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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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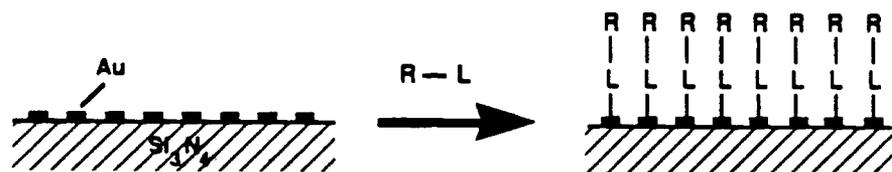
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Abstract

Secondary ion mass spectra of self-assembled monolayers (SAMs) of the thiol containing molecules ($\eta^5\text{-C}_5\text{H}_5$)Fe[($\eta^5\text{-C}_5\text{H}_4$)CO(CH₂)₁₀SH], **I**, and C₁₈H₃₇SH, **III**, and their isotopically labelled analogs ($\eta^5\text{-C}_5\text{D}_5$)Fe[($\eta^5\text{-C}_5\text{D}_4$)CO(CH₂)₁₀SH], **II**, and C₁₈D₃₇SH, **IV**, on polycrystalline Au films are presented. These spectra were taken using a VG IX70S magnetic sector SIMS instrument. Peaks corresponding to parent-like ions with the expected isotopic shifts for **I-IV** were detected, verifying the presence of intact molecules of **I-IV** on the Au. Molecular fragments of **I-IV** were also observed, eg. [(C₅H₅)Fe]⁺ for SAMs of **I** and [(C₅D₅)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 Si₃N₄ substrate) is demonstrated. Comparison of maps of Fe⁺ and the *molecular* fragment [(C₅H₅)Fe]⁺ with Au⁺ and Si⁺ maps show that **I** is found only on Au and not the Si₃N₄ 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 was acquired in less than 40 seconds; comparable element mapping of Au microwires by Auger electron spectroscopy takes 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

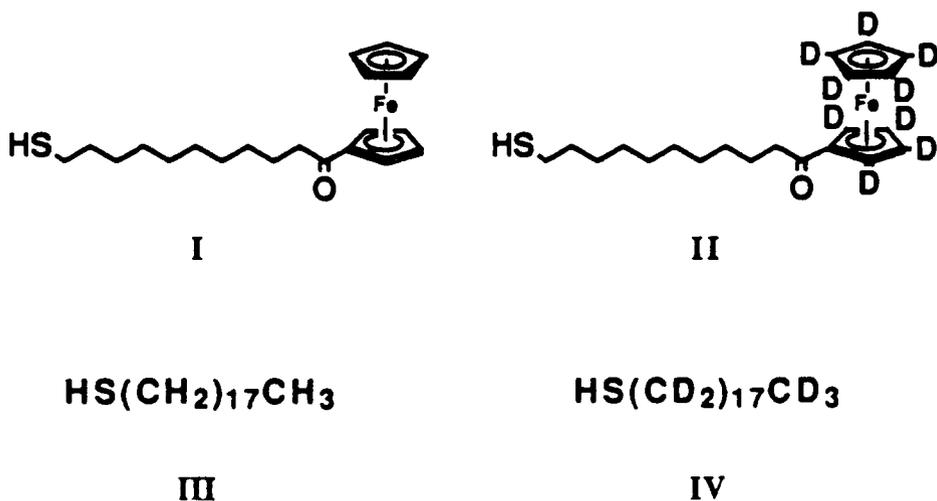
Scheme I. Cross Sectional View of a Au Microwire Array Selectively Modified with Redox Active Molecules R-L.



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 Si₃N₄ 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, eg. 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 molecular fragments as well as elemental ions. Therefore, the binding of intact molecules to microfabricated structures could be accomplished by simply mapping the location of the parent ion 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 silylated surfaces¹⁹ 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 as yet been no report on the SIMS characterization of SAMs, although closely related work on surface induced dissociation (SID) of alkane thiols on Au has recently appeared.²¹ We report here the first use of SIMS to characterize SAMs of thiols I-IV on 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.

11-Mercaptoundecanoylferrocene (I) was synthesized according to our previously published procedure.³

Cyclopentadiene-d₆. 100 ml of dicyclopentadiene (Fluka, 95%, 98.6 g) 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 D₂O (Cambridge Isotopes) and 2 g KOH. The flask was fitted with a dry ice condenser and stirred vigorously for 5 hours. The partially deuterated cyclopentadiene was distilled under Ar directly from the reaction pot using a 10 cm Vigreux column. The collection flask was kept on ice to prevent redimerization. This isotope enrichment reaction was repeated 4 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.

Ferrocene-d₁₀. 1.9 g (0.026 mol) of cyclopentadiene-d₆ 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 FeCl₂ (0.011 mol) dissolved in 250 ml dry THF. The mixture was stirred vigorously. After 3 hours 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.

11-Mercaptoundecanoylferrocene-d₉ (II) was prepared using ferrocene-d₁₀ and following an already published procedure.³

Octadecyl mercaptan (III) was purchased from Aldrich.

Octadecyl mercaptan-d₃₇ (IV) was a gift from Paul Laibinis at Harvard University.²²

Surface Modification of Au films and Au microwires. Au films were prepared by electron beam deposition of 1000 Å Au on a 4 inch Si wafer with a 50 Å Ti adhesion layer. The coated wafers were broken up into 1 cm x 3 cm slides and exposed to an O₂

plasma (100 watts, 150 mtorr) for 5 min. prior to derivatization. These slides were then immersed in 1 mM EtOH solutions of the appropriate thiol for 16 hours at 298 K. The derivatized Au was removed from solution and rinsed with EtOH and H₂O 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.^{3,23} Au microwire arrays on Si₃N₄ 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.²⁴ 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 Si₃N₄ substrate. On the same chip as the array were 7 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 hours. The microwire array was removed from this solution after 24 hours, rinsed with EtOH and H₂O, 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 XY recorder. Linear sweep cyclic voltammetry of both derivatized Au slides and Au microwires was performed in 1.0 M NaClO₄/H₂O 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 7 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 and rinsed with copious amounts of H₂O 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 focussing magnetic sector SIMS instrument.²⁵ The spectrometer was calibrated using a mixture of CsI, NaI, KI, RbI, and LiI salts dissolved in 3:1 MeOH:H₂O 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 measured at the sample were 50 pA over a 10⁻³ cm² area, yielding primary beam current densities of 5 x 10⁻⁸ A cm⁻². Microwire arrays which were examined electrochemically were prepared for SIMS analysis by grounding them to an 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. The maps obtained are a 256 x 256 pixel image of an approximately 2.5 x 10⁻⁵ cm² area, with a dwell time of 500 μs per pixel, so that each map took under 40 seconds to acquire. Base pressure in the instrument was 10⁻¹⁰ torr, and 5 x 10⁻⁹ torr in operation.

Results and Discussion

Figure 1a shows the principal peaks in a typical *positive* secondary ion mass spectrum (mass resolution, $m/\Delta m = 500$) of a Au surface derivatized with a monolayer of I (MW 386). At m/z values below 100, the dominant fragmentation pattern 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 $m/z = 384, 385$ and 386 correspond to parent-like ions of I, $[M-H]^+, M^+,$ and $[M+H]^+$. To confirm these assignments, a SIMS spectrum of a self-assembled monolayer of the deuterium labelled analog of I, species II (MW 395), on Au was obtained. Comparison of Figure 1a and 1b shows the expected shifts in the mass spectrum, e.g. 121 to 126, 186 to 195, 213 to 222, 384 to 393, 385 to 394, and 386 to 395.²⁶ No shift is found for peaks attributed to $Fe^+, Au^+,$ and $C_nH_m^+$.

Significantly, the detection of the parent-like 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 materials¹⁰ on metals has shown that $[M+H]^+$ and $[M-H]^+$ fragments, where M represents a molecular species, are commonly detected by SIMS. In this case, it may be important that M represents I less ¹H, consistent with the accepted mechanism of

thiol adsorption: loss of the thiol proton and formation of a Au-thiolate bond.²⁷ 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 Figures 1a and b, 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.

Figures 2a and 2b show the principal peaks in the positive SIMS spectra of self-assembled monolayers of **III** (MW 286) and its isotopically labelled analog, **IV** (MW 324), 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 Figures 1a and 1b. Parent-like ions of **III**, $[M-H]^+$, M^+ , $[M+H]^+$, were observed at 284, 285, and 286 as shown in 2a, where M is **III** less 1H . The analogous isotopically labelled ions for a SAM of **IV**, $[M-D]^+$, M^+ , $[M+D]^+$, appear at 321, 323, and 325 in Figure 2b. The peaks at 225 in 2a and 229 in 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. Of greater significance are the peaks at $m/z = 482$ in Figure 2a and $m/z = 520$ in Figure 2b, which correspond to the M^+ parent ions of **III** and **IV** plus one Au atom, respectively. Secondary ions of the general form $[M-Au]^+$ are known from earlier work.¹⁰ More experiments are needed to determine the significance of the M^+ and $[M+Au]^+$ peaks, specifically whether these peaks represent the detection of the thiolate of **III** and **IV**. However, together the survey spectra 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 $[(\text{C}_5\text{H}_5)\text{Fe}]^+$ for 10 of the roughly 600 microwires on a chip. As noted in the Experimental Section, each map is a 256×256 pixel image of an approximately $2.5 \times 10^{-5} \text{ cm}^2$ area, with a dwell time of $500 \mu\text{s}$ per pixel, so that each map took under 40 seconds to acquire. The Au^+ map highlights the positions of the Au microwires and the Si^+ map shows the corresponding Si_3N_4 gaps. Comparison of all the images shows that the Fe^+ and $[(\text{C}_5\text{H}_5)\text{Fe}]^+$ 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 $m/z = 121$. The important point is that the Fe^+ and $[(\text{C}_5\text{H}_5)\text{Fe}]^+$ maps demonstrate the use of SIMS to map the distribution of a monolayer of molecules at less than $1 \mu\text{m}$ lateral resolution. Since each of the derivatized wires shown in Figure 3 is roughly $1.9 \times 10^{-6} \text{ cm}^2$ ($190 \mu\text{m}^2$), the Fe^+ and $[(\text{C}_5\text{H}_5)\text{Fe}]^+$ maps in Figures 3c and d correspond to the detection of roughly 300 million molecules of I per microwire. As few as 2 million molecules in a $1 \mu\text{m}^2$ area could easily be detected with our instrument. Furthermore, the $[(\text{C}_5\text{H}_5)\text{Fe}]^+$ map in Figure 3d underscores the *molecular* sensitivity of SIMS. Elemental mapping at high lateral resolutions ($< 0.1 \mu\text{m}$) 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 parent ion on such structures. We re-iterate that each of these images was acquired in a matter of seconds. In contrast, it takes several hours 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 labelling was used to verify peak assignments. Work in this lab continues on molecular mapping of microstructures modified with self-assembling monolayers and on using SIMS to obtain structural information about molecularly modified surfaces.

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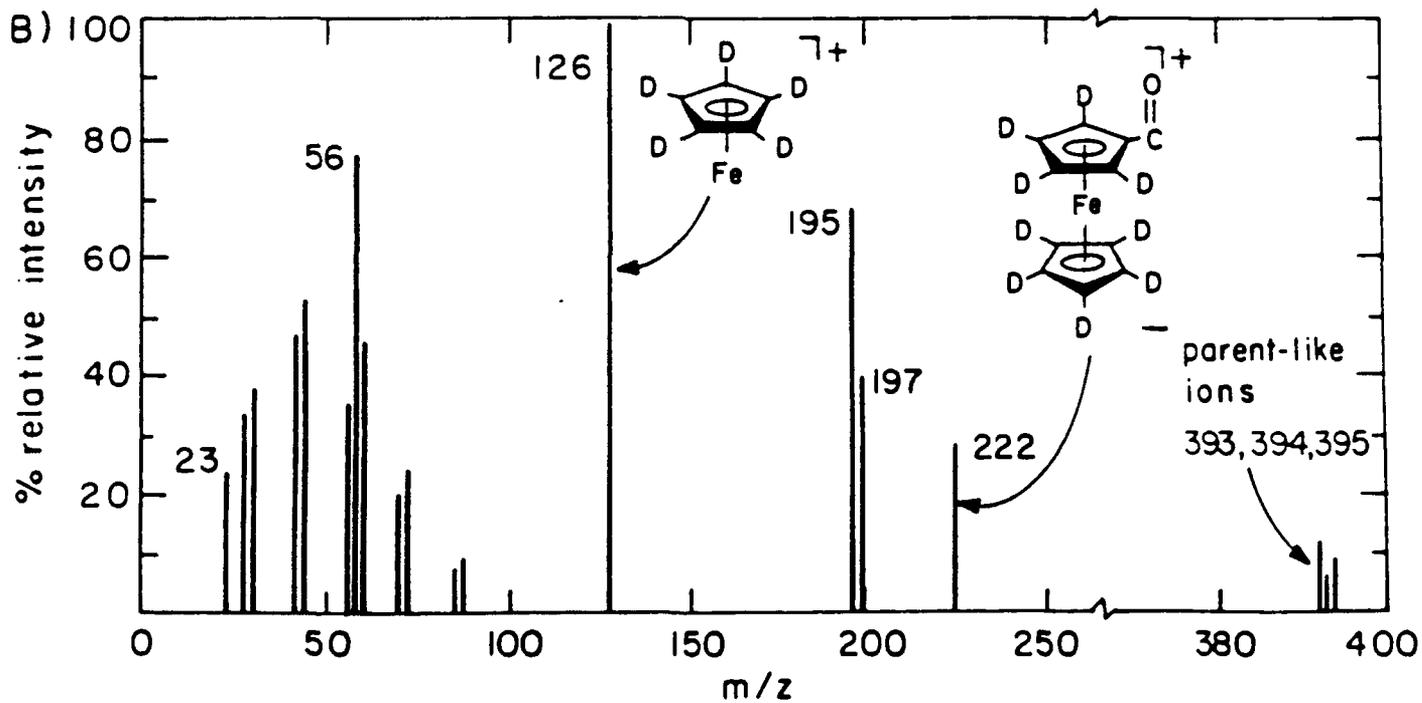
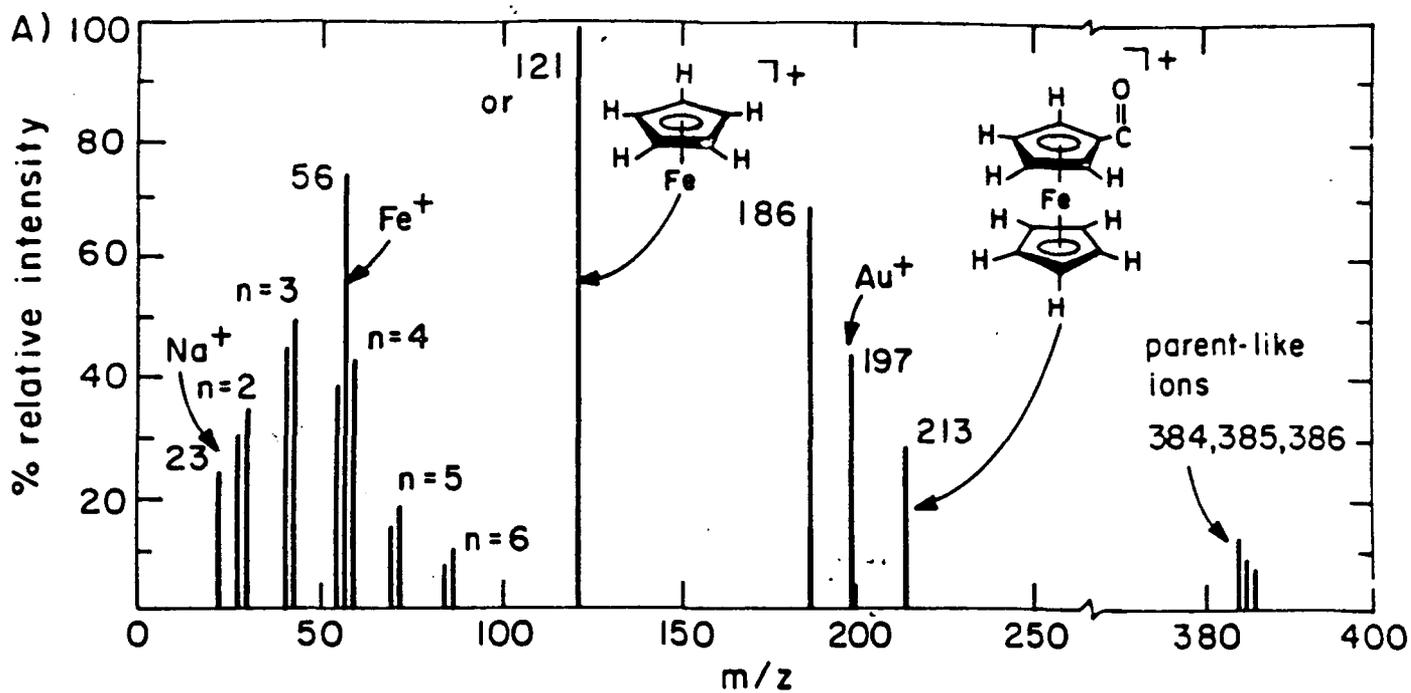
26. There is a possible mass interference at $m/z = 394$ and 395 due to Au_2^+ and Au_2H^+ , which are commonly observed clusters in SIMS spectra on Au substrates. However, control samples not exposed to **II** and run under the same conditions did not show the presence of these peaks. Also, samples derivatized with **I** did not show peaks at 394 and 395 . We are therefore confident that we have observed parent-like ions of **II**.
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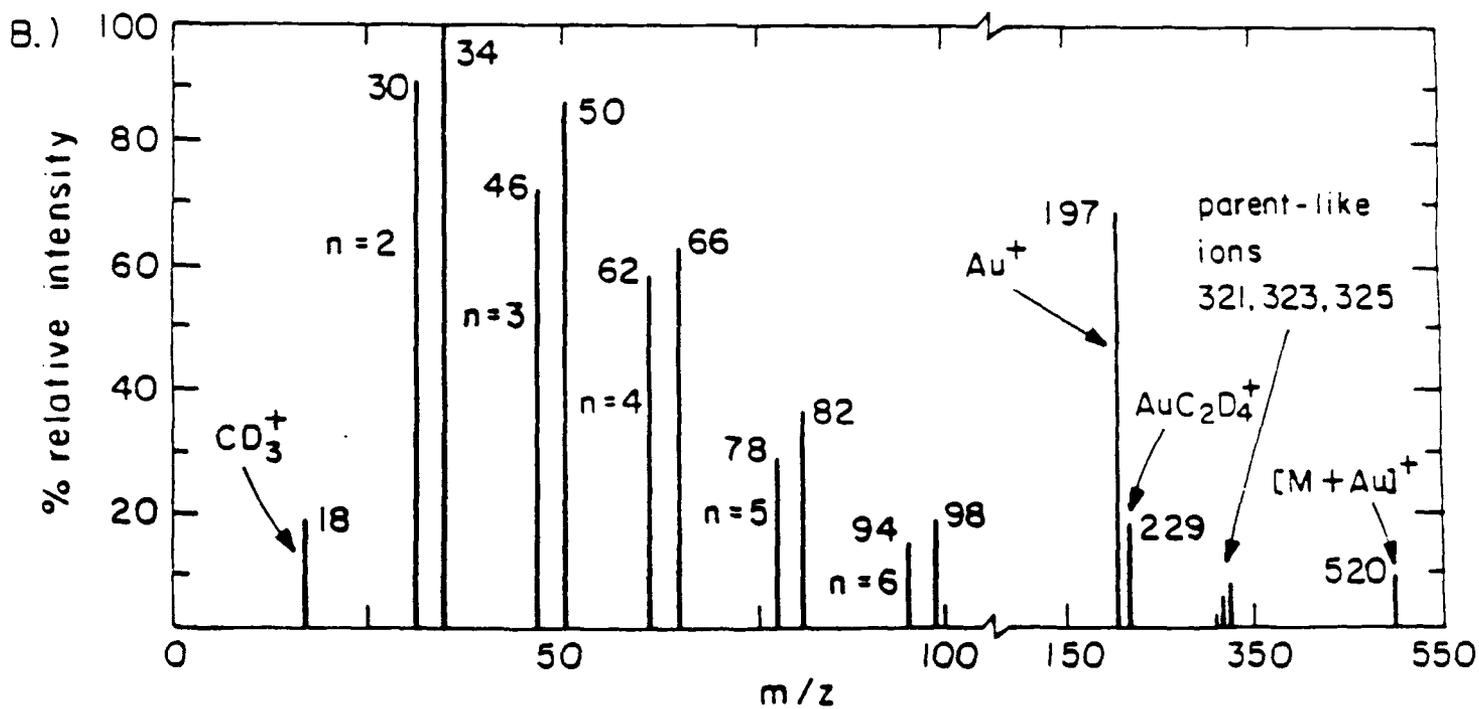
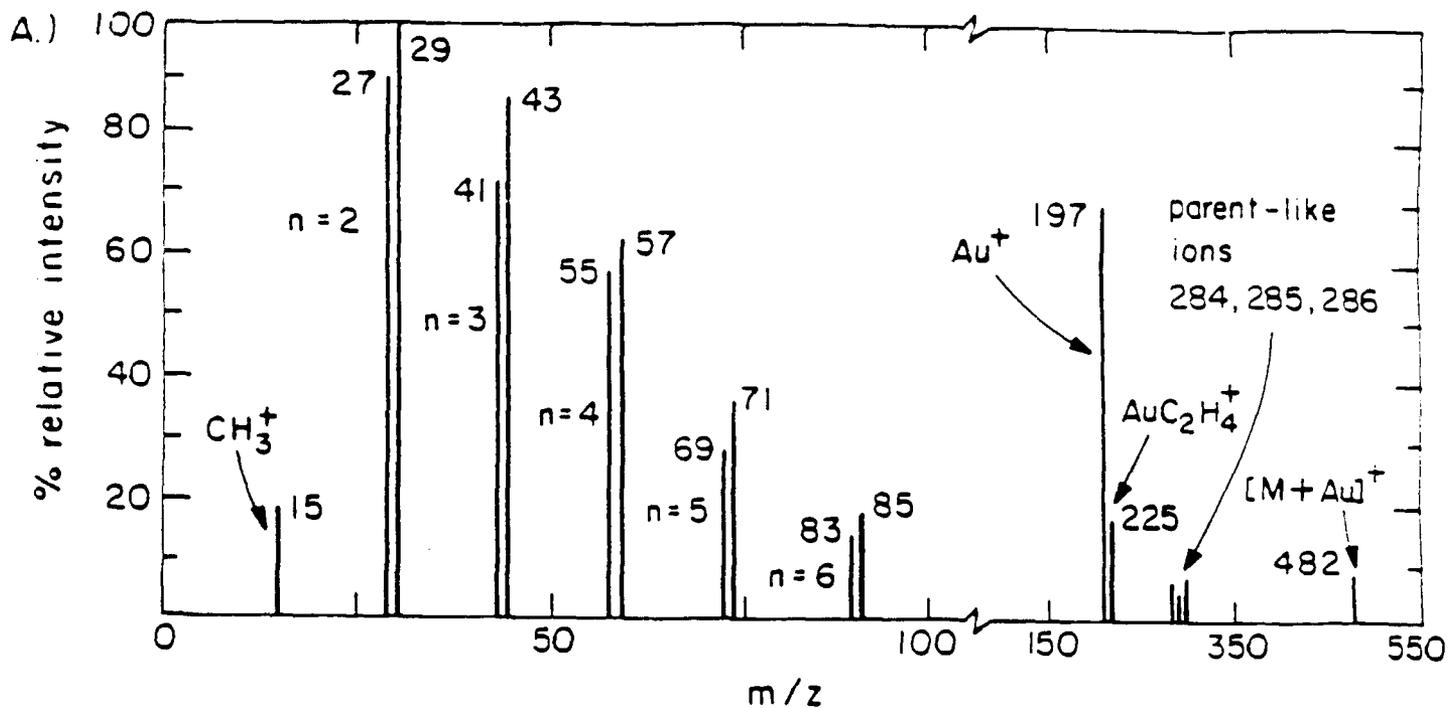
Figures:

Figure 1: 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 (A) is $[(C_5H_5)_2Fe]^+$, and the peak at $m/z = 195$ in (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, $m/\Delta m = 500$.

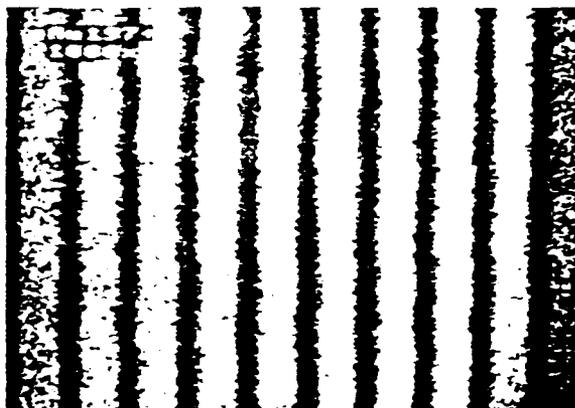
Figure 2: Positive secondary ion mass spectra of A.) a monolayer of **III** and B.) a monolayer of **IV** on evaporated Au. The values of n refer to the hydrocarbon fragments of the general form $C_nH_m^+$ where $m = 2n + 1$ or $2n - 1$. Both spectra were obtained using a 16 keV Ga^+ primary ion beam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

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 ($m/z = 121$). All maps obtained with a 16 keV Ga^+ primary ion beam at $10^{-5} A cm^{-2}$. Area imaged is $2.5 \times 10^{-5} cm^2$.

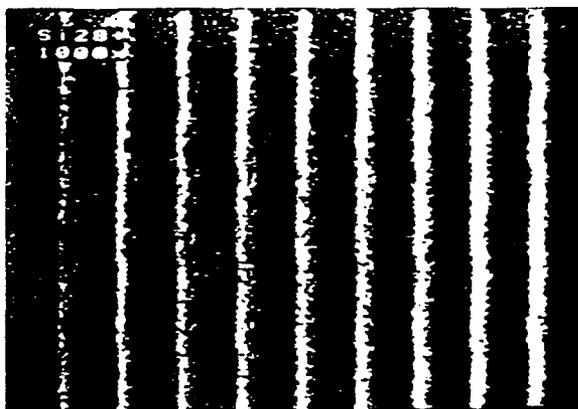




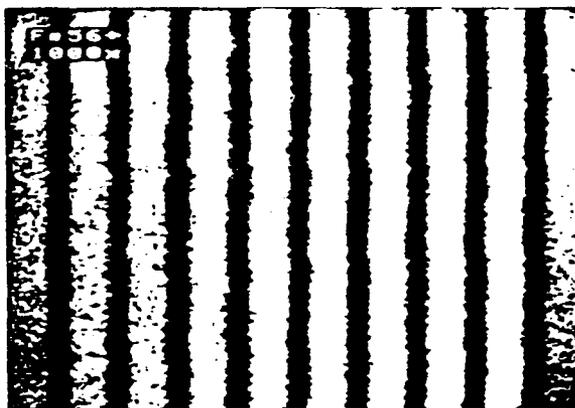
A.) Au⁺ Map



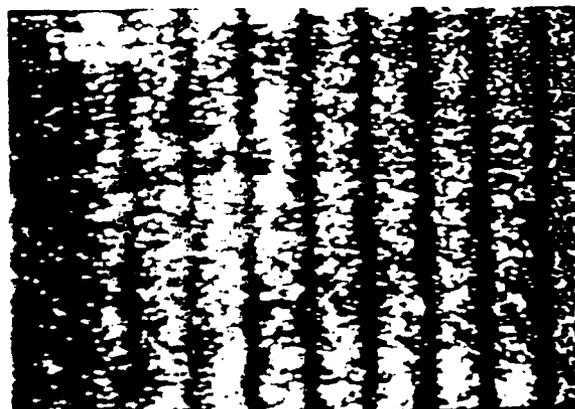
B.) Si⁺ Map



C.) Fe⁺ Map



D.) [(C₅H₅)Fe]⁺ Map



I
6μm

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