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Stability of Underpotentially Deposited Ag Layers on a Au(111) Surface Studied by Surface X-ray Scattering

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Abstract

Stability of underpotentially deposited (upd) Ag layers on Au(111) surface was investigated by surface X-ray scattering (SXS). While the complete pseudomorphic Ag bilayer on Au(111) surface obtained by upd at 10 mV (vs. Ag/Ag⁺) was maintained its structure even after the circuit was disconnected and the surface was exposed to ambient atmosphere, the pseudomorphic Ag monolayer obtained by upd at 50 mV was converted to a partial bilayer with the coverage of 0.66 ML and 0.46 ML for the 1st and 2nd layer, respectively. These results show that Ag bilayer is structurally more stable than Ag monolayer on Au(111) and Ag atoms of the upd monolayer move around on the Au(111) surface without potential control.

Keywords: Underpotential deposition (upd); Surface X-ray scattering (SXS); Ag on Au(111)

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1. Introduction

Ultrathin metal films with well-defined atomic arrangements on solid substrates have been extensively investigated because of their importance not only in fundamental surface science but also in modern nanotechnology. Underpotential deposition (upd) is one of the best techniques to prepare ultrathin metal films on single crystal electrode surfaces with well-defined atomic arrangements [1-3]. The potential dependent structures of upd metal films with atomic resolution have been studied *in situ* by scanning tunneling microscopy (STM) [1,4-21], atomic force microscopy (AFM) [22,23], and surface X-ray scattering (SXS) [24-32].

The upd thin films are known to exhibit unique catalytic activities [33-35] and have been used as substrates for self-assembled monolayers (SAMs) [36-39]. Upd films prepared in electrolyte solutions are usually used as electrocatalysts and substrates for SAMs after the circuit is disconnected and the substrate is transferred through ambient atmosphere. Thus, it is very important to know the structural stability of the upd films under these conditions.

Upd of Ag is one of the most studied systems and the structure of Ag upd layers prepared on Au(111) has been extensively studied with an atomic resolution [4-6,10,12,19,20,29]. We also have studied the structure of Ag upd layers on Au(111) using *in situ* SXS and found that pseudomorphic Ag monolayer and bilayer are formed on Au(111) surface at 50 mV (vs. Ag/Ag^+) and 10 mV, respectively [29]. Here we studied the structures of the Ag upd mono- and bi-layers on Au(111) surface as-prepared and those after the circuit was disconnected and the surface was exposed to ambient atmosphere with an atomic dimension by SXS.

2. Experimental

All chemicals were purchased from Wako Pure Chemicals and were used without further purification. Water was purified using a Milli-Q system (Yamato, WQ-500). Ultrapure N_2 was purchased from Tomoe Shokai Co., Ltd. A Au(111) single crystal disk was purchased from Surface Preparation Laboratory and was used after the treatments as previously reported

[40,41]. Prior to each measurement, the Au(111) disk was flame annealed using a Bunsen burner and slowly cooled in air. It was then transferred to an electrochemical cell with the surface being covered with a drop of ultrapure water to avoid any surface contamination. Upd Ag layers on the Au(111) electrode surface were prepared in a 50 mM H₂SO₄ solution containing 1 mM Ag₂SO₄ as previously reported [29] by scanning the potential from 650 mV (Ag/Ag⁺) to 50 mV and 10 mV, where Ag upd pseudomorphic mono- and bi-layers, respectively, are known to be formed on a Au(111)-(1×1) surface [29]. The electrode was then washed with ultrapure water, dried by blowing ultrapure N₂ gas, and then transferred to an SXS cell through ambient atmosphere. After the cell was set on a six axes diffractometer (HUBER, 5020) installed in a bending-magnet beamline BL4C at Photon Factory, SXS measurements were carried out as described in the previous report [41] and X-ray intensity variation along the (00) rod was obtained. Ultrapure N₂ gas was flowed into the cell during the SXS measurements to avoid X-ray induced formation of active species such as ozone and radicals.

Structures along the direction normal to the electrode surface were quantitatively determined from the least square fitting to the reflectivity data with a kinematical calculation based on a specific interfacial model [41] consisting of three layers on top of the Au(111)-(1×1) substrate. Coverage in each layer is described using ML as a unit where 1 ML corresponds to 1.39×10^{15} atoms cm⁻².

3. Results and Discussion

Figure 1 shows a linear sweep voltammogram (LSV) of Au(111) measured in a 50 mM H₂SO₄ solution containing 1 mM Ag₂SO₄ with a scan rate of 5 mV s⁻¹. The present result is in good agreement with those reported before [12,22,29]. When the potential was scanned to 50 mV and 10 mV, where it was known that Ag upd pseudomorphic mono- and bi-layers, respectively, are formed on the Au(111)-(1×1) surface [29], *in situ* SXS measurements were carried out. The formation of the Ag mono- and bi-layers was confirmed and structural parameters of these films are summarized in Table 1.

Figure 2 shows reflectivity profiles of the Au substrate, which were taken out from the

electrochemical cell and transferred through ambient atmosphere and measured under nitrogen flow. Values of standard errors of the scattered X-ray reflectivity were shown as error bars in the figure. The structural parameters of these films are listed in Table 1 and schematic sectional views of Ag upd layers on Au(111) based on the present results are shown in Fig. 3.

Although the *in situ* SXS measurement showed that the Ag upd film obtained at 50 mV in the 50 mM H₂SO₄ solution containing 1 mM Ag₂SO₄ was fitted well with Ag monolayer as mentioned before, the best fit data for the Ag upd layer obtained at this potential after the circuit was disconnected and the surface was exposed to ambient atmosphere were completely different from that of as-prepared film and a Ag bilayer on the Au(111)-(1×1) surface with the 1st, 2nd and 3rd layers of Au, Ag, and Ag, respectively, was required to fit. The best fit data showed that the Au(111)-(1×1) surface was covered with a bilayer composed of 0.66 ML Ag and 0.46 ML Ag (total Ag coverage: ca. 1.1 ML) as the 2nd and 3rd layers, respectively, with relatively large RMS values of the Ag bilayer (Fig. 3(A)). This result suggests that the deposited Ag atoms of Ag upd monolayer move on the Au(111) surface without potential control in ambient atmosphere.

On the other hand, the best fit data of the Ag upd bilayer obtained at 10 mV were exactly the same as those of the as-prepared sample, showing that the Ag upd bilayer was remained on the Au(111)-(1×1) surface intact (Fig. 3(B)), i.e., the Ag upd bilayer on the Au(111) surface is very stable under the same conditions.

4. Conclusions

Stabilities of Ag upd mono- and bi-layers prepared on a Au(111)-(1×1) surface after were investigated by SXS. While the Ag upd bilayer prepared on the Au(111) surface was very stable even after the circuit was disconnected and the surface was exposed to ambient atmosphere, the Ag upd monolayer prepared on the Au(111) surface was changed to partial bilayer under the same conditions, showing that the Ag upd bilayer is more stable than the Ag upd monolayer on the Au(111) surface.

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References

- [1] D. M. Kolb, *Adv. Electrochem. Sci. Eng.* 7 (2001) 107.
- [2] G. Herzog, D. W. M. Arrigan, *Tre. Anal. Chem.* 24 (2005) 208.
- [3] V. Sudha, M. V. Sangaranarayanan, *J. Chem. Sci.* 117 (2005) 207.
- [4] T. Hachiya, K. Itaya, *Ultramicroscopy* 42-44 (1992) 445.
- [5] P. Mrozek, Y.-E. Sung, A. Wieckowski, *Surf. Sci.* 335 (1995) 44.
- [6] K. Ogaki, K. Itaya, *Electrochim. Acta* 40 (1995) 1249.
- [7] K. Uosaki, S. Ye, H. Naohara, Y. Oda, T. Haba, T. Kondo, *J. Phys. Chem. B* 101 (1997) 7566.
- [8] H. Naohara, S. Ye, K. Uosaki, *App. Phys. A* 66 (1998) S457.
- [9] H. Naohara, S. Ye, K. Uosaki, *J. Phys. Chem. B* 102 (1998) 4366.
- [10] S. Garcia, D. Salinas, C. Mayer, E. Schmidt, G. Staikov, W. J. Lorenz, *Electrochim. Acta* 43 (1998) 3007.
- [11] H. Naohara, S. Ye, K. Uosaki, *J. Electroanal. Chem.* 473 (1999) 2.
- [12] M. J. Esplandiu, M. A. Schneeweiss, D. M. Kolb, *Phys. Chem. Chem. Phys.* 1 (1999) 4847.
- [13] L. A. Kibler, M. Kleinert, R. Randler, D. M. Kolb, *Surf. Sci.* 443 (1999) 19.
- [14] L. A. Kibler, M. Kleinert, D. M. Kolb, *Surf. Sci.* 461 (2000) 155.
- [15] X. H. Xia, L. Nagle, R. Schuster, O. M. Magnussen, *Phys. Chem. Chem. Phys.* 2 (2000) 4387.
- [16] L. Cagnon, A. Gundel, T. Devolder, A. Morrone, C. Chappert, J. E. Schmidt, P. Allongue, *Appl. Surf. Sci.* 164 (2000) 22.

- [17] T. A. Sorenson, K. Varazo, D. W. Suggs, J. L. Stickney, *Surf. Sci.* 470 (2001) 197.
- [18] A. M. El-Aziz, L. A. Kibler, D. M. Kolb, *Electrochem. Commun.* 4 (2002) 535.
- [19] J. Lee, I. Oh, S. Hwang, J. Kwak, *Langmuir* 18 (2002) 8025.
- [20] X.-M. Xu, H.-P. Zhong, H.-M. Zhang, Y.-R. Mo, Z.-X. Xie, L.-S. Long, L.-S. Zheng, B.-W. Mao, *Chem. Phys. Lett.* 386 (2004) 254.
- [21] S. Takakusagi, K. Kitamura, K. Uosaki, *J. Phys. Chem. C*, 112 (2008) 3073.
- [22] C. H. Chen, S. M. Vesecky, A. A. Gewirth, *J. Am. Chem. Soc.* 114 (1992) 451.
- [23] C. H. Chen, A. A. Gewirth, *Ultramicroscopy*, 42-44 (1992) 437.
- [24] M. F. Toney, J. G. Gordon, M. G. Samant, G. L. Borges, O. R. Melroy, D. Yee, L. B. Sorensen, *J. Phys. Chem.* 99 (1995) 4733.
- [25] M. Cappadonia, K. M. Robinson, J. Schmidberger, U. Stimming, *Surf. Rev. Lett.* 4 (1997) 1173.
- [26] A. C. Finnefrock, L. Buller, K. L. Ringland, J. D. Brock, H. D. Abrunã, *J. Am. Chem. Soc.* 119 (1997) 11703.
- [27] M. Takahasi, Y. Hayashi, J. Mizuki, K. Tamura, T. Kondo, H. Naohara, K. Uosaki, *Surf. Sci.* 461 (2000) 213.
- [28] J. W. Ndieyira, A. R. Ramadan, T. Rayment, *J. Electroanal. Chem.* 503 (2001) 28.
- [29] T. Kondo, J. Morita, M. Okamura, T. Saito, K. Uosaki, *J. Electroanal. Chem.* 532 (2002) 201.
- [30] T. Kondo, K. Tamura, M. Takahasi, J. Mizuki, K. Uosaki, *Electrochim. Acta* 47 (2002) 3075.
- [31] M. J. Ball, C. A. Lucas, N. M. Markovic, V. Stamenkovic, P. N. Ross, *Surf. Sci.* 540 (2003) 295.
- [32] K. Tamura, J. X. Wang, R. R. Adzic, B. M. Ocko, *J. Phys. Chem. B* 108 (2004) 1992.
- [33] H. Naohara, S. Ye, K. Uosaki, *Electrochim. Acta* 45 (2000) 3305.
- [34] L. A. Kibler, A. M. El-Aziz, D. M. Kolb, *J. Molecul. Catal.* 199 (2003) 57.
- [35] H. Naohara, S. Ye, K. Uosaki, *J. Electroanal. Chem.* 500 (2001) 435.
- [36] G. K. Jennings, P. E. Laibinis, *J. Am. Chem. Soc.* 119 (1997) 5208.
- [37] K. Shimazu, T. Kawaguchi, T. Isomura, *J. Am. Chem. Soc.* 124 (2002) 652.
- [38] M. Fonticelli, O. Azzaroni, G. Benítez, M. E. Martins, P. Carro, R. C. Salvarezza, *J. Phys. Chem. B* 108 (2004) 1898.

- [39] T. Kondo, K. Tamura, S. Takakusagi, K. Kitamura, M. Takahasi, J. Mizuki, K. Uosaki, J. Solid State Electrochem. in press.
- [40] S. Ye, C. Ishibashi, K. Uosaki, Langmuir 15 (1999) 807.
- [41] T. Kondo, J. Morita, K. Hanaoka, S. Takakusagi, K. Tamura, M. Takahasi, J. Mizuki, K. Uosaki, J. Phys. Chem. C 111 (2007) 13197.

Table 1. Structure parameters obtained from the analyses of the reflectivity profiles of the as-prepared Ag upd layers on Au(111) and those after the circuit was disconnected and exposed to ambient atmosphere.

*	50 mV		10 mV	
	as-prepared**	after air exposure	as-prepared	after air exposure
<i>Distance, z_{Au-Au} / Å</i>	2.36 ± 0.03	2.36 ± 0.01	2.36 ± 0.01	2.36 ± 0.01
<i>Distance, z_{Au-Ag} / Å</i>	2.35 ± 0.04	2.35 ± 0.04	2.35 ± 0.02	2.36 ± 0.01
<i>Distance, z_{Ag-Ag} / Å</i>	-	2.35 ± 0.05	2.36 ± 0.02	2.36 ± 0.02
<i>Coverage, ρ_{Au} / ML</i>	1.00 ± 0.01	1.00 ± 0.01	1.00 ± 0.01	1.00 ± 0.01
<i>Coverage, $\rho_{Ag(1)}$ / ML</i>	0.99 ± 0.03	0.66 ± 0.06	1.00 ± 0.03	1.00 ± 0.03
<i>Coverage, $\rho_{Ag(2)}$ / ML</i>	-	0.46 ± 0.07	0.99 ± 0.04	0.99 ± 0.04
<i>RMS, σ_{Au} / Å</i>	0.085 ± 0.001	0.085 ± 0.001	0.085 ± 0.001	0.085 ± 0.001
<i>RMS, $\sigma_{Ag(1)}$ / Å</i>	0.11 ± 0.02	0.19 ± 0.05	0.11 ± 0.03	0.13 ± 0.02
<i>RMS, $\sigma_{Ag(2)}$ / Å</i>	-	0.23 ± 0.08	0.15 ± 0.03	0.15 ± 0.02

*Distances of z_{Au-Au} , z_{Au-Ag} , and z_{Ag-Ag} represent atomic layer distances between the Au substrate and the top Au layer, between the Au substrate and the Ag layer, and between two Ag layers, respectively.

**For the as-prepared Ag upd monolayer obtained at 50 mV, the structure parameters were determined from the least square fitting based on the two, not three, layers model on the Au(111)-(1×1) substrate. Thus, the results of the 1st layer, i.e., Au, are not listed but only the results of the 2nd and 3rd layer, i.e., Au and Ag, are listed.

Figure Captions

- Figure 1 Linear sweep voltammogram of the Au(111) electrode measured in 50 mM H_2SO_4 + 1 mM Ag_2SO_4 with a scan rate of 5 mV s^{-1} . Scan was started at 650 mV (vs. Ag/Ag^+) to the negative direction. Arrows (**A**) and (**B**) represent the potentials (50 mV and 10 mV, respectively) where the *in situ* SXS measurements were carried out and the electrode were taken out for the SXS measurements.
- Figure 2 The reflectivity profiles of the Ag upd layers on the Au(111) surface obtained at (**A**) 50 mV (vs. Ag/Ag^+) and (**B**) 10 mV ($\div 10^3$) measured after the circuit was disconnected and surface was exposed to ambient atmosphere. Circles and solid lines are experimental data and calculated curves fitted by the least squares method with a kinematical calculation. Values of standard errors of the scattered X-ray intensity were shown as error bars in the figure.
- Figure 3 Schematic side views of Ag upd layers prepared at (A) 50 mV (monolayer) and (B) 10 mV (bilayer) on Au(111). Left: as prepared. Right: after the circuit was disconnected and the surface was exposed to ambient atmosphere.

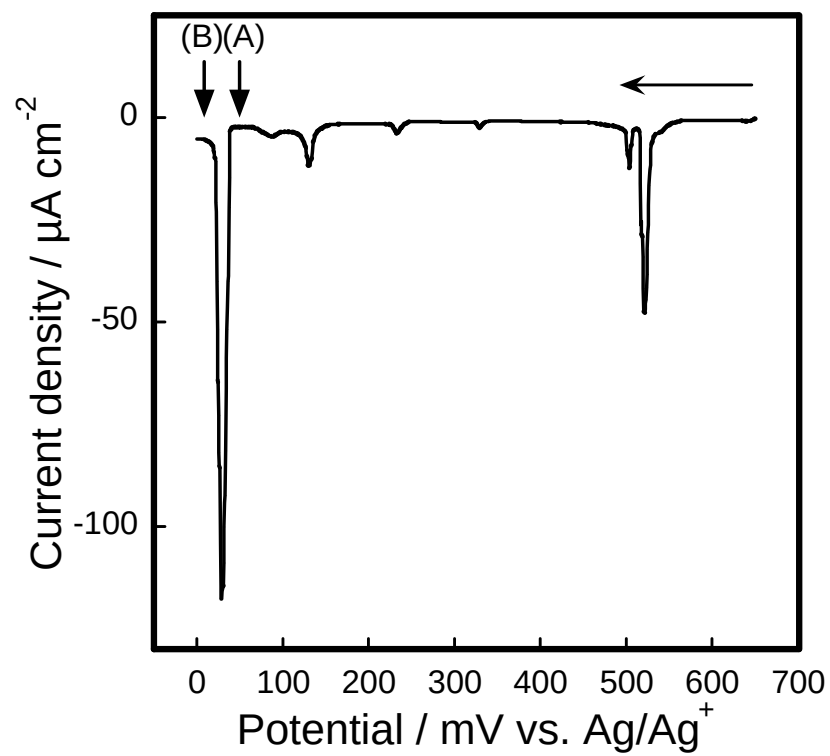


Fig. 1
K. Uosaki et al.

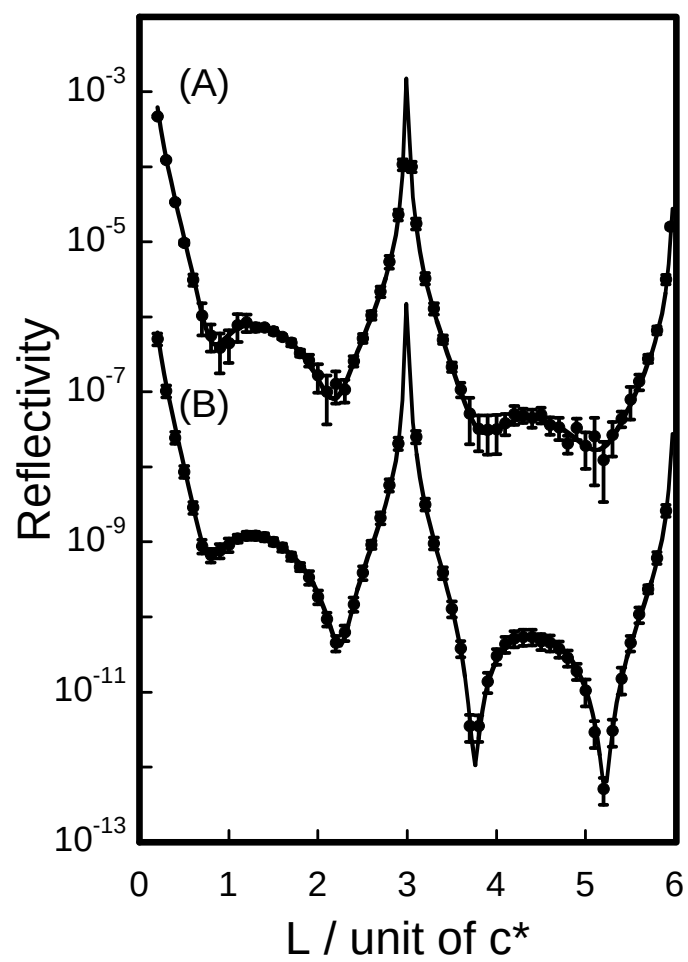


Figure 2
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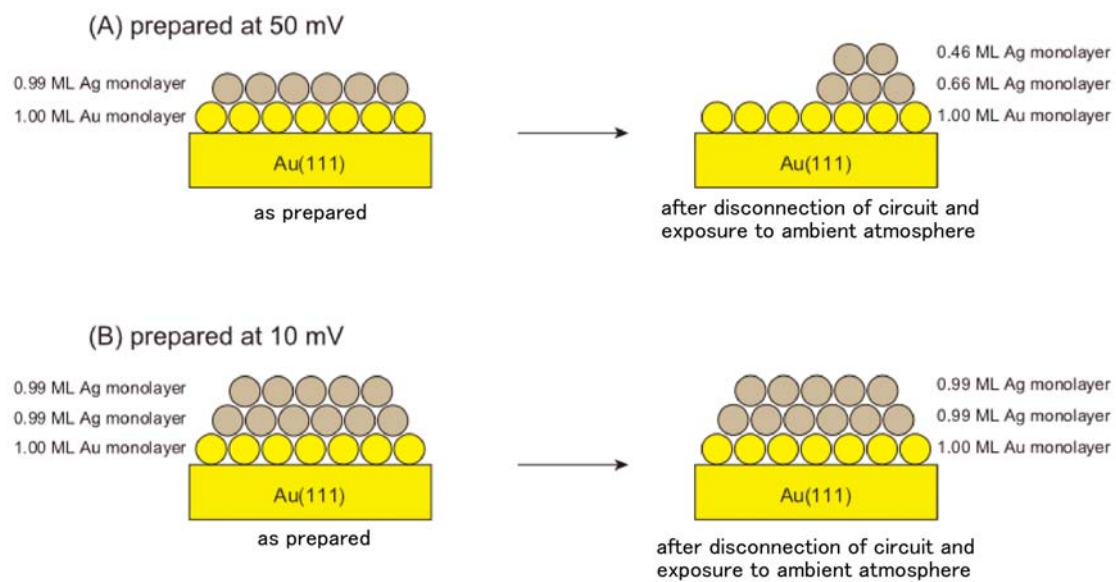


Fig. 3
K. Uosaki et al.