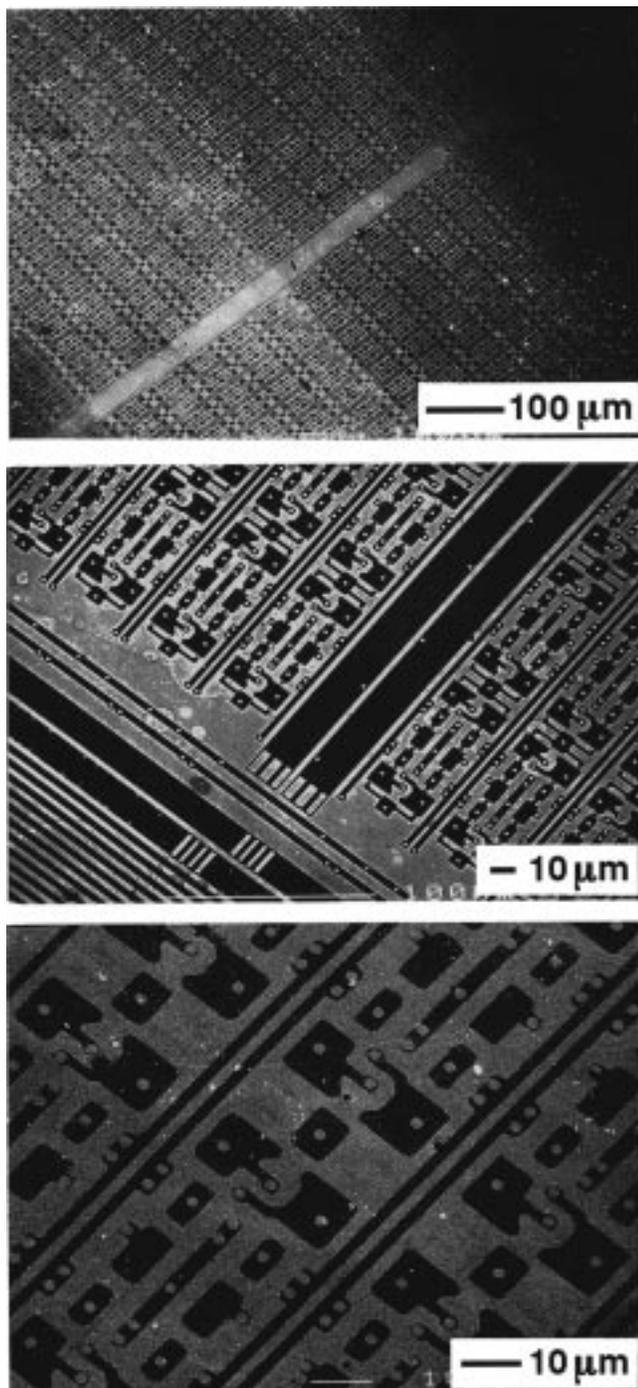
Figure 8. SEM images of test patterns of silver on the outside of a glass capillary that were fabricated using μCP with HDT, followed by selective wet etching in an aqueous ferricyanide solution for ~15 s. The thin film of silver was prepared using electroless deposition by immersion in the silvering bath for ~1 min. The capillary had a diameter of ~1 mm.

tion gratings and arrays of microelectrodes for sensors and electroanalytical chemistry.

Because no primer (typically Ti or Cr, with evaporated silver) was used when preparing electroless silver coatings, patterned structures of this silver could not stand the harsh condition usually used for the anisotropic etching of Si. The electroless silver was lifted off as soon as the substrate was immersed in the hot aqueous KOH solution. The patterns of electroless silver, however, could be used as masks in the isotropic etching of SiO_2 in a dilute aqueous HF solution. Figure 6 shows SEM images of submicron
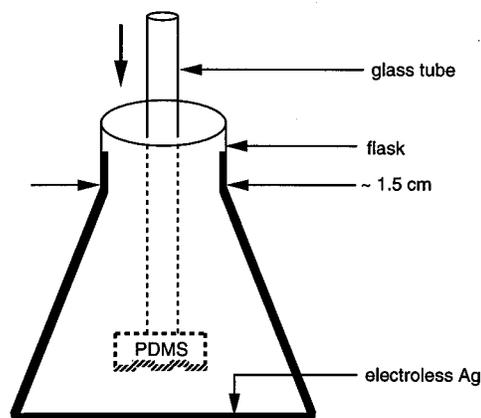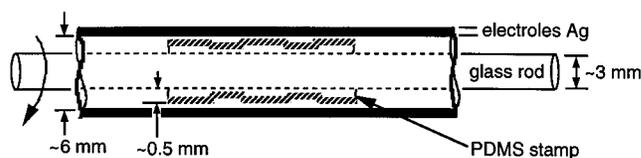
Figure 9. Schematic illustration of procedures used to form patterns of HDT SAMs on electroless silver deposited on (A) the bottom of the inside of an Erlenmeyer flask and (B) the inside surface of a hollow glass tube.

trenches that were etched in a 2-μm-thick SiO_2 layer with a pattern of electroless silver as the mask. The silver pattern was, in turn, generated using μCP with HDT, followed by selective chemical etching in an aqueous ferricyanide solution.

Conductivity and Isolation of Electroless Silver Patterns. Using the standard combination of μCP and selective wet etching, continuous silver wires (~50 μm in width, ~40 nm in thickness, ~0.2 m in length) suitable for the measurement of conductivity were fabricated on Si substrates that were covered by a 2-μm-thick layer of thermal SiO_2 (Figure 7A).[18] A resistivity of 2.2–2.6 $\mu\Omega$ cm was measured using the two-probe method (the resistivity reported for bulk silver is 1.6 $\mu\Omega$ cm);[19] this value indicates that the silver lines fabricated by the present method have the expected metallic conductivity.

An interdigitated array of silver lines (~40 nm thick, ~10 μm in width, separated by ~10 μm) was also fabricated on glass using a similar method (Figure 7B). The resistance across this array was measured to be ~2 MΩ. This value is about 6 orders of magnitude higher than that measured on the continuous region of the film of silver, indicating that the silver lines that are ~10 μm in separation are electrically isolated from each other.

Formation of Patterns of Electroless Silver on Nonplanar Surfaces. Microcontact printing has been extended to fabricate micropatterns and microstructures with well-defined edge resolution on curved substrates such as glass capillaries and optical fibers.[7] The incorporation of electroless deposition into this process further simplifies the procedure for patterning nonplanar surfaces.

(18) Qin, D.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 917.
(19) Kittel, C. *Introduction to Solid State Physics*, 6th ed.; John Wiley & Sons: New York, 1986; p 110.

(A) Ag pattern on the bottom of the inside of a flask

100 µm

10 µm
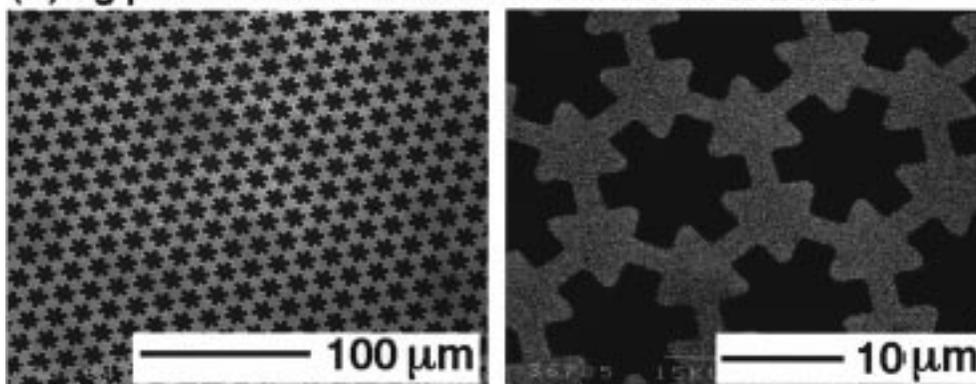
(B) Ag pattern on the inside of a glass tube

100 µm

10 µm
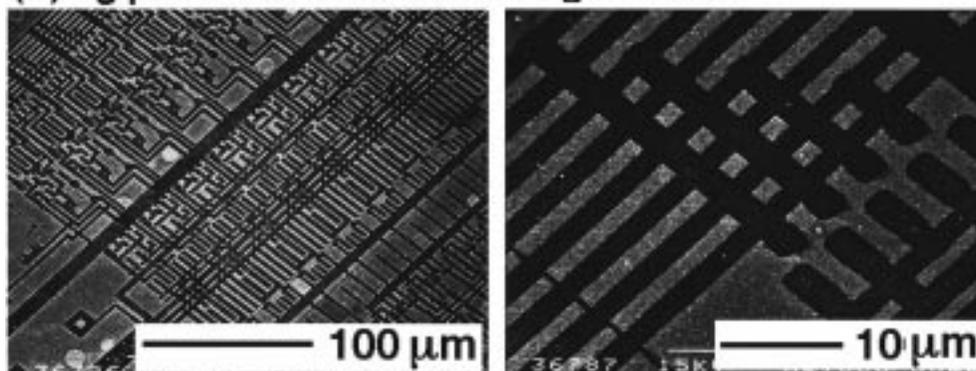
Figure 10. SEM images of test patterns of electroless silver formed on (A) the bottom of the inside of an Erlenmeyer flask and (B) the inside of a glass tube. The silver was deposited by immersing the substrate in the silvering bath for ~1 min. The silver patterns were generated using µCP with HDT, followed by selective etching in ferricyanide for ~15 s.

Figure 8 illustrates one example. A glass capillary (~1 mm in diameter) was coated with a thin film of electroless silver by immersion in the silvering bath for ~1 min, patterned with SAMs of hexadecanthiolate,[7] and selectively etched in an aqueous ferricyanide solution for ~15 s. The SEM images (at three different magnifications) of the test pattern clearly show well-defined features of silver with lateral dimensions of as small as ~1 µm. This procedure can be combined with electroplating and lift off to fabricate new types of electronic, optical, and analytical systems: for example, in-fiber gratings, capillaries for high-resolution NMR spectroscopy, micro inductors, microtransformers, intravascular stents, and microsprings.[20] This procedure should be especially useful where subsequent electrochemical deposition is used to thicken metallic patterns formed by µCP: in these fabrications, the edge roughness and defects in patterns produced on electroless silver will be buried by the electrodeposited metal.

Formation of Micropatterns of Electroless Silver on Hidden Surfaces. Figure 9 is a schematic illustration of procedures used to generate silver patterns on the bottom of the inside of an Erlenmeyer flask and on the inside of a glass tube. Figure 10 shows SEM images of test patterns of silver fabricated using the combination of µCP and selective wet etching. The silver was deposited by immersing the substrate in the silvering bath for ~1 min. After patterning with HDT using µCP, the substrate

was etched in an aqueous ferricyanide solution for ~15 s and then broken for SEM imaging. So far, it is impossible to generate patterns on these kind of hidden surfaces using photolithography or conventional µCP. We believe that this ability to form micropatterns and microstructures on hidden surfaces shown here will find applications in making new types of optical and analytical devices.

Summary

We have demonstrated electroless deposition as an alternative method for preparing thin films of silver to be used as substrates in microcontact printing of alkanethiols. This procedure allows us to prepare smooth coatings of silver on both planar and nonplanar surfaces and provides an effective route to microstructures of silver on these surfaces with submicron dimensions. It avoids the use of vacuum chamber, and can be applied to systems that will not stand vacuum or temperature (for example, a low-melting wax, an aqueous hydrogel, or a biological tissue). It can even be used to form micropatterns and microstructures on hidden surfaces such as the insides of hollow tubes and flasks. As a result of this study, we believe that thin films of silver prepared using other processes (for example, electrostatic spraying[21] and chemical vapor deposition (CVD)[22]) may also be satisfactory as substrates for use in microcontact printing of alkanethiols, although the edge resolution of the patterns formed will vary depending on the roughness of the surface. The ability

(20) See, for example: (a) Rogers, J. A.; Jackman, R. J.; Whitesides, G. M.; Wagener, J. L.; Vengsarkar, A. M. *Appl. Phys. Lett.* **1997**, *70*, 7. (b) Rogers, J. A.; Jackman, R. J.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 475. (c) Rogers, J. A.; Jackman, R. J.; Whitesides, G. M.; Olson, D. L.; Sweedler, J. V. *Appl. Phys. Lett.* **1997**, *70*, 2464.

(21) Hull, P. J.; Hutchison, J. L.; Salata, O. V.; Dobson, P. J. *Adv. Mater.* **1997**, *9*, 413.

(22) Dryden, N. H.; Vittal, J. J.; Puddephatt, R. J. *Chem. Mater.* **1993**, *5*, 765.

to prepare substrates using a wide range of methods extends the capability of μCP and will make it more useful and more widely accessible as a microfabrication technique.

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