## Measurements of Work Functions of Organic Monolayers Adsorbed on Gold Surfaces

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Electronic devices based on organic thin films are expected to realize device forms that are difficult to realize with conventional inorganic semiconductors due to the versatility of their molecular design. One of the characteristics of such excellent performance of organic compounds is the importance of delocalized  $\pi$ -electrons in the molecules. In general, organic compounds are insulating materials that are unsuitable for the development of conductivity, but by making extremely thin films of 100 nm or less, the transport of holes and electrons between electrodes and organic semiconductor layers becomes possible, making it possible to treat organic materials as semiconductors. Thus, the processes that hold the key to the operation of organic devices occur at the interface, and understanding the interface structure and electronic structure is essential for device development. The work function, which is the focus of this study, has been determined and evaluated as one of the important parameters that describe the interface.

The work function is the minimum energy required to extract electrons from the Fermi level into the vacuum and is intrinsic to the material. Even the presence of trace amounts of adsorbed molecules on a metal surface can change the electronic structure of the interface and significantly affect the work function. For example, the work function of a thin film of polycrystalline gold is  $4.4 \sim 4.7$  eV when exposed to air,  $5.0 \sim 5.1$  eV when cleaned at the atomic level under ultrahigh vacuum, and the largest value of  $5.3 \sim 5.4$  eV for a thin film sputtered and vacuum deposited with argon gas or so. These findings can also be used to evaluate the charge transport capability of organic monolayers (SAMs), which is the subject of our research work.

In this study, we measured in detail the secondary electron cut-off region in the photoelectron spectrum using synchrotron radiation in order to determine the change in work function of organic monolayers on gold surfaces due to differences in molecular backbones. Among the electrons emitted from the sample surface by light irradiation, those that reach the vacuum level are detected as photoelectron spectra. The electrons with zero kinetic energy are detected in large quantities as secondary electrons at the rising edge of the spectrum, and this region is called the secondary electron cut-off (SECO). On the other hand, photoelectrons with the highest kinetic energy are detected on the high-energy side of the spectrum as photoelectrons originating from the Fermi level. The relationship between the Fermi level  $E_{Fermi}$ , the energy of the SECO  $E_{SECO}$ , the energy of incident light hv, and the work function  $\phi$  is expressed as follows.

$$E_{Fermi} - E_{SECO} = h\nu - \phi \tag{1}$$

The Fermi level of each sample is coincident with that of a single molecule adsorbed on Au, so that the change in the work function  $\phi$  appears in the spectrum as a change in  $E_{SECO}$ . In this study, we investigate the relative change of the work function by measuring the  $E_{SECO}$  region of photoelectrons in detail by X-ray irradiation.

The experiments were performed using X-ray photoelectron spectroscopy (XPS) measurements at the beamline BL-13 of HiSOR, Hiroshima University. The cut-off region with zero kinetic energy was precisely measured by applying a negative voltage (typically -10 V) to the sample and shifting the photoelectron spectrum toward the high energy side. The SAMs used are shown in Fig. 1: MP0, MP1, and M2P composed of conductive aromatic rings in their molecular chains. On the other hand, MHDA and HD are aliphatic-chain SAMs with high insulating properties, and HD was used as a reference sample with a known work function.

Fig. 2 shows the photoelectron spectrum in the secondary electron region measured for MHDA SAM under the conditions of this experiment. Since a sample bias of -10 V is applied, the SECO is detected around 7 eV. A detailed measurement of this cut-off region for each sample is shown in Fig. 3. It can be seen that the SECO position varies greatly from sample to sample. The  $E_{SECO}$  was determined by linearly approximating the slope of this SECO. The work functions 4.37 eV for MHDA, 4.90 eV for MPO, and 5.00 eV for M2P were determined based on the work function of HD, 4.32 eV [1]. The work function of the Au surface deposited on a Si substrate at a deposition rate of 1 Å/s under high-vacuum was also determined to be in the range of 4.8-5.1 eV, lower than the value of 5.2 eV for a polycrystalline (111) clean surface [2]. This indicates that the surface is contaminated by exposure to air after deposition and that a perfectly clean surface cannot be maintained even if cleaned just prior to measurement.

Compared to HD and MHDA with aliphatic chains, M2P and MP0 with aromatic chains have work functions about 0.5~0.7 eV higher. This may be due to the push back effect. In this model, the interfacial electric bilayer ( $\delta^-$  and  $\delta^+$ ) that originally exists on the metal surface is reduced by molecular adsorption, resulting in a decrease in the work function. Since aromatic-chain SAMs have delocalized  $\pi$ -electrons in the ring, when they are adsorbed on the substrate, electrons in organic molecules are added to the  $\delta^-$  side of the metal surface, and the apparent decrease in  $\delta^-$  is considered to be smaller than that of aliphatic-chain SAMs. Therefore, the polarization of aromatic-chain SAMs is expected to be larger than that of aliphatic-chain SAMs, and the work function is also expected to be larger than that of aliphatic-chain SAMs.

## REFERENCES

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**FIGURE 2.** Photoelectron spectrum in the secondary electron region measured for MHDA SAM

FIGURE 3. Photoelectron spectrum in the secondary electron cut-off (SECO) region measured for aliphatic and aromatic SAMs.