# **Electroless, Electrolytic and Galvanic Copper Deposition with the Scanning Electrochemical Microscope (SECM)**

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Dedicated to Prof. Dr. Walther Jaenicke on the occasion of his  $85^{th}$  birthday

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The <u>S</u>canning <u>E</u>lectrochemical <u>M</u>icroscope (SECM) can be used with different techniques of microstructured copper deposition. A first approach involves the electrolytic copper deposition on noble metals, whereby copper ions are released from a complex by a suitable tip reaction and then reduced on the polarised conducting surface to form a copper microstructure. The second approach is very similar to the first, but does not involve polarising the substrate. It generates a tip-induced microgalvanic cell, the positive electromotoric force of which is constituted by two electrochemical reactions at different areas of the substrate. Finally the electroless copper deposition is performed on nonconducting surfaces like glass or semiconducting surfaces like silicon. This involves locally reducing a suitable precursor film whose surface has been previously immobilised.

# **1. Introduction**

Copper is widely used in the microelectronic industry on account of its high electric and thermal conductivities and its low electromigration [1, 2]. Hence,

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it is obvious that there is a demand for easy methods of generating copper microstructures. Wet chemical processes are mostly inexpensive and simple to perform; this applies when the scanning electrochemical microscope (SECM) is used in microfabrication, because this is a pure electrochemical method.

The SECM has been widely used to deposit metals [3–17], semiconductors [4, 18–21] and conducting polymers [22–35] on different substrates. Our group has already gained experience in silver deposition with the SECM [10. 12, 13, 16, 17], and now we are introducing the deposition of copper on various substrates. Copper was first deposited with the SECM by El Giar et al. [14]. In their work, the SECM was used in the direct mode, *i.e.* a potential was applied between tip and substrate. This mode could be compared with an STM-driven approach [15, 36]. The anodic oxidation of water to oxygen occurred at the tip and the cathodic reduction of soluble copper ions took place at the substrate. The growing copper columns eventually resulted in contact with the tip, thereby causing a short circuit, which triggered a motor to step up the tip electrode a few micrometers away, and the deposition of copper continued. This technique produced copper columns with very high aspect ratios (up to 150). Furthermore, it also demonstrated the lateral deposition of copper. The limitation of this procedure is that it can be used for copper deposition only on conducting surfaces as the substrate has to be biased by an external power source.

The deposition procedures developed in our laboratory are all based on the feedback mode of SECM instead. In this mode, the ultramicroelectrode (UME) transforms a redoxactive species to another redox state, which serves as a mediator and is able to react either with species in the gap between tip and surface or with the surface. Therefore, the substrate has to be biased only in some special cases.

As copper is the lower homologue of silver, their chemical and electrochemical properties are quite similar. Therefore, we decided to explore the applicability of the deposition strategies successfully employed for silver deposition and, despite the differences between copper and silver, they have been found to apply to copper deposition, too. We continued employing the electrolytic [10, 13] and galvanic deposition [17] approaches on one hand and electroless [12, 15] procedures on the other. The mediator produced at the tip releases free metal ions by reacting with a complex of the metal in question. If the substrate is cathodically polarised in such a way that only the free metal ions, and not the complexed metal species, can be discharged, the electrolytic deposition occurs at those places where the tip is moved. Furthermore, the substrate need not be connected to an external power supply if a suitable anodic reaction could occur either by providing a reducing agent dissolved in the aqueous phase [17] or a metal substrate that may undergo oxidation, which results in galvanic depositions induced by the tip reaction. Last but not least, the local reduction of a suitable metal precursor compound leads to the generation of metal structures on nonconducting surfaces. The reduction can be commenced by supplying a reducing agent produced at the tip.

## 2. Experimental

Three different substrates have been used for copper deposition throughout this work, namely gold, glass and steel. Gold specimens were employed in the electrolytic deposition process. They were fabricated by coating silicon [100] single crystals by evaporation in a two-step procedure involving the initial deposition of a few monolayers of chromium to promote adhesion, and the subsequent deposition of gold (Umicore Materials AG, Germany). Glass specimens were employed in the electroless deposition. The samples were also subjected to an evaporation process in which the glass sheets were covered with copper(I) iodide (Merck). In some selected experiments, the adhesion of the deposited layer on the glass sheets was improved by coating them, prior to the evaporation step, with MEM-213, a polydimethylsiloxane-polycarbonate block copolymer. In all these cases, the evaporation procedures were performed in a high-vacuum vapour depositer model Auto 306 (Edwards Company, USA). Finally, the specimens employed in the galvanic deposition process consisted of CK 105 steel after polishing.

The SECM apparatus was the home-made system described earlier [16, 37]. Ultramicroelectrodes were made from 10 and 25  $\mu$ m diameter platinum wires (Goodfellow Materials Ltd, UK), which where sealed in glass capillaries in such a way that the circular end surface of the metal was free, forming a disc-shaped microelectrode. The electrode geometry was sharpened by grinding the surrounding glass walls with a sequence of emery and SiO<sub>2</sub> (3 Micron Fibremet Disc<sup>®</sup> supplied by Buehler, USA) papers. Finally, the electrode surface was ground with a SiO<sub>2</sub> polish-disc (0.3 Micron Fibremet Disc<sup>®</sup>, Buehler, USA).

The specimens were mounted horizontally facing upwards at the bottom of a cell made of polytetrafluoroethene. They were either left unpolarised or polarised potentiostatically using the bipotentiostat associated with the SECM. When the specimen was polarised, an electrical contact was made *via* its back. The electrochemical setup was completed by using a reference electrode and a platinum wire (Goodfellow, UK) as auxiliary electrode. In our experiments different reference electrode systems have been employed, namely the saturated calomel reference electrode and pseudo-reference electrodes consisting of either a copper or a silver wire immersed in the electrolyte.

All SECM experiments were performed at ambient temperature with solutions of analytical grade chemicals (Merck, Germany) in 18.2 M $\Omega$  Millipore<sup>®</sup> water. The electrolytes contained CuSO<sub>4</sub> as the source of copper metal ions, NaNO<sub>2</sub> to create protons, and either NH<sub>3</sub> or Na<sub>2</sub>CH<sub>2</sub>(COO)<sub>2</sub> (sodium malonate) for the complexing copper ions. For both the electrolytic and the galvanic deposition processes, NaNO<sub>3</sub> was employed as supporting electrolyte, whereas methylviologen dichloride (MVCl<sub>2</sub>) was used as mediator in the electroless deposition process. KOH was used to adjust the pH of the electrolytes.

Imaging of the copper microstructures was performed with an Olympus SZ-STU2 optical microscope, provided with an Olympus DP10 digital camera.

## 3. Results

In this work several strategies have been investigated for the controlled generation of copper microstructures in an electrochemical cell with a scanning electrochemical microscope. In all the approaches the SECM operation was performed in the feedback mode. In this case, the ultramicroelectrode converts a redoxactive species to another redox state, which subsequently serves as a mediator by reacting with a species located either in the solution between the tip and the surface or directly at the surface. In the feedback mode, the substrate only needs to be biased in some special cases. The most favourable situation occurs when the reactant can be regenerated at the surface in a reversible redox reaction, originating a positive feedback effect as higher currents can be measured at the SECM tip.

#### 3.1 Microgalvanic deposition

A microgalvanic deposition strategy has been developed for the localised deposition of copper on steel substrates induced by the SECM tip, which is schematically depicted in Fig. 1. The solution must contain a complexing species for cupric ions to avoid the direct deposition of copper on steel through a galvanic coupling mechanism, as well as a mediator that releases protons during its electrochemical conversion at the tip. The mediator chosen for this purpose was the nitrite ion. The potential of the tip was thus set to a value at which the diffusion-limited oxidation of nitrite to nitrate occurred in accordance with

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-.$$
<sup>(1)</sup>

Protons are generated as a reaction by-product. These protons shift the complexation equilibrium for dimalonatecuprate(II) ions with the production of  $[Cu(H_2O)_6]^{2+}$  and  $CH_2(CO_2H)_2$  in the vicinity of the tip:

$$\left[\operatorname{Cu}\left(\operatorname{CH}_{2}(\operatorname{CO}_{2}^{-})_{2}\right)_{2}\right] + 4\operatorname{H}^{+} + 6\operatorname{H}_{2}\operatorname{O} \xrightarrow{} \left[\operatorname{Cu}(\operatorname{H}_{2}\operatorname{O})_{6}\right]^{2+} + 2\operatorname{CH}_{2}(\operatorname{CO}_{2}\operatorname{H})_{2}.$$
(2)

The hydrated cupric ions can subsequently be discharged at the steel surface:

$$\left[ Cu(H_2O)_6 \right]^{2+} + 2e^- \longrightarrow Cu + 6H_2O \qquad E^0 = +0.342 \text{ V vs. NHE}$$
 (3)



**Fig. 1.** Scheme of copper deposition on an iron substrate under a galvanic mechanism. Nitrite is oxidised to nitrate at the tip and protons are generated as by-product. In the gap between the tip and the surface the dimalonatocuprate(II) ion reacts with these protons. Free copper ions are reduced underneath the tip whereas the copper complex cannot be reduced due to thermodynamic restrictions. The electrons needed for the reduction are supplied by the oxidation of iron.

and the electrons are provided by the oxidation of iron atoms:

$$Fe \longrightarrow Fe_{aa}^{2+} + 2e^{-} \qquad E^0 = -0.447 \text{ V } \text{ vs. NHE}.$$
(4)

According to the redox potentials of these two half-cell reactions, copper deposition is thermodynamically favoured. A microgalvanic cell is thus developed under the SECM tip.

A line of copper spots deposited on a steel surface under a 10  $\mu$ m-diameter Pt tip is shown in Fig. 2a. During the experiment, the distance *d* between the tip and the surface was fixed at 20  $\mu$ m, and the deposits were produced at selected positions on the substrate by setting the tip potential at +1.40 V *vs*. Cu-QRE for varying durations (namely 10, 50, 100, and 300 s from left to right). Further inspection of the microphotograph allows for differences in the appearance of the deposits to be observed. Though the copper dot obtained for a 10 s polarization has a well-defined circular shape, longer durations result in less dense and more extended microstructures.

In order to investigate the determining factor for the effectiveness of the chemical lens, we next tried the electrolytic mechanism for the deposition of copper from a solution containing ammonia (concerning microgalvanic copper deposition from solutions containing ammonia see below). Copper dots were successfully generated on a biased gold substrate, and are shown in Fig. 2b. The localisation of the chemical lens below the tip is now confirmed



**Fig. 2. a** Copper dots generated on iron with the galvanic approach described in Fig. 1. Composition of the plating solution:  $0.01 \text{ M CuSO}_4 + 0.1 \text{ M NaNO}_2 + 0.04 \text{ M} \text{ Na}_2\text{CH}_2(\text{CO}_2)_2$  in water. Operating conditions for the SECM:  $10 \,\mu\text{m}$  tip;  $E_{\text{tip}} = +1.4 \text{ V}$  vs. Cu-QRE;  $d = 20 \,\mu\text{m}$ ; t = 10, 50, 100, and 300 s (from left to right, respectively). **b** Copper dots generated on gold with an electrolytic mechanism. Composition of the plating solution:  $0.25 \text{ M CuSO}_4 + 1 \text{ M NaNO}_2 + 1 \text{ M NH}_3$  in water. Operating conditions for the SECM:  $10 \,\mu\text{m}$  tip;  $E_{\text{tip}} = +1.4 \text{ V}$ ;  $E_{\text{sub}} = -0.38 \text{ V}$  vs. calomel (0.1 M KCl);  $d = 20 \,\mu\text{m}$ ; t = 10, 50, 100, and 150 s (from left to right, respectively).

by the observation that the size of the dots is independent of the duration of the tip reaction. On the other hand, it can be observed that the deposition of copper is progressively hindered towards the centre of the deposits in this case because the complexed copper species are effectively consumed in accordance with reaction (11) and cannot reach the centre of the deposit any longer.

An explanation for the different behaviour of the complexing agents malonate and ammonia can be derived from the comparison of their basicity constants ( $pK_{B,1} = 8.3$ ;  $pK_{B,2} = 12.1$ ;  $pK_{B,ammonia} = 4.75$ ). The protons generated at the tip by reaction (1), may participate in the following neutralization reactions:

$$H^+ + OH^- \longrightarrow H_2O$$
 (5)

$$2\mathrm{H}^{+} + \mathrm{CH}_{2}(\mathrm{CO}_{2}^{-})_{2} \xrightarrow{\leftarrow} \mathrm{CH}_{2}(\mathrm{CO}_{2}\mathrm{H})_{2}$$

$$(6)$$

$$\mathrm{H}^{+} + \mathrm{NH}_{3} \xrightarrow{\phantom{a}} \mathrm{NH}_{4}^{+}. \tag{7}$$

The reaction rate of Eq. (5) depends on the concentration of the hydroxide ion which is directly correlated to the basicity of the complexing agent as well as the reaction rate of Eqs. (6) or (7), respectively. Therefore, the basicity of the complexing agent is the determining factor for the effectiveness of the chemical lens.

The need for a biased gold surface arises from the nobler character of gold compared to copper, *i.e.*, an external source of electrons had to be available for the reduction of the copper ions. Copper deposition on unbiased steel from the copper tetraamine complex was also attempted, and produced completely different results. The deposits obtained in this case exhibited a light blue colour and had a very fine grained texture consistent with the conclusion that  $Cu(OH)_2$  or more probably  $Cu(OH)_{1.5}(SO_4)_{0.25}$  [38, 39] was deposited instead of copper (not shown in this work).

This effect can also be explained on the basis of the weak basic properties of the malonate ion. Thermodynamic data support the view that the onset of Cu(OH)<sub>2</sub> precipitation occurs at a pH value about 5.5, but copper ions at higher pH values are amphoteric. It is well known that the addition of ammonia to an aqueous solution of a copper salt solution initially leads to the precipitation of Cu(OH)<sub>2</sub> until ammonia is added in excess. Cu(OH)<sub>2</sub>precipitation does not occur in our experiments when copper ions are complexed by malonate, but would require the take place. From this follows that higher concentrations of the complexing agent are required for copper to be deposited from its copper(II)-tetraammine complex than from the copper(II)dimalonate complex. The big difference in basicity characteristics between malonate and ammonia also leads to the development of different pH values in their corresponding solutions; *i.e.*, a pH value of 11 was measured in the solution containing ammonia, whereas a pH value of 7.8 was found in the solution containing malonate. Such pH differences also have a direct effect on the thermodynamics of the system, as can be deduced from the inspection of the Pourbaix diagram for iron [40]. At low iron concentrations, iron reacts according Eq. (4) at pH 8 to produce a soluble iron species, whereas at pH 11  $Fe_3O_4$ is formed and thus the iron surface is passivated. This means that no microgalvanic cell is developed on the metal surface; hence, copper cannot be reduced. As a further consideration, the conversion of nitrite to nitrate at the tip in accordance with Eq. (1) in such a basic environment may not lower the pH below the tip to a sufficient extent, thus favouring the precipitation of  $Cu(OH)_2$  instead of copper deposition. Nevertheless, this does not appear to be case for the copper deposits generated on biased gold substrates from solutions containing ammonia, as shown in Figs. 2b and 3.

Fig. 3 displays an optical microscope image of two copper lines generated on a gold surface. The length of the lines is 200  $\mu$ m. Their width is nonuniform because the distance *d* between the tip and the surface was continuously varied during the scan of the tip. Thus, the value of *d* varied from an initial value of 10  $\mu$ m to 20  $\mu$ m at the end of the scan for the deposit depicted in Fig. 3a, whereas the inverse process was followed for the generation of that given in Fig. 3b. The thinning of the copper line in Fig. 3a was the direct result of the increase in the tip distance, and can be easily justified in terms of a chemical lens



**Fig. 3.** Copper lines generated with an electrolytic approach similar to that used for the microstructures in Fig. 2b. Composition of the plating solution:  $0.15 \text{ M CuSO}_4 + 0.1 \text{ M NO}_2 + 1 \text{ M NH}_3$  in water. Operating conditions for the SECM:  $10 \,\mu\text{m}$  tip;  $E_{\text{tip}} = +1.4 \text{ V}$ ;  $E_{\text{sub}} = -0.38 \text{ V}$  vs. calomel (0.1 M KCl). **a** Tip scan direction performed from left to right with  $d_{\text{initial}} = 10 \,\mu\text{m}$ , and  $d_{\text{final}} = 20 \,\mu\text{m}$ ,  $v = 0.5 \,\mu\text{m/s}$ ; **b** tip scan direction performed from left to right with  $d_{\text{initial}} = 20 \,\mu\text{m}$ , and  $d_{\text{final}} = 10 \,\mu\text{m}$ ,  $v = 0.5 \,\mu\text{m/s}$ .

[*cf.* Ref. 13]. Less straightforward is the justification for the lack of line thickening in the other case (see Fig. 3b). We assume that during the approach of the tip the diffusion field is compressed and therefore enlarges even if the tip velocity in the *z*-direction is quite low ( $0.025 \,\mu$ m/s). A careful observer may even wonder why the beginning of the line in Fig. 3b is not as narrow as the end of that in Fig. 3a, although tip distance is the same in both cases. This effect arises from the experimental observation that initial thickening of the lines is always observed as a direct consequence of the time required to reach the diffusioncontrolled steady state current. A rather high concentration of the tip product takes place which will not be reached again. Hence, the rate of deposition is also higher at the beginning than at any later stage.

The contours of the linear deposits in Fig. 3 are very sharp, which is a striking evidence for the effectiveness of the chemical lens. Since structures with very clear contours are desirable in industrial applications, we searched for a method to deposit copper on unbiased metals. As presented above, the microgalvanic cell does not apply in the case of iron substrates if ammonia is used as complexing agent due to the passivation of the substrate. On the other hand, the spontaneous oxidation of gold to maintain the corresponding anodic process in the galvanic cell is not feasible for thermodynamic reasons. An alternate procedure involves the formation of a microgalvanic cell by adding a reducing agent to the electrolyte, which can be oxidised at the gold surface as an anodic reaction. Such a procedure has been recently developed at our laboratory for the deposition of silver when hydroxide ions were used as the reducing agent, and is the subject of another publication currently in preparation [17]. An additional advantage of this process arises from the fact that the hydroxide ions are directly available in the experimental system since they are products of the hydrolysis of ammonia.

Unfortunately the redox potential of the system  $OH^-/O_2$  ( $E^0 = +0.401$  V vs. NHE at pH 14) is too high to reduce copper, and another reducing agent had to be chosen. Furthermore, additional care was required for the selection of the reducing agent, as too strong reducing agents would promote the reduction of nitrite, which can be easily reduced in many ways, *e.g.*:

$$2NO_{2}^{-} + 3H_{2}O + 4e^{-} \longrightarrow N_{2}O + 6OH^{-} \qquad E^{0} = +0.15 \text{ V vs. NHE}$$

$$2NO_{2}^{-} + 2H_{2}O + 4e^{-} \longrightarrow N_{2}O_{2}^{2-} + 4OH^{-} \qquad E^{0} = -0.18 \text{ V vs. NHE}$$

$$(9)$$

$$NO_{2}^{-} + H_{2}O + e^{-} \longrightarrow NO + 2OH^{-} \qquad E^{0} = -0.46 \text{ V vs. NHE}.$$

$$(10)$$

For this reason, ascorbic acid was chosen to create the microgalvanic cell. The processes below the tip could still be generally described by the scheme depicted in Fig. 1. In fact, the tip reaction is the same as in Eq. (1). Though the decomplexation reaction in the gap between tip and surface has to be modified to include the corresponding ammonia complexes, it is still quite similar to Eq. (2):

$$\left[\operatorname{Cu}(\operatorname{NH}_3)_4\right]^{2+} + 4\operatorname{H}^+ + 6\operatorname{H}_2\operatorname{O} \xrightarrow{} \left[\operatorname{Cu}(\operatorname{H}_2\operatorname{O})_6\right]^{2+} + 4\operatorname{NH}_4^+, \tag{11}$$

and the deposition of copper is still described by Eq. (3). The main difference between this situation and the scheme shown in Fig. 1 concerns the source for the electrons participating in Eq. (3). As mentioned above, the oxidation of ascorbic acid replaces Eq. (4):

$$\operatorname{ascH}_2 \longrightarrow \operatorname{asc}_{\operatorname{ox}} + 2\operatorname{H}^+ + 2\operatorname{e}^- \qquad E^0 = +0.06 \,\mathrm{V} \, vs. \text{ NHE; pH 7.} \quad (12)$$

The result obtained in this case was not as satisfactory as that for the deposition of silver [17]. Thus, we investigated stronger reducing agents, such as potassium borohydride or hydrazine, but without being successful. A photograph portraying a copper deposit produced with hydrazine in addition to ascorbic acid as reducing agents is shown in Fig. 4. Unfortunately, compared to the quality of the copper deposits obtained in the absence of hydrazine (not shown), the addition of hydrazine to the electrolyte did not significantly improve the quality of the copper deposits. The observed deposition was weak in both cases.

We next investigated a completely different approach for the generation of copper microstructures based on the local reduction of an insoluble copper



**Fig. 4.** Copper dot generated on gold with a tip-induced microgalvanic cell. The scheme given in Fig. 1 still applies when iron is replaced by gold, the tip reaction by Eq. (10) and the oxidation reaction by Eq. (11). Composition of the plating solution:  $0.005 \text{ M} \text{ CuSO}_4 + 0.05 \text{ M} \text{ NaNO}_2 + 0.05 \text{ M} \text{ NH}_3 + 0.1 \text{ M}$  ascorbic acid +  $0.0005 \text{ M} \text{ N}_2\text{H}_4$  in water, KOH added to adjust at pH 8. Operating conditions for the SECM:  $25 \,\mu\text{m}$  tip;  $E_{\text{tip}} = +1.3 \text{ V} vs.$  Ag-QRE;  $d = 10 \,\mu\text{m}$ ; t = 180 s.

precursor previously applied on the surface. This method is suitable for copper deposition on non-conducting surfaces as well. For this purpose, copper(I) iodide (solubility product constant  $K_{sp} = 1.27 \times 10^{-12} \text{ M}^2$ ) was evaporated on glass substrates. Good adhesion of the cuprous salt to the substrate was observed even when the glass specimen had not previously been coated with MEM-213, an adhesion promoter. The local reduction of copper is promoted by the reduced form of 1,1'-dimethyl-4,4'-dipyridinium-dichloride (methyl viologen dichloride, MVCl<sub>2</sub>). The methyl viologen radical cation is easily accessible from the electrochemical reduction of methyl viologen at the tip in accordance with:

$$MV^{2+} + e^- \longrightarrow MV^{\bullet+} \qquad E^0 = -0.56 V \text{ vs. NHE}.$$
 (13)

Subsequently, the radical cation reduces the copper precursor at the surface:

$$MV^{\bullet+} + CuI \longrightarrow Cu^0 + MV^{2+} + I^-$$
(14)

and the resulting microstructures are displayed in Fig. 5. This optical microscope image shows the copper microstructures produced on a glass substrate previously coated with MEM-213 using a tip of  $10\,\mu\text{m}$  in diameter. It must be pointed that we could find no differences between the structures generated on substrates with and without MEM-213.



**Fig. 5.** Copper dots generated on glass with an electroless approach. They were obtained by reducing CuI according to Eq. (14). Composition of the plating solution: parameter: 0.1 M MVCl<sub>2</sub> in water. Operating conditions for the SECM: 10  $\mu$ m tip;  $E_{tip} = -0.85$  V vs. Cu-QRE; d = 15, 11, 7, and 3  $\mu$ m from bottom to top; t = 10, 50, 100, and 200 s, from left to right.

The excess of the precursor remaining on the substrate after localised generation of copper microstructures can be easily removed by immersing the substrate in a diluted ammonia solution. The copper(I) iodide is oxidised by molecular oxygen dissolved in the electrolyte, and copper(II) ions subsequently undergo complexation by ammonia:

$$CuI + \frac{1}{2}O_2 + H_2O + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + I^- + 2OH^-.$$
 (15)

The metallic copper can undergo a similar oxidation process in this electrolyte. In this case  $Cu_2O$  is formed with molecular oxygen in the air:

$$2Cu + \frac{1}{2}O_2 \longrightarrow Cu_2O; \tag{16}$$

the copper(I) oxide subsequently reacts in a similiar way to that described by Eq. (15):

$$\frac{1}{2}Cu_2O + \frac{1}{4}O_2 + H_2O + 4NH_3 \longrightarrow \left[Cu(NH_3)_4\right]^{2+} + 2OH^{-}.$$
 (17)

Reaction (16) is slow enough for us to assume that only a few monolayers of the deposited copper may be dissolved in accordance with the reaction sequence given by Eq. (17). The reaction sequence given by Eqs. (16) and (17) may account for the bright zones observed around the individual copper spots after the treatment with ammonia solution. They may result from the conversion of a few monolayers of copper(I) iodide before the steady state current condition is attained.

Fig. 5 shows a matrix of copper spots deposited at various tip–surface distances (from bottom to top 15, 11, 7, and 3  $\mu$ m, respectively) and tip-reaction durations (from left to right 10, 50, 100, and 200 s, respectively). The size of the spots decreases slightly with increasing distance between the tip and the substrate, a feature that can be justified in terms of a chemical lens mechanism. Actually, the MV<sup>++</sup>-ion can react with molecular oxygen:

$$MV^{\bullet+} + \frac{1}{2}O_2 + H_2O \longrightarrow MV^{2+} + 2OH^-;$$
(18)

hence, dissolved oxygen is a scavenger for the chemical lens. On the other hand, the dependence of the spots' size on the duration of the tip reaction is very distinctive, as it results in less focused structures. This effect can be explained by a lateral reduction mechanism. If a sufficient fraction of the precursor below the tip is reduced during tip operation, then Eq. (14) takes place in two spatially resolved areas, as given below. At the substrate directly below the tip, the  $MV^{\bullet+}$ -ion undergoes oxidation, releasing electrons to the copper microdeposit in accordance with:

$$\mathrm{MV}^{\bullet+} \longrightarrow \mathrm{MV}^{2+} + \mathrm{e}^{-} \,. \tag{19}$$

The electrons released by reaction (19) migrate to the metal–precursor interface and are available to reduce the copper precursor on the contiguous substrate area:

$$\operatorname{CuI} + e^{-} \longrightarrow \operatorname{Cu}^{0}. \tag{20}$$

Such a mechanism actually counteracts the focusing effect of the chemical lens.

### 4. Conclusions

In this work we demonstrate the electrochemical generation of copper microstructures on a variety of substrates using scanning electrochemical microscopy. In all cases, the SECM is operated in the feedback operating mode. Copper structures, with dimensions on a micrometer scale were obtained with sharp delimitations of the deposited pattern by using the chemical lens concept. In this way, a suitable scavenger that reacts with the tip-generated species diffusing away from the centre of the ultramicroelectrode is used to promote a significant focusing of the diffusion field below the tip in the area where both species meet.

Three different approaches for generating controlled copper microdeposits on different kinds of substrates are developed. Firstly, an electrolytic method can be employed for generating copper deposits on noble metals. A suitable complexing agent is selected for the quantitative complexation of the copper(II) species present in the electrolytic phase. The solution must also contain a mediator which produces protons during its electrochemical conversion at the SECM tip. The local acidification of the solution below the tip results in the release of free copper(II) ions in the vicinity of the conducting sample, which are available to undergo reduction when the substrate is adequately biased. Both circular and linear copper deposits exhibiting a high lateral resolution have been produced on gold samples by this electrolytic procedure.

Secondly, copper deposition can be performed on less-noble metals using a galvanic procedure. Though quite similar in operation to the electrolytic deposition method described above, the main difference is the development of localised microgalvanic cells on the surface of the metal to be coated. As microanodes are spontaneously formed in the vicinity of the area covered by the tip, the electrons necessary for the reduction of the free copper(II) ions under the tip are readily supplied by the metallic substrate as it corrodes in the electrolytic environment. This process can be hindered by the onset of passivity at the metallic substrate. Optical microscope photographs of copper deposits generated on steel by this procedure are shown.

Thirdly, an electroless procedure has been developed for the generation of copper deposits on non-conducting and semiconducting surfaces. In this case, the electrochemical mediator species formed at the tip directly reacts with a copper-metal precursor immobilised on the substrate. This procedure has been successfully employed to form copper microstructures on glass substrates previously coated with CuI. After the local reduction of the salt to copper, the precursor left at the unexposed areas can be easily removed from the surface.

We believe that the experimental procedures described in this work have a great potential in the microfabrication techniques based on semiconductor technology, as controlled shape deposits can be produced at selected locations with high lateral resolution.

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