J|A|C|S
COMMUNICATIONS

Self-Assembled Monolayers of Alkanethiolates on Palladium Are Good Etch Resists

J. Christopher Love, Daniel B. Wolfe, Michael L. Chabinyc, Kateri E. Paul, and George M. Whitesides*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

Received November 20, 2001

Self-assembled monolayers (SAMs) formed from alkanethiols on palladium resist corrosion by solution-phase chemical etchants, regardless of the chain length and wettability of the SAM. This insensitivity to chain length contrasts with SAMs on gold, for which a hydrophobic, well-ordered, crystalline alkane film is required to prevent access of water-soluble etchants to the underlying metal.[1,2] This paper demonstrates that dense SAMs form on contact of hexadecanethiol ($C_{16}SH$) and palladium, and that these SAMs are notably more useful resists against wet-chemical etchants than are those on gold.[3] This system, however, differs from SAMs on gold in that the interfacial layer between the palladium and the organic film contributes the major part of the etch resistance of the system: a number of thiols differing substantially in hydrophobicity and chain length ($C_{16}SH$, $C_{12}SH$, $HO(CH_2)_2SH$, C_6H_5SH, HO_2CCH_2SH) provide comparable levels of contrast as etch resists.

SAMs of alkanethiolates on the coinage metals (Au, Ag, Cu) have been used for a range of purposes,[4] including etch resists for microcontact printing (μCP).[5] The use of μCP of SAMs is generally not practical for patterning sub-500-nm features on these metals for two reasons: (i) it leaves defects and surface pits during etching (for gold) and (ii) spontaneous formation of an oxide layer in air complicates the system (for copper and silver). In addition, the coinage metals are incompatible with complementary metal-oxide semiconductor (CMOS) fabrication, and require barrier layers to prevent their contamination of the silicon with deep-level traps for minority carriers.[6] Palladium and its alloys are commonly used in microelectronic elements such as resistors and capacitors.[7]

Palladium has several physical properties that suggest it would be a useful substrate for patterning SAMs of alkanethiolates: (i) it is very reactive toward sulfur-containing compounds, (ii) it has a slightly smaller lattice spacing in the (111) plane (2.75 Å) than gold and silver,[8] (iii) it resists oxidation in air below 400 °C, and (iv) it forms smaller grains (15−25 nm) by e-beam evaporation than either gold (50−100 nm) or silver (30−50 nm). Here we report that alkanethiols form well-ordered SAMs on palladium, and resist etching with greater selectivity than SAMs on gold.[9] The details of the formation and characterization of the hexadecanethiolate SAM on palladium are described in the Supporting Information. Infrared data indicate that a hexadecanethiolate monolayer forms rapidly on palladium with crystalline molecular packing, and that the order of the SAM is comparable to that of $C_{16}S$ SAMs on gold and silver. A high advancing contact angle of water ($\theta_a \sim 120°$) and high hysteresis ($\theta_a - \theta_r \sim 20°$) suggest that this SAM may be more heterogeneous or disordered at the molecular scale than $C_{16}S$-derived SAMs on either gold or silver.[10]

Figure 1 shows structures that we can generate by the combination of μCP and etching on palladium and on gold.[11] Both films were patterned with $C_{16}SH$ and exposed to the most selective etchants that we know for each of these systems: a semioptimized iron(III)-based solution[12] for SAMs on palladium, and a highly optimized ferri/ferrocyanide solution[13] for SAMs on gold. The structures on the palladium film show better edge definition and 85−95% fewer etch pits on the surface than on the gold film (particularly near the edges of the structures). Since we infer from the spectroscopic data that the organic layers formed on both substrates are similar in structure, these results suggest that the interface between the palladium and sulfur-containing species (which we call the RS/Pd interface, without specifying its structure in any detail) also contributes to the resist properties of SAMs on palladium.

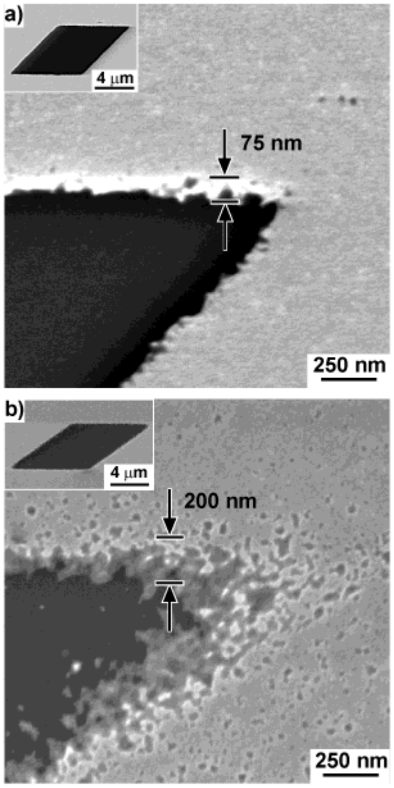

Figure 1. (a) Scanning electron micrograph (SEM) of the corner of a diamond patterned on Pd. The pattern was generated by two consecutive printings of 5 μm lines (10 μm pitch) at an angle of ~30° relative to one another. The edge roughness is ~30−75 nm and the radius of curvature at the point of the structure is ~ 40−50 nm. The insert shows the whole diamond. (b) SEM of a diamond patterned in gold. Note the increase in the number of pits in the surface of the gold and the radius of curvature in the point (~150 nm).

To investigate the effect of the RS/Pd interface on selective etching, we patterned a variety of organic thiols ($C_{16}SH$, $C_{12}SH$,

---

* Address correspondence to this author. E-mail: gwhitesides@gmwgroup.harvard.edu.

10.1021/ja012569l CCC: $22.00 © 2002 American Chemical Society

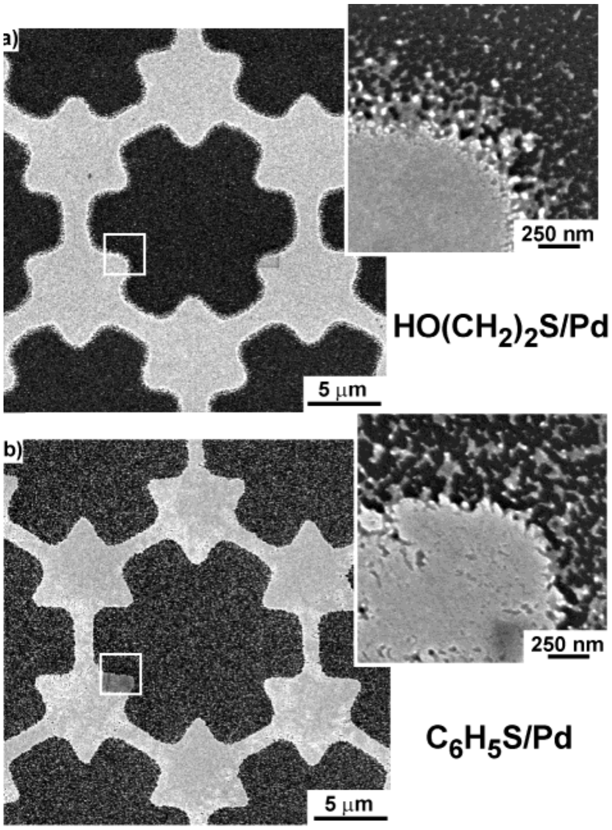

Figure 2. SEMs of palladium (bright areas) on Si/SiO$_2$ patterned by μCP with (a) HO(CH$_2$)$_2$SH and (b) C$_6$H$_5$SH and etched in an aqueous FeCl$_3$ solution. The white box marks the region of the structure shown in the magnified image offset to the right of each image. We attribute the increasing residue of unetched palladium (extending outward from the edges of the pattern) to the spreading of the volatile thiols by diffusion. The Supporting Information shows patterns generated with other thiols.

HO(CH$_2$)$_2$SH, C$_6$H$_5$SH, HO$_2$CCH$_2$SH) on palladium films by μCP and transferred those patterns by etching. Regardless of the structure of the organic layer, the SAMs protected the palladium from corrosion by wet etchants (Figure 2).[14] Although the density of defects increased with decreasing chain length, there was strong contrast between the protected and unprotected areas in all cases. Experiments using the same thiols on gold substrates, followed by treatment with the ferri/ferrocyanide etchant,[13] showed little or no selectivity. We believe that the etch resistance of alkanethiolate SAMs on Au depends entirely on a well-ordered, hydrophobic SAM to prevent the transport of oxidizing ions to the surface.[2] We exposed palladium substrates to a 10-mM ethanolic solution of Na$_2$S for 1 h and etched the treated films in aqueous solutions of KI/I$_2$ and FeCl$_3$.[12] The samples showed no significant corrosion over 1−2 min (periods ∼2−4 times longer than the time required to dissolve untreated palladium completely in the same etchants). Gold films treated with Na$_2$S dissolved as rapidly as untreated films. We infer that the RS/Pd interface—independent of attached organic groups and thickness of the SAM—contributes to the mechanism of etch resistance in this system.

We draw three conclusions from these studies: (i) SAMs of long-chain alkanethiolates form well-packed structures on palladium surfaces; the detailed structures of these SAMs remains to be resolved, but they are probably more heterogeneous than those on gold. (ii) A range of organic thiols can be patterned on palladium films by μCP; all provide good resistance to iron(III)-based etches, although C$_{16}$SH seems to give the best results. (iii) the RS/Pd interface contributes strongly to the ability of the film to resist chemical etching. This result suggests that an ion-impermeable organic layer is not essential to achieve high quality resist layers on palladium films.

We believe that the system of SAMs on palladium is superior to SAMs on gold and silver for patterning microstructures by μCP.[15] We suggest that the ability to fabricate palladium structures by μCP will provide new methods to functional micro- and nanostructures (e.g., in catalysis), for patterning contacts for CMOS structures, and for interfacing with metallic and organic electronic materials.[16]

Acknowledgment. This research was supported by DARPA and used the MRSEC Shared Facilities supported by the NSF under Award No. DMR-9400396. J.C.L. thanks the DoD for a graduate fellowship. D.B.W. thanks the NSF for a graduate fellowship. M.L.C. thanks NIH for a postdoctoral fellowship.

Supporting Information Available: Optical ellipsometry, contact angles, XPS, and PIERS for C$_{16}$S Sams on Pd (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Abbott, N.; Kumar, A.; Whitesides, G. M. *Chem. Mater.* **1994**, *6*, 596−602.

(2) Kumar, A.; Abbott, N. A.; Kim, E.; Biebuyck, H. A.; Whitesides, G. M. *Acc. Chem. Res.* **1995**, *28*, 219−226.

(3) Despite the technological significance of palladium, we are not aware of any reports in the literature on the characterization of monolayers of alkanethiolates formed on thin films of palladium. The use of thiols to stabilize palladium colloids and to protect palladium black catalysts has been reported. See for example: Chen, S.; Huang, K. J. *Cluster Sci.* **2000**, *11*, 405−422. Zamborini, F. P.; Gross, S. M.; Murray, R. W. *Langmuir* **2001**, *17*, 481−488. Berezin, M. Y.; Wan, K. T.; Friedman, R. M.; Orth, R. G.; Raman, S. N.; Ho, S. V.; Ebner, J. R. *J. Mol. Catal. A: Chem.* **2000**, *158*, 567−576.

(4) Hartwich, J.; Sundermann, M.; Kleineberg, U.; Heinzmann, U. *Appl. Surf. Sci.* **1999**, *144−145*, 538−542. Chapman, R. G.; Ostuni, E.; Yan, L.; Whitesides, G. M. *Langmuir* **2000**, *16*, 6927−6936. Friebel, S.; Aizenberg, J.; Abad, S.; Wiltzius, P. *Appl. Phys. Lett.* **2000**, *77*, 2406−2408. Mueller, H. U.; David, C.; Voelkel, B.; Grunze, M. *J. Vac. Sci. Technol., B* **1995**, *13*, 2846−2849. Jennings, G. K.; Laibinis, P. E. *Colloids Surf., A* **1996**, *116*, 105−114. Jennings, G. K.; Munro, J. C.; Yong, T.-H.; Laibinis, P. E. *Langmuir* **1998**, *14*, 6130−6139.

(5) Xia, Y.; Zhao, X.-M.; Whitesides, G. M. *Microelectron. Eng.* **1996**, *32*, 255−268. Michel, B.; Bernard, A.; Bietsch, A.; Delamarche, E.; Geissler, M.; Juncker, D.; Kind, H.; Renault, J. P.; Rothuizen, H.; Schmid, H.; Schmidt-Winkel, P.; Stutz, R.; Wolf, H. *IBM J. Res. Dev.* **2001**, *45*, 697−719.

(6) Wolf, S. *Silicon Processing fo the VLSI Era*; Lattice Press: Sunset Beach, 1990.

(7) Moniz, B. J. *Metallurgy*, 2nd ed.; American Technical Publishers: Homewood, 1994.

(8) The nearest neighbor spacing in the (111) planes of gold, silver, and copper is 2.88, 2.87, and 2.56 Å, respectively.

(9) The palladium substrates were prepared by evaporating 1.5 nm of titanium onto silicon wafers (Si/SiO$_2$) with an electron-beam thin film deposition system, followed by 30−200 nm of palladium.

(10) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley & Sons: New York, 1997.

(11) For μCP, the poly(dimethylsiloxane) stamp was wet with a 5-mM ethanolic solution of a thiol on a cotton swab and dried under a stream of nitrogen for 30 s. The stamp was in contact with the sample for 5−20 s for each printing.

(12) We purchased Gold Film Etchant TFA (KI/I$_2$) and Palladium Etch TFP (FeCl$_3$) from Transene, Inc., Danvers, MA.

(13) Xia, Y.; Zhao, X.-M.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 2332−2337.

(14) The uniformity of the samples printed with the short-chain thiols (C$_n$SH, $n < 10$) and etched was difficult to reproduce over large areas. Stamping the thiols with too much ink led to complete protection of the area covered by the stamp with no pattern. We attribute these difficulties to the high volatility of the short-chain alkanethiols.

(15) The relatively small difference in rates of etching of thin and thick SAMs on palladium will make it difficult to form patterns based on differential etching—e.g.: Black, A. J.; Paul, K. E.; Aizenberg, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 8356−8365.

(16) 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. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 4835−4840. Seminario, J. M.; De la Cruz, C. E.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 5616−5617.

JA012569L