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Microcontact printing (μCP)[1] is a convenient technique for generating patterned self-assembled monolayers (SAMs)[2] of alkanethiolates on gold[1] and silver[3] and of alkylsiloxanes on silicon dioxide and glass.[4,5] Patterned SAMs of hexadecanethiolate on gold and silver can be used directly as ultrathin resists in selective wet etching to fabricate patterned microstructures of these metals with dimensions of >0.2 μm.[1,3,6–9] The present study is a natural extension of this technique, since alkanethiols also form organized monolayers on evaporated films of copper.[10] The chemical reactivity of coinage metals increases in the order of Au < Ag < Cu; it is possible to find an etchant that dissolves only Cu but not Ag and Au or only Ag but not Au. For example, aqueous $FeCl_3$ solution, an etchant that is widely used in semiconductor industry to produce printed circuits of copper,[11] etches silver and gold very slowly or not at all.[3] This ability to carry out "orthogonal etching" offers an opportunity to generate junctions of Cu–Ag, Cu–Au, and Ag–Au by using a multistep procedure that includes metal evaporation, microcontact printing with hexadecanethiol, and selective wet etching.

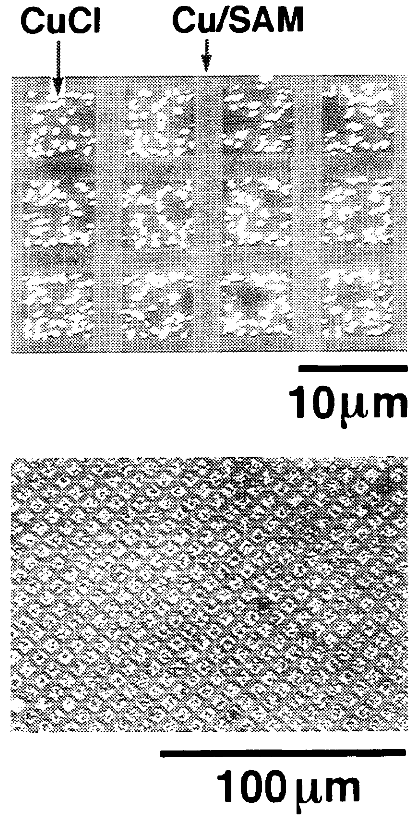

Figure 1. SEMs of copper films (~50 nm thick) that were patterned with SAMs of hexadecanethiolate and etched in an aqueous $FeCl_3$ solution for ~2–3 s. The microparticles (bright dots on SEMs) were CuCl that formed in situ on the bare regions of copper during etching.

Figure 1 shows scanning electron micrographs (SEMs) of copper samples (50 nm thick) that had been patterned with SAMs of hexadecanethiolate and etched in an aqueous $FeCl_3$ solution (0.012 M) for 2–3 s.[12] The microparticles (~0.5 μm in size) on the bare regions of copper are CuCl (shown by energy-dispersed spectroscopy, EDS). They were formed in situ during the dissolution of bare copper:

$$Cu(s) + FeCl_3(aq) = CuCl(s) + FeCl_2(aq) \quad (1)$$

Addition of HCl or NH_4Cl to the etching solution decreased the rate of etching and helped to dissolve the CuCl precipitate:[14]

$$CuCl(s) + 3Cl^-(aq) = [CuCl_4]^{3-}(aq) \quad (2)$$

(1) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002.
(2) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87. Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
(3) Xia, Y.; Kim, E.; Whitesides, G. M. *J. Electrochem. Soc.*, in press.
(4) Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576.
(5) Jeon, N. L.; Nuzzo, R. G.; Xia, Y.; Mrksich, M.; Whitesides, G. M. *Langmuir* **1995**, *11*, 3024.
(6) Kumar, A.; Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
(7) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274.
(8) Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 471.
(9) Wilbur, J. L.; Kim, E.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 649.
(10) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022.
(11) Glang, R.; Gregor, L. V. In *Handbook of Thin Film Technology*; Maissel, L. I., Glang, R., Eds.; McGraw-Hill: New York, 1970; Chapter 7.
(12) Copper (99.999%, Aldrich) films were prepared by e-beam evaporation onto Ti-primed (99.99%, Aldrich; 2.5 nm thick) Si(100) wafers (N/phosphorous doped, Silicon Sense, Nashua, NH). Microcontact printing was carried out according to published procedures.[6] Etchings of copper were conducted at room temperature; etching solutions were stirred at 300 rpm. We measured the thickness of hexadecanethiolate SAMs on copper using ellipsometry. SAMs formed by dipping copper films into an ~2 mM hexadecanethiol solution in ethanol for ~5 s had a thickness of ~58 Å (obviously, they were bilayers, for the reasons that are, however, not clear at the present time[13]); SAMs formed by μCP using a flat PDMS stamp had a thickness of ~20–26 Å (that is, they were very close to monolayers).
(13) Keller, H.; Simak, P.; Schrepp, W.; Dembowski, J. *Thin. Solid Films* **1994**, *244*, 799. Schlenoff, J. B.; Li, M.; Ly, Hiep *J. Am. Chem. Soc.* **1995**, *117*, 12528.
(14) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 759.
(15) Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 4581.
(16) Dirske, T. P. In *Zinc-Silver Oxide Batteries*; Fleischer, A., Lander J. J., Eds.; John Wiley & Sons: New York, 1971; p 100.
(17) UV Clean, Model 135500, Boekel Instruments, PA.
(18) The XPS of freshly prepared silver films only showed the characteristic peak of Ag(0) (3d, 368.08 eV). When the surfaces of these silver films were oxidized under UV/ozone, the peak of 3d shifted to lower energies: 368.03 eV (1 min); 368.02 eV (5 min), and 367.65 eV (10 min). The characteristic peak (3d) of Ag_2O is at 367.65 eV. In fabricating arrays of junctions, the surfaces of silver films were oxidized for ~6 min.
(19) When we were preparing this revised paper, we noticed that a similar work (μCP of hexadecanethiol on copper and selective etching) was just published: Moffat, T. P.; Yang, H. *J. Electrochem. Soc.* **1995**, *142*, L220. The etchant used by these authors was an aqueous solution containing H_2O_2 and HCl.

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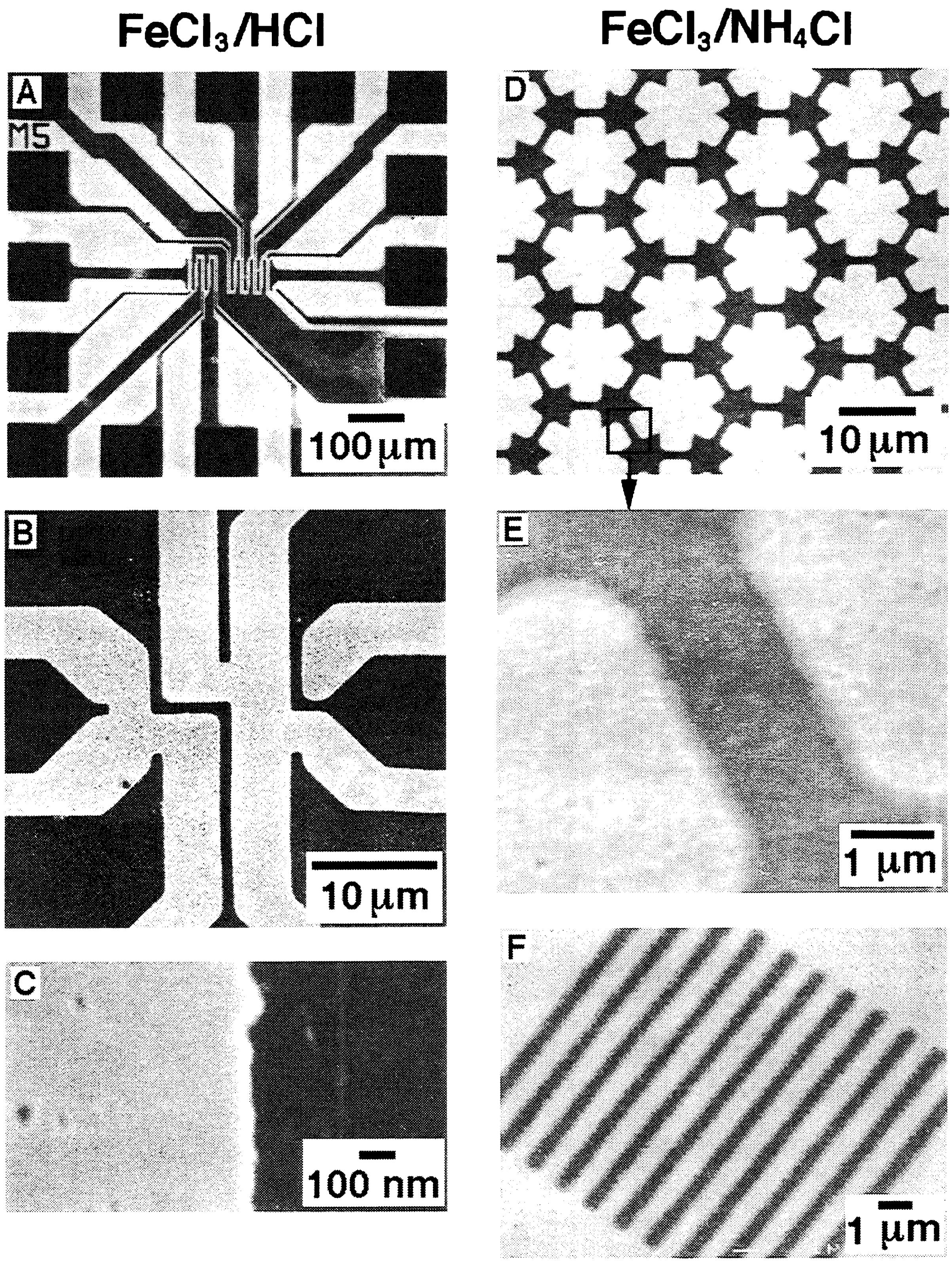

Figure 2. SEMs of copper films (~50 nm thick) that were patterned with SAMs of hexadecanethiolate and etched in aqueous solutions containing $FeCl_3/HCl$ (A–C) or $FeCl_3/NH_4Cl$ (D-F) for ~20 s. Addition of HCl or NH_4Cl to the $FeCl_3$ solution helped to dissolve the precipitates of CuCl and to generate clean structures of copper. The bright regions are copper covered by the SAM, and the dark regions are Si/SiO_2 where the underivatized copper has dissolved.

Figure 2A–C shows SEMs of test patterns of copper (at three different magnifications) that were fabricated by μCP with hexadecanethiol, followed by etching of the patterned samples in an aqueous solution containing $FeCl_3$ (0.012 M) and HCl (0.4–0.8 M) for ~20 s. The edge resolution of copper structures is ~100 nm (Figure 2C) when using a poly(dimethylsiloxane) (PDMS) stamp cast from lines made in a film of photoresist (Microposit 1813, Shipley) using photolithography; the edge resolutions are ~50 and ~20 nm for the systems of Au/C_{16}-

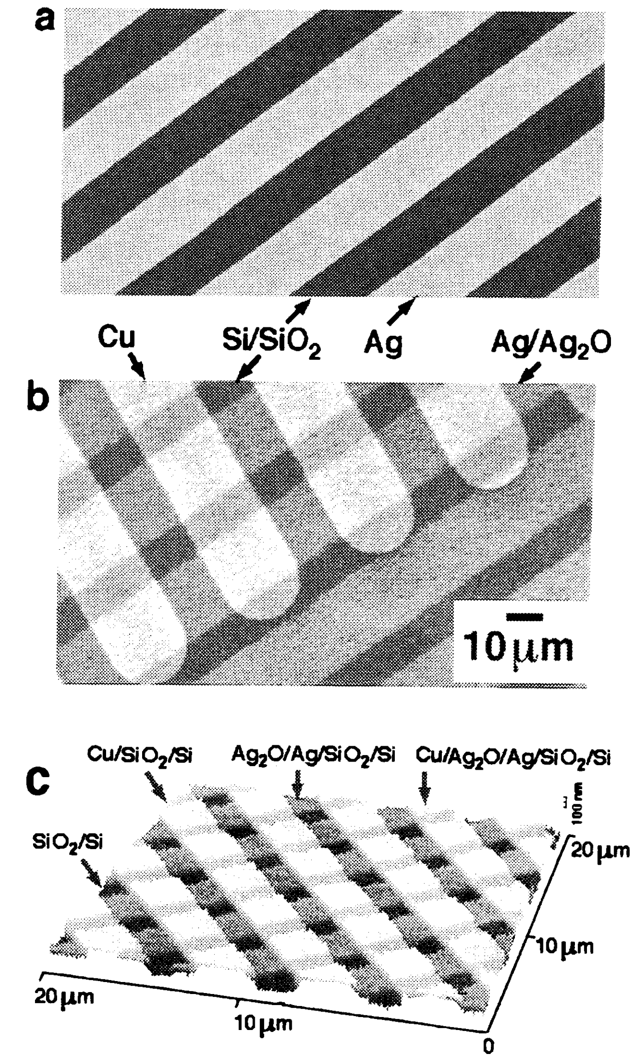

Figure 3. (a) SEM image of silver lines (~50 nm thick) that were generated by a combination of μCP and selective etching in $S_2O_3^{2-}$/ferri/ferrocyanide solution for ~15 s. (b) SEM image of $Ag/Ag_2O/Cu$ junction structures. Samples of (a) were oxidized under ozone for ~6 min, films of copper (~50 nm) were evaporated and patterned by μCP, followed by selective etching in aqueous $FeCl_3/HCl$ solutions. (c) AFM image of (b) to show 3-D profile.

SH[15] and $Ag/C_{16}SH$,[3] respectively. Figure 2D–F shows SEMs of other test patterns of copper that were generated using the combination of μCP with hexedecanethiol and selective wet etching in another aqueous solution containing $FeCl_3$ (0.012 M) and NH_4Cl (0.8 M) for ~20 s. The smallest features of copper that have been fabricated using the present procedure are parallel lines of copper that are ~0.6 μm in width and are separated by ~0.6 μm (Figure 2F).

Since aqueous $FeCl_3/HCl$ solutions only dissolve bare copper, not bare silver, we have been able to fabricate arrays of $Ag/Ag_2O/Cu$ junctions by a four-stage procedure. (i) Generate silver lines (50 nm thick) on Si/SiO_2 using a combination of μCP with hexadecanethiol and selective etching of silver in aqueous solutions containing $S_2O_3^{2-}$ and ferri/ferrocyanide (Figure 3a).[3] (ii) Form insulating layer of Ag_2O[16] on the surface of these silver lines using UV/ozone treatment.[17,18] (iii) Evaporate a copper film (50 nm thick) over the whole surface. (iv) Pattern the copper surface with lines of hexadecanethiolate perpendicular to the silver lines and etch in aqueous $FeCl_3/HCl$ solutions (Figure 3b). Each cross point of silver and copper lines represents a junction of metal/insulator/metal. Figure 3c is an AFM image of b to show the profiles of the junctions.

We have demonstrated that μCP could be used to generate patterned SAMs of alkanethiolates on the surface of evaporated thin films of copper.[19] These patterned SAMs were effective resists in protecting the underlying copper from dissolving in $FeCl_3/HCl$ and $FeCl_3/NH_4F$ solutions. The capability to etch Cu independently of Ag and Au adds another level of useful control to the ability to fabricate microstructures by using SAMs and μCP.

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