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High-Resolution X-ray Photoelectron Spectra of Organosulfur Monolayers on Au(111): S(2p) Spectral Dependence on Molecular Species

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We have used high-resolution X-ray photoelectron spectroscopy (XPS) to investigate the molecular dependence on sulfur chemical states of organosulfur monolayers of alkanethiol, dialkyl disulfide, monosulfide, thiophene, and aromatic thiols on a Au(111) surface. When monosulfides or thiophenes adsorbed on the Au surface, the S(2p) peaks appeared between 161 and 164 eV, and peak fitting revealed that these organosulfurs exhibited almost the same peaks as those of alkanethiol and dialkyl disulfide monolayers. The monolayer made from monosulfide with shorter alkyl chains exhibited almost the same S(2p) XPS spectrum as the typical alkanethiol or dialkyl disulfide monolayers. Another S(2p_{3/2}) peak appeared for aromatic derivatized thiol SAMs at around 161 eV, in addition to strong doublet S(2p) peak observed at 162.0 and 163.3 eV in the S(2p) spectra. The 161 eV peak was observed even in the S(2p) XPS spectra of alkanethiol or dialkyl disulfide monolayers, at the initial stage of monolayer growth or after low-temperature (~ 100 °C) annealing of low molecular density alkanethiol SAMs. We consider that this 161 eV peak can be formed without molecular decomposition as well as due to the atomic sulfur produced by C–S cleavage.

Introduction

The structures of alkanethiol or dialkyl disulfide or organosulfur self-assembled monolayers (SAMs) on a Au(111) surface have been extensively studied using many analytical tools such as X-ray photoelectron spectroscopy (XPS),^{1–12} scanning probe microscopy (SPM),^{13–24} X-ray

or helium diffraction techniques,^{25–27} electrochemical measurements,^{28–31} and thermal desorption spectroscopy (TDS)^{32,33} from a viewpoint of basic surface science.

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Although many reports have been published in the past decade, as reviewed by Ulman,³⁴ there still remain many unsolved questions, especially concerning the chemical state of sulfur on the Au surface. Also, a new class of molecules such as monosulfide^{28,35} and thiophene^{22,36} have recently attracted attention, from the viewpoint of their potential use in molecular devices, for example, in switch or optical memory applications.

To investigate the binding properties between the sulfur and Au surface, XPS is the most powerful analytical tool, because the chemical shifts and area intensity of XPS peaks can provide fruitful information. A high-resolution XPS system with a monochromatic X-ray source would be crucial for understanding Au-sulfur binding because such an XPS system could resolve the small peak shifts due to the chemical differences between sulfur species.

Here we review XPS sulfur peak of alkanethiol or dialkyl disulfide monolayers.^{10–12,18,28–30} It is believed that SAM films made from alkanethiols and disulfides were structurally the same, and that both species formed alkanethiolate on Au surfaces.⁵ Formerly, only broad sulfur 2p (S(2p)) XPS spectra of SAMs were observed using a conventional X-ray source.^{1–6} Generally, S(2p) spectra of alkanethiol or dialkyl disulfide SAMs exhibit two strong peaks at around 162 eV (S(2p_{3/2})) and 163.2 eV (S(2p_{1/2})). Since the spectrum consists of (2p_{3/2}) and (2p_{1/2}) peaks with the intensity ratio of 2:1, which has been theoretically determined by spin-orbit splitting effect,^{10–12} the two peaks should be assigned to one species, that is, thiolate. Porter and co-workers observed an additional 161 eV peak with the strong 162 eV S(2p_{3/2}) peak after the C–S cleavage of 4-mercaptopyridine.²⁹ They simply assigned this 161 eV peak to atomic sulfur. On the other hand, we also observed 161 eV peak at the initial stage of octadecanethiol

SAM growth and assigned it to another sulfur state where molecular decomposition such as C–S cleavage did not occur.¹⁰ Castner et al. demonstrated that the S(2p) spectra is influenced from the presence of a physisorbed multilayer at around 163–164 eV (hereafter we simply call unbound sulfur),¹¹ whose peak position was almost identical to that of bulk thiol or disulfide.³⁷ In relation to Castner's work, some papers appeared concerning with the S(2p) peak at around 163–164 eV.^{12,38} On the other hand, the 161 eV peak appearance in the alkanethiol and dialkyl disulfide is not generally accepted, although the 161 eV peak is often observed in the high-resolution XPS data.^{18,29}

Moreover, the sulfur adsorption states of monosulfide and thiophene onto the Au surface is poorly understood compared with alkanethiol and dialkyl disulfide SAMs. It is reported that monosulfide monolayers exhibited similar S(2p) spectra to that of alkanethiol SAMs at around 162 eV.^{28,35} On the other hand, there is no report concerning XPS data when the thiophene was adsorbed onto the Au surface. To reveal the sulfur chemical states of such compounds on a Au surface, high-resolution XPS measurements are essential and these results would be helpful for understanding the XPS peak assignments of the alkanethiol SAMs.

In the present study, we focus on high-resolution XPS measurements of organosulfur monolayers on Au in the course of our SAM studies^{17–21} and conducted the following experiments: (1) To investigate the molecular dependence on the sulfur chemical states of adsorbed monosulfides and thiophenes on a Au(111) surface, we compared S(2p) XPS data of these monolayers; (2) We measured XPS data of monolayers made from alkanethiol, dialkyl disulfide, and aromatic thiol to reexamine the S(2p) spectra of these SAMs.

Experimental Section

Au-Deposition. An atomically flat Au (111) surface was epitaxially grown on mica by vacuum deposition under a base pressure of about 4×10^{-8} Torr. The mica was preheated at 440 °C for 4 h before deposition. The Au deposition rate was kept at 0.2 nm/sec. After the deposition, the substrate was annealed at 480 °C for 60 min to obtain a large terrace of the Au surface. The terrace of the Au surface checked by SPM was atomically flat over 200 nm.

Chemicals. We used the following molecules: nonanethiol (CH₃(CH₂)₈SH, C9SH), octadecanethiol (CH₃(CH₂)₁₇SH, C18SH), dioctyl disulfide (CH₃(CH₂)₇S–(CH₂)₇CH₃, H8H8), 2-[(perfluorohexyl)ethane]-octyl-disulfide (CF₃(CF₂)₅(CH₂)₂S–(CH₂)₇CH₃, F8H8), dioctyl sulfide (CH₃(CH₂)₇S–(CH₂)₇CH₃, C8SC8). The molecular structures of bithiophene, 2-bromothiophene benzyl mercaptane (BM), 4-biphenylmethanethiol (BP) and [1,1'-4',1'-Terphenyl]–4–methanethiol (TP) are shown in Chart 1. C9SH, C18SH, C8SC8, and benzylmercaptane were purchased from Aldrich. Bithiophene molecules were synthesized as described below. F8H8 unsymmetric disulfide with hydrocarbon and fluorocarbon chains was synthesized by an iodine oxidation of an equimolar mixture of octanethiol and 2-(perfluorohexyl)ethanethiol in ethanol.¹⁷ H8H8 disulfide was also synthesized by the same method.¹⁹ BP and TP synthesis methods were followed as described elsewhere.^{21,39}

Monolayer Formation. To prepare monolayers, the Au substrates were immersed in 1 mM solution for 24 h unless otherwise specified. The solvent used here was mainly ethanol. For C8SC8 and thiophene derivatives (bromothiophene and

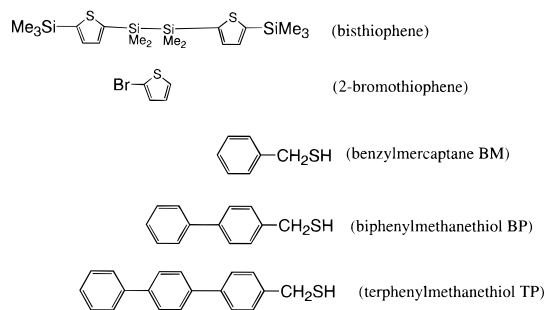
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Chart 1. Molecular Structures of Bisthiophene, 2-bromothiophene, Benzyl Mercaptane (BM), 4-biphenylmethanethiol (BP), and [1,1':4,1''-Terphenyl] – 4 – Methanethiol (TP)



bisthiophene), we used methylene chloride and chloroform as solvents, respectively. After removal from the solution, the Au substrates were rinsed with pure solvent to remove the physisorbed multilayer. For the C9SH monolayer, a 0.01 mM solution was used to control the coverage.^{2,7,16} Immersion times of 10 s, 1 min and 1 day were chosen. Annealing of monolayers was carried out at 100 °C for 8 h (in air) or 200 °C for 1 h (in the vacuum chamber of the XPS system). We confirmed that no oxidation of the molecules occurred in this annealing condition.

XPS Measurements. High-resolution XPS spectra were recorded using an ESCALAB 220iXL system (VG Scientific Inc.) with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV). The binding energy was calibrated using the Au ($4f_{7/2}$) peak energy (84.0 eV) as an energy standard. The X-ray power, the pass energy of the analyzer and the takeoff angle of the photoelectron were set at 180 W, 20 eV, and 90°, respectively. The energy resolution of this system is less than 0.6 eV, estimated by the Ag ($3d_{5/2}$) peak width at our measurement condition. All peaks were resolved by a mixture of Gaussian and Lorentzian, of ratio 4:1, using the spectral processing program in the XPS system. The coverage of the monolayer was estimated from XPS peak area and the value was normalized by a sensitivity factor of each element, 1.00, 1.19, and 9.58 for C(1s), S(2p), and Au($4f_{7/2}$), respectively.³⁷ In our system, the C(1s)/Au($4f_{7/2}$) ratios of the fully covered (long time immersed, more than 24 h) H8H8, C9SH, and C18SH are estimated to be 0.54, 0.60, and 1.25, respectively. The coverages or molecular densities of the monolayer were normalized by these values.

Recently, Schoenfish and Pemberton investigated the stability of alkanethiol SAMs on Au and Ag surfaces in air,⁴⁰ and they observed rapid oxidation of sulfurs in the monolayer. However, we confirmed using XPS that no oxidation of the sulfurs occurred under our annealing condition. If such a sulfur oxidation occurred by annealing or exposing to air for hours, we should have observed an oxidized sulfur (sulfonate) peak at around 167 eV. However, we only detected peaks in the range between 161 and 164 eV. Moreover, we could not detect any oxidized sulfur even after exposure to air for more than 10 days. For rapid oxidation, there must be uncharacterized factors such as ozone or UV, which do not seem to be sufficiently present in our environment.

Results and Discussion

1. S(2p) Spectra of Monosulfide and Thiophene Monolayers. Here we describe S(2p) spectra of organosulfur compound monolayers of monosulfide and thiophene. Figure 1 shows the S(2p) XPS spectra of a C8SC8 monosulfide monolayer prepared by 24 h immersion (Figure 1a); a bithiophene monolayer prepared by 24 h immersion (Figure 1b); and a Au surface immersed in bromothiophene solution for 24 h (Figure 1c). In the XPS spectrum of Figure 1a, we detected strong doublet peaks at 162.0 and 162.3 eV which were attributed to one sulfur species. On the other hand, we observed a broad S(2p) peak in the case of bithiophene SAM (Figure 1b).

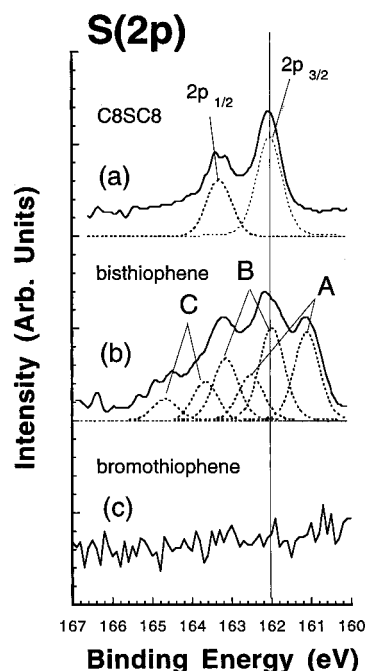


Figure 1. XPS spectra in S(2p) region of the (a) C8SC8 SAM (b) bisthiophene SAM; and (c) Au surface treated by bromothiophene solution. All the SAMs were prepared by immersion for 24 h into 1 mM solution. Hereafter, the upper and lower dotted line correspond to observed spectrum and resolved peaks, respectively. All the peaks were resolved by a mixture of Gaussian and Lorentzian, of ratio 4:1.

Hereafter, we resolve these spectra into the following six peaks attributed to three doublet peaks of mixture of Gaussian and Lorentzian: The lowest peaks were resolved into 161.1 and 162.4 ± 0.2 eV with the full width at half-maximum (fwhm) of 0.75 ± 0.05 eV (hereafter A peak); the major doublet peaks were resolved into 162.0 and 163.2 eV ± 0.1 eV peak with a fwhm of 0.75 ± 0.05 eV (hereafter B peak); the highest peaks were resolved into 163.7 and 164.7 ± 0.2 eV with a fwhm of 0.75 ± 0.05 eV (hereafter C peak).

First, we discuss the XPS spectra for the C8SC8 monosulfide monolayer (cf Figure 1a). Our C8SC8 monolayer exhibited strong doublet peaks which is almost identical to the typical alkanethiol or dialkyl disulfide SAMs.^{10,11} Recently, for the monosulfide monolayers, the problem concerning the C–S cleavage of one side alkyl chain has been examined.^{28,35,41–43} Zhong and Porter claimed for the first time that the side of C–S bonds in the monosulfide molecules with shorter alkyl chains or a phenyl ring cleaved on the Au surface during the SAM formation, because monosulfide monolayers exhibited this 162 eV B peak which was formerly assigned to alkylthiolate in the S(2p) XPS spectra.²⁸ Beulen et al. measured XPS spectra of the monosulfide (decyl sulfide C10) SAMs, and showed only a 162 eV S(2p_{3/2}) peak, which agrees with our and Porter’s data.³⁵ On the other hand, Beulen et al. reported that monosulfide molecules adsorbed onto the Au surface without the C–S cleavage of the side alkyl chain of monosulfide, because they detected a mass number attributed to monosulfide molecules as well as

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other mass numbers corresponding to adsorbed alkylthiolates in a time-of-flight secondary mass ion spectrum (TOF-SIMS).³⁵ We also measured TOF-SIMS, and confirmed the above results. (However, very recently, Porter and co-workers reexamined monosulfide adsorption phenomena onto the Au surface,⁴⁴ and then concluded that there was little possibility of C–S cleavage of one side alkyl chain in the monosulfide monolayer when well-purified monosulfide was used to form the monosulfide monolayer, i.e., impurities such as thiols strongly affect the character of monosulfide monolayers.)

From the area intensity of the XPS peaks, we found that excess sulfurs exist among the monosulfide SAMs, because the S(2p)/Au(4f_{7/2}) ratios of both the H8H8 and C8SC8 SAMs were almost the same (S(2p)/Au(4f_{7/2}) = 0.06 ± 0.05). The S(2p)/Au(4f_{7/2}) value of C8SC8 SAM should be 1/2 of that of H8H8 SAM, if C8SC8 SAMs adsorbed onto the Au surface simply as monosulfides with a same density of alkyl chains as alkanethiol SAMs. Hanley and co-workers reported a two-laser mass spectrometric study of alkanethiol, dialkyl disulfide, and dialkyl sulfide monolayers and concluded that there is an impurity effect on mass spectra for monosulfide monolayers,⁴¹ that is, the impurity originated from alkanethiol or dialkyl disulfide in solution adsorbed on gold with dialkyl sulfide and it therefore generated mass numbers corresponding to alkanethiol or dialkyl disulfide in TOF-SIMS spectra. Jung et al. also investigated the impurity effect on dialkyl sulfide SAMs using XPS and gave similar suggestions.⁴² It seems to be contradictory that XPS can observe only one sulfur species, while TOF-SIMS detected both the thiolate and monosulfide.

To explain the above results, we assume that the 162 eV binding energy of the B peak can be produced without C–S cleavage in the monosulfide SAMs, that is, the sulfurs in the monosulfide could bind onto the Au surface in the same configuration as alkylthiolate without C–S cleavage and could exhibit 162 eV B peak. It is well known that an XPS binding energy shift is caused by: (1) an electronegativity difference between the elements; (2) an interaction between molecule (sulfur) and metal surface even in the case of physisorption.⁴⁵ For example, when the sulfur bound other elements such as oxygen which has larger electronegativity than sulfur, the S(2p) binding energy become higher value, for example, the S(2p_{3/2}) peak of bulk alkanethiol and sulfonate species at 163–164 and 167–168 eV, respectively.³⁷ On the contrary, if it is the sulfur attached metal which has lower electronegativity, the S(2p) binding energy would decrease. In the case of alkanethiol SAMs, it has been considered that the binding energy shift from 163 to 162 eV is caused by such an interaction between the sulfur and Au (chemical bond formation).

On this basis, in the case of sulfur in the organosulfur compounds, the sulfur binding energy is mainly determined by (1) the electronegativity difference between the sulfur and carbon, and (2) the interaction between sulfur and the Au surface. For example, when monosulfide adsorbed onto a Au surface with a similar interaction between sulfur and Au, the structural difference between alkyl thiolates and monosulfides is the presence of an additional C–S bond in monosulfides. Interestingly, since sulfur and carbon have almost the same electronegativity,

ity,⁴⁶ the C–S bond should be electrically neutral. This same electronegativity could well explain the fact that the S(2p) binding energy of bulk materials of thiols, disulfides, and monosulfides are almost the same.³⁵ Furthermore, we observed a 162 eV B peak as well, in the case of monosulfide monolayers. If we assume the interaction between the sulfur and Au surface of monosulfide monolayer was identical to that of alkanethiol SAMs, the 162 eV peak formation could be explained by the same reason (cf. Figure 2).

Recently, Beulen et al.⁴⁷ detected a 163 eV rich S(2p) spectra of monosulfide with cyclodextrin structure, contrary to previous data of monosulfide monolayers. We also observed similar 163 eV rich S(2p) spectra of monosulfide monolayers with longer alkyl chains (octadecyl monosulfide, C18SC18) prepared by shorter immersing time (less than 6 h), and further confirmed that the S(2p) spectra gradually changed into 162 eV B peak rich spectra.⁴³ This discrepancy might be due to molecular structure. In the case of the longer alkyl chain monosulfide, the monolayer behaves like an LB film and needs few binding points because the van der Waals interaction is stronger than in a shorter monosulfide like a C8SC8, that is, all the sulfur do not necessarily bind on the Au surface. Thus, we consider that the 163 eV rich spectra simply indicated the presence of unbound sulfur among the monolayer, because of the weak reactivity of monosulfide molecules. Further study of monosulfide SAMs with more of the longer alkyl chains and the S(2p) spectra transition phenomena will be described in another paper.⁴³

Second, we discuss S(2p) spectra of bithiophene on the Au surface for comparison. In the S(2p) XPS spectrum of the bithiophene monolayer (Figure 1b), we observed a broad S(2p) spectrum consisting of three sulfur species, which appear in almost the same peak positions as those of alkanethiol and dialkyl disulfide SAMs. The reason for the generation of these same peaks was described above. We obtained a similar S(2p) spectrum in the case of tetrathiophene derivatives as well (data are not shown). This complicated spectrum indicated that the bithiophene can generate the 161 eV A peak. Since the thiophene ring is expected to be stable on the Au surface, spontaneous decomposition is unlikely.⁴⁸ Thus, this S(2p) spectrum of bithiophene SAM is evidence that the adsorbed sulfur in the organosulfur molecule can show the 161 eV peak without molecular decomposition.

We also detected a peak at around the 163 eV C peak in the S(2p) spectrum of the bithiophene monolayer. Two sulfur states have been assigned to the C peak. Castner et al.¹¹ pointed out that physisorbed molecules on the monolayer exhibit this peak. Recently, Rieley et al. concluded that dithiol molecules could generate the same 163 eV peak as well as a 162 eV bound sulfur peak.⁴⁹ They concluded that one side sulfur of dithiol does not bind onto the Au surface, and show the C peak, while another bound sulfur exhibits the B peak. In the bithiophene SAMs, there are two sulfurs in the bithiophene molecules (cf. Chart 1). It seems to be that one side sulfur of

(44) Zhong, C.-J.; Robert, C. B.; Andereg, J.; Porter, M. D. *Langmuir* **1999**, *15*, 518.

(45) For example, Kaindl, G.; Chiang, T.-C.; Eastman, D. E.; Himpsel, F. J. *Phys. Rev. Lett.* **1980**, *45*, 1808.

(46) For example, electronegativities are shown in the following book. Atkins, P. W. *Physical Chemistry*, 2nd ed.; Oxford University Press: London, 1982. According to this book, the electronegativities of the sulfur and carbon are 2.58 and 2.54, respectively.

(47) Beulen, M. W. J.; Bügler, J.; Lammerrink, B.; Geurts, F. A. J.; Biemond, E. M. E. F.; van Leerdam, K. G. C.; van Veggel, F. C. J. M.; Engbersen, J. F. J.; Reinhoudt, D. N. *Langmuir* **1998**, *14*, 6424.

(48) Scoles and co-workers reported that the thiophene ring can be adsorbed on the Au surface by TDS method.³³ On this basis, thiophene ring decomposition, i.e., spontaneous C–S cleavage, is unlikely on a Au surface.

(49) Whelan, C. M.; Smyth, M. R.; Barnes, C. J.; Brown, N. M. D.; Anderson, C. A. *Appl. Surf. Sci.*, **1998**, *134*, 144.

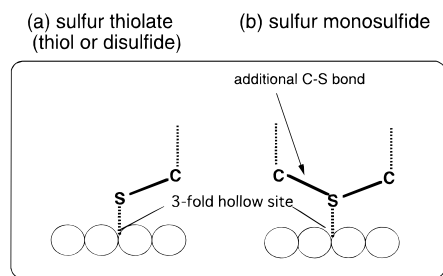


Figure 2. Schematic drawing of sulfur arrangements on a Au (111): (a) sulfur in alkanethiol SAMs; (b) sulfurs in monosulfide SAMs. An additional C–S bond formation does not affect the S(2p) binding energy, because the C–S bond is electrically neutral, sulfur and carbon having almost the same electronegativity.⁴⁷

bisthiophene is not bound to Au surface, exhibiting the C peak, while another bound sulfur generates the B peak, similar to the case of dithiol. The molecular arrangement of bisthiophenes on the Au surface is not revealed yet. It should be noted that the bisthiophenes cannot form an intact monolayer, because the structure of the bisthiophene molecule is complicated. Therefore, we consider that there should exist some possible sulfur states among the S(2p) spectra.

Dishner et al. obtained a clear STM image of adsorbed monothiophenes on Au(111) surface,³⁶ and reported that the single thiophene ring can form a stable monolayer in air. However, we could not obtain clear S(2p) peaks in the bromothiophenes adsorbed onto the Au surface (Figure 1c). Bromothiophene molecules might be so weakly adsorbed that they desorbed by introduction into the XPS vacuum chamber. This suggested that more than two thiophene rings are necessary to form a stable monolayer on the Au surface under a vacuum condition.

In concluding this section, when the monosulfides and thiophenes adsorbed on a Au surface, the S(2p) peaks appeared between 161 and 164 eV, and exhibited almost the same peaks as those of alkanethiol and dialkyl disulfide monolayers.

2. S(2p) Spectra of the Alkanethiol and Dialkyl Disulfide SAMs. For the alkanethiol and dialkyl disulfide SAMs, a 161 eV A peak is observed in specific cases as well as the 162 eV B peak. Figure 3 shows a series of S(2p) spectra of C9SH, prepared by immersion into 0.01 mM diluted solution. For the SAM prepared by 10 s immersion, corresponding to the molecular coverage of about 30% estimated from the STM image in this case,⁵⁰ three peaks appeared as shown in Figure 3a. This spectrum was resolved into the four peaks which correspond to the A and B peaks as described in Section 1. After immersion for 1 min, corresponding to the coverage of 80% estimated from the C/Au values, the peak around 161 eV disappeared in the S(2p) spectrum. We observed doublet peaks of B in the S(2p) region (Figure 3b). For the full-coverage SAM prepared by dipping into the 0.01 mM C9SH solution for 1 day, the S(2p) spectrum was almost the same as Figure 4b (Figure 3c). These results indicate that the presence of the A peak is characteristic of extremely low-coverage SAMs.¹⁰ The A species did not reappear when the SAM immersed for 24 h was annealed at 100 °C for 8 h in air as shown in Figure 3d. However, when the 70% coverage SAM prepared by immersion of 24 h into 0.01 mM

(50) For the low-coverage alkanethiol SAMs with a shorter alkyl chain, it is difficult to estimate exact coverage from the C/Au area intensity ratio because of the presence of contaminant on the Au surface (ref 8). Thus, we measured coverage using the STM image of this C9SH SAM prepared by 10 s immersion.

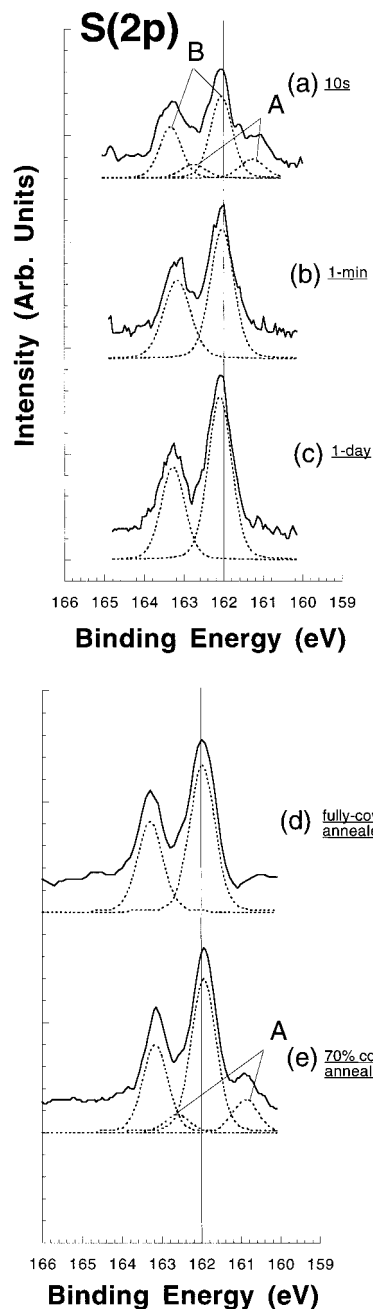


Figure 3. XPS spectra in S(2p) region of the C9SH SAMs. The surface conditions are as follows: (a) partial covered SAM prepared by the immersion for 10 s in 0.01 mM solution; (b) partial covered SAM prepared by the immersion for 1 min in 0.01 mM solution; (c) fully covered SAM prepared by more than 1 day immersion; (d) fully covered SAM (c) after annealing at 100 °C for 8 h; (e) partially covered SAM after annealing at 100 °C for 8 h, prepared by more than 1 day immersion. The partly covered C9SH SAM was accidentally formed when the SAM was prepared by the same procedure.

solution⁵¹ was annealed under the same conditions in air, the A peak reappeared as shown in Figure 3e, although the A peak was not detected before annealing. As clearly seen in Figure 3, the A peak is reproducibly observed in the high-resolution XPS spectra of alkanethiol SAMs prepared under the same conditions.

Table 1 summarizes the results of the A and B peaks obtained in alkanethiol and disulfide SAMs.^{10,25} In all the

(51) Even after immersion for 24 h into 0.01 mM C9SH solution, we often obtain a sample whose coverage is about 70%.

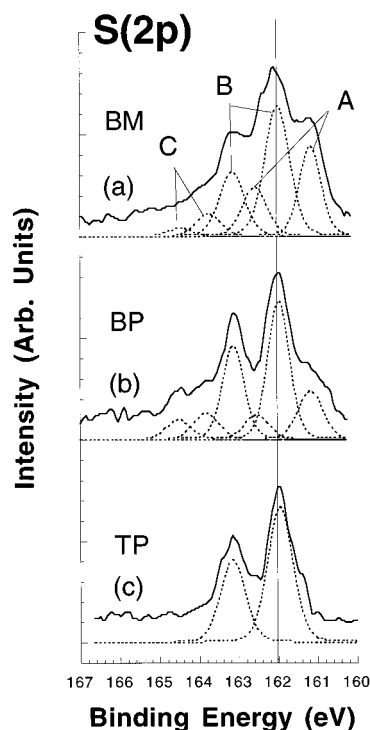


Figure 4. XPS spectra in S(2p) region of aromatic derivative thiol SAMs of (a) BM; (b) BP; and (c) TP SAMs. All the SAMs were prepared by immersion for 24 h into 1 mM solution. At around 161 eV, shoulder peaks were seen in (a) and (b).

Table 1. Molecular Dependence of Peak Presence of A and B Peaks of Alkanethiol or Dialkyl Disulfide SAMs. In All S(2p) Spectra, S(2p_{3/2}) Peak Positions of A and B Peaks Were Observed at 161.0 ± 0.3 and 162.0 ± 0.1 eV, Respectively. ○, × Indicate Presence, Absence of Peaks, Respectively

molecule	conditions ^a	Presence of Peaks ^b	
		A (161 eV)	B (162 eV)
C18SH (cf ref 10)	1 min immersion (50%)	○ (strong)	○
	1 h immersion (100%)	×	○
	1 day immersion (100%)	×	○
	annealed in vac at 200 °C (50%)	○ (strong)	○
C9SH	10 sec immersion (30%)	○ (weak)	○
	1 min immersion (80%)	×	○
	1 day immersion (100%)	×	○
	annealed in air (100%)	○ (weak)	○
	annealed in air (70%)	○ (weak)	○
H8H8	1 day immersion (100%)	×	○
	annealed in air (100%)	×	○
	annealed in air (80%)	○ (weak)	○
F8H8 ^c (cf ref 17)	1 day immersion	×	○
	annealed in air	○ (weak)	○
F8H8+ H8H8 ^c (cf ref 19)	1 day immersion	×	○
	annealed in air	○ (weak)	○

^a In these conditions, coverage values of C18SH, C9SH and H8H8 SAMs were noted. Values were normalized by the value of SAMs prepared immersion for 1 day. ^b Intensities of A peak were noted. When the relative area intensity of A peak to B peak more than 50%, we noted strong. In other weak case, the relative area intensity of A peak to B peak is c.a. 10%, we noted weak. ^c The molecular density of containing fluorocarbon chains the SAMs immersed for 1 day is estimated to be approximately 80% of that of H8H8 SAMs.

S(2p) spectra, the S(2p_{3/2}) peak position of the A and B peaks were observed at 161.0 ± 0.3 and 162.0 ± 0.1 eV, respectively. In the XPS spectra, an A peak was found when the C9SH and C18SH SAMs annealed in a vacuum for 1 h at 200 °C, corresponding to a coverage of

approximately 50%.¹⁰ The 161 eV A peak was also observed when the low-molecular density alkanethiol or disulfide SAM (cf. Figure 4e, with approximately 70–80% coverage) was annealed at 80–100 °C for 8 h in air. On the other hand, when the fully covered alkanethiol SAM was annealed at the same temperature, the A species peak did not appear (cf. Figure 3d). This tendency is observed in the case of annealed SAMs which contain fluorocarbon chains.^{17–19} AFM observations and C(1s) XPS peak intensity showed that fluorocarbon SAMs exhibited a lower molecular density than hydrocarbon SAMs.⁵²

3. S(2p) Spectra Dependence on the Molecular Species-Aromatic-Derivatized SAMs. Since the aromatic derivatized thiols are highly expected to be conductive molecules, we²¹ and Weiss and co-workers⁵³ investigated the molecular electrical conductance measurements of such aromatic molecules implanted into insulative *n*-alkanethiol SAMs using SPM. Sabatini et al.⁵⁴ and Tao et al.⁵⁵ evaluated the structure of these aromatic derivatized thiols with SPM or electrochemical measurements and concluded that the structure and molecular densities of these SAMs are dependent on the number of the aromatic rings and substituted groups.

Figure 4 shows the S(2p) XPS spectra of aromatic derivatized thiol SAMs prepared by 24 h immersion. Interestingly, we observed a clear A peak at around 161 eV in the spectra of BM and BP SAMs (Figures 4a and 4b). On the other hand, the A peak is very weak in the case of the TP SAM (Figure 4c). These XPS data indicated that the peak area intensity of the A peak decreased with the number of phenyl rings. Sabatini et al.⁵⁴ and Tao et al.⁵⁵ concluded that the molecular density of aromatic thiol SAMs is increased with the increase in the number of phenyl rings, as observed by electrochemical measurements. We compared the molecular density based on the C/Au ratios of these aromatic thiol SAMs. The C/Au ratios of BM, BP, and TP were estimated to be 0.24, 0.75, and 1.2, respectively, whose values correspond to those of C3SH, C10SH and C18SH alkanethiol SAMs. If these aromatic thiol SAMs arranged with $\sqrt{3} \times \sqrt{3}$ R 30°,⁵¹ the C/Au values of BM, BP, and TP should be identical to those of C7SH, C13SH, and C19SH. This is especially so in the case of BP which has only one phenyl ring, and cannot form an intact monolayer. This is consistent with the data by Sabatini et al.⁵⁴ Our data also confirmed that the molecular density of aromatic thiol SAMs is increased with the number of phenyl rings. Thus, the A peak intensity is dependent on the molecular density on the Au surface.

4. Summary of the S(2p) Peak Assignments. In this section, we summarize our XPS results and discuss possible S(2p) peak assignments. Figure 5 shows a schematic drawing of a possible S(2p) peak on the Au surface. At 163–164 eV, the unbound sulfur is observed whose value is almost the same as that of the bulk peak position (cf Figure 5a). At 162 eV, we observed a bound sulfur peak (cf Figure 5b). An interaction (or chemical

(52) In refs 23 and 24, the lattice parameter of fluorocarbon SAMs was estimated to be 0.58 nm which is larger than that of alkanethiol SAMs (0.5 nm). We also confirmed that the C/Au ratio of fluorocarbon SAMs was about 0.45–0.50 which correspond to approximately 80% of that of H8H8 SAMs with same alkyl chain length.¹⁷

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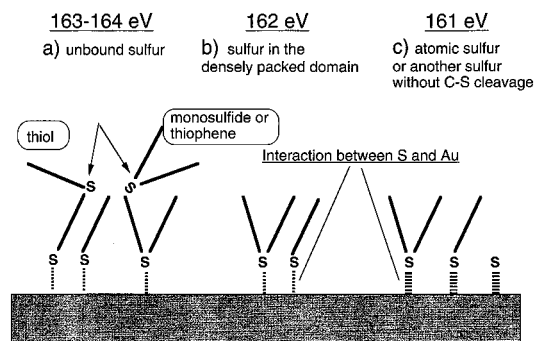


Figure 5. Schematic drawing of sulfur arrangements on a Au (111) of organosulfur monolayers: (a) unbound sulfurs; (b) bound sulfurs which cause the 162 eV B peak; (c) atomic sulfur or another bound sulfur with a binding energy of 161 eV.

bond formation) between the sulfur and the Au surface decreases the S(2p) binding energy. At 161 eV, the A peak was observed in particular conditions (cf Figure 5c). It should be noted that there is no strong dependence of the S(2p) peak position on the molecular species. The reason for this lack of dependence of S(2p) peak position on the molecular species is considered to be that an additional C–S bond formation of monosulfide or thiophene does not affect the S(2p) binding energy as mentioned before.

Here we discuss the A peak. Some of the features that we can conclude from Figures 1, 3, and 4 and Table 1 are as follows: (1) Some aromatic derivatized thiol SAMs exhibit the A peak; (2) In the case of alkanethiol or dialkyl disulfide SAMs, the A peak at around 161 eV was observed under one of the following conditions: (a) after annealing in a vacuum at higher temperatures; (b) in a low-coverage SAM after annealing in air; and (c) at the initial stage of SAM growth.¹⁰

There are two possible A peak assignments: (1) atomic sulfur²⁹ (2) another bound sulfur without molecular decomposition. In particular conditions, we agree with the presence of atomic sulfur. For example, in the case of vacuum annealing of SAMs at higher temperatures molecular decomposition should occur.^{10,49} However, in other cases where the A peak appeared as shown in the paper (cf Figures 1, 3, and 4 and Table 1), it is unlikely that the organosulfur molecules decompose on the Au surface at the above conditions (at room temperature on the Au surface). The appearance of the A peak in the bithiophene monolayer supported this assumption, because thiophene ring is stable on the Au surface.

Why is the A peak formed on the Au surface without molecular decomposition? To decrease the binding energy, there should be stronger interaction between the A peak sulfur and the Au surface than between the B peak sulfur and the Au (cf Figure 5c). Possible reasons are: (1) hybridization change;⁵⁶ (2) site difference; (3) defect or step effect;³⁰ (4) striped (lying down) phase formation etc.;^{13,15} (5) impurity of atomic sulfur.

Hybridization change is the likely cause of the peak shift.⁵⁶ For example, Leavitt and Beebe reported that the S(2p) binding energy of the sp^3 hybridized sulfur is about 1.0 eV higher than that of the sp hybridized sulfur in the case of H_2S adsorption onto a Au surface. IR–RAS measurements clearly imply a preference of sp^3 hybridization in the sulfur atoms in the case of fully covered alkanethiol SAMs, because the terminal methyl group of alkanethiol strongly appeared in the IR–RAS spectrum.⁵⁷

For example, if we assume that the S(2p_{3/2}) binding energy of sp^3 hybridized sulfur exhibits a 162 eV B peak, the binding energy of sp sulfur is estimated to be about 161 eV, which agrees with the A peak binding energy.

In another case, the site difference might change the S(2p) binding energy. It is generally accepted that the sulfurs of alkyl thiolate locate on the 3-fold hollow site of the Au(111) surface in the ordered domains of fully covered SAM.³² The isolated molecules outside of the ordered domains could adsorb onto other sites, such as bridge or on-top sites. Since the interaction between the sulfur orbital and Au surface depend on the site, the site change effect is also likely to be the reason for the A peak formation.

On the other hand, a defect or step effect³⁰ is not the likely cause of the A peak because we utilize an atomically flat Au surface. Sulfurs in the striped phase do not cause the A peak, either, because it was reported that the XPS S(1s) binding energies of the striped phase sulfurs and sulfurs in the ordered domains are identical.⁵⁸ Therefore, the sulfurs in the striped phase may exhibit the 162 eV B peak in the S(2p) region. It is difficult to deny the impurity effect. However, when we used well-purified molecules we often observed A peak, suggesting that A peak is not formed only by the presence of impurity.

However, at this moment, clear peak assignment for the A peak is impossible. To reveal the real structure at the Au–S interface, further study using more sensitive methods which could provide the exact location of sulfur atoms, for example, the X-ray fine adsorption structure method or electrochemical measurement, are essential.

Conclusions

We measured the S(2p) spectra of the SAMs on a Au (111) surface in order to investigate the S(2p) peak formation. These are summarized as follows.

1. The monosulfide SAM exhibited almost the same S(2p) XPS spectra as the typical alkanethiol or dialkyl disulfide SAMs. We consider that the 162 eV binding energy of the S(2p) spectra of the monosulfide SAMs was explained by considering it to be the case that the sulfurs were bound onto the Au surface without C–S cleavage of one side alkyl chain of monosulfide. Also, bithiophene SAMs showed S(2p) peaks at 161–164 eV. As a result of peak fitting, the thiophene derivative also exhibited almost the same peaks as those of alkanethiol and dialkyl disulfide monolayers. Therefore, there is no strong dependence of the S(2p) peak position on the organosulfur species. The reason for the lack of dependence of S(2p) peak position on the organosulfur species is considered to be that an additional C–S bond formation of monosulfide or thiophene does not affect the binding energy.

2. We also examined the S(2p) XPS spectra of alkanethiol, dialkyl disulfide, and aromatic derivatized thiol monolayer SAMs. The A peak at around 161 eV was observed under one of the following conditions: (a) after annealing in a vacuum at higher temperatures; (b) in a low-coverage SAM after annealing in air; and (c) at the initial stage of SAM growth. These XPS data indicated that the peak area intensity of A peak at around 161 eV depended on the molecular density. We considered that there are two possible assignments for A peak at 161 eV, ‘atomic sulfur’ and ‘another sulfur without molecular decomposition.’ In the case of sulfur without molecular decomposition, several formation mechanisms are con-

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sidered. However, at this moment, clear peak assignment for A peak is impossible.

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