

Vapor-Deposition of Aluminum on Thiophene-Terminated Self-Assembled Monolayers on Gold

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Thermal deposition of aluminum in ultrahigh vacuum on a monolayer of 12-(3-thienyl)dodecanethiol, a thiophene-terminated alkanethiol, self-assembled on gold has been investigated by X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) and compared to aluminum deposition on a monolayer of 1-tridecanethiol. Intensity variations of the C 1s and Au 4f peaks as a function of aluminum coverage demonstrate that thermally deposited aluminum forms an overlayer on top of the thiophene-terminated self-assembled monolayer (SAM). Strong interaction of interfacial aluminum with the thiophene functional group is evidenced by the appearance of a metal-induced, low-binding-energy component in the C 1s spectrum. XPS measurements performed at a 10° takeoff angle, where surface sensitivity is enhanced, show a metal-induced shift in the thiophene S 2p peak of 1.6 eV to lower binding energy. These are indicative of electron transfer from aluminum to the thiophene rings. Initially deposited aluminum exhibits a nonmetallic feature in the Al 2s spectrum at a binding energy of 119.4 eV, but further aluminum deposition leads to metallic overlayers on top of the thiophene-terminated SAM. UPS measurements also demonstrate that aluminum covers the thiophene-terminated SAMs, as evidenced by the complete absence of the spectral characteristics of thiophene by an Al coverage of 4.4×10^{15} atoms/cm². Work function measurements suggest that initially deposited aluminum grows as electrically isolated islands until this coverage is exceeded. This behavior is dramatically different from that of 1-tridecanethiol on which initially deposited aluminum interacts weakly with the alkanethiol and diffuses beneath the monolayer to the gold surface. The lack of penetration in the case of the thiophene-terminated SAM probably results from lower mobility of aluminum atoms on the organic surface, compared to methyl-terminated SAMs, and their inability to diffuse to defect sites and penetrate through the monolayer.

Introduction

A variety of experiments have been performed in recent years to investigate conjugated polymer/metal interfaces, and understanding their nature is critical in the area of optoelectronic devices, including field-effect transistors,^{1,2} organic light-emitting diodes (OLEDs),^{3–5} and photovoltaics.^{6–8} However, organic films, especially polymers, may have poor surface homogeneity, and this lack of structural uniformity may induce difficulties in studying the interfaces. The need for highly ordered, well-oriented functional groups exposed at the surface of organic films has inspired the use of self-assembled monolayers (SAMs)⁹ in the study of metal/organic interfaces.¹⁰

Various metals including Ag,^{10–13} Cu,^{10,13,14} Cr,^{10,15–17} Ti,^{10,18} Ni,¹⁰ K,¹⁰ and Na¹⁰ have been vapor-deposited onto alkanethiol SAMs terminated with methyl (–CH₃),^{10–15,18} alcohol (–OH),^{10,13} carboxylic acid (–COOH),^{10,12,13,16} methyl ester (–COOCH₃),^{10,13,18} and nitrile (–CN) groups.^{10,13,15,18} Depending on the reactivity between the metal and functional group, different degrees of penetration of the metal into the organic layer have been observed. Jung et al.¹⁹ ranked the reactivity of various metals and organic functional groups. In general, the reactivity of Ti and Cr are very high, Cu, Ni, and K are

intermediate, and Ag and Na are low. In the case of organic functional groups, the reactivity is highest for oxygen-containing groups, intermediate for nitrile groups, and lowest for methyl groups. They also ranked the degree of penetration for various metal/SAM systems and concluded that the degree of penetration increases as metal reactivity decreases. A recent investigation²⁰ has shown that deposited aluminum atoms penetrate methyl-terminated SAMs and insert into the Au–S bonds to form an aluminum thiolate species. In contrast, for oxygen-containing SAMs, deposited aluminum reacts with oxygen atoms in the –COOCH₃, –COOH, and –OH groups with no penetration into the monolayers.^{20–23} Aluminum atoms deposited on CH₃O-terminated SAMs exhibit intermediate behavior and partial penetration.²³

Thiophene and its derivatives comprise an important class of conjugated polymers, with potential optoelectronic device applications.²⁴ Recently, we synthesized thiophene-terminated alkanethiols, Th–(CH₂)_n–SH (Th = 3-thiophene) with *n* = 2, 6, and 12, and self-assembled them onto Au(111) surfaces.²⁵ It was found that 12-(3-thienyl)dodecanethiol, (Th–(CH₂)₁₂–SH), forms densely packed, well-ordered monolayers on gold with the thiophene rings at the periphery of the SAM. The chemical structure of this molecule is shown in Figure 1. In the present study, a 12-(3-thienyl)dodecanethiol SAM has been used as a model surface for investigating metal/thiophene interface formation. The interaction of thermally deposited aluminum with the

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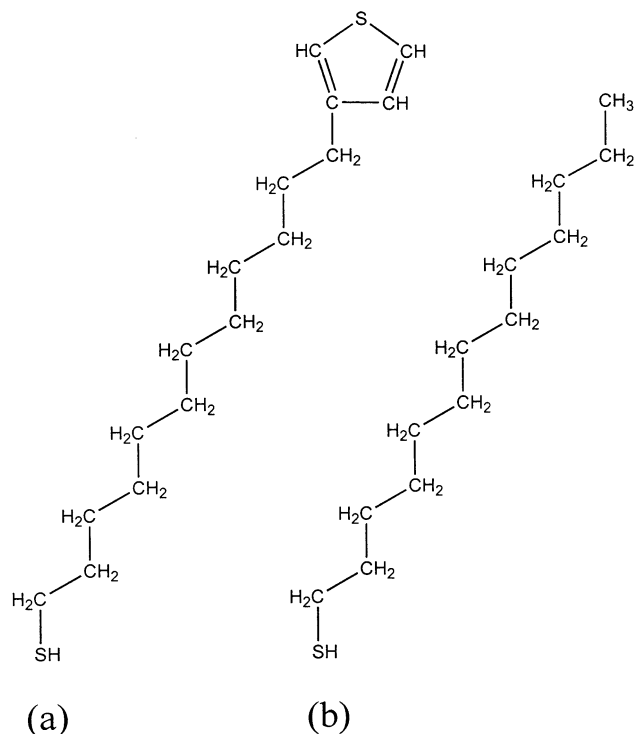


Figure 1. Chemical structures of (a) 12-(3-thienyl)dodecanethiol and (b) 1-tridecanethiol.

thiophene rings at the surface of the monolayers has been studied by X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). This is the first report regarding aluminum deposited on thiophene-terminated SAMs. However, theoretical and experimental studies have shown that vapor-deposited aluminum strongly interacts with thiophene monomer and oligo- and polythiophenes by bonding to the α -carbon atoms of the thiophene ring.^{5,26,27} The results of the present study indicate similar strong interaction of aluminum with the thiophene rings of the SAMs and demonstrate that initially deposited aluminum does not penetrate the monolayer. Comparison experiments have been performed on SAMs of 1-tridecanethiol, a methyl-terminated alkanethiol having the same number of methylene units as the thiophene-terminated molecule (Figure 1).

Experimental Section

Materials and SAMs Preparation. Details of the synthesis of 12-(3-thienyl)dodecanethiol and the preparation of SAMs on Au(111) have been previously described.²⁵ Briefly, 2000 Å of gold was thermally deposited in a ca. 5×10^{-7} mbar vacuum onto polished Si(111) wafers from a tungsten filament that had been wrapped with 99.999% gold wire. The gold deposition was performed with the substrates at room temperature. X-ray diffraction showed that the gold films were predominantly Au(111). Self-assembly of highly oriented, densely packed 12-(3-thienyl)dodecanethiol monolayers was formed by immersion of freshly prepared gold substrates in 1.0 mM 12-(3-thienyl)dodecanethiol solutions in chloroform for 24 h at room temperature. The SAMs were removed from the thiol solutions, rinsed carefully with chloroform, and dried in a nitrogen stream just prior to placing them in the sample introduction chamber of the photoelectron spectrometer for the metal deposition experiments. For comparative studies, the methyl-terminated alkanethiol, 1-tridecanethiol ($\text{CH}_3-(\text{CH}_2)_{12}-\text{SH}$), was used as received from Aldrich, with the SAMs prepared similarly to the 12-(3-thienyl)dodecanethiol ones.

Metal Deposition and Photoelectron Spectroscopy. XPS and UPS measurements were performed in a VG ESCALAB MK II photoelectron spectrometer consisting of three separate chambers: a sample introduction, a preparation, and an analysis chamber, as described in ref 26. The preparation and analysis chambers were pumped by liquid nitrogen-trapped diffusion pumps with base pressures in the low 10^{-10} mbar range. The analysis chamber was equipped with a Mg K α X-ray source ($h\nu = 1253.6$ eV), a He I ultraviolet lamp ($h\nu = 21.2$ eV), and a concentric hemispherical analyzer operating in constant pass energy mode and detecting photoelectrons approximately normal to the sample plane (unless otherwise noted). For a few experiments, as noted, XPS was performed at a takeoff angle (i.e., the angle between the surface of the sample and the photoelectron detector) of 10° to determine the extent that deposited aluminum atoms penetrate the monolayers and to obtain information about the electronic structure of the interface between Al and thiophene rings. The binding energy scale is referenced to the Fermi level of gold for both XPS and UPS.

To prevent charging during the experiments, silver paint was used to make electrical contact from the edges of the gold-coated Si(111) wafers to the sample stubs. The sample stub was held at electrical ground during XPS and approximately -6 V during UPS. In the latter case, the negative bias was necessary in order to be able to measure the entire width of the spectrum and calculate work functions. This voltage was accounted for in converting the measured kinetic energies to binding energies. The sample preparation chamber was equipped with an aluminum deposition source consisting of a resistively heated 0.5 mm diameter tungsten filament (99.95% purity) wrapped with multiple turns of 0.25 mm diameter 99.999% aluminum wire. The amount of deposited Al was monitored with a homemade quartz crystal microbalance (QCM) situated next to the samples. Prior to the metal deposition experiment, the Al source was outgassed, and the pressure in the preparation chamber did not exceed 1×10^{-9} mbar during Al deposition.

Prior to performing the aluminum deposition experiments, the SAMs were heated at 100°C in the sample preparation chamber for ca. 30 min to remove any oxygen and water contamination. As previously reported, 12-(3-thienyl)dodecanethiol SAMs are thermally stable at this temperature.²⁵ Subsequent metallization experiments were carried out at ambient temperature. Sample heating and temperature monitoring were accomplished with a commercial sample heater (VG model 240) into which a carousel holding multiple samples could be inserted. A thermocouple was attached to the carousel to monitor the temperature. No contamination, including oxygen, was detectable by XPS.

Results and Discussion

X-ray Photoelectron Spectroscopy (XPS). Figure 2 shows C 1s X-ray photoelectron spectra for 1-tridecanethiol on Au(111) before and after deposition of aluminum. In the case of the bare 1-tridecanethiol monolayer, the peak at 284.6 eV, with a fwhm of 1.5 eV, is assigned to methylene and methyl carbon atoms. This binding energy and fwhm agree with previously reported data¹¹ for an alkanethiol. As aluminum is added, the peak shifts to higher binding energy by 0.8 eV and gradually shifts back to approximately the original position. Such shifts in the C 1s peak position as a function of metal coverage have been observed in prior metal/SAMs studies,^{10,11,15–18,20,23} and several possible reasons have been discussed.¹¹ We shall return to this point later in the paper. Figure 3 shows analogous XPS measurements of the C 1s region for the thiophene-terminated

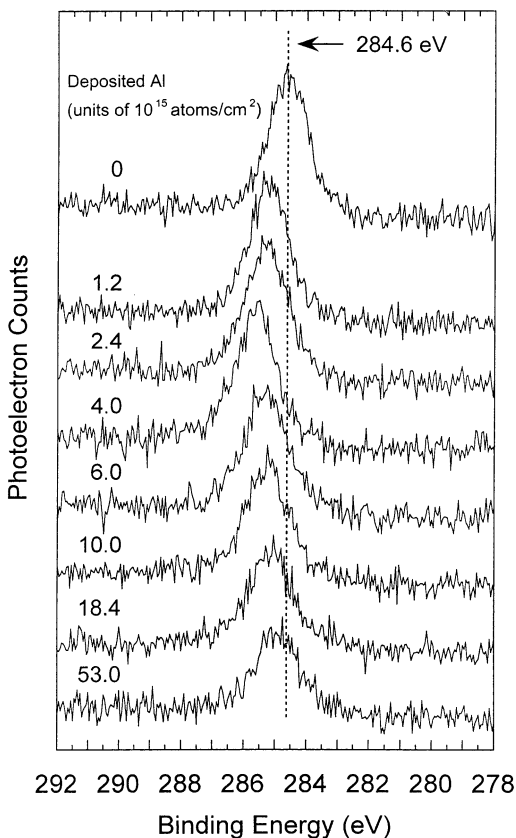


Figure 2. Mg K α XPS of the C 1s region of self-assembled tridecanethiol on Au/Si(111) as a function of aluminum coverage. The photoelectrons are detected at a takeoff angle of 90°, and the binding energy is referenced to the Fermi level of the gold substrate.

SAMs on Au(111). A shift of 0.6 eV to higher binding energy in progressing from 1.2 to 2.4×10^{15} atoms/cm² is observed, but the peak returns to its original position by a cumulative aluminum dose of 4.0×10^{15} atoms/cm². This peak is assignable to the carbons in methylene and thiophene groups. A metal-induced low-binding-energy shoulder occurs in the vicinity of 283.0 eV, in contrast to the case of metal deposition on 1-tridecanethiol films. To emphasize the Al-induced feature, Figure 4 presents peak fits of the C 1s spectra from Figures 2 and 3, for an Al dose of 10×10^{15} atoms/cm². Peak fitting was carried out with a Shirley-type background and 20% Lorentzian/80% Gaussian components. In the case of 1-tridecanethiol SAMs, no aluminum-induced features are observed, indicating minimal interaction of deposited Al with the C–C or C–H in methylene or methyl groups in the SAMs. This is consistent with previously reported results in ref 20. For 12-(3-thienyl)-dodecanethiol SAMs, however, a new C 1s peak appears at around 283.0 eV, indicating the interaction of aluminum with carbon atoms in thiophene rings. The lower binding energy component implies increased electron density on the thiophene ring induced by electron transfer from Al. Previous studies in which aluminum has been deposited on condensed thiophene,²⁶ oligothiophenes,^{5,27} and polythiophenes^{5,27} measured similar low-binding-energy components and attributed them to electron donation from aluminum atoms to the thiophene rings.

Because of its surface sensitivity, XPS can be used to infer information regarding metal penetration. Variations of the C 1s and Au 4f areas for 1-tridecanethiol and 12-(3-thienyl)-dodecanethiol SAMs as a function of Al coverage are shown in Figure 5. In the former case, the C 1s area shows no change up to an Al dose of 10×10^{15} atoms/cm². The Au 4f area, however, decreases by ca. 25% for this dose. If Al were forming

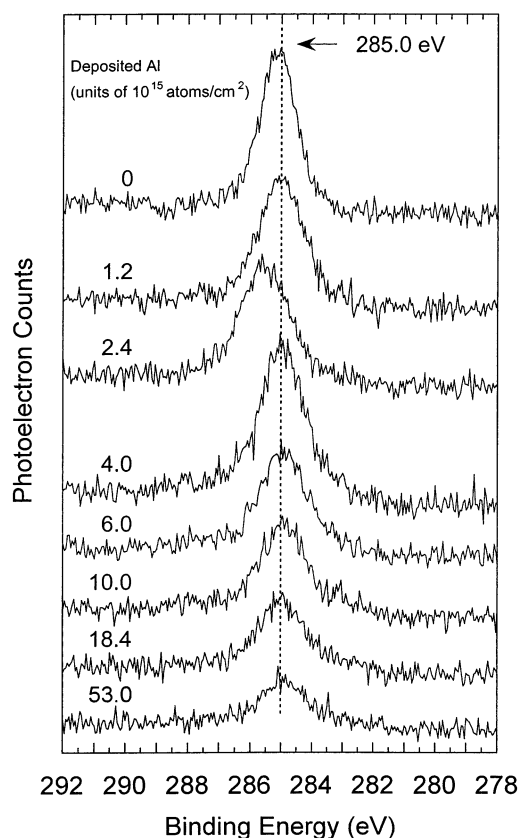


Figure 3. Mg K α XPS of the C 1s region of self-assembled 12-(3-thienyl)dodecanethiol on Au/Si(111) as a function of aluminum coverage. The photoelectrons are detected at a takeoff angle of 90°, and the binding energy is referenced to the Fermi level of the gold substrate.

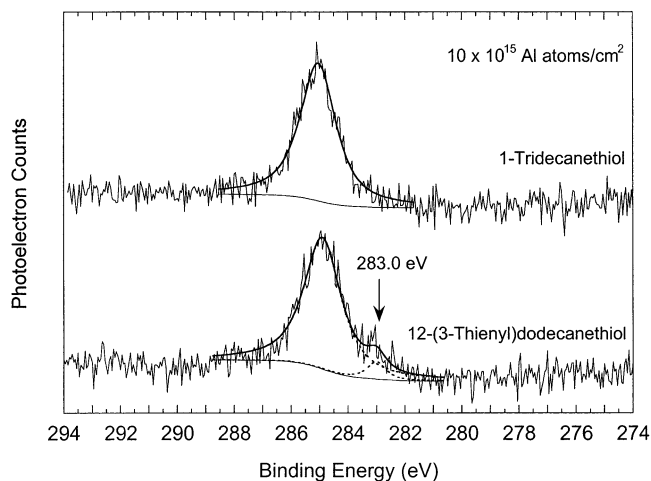


Figure 4. The results of peak fitting the Mg K α XPS C 1s spectra of self-assembled 12-(3-thienyl)dodecanethiol and 1-tridecanethiol on Au/Si(111) after an aluminum coverage of 10×10^{15} atoms/cm². The photoelectrons are detected at a takeoff angle of 90°, and the binding energy is referenced to the Fermi level of the gold substrate.

overlayers on top of the methyl-terminated SAM, both the C 1s and Au 4f areas would similarly decrease with Al deposition. The greater decrease in Au 4f intensity is consistent with aluminum penetration through the methyl-terminated SAM. Similar behavior was observed by Hooper et al.²⁰ who deposited aluminum on 1-hexadecanethiol monolayers and concluded that the metal diffused through the SAM to the Au–S interface and formed a uniform adlayer on Au. These results demonstrate that initially deposited aluminum penetrates the monolayer, up to

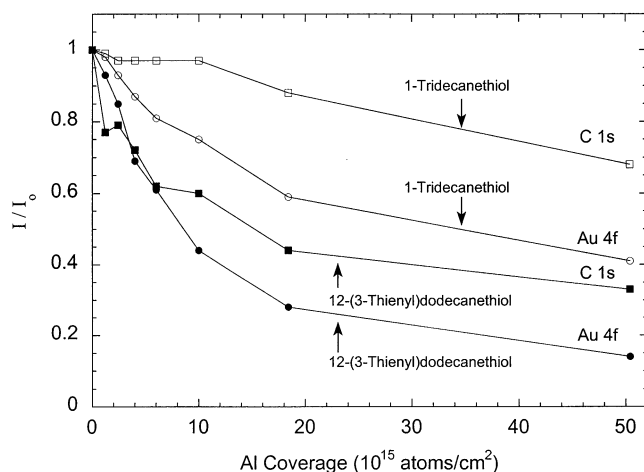


Figure 5. Areas of Au 4f and C 1s XPS peaks as a function of aluminum coverage for deposition on self-assembled monolayers of 12-(3-thienyl)dodecanethiol and 1-tridecanethiol. The areas are expressed as I/I_0 , where I is the measured area of the peak and I_0 is the area prior to metal deposition. The data correspond to measurements at a takeoff angle of 90° .

10×10^{15} atoms/cm². However, by 18×10^{15} atoms/cm², metal overlayer growth occurs. If the deposited aluminum were growing layer-by-layer, one monolayer would correspond to 1.4×10^{15} atoms/cm² and have a nearest-neighbor distance of 2.86 Å.²⁸ The present results thus indicate that approximately 7 layers worth of aluminum penetrate the 1-tridecanethiol SAM before overlayer formation occurs. For the thiophene-terminated SAM, dramatically different behavior is observed. Both the C 1s and Au 4f peaks decay similarly, even for low aluminum doses, indicating that Al does not penetrate significantly into the monolayer, but instead stays on top and forms an overlayer.

Figure 6 displays Al 2s XPS spectra for the 1-tridecanethiol SAM on Au(111) prior to and after Al deposition. Note that the Al 2p region could not be used because of a spectral interference from gold. For initial Al doses, a broad peak appears at a binding energy of 118.8 eV (fwhm of 2.6 eV) and dominates the spectra up to a coverage of 10×10^{15} atoms/cm². Further metallization leads to a shift to lower binding energy, with the peak at 118.0 eV (fwhm of 1.8 eV). This binding energy and fwhm are indicative of metallic aluminum.^{29,30} Hooper et al.²⁰ observed a similar higher binding energy component in the Al 2p spectrum in their studies of aluminum deposition on 1-hexadecanethiol SAMs.

Figure 7 contains Al 2s XPS spectra for the 12-(3-thienyl)dodecanethiol monolayer as a function of Al coverage. At low coverage, a broad peak appears with a component at a binding energy of 119.4 eV. This higher value relative to 118.8 eV indicates that the aluminum atoms interacting with the thiophene functional groups are more electron deficient than those inserted between the thiolate sulfur and gold surface. This is further evidence of strong charge transfer from aluminum to thiophene. By an aluminum dose of 6×10^{15} atoms/cm² the Al 2s spectra are dominated by the component having a binding energy of 118.5 eV, which shifts to 118.0 eV as more aluminum is added. As discussed previously, this value is indicative of metallic aluminum. The initially higher binding energy value of 118.5 eV may be due to reduced core hole screening from clusters compared to metallic layers. The different behaviors of deposited aluminum on the two SAMs are emphasized in Figure 8, which shows peak fits to the data for a coverage of 10×10^{15} atoms/cm². In the case of the methyl-terminated SAM, the spectrum is due to metallic aluminum. In the case of the thiophene-

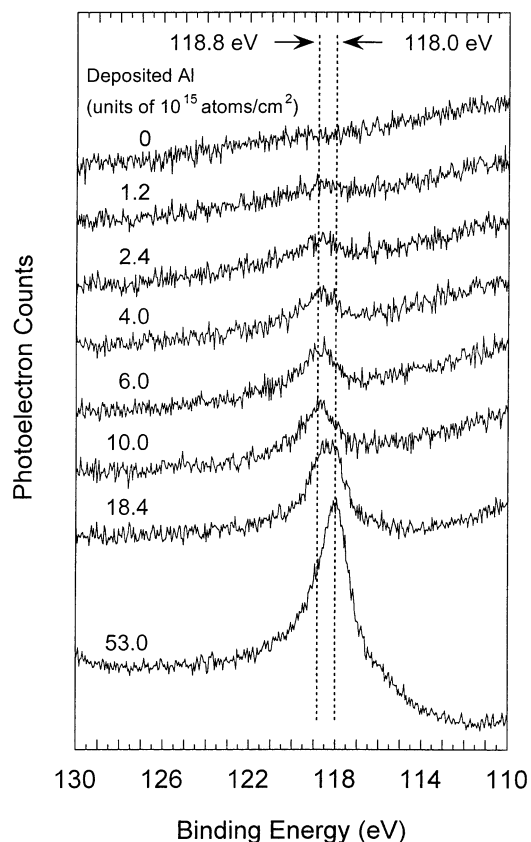


Figure 6. Mg $K\alpha$ XPS of the Al 2s region of self-assembled 1-tridecanethiol on Au/Si(111) as a function of aluminum coverage. The photoelectrons are detected at a takeoff angle of 90° , and the binding energy is referenced to the Fermi level of the gold substrate.

terminated SAM, the spectrum is comprised of two components: Al oxidized by its bonding to thiophene (at 119.4 eV) and a metallic Al peak (at 118.0 eV).

XPS has also been performed at a takeoff angle of 10° ; surface sensitivity increases as the takeoff angle decreases.³¹ At a 10° takeoff angle, the XPS sampling depths are in the range of 10 to 15 Å.³¹ Figure 9 displays variations of the Al 2s peak area as a function of Al coverage. For the methyl-terminated SAM, initially deposited Al atoms diffuse to the Au–S interface; no aluminum is detectable up to a coverage of about 4×10^{15} atoms/cm². For cumulative doses greater than 4×10^{15} atoms/cm², a dramatic increase in the Al 2s area is observed, consistent with aluminum growing on top of the SAM film (i.e., at the SAM/vacuum interface). In contrast, for the thiophene-terminated SAM, Al 2s intensity is measurable even for the lowest metal dose used and increases essentially linearly with doses up to 6×10^{15} Al atoms/cm². The onset of Al 2s signal at doses greater than 4×10^{15} atoms/cm² (2–3 monolayers worth of aluminum) disagrees with the C 1s results of Figure 5, which show overlayer growth only after a greater Al dose. However, the Al 2s data are probably a more reliable indicator, since this experiment detects the onset of a signal on a zero background instead of a decrease in a large signal.

All of the aforementioned results are consistent with initially deposited aluminum forming overlayers on the thiophene-terminated SAM, in contrast to the methyl-terminated one, which instead initially exhibits diffusion through the monolayer. Figure 10 shows the S 2p region for the 12-(3-thienyl)dodecanethiol SAM before and after an Al dose of 2.4×10^{15} atoms/cm². These data were, again, acquired with a 10° takeoff angle. Prior to any aluminum addition, the spin–orbit coupled peak has

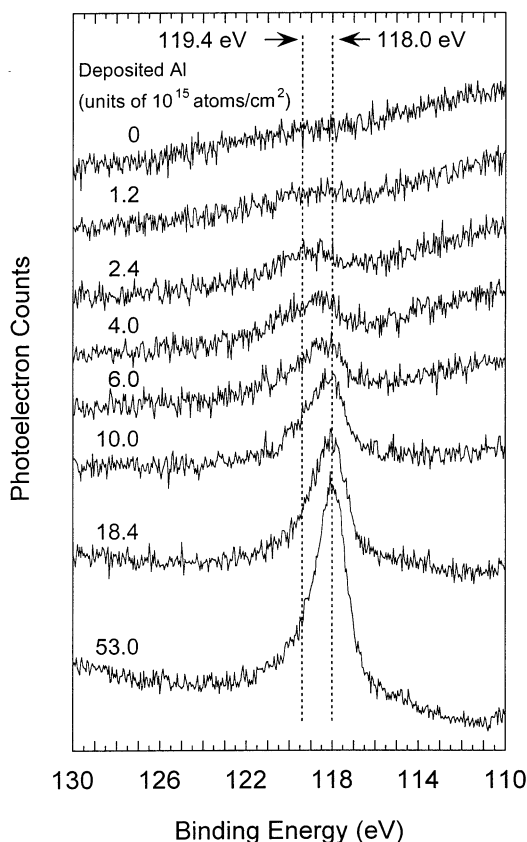


Figure 7. Mg K α XPS of the Al 2s region of self-assembled 12-(3-thienyl)dodecanethiol on Au/Si(111) as a function of aluminum coverage. The photoelectrons are detected at a takeoff angle of 90°, and the binding energy is referenced to the Fermi level of the gold substrate.

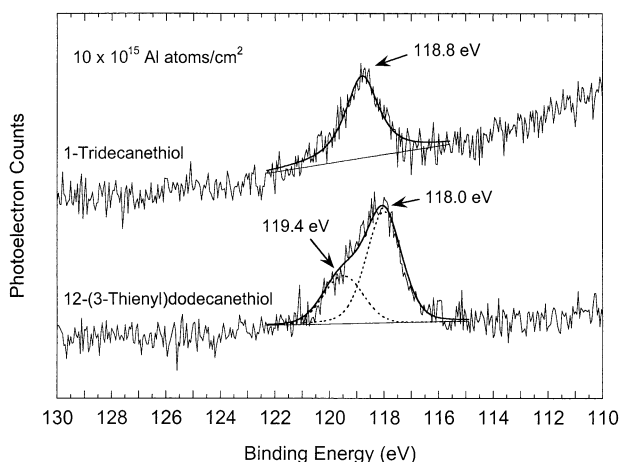


Figure 8. The results of peak fitting the Mg K α XPS Al 2s region of self-assembled 12-(3-thienyl)dodecanethiol and 1-tridecanethiol on Au/Si(111) after an aluminum coverage of 10×10^{15} atoms/cm 2 . The photoelectrons are detected at a takeoff angle of 90°, and the binding energy is referenced to the Fermi level of the gold substrate.

maximum intensity at 164.5 eV, with the S 2p $_{1/2}$ shoulder at 165.7 eV. The S 2p feature of thiolate, reported to appear at 162.1 eV with a shoulder at 163.3 eV (and observed by us at a takeoff angle of 90°²⁵), is not detected in this experiment due to the more limited escape depth at this angle. After an Al dose of 2.4×10^{15} atoms/cm 2 , the peak shifts to lower binding energy, with maximum intensity at 162.9 eV, ca. 1.6 eV lower in binding energy than the original feature. The spin-orbit splitting is no longer resolved, indicative of a loss of homogeneity. The shift is due to electron transfer from aluminum to thiophene rings

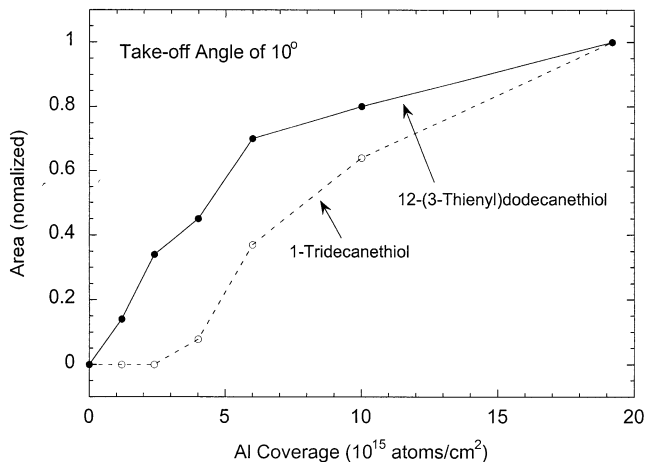


Figure 9. Areas of the Al 2s XPS peaks for the 12-(3-thienyl)dodecanethiol and 1-tridecanethiol monolayers as a function of aluminum coverage. The areas have been normalized to that corresponding to the greatest aluminum coverage used. The photoelectrons are detected at a takeoff angle of 10°.

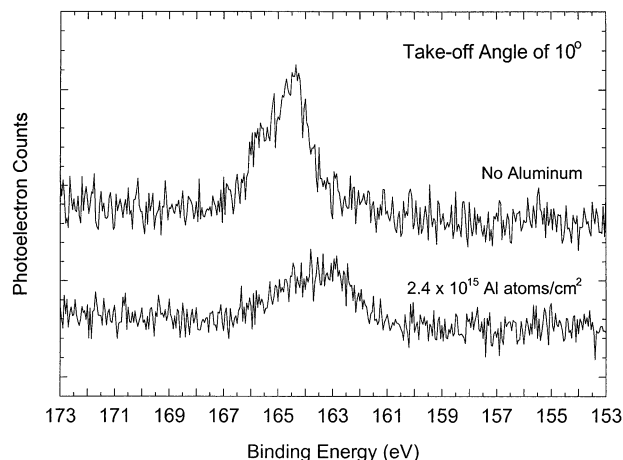


Figure 10. Mg K α XPS of the S 2p region of self-assembled 12-(3-thienyl)dodecanethiol on Au/Si(111) before and after an aluminum coverage of 2.4×10^{15} atoms/cm 2 . The photoelectrons are detected at a takeoff angle of 10°, and the binding energy is referenced to the Fermi level of the gold substrate.

(i.e., reduction of the thiophene). As for the C 1s results discussed previously, this conclusion is in general agreement with prior studies related to aluminum deposition on thiophenes, except for the intensity of the aluminum-induced feature in the S 2p spectrum. The previous studies for aluminum deposition on condensed thiophene monomer,²⁶ oligothiophenes,^{5,27} and polythiophenes^{5,27} observed only a small shoulder at lower binding energy. In the present study, the entire peak is observed to shift. This difference can be explained by the fact that most of the thiophene rings at the periphery of the monolayer interact with deposited aluminum. In all of the other studies, relatively thick organic films were used, causing the reduced thiophene ring S 2p spectra to be convoluted with that from unreacted rings.

Ultraviolet Photoelectron Spectroscopy (UPS). Figures 11 and 12 display ultraviolet photoelectron spectra for the methyl- and thiophene-terminated SAMs as a function of Al coverage. The He I UPS peak assignments for 12-(3-thienyl)dodecanethiol and 1-tridecanethiol have been discussed in detail in ref 25. Briefly, for 12-(3-thienyl)dodecanethiol, the peak in the vicinity of 3.6 eV is attributed to localized electronic states with a strong contribution from thiophene ring sulfur atoms and sulfur atoms in the thiol groups. The peaks at 6.6 and 8.5 eV are due to the

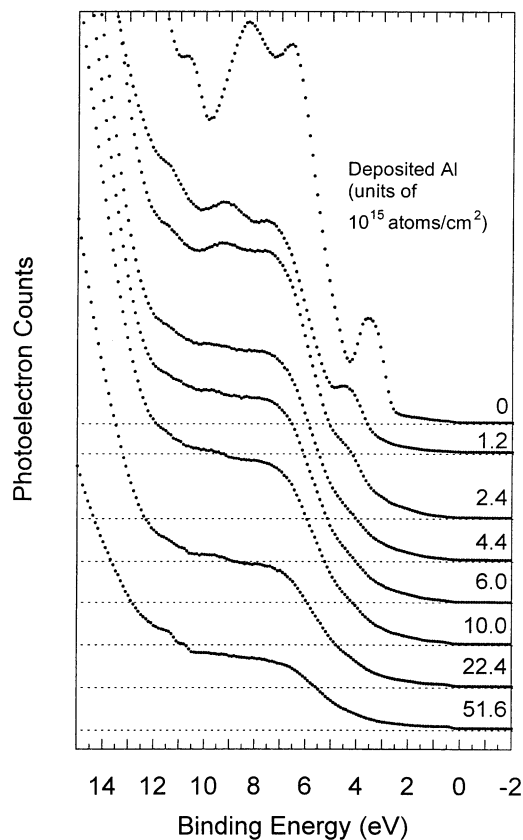


Figure 11. Low binding energy region of He I UPS of self-assembled 12-(3-thienyl)dodecanethiol monolayers on Au/Si(111) as a function of aluminum coverage. The photoelectrons are detected at a takeoff angle of 90° , and the binding energy is referenced to the Fermi level of the gold substrate.

nonbonding orbitals of sulfur atoms and some σ orbitals in the alkyl chains. In the case of 1-tridecanethiol SAMs, the feature at 3.2 eV is attributable to sulfur atoms in the thiol groups, and the peak near 7 eV and the shoulder at 10 eV are mainly attributable to σ orbitals in the alkyl chains and small contribution from the nonbonding orbitals of sulfur atoms in thiols. In Figure 11, the intensity of the peak at ~ 4 eV drastically decreases even after 1.2×10^{15} atoms/cm 2 , the lowest aluminum dose used. This is consistent with aluminum covering the thiophene functional groups. He I UPS is even more surface sensitive than XPS as a result of the lower kinetic energies of the escaping photoelectrons. All the characteristic binding energies of the 12-(3-thienyl)dodecanethiol SAM (at 3.6, 6.6, and 8.5 eV) completely disappear by a coverage of 4.4×10^{15} atoms/cm 2 . In contrast, as shown in Figure 12, except for the feature at 3.2 eV, the UPS spectra for the methyl-terminated SAMs remain essentially constant with increasing Al coverage up to 22.4×10^{15} atoms/cm 2 . The change in intensity at 3.2 eV is likely a result of perturbation of the thiolate sulfur orbitals as they bond to aluminum. These observations are consistent with aluminum diffusing through the methyl-terminated monolayer.

Figure 13 shows the work function of methyl- and thiophene-terminated monolayers on Au(111) as a function of Al coverage. These have been determined from the widths of the UPS spectra. 32 Values of 5.2 and 3.9 eV for clean gold and aluminum, respectively, have been obtained from similar measurements on an Ar ion-sputtered gold-covered Si(111) sample and an aluminum sample prepared by UHV deposition of 50×10^{15} Al atoms/cm 2 on a gold-coated Si(111) wafer. The work functions of the methyl- and thiophene-terminated monolayers

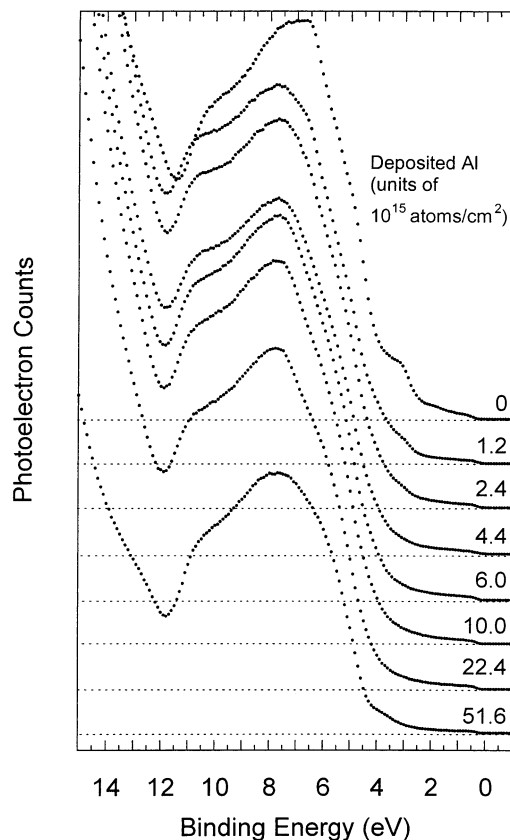


Figure 12. Low binding energy region of He I UPS of self-assembled 1-tridecanethiol monolayers on Au/Si(111) as a function of aluminum coverage. The photoelectrons are detected at a takeoff angle of 90° , and the binding energy is referenced to the Fermi level of the gold substrate.

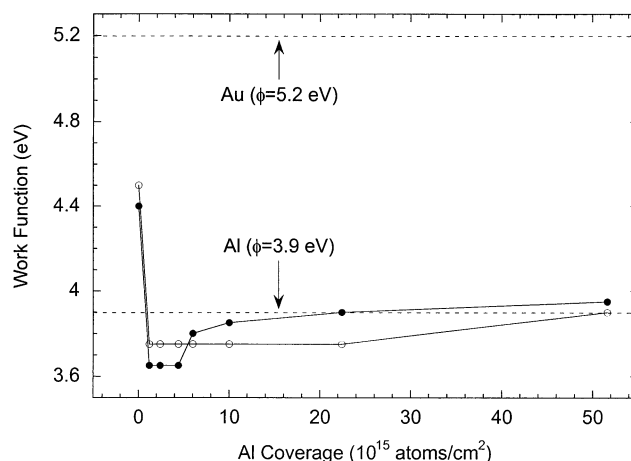


Figure 13. Work function of self-assembled 12-(3-thienyl)dodecanethiol (filled circles) and 1-tridecanethiol (hollow circles) monolayers on Au/Si(111) as a function of aluminum coverage. The work functions for bulk aluminum and gold are indicated by dashed lines.

are 4.5 and 4.4 eV, respectively, prior to aluminum deposition. In both cases, as aluminum is added, the work function decreases. In the case of the thiophene-terminated SAM, a minimum value of 3.65 eV is obtained at the smallest dose studied (1×10^{15} atoms/cm 2), and it remains at this level until a metal coverage of 4.4×10^{15} atoms/cm 2 . The addition of more aluminum causes the work function to gradually increase to the value of clean aluminum, which is achieved by a metal dose of 22×10^{15} atoms/cm 2 . In the case of the methyl-terminated SAM, deposition of aluminum causes the work function to decrease to 3.75 eV, and it stays at this value beyond 22×10^{15} atoms/cm 2 .

cm², until finally reaching the clean aluminum value by 50×10^{15} atoms/cm².

Metal-induced decreases in work function are commonly observed,^{33,34} with a minimum being due to depolarization of the surface dipoles as they get closer to each other with increasing coverage.³³ However, such minima for deposition on clean metals typically occur for submonolayer coverage.^{33,34} The data of Figure 13 suggest the following. 12-(3-Thienyl)dodecanethiol and 1-tridecanethiol adsorption results in the molecules having their negative poles (the thiol sulfurs) toward the gold substrates. For the 12-(3-thienyl)dodecanethiol, initially deposited aluminum grows in islands on top of the SAM up to a coverage of 6×10^{15} atoms/cm². Recall this corresponds to roughly 4 monolayers worth of aluminum. Higher aluminum dose results in the aluminum islands becoming electrically connected and forming overlayers, which exhibits the bulk aluminum work function by a coverage of 22×10^{15} atoms/cm². In the case of 1-tridecanethiol, initially deposited metal results in an entirely different situation in which the surface consists of the alkanethiol adsorbed on aluminum. The minimum in the work function is most probably not observed in our experiment since the lowest metal coverage studied is greater than submonolayer. The work function value of 3.75 eV should, therefore, correspond to that of 1-tridecanethiol self-assembled on an aluminum surface. It is interesting that even after 22×10^{15} atoms/cm², the work function still has not reached the value for bulk aluminum (as it did for the thiophene-terminated SAM). This is likely due to the fact that some of the organic layer is still adsorbed on top of the aluminum. Further dosing eventually leads to the SAM essentially being covered by the metal and reaching the work function of bulk aluminum, consistent with the XPS data in Figure 5.

In the case of 1-tridecanethiol, the changes in work function correlate with the observed shifts in the C 1s peaks. Referring to Figure 2, initial aluminum deposition causes the C 1s peak to shift 0.8 eV toward higher binding energy. It then gradually shifts back toward lower binding energy, reaching a value of 285.0 eV by 53×10^{15} atoms/cm². As shown in Figure 13, the work function decreases by 0.75 eV due to initial aluminum deposition and stays at this value until the metal dose exceeds 22×10^{15} atoms/cm², reaching a final value that is ca. 0.5 eV less than the original SAM/Au value. The trends in binding energy shift and work function with aluminum dose exactly correspond. If the data in Figure 2 were referenced to the vacuum level (by adding the work function to the binding energy for each spectrum) instead of the Fermi level, the C 1s spectra would exhibit no shifts (within experimental error). One interpretation of these results is that the C 1s orbital is pinned to the vacuum level, as first suggested by Tarlov¹¹ in the case of silver deposition on octadecanethiol. In the case of 12-(3-thienyl)dodecanethiol, the work function changes do not correspond to the shifts in the C 1s spectra observed in Figure 3. The shift of ca. 0.6 eV toward higher binding energy that occurs in progressing from 1.2 to 2.4×10^{15} atoms/cm² does not correspond to the measured work function change. This lack of correlation is further evidence that the observed XPS shifts are chemical in nature and are a result of interaction of aluminum with the SAM.

As discussed by Tarlov,¹¹ the first step in metal penetration of SAMs is metal diffusion on the surface of the organic layer until it finds defects through which it can migrate downward to the gold surface. In the case of gold deposited on Si(111) wafers, as used in the present study, the defects would most likely be along the edges of the Au(111) crystallites. For simple

alkanethiols, the interaction of aluminum atoms with the methyl groups is weak, and the atoms have high enough mobility to find the defect sites and subsequently penetrate the SAM. In contrast, for thiophene, the stronger interaction of aluminum with the thiophene rings limits the rate of diffusion. In other words, penetration of metal into the SAM is kinetically limited.

Conclusions

The interaction of vapor-deposited aluminum with a thiophene-terminated alkanethiol, 12-(3-thienyl)dodecanethiol, self-assembled on Au(111) has been investigated using XPS and UPS. Intensity variations of XPS C 1s and Au 4f peaks as a function of Al coverage demonstrate that thermally deposited aluminum forms overlayers at the vacuum/SAM interface. Strong chemical interaction of deposited aluminum with the thiophene functional groups is evidenced by the appearance of metal-induced low binding energy components in the S 2p and C 1s spectra. Both the Al 2s and work function data indicate that initially deposited aluminum (up to a dose of about 6×10^{15} atoms/cm²) is not metallic. This lack of metallic behavior presumably results from the aluminum atoms interacting with the thiophene rings and growing as electrically isolated islands on top of the SAM. UPS measurements are consistent with the formation of an Al overlayer on top of the SAMs, as evidenced by the complete absence of the spectral characteristics of the SAM after an Al dose greater than 2.4×10^{15} atoms/cm². These results have been compared with those of SAMs formed from a methyl-terminated alkanethiol of similar length (1-tridecanethiol). The results of XPS and UPS measurements demonstrate penetration of deposited Al through methyl-terminated SAMs to the gold interface. This is consistent with previously reported XPS and secondary ion mass spectrometry (SIMS) studies²⁰ which showed Al insertion between the thiol S and Au surface. In the case of the thiophene-terminated SAM, the overlayer growth of aluminum likely results from lack of mobility of aluminum atoms on top of the organic layer and their inability to "find" defect sites through which to penetrate the organic film. The results of this study demonstrate that thiophene-terminated self-assembled monolayers can be used as model surfaces in examining metal/thiophene reactivity. Possibilities also exist for constructing molecular capacitors by sandwiching a thiophene-terminated SAM between gold and aluminum electrodes.

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