

Reactive Surfaces under Electrochemical Control

Peter Broekmann³, Hubert Zajonz^{1,2}, Sascha Hümnn³

¹ Max-Planck-Institut für Metallforschung, Abteilung Dosch, Heisenbergstr. 3, D-70569 Stuttgart, Germany

² Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57/VI, 70550 Stuttgart, Germany

³ Institut für Physikalische and Theoretische Chemie, Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany

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1. Background and Motivation:

Copper as one of the *key materials* of the twenty-first century has attracted tremendous attention over the last two decades due to its nowadays realized application as a silicon chip interconnect material, here replacing the traditional vacuum deposited aluminum-based techniques. The mastering of copper-electrolyte interfaces with or without additional potential control can still be regarded as a particular challenge. It is the on-going trend of miniaturization towards the nanometer scale which requires a more sophisticated understanding of the relevant interface properties of those devices containing such reactive materials as copper. An atomic scale understanding of copper corrosion phenomena, corrosion inhibition by organics, oxidation and precursor films for oxidation, anodic dissolution and the formation of passivating films is thus of vital interest and has consequently been in the focus of numerous fundamental studies in the past.

Modern in-situ X-ray diffraction techniques have nowadays been well established as a powerful structure sensitive tool for the characterization of surfaces in an electrochemical environment. Most studies, however, focused on inert materials electrodes such as gold, silver or other noble metal surfaces such as Pt or Pd relevant for electrocatalysis. It has been demonstrated many times that these materials can easily be prepared by flame annealing resulting in clean and rather flat surfaces achieving similar quality standards as obtained after ion bombardment and subsequent annealing under UHV conditions.

By contrast to that, in-situ X-ray studies dealing with materials that are susceptible to oxidation are fairly rare. It appeared to be quite difficult to prepare clean and well ordered surfaces of those reactive materials since the conventional flame anneal techniques fails. Instead, electrochemical etching procedures have to be applied in order to remove the native oxide films from these surfaces. This, however, appears problematic for diffraction techniques due to the destructive character of the etching leaving substrates with a rather high defect

density within the first surface layers behind. While the quality of such prepared surfaces is sufficient for local observations with SPM techniques we need to significantly improve the surface quality for in-situ diffraction experiments characterizing the whole macroscopic sample on a microscopic scale. Therefore, we take advantage from so called “electrochemical annealing” after the initial electropolishing procedure. This treatment is based on the tremendous enhancement of the surface mobility by the presence of adsorbed anions which are excellent complexing agents such as chloride. By this we obtain surfaces revealing similar low defect densities as achieved by conventional flame annealing as demonstrated in the following section.

2. Results

X-ray diffraction analysis

We started to investigate electrosorbed monolayers of chloride (Cl) and iodide (I) on Cu(100) using surface sensitive x-ray diffraction techniques. The Cu sample was initially electropolished in 50% H₃PO₄ and subsequently treated in a 10 mM HCl solution. Under these conditions a single monolayer of chloride ions adsorbs at the Cu(100) surface even under “open circuit conditions” and prevents re-oxidation. The crystal was then mounted in an electrochemical cell that contains the 10 mM HCl electrolyte. Potential control of the sample was achieved through a potentiostat with Ag/AgCl serving as reference electrode.

Cl/Cu(100)-c(2x2) at -235mV to -400mV

The analysis of 2 symmetrically inequivalent copper crystal truncation rods (CTRs) confirms the formation of a c(2x2) reconstruction of the chloride ions on Cu(100) at -400mV. Further fit parameters of the c(2x2)-model include a surface roughness based on a statistical distribution of up and down steps [I.K. Robinson, PRB 33 (1986) 3830], ad- and surface layer occupancy and the first two interlayer spacings. Table 1a contains the fit results. The brackets behind the numbers indicate the error with respect to the last digit. The agreement between model and data (see Figure 1) expressed through a weighted residual is 5.5%. In contrast to a clean Cu(100) surface with a interlayer compression of the first two layers of 1.1% we find a 1.1% expansion due to Cl adsorption. This result is expected for two reasons:

At a potential of -400 mV vs. Ag/AgCl which is actually close to the on-set of the copper dissolution reaction the copper sample is positively polarized leading to a depletion of the electrons between the first Cu layers. The presence of electronegative chloride species on-top

is clearly pointing into the same direction. We find a Cl-Cu layer distance that is 3% larger than the c-lattice constant of Cu_{bulk} .

Electrochemical annealing

The occupancy of the $c(2 \times 2)$ -Cl layer on Cu(100) is 20% lower than expected. This might be attributed to a photon induced etching of the Cu(100) surface based on a radiation mediated Cl-radical and subsequent formation of mobile chloro-copper complexes. Consequently the equilibrium between chloride adsorption and chloro-complex formation may locally shift towards the latter where the synchrotron beam hits the sample. We propose an inverse step flow mechanism as transport phenomenon as previously observed by in-situ techniques.

Figure 2 shows the width of the surface sensitive Cu(2,0,0.3) reflection as a function of time of exposure to the synchrotron radiation. A 20% decrease of the width can be observed within 40 minutes. This process reflects an electrochemical annealing procedure of the surface leading to a 20% increase of the average domain size. The roughness of the surface is accordingly small with an σ_{RMS} of 3.0 Å.

Cl desorption at -825mV

At more negative potentials up to -825mV Cl^- desorbs from the Cu(100) surface. The analysis of the (2,0,L) CTR confirms the absence of Cl^- with a fitted occupancy of 0 ML for this species. However, along with hydrogen formation at the Cu surface the roughness increases by 26% to an σ_{RMS} of 3.8 Å in comparison to the electrochemically annealed surface at -400mV. The data and fit can be seen in Figure 3. The fit results in Table 1b show still a 0.9% expansion of the outmost layer spacing of Cu at those negative potentials.

I/Cu(100)- $c(2 \times 5)$ at -400mV

Iodide anions can be easily adsorbed on Cu(100) by replacement of the pre-existing chloride monolayer after adding trace amounts of iodide (1 mM KI) into the solution. In contrast to chloride, iodide forms several reconstructions on Cu(100) with different surface coverages depending on the substrate potential. Our x-ray diffraction data obtained at -400mV vs. Ag/AgI is shown in Figure 4. It delivers significant evidence for a $c(2 \times 5)$ -I reconstruction formed on Cu(100) under saturation conditions. Other competing models like a $p(2 \times 2)$, $c(2 \times 6)$ or $c(2 \times 8)$ observed in the STM experiments at lower potentials can be clearly ruled out since they do not fit the data. Besides interlayer spacings, a roughness and occupancy parameters the model includes the symmetrical lateral inward shift of iodine atoms by 1.5 Å that

improves the residual by 2.7% to 7.0%. Figure 5 shows an on top view of this model. The shift of two ions can be explained on the basis of steric effects for the distance to the next iodide would be otherwise smaller than in solid/molecular iodine. The shift relaxes the I-I distance but also moves iodide from 4-fold hollow to less coordinated pseudo bridge sites. Surprisingly, the interlayer spacing of the first 2 layers including the ad-layer is equal to ideal Cu bulk within the error range. The occupancy of iodide corresponds with 0.4 ML to that expected for the c(2x5) reconstruction observed by STM. The fitted value of the σ_{RMS} to 4.3 Å reflects the fact that I interacts strongly with Cu(100) surfaces in terms of a noticeable corrosive effect.

S/Cu(100)-c(2x2) at -850mV

Even more than the above adsorbents S has a pronounced corrosive effect on the Cu (100) surface. This is clearly expressed in the large σ_{RMS} of 17 Å deduced from the CTR data shown in Figure 6. The effect of roughness becomes noticeable in the data through a comparison of a model calculation of a clean smooth Cu(100) surface with its S covered roughened state in the experiment. The analysis of the data also includes a S coverage of 0.5 ML where S occupies the fourfold hollow sites of Cu forming a c(2x2) superstructure. The fitting of the first 2 interlayer spacings resulted in a 2% expansion of the S-Cu distance and a 3% compression of the following Cu-Cu layer separation. Both values show large errors due to weak scattering signal of this rough surface. All the above mentioned fitting results are summarized in Table 1d.

3. Discussion and future plans

Despite of the beauty and reliability of the results under the given realistic conditions the errors of our analysis are still relatively large. The primary reason for this is the choice of data that we measured. CTR data shows in the present case for different structural parameters like roughness, occupancy or atom displacements similar changes that provoke large dependencies between them during fitting and consequently large errors. The choice of data was limited to the experimental setup where the foil that seals the electrochemical cell creates a strong background throughout the reciprocal space. Avoiding this background would mean that not only CTRs could be measured with better accuracy but also in-plane data and superstructure rods that are individually more sensitive to the structural parameters of the model. To realize this idea we constructed an electrochemical cell that needs no foil to contain the electrolyte and prevents therefore the strong and structured scattering background. Instead of a foil we

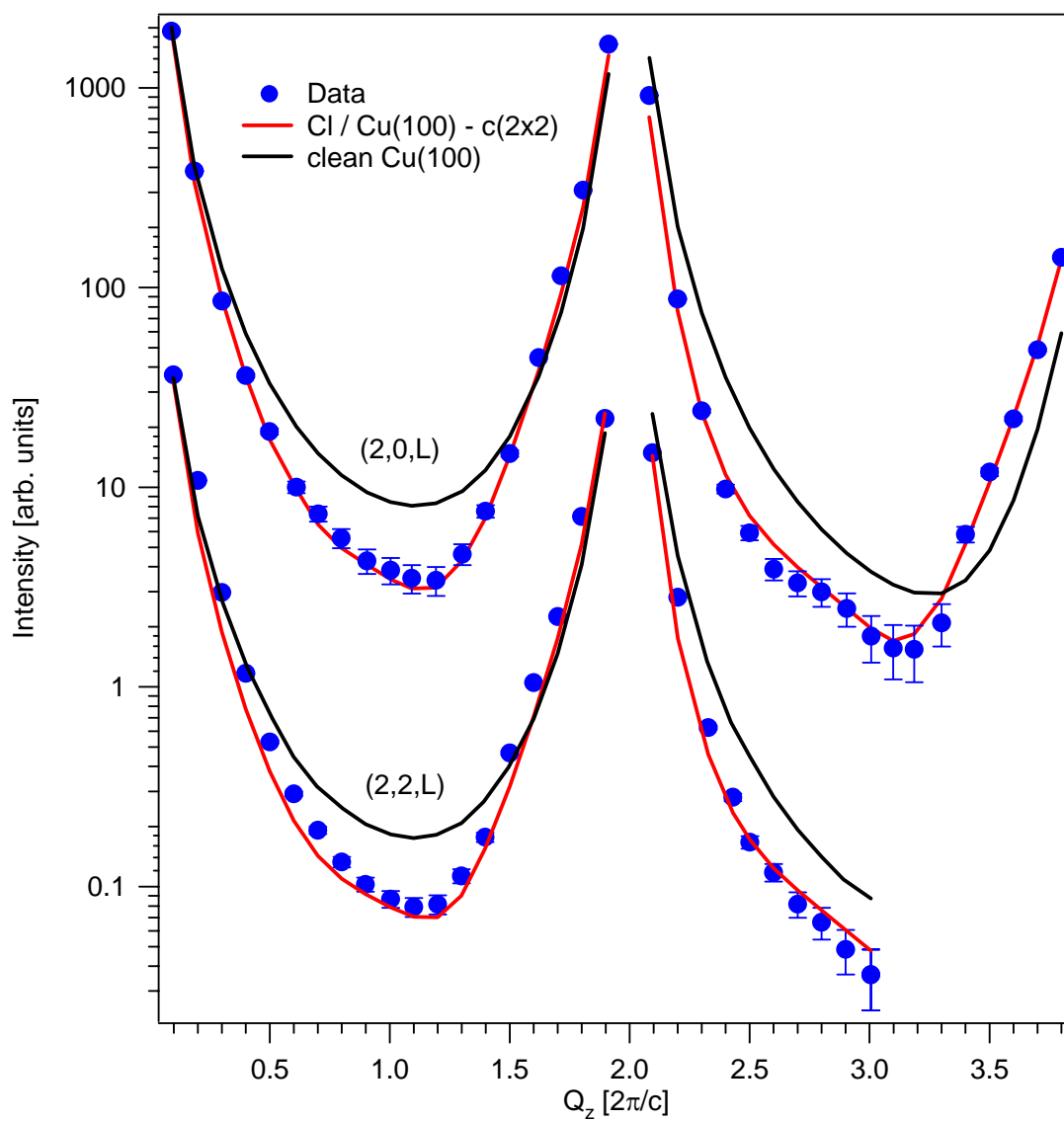
will use the surface tension of a hanging drop of an electrolyte to prevent its loss from the cell. Figure 7 illustrates this new setup.

Forthcoming X-ray experiments will focus on the formation of 2D-CuI phases at the onset of the copper dissolution reaction in the presence of the $c(2 \times 5)$ -I reconstruction phase. Previous STM results evidenced a clear potential separation between the surface confined 2D- and the subsequent 3D-CuI growth. Copper dissolution even proceeds in the presence of the 2D-CuI film via an inverse step flow mechanism until the entire surface is covered by an approximately 8 nm thick CuI_{bulk} film thus passivating the copper surface against further dissolution. One major goal will be the precise structural characterization of the 2D-CuI film which is expected to be closely related to the (111)-lattice of the crystalline CuI_{bulk} phase.

Fit results:

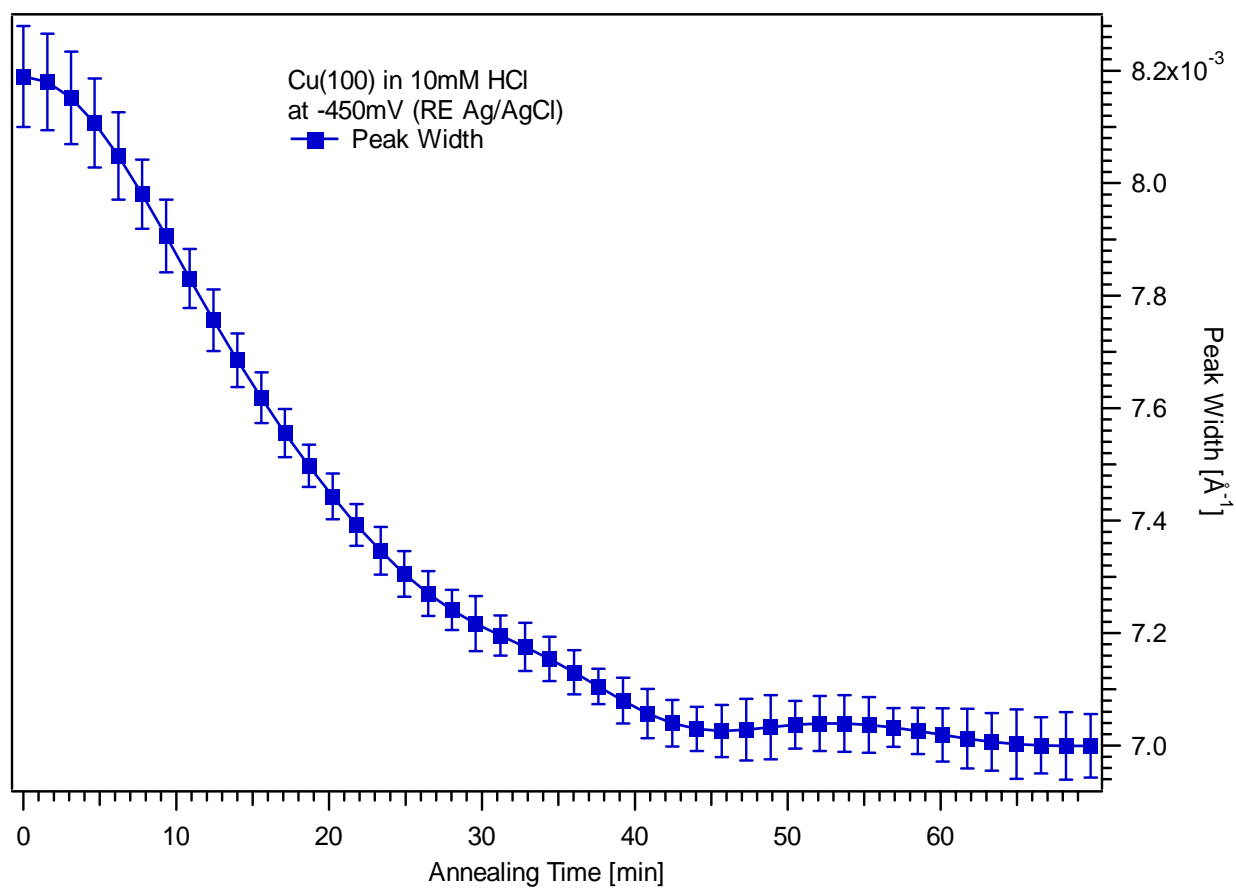
Table 1:	a			b			c			d		
RE Ag/AgCl	Cl/Cu(100) in 10 mM HCl U= -235mV/-400mV			Cl/Cu(100) in 10 mM HCl U= -825mV			I/Cu(100) in 1 mM KI U= -400mV			S/Cu(100) in 1 mM Na ₂ S U= -850mV		
	d _{ad-layer}	Cu-d ₁₂	Cu-d ₂₃	d _{ad-layer}	Cu-d ₁₂	Cu-d ₂₃	d _{ad-layer}	Cu-d ₁₂	Cu-d ₂₃	d _{ad-layer}	Cu-d ₁₂	Cu-d ₂₃
d-spacing [d/c]	0.53(1)	0.511(2)	0.5	-	0.509(5)	0.5	0.49(5)	0.5	0.5	0.52(1)	0.47(1)	0.5
lateral shift [Å]	-	-	-	-	-	-	1.5(4)	-	-	-	-	-
coverage [ML]	0.4(1)	1.0	1.0	0.0(1)	0.8(2)	1.0	0.40(5)	0.9(1)	1.0	0.5(1)	1.0	1.0
σ _{RMS} [Å]	3.0(1)			3.8(2)			4.3(2)			17(2)		
data	67			37			67			54		
R _w (Log ₁₀ (I))	5.5%			4.8%			7.0%			3.8%		

Figure 1



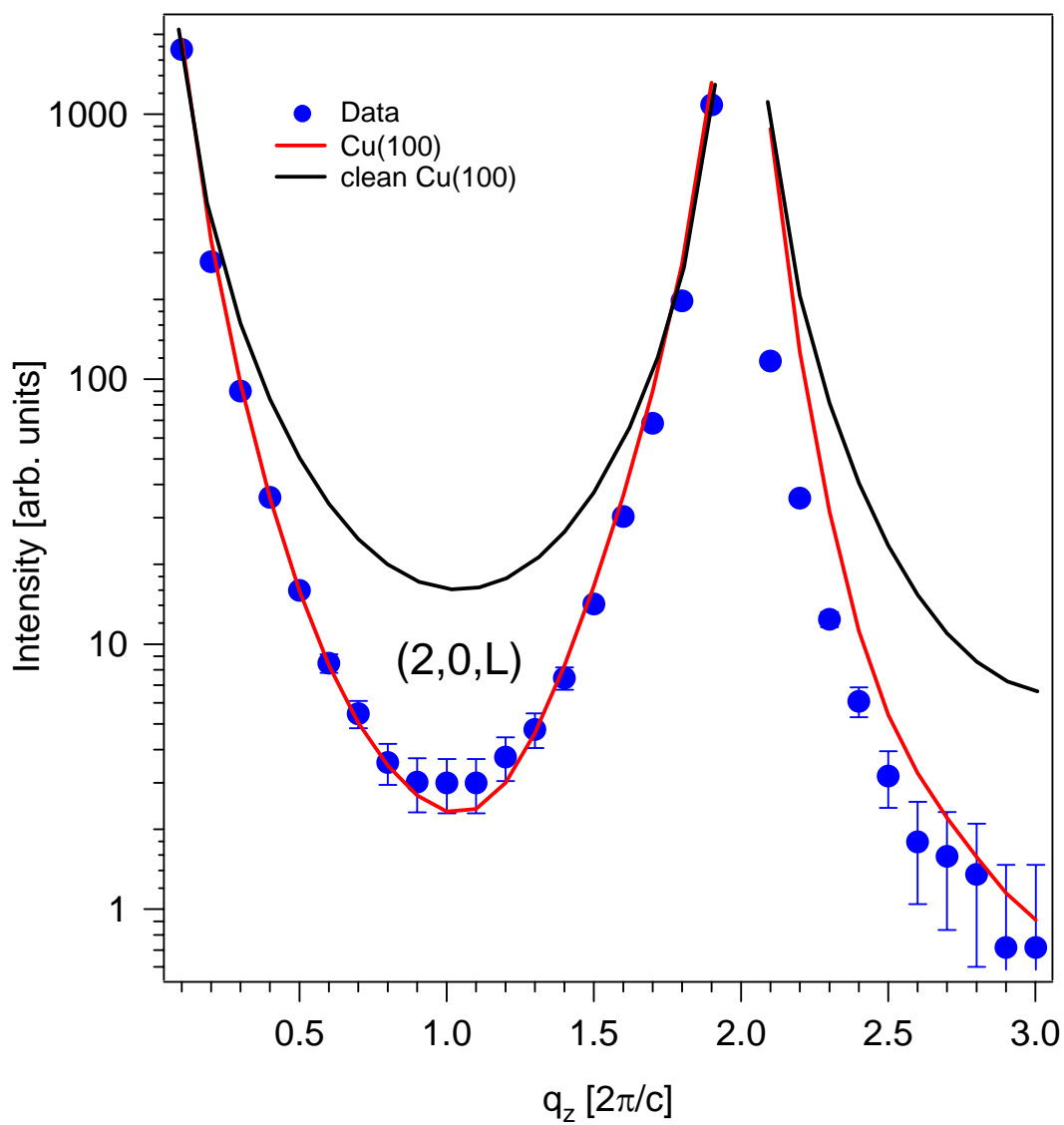
Cl/Cu(100)-c(2x2) at -235mV to -400mV

Figure 2



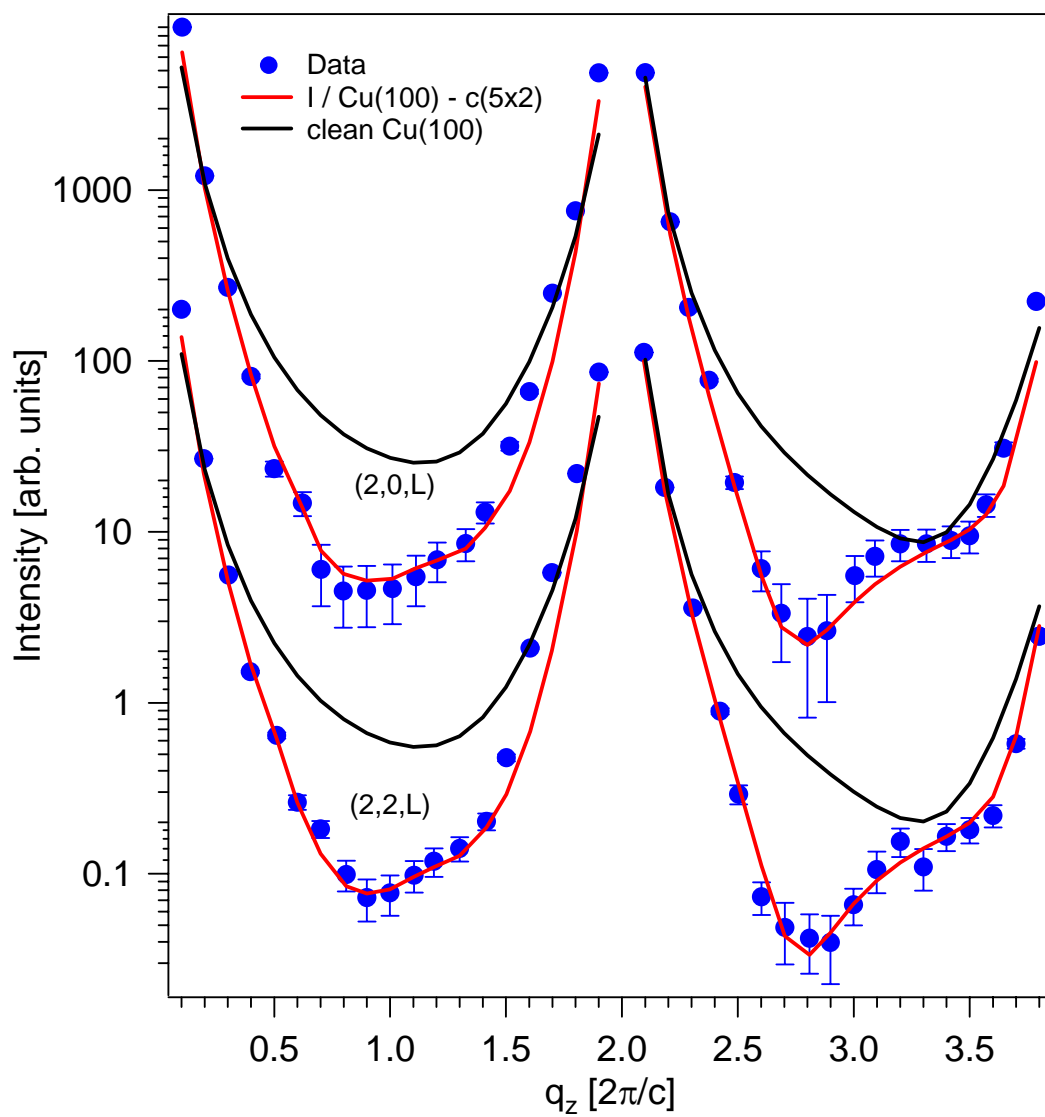
Electrochemical annealing:
Cl/Cu(100)-c(2x2) at -400mV

Figure 3



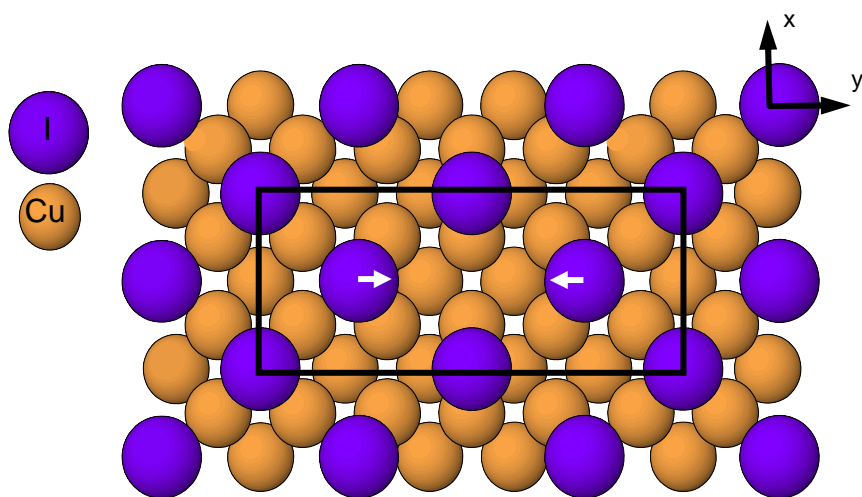
Cl desorption at -825mV

Figure 4



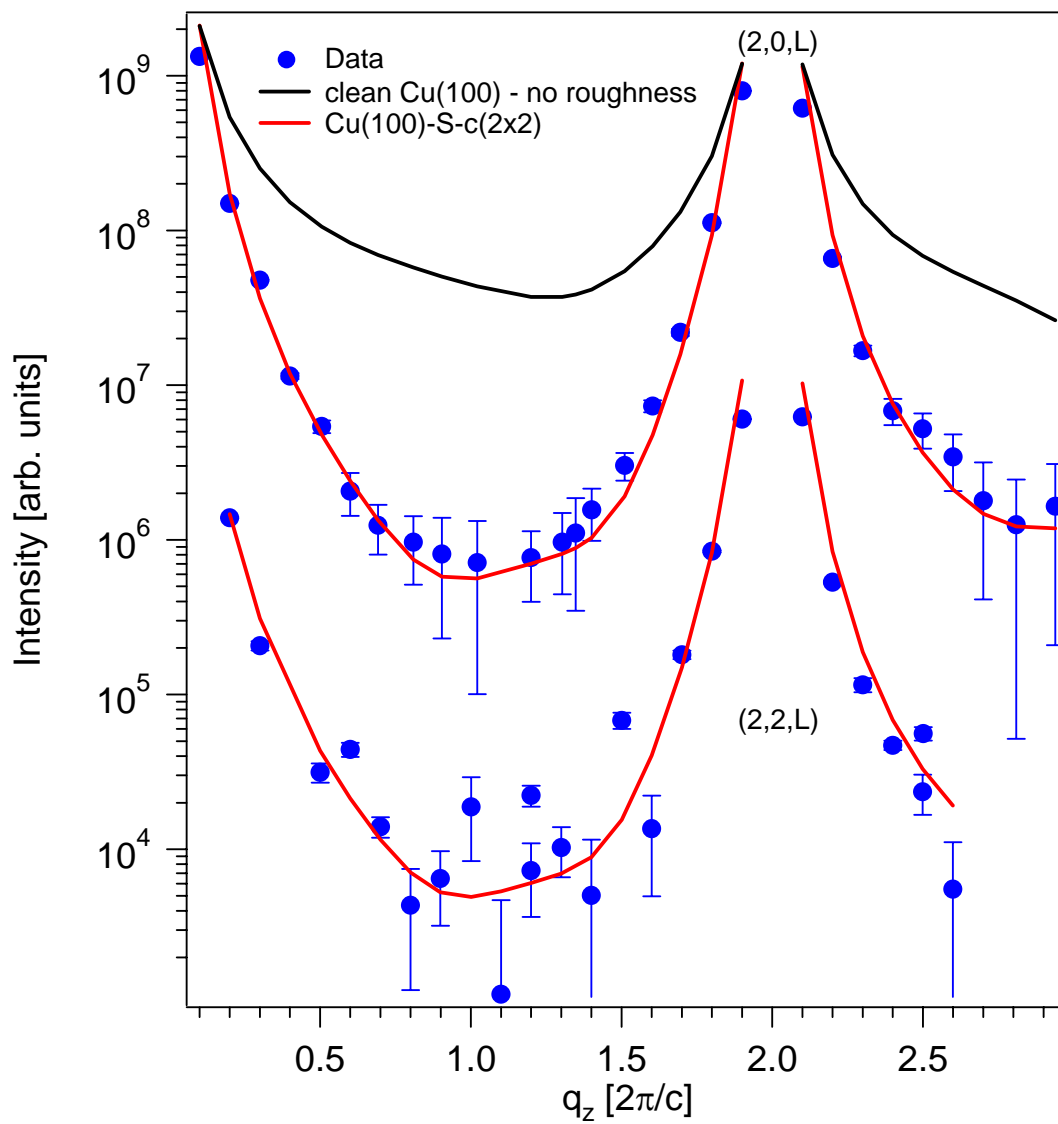
I/Cu(100)-c(2x5) at -400mV

Figure 5



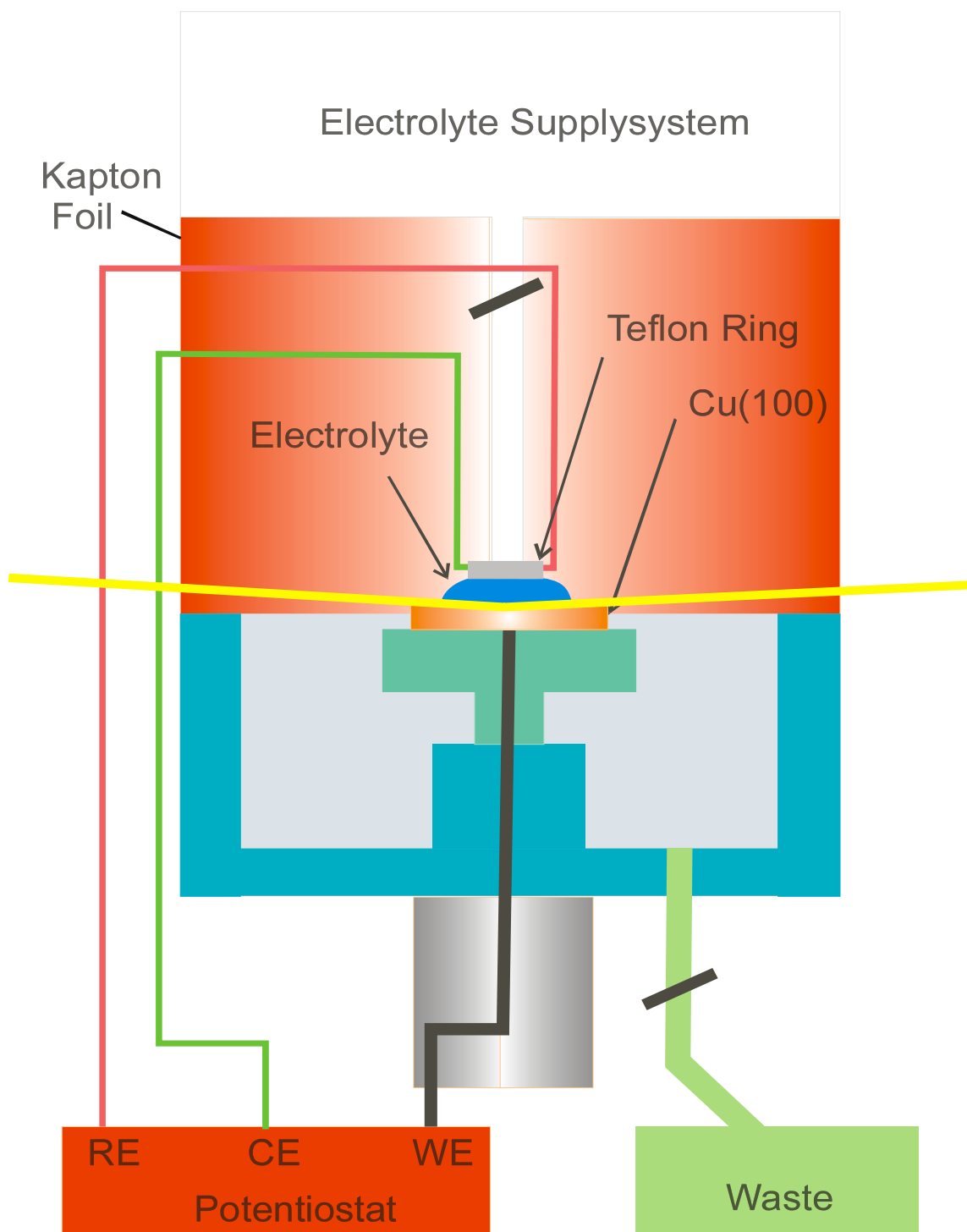
On top view of I-c(2x6) on Cu(100)

Figure 6



S/Cu(100)-c(2x2) at -850mV

Figure 7



Electrochemical cell without foil