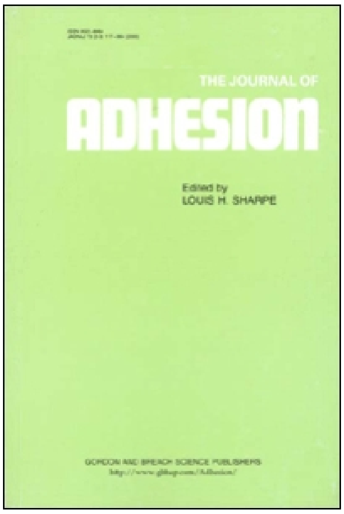

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Selective Metal Pattern Fabrication Through Micro-Contact or Ink-Jet Printing and Electroless Plating onto Polymer Surfaces Chemically Modified by Plasma Treatments

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Selective Metal Pattern Fabrication Through Micro-Contact or Ink-Jet Printing and Electroless Plating onto Polymer Surfaces Chemically Modified by Plasma Treatments

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Simple versatile processes combining plasma treatments, micro-contact printing (μCP) or ink-jet printing (IJP), and electroless deposition (ELD) have been developed to produce micrometer and sub-micrometer scale metal (Ni, Ag) patterns at the surface of polymer substrates. Plasma treatments were mainly used to graft the substrate surfaces with either nitrogen-containing functionalities on which a palladium-based catalyst can be subsequently chemisorbed (case of Ni deposition through a tin-free process in solution) or oxygen-containing functionalities on which a tin-based sensitization agent can be subsequently chemisorbed (case of Ag deposition through a redox reaction). μCP of the catalyst or of self-assembled monolayers (SAMs) as well as ink printing were used to obtain locally active or non-active areas at the polymer surfaces. The metal micro-patterns were characterized using optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Surface chemical characterization was carried out by X-ray photoelectron spectroscopy (XPS).

Keywords: Adhesion; Electroless deposition; Ink-jet printing; Metal patterning; Metal/polymer interface; Micro-contact printing; Palladium-based catalysis; Plasma treatments; Polymer substrates; Surface analysis; Tin-based sensitization

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1. INTRODUCTION

Over the last decades, a variety of discrete metal microstructures and nanostructures (exhibiting features with at least one lateral dimension lower than 100 µm and 100 nm, respectively) were fabricated at the surface of many insulating and dielectric substrates using conventional patterning techniques mainly based on photolithography and scanning beam lithography (electron and ion beam lithography) [1,2]. For example, these techniques have been applied successfully to manufacture integrated circuits and other microelectronic components, display units, biological, and chemical miniaturized sensors as well as optical, microelectromechanical (MEMs), information storage, and microfluidic devices [3,4]. In these processes, metal deposition was carried out by evaporation, ion sputtering, electroless plating, or electroplating. Unfortunately, these conventional patterning technologies require the implementation of sophisticated equipment, are time-consuming (low throughput), are not environmentally friendly (use of corrosive etchants and organic solvents), and mostly allow the patterning of only small areas on the planar surface of a limited number of rigid inorganic substrates. This explains why several alternative fabrication methods, commonly reported as "soft lithographic" techniques like micro-contact printing (µCP) [1,2,5–7] and ink-jet printing (IJP) [8–10], have more recently emerged. Briefly, µCP is a non-lithographic method in which an elastomeric stamp [usually made from poly(dimethylsiloxane) (PDMS)] with a selected relief (commonly obtained from a topographically patterned Si master) is wetted by the solution of the chemical species to be transferred and brought into intimate physical contact with the substrate surface. IJP consists in ejecting small volumes of a suitable liquid ink through a nozzle and in depositing them on the substrate either as continuous lines or as separated droplets (writing process). For this purpose, commercial piezoelectric desktop printers controlled by conventional computer software can be used to deliver picoliter volumes of the "ink" to be deposited. Both techniques (µCP and IJP) combined with electroless plating have been shown nowadays to be able to provide, under relatively environmentally friendly conditions, high speed patterning over large areas at the surface of various materials, including that of polymer substrates [11–22].

In the present work, special attention has been devoted to the selective electroless (Ni, Ag) metallization of poly(imide) (PI) substrates using several specific strategies which combine, on the one hand, plasma pre-treatments of the polymer surfaces, and on the other hand, µCP or IJP technologies. These strategies were implemented to make either the insulating polymer surface selectively active from a catalytic point of view or a homogeneously active surface selectively deactivated. Briefly, Ni and Ag patternings were carried out through NH_3 and O_2 plasma pre-treatments of the polymer surfaces, respectively. The so-functionalized surfaces are the key requirement leading to simplified routes for their activation before metallization.

2. STATE-OF-THE-ART REVIEW

2.1. Electroless Deposition

Electroless deposition (ELD) or plating is one of the most widely used industrial processes to metallize the surface of non-conducting materials, including that of polymers and polymer-based composites [23–26]. Basically, ELD is an autocatalytic process consisting in a redox reaction in aqueous solution between ions of the metals to be deposited and a strong reducing agent such as hypophosphite (in the case of Ni deposits) or formaldehyde (in the case of Ag deposits). In these examples, the redox reactions taking place in the plating baths are, respectively, as follows:

$$\mathrm{Ni^{+2} + 2H_2PO_2^- + 2H_2O \rightarrow Ni^0 + 2H_2PO_3^- + 2H^+ + H_2}$$

$$\mathrm{2[Ag(NH_3)_2]OH + R{-}CHO \rightarrow 2Ag + 4NH_3 + R{-}HCOO + H_2O.}$$

In addition, baths contain complexing agents ensuring the dissolution of the metal salt and a base permitting the reduction of the metal ions *via* a pH adjustment. Usually, these plating solutions are in a metastable state. This means that the redox reactions are triggered spontaneously only in the presence of a catalytically active surface. Then, when such reactions are initiated, the metal in the course of deposition serves as a catalyst, thus ensuring a continuous buildup of the electroless film (hence the "autocatalytic" term commonly used to describe the process). In the case of insulating substrates, the metallization initiation itself needs to be preceded by an activation step, whose primary purpose is to create suitable catalytic sites at the material surfaces. In industrial applications, the virgin polymer substrates are first surface-oxidized and etched in harmful chemicals involving, for example, sulphuric acid/chromic acid mixtures. Surface activation can then be performed using two main processes known as "two-step" or "one-step" processes. In the former case [27–30], the oxidized substrate surface is first sensitized by immersion in an acidic tin chloride ($SnCl_2$) solution and then activated by immersion in an acidic palladium chloride ($PdCl_2$) solution. In the latter case [31–33], the oxidized substrate surface is directly activated by immersion in a colloidal solution obtained from an acidic mixture of tin chloride and palladium chloride. A further treatment (acceleration step) is still needed to allow the catalyst to be efficient. More recently, several "tin-free" processes have also been developed. They are mainly based on the strong chemical affinity of Pd^{+2} species towards nitrogen-containing functionalities [34,35] and the chemisorption of Pd^{+2} species (direct activation in a $PdCl_2$-based solution) is carried out on surfaces which were previously either: (i) coated with specific self-assembled monolayers (SAMs) such as organosilanes containing amine or pyridine end-groups [36–43]; (ii) grafted with nitrogen-containing species through plasma or UV/VUV treatments in a nitrogenated (NH_3, N_2) atmosphere [44–49]; or (iii) coated with thin films obtained by plasma (or UV-induced) graft copolymerisation of either vinylimidazole or vinylpyridine precursors [50–56]. Whatever the activation mode, it should be noted that to initiate the metallization in the plating bath and make the adhesion at the metal/polymer interface as strong as possible, a key requirement consists in strongly anchoring the catalytic particles at the polymer surface.

2.2. Selective Electroless Deposition

To obtain metal patterns, several approaches have been used to nucleate selectively the palladium-based catalysts on the surface to be patterned: photolithography (PL), self-assembled monolayer (SAM) deposition, micro-contact printing (μCP), and ink-jet printing (IJP) technologies. For example, Dressick and co-workers [37–43] fabricated micrometer and sub-micrometer scale Ni, Co, and Cu patterns at the surface of various substrates including polymers such as poly(tetrafluoroethylene), poly(carbonate), epoxy, ABS, poly(sulfone), and poly(chloromethylstyrene). To chemically graft the Pd^0 catalyst (from a Pd (II)-based colloidal solution) to the substrate surface, they mainly used two fully additive processes based on both PL and the deposition of organosilane thin films (SAMs) containing specific ligand functional end-groups such as alkylamines, pyridines, or phosphines. In the first process [42,43], the substrate was coated successively with the organosilane film and a polymeric photoresist layer [channel constrained metallization (CCM) process]. Localized light exposure (using UV or VUV irradiation and a suitable mask) and development of the photoresist layer allowed the opening of channels in the underlying organosilane thin film, then the selective anchoring of the Pd-based catalyst to the SAM end-groups, and finally the ELD to be carried out.

Obviously, the remaining photoresist had to be removed by stripping. In the second process [43], the substrate coated with the organosilane film was directly irradiated (again through a suitable mask) in order to remove locally the SAM reactive functional end-groups [direct siloxane patterning (DSP)]. Under these conditions, the non-exposed areas of the SAM layer were directly catalyzed in the Pd-based solution, and further submitted to ELD. In both cases, metal microstructures as small as 100 nm were obtained.

Micro-contact printing (μCP) is a method making use of a stamp instead of a mask for pattern definition. This technique was introduced by Whitesides and others to pattern alkanethiol SAMs on evaporated thin films of Au and Ag [57,58], as well as silane-based SAMs on various other substrates [59,60]. It consists of applying onto the selected substrate an elastomeric stamp inked with the species to be patterned. The conformal transfer of these species occurs only in areas where the stamp and substrate come into contact. Obviously, the ink species must have a sufficient chemical affinity towards the substrate surface (hence, the requirement for suitable surface treatments) but must not diffuse or migrate laterally across the surface in order to give rise to well defined localized domains both at the micrometer and sub-micrometer scales. The selective EL metal deposition using μCP has been mainly carried out on glass and SiO_2/Si substrates [58–64] but some works have also been devoted to polymer substrates. Hidber *et al.* [11] used a stamp inked with a tetraoctadecylammonium bromide-stabilized palladium colloid to locally activate the surface of poly(imide) (PI) and biaxially oriented poly(styrene) (BOPS) substrates. Prior to this step and to the subsequent Cu ELD, the polymer surfaces were chemically oxidized in a H_2SO_4/CrO_3 solution and then silanized using, among others, an amino-terminated SAM, namely 3-amino propyltriethoxysilane. Similarly, Prissanaroon *et al.* [12] used μCP to deposit micrometer-scale patterns of Cu on flexible poly(tetrafluoroethylene) (PTFE) films. In that work, the PTFE surface was first Ar plasma pre-treated, then stamped by μCP using a N-[3(trimethoxysilyl)-propyl]diethylenetriamine (TMS) coupling agent, and subsequently activated in an acidic $PdCl_2$ solution. More recently, Hendricks and co-workers [13,14] described a versatile metal (Cu or Ni) patterning method combining the use of polyelectrolyte multilayer (PEM) coatings, μCP, and ELD. The PEM coatings were obtained by dipping the substrates [glasses, poly(styrene) microscope slides and flexible polyester transparency films] successively into solutions of positively charged poly(diallyldimethylammonium) chloride (PDAC) and negatively charged poly(styrene) sulfonate, the final layer of the outer surface being made of PDAC. Negatively charged palladium ions [from an aqueous solution of sodium tetrachloropalladate (II) ($Na_2[PdCl_4]$)] were then transferred to the positively charged PEM surface *via* electrostatic interactions. In another approach, Reinhoudt and co-workers [65,66] deposited cyclodextrin (CD) SAMs on Au and SiO_2 surfaces and used them as "molecular printboards" to host guest molecules through multivalent supramolecular interactions. Au nanoparticles stabilized by adamantyl-terminated poly(propylene imine) (PPI) dentrimers (G 5 generation) were transferred as catalysts by µCP within the CD cavities of the "molecular printboards". ELD was then carried out to fabricate Cu microstructures (10 µm wide and 85 nm thick Cu lines). In a last example, µCP was also used by Yoon *et al.* [15] to carry out micro-sized Au patterns on PI substrates. The substrate surface was locally hydrolyzed with a PDMS stamp inked with an aqueous KOH solution. This alkali treatment gave the formation of surface poly(amates) (potassium salts of the carboxylic acid) which were subsequently immersed in a $PdCl_2$ solution to obtain ion-exchange (K^+/Pd^{+2}). Finally, the so-adsorbed Pd^{+2} species were chemically reduced in a sodium borohydride $NaBH_4$ solution and the Pd-activated patterns were submitted to electroless Ni and then to electroless Au metallization. Dealing more especially with the electroless metallization of PI substrates, it should be noted that more details can be found in a recent review [67].

Like µCP, IJP [8–10] is a "soft lithography" technique. IJP was first used by Shah *et al.* [16] to pattern Pt colloids onto poly(ethylene terephthalate) (PET) substrates (pristine 3 M transparency sheets or NaOH-etched transparency sheets) and onto a Nafion® membrane, before electroless copper deposition. Similarly, Busato *et al.* [17] carried out IJP of an aqueous Pd^{+2} solution onto the surface of KOH–treated PI films. After this localized ion exchange step, the surface Pd^{+2} species were chemically reduced to Pd^0 in a $NaBH_4$ solution and electroless Cu patterns were then obtained in size down to 100 µm. IJP was also used by Konishi *et al.* [18] to seed selectively the surface of photoresists and PI substrates with γ-amino propyltrimethoxysilane. After drying, the seed material was activated using a conventional Pd/Sn colloidal catalyst and Ni ELD was carried out for the fabrication of micro-patterns (circuit lines with an average width of 55 µm). In addition, Wang *et al.* [19] and Guo *et al.* [20] used IJP to obtain a selective coating on polymer substrates (PET and PS, respectively) with PEMs, such as poly(acrylic acid) and poly(allylamine) hydrochloride, which were subsequently surface activated using positively or negatively charged Pd-based complexes, and finally plated with electroless Ni. Using a similar process, Cheng *et al.* [21] carried out Cu ELD on PET and glass-reinforced epoxy resins.

Concerning the Ag ELD patterning on polymer substrates, the literature clearly is less abundant than that dealing with the Cu and Ni ELD. Harkness *et al.* [68] described the selective electroless Ag deposition of a photolithographically patterned hydrogen silsesquioxane (HSQ) thin film spin-coated on a Si substrate. The process was initiated in the plating bath through an active reduction of the Ag^+ cations to the Ag^0 catalyst by the silyl hydride species and then further proceeded by autocatalysis. Bidoki *et al.* [22] used IJP to deposit Ag patterns and produce wiring boards, antenna devices, and electrodes on polyester transparency films. In this process, aqueous solutions of metal salt (silver nitrate) and reducing agent (ascorbic acid at neutral pH) were ink-jet printed consecutively onto the substrate surfaces.

3. EXPERIMENTAL

3.1. Substrates

All experiments carried out in this study were implemented using poly(imide) substrates (125 µm-thick Kapton® HN) indexed here as PI. They were supplied by Goodfellow (Cambridge, UK). Before any further treatment, the substrates were ultrasonically cleaned in ethanol in order to remove dusts and other solid particles from the sample surface.

3.2. Plasma Treatments

All plasma treatments were performed using a radio-frequency (RF) reactor (RIE model, Plasma Technology, Bristol, UK) operated at 13.56 MHz. This reactor is equipped with two water-cooled parallel and asymmetrical electrodes and with four gas lines. The samples to be surface treated are positioned on the RF-powered electrode (17 cm in diameter) which is capacitively coupled to the power supply through an impedance matching network. In this experimental device, the powered electrode is biased so that samples are bombarded by ions whose energy is dependent on the power density. All experiments were carried out at a $0.52\,W/cm^2$ power density (120 W), except when further indicated. At a $0.52\,W/cm^2$ power density, the energy of the ions bombarding the sample was then approximately 300 eV. The other experimental conditions were as follows: plasma gas—NH_3, O_2, Ar, or H_2; gasflow—100 sccm, working pressure—100 mTorr, treatment time—1 min. In surface functionalization experiments (NH_3 and O_2 plasma treatments), these experimental conditions correspond to a compromise allowing both the grafting of a sufficient amount of chemical groups at the polymer surface and a noticeable etching of this surface (favoring mechanical interlocking) without any overtreatment of the polymer surface.

3.3. Nickel Electroless Metallization

For experiments leading to Ni ELD, the activation step of the NH_3 plasma-treated areas was carried out at room temperature for 2 min using an acidic palladium chloride solution [0.1 g/L $PdCl_2 + 0.1$ mL/L HCl (37%)]. The formation of catalytic sites (Pd^0) was obtained at room temperature by immersion of the Pd^{+2}-based activated areas into a hypophosphite solution (10 g/L $NaH_2PO_2 \cdot H_2O$) for 3 min. ELD was performed for 2 min using a laboratory-made electroless Ni solution ($NiSO_4 \cdot 6H_2O$: 36 g/L; $NaH_2PO_2 \cdot H_2O$: 10 g/L; lactic acid: 29 mL/L; pH adjustment at 5 by NaOH addition; temperature: 85°C). Figure 1 displays the various steps of the electroless metallization process used in the case of Ni ELD. Note that the chemical reduction of the Pd^{+2} species to the Pd^0 state is required in the case of commercial Ni plating baths [47–49].

3.4. Silver Electroless Metallization

For experiments leading to Ag ELD, the sensitization step of the O_2 plasma-treated (90 W) areas was carried out at room temperature for 3 min using an aqueous tin chloride solution (0.2 g/L $SnCl_2$). The

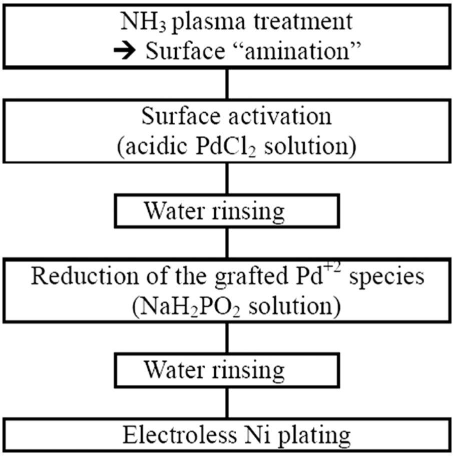


FIGURE 1 Schematic diagram of the electroless Ni plating process.

activation step was then performed at room temperature for 3 min using an aqueous silver nitrate solution (0.2 g/L $AgNO_3$) thanks to the redox reaction $Sn^{+2} + 2Ag^{+} \rightarrow Sn^{+4} + 2Ag^{0}$. The sample was then treated for 1 min by Ar or H_2 plasma (20 W) to improve the activation of the surface, possibly due to the reduction capabilities of such plasma treatments [69,70]. Ag ELD was then carried out at room temperature for 30 s using a laboratory made plating bath containing 10 g/L $AgNO_3$, 85 g/L NH_4OH, and 0.3 g/L formaldehyde as the reducing agent.

3.5. Micro-Contact Printing

PDMS stamps (μCP process) were fabricated by replica molding from silicon masters created *via* standard lithography and reactive ion etching (RIE) processes. In this work, the stamps were obtained by casting a 10:1 (v/v) mixture of PDMS and curing agent (Sylgard 184®, Dow Corning Corp., Midland, MI, USA) against the patterned master and then curing at 60°C for 120 min. They were used to transfer palladium-based catalytic species onto the areas to be metallized or to passivate the areas not to be metallized, respectively. In each case, the stamp was applied by hand by maintaining an intimate contact with the substrate under a slight pressure for a few seconds at room temperature. The stamps were then carefully removed to avoid, as far as possible, distortion of the printed pattern. SAMs of octadecylamine CH_3-$(CH_2)_{17}$-NH_2 (ODA) were used to passivate the PI surface covered with Pd^{+2}. Similarly, SAMs of octadecylmercaptan CH_3-$(CH_2)_{17}$-SH (ODM) were used to passivate the PI surface covered with Ag^0. Both SAMs were obtained from Sigma-Aldrich (L'Isle d'Abeau, France).

3.6. Ink-Jet Printing

In IJP experiments, patterns were created using a commercially available Canon Pixma® iP 4300 ink-jet printer and a standard drawing program (using Times New Roman 6 and 2 pt) to print locally the commercial ink to passivate the areas not to be metallized. The surface-treated polymer film was affixed to a supporting A4 paper sheet using a standard 3M adhesive tape. After writing, the print-out was allowed to dry under room conditions.

3.7. Characterization Techniques

The metal micro-patterns were observed by optical microscopy (Olympus BX41 M instrument; Olympus Corp., Tokyo, Japan), scanning electron microscopy (SEM) (Philips 515 apparatus; Philips, Eindhoven, The Netherlands), and atomic force microscopy (AFM) (Agilent PicoPlus® instrument operating in tapping mode; Agilent Technologies, Palo Alto, CA, USA). Spectroscopic analyses were carried out using a Riber SIA 200 (Cameca, Gennevilliers, France) X-ray photoelectron spectrometer (XPS) equipped with a non-monochromated Al K_α source. All spectra were referenced to the C 1s peak (C-C and C-H bonds) whose binding energy was fixed at 285.0 eV [71]. All of the samples for XPS analyses were introduced into the spectrometer, *i.e.*, under UHV, within 5 to 10 min after the corresponding surface modifications. Atomic concentrations as determined from the XPS peak areas are considered to be accurate within ±10%.

Practical adhesion of Ni microstructures to their substrates was evaluated using the standard ASTM Scotch® tape test (cross-cut tape test performed with a 3M 2503710 Scotch® tape).

4. RESULTS AND INTERPRETATION

The first part of the present work deals with Ni micro-patterning on PI. In this case, the palladium-based catalyst is used (Fig. 1). The second part of this work is devoted to Ag micro-patterning. In that case, the process does not require the use of the palladium-based catalyst as the polymer surface can be sensitized with tin-based species to directly graft the catalyst Ag^0 (Fig. 2).

4.1. Nickel Patterning

For Ni ELD experiments, plasma treatments were first carried out to prepare the polymer surface (cleaning, etching) and to graft nitrogen-containing groups on which the palladium-based species are subsequently chemisorbed (Fig. 1). For this purpose, only NH_3 plasma treatments were used in this work. Under these conditions, amino groups are mainly grafted onto the polymer surface [72]. Previous works illustrated that the maximum surface content in nitrogen (about 12 at.% as measured by XPS) is quickly obtained after a treatment time of about 10s [47–49] but longer durations (1–2 min) for which the N content is slightly lower (about 10 at.%) are required to strongly improve, at the end of the process, the mechanical anchoring, *i.e.*, the practical adhesion (thanks to the increase of the substrate etching) of the EL metal film [73]. After plasma treatment, the surface activation was implemented by immersion of the surface-grafted substrates in an acidic $PdCl_2$ solution (tin-free catalysis process). After

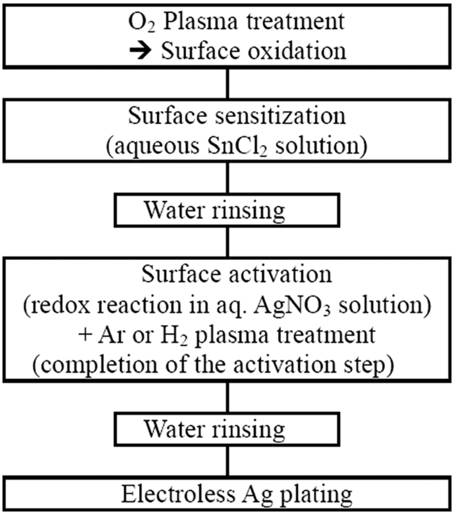


FIGURE 2 Schematic diagram of the electroless Ag plating process. Note that the activation is significantly improved when the sample, after immersion in an aqueous $AgNO_3$ solution, is Ar or H_2 plasma-treated, possibly due to the reduction capabilities of such plasma treatments.

rinsing, the chemical reduction of the Pd^{+2} species grafted on the surface nitrogen-containing groups was carried out by immersion in an aqueous hypophosphite solution but this reduction can also be carried out using H_2 or Ar plasma [69,70]. It should be kept in mind that Pd^0 is the actual catalyst able to initiate the EL metallization in the plating bath, especially when commercial electroless solutions are used [47–49].

Figure 3 displays a schematic illustration of the routes used to fabricate micro-patterned structures by combining the steps of the ELD process described in Fig. 1 and μCP. As an illustration of the (a) route (localized activation by stamping), Fig. 4 shows the optical micrograph of 1.0 μm-wide Ni dots obtained by immersion in the plating bath after a homogeneous NH_3 plasma-treatment of the PI substrate followed by a μCP transfer of the Pd-based catalyst (PDMS stamping). In this example, the μCP transfer was operated using a stamp with positive relief features which directly “ink” the areas to be metallized.

μCP can also be used to selectively deactivate the Pd-based catalyst homogeneously chemisorbed onto the PI surface subsequently to the NH_3 plasma treatment [route (b) in Fig. 3 (localized passivation by

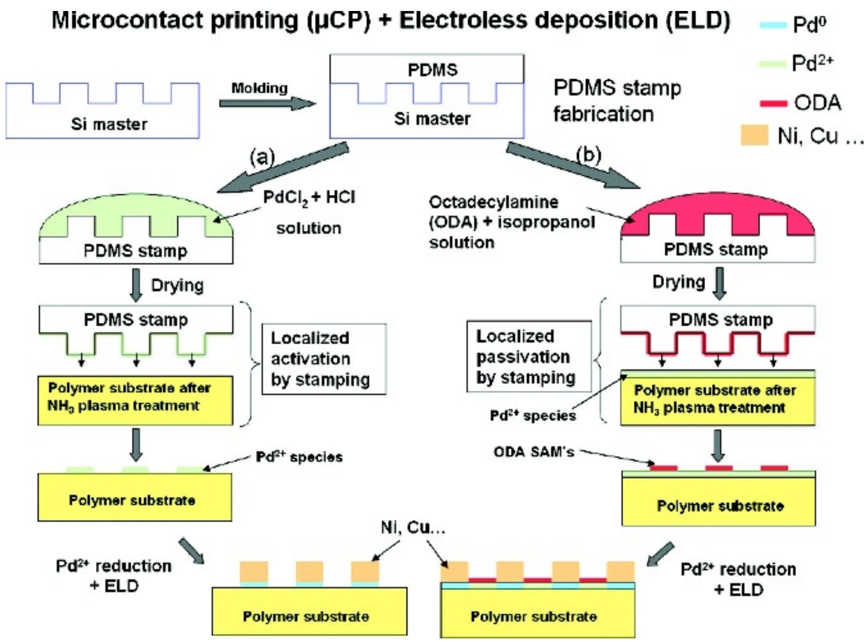


FIGURE 3 Schematic illustration of the routes used in this work to fabricate micro-patterned metal structure at polymer surfaces by combining plasma treatments, micro-contact printing (μCP) and electroless deposition (ELD). In route (a), the Pd^{+2}-based species are directly stamped onto the NH_3 plasma-treated polymer surfaces. The so-patterned substrates are then immersed in a hypophosphite solution in order to create the catalytic Pd^0 sites. After rinsing, the substrates patterned with the catalyst are dipped into the electroless bath for plating. On the other hand, in route (b), the octadecylamine (ODA) stamping is used to realize the localized passivation of the Pd^{+2} adsorbed species on the NH_3 plasma-treated polymer surfaces. Finally, the Pd^{+2} reduction and ELD steps are carried out as in route (a).

stamping)]. For this purpose, octadecylamine (ODA) SAMs containing terminal amino functionalities were used. As a result, the chemical affinity of the amino groups towards the chemisorbed Pd^{+2} species allows the local blocking of the reduction of Pd^{+2} to Pd^0 during the reduction step. The non-stamped areas are indeed those leaving free the surface Pd^{+2} species which can then be submitted to metallization after the reduction of Pd^{+2} to Pd^0. Figure 5 shows a SEM image of 2.5 μm lateral size micro-patterned Ni dots obtained through this process. In this example, the μCP transfer was carried out using a negative stamp, *i.e.*, a stamp with relief features which ink the areas not to

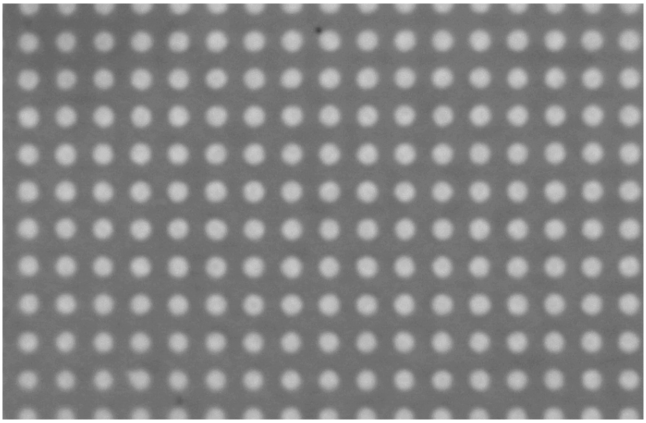


FIGURE 4 Optical micrograph of 1.0 μm lateral size micro-patterned Ni dots (2 μm periodic array) obtained by activating the PI surface according to route (a) (see Fig. 3). Here, μCP is used to transfer directly the Pd-based catalyst on the areas to be metallized.

be metallized. This method is, therefore, the reverse of that described in the previous example (Fig. 4). Under these conditions, in Fig. 5, the passivated areas appear dark while the metallized Ni dots appear bright.

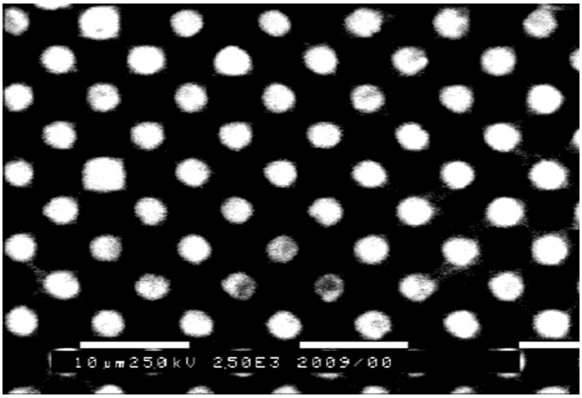
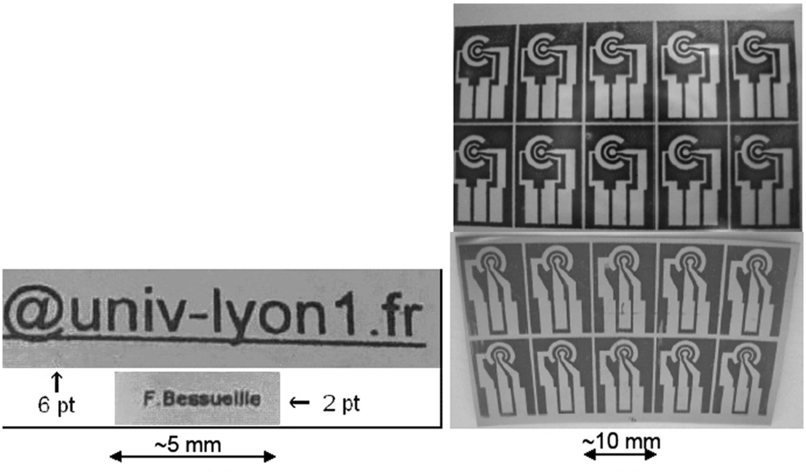


FIGURE 5 SEM image of 2.5 μm lateral size micro-patterned Ni dots (5 μm periodic array) obtained by activating the PI surface according to route (b) (see Fig. 3). Here, μCP transfer was operated using a negative stamp, i.e., a stamp with relief features which "ink" the areas not to be metallized (the passivated areas appear dark while the metallized Ni dots appear bright) (bar size = 10 μm).

Figure 6 is relative to Ni ELD of selected areas on PI substrates using IJP. This technology is here used to ink the areas not to be metallized. In this case, the ink (black print cartridge 5 PGBK from Canon, Tokyo, Japan) is deposited by the printer on areas defined by the operator. The ink operates as a mask and plays a role similar to the resist layer of a lift-off process. More in detail, inking was first carried out on the cleaned PI surface. The sample surface was then homogeneously NH_3 plasma-treated, activated by immersion in the acidic $PdCl_2$ solution, and metallized by ELD. Finally, ink removal was carried out through successive rinsing steps in ethanol and acetone. Metal deposits on the ink were thus also removed. Figure 6(a) displays a photograph of the E-mail address of the University Lyon 1 (Times New Roman 6pt) and name of the principal author (Times New Roman 2pt). This address was printed onto PI using IJP. After the whole process, only the framework around this address appears metallized, leaving the address not metallized.

Similarly, Fig. 6(b) is relative to Ni micro-electrodes also created on PI substrates and correspond to two different steps of the fabrication



(a) (b)

FIGURE 6 Photographs of: (a) the E-mail address of the University Lyon 1 (Times New Roman 6 pt) and name of the principal author (Times New Roman 2 pt) and (b) of two different steps of fabrication of micro-electrodes (illustrated for two different systems) (upper right: after the IJP step; bottom right: after the ELD step). In both cases, deposits were obtained by combination of IJP and Ni ELD (PI substrates) (smallest width of the Ni lines approximately between 50 and 100 μm).

(illustrated for two different micro-electrode systems). Dark areas in the upper right image are due to the inked areas while the bright areas correspond to the unprinted PI zones, the photograph being taken just after ink-jet printing. On the other hand, dark areas in the bottom right image for another microelectrode system correspond to the natural orange color characteristic of the PI substrate, again observable after ink removal (lift-off step) while the bright areas correspond to the metallic microelectrodes deposited on unprinted PI zones, the photograph being taken just after ELD.

4.2. Silver Patterning

For Ag ELD experiments, plasma treatments were carried out to prepare the polymer surface (cleaning, etching) and to graft oxygen-containing groups on which the tin-based species are subsequently chemisorbed (Fig. 2). For this purpose, only O_2 plasma treatments were used in this work but Ar or H_2 plasma treatments are also possible followed by a post-oxidation in air [52,74]. After O_2 plasma treatments, a significant oxygen content (about 30 at.% as measured by XPS, O/C ratio being equal to 0.40; in comparison, the oxygen content is about 17 at.% for the untreated PI substrate, O/C ratio being equal to 0.22) is detected for a 1-min treatment time. Afterwards, during the sensitization step, tin species are chemisorbed at a noticeable amount (about 7 at.% as measured by XPS) at the PI surface grafted with oxygen-containing functionalities. It should be noted that such a significant chemisorption of Sn^{+2} species has already been highlighted in previous works carried out in our laboratory which compared the capabilities of various polymer surfaces to be plasma-treated in nitrogenated and oxygenated atmospheres, with the view to attaching Pd/Sn or Pd-based particles used as catalysts for Ni or Cu ELD [47–49]. In other words, these results have confirmed the specific chemical affinity of the Sn^{+2} species towards oxygen-containing functionalities as that of the Pd^{+2} species had been previously confirmed towards nitrogen-containing functionalities. After sensitization and water rinsing, the Sn^{+2}-sensitized surface may be directly exposed to the electroless plating bath containing the Ag^{+} species and the redox reaction $Sn^{+2} + 2Ag^{+} \rightarrow Sn^{+4} + 2Ag^{0}$ takes place, leading to the formation of an ultra-thin layer of metallic Ag acting as the first catalytic layer before propagation by autocatalysis. However, activation is significantly improved when the sample is first immersed in an aqueous $AgNO_3$ solution. It is even better if this immersion is followed by Ar or H_2 plasma treatment, possibly due to the reduction capabilities of such plasma treatments [69,70]. On the other hand, it should be indicated that Ag ELD metallization does not occur when the O_2 plasma-treated surfaces are not subjected to the Sn^{+2}-based sensitization step before immersion in $AgNO_3$ solution and ELD bath.

The route used to fabricate micro-patterned Ag structures is different from those used for Ni patterning. A homogeneously distributed Ag ultra-thin layer is deposited and μCP of SAMS is then performed to block locally the catalytic activity of the Ag^0 species. Figure 7 shows

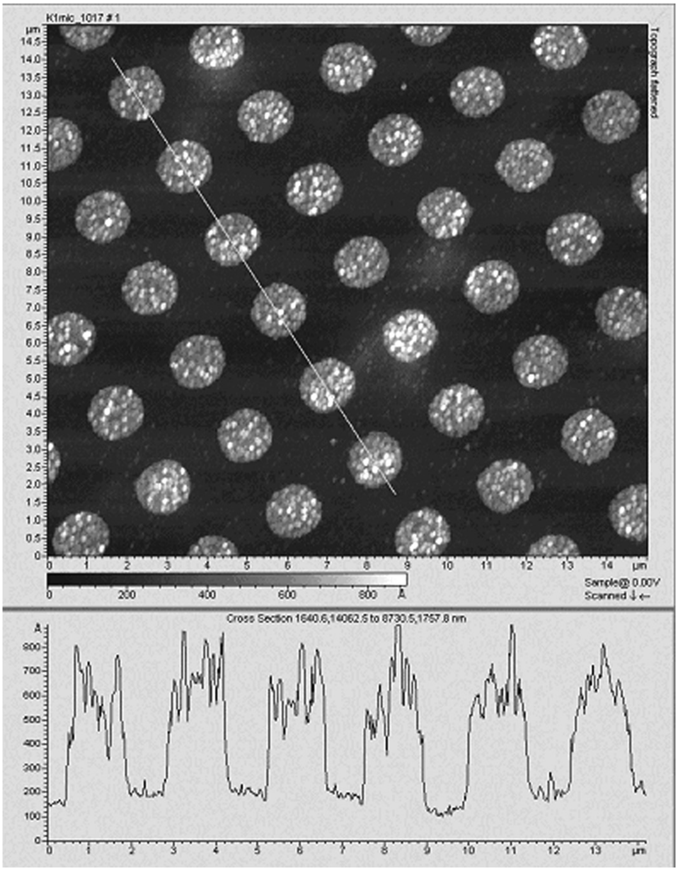


FIGURE 7 Tapping-mode AFM image of micro-patterned Ag structures (2 μm periodic array) obtained by electroless depostion (ELD) on PI substrates after a surface activation according to the route described in Fig. 2 (surface oxidation, sensitization, redox reaction between Sn^{+2} and Ag^{+} species, and H_2 plasma treatment). Note that the Ag grain size in the deposit is about 0.1 μm. In this experiment, the average thickness of Ag deposits (see height profile in the bottom illustration) is about 50 nm.

micro-patterned Ag structures grown by ELD on a PI substrate previously coated with the homogeneously distributed Ag ultra-thin layer (probably about 1 nm in thickness) obtained by carrying out the first part of the process described in Fig. 2 (O_2 plasma treatment, Sn^{+2} sensitization, Sn^{+2}/Ag^{+} redox reaction in the aqueous $AgNO_3$ solution, and reduction by H_2 plasma treatment). In this example, the μCP octadecylmercaptan (ODM) transfer was operated again using a negative stamp, *i.e.*, a stamp with relief features which ink the areas not to be metallized. In other words, the ODM SAMs containing thiol end-functionalities were used to block locally the catalytic activity of the ultra-thin Ag^0 layer obtained after the H_2 plasma reduction treatment. Indeed, it should be remembered that the ODM-stamped areas are passivated because the thiol (-SH) groups react chemically with silver through the formation of thiolate-type interfacial bonds [75]. Under these conditions, the Ag ELD patterning may be achieved over the non-stamped areas when the locally ODM passivated samples are immersed in the electroless Ag plating bath. Concerning the Ag micro-patterned ELD structures, it should be noted that individual Ag grains are observed by AFM, their size being estimated to be about 0.1 μm. Furthermore, the average thickness of the Ag deposits (see height profile in the bottom illustration) obtained after a 30 s ELD treatment time is about 50 nm.

In all of the examples described in this paper, the practical adhesion of metal deposits on the PI surface was checked on samples that were homogeneously treated following the processes described in Figs. 1 and 2 as well as on micro-patterned samples. The standard ASTM Scotch® tape test (cross-cut tape test performed with a 3M 2503710 Scotch® tape) was used and the practical adhesion of all deposits was considered as good (code 5 of the ASTM standard) since no metal was removed by peeling off the Scotch® tape. This is an expected result, given the selection of plasma treatment conditions avoiding any overtreatment of the polymer surface.

5. CONCLUSIONS

From the results presented and discussed in this paper, the following conclusions can be drawn:

1. Plasma treatments, micro-contact printing (μCP) or ink-jet printing (IJP), and electroless deposition (ELD) were used to develop well adhering micrometer-scale metal (Ni, Ag) patterns at the surface of PI substrates. The combination of these techniques is considered to have a great potential for the fabrication at low cost

(compared to conventional lithographic methods) and over large substrate areas of various innovative metal micro-patterned polymer-based devices, *e.g.*, for microelectronics and bioengineering applications. Studies are currently in progress in order to obtain higher resolution and uniformity of the so-formed metal micro-features. It should be noted that μCP has the capability of providing higher performances in terms of lateral resolution than IJP (in the latter case, the feature size is limited by that of the ink droplets as obtained from the printer). On the other hand, complex metal patterns of micrometer scale should be more easily fabricated using IJP than μCP as no master (to obtain stamps) is required for the former.

2. In these processes combining plasma treatments, micro-contact printing (μCP) or ink-jet printing (IJP), and electroless deposition (ELD), the versatility of plasma treatments has been highlighted by proposing different routes for Ni and Ag micro-patterning on PI. It opens a lot of possible variations in terms of either process steps or metals to be deposited. As an example, all processes proposed for Ni micro-patterning can also be easily adapted for Cu (similar catalysis route).

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