Dehydration processes of metal cations during electrodeposition

Metal deposition is an important subject from industrial viewpoints such as electrolytic refining, corrosion, and plating. Recently, well-designed plating techniques have become necessary for various fields, including the nanofabrication of electrodes for electronic devices and the surface modification of nanoparticles for catalysts. Underpotential deposition (upd) can achieve atomically controlled single- or double-layer modification of metal cations, which has been applied for the preparation of nanocatalysts [1].

During electrodeposition, counter anions often promote or inhibit metal deposition. Moreover, solvent species as well as ionic species also affect the approach of metal cations to a surface because of diffusion across an electrical double layer (EDL). In the EDL, ionic species are located at the Helmholtz layer and the solvent species are highly oriented by the layer structure of the charged species with a huge electric field. In an electrochemical reaction, when the reaction species approach the surface, these layered structures are destroyed. Since metal cations are hydrated in solution, the dehydration process is also important during deposition. However, these approaching and dehydration processes of metal cations are unknown. X-ray diffraction is the best method for the structural determination of ionic species in an EDL and can also carry out detection with high time and spatial resolution. In this study, we performed time-resolved X-ray diffraction to observe the upd process of various metal cations on Au(111) in real time.

X-ray diffraction measurements were performed with a multi-axis diffractometer at SPring-8 **BL13XU**. For the time-resolved experiment, a rectangular potential wave between non-upd and upd potentials with a frequency of 1.0 Hz was applied to an Au electrode. Diffracted photons were detected by a Ce-doped yttrium aluminum perovskite (YAP:Ce) detector, and the discriminated pulses were counted by a multichannel scaler synchronized with a function generator used for potential control [2].

We performed time-resolved measurements at peak positions along a crystal truncation rod (CTR). For Cu upd, a potential step was applied from the non-upd potential of 1.05 V *versus* standard hydrogen electrode (SHE), at which a well-ordered sulfate layer on Au (111) was formed, to the upd potential of 0.45 V, at which a $\sqrt{3} \times \sqrt{3}$ upd layer was formed. Figure 1 shows the time-resolved intensity transient along the specular CTR after the potential step. After 100 ms,

the intensity around $L = 1.2$ had decreased, whereas that around $L = 4.2$ had increased. These changes can be ascribed to the deposition of $\sqrt{3} \times \sqrt{3}$ Cu. However, an abnormal enhancement of the intensity appeared between $L = 1.2$ and 2.7 immediately after the potential step to 100 ms that cannot be attributed to the formation of an adsorbed layer. We constructed time-resolved structure factors along the specular CTR from the intensity transient in order to refine the structural parameters at each time. The structure factors were conventionally corrected from the integrated intensity measurement along the CTR. Figure 2 shows the time dependence of the structural parameters during Cu upd. The initial enhancement of the intensity after the step to the upd potential can be ascribed to the layer formation of the Cu species at a distance of around 0.32 nm from the surface. When Cu was deposited on a Au(111) surface directly, the distance between the first Au layer and the adsorbed Cu layer was 0.21 nm. Therefore, the distance of 0.32 nm indicates that this Cu species was not adsorbed directly but was located at the outer Helmholtz layer as a hydrated state [3]. During Cu deposition, hydrated Cu ions approached the outer Helmholtz layer, and Cu ions were then adsorbed on the Au(111) surface by the destruction of the hydration shell. The adsorbed
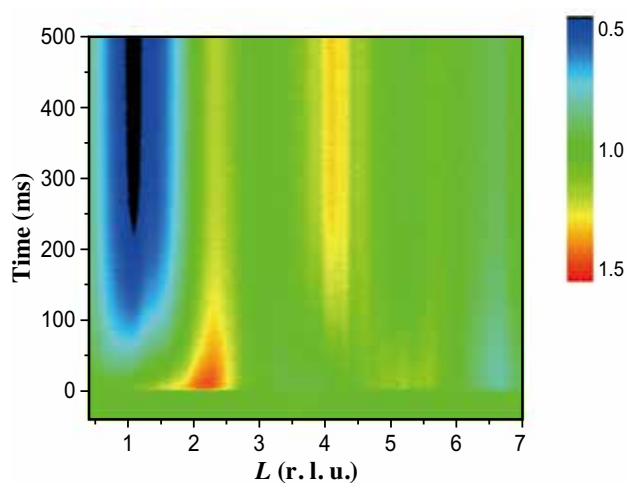

Fig. 1. Time-resolved specular CTR in 0.5 M H_2SO_4 + 1.0 mM $CuSO_4$ after the potential step from 1.05 V to 0.45 V with a time resolution of 500 μs. The transient intensities were normalized by those at the non-upd potential of 1.05 V. Red and blue regions indicate increases and decreases of intensity, respectively.
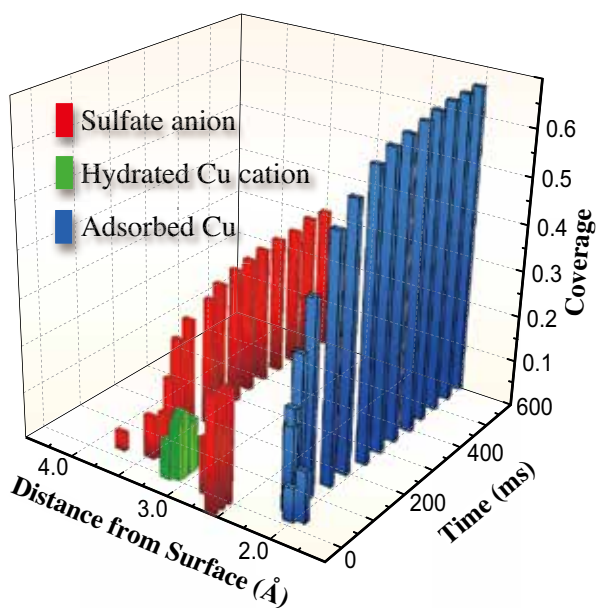
Fig. 2. Time dependence of the structural parameters optimized using the time-resolved specular CTR. The position of the adsorbed (bi)sulfate indicates the sulfur atom of tridentate (bi)sulfate.

strong interaction between water and the metal cation delays the adsorption on the surface. However, the decay time of the Cu deposition is longer than that of Bi showing a higher coordination energy. Since the decay of Cu upd becomes faster as the concentration of sulfuric acid increases, the slow decay of Cu upd is due to its complex formation with the sulfate anion. The complex formation process of Cu on Au(111), which requires SO_4 delays the Cu deposition and makes it slower than Bi upd.
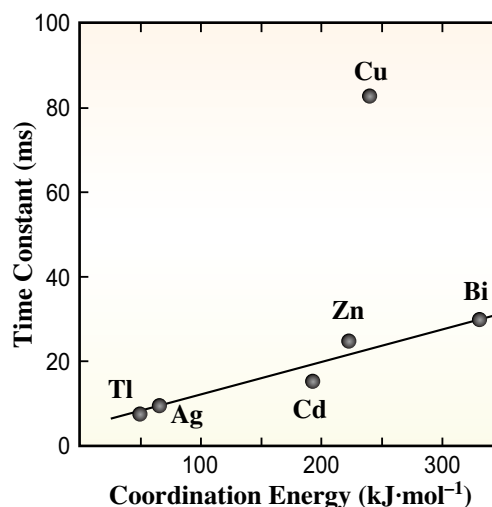

Fig. 3. Correlation between the time constant of X-ray intensity decay and the coordination energy of each hydration water of $M(H_2O)_6{}^{n+}$.

sulfate species at the non-upd potential were located 0.27 nm from the Au(111) surface. After the potential was decreased stepwise to 0.45 V, the sulfate species desorbed within 1 ms, and then the hydrated Cu^{2+} was immediately accumulated with a maximum coverage of 0.14. The coverage of the hydrated Cu^{2+} decreased after 40 ms, and the Cu and the sulfate anion were then adsorbed on Au(111) over the next 400 ms. The coverages of the adsorbed Cu and sulfate species correlated strongly, suggesting that these ions interacted in a complementary manner.

The initial deposition process was investigated for the upd of different metal cations (Tl^+, Ag^+, Zn^{2+}, Cd^{2+}, and Bi^{3+}). The time constants of metal deposition were estimated from the transient intensities at the reciprocal lattice point of 0 0 1.4. As described above, the metal cation with the hydration shell was metastably layered in the EDL before the deposition step. Therefore, the destruction of the hydration shell may have been the kinetically controlled step during deposition. Figure 3 shows a plot of the coordination energies of the hydrated water estimated by DFT calculations against the time constant of the intensity transient. The coordination energy is strongly correlated to the ionic valence due to the electrostatic interaction. The deposition rate of the metal cations has a linear relationship with the coordination energy, except in the case of Cu upd; this indicates that

Masashi Nakamura[a,*], Osamu Endo[b] and Osami Sakata[c]

[a] Graduate School of Engineering, Chiba University
[b] Graduate School of Engineering, Tokyo University of Agriculture and Technology
[c] Synchrotron X-ray Station at SPring-8, National Institute for Materials Science (NIMS)

*Email: mnakamura@faculty.chiba-u.jp

References
[1] F. Calle-Vallejo et al.: Chem. Soc. Rev. 42 (2013) 5210.
[2] M. Nakamura et al.: J. Phys. Chem. C 118 (2014) 22136.
[3] M. Nakamura, T. Banzai, Y. Maehata, O. Endo, H. Tajiri, O. Sakata, N. Hoshi: Sci. Rep. 7 (2017) 914.