UV Photopatterning of Alkanethiolate Monolayers Self-Assembled on Gold and Silver

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Recent interest in alkanethiolate monolayers on gold, silver, and copper surfaces stems from their simple preparation, well-defined structure, and outstanding flexibility in the study of organic interfaces.[1-6] One of the most attractive features of alkanethiolate self-assembled monolayers (SAMs) is the ease by which the surface chemical properties can be controlled simply by varying the terminal functional group.[7-9] It has also been demonstrated that alkanethiolate SAMs can be patterned in the plane of the surface both by mechanical removal of alkanethiolates[10] and photochemically by using photoactive pendant groups.[11] We describe here a new and straightforward method for photopatterning alkanethiolate SAMs on Au and Ag surfaces with micron-scale resolution. The method is compatible with optical imaging of a pattern and, consequently, does not require physical contact with the SAMs. In addition, we believe the method is generally applicable to all alkanethiol SAMS on Au and Ag. The effectiveness of this method is demonstrated with results from X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) imaging. SIMS has been shown to be useful in mapping the lateral distribution of photopatterned alkanethiol SAMs on Au.[11]

The photopatterning method used here is derived from results of two recent studies. First, Huang and Hemminger reported that, upon UV irradiation in air, alkanethiolates on Au are photooxidized to the corresponding alkanesulfonates.[12] Second, it was demonstrated that alkanesulfonate species that are formed from air oxidation can be readily displaced by immersion in a dilute thiol solution.[13] Our procedure combines these two observations. A pattern of alkanesulfonates is first formed on the alkanethiolate SAMs by UV irradiation in air through a mask. The sample is then immersed in a dilute solution of a different alkanethiol, and the alkanesulfonates in the exposed areas are displaced, resulting in the incorporation of the second alkanethiol in the photoexposed areas.

Alkanethiolate SAMs were formed on 200-nm Au and Ag thin films sputter-deposited on polished Si substrates as described previously.[14] UV radiation was provided by a high-pressure Hg lamp. The UV light was focused to irradiate uniformly a 0.5-cm-diameter portion of the samples with a total spectral power density of 3 W/cm^2. For all results presented here, 1-h exposure times in air were used.[15] For patterning of samples, 300- or 400-mesh Cu or Ni electron microscopy grids were placed directly on the SAM/Au or Ag samples. In experiments where a second thiol was exchanged into the UV-exposed areas, samples were first placed in pure ethanol for 5 min to rinse off sulfonated species in the UV-exposed regions, followed by immersion in ~1 mM alkanethiol–ethanol solution for 1–60 min.[16]

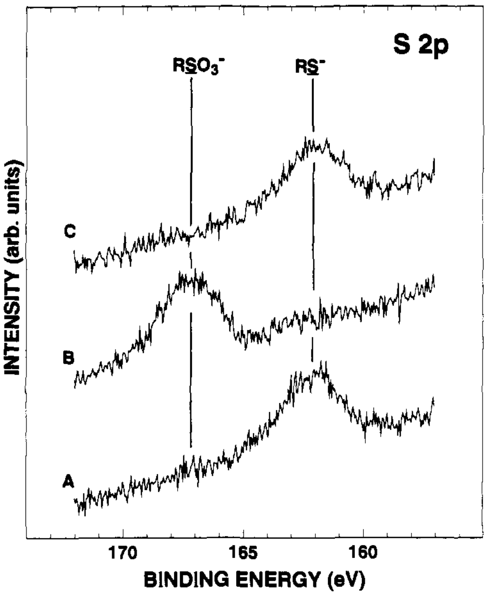

Figure 1. XPS spectra of S 2p region acquired from hexanethiol [CH$_3$(CH$_2$)$_5$SH] SAM/Au samples (A) as prepared, (B) after UV irradiation in air for 1 h, and (C) after UV irradiation for 1 h and immersion for 1 h in 1 mM hexanethiol–ethanol solution.

XPS was used to ascertain the extent of both the thiolate to sulfonate photoconversion and the sulfonate–thiol solution exchange reaction. In these experiments, the samples were irradiated without the patterning grids in place and the XPS analysis area was restricted within the photolyzed regions. Figure 1 shows a series of XPS spectra of the S 2p region acquired from hexanethiol [CH$_3$(CH$_2$)$_5$SH] SAM on Au samples (A) as prepared, (B) after irradiation, and (C) after solution exchange. The as-prepared monolayers exhibit a S 2p peak at a binding energy of 162 eV that is characteristic of thiolates on Au and Ag.[17] Following UV irradiation for 1 h, the 162-eV thiolate feature largely disappears and a new feature at 167 eV is observed that is assigned to sulfonate species formed from the photooxidation reaction.[12,17] The similarity of the S 2p peak areas before and after photolysis suggests that nearly complete conversion of the thiolate to sulfonate has occurred.[18] The third spectrum was obtained from a hexanethiol/Au sample that was UV exposed for 1 h followed by immersion in 1 mM hexanethiol–ethanol solution for 1 h. The sulfonate peak at 167 eV is now undetectable, and a thiolate peak at 162 eV has reappeared with approximately the same intensity as that for the as-prepared hexanethiol SAM. This suggests nearly complete exchange of alkanethiolates for alkanesulfonates in the

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(15) We have examined shorter UV irradiation times and found that exposure times of 15 min give comparable results.

(16) By removing sulfonate species prior to immersion in dilute thiol solutions, one can minimize the immersion time to limit exchange in unexposed regions. In addition, we have found that immersion times as little as 1 min in the thiol exchange solution give results comparable to 60-min immersions.

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(18) The appearance of an intense feature in the XPS O 1s region is also observed in the UV-photooxidized alkanethiol SAMs that we believe arises from the oxygen of the sulfonate groups. A decrease in the C 1s feature of approximately 60% following irradiation is also observed, however, indicating that substantial fragmentation and desorption of the hydrocarbon tails occur under the UV photolysis conditions used.

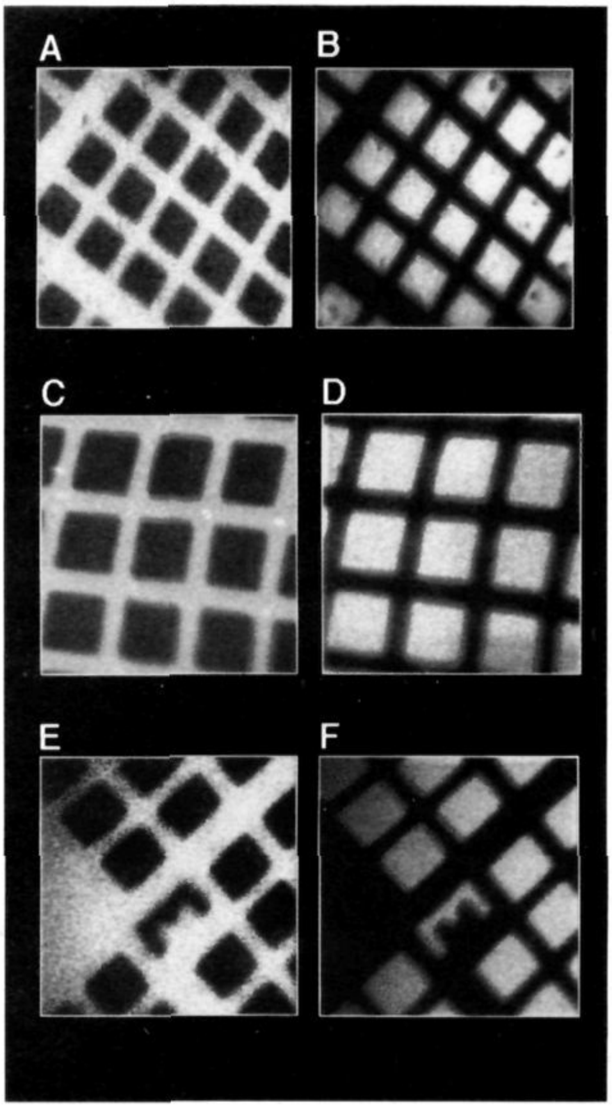

Figure 2. SIMS images obtained from UV-photopatterned alkanethiol SAMs on Au and Ag where lighter areas are regions of high secondary ion emission intensity: (A) SH^- (m/z=33) image of decanethiol SAM on Au irradiated for 1 h through 400-mesh grid (500-μm field of view); (B) same as A except HSO_4^- (m/z=97) image; (C) O^- (m/z=16) image of mercaptoundecanoic acid (MUDA) SAM on Au irradiated for 1 h through 300-mesh grid and immersed in 1 mM perfluoro mercaptan–ethanol solution for 1 h (350-μm field of view); (D) same as C except F^- (m/z=19) image; (E) $HOOC(CH_2)_{10}S^-$ (m/z=217) image of MUDA SAM on Ag irradiated for 1 h through 400-mesh grid and immersed in 1 mM octanethiol–ethanol solution for 1 min (335-μm field of view); (F) same as E except $CH_3(CH_2)_7S^-$ (m/z=145) image.

photolyzed areas. Similar XPS results were obtained from UV-photolyzed SAMs on Ag substrates.

Static SIMS spectra of UV-exposed and -unexposed areas of alkanethiol SAMs were acquired to identify secondary ions useful for imaging the photopatterned monolayers.[19] SIMS spectra acquired from UV-exposed areas display a dramatic increase in signals of sulfonate species including HSO_4^- (m/z=97), SO_3^- (m/z=80), and SO_2^- (m/z=64) and a corresponding large decrease in the SH^- (m/z=33) signal. These data suggested that photolyzed samples could be imaged by monitoring sulfonate or thiol secondary ions.

Typical SIMS images obtained from UV-photopatterned monolayers on Au and Ag are shown in Figure 2. Parts A and B of Figure 2 show SH^- and HSO_4^- secondary ion maps, respectively, acquired from a decanethiol [$CH_3(CH_2)_9SH$] SAM on Au that was irradiated in air through a 400-mesh grid for 1 h. In the unexposed areas, where the sample was covered by the grid bars, intense SH^- signals are observed (Figure 2A), while intense HSO_4^- signals are observed in the exposed areas (Figure 2B). The contrast, which we define as the ratio of counts in light areas to those in the dark areas, is approximately 10:1 and 15:1 for the SH^- and HSO_4^- images, respectively. We note that the photopatterned dimensions measured from the SIMS images agree well with the actual grid dimensions.

SIMS images of O^- (m/z=16) and F^- (m/z=19) acquired from a photopatterned mercaptoundecanoic acid [$HOOC(CH_2)_{10}SH$] (MUDA) SAM on Au are shown in parts C and D of Figure 2, respectively. The MUDA SAM was irradiated in air through a 300-mesh grid for 1 h and then immersed in a 1 mM $CF_3(CF_2)_7(CH_2)_2SH$–ethanol (perfluoro mercaptan–ethanol) solution for 1 h to displace, or exchange out, the sulfonates formed by UV photolysis in the exposed areas. O^- and F^- were selected to image the photopatterned and exchanged MUDA/Au sample because static SIMS spectra obtained from pure MUDA and perfluoro mercaptan SAMs displayed intense O^- and F^- signals, respectively. Strong O^- signals are observed in the unexposed areas (Figure 2C), while strong F^- signals are observed in the exposed (Figure 2D) areas where facile exchange of the perfluoro mercaptan is expected. The contrast ratios are approximately 20:1 and 8:1 for the O^- and F^- SIMS images, respectively. The lower contrast ratio and detection of F^- in unexposed regions of the F^- image indicate some displacement of MUDA by perfluoro mercaptan.[21]

Parts E and F of Figure 2 show SIMS images of parent alkanethiolate ions acquired from a MUDA SAM on Ag that was photopatterned in air for 1 h through a 400-mesh grid and then exchanged by immersion for 1 min in a 1 mM $CH_3(CH_2)_7SH$–ethanol (octanethiol–ethanol) solution. In contrast to alkanethiolate SAMs on Au, we have observed the emission of relatively intense SIMS molecular, or parent, thiolate ions from SAMs on Ag. The SIMS images in Figure 2E show strong $HOOC(CH_2)_{10}S^-$ (m/z=217) signals in the unexposed areas, while in the UV-exposed areas, where facile exchange of octanethiol is expected, intense octanethiolate [$CH_3(CH_2)_7S^-$ (m/z=145)] emission is observed. The contrast ratios are approximately 25:1 and 20:1 for the $HOOC(CH_2)_{10}S^-$ and $CH_3(CH_2)_7S^-$ images, respectively. We note that approximately 20 μm features associated with the letter E are easily resolved in the image.

In progress are studies to optimize conditions for the photolysis and exchange reactions with the goal of obtaining densely-packed alkanethiol films in the photoexposed regions while minimizing exchange in unexposed areas. One strategy to minimize exchange in unexposed areas is to perform the exchange reaction with a dialkyl disulfide.[10] Moreover, we are trying to elucidate the mechanism of the photooxidation reaction to better understand the factors that could limit the resolution of the photolithographic procedure for the alkanethiol SAMs.

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(19) A Cameca IMS 4F with a mass range of 0–300 was used to obtain SIMS spectra and images.[20] Negative ion spectra and images were acquired with 14.5-keV Cs^+ primary ions. Static SIMS spectra were acquired with primary ion currents of 10^{-12} A rastered over a 500 × 500 μm area. SIMS images were obtained in the microprobe mode at 10^{-11} A with typical acquisition times of 20–30 s.

(20) Commercial products and instruments are identified to adequately specify the experimental procedure; this identification does not imply endorsement by the National Institute of Standards and Technology.

(21) XPS spectra of the F 1s region acquired from 16-mercaptoundecanoic acid and decanethiol SAM/Au samples that have been irradiated and then immersed in 1 mM perfluoro mercaptan–ethanol solutions for 1 h indicate that the coverage of the perfluoro mercaptan in the irradiated areas is ~90% of that obtained for as-prepared perfluoro mercaptan SAMs on Au. In XPS control experiments with identical immersion times, the exchange of the perfluoro mercaptan in unexposed samples was estimated to be less than 5%.