The structure of the underpotential deposition of copper on to Pt(111) in the presence of chloride anions: a LEED structure analysis

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Abstract
The underpotential deposition (UPD) of copper on to Pt(111) in the presence of chloride anions was studied by full-dynamical LEED-intensity analyses. A deformed (4 × 4) LEED pattern was observed at an emersion potential of 0.36 V vs. Ag/AgCl, right in between the two characteristic and well-separated peaks of the cyclic voltammogram (CV). Corresponding LEED intensity measurements and simulations of the integral-order beams indicate that the UPD of Cu forms a single pseudomorphic Cu layer on Pt(111). © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction
The underpotential deposition (UPD) of Cu on Pt(111) in electrolytes has been studied extensively during the past two decades [1–17], rendering this system as a prototypical system in surface electrochemistry. It was found that the addition of small amounts of Cl\(^-\) anions changes the UPD of Cu drastically in that two well-separated voltammetric peaks are discernible in either cathodic or anodic direction (cf. Fig. 1a).

The interpretation of these peaks, however, is still controversial. Based on XPS measurements, Kolb et al. [8] assigned peaks I and II (cf. Fig. 1a) to Cu deposition and Cl desorption, respectively. By contrast, Ross and coworkers [9,13,14] performed in-situ X-ray scattering (SXS) and rotating ring disk electrode (RRDE) experiments from which both peaks were related to Cu deposition. Consequently, different real space models emerged for the Cu UPD adlayer on the Pt(111) substrate in the potential range between peak I and II: Kolb et al. [8] suggested that Cu UPD forms a pseudomorphic layer (1 ML Cu), whereas Ross et al. proposed a 0.59 ML Cu film on the substrate with a Cu–Cu distance of 3.63 Å [13].

This controversy, along with the prospect of performing the first LEED structure analysis of an electrochemically prepared surface, motivated us to analyze the structure of copper UPD on Pt(111) in the presence of Cl anions. Our analysis provides strong evidence that the Cu UPD layer (emerging the sample at potentials between peaks I and II) is pseudomorphically grown on Pt(111).

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The Pt(111) sample was cleaned in the main UHV chamber by cycles of Ar+ bombardment at about 800 K and/or oxidation in 3 × 10^-7 mbar oxygen at about 900 K followed by a final annealing at about 1100 K. After the cleaning procedure, no contaminants were detected by AES, and a sharp (1 × 1) pattern appeared in LEED/RHEED.

The electrolytes were prepared with supra-pure H2SO4, CuSO4·5H2O and HCl (Merck), and triply distilled water. All the potentials were referred to Ag/AgCl/KCl (sat.). Fig. 1a shows a typical cyclic voltammogram (CV) of Pt(111) in 0.05 M H2SO4/1 mM CuSO4/0.1 mM HCl, which is in excellent agreement with those reported in the literature [5,8,9,13,14]. Similar to the results derived from XPS measurements [8], we found with AES that the Cu coverage on Pt(111) did not change noticeably for potentials ≤ 0.38 V. Since there is general consensus in the literature that the Cu coverage is 1 ML for potentials smaller than 0.25 V, this suggests that also in between peaks I and II, the Cu coverage is close to 1 ML.

For the LEED investigations, the electrode was emersed at various potentials on the negative scan and transferred to the main UHV chamber. LEED I–V measurements were carried out at room temperature and confined to integral-order beams. Between 0.42 V and 0.50 V (point c in Fig. 1a), a \((\sqrt{3} \times \sqrt{3})R30^\circ\) LEED pattern showed up. At a potential of 0.38 V (peak I) to 0.2 V vs. Ag/AgCl in the cathodic direction, LEED showed a \((2 \times 4)\) pattern, whereas a \((2 \times \sqrt{7})\) or a slightly distorted structure was observed at 0.2 V. A representative LEED pattern at point b in the CV, which was also reported by Kolb et al. [8] and Ross et al. [9,13,14], is shown in Fig. 1b. To allow direct comparison with the results of Ross and coworkers, we took LEED intensity data under this experimental condition (point b in Fig. 1a). In addition, we collected LEED I–V data for two other potentials (points a and c in Fig. 1a). At points a and c in the CV, the Cu coverage is generally accepted to be 1 ML and 0 ML, respectively. The experimental LEED I–V curves of the (1, 1) and (1, 0) beams taken under the three pressure <1.5 × 10^-9 mbar). The experimental details can be found elsewhere [18].

2. Results and discussion

The experiments were performed in a UHV system consisting of a main chamber (base pressure <2 × 10^-9 mbar), housing LEED, RHEED, and AES, and an electrochemical chamber (base pressure <1.5 × 10^-9 mbar). The experimental details can be found elsewhere [18].
experimental conditions mentioned above are compiled in Fig. 2 and compared to corresponding LEED data of the clean Pt(111) surface. In total, we measured four integral-order beams: (1, 1), (1, 0), (2, 1), and (2, 2).

The LEED data were analyzed by a full-dynamical LEED program developed by Moritz [19], which is furnished with a least-squares optimization scheme [20–22] in order to allow for the simultaneous refinement of structural (as well as non-structural) parameters. The goodness of fit of calculated to experimental data was evaluated by Pendry’s reliability factor \( R_P \) [23], which was also the functional to be minimized.

As expected, the LEED \( I-V \) data taken at points a of the CV are clearly in favor of a pseudomorphically grown Cu layer on Pt(111), and those of point c are in favor of a clean Pt(111) surface. The latter conclusion can also be drawn by mere inspection of the experimental LEED \( I-V \) curves in Fig. 2. LEED \( I-V \) data of point c in the CV and of the clean Pt(111) data are similar, and therefore, the corresponding atomic geometries are similar. At point a, the Cu–Pt interlayer distance was determined to be 2.10 ± 0.04 Å, which is in agreement with that found by Ross and coworkers (2.2 ± 0.1 Å) [13].

More interesting is the atomic geometry of the Cu layer at point b of the CV (Fig. 1a), which is the subject of current controversy. Since the experimental LEED \( I-V \) data taken at points b and a are very much alike (cf. Fig. 2), a simple fingerprinting argument [24] shows that both surfaces consist essentially of the same pseudomorphic Cu layer. A complete LEED analysis confirms this notion and indicates, in addition, that the Cu coverage is at least 90% of a monolayer. Below this Cu coverage, the theory–experiment agreement deteriorates significantly. Since we confined the LEED analysis to integral-order beams, we probe mainly the \((1 \times 1)\)-averaged surface geometry. The LEED analysis turned out to be very sensitive to the adsorption site of Cu (cf. Table 1), preferring the fcc site over the hcp site. This finding already precludes the presence of a higher-order coincidence lattice with different adsorption sites of Cu as proposed in Ref. [13]. As previously discussed for the incommensurate growth of Mg on Ru(0001), the strong preference for a particular adsorption site is not compatible with incommen-

![Fig. 2. LEED \( I-V \) curves of the electrode surface at various emersion potentials: (a) 0.20 V, (b) 0.36 V and (c) 0.50. The uppermost LEED \( I-V \) curves correspond to the clean Pt(111) surface. The Pendry-R-factors between the LEED \( I-V \) curves (a)/(b), (a)/(c), (b)/(c), and (c)/clean are 0.15, 0.84, 0.63 and 0.35, respectively.](image-url)
surate and higher-order coincidence phases [25]. Moreover, we know that the Cl coverages at point a and b in the CV are different (as determined by AES and XPS [8] measurements). Therefore, the observed similarity in the (integral-order) LEED I–V curves at points a and b in the CV indicates that the contribution from the Cl overlayer to the $(1 \times 1)$ diffraction is negligible. This is consistent with the presence of higher-order coincidence phases of Cl on top of the pseudomorphic Cu film, i.e. there is no preference for a particular adsorption site of Cl; more details can be found in Ref. [25].

We also tested the proposed structure model from Ref. [13] to fit the LEED intensity data for point b in the CV. The optimum R-factor, however, is significantly worse than that for the pseudomorphic Cu layer (cf. Table 1). Therefore, this model can be clearly ruled out. In addition, it should be pointed out that a Cu–Cu distance of 2.59 ± 0.03 Å, as reported by Yee and Abruna [10], is also not consistent with the formation of a pseudomorphic Cu overlayer, i.e. the Cu–Cu distance being 2.78 Å.

3. Conclusion

LEED intensity analyses were used to determine the structure of underpotential deposited Cu adlay- ers on Pt(111). There is clear evidence that UPD of Cu forms a pseudomorphic layer on the Pt(111) electrode emerged between the two characteristic peaks in the cyclic voltammogram of Pt(111) in 0.05 M H$_2$SO$_4$/1 mM CuSO$_4$/0.1 mM HCl.

### References