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Use of High Lateral Resolution Secondary Ion Mass Spectrometry To Characterize Self-Assembled Monolayers on Microfabricated Structures

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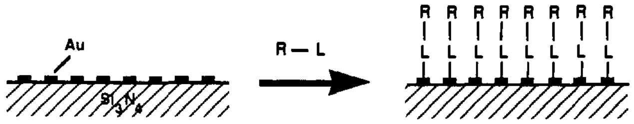
Abstract: Secondary ion mass spectra of self-assembled monolayers (SAMs) of the thiol-containing molecules $(\eta^5\text{-}C_5H_5)\text{-}Fe[(\eta^5\text{-}C_5H_4)CO(CH_2)_{10}SH]$ (I) and $C_{18}H_{37}SH$ (III) and their isotopically labeled analogs $(\eta^5\text{-}C_5D_5)Fe[(\eta^5\text{-}C_5D_4)CO(CH_2)_{10}SH]$ (II) and $C_{18}D_{37}SH$ (IV) on polycrystalline Au films are presented. These spectra were taken using a VG IX70S magnetic sector SIMS instrument. Peaks corresponding to parentlike ions $[M + H]^+$, $[M - H]^+$, or $[M + Au]^+$ with the expected isotopic shifts for I–IV were detected, verifying the presence of intact molecules of I–IV on the Au films. Molecular fragments of I–IV were also observed, e.g. $[(C_5H_5)Fe]^+$ for SAMs of I and $[(C_5D_5)Fe]^+$ for SAMs of II. Importantly, the use of SIMS to map the distribution of species I on a Au microwire array (wires 4.8 μm wide, separated by 1.2 μm on a Si_3N_4 substrate) is demonstrated. Comparison of maps of Fe^+ and the *molecular* fragment $[(C_5H_5)Fe]^+$ with Au^+ and Si^+ maps shows that I is found only on Au and not the Si_3N_4 substrate. The elemental and molecular ion maps represent the detection of 300 million molecules of I per microwire at a lateral resolution of less than 1 μm. Furthermore, each map covered 2500 μm² and was acquired in less than 40 s; comparable element mapping of Au microwire by Auger electron spectroscopy requires hours.

Our work on the surface coordination chemistry of microfabricated structures has inspired us to develop methodologies for detecting the presence of a monolayer of surface-confined molecules at high lateral resolution. Previous work from this laboratory has shown that it is possible to selectively derivatize microlithographically patterned Au and Pt surfaces with self-assembled monolayers (SAMs) of redox-active molecules, R–L, as shown in Scheme I, where L is –SH or –NC, known to coordinate to Au and Pt.[1-4] Verification of the selective binding of intact molecules in our studies to date has been provided by a combination of electrochemical and surface-sensitive spectroscopic techniques, including cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), and scanning Auger electron spectroscopy (AES). Of those techniques, only AES has the ability to image the location of a specific element on a patterned surface with a lateral resolution better than 1 μm. Elemental mapping by AES was therefore the key to demonstrating the selective binding of redox-active molecules R–L to microfabricated Au structures relative to the Si_3N_4 substrate. However, AES alone cannot establish the binding of *intact* molecules, R–L, to Au, but can only confirm the presence of certain characteristic elements, e.g. S, in the case where L is –SH. Cyclic voltammetry in combination with the AES element maps was necessary to show that molecules R–L were bound only to the Au, as shown in Scheme I.

Secondary ion mass spectrometry (SIMS) is a surface-sensitive technique which in principle could independently establish the binding of intact molecules to microfabricated structures.[5,6] While XPS and AES are only element sensitive, SIMS detects both ionized molecular fragments and intact molecules, as well as elemental ions. Therefore, the binding of intact molecules to microfabricated structures could be accomplished by simply mapping the location of the surface-confined molecules on the substrate. SIMS has already been shown to yield reliable "fingerprint" spectra of molecular materials,[7-11] and high lateral resolution imaging of both inorganic and organic materials has been demonstrated.[12,13] Characterizations of vapor-deposited organic films,[10,11] Langmuir–Blodgett assemblies,[14-18] and silated surfaces[19] have also been reported, verifying the ability of SIMS to detect monolayer quantities of organic materials. Furthermore, Schweiters et al. have shown the potential for using SIMS to characterize patterned surfaces modified with molecular reagents.[20] In spite of all this work, there has been only one very recent paper on the SIMS characterization of SAMs,[21] which reported the negative SIMS spectra of various alkanethiols adsorbed on Au.

Scheme I. Cross-Sectional View of a Au Microwire Array Selectively Modified with Redox-Active Molecules R–L



Important work on laser desorption Fourier transform mass spectrometry (FTMS)[22] and surface-induced dissociation (SID)[23]

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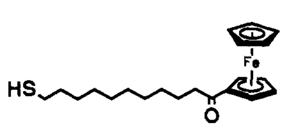
of alkanethiols on Au has also recently appeared. We report here the use of positive SIMS to characterize SAMs of thiols I–IV on



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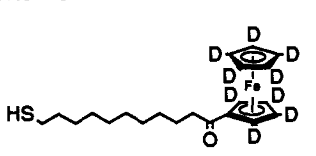

II

$HS(CH_2)_{17}CH_3$

III

$HS(CD_2)_{17}CD_3$

IV

evaporated Au films. Importantly, we also demonstrate the use of SIMS to map at high lateral resolution the location of redox-active molecules on microfabricated Au structures derivatized according to Scheme I.

Experimental Section

Chemicals. (a) (11-Mercaptoundecanoyl)ferrocene (I) was synthesized according to our previously published procedure.[3]

(b) Cyclopentadiene-d_6. Dicyclopentadiene (Fluka, 95%, 98.6 g, 100 mL) was cracked to cyclopentadiene monomer by distilling under Ar. A 250-mL round-bottomed flask was charged with 80 mL (64 g, 0.97 mol) of cyclopentadiene, 45 mL of dioxane (Fisher), 45 mL of D_2O (Cambridge Isotopes), and 2 g of KOH. The flask was fitted with a dry ice condenser, and the reaction mixture was stirred vigorously for 5 h. The partially deuterated cyclopentadiene was distilled under Ar directly from the reaction pot using a 10-cm Vigreaux column. The collection flask was kept on ice to prevent redimerization. This isotope enrichment reaction was repeated four times on the same 80 mL of cyclopentadiene. The entire procedure yielded 40 g of cyclopentadiene with at least 95% deuteration, as determined by ^1H NMR spectroscopy.

(c) Ferrocene-d_{10}. Cyclopentadiene-d_6 (1.9 g, 0.026 mol) was reacted with an excess of Na metal (~2 g) in dry THF under Ar. This reaction mixture was cannulated into a stoppered Schlenk flask containing 1.4 g of $FeCl_2$ (0.011 mol) dissolved in 250 mL of dry THF. The mixture was stirred vigorously. After 3 h, the solution was filtered and the solvent removed. The ferrocene was extracted with hexane, isolated, and sublimed. Mass spectrometry showed greater than 96% deuterium incorporation.

(d) (11-Mercaptoundecanoyl)ferrocene-d_9 (II) was prepared from ferrocene-d_{10} by following an already published procedure.[3]

(e) Octadecyl mercaptan (III) was purchased from Aldrich.

(f) Octadecyl-d_{37} mercaptan (IV) was a gift from Paul Laibinis of Harvard University.[24]

Surface Modification of Au Films and Au Microwires. Au films were prepared by electron beam deposition of a 1000-Å Au film on a 4-in. Si wafer with a 50-Å Ti adhesion layer. The coated wafers were broken up into 1-cm × 3-cm slides and exposed to an O_2 plasma (100 W, 150 mTorr) for 5 min prior to derivatization. These slides were then immersed in 1 mM EtOH solutions of the appropriate thiol for 16 h at 298 K. The derivatized Au was removed from solution and rinsed with EtOH and H_2O prior to analysis. Cyclic voltammetry established the binding of 3×10^{-10} mol cm^{-2}, or about one monolayer of I and II, to Au surfaces. Both species I and III are known to form SAMs on polycrystalline Au.[3,25]

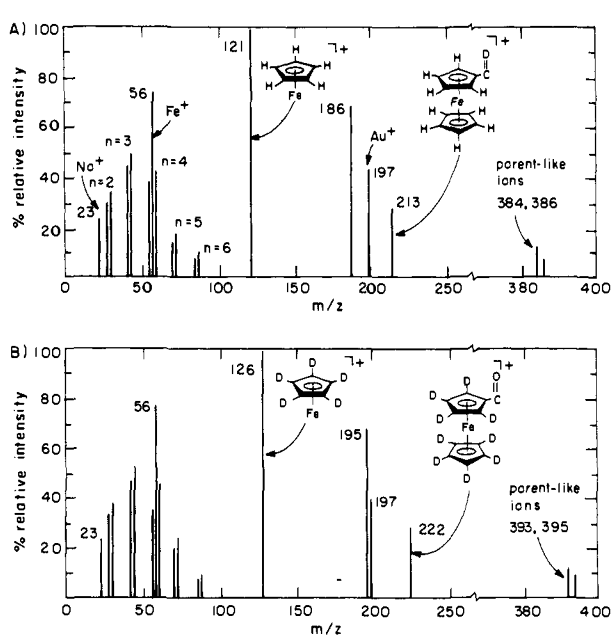

Figure 1. Major peaks in the positive secondary ion mass spectra of (A) a monolayer of I and (B) a monolayer of II on evaporated Au. The values of *n* refer to the hydrocarbon fragments of the general form $C_nH_m^+$ where $m = 2n + 1$ or $2n - 1$. The peak at $m/z = 186$ in spectrum A is $[(C_5H_5)_2Fe]^+$, and the peak at $m/z = 195$ in spectrum B is the deuterated analog, $[(C_5D_5)(C_5D_4H)Fe]^+$. Both spectra were obtained using a 16-keV Ga^+ primary-ion beam with primary current density $\sim 5 \times 10^{-8}$ A cm^{-2}. Mass resolution, $m/\Delta m$, is 500.

Au microwire arrays on Si_3N_4 substrates were made using standard lithography techniques; the detailed design and fabrication of the "chips" containing these microstructures will be described in a forthcoming paper.[26] Briefly, each array consisted of approximately 600 parallel Au microwires, each 200 μm long, 4.8 μm wide, 1000 Å tall, and separated by 1.2 μm on a flat Si_3N_4 substrate. On the same chip as the array were seven individually addressable Au microelectrodes of the same dimensions. After a plasma cleaning procedure described previously, the entire chip was immersed in a 1 mM EtOH solution of I for 24 h. The microwire array was removed from this solution after 24 h, rinsed with EtOH and H_2O, and characterized by electrochemistry.

Electrochemical Methods. Electrochemical measurements were carried out with a Pine Instruments Model RDE-4 bipotentiostat. Voltammetric traces were recorded with a Kipp and Zonen Model BD 91 X-Y recorder. Linear sweep cyclic voltammetry of both derivatized Au slides and Au microwires was performed in 1.0 M $NaClO_4/H_2O$ at 298 K in Ar-purged solutions. Pt gauze was used as a counter electrode. The reference was SCE. Integration of the voltammetric traces for each of the seven addressable Au microwires demonstrated $\sim 3 \times 10^{-10}$ mol cm^{-2} of I on each microwire, as has been shown previously.[3] After characterization, the Au microwire array was removed from solution, rinsed with copious amounts of H_2O, and prepared for SIMS analysis.

Secondary Ion Mass Spectrometry. Positive secondary ion mass spectra of SAMs of I–IV on macroscopic Au films were obtained using a Vacuum Generators IX70S double-focusing magnetic sector SIMS instrument.[27] The spectrometer was calibrated using a mixture of CsI, NaI, KI, RbI, and LiI salts dissolved in 3:1 $MeOH/H_2O$ and dispersed on a Au slide. The primary-ion beam consisted of 16-keV Ga^+ ions generated from a liquid metal field emission source. Typical primary-beam currents used in acquiring the mass spectra were 50 pA over a 10^{-3} cm^2 area, yielding primary beam current densities of 5×10^{-8} A cm^{-2}. Ten scans, each 20 s in duration, were taken over 10 separate 10^{-3} cm^2 areas of the sample. The 10 scans were then averaged to give a composite spectrum. Total ion dose to each area was $\sim 6 \times 10^{12}$ particles cm^{-2}. Mass resolution was 500. Microwire arrays which were examined electrochemically were prepared for SIMS analysis by grounding them to an

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aluminum stage with silver paint. Imaging SIMS was done using a 16-keV Ga^+ primary-ion beam operating at current densities of roughly 10^{-5} A cm^{-2}. Each map obtained is a 256 × 256-pixel image of an approximately 2.5×10^{-5} cm^2 area, with a dwell time of 500 μs/pixel, so that each map took under 40 s to acquire. Total ion dose under these conditions was 10^{15} particles cm^{-2}. Base pressure in the instrument was 10^{-10} Torr, and operation pressure was 5×10^{-9} Torr.

Results and Discussion

The currently accepted mechanism of thiol adsorption to Au surfaces involves the loss of the –SH proton and the formation of a Au–thiolate bond.[28] If this is the case, then adsorption of I (MW 386) to Au surfaces results in bound thiolates with MW 385. In assigning our secondary ion mass spectra, we use the symbol M to represent the deprotonated analogs of thiols I–IV, –SR, and not the respective thiol. This notation is most consistent with previous work,[10,14,16] as M therefore represents the molecular species presumably on the surface.

Figure 1A shows the principal peaks in a typical *positive* secondary ion mass spectrum of a Au surface derivatized with a monolayer of I. At m/z values below 100, the observed fragmentation is of the general form $C_nH_m^+$ where m is either $2n + 1$ or $2n - 1$. Peaks at m/z = 56, 121, 186, 197, and 213 are assigned to Fe^+, $[(C_5H_5)Fe]^+$, $[(C_5H_5)_2Fe]^+$, Au^+ (from the substrate), and $[(C_5H_5)(C_5H_4CO)Fe]^+$, respectively. The peaks at m/z = 384 and 386 correspond to parentlike ions of I, $[M - H]^+$ and $[M + H]^+$, where M represents the surface-confined, deprotonated thiol, as previously noted. To confirm these assignments, a SIMS spectrum of a self-assembled monolayer of the deuterium-labeled analog of I, species II (MW 395), on Au was obtained. Comparion of parts A and B of Figure 1 shows the expected m/z shifts in the mass spectrum, e.g. 121 to 126, 186 to 195, 213 to 222, 384 to 393, and 386 to 395.[29] No shift is found for peaks attributed to Fe^+, Au^+, and $C_nH_m^+$. Significantly, the detection of the parentlike ions in both spectra indicates the presence of intact molecules of I or II on the Au surface. Previous work on LB films[14,16] and vapor-deposited organic materials[10] on metals has shown that $[M + H]^+$ and $[M - H]^+$ ions, where M represents a molecular species, are commonly detected by SIMS. We also note that one might expect $[(C_5H_5)(C_5H_4)Fe]^+$ (m/z = 185) and $[(C_5D_5)(C_5D_4)Fe]^+$ (m/z = 194) fragments in parts A and B of Figure 1, respectively, due to fracture of the ferrocene–carbonyl bond. Instead, it appears that the ferrocenyl fragment in both cases abstracts ^1H before detection to make $[(C_5H_5)_2Fe]^+$ and $[(C_5D_5)(C_5D_4H)Fe]^+$, which are observed at m/z = 186 in Figure 1A and m/z = 195 in Figure 1B, respectively.

Figure 2 shows the principal peaks in the positive SIMS spectra of self-assembled monolayers of III (MW 286) and its isotopically labeled analog, IV (MW 323), on Au. Comparison of the two spectra again reveals the expected peak shifts and allows the peak assignments shown in Figure 2. The major feature of these data is the $C_nH_m^+$ fragmentation series, analogous to that shown at low m/z values in Figure 1. The peaks at m/z = 225 in Figure 2A and m/z = 229 in Figure 2B are most likely due to reaction of sputtered Au atoms and $[C_2H_4]^+$ fragments in the so-called selvedge immediately above the sample. Such sputter-induced reactions are common in SIMS,[5] and we do not think that these peaks represent any information on the actual chemical structure of the monolayer. In contrast to spectra of SAMs of species I and II, those of SAMs of III and IV do not show peaks for $[M + H]^+$ and $[M - H]^+$ ions. A low-intensity peak (<5% relative intensity) is observed at m/z = 285 (not shown), which could correspond to the M^+ ion of III, but preliminary SIMS data on SAMs of other alkanethiols show that this peak is not unique to SAMs of III.[30] However, significant peaks are observed at m/z = 482 and m/z = 519 in parts A and B of Figure 2, which correspond to the M^+ ions of III and IV plus one Au atom, respectively. Secondary ions of the form $[M + Ag]^+$ are common in SIMS studies of LB films on Ag.[14,16] Preliminary data suggest that $[M + Au]^+$ peaks are also observable for SAMs of I and II. Importantly, the $[M + Au]^+$ peaks in Figure 2 support the general conclusion from Figure 1 that SIMS can be used to detect intact surface-confined molecules in a self-assembled monolayer.

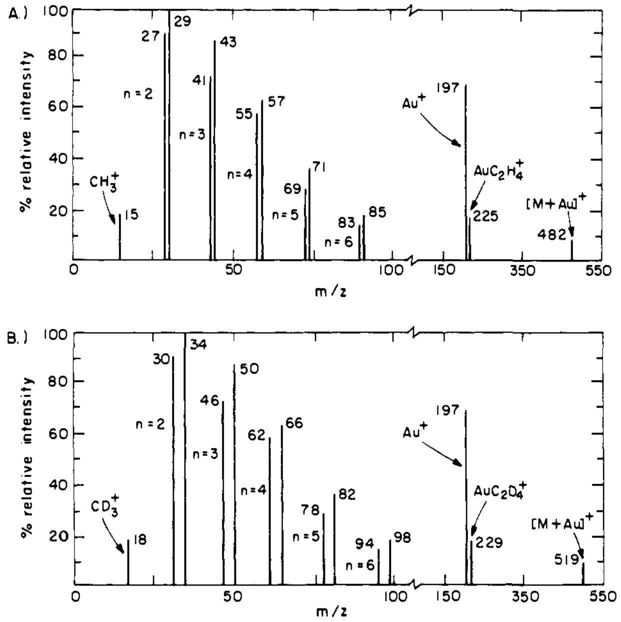

Figure 2. Major peaks in the positive secondary ion mass spectra of (A) a monolayer of III and (B) a monolayer of IV on evaporated Au. The values of n refer to the hydrocarbon fragments of the general form $C_nH_m^+$ where $m = 2n + 1$ or $2n - 1$. Both spectra were obtained using a 16-keV Ga^+ primary-ion beam with primary current density $\sim 5 \times 10^{-8}$ A cm^{-2}. Mass resolution, $m/\Delta m$, is 500.

It is interesting that $[M + H]^+$ and $[M - H]^+$ ions are relatively prominent in SIMS spectra of I and II but not III and IV. The most probable explanation is that the ferrocene substituent in I and II stabilizes the positive charge in the $[M + H]^+$ and $[M - H]^+$ ions. Ionization of the long alkyl chains of molecules III and IV most likely results in a series of fragmentations analogous to those known in conventional electron impact mass spectrometry of aliphatic hydrocarbons.[31] Ionization of the alkyl chains in I and II should also result in multiple fragmentations, giving rise to the peaks observed below m/z = 100 in Figure 1. However, the facile ionization of ferrocene in I and II and the subsequent localization of charge on the Fe center or Cp rings could account for the arrival of intact $[M + H]^+$ and $[M - H]^+$ ions of I and II at the detector, whereas $[M + H]^+$ and $[M - H]^+$ ions are not observed in SIMS spectra of III and IV, since positive charge cannot be stabilized in these species. More experiments are needed to determine the significance of the $[M + H]^+$ and $[M - H]^+$ peaks in Figure 1 and the $[M + Au]^+$ peaks in Figure 2, specifically as to whether they represent the detection of the surface-confined *thiolates*. In general, however, the data shown in Figures 1 and 2 demonstrate conclusively that SIMS can be used to detect the presence of intact molecules on Au at monolayer coverages.

Our most significant finding is the ability to exploit the high lateral resolution and sensitivity of SIMS to map the location of a monolayer of I on a microlithographically patterned surface. Figure 3 shows chemical maps of Au^+, Si^+, Fe^+, and $[(C_5H_5)Fe]^+$ for 10 of the roughly 600 microwires on a chip. The Au^+ map in Figure 3A highlights the positions of the 10 Au microwires, and the Si^+ map in Figure 3B shows the corresponding Si_3N_4 gaps. Comparison of all the images shows that the Fe^+ and $[(C_5H_5)Fe]^+$

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[28] Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87–96.

[29] There is a possible mass interference at m/z = 395 due to Au_2H^+, which is a commonly observed cluster in SIMS spectra on Au substrates. However, control samples not exposed to II and studied under the same conditions did not show the presence of this peak. Also, samples derivatized with I did not show a peak at m/z = 395.

[30] Positive SIMS spectra of SAMs of $C_{16}H_{33}SH$ and $C_{10}H_{21}SH$ on Au also show a peak at m/z = 285.

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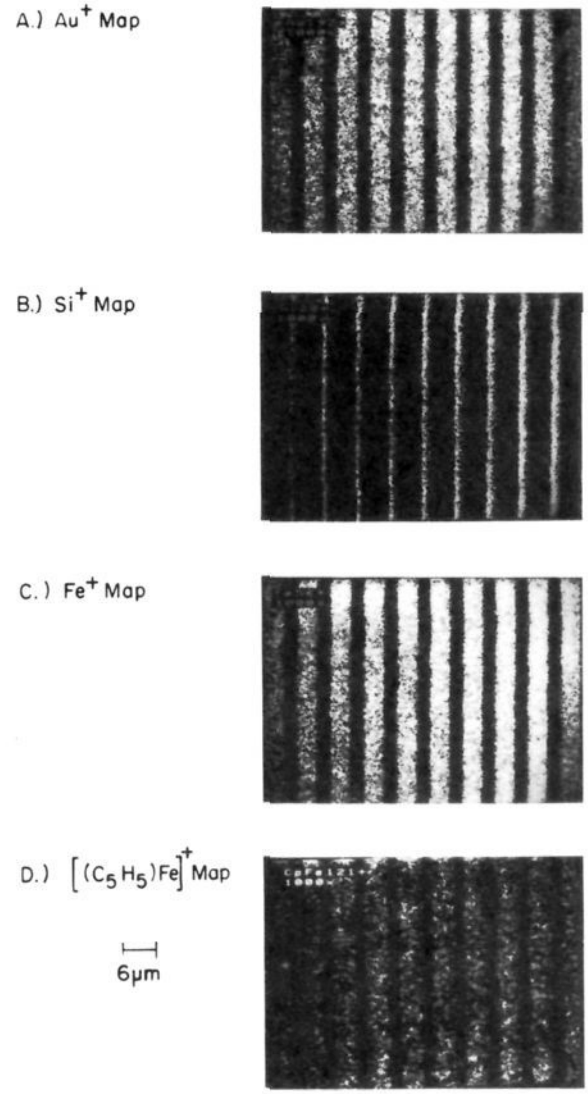

Figure 3. Elemental and molecular ion maps of 10 Au microwires (Si_3N_4 substrate) derivatized with a self-assembled monolayer of I as shown by cyclic voltammetry: (A) Au^+ map (m/z = 197); (B) Si^+ map (m/z = 28); (C) Fe^+ map (m/z = 56); (D) $[(C_5H_5)Fe]^+$ map (m/z = 121). Each map was acquired in less than 40 s using a 16-keV Ga^+ primary ion beam at 10^{-5} A cm^{-2}. Area imaged is 2.5×10^{-5} cm^2.

maps are in perfect registration with the Au^+ map, demonstrating the selectivity of I for Au relative to Si_3N_4, as has been shown previously.[3] Control samples, which were not derivatized, showed 1000 times less signal at $m/z = 56$ and no signal above noise at $m/z = 121$. As noted in the Experimental Section, each map is a 256 × 256 pixel image of an approximately 2.5×10^{-5} cm^2 area, with a dwell time of 500 μs per pixel, so that under 40 s was required for the acquisition of each map. Under these conditions, the total ion dose to the surface was roughly 10^{15} particles cm^{-2}, and several repeated mappings over the same area resulted in a complete loss of the Fe^+ and $[(C_5H_5)Fe]^+$ signals. Such doses so far have precluded mapping the parentlike ions of I, m/z = 384 or 386. Previous work has shown that an ion dose greater than 10^{13} particles cm^{-2} results in substantial damage to organic surfaces.[5a] However, we found that the Fe^+ and $[(C_5H_5)Fe]^+$ signals persisted sufficiently long for us to acquire the images shown in Figure 3.

Importantly, the Fe^+ *and* $[(C_5H_5)Fe]^+$ maps demonstrate the use of SIMS to map the distribution of a monolayer of molecules at less than 1-μm lateral resolution. Since each of the derivatized wires shown in Figure 3 is roughly 1.9×10^{-6} cm^2 (190 μm^2), the Fe^+ and $[(C_5H_5)Fe]^+$ maps in Figure 3C,D correspond to the detection of roughly 300 million molecules of I per microwire. As few as 2 million molecules in a 1-μm^2 area are easily detected with our instrument. Furthermore, the $[(C_5H_5)Fe]^+$ map in Figure 3D underscores the *molecular* sensitivity of SIMS. Elemental mapping at high lateral resolution (<0.1 μm) of monolayer-modified microstructures is possible by AES,[1,3,4] but such data must be accompanied by electrochemical or equivalent data to establish the selective binding of *intact molecules* to the patterned surfaces. SIMS alone can establish the selective binding of intact molecules of I to microfabricated structures by mapping the location of the surface-confined molecules on such structures. We reiterate that each of these images was acquired in a matter of seconds. In contrast, several hours are required to obtain equivalent element maps of SAMs on Au microwires by AES.[3]

Conclusion

In summary, we have taken advantage of three important characteristics of SIMS, namely its high lateral resolution imaging capability, its extreme sensitivity, and its ability to detect molecular species, to demonstrate the selective binding of a monolayer of molecules to Au microstructures. We have also used SIMS to generate secondary ion mass spectra of self-assembled monolayers of molecules I–IV on macroscopic Au surfaces. Isotopic labeling was used to verify peak assignments. Work in this laboratory continues on molecular mapping of patterned surfaces modified with self-assembling monolayers and on using SIMS to obtain structural information about molecularly modified surfaces.

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