In-situ electrochemical SPR study of gold surface smoothing by repetitive cathodic deposition and anodic dissolution of copper in an ionic liquid

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Abstract

We performed in-situ analysis of the initial process of copper electrodeposition in an ionic liquid (IL), 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)amide (C₄mimTFSA), using electrochemical surface plasmon resonance (ESPR), where the SPR resonance angle ($\Delta\theta$) was recorded simultaneously with cyclic voltammograms (CVs) at the gold interface of C₄mimTFSA. $\Delta\theta$ shifted at the potentials where faradaic current appears in the CVs, indicating that SPR probes the redox processes of copper between Cu²⁺, Cu⁺, and Cu metal. In stark contrast to the fact that the CVs are not cycle dependent, the amount of the $\Delta\theta$ shift due to the copper electrodeposition decreased with increasing the CV cycle. A model reflectivity analysis using the Bruggeman effective medium approximation predicted that this decrease in $\Delta\theta$ is due to the decrease in the roughness of the gold surface, and it was actually confirmed by ex-situ atomic force microscopy observation. Since the dissolution of gold was found to be negligible from the atomic absorption measurement of IL after the ESPR measurements, the roughness decrease of the gold surface is likely due to the surface diffusion of gold atoms promoted during copper electrodeposition and dissolution processes. It was found that ESPR can track the surface roughness change of the gold electrode in an in-situ manner in the order of Å.

KEYWORDS: Deposition; EMA; Ionic liquid/gold interface; Underpotential deposition; Tf₂N; Au

Introduction

Ionic liquids (ILs) are low-melting salts composed of cations and anions, and have characteristics such as wide potential window, ionic conductivity, nonvolatility, and flame retardancy, making them promising electrolytes for metal anode batteries [1,2] and electroplating [2]. For these applications, it is desirable to study the metal electrodeposition process and to monitor the change in the electrode surface roughness in an in-situ manner. Copper is widely used in the electronics industry due to its high electrical conductivity, for example, for electrical contacts on circuit boards. For industrial applications, it is necessary to investigate fine atomic-level electrochemical behavior at the electrode / electrolyte interface. In order to study the copper electrodeposition, mainly underpotential deposition (UPD), in aqueous electrolyte solutions, metal surface sensing techniques such as scanning tunneling microscope (STM) [3–8], atomic force microscope (AFM) [6], electrochemical quartz crystal microbalance (EQCM) [9], and extended x-ray absorption fine structure (EXAFS) [3] have been used in an in-situ manner, and those such as scanning electron microscope (SEM) [10], transmission electron microscope (TEM) [11,12], x-ray diffraction (XRD) [13], low energy electron diffraction (LEED), and reflection high energy electron diffraction (RHEED) [14] have been used in an ex-situ manner. In particular, insitu Scanning Probe Microscope (SPM) is a powerful method for electrodeposition studies in ILs to reveal morphological changes of the substrate surface at the atomic level [15–18]. The copper electrodeposition in ILs has also been investigated using several ex-situ techniques: SEM [2,19,28,20–27], TEM [19,29,30], and XRD [20–22,31], although there is a report of in-situ STM [15]. It has been reported that the surface roughness of the electrode increased with repeated cathodic deposition and anodic dissolution of copper in 1-etyl-3-methylimidazolium chloride (C₂mimCl) at 140 °C [28].

In the present study, we propose electrochemical surface plasmon resonance (ESPR) as a powerful in-situ method, to investigate the copper electrodeposition process in ILs. Several previous studies have investigated electrodeposition using ESPR in aqueous electrolyte solutions, aiming at SPR sensitivity enhancement to Cu electrodeposition using Ag/Au bilayers as a metal film [32], SPR sensitivity enhancement to small biomolecules using biocatalyzed Ag deposition [33], quantitative measurements of UPD of Cu using ESPR combined with chronoamperometry [34], and detection of a trace amount of heavy metal ions in water using ESPR combined with anodic stripping voltammetry [35]. However, there are no ESPR reports focusing on the surface roughness of the substrate during electrodeposition. ESPR is a method that simultaneously performs electrochemical measurements and surface plasmon resonance (SPR), and can analyze various changes on the substrate of thin film of metal, which is gold in the present study. Our previous research has shown that ESPR can sensitively track the composition changes in the electric double layer [36,37] and in the diffusion layer of redox species [38], which is in contrast to SPM or many other methods that have been applied to analyze the IL/metal interface. In this study, we used ESPR to measure the process of Cu electrodeposition on a gold electrode in an IL. It was found that ESPR can track the roughness decrease of the electrode surface in the order of Å during successive electrodeposition and dissolution processes, which was confirmed with ex-situ AFM and a reflectivity simulation using the Bruggeman effective medium approximation.

Experimental

• Reagent

1-butyl-3-methylimidazolium chloride (C₄mimCl) was synthesized as previously reported [38]. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (C₄mimTFSA) was prepared by mixing C₄mimCl and LiTFSA (Kanto Chemical) in dichloromethane and washing the solution repeatedly with pure water to remove the byproduct LiCl. Cu(TFSA)₂ was synthesized by dissolving CuO (Nacalai tesque) to HTFSA (70 wt% aqueous solution, Central Glass) until the pH of the solution reached 7, and then removing water with an evaporator. The synthesized $Cu(TFSA)_2$ was added to $C_4mimTFSA$ to obtain a 10 mM solution.

• Electrochemical surface plasmon resonance (ESPR)

SPRINGLE (Autolab) was used for ESPR measurements. A gold thin film (thickness: 50 nm) deposited on an SF15 glass substrate was used as the working electrode (surface area: 0.071 cm²). A Pt wire and an Ag / AgCl wire were used as the counter electrode and the quasi reference electrode, respectively. Before the measurement, the gold surface was cleaned by immersing the substrate in a piranha solution (concentrated sulfuric acid: hydrogen peroxide aqueous solution at a volume ratio of 3: 1) for 20 minutes followed by washing with Milli-Q water five times and then drying with N₂ gas. The Cu-containing IL was evacuated at 60 °C for 3 hours. Before the measurements, Ar gas was kept flowing at least for 1 hour, into the cell from the inlet needle on the silicone stopper on the cell, and out of the cell from the outlet needle. The flow rate of Ar gas was controlled at 30 mL / min using a Kofloc precision flow meter (50 mL / min). Ar gas was kept flowing into the cell during the measurements. ESPR measurement was performed at room temperature. The scan rate of CV was 10 mV s⁻¹. The resonance angle shift ($\Delta \theta$) at a wavelength of 670 nm was recorded simultaneously with the CV measurement, with $\Delta \theta = 0$ when the CV measurement started. The measurement was repeated with a waiting time for 300 s at the initial potential for the scan before the next scan.

• Ex-situ AFM observation of gold surface

The surface of the gold substrate was observed with AFM (SPM-9600, SHIMADZU). Prior to the AFM observation of the surface after ESPR measurement, the substrate was immersed in methanol to remove residual IL on the gold surface, and blown dry with N₂ gas. The substrate before the ESPR measurement was immersed first in methanol, then in a piranha solution for 20 minutes, last in Milli-Q water, and dried by blowing N₂ gas. The surface roughness was evaluated from the root mean square of the height deviation (R_q) of the AFM image data. Several methods for estimating the roughness thickness (d_0) from R_q have been reported [39–42]. We used a relation ($d_0 = (1.175 \pm 0.285)R_q$ [42]) proposed for polycrystalline silicon since the Au film used in this study was polycrystalline.



• Simulation of resonance angle shift during Cu electrodeposition

Fig. 1. Schematic diagram of the four layer model during the copper deposition; (a) before deposition and (b) after deposition.

Resonance angle shifts associated with copper deposition and roughness changes were simulated for comparison with experimental data. Fig. 1 shows a schematic diagram of a four-layer structure consisting of a prism, a gold film, a mixed layer, and an IL, before Cu deposition ($f_{Cu} = 0$, Fig. 1a) and after Cu deposition ($f_{Cu} > 0$, Fig. 1b). The roughness of the gold surface was modeled as a mixed layer composed of gold, copper, and IL using the Bruggeman effective medium approximation [43]. The resonance angle shift was calculated as a function of the mixed layer thickness d_{mix} and the fraction of copper f_{Cu} , which changed resulting from copper electrodeposition and dissolution. The surface roughness before the deposition, $d_{mix,0}$, which is d_{mix} at $f_{Cu} = 0$, was estimated by ex-situ AFM observation. The thickness of gold layer (d_{Au}) was $d_{Au} = d_{Au,0} - d_{mix} f_{Au}$ with $d_{Au,0} = 50$ nm.

The refractive index n_{mix} of the mixed layer was obtained using Bruggeman's effective medium approximation formula (1) [43].

$$\sum_{i} f_{i} \frac{{n_{i}}^{2} - {n_{\text{mix}}}^{2}}{{n_{i}}^{2} + 2{n_{\text{mix}}}^{2}} = 0$$
(1)

where i is either of Au, Cu, and IL, n_i is the refractive index of i, f_i is the fraction of i satisfying $\sum_i f_i = 1$. The refractive index values at 670 nm are $n_{\text{prism}} =$ 1.669, $n_{\text{Au}} = 0.1 + 4.0i[44]$, $n_{\text{Cu}} = 0.2 + 3.6i[44]$, and $n_{\text{IL}} = 1.425$. n_{IL} was measured with an Abbe refractometer (DR-M2, Atago, interference filter 656 nm). For simplicity, $f_{Au} = f_{IL} = \frac{1-f_{Cu}}{2}$ was assumed. Since it is difficult to determine f_i independently, we have made the simplest assumption.

Among the six solutions of n_{mix} from eq (1), only one solution was adopted that had positive values for both the real and imaginary parts. The reflectance *R* due to the Fresnel reflection was obtained as follows [45].

$$n_{j}\cos\theta_{j} = n_{prism}\cos\theta_{prism}$$

$$q_{j} = \cos\theta_{j}/n_{j}$$

$$\beta_{j} = \frac{2\pi}{\lambda}n_{j} \ \cos\theta_{j}d_{j}$$

$$M_{j} = \begin{pmatrix} \cos\beta_{j} & -i\sin\beta_{j}/q_{j} \\ -i \ q_{j}\sin\beta_{j} & \cos\beta_{j} \end{pmatrix}$$

$$M = M_{Au}M_{mix}$$

$$(M^{11} + M^{12}q_{u})q_{prism} - (M^{21} + M^{22}q_{u})$$

$$R = \left| \frac{\left(M^{11} + M^{12} q_{\rm IL} \right) q_{\rm prism} - \left(M^{21} + M^{22} q_{\rm IL} \right)}{\left(M^{11} + M^{12} q_{\rm IL} \right) q_{\rm prism} + \left(M^{21} + M^{22} q_{\rm IL} \right)} \right|^2$$

where θ_j is the incident angle in the j-layer, λ is the wavelength (670 nm), *d* is the thickness, j is either prism, Au, mix, or IL.

In the total internal reflection condition in the range of $\operatorname{arcsin}\left(\frac{n_{\text{IL}}}{n_{\text{prism}}}\right) \leq \theta_{\text{prism}} < 90^{\circ}, \ \theta_{\text{prism}} = \theta_{\text{SPR}}$ was searched at which *R* takes a minimum value. θ_{SPR} was obtained at various f_{Cu} and d_{mix} values, and the contour map of $\Delta\theta$ (f_{Cu} , d_{mix}) was made (see Fig. 4).

Results and Discussion

• ESPR



Fig. 2. (a) CVs and (b) ESPR curves at the Au electrode in C_4 mimTFSA with 10 mM $Cu(TFSA)_2$, The gray lines indicate the data for C_4 mimTFSA without $Cu(TFSA)_2$.

Fig. 2 shows the CVs (Fig. 2a) and ESPR (Fig. 2b) recorded simultaneously. The CVs in Fig. 2a are similar to that in a previous report [19] for Cu electrodeposition on the GC electrode at 35 °C in C₂mimTFSA. It has been reported that the reduction process from Cu²⁺ to Cu in IL occurs via Cu⁺ [2,19]. In Fig. 2a, the cathodic currents around 0.1 V and -0.35 V are ascribable to Cu²⁺ \rightarrow Cu⁺ and Cu⁺ \rightarrow Cu, respectively, and the anodic currents around -0.15 V and 0.2 V are ascribable to Cu \rightarrow Cu⁺ and Cu⁺ \rightarrow Cu²⁺, respectively [19]. Both of the anodic currents show sharper peaks than the corresponding cathodic currents, which is due to the large difference in the mass transfer rate between the oxidation and reduction, by stripping from the surface and by diffusion from the IL bulk, respectively. During the eight cycles, the CVs were almost the same as each other.

The SPR resonance angle (Fig.2b) shifted corresponding to the redox processes shown in the CVs (Fig. 2a). In the negative scan, $\Delta\theta$ shifted negatively corresponding to $Cu^{2+} \rightarrow Cu^{+}$ around 0.1 V. Both of Cu^{2+} and Cu^{+} are dissolved redox species, and the resonance angle shifts with a sigmoidal shape in such a redox process [36]. A narrower potential scan actually led to a sigmoidal shape (Fig. S1). Since $\Delta\theta$ negatively shifted during the Cu²⁺ \rightarrow Cu⁺ process, Cu⁺ complexed with TFSA⁻ is likely to have a lower polarizability than the Cu²⁺ counterpart [36]. In the further negative scan where Cu⁺ \rightarrow Cu occurs, $\Delta\theta$ shifted positively (Fig. 2), which is due to the deposition of metallic Cu as confirmed with the simulation below and agrees with a ESPR study in aqueous solutions [32]. In $Cu^+ \rightarrow Cu, \Delta\theta$ shifts negatively first before the positive shift, which is caused by the depletion of Cu⁺ near the surface of the gold electrode. We performed the digital simulation to elucidate the depletion effect on $\Delta \theta$ (see Supporting Information for details). Fig. S2 shows the simulated CV (Fig. S2a) with the surface concentration of Cu²⁺ and Cu⁺ on the gold electrode (Fig. S2b) and $\Delta \theta_{DL}$ (Fig. S2c) during the CV. Note that $\Delta \theta_{\rm DL}$, the diffusion layer contribution to $\Delta \theta$, from the simulation does not contain other contributions such as Cu deposition and the surface roughness change. Fig. S2b shows the depletion of Cu⁺ around -0.3 V in the forward negative scan and simultaneously Fig. S2c shows the negative shift of $\Delta \theta_{DL}$ (red dashed line), indicating that ESPR tracks the depletion of Cu⁺ in the diffusion layer.

In the backward positive scan, $\Delta\theta$ shifted negatively in Cu \rightarrow Cu⁺ and positively in Cu⁺ \rightarrow Cu²⁺. In Cu⁺ \rightarrow Cu²⁺, $\Delta\theta$ shifts negatively once before $\Delta\theta$ curves are flat, which is caused by the accumulation and diffusion of Cu⁺ near the surface of the gold electrode. This behavior is also confirmed by the simulation; Fig. S2c shows the negative $\Delta\theta_{DL}$ shift around -0.1 V in the positive scan, which is caused by the decrease in the surface concentration of accumulated Cu⁺ due to the diffusion toward the bulk (Fig. S2b).

The gray line in Fig. 2b shows the $\Delta\theta$ in the absence of Cu, i.e., in neat C₄mimTFSA. One can see little $\Delta\theta$ shift, indicating that the behaviors of $\Delta\theta$ in the presence of Cu described above are definitely due to the redox process of Cu. It should be noted that even without Cu ions $\Delta\theta$ shows a slight negative shift around -0.5 V, the negative edge of the scan range. The negative shift is due to the ionic composition change in the electric double layer, which becomes non-negligible around the potential of zero charge of this system (-0.6 V at the gold/C₄mimTFSA interface) [37].

Although the CVs did not depend on the number of cycles (Fig. 2a), the change in SPR resonance angle $(\Delta\Delta\theta)$ due to the copper deposition $(Cu^+\rightarrow Cu)$ decreased with each measurement (Fig. 2b). The decrease in $\Delta\Delta\theta$ is apparently not due to the change in the amount of Cu deposited since there was no difference in CVs. Fundamental SPR studies in 1970s confirmed that the surface roughness of metal thin film contributes to positive shift in SRP angle [46,47]. This suggests that the surface roughness of gold decreased by the repeated electrodeposition of copper. At the same time, it suggests that a minute change in surface roughness that could not be detected by CV is observable in-situ by using ESPR. To check

the reproducibility of this behavior, we performed this 8-cycle ESPR measurement several times using a new substrate each time. The results in Fig. S3a show the same tendency; $\Delta\Delta\theta$ decreases with increasing the cycle number. Since $\Delta\Delta\theta$ is expected to be approximately proportional to the deposition amount of Cu, $\Delta\Delta\theta$ was normalized by the charge for the Cu electrodeposition, q. Fig. S3b is a normalized version of Fig. S3a with q, which was calculated by integrating oxidation peak (Cu \rightarrow Cu⁺) in the CVs with baseline subtraction. Fig. S3b shows better quantitative reproducibility than Fig. S1a, indicating that $\Delta\Delta\theta$ certainly reflects the amount of Cu deposition. But since there is still some variability in the data even after the normalization, other factors such as the initial surface roughness should affect the absolute value of $\Delta\Delta\theta$. However, all the data in Fig. S3 show decaying tendency as the cycle number increases, revealing that the roughness of the gold surface decreased to a certain level by the successive electrodeposition and dissolution of copper.

• Ex-situ atomic force microscope (AFM) observation of gold surface

In order to examine the surface roughness change due to the successive electrodeposition and dissolution of copper, AFM observation was carried out in an ex-situ manner on the gold surface before and after the ESPR measurements,

Table 1. AFM measurement resul	ts.
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	$R_{ m q}$ / nm	$d_{ m mix,0}$ / nm $^{ m a)}$
Before ESPR	4.2	4.9 ± 1.2
After ESPR	1.7	2.0 ± 0.5

^{a)} Estimated using the relation $d_{\text{mix},0} = (1.175 \pm 0.285)R_q$ [37].

and the AFM images are shown in Fig. 3a and Fig. 3b, respectively. Large particles observed in Fig. 3a disappeared in Fig. 3b, indicating the decrease in gold surface roughness. Table 1 lists R_q obtained from Fig. 3 and the surface roughness thickness $d_{\text{mix},0}$ calculated from R_q . This ex-situ experimental result clearly indicates that the surface roughness of gold decreased by copper electrodeposition.



Fig. 3. Ex-situ AFM observation of the gold surface (a) before and (b) after SPR measurements.

Possible reasons for the decrease of the surface roughness in the copper electrodeposition process include (i) that the surface diffusion of gold was promoted and (ii) that gold was dissolved by the copper electrodeposition. For (ii) to be examined, the amount of gold dissolved was measured by atomic absorption spectrometry (see SI for details) of the IL after ESPR measurement. Assuming that the gold film has the same density as the bulk, the amount of gold dissolved was estimated to correspond to a thickness of 0.06 ± 0.12 Å (Fig. S4). Since this value is negligible, even smaller than the atomic diameter of gold (2.88 Å), we concluded that gold was not dissolved into IL during the ESPR measurement. This result is

contrary to a study where the surface roughness of Au electrode increased as a result of repeated cathodic deposition and anodic dissolution of copper via CV at 140 °C in C₂mimCl [28]. The difference is likely to be caused by the difference in the constituent anions of ILs and temperature. The high concentration of Cl⁻ in ref. 20 will facilitate the dissolution of gold from the electrode by forming AuCl₄⁻. Furthermore, the alloying of Cu and Au is practically negligible at room temperature in the present study [48], while it is not negligible at 140 °C in ref. 20. Therefore, it is highly likely that in ref. 20 the Au dissolution is promoted by the alloying during the Cu cathodic deposition followed by dealloying and forming AuCl₄⁻ during the Cu anodic dissolution.

Since we confirmed that the dissolution of gold is negligible, the decrease in the roughness of the gold surface is highly likely due to the surface diffusion of gold atoms accelerated by copper electrodeposition. In a previous study [49], Cu electrodeposition on polycrystalline gold electrodes in 0.01 M $H_2SO_4 + 0.01$ CuSO₄ aqueous solution was observed by in-situ STM. The authors reported that a Cu-Au alloy layer is formed because the morphology of the gold surface changes when copper is electrodeposited on the gold electrode [49]. Such a surface alloying process may be the cause of the diffusion acceleration.

Simulation of roughness dependence of SPR angle shift

Fig. 4 shows the simulation results on SPR angle changes in the copper deposition process (Cu⁺ \rightarrow Cu) during the 1st (Fig. 4a) and 8th (Fig. 4b) cycles of Fig. 2b as the blue arrows. The $d_{\text{mix},0}$ value in Table 1, which is the surface

roughness before deposition ($f_{Cu} = 0$), was used as the starting point of the arrows, which is at $\Delta \theta = 0$.



Fig. 4. Change in SPR resonance angle $(\Delta \theta)$ with electrodeposition of copper for (a) 1st cycle ($\Delta \theta = 0$ in (0, 4.9)), and (b) 8th cycle ($\Delta \theta = 0$ in (0, 2.0)). The blue arrows are from eq (3).

Since the CVs did not change during the eight cycles (Fig. 2a), the amount of copper electrodeposition does not change, and therefore Δd_{mix} does not depend on the cycle number. Then, Δd_{mix} was obtained as follows. By integrating the oxidation (Cu \rightarrow Cu⁺) peak of the CVs (Fig. 2a) with baseline subtraction, the amount of charge q used in the oxidation reaction was estimated to be 6.9 μ C cm⁻². The thickness $\Delta d_{\text{mix,max}}$ of the total deposited copper was obtained

$$\Delta d_{\rm mix,max} = \frac{q M_{\rm Cu}}{F \rho} \tag{2}$$

where $M_{\rm Cu}$ is the atomic weight (= 63.5 g mol⁻¹) of copper, ρ is the density (= 8.96 g cm⁻³) of bulk copper, and *F* is the Faraday constant. $\Delta d_{\rm mix,max}$ from eq (2) was 0.51 nm. Further, the relation of $f_{\rm Cu}$ with $\Delta d_{\rm mix}$ may be represented as

$$f_{\rm Cu} = \frac{\Delta d_{\rm mix}}{d_{\rm mix}} = \frac{\Delta d_{\rm mix}}{d_{\rm mix,0} + \Delta d_{\rm mix}} \tag{3}$$

The blue arrows in Fig. 4 is from eq (3), and the end point of the arrows was at $\Delta d_{\text{mix,max}} = 0.51$ nm. The blue arrows in Fig. 4 indicates that the resonance angle shifts positively with copper deposition as observed in experiments. The $\Delta\theta$ change with Cu deposition is about 500 mdeg when the roughness is large as shown in Fig. 4a whereas about 450 mdeg when the roughness was small in Fig.4b. That is, the smaller the roughness of the gold surface, the smaller the amount of change in the resonance angle when copper is deposited. These results confirm that $\Delta\Delta\theta$ decreases with decreasing the surface roughness, supporting the ESPR results (Fig.2). However, these $\Delta\Delta\theta$ values are much larger than the $\Delta\Delta\theta$ associated with copper deposition obtained from ESPR measurements, $\Delta\Delta\theta < 300$ mdeg (Fig. 2b). This is probably because $\Delta\theta$ negative shift contribution (Fig. 2b), in which Cu⁺ and Cu²⁺ are depleted in the diffusion layer, cancels out the $\Delta\theta$ positive shift due to Cu deposition.

The dependence of the resonance angle change ($\Delta\Delta\theta$) on the initial roughness ($d_{\text{mix},0}$) at 0.51 nm deposition conditions was also investigated (Fig. S5). $\Delta\Delta\theta$ shows a large initial (1st and 2nd, 2nd and 3rd) change, but converges to a value in a certain range when the measurement is repeated (Fig.S3). Therefore, it is considered that the roughness of the gold surface rapidly changed in the initial stage of measurement. A small but noticeable $\Delta\Delta\theta$ decrease still appeared in the 6-8th ESPR measurement with a small roughness reduction, indicating that ESPR can distinguishes surface roughness difference in the Å order.

Fig. S6a shows ESPR curves in Fig. 2b with $\Delta\theta$ set to zero only at the beginning of the 1st cycle and not the subsequent cycles. For each cycle, the resonance angle shifts positively at the end compared to the beginning. This is opposite to the simulation results where the resonance angle shifts negatively as the surface roughness decreases (Fig. 4). A model simulation assuming Cu-Au alloying in the gold film failed to explain the positive shift (data not shown). It is necessary to examine another model to explain this. This positive shift is not an artifact. Fig. S6b shows an example exhibiting an artifact, temperature drift, in similar ESPR measurement of IL without Cu. As shown in Fig. S6b, the resonance angle shifts not only during measurement, but also between measurements, so each SPR curve appears separately. On the other hand, in Fig. S6a, the successive SPR curves look continuous because there is no change in the resonance angle between measurements. Therefore, it is considered that the positive shift is not caused by the measurement conditions such as temperature drift.

Conclusions

Copper electrodeposition on a gold electrode in IL was measured in an in-situ manner using ESPR. $\Delta\Delta\theta$ due to copper electrodeposition decreased with increasing the number of CV cycles. AFM ex-situ observations showed that repeated electrodeposition of copper at the IL / gold interface decreased the gold

surface roughness. It was also suggested by atomic absorption spectrometry that the roughness decrease in the gold surface was due to the surface diffusion of gold atoms. A model simulation showed that the $\Delta\Delta\theta$ due to copper electrodeposition decreased with decreasing the surface roughness, and it was concluded that the $\Delta\Delta\theta$ decrease in ESPR was due to the decreasing roughness of the gold surface. Through a series of measurements, it was found that ESPR can distinguish the Å order difference of the surface roughness of the gold electrode in the Cu electrodeposition process.

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References

- T.-I. Leong, I.-W. Sun, M.-J. Deng, C.-M. Wu, P.-Y. Chen,
 Electrochemical Study of Copper in the 1-Ethyl-3-Methylimidazolium
 Dicyanamide Room Temperature Ionic Liquid, J. Electrochem. Soc. 155
 (2008) F55. https://doi.org/10.1149/1.2840627.
- P.Y. Chen, I.W. Sun, Electrochemical study of copper in a basic 1-ethyl-3methylimidazolium tetrafluoroborate room temperature molten salt, Electrochim. Acta. 45 (1999) 441–450. https://doi.org/10.1016/S0013-4686(99)00275-3.
- [3] S. Manne, P.K. Hansma, J. Massie, V.B. Elings, A.A. Gewirth, Atomic-resolution electrochemistry with the atomic force microscope: Copper deposition on gold, Science (80-.). 251 (1991) 183–186. https://doi.org/10.1126/science.251.4990.183.
- [4] T. Hachiya, H. Honbo, K. Itaya, Detailed underpotential deposition of copper on gold(III) in aqueous solutions, J. Electroanal. Chem. 315 (1991) 275–291. https://doi.org/10.1016/0022-0728(91)80076-3.
- [5] D.M. Kolb, Atomic structure of Cu Adlayers on Au, Phys. Rev. Lett. 21 (1968) 1441–1443. https://doi.org/10.1103/PhysRevLett.21.1441.
- [6] A.A. Gewirth, B.K. Niece, Electrochemical applications of in situ scanning probe microscopy, Chem. Rev. 97 (1997) 1129–1162. https://doi.org/10.1021/cr960067y.
- [7] J. Okada, J. Inukai, K. Itaya, Underpotential and bulk deposition of copper on Pd(111) in sulfuric acid solution studied by in situ scanning tunneling

microscopy, Phys. Chem. Chem. Phys. 3 (2001) 3297–3302. https://doi.org/10.1039/b101093j.

- [8] M. Wilms, P. Broekmann, C. Stuhlmann, K. Wandelt, In-situ STM investigation of adsorbate structures on Cu (111) in sulfuric acid electrolyte, Surf. Sci. 416 (1998) 121–140. https://doi.org/10.1016/S0039-6028(98)00550-0.
- [9] E. Gileadi, V. Tsionsky, Studies of Electroplating Using an EQCM. I.
 Copper and Silver on Gold, J. Electrochem. Soc. 147 (2000) 567.
 https://doi.org/10.1149/1.1393234.
- [10] N.D. Nikolić, K.I. Popov, L.J. Pavlović, M.G. Pavlović, Morphologies of copper deposits obtained by the electrodeposition at high overpotentials, Surf. Coatings Technol. 201 (2006) 560–566. https://doi.org/10.1016/j.surfcoat.2005.12.004.
- [11] M.J. Williamson, R.M. Tromp, P.M. Vereecken, R. Hull, F.M. Ross, Dynamic microscopy of nanoscale cluster growth at the solid-liquid interface, Nat. Mater. 2 (2003) 532–536. https://doi.org/10.1038/nmat944.
- [12] A. Radisic, F.M. Ross, P.C. Searson, In situ study of the growth kinetics of individual island electrodeposition of copper, J. Phys. Chem. B. 110 (2006) 7862–7868. https://doi.org/10.1021/jp057549a.
- [13] B. Hong, C. hai Jiang, X. jian Wang, Influence of complexing agents on texture formation of electrodeposited copper, Surf. Coatings Technol. 201 (2007) 7449–7452. https://doi.org/10.1016/j.surfcoat.2007.02.011.
- [14] M.S. Zei, G. Qiao, G. Lehmpfuhl, D.M. Kolb, The influence of anions on the structure of underpotentially deposited Cu on Au(111): A LEED,

RHEED and AES study, Berichte Der Bunsengesellschaft Für Phys. Chemie. 91 (1987) 349–353. https://doi.org/10.1002/bbpc.19870910423.

- [15] F. Endres, Ionic liquids: Solvents for the electrodeposition of metals and semiconductors, ChemPhysChem. 3 (2002) 144–154. https://doi.org/10.1002/1439-7641(20020215)3:2<144::aid-cphc144>3.0.co;2-%23.
- [16] F. Endres, S. Zein El Abedin, Nanoscale electrodeposition of germanium on Au(111) from an ionic liquid: An in situ STM study of phase formation. Part I. Ge from GeBr4, Phys. Chem. Chem. Phys. 4 (2002) 1640–1648. https://doi.org/10.1039/b110268k.
- [17] T. Carstens, A. Ispas, N. Borisenko, R. Atkin, A. Bund, F. Endres, In situ scanning tunneling microscopy (STM), atomic force microscopy (AFM) and quartz crystal microbalance (EQCM) studies of the electrochemical deposition of tantalum in two different ionic liquids with the 1-butyl-1methylpyrrolidinium cation, Electrochim. Acta. 197 (2016) 374–387. https://doi.org/10.1016/j.electacta.2015.07.178.
- [18] X. Hu, C. Chen, S. Tang, W. Wang, J. Yan, B. Mao, An in situ STM investigation of EMITFSI ionic liquid on Au(111) in the presence of lithium salt, Sci. Bull. 60 (2015) 877–883. https://doi.org/10.1007/s11434-015-0746-7.
- T. Liu, R. Vilar, S. Eugénio, J. Grondin, Y. Danten, Electrodeposition of copper thin films from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, J. Appl. Electrochem. 45 (2015) 87–93. https://doi.org/10.1007/s10800-014-0773-0.

- [20] P. Giridhar, S. Zein El Abedin, F. Endres, Electrodeposition of nanocrystalline aluminium, copper, and copper-aluminium alloys from 1butyl-1-methylpyrrolidinium trifluoromethylsulfonate ionic liquid, J. Solid State Electrochem. 16 (2012) 3487–3497. https://doi.org/10.1007/s10008-012-1800-x.
- [21] Q. Zhang, Q. Wang, S. Zhang, X. Lu, X. Zhang, Electrodeposition in Ionic Liquids, ChemPhysChem. 17 (2016) 335–351.
 https://doi.org/10.1002/cphc.201500713.
- [22] T. Liu, R. Vilar, S. Eugénio, J. Grondin, Y. Danten, Electrodeposition of nanocrystalline copper thin films from 1-ethyl-3-methylimidazolium ethylsulphate ionic liquid, J. Appl. Electrochem. 44 (2014) 189–198. https://doi.org/10.1007/s10800-013-0630-6.
- [23] S.Z. El Abedin, M. Pölleth, S.A. Meiss, J. Janek, F. Endres, Ionic liquids as green electrolytes for the electrodeposition of nanomaterials, Green Chem. 9 (2007) 549–553. https://doi.org/10.1039/b614520e.
- [24] S. Zein El Abedin, A.Y. Saad, H.K. Farag, N. Borisenko, Q.X. Liu, F. Endres, Electrodeposition of selenium, indium and copper in an air- and water-stable ionic liquid at variable temperatures, Electrochim. Acta. 52 (2007) 2746–2754. https://doi.org/10.1016/j.electacta.2006.08.064.
- [25] G. Saravanan, S. Mohan, Nucleation of copper on mild steel in copper chloride (CuCl 2·2H2O)-1-ethyl-3-methylimidazolium chloride
 [EMIM]Cl-ethylene glycol (EG) ionic liquid, New J. Chem. 37 (2013) 2564–2567. https://doi.org/10.1039/c3nj00245d.

- M. Mascia, A. Vacca, L. Mais, S. Palmas, E. Musu, F. Delogu,
 Electrochemical deposition of Cu and Nb from pyrrolidinium based ionic liquid, Thin Solid Films. 571 (2014) 325–331.
 https://doi.org/10.1016/j.tsf.2014.05.030.
- [27] S. Caporali, P. Marcantelli, C. Chiappe, C.S. Pomelli, Electrodeposition of transition metals from highly concentrated solutions of ionic liquids, Surf. Coatings Technol. 264 (2015) 23–31.
 https://doi.org/10.1016/j.surfcoat.2015.01.031.
- [28] J. Jiang, Copper-Assisted Etching of Gold through Electrochemical Deposition and Dissolution of Copper in Ionic Liquids, J. Electrochem.
 Soc. 166 (2019) D940–D945. https://doi.org/10.1149/2.0591916jes.
- [29] S. Schaltin, L. D'UZrzo, Q. Zhao, A. Vantomme, H. Plank, G. Kothleitner, C. Gspan, K. Binnemans, J. Fransaer, Direct electroplating of copper on tantalum from ionic liquids in high vacuum: Origin of the tantalum oxide layer, Phys. Chem. Chem. Phys. 14 (2012) 13624–13629. https://doi.org/10.1039/c2cp41786c.
- [30] S. Schaltin, A. Shkurankov, K. Binnemans, J. Fransaer, Direct Cu-on-Ta Electroplating from Ionic Liquids in High Vacuum, 25 (2010) 119–128. https://doi.org/10.1149/1.3318510.
- [31] K. Murase, K. Nitta, T. Hirato, Y. Awakura, Electrochemical behaviour of copper in trimethyl-n-hexylammonium bis((trifluoromethyl)sulfonyl)amide, an ammonium imide-type room temperature molten salt, J. Appl. Electrochem. 31 (2001) 1089–1094. https://doi.org/10.1023/A:1012255601793.

- [32] P. Zhai, J. Guo, J. Xiang, F. Zhou, Electrochemical surface plasmon resonance spectroscopy at bilayered silver/gold films, J. Phys. Chem. C. 111 (2007) 981–986. https://doi.org/10.1021/jp065525d.
- [33] J. Wang, F. Wang, X. Zou, Z. Xu, S. Dong, Surface plasmon resonance and electrochemistry for detection of small molecules using catalyzed deposition of metal ions on gold substrate, Electrochem. Commun. 9 (2007) 343–347. https://doi.org/10.1016/j.elecom.2006.09.011.
- Q. Liu, X. Wang, A. Benedict, L. Janibekyan, S.W. Su, Y. Wang, F. Zhou, Surface Plasmon Resonance Coupled with Potential-step Chronoamperometry: Theory and Applications for Quantitative Measurements of Electrodeposited Thin Films, Electroanalysis. 31 (2019) 2155–2161. https://doi.org/10.1002/elan.201900006.
- [35] S. Wang, E.S. Forzani, N. Tao, Detection of heavy metal ions in water by high-resolution surface plasmon resonance spectroscopy combined with anodic stripping voltammetry, Anal. Chem. 79 (2007) 4427–4432. https://doi.org/10.1021/ac0621773.
- [36] N. Nishi, Y. Hirano, T. Motokawa, T. Kakiuchi, Ultraslow relaxation of the structure at the ionic liquid-gold electrode interface to a potential step probed by electrochemical surface plasmon resonance measurements: Asymmetry of the relaxation time to the potential-step direction, Phys. Chem. Chem. Phys. 15 (2013) 11615–11619. https://doi.org/10.1039/c3cp51463c.
- [37] S. Zhang, N. Nishi, T. Sakka, Electrochemical surface plasmon resonance measurements of camel-shaped static capacitance and slow dynamics of

electric double layer structure at the ionic liquid/electrode interface, J. Chem. Phys. 153 (2020) 044707. https://doi.org/10.1063/5.0011671.

- [38] N. Nishi, Y. Ikeda, T. Sakka, Electrochemical surface plasmon resonance as a probe of redox reactions at the ionic liquid|gold interface, J. Electroanal. Chem. 817 (2018) 210–216. https://doi.org/10.1016/j.jelechem.2018.03.067.
- [39] J. Koh, Y. Lu, C.R. Wronski, Y. Kuang, R.W. Collins, T.T. Tsong, Y.E. Strausser, Correlation of real time spectroellipsometry and atomic force microscopy measurements of surface roughness on amorphous semiconductor thin films, Appl. Phys. Lett. 69 (1996) 1297–1299. https://doi.org/10.1063/1.117397.
- [40] D. Franta, I. Ohlídal, Comparison of effective medium approximation and Rayleigh-Rice theory concerning ellipsometric characterization of rough surfaces, Opt. Commun. 248 (2005) 459–467. https://doi.org/10.1016/j.optcom.2004.12.016.
- [41] A. Yanguas-Gil, B.A. Sperling, J.R. Abelson, Theory of light scattering from self-affine surfaces: Relationship between surface morphology and effective medium roughness, Phys. Rev. B - Condens. Matter Mater. Phys. 84 (2011) 1–8. https://doi.org/10.1103/PhysRevB.84.085402.
- P. Petrik, L.P. Biró, M. Fried, T. Lohner, R. Berger, C. Schneider, J. Gyulai, H. Ryssel, Comparative study of surface roughness measured on polysilicon using spectroscopic ellipsometry and atomic force microscopy, Thin Solid Films. 315 (1998) 186–191. https://doi.org/10.1016/S0040-6090(97)00349-0.

- [43] D.A.G. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen, Ann. Phys. 416 (1935) 636–664. https://doi.org/10.1002/andp.19354160705.
- [44] K.M. McPeak, S. V. Jayanti, S.J.P. Kress, S. Meyer, S. Iotti, A. Rossinelli,
 D.J. Norris, Plasmonic films can easily be better: Rules and recipes, ACS
 Photonics. 2 (2015) 326–333. https://doi.org/10.1021/ph5004237.
- [45] M. Born, E. Wolf, A.B. Bhatia, P.C. Clemmow, D. Gabor, A.R. Stokes,
 A.M. Taylor, P.A. Wayman, W.L. Wilcock, Principles of Optics,
 Cambridge University Press, 1999.
 https://doi.org/10.1017/CBO9781139644181.
- [46] A.J. Braundmeier, E.T. Arakawa, Effect of surface roughness on surface plasmon resonance absorption, J. Phys. Chem. Solids. 35 (1974) 517–520. https://doi.org/10.1016/S0022-3697(74)80005-3.
- [47] D. Hornauer, H. Kapitza, H. Raether, The dispersion relation of surface plasmons on rough surfaces, J. Phys. D. Appl. Phys. 7 (1974) 7–9. https://doi.org/10.1088/0022-3727/7/9/102.
- [48] M.R. Pinnel, Diffusion-related behaviour of gold in thin film systems,Gold Bull. 12 (1979) 62–71. https://doi.org/10.1007/BF03216542.
- [49] J.E.T. Andersen, Growth of a Copper-Gold Alloy Phase by Bulk Copper Electrodeposition on Gold Investigated by In Situ STM, J. Electrochem. Soc. 142 (1995) 2225. https://doi.org/10.1149/1.2044279.