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An XPS Study of the Ag-S interface of L-Cysteine Films on Silver Surface

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Abstract: L-cysteine has gained much attention as a versatile amino acid to create bioactive surfaces by assisting the bonding of proteins to metal surfaces. When L-cysteine interacts with metallic partners such as gold, silver and copper, the SH functional group is known to interact strongly with the metallic surface. The interaction of the L-cysteine with silver surfaces is particularly interesting because, L-cysteine adsorption on silver has been suggested to be stronger than on gold or copper surfaces and the interactions may strongly influence the formation of novel interface states of the L-cysteine-Ag interface. On the other hand, some studies report a weakening of silver-sulfur bond with increasing coverage. However, research has not been sufficiently addressed for experimental investigation to understand the interaction of L-cysteine with silver metallic surfaces. As the first step, we reported the results of experimental investigation of L-cysteine and silver interface electronic structure by thickness-dependent ultraviolet photoelectron spectroscopy (UPS) with a clear spectral feature in between Fermi edge and highest occupied molecular orbital (HOMO) of L-cysteine due to the formation of Ag-S bonding together with a weakening of the silver-sulfur bond with increasing of L-cysteine. In this study, the formation of Ag-S bond at the L-cysteine modified silver surface was systematically elucidated by X-ray photoelectron spectroscopy (XPS) for three different coverages, namely monolayer, two-layered and multi-layered. A prominent shoulder at 2475.2 eV of the main peak at 2473.2 eV was observed for the S 1s XPS spectrum for monolayer film, while only a single peak was observed in the case of two-layered and multi-layered. The spectral feature at 2475.2 eV can be attributed to the interaction of L-cysteine with silver. In addition, the disappearance of the spectral feature for the two-layered film can be attributed to the weakening of silver-sulfur bond by over layer of L-cysteine.

Keywords: Interface electronic structure, L-cysteine, silver, X-ray photoelectron spectroscopy.

1 Introduction

Bioelectronics is a discipline at the intersection of electronics and living systems by interfacing the knowledge from biology, electronics and nanotechnology. In bioelectronics device fabrication a viable mechanism is required to link the selected biomolecules to metallic substrates. Proteins, being the most versatile biomolecules, play an outstanding role in bioelectronics as a connector between the organic world and the inorganic world especially when metal electrodes are involved. Therefore, knowledge about metal-protein interactions is crucial, and the interaction should be well understood to apply protein-based structures in bioelectronics [1, 2, 3, 4]. It is well known that the design of devices with high efficiency relies on an in-depth understanding of the physical and chemical properties of the molecule-metal interface. When designing bio-electronic devices and biosensors using proteins, it is essential to find the carrier exchange between electrodes and bioactive layers that provide the connection between biomolecule and metal [5, 6]. L-cysteine [HS-CH2-CH(NH2)-COOH] is a Sulfur containing amino acid with a unique metal-binding ability. It is a promising bioactive layer that can anchor metal surfaces such as Au(111) by virtue of its ability to form chemical

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bonds between Au atoms and the sulfur atoms in the molecule itself [7, 8, 9, 10, 11, 12]

Sulfur containing molecules and their interactions on surfaces have gained much attention due to their potential application for organic thin film devices such as self-assembled monolayers (SAMs) and it has been shown that molecules like alkanethiols (R-SH) are adsorbed on metals such as Au(111), often leading to well ordering of molecules at surfaces [13, 14]. Sulfur containing biomolecules such as L-cysteine have an outstanding role in bioelectronics as a connector between biomolecules like proteins and metal electrodes based on inorganic metals through the lateral interactions facilitated by multiple functional groups such as the carboxylic group [-COOH], amino group [-NH2], and thiol group [-SH]. It has been reported that L-cysteine anchors to the metal surface using either chemisorption (similar to thiolate-metal bonding) or physisorption (similar to the bonding to metal surfaces by the amino and carboxyl functional groups) leading to the formation of highly ordered layers [12, 15]. Therefore, L-cysteine can be considered as a versatile SAM molecule.

Several experimental and theoretical research studies have been conducted previously to elucidate the absorption behaviors of L-cysteine on different metals and according to them L-cysteine adsorption on metallic surfaces is very strong due to the multifunctional anchoring behavior coordinated by the functional groups, particularly the thiol (-SH) group [16, 17, 18, 19, 20]. This strong interaction may affect the different interface electronic structure depending on the metallic partner and the new properties at the interface should be considered for the applications in electronics. Therefore, it is essential to investigate the adsorption behavior of L-cysteine on metallic partners, especially the detailed understanding of the interface electronic structure of L-cysteine on metallic surfaces. Silver has been identified as a promising candidate in many recent applications involving bioelectronic interfaces [16, 21]. Therefore, studies with a focus on the interaction of L-cysteine on the Ag surface are interesting from a bioelectronics perspective and to compare the results with other metals like Au and Cu. The L-cysteine adsorption on silver has been suggested to be stronger than on gold or copper surfaces and the interactions may strongly influence the formation of novel interface states of the L-cysteine-Ag interface [22, 23]. On the other hand, there has been theoretical investigation by means of density functional theory (DFT) studies report a weakening of silver-sulfur bond with increasing coverage. This will be a drawback of anchoring the biomolecules on silver surface through the L-cysteine-silver strong interaction [24]. However, research has not been sufficiently addressed for experimental investigation to understand such change in interaction via over layer of L-cysteine in the case of silver surfaces.

As the initial step, in our previous study we have examined the electronic structure of the L-cysteine/Ag interface using thickness dependent ultraviolet photoelectron spectroscopy (UPS) to obtain the information of interaction at the interface [25]. UPS has turned out to be one of the most important techniques in order to clarify the formation of such an electronic structure [26, 27, 28, 29]. Further, we have also reported photoelectron yield spectroscopy (PYS) of L-cysteine on evaporated silver and palladiaum surfaces in order to support the UPS analysis [25, 30]. It was clearly observed an interface state and, which was assigned to the antibonding state due to coupling of S 3p orbital of L-cysteine with Ag 4d orbital. The results of UPS together with PYS confirmed that the work function of silver decreased once and then recovered at low coverage which also suggests a weakening of the interaction of L-cysteine with silver by increasing of L-cysteine coverage.

In this study, formation of Ag-S bond was further studied using x-ray photoelectron spectroscopy (XPS). XPS is an effective and one of the most widely used methods to investigate metal-molecular interfaces [31, 32, 33]. Synchrotron radiation has a variety of properties which make it an attractive source for XPS analysis [34, 35]. In the case of Lcysteine on silver surface, chemical bonding of L-cysteine with silver surface can be identified via XPS because it provides information on the local structure around the sulfur atom

2 Experimental Details

All experiments were carried out at the BL 27A soft x-ray station in the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Japan. The double crystals of InSb (111) were used as a monochromator. The energy resolution of the monochromator was 1.1 eV at 2.5 keV (sulfur K-edge). This beam line has the end station consisting of two ultra high vacuum systems (UHV system), i.e., main analyzing chamber and sample preparation chamber. The base pressure of both chambers was in the order of 10^{-7} Pa. The main analyzing chamber consists of a hemispherical electron energy analyzer (VSW Co. Class-100) for XPS measurements and manipulator. L-cysteine was purchased from Sigma Aldrich (purity: 99%) and inserted into a quartz cylindrical tube wound with a tungsten wire for heating. The surface of Au was rinsed with acetone before introducing into the vacuum chamber and then the surface was sputtered by 1 keV Ar+ ions. L- Cysteine evaporated at a constant rate of 0.3 A°/s which was measured by a crystal monitor. Hence, the thickness values for L-cysteine coverage are nominal film thicknesses and predetermined the thickness of L-cysteine coverage with our previous experiences of evaporation rate and time. When the desired rate of evaporation was reached the sample was moved into position from a preparation chamber, turned to face the evaporator for the desired time, turned upright again, and moved into the measurement chamber. Here, three types of films were prepared with different evaporation times namely monolayer, two-layered and multi-layered.

Subsequently, a set of XPS measurements were performed at each step of the thickness accumulation.

3 Results and Discussion

Figure 1 shows XPS S 1s spectra of L-cysteine on silver surface. The spectra (a), (b) and (c) represent monolayer, twolayered and multi-layered films, respectively. It is clear from the figure that the main peak and a prominent shoulder can be observed in the monolayer in contrast to thick layers. The main peak position of all three layers are nearly the same. It is deduced that the higher-energy shoulder at 2475.2 eV (x line) may originate due to an interaction of Ag with L-cysteine. It is also attributed considering the higher binding energy peak as the electrons are donated from sulfur atom to the silver and the sulfur can be positively charged. Such a positive charge may apply an additional coulomb repulsion on photoelectron which implies photoelectrons loss kinetic energy and as a result there should be a peak in the high binding energy side. However, any spectral change apart from the main peak cannot be observed in the case two-layered and multi-layered films. There is a small difference of the peak position of 0.3 eV (y and z lines) of two-layered and multi-layered films can be attributed to the accumulation of surface charge which can affect to the loss of kinetic energy of photoelectrons. Also, there may be a peak shift because over layers possible to be formed in the zwitterionic form [23, 36].

Honda et al, performed XPS for L-cysteine on Au surface and observed two peaks at peak at 2472.2 eV and 2480.4 eV for thin L-cysteine layer on Au [32]. In contrast, only one main peak was observed closer to 2472.2 eV for the thick film. It was presumed that the peak at 2472.2 eV corresponds to the S 1s of molecular L-cysteine. Honda et al, assigned that the higher-energy peak at 2480.4 eV originates from the formation of Au-S configuration between sulfur and gold atoms [32]. Our XPS results are consistent with Honda et al with the observation of the main the peak at low binding energy side (i.e. at 2472.2 eV) with higher binding energy shoulder. This allows us to assign the higher-energy shoulder at 2475.2 eV to the formation of Ag-S. In our previous UPS results, we have reported interaction of a sulfur-originated state of L-cysteine HOMO interaction with Au d orbitals forming bonding and antibonding states coupling of S 3p orbital with Ag 4d orbital in line with previous studies [36]. The antibonding state is assigned as the interface state and such an interface state possibly enhance the charge transfer between L-cysteine and silver substrate. Generally, the Fermi level of the substrate should lie in the middle of molecular adlayer HOMO-LUMO bandgap. However, we observed a clear spectral feature between the Fermi edge and the HOMO of L-cysteine which can be attributed to the formation of Ag-S bonding. However, the charge transfer between L-cysteine and silver is much more complicated to understand via UPS results as the secondary electron cutoff (SECO) direction behave differently compared to the case of gold and copper. In the case of L-cysteine on silver surface, we have observed SECO shifted toward higher binding energies and shifted back to the lower binding energy side and eventually cancel the initial vacuum level shift. This might be attributed to different charge transferring of in the case of interaction of L-cysteine and Ag(111) with the forming of over layers. Luque et al performed calculation for L-cysteine and silver system and reported that excess negative charge on the sulfur atom and the positive charge on the silver surface [24]. The electronic properties of thiolate/Au(111) interface have been reported by De Renzi [36]. Accordingly, the interaction of a localized atomic orbital with an extended metallic orbital can be explained with reference to the Anderson-Newns model for atomic and molecular chemisorption on transition metal surfaces. It outlines that the interaction between a localized atomic or molecular orbital and the narrow d band of the metal produces hybrid orbitals of both bonding and antibonding type. The one-electron states on the substrate or adsorbate start to interact with all the valence states on the transition metal as it approaches the surface. These metal states form an almost continuous band of states. Depending on the shape of these bands the interaction will result in a broadened single resonance if the metals states are broad and delocalized or split into bonding and anti-bonding resonances if the metal states are narrow and localized. This in turn gives rise to strong chemisorption [37]. Accordingly, bonding and antibonding states are possibly formed by a coupling of S 3p orbital with Ag 4d orbital when L-cysteine interacts with Ag. It is suggested that the bonding and antibonding states between sulfur and metal are located below and above the d band of metal. Therefore, the peak shift and the slight change of spectrum feature together with the decrement of d band can be attributed to bonding and antibonding states as coupling of S 3p orbital with Ag d orbital. The bonding and antibonding states might be located near the HOMO of L-Cysteine and the Fermi level of Ag, respectively. Such a change in the valance level due to the interaction of Ag-S may clearly influence the change of XPS S 1s spectra thus the clearly visible spectral shoulder can be attributed due to the formation of Ag-S bonding.

It is hardly observed the higher-energy peak at 2475.2 eV in the case of two-layered film. This might be due to the weakening of silver-sulfur bond by the over layer of L-cysteine. Otherwise, there should be a spectral change in the high binding side if the interaction of L-cysteine with silver surface existing in the case of the monolayer level. We have reported the weakening of the silver-sulfur bond

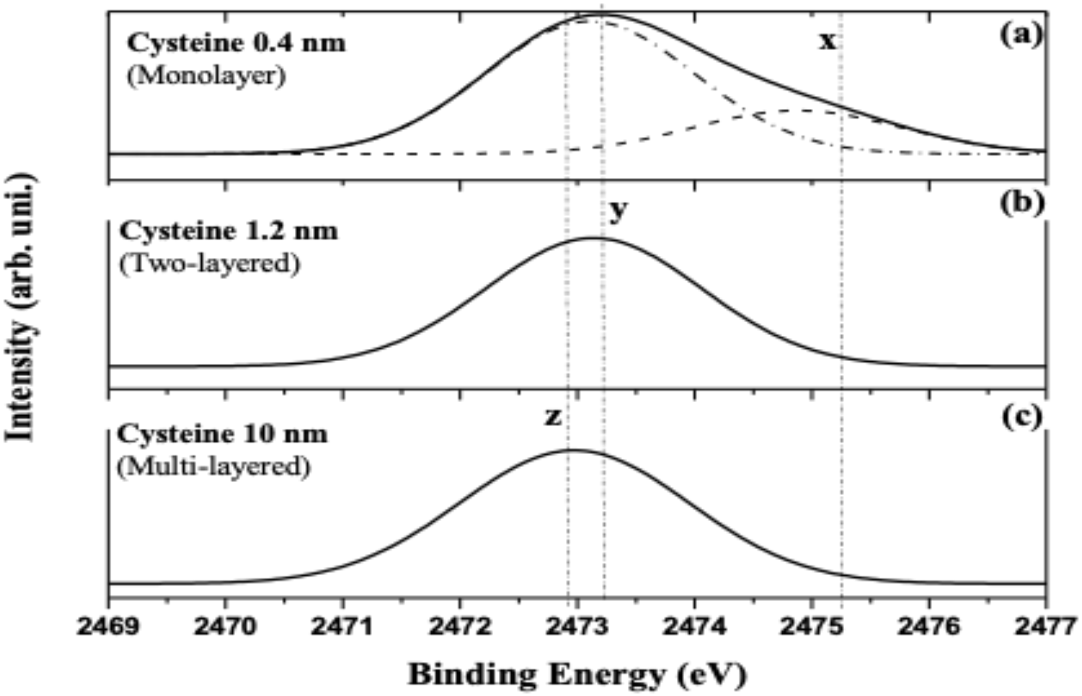

Fig. 1: Thickness-dependent XPS S 1s spectra of L-cysteine on Ag.

with increasing of L-cysteine coverage on silver via work of UPS together with PYS [25].

We have measured UPS spectra of L-cysteine on Ag(111) with various thickness and found that the SECO starts to decrease at low coverage from 2 A°, and at 16 A°, the SECO shifted to a value of around 0.4 eV toward lower binding energies where at 16 A° SECO shifted back to the lower binding energy side by 0.4 eV to eventually cancel the initial vacuum level shift. This was attributed to reduction of the amount of charge transfer cause decrease the interface dipole moment by weakening the interaction of L-cysteine and Ag(111) with the forming of over layers.

Luque et al. have suggested similar behavior as weakening of the silver-sulfur bond with increasing of L-cysteine coverage on silver [24]. We performed PYS for further clarification the SECO behavior of UPS as the SECO shifts toward the low binding energy side at low coverage with increasing thickness as here it is attributed to weakening of the silver-sulfur bond with increasing of L-cysteine coverage on silver. We have observed similar behavior via PYS results of L-cysteine on silver where the work function of Ag is decreased until 5 A° thickness of L-cysteine layer and at thickness 10 A°, it is increased again [25]. This can be due to a weakening of silver-sulfur bond with increasing the coverage which is consistent with SECO behavior of UPS results. Here, the XPS results of two-layered support to the discussion through our previous UPS and PYS results of a weakening of silver-sulfur bond with increasing the coverage.

4 Conclusions

The current study is carried out to support our previous findings on interaction of L-cysteine with silver surface.

Where UPS and PYS data suggested that the weakening of Ag-S bond with the increase of coverage. Here we differentiated spectral changes of monolayer and multilayer (two layers and more) L-cysteine films. The spectral change attributed to the Ag - S bond formation at the interface. Further the fact that, complete disappearance of spectral change in two - layered film strengthens the proposed hypotheses of Ag - S bond weakening with coverage. Thus, based on UPS, PYS, and XPS results we can conclude that the L-cysteine - Ag system could not be the ideal candidate for anchoring biomolecules with metals in bioelectronic applications.

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