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Control of the Electrode−Molecule Interface for Molecular Devices

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The gold−sulfur bond is extremely important for applications in the formation of self-assembled monolayers,[1] markers of biological molecules,[2] such as DNA and proteins, and the connection of electrodes and molecules in single molecule devices.[3] However, it has been pointed out, since the development of single molecule devices started, that this bond is not an advantageous device property.[4] In an effort to realize quantum conduction in the electric conduction or device property of a single molecule or a small number of molecules and to advance nanoscale molecular electronics, it is essential to develop an electrode−molecule interface with highly stable electrode−molecule bonding and a low charge injection barrier from electrode to molecule.[5]

To find a substitute for the gold−sulfur bond, the most promising way involves the use of a gold−selenium or gold−tellurium bond by replacing sulfur atoms with selenium or tellurium atoms. The gold−chalcogen bond has been examined with monolayers of dialkyl dichalcogenide molecules (dioctyl disulfide, diselenide, and ditelluride),[6] while the gold−selenium bond was also studied by using monolayers of biphenyl selenol.[7] However, no systematic study on the gold−chalcogen (S, Se, and Te) bond has been conducted with monolayers of π-electron system chalcogen molecules. Also, the electronic states of monolayers of π-electron system chalcogen molecules have not been investigated, although the electronic states are very important to estimate the charge injection barrier from electrode to molecule.[3,5,8]

In this study, we conducted photoelectron spectroscopy to investigate the bonding condition between gold and chalcogen atoms and the electronic states of the interface, by employing benzenethiol, benzeneselenol, and biphenyl ditelluride. We found that bonding was formed between gold and benzenethiol or benzeneselenol. We also observed various spectra, depending on the production condition of a monolayer of biphenyl ditelluride. By examining the bonding property and the electronic states, we clarified that a gold−selenium bond is more suitable for molecular electronics than the other bonds.

We produced a gold (111) plane on a mica substrate using the thermal deposition method. We placed the gold substrate into 10 mM methanol solution of benzenethiol, that of benzeneselenol, or 5 mM methanol solution of biphenyl ditelluride for 12 h, then washed off the substrate with methanol, and dried it to produce a monolayer. As light promotes the generation of oxides in the methanol solution of biphenyl ditelluride,[9] we shielded the light to form the biphenyl ditelluride monolayer. After making the monolayers, we immediately placed them in a vacuum chamber and conducted spectroscopy measurement. Detailed experimental procedures are described in the Supporting Information.

We then used X-ray photoemission spectroscopy (XPS) to measure the bonding condition between gold and each molecule and observed a chemical shift corresponding to each bond, that is, the bond between gold and sulfur, selenium, or tellurium. In the gold−sulfur bond, the bonding energies corresponding to $S(2p_{3/2})$ and $S(2p_{1/2})$ were found to be 161.4 and 163.0 eV, respectively.[1b] In the gold−selenium bond, the bonding energies corresponding to $Se(3p_{3/2})$ and $Se(3p_{1/2})$ were 160.3 and 164.7 eV, respectively.[6,7] Therefore, the chemical shifts[10] of the $S(2p_{3/2})$ and $Se(3p_{3/2})$ peaks were −1.1 and −0.4 eV, respectively, indicating that the gold−sulfur bond was a stronger ionic bond than the gold−selenium bond. Namely, we can expect frontier molecular orbitals to be localized more significantly in the gold−sulfur bond than in the gold−selenium bond, meaning the gold−sulfur bond has a higher charge injection barrier.

Figure 1 shows the XPS spectrum of the monolayer of biphenyl ditelluride. The observed spectrum differed, depending on whether or not light shielding was used to produce the monolayer. In the spectrum of the monolayer produced with light, we observed strong peaks of Y1 (575.4 eV) and Y2 (585.7 eV), while in the spectrum of the monolayer produced with no light, we found strong peaks of X1 (572.3 eV) and X2 (582.7 eV). Since the bonding energies of $Te(3d_{5/2})$ and $Te(3d_{3/2})$ are 572.5 and 582.2 eV, respectively, the chemical shifts of the peaks Y1 and Y2 are 2.9 and 3.5 eV, respectively,[10] suggesting that the tellurium atoms formed strong ionic bonds with the elements of high electronegativity. On the other hand, the adsorbed oxygen peak O(1s) was observed at 531.8 eV[11] in the monolayer produced with no light, but the peak O(1s) was observed at 530.0 eV in the monolayer produced with light. This indicates that oxygen atoms were negatively charged under the lighting condition. With this in mind, the peaks Y1 and Y2 should come from the bonding energy of $Te(3d_{5/2})$ and $Te(3d_{3/2})$ of tellurium oxides. It is possible to control the ratio of the tellurium oxides to the gold−tellurium bonds by changing the production conditions, but the gold−tellurium bond that tends to generate oxides is inappropriate for molecular devices because the tellurium oxide is an insulator.

To investigate the electronic states of the gold−molecule interfaces, we then conducted ultraviolet photoemission spectroscopy (UPS) for the monolayer of gold−benzenethiol or gold−benzeneselenol that can be bound to gold without generating oxides. Figure 2 shows the spectrum of around the Fermi level of gold. In the monolayer of benzenethiol, the density of states (the intensity) increases from around 1.2 eV measured from the Fermi level of gold, while in the monolayer of benzeneselenol, the density of states increases from around 0.9 eV. The increase in the density of states around the Fermi level of gold comes from the density of states of the p_z orbitals of the sulfur or selenium atoms that form the π-electron orbitals of the molecule bound to the electrode.[12] This indicates that the charge injection barrier from the electrode to the frontier molecular orbitals of the molecule is smaller in the gold−selenium interface than in the gold−sulfur interface.

To obtain quantum conduction in an electrode−molecule−electrode structure, the coupling between the electrode and molecule has to be strong.[13] The coupling is stronger with larger overlap integrals between the Fermi level orbitals of the electrode and the frontier orbitals of the molecule.[13] Let us consider the bonding property and the charge injection barrier of the electrode−molecule

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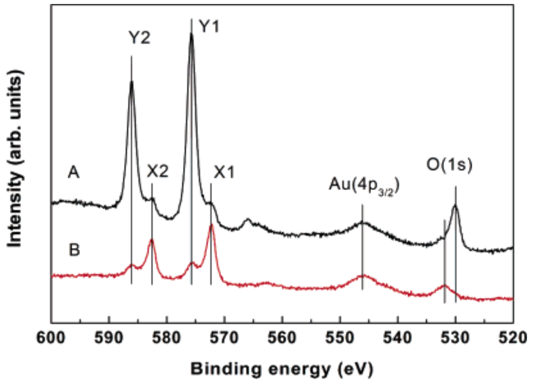

Figure 1. XPS spectra of the Te(3d), O(1s), and Au(4p) core levels from the biphenyl ditelluride monolayer on the Au(111) surface. The spectra A and B were obtained on the monolayers produced with light and no light, respectively.

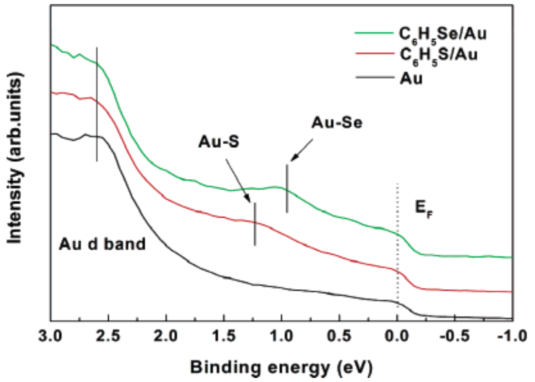

Figure 2. UPS spectra of benzenethiol and benzeneselenol adsorbed on the Au(111) surface, and the Au(111) surface near the Fermi level. E_F shows the Fermi level of a gold.

interface, with the electrode−molecule coupling in mind. The strong ionic binding property in the coupling indicates that the frontier orbitals of the molecule bound to the electrode are strongly localized.[14] Therefore, in the strong ionic binding, the overlap integral between the Fermi level orbitals of the electrode and the frontier orbitals of the molecule is small. On the other hand, if the charge injection barrier is high, the energy level difference between the Fermi level orbitals of the electrode and the frontier orbitals of the molecule is considerable, and the overlap integral between the two orbitals is modest.[14] We therefore expect stronger coupling to be formed in the gold−selenium interface than in the gold−sulfur interface since the gold−sulfur bond has stronger ion binding property than the gold−selenium bond and the gold−selenium interface has a smaller charge injection barrier than the gold−sulfur interface.

In summary, we conducted XPS and UPS measurements of the gold−sulfur, gold−selenium, and gold−tellurium interfaces by using three benzene derivatives to find an appropriate electrode−molecule interface for the development of molecular devices with quantum conduction property. The gold−sulfur and gold−selenium bonds were formed in a stable manner. The gold−tellurium bond was formed on a gold surface, but it is not suitable for molecular devices as it produces tellurium oxides. In a comparison of the gold−sulfur and gold−selenium interfaces, we found that the charge injection barrier from gold to the frontier molecular orbitals of the molecule was smaller in the gold−selenium interface, from which we expected that a large electric current could be obtained at a lower voltage in the gold−selenium interface. We therefore concluded that the gold−selenium interface was more appropriate for molecular devices than the gold−sulfur or gold−tellurium interface. These bondings can be used as new anchors of electrochemical applications, and higher-performance molecular devices can be developed by combining the result and the self-organized interconnect method.[15]

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Supporting Information Available: Sample preparation and XPS spectra from monolayers on the Au surface. This material is available free of charge via Internet at http://pubs.acs.org.

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