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Polymeric Self-Assembled Monolayers. 3. Pattern Transfer by Use of Photolithography, Electrochemical Methods, and an Ultrathin, Self-Assembled Diacetylenic Resist

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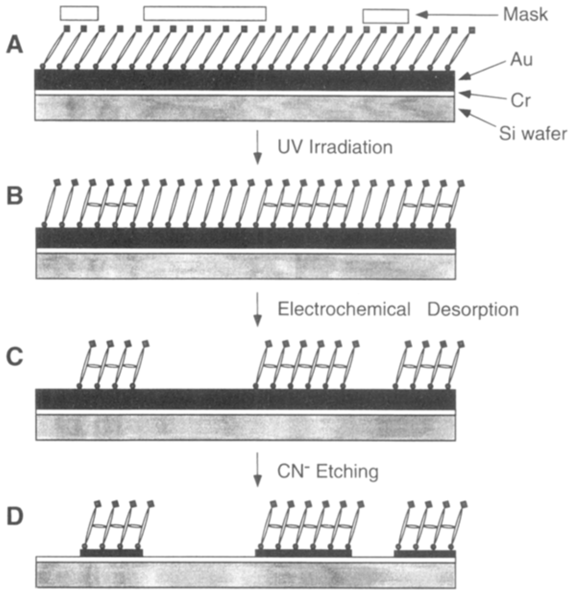
We report herein that a substrate can be patterned using a diacetylenic, self-assembled monolayer (SAM) resist and photolithographic and electrochemical methods. Our proof-of-concept experiments result in micron-scale pattern transfer onto Au substrates, but extension to other materials, including Si,[1] Al,[2] and GaAs,[3] and nanometer-scale patterning will be straightforward.

For a number of reasons there has been considerable recent interest in using ultrathin SAM resists for patterning surfaces. First, since such resists consist of single, small molecules, the theoretical resolution of lithographically defined features can be as small as a few nanometers if the resist is patterned with an appropriate tool, such as the tip of a scanning tunneling microscope (STM).[4−6] Second, SAMs are extremely dense and in some cases their structure approaches that of a two-dimensional crystal even when the SAM is formed by vapor-phase dosing.[7−9] This insures low defect density and simplified resist application and stripping (*vide infra*). Finally, the terminal groups of the SAMs can be varied to enhance selective chemical or physical vapor deposition of materials.[4,10]

Prior to the work discussed here, several reports had appeared that illustrate the viability of SAMs as resist materials. Examples of patterning based on the removal or the application of SAMs by photo-oxidation,[11−13] stamping,[14−18] STM,[4−6] electron beam,[6,19] and physical abrasion[20−22] have been illustrated.

Scheme 1



In this report, we use a diacetylenic SAM as a negative photoresist and transfer the image of a transmission electron microscope (TEM) minigrid into a Au substrate using the three steps illustrated in Scheme 1. We begin by placing the minigrid in contact with a SAM composed of close-packed HS-$(CH_2)_{10}C\equiv CC\equiv C(CH_2)_{10}COOH$, **1**, molecules[23−25] confined to a Au/Cr/Si surface (Scheme 1, Frame A).[26] The entire assembly is then exposed to UV light, which induces polymerization in the unmasked regions of the SAM (Scheme 1, frame B).[23−25,27,28] Next the unpolymerized portion of the resist is selectively desorbed using an electrochemical reductive stripping method (Scheme 1, frame C).[29,30] Selective stripping is possible because the polymeric SAM is sufficiently insoluble and strongly bound to the surface through multiple Au/S and van der Waals interactions that it survives potential excursions that remove monomeric organomercaptan SAMs.[23,25,29,30] Resist removal results in a negative image of the mask, which can be elaborated by etching the grid image into the Au surface with an O_2-saturated 1 M KOH plus 10 mM KCN aqueous solution (Scheme 1, frame D).[12,15,20,22]

Figure 1a is an optical micrograph of the 400-mesh (holes per linear inch) Cu TEM minigrid, which was used to pattern

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(1) Maoz, R.; Sagiv, J. *J. Colloid Sci.* **1984**, *100*, 465.
(2) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45.
(3) Sheen, C. W.; Shi, J.-X.; Martensson, J.; Parikh, A. N.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, *114*, 1514.
(4) Schoer, J. K.; Ross, C. B.; Crooks, R. M.; Corbitt, T. S.; Hampden-Smith, M. J. *Langmuir* **1994**, *10*, 615.
(5) Ross, C. B.; Sun, L.; Crooks, R. M. *Langmuir* **1993**, *9*, 632.
(6) Marrian, C. R. K.; Perkins, F. K.; Brandow, S. L.; Koloski, T. S.; Dobisz, D. A.; Calvert, J. M. *Appl. Phys. Lett.* **1994**, *64*, 390.
(7) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
(8) Poirier, G. E.; Tarlov, M. J.; Rushmeier, H. E. *Langmuir* **1994**, *10*, 3383.
(9) Chailapakul, O.; Sun, L.; Xu, C.; Crooks, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 12459.
(10) Dressick, W. J.; Calvert, J. M. *Jpn. J. Appl. Phys.* Part 1 **1993**, *32*, 5829.
(11) Huang, J. Y.; Hemminger, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3342.
(12) Huang, J. Y.; Dahlgren, D. A.; Hemminger, J. C. *Langmuir* **1994**, *10*, 626.
(13) Tarlov, M. J.; Burgess, D. R. F.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305.
(14) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60.
(15) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
(16) Lopez, G. P.; Biebuyck, H. A.; Frisbie, C. D.; Whitesides, G. M. *Science* **1993**, *260*, 647.
(17) Lopez, G. P.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1993**, *9*, 1512.
(18) Frisbie, C. D.; Wollman, E. W.; Martin, J. R.; Wrighton, M. S. *J. Vac. Sci. Technol. A* **1993**, *11*, 2368.
(19) Tiberio, R. C.; Craighead, H. G.; Lercel, M.; Lau, T.; Sheen, C. W.; Allara, D. L. *Appl. Phys. Lett.* **1993**, *62*, 476.
(20) Kumar, A.; Biebuyck, H. A.; Abbott, N. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9188.
(21) Abbott, N. L.; Whitesides, G. M.; Racz, L. M.; Szekely, J. *J. Am. Chem. Soc.* **1994**, *116*, 290.
(22) Abbott, N. L.; Kumar, A.; Whitesides, G. M. *Chem. Mater.* **1994**, *6*, 596.
(23) Kim, T.; Crooks, R. M.; Tsen, M.; Sun, L. *J. Am. Chem. Soc.* **1995**, *117*, 3963.
(24) Kim, T.; Crooks, R. M. *Tetrahedron Lett.* **1994**, *35*, 9501.
(25) Kim, T.; Crooks, R. M.; Tsen, M.; Sun, L. Manuscript in preparation.
(26) Au films (2000 Å) were electron-beam deposited on Cr-primed (50 Å) Si(100) wafers. The substrates were cleaned by rinsing with acetone and water several times and then drying with N_2. The SAMs were prepared by immersing the substrates in a 1 mM solution of diacetylenic alkanethiol **1** in $CHCl_3$ for about 1 h. The SAM-modified Au substrates were rinsed with acetone and water several times prior to lithography.
(27) Wegner, G. *Z. Naturforsch.* **1969**, *24b*, 824.
(28) Photolithography was performed in a N_2-purged chamber. The substrate was exposed to UV light, 254 nm (Oriel, Model 6035) for about 1 h (the exact time required for the polymerization depends on the distance between the light source and the SAM). Control experiments indicate that no pattern forms if a simple n-alkanethiol SAM is substituted for the diacetylenic resist.
(29) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.
(30) Electrochemical desorption of the monomeric resist was carried out by reductive stripping voltammetry in a single-compartment cell. The Au substrate potential was scanned between −0.5 and −1.4 V (vs Ag/AgCl (3 M NaCl)) 32 times over a period of 25 min at 50 mV/s in an electrolyte consisting of a 1:1 mixture of 1 M aqueous KOH and ethanol using a Pine (Model AFCBP1) potentiostat. Control experiments involving FTIR-ERS and XPS analysis of unpatterned monomeric and polymeric diacetylenic resists indicate that this electrochemical procedure completely (within the resolution of the techniques) removes the monomeric resists, but removes little, if any, of the polymerized resist.

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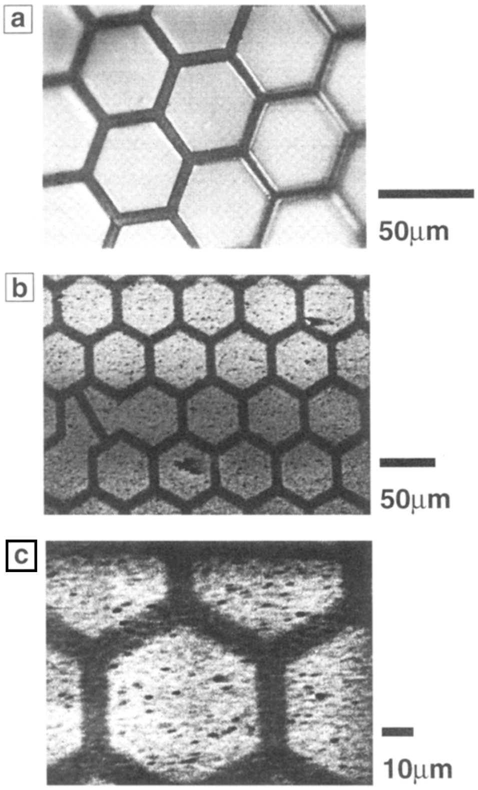

Figure 1. (a) Optical micrograph of the 400-mesh minigrid used to generate the patterns shown in panels b and c. Note that the right and left sides of this micrograph are slightly out of focus. (b, c) Scanning electron micrographs of a Au surface patterned using the 400-mesh TEM minigrid shown in panel a.

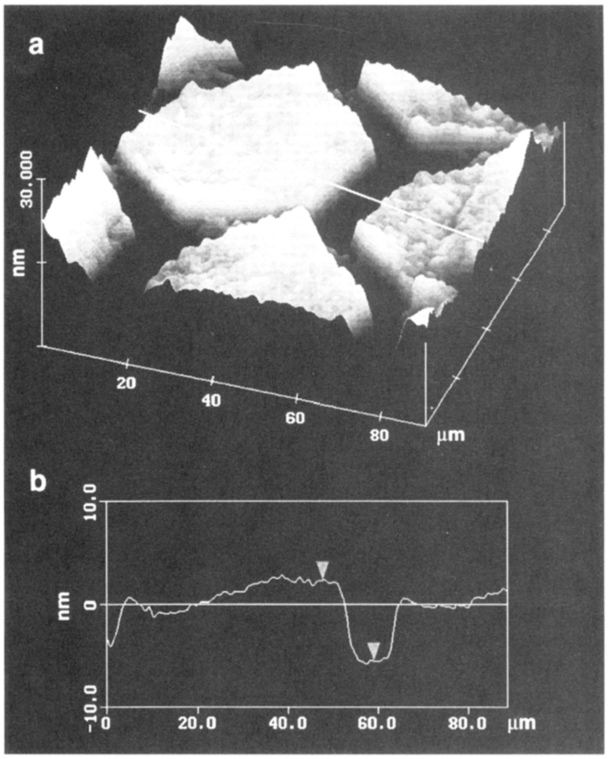

Figure 2. (a) A three-dimensional STM image of a Au surface patterned using the 400-mesh TEM minigrid shown in Figure 1a. Note that the image has been filtered to emphasize the lithographically-defined pattern. (b) A depth profile centered on the line shown in panel a. The profile is an average of several line scans.

the Au surface. Panels b and c of Figure 1 are scanning electron micrographs (SEMs) of a patterned Au surface, such as that illustrated in Scheme 1, frame D, obtained at two different magnifications. At this level of resolution, we observe excellent reproduction of the mask features. However, close inspection reveals that the lateral dimensions of the hexagonal raised regions are somewhat less than those of the original mask. This may arise from diffraction off the mask edges, that is, from the modulation transfer function, which will tend to reduce the photon flux in areas near the vicinity of the mask edges. We are uncertain of the origin of the dark spots that are especially apparent in Figure 1c; however, they appear in both regions of the pattern, they are not apparent on the naked Au substrates or on substrates modified with the polymerized or unpolymerized SAMs, and they are not visible in STM images (*vide infra*).

Figure 2a is a three-dimensional STM image (90 µm × 90 µm) of the pattern shown in Figure 1b,c. The grooves in this image are regions of the Au surface that have been etched by the KCN/KOH solution, while the hexagonal regions are those parts of the Au surface that etch at a reduced rate as a result of the presence of the polymeric SAM resist. That the organomercaptan survives CN^- etching is consistent with our previous findings[31,32] and those from other groups.[13,15,20,33,34] The critical issue in this regard is that dissolution requires that CN^- make intimate contact with the Au surface, and the strongly complexed mercaptan retards this process. STM depth profiles (Figure 2b) indicate that the grooves are about 7–8 nm deep. Note that we did not determine the extent to which the raised regions etched, but we believe that defects within the polymeric resist do result in at least some loss of Au from the SAM-coated, hexagonal regions. For example, the top of the hexagon in Figure 2 is not flat, which could result from the etchant undercutting the resist (the depth of this feature might be enhanced somewhat by the flattening software, since we used the maximum travel of the tube scanner to obtain this image). Optimization of the etching conditions, which is an issue we have not addressed, should reduce this effect.

In summary, we have demonstrated that a SAM composed of diacetylenic organomercaptans can be used as a negative photolithographic resist. The importance of this method results from the fact that the resist is highly organized, thin, and largely defect free. These factors ensure high-resolution patterning and control over the surface energy and reactivity of the resist itself, which permits an added dimension of control over surface processing. In addition, resist stripping involves only gentle and easily controlled electrochemical methods. Moreover, we have previously shown that organized multilayers of polydiacetylenic SAMs can be easily formed, so resist thickness can be controlled over a broad range.[23] Finally, unique electronic and photonic properties of the polymeric SAMs might themselves be integrated into Si-based devices using this lithographic approach in the future.

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[31] Li, Y.; Chailapakul, O.; Crooks, R. M. *J. Vac. Sci. Technol. A*, in press.

[32] Sun, L.; Crooks, R. M. *Langmuir* **1993**, *9*, 1951.

[33] Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022.

[34] Abbott, N. L.; Rolison, D. R.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2672.