

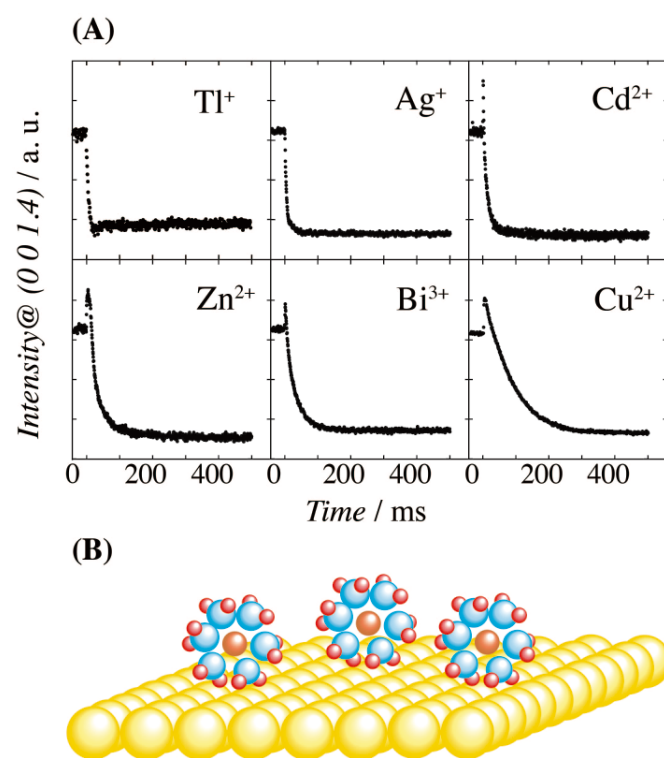
## Structural Dynamics during Metal Deposition on Au(111) Electrode

The transitional structures at the initial electrocrystallization of various metal cations on an Au(111) electrode have been determined by using time-resolved surface X-ray diffraction. At the initial stage of metal deposition, a characteristic intensity transient appears depending on the metal cations. Metal cations with relatively high hydration energies are deposited in two steps: first, the hydrated metal cations approach the surface and are metastably located at the outer layer, then they are deposited via destruction of the hydration shell. Metal cations strongly interacting with the counter coadsorbed anions slow down the deposition rate because of the formation of metal-anion complexes.

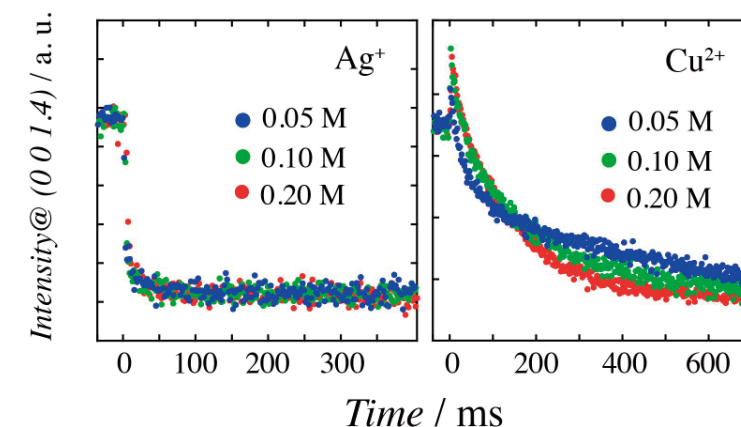
Electrochemical deposition of metal cations is widely used in various industrial processes such as electrolytic refinement and wet metallization on semiconductor. Recently, it was reported that core-shell catalysts modified by hetero-atoms could significantly enhance chemical reactions [1]. Atomically controlled first or second layer deposition techniques are a major issue for the preparation of nano-catalysts. The under-potential deposition (upd) of metal cations can control a well-defined deposition structure in a few atomic layers, which can be used for catalyst preparation, and it is also useful for fundamental research as a model of the initial stage of metal deposition [2]. An understanding of transient structures is also necessary to elucidate deposition/dissolution processes. In this study, the deposition processes of  $Tl^+$ ,  $Ag^+$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ , and  $Bi^{3+}$  on Au(111) were studied by using time-resolved surface X-ray diffraction (TRSXRD). Transient structures of metal cations in the

electrical double layer were captured with a time resolution of 500  $\mu s$  [3].

Diffraction X-ray was counted by a multichannel scaler synchronized with a function generator [4]. **Figure 1(A)** shows TRSXRD profiles at the 0 0 1.4 reflection that is sensitive to each upd layer. After the potential is stepped from non-upd potential to upd potential, the X-ray intensity at 0 0 1.4 between Bragg peaks is reduced because of interference between the Au substrate and the upd layer. However, the intensity at this reflection increases within a few ms and then decreases over the next 100–300 ms in solutions containing  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ , and  $Bi^{3+}$ . At the non-upd potentials for Cd, Zn, and Bi upd, no specifically adsorbed anions are adsorbed on Au(111); this supports the observation that the intensity increase is not because of the desorption of anions but rather because of the existence of a temporal hydrated cation layer. Structural analysis was performed from



**Figure 1:** (A) TRSXRD at 0 0 1.4 with the time resolution of 500  $\mu s$ . (B) Schematic model of metastable structure of hydrated cation during upd.



**Figure 2:** TRSXRD at 0 0 1.4 in  $x M H_2SO_4 + 0.5 mM Ag_2SO_4$  and  $x M H_2SO_4 + 1.0 mM CuSO_4$  ( $x = 0.20$  (red), 0.10 (green), and 0.05 (blue)) with the time resolution of 1.0 ms.

time-resolved measurements at the peak positions along the crystal truncation rod. Intensity increase at the initial step suggests the presence of outer layer species in the electrical double layer, which we assigned to the hydrated metal ion as shown in **Fig. 1(B)**. During  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ , and  $Bi^{3+}$  deposition, hydrated metal cations approach the outer layer in the electrical double layer and then metal ions are deposited on Au(111) with destruction of the hydration shell. However,  $Tl^+$  and  $Ag^+$  upd processes are different from the other upd processes; the intensity transients decrease without any temporary enhancement. The initial enhancement did not appear even at the faster time resolution of 100 ms. The intensity transients of other reciprocal lattice space also rapidly converge to the diffraction intensity of the upd potential, which indicates that  $Tl^+$  and  $Ag^+$  are deposited without a metastable state at the outer layer. These results indicate that the dehydration process is a kinetically controlled step during metal upd.

For  $Tl^+$ ,  $Ag^+$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ , and  $Bi^{3+}$ , the deposition rate estimated from the intensity decay of **Fig. 1(A)** has a linear relationship with the hydration energy calculated from the hexa-aqua metal complexes, supporting the conjecture that the interaction between hydration water and the metal cation affects the deposition of metal cations. However, although the hydration energy of  $Bi^{3+}$  is higher than that of  $Cu^{2+}$ , the deposition rate of  $Cu^{2+}$  is slower than that of the Bi upd. This slow deposition rate of  $Cu^{2+}$  is due to the formation of a complex with the (bi) sulfate anion. The concentration dependence of the (bi) sulfate anion was investigated for the deposition rate

of Cu and Ag upd to confirm the effect of the formation of the complex. **Figure 2** shows the concentration dependence of TRSXRD on sulfuric acid for Ag and Cu upd. The solutions were adjusted to the same pH by adding  $HClO_4$  to equalize the ratio between  $[SO_4^{2-}]$  and  $[HSO_4^-]$ . Although the decay of Ag upd was constant and did not depend on the concentration of sulfuric acid, the decay of Cu upd was faster as the concentration of sulfuric acid increased. In the case of Cu upd in 0.05 M  $H_2SO_4$ , the decay convergence did not occur even at 600 ms. The complex formation process during the Cu upd requires (bi)sulfate anion in the interface. For metal depositions that are accompanied by strong complex formation with the counter anion, the concentration of the counter anion is the rate-determining factor of metal deposition.

### REFERENCES

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### BEAMLINE

BL-4C

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