Early stages of copper electrocrystallization

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The objective of our work is to understand the role played by anions in controlling a two-dimensional (2D) ordering of copper atoms electrons deposited at the metal-electrolyte interface. Copper electroplating is involved in the manufacturing of electronic devices. It is also used for decoration and for the final finish of many commercial goods. Copper electroplated for commercial or industrial applications must adhere strongly to the support, be of high purity, well leveled and have a shiny appearance.

The quality of electrodeposited metal is to a large extent determined by the composition of the electrolyte used for electroplating, and particularly by the type of anions and organic additives present in the electrolytic bath. The anions and additives are frequently codeposited with copper atoms and hence they affect the rate of crystallization, the rate of crystallite growths, and the crystallographic direction of growth. The structure of three-dimensional (3D) crystallization in metal electroplating is determined by the structure and composition of the first one or two monolayers formed at the surface of the electrodeposited material. A proper understanding of the processes taking place at the surface, and particularly an understanding of the driving forces responsible for 2D ordering of the deposited atoms, is a prerequisite to the understanding of electrocrystallization as a whole. This knowledge is needed for improved control of electroplating technologies.

In order to investigate two-dimensional ordering of electrodeposited metal one has to isolate 2D from 3D crystallization processes. This can be achieved easily by using gold (or platinum) as a substratum material. The deposition of the first monolayer of copper at the surface of a gold (or platinum) electrode proceeds at potentials which are between 0.3 to 0.5 V more positive than potentials needed for the deposition of copper on copper. The substratum material of our choice is a gold (311) single crystal electrode. Copper is known to form isomorphous, epitaxial (1x1) overlayers on gold single crystal surfaces if deposited in vacuum. The surface crystallography of the substrate is therefore the first factor which influences 2D ordering of electrodeposited copper atoms (adatoms). The second factor is the presence of anions which are codeposited with copper at the electrode surface.

Figure 1 shows the composition of an overlayer formed at the Au(III) electrode surface by Cu deposition in the presence of chloride ions. The formation of the first monolayer of Cu at the Au(III) surface starts at potentials that are about 0.25V more positive than potentials required for bulk copper deposition. This surface concentration of Cu rises steeply until a concentration of 1.65 x 10^12 atoms/cm^2 is reached. This corresponds to the coverage of 0.7% ML, where (ML) the monolayer coverage corresponds to the surface concentration of gold atoms at an ideal (111) surface (1.36 x 10^14 atoms/cm^2). The copper coverage increases slowly with decreasing potential until, just before the onset of the bulk copper deposition, the formation of the first monolayer is completed. The adsorption of copper apparently promotes a nucleation of chloride ions. The surface concentration of Cl^- with copper coverage up to a value of 7 x 10^14 ions/cm^2. Further increase of the surface concentration of copper has only a very weak effect on the surface concentration of chloride. The surface concentration corresponding to a close-packed hexagonal monolayer of chloride...
ions is \(9 \times 10^{10} \text{ ions/cm}^2\), when estimated using the ionic radius (1.8 Å). Therefore, the concentration of chloride co-adsorbed with Cu(111) is approximately 0.8 ML of a hexagonal monolayer of Cl.

The co-adsorbed copper and chloride form a bilayer. It is known from X-ray absorption spectroscopy [6, 7] and STM imaging [6, 7] that the bilayer is well ordered and has a (0001) long range structure. However, it is not known how the copper atoms and co-adsorbed chloride ions are packed within a unit cell of this structure. Are the copper atoms sandwiched between the bottom layer of gold atoms and the top layer of chloride ions? Do they adsorb in registry with the underlying gold layer as illustrated in Figure 2a, or are they packed in registry with the top layer of chloride as shown schematically in Figure 2b? Both types of the surface configuration have been suggested in the literature [5, 6]. We have used X-ray absorption spectroscopy at CHESS station C2 to investigate these questions. We expected that differences between the spectra determined for copper using X-ray photons polarized normal to the surface (s-polarized) and parallel to the surface (p-polarized) will provide information about the location of copper atoms in the bilayer. We believed that these experiments should tell us whether copper atoms are sandwiched, as shown in Figure 2a, or are adsorbed on top of a chloride layer, as suggested in [7]. In addition, we expected that the spectra should help us to determine whether the copper is in registry with the gold layer (Figure 2a) or with the chloride layer (Figure 2b).

The experiments were performed using a thin layer electrochemical cell which was a modified version of a cell described by Abrate et al. [6]. By controlling the electrode potential, known amounts of copper and chloride were deposited at the Au(111) single crystal electrode surface from a dilute solution of copper which contained chloride ions. The Anode electrode was then immersed against a polystyrene window so that a very thin layer of the solution (only a few micrometer thick) was trapped between the electrode and the window. This thin layer of the electrolyte ensured potential control and therefore control of the surface composition and structure. The Cu K-edge X-ray absorption spectrum was recorded by detecting Cu K-fluorescence X-rays which pass through the thin layer of the electrolyte and the polystyrene window.

Figure 3 shows the magnitude of the Fourier transform of the Cu K-edge (labelled radial distribution function (RDF)) for the co-adsorbed copper and chloride at the Au(111) electrode surface. Figure 3a shows the RDFs determined with the electric field of the photon oriented parallel to the surface while Figure 3b shows the RDFs for the electric field normal to the surface. The RDFs were derived from spectra acquired at the electrode potentials indicated in the figure. The surface concentrations of Cu and Cl at these voltages are given in Figure 1. These are significant differences between the RDFs determined for the two photon polarizations. The function determined using light polarized parallel to the surface (p-polarized) is almost of lower magnitude than that measured using light polarized in the direction normal to the surface (s-polarized). This suggests that the surface has a relatively large static disorder. To overcome this problem we decided to perform the theoretical XAS calculations for different models to compare the simulated results with the experimental spectra. We have used the FEFF 6.5 [8] multiple scattering calculations of the X-ray absorption spectra of both the near edge (XANES) and extended (EXAFS) fine structure in our analysis. We have used our efforts on obtaining data for E=200mV where the ratio of co-adsorbed copper to co-adsorbed chloride ions is approximately 1:1. Feff calculates the polarization resolved X-ray absorption spectrum of an atom in a most defined environment. We have represented our system as a 25-atom cluster consisting of a top layer of 13 chloride ions, a middle layer of 33 copper atoms and a hexagonal layer of gold which contained 142 gold atoms in total. Copper atoms in the middle layer are assumed to be adsorbed either with registry to the bottom gold layer (as in Figure 2a) or in registry to the top chloride layer (as in Figure 2b). The Feff calculations were performed for each of the models and atom sites and were
averaged over all of these sites. The results of the Koo calculations are compared to the experimental XANES spectrum in Figures 6a and b for photon polarization parallel and normal with respect to the electrode surface, respectively. The spectra calculated assuming the copper atom is adsorbed in registry with the top chloride layer match the experimental results better than the spectra calculated for copper coordination in registry with the bottom gold layer. The differences between the curves simulated for the two copper coordinations are particularly strong when the photon is polarized in the direction parallel to the electrode surface.

Our X-ray absorption experiments have revealed significant information about the surface coordination of copper co-deposited with chloride at the Au(111) electrode. Similar experiments are being performed to determine the structure of mixed overlayers (Figure 4). Comparison of Koo calculations and experimental XANES spectra of Cu co-deposited with chloride at the Au(111) electrode surface at an absolute or 200 F/cm² V.S.C. The model used in the calculations consisted of 200 atoms (32 Au, 33 Cl, 33 O, 33 Cu) with the Cu atoms co-ordinated between the Au surface and a Cl monolayer. The Cu atoms are in registry with the bottom layer of Au atoms, and in registry with Cl in model B.

Curves C in the experimental result are formed by copper adatoms co-deposited with other atoms such as SO³⁻ and Br⁻. The structural studies will also be extended by cryo-transmission electron microscopy to measure the composition of mixed overlayers, which may lead to a complete description of the surface coordination chemistry and electron crystallization of copper. This is an important step in our efforts to understand the mechanisms of metal electropolishing.