Modification of metal surfaces through the adsorption of small molecules has been used to alter the adhesion, corrosion, lubrication, and wetting properties of metals. Self-assembled monolayers (SAMs) of alkanethiols on gold have been studied extensively in this regard. The ability to vary alkane chain lengths and end groups has made them valuable for extending the fundamental understanding of surface phenomena.

Expansion of the variety of chemistry possible at the interface would greatly enhance efforts to achieve the wide-ranging promises of this technology. It has been demonstrated that silane will greatly enhance efforts to achieve the wide-ranging promises of this technology. It has been demonstrated that silane will make them valuable for extending the fundamental understand-

Chemisorbed monolayers of n-alkanesulfide (H_{1n}C_{n}S_{n}H_{2n+1}), n-octylsulfide (H_{1n}C_{n}S_{2n}H_{2n+1}), and n-octadecylsulfide (H_{13}C_{18}S_{2n}H_{30}) are formed by exposing freshly evaporated gold surfaces to saturating doses (>440 L, 1 L = 1 × 10^{-6} Torr) of one of these alkanesulfides in an ultrahigh vacuum (UHV) chamber. The samples have been characterized in UHV by reflection-absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS).

The RAIRS spectra of the octyl- and hexylsulfide monolayers (Figure 1, B and C) each exhibit four ν(C−H) vibrational modes. The peak frequencies and vibrational mode assignments for the octylsulfide-based layer are the following: ν(CH) 2923 cm^{-1}, ν(CH) 2925 cm^{-1}, and ν(CH) 2967 cm^{-1} (Figure 1B). For the hexylsulfide layer, the features are observed at ν(CH) 2850 cm^{-1} (observed as a shoulder), ν(CH) 2856 cm^{-1}, and ν(CH) 2964 cm^{-1} (Figure 1C). The spectrum of chemisorbed octadecylsulfide (Figure 1A) contains only three features in the ν(CH) region: ν(CH) 2830 cm^{-1}, ν(CH) 2850 cm^{-1}, and ν(CH) 2968 cm^{-1}. A direct comparison to the solution IR spectrum of octadecylsilane (Figure 1D) illustrates the absence of the prominent ν(Si−H) at 2150 cm^{-1} from RAIRS spectra for the silane-based layers.

Soft X-ray photoelectron spectroscopy data are summarized in Table 1. The Si 2p core-level spectra (Figure 2B) have been obtained (photon energy, hν = 160 eV) and consist of a spin-orbit doublet (2p_{3/2} and 2p_{1/2}) with binding energies of −99.8 eV and −100.4 eV and full width at half-maximum (fwhm) of 0.4 eV for each of the chemisorbed layers. The Au 4f core-levels for a clean gold surface are included for reference (Figure 2B, 4). A single C 1s (hν = 342.5 eV) feature is observed at −285 eV (Figure 2A). The area ratio of 6:8:1 observed for the C 1s silane data is the same as that detected for thiol-based SAMs when no correction for the attenuation of the photoelectrons through the alkane chains is made. Contrary to many thiol-based SAMs, no changes in the area ratio of 6:8:1 for the C 1s silane data is the same as that detected for thiol-based SAMs when no correction for the attenuation of the photoelectrons through the alkane chains is made. No changes in the area ratio of 6:8:1 for the C 1s silane data is the same as that detected for thiol-based SAMs when no correction for the attenuation of the photoelectrons through the alkane chains is made.

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Figure 1. RAIRS data (3050−2750 and 2350−2000 cm\(^{-1}\)) for monolayers of (A) octadecylsilane, (B) octylsilane, and (C) hexylsilane on Au. The RAIRS spectra represent −3000 scans at 8 cm\(^{-1}\) resolution ratioed to a clean gold background. A solution IR spectrum of octylsilane (D) is included for comparison.

Table 1. Selected Curve Fitting Parameters for Core-Level XPS Data

<table>
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<tr>
<th>Parameter</th>
<th>H_{1n}C_{n}S_{n}H_{2n+1}</th>
<th>H_{1n}C_{n}S_{2n}H_{2n+1}</th>
<th>H_{13}C_{18}S_{2n}H_{30}</th>
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</thead>
<tbody>
<tr>
<td>Si 2p B.E. (eV)</td>
<td>−99.7</td>
<td>−99.8</td>
<td>−99.8</td>
</tr>
<tr>
<td>Si 2p fwhm (eV)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>C 1s B.E. (eV)</td>
<td>−284.7</td>
<td>−284.9</td>
<td>−285.0</td>
</tr>
<tr>
<td>C 1s fwhm (eV)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>C 1s area</td>
<td>2.2</td>
<td>2.9</td>
<td>4.5</td>
</tr>
<tr>
<td>rel. C 1s area ratio(a)</td>
<td>6</td>
<td>8</td>
<td>12</td>
</tr>
</tbody>
</table>

\(a\) Ratio calculated by setting the hexylsilane C 1s area equal to six carbons.

The RAIRS data for the silane-based layers are reminiscent of the straight chain alkanes. The ν-(C−H) features for n-octadecanethiol are observed at 2965, 2919, 2878, and 2851 cm\(^{-1}\). The peaks correspond to the assignments of ν(CH) 2830 cm\(^{-1}\), ν(CH) 2850 cm\(^{-1}\), and ν(CH) 2968 cm\(^{-1}\). A direct comparison to the solution IR spectrum of octadecylsilane (Figure 1D) illustrates the absence of the prominent ν(Si−H) at 2150 cm\(^{-1}\) from RAIRS spectra for the silane-based layers.

Soft X-ray photoelectron spectroscopy data are summarized in Table 1. The Si 2p core-level spectra (Figure 2B) have been obtained (photon energy, hν = 160 eV) and consist of a spin−orbit doublet (2p_{3/2} and 2p_{1/2}) with binding energies of −99.8 eV and −100.4 eV and full width at half-maximum (fwhm) of 0.4 eV for each of the chemisorbed layers. The Au 4f core-levels for a clean gold surface are included for reference (Figure 2B, 4). A single C 1s (hν = 342.5 eV) feature is observed at −285 eV (Figure 2A). The area ratio of 6:8:1 observed for the C 1s silane data is the same as that detected for thiol-based SAMs when no correction for the attenuation of the photoelectrons through the alkane chains is made. Contrary to many thiol-based SAMs, no changes in the area ratio of 6:8:1 for the C 1s silane data is the same as that detected for thiol-based SAMs when no correction for the attenuation of the photoelectrons through the alkane chains is made.
not been observed for the octadecylsilane monolayer. This may be a result of the position of the CH$_3$ group with respect to the surface or simply signal-to-noise limitations. This feature is observed for the shorter chain alkylsilane-based layers; however, the $\nu(CH_3)$ mode is far more intense (Figure 1, B and C). Similar RAIRS comparisons between thiol and alkylsilane monolayers on gold can be drawn for the shorter chains. The ratio of the intensities of the $\nu(CH_3)$ to $\nu(CH_2)$ features decreases with increasing chain length. This is consistent with the decrease in the CH$_3$ to CH$_2$ ratio with increasing chain length in the alkyl chain. Both RAIRS and XPS data strongly suggest the three Si−H bonds of the alkylsilane are broken during the formation of these monolayers. Recall, the prominent $\nu(Si−H)$ feature in the solution spectrum of the alkylsilanes is not observed for the monolayers (Figure 1). In addition, the binding energy observed in the XPS data is consistent with the loss of all three hydrogen atoms. For systems with Si−H bonds, a shift of 0.3 to 1 eV is observed in the Si 2p core-levels, depending on the number of hydrogen atoms bound to the Si atom. These observations suggest that the silicon atom has formed three covalent bonds to the gold surface. The RAIRS correlation to the thiol case, this suggests that the Si−H bond activation. It is envisioned that control of the number of Au−Si bonds could be attained by the use of di- and trisubstituted silanes. This may permit a unique tailoring of the monolayer’s functional properties via selection of a specific bonding geometry.

In conclusion, alkylsilanes form monolayers on freshly evaporated gold surfaces in UHV. The silane remains intact on the gold surface, likely forming three covalent Au−Si bonds by means of Si−H bond activation. It is envisioned that control of the number of Au−Si bonds could be attained by the use of di- and trisubstituted silanes. This may permit a unique tailoring of the monolayer’s functional properties via selection of a specific bonding geometry.

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Supporting Information Available: Materials and experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(14) Assignments from ref 13a.
(18) Owens, T. M.; Sützer, S.; Banaszak Holl, M. M. To be submitted for publication.

Figure 2. X-ray photoemission data for (A) C 1s core-levels, (B) Si 2p and Au 4f core-levels, and (C) the valence band region of (1) octadecylsilane, (2) octylsilane, and (3) hexylsilane chemisorbed on (4) freshly evaporated Au. The binding energies are referenced to Au 4f$_{7/2} = \sim 84$ eV.