J|A|C|S
ARTICLES

Selectively Metallized Polymeric Substrates by Microcontact Printing an Aluminum(III) Porphyrin Complex

Michael S. Miller, Heather L. Filiatrault, Gregory J. E. Davidson, Minmin Luo, and Tricia Breen Carmichael*

Department of Chemistry and Biochemistry, University of Windsor,
Windsor, Ontario, Canada N9B 3P4

Received October 3, 2009; E-mail: tbcarmic@uwindsor.ca

Abstract: We report a simple, low-cost method for the fabrication of copper wires and contacts on a wide range of flexible, rigid, and inert polymeric substrates. This method relies on procedures to oxidize the polymeric substrates to form surface-bound carboxylic acid groups. Patterning of an aluminum porphyrin ink using microcontact printing results in the formation of an aluminum porphyrin monolayer that is covalently anchored to the oxidized polymer surface via an aluminum−carboxylate bond. We characterize this monolayer using ultraviolet−visible absorption spectra, reflection−absorption infrared spectroscopy, and contact angle measurements. Patterned aluminum porphyrin monolayers bind a Pd/Sn colloidal catalyst from solution that subsequently initiates the selective deposition of copper in an electroless plating solution. We demonstrate the fabrication of patterned copper films on a variety of both flexible and rigid polymers with minimum feature sizes of 2 μm over 2 cm^2 substrates. Measurements of electrical resistivity of copper wires fabricated on flexible poly(ethylene naphthalate) (PEN) substrates as a function of the bending radius show no negative impact on electrical performance at bending radii as small as 500 μm. Permanently damaging the PEN substrate by creasing (corresponding to a bending radius of 100 μm) results in only a modest increase in resistivity.

Introduction

In this paper we describe a simple, low-cost method based on microcontact printing and electroless metal deposition to fabricate metallic contacts and wires on polymeric substrates for use in lightweight plastic electronic devices. Plastic electronics span a wide range of applications and polymeric substrates: Flexible polymers, such as poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), and polyimide (PI), enable the fabrication of devices such as conformal displays, wearable electronics, and bioelectronic devices such as sensors and artificial nerves.[1] Rigid polymers that can be rapidly molded or lithographically patterned into thick, high-aspect-ratio structures, such as poly(methyl methacrylate) (PMMA) or the epoxy-based negative-tone photoresist SU-8, are useful as structural materials for microanalytical and microfluidic systems.[2] Coating these rigid structures with metal enables the transmission of electrical signals in devices such as microactuators,[3] electrochemical detectors,[4] millimeter-wave antennae for broad-bandwidth wireless communications,[5] and radio frequency conductors for microelectromechanical systems (MEMS).[6] The selective metallization method described in this paper is applicable to the range of substrates used for plastic electronics, as well as to inert polymers such as polyethylene (PE), polypropylene (PP), and poly(tetrafluoroethylene) (PTFE). Oxidizing these polymer surfaces generates a common surface chemistry consisting of surface-bound carboxylic acid groups. We use microcontact printing to form a patterned monolayer of an aluminum porphyrin complex that binds to the oxidized surface of the polymer through a covalent aluminum−carboxylate bond and subsequently captures a palladium−tin colloidal catalyst from solution, which initiates the electroless deposition (ELD) of copper from solution. This selective metallization process reduces fabrication costs by replacing complex and expensive processes—conventional photolithography and physical vapor deposition (PVD) of metals—with the simple, low-cost methods of microcontact printing and ELD. We demonstrate the process by fabricating patterned copper films on a variety of both flexible and rigid polymers with minimum feature sizes of 2 μm over 2 cm^2 substrates. We also establish an important practical advantage to this process by demonstrating that copper wires fabricated on flexible PEN substrates withstand substantial

---

(1) (a) Special issue on “Flexible Electronics”. *Mater. Today* **2006**, *9*, 24−52. (b) Special issue on “Macroelectronics”. *Mater. Res. Soc. Bull.* **2006**, *31* (6), 447−475. (c) Special issue on “Flexible Electronics Technology, Part 1: Systems and Applications”. *Proc. IEEE* **2005**, *93* (7), 1235−1378. (d) Special issue on “Flexible Electronics Technology, Part 2: Materials and Devices”. *Proc. IEEE* **2005**, *93* (8), 1391−1510. (e) Someya, T.; Sekitani, T.; Iba, S.; Kato, Y.; Kawaguchi, H.; Sakurai, T. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 9966–9970.

(2) Velten, T.; Ruf, H. H.; Barrow, D.; Aspragathos, N.; Lazarou, P.; Jung, E.; Malek, C. K.; Richter, M.; Kruckow, J.; Wackerle, M. *IEEE Trans. Adv. Packag.* **2005**, *28*, 533–546.

(3) Dai, W.; Wang, W. *Proc. SPIE*−*Int. Soc. Opt. Eng.* **2007**, *6464*, 64640I.

(4) Henry, A. C.; McCarley, R. L. *J. Phys. Chem. B* **2001**, *105*, 8755–8761.

(5) Yoon, Y.-K.; Pan, B.; Papapolymerou, J.; Tentzeris, M.; Allen, M. G. *International Conference on Solid-State Sensors, Actuators, and Microsystems (Transducers ’05)*; IEEE: New Jersey, 2005; pp 1986−1989.

(6) Yoon, Y.-K.; Allen, M. G. *J. Microelectromech. Syst.* **2005**, *14*, 886–894.

10.1021/ja908433p

mechanical deformation without a loss in performance: Wire resistivity is unaffected by bending the metallized PEN around a cylinder of <1 mm radius.

The emergence of plastic electronic products has intensified the drive to reduce the cost and complexity of their fabrication. Academic research leads this effort by developing fabrication processes that replace conventional technologies such as photolithography and PVD, both of which are slow processes with high capital and operating expenses, with simple patterning methods such as microcontact printing, inkjet printing, or screen printing and fast materials deposition methods from solution such as spin-coating or dip-coating.[7] For the deposition of metallic wires and contacts on polymeric substrates, researchers have developed several low-cost printing methods to replace photolithography; however, many of these methods rely on metal PVD. Examples include patterning methods based on shadow masks,[8] microcontact printing and etching,[9] nanotransfer printing,[10] and lamination.[11] These methods have all successfully contributed to the fabrication of flexible devices on polymeric substrates; in addition, Rogers et al. demonstrated that microcontact printing and etching can produce high-quality plastic electronics over large substrate areas.[9a] To further reduce costs, however, it is necessary to eliminate our dependence on PVD and instead combine a low-cost patterning method with solution-based metal deposition. One approach is to directly pattern a conductive metallic ink or a suspension of metallic nanoparticles. Conductive silver inks have been patterned using screen printing, which uses a physical mask to block the flow of the ink.[12] Although this method is compatible with large-area patterning, it is limited by the relatively modest resolution that can be achieved (~75 μm).[7b] Solutions of metallic nanoparticles have been patterned using inkjet printing[13] and direct ink writing.[14] Annealing the printed nanoparticles to create conductive metallic films can be accomplished at relatively low temperatures due to melting point depression of metal nanoparticles, making this process compatible with many polymeric substrates. A second approach is to combine a low-cost patterning method such as inkjet printing or microcontact printing with a solution-based metal deposition process such as ELD.[15] ELD is widely used in the microelectronics industry to form patterned conducting lines and interlevel connections on printed circuit boards, to cap copper damascene interconnects in semiconductor devices, and to fabricate thin metal etch masks.[16] It can be used to deposit metals such as copper, nickel, gold, silver, and cobalt onto either metallic or insulating substrates. In ELD, metal ions in the electroless plating solution are chemically reduced to metal by a Pd catalyst chemisorbed on the surface of the substrate. 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. Inkjet printing and microcontact printing have both been used with ELD to fabricate metal contacts and wires on plastic substrates. Inkjet printing of either a Pd catalyst[17] or a polyelectrolyte adhesion layer that subsequently binds a Pd catalyst from solution,[18] followed by ELD, has been demonstrated on PET substrates. Microcontact printing has been used with ELD in either subtractive or additive patterning approaches. Subtractive patterning uses ELD to deposit a blanket metal film that is then patterned by microcontact printing an alkanethiol self-assembled monolayer (SAM) and wet etching.[19] Although this approach is presumably compatible with plastic substrates, the process of depositing and then removing metal generates waste. Additive patterning eliminates this drawback by using microcontact printing to define a chemical pattern on a polymeric substrate and then depositing metal within that pattern using ELD. There are few reports of additive patterning methods on polymeric substrates, and they can be divided into two categories. The first category uses microcontact printing to directly transfer the Pd catalyst to the surface of a polymeric substrate, followed by ELD. Whitesides et al. demonstrated this approach by microcontact printing tetraalkylammonium bromide-stabilized Pd nanoparticles to a polymeric substrate that had previously been oxidized and treated with an organosilane bearing amino or thiol groups.[20] The organosilane is an adhesion promoter: It covalently binds to the oxidized surface and presents amino or thiol groups that bind the Pd catalyst. In the second category, it is the organosilane layer that is initially patterned by microcontact printing; Pd or

---

(7) For two excellent reviews of the use of low-cost fabrication methods, see: (a) Menard, E.; Meitl, M. A.; Sun, Y.; Park, J.-U.; Shir, D. J.; Nam, Y.-S.; Jeon, S.; Rogers, J. A. *Chem. Rev.* **2007**, *107*, 1117–1160. (b) Ling, M. M.; Bao, Z. *Chem. Mater.* **2004**, *16*, 4824, and references therein.

(8) Klauk, H., Ed. *Organic Electronics: Materials, Manufacturing and Applications*; Wiley-VCH: Weinheim, Germany. 2006.

(9) (a) Rogers, J. A.; Bao, Z.; Baldwin, K.; Dodabalapur, A.; Crone, B.; Raju, V. R.; Kuck, V.; Katz, H.; Amundson, K.; Ewing, J.; Drzaic, P. *Proc. Nat. Acad. Sci. U.S.A.* **2001**, *98*, 4835–4840. (b) Mach, P.; Rodriguez, S. J.; Nortrup, R.; Wiltzius, P.; Rogers, J. A. *Appl. Phys. Lett.* **2001**, *78*, 3592–3594. (c) Rogers, J. A.; Bao, Z.; Dodabalapur, A. *IEEE Electron Device Lett.* **2000**, *21*, 100–103. (d) Rogers, J. A.; Bao, Z. N.; Makhija, A.; Braun, P. *Adv. Mater.* **1999**, *11*, 741–745.

(10) (a) Cosseddu, P.; Bonfiglio, A. *Appl. Phys. Lett.* **2006**, *88*, 023506. (b) Hur, S. H.; Khang, D. Y.; Kocabas, C.; Rogers, J. A. *Appl. Phys. Lett.* **2004**, *85*, 5730–5732. (c) Wang, Z.; Xing, R. B.; Zhang, J.; Yuan, J. F.; Yu, X. H.; Han, Y. C. *Appl. Phys. Lett.* **2004**, *85*, 831–833. (d) Loo, Y. L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *Appl. Phys. Lett.* **2002**, *81*, 562–564.

(11) (a) Loo, Y. L.; Someya, T.; Baldwin, K. W.; Bao, Z. N.; Ho, P.; Dodabalapur, A.; Katz, H. E.; Rogers, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 10252–10256. (b) Guo, T. F.; Pyo, S.; Chang, S. C.; Yang, Y. *Adv. Funct. Mater.* **2001**, *11*, 339–343.

(12) Gray, C.; Wang, J.; Duthaler, G.; Ritenour, A.; Drzaic, P. S. *Proc. SPIE—Int. Soc. Opt. Eng.* **2001**, *4466*, 89–94.

(13) (a) van Osch, T. H. J.; Perelaer, J.; de Laut, A. W. M.; Schubert, U. S. *Adv. Mater.* **2008**, *20*, 343–345. (b) Smith, P. J.; Shin, D.-Y.; Stringer, J. E.; Derby, B. *J. Mater. Sci.* **2006**, *41*, 4153–4158. (c) Deardon, A. L.; Smith, P. J.; Shin, D.-Y.; Reis, N.; Derby, B.; O'Brien, P. *Macromol. Rapid Commun.* **2005**, *26*, 315–318. (d) Kamyshny, A.; Ben-Moshe, M.; Aviezer, S.; Magdassi, S. *Macromol. Rapid Commun.* **2005**, *26*, 281–288. (e) Redinger, D.; Molesa, S.; Yin, S.; Farschi, R.; Subramanian, V. *IEEE Trans. Electron Devices* **2004**, *51*, 1978–1983. (f) Szczech, J. B.; Megaridis, C. M.; Gamota, D. R.; Zhang, J. *IEEE Trans. Electron. Packag. Manuf.* **2002**, *25*, 26–33.

(14) Ahn, B. Y.; Duoss, E. B.; Motala, M. J.; Guo, X.; Park, S.; Xiong, Y.; Yoon, J.; Nuzzo, R. G.; Rogers, J. A.; Lewis, J. A. *Science* **2009**, *323*, 1590–1593.

(15) Mallory, G. O., Hajdum, J. B., Eds. *Electroless Plating: Fundamentals and Applications*; American Electroplaters and Surface Finishers Society: Orlando, FL, 1990.

(16) (a) Nakano, H.; Itabashi, T.; Akahoshi, H. *J. Electrochem. Soc.* **2005**, *152*, C163. (b) Mak, C. Y. *MRS Bull.* **1994**, August, 55−62. (c) Cho, J. S. H.; Kang, H.-K.; Wong, S. S.; Shachem-Diamand, Y. *MRS Bull.* **1993**, June, 31−38. (d) Li, J.; Blewer, R.; Mayer, J. W. *MRS Bull.* **1993**, June, 18. (e) Ting, C. H.; Paunovic, M.; Pai, P. L.; Chiu, G. *J. Electrochem. Soc.* **1989**, *136*, 462–466. (f) Ting, C. H.; Paunovic, M. *J. Electrochem. Soc.* **1989**, *136*, 456–462.

(17) (a) Cheng, K.; Yang, M.-H.; Chiu, W. W. W.; Huang, C.-Y.; Chang, J.; Ying, T.-F.; Yang, Y. *Macromol. Rapid Commun.* **2005**, *26*, 247–264. (b) Shah, P.; Kevrekidis, Y.; Benziger, J. *Langmuir* **1999**, *15*, 1584–1587.

(18) (a) Wang, T. C.; Chen, B.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2001**, *17*, 6610–6615. (b) Guo, R.-F.; Chang, S.-C.; Pyo, S.; Yang, Y. *Langmuir* **2002**, *18*, 8142–8147.

(19) Tate, J.; Rogers, J. A.; Jones, C. D. W.; Vyas, B.; Murphy, D. W.; Li, W.; Bao, Z.; Slusher, R. E.; Dodabalapur, A.; Katz, H. E. *Langmuir* **2000**, *16*, 6054–6060.

(20) Hidber, P. C.; Helbig, W.; Kim, E.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1375–1380.

Pd/Sn colloids subsequently bind from solution selectively either within or outside the patterned organosilane. For example, Prissanaroon et al. used microcontact printing of an organosilane adhesion promoter bearing an amino group and subsequent binding of Pd colloids from aqueous solution to selectively metallize plasma-modified PTFE.[21] Li et al. also used microcontact printing to pattern an organosilane adhesion promoter for the selective metallization of PI; however, this method was only applicable to a siloxane-containing polyimide substrate.[22] Zschieschang et al. used microcontact printing to transfer a patterned fluorinated organosilane to the surface of a PEN substrate; the fluorinated layer subsequently acted as a resist to Pd catalyst adsorption, allowing for the selective deposition of nickel gate electrodes on the PEN surface and fabrication of flexible circuits.[23]

The problem with the reported additive approaches to selective electroless metallization is the incompatibility of poly(dimethylsiloxane) (PDMS) stamps used in microcontact printing with the solvents used to suspend Pd nanoparticles, with polar catalysts such as Pd or Pd/Sn colloids, and with organosilanes. Tetraalkylammonium bromide-stabilized Pd nanoparticles require the use of solvents such as toluene or THF, which swell the stamp[24] and lead to distortion of the metallized pattern. Distortion is highly detrimental to device fabrication, where registration between patterned material layers is crucial. Pd/Sn colloids or other polar catalysts use aqueous solvents that inhibit the deposition of the catalyst onto the surface of the hydrophobic PDMS stamp. Rendering the PDMS surface hydrophilic by plasma oxidation is only a temporary solution due to the tendency of PDMS to undergo hydrophobic recovery over a period of only a few hours.[25] Microcontact printing of functionalized organosilanes also requires plasma oxidation of the stamp to enable inking and additionally presents a serious manufacturing problem: The hydrolytic instability of alkyltrichloro- and alkyltrialkoxysilanes results in cross-linking on the surface of the PDMS stamp, curtailing its lifetime.

Our approach to the selective electroless metallization of polymeric substrates incorporates the economic advantages of microcontact printing and ELD with a new microcontact printing ink—an aluminum(III) porphyrin complex—to eliminate the problems plaguing previous methods that use unsuitable printing inks. In the past, applications of metalloporphyrins immobilized on solid substrates have predominantly been based on the optical and electrochemical properties of the metalloporphyrin: Optical and photoelectrochemical sensors,[26] molecular electronics,[27] and sensitizers in dye-sensitized solar cells[28] are all well-studied examples. Our work exploits different metalloporphyrin properties—solubility, hydrophobicity, and chemical reactivity at the metal center—to demonstrate that (tetraphenylporphyrinato)aluminum(III) methoxide ((TPP)Al−OMe) is an ideal microcontact printing ink when paired with oxidized polymeric substrates bearing carboxylic acid groups. There are four important advantages to using (TPP)Al−OMe as a microcontact printing ink and subsequent foundation for ELD: First, (TPP)Al−OMe is soluble in 2-propanol, an ideal solvent for microcontact printing because it minimizes swelling and distortion of the PDMS stamp. Second, (TPP)Al−OMe is a hydrophobic material that can effectively wet the surface of a native PDMS stamp, eliminating the need for stamp surface modification. Third, the reaction of (TPP)Al−OMe with carboxylic acid groups at the interface between the inked stamp and oxidized polymer occurs rapidly to form highly stable aluminum−carboxylate bonds that covalently anchor the (TPP)Al monolayer to the substrate (Figure 1). The byproduct of the reaction, methanol, evaporates or dissipates into the PDMS stamp, but does not cause swelling or distortion. The reactivity of aluminum(III) porphyrin complexes is well-established in solution: (TPP)Al−OH reacts rapidly with benzoic acid to generate the five-coordinate aluminum benzoate complex (TPP)Al−benzoate and liberate an equivalent of water.[29] The axially bound benzoate ligand is highly stable. It is not displaced by alcohols or water; rather, it requires a competitive carboxylic acid to be present in excess. Fourth, the (TPP)Al−carboxylate monolayer rapidly binds Pd/Sn colloids from solution to subsequently initiate ELD.

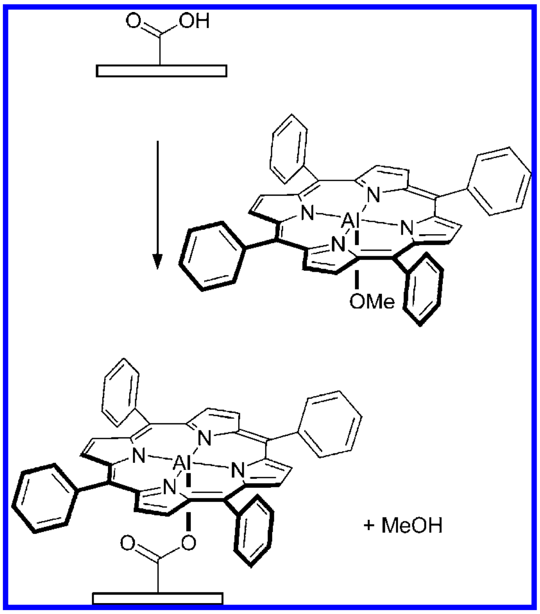


Figure 1. Reaction of (TPP)Al−OMe with carboxylic acid groups on the surface of an oxidized polymeric substrate.

Experimental Section

Materials. All materials and chemicals were purchased commercially and used as received. PDMS stamps were prepared by

---

(21) Prissanaroon, W.; Brack, N.; Pigram, P. J.; Hale, P.; Kappen, P.; Liesegang, J. *Thin Solid Films* **2005**, *477*, 131–139.

(22) Li, Y.; Chen, D.; Lu, Q.; Qian, X.; Zhu, Z.; Yin, J. *Appl. Surf. Sci.* **2005**, *241*, 471–476.

(23) Zschieschang, U.; Klauk, H.; Halik, M.; Schmid, G.; Dehm, C. *Adv. Mater.* **2003**, *15*, 1147.

(24) Lee, J. N.; Park, C.; Whitesides, G. M. *Anal. Chem.* **2003**, *75*, 6544–6554.

(25) Kim, J.; Chaudhury, M. K.; Owen, M. J.; Orbeck, T. *J. Colloid Interface Sci.* **2001**, *244*, 200–207.

(26) See, for example: (a) Spadavecchia, J.; Rella, R.; Siciliano, P.; Manera, M. G.; Alimelli, A.; Paolesse, R.; DiNatale, C.; D'Amico, A. *Sens. Actuators, B* **2006**, *115*, 12–16. (b) Andersson, M.; Holmberg, M.; Lundstrom, I.; Lloyd-Spetz, A.; Martensson, P.; Paolesse, R.; Falconi, C.; Proietti, E.; DiNatale, C.; D'Amico, A. *Sens. Actuators, B* **2001**, *77*, 567–571. (c) Flink, S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Adv. Mater.* **2000**, *12*, 1315–1328.

(27) See, for example: (a) Li, C.; Ly, J.; Lei, B.; Fan, W.; Zhang, D.; Han, J.; Meyyappan, M.; Thompson, M.; Zhou, C. *J. Phys. Chem. B* **2004**, *108*, 9646–9649. (b) Yasseri, A. A.; Syomin, D.; Malinovskii, V. L.; Loewe, R. S.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 11944–11953. (c) Roth, K. M.; Dontha, N.; Dabke, R. B.; Gryko, D. T.; Clausen, C.; Lindsey, J. S. *J. Vac. Sci. Technol., B* **2000**, *18*, 2359–2364.

(28) (a) Imahori, H.; Umeyama, T.; Ito, S. *Acc. Chem. Res.* **2009**, *42*, 1809–1818, and references therein. (b) Campbell, W. M.; Burrell, A. K.; Officer, D. L.; Jolley, K. W. *Coord. Chem. Rev.* **2004**, *248*, 1363–1379, and references therein.

(29) Davidson, G. J. E.; Tong, L. H.; Raithby, P. R.; Sanders, J. K. M. *Chem. Commun.* **2006**, 3087–3089.

casting PDMS prepolymer against photolithographic masters according to published procedures.[30] (TPP)Al−OMe was prepared using the literature method reported for (TPP)Al−OEt,[31] but the reaction was quenched with methanol rather than ethanol. (TPP)Al−benzoate was prepared according to the literature method. The following polymer films were purchased from Goodfellow (Oakdale, PA) and used as received (thickness of polymer films in parentheses): poly(ethylene terephthalate) (75 μm), poly(ethylene naphthalate) (75 μm), polyimide (75 μm), polypropylene (75 μm), polyethylene (125 μm), poly(tetrafluoroethylene) (100 μm), and poly(methyl methacrylate) (500 μm). SU-8 films were prepared as directed by the manufacturer. For details, see the Supporting Information.

Substrate Preparation. The surfaces of PET,[32] PEN,[32] PI,[33] PE,[34] PP,[34] PTFE,[35] PMMA,[36] and SU-8[37] were oxidized according to literature methods. For details, see the Supporting Information.

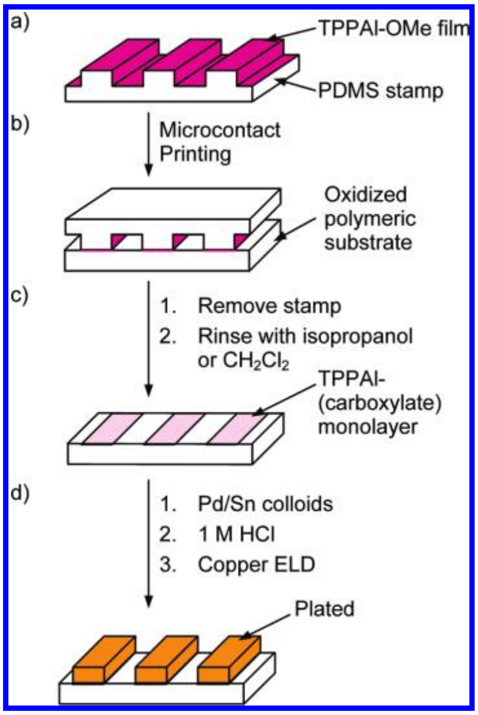
Stamp Inking and Printing. An ink solution of (TPP)Al−OMe in 2-propanol (1 mg/mL) was filtered through a 0.2 μm PTFE Acrodisc syringe filter. The surface of a PDMS stamp was flooded with the filtered ink solution and left for 30 s. A stream of nitrogen was used to first blow off excess solution and then to thoroughly dry the stamp for 30 s, leaving a film of neat (TPP)Al−OMe. Inked stamps were placed on the surface of oxidized polymeric substrates using tweezers, left for 1 min, and then removed. Porphyrin multilayers were removed by rinsing the printed substrate with 2-propanol for 1 min.

Electroless Metallization. The patterned polymeric substrate was immersed in a Pd/Sn colloidal catalyst solution (Cataposit 44 and Cataprep 404 (Shipley), prepared as directed by the manufacturer) for 1 min and an accelerator solution (1 M HCl) for 1 min and then metallized in the copper ELD bath (10:1, v/v, mixture of solutions A (copper(II) sulfate pentahydrate (4.5 g/L), sodium potassium tartrate tetrahydrate (21.0 g/L), and sodium hydroxide (6.0 g/L) in water) and B (37.2% formaldehyde in water)). Plating times were typically 3−5 min.

Reaction of (TPP)Al−Benzoate with HCl. A 0.03 mmol portion of (TPP)Al−benzoate was dissolved in 3.0 mL of CH_2Cl_2, 2.0 mL of 1 M HCl was added, and the mixture was shaken vigorously for 3 min. The mixture was allowed to stand for 3 h; the organic layer was then separated and dried over sodium sulfate. The solvent was removed by evaporation under vacuum and the residue dissolved in $CDCl_3$ for ^1H NMR spectroscopic analysis, which showed only the presence of (TPP)Al−benzoate.

Tape Test. Adhesion of copper films deposited by ELD was tested using the ASTM D3359B-02 tape test.[31] A 30 × 30 mm copper film was metallized on a polymeric substrate as described (a flat slab of PDMS was used as the microcontact printing stamp). A cutter equipped with 11 blades spaced by 1 mm was used to cut a lattice pattern measuring 20 × 20 mm in the copper film. Pressure-sensitive tape was applied to the cut area and then removed. Adhesion was assessed qualitatively on a 0−5 scale according to ASTM guidelines.[38]

Scheme 1. Schematic of the Process Steps Used To Fabricate Patterned Copper Films on Oxidized Polymeric Substrates



Fabrication of Copper Wires and Electrical Testing. Copper wires on PEN were fabricated with $l = 1.0$ cm, $w = 1.0$ mm, and $h = 40$ nm. A small drop of eutectic gallium−indium (EGaIn) was applied to each end of the wire. The wire was then bent around a metal cylinder with the desired radius of curvature, and then electrical contact was made via the EGaIn drops using stainless steel probes connected to a Keithley 2601 source meter (Keithley Instruments, Cleveland, OH). The resistance of the wire was measured at 0.005 V increments as the voltage was swept from −0.5 to +0.5 V. The average of these 210 measurements was used, and three separate measurements were taken for two wires at each radius of curvature. Radii of curvature ranged from 12.5 mm to 100 μm.

Characterization. Ultraviolet−visible (UV−vis) absorption spectra were collected using a CARY 50 Conc UV−vis spectrophotometer. Reflection−absorption infrared spectroscopy (RAIRS) spectra were collected using a Bruker IFS 66/v spectrometer equipped with a mercury cadmium telluride (MCT) detector and Harrick Autoseagull accessory. The p-polarized light was incident at 85° from the surface normal; 1024 scans were collected at a resolution of 2 cm^{-1}. Water contact angles were measured using the sessile drop method on a Rame-Hart contact angle goniometer. Three readings from at least two samples were averaged. ^1H NMR spectroscopy was performed using a Bruker DRX spectrometer operating at 500 MHz in $CDCl_3$, using residual $CHCl_3$ as the internal reference. Optical inspection was performed using an Olympus BX51 microscope. Scanning electron microscopy (SEM) images were obtained using an FEI Quanta 200 scanning electron microscope. Atomic force microscopy (AFM) measurements were made using a Digital Instruments Multimode atomic force microscope.

Results and Discussion

A Single Process Selectively Deposits Copper on a Variety of Oxidized Polymeric Substrates. We used a single process for the selective electroless metallization of flexible polymers (PET, PEN, and PI), rigid polymers (PMMA, SU-8), and polymers with low surface free energies (PE, PP, and PTFE). This process begins with oxidation of the polymer surfaces to create surface carboxylic acid groups. Scheme 1 outlines the

---

(30) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498–1511.

(31) Davidson, G. J. E.; Lane, L. A.; Raithby, P. R.; Warren, J. E.; Robinson, C. V.; Sanders, J. K. M. *Inorg. Chem.* **2008**, *47*, 8721–8726.

(32) Roux, S.; Demoustier-Champagne, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1347–1359.

(33) Stephans, L. E.; Myles, A.; Thomas, R. R. *Langmuir* **2000**, *16*, 4706–4710.

(34) Rasmussen, J. R.; Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736–4745.

(35) Kim, S. R. *J. Appl. Polym. Sci.* **2000**, *77*, 1913–1920.

(36) Brown, L.; Koerner, T.; Horton, J. H.; Oleschuk, R. D. *Lab Chip* **2006**, *6*, 66–73.

(37) Walther, F.; Davydovskaya, P.; Zurcher, S.; Kaiser, M.; Herberg, H.; Gigler, A. M.; Stark, R. W. *J. Micromech. Microeng.* **2007**, *17*, 524–531.

(38) *ASTM Annual Book of Standards*; American Society for Testing and Materials International: West Conshohocken, PA, 2002; Vol. 06.01.

subsequent process steps: (a) Inking a PDMS stamp with (TPP)Al−OMe forms a film of (TPP)Al−OMe on the surface of the stamp. (b) Microcontact printing brings the film of (TPP)Al−OMe in contact with the surface carboxylic acid groups of the substrate to form a (TPP)Al−carboxylate monolayer and 1 equiv of methanol, as depicted in Figure 1. It also transfers a film of unreacted (TPP)Al−OMe to the surface. (c) Rinsing with dichloromethane or 2-propanol removes the physisorbed (TPP)Al−OMe, leaving the (TPP)Al−carboxylate monolayer covalently bound to the surface. (d) Immersion in a solution of Pd/Sn colloids, which consist of a Pd-rich core protected from oxidation by a hydrolyzed Sn^{2+}/Sn^{4+} shell, binds the colloids selectively to the (TPP)Al−carboxylate monolayer. The acceleration step uses 1 M HCl to dissolve a portion of the Sn^{2+}/Sn^{4+} protective shell to expose the catalytic, Pd-rich core of the bound Pd/Sn colloids.[39] Immersion in an electroless copper plating bath deposits copper selectively over the catalyzed regions of the substrate.

Microcontact Printing Transfers a (TPP)Al−OMe Multilayer to Oxidized Polymeric Substrates. UV−vis absorption spectra of printed (TPP)Al−OMe films on oxidized PET confirm the initial formation of a multilayer of (TPP)Al−OMe and are consistent with the removal of physisorbed (TPP)Al−OMe by rinsing with dichloromethane or 2-propanol to leave a (TPP)Al−carboxylate monolayer on the surface (Figure 2a). For these experiments we used a flat slab of PDMS as the printing stamp to create a printed area on oxidized PET for UV−vis absorption spectroscopy. The very broad Soret band at 432 nm in the UV−vis spectrum of the as-printed layer is due to the random orientation of (TPP)Al−OMe molecules in the multilayered film: The absorption spectrum is the sum of the absorption bands resulting from the various types of excitonic couplings between molecules in the film.[40] Two Q-bands at 555 and 602 nm are also visible. After repeatedly rinsing the printed film with either dichloromethane or 2-propanol, the Q-bands are no longer detectable and the Soret band decreases in absorbance and narrows relative to the Soret band of the unrinsed film, consistent with the removal of physisorbed (TPP)Al−OMe. The bathochromic shift of the Soret band (426 nm) relative to the solution spectrum (414 nm) is typical of head-to-tail dipolar interactions between π-systems of neighboring adsorbates[41] and is thus consistent with the formation of a (TPP)Al−carboxylate monolayer.

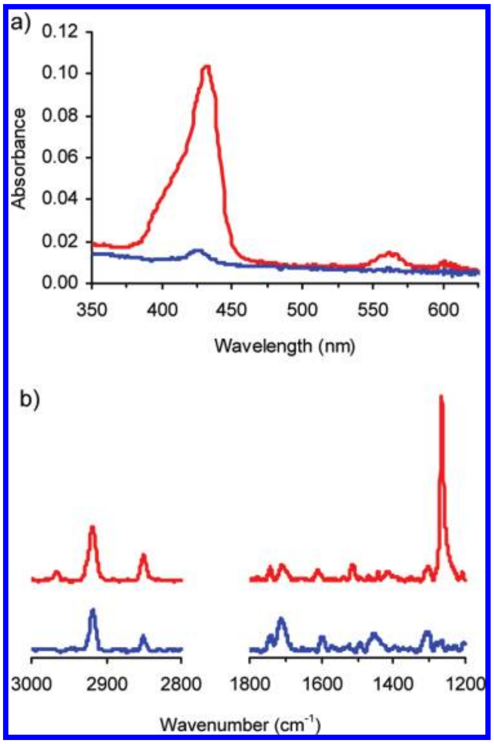


Figure 2. Characterization of a (TPP)Al−OMe film transferred by microcontact printing to the surface of an oxidized PET substrate. (a) UV−vis absorption spectrum of a (TPP)Al−OMe film transferred by microcontact printing to the surface of oxidized PET before (red) and after (blue) rinsing with 2-propanol. (b) RAIRS spectra (3000−2800 and 1800−1200 cm^{-1}) of a (TPP)Al−OMe film transferred by microcontact printing to the surface of an MHDA SAM on gold before (red) and after (blue) rinsing in dichloromethane.

Table 1. Assignments of Selected Absorption Bands in the RAIRS Spectra of an MHDA SAM on Gold, a (TPP)Al−OMe Multilayer Printed on the MHDA SAM, and a (TPP)Al−OMe Multilayer Printed on the MHDA SAM after Rinsing with Dichloromethane[a]

wavenumber (cm^{-1})			
MHDA SAM	as-printed (TPP)Al−OMe multilayer	(TPP)Al−OMe multilayer after rinsing	assignment
	2963		$\nu_{as}(CH_3)$ (from Al−OMe)
2917	2917	2917	$\nu_{as}(CH_2)$
2849	2849	2849	$\nu_s(CH_2)$
1742	1740	1739	ν(C=O) (free)
1709	1706	1709	ν(C=O) (H-bonded)
	1607	1594	ν(C=C) (phenyl)
	1510	1520	ν(C=O) (from Al−CO_2−R)
	1486	1488	δ(C−H) (pyrrole)
1303	1297	1300	ν(C−O) (from C−OH of MHDA)
	1265		ν(C−O) (from Al−OMe)

[a] Assignments taken from Yan, L.; Marzolin, C.; Terfort, A.; Whitesides, G. M. *Langmuir* **1997**, *13*, 6704−6712 and Thomas, D. W.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 5111−5119.

Rinsing Removes Physisorbed (TPP)Al−OMe and Leaves a (TPP)Al−Carboxylate Monolayer on Oxidized Polymeric Substrates. RAIRS spectra confirm that rinsing removes physisorbed (TPP)Al−OMe from microcontact-printed multilayers and leaves a (TPP)Al−carboxylate monolayer on the surface. The RAIRS spectrum of a printed (TPP)Al−OMe multilayer formed on a 16-mercaptohexadecanoic acid (MHDA) SAM on gold—a reflective model surface for oxidized polymeric substrates—and the RAIRS spectrum of a multilayer rinsed with dichloromethane both contain characteristic bands that confirm the presence of the MHDA SAM and the porphyrin ring (Figure 2b, Table 1). The presence of free and hydrogen-bonded carbonyl stretches of the MHDA carboxylic acid group indicates that the large size of the aluminum porphyrin precludes a 1:1 reaction between (TPP)Al−OMe and MHDA carboxylic acid groups. The decrease in the average water contact angle from 82.8° for a multilayer printed on oxidized PET to 53.9° after

---

(39) (a) Horkans, J.; Kim, J.; McGrath, C.; Romankiw, L. T. *J. Electrochem. Soc.* **1987**, *134*, 300. (b) Osaka, T.; Nagasaka, H.; Goto, F. *J. Electrochem. Soc.* **1980**, *127*, 2343. (c) Osaka, T.; Rakematsu, H.; Hikei, K. *J. Electrochem. Soc.* **1980**, *127*, 1021. (d) Cohen, R. L.; Meek, R. L. *J. Colloid Interface Sci.* **1976**, *55*, 156. (e) Feldstein, N.; Schlesinger, M.; Hedgecock, N. E.; Chow, S. L. *J. Electrochem. Soc.* **1974**, *121*, 738. (f) Cohen, R.; West, K. W. *J. Electrochem. Soc.* **1973**, *120*, 502.

(40) Satake, A.; Kobuke, Y. *Org. Biomol. Chem.* **2007**, *5*, 1679–1691.

(41) Zak, J.; Yuan, H.; Ho, M.; Woo, L. K.; Porter, M. D. *Langmuir* **1993**, *9*, 2772–2774.

(42) IR of (TPP)Al−OMe (KBr pellet, cm^{-1}): 1723 (br), 1594 (br), 1486 (w), 1441 (w), 1405 (sh), 1384 (s), 1351 (m), 1321 (sh), 1260 (m), 1203 (m), 1174 (w), 1108 (br), 1069 (m), 1008 (s).

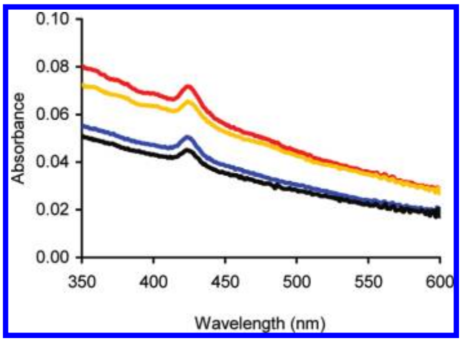


Figure 3. UV−vis absorption spectra of two samples of (TPP)Al−carboxylate monolayers on oxidized PET exposed to a solution of Pd/Sn colloids for 1 min. The first sample was rinsed with water (red), then accelerated in 1 M HCl, and rinsed with water again (blue). The second sample was rinsed with 2-propanol (yellow), then accelerated in 1 M HCl, and rinsed with 2-propanol again (black).

rinsing with 2-propanol supports this model: When the multilayer is rinsed off, the water drop then senses the underlying hydrophilic carboxylic acid groups, thus reducing the contact angle. The bands due to MHDA and the porphyrin ring likely obscure one of the two carboxylate stretches expected for the (TPP)Al−carboxylate monolayer covalently bonded to the MHDA surface; nonetheless, we are able to assign the absorption band at 1510 cm^{-1} in the spectrum of the unrinsed film and 1520 cm^{-1} in the spectrum of the rinsed film to a carboxylate stretch since it does not appear in either the RAIRS spectrum of the MHDA SAM or the transmission spectrum of (TPP)Al−OMe.[42] Although observation of both the symmetric and antisymmetric carboxylate stretches is necessary to establish the binding mode of the carboxylate to aluminum,[43] we propose a unidentate coordination mode for this carboxylate in agreement with the crystal structure reported for (TPP)Al−benzoate.[29] The major change that occurs upon rinsing is the loss of absorption bands due to the methoxy group bound to aluminum ($\nu_{as}(CH_3)$ at 2963 cm^{-1} and ν(C−O) at 1265 cm^{-1}) in (TPP)Al−OMe. This loss confirms that physisorbed (TPP)Al−OMe is completely removed by rinsing.

Pd/Sn Colloids Adsorb from Solution on (TPP)Al−Carboxylate Monolayers. The selective adsorption of Pd/Sn colloids on (TPP)Al−carboxylate monolayers patterned on oxidized polymeric substrates—the foundation of selective ELD—was established by UV−vis absorption spectroscopy (Figure 3). We exposed unmodified oxidized polymeric substrates and oxidized polymeric substrates bearing a (TPP)Al−carboxylate monolayer (formed using a flat PDMS stamp) to an aqueous solution of Pd/Sn colloids for 1 min and rinsed with water. The former substrates showed no evidence of colloid adsorption in the UV−vis absorption spectrum; the latter substrates showed the Soret band at 426 nm of the (TPP)Al−carboxylate monolayer riding on top of the broad absorption continuum extending through the visible−ultraviolet range that is characteristic of Pd/Sn colloids. After acceleration in 1 M HCl, the absorption due to the Pd/Sn colloids decreased due to colloid loss during the acceleration process, which is typically due to overetching of the Sn^{2+}/Sn^{4+} shell,[39] but the Soret band remains at 426 nm.

Although the nature of the interaction between Pd/Sn colloids and the (TPP)Al−carboxylate monolayer remains unclear, we were able to establish that Pd/Sn colloids adsorb on an intact (TPP)Al−carboxylate monolayer. Exposure to HCl, present in both the Pd/Sn colloid and accelerator solution, does not protonate the aluminum−carboxylate bond or the Al−N bonds of the aluminum porphyrin to liberate $AlCl_3$ and leave physisorbed H_4TPP^{2+} on the surface. It is plausible that physisorbed H_4TPP^{2+} could bind Pd/Sn colloids: Chloride ions associated with the Sn^{2+}/Sn^{4+} colloidal shell give Pd/Sn colloids a net negative charge that inhibits aggregation and allows the colloids to be electrostatically bound to cationic functional groups on a substrate.[39] Two studies eliminated this possibility: First, rinsing (TPP)Al−carboxylate monolayers with 2-propanol after Pd/Sn colloid adsorption and after acceleration should easily remove physisorbed H_4TPP^{2+}. UV−vis absorption spectra show an increased loss of Pd/Sn colloids relative to that of samples rinsed with water, but still exhibit the Soret band at 426 nm (Figure 3). Second, a solution study that used (TPP)Al−benzoate as a model for surface-bound (TPP)Al−carboxylate showed no reaction with excess HCl. The ^1H NMR spectrum showed only the presence of unchanged (TPP)Al−benzoate,[29] with no trace of benzoic acid or H_4TPP^{2+}.

Pd/Sn Colloids Adsorbed to Microcontact-Printed (TPP)Al−Carboxylate Monolayers Initiate Electroless Metallization. Pd/Sn colloids adsorbed on patterned (TPP)Al−carboxylate monolayers initiate copper metal deposition in the ELD solution. We used 2 cm^2 PDMS stamps bearing an arbitrary pattern with feature sizes ranging from 200 to 2 μm to create (TPP)Al−carboxylate monolayers on oxidized polymeric substrates. After adsorption of the Pd/Sn colloids and acceleration, the samples were plated with copper by immersion in the copper ELD solution for 3−5 min. Optical and SEM images show that copper deposits exclusively within the printed regions for all oxidized polymeric substrates in this study (shown in Figure 4 for selectively metallized oxidized PET).[44] Defects in the metallized patterns are limited to errors associated with microcontact printing: Dust particles or air bubbles trapped between the stamp and substrate prevent the deposition of (TPP)Al−carboxylate, producing unmetallized voids; collapse of recessed regions of the PDMS stamp deposits (TPP)Al−carboxylate in unwanted areas, producing superfluous metallized areas. These defects can be avoided by engineering the microcontact printing process, such as conducting the experiments in a cleanroom to eliminate dust particles and incorporating nonfunctional support posts in the PDMS stamp to prevent collapse.

Contact mode AFM studies of the copper films indicate that a plating time of 3 min yields patterned copper films that are 40 nm thick. Longer plating times yield thicker metal films, but >5 min in the ELD bath resulted in the formation of large, dome-shaped blisters and eventual delamination of the copper film. The formation of blisters during copper ELD has been widely observed and is attributed to incorporation of hydrogen gas that evolves during copper plating.[45] Although blistering can be remedied through manipulation of the ELD bath chemistry and deposition temperature, keeping plating times <5

---

(43) Alcock, N. W.; Tracy, V. M.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2243–2246.

(44) In principle, unrinsed (TPP)Al−carboxylate monolayers that are covered with a film of physisorbed (TPP)Al−OMe can also be used for the selective deposition of copper. UV−vis spectra of printed multilayers on PET after exposure to Pd/Sn colloids (Figure S2, Supporting Information) show a slight reduction of the Soret band absorbance, indicating that the physisorbed (TPP)Al−OMe layers do not desorb to an appreciable extent in the colloidal solution. However, the economic advantage of using ELD decreases if contamination of the plating solutions—particularly for Pd/Sn colloids—reduces their lifetime. For this reason, we have focused on the use of (TPP)Al−carboxylate monolayers as a base for selective ELD.

(45) Nakahara, S.; Okinaka, Y. *Annu. Rev. Mater. Res.* **1991**, *21*, 93–129.

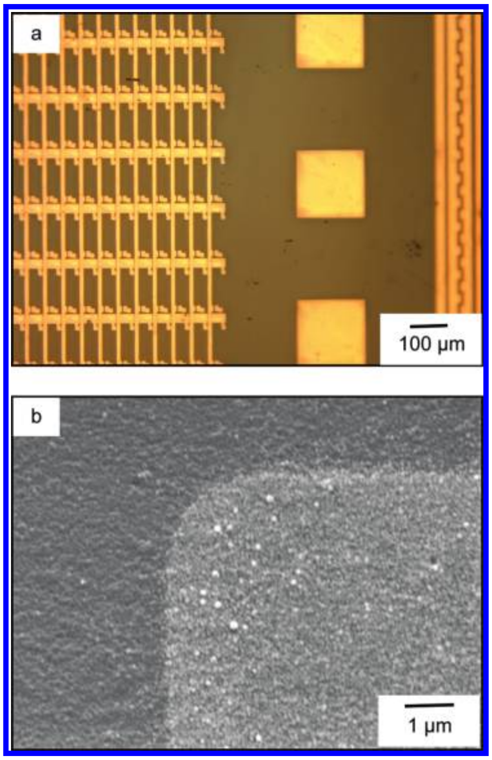


Figure 4. Optical and SEM images of patterned copper films on oxidized PET. (a) Optical image of an arbitrary copper pattern. (b) SEM image of a portion of the metallized substrate in (a). In both images, the light areas are copper; these areas correspond to the raised portion of the PDMS microcontact printing stamp.

min produced uniform, blister-free copper films on oxidized polymeric substrates that we used for further characterization.

Copper Wires Fabricated on Oxidized PEN Are Resilient to Mechanical Stress. Copper wires fabricated by selective ELD on flexible polymeric substrates retain their conductivity even when subjected to substantial mechanical deformation. The average resistivity of unstrained copper wires fabricated on flexible PEN substrates was 2.7 ± 0.27 $\mu\Omega$ cm, which compares well with the reported resistivity for ELD copper ($\sim$2 $\mu\Omega$ cm).[46] Inducing tensile strain in the wire by bending the PEN substrate around cylinders with radii decreasing from 12.5 mm to 500 μm did not increase the resistivity (Figure 5), indicating that the wires deform with the PEN substrate and that the testing process, which subjected the wires to $\sim$30 cycles of repetitive strain, did not induce metal fatigue. We observed a modest increase in resistivity (to 4.3 $\mu\Omega$ cm) only when the PEN substrate was creased, corresponding to a radius of curvature of $\sim$100 μm. Permanent damage to the PEN substrate occurs before copper wires fabricated on the surface cease to function electrically.

We attribute the ability of copper wires on PEN to tolerate high tensile strain to strong adhesion between the wire and the substrate. Strong adhesion is essential to strain tolerance because it distributes the strain over the entire area of the wire, thus allowing the wire and substrate to deform together. We tested the adhesion of copper films deposited on oxidized polymeric substrates using the ASTM D3359B-02 tape test.[38] There was no removal of copper after scoring the copper films into 1 mm × 1 mm squares, applying tape to the cut surface, and peeling it off. Copper films deposited on all polymeric substrates achieved the highest ASTM adhesion classification (5B). This strong adhesion is likely due to both chemical and mechanical adhesion: Chemical adhesion is caused by strong bonds between the interfaces present in the film. A significant contribution to chemical adhesion may be from the (TPP)Al−carboxylate monolayer, which is covalently bound to the oxidized polymeric substrate. Mechanical adhesion is caused by physical interlocking between the metal film and a rough substrate. Roughening of the polymeric substrates used in this work is a result of surface oxidation. For example, the root-mean-square roughness of PET substrates increases from 0.96 to 10.4 nm after oxidation, as measured by AFM (Figure S2, Supporting Information).[47]

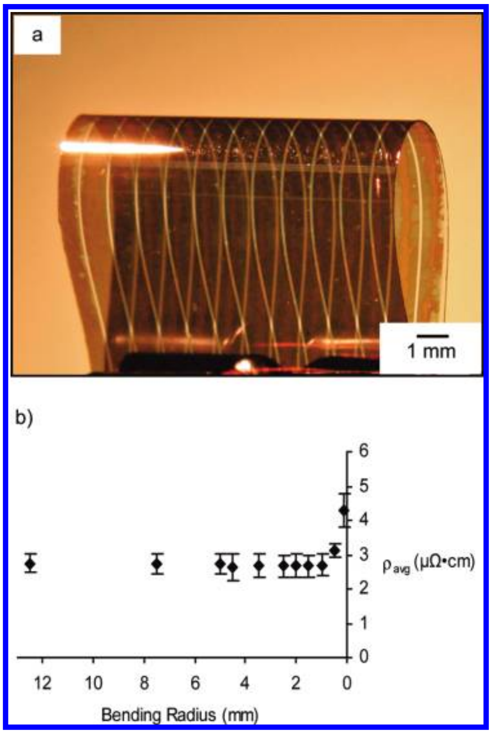


Figure 5. Electrical characterization of copper wires fabricated on PEN. (a) Photograph of copper wires (l = 5.0 cm, w = 1.0 mm, h = 40 nm) fabricated on a 75 μm thick PEN substrate. (b) Resistivity of copper wires (l = 1.0 cm, w = 1.0 mm, h = 40 nm) as a function of the bending radius.

Conclusions

In conclusion, we have shown that (TPP)Al−OMe is an ideal material for the selective electroless metallization of a wide range of polymeric substrates: It is inexpensive, stable, and compatible with native PDMS stamps, and it reacts quickly with surface carboxylic acid groups to form robust (TPP)Al−carboxylate monolayers that are stable to the harsh processing conditions of electroless copper deposition, particularly the low pH of Pd/Sn colloidal catalyst solutions. The use of (TPP)Al−carboxylate monolayers as a base for selective electroless metallization is

---

(46) Li, T.; Seidel, T. E.; Mayer, J. W. *MRS Bull.* **1994**, August, 15−18.

(47) It is interesting to note that copper deposited on unrinsed (TPP)Al−carboxylate monolayers covered with a film of physisorbed (TPP)Al−OMe achieves the same ASTM adhesion classification (5B) as copper deposited on (TPP)Al−carboxylate monolayers. The presence of physisorbed (TPP)Al−OMe introduces a potentially weak interface since physisorbed (TPP)Al−OMe multilayers are held together by weak intermolecular forces. The fact that the presence of this interface does not impact the adhesion of the copper likely indicates that the adhesion of copper films is dominated by mechanical interlock to the rough polymeric substrate.

also applicable to the selective electroless deposition of other metals that are initiated by Pd/Sn colloids, such as nickel and cobalt. Copper wires fabricated in this way exhibit remarkable adhesion to polymeric substrates, allowing the copper/polymer to withstand substantial deformation without a negative impact on electrical performance. This simple, inexpensive fabrication method is well-suited to the fabrication of low-cost plastic electronic devices, such as flexible displays. It is adaptable for use in the fabrication of large-area plastic electronic devices by simply scaling up the size of the microcontact printing stamp.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). SU-8 films were fabricated at the University of Western Ontario Nanofabrication Facility in London, Ontario. M.S.M. is grateful for the award of an NSERC Summer Research Fellowship and an Ontario Graduate Scholarship. M.L. is grateful for the award of an NSERC Summer Research Fellowship. We thank Sharon Lackie for help with the scanning electron microscope and J. Mueller for help with atomic force microscopy.

Supporting Information Available: Experimental details for the fabrication of SU-8 films and for the oxidation of PET, PEN, PI, PE, PP, PTFE, PMMA, and SU-8, RAIRS spectrum of the MHDA SAM on gold, UV−vis absorption spectrum of an unrinsed (TPP)Al−carboxylate monolayer covered with a film of physisorbed (TPP)Al−OMe on an oxidized PET substrate before and after exposure to a solution of Pd/Sn colloids, and AFM images of native and oxidized PET substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

JA908433P