Adsorbate Isotherm Analysis by Reflection Anisotropy Spectroscopy on Copper (110) in Hydrochloric Acid

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ABSTRACT: Reflectance anisotropy spectroscopy (RAS) is a powerful optical probe that works on a polarization contrast basis. It can be operated in any environment, ranging from ultrahigh vacuum to vapor phases and liquids. The measured optical anisotropies are caused by several symmetry breaking effects and are exclusively assigned to the surface for otherwise bulk isotropic materials. In this work, we present a systematic study comprising in situ RAS-transient to assess the surface thermodynamics of the chloride adsorption on Cu(110) upon systematic variations of the applied electrode potentials in comparison to cyclic voltammetry (CV). Numerical time-derivatives of the measured RAS-transients are shown to be exclusively associated with electrical currents of those electrochemical reactions, which change the properties of the electrode surface. The recorded transient line-shapes track the Frumkin type isotherm properties related to chloride coverage. Both connections are theoretically discussed. Owing to the surface and interface specificity, RAS is shown to exhibit a high surface sensitivity. In particular, processes taking place in parallel, namely, the hydrogen evolution reaction (HER) as well as the copper dissolution as Cu" and Cu"", do not contribute to the RAS response.

1. INTRODUCTION

When foreign ions or molecules adsorb on metals they cause changes in their surfaces. Such surface modifications are complex and deserve detailed studies in any environment. As a matter of fact, in ultrahigh vacuum (UHV), molecular chlorine (Cl2) adsorption on Cu(110) has been extensively studied with scanning tunneling microscopy (STM) and low energy electron diffraction (LEED).1,2 In liquid environments, atom species are prone to alter the liquid-metal interface in a different way; i.e., ions are adsorbed instead of neutral atoms and molecules. In electrochemical conditions, for instance, electron-based probes (like LEED) are clearly incompatible, and therefore noninvasive analytical techniques are much preferred. Photonic probes (PP) have been employed because they use light and are transparent to the liquid hosting the metal surface. However, as the heart of the reaction mechanism stems mainly from the surface region, PPs need to exploit an anisotropic surface in order to retrieve information solely from the surface, filtering out the isotropic, albeit dominant, bulk contribution.3 One of such linear optical probes is termed reflectance anisotropy spectroscopy (RAS), which measures the optical anisotropies through a contrast of two in-plane orthogonal crystallographic directions. This is advantageous when dealing with low index metal surfaces which are chemically more active to adsorption phenomena. In particular, the Cu(110) surfaces have been exploited under several conditions,4,5 including electrochemical (EC) reaction regimes.6−9

In this paper, we demonstrate the power of RAS as an analytical probe capable to measure the complex reaction of chlorine ions Cl" adsorption on low index metal surfaces. Special attention is paid to the possibility of quantifying certain surface structures and deriving respective thermodynamic potentials. In a previous work, we showed by EC-STM that the Cu(110) surface structures change in several steps due the anodic adsorption of chloride.7,9 Most prominent is the formation of a stripe/groove-structures in the [001] surface direction. The latter are about 2.6 nm wide and keep a minimum distance of the same order. A second major surface oxidation step results in a faceting of the surface. When using the appropriate photon energy, in operando kinetic RAS is able to detect electrosorption isotherms of the Frumkin type for this Cl" induced structuring.

The relationship between the polarization optical response as determined with RAS and the adsorbate induced surface structures, on one hand, and the currents measured (e.g., in cyclic voltammetry (CV)), on the other hand, needs to be clarified first. The rest of the paper is organized as follows. In the Theory section, we summarize first the conceptional approach and review approximations made therein. In the

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Results and Discussion section, we verify our theoretical model based on experimental data. With the previous findings, we discuss peculiarities of the Cu(110) surface. The experimental arrangements and measuring conditions are given in the Experimental Details section.

2. THEORY

2.1. RAS: a Measure of Surface Adsorbates. Chemical bonds, whether they are ionic, covalent, or even weaker of the van der Waals type, increase the concentration of species (ions) at an electrochemical interface. In the picture of the electrochemical double layer structure, such species are transferred either from the bulk electrolyte or from the outer to the inner Helmholtz layer to the surface during the adsorption process.\(^\text{10}\) The amount of adsorbed species is usually given in terms of the relative coverage

\[
\Theta = \frac{\Gamma_l}{\Gamma_{l,max}}
\]

which describes the fraction of the electrode surface coverage \(\Gamma_l\) with respect to the maximum value \(\Gamma_{l,max}\) of the respective adsorbate type at a certain absorption site.

RAS measures at normal incidence, as a function of photon energy, the difference in reflectivity between two orthogonal in-plane directions, \(r_x\) and \(r_y\)

\[
\Delta r = \frac{r_x - r_y}{r_x + r_y}
\]

The two reflectivities \(r_x\) and \(r_y\) are in general, i.e., in case of absorbing materials, complex entities leading to relative amplitude and phase changes. In our experiments, we measure both the real and imaginary parts of \(\Delta r/r\). For a planar interface between two isotropic media, \(r_x\) and \(r_y\) can be calculated with the Fresnel equations.\(^\text{11}\) Our angle of incidence is \(\phi \approx 0\). For an isotropic interface between the cubic copper and the electrolyte (water), we would obtain \(\Delta r/r \approx 0\). The Cu(110) surface, however, appears to be intrinsically anisotropic due to the reduced symmetry of the respective surface unit cell. Such a situation can be approximated by a so-called optical “3-phase model”. From now on, the interface is represented by the half infinite substrate (our cubic single crystal Cu(bulk)), by the half infinite ambient (electrolyte in our case), and in-between by an anisotropic interface layer of thickness \(d\). The substrate and ambient dielectric functions (DF) are \(\varepsilon_s\) and \(\varepsilon_\text{eff}\), respectively. The latter is a real number since the ambient is assumed to be transparent (\(\varepsilon_\text{eff} = n^2\)).

With the approximation \(d \ll \lambda\) \((d \lesssim 1\ \text{nm})\) one can show that\(^\text{12,13}\)

\[
\frac{\Delta r}{r} = -i \frac{4\pi \sqrt{\varepsilon_s}}{\lambda (\varepsilon_s - \varepsilon_\text{eff})} (\varepsilon_{\text{eff},x} - \varepsilon_{\text{eff},y})
\]

For solid–liquid interfaces, we derived the latter expression including the ambient DF \(\varepsilon_s\), which is set equal to one in the majority of cases. For our purpose of low concentration hydrochloric acids, we use the DF of pure water \((\varepsilon_s = 41.8), \approx 1.33\).\(^\text{14}\) For the substrate DF, we use the Cu-DF measured in situ in hydrochloric acids at electrochemical potentials where no surface adsorbates are detectable by ECSTM. The Cu Bulk-DF has been obtained with an optical layer model where surface charges are take into account in a separated layer contribution.\(^\text{5}\) The term \(\Delta(\varepsilon d) = d(\varepsilon_{\text{eff},x} - \varepsilon_{\text{eff},y})\) is regarded as the surface dielectric anisotropy (SDA).

Accordingly, \(\Delta r/r\) as measured by RAS, is proportional to the SDA. The complex proportionality factor that includes the bulk dielectric properties is a constant, as we will consider only changes in the anisotropic surface response at a single wavelength. Note that the amplitude of the optical anisotropies measured during the chemical reaction are larger than the respective experiments performed in air or vacuum for the substrates, because of the higher refractive indexes of the surrounding liquids.

The connection between the coverage \(\Theta\) of a certain adsorbate and the change in the SDA requires a critical analysis. Two major scenarios are conceivable. Surface adsorbates can change global surface properties as a function of the surface coverage \(\Theta\). For example, a change in the electron excess \(\Gamma_e\) on the metal side of the interface is likely. Such an assessment is generally accepted because the Mott criterion remains always satisfied, and the copper surface maintains its metallic properties.\(^\text{8}\) Indeed, spectroscopic ellipsometry experiments have shown this proportionality by means of the ellipsometric angle \(\Delta\) and the electron excess \(\Gamma_e\).

A second part concerns local changes of the surface due to the adsorbed (Cl\(^-\)) ions. The latter could generate, for example, new electronic resonances at adsorbate sites or in between them. Local morphology changes like surface stripes, grooves, and facets, which were reported for Cu(110),\(^\text{2,7}\) fall into the same category. In the long wavelength limit, where lateral structures are assumed to be much smaller than the wavelength, the measured SDA is an “average” between covered and uncovered surface areas. Without screening effects, the effective SDA becomes a linear combination between two different surface dielectric functions

\[
\Delta(\varepsilon d) = \Theta \Delta(\varepsilon d)_2 + (1 - \Theta) \Delta(\varepsilon d)_1
\]

where \(0 < \Theta < 1\) denotes the surface coverage. In the maximum screening situation, the two states add up reciprocally

\[
\frac{1}{\Delta(\varepsilon d)} = \Theta \frac{1}{\Delta(\varepsilon d)_2} + (1 - \Theta) \frac{1}{\Delta(\varepsilon d)_1}
\]

which are the so-called Wiener bounds\(^\text{15,16}\) and the actual value of the effective dielectric properties appears between these two extreme cases depending on the geometry of the structure. Nevertheless, the reciprocal averaging given by eq 5 is actually obtained only for a bulk structures consisting of 2D layers. For 1D structures on a surface, the effective dielectric relationship tends to be linear. Furthermore, one should note that eq 5 attains a linear dependency for the limit \(\Delta\varepsilon_{\text{eff}} \ll \varepsilon_{\text{eff}}\).

2.2. Adsorption Isotherm Kinetics in RAS-Transients.

A comprehensive discussion of the physics and chemistry of adsorption isotherms was presented, for example, by J.O’M. Bockris et al.\(^\text{17}\) For the interpretation of our in situ optical results, it is important to bear the following aspects in mind.

The adsorbed (Cl\(^-\)) ions may have a concentration \(c_2\) in the bulk of the solution. The variation of the coverage \(\Theta\), depending either on \(c_2\) or the applied electrode potential, is known as the adsorption isotherm. A typical surface has \(10^{14}\) to \(10^{15}\) cm\(^{-2}\) atoms in the uppermost layer, whereas the number of adsorption sites is typically less. The used electrochemical cell employed in the present work, on the other hand, has a volume of 1 cm\(^3\). By using a concentration of \(c_2 = 10\ \text{mM}\), the
number of ions in the solution is about $6 \times 10^{18}$ and is thus $(3-4)$ orders of magnitude higher than the number of possible adsorption sites. Therefore, we regard the concentration $c_i$ in the bulk of the electrolyte as a constant. The change in the Gibbs energy $G$ of the electrochemical adsorption/desorption of an ion in equilibrium is thus

$$0 = \Delta G = \Delta G_0 + eU + \Delta G_x(\Theta)$$

(6)

The first term ($\Delta G_0$) in eq 6 contains the constant formation energy of the adsorption of an isolated ion and also includes the constant activity of the respective ion in the solution, $kT \ln(c_i/c_s)$. The second term accounts for the applied working electrode potential $U$ versus the reference electrode. In a rigorous discussion, it depends on the vertical position of the ion in the outer Helmholtz layer before and in the inner Helmholtz layer after adsorption as well as on the water molecule configuration near the surface. The third term adds all contributions dependent on $\Theta$. For $T = 0$ K and for the adsorption of isolated ions, it would be constantly zero and the surface coverage depending on the applied potential would change as a step like function. However, at temperatures different from zero, at least an entropy related continuous potential change has to be considered because the number of possible surface coverage realizations has a maximum at $\Theta = 0.5$. The simplest possible model, in which adsorption occurs, is thus the so-called Langmuir isotherm

$$0 = \Delta G_0 + eU + \frac{kT}{n} \ln \left( \frac{\Theta}{1 - \Theta} \right)$$

(7)

where $n$ is the number of ions and $e$ is electron charge. RAS-transients should resemble the hereby defined dependency of $\Theta$ on the applied potential $U$ if we consider a linear relation between the SDA and $U$ (eq 4). A relatively simple extension of the Langmuir isotherm is the Frumkin isotherm where the interaction between ions is taken into account by an additional linear term in $\Theta$:

$$0 = \Delta G_0 + eU + \frac{kT}{n} \ln \left( \frac{\Theta}{1 - \Theta} \right) + w\Theta$$

(8)

Positive and negative values of $w$ consider repulsive and attractive interactions between the adsorbed species, respectively. Figure 1a shows a Langmuir isotherm (solid line) and two Frumkin isotherms (dashed and dotted lines) at room temperature ($n = 1$). (a) Coverage $\Theta$ and (b) derivative of $\Theta$, which is proportional to the current, both as a function of the changing potential.

UHV environment as well as with ab initio calculations for the water absorption in equilibrium with water in gas phase are considered. Accordingly, the water molecule concentration at the surface is about 0.5–0.7 times the number of the uppermost Cu atoms per unit area. The lattice constant of the Cu(110) surface unit cell is 0.363 $\times$ 0.256 nm. The ionic diameter of Cl$^-$ is 0.362 nm. As mentioned already, the true configuration is unknown for the solid liquid. Therefore, we use, in the following discussion, values of $m = 1$ and 0.6 as upper and lower boundaries.

J.O'M. Bockris et al. pointed out that Frumkin isotherms are probably not sufficient to represent the adsorption of ions. They describe two different interactions upon ion absorption. The first one is a lateral repulsive component due to coulomb interactions which for small coverages is proportional to $\Theta^{1/2}$. A second component is an attractive lateral dispersive interaction which is for small coverages proportional to $\Theta^3$. However, the underlying model suppose a homogeneous distribution of the adsorbed ions at the surface which is, as we will discuss later, questionable in case of the Cl$^-$ adsorption on Cu(110). Nevertheless, repulsive as well as attractive potentials are conceivable and deviations from the Frumkin-like isotherm are possible. The Langmuir isotherm, however, has a benchmark character. At room temperature, for instance, an electrochemical adsorption process will extend over 150 mV if...
we consider: (i) only one type of adsorption site, (ii) a nondissociative desorption/adsorption process, (iii) a vanishing overall lateral interaction \((w = 0)\), (iv) \(m = 0.6\), and (v) a quasi static change of the electrode potential. As depicted in Figure 1, an overall repulsive lateral interaction results in a broadening of the process, while attractive interactions compress it. A similar effect is obtained for different values of \(m\). Quantities bigger or smaller than one induce broadening or compression, respectively.

2.3. Relation to Electric Currents in CV. Several processes at the solid–liquid interface contribute to the measured currents over the applied electrode potential range in CV. For Cu(110) in hydrochloric acid, the electrochemical window is limited at negative cathodic potentials by the hydrogen evolution reaction (HER) and at positive anodic potentials by the copper dissolution as \(\text{Cu}^{2+}\). In between these potential ranges, a number of Faradaic and non Faradaic processes including the adsorption of \(\text{Cl}^-\) ions take place. The total electrical current is approximated by three principal contributions

\[
I(U(t)) = C \frac{dU}{dt} + n\Gamma_{\text{max}} \frac{\delta \Theta}{\delta U} \frac{dU}{dt} \theta_{\text{max}} + \frac{A}{R_{\text{CT}}} \left( f(U(t) - U_0) \right)_{\text{corr}}
\]

In eq 10, term (1) considers the charging of the interface due to the applied potential. The capacitance \(C\) is a constant only in the very simple Helmholtz double-layer model, which implies that any excess charge on the metallic face and the counter-charge in the solution reside planar at the interface; otherwise, it is a function of the charge density \(\sigma\) and thus dependent on the applied potential. In the latter case, the constant \(C\) has to be replaced by \(C + U(t)(\delta C/\delta U)\). In CV experiments, the potential sweep is linear in time and \(dU/dt\) is constant. The related change in the electron excess \(d\Gamma_e\) \(\propto C\), which could show up as a continuous background in RAS-transients, is small compared to the respective changes during the adsorption of ions.

Term (3) in eq 10 represents a Faradaic (charge transfer) current due to a redox reaction of diluted ions. This term considers, for example, the HER or the dissolution of the electrode at the edge of our potential window. The measured current depends on the applied potential \(U\), the surface area \(A\), and the charge transfer resistance \(R_{\text{CT}}\) (the exchange current density \(j_0 \propto 1/R_{\text{CT}}\)). In contrast to the heteroepitaxial adsorption and desorption of ions, the HER and the copper dissolution as \(\text{Cu}^{2+}\) remain in a nonequilibrium state within the experimental time frame. In the Butler–Volmer theory, the function \(f(U - U_0)\) is an exponential relation, where \(U_0 = \Delta G_0/e\) is the standard equilibrium potential of the respective reaction. In the limit of small currents, the electrode surface does not change upon such reactions and the optical response remains constant. The copper dissolution, in our particular case, appears in EC-STM as an step function and the general appearance of the surface does not change. At higher dissolution currents, however, roughening sets in and causes clear changes in the RAS response.

Contribution (2) in eq 10 takes into account the adsorption and desorption of an ion (\(\text{Cl}^-\)). The measured current and thus the change of the electronic excess \(\Gamma_e\) are proportional to the change of the surface coverage \(\Theta\). Note that the sum of all charges on both sides of the interface has to be zero. The countercharge to the electronic charge can be divided into the charge stored in the diffuse double layer and the charge stored in the adsorbate” (Schmickler and Santos). The charge stored in the adsorbate is obviously proportional to the number of adsorbate ions \(\Gamma_e = \Theta \Gamma_{\text{max}}\) (eq 1). We call the number of ions in the diffuse double layer \(\Gamma_{\text{free}}\). In term (2) of eq 10, \(\Gamma_{\text{free}}\) is kept constant because the relative small capacitive currents were already considered in term (1).

We can conclude that the surface optical anisotropy, measured by RAS, changes in proportion to the surface coverage, whereas the current measured in CV contains the time derivative of the surface coverage. The time (potential) derivative of the RAS-transients should therefore selectively resemble all such peaks measured in CV which relate to adsorption and desorption processes changing the surface anisotropy. The measured amplitude depends on the type of adsorption and the chosen photon energy (wavelength).

The potential evolution of the surface coverage and thus the RAS transient is finally determined by the respective isotherm (Figure 1b). The latter correlation is only correct for quasi static potential changes. Under such conditions, the current maximum appears in anodic and cathodic scan directions at the same potential without overpotentials. In the case of a vanishing lateral interaction \((w = 0)\), the standard equilibrium potential is \(U_0 = \Delta G_0/e\). In real experiments, however, currents can only be measured at finite scan speeds. In our particular case, it turned out that the Cu(110) surface is additionally irreversibly harmed at very low scan speeds (<0.5 mV/s) after a few cycles; therefore, we chose a scan speed of 1 mV/s for the experiments. The resulting overpotentials were determined by means of CV experiments with different sweep rates (not shown here). For 1 mV/s, we found activation overpotentials smaller than 2 mV.

3. EXPERIMENTAL DETAILS

In-situ cyclic voltammetry and RAS experiments were performed in a homemade electrochemical cell (ECC) made of polyetheretherketon with an opening at the top for the optical experiments. The Cu sample was attached from the bottom with an O-ring so that only the (110) surface was in contact to the electrolyte. The ECC is introduced into a gastight chamber filled with Ar to provide an inert atmosphere. The 10 mM solution of HCl is supplied to the cell after mounting it inside the chamber. CV measurements were performed in a three-electrode configuration using a potentiostat (Ivium Technologies B.V., CompactStat). A Pt and Ag/AgCl wire were used as counter and quasi reference electrode, respectively.

All the employed electrode potentials are calibrated against a classical Ag/AgCl reference electrode in 3 M NaCl. CV scans, measured before and after each experiment, indicate the successive protection of the electrolyte and the sample against (oxygen) contaminations. The Cu(110) single crystal is set as the working electrode with a rectangular area of \(\approx 0.72 \text{mm}^2\) exposed to the electrolyte. All the solutions introduced into the system were deaerated by bubbling with Ar for 2 h prior the experiment. The Cu(110) sample was supplied by MaTeck GmbH, with an orientation accuracy of better than 1°. The as-received samples were 99.9999% pure with a surface roughness of less than 30 nm. Native oxides were removed by
electropolishing in a 85% ortho-phosphoric acid for several minutes at an applied voltage of +0.5 V, until the surface appearance became mirror like.8,23 The residues of electropolishing process were removed by dipping the sample into an ultrasonic bath with deaerated ultrapure water (18.2 MΩm) under Ar ambient. Hydrochloric and phosphoric acids were supplied by Merck KGaA (Suprapur grade), and ultrapure water was used to prepare the electrolyte solutions.

The optical arrangement of the RAS system is a homemade instrument, according to the design by Aspnes et al.24 The core of the system comprises three optically active elements: a linear polarizer, a 50 kHz photoelastic modulator (PEM), and an analyzer. The sample was oriented in a way that x and y corresponded to [1 ̅ 0] and [001] crystallographic directions, respectively. The measured anisotropy is averaged over the area of the light spot, which was half of the sample area exposed to the electrolyte. The covering electrolyte is optically isotropic, and the back reflection from the air–water interface was removed by a small tilting of the ECC. All the measurements were performed at a room temperature of 22 °C.

4. RESULTS AND DISCUSSION

Figure 2 shows a sequence of CV’s with a common scan rate of 10 mV/s for Cu(110) in a HCl solution (10 mM). The potential window spans a range from −90 to −516 mV limited by the copper dissolution as Cu2+ in the anodic and hydrogen evolution reaction (HER) in the cathodic direction. The full range CV depicted by the solid blue line confirms the typical line shape of Cu(110)7,8 with two quasi redox coupled peaks. Two oxidation peaks in anodic direction are labeled A and B/C. In reference 7, we have discussed in detail, by means of EC-STM results, the correlation of these peaks with changes in the structures. With the assumed Cl− adsorption occurring at peak A, we observe the formation of stripes/grooves extending in the [001] surface direction (upper EC-STM inset in Figure 2). At more negative potentials from peak A, the surface appeared adsorbate-free and we resolved the 1 × 1 Cu(110) unit cell. At more positive potentials, the surface undergoes a complete faceting (lower EC-STM inset in Figure 2). Possibly, at the same time, [CuCl2]− dissolution as well as the formation of a CuCl aggregate film set in. It extends as a plateau-like current due to kinetic limitations in the mass transport through the aggregate film or the [CuCl2]− complex in the electrolyte.7,25

The two reduction peaks in cathodic direction are denoted with D and E/A, respectively. In this potential range, the surface returns in the pristine state with wide terraces showing EC-STM again the 1 × 1 Cu(110) unit cell. As will be discussed further, these peaks are more complex in a sense that they do not reverse as ordinary redox couples peak A, B, and C.

In this work, we have studied the surface properties by RAS and CV under quasi static potential changes (regarding the Cl− adsorption) with a scan rate of 1 mV/s. Kinetic effects due to diffusion and activation barriers are thereby almost omitted for all surface modifications. As pointed out before, even lower sweep rates could damage the sample but peak positions do not change further. In this regard, extended anodic dissolution would cause surface roughening, and at cathodic potentials, hydrogen may creep into the copper bulk inducing irreversible changes. For the single wavelength RAS-transients, we have chosen a photon energy of 2.3 eV (539 nm). It was selected from spectral resolved RAS measurements at fixed potentials7 where the real part of Δr/r at 2.3 eV turned out to be very sensitive to the Cl− adsorption.

Figure 3 shows a CV as a function of time/potential measured at 1 mV/s together with the parallel recorded real part of Δr/r. In the CV response shown in (Figure 3a), the HER appears now with higher relative currents and peaks B and C seem to be quenched or redistributed. As shown by EC-STM experiments, the peaks B/C depend very much on the kinetic properties of the contributing processes.7 The currents measured at potentials more anodic than peak A include a diffusion limited dissolution of [CuCl2]−.25 The solubility of this copper-cloride complex is low but still higher than that of the bare copper dissolution as Cu+ ion, and at even more positive potentials above about −150 mV, it vanished by the copper dissolution as Cu2+.

The currents measured in the first half of the subsequent cathodic scan (blue line) are interpreted as a superposition of the partial redeposition of copper (Cu2+) and the ongoing [CuCl2]− dissolution and therefore the overall current remains positive. In the second half, the diffusion limited redeposition of copper clearly overlaps with defacetting which was detected in connection with the two cathodic peaks D and E/A. Basically, the CV resembles all the features known from higher scan rates. Note that they are slightly shifted in potential due to the vanishing activation overpotentials.

The temporal RAS transient of the real part of Δr/r at 2.3 eV (Figure 3b) nicely resembles the stepwise change as expected for a Frumkin isotherm like adsorption/desorption (Theory section; Figure 1a). The RAS transient exhibits four sections in anodic as well as in cathodic directions. It is worth mentioning that the kinetic behavior of the RAS signal remains basically unaltered also for measurements with faster scan speeds.

The first section from −450 up to −400 mV in the anodic direction corresponds to the HER with relatively strong
The real part of the previous one by a shallower slope of the RAS-transient. The signal from \(-2.1\) to \(-0.5\) \(10^{3}\). In particular, we cannot recall any connection between the broad current maximum C and the remaining slope of the RAS transient. The \(\Delta r/r\) signal changes only due to modifications in the surface properties, for instance, as induced by the adsorption of Cl\(^-\) ions. The current at maximum point C, which shows up only in CV (Figure 2 and Figure 3a), is attributed to the diffusion hindered copper dissolution of [CuCl\(_2\)]\(^-\) while the surface properties do not change. The same argument applies for the copper dissolution as Cu\(^{2+}\) at the positive end of the investigated potential range. The RAS signal does not change, although the current exponentially increases. The very small positive slope in the real part of \(\Delta r/r\) above \(-300\) mV continues in the following cathodic scan direction. We attribute this slope to a marginal roughening or an accumulation of the CuCl aggregate film at the surface.

The local minimum in the current, after changing the potential sweep direction due to the partially redeposition of copper as Cu\(^2+\), does not change the RAS signal. Thereafter, follow the two sections where the RAS signal changes back to negative values stepwise. The two changes in RAS are labeled with D and E/A\(^t\). The process D and E/A\(^t\) are reversed quite similarly following the changes induced by B and A. The overall appearance resembles a Frumkin isotherm like behavior again. Slopes, amplitudes, and potential positions deviate from the line shapes of B and A. The most obvious difference, however, is that both coincide with respective negative peaks in the CV. The chemical pathway, which finally restores the smooth pristine Cu(110) surface, obviously differs significantly from the reaction steps in the anodic scan.

According to eq 10, the first derivative of the potential dependent RAS signal should equal the measured currents for all those reactions which change the electrode surface anisotropy. Figure 4 shows a respective comparison between the numerical derivative of the RAS transient vs potential

![Figure 3](https://dx.doi.org/10.1021/acs.jpcc.9b11326)

Figure 3. Comparison of the current (red and blue line in panel a) and the real part of \(\Delta r/r\) measured in a RAS transient at 2.3 eV (black squares in panel b) over a CV loop with 1 mV/s. The green line in panel b was smoothed with a Savitzky-Golay smoothing algorithm in order to highlight the potential dependency of the RAS transient. The black lines in panel b are adapted as a guide to the eye and represent the Flory–Huggins isotherm line shapes based on the fitting shown in Figure 4. The potentials are referenced vs Ag/AgCl in 3 M NaCl.

Faradaic current. The RAS signal at 2.3 eV is not at all affected by this process. It is not shown here, but this independence is observed also at all other accessible photon energies between 1.5 and 5 eV (825–248 nm). Deviations, which emerge at 3.5 eV in this potential range, are clearly independent from the Faradaic current of the HER and are not further discussed here. Note that the capacitive charging of the interface due to the potential variation (term 1 in eq 10) is also not detectable: neither at potentials below \(-400\) mV or at potentials higher than \(-300\) mV.

The second part in the anodic scan direction from \(-400\) up to \(-350\) mV is characterized by a rapid change of the RAS signal from \((-2.1\) to \(-0.5\) \(10^{3}\). This change of the optical anisotropy matches peak A in CV and appears at potentials where the adsorption of Cl\(^-\) induces the formation of stripe like structures at the surface. The respective oxidation process is completed in a remarkable narrow potential range of \(\approx 50\) mV. Considering the Frumkin isotherm-like line shape, this would indicate a negative \(\omega\) value.

The third part from \(-350\) up to \(-270\) mV differs from the previous one by a shallower slope of the RAS-transient. The real part of \(\Delta r/r\) changes here from \((-0.5\) to \(0.5\) \(10^{3}\). The potential range matches with the formation of the surface facets. But in CV, we can not recognize an oxidation peak at these potentials anymore. The faceting process recorded in RAS and the current maximum, which is now shifted to higher potentials, are thus denominated with two different labels B and C. At scan speeds of 10 mV/s, they merge together.

In the fourth part, from \(-270\) up to \(-150\) mV, the RAS response almost stabilizes at a value of \(0.7 \times 10^{-3}\). In particular, we cannot recall any connection between the broad current maximum C and the remaining slope of the RAS transient. The \(\Delta r/r\) signal changes only due to modifications in the surface properties, for instance, as induced by the adsorption of Cl\(^-\) ions. The current at maximum point C, which shows up only in CV (Figure 2 and Figure 3a), is attributed to the diffusion hindered copper dissolution of [CuCl\(_2\)]\(^-\) while the surface properties do not change. The same argument applies for the copper dissolution as Cu\(^{2+}\) at the positive end of the investigated potential range. The RAS signal does not change, although the current exponentially increases. The very small positive slope in the real part of \(\Delta r/r\) above \(-300\) mV continues in the following cathodic scan direction. We attribute this slope to a marginal roughening or an accumulation of the CuCl aggregate film at the surface.

The local minimum in the current, after changing the potential sweep direction due to the partially redeposition of copper as Cu\(^2+\), does not change the RAS signal. Thereafter, follow the two sections where the RAS signal changes back to negative values stepwise. The two changes in RAS are labeled with D and E/A\(^t\). The process D and E/A\(^t\) are reversed quite similarly following the changes induced by B and A. The overall appearance resembles a Frumkin isotherm like behavior again. Slopes, amplitudes, and potential positions deviate from the line shapes of B and A. The most obvious difference, however, is that both coincide with respective negative peaks in the CV. The chemical pathway, which finally restores the smooth pristine Cu(110) surface, obviously differs significantly from the reaction steps in the anodic scan.

According to eq 10, the first derivative of the potential dependent RAS signal should equal the measured currents for all those reactions which change the electrode surface anisotropy. Figure 4 shows a respective comparison between the numerical derivative of the RAS transient vs potential

![Figure 4](https://dx.doi.org/10.1021/acs.jpcc.9b11326)

Figure 4. Derivative vs potential of the real part of the RA transient measured at 2.3 eV (green line) and the CV-current (red and blue line) both measured parallel with a sweep rate of 1 mV/s. The black lines represent a numerical fit with Flory–Huggins isotherms. The potential is referenced vs Ag/AgCl in 3 M NaCl.
contributions are arbitrarily chosen in Figure 3. In this representation, the strong correlation between the RAS response and the currents of peak A and the two reduction peaks D and E/A becomes clear. Note that the process contributes with different proportionality factors; hence, the relative amplitudes cannot be correct. Nevertheless, the derivative of the RAS transient recalls precisely all sharp current peaks in CV. In case of the HER and the copper dissolution as ([CuCl₂] ± 25 (+15) / readsorption), the surface appears quasi static. These process superimpose only the currents measured in CV but the derivative of the RAS signal is constantly zero. The latter again underlines the fact that term (1) in eq 10 does not contribute to the changes in the RAS signal either.

In particular, it becomes clear in such a comparison that the anodic B/C current peak, which is measured in CV’s at higher sweep rates, has two components. The first part, denoted with B, corresponds to an adsorption induced faceting. The second part is related to the diffusion limited dissolution of, e.g., [CuCl₃]⁻.

The selective sensitivity of the RAS signal to surface modifications is used to analyze the underlying adsorption/desorption processes concerning their thermodynamic properties. Assuming Frumkin (Flory–Huggins) type isotherms, we apply a parametric fit of eq 9 to the derivative of the RAS transient. Therefore, we numerically solved eq 9 for Θ and calculated the derivative according to the potential. By fitting the derivatives, it will not be necessary to consider absolute anisotropies and the individual processes separately. Each of the four peaks is fitted with a single Flory–Huggins isotherm and adapted with an individual proportionality factors. The amplitude values have right now no physical significance and will not be discussed further. For all processes, we assumed n = 1 and m = 0.6 (m = 1). The obtained w and ΔG₀ values are summarized in Table 1. The fit result with the four different

| Peak | w in meV | ΔG₀ in meV |
|------|----------|------------|
| A    | −40 (−50)| −354       |
| B    | +25 (+15)| −349       |
| D    | −35 (−45)| −379       |
| E/A  | −38 (−48)| −428       |

The error of all values is estimated with ±5 mV. The potentials are referenced vs. Ag/AgCl in 3 M NaCl.

Like structures in the [001] surface direction. To form these structures, attractive forces along the rows are conceivable, regardless of their type.

The second surface oxidation step, peak B, appears much wider and overlaps strongly with process A. According to the EC-STM experiments, the faceting finishes right after peak A. Afterward, the surface structure, as imaged by EC-STM, is left without changes. The isotropic dissolution may result in the movement of the facets but the integrative appearance probed by optics remains constant. A closer inspection of the EC-STM images near peak A, however, shows already the parallel evolution of surface stripes and facets. In the upper inset in Figure 2, one can already observe first facets while the stripe structures in the middle of the EC-STM image are not yet fully formed. A separation of both processes in quasi static experiments is thus only at reduced temperatures possible. The adsorbate which induce the faceting at process B is clearly of repulsive type (wₐ = +25 meV). Obviously, the lateral Coulomb repulsion is getting stronger as more negative ions are collecting at the surface. Together with attractive forces to the Cu substrate, the faceting becomes comprehensible.

The absence of a respective peak B in the CV could have several reasons. The facets could require a relatively small number of ions or a redistribution in terms of a phase transition. Furthermore conceivable is also an exchange of the adsorbed Cl⁻ ions by an oxygenated species as described in reference 26.

The fit results for the peaks D and E/A’ underline again the mentioned differences compared to those of peak A and B. Neither the formation potentials nor the values for the lateral interaction w coincide as expected for redox pairs. Additional insights are obtained from Figure 2, which shows a sequence of cyclic voltammograms (10 mV/s) with different anodic turning points. From these sequential scans, it becomes evident that oxidation peak A and reduction peak E/A’ form at least a “quasi” redox pair. These two peaks depend on each other, and the w value matches within the approximated error limits. But the potential of the maximum current depends on the time in which the copper electrode was in the “[CuCl₃]⁻” dissolution range before.

Peak D emerges always at the same potential alongside to the defaceting, but its amplitude is maximized just after the scan evolves to the constant current region. In another experiment, which is not shown here, both the potential positions and shapes of the current peaks D and E/A’ are the same, whether a 10 mV/s sweep up to −80 mV is made or if the potential is kept constant at −250 mV for the respective time. D and E/A’ current peaks on one hand and the defaceting and the disappearance of the surface stripes/grooves on the other hand both belong to the same processes if we keep in mind the perfect match of the current and the derivative of the RAS transient. Furthermore, the RAS signal reverses with the respective changes. But the chemical process behind it seems to be different and involves the reduction of the before dissolved [CuCl₃]⁻ or the CuCl aggregate film or other species.

5. CONCLUSIONS

In this work, single-wavelength RAS transients were used to investigate the electrochemical adsorption/desorption process on Cu(110) surfaces in hydrochloric acid. It was found that the adsorption/desorption of Cl⁻ ions and the subsequent surface modifications resemble the thermodynamics of Frumkin-type
isotherms (Flory–Huggins isotherm statistics). Accordingly, the respective currents, as retrieved with CV measurements, and the first derivatives of the RAS-transients to the potential coincide; a fact that was affirmed theoretically as well as experimentally.

Specifically, we detected two anodic and two cathodic adsorption/desorption processes. According to previously reported EC-STM experiments, these four processes correlate to (i) the formation of stripes/grooves along [001] direction of Cu(110) and (ii) a faceting of the surface. For the formation of the stripe phase, a numerical analysis based on the Flory–Huggins isotherm statistics reveals an overall attractive lateral interaction between Cl\(^-\) adsorbate species. On the basis of the measured electrochemical current, the surface coverage is less than a monolayer at these potentials and the adsorption/desorption process extends over a range of 50 mV.

With increasing potentials and coverages, we deduce an overall repulsive interaction between the adsorbates parallel to the faceting. These, however, overlap strongly and the faceting is barely visible with CV measurements. Additionally, both surface oxidation steps overlap with a Cu([CuCl\(_2\)])\(_{\text{L}}\) dissolution, which is superimposed in CV but visible with RAS experiments. In cathodic scans, the pristine and well ordered surface recovers in two distinct steps: on one hand, we found a correlation between current peaks measured in CV and the derivative of the RAS-transients, which prove that the electrochemical reactions induce surface modifications. On the other hand, both reactions depended very much on the time for which the Cu surface was kept at potentials with an ongoing [CuCl\(_2\)]\(_{\text{L}}\) dissolution.

Furthermore, we deduced different formation potentials and lateral interaction values in the anodic and cathodic transients, although the scan speed of 1 mV/s is regarded as quasi static. We conclude that the reaction paths of both, the cathodic defaceting and removal of the stripe structure due to Cl\(^-\) desorption, differ significantly from the anodic reactions and contain the redeposition of [CuCl\(_2\)], CuCl aggregates, or other species.

Finally, as the changes in the surface optical anisotropies are strongly correlated with changes in current, it is attractive to have noninvasive probes, such as RAS, that elucidate atomic details in real-time in order to shed light onto subsequent evolution steps in the electrochemical process. In this sense, the CV-RAS combination, as presented in this work, is of great potential to other systems such as the decomposition of CO\(_2\) on copper surfaces.

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