Letters

Patterned Electroless Deposition of Copper by Microcontact Printing Palladium(II) Complexes on Titanium-Covered Surfaces

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The capability of microcontact printing (μCP) to transfer chemical reagents from an elastomeric stamp to a substrate is used here to direct electroless deposition of Cu. The stamp is inked with a Pd(II) catalytic precursor, which it prints onto a Ti-coated substrate. This application of μCP is challenged by several interdependent parameters such as the appropriate surface chemistry of the stamp, the choice of the ink, the control over the transfer of the catalyst during printing, the activation of the catalyst, and the electroless plating of Cu in general. We address these issues and suggest a reliable, but not general, method to combine microcontact printing and electroless deposition of Cu. This method uses hydrophilization of poly(dimethyl)-siloxane stamps and inking with the ethanol-soluble $[(CH_3-(CH_2)_{16}-CN)_2PdCl_2]$ catalytic precursor. Printing this complex onto a thin Ti layer evaporated onto Si/SiO_2 provides a high-level transfer of the Pd(II) complex from the stamp to the surface with simultaneous activation and fixation of the catalyst by reduction of Pd(II) to Pd(0) before the electroless deposition of Cu. Fabrication of high-resolution and high-contrast patterns of Cu electroless deposited with this method is possible.

1. Introduction

Electroless deposition (ELD) of metals is based on the deposition and reduction of metallic ions from a solution to a surface in the absence of an external electric current source. This deposition requires the immersion of a surface catalytically activated in a plating bath containing complexed metal ions and a reducing agent.[1-9] This bath needs careful control with respect to its chemistry, stirring, temperature, and pH for reliable and high-quality platings. ELD proceeds after its initiation on the surface via autocatalysis and uses the reducing agent from the solution as a source of electrons. The autocatalytic character of ELD renders this technique attractive to many fields of technology, but the catalysis associated with ELD

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and the absence of a directly measurable control like a current to control or monitor this reaction makes its application difficult. Many parameters can affect the ELD of metals, such as the density of the catalyst and its degree of activity on the surface, the adhesion of the deposit to the substrate, and the composition and conditions of the plating bath. Understanding the chemical reactions in ELD requires insight into the chemical and physical state of the catalytic interface, which can only be addressed using a restrictive scope of instrumentation.[10] Exploration of which parameters are significant and how they contribute to the observed effects can be cumbersome, in particular when ELD is sought to metallize only a subset of a substrate because contrast and accuracy of the metallized patterns are additional concerns.

ELD is nevertheless a remarkable method to metallize substrates selectively. It is proving increasingly useful in semiconductor and packaging technologies, for example. A major requirement prior to performing ELD is the seed (the placement and activation of the catalyst on the surface) and its selectivity: the catalyst must be confined to certain regions of the substrate and be completely absent from adjacent regions. This can be achieved either by selective deactivation of a catalytically active substrate or by the selective activation of a nonreactive surface. Several approaches that seek to create catalytic patterns with high activity and contrast have been explored. They include photopatterning of pretreated substrates combined with the deposition of metal films,[11−14] selective modification of catalyst-binding monolayers,[15−17] and microcontact printing (μCP) of a catalyst onto substrates.[18,19]

In this article, we explore various problems encountered when μCP[20−24] provides the catalytic pattern on the substrate. Briefly, μCP uses here a patterned and inked elastomeric stamp to print a catalytic precursor (a Pd(II) complex) as a pattern onto a substrate, Figure 1. A chemical reaction between the Pd(II) from the ink and Ti evaporated onto the substrate prior to the print creates the Pd(0) catalytic pattern. Deposition of Cu follows from the immersion of the printed substrate into a Cu plating bath. We suggest that hydrophilization of the stamp before inking, the use of a molecular Pd(II)-based catalyst which is soluble and stable in ethanol, and precoating substrates
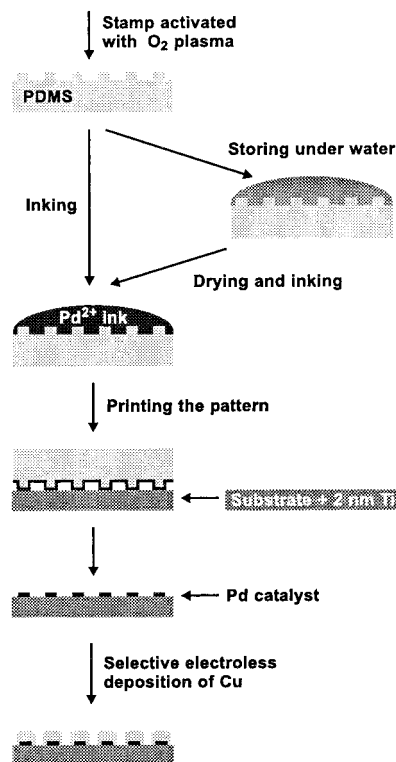

Figure 1. Procedure for selective electroless deposition of Cu by microcontact printing Pd-based catalytic precursors onto a Ti-coated silicon wafer. A PDMS stamp is first hydrophilized with an oxygen plasma and stored in deionized water if not used immediately. The stamp is then inked with a solution of Pd(II) catalytic precursors in ethanol. Microcontact printing the Pd complexes onto a freshly Ti-coated substrate immobilizes and activates the catalyst onto the substrate. Cu electroless deposition proceeds by immersion of the printed substrate in the Cu plating bath.

with a thin layer of Ti provide a reliable method of using μCP to pattern substrates with Cu in the micrometer and submicrometer scales using ELD.

2. Experimental Section

2.1. Formation of Stamps and Substrates. Unpatterned poly(dimethylsiloxane) (PDMS) stamps were prepared from Sylgard 184 (Dow Corning, Midland MI), dispensed with an automatic mixer/dispenser (DOPAG MICRO-MIX E, Cham, Switzerland), and cured for at least 12 h at 60 °C on a flat polystyrene surface (Petri dish, Falcon 1001 & 1013, Becton Dickinson Labware, NJ).[25] Patterned stamps were prepared similarly to flat stamps but cured on masters prepared by contact photolithography using Novalac resist and fluorinated with a monolayer of (1,1,2,2,-tetrahydroperfluorodecyl)trichlorosilane (ABCR, Karlsruhe, Germany). Stamps with high-resolution features (<500 nm) were molded using commercially available copolymers from ABCR and fluorinated masters prepared by electron beam (e-beam) lithography on a silicon-on-insulator (SOI) wafer.[26] Both types of stamps had a thickness of ~4−5 mm. We used an O_2 plasma treatment of the stamps (oxygen pressure ~0.8 Torr, load coil power ~100 W, 15 s; Technics Plasma 100E, Florence, KY) to render their surface hydrophilic prior to inking. Hydrophilized stamps were used immediately or stored in deionized water. Ti-covered substrates were prepared by e-beam evaporation of Ti (99.99%, Johnson Mattey) onto Si/SiO_2 wafers (Siltronix, Neuchâtel, Switzerland) and glass microscope slides at a pressure of ~2×10^{-7} Torr and a rate of ~0.01 nm s^{-1}. All Ti substrates were used within 1 h after the evaporation of Ti to limit aging effects by oxidation and contamination of the Ti on subsequent printing and plating steps.

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2.2. Inking and Printing. The ink was made of solutions of bis(stearonitrile)palladium(II) dichloride [$(CH_3-(CH_2)_{16}-CN)_2-PdCl_2$] in ethanol with concentrations ranging from 0.01 to 1.0 mM. All ink solutions were used within 6 h after their preparation to prevent oligomerization and evolution of the palladium(II) toward colloidal species (directly detectable by the change of color of the ink solution and by the precipitation of the colloids). The Pd complex was synthesized as follows: 1.0 g (5.6 mmol) of $PdCl_2$ (Fluka) was dissolved in 6.0 g (22.6 mmol) of stearonitrile (Aldrich, recrystallized from 20 mL of ethanol) and stirred at 100 °C for 3 h. After cooling, 30 mL of pentane (Fluka) was added, and the Pd complex was filtered and washed with cold pentane. The stearonitrile-substituted complex was separated from $PdCl_2$ and metallic Pd by extraction with toluene (Fluka). Removing of the solvent yielded 2.9 g (4.1 mmol, yield: 73%) of bis-(stearonitrile)palladium(II) dichloride as a yellow powder. ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 0.83 (t, 6H, CH_3), 1.28 (m, 56H, CH_2), 1.52 (q, 4H, $CH_3-\mathbf{CH_2}$), 2.42 (t, 4H, $NC-\mathbf{CH_2}$). ^{13}C NMR (DMSO-d_6, 250 MHz) δ (ppm): 14.11 (CH_3), 16.28, 22.25, 23.51, 24.85, 28.20, 28.29, 28.83, 28.91, 29.14, 31.44, 120.96 (CN). Anal. Calcd for $C_{36}H_{70}N_2PdCl_2$ (708.29 g mol^{-1}): C, 61.05; Cl, 10.01; H, 9.96; N, 3.96; Pd, 15.02. Found: C, 60.68; Cl, 9.70; H, 10.16; N, 3.96.

Inking was achieved by covering a flat or patterned stamp with a 0.5 mM solution of the Pd complex in ethanol for 60 s and drying the stamp for 10 s under a stream of N_2. Inked stamps were used within ~15 s of their inking. Printing was done by placing stamps on substrates by hand and removing them after a contact duration of 15 s. Each print used a new patterned stamp to prevent interference from the history of the stamps with the next print.

2.3. Electroless Cu Deposition. Cu solutions were prepared by dissolving 3 g of $CuSO_4$, 14 g of sodium potassium tartrate, and 2 g of NaOH in 100 mL of distilled water.[27] A 100-μL portion of formaldehyde (37.2 wt %, Fluka) was added to 10 mL of the Cu solution to supply the reducing agent to the plating bath. Cu electroless plating baths were prepared immediately (~30 min) prior to plating samples or series of samples. Printed samples were immersed in the Cu plating bath for 30–120 s at room temperature. The duration of plating was kept constant for a series of experiments. Plating was stopped by removing the sample from the bath and rinsing it with distilled water. Occasionally, small (100 nm) Cu particles were developed or deposited from the bath onto nonprinted areas of the sample and appeared in the optical microscope as a diffuse background. This problem was reduced or suppressed by filtration of the bath before plating with a 0.22-μm pore filter (Millipore). Mechanical stirring and air bubbling were not used but could reduce "plating fog" of this type as well.[28] The Ti film between the Cu structures could be removed within a few seconds, if desired, by dissolution in 1% HF or other strong acids.

2.4. Instrumentation. Contact angles of water with substrates were determined with a Krüss (Hamburg, Germany) contact angle goniometer equipped with a motorized pipet (Matrix Technology, Nashua, NH). Advancing and receding angles were measured at three or more locations on each sample. Roughness measurements were performed with a commercial Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) operated under ambient conditions in tapping mode. Optical inspection of the samples was carried out in reflection with a Leica Polyvar SC microscope equipped with a charge-coupled camera (3-CCD Donpisha, Sony) and a high-resolution (768 × 512 pixels) frame grabber to digitize images (Image-Pro Plus, Version 1.3, Media Cybernetics). High-resolution patterns of plated Cu were examined using a Hitachi S-4000 scanning electron microscope (SEM). X-ray photoemission spectroscopy (XPS) spectra were acquired on a Sigma Probe VG Scientific spectrometer operating at a base pressure of <10^{-9} mbar and equipped with a monochromatized Al Kα source ($E = 1486.6$ eV). The X-ray spot was focused down to 100 μm to perform a series of XPS measurements at several locations on the same sample. The analyzer had an angle of 45° to the sample, and samples were mounted on a multisample holder stage for examination under the same conditions. Spectra are referenced to the C 1s peak at 285 eV. For all samples, survey spectra were acquired first with a pass energy of 80 eV, and high-resolution spectra for the various elements investigated were acquired in the same sequence for all samples with a pass energy of 40 eV. The comparison of the peak of Si 2p or Ti 2p acquired first and last for each sample indicated no noticeable damages on the surface of the sample during the measurements. XPS on PDMS stamps was done with a flood gun (~1 μA emission current) and partial pressure of Ar of ~5 × 10^{-8} mbar for charge compensation of these insulating samples.

3. Results and Discussion

Stamps for μCP must have the following features: they must provide a stable, accurate pattern for the printing of an ink on a substrate, they must have an affinity for the relevant molecules in the ink without being swollen or damaged by them, and finally they must conform to the substrate to provide a homogeneous derivatization of the substrate during printing. There is now experimental evidence that stamps with stable patterns down to 500 nm can be fabricated.[25] When alkanethiols diluted in ethanol form the ink, these molecules partition in and on the stamp so that stamps can easily be loaded with an excess of reactant before printing.[29] Inking a PDMS stamp with a catalyst for ELD represents a different paradigm for μCP, however. Hidber et al.[18] have used colloidal Pd catalysts stabilized with tetraoctadecylammonium bromide dissolved in toluene for μCP and plated catalytic patterns with success. We use in this work an alternative for the inking of the stamp: hydrophilization of the PDMS surface using an O_2-based plasma increases the affinity between polar Pd(II) species and the stamp, Figure 1.[30–32] This treatment is simple and not detrimental to PDMS stamps because it oxidizes only a few nanometers of the surface of the stamp and preserves its elasticity and the accuracy of its pattern. Hydrophilization is a key step as it increases considerably the affinity between the stamp and a large variety of water and ethanol-soluble catalytic precursors for ELD. Once hydrophilic, stamps are subsequently inked with a solution of Pd(II) and used for printing or stored in deionized water to prevent the evolution of their surface toward a more hydrophobic-like state. The use of catalytic precursors soluble in water and ethanol is important because it represents an improvement over using solvents interfering with the chemical and topological integrity of stamps made in PDMS. Ethanol offers the additional advantage of drying and evaporating without leaving noticeable drying traces on the pattern of the stamp, in contrast to water-based inks, which dry over the surface of the stamp in a noncontrolled manner.

We synthesized a series of bis(alkylnitrile)palladium-(II) dichloride complexes as catalytic precursors for the ELD of Cu because (i) these complexes are simple to prepare and easy to reduce to Pd(0), (ii) Pd(0) is a strong catalyst for ELD of Cu, (iii) these Pd(II) catalytic precursors are soluble in ethanol, (iv) long alkyl chains on the nitrile ligands considerably improve the stability of the Pd(II) complexes in the ink versus the formation of colloidal species, and (v) molecular catalytic precursors may be

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printed at higher resolutions than colloidal species.[33] Interestingly, increasing the length of the alkyl part of both nitrile ligands did not improve the affinity between hydrophobic PDMS stamps and the catalytic precursor in the ink. We consequently used hydrophilic PDMS stamps and $[(CH_3-(CH_2)_{16}-CN)_2PdCl_2]$ for all experiments because this complex is more stable in ethanol than its shorter analogues.

Transferring the catalytic precursor from the stamp after inking and drying to the substrate is the next step but is also critical for obtaining adhesive and high-quality deposits. Deposition of a catalyst for ELD usually follows the immersion of a preconditioned substrate in a solution of colloidal Pd and Sn particles. The preconditioning step can be simple or composed of a long series of dips and rinses resulting in a homogeneous fixation of the catalytic particles on the surface to be plated. The art of elaborating a successful ELD method lies therein. Here, we seek to use μCP to pattern the catalyst such that the scope of possible pretreatment of the substrate before printing is different from more conventional and proprietary approaches. Derivatization of surfaces carrying silanol ($-$SiOH) groups with ω-functionalized alkylsilanes proved useful in previous work for printing colloidal Pd onto the surface of oxides.[18] In our case, Si/SiO$_2$ was selected as a substrate because it has important technological applications, it is available pure and clean, it is not conductive nor active for ELD, it is compatible with silane-coupling chemistry, and a variety of analytical techniques can readily be performed on wafers. Microcontact printing the Pd(II) complex onto Si wafers cleaned with strong chemical oxidants, or sonicated with detergents and ethanol, or as received from manufacturers did not seem to lead to homogeneous ELD of Cu. Neither conventional pretreatment of the substrate with SnCl$_2$, nor proprietary vendor treatments, nor etch-induced roughening of the substrates, nor silanization of the substrates was satisfactory for our application.

Ti was evaporated onto the wafers as an alternative to wet chemical treatments or cleaning. Evaporation of metals such as Ti on substrates is a well-defined and controllable method to derivatize a substrate. Ti, like Cr, is often used as an adhesion promoter for metals on oxides. Partially oxidized Ti can reduce Pd(II), and we hypothesized that it could bind Pd(II) during printing and reduce it to its metallic state.[34] Figure 2 reveals that the quality of the Cu deposits is optimal and similar when at least 2 nm of Ti have been evaporated onto the Si/SiO$_2$ wafers.[35] Interestingly, the quality of the deposits increases with the thickness of evaporated Ti despite equivalent inking, printing, and plating conditions for all experiments in Figure 2. This indicates that more active Pd is present on surfaces coated with more than 2 nm Ti because ELD of Cu represents a very sensitive diagnostic of how much catalyst is available and how active it is on the surface.

The roughness of a substrate can be an extremely important factor in influencing the quantity and the adhesion of a catalyst transferred to a substrate in ELD methods. Substrates are often roughened and etched prior to their derivatization with a catalyst for this reason. An atomic force microscopy (AFM) investigation of the
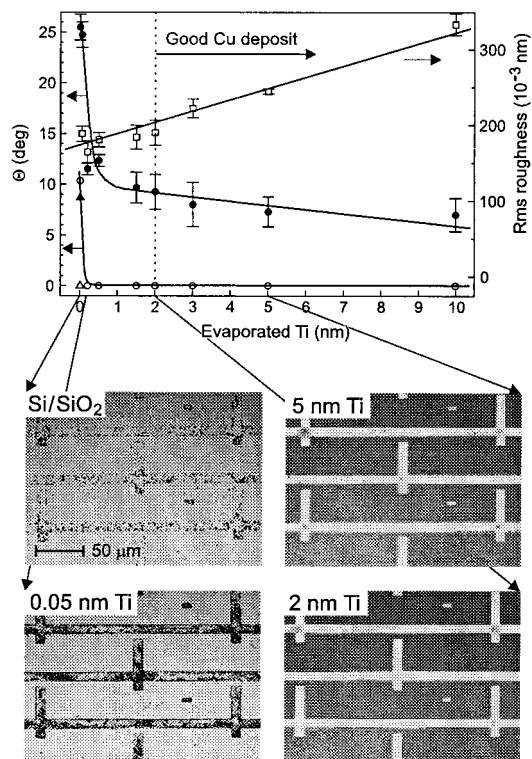
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(35) Optical microscope images are shown here because the color of Cu is an important criterion for its quality: Cu plated poorly on thin Ti films (<1 nm) has a dark nonmetallic color. For a Ti layer thicker than 2 nm, the Cu metal deposits a bright, reddish color corresponding to thicker and metallic Cu.
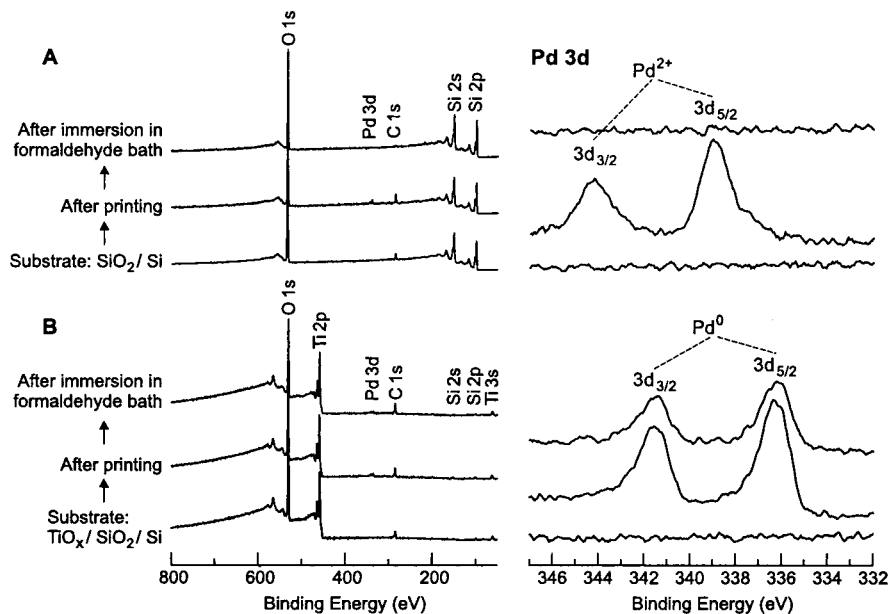
Figure 2. Dependence of roughness, contact angle, and thickness of a Ti layer evaporated onto a Si/SiO$_2$ wafer on the electroless deposition of Cu that followed microcontact printing a Pd(II) catalytic precursor onto the Ti surface. The roughness (open squares) of the Ti layer and its advancing (solid circles) and receding (open circles) contact angles with water are reported in the graph as a function of the Ti thickness. The optical microscope images show the quality of the electroless Cu deposits for some particular thicknesses of Ti. The roughness and wettability by water of the evaporated Ti layer do not correlate with the quality of the Cu electroless deposit, but rather 2 nm is the critical thickness of Ti necessary for good Cu deposits.

roughness of the substrates as a function of the Ti thickness suggests no evident correlation between the quality of the Cu deposits and the roughness of the modified substrates. Changes in this roughness seem marginal, and the quality of the Cu deposits is independent of this roughness for Ti films thicker than 2 nm. Similar to the roughening of substrates, changing their wettability can strongly influence their ability to interact productively with a catalyst from a solution. Substrates coated with only a few angstroms of Ti have an excellent wettability by water but have corresponding Cu deposits of mediocre quality. For this reason, the wetting properties of the substrates are not the determinant cause for getting high-quality Cu, but Ti seems to play the role of a reactant during the printing of the Pd complex to the surface. We reproduced the results presented in Figure 2 in a single operation by evaporating Ti on a Si/SiO$_2$ wafer with a gradient of thickness from 0 nm up to ~5 nm. This indicated that changes in the Cu quality are not induced by uncontrolled printing conditions or by aging effects of the plating bath or the Ti substrates. The adhesion of the Cu structures was measured by a standard Scotch tape test and followed the correlation between the quality of the Cu deposit and the thickness of Ti on the substrate: Cu is not removed by peeling off the Scotch tape when more than 2 nm of Ti is present on the surface.

XPS experiments in Figure 3 indicate that Ti provides two simultaneous advantages for μCP of a Pd(II) catalyst onto a surface: Ti fixes and reduces the Pd(II), whereas

Figure 3. XPS survey and high-resolution spectra of the Pd 3d region of (A) Si/SiO_2 substrates and (B) 2.5 nm of Ti evaporated on the Si/SiO_2 substrates before and after microcontact printing a Pd(II) catalytic precursor and after immersion of the printed samples in an electroless Cu plating bath containing no Cu ("formaldehyde bath"). The action of the Ti layer evaporated prior to printing the Pd(II) catalytic precursor is dual: it reduces Pd(II) to metallic Pd during printing, and prevents its being washed off the surface during the immersion of the printed sample in the formaldehyde bath.

printing Pd(II) on the native oxide of a Si wafer renders it in the same oxidation state (II) as it was initially in the ink.[36] Several approaches exist to place and fix a Pd catalyst on a surface. The majority of these techniques uses direct deposition of colloidal Pd and Sn species from solution on preconditioned substrates.[1,4−9] Activation of the catalyst on the surface can then proceed by reaction with hydrofluoroboric acids to liberate Pd atoms or clusters from the colloids. The fraction of the catalysts present in an oxidized state may additionally be reduced by reducing agents in the plating baths. We tried several of these approaches to μCP catalytic patterns for ELD but always found low-quality Cu structures with poor resolution. Other interesting approaches involve the silanization of substrates with ligands for the fixation of Pd complexes from solution or placed on the substrate by printing.[16,18] We favored the evaporation of Ti in this work as it is a simple and reliable technique and may be more generally applicable to the fixation and activation of a large variety of catalytic precursors. Moreover, Ti can easily be selectively etched.

Figure 3B illustrates how Ti acts on the printed palladium. An equivalent amount of Pd(II) appears to transfer from the stamp to Si/SiO_2 and Ti on Si/SiO_2 but the Pd(II) is reduced to Pd(0) when Ti is present on the substrate and is not washed away after the substrate is immersed in the plating bath from which Cu was omitted. This reduction is consistent with the standard electrochemical potentials of partially oxidized Ti and Pd(II), but it also implies that fully oxidized Ti should lose its ability to coordinate and reduce Pd(II).[34] This was confirmed (i) by a complete oxidation of Ti evaporated on Si/SiO_2 in a O_2 plasma after which the surface behaved similarly to Si/SiO_2 and (ii) by the observation that exposure of Ti-coated substrates to ambient for more than a few hours reduced the benefits of the Ti evaporation considerably. Printing the Pd catalytic precursors directly onto Si/SiO_2 yields deposition of Pd on the substrate (XPS

spectra in Figure 3A). After immersion of the sample into the formaldehyde reducing bath, the Pd complexes are lost into the bath to a large extent, which accounts for the poor quality of subsequently deposited Cu.

We observed that changing the inking time of the stamp from a few seconds to 10 min does not affect the quality of the Cu deposit, indicating that the density and distribution of the catalytic precursor on the stamp surface remain comparable in either case. Three phenomena may account for this observation: (i) the stamp may be limited in its ability to incorporate the Pd(II) complex at its surface, (ii) the overall transfer may be limited by the printing time, or (iii) the reaction between Pd complexes and Ti on the surface is optimal and reaches completion. Changing printing times from 1 s to several minutes did not have obvious effects on the quality of the Cu-plated patterns. Immersion of Ti-coated substrates in a solution of the Pd(II) catalyst resulted in Cu deposits of slightly higher quality (denser and smaller Cu grains). This suggests that the stamp represents the limiting factor for printing the Pd(II) on the surface.

Figure 4 corresponds to the investigation using XPS of the amount of Pd(II) that can be inked onto the surface of a hydrophilized stamp and transferred by printing onto a Ti-coated substrate. Several stamps were prepared for the three different steps investigated in Figure 4, exposed to ultrahigh vacuum conditions, and analyzed under the same conditions. The principal components of the PDMS stamps after O_2 plasma treatment are oxygen, carbon, and silicon. The presence of an important peak of carbon at 285 eV denotes the presence of methyl groups on or near the surface of the siloxane polymer. This suggests that "reconstruction" of the oxidized air−polymer interface occurred after the plasma treatment and before the XPS experiments or that combustion of these groups by the O_2 plasma remains confined to a very thin surface layer.[29−31] Inking the stamp with a 0.5 mM solution of the Pd(II) in ethanol for 30 s provides an observable quantity of catalytic precursors. The broadening of the Pd 3d region is due to a slight charging of the sample during data acquisition.

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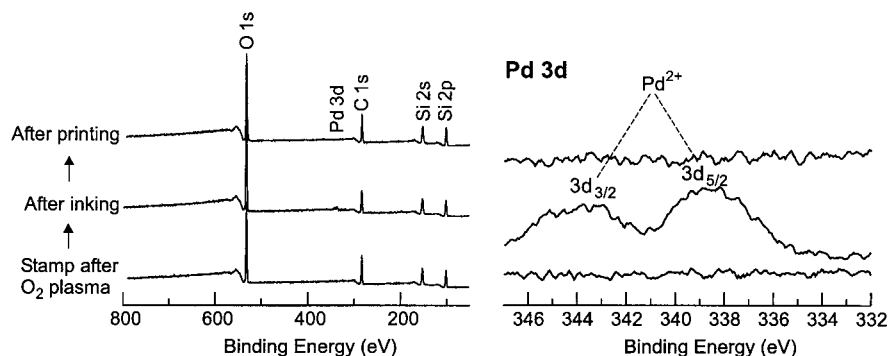
Figure 4. XPS survey and high-resolution spectra of the Pd 3d region before and after inking, and after printing a hydrophilized stamp inked with a 0.5 mM ethanolic solution of $[(CH_3-(CH_2)_{16}-CN)_2PdCl_2]$ onto Ti-pretreated Si/SiO$_2$ wafers for 30 s. After inking, the catalytic precursor remains in the +II oxidation state and apparently transfers entirely from the stamp to the substrate after printing.

Taking this charging into account, the species found on the stamp could always be attributed to Pd(II). No palladium apparently remains on the stamp after printing. The XPS results in Figure 4 are qualitative in nature but demonstrate that it is possible to ink a hydrophilic PDMS stamp with the Pd(II) complex and that its transfer during printing appears to be complete. The quantity of Pd(II) on the inked stamp was variable[37] but could never be increased noticeably by increasing the duration of the plasma oxidation, the concentration of the complex in the ink, or the duration of inking. This reinforces the idea that the stamp is limited in its ability to capture the complex during inking. Two coinciding factors contribute to this limit. First, the solubility of the Pd(II) compound in the PDMS stamp is poor. In contrast to μCP alkanethiols on gold, no multiple printing is possible without reinking the stamp. No reserve of Pd(II) exists in the bulk of the stamp, which could progressively release Pd by diffusion. Second, the affinity between nonhydrophilized PDMS stamps and the Pd complex is very low: not enough palladium for good ELD of Cu could be transferred when using a nonhydrophilized stamp. The hydrophilic layer on the plasma-treated stamp provides a small reservoir for the catalytic precursor. The depth of this hydrophilic layer cannot be increased noticeably with a treatment such as an O$_2$ plasma because the plasma apparently forms a self-passivating silicate layer on the surface of the stamp.[30,31]

The resolution and accuracy of Cu patterns produced by ELD and μCP, in addition to the quality, homogeneity, and adhesion to the substrate of Cu deposits, are important criteria to evaluate the virtues of this technique. The SEM image in Figure 5A demonstrates that microcontact printing of the Pd(II) catalytic precursor can lead to Cu structures with a line width of 170 nm when high-resolution stamps provide the pattern.[26] The size of the Cu grains is between 80 and 120 nm in width and thickness. The very high contrast indicates that no catalyst has diffused away from the zones of print and that ELD of Cu remained confined to the catalytic areas of the substrate. Printing $[(CH_3-(CH_2)_{16}-CN)_2PdCl_2]$, which has a higher molecular weight (708.29 g mol^{-1}) than printing eicosanethiol (314.62 g mol^{-1}) on gold, may be beneficial for the fabrication of high-resolution patterns by μCP without the need to invert patterns and improve inking

Figure 5. Scanning electron microscope images of electroless Cu deposits at an early stage over a high-resolution microcontact print of $[(CH_3-(CH_2)_{16}-CN)_2PdCl_2]$ onto a Ti-coated Si/SiO$_2$ wafer. In both cases, the Cu lines match with accuracy and contrast the (A) 170-nm and (B) 500-nm-wide lines that were present on the stamps used here.

schemes or to optimize inking/printing conditions.[29,38] We found in general that optimization of the concentration of the Pd complex in the ink and of the duration of the print was less important than when printing eicosanethiol on gold, suggesting that the Pd ink had little diffusion on the substrate during printing. Cu grains of 170 nm appear to be continuously connected and form the lines in these samples. It is equally possible to form 170-nm nonplated gaps with high resolution and contrast, Figure 5B. There, the distribution of the Cu grains in the 500 nm lines suggests that the catalytic pattern underneath is homogeneous. The thickness of the Cu structures in both images is ~100 nm. It is difficult in these experiments, however, to deconvolve the influence of the plating conditions (strength, stirring, temperature, and stability of the bath) on the highest achievable resolution of μCP for Cu ELD, but the particle grain size of Cu can range, in the limit, between 5 and 200 nm for deposits onto activated

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(37) XPS indicated that the amount of Pd(II) present on inked stamps varied within 20%. Interestingly, this variability had no influence on the quality of the Cu deposit. This suggests that the critical amount of of Pd on the sample to have good catalytic activity was reached in all cases.
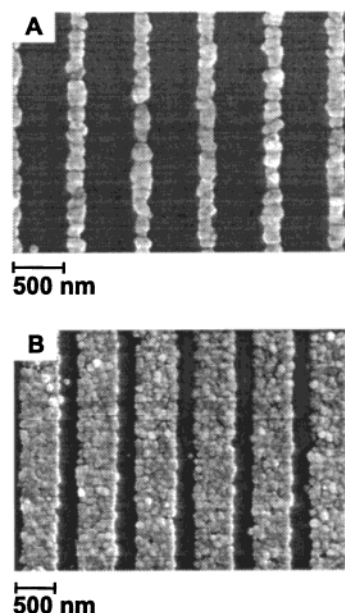
(38) Libioulle, L.; Bietsch, A.; Schmid, H.; Michel, B.; Delamarche, E. *Langmuir* **1999**, *15*, 300−304.

surfaces.[39] In choosing an appropriate Cu bath, a minimal line width of about 30−50 nm may be achievable.

4. Conclusion

Microcontact printing a catalyst onto a substrate to initiate selective ELD of Cu is a challenge because it requires that this contact patterning technique be used in a markedly different way than for microcontact printing alkanethiols on gold. This raises such questions as, What is the preferred surface chemistry for the relatively chemically inert PDMS stamps in the former case? How can one compose the catalytic ink for ELD? How can one fix the catalyst firmly to the substrate during the printing step, and what is its catalytic state? ELD of Cu itself contributes to some of these challenges, ELD being a technique that is difficult to understand in detail. Hidber et al. boldly opened the exploratory route paved with these questions. Our use of microcontact printing combined with ELD of metals extends the work of these authors to a different paradigm. We relied on surface chemistry to control the operations necessary for good printing of a catalyst and satisfactory electroless plating. The catalyst used here is stabilized with two organic ligands and can be inked with stamp-compatible solvents such as ethanol onto a hydrophilic surface-treated stamp. The stamp is not yet permanently hydrophilic and the ink only contains a catalytic precursor, which can be reduced to a catalytic state and fixed to the substrate during the printing on a Ti-coated surface. Surface chemistry here again ensures that ELD of Cu proves satisfactory in terms of the amount plated on the surface and the resolution and contrast of the Cu pattern on the surface.

(39) Weber, C. In Situ Scanning Tunneling Microscopy Study of Morphological and Mechanistic Aspects of Electroless Cu Deposition. PhD Thesis; The Pennsylvania State University, 1998.