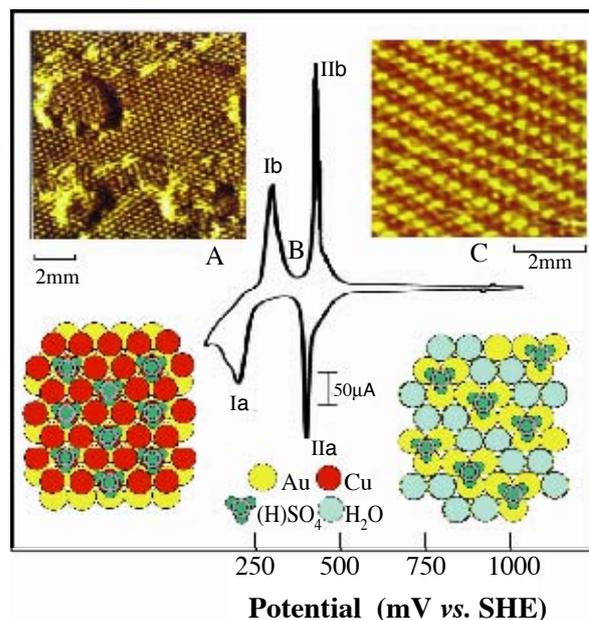


**STRUCTURES OF ELECTRODE SURFACES STUDIED  
BY *IN SITU* SURFACE X-RAY DIFFRACTION:  
NEW STRUCTURES OF WATER ADSORBED ON Au(111) ELECTRODE SURFACE**

The adsorption of a water molecule and coadsorption of a water molecule with electrolyte ions on a metal electrode surface is a fundamental issue of electrochemical surface science. So far, the role of the hydration water molecule in electrode reactions on an electrode surface remains unclear. The two-dimensional structure of water molecules on a surface gives an insight into important mechanisms concerning electron and proton transfer or weak interactions of water molecules with surfaces. Recent studies of water adsorption on metal surfaces are almost entirely limited to the adsorption of water under UHV conditions. *In situ* observation of water adsorption on a real electrode surface is quite difficult due to the hindrance of electrolyte solution on the electrode surface. To understand the role of hydration water molecules on electrochemical double layers on an electrode surface, it is imperative to reveal the structure of hydration water molecules in the double layers under an electrode potential control.

It is well known that water forms a tetrahedral network structure not only in ice (solid), but also in liquid (solution) phases. The density of these phases is approximately one unit. Recently, however, the existence of a high-density water (1.5 - 2.0) has been observed for a water structure on an electrode surface [1]. Thus, it might be possible to find a new two-dimensionally extended water phase on a metal electrode surface. Recent progress with synchrotron radiation has made it possible to observe structures extended on surfaces or interfaces by two- or three-dimensional structure analysis, and we have applied this surface X-ray diffraction technique to one of the

most important systems of electrochemistry: the underpotential deposition (UPD) of copper on an Au(111) electrode surface. Figure 1 shows a cyclic voltammogram (CV, current-potential curve) associated with copper deposition on an Au(111) electrode surface in  $\text{H}_2\text{SO}_4$  solution. In general, metal monolayer deposition was observed to occur at a certain “undervoltage” with respect to the equilibrium Nernst potential of the reaction  $\text{M}(z+) + ze^- \rightarrow \text{M}$ . Here,  $\text{M}(z+)$  designates a metal ion in



*Fig. 1. CV of an Au(111) electrode in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 mM  $\text{CuSO}_4$  at a scan rate of 50 mV/s. In situ STM images at the A range (0.35V RHE) and C range (1.20 V, RHE) of adsorbed molecules on the Au(111) electrode in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 mM  $\text{CuSO}_4$  solution are shown in the inset. STM (A range): in situ STM of sulfate + UPD copper adsorbed on the Au(111) electrode surface.  $I_1 = 2.8$  nA,  $V_{\text{bias}} = -65.6$  mV. STM (C range): in situ STM of  $\text{HSO}_4^-$  +  $\text{H}_5\text{O}_2^+$  adsorbed on the Au(111) electrode surface.  $I_1 = 4.2$  nA,  $V_{\text{bias}} = -967.2$  mV.*

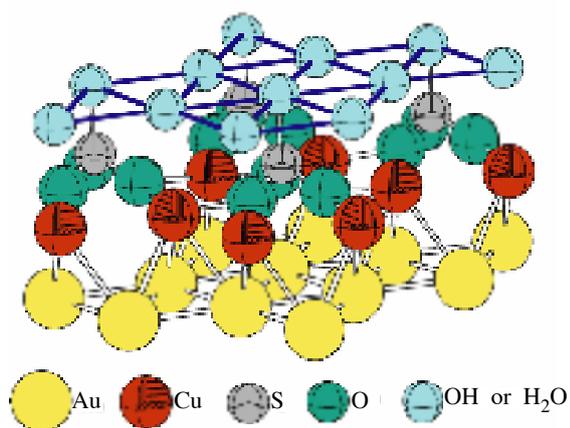
solution, and M, a metal atom in a lattice position on a surface. It was recognized that the undervoltage results energetically from the contribution of the heat of adsorption of the metal atoms on the inert substrate metal electrode surface on the energy of activation of the discharge reaction. The current peaks, IIa and IIb, are attributed to adsorption or deposition of Cu and desorption or stripping of  $\text{Cu}^{2+}$  in honeycomb copper atoms ( $2/3$  coverage), respectively. The peaks, Ia and Ib, appear to be those of honeycomb-centered copper atoms for  $1/3$  coverage, respectively. We have determined the structures in those three potential ranges at A (more negative than Ia), B (between Ia and IIa) and C (more positive than IIa).

The *in situ* specular X-ray reflectivity measurements were carried out using a multi-axis diffractometer installed on beamlines **BL09XU** and **BL13XU**. The wavelength of X-ray radiation was 0.130 nm. The total number of unique reflections observed for the symmetry (P31m) was 53 at the potential of 0.32 V (RHE: Reversible Hydrogen Electrode) where UPD copper forms a honeycomb structure. The final R-factor converged to 8.8%. **Figures 2 and 3** show the Cu UPD honeycomb structure formed on the Au(111) electrode in 0.5 M

$\text{H}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$  solution at 0.32 V in the potential range B. We succeeded in locating the hydration water molecules on top of each UPD copper atom, so that a  $1 \times 1$  closest-pack oxygen adlayer dominates on the UPD copper Au(111) surface.

The honeycomb copper layer on Au(111) does not show a metallic state. The difference in diameter between copper (0.256 nm) and gold (0.288 nm) causes a gap in the copper-copper distance of the honeycomb structure. The hydration water that is formed on copper is a new phase of water with a high density. The hydration water phase consists of a  $1 \times 1$ -O structure on the Au(111) surface,  $1/3$  of which is an oxygen atom of sulfate O and  $2/3$  of which is hydration water molecule on each copper atom. The distance (OH...O), 0.288 nm, is typical of the hydrogen bonding value of O...O seen in an ice structure under high pressure. The important point is that all of the oxygen atoms form a coplanar structure, which is in remarkable contrast to an ice structure. The ice structures have the common feature of tetrahedral bonding of water oxygen atoms. In contrast, the new water phase is formed by a closest-packed oxygen structure with a coplanar layer.

In region C, with a more positive potential than the small dip in CV at 940 mV, the *in situ* STM image shows a  $\sqrt{3} \times \sqrt{7}$  structure as seen in the inset in **Fig. 1**. Intensities in a non-integer reflection ( $1/5, 1/5, 0.2$ ) and its equivalent reflections, developed in region C, measure the growth of  $\sqrt{3} \times \sqrt{7}$  structure domains of bisulfate anion on the surface. The ball model in **Fig. 1** shows the best fit of the observation. The bright and the dimmer spots in the STM image correspond to the  $\text{HSO}_4^-$  anion and proton dimer  $\text{H}_5\text{O}_2^+$  molecules, respectively. There exist a number of hydrogen bonding pairs between anions and water molecules. The ideal and most stable OH...O hydrogen bonding distance of 0.280 nm matches



**Fig. 2.** ORTEP drawing of the structure based on the final positional parameters and temperature factors for Cu UPD on the Au(111) electrode in 0.5 M  $\text{H}_2\text{SO}_4 + 1 \text{ mM CuSO}_4$  solution. Electrode potential was 0.32 V (RHE).

the substrate Au lattice unit, yielding a high degree of stabilization due to the hydrogen bond network formation. In the ball model, oxygen atoms occupy the top surface of gold atoms which exhibit closest packing accommodation of oxygen, although the oxygen is not coplanar in this case.

In region A, which has a more negative potential than the current peak Ia in CV, where  $1 \times 1$  full monolayer coverage of copper or further overlayers (OPD) of copper are deposited on the Au(111) electrode surface, high-intensity at  $(1/3, 1/3, 1.5)$  reflection continues to evolve even at the potential more negative than 100 mV, where multilayers of copper deposit epitaxially on Au(111). The further-enriched intensity of the reflection at potentials more negative than 100 mV indicates that hydration water and sulfate anions still form the similar  $\sqrt{3} \times \sqrt{7}$  structure shown in Fig. 2 on  $1 \times 1$  epitaxially grown copper layers on the Au(111) electrode.

We have recently observed zinc UPD on Au(111) in 0.1 M  $\text{KH}_2\text{PO}_4$  and 1 mM  $\text{Zn}(\text{ClO}_4)_2$  solution. While the surface structure of the Au(111) electrode in the topmost layer of copper UPD is the same as a bulk structure ( $1 \times 1$ ), and lifting of a surface reconstruction takes place at a surface, surface reconstruction of the Au(111) electrode continues to occur in the case of zinc UPD associated with a zinc phosphate formation (Zn-UPD), even in very negative electrode potential ranges [3]. This indicates that copper sulfate with a closest-packed hydration water sheet causes a strong interaction with the Au(111) electrode, whereas the Zn-phosphate surface complex is only weakly adsorbed on the Au(111) electrode. Consequently, the top layer gold surface is only weakly affected by the overlayer Zn-phosphate complex, resulting in the occurrence of surface reconstruction.

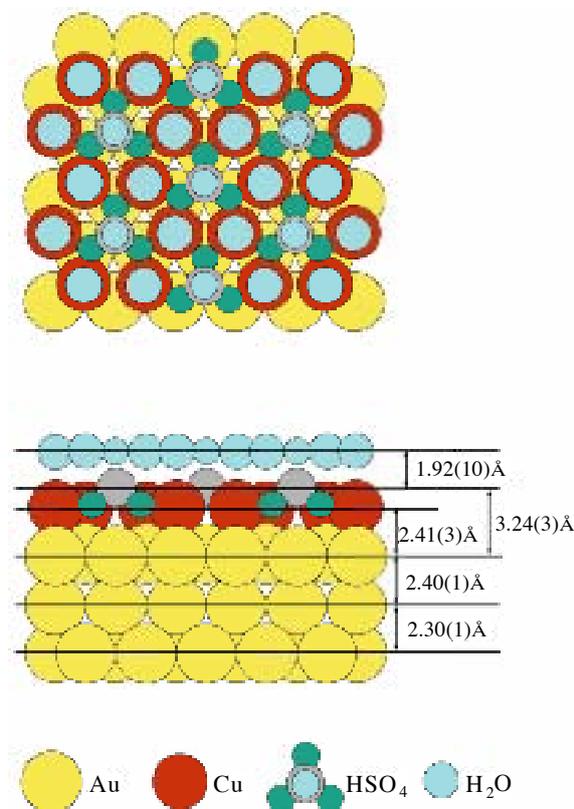


Fig. 3. Schematic model (top and side view) of UPD copper, hydration water molecule and sulfate anion adsorbed on an Au(111) electrode at the potential, 0.32 V (RHE).

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