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Formation of a monolayer on a gold surface with high thermal stability using benzenedithiol

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The formation and stability of a benzenedithiol monolayer on a Si substrate with a Au layer have been investigated to obtain a monolayer having high thermal stability as compared to that formed by use of a benzenethiol derivative. The monolayer was formed by immersing into an ethanol solution of 1,2-benzenedithiol (BDT). The work function of BDT-monolayer surface was measured for the investigation. The association constant for the adsorption of the molecules was estimated from the change of the work function. The subsequent annealing of the substrate with a BDT-monolayer at 500 K or lower did not lead to the change of the work function. Substrates with a BDT-monolayer were also examined using X-ray photoelectron spectroscopy (XPS). The work function and XPS spectra measured indicated that a BDT-monolayer formed on a Au surface is stable to annealing at temperatures up to about 473 K.

1. Introduction

The surface properties of a metal modified with an organic thiol such as a benzenethiol derivative have been intensively studied because of the technological importance and scientific interest.1-3) For benzenethiol, surface modification, resulting in a monolayer formation, were demonstrated using benzenethiol (BT)4-7) and various BT derivatives including 4-nitorobenzenethiol,7-10) 4-methylbenzenethiol (MBT),6,9,10) 4-fluorobenzenethiol (FBT),6,7,11) pentafluorobenzenethiol (PFBT).7,12,13) A monolayer formed on a metal surface leads to the change of work function on the surface.14,15) The change induced by modification is explained based on the dipole moment of a thiol molecule used for the modification.

Work function change has been applied to improve the performance of organic thin-film transistors (TFTs).8-10,16-20) This is because the change contributes to reducing the contact resistance between the contact metal and organic semiconductor in an organic TFT.9,19,20) The thermal stability of a monolayer used in an organic device limits fabrication process to be adopted for the organic device. We have investigated the thermal stability of monolayers formed using benzenethiol derivatives.21,22) The thermal desorption spectra revealed the presence of molecules desorbing from the modified surface at 373 K or higher.21) The temperature is quite low even when considering process temperature for organic devices, which have an advantage of application to flexible devices. Organic semiconductors for organic TFTs are sometimes deposited on substrates heated at temperatures of 373 to 473 K.23-25)

The thermal stability of a monolayer formed on a Au layer using a thiol molecule relates to the strength of chemical bonding between the metal atom and sulfur atom. The desorption described above indicates that a S-Au bond for a thiolate molecule on a Au layer is not sufficient for stability at temperatures of higher than 373 K. Thus, it is expected that use of a molecule with two or three SH terminals for monolayer formation improves the thermal stability of the monolayer. In fact, some groups have reported the synthesis of such molecules and the formation of a monolayer using the molecule.26-34) Shon and Lee investigated the stability of a monolayer formed using 2,2-dipentadecylpropane-1,3-dithiol (d-C17, $[CH_3(CH_2)_{14}]_2C[CH_2SH]_2$) in the range of 343 to 383 K, and confirmed the desorption at the temperature.28) Srisombat *et al.* reported that a monolayer formed using 1,1,1-tris(mercaptomethyl)heptadecane (t-C18, $CH_3(CH_2)_{15}C[CH_2SH]_3$) had high thermal stability as compared to that for 2-hexadecyl-2-methylpropane-1,3-dithiol (C18C3, $CH_3(CH_2)_{15}C(CH_3)[CH_2SH]_2$) when annealing at temperatures up to 498 K.32) However, a thiol molecule having a long chain is not suitable for modification on contact electrodes in organic TFTs.[35)] Although Garg and Lee reported a monolayer formed from xylene-α_1,α_2-dithiol, the thermal stability of the monolayer was unclear.[27)] We have proposed use of 1,2-benzenedithiol (BDT), having a short length, for formation of a monolayer, and reported the thermal stability of a BDT-monolayer formed on a Au surface.[36)]

In this paper, we report the formation and stability of a BDT-monolayer on substrates with a Au layer in more detail. The formation of the monolayer is examined as the work function change of the monolayer surface. The area density of molecules, benzenedithiolate, forming the monolayer is discussed based on the dipole moment calculated for the benzenedithiol molecule. In addition, the work function of the substrate annealed is presented to investigate the thermal stability of the BDT-monolayer. X-ray photoelectron spectroscopy (XPS) spectra for the substrate annealed 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 BDT-monolayer formed on a Au layer examined in this study. Figure 1(b) is the chemical structure of BDT used for the monolayer formation. To obtain a Au surface on a substrate, 5-nm-thick adhesive Cr and 60-nm-thick Au layers were deposited by thermal evaporation at a room temperature onto a SiO_2/Si substrate. Post-annealing of a substrate with a monolayer may affect not only the monolayer but also the Au layer. So, substrates were pre-annealed on a hot plate at 473 K for 10 min in a dry-nitrogen filled glovebox after the deposition of the Cr and Au layers. In general, organic semiconductor devices including organic TFTs are fabricated at temperatures below 473 K. We decided the pre-annealing temperature considering the fabrication temperatures. The resulting substrates were then stored in the glovebox until required for surface modification.

To obtain a monolayer, the substrate with a Au layer was immersed for a time t_R of between 1 and 10 min in an ethanol solution containing a BDT concentration C ranging from 1 μ to 1 m mol/L. The substrate was subsequently rinsed with ethanol several times. The monolayer formation was performed in air at room temperature of about 300 K. Following modification, some substrates were post-annealed on a hot plate at temperatures t_A in air to investigate the thermal stability of the monolayer.

The work functions of Au surfaces were measured with an atmospheric photoelectron spectrometer (Riken Keiki AC-2). In addition, the XPS spectra of Au surfaces were measured by a PHI-X-tool (ULVAC-PHI) with a monochromatized Al Ka X-ray source. The Au 4 *f*7/2 lines directly measured has a peak at 84.0 eV, which is close to 83.95 eV expected for a Au 4 *f*7/2.[37] Thus, we did not perform additional calibration to the binding energy scale of XPS spectra.

3. Results and discussion

3.1 Monolayer formation

A monolayer formed on a metal surface induces the change of the work function W according to the dipole moment $\mathbf{d}$ and area density N of molecules constructing the monolayer as shown in Fig. 1(c). Thus, the N value can be roughly estimated from the measurement of the work function if the value of $|\mathbf{d}|$ is known. This is because the work function change ΔW is given by

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

where q is the elementary charge, α is the average angle of the dipole direction relative to the surface normal, and ε is the permittivity of the molecule layer.[38] When the negative charge of the dipole moment is placed on the metal surface, α is between 90 and 180°. In this case, cos α is negative, and the monolayer leads to decrease in the work function.

For estimation of N, we calculated the dipole moment of BDT based on density functional theory DFT, using the Gaussian 09 software package with the B3LYP method and LanL2DZ basis set.[39] The dipole moment obtained has the direction of the arrow shown in Fig. 1(b), and $|\mathbf{d}|$ = 2.70 debye (D). Thus, a BDT-monolayer is expected to cause a decrease in work function.

The progress of a monolayer formation was examined by measurement of the work function. The work function of a Au bare surface without monolayer, W_0, was about 4.82 eV. The value is used as a reference. Figure 2 shows the measured work function for the substrate with a BDT-monolayer formed on a Au layer. The work function is plotted as a function of $t_R C$. This is because ΔW can be written as

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

where $\Delta W_{\mathrm{SAT}} = W_{\mathrm{SAT}} - W_0$, , W_{SAT} is the work function saturated at large $t_R C$, and k_A is the association constant for the adsorption of the molecule.[40] Equation (2) is derived by assuming that adsorption progresses according to the Langmuir adsorption model, and desorption is neglected. The work function shown in Fig. 2 gradually decreases with an increase of $t_R C$. The decrease indicates that the negative charge of the dipole moment is placed on the Au surface, and suggests that S atoms in BDT molecules bonds to the Au surface as shown in Fig. 1(a). The work function is saturated toward about 4.69 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 about 100 s^{-1} mol^{-1} L. This value is almost the same as 106 s^{-1} mol^{-1} L obtained for formation of a PFBT-monolayer.[21)] On the other hand, this value is obviously small as compared to 386 for MBT[21)], 1776 for FBT[41)] and 1126 s^{-1} mol^{-1} L for 1-octadecanethiol.[41)] Main reason for slow reaction of BDT may be due to the need for two S-Au bonds.

In order to estimate N, it is necessary to assume a value of α. When assuming that $\alpha = 180$, 150, and 120°, N values are estimated to be 3.84×10^{13}, 4.44×10^{13}, and 7.68×10^{13} cm^{-2}, respectively. The values were obtained by assuming that the relative permittivity for Eq. (1) is 3.0 for the estimation.[7,42)] It seems that the N values estimated in this study is slightly low as compared to those obtained for other thiols. We have reported N values estimated for monolayers formed on Au surfaces by use of various benzenethiols.[21,43)] The N values were in the range from 2.3×10^{13} to 1.86×10^{14} cm^{-2}. The $|\mathbf{d}|$ value for 4-methylbenzenethiol (MBT) was calculated to be 2.46 D, which is close to 2.70 D for BDT. The N value for MBT was 1.00×10^{14} cm^{-2}. The N value for BDT is less than that for MBT even when assuming $\alpha =$ 120° for BDT. Probably, each S atom of BDT chemically bonded to Au atoms. It is possible that the bonding of two S atoms suppresses the area density. 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 value for BDT suggests that a molecule, 1,2-benzenedithiolate, for formation of a BDT monolayer is roughly present on a surface area consisting of 18 to 36 Au atoms. Figure 3 shows an illustration of two 1,2-benzenedithiolate standing on an atomic layer consisting of 42 Au atoms. The illustration corresponds to $N = 6.57\times10^{13}$ cm^{-2}.

3.2 Thermal stability

We used the substrates prepared with $C = 10$ mmol/L and $t_R = 5$ min to evaluate the thermal stability of BDT monolayers. This is because a value of $t_R C > 1$ m min mol/L is enough to form the saturated BDT monolayer as seen in Fig. 2. Figure 4 shows the work functions measured for substrates with a BDT monolayer and those with a Au bare surface annealed at a temperature (T_A) of 353 to 573 K. Each substrate was annealed at a temperature for 10 min, and then the work function was measured. A substrate annealed at a temperature was not used for annealing at another temperature. The work functions for un-annealed substrates are plotted at $T_A = 300$ K.

The annealing up to 473 K did not affect the work functions as seen in Fig. 4. The work function for the BDT-monolayer increased with an increase of T_A for $T_A \geq 513$ K. This indicates that a BDT-monolayer formed on a Au surface is stable at temperatures up to about 500 K. This temperature is much high as compared to the lowest temperature at which monolayers formed from BT derivatives desorb.21,43) This suggests that two S atoms in a benzenethiolate constructing a monolayer chemically bond to Au atoms, and two S-Au bonds contribute to the thermal stability. The BDT-monolayer exhibited thermal stability higher than monolayers of d-C17[28)] and C18C3 having dithiol and comparable to that of t-C18 having trithiol.32) Two or three S atoms in d-C17, C18C3, and t-C18 bond to a carbon atom as mercaptomethyl (-CH_2-SH). On the other hand, the S atom in 1,2-benzenedithiol (BDT) directly bonds to a carbon in the benzene ring. In addition, the structure of a benzene ring is more structurally stable compared to an alkyl chain. Probably, the chemical structure concerning S atoms in BDT contributes to the high thermal stability.

The work function for the Au bare surface also increased with T_A for $T_A \geq 493$ K. It seems that the stability of a BDT-monolayer formed on a Au surface is limited by pre-annealing temperature. The increase in the work function for the BDT-monolayer implies the change in surface condition of the BDT-monolayer surface. Desorption of species from the BDT-monolayer surface may cause the increase in the work function. Another possible reason is diffusion of metal atoms in the Au/Cr layer on the SiO_2 layer. If the hypothesis is correct, the diffusion occurs in a substrate without BDT-monolayer, and affects the work function. In fact, the work function for the Au bare surface increases with T_A for $T_A \geq 493$ K as described above. If a substrate with a Au/Cr layer were pre-annealed at temperatures higher than 500 K, a BDT-monolayer formed on the substrate would be stable up to the annealing temperature. The stability observed using a substrate annealed at temperatures higher than 500 K is under investigation.

3.3 XPS spectra

To confirm atoms present in a BDT-monolayer formed on a Au/Cr layer, XPS spectra were measured. Figure 5 shows the XPS spectra taken on substrates with a BDT-monolayer annealed at 373, 473, and 573 K, and with a Au bare surface un-annealed. Atomic ratios of peaks associated with C 1*s*, S 2*p*, Cr 2*p*, O 1*s*, and Au 4*f* are summarized in Table I. The atomic ratio was calculated from ratios of integrated areas of the peaks using MultiPak software (Ulvac-phi, Inc.), being corrected with relative sensitivity factors.

Figure 5(a) shows C 1*s* XPS spectra, which are decomposed into three curves fitted to plots as solid lines. Two fitting curves with peaks at 284.1 and 284.6 eV was observed for the Au bare surface. Thus, the peaks are probably attributed to contaminations embedded in the Au layer and/or on the surface. For the BDT-monolayers of T_A = 373 and 473 K, the peak intensities for 284.1 eV are higher than that for the Au bare surface. The peak at 284.1 eV may be partially attributed to the C atoms in the benzenedithiolate. The peak at 287.8 eV was observed for the BDT-monolayer of T_A = 573 K. A C=O specie causes a peak at about 288.0 eV. Annealing at 573 K leaded to increase in concentration of O atoms as seen in Table I. The O atom may relate to the peak at 287.8 eV.

Figure 5(b) shows S 2*p* XPS spectra, which are decomposed in two curves fitting to plots as solid line, corresponding to 2*p* 1/2 and 2*p* 3/2 levels of S atoms in Au–S–C_6H_4–S–Au species. Actually, no peak at 163.4 and 162.1 eV was observed for the Au bare surface. On the other hand, XPS spectra measured for the BDT-monolayers of T_A = 373 and 473 K had peaks at 163.4 and 162.1 eV. The result supports the presence of a BDT-monolayer on the Au surface. A XPS spectrum measured for the BDT-monolayer of T_A = 573 K had a quite low or no peak at 163.4 and 162.1 eV. This indicates that a benzenethiolate desorbed from the Au surface at T_A = 573 K. The result of the XPS spectra for T_A = 373, 473, and 573 K is consistent with change of the work function measured for substrates post-annealed.

We also measured Cr 2*p*, O 1*s*, and Au 4*f* spectra to investigate influence of annealing on the stability of Au/Cr layers, and to estimate atomic ratios on the surface. The Cr 2*p*, O 1*s*, and Au 4*f* spectra are shown in Figs. 5(c), 5(d), and 5(e), respectively. The Cr 2*p* spectrum at T_A = 573 K had high intensity. This indicates that annealing at a temperature of 573 K leads to diffusion of Cr atoms in the Au/Cr layer. Also, the O 1*s* spectrum at T_A = 573 K had high intensity. Probably, this is because Cr atoms on the surface were oxidized. This result implies that the increase in work function with T_A shown in Fig. 4 relates to the increases in the concentration of Cr and O atoms.

The atomic ratio of S atom for T_A = 373 and 473 K are 1.8 and 2.5 %, as seen in Table I, respectively. Considering *N* values described in Sect. 3.1, the atomic ratio is not small. The *N* value estimated is in the range of 3.84×10^{13} to 7.68×10^{13} cm^{-2}, corresponding to presence of a benzenedithiolate on a surface area consisting of 18 to 36 Au atoms. Thus, atomic ratio of S atom is estimated to be 8.3 to 11% from the work function. In addition, S atoms in the monolayer are closer to the Au surface as compared to C atoms in the monolayer, and the location suppresses the intensity of S 2p spectra. As a result, the atomic ratio of 1.8 and 2.5 % does not deny the presence of a monolayer consisting of benzenedithiolate.

4. Conclusions

We measured the work function and XPS spectra for substrates having a Au layer covered with a BDT-monolayer to investigate the formation and thermal stability of the monolayer. The association constant for adsorption of BDT k_A was estimated to 100 s^{-1} mol^{-1} L. The reaction of $t_R C$ > 1 m min mol/L was found to be enough to form a saturated BDT-monolayer. Annealing a substrate with a BDT monolayer indicated that a BDT-monolayer is thermally stable up to about 500 K. XPS spectra for S 2*p* lines was consistent with the indication. Probably, two S-Au bonds in 1,2 benzenedithiolate contribute to the thermal stability. This suggests that a monolayer formed using benzenedithiol derivatives also has high thermal stability. Such a monolayer with high thermal stability is suitable for application to contact electrodes in organic devices.

Acknowledgments

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Figure Captions

Fig. 1. (a) Cross section a Si substrate with a BDT-monolayer formed on a Au surface. (b) Chemical structure of BDT. (c) Energy levels induced by dipoles on a metal surface, and the metal.

Fig. 2. Work function for BDT-monolayers on Au surfaces obtained with $t_R C$ where t_R is the immersion time and C is the concentration of BDT in the solution.

Fig. 3. Illustration of two 1,2-benzenedithiolates adsorbed on a Au layer consisting of 42 atoms, corresponding to a molecular area density of 6.57×10^{13} cm^{-2}.

Fig. 4. Work function for substrates with a BDT-monolayer and Au bare surfaces annealed at temperatures of 353 to 573 K for 10 min. Work functions for un-annealed substrates are plotted as $T_A = 300$ K.

Fig. 5. XPS spectra taken on substrates with a BDT-monolayer annealed at 373, 473, and 573 K, and with a Au bare surface un-annealed: (a) C 1*s*, (b) S 2*p*, (c) Cr 2*p*, (d) O 1*s*, and (e) 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*, S 2*p*, Cr 2*p*, O 1*s*, and Au 4*f*, calculated from XPS spectra obtained for substrates with a BDT-monolayer of T_A = 373, 473, and 573 K, and with a Au bare surface un-annealed.

Surface	T_A (K)	C 1*s* (%)	S 2*p* (%)	Cr 2*p* (%)	O 1*s* (%)	Au 4*f* (%)
Au	–	25.0	0.0	6.9	14.5	25.0
BDT	573	25.5	0.4	19.5	38.1	25.5
BDT	473	28.0	2.5	7.5	17.0	28.0
BDT	373	26.3	1.8	7.2	18.7	26.3

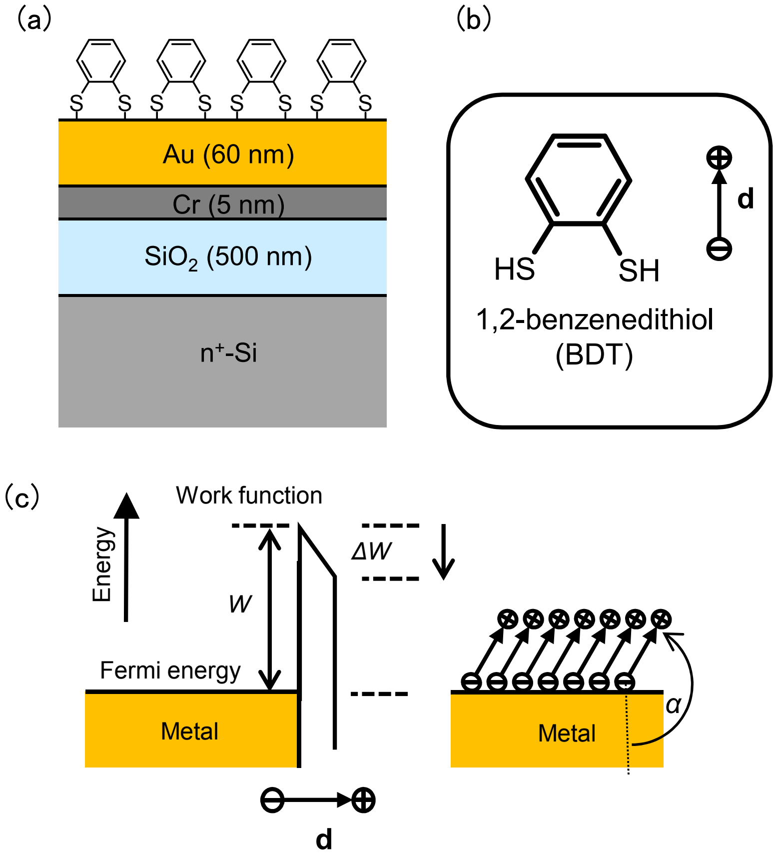

(a)
S S S S S S S S
Au (60 nm)
Cr (5 nm)
SiO$_2$ (500 nm)
n$^+$-Si
(b)
HS
SH
d
1,2-benzenedithiol
(BDT)
(c)
Energy
Work function
W
ΔW
Fermi energy
Metal
d
Metal
α

Fig.1.

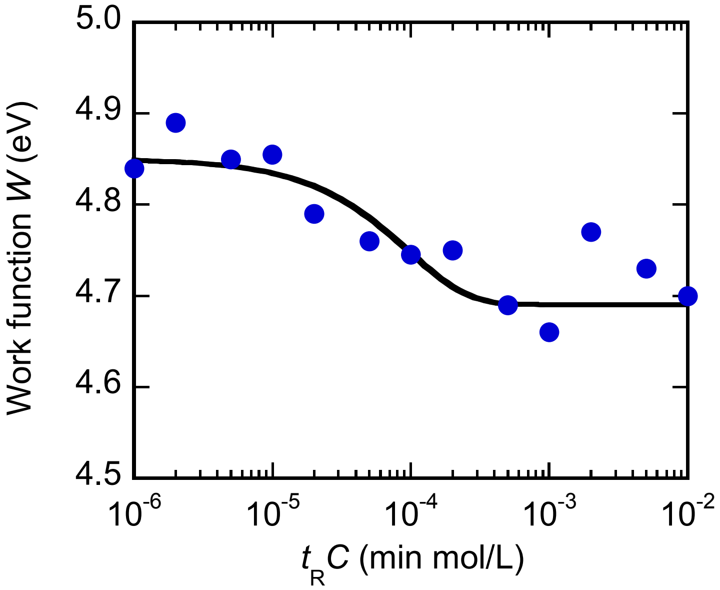

5.0
4.9
4.8
4.7
4.6
4.5
Work function W (eV)
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
$t_R C$ (min mol/L)

Fig. 2.

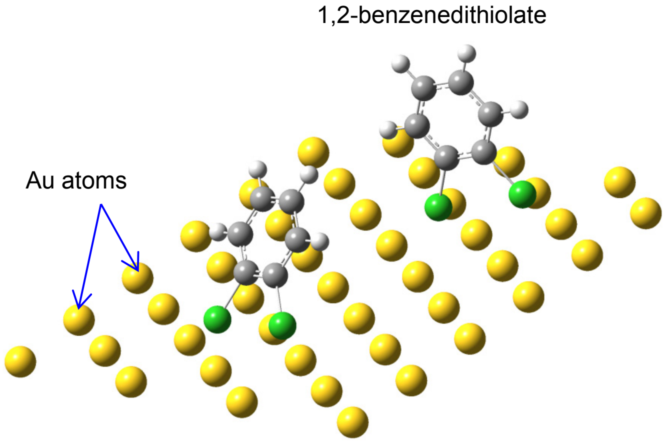
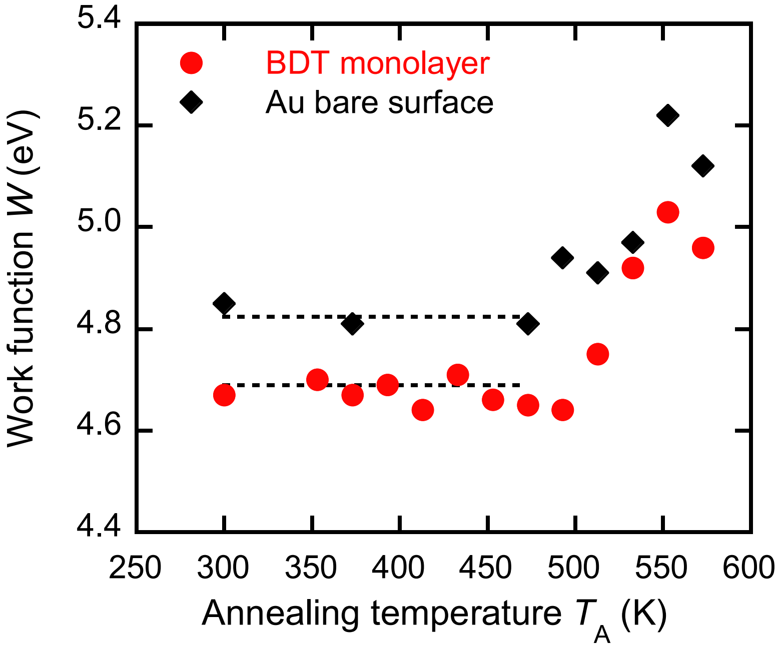


Fig. 3.


BDT monolayer
Au bare surface
Work function W (eV)
Annealing temperature T_A (K)
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5.2
5.0
4.8
4.6
4.4
250
300
350
400
450
500
550
600

Fig. 4.

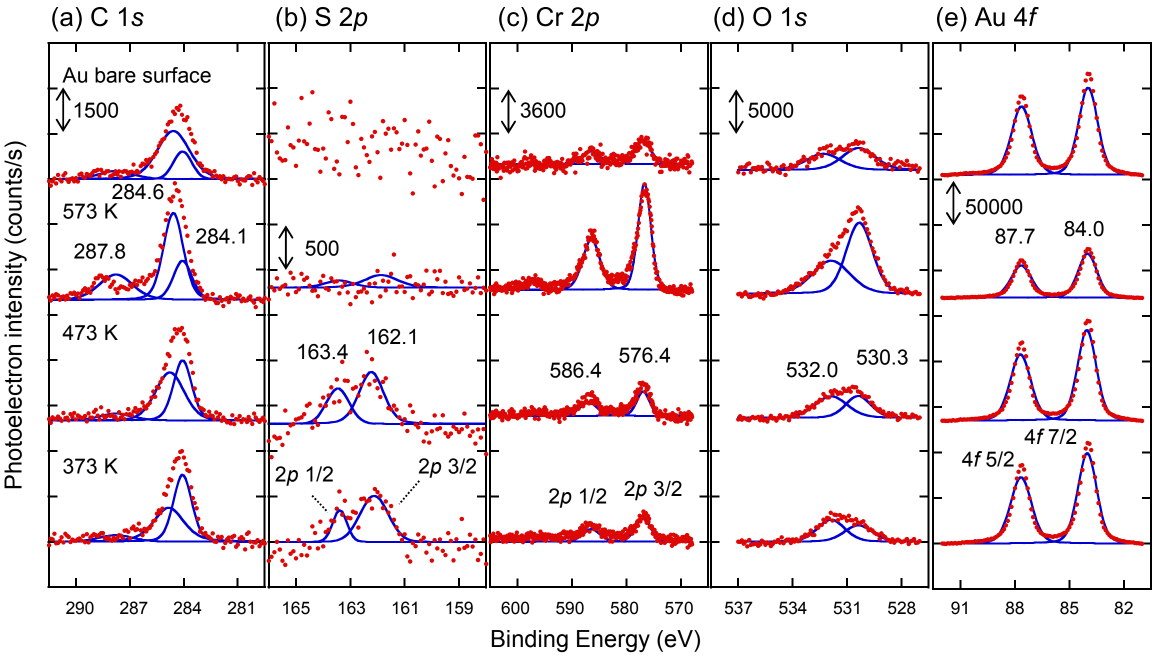
(a) C 1s
(b) S 2p
(c) Cr 2p
(d) O 1s
(e) Au 4f
Au bare surface
1500
500
3600
5000
50000
573 K
473 K
373 K
284.6
287.8
284.1
163.4
162.1
2p 1/2
2p 3/2
586.4
576.4
532.0
530.3
87.7
84.0
4f 5/2
4f 7/2
Photoelectron intensity (counts/s)
Binding Energy (eV)
290
287
284
281
165
163
161
159
600
590
580
570
537
534
531
528
91
88
85
82

Fig. 5.