

## X-ray standing-wave fluorescence analysis of electrodeposited Tl on clean and oxygen-reconstructed Cu(111)

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Tl submonolayers were deposited from an aqueous electrolyte on a Cu(111) surface. The emersed electrodes were studied with standing x-ray wave fields to determine the position of the Tl atom relative to the bulk diffraction planes. The results reveal that well-ordered Tl planes are stable outside the electrolyte. In addition, trace amounts of oxygen present in the electrolyte cause a 0.4-Å inward shift of the Tl adsorbate which is attributed to an oxygen-induced reconstruction of the Cu surface.

It is well known<sup>1</sup> that the dynamical reflection of an x-ray plane wave by a perfect single crystal leads to the formation of an interference field within a shallow layer on either side of the surface. This standing-wave field has for each reflection the same spatial periodicity as the corresponding diffraction planes which are described by the reciprocal-lattice vector  $\mathbf{H}$ . The antinodal planes of the electrical field intensity lie parallel to the diffraction planes. They move with increasing reflection angle in the  $-\mathbf{H}$  direction from being out of phase with the  $\mathbf{H}$ -Fourier component of the elastically scattering electron density to being in phase with the diffraction planes.

As was first demonstrated by Cowan, Golovchenko, and Robbins,<sup>2</sup> the controlled movement of this standing-wave field can be used to determine the position of submonolayer coverages of foreign atoms on a surface if their characteristic fluorescence radiation is detected simultaneously with the shift of the antinodal planes. The application of synchrotron radiation<sup>3-5</sup> has decreased the measuring time and the detection limit and has increased the position resolution. This method can therefore be used to study a large variety of surface-adsorbate systems. It is important to note that the spectrum of applications is not restricted to the surface in vacuum, but solid-solid<sup>4,6-8</sup> and solid-liquid<sup>2</sup> interfaces can be analyzed as well.

The data evaluation is based on the dynamical theory of x-ray diffraction by a perfect crystal lattice. Thus, as long as the theory is not modified to include lattice strains, high-quality single crystals are needed as substrates. Previously, Si,<sup>2,3</sup> Ge,<sup>5</sup> III-V crystals<sup>9</sup> as well as gadolinium gallium garnet (GGG)<sup>10</sup> single crystals and layered structures<sup>11</sup> were used successfully for measurements with standing x-ray wave fields. The present study, which uses for the first time a Cu substrate, demonstrates that metal crystals of sufficiently high quality can be prepared and handled as well.

Since surfaces of metals are of major importance in electrochemical and catalytic processes, it is especially exciting to determine with standing x-ray wave fields (SXW) the structure of such "realistic" interfaces and overcome the limitations of ultrahigh vacuum methods. We have therefore applied SXW to characterize electrodeposited Tl adsorbates on Cu(111) electrodes under normal atmospheric conditions. Many studies with different surface sensitive

methods have been carried out to investigate the nature of electrochemical reactions which take place at the electrode surface when the electrode potential is changed. The present knowledge of this interface process has been reviewed in several articles,<sup>12-14</sup> and the lack of any detailed structural information about the geometrical atomic arrangement is quite obvious.

Despite the complicated nature of the solid-electrolyte interface, the very special feature of it is that its properties can be controlled reproducibly via the electrode potential.<sup>12,15</sup> In the potential range positive of the reversible Nernst potential for the respective bulk metal deposition, underpotential deposition (UPD) of metal ions on an electrode surface can occur in submonolayer quantities.<sup>13</sup> Adsorbed atoms are desorbed as ions again from the surface simply by reversing the potential scan and the process can be repeated in a cyclic manner (cyclic voltammetry).

The electrode may even be removed from the electrolyte at a fixed potential without significant loss of the deposit.<sup>16-18</sup> However, it cannot be ruled out that such removal disturbs or even destroys the adsorbate structure due to the sudden loss of potential control or to the drastic change in environment as the liquid phase is replaced by the gaseous atmosphere. The Czochralsky-grown copper single crystals which were used in our present study were cut and polished electrolytically. The surface plane was oriented parallel to the (111) diffraction planes. The crystalline perfection was checked by high-resolution double crystal topography and samples with  $< 2000$  dislocations per  $\text{cm}^2$  were chosen as substrates.<sup>18,19</sup>

The UPD was performed in an electrochemical cell (insert of Fig. 1) with a Pt counterelectrode (C), a saturated calomel (SCE), reference electrode (R), and with the Cu electrode (X) dipping into the 0.5M Na<sub>2</sub>SO<sub>4</sub> and 10<sup>-3</sup>M TiNO<sub>3</sub> electrolyte. The potential was controlled by a potentiostat (Pot.) and the voltage-to-current diagram was recorded with an X-Y recorder (Rec.). Voltage-to-current diagrams which are characteristic for two different sets of preparations are shown in Fig. 1. Curve (a) was recorded with nitrogen flowing through the electrolyte to reduce the oxygen partial pressure. In this case the N<sub>2</sub> left the electrochemical cell through a small open hole in the cover. Curve (b) was recorded when the gas outlet was closed such that

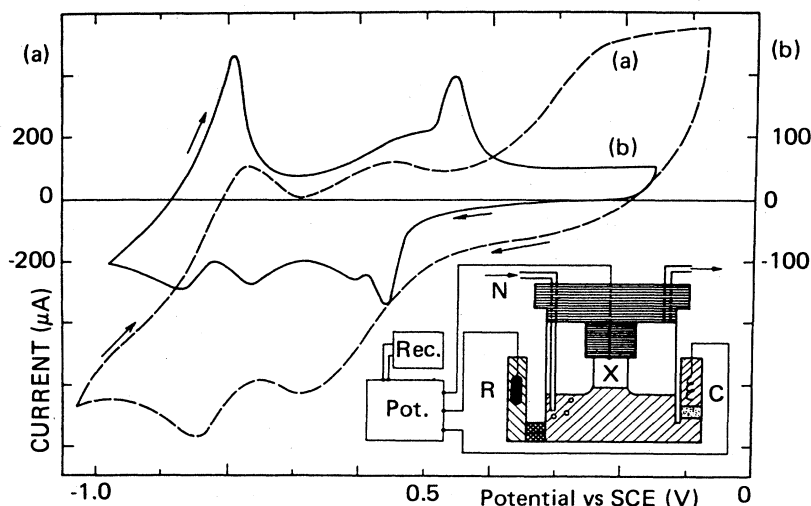


FIG. 1. Voltage-to-current diagrams recorded with an electrolyte containing a trace amount of oxygen (a) and without oxygen contamination (b). The inset shows the electrochemical setup (see text). Immersed Cu surface areas: (a) 1.13 cm<sup>2</sup>, (b) 0.8 cm<sup>2</sup>. Potential sweep rate: (a) 200 mV s<sup>-1</sup>, (b) 100 mV s<sup>-1</sup>. Arrows indicate sweep direction.

N<sub>2</sub> was flowing at the outlet through a vapor lock to prevent any oxygen from diffusing back into the atmosphere inside the electrochemical cell. The influence of spurious amounts of oxygen is clearly visible in these voltage-to-current diagrams.<sup>20</sup>

Before the electrode was removed from the electrolyte, the scan was stopped during a cathodic scan in a range  $-0.7 \text{ V} < U_{\text{SCE}} < -0.6 \text{ V}$  to allow for metal deposition. The electrolyte was carefully peeled off the surface and the samples were stored afterwards under normal atmosphere conditions. It is important to note that voltage-to-current diagrams from oxidized Cu crystals which are immersed in an oxygen-free solution slowly change their shape from (a) to (b), while a comparatively fast change occurs in the opposite direction [(b) to (a)] when the electrolyte is slightly enriched with oxygen.

The synchrotron x-ray standing-wave measurements were done at the ROEMO station of the Hamburg Synchrotron Radiation Laboratory HASYLAB. The experimental arrangement is shown schematically in Fig. 2. Synchrotron radiation emitted from the storage ring DORIS was monochromatized by a double crystal arrangement<sup>4,21</sup> which consisted of a symmetric Ge(220) (X1) and an asymmetric Si(220) (X2) crystal. This combination of crystals allowed the proper photon energy (15.3 keV) to be set and the monochromator angular emittance to be reduced to about one tenth of the Cu(111) reflection curve. The ion chambers

were used to keep the monochromator aligned (I1), and to monitor (I2) the flux incident on the sample (XS). Collimators were used to reduce the radiation background (S1, S2) and to choose a proper sample area (S3). The NaI(Tl) detector measured the Cu reflectivity as a function of reflection angle  $\theta$  and an energy-dispersive Si(Li) detector recorded simultaneously the scattered photons at up to 32 different angular settings of the sample (see Fig. 3). A 0.4-mm-thick Al absorber (A) was placed in front of the Si(Li) to avoid overloading the detector system with the strong Cu *K* substrate fluorescence. The collimator S3 limited the beam to 6 mm horizontally and 1 mm vertically such that a 30-mm<sup>2</sup> sample area was illuminated. Measuring times ranged from 0.5 to 2 h with a mean photon flux of 10<sup>9</sup> photons cm<sup>-2</sup>s<sup>-1</sup>. The whole standing-wave instrument is described in detail elsewhere.<sup>4,21,22</sup>

The peak areas of the Tl *L* $\alpha$  and *L* $\beta$  lines were summed up to determine the angular-dependent fluorescence yield  $A_{\text{Tl}}(\theta)$  (Fig. 3). These data were subsequently given a least-squares fit to the expression:<sup>7,19</sup>

$$A_{\text{Tl}}(\theta) = A_0^{\text{Tl}} \{1 + R(\theta) + 2\sqrt{R(\theta)} f_c^{\text{Tl}} \cos[\nu(\theta) - 2\pi\Phi_c^{\text{Tl}}]\} \quad (1)$$

The phase  $\nu(\theta)$  of the reflected beam relative to the incident beam and the reflectivity  $R(\theta)$  were calculated from dynamical theory.<sup>1</sup> A  $\chi^2$  fit of the measured data to the

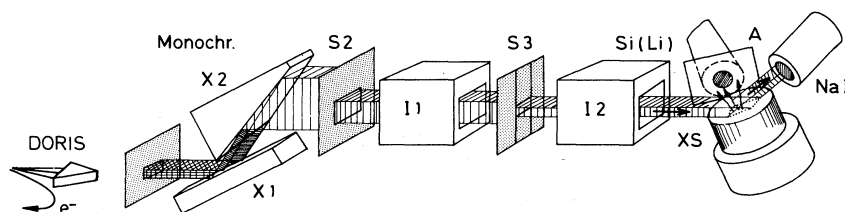


FIG. 2. Schematic experimental arrangement for standing-wave measurements (see text).

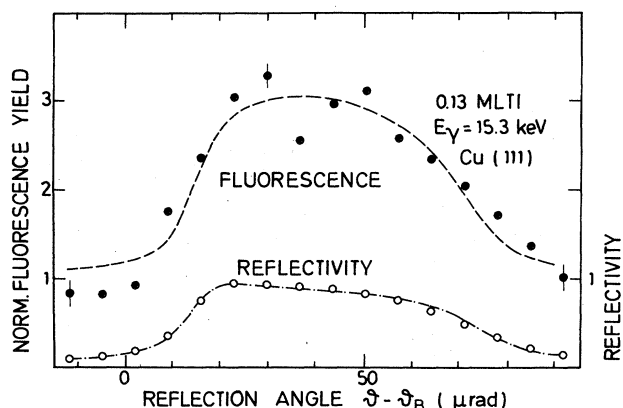


FIG. 3. Angular dependence of the Cu(111) reflectivity and the normalized Tl *L* fluorescence yield  $Y_{\text{Tl}}(\theta) = A_{\text{Tl}}(\theta)/A_0^{\text{Tl}}$  [see Eq. (1)]. O, ●: experimental data; - - - - -: result of least-squares fit.

theoretical  $R(\theta)$  curve determined the angular scale. Three parameters are accordingly determined from Eq. (1). These are the fluorescence counts  $A_0^{\text{Tl}}$  at zero reflectivity of the Cu(111) reflection, the coherent fraction  $f_c^{\text{Tl}}$ , and the coherent position  $\Phi_c^{\text{Tl}}$ .

Since  $A_0^{\text{Tl}}$  is proportional to the Tl coverage  $\Theta_{\text{Tl}}$ , the comparison of  $A_0^{\text{Tl}}$  and  $A_0^{\text{Cu}}$ , which is the corresponding factor of a  $\chi^2$  fit to the substrate Cu *K* fluorescence yield, was used to determine  $\Theta_{\text{Tl}}$ .<sup>19</sup> The coherent fraction  $f_c$  is directly related to the amount of atoms which register coherently with the (111) diffraction planes. If the Tl atoms are adsorbed in only one binding geometry,  $f_c^{\text{Tl}} = D_H^{\text{Tl}}$ , which is the Tl surface Debye-Waller factor, and as such determined by the mean-square vibrational amplitude of the Tl atoms.<sup>23</sup>  $f_c$  is smaller than this value if more than one position is occupied coherently, or if part of the overlayer is distributed randomly in the direction of *H*.

The coherent position  $\Phi_c^{\text{Tl}}$  can be expressed as a distance in units of the Cu lattice plane spacing  $d_{111}$  by  $\bar{z}_{\text{Tl}} = (n + \Phi_c^{\text{Tl}})d_{111}$ , where  $n$  is an integer  $\geq 0$ .  $\bar{z}_{\text{Tl}}$  gives the mean position of the Tl atoms in the *H* direction if one position is occupied with a Gaussian distribution profile or if the adsorbate resides on two places with identical occupation numbers.

The results of the standing-wave analysis are compiled in Table I for coverages below 0.3 ML (monolayers).<sup>24</sup> After preparation a3 had been measured, the surface was rinsed with water and measured again. The drastic increase of  $f_c^{\text{Tl}}$  accompanied by a marked reduction of  $\Theta_{\text{Tl}}$  (see Table I) without significant change in position  $\bar{z}_{\text{Tl}}$  indicates that almost exclusively randomly distributed Tl was removed from the surface, leaving a well-ordered Tl phase on the Cu(111) surface. This is further supported by the fact that  $\bar{z}_{\text{Tl}}$  remains independent of the  $f_c^{\text{Tl}}$  values reached in either preparation condition (a) or (b).

The average of  $\bar{z}_{\text{Tl}}$  for the oxygen-contaminated electrolyte is  $2.27 \pm 0.04$  Å, whereas the corresponding value in the oxygen-free solution is  $2.67 \pm 0.02$  Å. This latter distance is in good agreement with an adsorbate model in which the Tl atom occupies a twofold position on the Cu(111) surface with a contraction of the metallic Tl radius (1.73 Å) by 3%.

TABLE I. Quantitative comparison of different sample preparations (Prep.). The mean Tl position  $\bar{z}_{\text{Tl}}$  is calculated by using  $\bar{z} = (n + \Phi_c)d$  with  $n = 1$ .  $\langle \bar{z}_{\text{Tl}} \rangle$  is the average of preparations a1 to a3 (with oxygen) and b1 to b2 (without oxygen), respectively. a3 rinse: preparation a3 after H<sub>2</sub>O rinse.

Prep.	$\Theta_{\text{Tl}}$ (ML)	$f_c^{\text{Tl}}$	$\bar{z}_{\text{Tl}}$ (Å)	$\langle \bar{z}_{\text{Tl}} \rangle$ (Å)
a1	0.22	$0.25 \pm 0.04$	$2.27 \pm 0.06$	
a2	0.24	$0.26 \pm 0.04$	$2.26 \pm 0.06$	$2.27 \pm 0.04$
a3	0.27	$0.19 \pm 0.03$	$2.29 \pm 0.07$	
b1	0.16	$0.40 \pm 0.06$	$2.68 \pm 0.02$	
b2	0.13	$0.63 \pm 0.08$	$2.65 \pm 0.02$	$2.67 \pm 0.02$
a3 rinse	0.08	$0.65 \pm 0.11$	$2.31 \pm 0.05$	

This binding geometry will be discussed in detail elsewhere.<sup>18</sup>

The 0.4-Å smaller distance for deposition out of the oxygen-contaminated electrolyte, however, cannot be explained by a model with Tl atoms residing on a pure Cu(111) surface. This falls in line with recent low-energy ion-scattering studies,<sup>25</sup> which showed that this surface reconstructs by adsorption of ( $\sim 0.5$  ML) oxygen leading to an inward shift of the copper surface atoms by about 0.3 Å. This value agrees very well with our measurement if we assume that the Tl atoms are adsorbed on the oxygen-reconstructed (111) surface.

The effect of the oxygen, as visible in the voltage-to-current diagrams, is such that irreversible processes occur which lead to an unbalanced relation between the cathodic and anodic charges.<sup>26</sup> The standing-wave results show the reason for this difference. Without any doubt the geometrical Cu surface structure is changed. They indicate further that as under UHV conditions<sup>27</sup> oxygen is built into the surface layer leading to a surface reconstruction. However, it is remarkable to find a well-ordered Tl phase on a reconstructed surface which was described as rough and disordered under UHV conditions.<sup>25,27</sup>

Since the adsorbate structure remained stable after removal from the oxygen-free as well as from the oxygen-contaminated electrolyte for up to at least 24 h, it can be concluded that the Tl layer prevents the Cu surface from direct oxidation. A reordering of the whole adsorbate during removal or just afterwards cannot be excluded from our present results. This question can only be answered by an *in situ* structural study of this system, which is presently in progress.

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