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Adsorption Behavior of TBPS in the Process of Cu Electrodeposition on an Au Film

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Abstract: The adsorption behavior of an Cu electroplating additive, 3,3 thiobis-(1-propanesulfonic acid sodium salt) (TBPS) in a process of Cu deposition onto a single crystalline Au(111) surface is studied by an *in-situ* Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS). The SEIRAS spectra of the TBPS adlayer on a Cu film is investigated first and compared to that on an Au film. These results are utilized to evaluate the characteristics of TBPS adlayer on the electrode surface during the Cu deposition and stripping processes. The results show that the SEIRAS spectra of TBPS adsorbed on the Cu film resembles closely to that on the Au film, and the most pronounced peaks are symmetric S-O (ss-SO) and asymmetric S-O (as-SO) stretching modes. However, the as-SO band is sharper with a higher intensity on the Cu film. Since the ss-SO and as-SO peaks correspond to the molecular with upright and lie-down orientations, respectively, it implies that the TBPS molecules have higher ratio of lie-down orientation on the Cu film. In the Cu electrodeposition process, the cyclic voltammetry (CV) result shows that the presence of the TBPS in the $HClO_4$ solution can decrease the inhibition effect of $HClO_4$ to the Cu deposition. For the spectra measured at various potential during cathodic and anodic sweeping, an obvious change of the spectra occurs at ca. 0.6 V, the initiation of Cu underpotential deposition (Cu-UPD). For potentials higher and lower than 0.6 V, the spectra are similar, respectively, to those measured for the Au and Cu films. This result indicates that the TBPS molecules originally adsorbing on the Au film transfer to the surface of deposited Cu layer. This inference is also confirmed by the variation in wavenumber and peak intensity of ss-SO and as-SO peaks during the potential sweeping.

Key words: Surface Enhanced Infrared Absorption Spectroscopy, cyclic voltammetry, electroplating additive, adsorption

1 Introduction

In the fabrication process of microelectronic devices, electrochemical deposition is a widely used and well-established method. For performing the damascene electroplating of copper, deposition additives were usually required, not only to facilitate a void-free filling, but also to obtain superfilling of trenches and vias with high aspect ratios[1-3]. In the literature, many studies had performed to study the effects of the additives on the growth behavior of copper in the electroplating process. These studies had shown that the bottom-up copper filling of microvias is achieved in the presence of two plating additives at least. The first one was termed as the accelerator which promotes the Cu deposition rate, and the other decreases the deposition rate, referred as the suppressor. In the literature, 3-Mercapto-1-propanesulfonic acid sodium salt（MPS）and Bis-（Sodium Sulfopropyl）-Disulfide（SPS）were the most commonly used

as Cu growth accelerator. The electrochemical properties and accelerating mechanisms of these two compounds have been extensively studied[4-15]by many electrochemical and structure-sensitive methods. Several growth models of deposits have been proposed for the electroplating systems containing these additives[16-19]. However, the detailed, molecular-scale mechanisms are still not fully clarified and require further investigations, preferably by the applications of new experimental methods or new electroplating additives.

According to the studies in the literature, a molecule utilized as an accelerator must contain both thiol and sulfonate functional groups. In the recent years, a new accelerator, 3,3-thiobis（1-propanesulfonate）（TBPS）, was considered as a promising accelerator for copper damascene plating. TBPS has a molecular structure of（NaO_3S-$(CH_2)_3$-S-$(CH_2)_3$-SO_3Na）, which contains a thioether group

and two sulfonic acid groups. The acceleration effects of TBPS on the copper electrodeposition and been studied and the acceleration mechanisms were proposed in previous work[20-23]. However, the real mechanism is still not clear.

Since the accelerators always contain thiol groups, the adsorption behavior of the accelerator molecules on the electrode surface are considered to be an important step in determining the acceleration effect of an accelerator. Therefore, adsorption behavior of the several accelerators had been studied in the literature by cyclic voltammetry (CV) or scanning tunneling microscopy techniques[12-15]. In a previous study, surface Enhanced Infrared Adsorption Spectroscopy (SEIRAS) was utilized to study the adsorption behavior of TBPS on an Au film[24]. SEIRAS in attenuated total reflection mode (ATR-SEIRAS) facilitates the investigation of the structural composition at the interface with a specific sensitivity to adsorbed molecules much higher than that obtained by an Infrared Reflection Absorption Spectroscopy (IRRAS). Furthermore, this equipment is not restricted by the side-effects in the bulk solution, such as mass transport limitations or advanced potential perturbations. According to the surface selection rule, only molecular vibrations that have dipole changes normal to the surface can give IR adsorption in the SEIRAS measurement[16, 17, 25]. In this way, the spatial orientation of both adsorbed molecules and co-adsorbed species (e.g., water) can be evaluated simultaneously[17, 18]. In this work, we extend the study by using the SEIRAS to probe the adsorption behavior of TBPS molecules in the cupper electrodeposition process. In this work, the adsorption behavior of TBPS onto a Cu film was investigated first and compared to that reported previously on an Au film. The Cu deposition onto an Au film was then performed by sweeping the electropotential in a solution containing TBPS. The SEIRAS spectra were measured at various potential during the cathodic and anodic scanning.

2 Experimental Section

Cyclic voltammetry (CV) experiments were performed using a potentiostat supplied by CH Instruments (model CHI703A). The potentials reported in this work were referred to a reversible hydrogen reference electrode (RHE). For the electrochemical SEIRAS experiments, the cell consists a RHE, a platinum counter electrode (CE) and a hemispherical, Au-coated Si prism or Cu-coated Ge prism as working electrode (WE). The Au and Cu films used for the SEIRAS studies were produced by an electroless deposition technique described elsewhere[26]. The current-potential response of the SEIRAS system was monitored using a standard potentiostat (EG&G PAR Model 263A).

The electrolyte solutions were prepared from ultrapure

$HClO_4$ (70% $HClO_4$, Merck), TBPS (Sigma Aldrich), cupric perchlorate (98% $Cu(ClO_4)_2$, Merck), and Millipore water (Milli-Q, ≥ 18.2M-cm). To reduce the oxygen content, the cell and the solutions were purged with nitrogen gas (N 5.5). The details principle and process and of the SEIRAS experiments were described in a previous work[24]. A Fourier Transform IR Spectrometer (Bio-Rad FTS 60A/896 with MCT detector) in attenuated total reflection mode (ATR-SEIRAS) was utilized for this analysis. Spectra were shown as absorbance curves, obtained after the subtraction of a reference spectrum. The assignment of spectral bands to vibrational frequencies of TBPS is based on theoretical density functional theory (DFT) calculations as given in our previous work[24].

3 Results
3.1 Cyclic Voltammetry Analysis

The CV and SEIRAS experiments were performed using an Au(111) single crystal electrode and an Au-coated Si prism, respectively. In a previous work[24], it had been shown that the characteristic of the CV curves obtained for the two electrodes have good qualitative agreement, indicating that the terraces on the polycrystalline Au film (on Si prism) has mainly a (111) orientation. Therefore, an Au (111) single crystal electrode was used to study the CV behavior of Cu deposition on the Au-coated film. **Figure 1** shows that CV curves obtained in solutions containing 0.1 M $HClO_4$ and 100 μM Cu^{2+}, without (**Fig. 1a**) or with (**Fig. 1b**) TBPS, at a scanning rate of 10 mV/s. In the TBPS-free solution (**Fig. 1a**), a broad cathodic peak (C) associated with the underpotential deposition (UPD) of Cu appears at ca. 0.51 V, and the corresponding anodic peak (A) at ca. 0.54 V is the dissolution of the deposited Cu monolayer. It is noteworthy that, by negative shifting the electrode potential, the overpotential deposition (OPD) of Cu doesn't occur before the potential of hydrogen evolution (ca. −0.15 V). These results are in good agreement with those reported in the literature[21], ascribing to the inhibition effect of $HClO_4$ to the UPD and OPD of Cu.

For the experiment containing TBPS (155 μM), the potential was first controlled at 0.8 V. After approaching the equilibrium adsorption state of TBPS on the Au electrode, the potential was swept negatively. The corresponding CV spectrum (**Fig. 1b**) demonstrates a significant difference compared to that of the TBPS-free system. Two broad cathodic peaks corresponding to the Cu-UPD and Cu-OPD appear at 0.44 V (C1) and 0.09 V (C2), respectively. However, the C2 peak is very broad and not easy to be identified, probably due to the high scanning rate. In the reverse anodic scan, the A1 (ca. 0.62 V) and A2 (between 0.25 − 0.52 V) peaks correspond, respectively, to the striping of Cu deposits caused by the UPD and OPD. The occur-
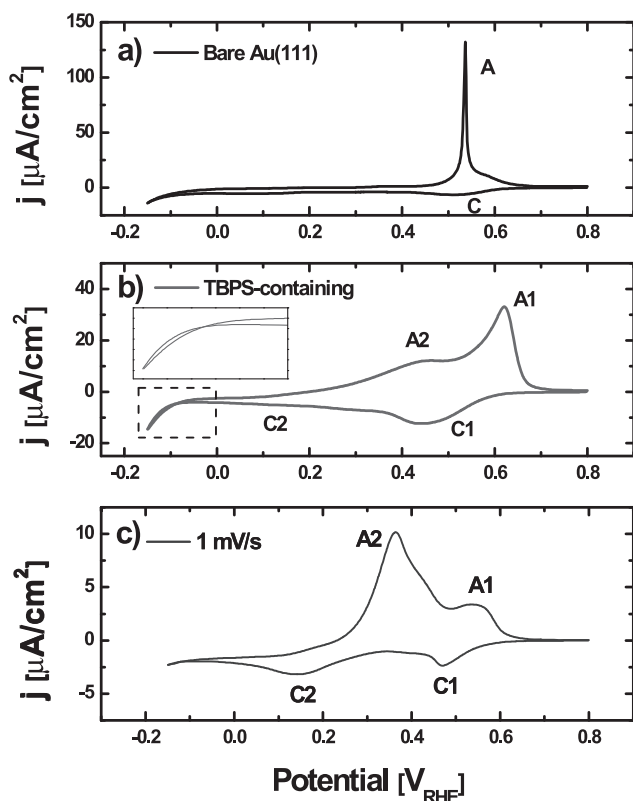
Fig. 1 Cyclic voltammograms measured for an Au(111) electrode in 0.1 M HClO₄ + 100 μM Cu²⁺ solutions without(a), or with 155 μM TBPS(b, c). The scanning rates are 10(a,b)or 1 mV/s(c).

rence of the Cu-OPD indicates that the inhibition effect of HClO₄ is significantly decreased at the presence of TBPS. The anodic current integrated from the A1 peak(stripping of the UPD layer)is ca. 236 μC cm⁻², which is smaller than the theoretical value of a Cu UPD monolayer(ca. 284 μC cm⁻²). This result is ascribed to the co-adsorption of TBPS and other anions[21]. Furthermore, around the hydrogen evolution potential(HEP, ca. −0.15 V), the current measured for the cathodic scan is smaller than that for the anodic scan, resulting a hysteresis behavior of I-V curves as shown in the insect of **Fig. 1b**. The inhibitive effect of TBPS adlayer toward the charge transfer was proposed to explain this behavior. Since the HEP(ca. −0.15 V)is more negative to the potential of Cu-OPD(ca. 0.13 V), it is inferred that the TBPS molecules adsorb on the pre-deposited Cu film, resulting this inhibition effect. This result also implies that, for a TBPS adlayer on Cu film, a more negative potential is required to desorb the adlayer in comparison to that required on an Au(111)surface(ca.0.06 V vs RHE).

The CV spectrum of the Cu deposition is affected by the scanning rate, as well as by the adsorption condition of TBPS. For a smaller scanning rate of 1 mV/s(**Fig. 1c**), the Cu-UPD and Cu-OPD peaks shift more positively to 0.46 V

(C1)and 0.14 V(C2), respectively. This result implies that the charge transfer rate may involve in the cupper reductive deposition. At a slower scanning rate, the longer charge transfer time allows the reductive reaction to perform at a more positive potential.

3.2 SEIRAS Analysis

3.2.1 SEIRAS Analysis of TBPS adsorption on a Cu electrode

To study the adsorption of TBPS adlayer on Cu electrodes, a Cu film was deposited on a Ge prism using an electroless deposition technique. The Cu-coated Ge prism was first immersed in a 0.1 M HClO₄ solution at 0.05 V. After measuring the spectrum of the background(0.1 M HClO₄ solution, t = −5 sec), 155 μM TBPS was introduced into the electrolyte. **Figure 2a** shows the SEIRAS spectra measured after various adsorption time(5, 250, and 500 sec). It shows that, after adding TBPS, a sharp peak appears at 1045 cm⁻¹ which is assigned to the symmetry S-O stretching(ss-SO)vibration of sulfonate(SO₃⁻)group.
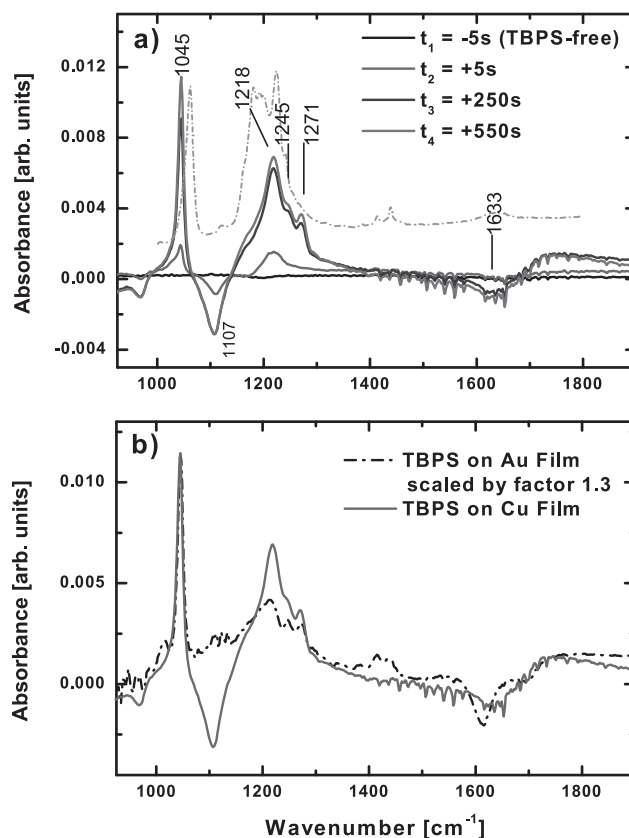

Fig. 2 (a). The SEIRAS spectra of TBPS adsorbed on a Cu-coated Ge prism in 0.1 M HClO₄ + 155 μM TBPS solution at 0.05 V. The spectra were obtained before addition of TBPS(t = −5 s)or at various adsorption time after adding TBPS. (b)A comparison between the SEIRAS spectra of TBPS adsorbed on Au and Cu films.

Furthermore, a board peak corresponding to the asymmetry S-O stretching (as-SO) mode was observed around 1200 cm^{-1}. On the other hand, two negative peaks around 1107 and 1633 cm^{-1} were also exhibited. The negative-going band around 1633 cm^{-1} is ascribed to the desorption of adsorbed water species by adsorption of TBPS molecules. However, the reason leading to the negative peak at 1107 cm^{-1} is presently not clear.

The intensities of the peaks increase with increase of adsorption time and approach an equilibrium value at ca. 250 sec. Compared to the spectrum of free-TBPS measured under air atmosphere (shown as dash line in **Fig. 2a**), the corresponding peaks demonstrate a good agreement in the peak positions, although a slight shift exists and, furthermore, the as-SO peak becomes boarder with a lower intensity. This result is similar to the SEIRAS spectra of TBPS adsorbed on Au-coated Si prism[24]. Since the as-SO stretching mode is associated with a lie-down orientation of adsorbed molecular on the surface, the lower intensity of as-SO peak for the TBPS adlayer, compared to that of free TBPS in the air, suggests that the adsorbed molecules incline slightly to the surface normal. This inference is reasonable since the SO_3^- group is difficult to orient closely to the negatively charged Cu electrode due to the electrostatic interaction.

Comparing the adsorption characteristics of TBPS on Au-coated[24] and Cu-coated surfaces, the two spectra are quite similar. However, the ss-SO peak shifts slightly from 1047 (for Au) to 1045 cm^{-1} (for Cu) which can be ascribed to the effect of different molecule-substrate interactions. Similar phenomena were also found for other peaks. Furthermore, it also appears that the intensities of the peaks for the Cu film are higher than those for the Au film. It should be noted that the intensities of ss-SO and as-SO peaks depend not only on the molecular orientation, but also on the number of adsorbed molecules. Therefore, it is difficult to identify the two effects individually base on the SEIRAS spectra. However, it is possible to compare qualitatively the orientation of TBPS adsorbing on Au and Cu films. Since the spectrum measured for the Au film has lower intensity, the spectrum measured for the Au film was scaled up by a factor of 1.3 to get an identical intensity of the ss-SO peak (at 1045 cm^{-1}) for both Au and Cu films. The result shown in **Fig. 2b** indicates that, when the intensities of ss-SO peak are identical, the as-SO peak (around 1200 cm^{-1}) intensity is higher for the Cu film. Since the as-SO stretching corresponds to the lie-down orientation of adsorbed TBPS molecules, this result implies that the adsorbed TBPS molecules on Cu film have higher ratio of lie-down orientation in comparison to that on the Au film.

3.2.2 SEIRAS Study of TBPS adsorption during the Electrodeposition of Cu on Au Film

The adsorption behavior of TBPS molecules during a Cu electrodeposition process, onto an Au-coated electrode, was studied by SEIRAS. The investigation was performed by sweeping the potential between 1.00 and 0.05 V in a solution containing 155 μM TBPS, 0.1 M HClO$_4$, and 100 μM Cu(ClO$_4$)$_2$. Initially, a TBPS adlayer was formed on an Au film in the Cu-free solution at 1 V. After approaching the equilibrium adsorption state of TBPS, Cu(ClO$_4$)$_2$ was added to obtain a concentration of 100 μM. **Figure 3** shows a series of SEIRAS spectra acquired at various potentials during the cathodic (**Fig. 3a**) and anodic (**Fig. 3b**) sweepings. Of note, these SEIRAS spectra were shown with respected to the spectrum of a solution containing only 0.1M HClO$_4$ solution without TBPS and Cu^{2+} ions. It is found that the spectrum measured at 1 V is closely resembled to that reported for the TBPS adsorbing on Au film[24]. This result is reasonable because Cu film doesn't deposit on the Au electrode at 1 V and the spectrum is mainly caused by the adsorption of TBPS on the Au film. If attention was paid on the ss-SO peak (ca. 1045 cm^{-1}) and as-SO band (around 1022 cm^{-1}), no apparent change was found for potentials higher than 0.6 V (i.e. E > 0.6 V) during the cathodic scanning. However, for E ≤ 0.6 V, the intensity and shape of the two peaks demonstrate a significant dependence to the applied potential. The transition potential (0.6 V) found here can be ascribed to the initiation of Cu UPD deposition, leading to a different adsorption characteristic of TBPS adlayer on the electrode surface. This inference is confirmed by the CV spectra shown in **Fig. 1** which indicate that the Cu-UPD initiates at ca. 0.6 V.

In the reverse anodic potential sweep (**Fig. 3b**), the SEIRAS spectra are similar for E < 0.4V, i.e., negative of the anodic Cu stripping peak as shown in the corresponding CV spectrum. For E ≥ 0.4 V, the deposited Cu layer is stripped from the electrode surface. The corresponding SEIRAS spectra show a sharp intensity increase in the ss-SO peak and a significant change in the shape of as-SO band (**Fig. 3b**). Apparently, the Cu stripping process disrupts the TBPS adlayer, leading to a re-orientation of adsorbed TBPS molecules. It is important to note that, after dissolution of the Cu deposit, the SEIRAS spectrum resembles the original spectrum before the potential sweeping (**Fig. 3a**, E = 1.0 V). Therefore, it is inferred that the TBPS molecules still adsorb on the Au electrode surface after Cu stripping.

Comparing the spectra shown in **Figs. 2** and **3**, the intensity ratio of ss-SO peak to as-SO band is higher for TBPS adsorbing directly on a Cu film (**Fig. 2**), but is much lower measured in the Cu deposition process (**Fig. 3**). This result implies that the TBPS molecules tend to adsorb as a lie-down conformation when the adsorption was performed in the Cu deposition process. Two possible reasons are proposed to explain the different results. The first is the presence of the Cu^{2+} ions in the solution which is anticipated to affect the TBPS-substrate interaction and, therefore, the molecular conformation. The other is the different adsorp-
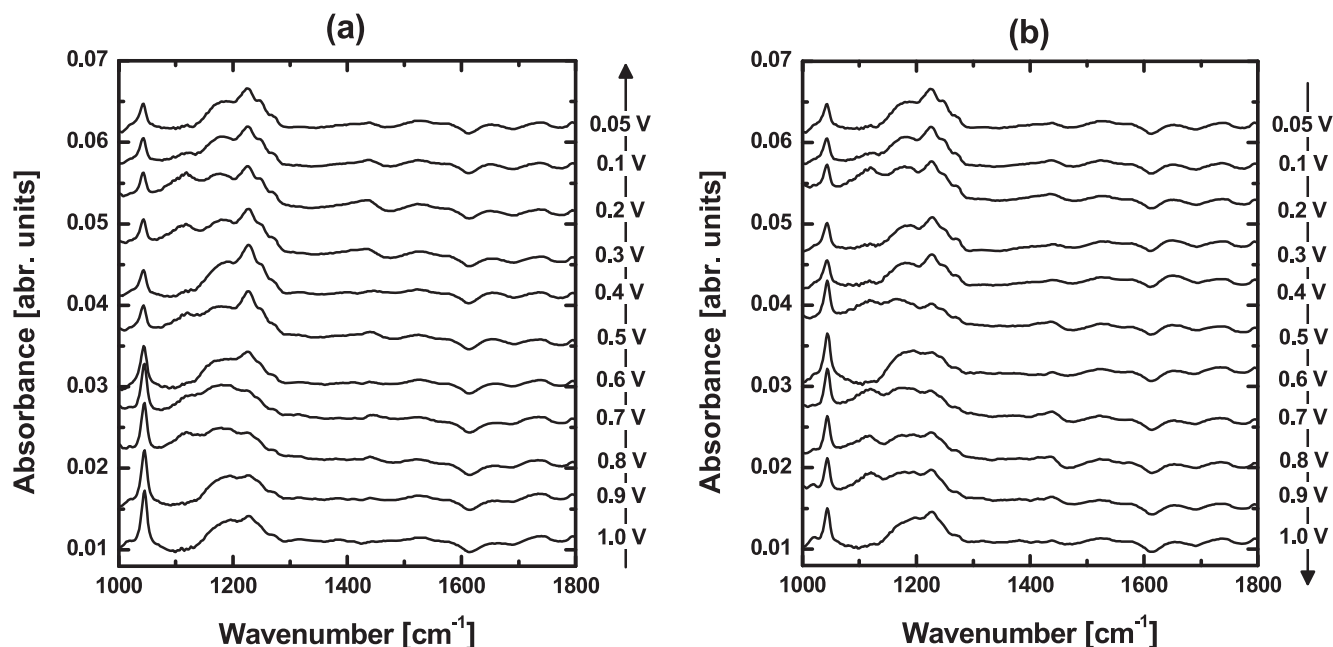
Fig. 3 *In-situ* SEIRAS spectra of TBPS during the Cu electrodeposition onto an Au film acquired at various potentials in the cathodic(a), and anodic(b)sweeping. The solution has a composition of 0.1 M $HClO_4$ + 155 μM TBPS + 100 μM $Cu(ClO_4)_2$ and the scanning rate is 1 mV/s.

tion mechanisms. Since the TBPS molecules were originally adsorbed on the Au film, the TBPS detected after Cu deposition is inferred to be the molecules transferred from Au electrode to the surface of deposited Cu film. The molecular conformation obtained from the transferring may be different from that adsorption directly.

4 Discussions

For detail studying the effects of potential on the adsorption-desorption behavior of TBPS during the Cu electroplating, the position of ss-SO peak at various potential was shown in **Fig. 4a**. Furthermore, the ss-SO(ca. 1045 cm^{-1}) and as-SO(around 1022 cm^{-1})peaks were integrated and the dependences of the integrated peak intensities with the applied potential were shown in **Figs. 4b** and **4c**, respectively. For comparison, the CV curve measured in this system was also shown as solid line in these figures. **Figure 4a** shows that, at the initiation potential(1 V), the position of ss-SO peak is 1044.5 cm^{-1}, which is ca. 2 cm^{-1} smaller than that obtained in a Cu-free solution(1047 cm^{-1}). This result is inferred to be caused by the interaction between adsorbed TBPS and Cu^{2+} ions in the solution.

With negative shifting of the potential, a sharp decrease of the wavenumber occurs at ca. 0.6 V which is associated with the initiation of Cu-UPD as observed from the CV curve. The wavenumber decreases and approaches a constant value of 1042.5 cm^{-1} at ca. 0.4 V which suggests the

formation of a complete UPD Cu layer. The difference in the wavenumber before(1044.5 cm^{-1})and after(1042.5 cm^{-1}) formation of Cu UPD layer is about 2 cm^{-1}, a value identical to the difference of the ss-SO peak for TBPS adsorbed on Au(1047 cm^{-1})and Cu(1045 cm^{-1})films in a Cu-free solution. This result suggests that the adsorbed TBPS molecules on the Au surface transfer to the outer Cu surface when the Cu layer was formed. Regarding the red-shift of the ss-SO peak in the Cu-containing solution, the interaction between adsorbed TBPS and Cu^{2+} ion in the solution is considered as a responsibility. In the reverse anodic scan (open square), the wavenumbers resembles closely to those of cathodic scan(full square)at low potentials(E < 0.5 V). However, the wavenumber cannot increase to the original value before Cu deposition. It is inferred that, after Cu stripping, the Cu^{2+} ions may involve in the adsorption of TBPS on Au film and affect the TBPS-Au interaction.

Figures 4b and **4c** show the normalized integrated intensities as a function of applied potential for ss-SO and as-SO modes, respectively. **Figure 4b** shows that, in the cathodic scanning, the ss-SO peak intensity decreases slightly for potentials higher than 0.6 V.(i.e. E > 0.6 V)and a sharp decrease begins at about E = 0.6 V. This behavior is similar to the effect of the potential on the wavenumber shown in **Fig. 4a** and the sharp transition can also be ascribed to the occurrence of Cu-UPD. On the other hand, the as-SO peak intensity increase gradually with negative shift of the potential(**Fig. 4c**). It has been shown that the ss-SO and as-SO peaks correspond to the adsorbed TBPS molecules
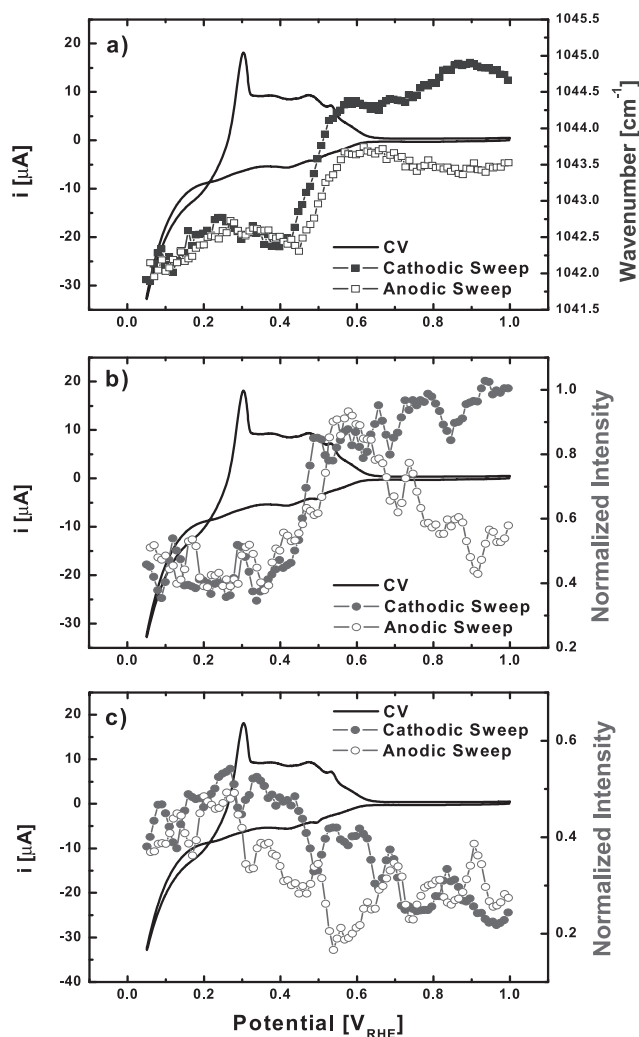
Fig. 4 The effects of the applied potential on the wavenumber of ss-SO peak（a）, and the integrated intensity of ss-SO peak（b）and as-SO band（c）obtained from the SEIRAS spectra shown in Fig. 3. The solid line shows the CV curve of the system at a scanning rate of 1 mV/s.

with "upright" and "lie-down" orientations, respectively. Therefore, the intensity decrease of ss-SO peak, as well as the increase of the as-SO band, toward negative potentials indicates a decrease of "upright" and an increase of "lie-down" TBPS molecules. This behavior is opposite to the potential-dependence of the TBPS adlayer on an Au film in the absence of Cu deposition where the intensity of ss-SO peak（~1047cm^{-1}）increases, but that of the as-SO mode （~1200cm^{-1}）decreases toward more negative potentials[24]. That is, an orientation transition from "lie-down" to "upright" configuration was proposed for system without Cu deposition.

Base on the results obtained here, it can be concluded that the adsorbed TBPS molecules transfer from Au surface to the surface of deposited Cu layer. This inference

was made by the following reasons. First, during the negative sweeping, the increase of lie-down configuration for E ＜0.6 V is in agreement with the TBPS adsorption behavior on Cu films. If Cu deposits on top of the TBPS adlayer, the TBPS molecules must be strongly bound to the Au surface. In such a case, the conformation of lie-down TBPS will not increase and, furthermore, the Cu stripping process is not expected to disrupt the TBPS adlayer or to induce an orientation change from lie-down to upright configuration as obtained in this study.

5 Conclusion

The results of this study show that the SEIRAS spectrum of TBPS on a Cu film is quite similar to that measured on an Au film. However, the molecules tend to adsorb with a more lie-down orientation on Cu film, inferred from the more obvious and higher intensity of the as-SO band. In the cathodic sweeping of the electrodeposition process, the wavenumber and peak intensity of the ss-SO peak decrease with decreasing potential and a sharp transition occurs at the initiation of Cu-UPD potential（0.6 V）. For the as-SO band, the integrated intensity increases gradually during the negative scanning. An opposite change of the spectra was observed during the anodic scanning. These results revels that the TBPS molecules, which originally adsorb on the Au surface, transfer to the surface of deposited Cu layer.

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