Electronic and Structural Characterization of Underpotentially Deposited Submonolayers and Monolayer of Copper on Gold (111) Studied by *In Situ* X-Ray-Absorption Spectroscopy

A. Tadjeddine
Laboratoire d'Electrochimie Interfaciale du Centre National de la Recherche Scientifique,
1 Place A. Briand, 92195 Meudon CEDEX, France

D. Guay, M. Ladouceur, and G. Tourillon
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Centre National de la Recherche Scientifique,
Bâtiment 209A, 91405 Orsay, France

(Received 26 November 1990)

We report on the first *in situ* study of the electronic state and the structure of underpotentially deposited submonolayers of Cu on Au(111) by x-ray-absorption spectroscopy. We found (i) various ordered adlayer structures, dependent on coverage, time, and direction of the potential scan, and (ii) strong interactions of Cu and oxygen and charge transfer from Cu to Au. During the deposition, the initial $(\sqrt{3}\times\sqrt{3})$ structure at 0.3 monolayer evolved to an equilibrium with the $c(5\times5)$. The latter and the (1×1) phases were observed at 0.6 and 1 monolayer, respectively. The three structures are present at 0.6 monolayer during the stripping scan.

PACS numbers: 78.70.Dm, 68.45.Da, 82.45.+z

The lack of *in situ* structural and electronic information has prevented the development of a coherent microscopic model of the electrochemical interface, which is a main step towards a better understanding of the electrode reaction processes. The structure and properties of the interfacial species, the charge distribution, the electronic and geometric structure of the adsorbate and of the electrode surface, and their changes with the electrode potential need to be described in their real media, to prevent any perturbation due to the removal of the potential control and of the electrochemical environment inherent in any *ex situ* characterization technique. The development of new surface sensitive techniques is opening a wide field for *in situ* investigation of the structural and electronic properties of the electrochemical interface. As an example, the generation of second-harmonic radiation at the metal-electrolyte interface appears as a suitable tool to probe the potential dependence of the surface electronic distribution[1] and the potential-induced surface structural transition.[2]

Recently, structural information has become accessible from *in situ* scanning tunneling microscopy[3] and *in situ* x-ray reflectivity, diffraction,[4,5] and absorption spectroscopy (XAS).[6,7] The latter technique combined with a fluorescence detection mode is very well adapted to study the local arrangement properties of adsorbate films deposited on foreign substrate. Indeed, information on the adsorbate electronic structure comes from the x-ray-absorption near-edge structure (XANES) since the energy position of the edge is related to the effective charge density of the absorber and its shape depends on the type and symmetry of the ligands.[8] The structure of the adsorbate can be obtained from the extended x-ray-absorption fine structure (EXAFS), which allows the determination of the nature, the numbers, and the bond lengths of the near neighbors.

In this Letter we report on a XAS study of the electronic and geometric structure of submonolayers and a monolayer of copper underpotentially deposited onto a gold (111) electrode. We were able to record *in situ* XANES and EXAFS spectra down to 0.3 monolayer (ML), and thus to access the structure of the adsorbate as a function of the coverage. The experiments were performed at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay, using the the synchrotron radiation from the DCI storage ring running at 1.85 GeV with a current of 300 mA and a lifetime of 45 h. The x rays were monochromatized by a Si(331) channel-cut single crystal with a resolution of 1 eV at the Cu *K* edge. The beam was polarized in the sample surface plane and XAS spectra were obtained in the fluorescence mode[9] using an especially designed electrochemical cell which reproduces the data obtained with a standard three-electrode cell.[7] For each copper coverage, fifteen XANES spectra have been collected with a step of 0.5 eV (2.5 h) and fifteen EXAFS spectra over a 600-eV range with a step of 2 eV (5 h). The analysis of the EXAFS oscillations involves a background subtraction. The various neighboring shells are sorted out by a Fourier transformation (FT) of the EXAFS signal: The peaks occur at R values that differ by a phase shift from the real interatomic distances.[10] By an inverse FT into k space, the EXAFS oscillations corresponding to only one neighbor shell are obtained. Comparison of the phase and amplitude of model compounds (metallic copper, Cu^{2+} in aqueous solution, and Au_3Cu) with those of the sample yields the structural parameters.

The gold (111) single-crystal electrode was a disk of 8-mm diameter and 2-mm thickness, cut from a single-crystal rod by electroerosion. It was mechanically and electrochemically polished to a mirrorlike finish and chemically cleaned. The electrolyte ($0.5M$ Na_2SO_4 + 10^{-4} $CuSO_4$ adjusted to a pH of 3 with H_2SO_4) was made of high-purity reactants and triply distilled water and was deoxygenated with 99.999% grade argon. Cu deposition was studied by sequential XAS measurements at stepwise more cathodic potentials up to a full monolayer, similar to the procedure used by Magnussen *et al.* in their STM study of the same system,[11] and at a coverage of 0.6 ML during the positive-potential scan.

The electronic characteristics of the Cu adlayer have been deduced from XANES spectra measured at each coverage and compared to the spectra of copper foil, Cu_2O, and $CuCl_2$ in aqueous solution. Similar features are observed in all cases, the only difference being the magnitude of the edge jump which depends on the amount of deposited copper. We have indeed found a good agreement between the Cu coverage given by the charge of the stripping peak and the height of the edge-jump absorption. As already discussed for a Cu monolayer on Au(100) and Au(111),[7] the energy position and the shape of the edge of the adlayer is close to that of Cu^+ in Cu_2O, indicating an oxidation state of the copper adatoms close to Cu^{+1} and a large charge transfer from the copper to the gold substrate. This conclusion is supported by results recently presented by McBreen *et al.*[12] on underpotentially deposited copper on carbon-supported platinum. XANES spectra recorded at both Cu K and Pt L_{III} edges indicate a Cu^{+1} oxidation state and a partial filling of the Pt d bands.

The k^3-weighted FT of the EXAFS oscillations above the Cu K edge are reported in Fig. 1(A) at various electrode potentials corresponding to different copper coverages. Curves a and b were obtained for 0.3 ML at different times. They correspond, respectively, to a "freshly" deposited Cu layer (1-h acquisition, curve a) and to a steady state of the adlayer (curve b) reached after 1 h in our experimental conditions. Curve c was obtained for 0.6 ML during the negative-potential scan, curve d for 1 ML, and curve e for 0.6 ML during the anodic-stripping-potential scan. The different shapes of the FT are indicative of the very different structures of the adlayer. In order to obtain a quantitative estimation of the bond lengths, and the nature of the neighbors and their numbers, we have fitted the inverse filtered FT of each peak using the phase and the amplitude functions of

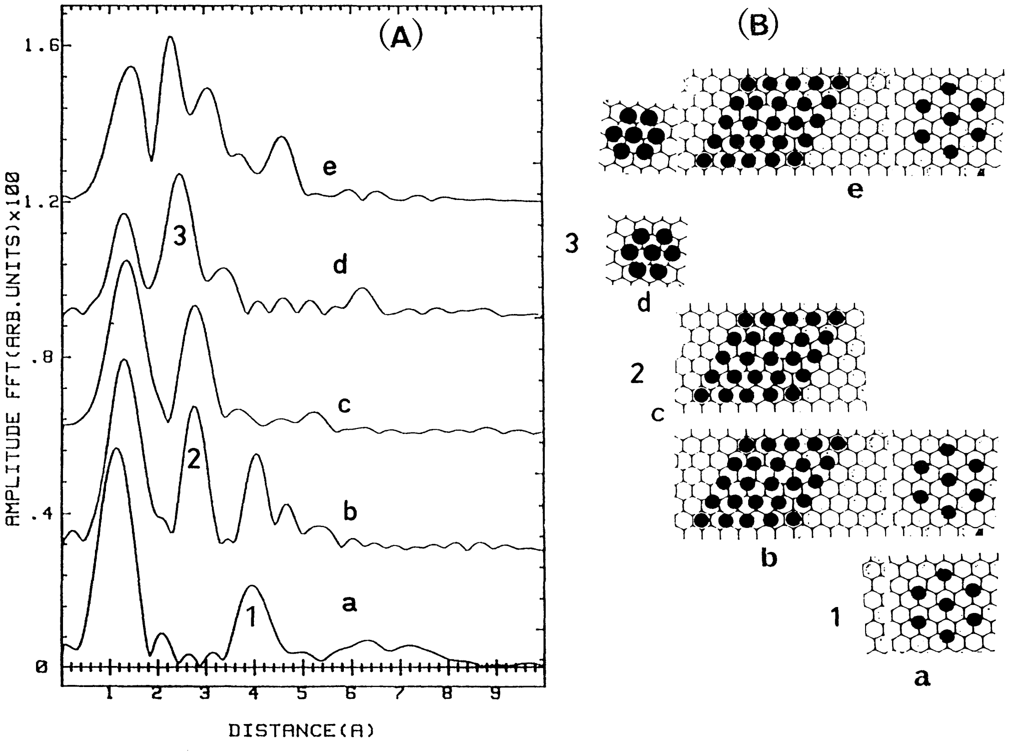

FIG. 1. (A) Fourier transforms of the Cu k^3-weighted EXAFS spectra and (B) corresponding model structures for Cu adlayers on Au (111): a, "freshly" deposited 0.3 ML; b, 0.3 ML after 1 h; c, 0.6 ML during the deposition scan; d, 1 ML; and e, 0.6 ML during the stripping scan. Labels 1,2,3 refer, respectively, to the ($\sqrt{3}\times\sqrt{3}$), the $c(5\times5)$, and the (1×1) hexagonal arrangements of the adlayer. [(B) Open circles, Au atoms; solid circles, Cu atoms.]

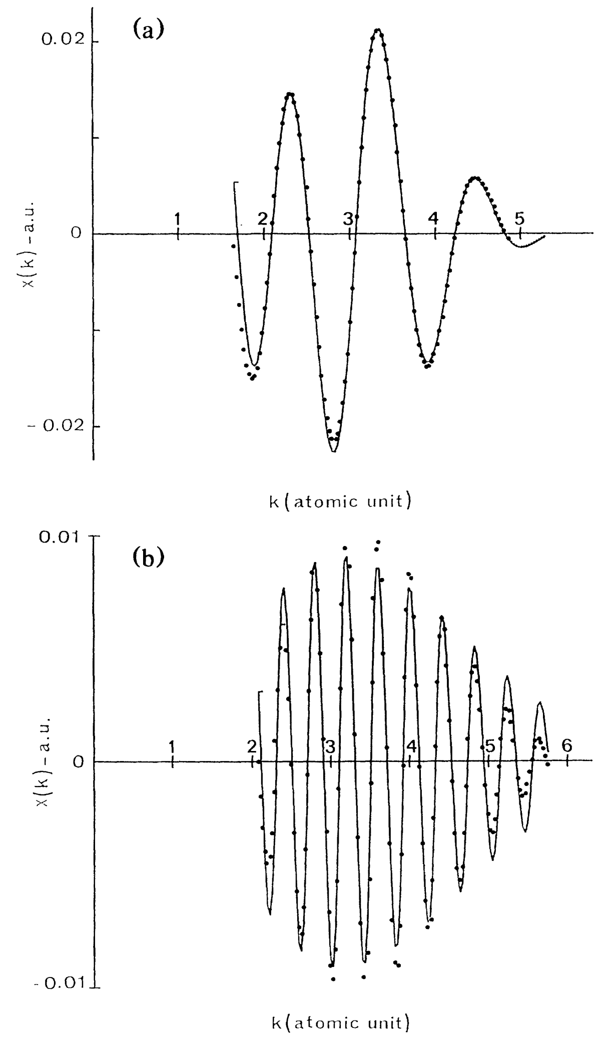

FIG. 2. Inverse Fourier transforms of the Cu *K*-edge EXAFS spectrum of a "freshly" deposited 0.3 ML: experimental curve (solid line) and fit (dotted line) for the (a) first and the (b) second peak of Fig. 1(B), model *a*.

model compounds. An example of the fits is shown in Fig. 2 for the freshly deposited 0.3 ML [from Fig. 1(A), curve *a*]. Results are summarized in Table I where we have collected, for each state of the adlayer, the bond lengths R, the effective coordination number N_{eff}, the Debye-Waller factor $\Delta\sigma$, and the energy variation ΔE.

At all coverages, scattering from oxygen atoms is observed from the fit of the first peak where the Cu-O distance is 0.195 nm and N_{eff} is close to 4.5. These results could be accounted for by a hexagonal structure of the oxygen atoms with an angle of 30° between the vector connecting the absorber and its oxygen neighbors and the substrate surface. They confirm the strong interaction between the adsorbed copper and the oxygen (coming from the solvent or from the sulfate ions) deduced from XANES data. This should influence the structure of the adsorbed layer and could explain the large charge-transfer processes.

The fits of the inverse filtered FT of the other peaks reveal in all cases (i) the presence of Cu-Cu scattering atoms with the same coordination number of 6 within an accuracy of ±10%, and (ii) the formation of well-ordered hexagonal structures. However, the Cu-Cu distances strongly depend on the coverage, the time at the smallest coverage, and the direction of the potential scan at medium coverage. It is then possible to get from the Cu-Cu distance the structure of the adsorbate at each stage corresponding to curves *a*-*e* in Fig. 1(A). For a freshly deposited 0.3 ML [$E = 0.22$ V per standard calomel electrode (SCE)] the Cu-Cu distance of 0.488 nm, close to $0.289\times\sqrt{3}$ nm, where 0.289 nm is the gold-gold spacing, leads straight to the $(\sqrt{3}\times\sqrt{3})$ structure [Fig. 1(B), model *a*] identified in *ex situ* LEED (Ref. 13) and *in situ* STM (Ref. 11) works. However, the XAS data clearly reveal that this structure is not stable in the electrochemical environment since two Cu-Cu distances are observed in the FT between 1- and 5-h aquisition time [Fig. 1(A), curve *b*]: a Cu-Cu distance of 0.488 nm due to the $(\sqrt{3}\times\sqrt{3})$ phase and a new Cu-Cu

TABLE I. EXAFS parameters. Bond lengths R, effective coordination number N_{eff}, Debye-Waller factor $\Delta\sigma$, and energy variation ΔE (accuracy: R, ±0.003 nm; N_{eff}, ±10%).

θ (ML)		R (nm)	N_{eff}	$\Delta\sigma$ (nm^{-1})	ΔE (eV)
0.3(*a*) [a]	Cu-O [b]	0.195	4.5	0.01	0.12
	Cu-Cu(1) [c]	0.488	5.9	0.015	0.13
0.3(*b*)	Cu-Cu(2)	0.359	5.85	−0.01	0.24
	Cu-Cu(3)	0.487	5.8	−0.01	0.25
0.6(*c*)	Cu-Cu(2)	0.357	5.85	−0.02	0.15
1(*d*)	Cu-Cu(3)	0.289	5.9	−0.01	0.12
0.6(*e*)	Cu-Cu(3)	0.286	5.7	−0.025	0.1
	Cu-Cu(4)	0.356	6.3	0.015	0.1
	Cu-Cu(1)	0.496	5.8	0.02	0.15

[a] The *a*-*e* relate to the curves *a*-*e* in Fig. 1.

[b] The same Cu-O EXAFS parameters have been obtained for all Cu coverages.

[c] The 1,2,3 relate to the labeled peaks in Fig. 1.

distance of 0.359 nm expected for a densely packed hexagonal $c(5\times5)$ structure [Fig. 1(B), model *b*]. Thus an equilibrium between these two phases is reached in about 1 h and preserved during the 5 h of the EXAFS experiment. After the potential has been stepped to 0.15 V corresponding to 0.6 ML, only the $c(5\times5)$ phase structure is observed with a Cu-Cu distance equal to 0.357 nm [Fig. 1(B), model *c*]. When a full Cu ML is adsorbed ($E=0.08$ V) the Cu-Cu distance of 0.289 nm corresponds exactly to an (1×1) epitaxial arrangement on an unreconstructed gold substrate, the copper atoms sitting in a threefold hollow site [Fig. 1(B), model *d*], in agreement with the results of Melroy *et al.*[6]

Finally, the structure of the adlayer appears to be sensitive not only to the coverage, but also to the direction of the potential scan—as seen from the very different shapes of the FT obtained for 0.6 ML during the scans with the cathodic deposition (curve *c*) and the anodic copper stripping (curve *e*) potentials. During the anodic scan, we observe three different copper-copper distances indicative of an equilibrium between the three above identified phases [Fig. 1(B), model *e*]. This observation could be explained by an inhomogeneous process of copper oxidation over the electrode surface. The stripping rate is then higher in the area covered by the $(\sqrt{3}\times\sqrt{3})$ phase than in the area covered by the $c(5\times5)$ phase and very weak in the surface region where the (1×1) phase is present.

As far as the Cu-Cu distances are concerned our results are in perfect agreement with the *in situ* STM data recently published by Magnussen *et al.*,[11] who also observed two phases at 0.3 ML and a decrease with time of the strongly corrugated phase identified as a $(\sqrt{3}\times\sqrt{3})R30°$ superstructure and a concomitant expansion of the weakly corrugated structure which was still present at 0.64 ML. Thus, the agreement between both sets of results clearly shows that the structures of the Cu adlayers are a genuine structure of the electrochemical interface and were not induced by the presence of the polarized tip in STM measurements. Further information can be gained from the unique ability of XAS to determine the chemical nature of the neighbors. Hence our results show the presence of Cu-O interactions at all coverages. Thus both techniques appear to be very complementary since STM probes the geometry and the long-range order while XAS accesses the oxidation state and the local chemical and structural environment of the adatoms.

In summary, we have used for the first time *in situ* XAS to determine the electronic and structural characteristics of submonolayers and a monolayer of Cu underpotentially deposited onto Au(111) in the electrochemical environment. Several ordered phases for Cu adlayers were observed, depending on the coverage, the time, and the direction of the potential scan. We have also found strong interactions of the adsorbed Cu with O atoms coming from the solvent or the sulfate ions and a charge transfer from Cu to Au. These effects should influence the structure of the adsorbate in the electrochemical interface. They could also participate in the stabilization of superstructures like the $c(5\times5)$, which has not been observed in *ex situ* measurements. The oxidation state of Cu, close to +1 in all cases, could also explain the repulsive interaction between the closely spaced Cu adatoms reflected by their hexagonal arrangement.

---

[1] P. Guyot-Sionnest, A. Tadjeddine, and A. Liebsch, Phys. Rev. Lett. **64**, 1678 (1990).

[2] A. Friedrich, B. Pettinger, D. M. Kolb, G. Lupke, R. Steinhoff, and G. Matowshy, Chem. Phys. Lett. **163**, 123 (1989).

[3] R. Christophe, H. Siegenthaler, H. Rohrer, and H. Wiese, Electrochim. Acta **34**, 1011 (1989); J. Wiecher, T. Twomey, D. M. Kolb, and R. J. Behn, J. Electroanal. Chem. **248**, 451 (1988).

[4] L. Bosio, R. Cortes, M. Denoziere, and G. Folcher, J. Phys. (Paris), Colloq. **50**, C7-23 (1989).

[5] B. M. Ocko, Jia Wang, A. Davenport, and H. Isaacs, Phys. Rev. Lett. **65**, 1466 (1990).

[6] O. R. Melroy, M. G. Samant, G. L. Borges, J. G. Gordon, L. Blum, J. H. White, M. J. Albarelli, M. McMillan, and H. D. Abruna, Langmuir **4**, 728 (1988).

[7] G. Tourillon, D. Guay, and A. Tadjeddine, J. Electroanal. Chem. **289**, 263 (1990); A. Tadjeddine, G. Tourillon, and D. Guay, Electrochim. Acta (to be published).

[8] T. A. Smith, J. Penner-Hahn, M. A. Berding, S. Doniach, and K. O. Hodgson, J. Am. Chem. Soc. **107**, 5945 (1985).

[9] G. Tourillon, D. Guay, M. Lemonnier, F. Bartol, and M. Badeyan, Nucl. Instrum. Methods Phys. Res., Sect. A **294**, 382 (1990).

[10] J. Stohr, J. Jeager, and R. Brennan, Surf. Sci. **117**, 503 (1982).

[11] O. M. Magnussen, J. Hotlos, R. J. Nichols, D. M. Kolb, and R. J. Behm, Phys. Rev. Lett. **64**, 2929 (1990).

[12] J. McBreen, W. E. O'Grady, G. Tourillon, E. Dartyge, and A. Fontaine, J. Electroanal. Chem. (to be published).

[13] Y. Nakai, M. S. Zei, D. M. Kolb, and G. Lehmpfuhl, Ber. Bunsenges. Phys. Chem. **88**, 340 (1984).