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Characterization of Photooxidized Self-Assembled Monolayers and Bilayers by Spontaneous Desorption Mass Spectrometry

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We show that selected self-assembled monolayers (SAMs) and bilayers are readily characterized by the application of controlled photooxidation and spontaneous desorption mass spectrometry (SDMS) in the negative ion mode. Additionally, SDMS is used to characterize organic and inorganic anionic species adsorbed to the surface of a positively charged SAM surface, 2-aminoethanethiol (AET). Prominent peaks are observed that correspond both to the sulfonate form of each SAM and bilayer and to the anion form of each molecule adsorbed to AET. In addition, fragments of the oxidized thin films were also observed at m/z 80 (SO_3^-) and 97 (HSO_4^-). Other prominent fragment peaks more characteristic of the molecule are also seen in the mass spectra.

The formation, chemistry and surface properties of self-assembled monolayers (SAMs) and multilayer architectures on gold surfaces have been extensively studied with a suite of analytical methods, including infrared (IR), X-ray photoelectron spectroscopy (XPS), ellipsometry, electrochemistry, contact-angle measurements, Raman spectroscopy, ion scattering, and mass spectrometry.^{1–22} The mass spectrometric methods of choice have

been laser desorption/ionization (LD) and secondary ion mass spectrometry (SIMS).^{23–29} LD produces prominent secondary ions that are characteristic of the SAM surface, primarily AuM_2^- and $(\text{M} - \text{H})^-$ (where M represents the thiol species). SIMS spectra of SAMs are more complicated, exhibiting peaks such as AuM_2^- and $(\text{M} - \text{H})^-$ along with nonspecific cluster ions composed of Au, S, C, and H atoms. In addition, the yield of analytically significant ions from monolayer systems in SIMS is low, perhaps due to the strength of the Au–S bond and/or the low electron affinity of the thiol. An approach that sidesteps this limitation is to photooxidize the SAM prior to SIMS.^{12,23–26,30–33} The photooxidation step converts the thiolate to a sulfonate moiety, producing a species that is characteristic of the intact monolayer molecule that is easily sputtered/ionized and detected using TOF-SIMS. The high yield of the sulfonate version of the monolayer molecule is attributed to the weak $-\text{SO}_3^-/\text{Au}$ bond and the high electron affinity of the sulfonate group.

We show here that the photooxidation/analysis procedure can be implemented with a simplified version of SIMS. We are referring to spontaneous desorption mass spectrometry (SDMS),^{34–36}

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which relies on low-cost instrumentation yet provides adequate analytical performance for the characterization of SAMs and multilayers. We demonstrate the photooxidation–SDMS procedure with both the characterization of SAMs that are produced via novel derivatization pathways and the assay of anionic species that are adsorbed on positively charged SAMs.

EXPERIMENTAL SECTION

Substrates. Si wafers (4 in., PB100) were purchased from Wafer World, Inc. (W. Palm Beach, FL). The wafers were coated with a 10-nm Ti adhesion layer, followed by a 200-nm layer of Au (Lance Goddard Associates, Foster City, CA). Prior to preparing SAM surfaces, the Au-coated Si wafers were cut into 1 cm² pieces using a diamond scribe, were rinsed with EtOH, and ozone-cleaned for 10 min under UV light (Boekel Industries, Inc., model 135500).

Chemicals. The following chemicals were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and used as received: 4-(trifluoromethyl)benzoyl chloride (TFMBC), 97%; heptanoyl chloride (HC), 99%; mercaptoundecanol (MUD), 97%; dichloromethane (DCM), 99.8%; triethylamine (TEA), 99.5%; 1-propanethiol, 99.5%; 1-octanethiol, 98%; 1-hexadecanethiol, 92%; 2-aminoethanethiol hydrochloride (AET); sodium tetradecyl sulfate (NaTDS); sodium octyl sulfate (NaOS); sodium dodecyl sulfate (NaDS); potassium perrhenate (KReO₄); sodium tetrafluoroborate (NaBF₄); sodium tetraphenylborate {NaB(Ph)₄}; 4-hydroxythiophenol (HTP), 90%; and 4-aminothiophenol (ATP), 90%. HTP was purified by vacuum sublimation before use. Mercapto-6-hexanol (MXHOL), 97%, was purchased from Fluka (Milwaukee, WI) and used as received. High-purity ethanol (EtOH) was purchased from AAPER Alcohol and Chemical Co. (Shelbyville, KY). Water was purified using a Milli-Q reagent water system (Millipore, Bedford, MA). N₂ from gas cylinders had a purity of at least 99.995% and was passed through three Drierite gas-drying units (Hammond 26800, Fisher Scientific Co., Pittsburgh, PA) before use.

n-Alkanethiol Monolayer Preparation. To prepare *n*-alkane-thiol SAMs, the Au substrates were immersed in 1 mM 1-propanethiol, 1-octanethiol, or 1-hexadecanethiol solutions in EtOH and allowed to soak for 18–25 h. The monolayer-coated substrates were removed from the thiol solution, rinsed with EtOH, and dried with a stream of dry nitrogen. Unless otherwise noted, all monolayers were immediately inserted into the mass spectrometer for analysis. After acquiring a mass spectrum from the unoxidized substrate, the SAM was removed from the chamber, oxidized with a UV light source (vide infra), and reinserted into the mass spectrometer for further analysis.

Bilayer Preparation. The procedure for the preparation of the ester-linked bilayer films has been described in detail elsewhere.³⁷ Briefly, Au-coated wafers were soaked for >18 h in a 1 mM ethanol solution of HTP or ATP to form a base monolayer. Upon removal from the solution, the substrates were rinsed with

EtOH, sonicated for 1–2 min in EtOH to remove any physisorbed material, rinsed with EtOH, and then dried in a gentle stream of N₂.

For vapor-phase functionalization, the Au substrate modified with the ATP base monolayer was transferred to a clean borosilicate glass vial that was fitted with a Teflon/silicone septum. N₂ was purged for 20 min through the vessel prior to dosing with the vapor-phase reactants. Vapor-phase TFMBC was generated by passing N₂ over the headspace of a vial containing neat liquid TFMBC. The resulting sub-saturated vapor was passed over the base-layer-modified substrate via a 1.5-mm i.d. Teflon tube for 20–30 min. Excess reactant was removed from the reaction vial and substrate surface by purging with pure N₂ for 20 min prior to bilayer characterization. Vapor-phase functionalization experiments were carried out at 23 ± 2 °C.

For liquid-phase functionalization, HTP, MXHOL, MUD, and ATP base monolayer substrates were immersed in 0.1 M solutions of HC in dry DCM containing an excess (0.2 M) of TEA or immersed in 0.1 M TFMBC in DCM containing an excess (0.2 M) of TEA. Liquid-phase functionalization experiments were carried out at 23 ± 2 °C. The formation of bilayer substrates by the vapor-phase and liquid-phase procedures was confirmed using Fourier transform infrared–external reflectance spectroscopy (FT-IR–ERS) and ellipsometry (data not shown) prior to mass spectrometric analysis.

Oxidation Procedure. The substrates were oxidized for 15–40 min (oxidation time dependent on the sample) using a Hg/Ar spectral calibration lamp (Oriol Instruments, Stratford, CT) inside a fume hood. The lamp was covered by plexiglass walls and shielded from stray light in the room. The user wore polycarbonate protective lenses (Uvex Safety, Smithfield, RI) which blocked over 99% of UVB and 99% of UVA. The photooxidized sample was removed from the hood after waiting a few minutes for excess ozone to leave the surrounding area so as to not inhale any UV-generated ozone. The distance from the UV source to the monolayer surface was optimized and found to be 4 cm, which provided a photon dose of ~1 μW/cm.^{2,33} The fraction of the monolayer lost to photodesorption or photodegradation following exposure to UV radiation is not known. Immediately after oxidation, the sample was inserted into the mass spectrometer for subsequent analysis.

Preparation of Surfaces with Adsorbed Anions. To prepare SAM surfaces, the Au substrates were immersed in 1 mM solutions of AET in EtOH and allowed to soak for >10 h. The monolayer-coated substrates, once removed from the AET solution, were rinsed with EtOH and 0.1 M HCl to ensure protonation of the terminal amine, rinsed with Milli-Q water to remove excess chlorine, and dried with a stream of dry nitrogen. The AET monolayer substrates were then soaked in the following 0.3 M solutions in deionized water: (organic) NaOS, NaDS, and NaTDS; (inorganic) NaBF₄, NaB(Ph)₄, and KReO₄. These substrates were removed from the soak solutions, rinsed with EtOH, and dried with a stream of dry nitrogen.

Mass Spectrometry. The structure and molecular weight for the oxidized monolayers/bilayers are provided in Table 1. The monolayer and bilayer films on Au-coated Si wafers were mounted to the sample support for the mass spectrometer using double-sided tape and conductive silver paint. Negative ion mass spectra

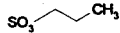


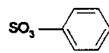
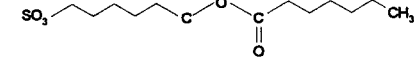
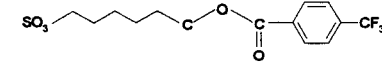
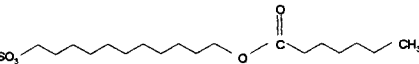
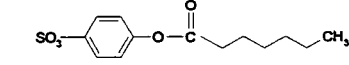
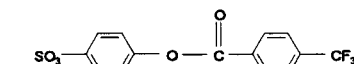
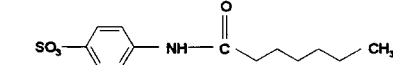
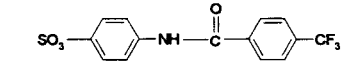
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Table 1. Name, Molecular Weight and Structure for Each Photooxidized Self-Assembled Monolayer and Bilayer

Monolayer - Unoxidized	Molecular Weight - oxidized to sulfonate	Structure - oxidized to sulfonate
1-propanethiol	123 g/mol	
1-octanethiol	193 g/mol	
1-hexadecanethiol	305 g/mol	
1-thiophenol	157 g/mol	
Bilayer - Unoxidized	Molecular Weight - oxidized to sulfonate	Structure - oxidized to sulfonate
MXHOL/HC	293 g/mol	
MXHOL/TFMBC	353 g/mol	
MUD/HC	363 g/mol	
HTP/HC	285 g/mol	
HTP/TFMBC	345 g/mol	
ATP/HC	284 g/mol	
ATP/TFMBC	344 g/mol	

were collected using a custom dual TOF-SIMS instrument. The configuration and operation of the instrument have been described in detail elsewhere.^{38,39} To operate the instrument in the SD mode, the primary ion source was turned off.

To obtain an SD mass spectrum, a voltage between -6 kV and -9 kV (for the monolayers and bilayers, respectively) was applied to the stainless steel sample support. A grounded 90% transmission acceleration grid, located 3 mm from the sample surface, generated electric field strengths of 2 and 3 kV/mm, respectively, for the two applied voltages. The threshold field strength for initiating the SD process has been reported to be approximately 1 kV/mm.⁴⁰

Secondary electrons (SE) emitted from the target by the impact of the ions that were field ionized/desorbed from the acceleration grid were steered by a weak magnetic field into a microchannel plate (MCP) (Galileo Electrooptics Corporation, Sturbridge, MA) detector. The voltage pulse provided by the electrons was used as a start pulse for the flight-time measurement (the flight times of the SEs are assumed to be negligible as compared to the flight times of the SIs emitted from the target). The negative SIs were accelerated, using the voltage applied to the sample target, through the grid into a 65-cm TOF region and detected at a second MCP detector. Signals from both of the detectors were processed through constant fraction discriminators (Tennelec, Oak Ridge, TN) and routed to a high-resolution time-to-digital converter (CTN-M2, Orsay, France). The SD mass spectra were collected using software designed in-house and displayed on a Pentium computer. Mass spectral data from all monolayer and bilayer substrates were acquired for 15–45 min for good peak statistics. The ion intensities

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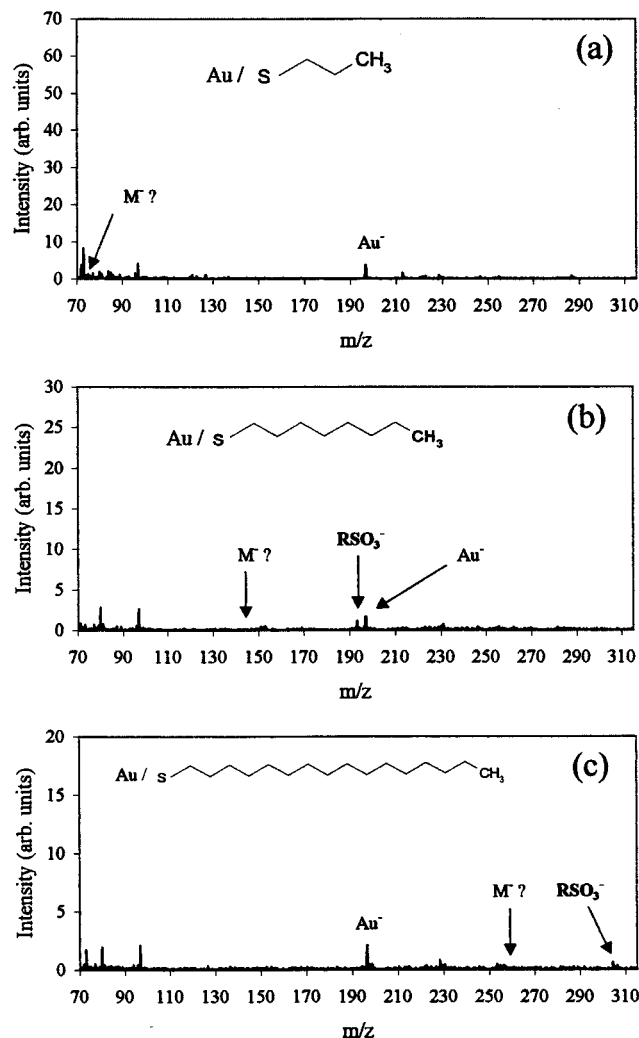


Figure 1. Negative spontaneous desorption mass spectra of the following unoxidized monolayer substrates: (a) 1-propanethiol monolayer on Au, (b) 1-octanethiol monolayer on Au, and (c) 1-hexadecanethiol monolayer on Au. The spectra were acquired using an acceleration voltage of -9 kV with acquisition times of 20, 30, and 30 min, respectively. The ion intensities in the spectra are relative to the most abundant peak in the spectra, H^- .

in the mass spectra shown in Figures 1–5 are plotted relative to the most abundant peak, which in the SD mode is H^- .

RESULTS AND DISCUSSION

Mass Spectra Produced from Unoxidized and Oxidized Monolayers. For the sake of clarity, the term “unoxidized monolayers” refers to substrates analyzed immediately after monolayer formation. The term “oxidized monolayers” refers to substrates analyzed immediately following UV photooxidation.

Figure 1 shows the negative ion SD mass spectra collected from unoxidized 1-propanethiol (Figure 1a), 1-octanethiol (Figure 1b), and 1-hexadecanethiol monolayer substrates (Figure 1c). Within the time-scale used for these experiments (min/h), SI peaks representative of the unoxidized alkanethiolate species (which would appear at m/z 76, 146, and 258 Da for 1-propanethiol, 1-octanethiol, and 1-hexadecanethiol, respectively) were not observed. Extended acquisition times failed to produce abundant thiolate peaks. It may be noted that a comparison of these

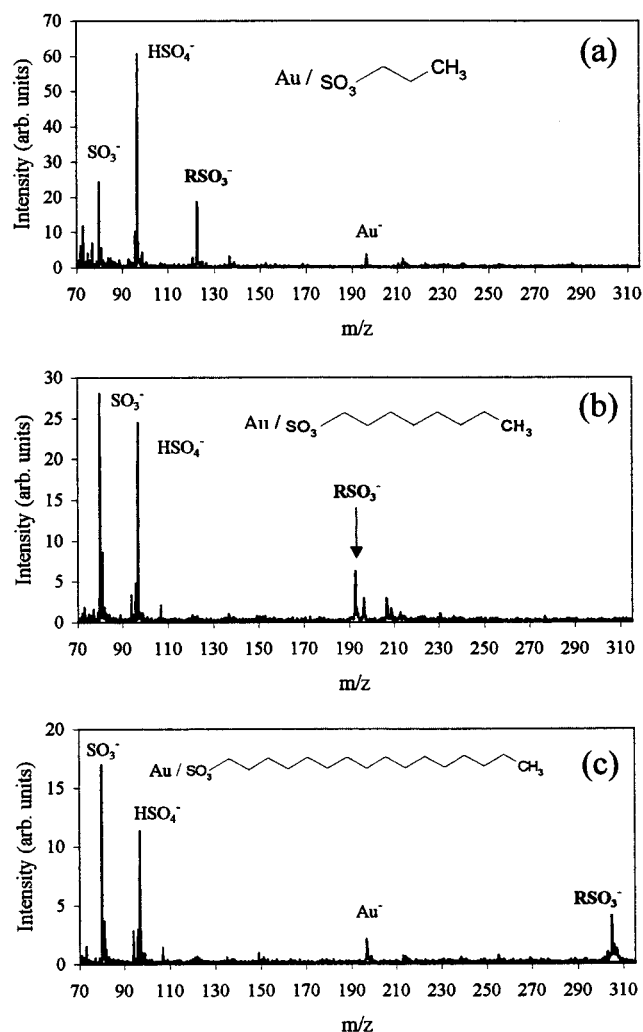


Figure 2. Negative spontaneous desorption mass spectra of the following photooxidized monolayer substrates: (a) 1-propanethiol monolayer on Au, (b) 1-octanethiol monolayer on Au, and (c) 1-hexadecanethiol monolayer on Au. The monolayers were oxidized for 25 min using a Hg/Ar spectral calibration lamp. The distance from the UV source to the monolayer surfaces was 4 cm, which provided a photon dose of $\sim 1 \mu W/cm^2$. The spectra were acquired using an acceleration voltage of -9 kV with acquisition times of 20, 45, and 45 min, respectively. The ion intensities in the spectra are relative to the most abundant peak in the spectra, H^- .

observations to the mass spectrometric data from SAMs obtained in conventional SIMS must take into account the difference in ion doses used to generate the analytical information, that is, $10^{10} - 10^{11}$ ions/ cm^2 in static SIMS vs $10^5 - 10^6$ ions/ cm^2 in SDMS.

In Figure 1b and c, SI peaks of low relative intensity were observed at m/z 193 and 306 which correspond to the oxidized form (RSO_3^- , where R corresponds to the hydrocarbon portion of the molecule) of the 1-octanethiol and 1-hexadecanethiol monolayers, respectively. It is possible that a very small fraction of the SAM oxidized quickly, that is, prior to its insertion into the mass spectrometer.⁴¹ It is also possible that a small fraction of oxidized thiolate was present in the solution that was used for preparing the SAM, and that some of it was incorporated into the

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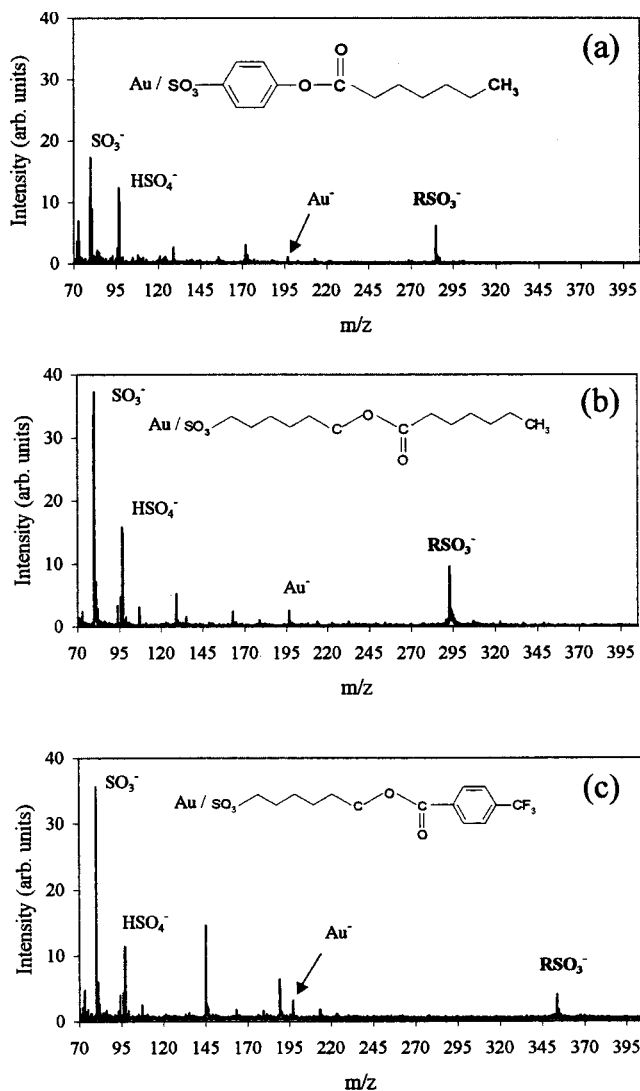


Figure 3. Negative spontaneous desorption mass spectra of the following photooxidized bilayer substrates: (a) HTP/HC (see Table 1) on Au, (b) MXHOL/HC (see Table 1) on Au, and (c) MXHOL/TFMBC on Au (see Table 1). The spectra were acquired using an acceleration voltage of -6 kV with 5-h, 30-min, and 4-h acquisition times, respectively (although shorter acquisition times could be used to obtain reasonable mass spectra). The bilayers were oxidized for 15 min using a Hg/Ar spectral calibration lamp. The distance from the UV source to the monolayer surface was 4 cm, which provided a photon dose of ~ 1 $\mu\text{W}/\text{cm}^2$. The ion intensities in the spectra are relative to the most abundant peak in the spectrum, H^- .

SAM. For these experiments, the monolayer samples were placed into the mass spectrometer immediately following their removal from the thiol solution, so the latter seems more likely.

Figure 2a–c, shows three negative ion SD mass spectra collected from photooxidized 1-propanethiol, 1-octanethiol, and 1-hexadecanethiol monolayer substrates, respectively. The spectra illustrate that upon UV photooxidation (25 min), the appearance of the mass spectra and the peak intensities change significantly. Prominent peaks are observed corresponding to the sulfonate form of each n -alkanethiol monolayer (m/z 123, 193 and 305 Da, respectively). In addition, fragments of the oxidized monolayers were also observed at m/z 80 (SO_3^-) and 97 (HSO_4^-). Similar low-mass peaks have also been observed in SIMS investigations of oxidized monolayer surfaces.¹² The SO_3^- , HSO_4^- , and RSO_3^-

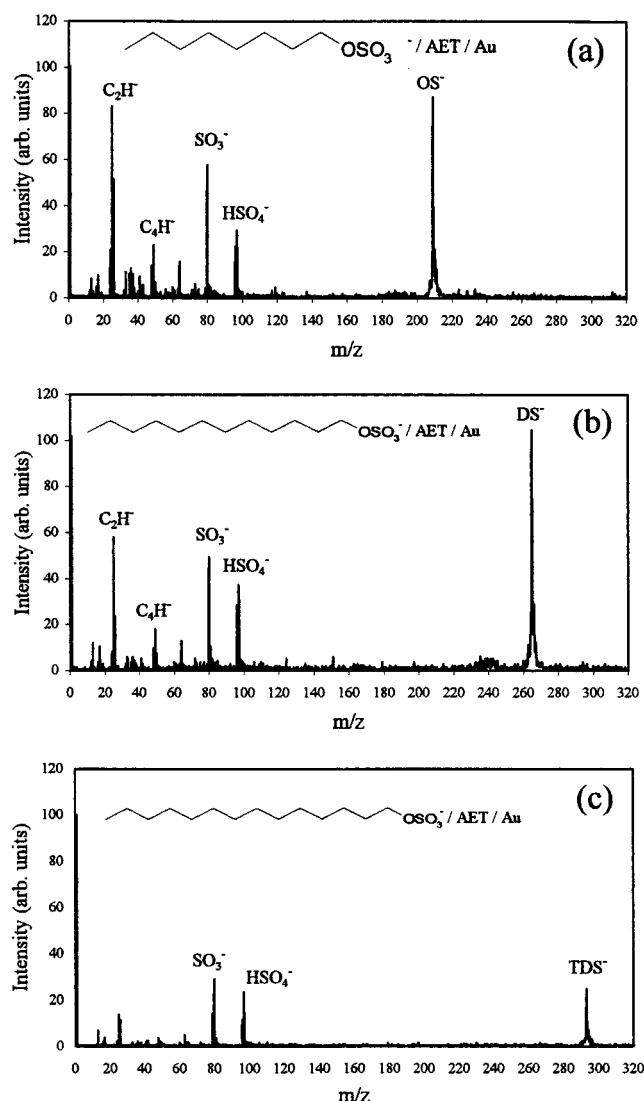


Figure 4. Negative spontaneous desorption mass spectra of (a) OS^- adsorbed to an AET monolayer surface, (b) DS^- adsorbed to an AET monolayer, and (c) TDS^- adsorbed to an AET monolayer. The spectra were acquired using an acceleration voltage of -7 kV and 30-min acquisition times. The ion intensities in the spectra are relative to the most abundant peak in the spectra, H^- .

peaks are up to 10 times more abundant in the spectra of photooxidized 1-octanethiol and 1-hexadecanethiol monolayers than in the spectra of the same monolayers in the unoxidized form. Clearly, over the same acquisition times, the characterization of the monolayer surfaces using SD, as with SIMS, is aided by the use of controlled photooxidation to convert the thiolate to a sulfonate species.

Mass Spectra Produced from Oxidized Bilayers. Methods to prepare bilayer films are described in the Experimental Section and in detail in references.^{37,42} The molecular weights and structures of the bilayers that were examined in these experiments are provided in Table 1. As with the mass spectra from the unoxidized monolayers, those of the unoxidized bilayer surfaces exhibit few peaks that are related to the bilayer composition. Therefore, only the mass spectra that were collected after photooxidation of the synthetic bilayers are shown here.

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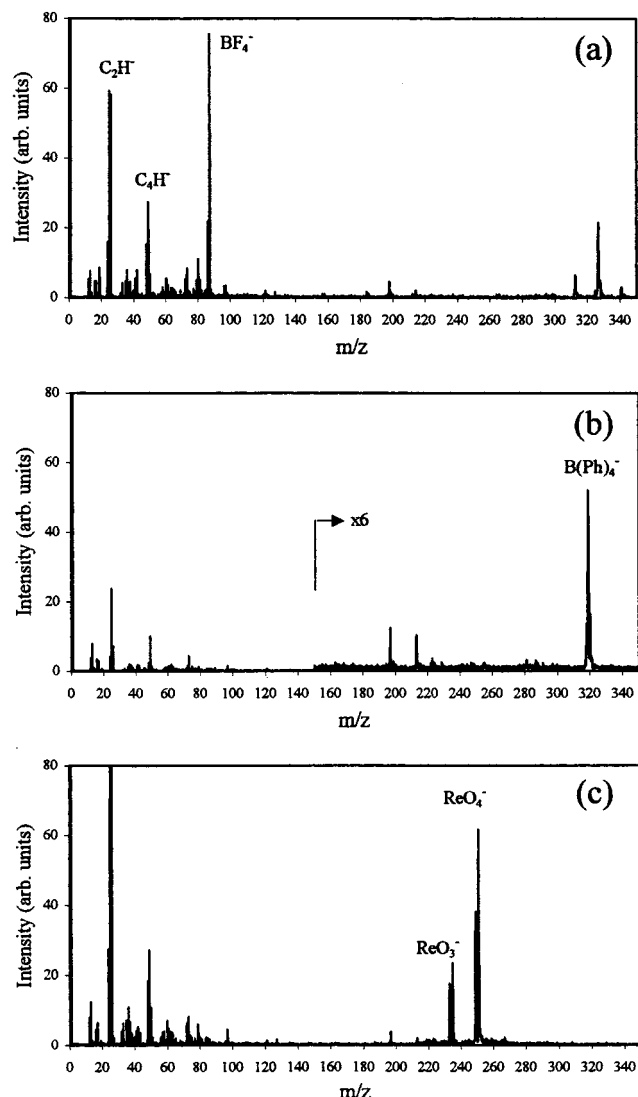


Figure 5. Negative spontaneous desorption mass spectra of (a) BF_4^- adsorbed to an AET monolayer surface, (b) B(Ph)_4^- adsorbed to an AET monolayer, and (c) ReO_3^- and ReO_4^- adsorbed to an AET monolayer. The spectra were acquired using an acceleration voltage of -7 kV and 30-min acquisition times. The ion intensities in the spectra are relative to the most abundant peak in the spectra, H^- .

Figure 3a–c shows three negative ion SD mass spectra that were collected from the following oxidized (15 min) bilayers: (a) HTP/HC, (b) MXHOL/HC, and (c) MXHOL/TFMBC (see Table 1 for definitions of acronyms). Prominent peaks are observed that correspond to the sulfonate form of each bilayer (m/z 285, 293, and 353 Da, respectively). In addition, fragments of the oxidized bilayers were also observed at m/z 80 (SO_3^-) and 97 (HSO_4^-). Other prominent fragment peaks more characteristic of the molecule are also seen in the mass spectra. For example, Figure 3a shows a peak at m/z 172 that is indicative of the fragment ion $\text{SO}_3\text{C}_6\text{H}_4\text{O}^-$. This represents the first one-half of the bilayer combined with three oxygen atoms from the photooxidation. In Figure 3b, a fragment ion peak at m/z 129 is observed for $\text{OCOC}_6\text{H}_{13}^-$, an ion that results from the breaking of the ester bond. Fragment ions at m/z 19 and 145 (F^- and $\text{C}_6\text{H}_4\text{CF}_3^-$, respectively) are present in Figure 3c (the F^- peak is not seen due to the m/z range shown). These results show that the bilayer films as well as the monolayers that were previously discussed

can be successfully characterized using SDMS by (a) photooxidizing the surface prior to mass spectrometric analysis, (b) identifying the RSO_3^- peak representative of the oxidized molecule, and (c) identifying characteristic fragment ion peaks.

Amount of Fragmentation Observed in SDMS and SIMS.

A series of reports have shown that the amount of fragmentation observed in a SIMS spectrum varies with primary ion characteristics.^{43–45} The most dramatic differences in fragmentation are observed when polyatomic projectiles are substituted for atomic primary ions. We were, therefore, interested in the fragmentation produced and, in particular, the ratio of intact ions to fragment ions ($\text{RSO}_3^-/\text{SO}_3^-$ and $\text{RSO}_3^-/\text{F}^-$) that were produced when the instrument was operated in the SD and SIMS modes on the same substrates. For example, the SD spectrum of the photooxidized 1-propanethiol monolayer on Au can be compared to a SIMS spectrum, collected using 20 keV Cs^+ primary projectiles, of the same monolayer. The data show that $\text{RSO}_3^-/\text{SO}_3^-$ intensity ratio is 0.44 for SDMS and 1.07 for SIMS (Cs^+ projectiles). The $\text{RSO}_3^-/\text{SO}_3^-$ ratio that was collected from the same monolayer surface, but with a polyatomic (CsI) Cs^+ projectile (spectrum not shown), is 0.59. Table 2 summarizes the data that was produced from a suite of monolayer and bilayer substrates using SD and Cs^+ , (CsI) Cs^+ , and (CsI) $_2\text{Cs}^+$ projectiles impacts for SI generation. In previous studies we used the intact ion-to-fragment ion ratio as an indicator of the relative amount of fragmentation that was induced by discrete primary projectile impacts. For each of the monolayer and bilayer samples, the $\text{RSO}_3^-/\text{SO}_3^-$ and $\text{RSO}_3^-/\text{F}^-$ ratios indicate that SDMS produces more fragmentation relative to intact RSO_3^- than SIMS with atomic projectiles and fragmentation comparable to that produced by the polyatomic projectiles. Thus, these ratios suggest that the primary ion operative in the SD process is molecular, and may be an ionized species originating from one or more of the residual gases in the vacuum chamber, such as H_2O , N_2 , and various components from the oil diffusion pump system.

We attribute the increase in fragmentation to the increase in energy density, or the amount of energy per unit volume at the surface region, that was deposited by molecular or cluster projectile impacts. A number of studies have established that increased yield of artifact and fragment ions results from polyatomic projectile impacts on organic and inorganic solids.⁴⁶ Specific to the case of organic thin films, recent molecular dynamic (MD) simulations have been used to model the impacts of atomic and polyatomic projectiles on model organic monolayers on Si and Cu surfaces.^{47,48} The simulations predict that the ratio of intact molecules to damaged ions (prompt fragments and metastable ions that fragment above the surface) is lower using the polyatomic projectile. The simulations also predict that the yield of ejected molecules is greater when using SF_5^+ rather than when

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Table 2. Intact-to-Fragment Ion Ratios for a Suite of Self-Assembled Monolayers and Bilayers on Au by SD and SIMS

oxidized target	$\text{RSO}_3^-/\text{SO}_3^-$	$\text{RSO}_3^-/\text{F}^-$	projectile
1-propanethiol	0.44 1.07 0.59		SD Cs^+ (CsI) Cs^+
1-hexadecanethiol	0.24 1.33 0.42		SD Cs^+ (CsI) Cs^+
thiophenol	1.42 3.74		SD Cs^+
MXHOL/HC	0.38 0.67 0.29 0.22		SD Cs^+ (CsI) Cs^+ (CsI) $_2\text{Cs}^+$
MXHOL/TFMBC	0.27 0.70 0.24 0.20	0.30 0.56 0.39 0.32	SD Cs^+ (CsI) Cs^+ (CsI) $_2\text{Cs}^+$
MUD/HC	0.32 0.75 0.21		SD Cs^+ (CsI) Cs^+
HTP/HC	0.53 1.15 0.47 0.23		SD Cs^+ (CsI) Cs^+ (CsI) $_2\text{Cs}^+$
HTP/TFMBC	1.08 4.75 1.87 1.22	0.20 0.65 0.49 0.34	SD Cs^+ (CsI) Cs^+ (CsI) $_2\text{Cs}^+$
ATP/HC	0.31 0.62 0.35 0.37		SD Cs^+ (CsI) Cs^+ (CsI) $_2\text{Cs}^+$
ATP/TFMBC	0.18 0.72 0.28 0.21	0.16 0.30 0.41 0.46	SD Cs^+ (CsI) Cs^+ (CsI) $_2\text{Cs}^+$

using Xe^+ . The simulations showed that fragments generated from projectile impact were due to atoms or fragments of molecules, directly hit by the primary ion, that project out to fragment other surface molecules, not due to multiple hits from substrate atoms.⁴⁸

Mass Spectra Produced from Anions Adsorbed onto AET Surfaces. We previously showed that increased SI yields are obtained in SIMS by adsorbing inorganic⁴⁹ and organic anions⁵⁰ from solution onto the surface of a positively charged AET (aminoethanethiol) SAM. We have also shown that such anions are bound to the surface via weak electrostatic interactions, and that exchange is reversible. The increased ion yields are believed to be due to the adsorption and isolation of preformed ions at the surface, thereby decoupling the desorption/ionization steps.

Figure 4 shows negative ion mass spectra acquired from AET's adsorbing octyl sulfate (OS^-), dioctyl sulfate (DS^-), and tetradecyl sulfate (TDS^-) (Figure 4, panels a–c, respectively). Prominent peaks are observed for SO_3^- , HSO_4^- , and the respective intact negative ions in all three spectra. In these cases, the SO_3^- and HSO_4^- peaks are present due to the sulfate group of the adsorbed molecule and not because of a photooxidation step or the

accidental oxidation of the AET SAM. Peaks corresponding to SO_3^- and HSO_4^- were absent in the mass spectrum of an AET-only (no anions exchanged) substrate. Peaks corresponding to the intact anions are present for OS, DS, and TDS at m/z 209, 265, and 293, respectively.

Figure 5 shows negative ion spectra that were acquired from AET surfaces with the adsorption of the following inorganic anions: BF_4^- , B(Ph)_4^- , and ReO_4^- (Figure 5, panels a–c, respectively). Peaks corresponding to the intact anions are present for BF_4^- and B(Ph)_4^- at m/z 87 and 319, respectively. Prominent peaks corresponding to ReO_3^- and ReO_4^- are present in Figure 5c. Apparently, the SD process causes significant reduction of the perrhenate (ReO_4^-) ion during the desorption event to produce ReO_3^- . Similar reduction/oxidation reactions have been observed for a variety of inorganic molecules.⁵¹ Cs^+ primary ion impacts, measuring 20 keV, on the same ReO_4^- -exchanged monolayer produced predominantly ReO_4^- , with the ReO_3^- peak intensity only ~10% that of the ReO_4^- abundance. A comparison of the spectra of the same monolayer as generated by Cs^+ impacts and SD demonstrates that the reduction of ReO_4^- occurs during ion formation/emission and not during the anion uptake/adsorption process.

CONCLUSIONS

We have shown that SDMS can be used to characterize SAMs and self-assembled bilayers when coupled with deliberate photooxidation of the surface. The photooxidation step produces RSO_3^- ions that are diagnostic of the molecular composition of the monolayer and bilayer samples and are easily sputtered and detected by TOFMS. SD also proved to be effective for the characterization of anions that are adsorbed to a protonated surface such as AET. SDMS offers the advantage of simplicity in that no formal primary ion source is necessary; only a potential difference of ~10 kV between the sample and the acceleration grid is required to induce SI desorption.

Techniques such as XPS, IR, and ellipsometry provide elemental, functional group, and thickness information, respectively, when applied to the characterization of SAM and bilayer surfaces. Mass spectrometry offers both elemental and molecular (fragment and intact ions) information about a surface. SD mass spectrometers can be small enough to fit on a benchtop, and vacuum in the 10^{-6} Torr range is sufficient for operation. Even though the photooxidation process permanently damages the SAM or bilayer surface, doing so provides molecular information about the success of chemical modification that is significantly more specific than the other techniques. Only a small portion of the substrate need be exposed to the light; thus, one might imagine using this technique for diagnostics in which only (e.g.) 1% of the substrate is damaged. With the growing interest of monolayers and bilayers in the applied fields of chemical sensors,^{52,53} molecular recognition,^{54–56}

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and protein adsorption,⁵⁷⁻⁵⁹ to characterize monolayers and bilayers using a simple MS technique such as SD will be a valuable complement to the existing tools that are available for thin-film characterization. SDMS is an inexpensive and simple technique for the qualitative identification of monolayer and bilayer films,

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and gives the much-needed molecular, rather than just elemental or functional group, information about the surface.

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