Self-Assembled Monolayers Exposed to Metastable Argon Beams Undergo Thiol Exchange Reactions

Michael L. Chabinyc,† J. Christopher Love,† Joseph H. Thywissen,‡ Federico Cervelli,‡ Mara G. Prentiss,*,‡ and George M. Whitesides*,†

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, and Department of Physics, Harvard University, 9 Oxford Street, Cambridge, Massachusetts 02138

Received August 29, 2002

Self-assembled monolayers (SAMs) formed from alkanethiols on thin films of gold were exposed to a beam of metastable argon atoms through a stencil mask. The changes in the organizational structure of the alkyl chains in the SAM that resulted from exposure were characterized using reflection–absorption infrared spectroscopy. All spectroscopic evidence suggested that the SAMs become disordered after exposure to metastable argon atoms and that no apparent oxidation of the alkane chain occurred. The alkanethiolates in the regions of a SAM of dodecanethiolate damaged by the atom beam exchanged readily upon immersion in a solution of 16-mercaptohexadecanoic acid. The exchange reaction was selective for the regions of the SAM exposed to metastable argon atoms with patterns containing critical dimensions of <50 nm. A thin (<5 nm) polymeric multilayer was covalently linked to the carboxylic acid groups in the exposed regions of the SAM. The polymeric layer served as an improved resist against a commercial KI/I_2-based etchant used to transfer the pattern into the thin film of gold.

Introduction

This paper examines the effect of limited dosages of metastable argon (Ar*) atoms on the structural organization of self-assembled monolayers (SAMs) of alkanethiolates formed on thin films of gold and demonstrates a method for the chemical functionalization of the substrate after exposure to low dosages of Ar* (less than 1 Ar* per molecule in the SAM). Metastable atom beams have been used to pattern SAMs on metals and silicon dioxide.[1–3] Little information concerning the chemical effects of the bombardment of metastable atoms on SAMs is known.

Atomic beam lithography (ABL) has been proposed as a technique for nanolithography.[1,4–7] The de Broglie wavelength of most thermal atoms is sufficiently small (~10 pm) that diffraction does not limit the resolution of the attainable features. ABL has two advantages over serial lithographic techniques (e.g., electron beam lithography).[8–10] First, the electronic energy contained in a metastable atom of a rare gas is ~8–20 eV; these values are near the ionization energies of organic materials (~10–12 eV) frequently used as resists.[11] Second, sources for atomic beams can be configured to expose relatively large areas (>10 cm^2). The difficulty of creating high-flux metastable beams, however, has limited the use of metastable ABL because long exposure times are required to produce useful contrast in resistance to chemical etchants between the exposed and unexposed regions.

SAMs have been used almost exclusively as resists for ABL[1–3] because metastable atoms are unable to penetrate polymeric layers more than ~5 nm thick.[12,13] SAMs have particular advantages for the fabrication of nanometer-scale features relative to polymeric resists because (i) the molecular diameter of the species in the SAM is small (<1 nm) and (ii) they are sufficiently thin that they minimize scattering of incident particles or electrons in the film.[14,15] Two disadvantages of SAMs as resists for ABL are that (i) SAMs are relatively poor resists against common processing techniques such as reactive ion etching and (ii) the fluxes of many atomic beam sources are unable to achieve the dosages (e.g., >10 Ar* per thiolate)[2] that are required to generate useful contrast to chemical etchants between the exposed and unexposed regions of the SAM in short amounts of time (<1 h).

* To whom correspondence should be addressed. George M. Whitesides: telephone, 617-495-9430; fax, 617-495-9857; e-mail, gwhitesides@gmwgroup.harvard.edu. Mara G. Prentiss: telephone, 617-495-4483; fax, 617-495-0416; e-mail, mara@atomsun.harvard.edu.

† Department of Chemistry and Chemical Biology.

‡ Department of Physics.

(1) Berggren, K. K.; Bard, A.; Wilbur, J. L.; Gillaspy, J. D.; Helg, A. G.; McClelland, J. J.; Rolston, S. L.; Phillips, W. D.; Prentiss, M.; Whitesides, G. M. *Science* **1995**, *269*, 1255–1257.

(2) Bard, A.; Berggren, K. K.; Wilbur, J. L.; Gillaspy, J. D.; Rolston, S. L.; McClelland, J. J.; Phillips, W. D.; Prentiss, M.; Whitesides, G. M. *J. Vac. Sci. Technol., B* **1997**, *15*, 1805–1810.

(3) Younkin, R.; Berggren, K. K.; Johnson, K. S.; Prentiss, M.; Ralph, D. C.; Whitesides, G. M. *Appl. Phys. Lett.* **1997**, *71*, 1261–1263.

(4) Timp, G.; Behringer, R. E.; Tennant, D. M.; Cunningham, J. E.; Prentiss, M.; Berggren, K. K. *Phys. Rev. Lett.* **1992**, *69*, 1636–1639.

(5) Johnson, K. S.; Thywissen, J. H.; Dekker, N. H.; Berggren, K. K.; Chu, A. P.; Younkin, R.; Prentiss, M. *Science* **1998**, *280*, 1583–1586.

(6) Bell, A. S.; Brezger, B.; Drodofsky, U.; Nowak, S.; Pfau, T.; Stuhler, J.; Schulze, T.; Mlynek, J. *Surf. Sci.* **1999**, *433–435*, 40–47.

(7) Hill, S. B.; Haich, C. A.; Dunning, F. B.; Walters, G. K.; McClelland, J. J.; Celotta, R. J.; Craighead, H. G. *Appl. Phys. Lett.* **1999**, *74*, 2239–2241.

(8) Lercel, M. J.; Redinbo, G. F.; Pardo, F. D.; Rooks, M.; Tiberio, R. C.; Simpson, P.; Craighead, H. G.; Sheen, C. W.; Parikh, A. N.; Allara, D. L. *J. Vac. Sci. Technol., B* **1994**, *12*, 3663–3667.

(9) Seebohm, G.; Craighead, H. G. *Electron. Mater. Ser.* **2000**, *6*, 97–138.

(10) Ito, T.; Okazaki, S. *Nature* **2000**, *406*, 1027–1031.

(11) Ozaki, H.; Harada, Y. *J. Am. Chem. Soc.* **1990**, *112*, 5735–5740.

(12) Harada, Y.; Masuda, S.; Ozaki, H. *Chem. Rev.* **1997**, *97*, 1897–1952.

(13) Recent work has shown that contamination lithography is a useful resist scheme but also requires long exposure times for development (>1 h): Johnson, K. S.; Berggren, K. K.; Black, A. J.; Black, C. T.; Chu, A. P.; Dekker, N. H.; Ralph, D. C.; Thywissen, J. H.; Youkin, R.; Prentiss, M.; Tinkham, M.; Whitesides, G. M. *Appl. Phys. Lett.* **1996**, *69*, 2773–2775.

(14) Tiberio, R. C.; Craighead, H. G.; Lercel, M.; Lau, T.; Sheen, C. W.; Allara, D. L. *Appl. Phys. Lett.* **1993**, *62*, 476–478.

(15) Lercel, M. J.; Craighead, H. G.; Parikh, A. N.; Seshadri, K.; Allara, D. L. *Appl. Phys. Lett.* **1996**, *68*, 1504–1506.

10.1021/la026495i CCC: $25.00 © 2003 American Chemical Society
Published on Web 02/04/2003

The mechanism by which organic molecules are damaged by metastable atoms has been studied and seems to involve a Penning ionization process.[11,12,16] There are, however, relatively few studies of the chemical identity of the molecules remaining after exposure to metastable atom beams. We have examined the results of the exposure of SAMs of alkanethiolates to an Ar* beam using reflection–absorption infrared spectroscopy (RAIRS).[17] These spectra indicated that the Ar*-exposed SAMs become more disordered with increasing exposure to a beam of Ar*. These data further suggested that a thiolate exchange reaction[18] could enhance the chemical contrast of the regions exposed to low dosages of Ar* (<1 atom per thiolate). We report our initial results on the selectivity and the kinetics of exchange reactions with Ar*-damaged SAMs and demonstrate the utility of the reaction by using it to create a negative-tone etch resist consisting of a combination of a SAM and a thin (~5 nm), covalently attached polymeric multilayer.

Results and Discussion

Exposure to Ar* Causes Structural Disorder in Alkanethiolate SAMs. Previous studies have shown that SAMs formed from alkanethiols exhibit a decreased ability to resist wet chemical etches after exposure to the Ar* beam.[1–3] We obtained RAIR spectra of SAMs formed from several alkanethiols that had been damaged by the Ar* beam. The vibrational spectra of a SAM, particularly in the region of the C–H stretching modes, help to define the organizational structure of the alkyl chains of the SAM.[17] The methylene stretching modes exhibited pronounced spectral shifts for all of the SAMs of alkanethiolates studied (C_n = 10, 12, 14, and 16 where C_n refers to $CH_3(CH_2)_{n-1}SH$). For a SAM formed from C_{12}, the symmetric methylene stretching mode shifts from 2918 to 2924 cm^{-1} and the antisymmetric mode shifts from 2851 to 2854 cm^{-1} (Figure 1a,c). These spectral shifts indicate that the local molecular environment of the hydrocarbon chains in the SAM has become more disordered, or liquidlike, with exposure to Ar*.[17] In addition, the intensity of the methyl stretching modes decreases with increasing dosages of Ar*.[19] Possible explanations for these observations include (i) a decrease in the mass coverage of alkanethiolates due to desorption of the molecules in the SAM from the surface upon Ar* impact or (ii) an increase in the conformational freedom of the alkyl chains in the SAM due to cleavage of the chains. We are unable to choose unequivocally between these two hypotheses based on our data, but we believe that it is possible that both mechanisms occur.

After exposure to Ar*, there are no detectable features in the carbonyl spectral region. This information suggests that little or no oxidation of the alkyl chains in the SAM due to processes such as radical capture by O_2 occurred during or after exposure to the Ar* beam (~1 h at an Ar* flux of $3.5 \pm 1.4 \times 10^{11}$ Ar* cm^{-2} s^{-1}).

Ar*-Damaged SAMs Undergo a Thiol Exchange Reaction. We hypothesized that the disorder (or material loss) caused by exposure to Ar* would allow us to replace the molecules in the exposed regions of the SAM selectively with another alkanethiol, while not affecting the unexposed regions.[20] The RAIR spectrum of a SAM damaged by the Ar* beam and subsequently exposed to a solution of a carboxylic acid terminated thiol shows two features that indicate the carboxylic acid terminated thiol is inserted into the SAM. First, the methylene stretches are more intense than those in the spectra taken prior to the exposure of the substrate to the acid-terminated thiol and the methyl stretches are slightly above the baseline (Figure 1d). Second, two peaks at 1718 and 1742 cm^{-1} appear in the spectra upon exposure to the acid-terminated thiol (Figure 2d). These two peaks are consistent with carbonyl stretching modes. The RAIR spectrum of a SAM of dodecanethiolate undamaged by the Ar* beam, but exposed to the same carboxylic acid terminated thiol, does not show any spectral evidence of an exchange of the thiol (Figures 1b and 2b). The spectra show no changes in the organizational structure of the alkyl chains and no peaks corresponding to carbonyl stretches. These results demonstrate that we can achieve chemical contrast between the Ar*-exposed and unexposed regions of a SAM using a simple exchange reaction. From these measurements, we cannot determine quantitatively the percentage of the damaged SAM that is replaced by the acid-terminated thiols.

We investigated the rate of exchange of 16-mercaptohexadecanoic acid, $C_{15}COOH$, into both unexposed and Ar*-exposed SAMs in order to determine the minimum dosage of Ar* and the minimum time of chemical exchange that was required to differentiate two regions on a patterned substrate chemically. We found that the exchange of the carboxylic acid terminated thiol into undamaged SAMs of alkanethiolates of C_{10} was too rapid to provide strong contrast between the damaged and undamaged regions based on RAIR spectra (Figure 3).

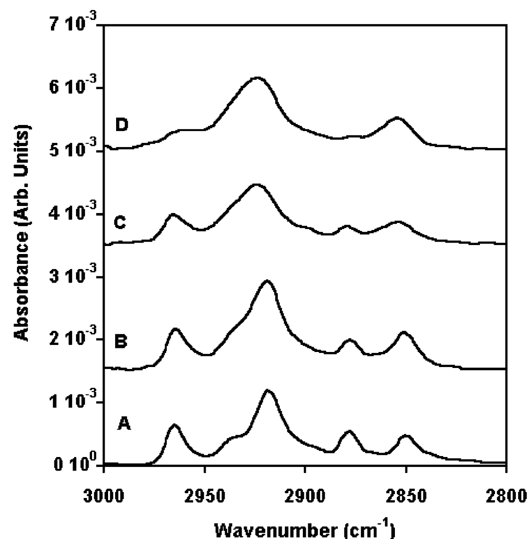

Figure 1. Methylene region of the RAIR spectra of SAMs formed from dodecanethiol (C_{12}) on gold thin films (200 nm of Au on a 6-nm Cr adhesion layer). (A) SAM formed from C_{12}. (B) SAM formed from C_{12} and immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 15 min. (C) SAM formed from C_{12} and exposed to the metastable argon beam for 60 min at a flux of $\sim 3.5 \times 10^{11}$ Ar* s^{-1} cm^{-2}. (D) Sample from (C) immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 15 min.

(16) Heinz, B.; Morgner, H. *Surf. Sci.* **1997**, *372*, 100–116.
(17) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.
(18) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–325.
(19) These changes in the spectral features are similar to those observed for SAMs that had been exposed to low-energy electron beams: Seshadri, K.; Froyd, K.; Parikh, A. N.; Allara, D. L.; Lercel, M. J.; Craighead, H. G. *J. Phys. Chem.* **1996**, *100*, 15900–15909. Müller, H. U.; Zharnikov, M.; Völkel, B.; Schertel, A.; Harder, P.; Grunze, M. *J. Phys. Chem. B* **1998**, *102*, 7949–7959.
(20) Previously, exchange reactions in SAMs have been used to fabricate sub-100-nm features using topographically directed etching: Black, A. J.; Paul, K. E.; Aizenberg, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 8356–8365.

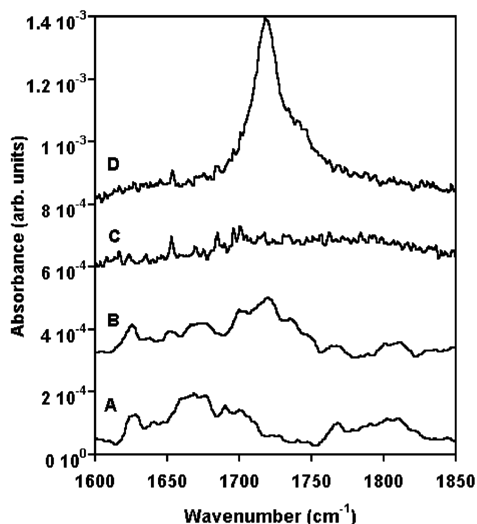

Figure 2. Carbonyl region of the RAIR spectra of SAMs formed from dodecanethiol (C_{12}). (A) SAM formed from C_{12}. (B) SAM formed from C_{12} and immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 15 min. (C) SAM formed from C_{12} and exposed to the metastable argon beam for 60 min at a flux of $\sim 3.5 \times 10^{11}$ Ar* s^{-1} cm^{-2}. (D) Sample from (C) immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 15 min.

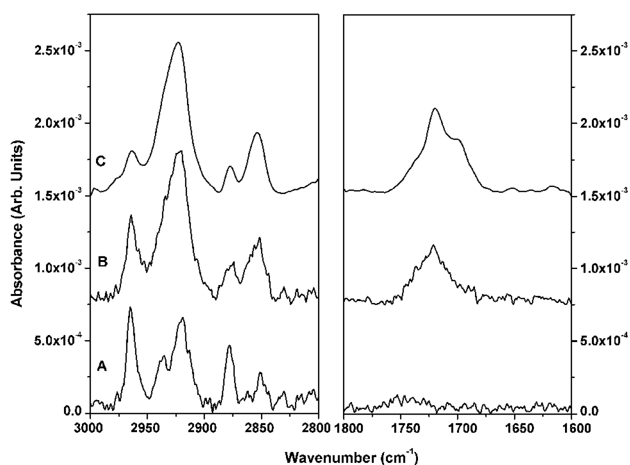

Figure 3. Methylene and carbonyl stretching regions of the RAIR spectra of SAMs formed from decanethiol (C_{10}) on gold thin films (200 nm of Au on a 6-nm Cr adhesion layer). (A) SAM formed from C_{10}. (B) SAM formed from C_{10} and immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 10 min. (C) SAM formed from C_{10} that was exposed to the metastable argon beam for 15 min at a flux of $\sim 3.5 \times 10^{11}$ Ar* s^{-1} cm^{-2} and immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 10 min.

For the SAMs composed of C_{12} and greater, we found that the exchange reactions with undamaged SAMs were substantially slower (greater than a factor of 2) than those for SAMs damaged by low dosages of Ar* (one per molecule in the SAM). The decrease in the rate of exchange correlates well with previous spectroscopic studies that show that a transition to greater ordering occurs in SAMs of alkanethiolates between C_{10} and C_{12}.[17]

For a SAM formed from C_{12}, we found that dosages that correspond to approximately 0.2−0.5 Ar* atoms per molecule in the SAM provided a useful difference in the rate of exchange between the two regions in the patterned SAM. This dosage is significantly lower than those used previously for patterning SAMs with Ar* for wet chemical etchants (typically >10 atoms per molecule in the SAM).[21]

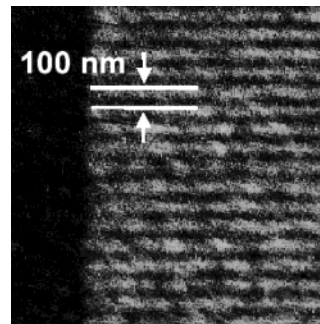

Figure 4. Lateral force atomic force micrograph of an Ar*-patterned surface after the thiolate exchange reaction. A SAM formed from C_{12} on palladium was exposed to the Ar* beam (15 min at a flux of $\sim 3.5 \times 10^{11}$ Ar* s^{-1} cm^{-2}) through a silicon nitride shadow mask consisting of suspended 30-nm-wide lines separated by 70-nm-wide gaps. The mask was fabricated using achromatic interferometric lithography (ref 24) and was available from a previous study (ref 25). The substrate was subsequently immersed in a 10 mM solution of 16-mercaptohexadecanoic acid for 15 min. The lighter regions corresponded to greater friction between the tip and the substrate.

The benefit of the low dosage is a reduced exposure time; typical exposures lasted less than ∼15 min at a typical Ar* flux of $\sim 3.5 \times 10^{11}$ Ar* s^{-1} cm^{-2}. At these dosages, the damaged SAM could be replaced by the carboxylic acid terminated thiol by immersion of the substrate in a 10 mM ethanolic solution of the thiol for less than 15 min. SAMs formed from C_{14} that were damaged by the metastable argon beam showed no evidence of exchange after immersion in 16-mercaptohexadecanoic acid for 15 min.

Exchange Reaction Can Fabricate Submicron Features. We further tested the selectivity of the reaction to exchange thiolates by exposing a SAM of C_{12} to Ar* through a silicon nitride shadow mask with <50 nm features. We formed the SAM on a film of palladium instead of gold to aid in the imaging of small features on the surface; the grain size of palladium is ∼15 nm, whereas that of gold is ∼50 nm.[22] After exposure to Ar* and immersion in an ethanolic solution of mercaptohexadecanoic acid for 15 min, the SAM was imaged using lateral force microscopy (LFM). The resulting image showed strong frictional contrast between the exchanged and unexchanged regions (Figure 4). The contrast measured is greater than that observed for the damaged SAMs prior to the exchange reaction. These observations suggest that this method should be useful for producing arrays of sub-100-nm patterns with chemical contrast and functionality and for detecting atomic fluxes with subwavelength resolution in atomic physics experiments.

Negative Tone Resists for Ar* Lithography. The ability to introduce chemical functionalities selectively into Ar*-patterned substrates provides a simple method to differentiate the two regions chemically. We demonstrate its use by covalently attaching a thin polymeric film to the exposed surface of the SAM; this film provides a greater resistance to wet chemical etchants than the SAM alone (Figure 5). (We have used this procedure previously as a method to increase the etch resistance of microcontact-printed SAMs formed from carboxylic acid terminated thiols on gold.[23]) The use of a thin layer of polymer (<5 nm) should preserve the edge resolution of

(21) A similar scheme to perform an exchange reaction using electron-beam-damaged SAMs was demonstrated in: Harnett, C. K.; Satyalakshmi, K. M.; Craighead, H. G. *Langmuir* **2001**, *17*, 178−182.

(22) Love, J. C.; Wolfe, D. B.; Chabinyc, M. L.; Paul, K. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1576−1577.

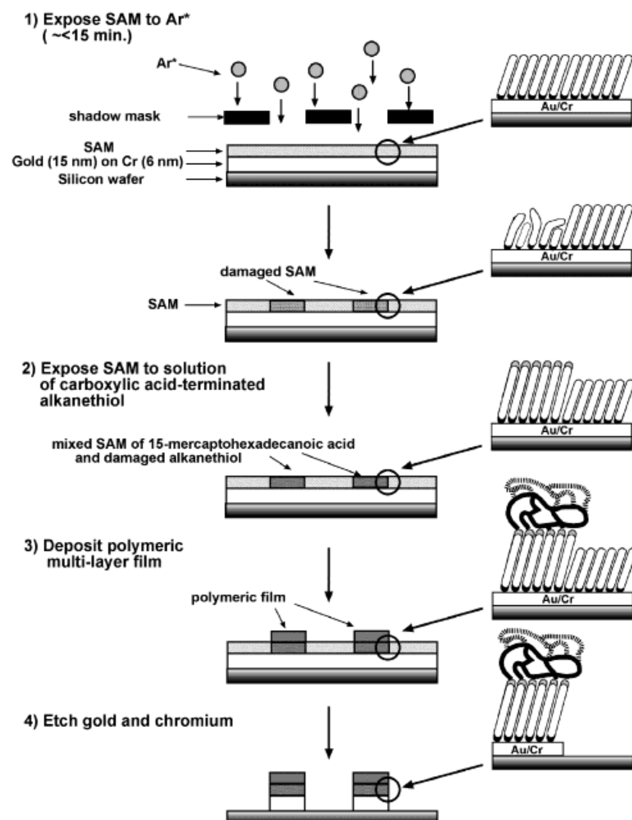

Figure 5. Schematic illustration of the lithographic process. (1) A SAM formed from dodecanethiol on a 15-nm gold film supported by a silicon wafer was exposed to the metastable argon beam through a TEM grid. The periods of exposure ranged from 15 min to 1 h. (2) The sample was removed from the vacuum system and placed in a 10 mM ethanolic solution of 16-mercaptohexadecanoic acid. The adsorbates in the damaged regions of the SAM were displaced by the carboxylic acid terminated thiol after a period of 15 min. (3) A thin film of polymer was then linked to the exposed regions on the substrate by the following steps: (i) immersion in a 10 mM solution of trifluoroacetic anhydride in dimethylformamide for 20 min, (ii) immersion in a 0.05 wt % solution of linear poly(ethylene imine), $M_n = 230$, in ethanol for 30 min, and (iii) immersion in a 0.05 wt % solution of poly(ethylene-*alt*-maleic anhydride), $M_n = 100{,}000-500{,}000$, in *N*-methyl-2-pyrrolidone for 30 min. The substrate was rinsed well between each step. (4) The pattern in the gold film was developed by immersing the sample in a commercial etchant composed of KI and I_2 that had been diluted by 1/3 in water.

the features patterned by metastable atom lithography. The molecular weight of the deposited polymer can also be optimized for the feature sizes required for a particular application.

We deposited two polymeric layers to improve the etch resistance of the patterned regions of the substrate (Figure 5). RAIR spectra and ellipsometry were used to characterize the deposited layers. The thickness of the SAM and the polymeric multilayer combined was ~4−5 nm (the thickness of the SAM prior to deposition of the polymeric layer was ~2 nm). Figure 6 shows the results of wet chemical etching of the gold substrates that had been patterned by exposure to the Ar* beam using a transmission electron microscopy (TEM) grid as a physical mask. The pattern was uniform over the area of the TEM grid (~0.1 cm^2). Etching of the substrates prior to deposition of the polymeric multilayer resulted in poor contrast between the exposed and unexposed regions, as well as significant pitting in the exposed regions.

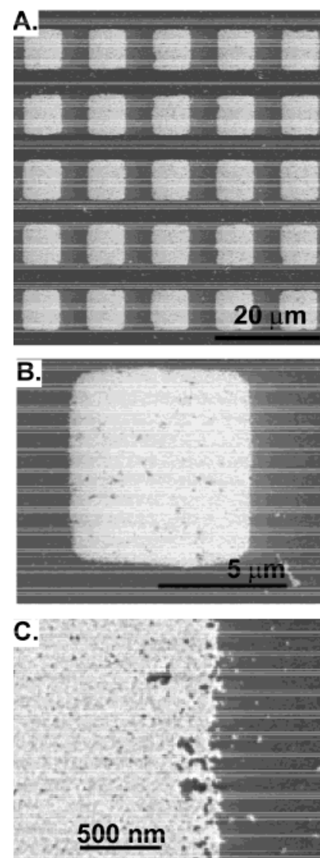

Figure 6. Scanning electron micrographs of a gold film patterned using metastable atom lithography and etched using a KI/I_2-based etchant (Transene Inc., Danvers, MA). The gold film was 15 nm thick and was evaporated onto a silicon wafer. The substrate was exposed to the metastable argon beam through a TEM grid for 15 min. The substrate was then treated using the scheme in Figure 5. Parts A−C show successive magnifications of the patterned regions.

We were unable to etch submicron features into gold substrates using the shadow masks available to us. The pitch of the features in our masks was near the grain size of gold in our evaporated films (~50 nm). Because of this factor, we are not certain if the method is able to pattern features at this scale using wet chemical etchants. Even so, we believe that this method should be still useful for the fabrication of chemically distinct submicron features over relative large (cm^2) areas that do not require chemical etching.

Conclusions

We have studied the chemical damage to SAMs of alkanethiolates by exposure to Ar* beams. Infrared spectra suggest that the SAMs become disordered after exposure to Ar*. The structural disorder may be caused by loss of molecules from the SAM or by chemical degradation. No evidence for chemical oxidation of the alkyl chains was observed. The gold surface supporting the damaged SAMs can be chemically derivatized by an exchange reaction with a second thiol.

We have used the thiolate exchange reaction to demonstrate a simple scheme to modify the chemical reactivity

(23) Huck, W. T. S.; Yan, L.; Stroock, A.; Haag, R.; Whitesides, G. M. *Langmuir* **1999**, *15*, 6862−6867.
(24) Savas, T. A.; Shah, S. N.; Schattenburg, M. L.; Carter, J. M.; Smith, H. I. *J. Vac. Sci. Technol., B* **1995**, *13*, 2732−2735.
(25) Thywissen, J. H.; Johnson, K. S.; Dekker, N. H.; Prentiss, M.; Wong, S. S.; Weiss, M.; Grunze, M. *J. Vac. Sci. Technol., B* **1998**, *16*, 1155.

of regions of SAMs exposed to metastable argon atoms by a thiol exchange reaction. The advantages of this method for atom beam lithography include (i) the ability to pattern SAMs using low dosages of Ar* (<1 Ar* atom per molecule in the SAM), (ii) the ability to insert molecules with contrasting chemical functional groups in the Ar*-damaged regions of the SAM, and (iii) the ability to create a negative-tone resist for Ar* lithography by deposition of a thin polymeric layer (<5 nm) in the patterned region. The main disadvantage of this method is the possibility of substitution of the molecules in the undamaged SAM during the exchange reaction. This limitation can, we believe, be minimized by careful study of the kinetics of the exchange reaction with the undamaged SAM. We believe that this technique will be of general utility for lithography using metastable atoms beams and also for the detection of the impact of metastable atoms in low-flux beams.

Experimental Section

Materials. Alkanethiols ($HS(CH_2)_{n-1}CH_3$ ($n = 10, 12, 14, 16$)), 16-mercaptohexadecanoic acid, poly(ethyleneimine), and poly(ethylene-*alt*-maleic anhydride) were purchased from Aldrich or TCI and were used without further purification. Etchant solutions were obtained from Transene Inc. (Danvers, MA).

Formation of SAMs. The gold films were prepared by thermal evaporation (Edwards Auto 306) of an adhesion layer of chromium (~60 Å thick) onto a 3-in. Si/SiO_2 wafer (Silicon Sense, test grade (100)) followed by a layer of gold (~2000 Å thick). SAMs on gold films were formed by immersion of a freshly evaporated thin film in a 1−5 mM ethanolic solution of the alkanethiol for 12 h.

Metastable Atom Beam Chamber. The experimental apparatus has been described in detail previously.[1] The metastable argon beam is created in a high-pressure region ($\sim 1 \times 10^{-3}$ Torr) by application of a static dc discharge. The Ar* atoms then travel through a skimmer into a low-pressure region ($\sim 1 \times 10^{-6}$ Torr), and any ionized particles are removed by two biased electrodes. The diameter of the metastable beam is approximately 9 cm when it reaches the surface. The flux of metastable atoms was detected by electron emission from a gold electrode and measured using an electrometer (Keithley model 6512).

Ar* Exposure of SAMs. Substrates were cleaned with ethanol and dried under a stream of N_2 before introduction into the Ar* chamber. The samples were exposed to the Ar* beam and then rinsed with ethanol and stored under ethanol. No signatures of contamination by pump oil were observed by RAIRS after removal from the vacuum chamber. Substrates were chemically derivatized within 2 h of being removed from the Ar* apparatus.

Infrared Spectroscopy. RAIR spectra of the monolayers of alkanethiolates were obtained using a Nexus 670 FT-IR (Thermo Nicolet, Madison, WI) equipped with a surface grazing angle attachment (SAGA, Thermo Spectra-Tech, Shelton, CT) and a liquid-nitrogen-cooled MCT detector. The grazing angle was 80°. Spectra were averaged over 512 scans at 1 cm^{-1} resolution.

Covalent Attachment of a Polymer Film. The Ar*-damaged substrate was placed in a 10 mM ethanolic solution of 16-mercaptohexadecanoic acid for 15 min. The substrate was then immersed in a 10 mM solution of trifluoroacetic anhydride in dimethylformamide for 20 min. After the reaction was complete, the substrate was cleaned by washing with dry dichloromethane and dried under a stream of nitrogen. The substrate was allowed to react with a 0.05 wt % solution of linear poly(ethylene imine), $M_n = 230$, in ethanol for 30 min. After deposition, the substrate was sonicated in ethanol for 30 s to remove any physisorbed polymer. The substrate was then immersed in a 0.05 wt % solution of poly(ethylene-*alt*-maleic anhydride), $M_n = 100{,}000-500{,}000$, in *N*-methyl-2-pyrrolidone (NMP) for 30 min. After reaction, the substrate was sonicated in NMP for 30 s.

Acknowledgment. This work was supported by the ONR, DARPA, and the NSF (ECS-9729405). M.L.C. thanks the National Institutes of Health for postdoctoral fellowships. J.C.L. thanks the DoD for a graduate research fellowship.

LA026495I