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## ELECTRODEPOSITION OF GOLD FROM FORMALDEHYDE-SULFITE BATHS: BATH STABILITY AND DEPOSITS CHARACTERIZATION

Juliana L. Cardoso\* e Sebastião G. dos Santos Filho

Escola Politécnica, Universidade de São Paulo, Av. Prof. Luciano Gualberto, 158, trav. 3, Bl. A, 05508-900 São Paulo - SP, Brasil

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It was investigated Au(I)-sulfite baths containing formaldehyde. As a result, high stability was achieved for baths containing formaldehyde concentration close to 10 mL L<sup>-1</sup> with a lifetime superior to 600 days. On the other hand, cyclic voltammograms indicated that the increase of formaldehyde concentration in the bath promotes decreasing of the maximum cathodic current, so that, if the formaldehyde concentration is high, the surface areal concentration of gold will be low. Also, the lowest surface roughness was obtained for 10 mL L<sup>-1</sup> of formaldehyde.

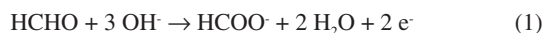
Keywords: electrodeposition; formaldehyde; gold bath.

### INTRODUCTION

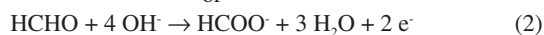
Cyanide based gold baths have been widely used for gold plating, because of the high stability constant of cyanide with gold ([Au(CN)<sub>2</sub>]<sup>-</sup>, K<sub>f</sub> = 38.3 mol L<sup>-1</sup>);<sup>1</sup> although its toxicity.<sup>1</sup> Non-cyanide baths have been developed to overcome the problem of toxicity, most of them based on Au(I)-sulfite complex.<sup>2,3-7</sup> Different reducing agents are commonly add to the Au(I)-sulfite bath, as thiourea,<sup>5,6</sup> hypophosphite,<sup>4,6</sup> borohydride,<sup>6</sup> dimethylamine borane (DMAB),<sup>6</sup> hydrazine<sup>6</sup> and formaldehyde.<sup>2,6,8</sup> Redox potentials of all reducing agents are negative, showing dependence with pH ranging from 4 to 14, except when thiourea is added to the bath.<sup>6,9</sup>

Au(I)-sulfite baths can be unstable, due the low stability constant of the Au(I)-sulfite complex ([AuSO<sub>3</sub>]<sup>-</sup>, K<sub>f</sub> = 12.3 mol L<sup>-1</sup>; [Au(SO<sub>3</sub>)<sub>2</sub>]<sup>3-</sup>, K<sub>f</sub> = 26.8 mol L<sup>-1</sup>), which may cause a disproportionation reaction from Au(I) to Au(III).<sup>1,3</sup> However, the increase of the pH makes Au(I)-sulfite baths more stable since the amount of free sulfite ions decreases.<sup>1</sup>

Formaldehyde has been used as additive in baths for electro- and electroless plating over the past decades<sup>8,10,11-14</sup> because of its electrocatalytic oxidation effect on various metals, including Pd, Ag, Au, Ni, Pt, Cu, and Ir, described by the following chemical equations:<sup>8,12</sup>



or



In addition, formaldehyde has been used as reducing agent in Au(I)-sulfite baths<sup>8,10,12</sup> for gold electroless deposition. Although mixed deposition using gold electroless and electroplating reported on literature,<sup>15</sup> details about bath stability and deposits characteristics were not presented yet. Considering this lack, the purpose of this paper is to investigate the influence of formaldehyde on the stability of Au(I)-sulfite baths and its role on the growth characteristics of the electroplated gold.

### EXPERIMENTAL

Baths were prepared from chemicals of analytical grade or better, and Milli-Q deionized water (18.2 MΩ cm), using anhydrous sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>), 35% formaldehyde (HCHO) solution and potassium tetrachloroaurate (III) (KAuCl<sub>4</sub>). All baths were fresh, and a magnetic stirrer was used for bath agitation. pH was measured using pHmeter (pHbanc II from Tekna).

Cyclic voltammetry was performed using a CV-50W potentiostat from BAS and a glass cell. All the experiments were performed at room temperature (25 ± 2 °C). Prior to the measurements, nitrogen gas were bubbled through the bath during 30 min and, following, it was kept flowing near the bath surface. Potential was ranged from -100 to -1200 mV and was cycled 3 times at 1 mV s<sup>-1</sup>.

The employed working electrode was a metalized Si wafers with evaporated Ti and Au layers, 14.0 and 50.8 nm thick, respectively. The area of the working electrode exposed to the bath was 0.923 cm<sup>2</sup>, delimited with tape (Scotch, 3M) and they were previously dipped in 1 HF (49%):20 H<sub>2</sub>O (d-HF) during 100 s and washed in deionized water (5 min). The counter-electrode was a Pt wire and the reference was an Ag/AgCl electrode (3 mol L<sup>-1</sup> KCl).

The voltammograms were recorded for baths with 5 g L<sup>-1</sup> of KAuCl<sub>4</sub> and 1, 10 or 100 mL L<sup>-1</sup> of HCHO. Also, baths with 5 g L<sup>-1</sup> of KAuCl<sub>4</sub>, 60 g L<sup>-1</sup> of Na<sub>2</sub>SO<sub>3</sub> and 1, 10 or 100 mL L<sup>-1</sup> of HCHO were prepared and analyzed.

Before the voltammetric measurements, baths containing gold and formaldehyde or baths containing gold, sulfite and formaldehyde (1, 10 or 100 mL L<sup>-1</sup>), were prepared in a polypropylene ependorph and stored for tests of stability. The analysis of the voltammograms were also based on the results obtained through a program for chemical equilibrium simulation (CHEAQS Pro).<sup>16</sup>

Electrodeposits of gold were obtained at -800 mV<sub>Ag/AgCl</sub> during 30 min, before and after purge of 30 min with N<sub>2</sub>. The electrodepositions were performed with PalmSens from Ivrium Technology, during constant agitation.

Rutherford backscattering spectrometry (RBS) analysis was used to determine the deposits composition, roughness and areal concentration in the electrodeposited samples, using the program SIMNRA 6.04.<sup>17</sup> The areal concentrations of the layers previously

\*e-mail: [jcardoso@lsi.usp.br](mailto:jcardoso@lsi.usp.br)

deposited at the working electrode were discounted from the total areal concentration obtained from the RBS spectra. The surface roughness was obtained from RBS spectra through a Gaussian distribution, defined by the full width at half maximum (FWHM).<sup>17</sup>

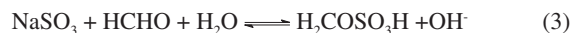
In addition, profilometry was employed to evaluate the peak-valley surface roughness of CV samples and field emission scanning electron microscopy (FESEM) was employed to evaluate the surface morphology of the electrodeposited films.

## RESULTS AND DISCUSSION

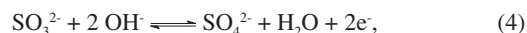
### Stability

At first, baths containing HCHO and KAuCl<sub>4</sub> presented yellow color and the time interval for precipitation decreased as the concentration of HCHO increased. As can be seen in Table 1, the bath with 100 mL L<sup>-1</sup> of HCHO allowed one deposits with small amount of gold on the wall of the ependorph after 5 days. In contrast, the bath with 10 mL L<sup>-1</sup> of HCHO also allowed deposits with small amount of gold, but only after 45 days. Finally, the bath with 1 mL L<sup>-1</sup> of HCHO was stable for 250 days. Therefore, addition of less than 1 mL L<sup>-1</sup> HCHO (35%) in a solution of KAuCl<sub>4</sub> does not markedly change the grade in which Au(I) remains complexed with chlorine at room temperature.

On the other hand, addition of Na<sub>2</sub>SO<sub>3</sub> to the KAuCl<sub>4</sub> bath, followed or not by the addition of HCHO, makes the bath colourless. The time interval for precipitation of these baths became 400 days for HCHO concentration of 1 mL L<sup>-1</sup> and more than 600 days for 10 mL L<sup>-1</sup>. It should be caused due to the complexation of the sulfite by the HCHO.<sup>18</sup> In this case, Au(I) complexes with sulfite ions and their excess also complexes with formaldehyde as shown by the following reaction:<sup>19</sup>



Reaction 3 was corroborated by measuring pH before and after addition of sodium sulfite in the bath (Table 1). In this case, pH varied from about 2.7-3.2 (before) to 8.3-13.0 (after). Also, it was noteworthy that the pH varied from 8.3 to 13.0 when formaldehyde concentration varied from 0 to 100 mL L<sup>-1</sup>, respectively, which is predicted by the increase of the OH<sup>-</sup> concentration in reaction 3. In addition, the complex molecules Au(I)-sulfite and HCHO-sulfite avoids the oxidation of sulfite to sulfate in alkaline media, according to reaction 4 as follows:<sup>19,20</sup>



Despite the HCHO-sulfite complexation (reaction 3), for higher formaldehyde concentrations (100 mL L<sup>-1</sup>), it was observed spontaneous precipitation of gold due to the electrocatalytic oxidation of the formaldehyde excess (reaction 1).

### Voltammetry measurements

Since the bath containing Au salt and 100 mL L<sup>-1</sup> HCHO is very unstable, as mentioned before, cyclic voltammograms were extracted only for baths with 1 or 10 mL L<sup>-1</sup> HCHO.

Simulations of ionic strength for solutions containing only KAuCl<sub>4</sub> or KAuCl<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub> give values of 0.0314 and 0.886 mol L<sup>-1</sup>, respectively, which indicated that baths containing only KAuCl<sub>4</sub> can present high ohmic drop. Indeed, this was observed for cyclic voltammograms recorded at 1 mV s<sup>-1</sup> for Au electrode in a 5 g L<sup>-1</sup> KAuCl<sub>4</sub> bath in comparison with a 5 g L<sup>-1</sup> KAuCl<sub>4</sub> + 60 g L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> bath. In addition, the bath containing only KAuCl<sub>4</sub> presented non-repetitive shapes with increasing cathodic current (at -1200 mV<sub>Ag/AgCl</sub>) from 2.2 to 8.0 mA cm<sup>-2</sup> for sequential cycles in the range of -100 to -1200 mV<sub>Ag/AgCl</sub> (Figure 1), possibly due to the influence of ionic strength changing during the cycles.<sup>21</sup> As the ionic strength of the 5 g L<sup>-1</sup> KAuCl<sub>4</sub> bath is low, the ionic strength may substantially increase during the cycles what could be made responsible by the increase of the cathodic current (arrow 1 in Figure 1) and the decrease of the ohmic drop (arrow 2 in Figure 1). The beginning of the Au(I) reduction was obtained when the current density varied 50 μA cm<sup>-2</sup> from the current base line in the cathodic region.

The reduction of gold (Figure 1) at the working electrode occurred when the scanning potential overcomes -650 mV<sub>Ag/AgCl</sub> at the first cycle, and this value decreased in the next cycles to a fixed value of approximately -480 mV<sub>Ag/AgCl</sub> (beginning of the reduction). Initial surface conditioning can be made responsible for this difference between the first and the other cycles, this is to say, the surface concentration of active sites must have changed when surface gold, previously treated in d-HF, is introduced in the gold bath.<sup>22</sup>

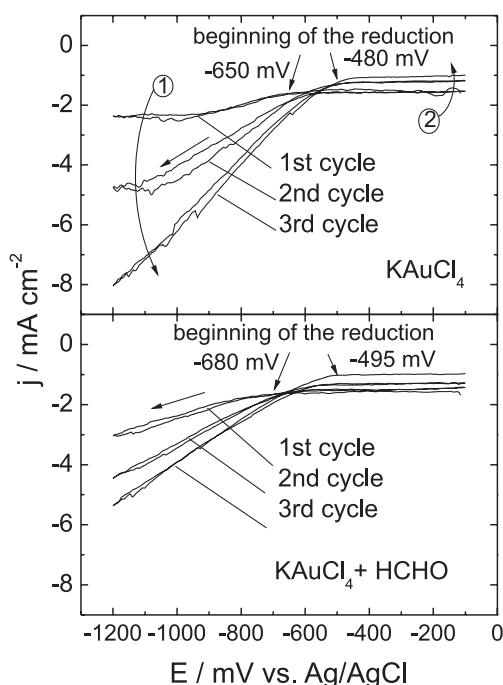
A possible single step reaction of gold reduction is:<sup>19,20</sup>



Adjusting the potential with the Nernst equation, considering the simulated chloride activity of 4.45 10<sup>-2</sup> mol L<sup>-1</sup>, the simulated AuCl<sub>2</sub><sup>-</sup> activity of 4.85 10<sup>-27</sup> mol L<sup>-1</sup> and the reference electrode potential of 210 mV<sub>H</sub>, the potential of the reaction 5 became -453 mV<sub>Ag/AgCl</sub>, which is very close of the extracted value at the beginning of reduction in Figure 1.

**Table 1.** Bath stability, color, pH, areal concentration and roughness of baths containing 5 g L<sup>-1</sup> of KAuCl<sub>4</sub>, used to evaluate HCHO and Na<sub>2</sub>SO<sub>3</sub> concentration or N<sub>2</sub> purge influences

HCHO (mL L <sup>-1</sup> )	Na <sub>2</sub> SO <sub>3</sub> (g L <sup>-1</sup> )	Bath color	pH	Bath stability (days)	N <sub>2</sub> purge	Areal concentration (10 <sup>15</sup> at. cm <sup>-2</sup> )	Roughness (10 <sup>15</sup> at. cm <sup>-2</sup> )	
0			3.1	>600				
1	0	Yellow	3.2	250				
10			2.7	45				
100			3.0	5				
0			8.3	300				
1	60	Colourless	9.5	400	no	3100.1	301.9	
10			12.1	>600	yes	2803.7	354.9	
						no	828.4	82.0
						yes	1021.6	143.3
100			13.0	4				



**Figure 1.** Cyclic voltammograms recorded at  $1 \text{ mV s}^{-1}$  for Au electrode in  $5 \text{ g L}^{-1} \text{ KAuCl}_4$  and,  $5 \text{ g L}^{-1} \text{ KAuCl}_4$  and  $10 \text{ mL L}^{-1} \text{ HCHO}$

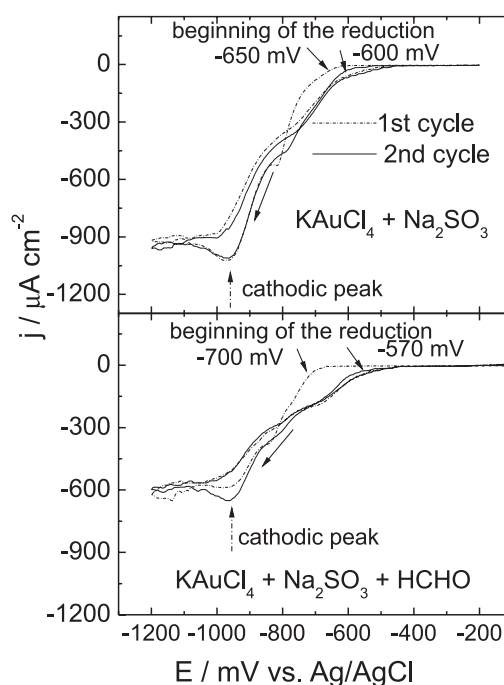
The gold reduced during the first cycle remains on the electrode surface during the anodic scanning. At potentials higher than  $-650 \text{ mV}_{\text{Ag/AgCl}}$ , Au electroplating rate is very slow, while at potentials lower than  $-650 \text{ mV}_{\text{Ag/AgCl}}$  plating is possibly controlled by diffusion (constant current levels). The deposited gold was rough ( $16 \mu\text{m}$  peak-valley roughness after the three cycles shown in Figure 1a) and porous, enlarging the electrode area and increasing the current density of the following cycles. A gas evolution was also observed as bubbles formed at the working electrode, indicating probably the evolution of  $\text{H}_2$ .

The contribution of formaldehyde to the current density can be analyzed comparing the voltammograms of the Figure 1b. The first cycle is very similar for both voltammograms. The area of the electrode from the bath without sulfite ions increased, because of the rougher deposit associated to higher current density. The addition of formaldehyde has low influence at the pH of the  $\text{KAuCl}_4$  bath, as indicated in Table 1.

Formaldehyde induces decreasing of the electrodeposition current density. The addition to the bath of only  $\text{Na}_2\text{SO}_3$  reduces the roughness ( $4 \mu\text{m}$  peak-valley roughness after three cycles shown in Figure 1b) but the deposit is not as flat as with the presence of formaldehyde ( $600 \text{ nm}$  peak-valley roughness after the three cycles). The  $\text{Na}_2\text{SO}_3$  also changed the pH of this bath to alkaline values, as already mentioned (Table 1).

The visual appearance of the electrode after cyclic voltammetry experiments changed drastically. Deposits obtained from bath containing only Au(I)-sulfite complex are usually light yellow, but they are opaque. The addition of formaldehyde to this bath substantially improved the deposit characteristics (bright light-yellow deposits).

The addition of  $\text{Na}_2\text{SO}_3$  to the bath changed the bath color from yellow to colourless and the aspect of the voltammogram, as shown in Figure 2a, due to the complexation gold-sulfite ( $[\text{AuSO}_3]^-$  and  $[\text{Au}(\text{SO}_3)_2]^{3-}$ ).<sup>1</sup> Now, the beginning of the reduction changes to approximately  $-600 \text{ mV}_{\text{Ag/AgCl}}$ , possibly due to a different surface conditioning promoted by sulfite. Also, it is observed a cathodic peak, indicated by a dashed arrow at  $-950 \text{ mV}_{\text{Ag/AgCl}}$ . This cathodic peak suggests a diffusion limiting current,<sup>23</sup> possibly due to reduction of Au(I)-sulfite complex ions.



**Figure 2.** Cyclic voltammograms recorded at  $1 \text{ mV s}^{-1}$  for Au electrode in  $5 \text{ g L}^{-1} \text{ KAuCl}_4$  with  $60 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$  and,  $5 \text{ g L}^{-1} \text{ KAuCl}_4$  with  $60 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$  and  $10 \text{ mL L}^{-1} \text{ HCHO}$

On the other hand, the values of the achieved current density (at  $-1200 \text{ mV}_{\text{Ag/AgCl}}$ ) are ten times lower than that for the bath with only  $\text{KAuCl}_4$  and  $\text{HCHO}$ . The complexation of sulfite ion with Au(I) decreases the content of free Au(I) and diminishes the current and deposition rate of metal. Possibly, the Au(I)-sulfite complex, due its higher energetic barrier, decreased the maximum current density, which meant lower deposition rate and better quality of deposition to obtain a better deposit with high deposition rate.<sup>24</sup>

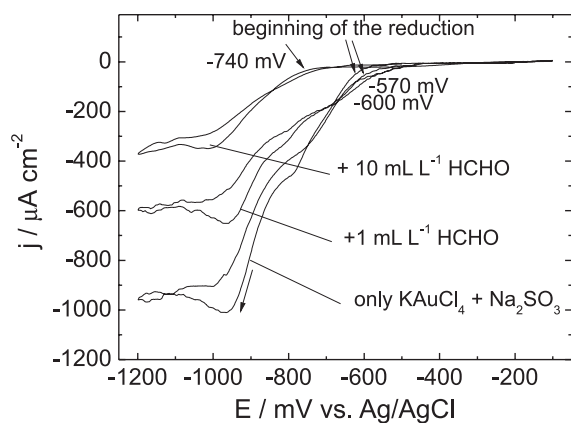
The adherence of deposits obtained from baths containing only  $\text{KAuCl}_4$  are poor (qualitatively evaluated using a sellotape), mainly because of the high deposition rate. The addition of sodium sulfite to the Au bath improves the adherence, which is kept after the addition of formaldehyde.

The influence of oxygen in the solution containing gold, sulfite and formaldehyde was also investigated. After purge, the voltammogram presented a slight improvement in the current density achieved at the peak, indicating that the presence of oxygen reduces the efficiency of gold deposition from this solution.

The addition of formaldehyde in the Au(I)-sulfite solution reduces the maximum of current achieved during the voltammetry (Figure 3), which justify the decreasing of the areal concentration. The reduction of the current permits a better control of the gold deposition, with deposits thinner and flatter. The potential which the deposition begins are also changed, this is to say, they are approximately  $-570$  and  $-740 \text{ mV}_{\text{Ag/AgCl}}$  for  $1 \text{ mL L}^{-1}$  and  $10 \text{ mL L}^{-1}$  of formaldehyde, respectively.

### RBS analysis and SEM images

Considering the results obtained through cyclic voltammetry, electrodepositions were carried out with the baths containing  $5 \text{ g L}^{-1} \text{ KAuCl}_4$ ,  $60 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$  and  $1$  and  $10 \text{ mL L}^{-1}$  of  $\text{HCHO}$ , at  $-800 \text{ mV}_{\text{Ag/AgCl}}$  during 30 min. This potential was elected because it is a middle point between the base line and the cathodic peak in the voltammogram, which should avoid achieve any reduction reaction associated to the cathodic peak.

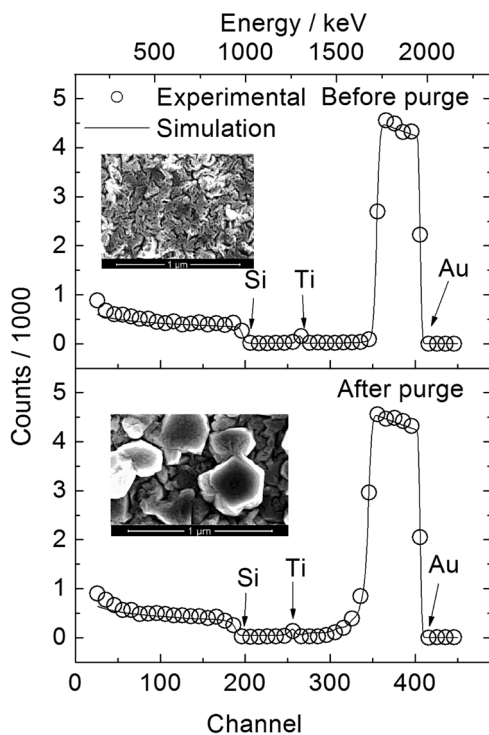


**Figure 3.** Cyclic voltammograms recorded at  $1 \text{ mV s}^{-1}$  for Au electrode after 30 min  $\text{N}_2$  purge, for solution containing  $5 \text{ g L}^{-1} \text{ KAuCl}_4$  and  $60 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$ , and after addition of  $1 \text{ mL L}^{-1}$  formaldehyde and  $10 \text{ mL L}^{-1}$  formaldehyde

The values of areal concentration and roughness from all the samples obtained through RBS are in Table 1.

From the bath containing  $1 \text{ mL L}^{-1}$ , the RBS results indicated that the areal concentration of the deposit decreased with the  $\text{N}_2$  purge and or the presence of  $\text{O}_2$  (without purge) contributes to improve the deposition, increasing the areal concentration of the deposited layer. The roughness is lower for the deposit obtained before purge and higher after the purge, as indicated in Table 1, probably due to a change in the deposition rate, which was confirmed in the FESEM images of these deposits.

Figure 4 presents the RBS results for the bath containing  $10 \text{ mL L}^{-1}$ . The increase in the HCHO concentration decreased the areal concentration achieved in the deposits, around 3.2 times compared to the bath containing  $1 \text{ mL L}^{-1}$  of HCHO and the roughness was also reduced.



**Figure 4.** RBS spectrum and FESEM surface images of electrodeposits obtained from electrodeposition at  $-800 \text{ mV}_{\text{Ag/AgCl}}$  during 30 min in  $5 \text{ g L}^{-1} \text{ KAuCl}_4$ ,  $60 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$  and  $10 \text{ mL L}^{-1}$  formaldehyde, before and after  $\text{N}_2$  purge during 30 min

FESEM images of the deposits from solution containing  $10 \text{ mL L}^{-1}$  of HCHO are shown in Figure 4. The deposit aspect before the purge is flatter, however, after the purge, the current density increased, and whiskers were observed on the surface (Figure 4b). The formation of whiskers is a typical indicator of the increase of the current density.<sup>25</sup> In this case, the current achieved after purge in  $\text{N}_2$  should be closer to the limiting current for whisker formation.<sup>25</sup> In addition, whiskers were also observed for baths containing  $1 \text{ mL L}^{-1}$  due to higher current density (before and after purge) at  $-800 \text{ mV}_{\text{Ag/AgCl}}$ .

## CONCLUSION

It was investigated the influence of formaldehyde on the stability of Au(I)-sulfite baths and its role on the growth characteristics of the electroplated gold. The most stable gold bath was obtained for  $10 \text{ mL L}^{-1}$  of formaldehyde,  $5 \text{ g L}^{-1}$  of  $\text{KAuCl}_4$  and  $60 \text{ g L}^{-1}$  of  $\text{Na}_2\text{SO}_3$ , without any precipitation for time intervals higher than 600 days. That superior lifetime is possibly due to the additional complexation of formaldehyde with sulfite ions in the baths.

From cyclic voltammograms (CV), it was observed for  $\text{KAuCl}_4$ -only or  $\text{KAuCl}_4$ - $\text{Na}_2\text{SO}_3$  baths that the higher the concentration of both formaldehyde and dissolved  $\text{O}_2$ , the lower the electrodeposition current density and, the thinner and the flatter are the deposits.

In addition, RBS analysis revealed that the thinnest and the flattest deposits were obtained for baths containing  $10 \text{ mL L}^{-1}$  of formaldehyde,  $5 \text{ g L}^{-1}$  of  $\text{KAuCl}_4$  and  $60 \text{ g L}^{-1}$  of  $\text{Na}_2\text{SO}_3$  and FESEM images showed that the nitrogen purge of the bath promotes the appearance of "whiskers" on the surface of the deposits, which can be made responsible for the increase of the surface roughness.

## ACKNOWLEDGMENTS

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