Fabrication of palladium-based microelectronic devices by microcontact printing

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(Received 4 December 2001; accepted for publication 23 January 2002)

This letter demonstrates the patterning of thin films of metallic palladium by microcontact printing (μCP) of octadecanethiol, and the use of the patterned films in the fabrication of a functional sensor. This technique was also used to prepare templates of palladium for the electroless deposition of copper. The resistivity of the palladium and copper microstructures was 13.8 and 2.8 $\mu\Omega$ cm, respectively; these values are approximately 40% larger than the values for the pure bulk metals. Palladium patterned into serpentine wires using μCP functioned as a hydrogen sensor with sensitivity of 0.03 vol % H_2 in N_2, and a response time of ~10 s (at room temperature). © *2002 American Institute of Physics.* [DOI: 10.1063/1.1463719]

Microcontact printing (μCP) of long-chain alkanethiols on gold films forms self-assembled monolayers (SAMs) of alkanethiolates. Selective removal of the unprotected regions of the films by etching provides a useful, nonphotolithographic method for the fabrication of conducting gold microstructures.[1] The structures generated by this procedure have pinhole defects, and their edges have a roughness of ~100–150 nm. The defects in the etched microstructures are probably due to defects in the SAMs; the roughness of the edges seems to correlate with the size of the grains produced by e-beam deposition of gold.[2] Gold has the additional disadvantage as a substrate that it is not compatible with many technologies for fabrication of semiconductor-based microelectronic devices.[3] These characteristics limit the applications of μCP on gold in the microfabrication of electronic and optical devices.

To fabricate electronically functional devices using μCP, we needed a system that could generate microstructures with fewer functionally significant defects and smaller grain sizes than those produced using alkanethiolates on gold, and that was compatible with complementary metal–oxide semiconductor (CMOS) technologies. Here, we describe the results of a study of μCP of alkanethiolates on palladium.[4] Our initial evidence indicates that this system does, in fact, allow production of microstructures with substantially higher quality than those generated using gold. We believe that this fabrication process will be directly CMOS compatible.

Soft lithography is a suite of techniques, including μCP, whose members are useful for patterning of SAMs of thiol-containing organic molecules (RSH) onto surfaces.[1] For μCP, an elastomeric stamp made of poly(dimethylsiloxane) (PDMS) with bas-relief features is coated with an alkanethiol and placed in contact with a metal surface. This process leaves SAMs where the stamp contacted the metal. If the group R has an appropriate structure, the patterned SAMs act as a resist and protect the underlying metal films from wet-chemical etchants.[1]

Palladium shares three desirable properties with gold for use in μCP. First, it is resistant to spontaneous formation of surface oxides (up to 400 °C).[5] Second, it can be evaporated onto surfaces using standard techniques.[6] Third, it reacts readily with alkanethiols to form well-ordered monolayers. These SAMs are analogous to those formed on gold and silver.[4] The resulting Pd/SR surface is a resist for wet-chemical etchants; etching yields structures with smaller etch pits than are observed with SAMs on gold.[4,7] Palladium in films prepared by e-beam evaporation has a typical grain size (~15–20 nm) that is smaller than that of gold (~40–75 nm);[8] this characteristic leads to etched patterns of palladium with smaller roughness than etched patterns of gold. Palladium is also catalytically active, and the ability to pattern it may be useful in catalysis.[9,10] Although the resistivity of palladium is a factor of 5 greater than that of gold, palladium is used commonly in microelectronic devices such as capacitors, resistors, and contacts. Patterned films and colloids of palladium serve as seed layers for the electroless deposition of copper to form electrical interconnects.[9,11,12] Many alloys of palladium are used routinely in microelectronic devices—e.g., in resistors (AgPd) and finishes (NiPd and CoPd).[5]

We prepared the substrates by e-beam evaporation of titanium (2 nm, 1 Å/s, as an adhesion layer) and then palladium (25 nm, 8 Å/s) onto a 3 in. Si/SiO_2 ⟨100⟩ wafer (Silicon Sense, NH).[13] We used rapid prototyping techniques[1] to generate the stamps for μCP made of PDMS (Sylgard 184, Dow Corning; Midland, MI). The stamp was coated with C18SH by wiping a cotton swab wet with an ethanolic solution of octadecanethiol (5 mM) across the surface. After wetting with C18SH, the stamp was then dried under a stream of N_2 for 1 min. The stamp was placed in contact with the palladium surface, allowed to wet the surface without additional pressure for 3–7 s, and then removed manually. The unprotected palladium was removed by etching in a commercially available $FeCl_3$-based etchant (TFP, Transene, Inc.; Danvers, MA) that had been diluted to a ratio of H_2O:etchant of 5:1.[14]

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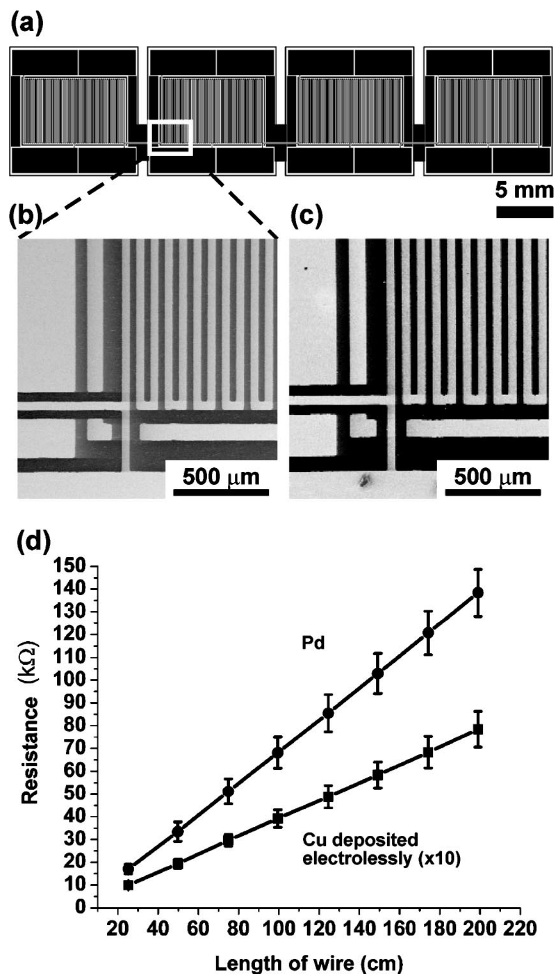

FIG. 1. (a) Design of the wire and contact pad system. Each contact pad is connected to the wire at different locations along its length. The individual sections of wire are all connected to each other. (b) Scanning electron microscope (SEM) image of a section of the palladium wire (42.5 μm wide and 25 nm thick) generated using the pattern in (a). (c) SEM image of a section of the copper wire (45 μm wide and 170 nm thick) deposited electrolessly onto the patterned, thin film of palladium. (d) Resistance measured as a function of length on both the palladium and copper wire.

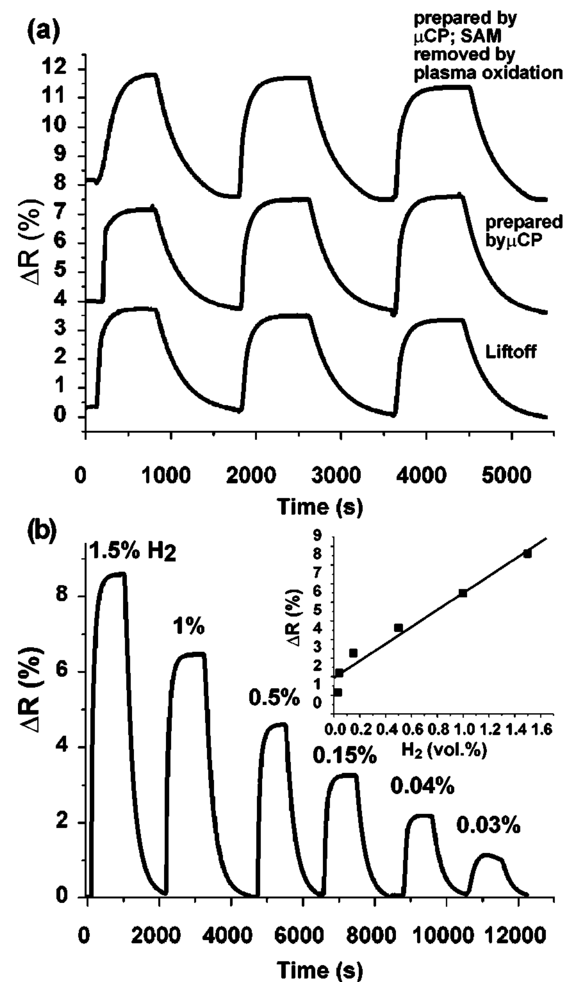

FIG. 2. Resistance measured as a function of time of the palladium wire from Fig. 1(b) when exposed to a H_2/N_2 mixture at 25 °C. (a) Response of palladium wires that were prepared by μCP and by lift-off to exposure to 0.5 vol % H_2 in N_2. The H_2/N_2 mixture was turned on at 60, 1800, and 3600 s. The pure N_2 was turned on at 1000, 2800, and 4600 s. (b) Response of a palladium wire prepared by μCP and subsequent removal of the SAM to decreasing concentrations by volume of H_2 in N_2. The inset is a plot of ΔR as a function of H_2 concentration.

We printed octadecanethiol on palladium, and etched to fabricate a long wire (~2 m; width of 42.5 μm; thickness of 25 nm) with contact pads spaced along the length of the wire to facilitate the measurement of the resistance as a function of length [Figs. 1(a) and 1(b)]. The underlying substrate was a thermally grown SiO_2 layer (200 nm). The resistance was measured by a two-probe technique. The resistance values depended linearly on length [Fig. 1(d)]. The average resistivity was calculated to be 13.8 μΩ cm; the literature value for the resistivity of bulk palladium is 10.8 μΩ cm.[5] We also deposited copper electrolessly on this palladium wire.[15] The palladium wire from Fig. 1(b) was immersed in aqueous HF (1 vol %) for 10 min to remove the exposed Ti and then cleaned in an oxygen plasma for 30 s to remove the alkanethiolates from the surface. The cleaned wire was immersed in an electroless-plating solution[16] for 30–240 s.[11] Figure 1(c) indicates that the copper structures produced by the technique are restricted to the template made of palladium; they do not possess visible defects, and they have electrical characteristics consistent with those expected from bulk metal. Figure 1(d) plots the resistance of the copper wire measured as a function of its length. The average resistivity was 2.8 μΩ cm; the literature values for the resistivity of bulk and electrolessly plated copper are 1.7 and 2 μΩ cm, respectively.[5,11]

Palladium can be used to detect trace amounts of H_2,[17] because palladium reacts reversibly with hydrogen gas to form PdH_x at room temperature or above;[18] this reaction results in changes in its physical properties—resistivity and reflectivity—that can be measured easily.[17,19] Hydrogen-based fuel cells (among other applications) have spurred interest in the development of inexpensive sensors of H_2 in both the research and commercial sectors.[20,21] Mainstream adoption of H_2-based fuel cell technology requires devices that can detect small H_2 concentrations (<4 vol %) rapidly.[22]

The palladium wire [Figs. 1(a) and 1(b)] was placed in a flow chamber and electrical leads were connected to the contact pads. The wire was exposed to a stream of gas (either a H_2/N_2 mixture or pure N_2), and the resistance was monitored. Figure 2(a) shows that the magnitude of the change in resistance (~3.5% ΔR) and the response time (~10 s) as a function of exposure to H_2 for palladium wires prepared by μCP [either with or without a SAM (Ref. 23) on their sur-

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face] is similar to those of a palladium wire prepared by photolithography and lift-off.[24] All three samples had a slow initial response time ($\sim$120 s) for the first exposure to H_2; subsequent exposures all had response times of $<$10 s. The sensor prepared by μCP detected H_2 concentrations as low as 0.03 vol % in N_2 [Fig. 2(b)] with sensitivity equivalent to that of other palladium-based devices for sensing H_2.[20] These data show that the thin film of palladium retains its bulk ability to adsorb H_2 after patterning by μCP of alkanethiolates with no increase in response time or decrease in sensitivity.

Sulfur is known to poison the catalytic activity of palladium and affect the response time of palladium-based H_2 sensors, and it seemed possible that exposure to H_2 might influence the interface between alkylthiolates and palladium, and thus the SAM.[17] Infrared spectra of a SAM of octadecanethiol on palladium show no change in frequency (within $+/-1$ cm^{-1}) or intensity ($+/-10\%$) after exposure to H_2 (0.5 vol % in N_2) for 10 min (see supplemental information). We infer that exposure of the SAM to H_2 does not change it significantly. Thus, the RS/Pd interface seems to be transparent to H_2.

The ability to pattern palladium films directly by μCP extends the utility of the soft-lithographic technique in generating functional micro- and nanostructures. We believe that palladium is superior to gold for use with μCP in the fabrication of devices for five reasons. (i) The features produced by μCP on palladium have a relatively low density ($\sim$70 defects/mm^2) of small pits ($<1\ \mu$m^2) and have relatively smooth edges (30–50 nm). (ii) Palladium is commonly used as a substrate for electroless deposition of copper and other metals. (iii) Many alloys of palladium are already used as finishes to connectors and as precision resistors in microelectronic devices. (iv) The chemical etchant used for palladium is less toxic than the $Fe(CN)_6^{3+}$ etch used for gold (which can generate HCN if treated incorrectly). (v) Palladium is catalytically active, and the ability to pattern palladium by μCP may be useful in generating substrates for use in catalysis.[25] The disadvantage of using palladium is that it is $\sim$5 times more resistive than gold (10.8 $\mu\Omega$ cm for palladium and 2.1 $\mu\Omega$ cm for gold).[5] We believe that fabrication of micro/nanostructures in palladium by soft lithography can be incorporated into the fabrication of Si-based microelectronic devices because palladium is CMOS compatible.

Note added in proof. Carvalho *et al.* at IBM in Zurich have carried out a similar study of the patterning of palladium by microcontact printing of alkanethiols. Although our inferences concerning the mechanism by which alkanethiolate SAMs confer protection against etching differ from theirs, we agree on the characteristics and utility of the method. See: A. Carvalho, M. Geissler, H. Schmid, B. Michel, and E. Delamarche. Langmuir, 2002 (in press) (availalbe on ASAP, http://pubs.acs.org).

This research was supported by DARPA and used MRSEC Shared Facilities supported by the NSF under Award No. DMR-9809363. One of the authors (D.B.W.) thanks the NSF for a graduate fellowship. One of the authors (J.C.L.) thanks the DoD for a graduate fellowship. One of the authors (M.L.C.) thanks the NIH for a postdoctoral fellowship.

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[13] The substrates were stored under ambient conditions but away from thiol-containing compounds until use. We found that the best results from μCP resulted if the substrates were used within 48 h of their preparation.
[14] The dilution slows the rate of etching to a controllable rate (i.e., 10–30 s).
[15] Palladium-based substrates for electroless deposition of copper were patterned previously by techniques that required lasers and positioning stages (see Refs. 9, 10, and 12). We, and others, have demonstrated the patterning of palladium colloid and palladium (II) catalytic precursors μCP (see Refs. 9 and 11). The direct patterning of palladium metal by μCP does not require special equipment or synthesis of precursors.
[16] The electroless-plating solution for copper consisted of $CuSO_4$ (3 g), sodium potassium tartrate (14 g), and NaOH (4 g) in water (100 mL). An aqueous solution of formaldehyde (37.2 wt %, 10 mL) was added just before use.
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