

Interface Electronic Structures of the L-Cysteine on Noble Metal Surfaces Studied by Ultraviolet Photoelectron Spectroscopy*

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L-cysteine, one of amino acids, is well known in the bioelectronics field as a linker between proteins and metal electrodes. The interface electronic structures between L-cysteine and metals are therefore very crucial because they dominate the charge carrier injection characteristics into such biological systems. However the interface electronic structures of L-cysteine and metals have been not well understood. In this study, the electronic structures at the interfaces of sequentially deposited L-cysteine layers on the metal surfaces of Au(111), Ag(111), and Cu(111) were investigated by thickness-dependent ultraviolet photoelectron spectroscopy (UPS). At the contact regions, the electronic structures of L-cysteine revealed modification with respect to its bulk phase and significant variation depending on the substrate. The electronic structure at the interfaces including work function, secondary electron cutoff (SECO), highest occupied molecular orbital (HOMO) onset, position of an interface state, charge injection barrier, and ionization energy were estimated for each case. [DOI: 10.1380/ejsnt.2015.373]

Keywords: Photoelectron spectroscopy; L-cysteine; Single crystal surfaces; Gold; Silver; Copper; Electronic structure

I. INTRODUCTION

L-cysteine, as an amino acid on the outer fringes of large proteins, can provide a link between those proteins and inorganic metal substrates. For the application of biomolecules (*e.g.*, proteins) in electronic devices, it is essential to bond and organize the biomolecules on metal electrodes. It is expected that the L-cysteine presumably employs multiple functional groups (*i.e.*, SH, NH₂, and COOH) in its bonding to metal surfaces and 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). These bonding strengths of L-cysteine, in particular the involvement of SH with the other functional groups, depend on the metallic partner properties [1]. Therefore, an understanding of the interaction of L-cysteine with metal surfaces is necessary. There have been experimental and theoretical research studies that examined the behavior of L-cysteine adsorbed on different faces of gold [2–19], silver [20–23], and copper [24–26] metallic single crystals as model systems for understanding the interaction of L-cysteine with metal surfaces and also L-cysteine adsorbed on some other surfaces considering technological interests [27–35]. In the

experimental studies, the L-cysteine sample for investigation was formed using either the self-assembly or evaporation method.

Some studies reported that L-cysteine adsorption on metallic surfaces involved a strong chemical and electronic interaction between the cysteine and the surface, and that the interactions may strongly influence the properties of the L-cysteine–metal interface. For instance, cysteine–substrate bonding may result in the formation of electronic states in the energy gap of the molecular system, which are interesting and important to investigate the use of L-cysteine for electronics applications because such a state influence the charge carrier injection characteristics across the cysteine/electrode junction [18]. Even though some research efforts have been focused on understanding of the behavior of cysteine on metallic surfaces, it remains difficult to compare the experimental results because of differences among experimental conditions, sample preparation, *etc.* Thus, it is necessary to perform a research study in which a comparison of the behavior of cysteine on different metallic surfaces in the same experimental conditions. Furthermore, detailed understandings of the interface electronic structure of cysteine on metallic surfaces including charge injection barrier across the interface, existence of possible interface state and behavior of vacuum level shift have been hardly reported. Such findings are necessary for designing the function of devices such as bio-electronic devices and biosensors, because carrier exchange between electrodes and bio-active layer is an essential process. Consequently, as the initial step, this study focuses on elucidating the electronic structures at

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the interfaces of successive L-cysteine layers and the metal surfaces Au(111), Ag(111), and Cu(111) by ultraviolet photoelectron spectroscopy (UPS) using synchrotron radiation, where thickness-dependent UPS is employed for a detailed analysis of the electronic structure at the interfaces.

So far, Beerbom, *et al.* [36] performed a multistep deposition sequence of cysteine on Au surfaces to investigate electronic and chemical structure of the interface between L-cysteine and Au, depositing L-cysteine by repeatedly dipping the Au substrate into a solution of L-cysteine. Based on their UPS results, they have suggested the formation of an interface state around 1.5 eV above the HOMO of L-cysteine. However, this interface state is difficult to be distinguished in their results; they consider the conclusion to be an assumption limited by weak emission under the experimental conditions. Further, Ogawa, *et al.* [33, 34] has performed UPS to study the electronic structures of dental alloys and their interaction with L-cysteine. In the study, they have performed UPS of vacuum evaporated thin films of nominal thickness 3 Å and thick films of nominal thickness 60 Å on polycrystalline Au, Ag, Pd, Cu in order to analyze L-cysteine interaction with dental alloys. They have observed the interface electronic structure which was assumed by Beerbom, *et al.* [36] through their UPS results; however Ogawa, *et al.* [33, 34] results are not sufficient for a systematic elucidation and comparison of the interfaces of L-cysteine on metallic surfaces because there is no experimental evidence to understand the vacuum level shift at interfaces and, it is difficult to perform a systematic evaluation of the interfaces because limited thickness of the films are considered.

In the present study, a vacuum evaporation method was used to form the L-cysteine films on the metallic substrates due to the following advantages for the investigation. Vacuum deposition can control the L-cysteine coverage precisely on the substrate, which is important for such an interface investigation employing thickness-dependent UPS. In the case of cysteine on metallic substrates, the adsorption configuration involving all the functional groups has been determined to be energetically favored at low coverage and the adsorption mechanism changes (chemisorption to physisorption, weakening of the cysteine-metal bond, *etc.*) with increase of coverage [21]. Thus, the precise control of the thickness, especially at low coverages, is essential in the present study. It has been reported that smooth L-cysteine films can be formed without decomposition using a vacuum deposition method [37]. Furthermore, although most amino acids in the solid states and aqueous solutions tend to exist in zwitterionic isomers where the amino group is protonated to ammonium and the carboxyl group is deprotonated to carboxylate, while amino acids in the gas phase commonly exist in nonzwitterionic neutral forms. In aqueous solution, the zwitterionic form is stabilized by hydrogen bonding with water molecules. However, it has been suggested that different chemical states of L-cysteine adsorbed on metallic substrates using aqueous solution are strongly correlated to the pH of the solution during adsorption [38–41]. Thus, investigations of cysteine-metal bonding using aqueous solutions have revealed complex scenarios. In addition, it is essential to perform cysteine

adsorption processes in an ultraclean condition to enable essential contamination-free deposition during the experiments, where such a contamination may affect the intermolecular interaction and hence the ordering on the surface.

II. EXPERIMENTAL

The clean, atomically flat surfaces of the Au(111), Ag(111), and Cu(111) single crystals were prepared by repeated cycles of Ar-ion sputtering and annealing. Low-energy electron diffraction measurements of the metallic substrates were performed to verify the surface quality. The L-cysteine was purchased from Aldrich (Aldrich, 99% L-cysteine), which was inserted into a quartz cylindrical crucible wound with a tungsten wire for heating and evaporated at a constant rate of 0.3 Å/s (as measured by a quartz microbalance to form cysteine layers on the substrates). Hence, the thickness values for L-cysteine coverage are nominal film thicknesses. 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. Subsequently, a set of UPS measurements was performed at each step of the thickness accumulation.

The UPS measurements were performed at the beamline BL8B of the Ultraviolet Synchrotron Orbital Radiation (UVSOR) facility of the Institute for Molecular Science, Japan [42]. The UPS spectra were measured using an analyzer with a multichannel detector system (VG, ARUPS10). The angles of incident photons and the detected photoelectrons were 45° and 0°, respectively, relative to the substrate surface normal. The SECO was measured with the sample biased at −5 V. All the preparation steps and the measurements were performed at room temperature. To control for beam damage, adjustment for different photon energies of the intense synchrotron beam and sequential short periods of acquisition on different zones of the sample were performed. Further, for thicker films, photoemission-induced sample charging was carefully monitored by comparing consecutive UPS measurements at the same experimental conditions.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the thickness-dependent UPS spectra of L-cysteine on (a) Au(111), (b) Ag(111), and (c) Cu(111) for the photon energy of 28 eV. In each figure, on the left, the SECO is shown on a magnified scale. On the right, the region between Fermi level of the metal substrate and the HOMO of the L-cysteine measured with a relatively small energy step is also shown. The work functions for clean Au(111), Ag(111) and Cu(111) were estimated to be 5.2, 4.5, and 4.9 eV, respectively.

Each *d* band peak of the metallic substrates can be assigned as follows: for Au, the peaks at around 3.6 and 6 eV are Au 5*d*_{5/2} and Au 5*d*_{3/2}; for Ag, the peaks at around 4.8 and 6.1 eV are Ag 4*d*_{5/2} and Ag 4*d*_{3/2}; and for Cu, the peaks at around 2.8 and 3.6 eV are Cu 3*d*_{5/2} and

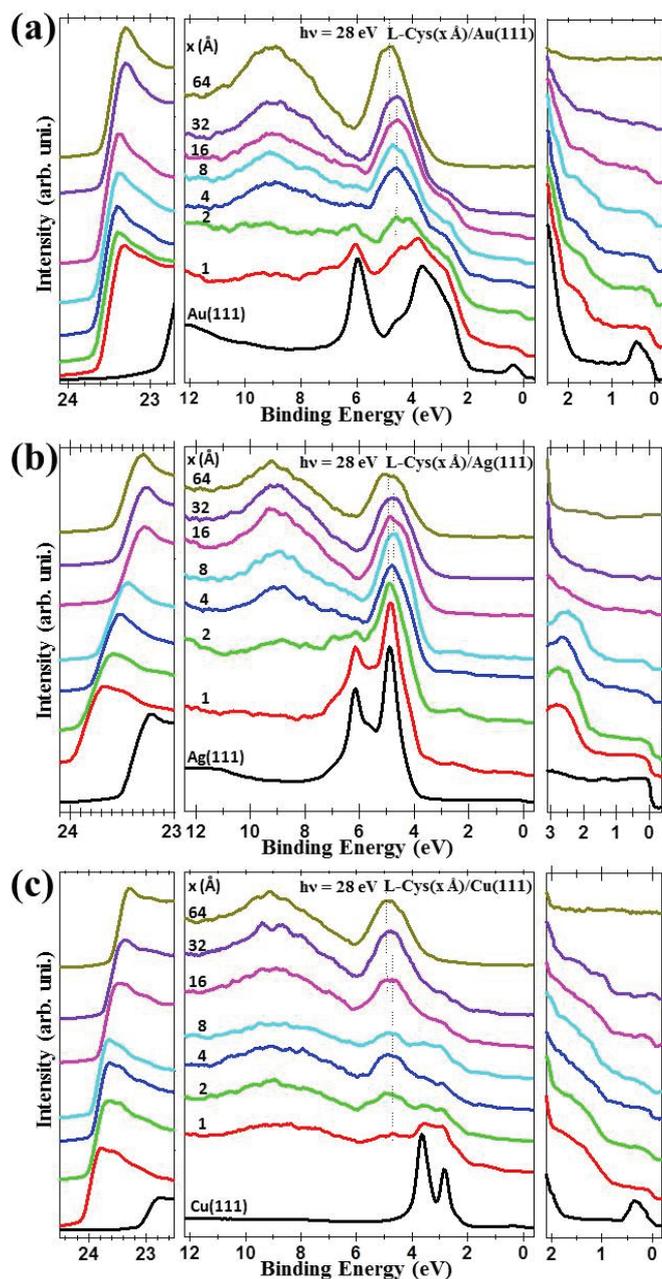


FIG. 1: Thickness-dependent UPS spectra of L-cysteine on (a) Au(111), (b) Ag(111), and (c) Cu(111) at a photon energy of 28 eV. In each figure, on the left, the secondary energy cutoff (SECO) is shown on a magnified scale. On the right, the region between the Fermi level of the metal substrate and the HOMO of the L-cysteine measured with relatively small energy step is also shown.

Cu $3d_{3/2}$ [43, 44]. In the case of Au and Cu, the Shockley surface state was observed. For all the substrates, the metal Fermi edges are no longer visible at 64 Å; therefore, at 64 Å, the L-cysteine spectra may represent only the electronic structure of L-cysteine and the spectra are consistent with the previous reports of UPS spectra of thick films of L-cysteine [33, 34, 36, 37].

It is clear from Fig. 1 that thin film spectra in valence top region depends on substrate and they are different also from the L-cysteine thick films. These features imply that the electronic structures of L-cysteine on metallic

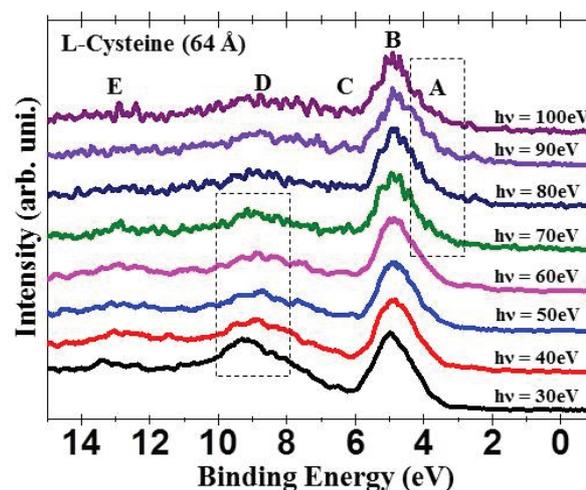


FIG. 2: Photon-energy dependent UPS spectra of L-cysteine thick films obtained with photon energies from 30 to 100 eV.

substrates are strongly dependent on the metallic partner. In Fig. 1, the feature centered at around 4.8 eV binding energy for L-cysteine can be attributed to the HOMO of L-cysteine where the HOMO threshold is estimated to be 3.2 eV and the HOMO positions of all of the thickest layers are almost identical for all the substrates. This value agrees with the HOMO threshold value which we have roughly estimated from the UPS data of L-cysteine thick film of Kamada, *et al.* [37]. However, it is different from the value by Beerborm, *et al.* 3.0 eV [36]. This discrepancy may be due to the difference in zwitterionic form.

For the thin films on all the substrates, a new structure appears between the Fermi level and the HOMO of L-cysteine. The structure may be due to the bonding of orbitals of the S atom in the thiol group with the Au 5*d*, Ag 4*d*, and Cu 3*d* states separately for all the substrates. However, in the case of Au and Cu, it is difficult to distinguish this new feature from the *d*-bands contribution of the substrates. In the case of Ag, the new feature appears as one peak. Furthermore, it is also observed in Fig. 1 that there is a shift of the peak at ~5 eV and at ~9 eV (dotted lines). These shifts may be due to the formation of additional chemical bonds between the metal and cysteine (oxygen or nitrogen metal bonds). We will discuss briefly this interface state and bonding configuration after discussing the valence electronic structure of L-cysteine.

It has been verified that the top of the valence band of cysteine originates with sulfur using photon-energy dependent UPS measurements and theoretical calculations [7, 8, 37]. In this experiment, we also performed photon-energy dependent UPS measurements for the thickest films where the UPS spectra were obtained with photon energies from 30 to 100 eV, and the results are shown in Fig. 2. The spectra are almost identical to those of Kamada, *et al.* [37], and thus the structures A to E shown in Fig. 2 are labeled in terms of their assignments. In Fig. 2, it is clear that with increasing photon energy, the intensity of structure A increases, while those of structures C to E decrease. This indicates that the top

of the valence band has a different origin from the other structures. The structure around the top of the valence band can be attributed to sulfur, while structures C to E can be to carbon, nitrogen, and oxygen, respectively, considering the photon-energy dependence of the ionization cross-sections of the atoms in the L-cysteine. Hence, it can be concluded that the sulfur-originated state is located at the top of the valence band and peak at ~ 5 eV and at ~ 9 eV are mainly contributed by O, C, and N atom-originated states of O $2sp$, C $2sp$, and N $2sp$, respectively.

In the following, the new structure between the Fermi level and the HOMO of the L-cysteine thin film will be briefly discussed considering L-cysteine on Au(111). As can be found in Fig. 1(a), in particular, an intensity increase is clearly observed in the 1–2 eV binding energy region, while the Au d bands in the 2–7 eV region show intensity reduction and shape modification. These spectral changes appear to be due to a sulfur-originated state of L-cysteine HOMO interaction with Au d orbitals. This interaction can be discussed and interpreted in the framework of an Anderson–Newns model, which describes the interaction of a localized atomic orbital with an extended metallic orbital [7, 8, 18]. In this model, for a metal surface, whose electronic structure is characterized by a half-filled broad s band and completely occupied narrow d bands, the model predicts that the atomic orbitals of adatoms are modified by the hybridization of both these bands. Compared to the broad s band, the narrow d bands may be viewed as a localized level, and therefore the coupling of the atomic orbital with such bands causes both bonding and antibonding states, analogous to the bonding and antibonding molecular orbitals, which are formed by the orbitals of two interacting atoms. Thus in the case of L-cysteine on Au(111), the sulfur $3p$ orbitals of the L-cysteine molecule (which correspond to its HOMO) couple to the Au(111) metal d orbitals. That is, molecule–metal hybridization can occur forming bonding and antibonding states [18, 45]. Therefore, the spectral change in the UPS spectra can be attributed to a hybridization of the Au d state with the S $3p$ orbitals where the spectral changes in the 1–2 eV region and above the d band edge can be attributed to S–Au antibonding and bonding states. In particular, some theoretical studies have predicted that in the L-cysteine on Au system, the S–Au antibonding state is located at around 1.5 eV binding energy and that the S–Au bonding region is around the lower edge of the Au d bands [7, 8]. Thus, the increase in the 1–2 eV region can be attributed to the formation of the S–Au antibonding state, which corresponds to the interface state. This attribution is in substantial agreement with previous experimental interpretations by Beerborn, *et al.* though the observed features in their results are broad and thus precise determination of the location of these states is difficult [36]. Furthermore, the shape modification of the d bands region of Au around 2–7 eV is consistent to formation of the S–Au bonding state [7, 8, 18].

Considering the SECO shift that is apparent in the work function change at the interface can be interpreted as an interface dipole. In the case of L-cysteine on Au(111), the maximum shift of SECO is 1.1 eV to a higher binding energy side at 2 Å, and the value is in agreement with the results of Beerborn, *et al.* [36] for cysteine

deposition from solution, where the SECO change (as an interface dipole) was attributed to molecule–metal charge transfer. However, for a system such as L-cysteine on metallic surfaces, the formation of interface dipoles can be attributed mainly to the intrinsic dipole of the adsorbed molecule and the charge transfer across the interface. Thus, there can be possible important contributions of the intrinsic molecular dipole moment that needs to be considered for the attribution of SECO. However, under the circumstances, it is not so straightforward to assign amount of contributions separately from intrinsic dipole moments and charge transfer to interface dipoles because L-cysteine adsorption on gold in different adsorption geometries and chemical forms (radical, anion, and zwitterion) has been theoretically reported to include an induced intrinsic dipole moment (for the interface dipole); the interface charge transfer depends strongly on the molecular configurations [46]. By considering the SECO value, the electrostatic energy difference across the interface (eD) due to the dipole layer is derived to be 1.10 eV, which puts the work function of the L-cysteine layer to 4.1 eV. Adding the work function of the cysteine on Au(111) and the charge injection barrier yields, an ionization energy for the L-cysteine layer can be estimated as 7.30 eV.

In the case of L-cysteine on Ag(111), the maximum SECO shift was 0.46 eV to the higher binding energy side at the nominal thickness of 1 Å. However from the nominal thickness of 2 Å, SECO started to shift to the lower binding energy side, and at 16 Å, the SECO shifted to a value of around 0.4 eV to the lower binding energy side where eventually cancel the initial vacuum level shift. This might be attributed to either of the following reasons concerning over layer formation: 1) weakening the interaction of L-cysteine with Ag(111) reduces the amount of charge transfer, therefore the strength of the interface dipole can be decreased, 2) change of the adsorption orientation affects the intrinsic dipole moment of cysteine; parallel to the metal surface reduces the intrinsic dipole moment contribution to the interface dipole, and 3) a combination of these two phenomena. Fischer, *et al.* [20] addressed evaporated L-cysteine on Ag(111) and reported that L-cysteine forms a dense-packed layer on Ag(111). In this case, the monolayer coverage is chemisorbed to Ag(111) forming silver–sulfur bonding, and L-cysteine exists mainly as a zwitterion for all the layers. Furthermore, when the L-cysteine coverage is increased outside the monolayer, the next cysteine layers physisorb on top of the chemisorbed monolayer. However, Luque, *et al.* [21] have reported that there is a weakening of the silver–sulfur bond with increasing coverage of L-cysteine on silver; this suggestion is consistent with our UPS results where the SECO shifts toward the low-BE side at low coverage with increasing thickness.

In the case of L-cysteine on Ag(111), the feature related to interface structure appeared as a clear peak centered at 2.5 eV with a cutoff at 1.9 eV. The reason for the clear feature is due to a deeply available d band and strong interaction of thiolate upon the adsorption of L-cysteine on Ag(111). However, it has been reported in the case of L-cysteine on Ag(111) that the only situation where the bonding and antibonding states are possible if the adsorbate cysteine is “pushed” into the surface at shorter

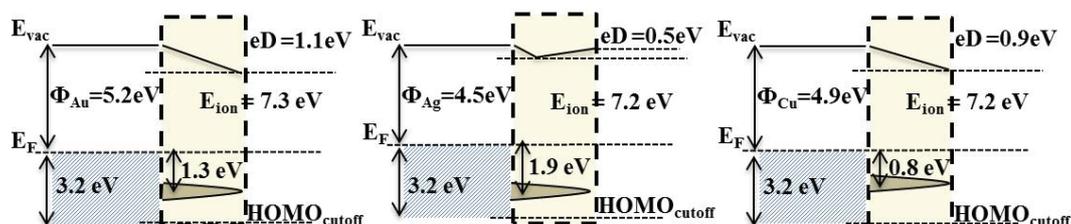


FIG. 3: Schematic of the determined electronic structure at the interface of L-cysteine on (a) Au(111), (b) Ag(111), and (c) Cu(111).

distance than the equilibrium position. The shifting of the peaks at ~ 5 and ~ 9 eV for thick films toward the higher binding energy side, as is shown in Fig. 1 (dotted lines), may explain the bonding of amino or carboxylate groups to metal surfaces. As we have described in the photon-energy dependent UPS results, the features around ~ 5 and ~ 9 eV can be assigned as O, C, and N atom-originated states. Thus, the shifting of peaks at ~ 5 and ~ 9 eV may be due to the interaction of amino and carboxylate groups (O $2sp$ and N $2sp$ orbitals) with silver surface. This interaction may allow pushing adsorbate L-cysteine in to silver surface at shorter distance and consequently, satisfying the the possible situation to form bonding and antibonding states due to sulfur-silver interaction

In the case of L-cysteine on Ag(111) in the Fig. 1 (b), clear spectral changes can be observed comparing 8 Å and 16 Å thickness. Those spectral changes are SECO shifted to the lower binding energy side by 0.3 eV, the peak centered at ~ 9 eV shifting to higher binding energy side, and a disappearance of the peak corresponding to the interface state. These changes may be due to a formation of second layer or more on the chemisorbed first layer. Because, the formation of over layers can be weakening the interaction between first layer and as a result the SECO shift and disappearance of the peak of the interface state are possible [21, 22]. Further, the over layers on Ag(111) are possible to be formed in the zwitterionic form and consequently a shift of the peak ~ 9 eV is possible [21, 22]. Thus, it may be possible to assign the nominal thickness of 8 Å layer as around monolayer of L-cysteine.

In contrast to the L-cysteine on Ag(111), the absence of a clear feature of the L-cysteine on Au(111) from 1 to 2 eV can be ascribed to the emission of Au(111) and partial physisorption of L-cysteine on Au(111). There have been experimental verifications at room temperature the L-cysteine molecule is mainly weakly adsorbed on the gold surface, based on the L-cysteine on Au(111) system [19, 23].

Canepa, *et al.* [19] has performed metastable deexcitation spectroscopy (MDS) investigation of the growth of L-cysteine layer deposited under UHV conditions on Au(111) and suggested that the early stages of growth contains of strongly and weakly bound cysteine molecules. Santos, *et al.* [23] has reported that L-cysteine is adsorbed on Ag(111) stronger than on Au(111) through their investigation of electrochemical behavior and nonlinear optical properties of L-cysteine on Ag(111).

According to an XPS study of Uvdal, *et al.*, [1] L-cysteine adsorbed on copper is not well organized. When

compared with S $2p$ XPS results, L-cysteine adsorbed on copper shows analogous results to S $2p$ XPS results of L-cysteine adsorbed on gold. However, the N $1s$ spectra show some new features for the adsorbate, where neither the N $1s$ nor the O $1s$ XPS spectra show significant changes in peak position during adsorption on gold, when compared with the multilayer films. Furthermore, the angle dependence of the XPS results of O $1s$ suggests carboxylate groups may be oriented toward the surface. Consequently, Uvdal, *et al.* [1] suggested that L-cysteine adsorbed on copper employs at least two functional groups where both the thiol and amino groups participate in the reaction with the copper and the carboxylate groups interact weakly. However, according to our results, the formation of bonding between amino and carboxylate groups with metal surfaces are possible for Cu as well as Au and Ag. There are research works suggesting L-cysteine adsorption process involves not only contribution of thiol but also those of the other existent functional group in the cases of Au and Ag by various experimental methods. Tawil, *et al.* [47] has performed surface plasmon resonance investigation on L-cysteine on gold and indicate that the adsorption of L-cysteine involving both amino and thiol interactions. Brolo, *et al.* [48] has performed surface-enhanced Raman spectroscopy (SERS) and surface-enhanced second-harmonic generation measurements to investigate adsorption behavior of L-cysteine onto a polycrystalline Ag and found that L-cysteine adsorption on Ag through the sulfure group together a weak bonding through either carboxylate or amino group. Our UPS results are consistent with above studies as formation of bonding between amino and carboxylate groups with metallic surfaces are possible in the case of Au and Ag which is not consistent with the earlier study of Uvdal, *et al* [1]. Furthermore, Honda, *et al.* [49, 50] has investigated chemical bonding states of Au-cysteine interface and successfully observed specific Au-S bond formation only in mono-layered L-cysteine on gold through S K-edge NEXAFS and S $1s$ XPS measurements. They suggested specifically strong electron donation from sulfur to gold which is absent for other metal such as copper due to a weak bonding. However, our results contradict with their suggestion as strong Cu-S bond is possible from our UPS results.

The charge injection barrier from the L-cysteine HOMO to the metal Fermi level can be determined as 3.2 eV in the case of Au, Cu, and Ag. This barrier height is too high to inject carrier, however existence of interface state can be facilitated carrier injection and the interface state can be less than 1 eV from the Fermi level for Cu substrate

expecting better carrier injection. Considering the work function of metallic substrates and SECO, the ionization energies are identical on all three substrates within the uncertainty of 0.1 eV, namely 7.3 eV on Au(111), 7.2 eV on each Ag(111) and Cu(111).

Finally, Fig. 3 shows a schematic representation of the electronic structure at the interface in the cases of L-cysteine on Au(111), Ag(111), and Cu(111), including estimated values of work function, SECO, HOMO cutoff, position of the interface state, charge injection barrier, and ionization potential for each case separately. As is clear from Fig. 3, the position of the interface state from the Fermi level of the metal is different on the kind of metallic partner. It can be suggested that the position of the interface is dependent on the position of the *d* band of the metal.

IV. CONCLUSIONS

We have demonstrated different interaction strength and configurations of L-cysteine on the metallic surfaces of Au(111), Ag(111), and Cu(111) using photoemission

spectroscopy. In all cases, we have determined the existence of a new state near the Fermi edge and interpreted it as a metal–cysteine antibonding state. Based on the literature, the corresponding bonding state is assumed to appear at the lower edge of the *d* band, which is difficult to distinguish because of the emission from the *d* band. The formation of such interface electronic states, which are induced by the interaction between the molecule and the metallic surfaces, can strongly affect the charge transport across the junction. Thus, the position of these new states relative to the Fermi level is clearly fundamental in determining the junction properties.

Acknowledgments

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