

Binary Compound Formation During Copper Corrosion

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Experiment SI-1444 at ID32

1. Background and Motivation

Our efforts are motivated by experiments demonstrating that already trace amounts of halides in combination with certain organic additives are sufficient in order to improve the copper plating process. This process plays a key role in the course of on-chip wiring of state of the art integrated logic devices. However, the formation of binary Cu-halide compounds during the plating process leads to functionality problems when the features of the electrodeposited Cu structures reach nanometer size. An understanding of the involved atomic scale processes is still lacking but highly desirable since no progress or specific control of this phenomenon can be achieved without it.

The main objective of this experiment was concerned with the potential dependent formation of ordered binary compounds on Cu surfaces in halide containing electrolytes. The first step towards an understanding of these binary phases is based on a detailed knowledge of the potential dependent formation and structure of preadsorbed halide layers. The scientific goal of this contribution is, therefore, to achieve a more sophisticated understanding of the interaction of different electroadsorbed halide monolayers with copper electrodes. We particularly address here the entire *out-of plane structure* of halide modified copper surfaces by measuring and analyzing potential dependent crystal truncation rod and superstructure data under electrochemical conditions.

2. Preliminary Results (Experiment ended February 7, 2007)

Experimental Setup

A new electrochemical cell design for surface X-ray diffraction experiments has been used for the first time in this experiment. The cell can be seen in Figure 1 and 2a). It generally provides an inert sample environment that enables diffraction experiments from reactive surfaces such as Cu, Co or Ni under electrochemical conditions. As shown in Figure 2 b) the sample was placed below a capillary and covered by a droplet of electrolyte hanging from it. X-ray absorption by the electrolyte was adjustable by controlling the shape and volume of the droplet through a balance between its surface tension and the gravitational force of an electrolyte reservoir connected to it. The reference and counter electrode were placed just at the end of the capillary and with a resulting distance of only 5-7mm to the sample. The high quality of electrochemical conditions and control can be seen from Figure 1(b) which shows a voltammogram of a Cu(100) surface in a 5mM H₂SO₄ / 10mM KCl containing droplet. The scattering geometry is indicated by the vectors k_i for the incoming and k_f for the diffracted beam. Accessibility to reciprocal space was practically unrestricted and allowed the collection of in- and out-of-plane data up to momentum transfers of 6.6 Å⁻¹. Oxygen or other contaminations were avoided through flushing of the cell with ultra pure nitrogen or argon gas.

The stability and cleanliness of Cu(100) surfaces was monitored by reference reflections that were sensitive to the full 3D geometry and roughness of the surface. Stable and clean conditions on Cu(100) were achieved for more than 12 hours during surface sensitive X-ray diffraction experiments.

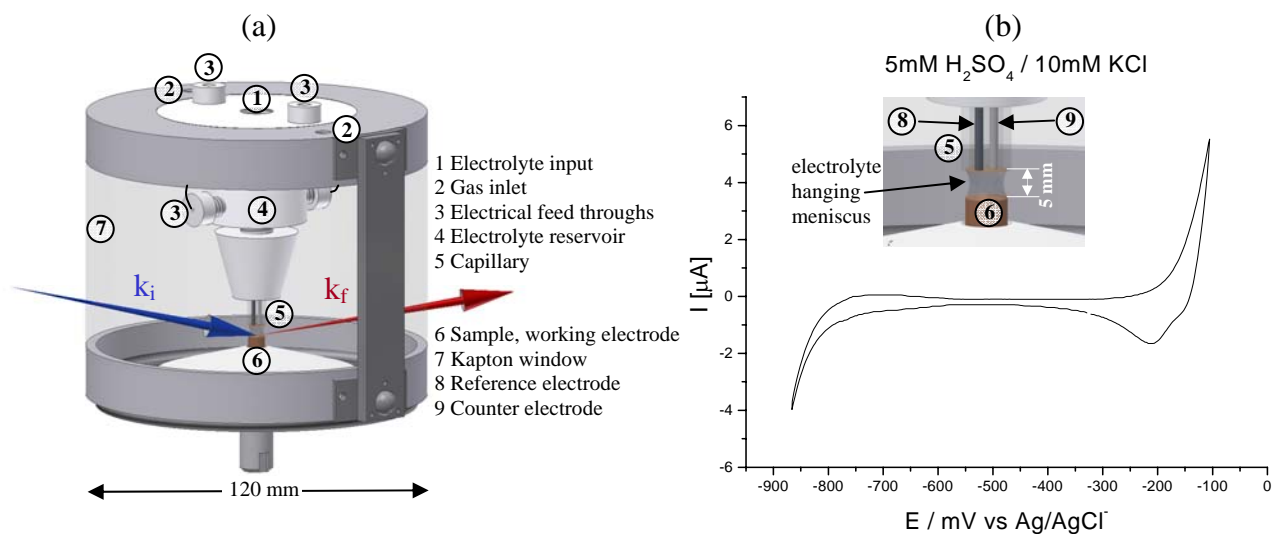


Figure: 1a): Sketch of electrochemical cell and b): Voltammogram of Cu in 5mM H₂SO₄ / 10mM KBr.

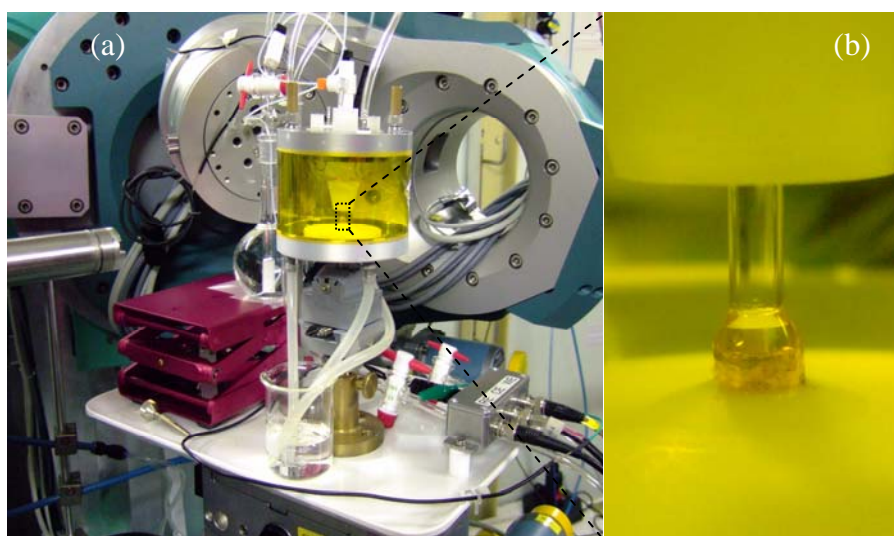


Figure: 2a): Picture of the cell on diffractometer at ID32 b): Picture of the capillary, droplet and Cu-sample.

Electrosorption and Surface Charging Effects of Halide Covered Cu Surfaces

The measured data is addressed in terms of a conventional crystallographic surface notation for the Cu(100) surface. The surface unit cell equals the bulk cell and forms a face centred square Cu lattice with a lattice constant of $a = 3.61 \text{ \AA}$ at room temperature. Previous STM studies under electrochemical conditions proposed a p-(1x1) ad-layer geometry for Cl⁻ and Br⁻ ions on Cu(100) which amounts to a coverage of 1 halide ion per Cu unit cell. Most references refer in this case to a c-(2x2) halide superlattice on Cu(100) taking only a primitive Cu surface unit cell into account. However, this does not accurately describe the surface geometry since subsequent Cu layers are not included in it. When doing surface sensitive diffraction experiments we always see the full 3D surface structure and cannot neglect this fact.

Open questions with reference to the ad-layer structures formed by Cl- and Br-ions and their impact on the substrate are:

- The ad-layer induced reconstruction of the substrate
- The potential dependence of ad-layer and substrate structure
- The interlayer spacings and
- The symmetry of the full 3D surface structure.

In order to address these topics we measured the (20L)-, (11L)-, (22L)-CTRs (crystal truncation rods) and additionally the (10L)-, (30L)-rods for Cl and Br covered Cu(100) surfaces as well as symmetry equivalent rods for all of the above. Data from Cl and Br covered Cu(100) was taken for potentials between -400mV and -800mV vs a Ag/AgCl and Ag/AgBr reference electrode, respectively. The intensity distribution along the latter 4 rods is purely sensitive to the relaxed surface structure since Cu does not scatter to these coordinates due to systematic extinctions of its lattice type. Higher order scattering from the monochromator did not interfere with our measurements.

Figure 3 a) and b) show a surface plots of the intensity distribution along the (20L)-CTR and (10L)-rod for a Br covered Cu(100) surface at -700mV (vs Ag/AgBr). This kind of plot displays a series of transverse scans taken along a rod in order to integrate its intensity. It gives an impression of the scattering background and the intensity distribution in Fourier space with our new cell. A comparison of the (10L)-rod intensity with model calculations based on a simple p-(1x1) structure for Br on Cu(100) indicates that the features of the measured intensities cannot simply be explained by this model. Small lateral relaxations that would slightly break the square symmetry of the surface must be taken into account in order to reproduce the experimental observation (\rightarrow "p-(1x1)"). Model calculations based on the formation of binary halide compounds on Cu(100) would again lead to a more complex modulation of the intensity distribution along the CTRs in comparison to that shown in Figure 3b). The presence of binary halide compounds is, therefore, unrealistic. The search for a suitable model is still ongoing.

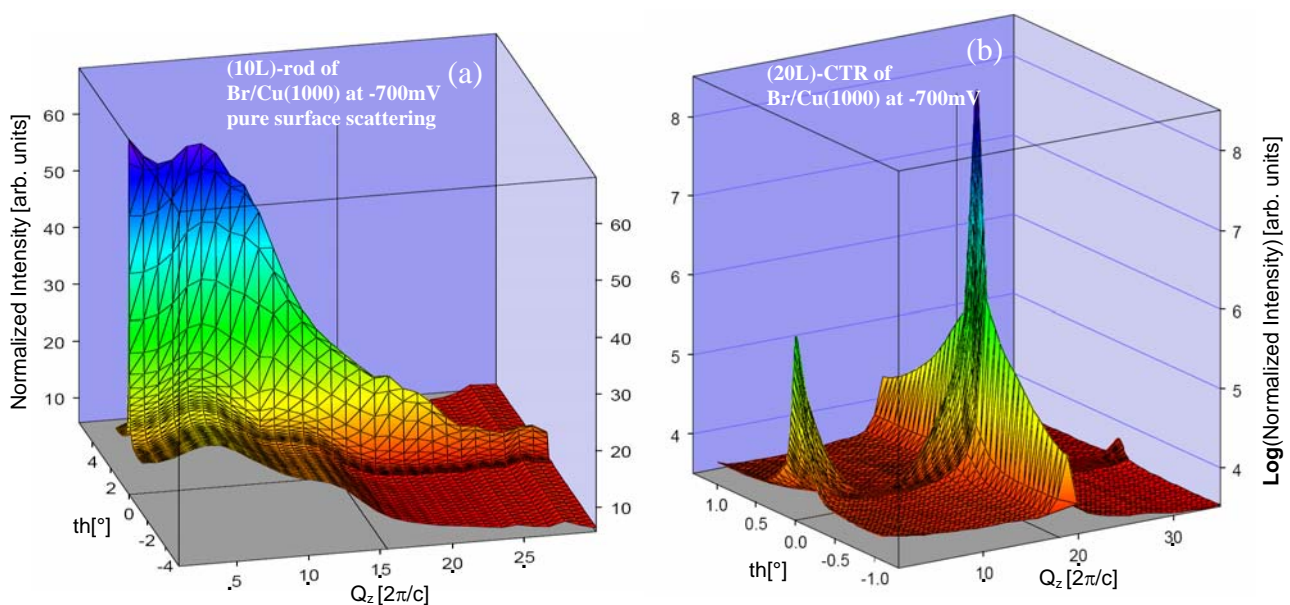


Figure 3: Surface plots of a) (10L)-rod and b) (20L)-CTR (intensity on log-scale) both for Br/Cu(100) at -700mV

One of the key questions in electrochemistry relate to the very delicate interplay between “pure” surface charging effects on one hand and related electroadsorption phenomena on the other hand. Without a clarification of the individual structural impact of these phenomena, the chances to obtain a full understanding of relaxation effects at the electrified solid/liquid interface remain slim. Figure 4 shows a surface plot for (10L)-rod intensities of Br/Cu(100) as function of their potential that was cycled between -500 and -800mV.

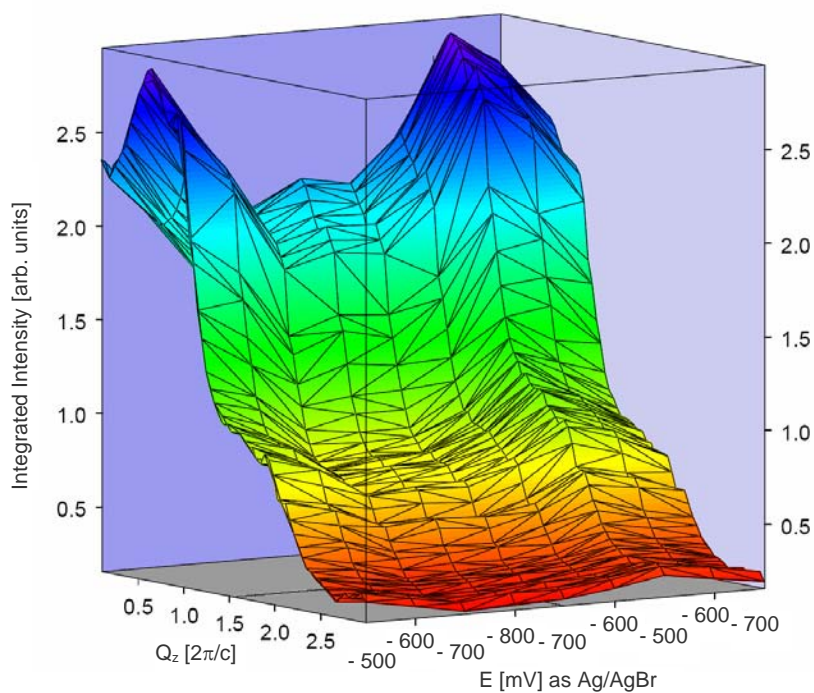


Figure 4: Intensity along (1,0,L)-rods of Br/Cu(100) for potentials that were cycled between -400 and -800mV.

Figure 5 shows more specifically the integrated intensity of surface sensitive inplane scattering at (1,0,0.1) from Cl and Br covered Cu(100) surfaces as function of their potential. The different changes of the intensities for the (1,0,0.1) reflection with decreasing potential reveal an unlike structural behaviour for the two halide species. Cycling of the potential within the known stability range of the “p-(1x1)” halide phases shows deviations of the intensity in the range of 10% at the upper borders of the potential window. The starting point of the potential cycles are marked by an arrow for Br and Cl covered Cu(100) respectively. While for Br the (1,0,0.1) intensity clearly decreases by 20% with a potential drop of 300 mV, the Cl covered Cu(100) surface exhibits a plateau between -500 and -600mV and shows only slightly lower intensities at both borders of the potential window. This means that Br reacts more strongly and in a different manner on potential changes which is intuitively expected because of its larger polarizability in comparison to the more electronegative Cl.

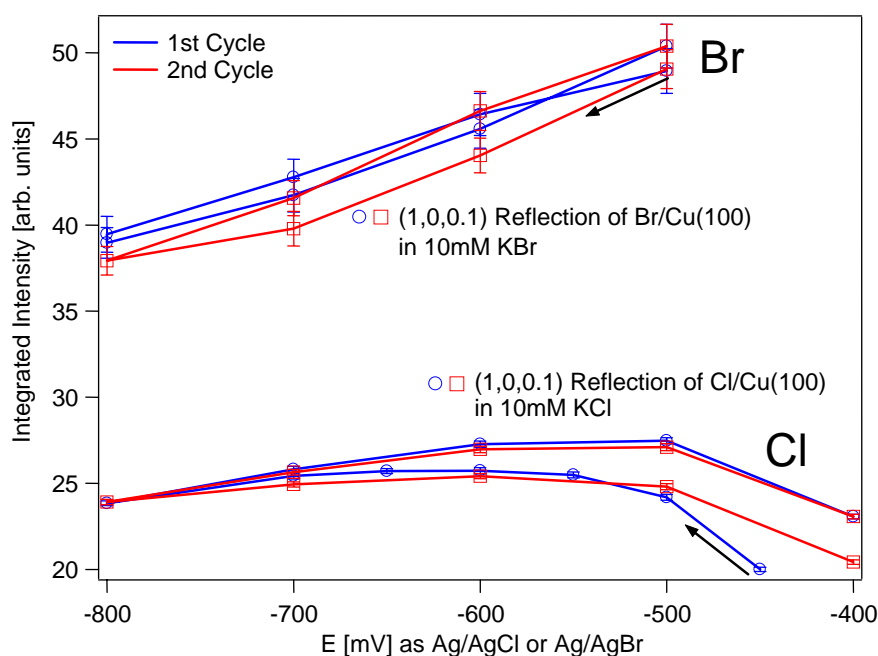


Figure 5: (1,0,0.1) intensity as a function of potential that was cycled between -400 and -800mV.

The fitting of the potential dependent (1,0,0.1) reflection profiles lead to a constant peak position and full width at half maximum that indicate an average domain size of 800Å. Out of plane reflections with $Q_z = 0.5, 0.97$ and 1.94 that were scanned together with the inplane data in Figure 5 showed also no obvious or systematic peak broadening. The potential induced change of intensity implies, therefore, that no disorder or roughening is induced. The change in structure factor could therefore be caused by a small displacive modification of the surface geometry, that is e.g. related to an electro-compression or -expansion of the surface and interfacial structure.

The electrosorption induced structural influence of different halide species on Cu surfaces becomes obvious in the variation of their intensity along the CTRs for equal electrode potentials as illustrated in Figure 6 a). It shows the (20L) CTR for Cl and Br covered Cu(100) at a potential of -500mV vs Ag/AgCl and Ag/AgBr respectively. The differences in structure of Cl and Br covered Cu(100) are expressed through their deviation of intensity between the Bragg points at $Q_z = 0, 2$ and 4. This deviation becomes also clear from a comparison of (10L)-rods intensities from Cl and Br-covered Cu(100) surfaces which represent only the surface structure and contain no bulk contribution. These discrepancies can not simply be explained by a difference in scattering power of Cu and Br since this would lead to similar shapes for the CTRs and more coinciding positions for the local rod minima of the (10L)-rod in Figure 6 b). Different geometric parameters have to be taken into account in order to fit a model to these data.

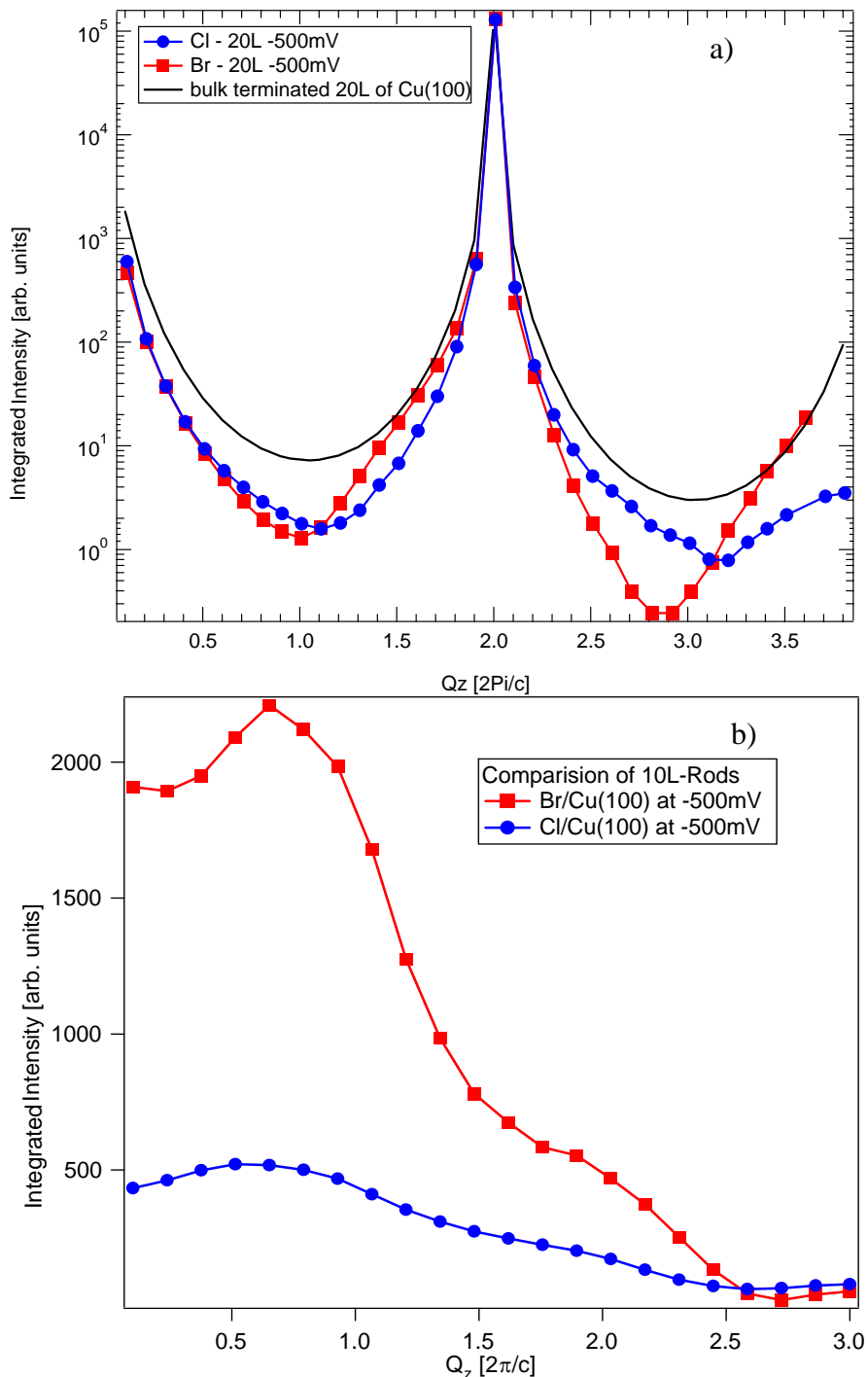


Figure 6: a): (20L)-CTRs and b): (10L)-rods for Cl and Br on Cu(100), both at -500mV vs Ag/AgCl and Ag/AgBr respectively.

Outlook

The above experiments deliver for the first time high quality surface sensitive diffraction data from a reactive surface like Cu. The results will generally allow a deeper insight into electrosorption and surface charging effects of halide covered metal surfaces and in particular help to describe the details of the charge induced structural changes of halide covered Cu(100).

Future experiments will aim towards an analysis of the formation and geometric structure of binary Cu-halide compounds and their direct influence on the Cu plating process.