



Effect of molecular desorption on the electronic properties of self-assembled polarizable molecular monolayers



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ABSTRACT

We investigated the interfacial electronic properties of self-assembled monolayers (SAM)-modified Au metal surface at elevated temperatures. We observed that the work functions of the Au metal surfaces modified with SAMs changed differently under elevated-temperature conditions based on the type of SAMs categorized by three different features based on chemical anchoring group, molecular backbone structure, and the direction of the dipole moment. The temperature-dependent work function of the SAM-modified Au metal could be explained in terms of the molecular binding energy and the thermal stability of the SAMs, which were investigated with thermal desorption spectroscopic measurements and were explained with molecular modeling. Our study will aid in understanding the electronic properties at the interface between SAMs and metals in organic electronic devices if an annealing treatment is applied.

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1. Introduction

The use of self-assembled monolayers (SAM) of polarizable molecules has been recognized to be a convenient and useful chemical approach to enable the tuning of the electrical properties of organic-based devices [1–12]. In particular, a dipolar molecular layer on an electrode surface can control the two important electronic properties: the work function [2,4–9,11,12] and the injection barrier height [1,3–5,7–10] (which is the difference between the Fermi level of the electrode and the molecular orbital level) of the subsequently deposited organic active material. These two parameters, which depend on the dipole moment at the SAM/electrode interface, have been considered to be the main factors to be adjusted for efficient charge injection properties in organic electronic devices in various applications. For this reason, a considerable number of studies have investigated the influence of SAMs on the electronic properties of the metal surface and organic devices [1,3–5,7–10]. In addition, in organic electronic devices, the effect of thermal annealing on the properties of the interface between the SAM and the electrode surface is an interesting subject because annealing treatments of organic-based devices with SAMs are often employed to enhance the morphological and

interfacial electronic properties of the organic materials in the devices [5,13–15]. In particular, annealing can change the work function of a SAM-modified metal [5,16,17], that leads to change the electrical properties of organic electronic device. Therefore, it is important to understand the influence of the dipole moments for various types of SAM on the electronic properties of the metal surface at different temperatures for organic device application.

In this study, we investigated the influence of molecular desorption on the work function of SAM-modified Au metal surfaces under different temperature conditions with a Kelvin probe technique and compared the experimental results with those of theoretical calculations derived from the Helmholtz equation. We developed a comprehensive explanation for the values of the temperature-dependent work function of SAM-modified Au metal based on the molecular binding energy and the thermal stability of the SAM. These properties were also investigated with thermal desorption spectroscopic (TDS) measurements and molecular modeling.

2. Experimental

2.1. Preparation of the metal substrate

To prepare the metal substrate, a p-type (100) Si wafer (1 cm × 1 cm) covered with thermally grown, 300 nm thick SiO₂ was cleaned with a detergent and was ultrasonicated in acetone,

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methanol, and DI (deionized) water for ~ 10 min each. Then, the substrates were treated with UV (ultraviolet)/ozone to remove the remaining organic residues. Next, Ti (5 nm) and Au (100 nm) (99.999%) were deposited on the substrates with an electron beam evaporator under a pressure of $\sim 10^{-7}$ Torr at a low deposition rate of 0.1–0.2 Å/s. The average root-mean-square (RMS) roughness for the Au/Ti substrate was found to be ~ 0.8 Å by atomic force microscopy (AFM, Park Systems XE-100) for scan sizes of $2 \mu\text{m} \times 2 \mu\text{m}$ (not shown here).

2.2. SAM preparation

Three molecular species ((i) 2-naphthalenethiol (denoted Naph-S), (ii) 2-naphthyl isocyanide (Naph-NC), and (iii) 1H,1H,2H,2H-perfluorodecanethiol (Perfluoro-C10-S)) were self-assembled on the Au surface from molecular solutions in anhydrous ethanol. To form SAM of these molecules on the Au surface, we used 3 mM molecular solutions and an incubation time of at least two days in a nitrogen-filled glove box with an oxygen level of less than ~ 10 ppm to avoid potential oxidation problems. Before the Kelvin probe measurement, the SAM-modified Au substrate was rinsed with anhydrous ethanol and was dried under flowing N_2 . All molecular species in this study were purchased from the Aldrich Chem. Co.

2.3. Kelvin probe measurement

The work function of each SAM-modified Au sample was detected with a Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services, Co.). To investigate the work function of the samples at elevated temperatures, the samples were annealed on a calibrated hotplate in a glove box for at least 10 min at different temperatures (300, 323, 343, 363 and 383 K). After cooling to room temperature, the samples were rinsed again with anhydrous ethanol and were dried under flowing N_2 to remove the residual desorbed molecules on the substrate. Then, the work function of the samples was measured with the Kelvin probe in the glove box. The contact potential difference was calibrated to highly ordered pyrolytic graphite (HOPG) at 4.58 ± 0.03 eV. The work function of the deposited Au/Ti metal on the SiO_2/Si substrate was found to be 4.94 ± 0.06 eV.

2.4. Thermal desorption spectroscopy measurement

To examine and compare the thermal desorption behavior and stability of the SAMs on the Au surfaces, thermal desorption spectroscopy (TDS) measurements (WA-1000S system, ESCO, Ltd.) were performed with a quadrupole mass spectrometer (QMG422; Balzers). The heating rate was approximately 1 K/s, and the surface temperature was measured with a chromel–alumel thermocouple in contact with the SAM/Au samples. The vacuum pressure in the chamber was less than 10^{-10} Torr. The desorption fragments for each SAM sample were detected as a function of surface temperature.

2.5. Molecular modeling

The potential drop ($\Delta\Phi$) of the SAM-modified Au metal substrates with various molecular species can theoretically be extracted from the Helmholtz equation (Eq. (1)) [4,18]. The dipole moments (μ in Table 1) of the molecular species (Naph-S, Naph-NC, and Perfluoro-C10-S) used in the equation were calculated for geometries optimized in the gas phase with density functional theory (DFT) at the B3LYP/6-311++G** level of theory and implemented in Jaguar v6.5. And the binding energies of the molecules adsorbed on the Au(111) surface were estimated with a classical

molecular mechanics calculation based on the final geometries, which were optimized with the conjugate gradient method for the universal force field (UFF) [19,20] (see Table 2).

3. Results and discussion

We used three types of molecules (Fig. 1) to study the influence of the density and magnitude of the dipole moment on the SAM-modified metal surfaces. The molecular systems investigated in this study can be categorized by three different features based on chemical anchoring group ($-\text{S}$ or $-\text{NC}$), molecular backbone structure (naphthalene or perfluorodecane), and the direction of the dipole moment (from metal to molecule or vice versa). The direction of the molecular dipole moment is defined by the direction from the negative charge (δ^-) to the positive charge (δ^+) for molecules whose charge distribution has non-uniform polarity [8]. In our molecular systems, the direction of the dipole moment for Naph-S and Naph-NC is oriented from Au metal (δ^-) to the molecular material (δ^+). In contrast, the direction of the dipole moment for Perfluoro-C10-S is oriented from the molecular material (δ^-) to the Au metal (δ^+) because of the relatively high electronegativity of the fluorine atoms [4]. The direction and magnitude of the dipole moments of the molecular systems were calculated with DFT for unbound and isolated (gas phase) molecules (see Table 1).

In the energy level diagrams for the SAM/Au interface shown in Fig. 2, the directionality of the dipole moment determines the sign of the interfacial potential drop ($\Delta\Phi$) with respect to the Fermi level of the Au reference metal. Therefore, the direction of the dipole moment can change the work function (Φ_{W}) of the SAM-modified Au metal. For example, Naph-S and Naph-NC molecules, with dipole moments directed from the metal to the molecule, have negative values for $\Delta\Phi$, which lead to lower work functions for the Au metal (Φ_{Au}) (Fig. 2a). In contrast, Perfluoro-C10-S molecules increase the work function of the Au metal (Φ_{Au}) (Fig. 2b). From the perspective of classical electronics, this potential drop, $\Delta\Phi$ (the change in the work function), between the molecule and the metal can be derived from the Helmholtz equation (Eq. (1)) [4,18],

$$\Delta\Phi = -\frac{N_o\mu_{\perp}}{\epsilon_o K_{\text{SAM}}} = -\frac{N_o\mu}{\epsilon_o K_{\text{SAM}}} \cos\theta \quad (1)$$

where N_o is the grafting density (or the dipole moment density) of the SAM ($\#/m^2$) at room temperature, μ_{\perp} is the effective dipole moment of the SAM along the direction perpendicular to the metal substrate, θ is the tilt angle of the molecules with respect to the surface normal of the metal substrate ($\mu_{\perp} = \mu \cos\theta$), ϵ_o is the permittivity of vacuum, and K_{SAM} is the dielectric constant of the SAM. The grafting density (N_o) of the SAM on the Au surface depends on the type of close-packed structure of the molecules on the Au surface. For Naph-S on an Au(111) surface, the molecular chains are oriented closer to the plane of the Au surface ($\theta = \sim 44^\circ$) and adopt an ordered $3 \times 3\sqrt{3}$ (Wood's notation) structure with a rectangular unit cell because of the contributions from the larger nearest-neighbor spacing and the molecular structure, which yields a less dense packing than that of alkanethiol [4,21]. This results in a grafting density (N_o) for the Naph-S SAM of $\sim 2.9 \times 10^{18} \text{ m}^{-2}$ on the Au(111) surface [21]. It is known that Perfluoro-C10-S on an Au(111) surface adopts an ordered $c(7 \times 7)$ superlattice of closed-packed molecules with a lattice constant of 5.8 ± 0.1 Å and a smaller tilt angle ($12\text{--}20^\circ$) [4,22,23]. From these values, the grafting density for the Perfluoro-C10-S SAM can be estimated to be $\sim 3.4 \times 10^{18} \text{ m}^{-2}$ on Au(111) [4]. For the Naph-NC SAM, the exact values of N and θ are not known. Here, we assume that N and θ for the Naph-NC SAM are the same as those for the Naph-S SAM because the molecular structure is the same although a different chemical anchoring group on Au surface. The physical properties

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