

Formation of Alkylsilane-Based Monolayers on Gold

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Modification of metal surfaces through the adsorption of small molecules has been used to alter the adhesion, corrosion, lubrication,¹ and wetting² properties of metals. Self-assembled monolayers (SAMs) of alkanethiols on gold³ have been studied extensively in this regard.⁴ The ability to vary alkane chain lengths and end groups⁵ 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 chemisorb to several clean metal surfaces⁶ and alkylsilanes have been used to modify oxidized surfaces.⁷ Recently, $\text{H}_8\text{Si}_8\text{O}_{12}$ was reported to chemisorb on clean gold surfaces at 20 °C via a novel Si–H activation.⁸ These discoveries set the stage for the synthesis of a new class of alkylsilane-based monolayers.

Chemisorbed monolayers of *n*-hexylsilane ($\text{H}_{13}\text{C}_6\text{SiH}_3$), *n*-octylsilane ($\text{H}_{17}\text{C}_8\text{SiH}_3$), and *n*-octadecylsilane ($\text{H}_{37}\text{C}_{18}\text{SiH}_3$) are formed by exposing freshly evaporated gold surfaces to saturating doses ($>440 \text{ L}$, $1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$) of one of these alkylsilanes 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 hexylsilane monolayers (Figure 1, B and C) each exhibit four $\nu(\text{C–H})$ vibrational modes. The peak frequencies and vibrational mode assignments for the octylsilane-based layer are the following: $\nu_s(\text{CH}_2)$ 2856 cm^{-1} , $\nu_s(\text{CH}_3)$ 2879 cm^{-1} , $\nu_a(\text{CH}_2)$ 2925 cm^{-1} , and $\nu_a(\text{CH}_3)$ 2967 cm^{-1} (Figure 1B). For the hexylsilane layer, the features are observed at $\nu_s(\text{CH}_2)$ 2850 cm^{-1} (observed as a shoulder), $\nu_s(\text{CH}_3)$ 2879 cm^{-1} , $\nu_a(\text{CH}_2)$ 2925 cm^{-1} , and $\nu_a(\text{CH}_3)$ 2964 cm^{-1} (Figure 1C). The spectrum of chemisorbed octadecylsilane (Figure 1A) contains only three features in the $\nu(\text{CH})$ region: $\nu_s(\text{CH}_2)$ 2850 cm^{-1} , $\nu_a(\text{CH}_2)$ 2923 cm^{-1} , and $\nu_a(\text{CH}_3)$ 2968 cm^{-1} . A direct comparison to the solution IR spectrum of octylsilane (Figure 1D) illustrates the absence of the prominent $\nu(\text{Si–H})$ 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, $h\nu = 160 \text{ eV}$) 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 ($h\nu = 342.5 \text{ eV}$) feature is observed at -285 eV (Figure 2A). The area ratio of 6:8:12 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.⁹ Contrary to many thiol-based SAMs,¹⁰ no changes in the

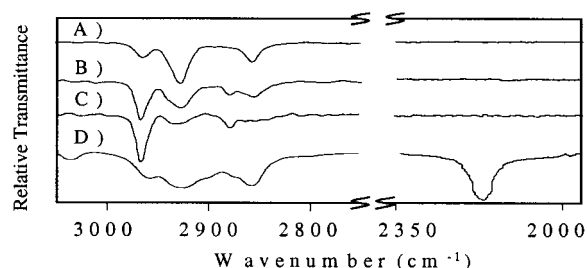


Figure 1. RAIRS data (3050–2750 and 2350–2000 cm^{-1}) for monolayers of (A) octadecylsilane, (B) octylsilane, and (C) hexylsilane on Au. The RAIRS spectra represent ~ 3000 scans at 8 cm^{-1} resolution ratioed to a clean gold background. A solution IR spectrum of octylsilane (D) is included for comparison.

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

parameter	$\text{H}_{13}\text{C}_6\text{SiH}_3$	$\text{H}_{17}\text{C}_8\text{SiH}_3$	$\text{H}_{37}\text{C}_{18}\text{SiH}_3$
Si 2p _{3/2} B.E. (eV)	−99.7	−99.8	−99.8
Si 2p fwhm (eV)	0.4	0.4	0.4
C 1s B.E. (eV)	−284.7	−284.9	−285.0
C 1s fwhm (eV)	1.2	1.2	1.1
C 1s area	2.2	2.9	4.5
rel. C 1s area ratio ^a	6	8	12

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

Si 2p, C 1s, and valence band region ($h\nu = 160 \text{ eV}$) are detected after more than 24 h of irradiation.

Only features originating from the Au 5d and Au 6s levels are observed in the valence band region for a clean gold surface (Figure 2C, 4). Upon chemisorption of the alkylsilane-based layer, features arising from the C 2s and C 2p levels are detected (Figure 2C, 1–3). These features are highly reminiscent of those observed for straight chain alkanes.¹¹

The RAIRS and XPS data collected for the silane-based layers support a proposed bonding geometry in which the alkyl chain remains intact and the Si atom forms three covalent bonds to the gold surface. Empirically, the simplest bonding geometries situate the Si atom either above the Au 3-fold hollow or on top of one of the Au surface atoms as proposed for reactions of silanes with other metal surfaces.^{12,6b}

The RAIRS data for the silane-based layers are reminiscent of straight chain, thiol-based SAMs on gold.¹³ For example, the $\nu(\text{C–H})$ features for *n*-octadecanethiol are observed at 2965, 2919, 2878, and 2851 cm^{-1} . The peaks correspond to the assignments of $\nu_a(\text{CH}_3)$, $\nu_a(\text{CH}_2)$, $\nu_s(\text{CH}_3)$, and $\nu_s(\text{CH}_2)$, respectively.¹⁴ The RAIRS spectra of octadecylsilane-based layers have features of similar intensity at $\nu_a(\text{CH}_3)$ 2968 cm^{-1} , $\nu_a(\text{CH}_2)$ 2923 cm^{-1} , and $\nu_s(\text{CH}_2)$ 2850 cm^{-1} (Figure 1A). The frequency of $\nu_a(\text{CH}_2)$ indicates that the alkyl chain for the silane-based monolayer is not as well packed as the alkyl chains of thiol-based SAMs. The $\nu_s(\text{CH}_3)$ feature has

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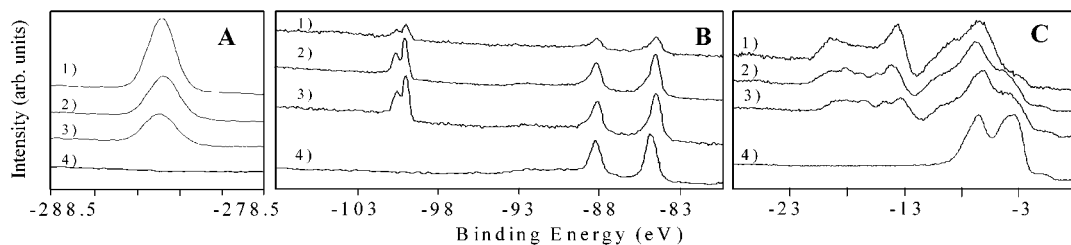


Figure 2. X-ray photoemission data for (A) C 1s core-levels, (B) Si 2p and Au 4f core-levels, and (C) the valence band region of (1) octadecylsilane, (2) octylsilane, and (3) hexylsilane chemisorbed on (4) freshly evaporated Au. The binding energies are referenced to Au $4f_{7/2} = -84$ eV.

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 $\nu_a(\text{CH}_3)$ mode is far more intense (Figure 1, B and C). Similar RAIRS comparisons between thiol¹⁵ and alkylsilane monolayers on gold can be drawn for the shorter chains. The ratio of the intensities of the $\nu(\text{CH}_3)$ to $\nu(\text{CH}_2)$ 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 $\nu(\text{Si–H})$ 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.¹⁶ These observations suggest that the silicon atom has formed three covalent bonds to the gold surface. The reaction may proceed by the oxidative addition of Si–H bonds to the gold surface and the reductive elimination of H_2 .¹⁷ The XPS and RAIRS data suggest the monolayers are chemically homogeneous. The chemical homogeneity of these monolayers is best assessed by the surprisingly narrow fwhm of 0.4 eV for the Si 2p core-levels (Figure 2B). In addition to the previously described RAIRS correlation to the thiol case, this suggests that the Si–C bond as well as the entire alkyl chain remains intact for the silane-based monolayers. The intensity of the Si 2p core-levels diminishes with increasing alkyl chain length, as expected with exponential photoelectron attenuation (Figure 2B). Variable photon energy XPS has been shown to be sensitive to surface coverage.⁹ Using a range of photon energies (160–400 eV), it has been determined that at least 95% of the Au surface is covered by the monolayer.¹⁸

The silanes do not form multilayers on gold surfaces at room temperature. If multilayers had formed, the silicon atoms would not be in a chemically homogeneous environment as suggested by the observed fwhms of the Si 2p core-levels (Figure 2B). Furthermore, a second, more intense Si 2p feature arising from silicon atoms not bonded directly to the gold surface would be observed. The binding energy of this core-level would be several electronvolts higher due to the hydrogen atoms on the silicon, sample charging, and a greater influence from final state effects than those experienced by the Si atoms bound directly to the surface. In addition, the intensity of the Au 4f and the observed Si 2p core-levels would be attenuated by the presence of the multilayers.

All three alkylsilane monolayers are stable to $>36\,000$ L H_2O or O_2 exposure. However, exposure to ambient conditions results in the oxidation of the silicon atoms as judged by a 2.3 eV shift in the Si 2p core-level. Similar instabilities, ascribed to reactions with ozone, have been noted for alkanethiol systems.¹⁹ The oxidized

monolayers are stable to water, methanol, and *n*-hexane rinses as judged by conventional XPS.

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>.

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