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Formation of a mixed monolayer on a gold surface using fluorobenzenethiol and alkanethiol

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Mixed monolayers consisting of 4-fluorobenzenethiolate and 1-octadecanethiolate on Au surfaces were formed by immersing in an ethanol solution of 4-fluorobenzenethiol (FBT), and subsequently by immersing in that of 1-octadecanethiol (ODT). To obtain systematically a mixed monolayer, the formation of FBT- and ODT-monolayers was investigated with respect to the reaction time and concentration of the solution. The monolayer formed on a Au surface was evaluated based on the work function, the water contact angle, and the X-ray photoelectron spectroscopy (XPS) spectra measured. The XPS measurement of substrates prepared for formation of a mixed monolayer exhibited F 1*s* and C 1*s* spectra supporting the presence of a mixed monolayer consisting of 4-fluorobenezenethiolate and 1-octadecanethiolate.

1. Introduction

The surface properties of a metal modified with organic thiols such as alkanethiol[1-5] and aromatic thiols[6-10] strongly depend on the thiol used for the modification. The surface modification, resulting in a monolayer formation, has been attracting attention not only as scientific interest but also as application to organic devices.[11-14]

Metal electrodes modified with benzenethiol derivative have been actually used to improve device performance of organic transistors[15-19] and organic light-emitting diodes.[20] A monolayer formed on a metal surface induces the work function change on the surface according to the dipole moment in molecules composing the monolayer.[20-25] The work function change improves the carrier injection from a metal electrode into an organic layer, and contributes to the improvement of device performance. Surface modification also has the influence on wettability[25-30] and chemical reactivity.[31,32] Changes in surface properties are related to changes in surface energy induced by monolayer formation. It is possible that such a monolayer with a different surface energy results in selective adsorption of gas molecules. In fact, Au nanoparticles covered with various thiols have been used for selective gas sensing.[33]

It is possible that the use of a mixed monolayer containing two kinds of thiols provides complex surface and enables the fine control of the surface properties. Whitesides *et al*. and Shimazu *et al*. have reported mixed monolayers formed by two kinds of molecules with an alkyl chain.[34-37] On the other hand, Caprioli et al. have investigated the formation of mixed monolayer consisting of two kinds of benzenethiol derivatives.[38] It is expected that a mixed monolayer formed from alkanethiol and benzenethiol derivative provides more complex surface with molecular scale roughness, and broadens scope of the application. We have proposed designable formation of a mixed monolayer based on reaction rate of a kind of thiol onto a surface. [39]

In this paper, we report the formation of a mixed monolayer on SiO_2/Si substrates with a Au layer using benzenethiol derivative and alkanethiol in detail. The mixed monolayer was formed by immersing in an ethanol solution of 4-fluorobenzenethiol (FBT), and subsequently by immersing in that of 1-octadecanethiol (ODT). The work function W of a substrate covered with a FBT- or ODT-monolayer is shown as a function of the product of immersion time t_R and concentration of the solution C. This relation between W and t_RC is used to determine a t_RC value suitable for formation of a mixed monolayer. The work function of the substrate prepared under a condition that a mixed monolayer will be obtained is also shown. Water contact angles on FBT-monolayers, ODT-monolayers, and a

mixed monolayer are examined as a surface property. X-ray photoelectron spectroscopy (XPS) spectra for the substrates with a monolayer are shown to confirm atoms present on the surface.

2. Experimental methods

Figures 1(a) shows the schematic illustration of a Si substrate with a mixed monolayer formed on a Au layer, intended to be obtained in this study. Figures 1(b) and 1(c) are the chemical structures of FBT and ODT used for the mixed monolayer, respectively. We selected an alkanethiol with a long chain and a benzenethiol derivative to construct structure of molecular scale on a metal surface. Although any benzenethiol would be used to achieve the purpose, we chose FBT having a fluorine atom to be detected by XPS.

The substrate has 60-nm-thick Au and 5-nm-thick adhesive Cr layers deposited by thermal evaporation at room temperature onto a SiO_2/Si substrate. The substrate was pre-annealed on a hot plate at 473 K for 10 min in a dry-nitrogen filled glovebox to improve the stability. The resulting substrates were then stored in the glovebox until required for surface modification. Before formation of a monolayer, the substrate was cleaned in 2-propanol with an ultrasonic cleaner, and was exposed to UV/ozone for removing carbon contaminations. Then, the substrate was immersed in ethanol for 10 min. The substrate was used for measurement of water contact angle and work function as a Au bare substrate. The immersion into ethanol is expected to contribute to reproducibility of monolayer formation and surface properties. UV/ozone treatment causes formation of AuO_x, which leads to an increase of the work function.[19] AuO*x* is unstable and gradually decomposes at room temperature.[40] The immersion promotes the decomposition of AuO_x into Au. This is why the immersion in ethanol was added for preparation of a Au bare substrate.

To obtain FBT- and ODT-monolayers, a substrate with a Au layer cleaned was immersed in an ethanol solution containing FBT or ODT with C for t_R. The C value was in the range from 1 μmol/L to 10 mmol/L, and t_R was in the range from 1 to 10 min.

For formation of a mixed monolayer, a substrate with a Au layer cleaned was immersed in an ethanol solution of FBT of C = 1−10 μmol/L for t_R = 1−10 min. Subsequently, the substrate was immersed in an ethanol solution of ODT of C = 10 μmol/L for t_R = 10 min. ODT has a long alkyl chain. Thus, if a ODS-monolayer were formed at first, the long alky chain would disturb the formation of a FBT-monolayer. Therefore, we performed the reaction of FBT at first for formation of a mixed monolayer. All monolayer formation was performed in air at room temperature of about 300 K.

For measurement of water contact angle, de-ionized water was used as a liquid. The volume of a water droplet is about 2 μL, which is small enough to exclude the influence of gravity. The image of a water droplet on a substrate was captured with a digital microscope, and was used to measure the dimensions of the droplet. Water contact angle was calculated from the dimensions. The work function of substrates with a monolayer was measured with an atomospheric photoelectron spectrometer (Riken Keiki AC-2). The XPS spectra of surfaces with a monolayer were measured by a PHI-X-tool (ULVAC-PHI) with a monochromatized Al Ka X-ray source. The Au 4*f*7/2 lines obtained without calibration had a peak at 83.94−83.99 eV, which is close to 83.95 eV expected as a peak of a Au 4*f*7/2 line.[41] Thus, we did not perform additional calibration to the binding energy scale of XPS spectra.

3. Results and discussion

3.1 Work function

When dipoles with a moment **d** are placed on a plane surface at an area density N, the dipole changes the work function on the surface W. The work function change ΔW is given by

$$\Delta W = \frac{qN|\mathbf{d}|\cos\alpha}{\varepsilon} \quad (1)$$

where q is the elementary charge, α is the average angle of the dipole direction relative to the surface normal downward vector, and ε is the permittivity of the molecule layer.[42] When the positive (negative) charge of the dipole is placed on the surface, cos α is positive (negative). The N value can be calculated from W measured if $|\mathbf{d}|$, α and ε values are known.

The progress of a monolayer formation was examined by measurement of W. The work function of a Au bare surface without monolayer, W_0, was about 4.83 eV. The value is used as a reference. UV/ozone treatment to Au surface has leaded to increases up to 5.5 eV.[19] Thus, the value of 4.83 eV obtained in this study supports effect of the immersion into ethanol about decomposition of AuO_x. Figure 2 shows W measured for the substrates with FBT- and ODT-monolayers formed on a Au layer. The work function change ΔW can be written as

$$\Delta W = \Delta W_{\mathrm{SAT}}\left[1 - \exp(-k_{\mathrm{A}} t_{\mathrm{R}} C)\right] \quad (2)$$

where $\Delta W_{\mathrm{SAT}} = W_{\mathrm{SAT}} - W_0$, , W_{SAT} is the work function saturated at large $t_{\mathrm{R}}C$, and k_{A} is the association constant for the adsorption of the molecule.[43] Thus, the W value in Fig. 2 is plotted as a function of $t_{\mathrm{R}}C$. The W measured for a FBT-monolayer gradually increases with

an increase of $t_R C$. The increase indicates that the positive charge of the dipole moment in FBT is placed on the Au surface. The W value is saturated toward about 5.18 eV. This value is close to 5.21 eV obtained in our previous work, though the substrate preparation is slightly different from that in this study.[24] On the other hand, the W measured for an ODT-monolayer gradually decreases with $t_R C$. The decrease indicates that the negative charge of the dipole moment in ODT is placed on the Au surface. The W value is saturated toward about 4.50 eV. The solid line in Fig. 2 is a curve to fitting to the plots using Eq. (2). From the fitting, k_A is estimated to be 1776 s^{-1} mol^{-1} L for FBT and 1126 s^{-1} mol^{-1} L for ODT. These values are much large as compared to 106 s^{-1} mol^{-1} L for PFBT and 386 s^{-1} mol^{-1} L for MBT reported in Ref. 24. The comparison shows that the formation of FBT- and ODT-monolayers proceeds rapidly as compared to previous work. The UV/ozone cleaning adopted before the monolayer formation may contribute to the high reaction rate.

Figure 3 shows W measured on substrates prepared for formation of a mixed monolayer. The horizontal axis is $t_R C$ for formation of a FBT-monolayer. The data for a single FBT-monolayer shown in Fig. 2 is re-plotted with a fitting curve in Fig. 3. The second treatment for a mixed monolayer formation was performed by immersing in an ethanol solution of ODT of C = 10 μmol/L for t_R = 10 min. The W measured for a single ODT-monolayer formed under the condition of $t_R C$ = 100 μ min mol/L is also plotted with a dashed line in Fig. 3. The W measured on substrates prepared for formation of a mixed monolayer is between the fitting curve and dashed line at a value of $t_R C$. It is expected that ODT molecules adsorb on a Au surface uncovered with 4-fluorobenzenethiolate and the Au surface is partially covered with 4-fluorobenzenethiolate and 1-octadecanethiolate. This result of the W measured supports the expectation.

3.2 Area density of molecules

For estimation of N, we calculated the dipole moment of FBT and ODT based on density functional theory DFT, using the Gaussian 09 software package with the B3LYP method and LanL2DZ basis set.[44] The direction of dipole moment calculated are roughly shown as an arrow with the |**d**| value in Figs. 1(b) and 1(c). The value of |**d**| is 1.35 debye (D) for FBT and 2.12 D for ODT.

Here, we estimate area densities for a FBT-monolayer (N_{FBT}) and for an ODT-monolayer (N_{ODT}) from the work function saturated at large $t_R C$. In order to estimate N, it is necessary to assume a value of α. When assuming that α = 0, 30, and 60° for FBT, N_{FBT} values are estimated to be 2.12×10^{14}, 2.45×10^{14}, and 4.25×10^{14} cm^{-2}, respectively. When assuming that

α = 180, 150, and 120° for ODT, N_{ODT} values are estimated to be 1.20×10^{14}, 1.39×10^{14}, and 2.40×10^{14} cm^{-2}, respectively. The values were obtained by assuming that the relative permittivity for Eq. (1) is 3.0 for the estimation.[45] Here, we refer N values estimated for monolayers formed on Au surfaces by use of various benzenethiols[24,25] in order to evaluate the N value obtained in this study. The N values for earlier works were in the range from 2.3×10^{13} to 1.86×10^{14} cm^{-2}. The N_{FBT} and N_{ODT} values are slightly large as compared to those in previous reports. In Refs. 24 and 25, |**d**| obtained from a molecule with a S-Au group instead of a S-H group was used for the estimation. The |**d**| value is larger than that of the original molecule with a S-H group. The difference in the |**d**| value may cause the difference in the N estimated.

The atomic density on a Au(111) surface is calculated to be about 1.38×10^{15} cm^{-2} from the lattice constant. The N_{FBT} value suggests that a 4-fluorobenzenethiolate constructing the FBT-monolayer is approximately present on a surface area consisting of three to seven Au atoms. On the other hand, the N_{ODT} value suggests that a 1-octadecanethiolate doing the ODT-monolayer is approximately present on a surface area consisting of six to twelve Au atoms.

The area densities for 4-fluorobenzenethiolate and 1-octadecanethiolate in a mixed monolayer are roughly estimated from Fig. 3. The difference between the work function for a FBT-monolayer and that for a mixed monolayer at a t_RC is in the range from 0.265 and 0.368 eV. The ΔW for an ODT-monolayer at large t_RC is about 0.35 – 0.38 eV. Thus, ODT treatment for a mixed monolayer provides formation of 1-octadecanethiolate with an area density of $0.7N_{ODT}$ to N_{ODT} ,which are expected from 0.265 eV/0.38 eV≃ 0.70 and 0.368 eV/0.38 eV≃ 0.98. In the same way as the estimation, a mixed monolayer prepared at t_RC = 10 μ min mol/L approximately has area densities of $0.5N_{FBT} = 1.3\times10^{14}$ and $N_{ODT} = 1.4\times10^{14}$ cm^{-2}, for example. The area density corresponds to that one 4-fluorobenzenethiolate and one 1-octadecanethiolate are present on a surface area consisting of ten Au atoms.

3.3 Water contact angle

The measurement of water contact angle is an effective method to know the change of surface condition at molecular scale as the change of micro scale phenomenon.[25] The contact angle of a water droplet on a substrate θ can be calculated using

$$\theta = 2\tan^{-1}\left(\frac{2H}{L}\right) \qquad (3)$$

where H and L are the height and the length in the contact side of the droplet, respectively. The contact angle of a surface consisting of two different kinds of regions with contact angles θ_1 and θ_2 is given by

$$\theta = f \cos \theta_1 + (1 - f) \cos \theta_2 \quad (4)$$

where f and $(1 - f)$ are the occupation ratios of the two regions.[28,46] Measurement of the contact angle for a metal surface partially covered with a thiol provides the percentage of the covered region if the contact angle for a surface fully covered with the thiol and that for a bare metal surface are known.[30] In this study, a surface covered with a monolayer prepared with a large $t_R C$ was adopted as a surface fully covered with the thiol. The contact angle on a surface covered with an alkanethiol may depend on the tilt angle of the molecule relative to the surface normal. At initial stage of a monolayer formation, the thiols possibly orient parallel to the surface.[47] However, a simulation has predicted that the tilt angle rapidly decreases to less than 45° until the coverage ratio reaches 20%.[48] Moreover, this tendency was remarkable for thiols with a long alky chain. Thus, it was assumed that no thiol orients parallel to the surface and occupation rations are roughly calculated from Eq. (4).

Figure 4 shows microphotographs of a water droplet on surfaces of a Au bare, FBT-monolayers, a mixed monolayer, and ODT-monolayers with θ values measured. The $t_R C$ values for the monolayer formation are also shown. For a Au bare surface, the substrate was immersed in ethanol, and the contact angle was immediately measured. For FBT-monolayers, the reaction of $t_R C$ = 100 m min mol /L provides a saturate area covered with 4-fluorobenzenethiolate. Thus, the contact angle for a surface fully covered with 4-fluorobenzenethiolate θ_{FBT} is determined to be 77.1°. By substituting θ = 75.0°, $\theta_1 = \theta_{FBT}$ = 77.1°, and θ_2 = 71.9° into Eq. (4), the f value for $t_R C$ = 10 μ min mol /L is estimated to be 58.7%. On the other hand, the W value for $t_R C$ = 10 μ min mol /L is 5.09 eV from Fig. 2. This corresponds to an area density of $0.68 N_{FBT}$, and f = 68%. The f value is not far from that estimated from the water contact angle. For ODT-monolayers, the reaction of $t_R C$ = 100 m min mol/L also provides a saturate area covered with 1-octadecanethiolate. Thus, the contact angle for a surface fully covered with 1-octadecanethiolate θ_{ODT} is determined to be 98.1°. By substituting θ = 95.0°, $\theta_1 = \theta_{ODT}$ = 98.1°, and θ_2 = 71.9° into Eq. (4), the f value for $t_R C$ = 10 μ min mol/L is estimated to be 88.1%. On the other hand, the W value for $t_R C$ = 10 μ min mol /L is 4.66 eV from Fig. 2. This corresponds to an area density of $0.51 N_{ODT}$, and f = 51%. The f value is obviously much smaller than 88.1% estimated from the water contact angle. Equation (4) may not be applicable for estimation of f in case

which molecules having a long alkyl chain partially cover a surface.

An important result is the water contact angle of the substrate prepared for formation of a mixed monolayer. The θ value of 88.3° is between θ_{FBT} = 77.1° and θ_{ODT} = 98.1°. This result indicates that a mixed monolayer consisting of 4-fluorobenzenethiolate and 1-octadecanethiolate is formed as expected. Assuming that no Au bare surface is present under this condition, the occupation ratio is calculated to be 53.3% for 4-fluorobenzenethiolate and 46.7% for 1-octadecanethiolate by substituting θ = 88.3°, θ_1 = θ_{FBT} = 77.1°, and θ_2 = θ_{ODT} = 98.1°. The occupation ratio is close to the density ratio of $0.5N_{FBT} = 1.3\times10^{14}$ and $N_{ODT} = 1.4\times10^{14}$ cm^{-2} derived in Sect. 3.2.

3.4 XPS spectra

To confirm atoms present in FBT-, mixed, and ODT-monolayers formed on a Au/Cr layer, XPS spectra were measured. Figure 5 shows C 1*s*, F 1*s*, S 2*p*, and Au 4*f* XPS spectra taken on substrates prepared for formation of monolayers. The substrates were prepared under the following condition: t_RC = 5 μ min mol/L for the FBT-monolayer, t_RC = 20 μ min mol /L for FBT and t_RC = 100 μ min mol/L for ODT of the mixed monolayer, t_RC = 100 μ min mol /L for the ODT-monolayer.

Figure 5(a) shows C 1*s* XPS spectra, which are decomposed into three or two curves fitted to plots as solid lines. For the ODT-monolayer, the C 1*s* spectrum is almost composed of a fitting curve. Thus, the curve with a peak at 284.77 eV is mainly attributed to the alkyl chain, though the curve may partially contain influence relating to contaminations. On the other hand, the C 1*s* spectrum for the FBT-monolayer is decomposed into three curves with peaks at 288.63, 285.87, and 284.21 eV. The intensity at 288.63 eV is quite low, and the peak at 285.87 eV is probably attributed to the carbon atom within the benzene ring bonding to the fluorine atom. This is because a XPS spectrum from a carbon atom in a benzene ring bonding to a fluorine atom appears around 286-287 eV.[30,38] Although a peak assigned to a C atom bonding to a F atom is not clear for the mixed monolayer, the shape of the spectrum is obviously different from that for the ODT-monolayer. For the mixed and FBT-monolayer, the presence of fluorine atoms is directly confirmed from the F 1*s* spectra. On the other hand, the spectrum for the ODT-monolayer had no clear peak around 687 eV. For all monolayers, peaks assigned to S atoms were observed.

The atomic ratio of peaks associated with C 1*s*, F 1*s*, S 2*p*, and Au 4*f* is summarized in Table I. The atomic ratio was calculated from ratios of integrated areas of the peaks using

MultiPak software (Ulvac-phi), being corrected with relative sensitivity factors. Since a 4-fluorobenzenethiolate has a F atom and six C atoms and the atomic ratio of F 1*s* spectrum is 1.5%, 9% in the percentage 33.6% for C 1*s* spectrum may relates to carbon atoms in 4-fluorobenzenethiolate for the FBT monolayer, and the other, 24.6%, may relates to contaminations. In fact, a XPS spectrum measured for a Au bare surface had a peak assigned to C 1*s*.[49] Assuming that an atomic ratio of 25% is assigned to C atoms of contaminations on a surface, atomic ratios of about 20% and 9% for the mixed monolayer relate to C atoms in 1-octadecanethiolate and 4-fluorobenzenethiolate, respectively. A 1-octadecanethiolate has 18 C atoms and a 4-fluorobenzenethiolate has 6 C atoms. Thus, the atomic ratio of 20% and 9% roughly corresponds to a molecular ratio of 1 to 1. In this condition, the occupation ratio of 4-fluorobenzenethiolate is close to that of 1-octadecanethiolate as discussed in Sect. 3.3. The molecular ratio is consistent with the occupation ratio of 53.3% and 46.7% shown in Sect. 3.3 More accurate quantitative analysis of atomic ratio and molecular ratio will require more XPS measurements.

4. Conclusions

We attempted to form a mixed monolayer consisting of 4-fluorobenzenethiolate and 1-octadecanethiolate. From the work function measured for FBT- and ODT-monolayers, the association constants for adsorption of FBT and ODT were estimated to be 1776 and 1126 s^{-1} mol^{-1} L, respectively. The reaction of $t_RC > 200$ μ min mol/L was found to be enough to form saturated FBT- and ODT-monolayers. The t_RC values suitable for formation of a mixed monolayer was determined based on the relation between W and t_RC obtained from the work function measurement. The presence of a mixed monolayer was supported by the work function and water contact angle measured for a substrate prepared under conditions that a mixed monolayer would be obtained. XPS spectra measured for the substrate exhibited an F 1*s* spectrum with a peak, and supported the presence of 4-fluorobenzenthilate. As a result, the method examined based on reaction rate is suitable to obtain a mixed monolayer.

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Figure Captions

Fig. 1. (a) Illustration of a Si substrate with a mixed monolayer consisting of 4-fluorobenzenethiolate and 1-octadecanethiolate formed on a Au surface. Chemical structures of (b) FBT and (c) ODT.

Fig. 2. Work function for FBT-monolayers and ODT-monolayers formed on Au surfaces obtained with $t_R C$ where t_R is the immersion time and C is the concentration of FBT or ODT in the solution. t_R = 1 to 10 min. C = 1 μ (●), 10 μ (■), 100 μ (◆), and 1 m mol/L (▲). Illustration of a monolayer expected is shown in the inset.

Fig. 3. Work function for mixed monolayers (green filled circles), FBT-monolayers (blue filled diamonds), and an ODT-monolayer (blue filled square) formed on Au surfaces.

Fig. 4. Microphotographs of a water droplet for measurement of water contact angle, on (a) a Au bare, [(b) and (c)] FBT-monolayers, (d) a mixed monolayer, and [(e) and (f)] ODT-monolayers. The $t_R C$ values for the monolayer formation are shown in unit of min mol/L.

Fig. 5. XPS spectra taken on substrates with a FBT-monolayer, a mixed monolayer, and a BDT-monolayer: (a) C 1*s*, (b) F 1*s*, (c) S 2*p*, and (d) Au 4*f*. A single tick value for photoelectron intensity is shown with a double arrow in the figure. The value is common to all substrates in the figure.

Table I. Atomic ratios of peaks associated with C 1*s*, F 1*p*, S 2*p*, and Au 4*f*, calculated from XPS spectra obtained for substrates with a FBT-monolayer, a mixed monolayer, and an ODT-monolayer.

Surface	FBT	ODT	C 1*s* (%)	F 1*s* (%)	S 2*p* (%)	Au 4*f* (%)
	$t_R C$ (min mol/L)					
FBT	5 μ	−	33.6	1.5	0.7	64.2
Mixed	20 μ	100 μ	53.5	1.5	2.5	42.5
ODT	−	100 μ	65.3	0.5	2.0	32.2

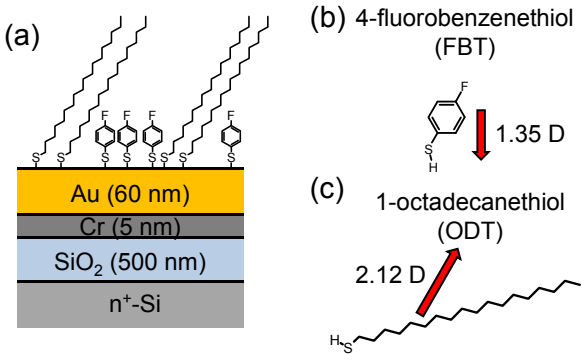
(a)
Au (60 nm)
Cr (5 nm)
SiO2 (500 nm)
n+-Si
(b) 4-fluorobenzenethiol
(FBT)
1.35 D
(c)
1-octadecanethiol
(ODT)
2.12 D

Fig.1.

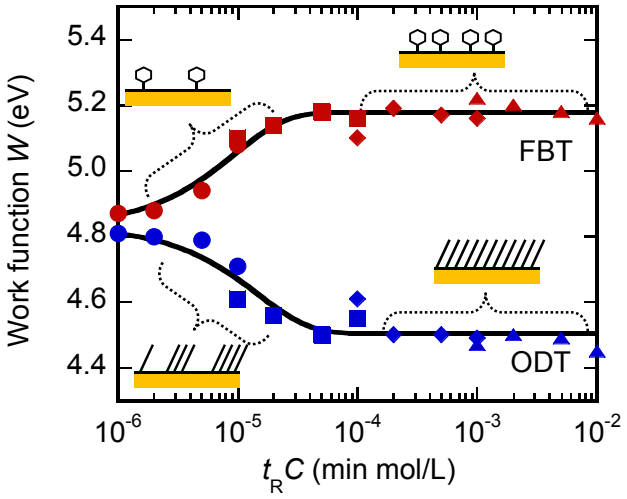
Work function W (eV)
5.4
5.2
5.0
4.8
4.6
4.4
FBT
ODT
10-6
10-5
10-4
10-3
10-2
tRC (min mol/L)

Fig. 2.

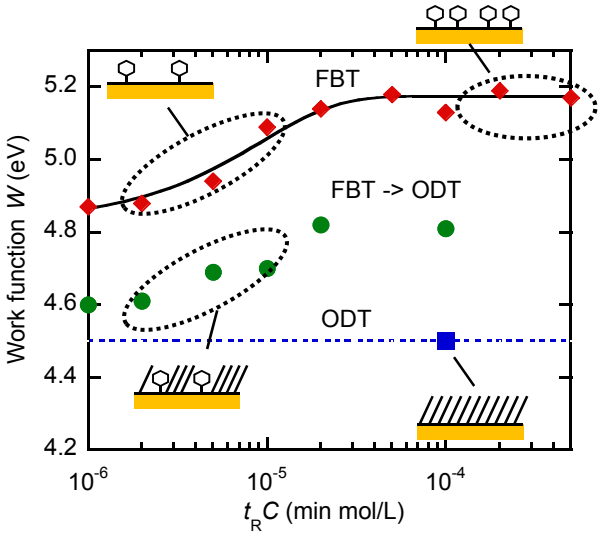
FBT
FBT -> ODT
ODT
Work function W (eV)
5.2
5.0
4.8
4.6
4.4
4.2
10^-6
10^-5
10^-4
t_R C (min mol/L)

Fig. 3.

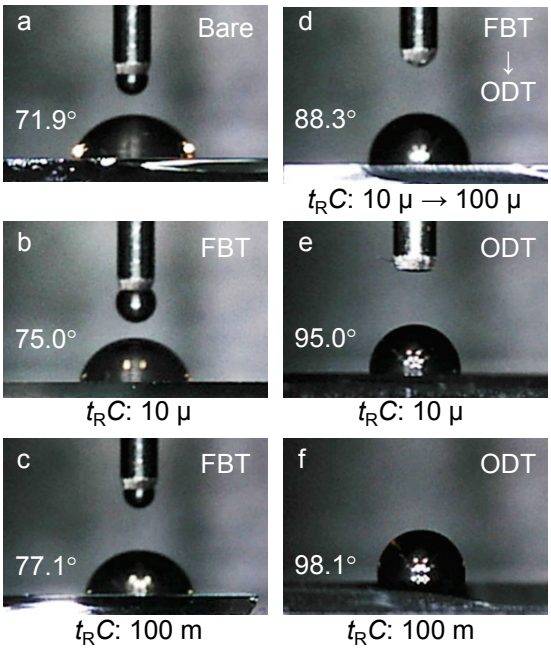
a
Bare
71.9°
d
FBT
↓
ODT
88.3°
$t_R C$: 10 μ → 100 μ
b
FBT
75.0°
$t_R C$: 10 μ
e
ODT
95.0°
$t_R C$: 10 μ
c
FBT
77.1°
$t_R C$: 100 m
f
ODT
98.1°
$t_R C$: 100 m

Fig. 4.

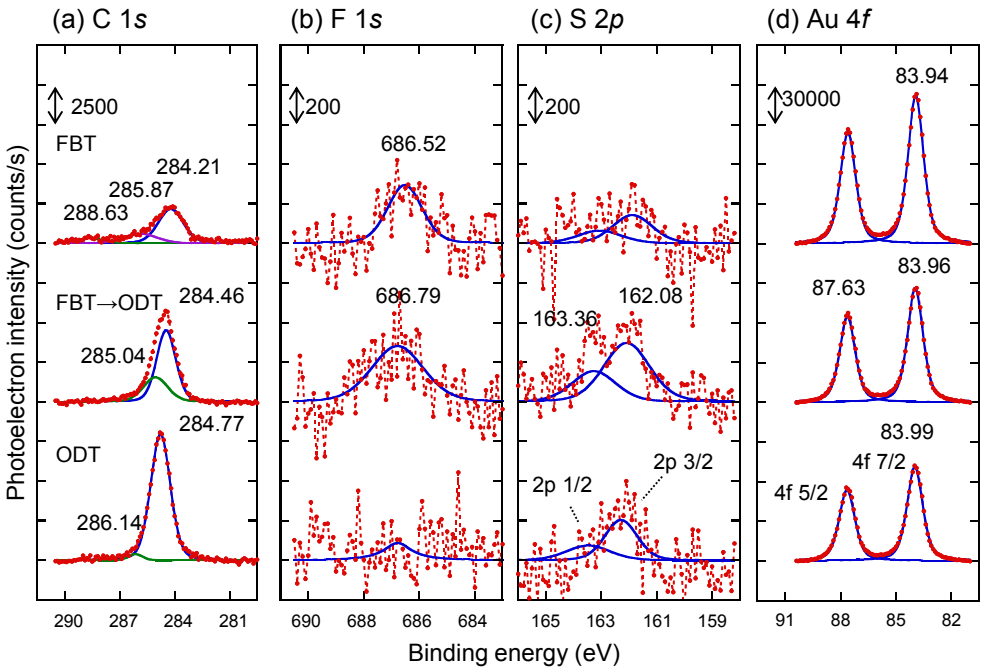
(a) C 1s
(b) F 1s
(c) S 2p
(d) Au 4f
2500
200
200
30000
FBT
284.21
285.87
288.63
686.52
FBT→ODT
284.46
285.04
686.79
163.36
162.08
ODT
284.77
286.14
2p 1/2
2p 3/2
83.94
83.96
87.63
83.99
4f 7/2
4f 5/2
Photoelectron intensity (counts/s)
290 287 284 281
690 688 686 684
165 163 161 159
91 88 85 82
Binding energy (eV)

Fig. 5.