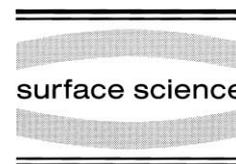




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# XPS study of the displacement of an electrodeposited Cu monolayer on Pt by mercaptopyridines

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## Abstract

The displacement of an electrodeposited Cu monolayer on polycrystalline Pt by 2- and 4-mercaptopyridine in solution has been investigated by XPS. The results indicate that, in both cases, the Cu adatoms are completely removed and substituted by mercaptopyridine molecules. An analysis of the S 2*p* spectra reveals a binding energy shift between adsorbed 2- and 4-mercaptopyridine, associated with the different electronic environment around the S atom in each case. An additional component, whose intensity correlates with that of the N–Pt component in the N 1*s* spectra, is assigned to S atoms in dimers, suggesting that N–Pt interaction decreases the probability of dimer formation. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Adatoms; Adsorption kinetics; Aromatics; Copper; Electrochemical methods; Platinum; Surface chemical reaction; X-Ray photoelectron spectroscopy

## 1. Introduction

Electrodeposition of metal adlayers on foreign metal substrates at potentials more positive than the reversible Nernst potential is known as underpotential deposition (*upd*). It occurs when the binding energy of an adsorbed metal atom on a foreign metal substrate is higher than the binding energy of a deposited metal atom on a surface of its own kind [1]. Consequently, the theoretical limit for the coverage obtained in the *upd* regime corresponds to one monolayer (ML). *upd* of Cu on Pt has been one of the systems studied most extensively in the last years [2–7], and much has been learned about the structure and bonding

mechanisms of the adsorbed Cu ML. However, the adsorption kinetics, whose complexity is evidenced by the many peaks observed in the voltammetric curves for adsorption and desorption of Cu [5–8], is not yet fully understood.

One of the possible effects of *upd* adlayers is to modify the catalytic activity of the substrate. For instance, Cu adlayers on Pt inhibit oxygen reduction [9], promote the oxidation of carbon monoxide [10], enhance the reduction of ethylene [11], and inhibit oxidation of hydrogen [12]. On the other hand, the presence of coadsorbates during the *upd* process can modify the bonding mechanisms of the Cu atoms on the Pt substrate [13]. The interaction between coadsorbates and Cu can, thus, give information on the dynamics of Cu bonding on Pt itself. It has been shown that certain organic molecules, based on pyridine rings, are

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able to inhibit Cu *upd* [8,14]. In the case of mercaptopyrindines (pyridine rings with a SH radical), there has been evidence not only that the Cu *upd* process is inhibited, but also that a Cu ML previously deposited on Pt can be displaced by these molecules in solution at open circuit [8,15]. Adsorption of such organic molecules alone on Pt has been subject of several works [16–21] because of their potential application as biosensors due to their ability to promote charge transfer between Pt electrodes and certain hemoproteins [22–26]. In general, the adsorption geometry is perpendicular to the substrate surface and the bonding occurs through the sulfur atom. The aim of this work is to investigate the effects of 2-mercaptopyridine (2MP) and 4-mercaptopyridine (4MP) molecules in solution on a predeposited *upd* monolayer of Cu on polycrystalline Pt by XPS.

## 2. Experimental details

The Pt electrodes were first polished with 1  $\mu\text{m}$  diamond paste, rinsed with water, and subsequently submitted to a potential sweep ( $100\text{ mV s}^{-1}$ ) between +1.55 and 0.0 V versus SHE (standard hydrogen electrode) in 0.50 M  $\text{H}_2\text{SO}_4$  until a steady voltammogram was obtained. The last cycle was stopped at 0.45 V versus SHE (double layer region) on the positive sweep, where faradaic reactions do not take place. The electrochemical area of the platinum electrode ( $\approx 1\text{ cm}^2$ ) was evaluated by integration of the voltammetric peaks for hydrogen adsorption on 0.50 M  $\text{H}_2\text{SO}_4$ , using a conversion factor of  $210\text{ mC/cm}^2$ .

Cu monolayers were deposited in the *upd* regime onto the polycrystalline Pt electrodes by exposing them to a  $1 \times 10^{-3}\text{ M}$   $\text{CuSO}_4$  solution in 0.50 M  $\text{H}_2\text{SO}_4$ . The coulometric charge, obtained by integrating the voltammetric peaks (*upd* region), was  $417\text{ mC/cm}^2$ , which corresponds to one copper monolayer [8]. A three-compartment cell, with provision for addition and withdrawal of solution under prepurified nitrogen atmosphere, was used during the electrochemical preparation. Consequently, rinsing of the electrode and solution exchanges were carried out in a flow-through fash-

ion inside the cell, without exposing the electrode to the environment. All solutions were prepared using water purified with a Millipore Milli-Q system. 4MP was purified by sublimation. All other reagents were of high purity and were used as received.

Once the Cu ML had been deposited, the  $\text{CuSO}_4$  solution was substituted by a  $1 \times 10^{-3}\text{ M}$  2MP or 4MP aqueous solution, which was led interact with the electrode at open circuit. The Pt electrode was then transported to the XPS chamber in a glass cell under nitrogen atmosphere while immersed in the corresponding MP solution. By transferring the samples to the UHV chamber, they were briefly exposed (few seconds) to the atmosphere. Direct contact with the air was, however, avoided by leaving a solution drop on the electrode surface. This remanent solution was removed during pumping in the vacuum chamber, where the very low pressures of the UHV regime ( $< 10^{-8}\text{ mbar}$ ) in comparison with the vapor pressure of water and mercaptopyrindines, warranted that both components of the solution evaporate.

For the XPS measurements, a conventional surface-analysis chamber was used, equipped with a commercial VG-CLAM hemispherical electron energy analyzer and a twin-cathode X-ray source, set to the Mg-K $\alpha$  excitation. Measurements were performed in normal emission geometry. The overall energy resolution was 0.6 eV, and the base pressure inside the UHV chamber during measurements was  $1 \times 10^{-9}\text{ mbar}$ . No sputtering was carried out to avoid possible damage of the adsorbed molecules under the effect of the ion beam [27–29], and bearing in mind the passivating nature of these organic molecules [19–21]. Depth profiling was performed on Cu/Pt samples without MP adsorption. In this case, the sputtering parameters were 3 kV and 1  $\mu\text{A}$  sample current.

## 3. Experimental results

Prior to the measurements of the displacement of the Cu adlayer on Pt by 2MP and 4MP, XPS spectra were obtained of the Cu monolayer itself, and compared with the spectra obtained on a thicker Cu layer ( $\sim 10\text{ ML}$ ). The results are shown

in Fig. 1, where the evolution of the Cu  $2p_{3/2}$  binding energy (BE) position and the photoemission (PE) intensity with respect to the sputtering time are shown. The BE is sensitive to the environment around the emitter atom. It is not the same when the Cu emitter atom is completely surrounded by other Cu atoms (bulk copper) as when the Cu neighbours are confined into one plane (Cu ML), or even when the number of in-plane Cu atoms is not enough to surround the emitter atom (islands, rows, or Cu isolated atoms). This has been illustrated in Fig. 1a, where it can be observed that the Cu  $2p_{3/2}$  BE decreases as the coverage

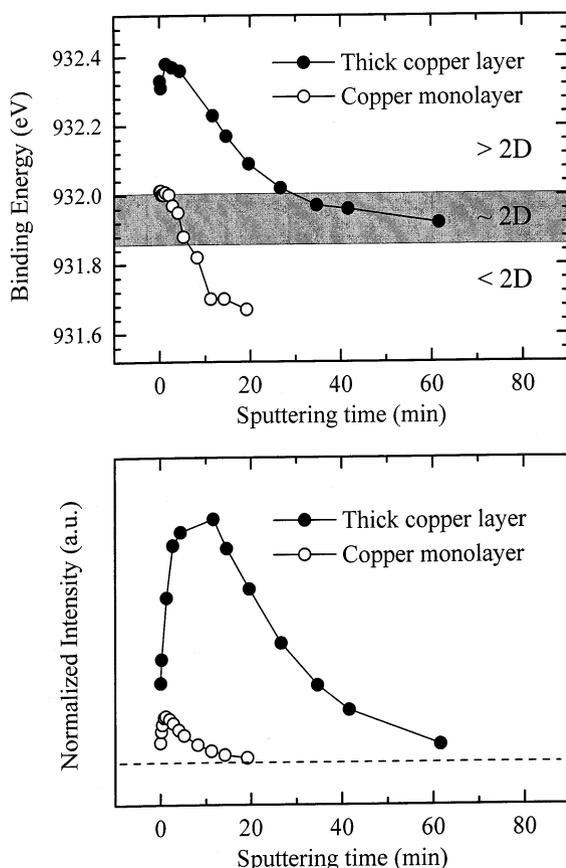


Fig. 1. Evolution with depth of the Cu  $2p_{3/2}$  binding energy (a) and the Cu  $2p_{3/2}$  photoemission intensity (b) of an electrodeposited Cu ML on Pt (open circles) and a thick Cu layer ( $\sim 10$  ML, black circles). The shaded area in (a) gives an approximate range for the binding energy of bidimensional copper.

decreases (except for a small increase at very short sputtering times, where the copper layer is covered by surface oxides and contamination). The correlation of the BE with the PE intensity (Fig. 1b) can give an approximate idea of the dimensionality of the Cu adlayer. Assigning the BE of bulk copper to the maximum binding energy at the first region of the thick Cu adlayer (solid circles), and that of low dimensional Cu adatoms to the last stages of the Cu ML (sputtering times between 10 and 20 min, open circles), the intermediate region would correspond to approximately bidimensional Cu. Both the first region of the Cu ML (sputtering times less than 5 min) and the last one of the thick layer (sputtering times above 35 min), lay into this region. The separation of the Cu  $2p_{3/2}$  BE into three regions shown in Fig. 1a does not intend to be rigorous, but just to give an approximate range of the BE for a Cu ML on Pt. The substrate should also play an important role in the Cu  $2p_{3/2}$  BE in the monolayer and submonolayer regime, corresponding the lowest-dimensional limit (one Cu adatom) to the binding energy of Cu–Pt bonding. Cu incorporation into the Pt-substrate due to knock-on processes during sputtering can not be excluded. However, the binding energy of a buried Cu atom is not expected to be very different to that of a Cu adatom on Pt. The assignment of the 2D region is supported by results obtained in previous works [30–32].

As can be observed in Fig. 1b, the Cu ML is almost completely removed after  $\sim 7$  min sputtering time with the sputtering conditions and geometry ( $\sim 45^\circ$  incidence angle) used. The exponential decay of the PE intensity observed after this point is probably due to the shadowing effect of the surface roughness ( $1 \mu\text{m}$  r.m.s.), that prevents some regions being directly hit by the ion incident beam. This effect is even more pronounced in the case of the thicker layer, where the roughness is larger.

Fig. 2 shows XPS spectra at the Cu  $2p$  core level region of the *upd* Cu ML electrodeposited on the polycrystalline Pt electrode (Fig. 2a), and the same electrode after interacting with the 2MP and 4MP aqueous solutions (Fig. 2b and c, respectively). As can be observed, the Cu  $2p$  photoemission signal disappears after interaction with both

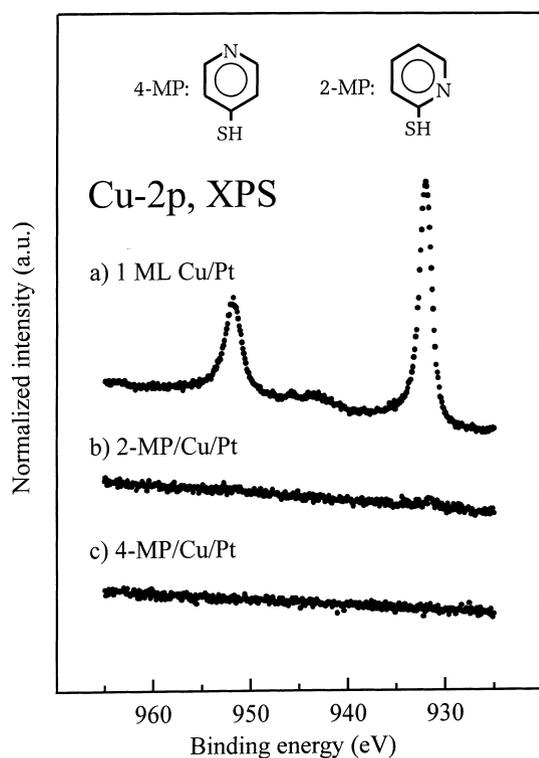


Fig. 2. Cu 2p photoelectron spectra of an electrodeposited Cu ML on Pt (a), and the same ML after interacting with 2MP (b) and 4MP (c). The upper inset shows both molecules.

MP solutions. The Pt 4f photoemission signal coming from the substrate is still present, with a similar intensity to the case of the adsorbed Cu ML, so we conclude that this Cu ML has been completely removed after interaction with the MP solutions. Two different mechanisms can be proposed to explain this behaviour. One possibility is that the MP molecules react with the Cu adatoms, forming Cu-containing intermediate compounds. In this case it would be possible that some non-copper-containing products remain on the surface. A second possibility would be a direct substitution of Cu by MP molecules without intermediate products. It is known that S–Pt bonding is more favorable than S–Cu bonding ( $\Delta H = -20$  kcal mol<sup>-1</sup> versus  $\Delta H = -13$  kcal mol<sup>-1</sup> in the case of sulfides). On the other hand, a Cu layer on Pt has shown to promote the formation of Pt–S compounds [33]. Since, as mentioned above, MP

adsorbs through the sulfur atom [16–18], the Cu adlayer could act as a catalyst for MP–Pt reaction.

To find out which is the right mechanism of the Cu ML displacement, XPS measurements at the S 2p region were obtained. The results are shown in Fig. 3b, d, where spectra of 2MP and 4MP adsorbed at open circuit on clean Pt (without the Cu ML) are also shown for comparison (Fig. 3a, c). Also shown in Fig. 3e is a spectrum of aldrithiol (a molecule composed of two 4MP rings bound by the S atoms) adsorbed on Pt. The solid line through the data points as well as the subspectra are the results of a least-squares fit analysis. Each subspectrum consists of two Lorentz lines, convo-

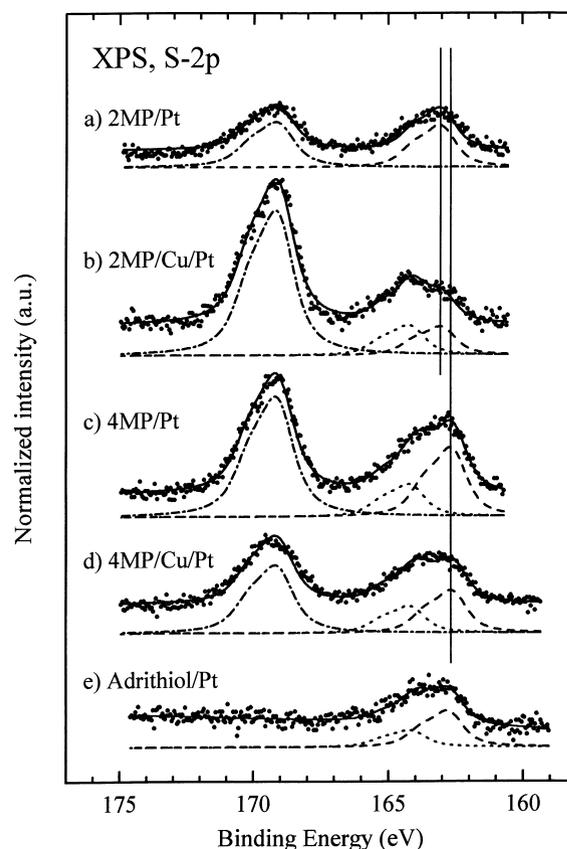


Fig. 3. S 2p photoelectron spectra of 2MP adsorbed on Pt (a), 2MP after interacting with one Cu ML on Pt (b), 4MP adsorbed on Pt (c), 4MP after interacting with one Cu ML on Pt (d), and aldrithiol adsorbed on Pt (e). The solid line through the data points, as well as the subspectra, are the results of a least-squares fitting procedure (see text).

luted with a Gaussian curve to take into account the experimental resolution, representing the S  $2p$  spin-orbit-split doublet, with a splitting of 1.18 eV and an intensity ratio of approximately 2:1. The dash-dotted subspectrum at  $\sim 169.2$  eV, present in all MP samples, can be assigned to sulphates [34]. They must originate by partial oxidation of the MP molecules, either in the aqueous solution or by oxygen diffusion through the water drop during transport to the UHV chamber. Two additional subspectra appear in Fig. 3, represented by the dashed and dotted lines. Except for the absence of the dotted subspectrum in Fig. 3a, no differences are observed between the MP/Pt spectra and those of the corresponding MP/Cu/Pt system. This indicates that the MP molecules displace the Cu monolayer without decomposition, remaining afterwards adsorbed on the Pt surface. This result is in agreement with previous voltammetric observations [8,14]. The attenuation of the XPS Pt signal with respect to the clean Pt surface corresponds to less than 1 ML of adsorbed MP.

A small difference in the BE position of the dashed component (see vertical lines) is observed between the 2MP and the 4MP samples, both with and without the Cu ML: 162.7 eV in the case of 4MP and 163.1 eV for 2MP. This must be related to the different electronic environment around the S atom in both molecules. In 2MP, the N atom is close to the S atom, allowing the formation of chelate structures of type S–Pt–N, whereas in 4MP the N atom is at the opposite side ('para' position), and the S atom only interacts with Pt. This fact can explain the observed BE difference, which has not been reported previously. Similar S  $2p$  BE values for S containing organic molecules have been obtained in previous works [35,36].

The dotted subspectrum appears in the case of the 4MP/Pt sample, but is absent for the 2MP/Pt sample. 4MP molecules have the ability to form dimers, bound by the S atom, whose electronic environment is different to that of the S atoms in 4MP alone [15]. This situation is similar to that of the aldrithiol molecule, whose spectrum is shown in Fig. 3e. The similarity of this spectrum to the 4MP spectra suggests that the dotted component can be associated with the formation of dimers. In the spectra of 2MP, the dotted compo-

nent is absent from the 2MP/Pt system, suggesting that the formation of chelates hinders dimerization. On the other hand, the dotted component is observed for the 2MP/Cu/Pt system. In this case, the presence of the Cu adlayer seems to play a determinant role, probably by decreasing the N–Pt interaction. In order to clarify the mechanisms that are taking place, N  $1s$  spectra were also recorded. The results are shown in Fig. 4, where a spectrum of 4MP adsorbed on Pt in acidic medium (0.5 M  $H_2SO_4$  aqueous solution) is also shown for comparison (Fig. 4e). In order to properly fit the data, two components were needed, located at 399.3 eV (dotted lines) and 400.9 eV (dashed lines),

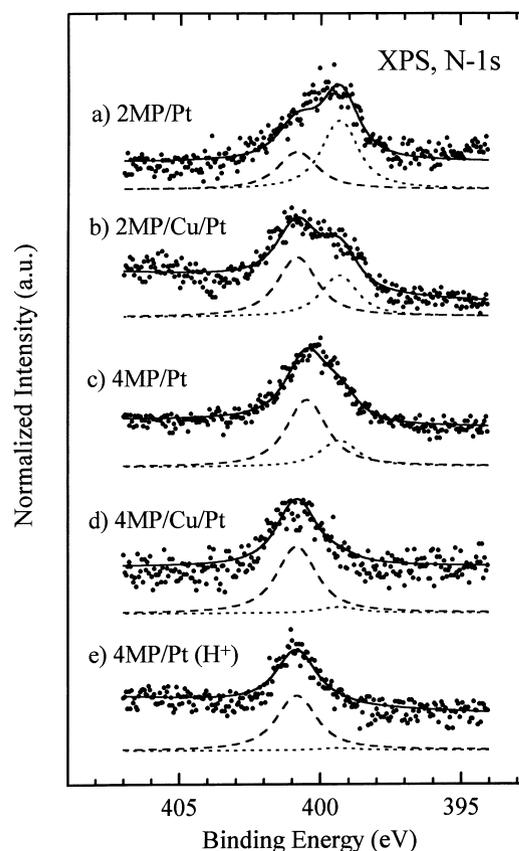


Fig. 4. N  $1s$  photoelectron spectra of 2MP adsorbed on Pt (a), 2MP after interacting with one Cu ML on Pt (b), 4MP adsorbed on Pt (c), 4MP after interacting with one Cu ML on Pt (d), and 4MP adsorbed on Pt in acidic medium (e). The solid line through the data points, as well as the subspectra, are the results of a least-squares fitting procedure (see text).

respectively. A similar double structure has been observed in previous works on adsorbed pyridine molecules and similar systems [37,38]. According to these works, the component at higher binding energy (dashed lines in Fig. 4) can be assigned to N in the pyridine ring, with weak or null N–Pt interaction [37], and that at lower binding energy (dotted lines in Fig. 4) to N–Pt bonding [38]. The possibility of 2MP forming chelate structures (S–Pt–N) can explain the higher intensity of the dotted component in spectra 4a and 4b as compared with spectra 4c and 4d. On the other hand, the presence of the dotted component in the case of 4MP, where the N atom is in ‘para’ position, indicates some interaction between N and Pt, probably through deviations of the adsorption geometry with respect to normal geometry. When 4MP is adsorbed on Pt in acidic medium (spectrum 4e), the N atom is protonated due to the excess  $H^+$  [8], and the N–Pt interaction is not possible, as is evidenced by the absence of the dotted component in this case.

The formation of chelates should hinder dimerization, since all valence electrons are employed to bonding with Pt. A correlation between the dotted subspectra of Figs. 3 and 4, corresponding to the dimer component in the S 2*p* spectra and to the N–Pt component in the N 1*s* spectra, respectively, is indeed observed. In particular, spectra of 2MP/Pt show the highest intensity of the N–Pt component (Fig. 4a) and the lowest of the dimer component (Fig. 3a). The presence of the Cu adlayer seems to promote dimer formation and to hinder N–Pt interaction, as is observed in Figs. 3 and 4. Cu adatoms seem to favor the formation of strong S–Pt bonding, in a similar way to the Cu-promoted sulfidation of Pt [33], diminishing the interaction of N with Pt.

#### 4. Conclusions

We have investigated by XPS the effects of 2- and 4-mercaptopyridine molecules in aqueous solution on a Cu monolayer electrodeposited on a polycrystalline Pt electrode in the *upd* regime. The results indicate that the Cu monolayer is completely displaced in both cases. The presence at

the Pt surface of mercaptopyridines after Cu removal suggests that the displacement mechanism is substitutional, and, consequently, that MP–Pt bonds are much stronger than Cu–Pt bonds. The role of the Cu adlayer is, probably, to catalyze the reaction between Pt and MP molecules, which adsorb through the S atom. Two components are observed in the S 2*p* XPS spectra, assigned to S–Pt bonds in single molecules and dimers. A small binding energy difference is observed between 2MP and 4MP due to the different electronic environment of the S atom in both cases, allowing the formation of chelate structures in the case of the 2MP molecules. N 1*s* spectra show two components, the one at lower binding energy being associated with N–Pt interactions. A correlation is observed between the intensity of the N–Pt component and the probability of dimer formation, being the latter minimum for the 2MP/Pt system, where the intensity of the N–Pt component is maximum due to the formation of chelate structures. The Cu adlayer seems to reduce the N–Pt interaction, favouring dimer formation.

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