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Selective Electroless Metal Deposition Using Microcontact Printing of Phosphine–Phosphonic Acid Inks

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Received January 14, 2004

We report a low-cost approach to selectively deposit films of nickel and copper on glass substrates. Our approach uses microcontact printing of organic inks containing phosphonic acid groups to bind the ink to a glass substrate and phosphine groups to bind a colloidal catalyst that initiates electroless metallization. We demonstrate this procedure by fabricating patterned nickel and copper films with areas as large as 15 cm² and minimum feature sizes of $\sim 2\ \mu\text{m}$. We present studies on the use of two ink types, an oligomer and a bifunctional molecule, and demonstrate that pattern quality and adhesion of the metallized films depends on the molecular weight of the ink and the ratio of phosphine and phosphonic acid groups.

Introduction

Electroless metallization is a solution-based, low-cost method of depositing metals such as copper, nickel, gold, silver, and cobalt onto either metallic or insulating substrates.¹ It is an important process widely used in microelectronics, packaging, and storage technologies to fabricate, for example, circuit lines in printed circuit board manufacturing, chip-level metal interconnects and contacts, and thin metal etch masks.² Current demand for low-cost electronics has generated great interest in developing methods for selective electroless metallization: that is, a method in which metal is electrolessly plated up from a predetermined pattern.³ Using a low-cost patterning method, such as microcontact printing, ink-jet printing, or screen printing, to define the metallization pattern would further lower manufacturing costs because these methods avoid the high capital and operating expenses associated with conventional photolithography. They are ideal for use in applications that do not require submicrometer fabrication: display technologies, such as liquid crystal displays, organic light-emitting diodes, and electronic paper, are leading targets. In this paper, we describe a new strategy for selective electroless metallization that uses microcontact printing to define a metallization pattern on a glass (SiO₂) substrate. We demonstrate its use by fabricating patterned electroless nickel and copper films with minimum feature sizes of 2 μm , over substrates as large as 15 cm².

The key to selective electroless metallization is the need for a catalyst to initiate metal deposition. In electroless metallization, metal ions in the electroless plating solution are chemically reduced to metal at the surface of a catalytic substrate or by a catalyst chemisorbed on the surface of an inert substrate. Palladium catalysts, in particular

palladium–tin colloids, are frequently used to activate inert substrates.⁴ After metallization is initiated, the initial layer of deposited metal autocatalyzes further metal deposition as a reducing agent in the electroless plating solution is oxidized. Two selective metallization approaches are, thus, possible: the selective deactivation of a catalytic substrate or the selective activation of an inert substrate.³ Selective electroless metallization schemes based on both approaches have been reported in the literature, the majority of which use photolithography for pattern definition.^{2d,5} The activation of inert substrates has also been accomplished using schemes based on microcontact printing^{6,7} and ink-jet printing.⁸ These low-cost patterning methods have been used to directly transfer a palladium catalyst onto an inert substrate.

The main drawback to using microcontact printing to transfer a palladium catalyst onto a substrate is the incompatibility of poly(dimethylsiloxane) (PDMS) stamps with many palladium catalyst solutions, including palladium–tin colloids. Polar solvents, the polarity of the catalyst itself, or a combination of these factors inhibit the deposition of the catalyst onto the surface of the hydrophobic PDMS stamp. Two approaches have been used to ameliorate this problem: either using a less polar catalyst solution with native PDMS stamps or rendering the surface of a PDMS stamp more hydrophilic for use with polar catalyst solutions. Using a less polar catalyst, such as tetraalkylammonium bromide-stabilized palladium nanoparticles, requires the use of solvents [toluene, tetrahydrofuran (THF)] that swell the stamp and can lead to distortion of the metallized pattern.⁶ This distortion is a serious drawback for microelectronic device fabrication,

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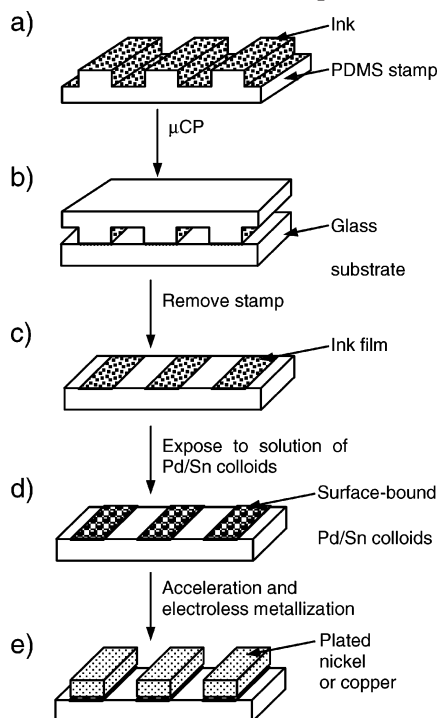
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Scheme 1. Schematic Outline of the Procedure for Selective Electroless Deposition

which requires registration of the selectively metallized pattern with other patterned layers. The best solvents for microcontact printing inks (i.e., those that cause the least amount of stamp swelling) are alcohols.⁹ Treatment of the PDMS stamp with an oxygen plasma renders the stamp surface more hydrophilic, thus allowing polar catalyst solutions to be used as microcontact printing inks.⁷ Unfortunately, this approach only temporarily alters the PDMS surface properties.

We present a new approach to selective electroless metallization that uses microcontact printing of 2-propanol-soluble organic inks containing phosphonic acid groups to bind the ink to a glass substrate and phosphine groups to bind palladium–tin colloids. We explore the use of two ink types, an oligomer and a bifunctional molecule, and demonstrate that pattern quality and adhesion of the metallized films depend on the type of ink. Scheme 1 outlines the steps for selective electroless metallization: (a) inking a PDMS stamp with the organic linker; (b, c) microcontact printing to transfer a film of the organic linker, which serves as a base for electroless metallization, to the SiO₂ surface; (d) uptake of a palladium–tin colloidal catalyst by the printed organic film; and (e) acceleration of the adsorbed catalyst and electroless metal deposition.

Experimental Section

Materials. 2,2'-Azobisisobutyronitrile (AIBN), *n*-butanethiol, trimethylsilylbromide, methyl ethyl ketone, and methylene chloride (Aldrich, Milwaukee, WI); octadecylphosphonic acid (ODPA; Lancaster Synthesis, Inc., Windham, NH); methanol, ethanol, and 2-propanol (Mallinckrodt Baker, Inc., Phillipsburg, NJ); Cataposit 44 concentrate, Cataprep 404, and Niposit 468 electroless nickel–boron plating bath (Shipley Co., Newton, MA); 1025 electroless copper plating bath and 1019 accelerator (Fidelity Chemical Products, Newark, NJ); and PDMS Sylgard 184 (Dow Corning Corp., Midland, MI) were all used as received. Vinyl-

benzenediphenylphosphine **1**¹⁰ and 2-(diphenylphosphino)ethylphosphonic acid **5**¹¹ were synthesized as reported in the literature. Diethyl 4-vinylbenzenephosphonate **2** was prepared using the synthetic procedure for phosphonation described in ref 12.

Poly(4-vinylbenzenediphenylphosphine-co-diethyl 4-vinylbenzenephosphonate) 3. AIBN (20 mg, 0.12 mmol) was added to a solution of 4-vinylbenzenediphenylphosphine **1** (1.73 g, 6 mmol) and diethyl 4-vinylbenzenephosphonate **2** (300 mg, 1.25 mmol) in 6 mL of 2-butanone containing 0.2 g of *n*-butanethiol. The resulting solution was refluxed for 3 h. After cooling to room temperature, the solvent was evaporated on a rotary evaporator. The oily residue was dissolved in 2 mL of dichloromethane and added dropwise to 100 mL of hexane with vigorous stirring. The precipitate was filtered, washed thoroughly with hexane, and dried in a vacuum oven to yield 751 mg of an off-white powder (37%). *M_n* = 1082; *M_w*/*M_n* = 1.04. ¹H NMR (400 MHz, 25 °C, CDCl₃): δ 7.60–6.84 (br, Ar-*H*), 4.02 (br, POCH₂-CH₃), 2.40–1.10 (br, POCH₂CH₃, CH₂, and CH). ³¹P NMR (162 MHz, 25 °C, CDCl₃): 4.9, 20.1.

Poly(4-vinylbenzenediphenylphosphine-co-4-vinylbenzenephosphonic acid) 4. Oligomer **3** (0.7 g) was dissolved in 5 mL of anhydrous dichloromethane and treated with 0.5 mL of bromotrimethylsilane. The solution was stirred under nitrogen for 18 h, after which time the solvent was evaporated under a reduced pressure. The oily residue was dissolved in 2 mL of anhydrous methanol and added dropwise to 50 mL of anhydrous diethyl ether. The white precipitate was filtered, washed with diethyl ether, and dried in a vacuum oven at 50 °C overnight to yield 644 mg (92%). ¹H NMR (250 MHz, 25 °C, CDCl₃): δ 7.41–6.93 (br, Ar-*H*), 2.51–2.23 (br, CH, and CH₂).

Solution Preparation. Solutions of colloidal palladium–tin catalyst were prepared from Cataposit 44 concentrate and solid Cataprep 404, as directed by the manufacturer. The Niposit 468 electroless nickel–boron plating bath and the 1025 electroless copper plating bath were prepared according to the manufacturers and then diluted by mixing 1 vol of the standard bath with 1 vol of water. The accelerator solution was a 5% solution of 1019 accelerator in water.

Substrate Preparation. Silicon wafers and glass substrates were cleaned for 10 min either by UV ozone treatment (Jelight, Inc., UVO-Cleaner model 144) for 10 min or by immersion in Piranha solution [a 7:3 (v/v) mixture of 98% H₂SO₄ and 30% H₂O₂], followed by rinsing in deionized water and drying on a 120 °C hotplate. *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.*

Stamp Preparation. Stamps were fabricated using a photolithographically defined master, according to published literature procedures.¹³

Stamp Inking and Printing. An ink solution of ODPA in 2-propanol (5 mM), **4** in 2-propanol (0.5 mg/mL), or **5** in 2-propanol (2 mM) was filtered through a 0.2-μm poly(tetrafluoroethylene) Acrodisc syringe filter. The surface of a PDMS stamp was flooded with the ink solution and left for 30 s. A stream of nitrogen was used to first blow off excess solution and then to thoroughly dry the stamp for 30 s, leaving a film of neat ink. Inked stamps were placed on the surface of clean glass or Si/SiO₂ substrates using tweezers, left for 1 min, and then removed. The patterned substrate was baked on a hotplate at 120 °C for 5 min and then allowed to cool.

Electroless Metallization. The printed samples were immersed in a solution of colloidal palladium–tin catalyst for 10 min with mild agitation, then removed, and rinsed thoroughly under a stream of deionized water. The wet substrate was then immersed in the accelerator solution for 2 min, removed, and rinsed gently with deionized water. The catalyzed and accelerated substrate was then metallized by immersion in either the Niposit 468 electroless nickel–boron plating bath (at 50–55 °C) or the 1025 electroless copper plating bath (at 25 °C). Plating times were typically 2–5 min.

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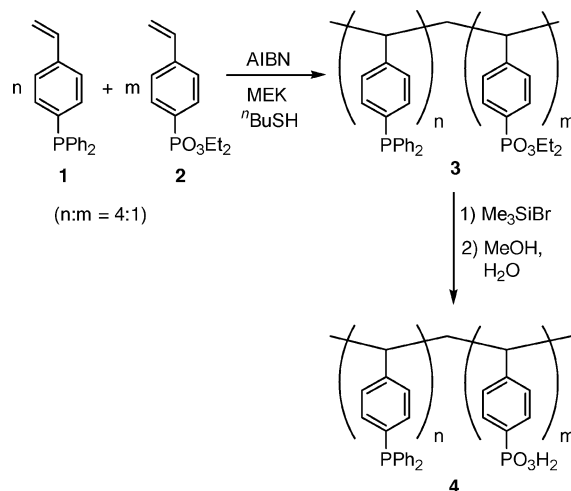
Characterization. ^1H , ^{31}P , and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were collected on a Bruker Avance 400 spectrometer (400 MHz for ^1H , 162 MHz for ^{31}P). Water contact angles were measured using the sessile drop method on an AST VCA-Optima 2500XE surface analysis system. Three readings from at least two samples were averaged. Optical inspection was performed using a Leitz Ergolux microscope. Scanning electron microscope (SEM) images were obtained using a LEO 1560 digital scanning microscope. Gel permeation chromatography (GPC) was performed on a Waters chromatograph (four Waters Styragel HR columns HR1, HR2, HR4, and HR5E in series) connected to a Waters 410 differential refractometer and tandem UV diode array detector with THF as the eluent. Molecular weight standards were narrow polydispersity polystyrene standards.

Results and Discussion

Design and Synthesis of Inks. In our approach to selective electroless metallization, the material ("ink") patterned on the substrate by microcontact printing acts as a base for electroless metallization. It performs the function of binding both to the substrate and to an electroless plating catalyst, thus requiring two different types of functional groups. These groups must not react with the PDMS stamp, and it is essential that the ink be soluble in ethanol or 2-propanol to minimize stamp swelling. The ink must also be sufficiently hydrophobic to coat the surface of the PDMS stamp yet have sufficient affinity to the glass substrate to transfer from the stamp to the substrate during printing. We chose phosphonic acid and phosphine functional groups to incorporate into microcontact printing inks. The first functional group, phosphonic acid, binds the ink to the surface of the glass substrate. Alkanephosphonic acids are convenient microcontact printing inks. They are stable to air and water and have previously been used as microcontact printing inks on aluminum oxide and indium tin oxide substrates.^{14,15} Alkyltrichloro- and alkyltrialkoxysilanes, which have been more commonly used as printing inks on SiO_2 ,¹⁶ are hydrolytically unstable and must be handled in an inert atmosphere to prevent cross-linking on the surface of the stamp. The second functional group, phosphine, binds the palladium–tin colloidal catalyst. Palladium–tin colloids consist of a palladium-rich core, which is the actual catalyst that initiates electroless metallization, protected from oxidation by a hydrolyzed $\text{Sn}^{2+}/\text{Sn}^{4+}$ shell. The chloride ions associated with this shell give the colloids a net negative charge to inhibit aggregation and allow the colloids to be electrostatically bound to positively charged functional groups on a substrate.⁴ We chose the phosphine group to bind the colloids for two reasons: First, its hydrophobicity balances the hydrophilicity of the phosphonic acid group to permit stamp inking. Second, phosphines react with acids to form positively charged phosphonium salts¹⁷ that electrostatically bind palladium–tin colloids. Although amine groups could also perform this function, we found that materials incorporating amines and phosphonic acids were less soluble and too hydrophilic to be transferred using a PDMS stamp.¹⁸

We incorporated phosphine and phosphonic acid functional groups in the ink material by synthesizing two types

Scheme 2. Synthesis of 4



of inks: an oligomer and a bifunctional molecule. Oligomer **3** was prepared by reacting styrene monomers functionalized with phosphine (**1**) and phosphonic ester (**2**) groups (Scheme 2). The phosphonic ester groups of oligomer **3** were then hydrolyzed to form oligomer **4**. The ratio of the two functional groups and the molecular weight were the key factors that determined the solubility of the oligomer and the ability of its solutions to wet PDMS stamps. A feed ratio of 5:1 phosphine/phosphonic acid monomers and drastically reducing the molecular weight using the chain transfer agent *n*-butanethiol produced an oligomer ink with $M_n = 1082$ that was soluble in both ethanol and 2-propanol. The broad ^{31}P NMR signals (4.9, 20.1) and multimodal GPC trace of **3** indicate that this material is likely a mixture of 2-, 3-, and 4-mers. Oligomers (or copolymers) with either higher molecular weights or a higher fraction of phosphonic acid were insoluble in ethanol and 2-propanol. The second ink, bifunctional molecule $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PO}_3\text{H}_2$ **5**, was prepared in a convenient three-step synthesis.¹¹ Bifunctional molecule **5** is soluble in ethanol and 2-propanol at concentrations suitable for microcontact printing (2–10 mM).

Affinity of Phosphonic Acid Groups to Glass Substrates. We tested the affinity of phosphonic acids for our glass substrates by printing a simple alkanephosphonic acid (ODPA, 2 mM in 2-propanol) with an unpatterned PDMS stamp onto a glass substrate. After removing the stamp, a visible film of the phosphonic acid remained on the substrate, indicating the formation of a multilayer film on the surface. Similar multilayers form when printing alkanephosphonic acids on aluminum oxide¹⁴ and indium tin oxide.¹⁵ Contact angle experiments showed that ODPA films on glass substrates required heating to drive the dehydration reaction between phosphonic acid groups and terminal hydroxide groups on the substrate surface. The contact angle of water on unbaked printed films (44.6°) was significantly lower than on films baked on a 110 °C hotplate for 5 min (100.6°). Although baked and unbaked films consist of equivalent amounts of printed ODPA, the water drop used in the contact angle measurement easily removes the ODPA in the unbaked film. Rinsing the unbaked film with water and ethanol yields similar water contact angles (38.5°). In contrast, rinsing baked ODPA films only slightly decreases the contact angle of water (93.7°). This decrease is probably due to the

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removal of ODPA multilayers, but no amount of rinsing could fully remove ODPA bound to the substrate by heating.

Conversion of Phosphine Groups to Phosphonium Salts. We studied the conversion of phosphine groups to phosphonium salts in **4** and **5** by solution ^{31}P NMR studies of **5** and contact angle measurements of water on printed films of both **4** and **5**. The resonance attributable to the phosphine group in compound **5** occurs at -10.3 ppm in CDCl_3 as a phosphorus-coupled doublet ($|J_{\text{P-H}}| = 64$ Hz) with no P-H coupling. Dissolving **5** in concentrated hydrochloric acid converted the phosphine groups to phosphonium salts: the phosphine resonance shifted to 9.1 ppm and exhibited P-H coupling ($|J_{\text{P-H}}| = 579$ Hz), in addition to the P-P coupling. The chemical shift and magnitude of the P-H coupling constant are comparable to spectral data for triphenylphosphonium chloride.¹⁹ Similar solution NMR experiments with oligomers **3** and **4** were precluded by their insolubility in concentrated hydrochloric acid. Contact angle measurements on printed films of **4** and **5** printed using unpatterned PDMS stamps support the notion that the phosphine groups convert to more polar phosphonium salts upon exposure to concentrated hydrochloric acid. The contact angle of water on printed films decreased significantly after immersion in concentrated hydrochloric acid for 1 min (from 82.6 to 48.9° for films of **4**, from 50.3 to 28.4° for films of **5**).

Selective Electroless Metallization. We used 2-cm^2 and 15-cm^2 PDMS stamps bearing an arbitrary pattern with features ranging from 200 to $2\text{ }\mu\text{m}$ to fabricate patterned films of **4** and **5** on clean glass substrates. Immersion of the patterned substrate in an aqueous solution of commercial palladium-tin colloids, which contains hydrochloric acid, accomplished the conversion of the phosphine groups to phosphonium salts and the binding of palladium-tin colloids. This step was followed by acceleration, in which the accelerator solution dissolves a portion of the $\text{Sn}^{2+}/\text{Sn}^{4+}$ protective shell to expose the catalytic core of the bound palladium-tin colloids. Immersion in either an electroless nickel plating bath or an electroless copper plating bath resulted in metal deposition selectively over the catalyzed regions of the substrate.

Figure 1 shows optical and SEM images of selectively metallized nickel films using oligomer **4** as the micro-contact printing ink. The patterned nickel films had thicknesses ranging from 200 to 500 nm, depending on the plating time. We observed three types of defects in the metallized patterns: first, small particles (<50 nm) deposited over both metallized and unmetallized regions of the substrate (Figure 1c,d). These were likely deposited by the plating bath, which we did not filter. Sonicating the metallized substrates in acetone removed many, but not all, of these particles and did not damage the nickel film. Second, large ($>3\text{ }\mu\text{m}$) holes were found in the patterned film. We attribute these to dust or air bubbles trapped between the stamp and the substrate because of ambient laboratory conditions and manual positioning of the stamp on the substrate. Third, nickel deposited on regions of the substrate outside the printed pattern. These defects are due to the transfer of **4** to these regions of the substrate, probably caused by manual stamp handling. In selective metallization, this type of defect is amplified, in contrast to other microcontact printing methods in which a patterned self-assembled monolayer is used as an etch resist and wet etching times can be tailored to remove such defects.¹⁵

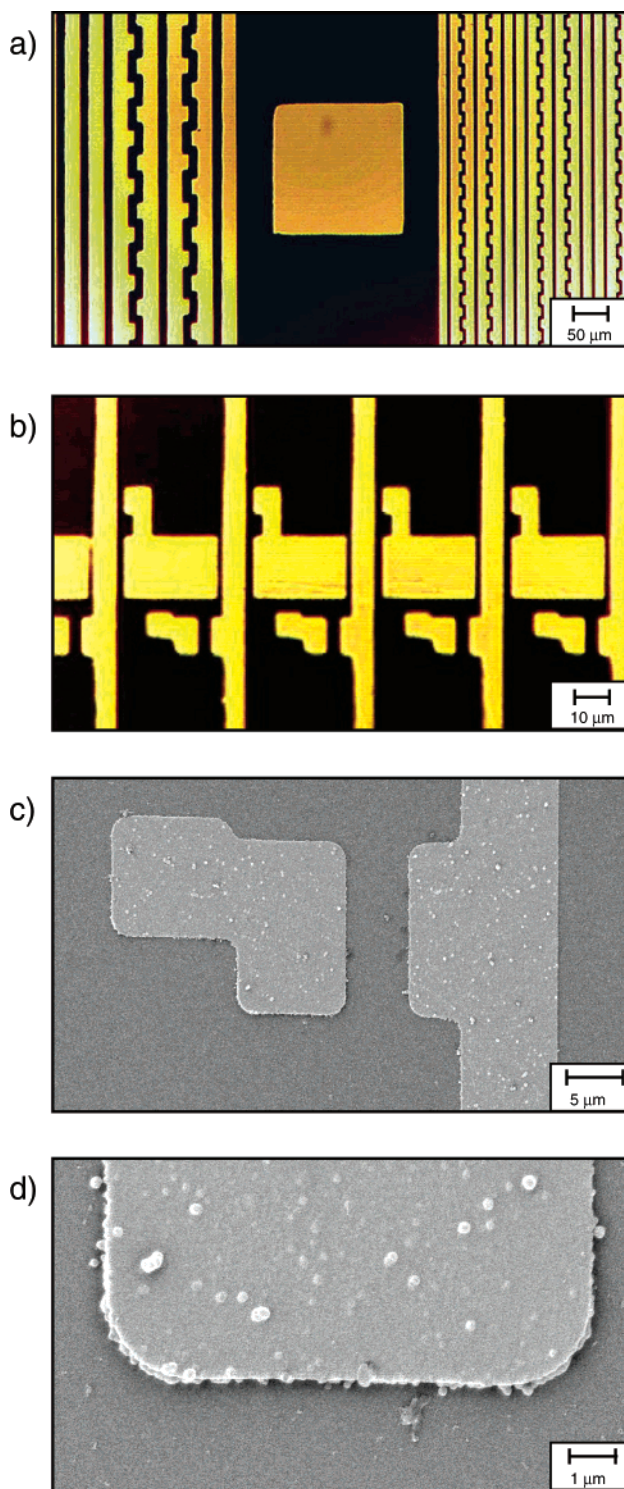


Figure 1. (a, b) Optical images of patterned nickel films fabricated by selective electroless metallization of a glass substrate printed with an arbitrary pattern of **4**. (b, c) SEM images of portions of the patterned, metallized substrate in part b.

Figure 2 shows optical and SEM images of selectively metallized copper films using oligomer **4** as the printing ink. We observed the same defects described for selectively metallized nickel films; in addition, the copper films with thicknesses >200 nm did not adhere well to the glass substrate. Figure 2b,c shows typical SEM images of a selectively metallized copper film, in which the corners of the patterned features have lifted off the glass substrate. Poor adhesion of electroless copper on smooth surfaces

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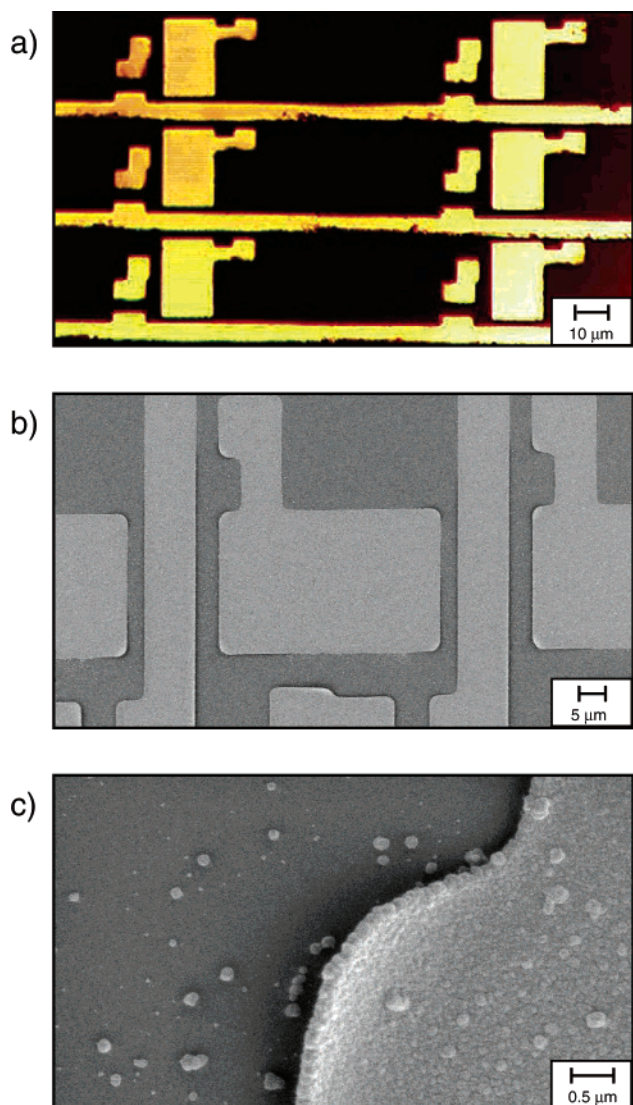


Figure 2. (a) Optical image of a patterned copper film fabricated by selective electroless metallization of a glass substrate printed with an arbitrary pattern of **4**. (b) SEM image of a portion of the metallized substrate in part a. (c) SEM image showing delamination of the copper film of the substrate in part a.

such as glass is well-known and can be remedied by strengthening either chemical or mechanical bonds to the substrate.²⁰ Our attempts to enhance the bonding of copolymer **4** to the substrate by using a copolymer formulation with a greater fraction of phosphonic acid monomer relative to phosphine monomer were thwarted by the poor solubility of these materials in 2-propanol. In addition, methanol solutions of these copolymers were too polar to wet the PDMS stamp; thus, they could not be used in microcontact printing.

Bifunctional molecule **5** has a ratio of phosphine to phosphonic acid of 1:1; we anticipated that this ratio might improve the adhesion of selectively metallized copper films. Figure 3a shows an optical image of a film of bifunctional molecule **5** selectively metallized with copper. The adhesion of these copper films is vastly improved over copper films plated on oligomer **4**. The films withstand the adhesive tape test easily. However, we observed poor resolution of the metallized pattern, the extent of which

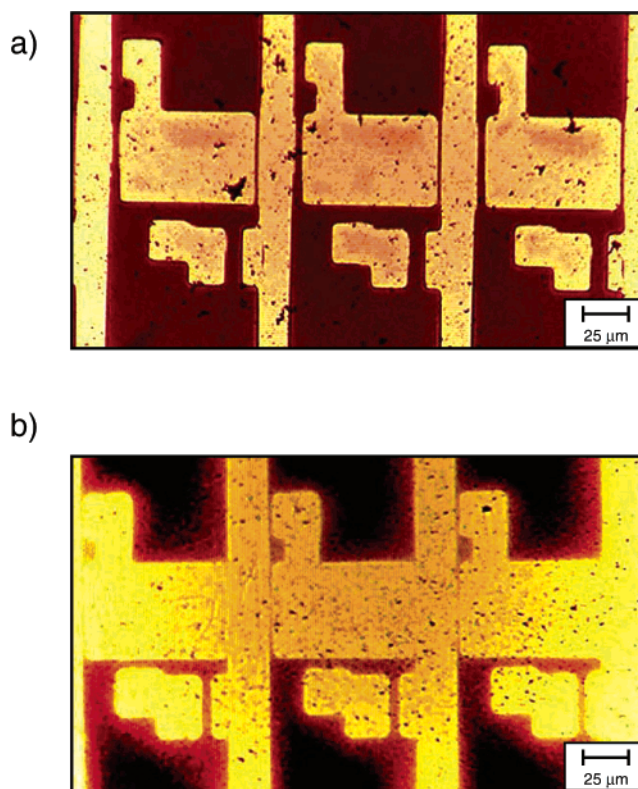


Figure 3. Optical images of patterned copper (a) and nickel (b) films fabricated by selective electroless metallization of a glass substrate printed with an arbitrary pattern of bifunctional molecule **5**. The concentrations of **5** used in printing were 2 mM (a) and 5 mM (b).

was dependent on the concentration of **5**. Using >10 mM solutions of **5** resulted in extremely poor resolution: metal deposited both inside and outside the patterned areas, although the pattern was still discernible because the metal film was thinner outside the patterned regions. Reducing the concentration of **5** to 5 mM, as shown in Figure 3b for selectively metallized nickel, improved the resolution but still resulted in a metallized pattern broadened by $\sim 2\ \mu\text{m}$. The optimum concentration was 2 mM, as shown in the metallized copper film in Figure 3a. Pattern broadening relative to the concentration of **5** was consistent for both nickel and copper electroless plating. Both plating baths also resulted in the deposition of numerous particles on the surface of the substrate, more so than for metallized films on oligomer **4**.

Our results suggest that diffusion of **5** on the surface of the substrate causes the pattern broadening. Previous studies of the diffusion of thiols on gold substrates during microcontact printing indicate that lower ink molecular weights, higher ink concentrations, and increasing the length of time the stamp is in contact with the substrate amplify the extent of ink diffusion.²¹ We determined that the first two factors have the greatest impact on the diffusion of **5**: we observed diffusion of **5** ($294\ \text{g mol}^{-1}$) but not of oligomer **4** ($M_n = 1082$), and the extent of diffusion of **5** is concentration-dependent. In addition to the factors listed above, we hypothesize that the heating step required after stamping **5** increases the extent of surface diffusion.

Conclusions

We have demonstrated a new approach to selective electroless metallization that uses microcontact printing

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of a new material possessing functional groups to anchor the material to the substrate and to bind an electroless plating catalyst. This approach is an effective, low-cost way to fabricate patterned metal films over large areas (15 cm²) with feature sizes >2 μ m. It circumvents many of the problems associated with direct microcontact printing of palladium catalysts. Its implementation in the fabrication of microelectronic devices requires the reduction of defects in the metallized films and improvement of metal adhesion to the glass substrate. Defects in the selectively metallized films may be reduced or eliminated by constant filtration of the plating bath to reduce particle deposition, the use of a "printing press"²² to eliminate smudging of the stamp and trapped air bubbles, and the

use of a clean room to reduce contamination by airborne particles. Our studies of bifunctional molecule **5** indicate that the proportion of phosphonic acid groups in the ink improve the adhesion of metallized films. It will be necessary to develop oligomer or copolymer inks that incorporate a higher fraction of phosphonic acid groups while maintaining solubility in alcohols, adequate hydrophobicity for stamping, and a sufficiently high molecular weight to reduce surface diffusion.

Acknowledgment. We thank W. Graham for help with electroless plating solutions, K. Carter and T. Magbitang for GPC, and R. Nunes, S. Hall, and M. Mastro for helpful discussions.

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LA049870A