Self-assembled monolayers (SAMs) are used for adjusting the work function of metal electrodes in organic devices. Since the energy level difference between the HOMO or LUMO and the work function affects the electron injection through the metal-organic interfaces, fine tuning of the work function is of importance. To control the work function from external environment, external large electric field on low-density SAMs is reported to be effective. In order to obtain a direct evidence for the structural switching of the SAM, X-ray reflectivity measurements were performed. The result shows that the molecular tilting of $10^\circ$ is induced by the external voltage application. [DOI: 10.1380/ejssnt.2018.76]

Keywords: X-ray scattering; Diffraction and reflection; Solid-liquid interfaces; Self-assembled monolayer; Ionic liquid

I. INTRODUCTION

Self-assembled monolayers (SAMs) are used as the buffer layer for organic devices [1–5]. One of the main functionalities of the SAM is adjusting the work function of metal electrodes [6–9]. Since the energy level difference between the HOMO or LUMO and the work function affects the electron injection through the metal-organic interfaces, fine tuning of the work function is of importance. Possible controlling mechanisms of the work function are (1) electric double layer caused by the polarization of the SAM molecule [1–3, 9], and (2) electrons spilled at the metal surfaces are pushed back inside the metal due to Pauli repulsion, resulting in a dipole moment at the surface [10]. In case of the helicene derivative 1,12-dimethyl-5,8-[4]helicenedithiol SAM, the latter mechanism is known to be dominant [11, 12]. Both mechanisms are strongly related to the surface structure. Although the work function is controlled by the SAM formation, controlling the work function after the formation of SAMs is difficult. To achieve the surface switching, low-density SAMs are found to work [11–13]. Especially the method reported in refs. [11, 12] is simple and stable, which are required for technological applications. However, the direct observation of the molecular switching has not been performed. Therefore, we performed an x-ray reflectometry measurement on the low-density SAM with applying external electric fields.

X-ray reflectivity observes the electron density around the surface or interface. Since this is a non-contact technique, it would give little disturbance on the external electric field effect on the interfacial structure. For example, electric double layer (EDL) formed at the interface between gold and an ionic liquid (IL) interface is observed by this method [14]. The external voltage effect on the interfacial structure is usually small, and the differential detection is found to be useful. By performing the parameter fitting on the intensity ratio measured at positive voltage $I_+$ and negative voltage $I_-$, one can derive the electron density change induced by the external voltage. In the present study, we also use this procedure.

II. EXPERIMENTAL

SAMs of 1,2-benzenedithiol were made on vacuum evaporated made Au(111) surface on cleaved mica (purchased from Phasis, Switzerland) by overnight immersion in 1 mM 1,2-benzenedithiol solution in tetrahydrofuran, followed by rinsing with copious amounts of tetrahydrofuran. The surface molecular density is estimated to be $3.8\times10^{14}$ cm$^{-2}$ [12]. The sample was covered with the IL 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI), and applied an electric voltage by using the device structure presented in Fig. 1. Strong electric field is applied to the SAM through the EDL formed at the interface. Using the van der Waals radius of the atoms, the length of the SAM molecule measured from the Au surface is estimated to be 7.48 Å. Typical intensity of the local electric field caused by the EDL is 1 V/µm or 10 MV/cm.

The X-ray reflectivity measurements were performed at the SPring-8, BL13XU. The energy of the X-ray used was 10 keV. Typical beam size is 0.3 mm × 0.3 mm. During the measurements, the samples were kept in a vacuum chamber and cooled to 100 K to avoid radiation damage. Measurement procedure was (1) apply the voltage

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at room temperature, (2) cool down the sample to 100 K, (3) measure the reflectivity, (4) heat up to room temperature, and return to (1) for next measurement at different voltage.

III. RESULTS AND ANALYSIS

Figure 2 shows the reflectivity profiles at +1 V. Au 111 Bragg reflection was observed at 30°, and the results are well reproduced. Slight deviation in the range of 2θ < 5° was originated from the change in the thickness of frozen IL, as the sample was heated up to room temperature between the measurements. The change in the thickness causes the change in absorption of x-ray in the small incident angles. For example, the intensity taken in the first run differs a few percents from that in the second run, which is well explained by the change in the liquid thickness by 0.19 ± 0.01 µm. In the higher incident angle conditions, the absorption difference was too small to be seen in the log-scale plot. The absorption correction was made for the later analysis.

The reflectivity measured at +1 V and −1 V, I+(2θ) and I−(2θ), are not precisely measured as there is an uncontrollable parameter, thickness of the IL layer; The absorption correction introduced in the previous paragraph gives the correction for the difference in IL thickness among the datasets. Instead, the ratio I+(2θ)/I−(2θ) can be obtained precisely as the effect of the uncontrollable IL thickness is canceled out.

The intensity ratio for the Au/IL interface is plotted in Fig. 3(a). It shows clear oscillation as a function of the scattering angle. This is originated from the formation of the EDL at the Au/IL interface [14]. The IL used was EMI-TFSI, whose cation (EMI) is made of C, N and H, while the anion (TFSI) contains F and S, thus the electron density of the anion is higher than that of the cation. X-ray reflectivity signal is sensitive to the electron density contrast, and thus the intensity oscillation is caused by the layered structure of the anions and cations. The electron density profile of the IL (SAM/IL) layer around the positively charged Au ρ+(z) and around the negatively charged Au ρ−(z) are expressed by the slab models, i.e., models composed of a bulk liquid region with constant electron density and slabs with certain electron densities at the interface. The electron density difference ρ−(z) − ρ+(z) is plotted in Fig. 3(b). The interfacial layer contains much cations in ρ−(z) and much anions in ρ+(z). Since the anions have larger electron density than cations, ρ−(z) − ρ+(z) at the Au/IL interface is expected to be negative, and so do the result of the analysis.

The intensity ratio for Au/SAM/IL interface is also plotted in Fig. 3(a). Although it is rather noisy, it is clear that the reflectivity differs from that of the Au/IL interface. In order to extract some real space structure, we imposed an assumption that the IL structure in the Au/SAM/IL interface is the same as Au/IL interface. Assuming this, we made the slab models for Au/SAM/IL interfaces by inserting a slab representing the SAM layer. Total number of electron for the slab is kept unchanged with changing the voltage, and the thickness of the slab represents the angle of the SAM molecules. The electron density change induced by the external voltage for this interface is obtained as shown in panel (b), which gives the fit to the experimental result shown in panel (a) by
FIG. 3. (a) Reflectivity ratio $I_{+1V}/I_{-1V}$ measured for Au/IL interface (black plots) and Au/SAM/IL interface (red plots). Solid curves show the result of model fitting based on the slab-model. (b) Resulting electron density difference $\rho_- - \rho_+$ for Au/IL interface (black curve) and Au/SAM/IL interface (red curve) as a function of the distance from the Au surface.

FIG. 4. Schematic view of the resulting structures.

the red curve. Here, $\rho_-(z) - \rho_+(z)$ at the Au/SAM interface is positive. This means that the tilting of the SAM molecule is as presented in Fig. 4. According to Ref. [15], the SAM molecule is $51^\circ$ tilted from the surface normal direction. Our analysis derives about $10^\circ$ tilt is induced on the SAM molecule by the applied voltage.

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