Potentiostatic Electrodeposition of Au-Sn Alloys from a Non-Cyanide Bath for Soldering: Influence of Reagents Concentrations

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ABSTRACT

This work presents an extensive study of a non-cyanide Au-Sn bath to obtain potentiostatically deposited Au-Sn alloys. In addition, Au-Sn bath speciation was studied through a program for chemical equilibrium simulation (CHEAQS Pro) and the electrochemical mechanisms were investigated using Cyclic Voltammetry (CV). Also, Rutherford Backscattering Spectroscopy (RBS) was used to determine the deposits characteristics and composition. Some recipes using different concentrations of ammonium citrate, SnCl₂ and Na₂SO₃, and L-ascorbic acid presented the formation of colloidal gold during the electrodeposition processes. The incorporation of tin in the deposits obtained varied from 2 to 16 atomic % (at%).

Index Terms: Gold-tin alloy, Electrodeposition, RBS analysis, Chemical simulation.

1. INTRODUCTION

Gold-tin (Au-Sn) solders have been widely used in the optoelectronics and microelectronics industry. Some applications of Au-Sn alloys are flip chip package [1, 2], optical packages [2, 3], optical fiber feedthrough joint [4], and die-attachment for ASIC (Application-Specific Integrated Circuit) [2]. Their passive alignment characteristic, good thermo-mechanical behavior, fluxless soldering capability, suitable thermal conductivity and thermal expansion coefficient, as well as leadfree feature make the Au-Sn solders suitable for high temperature applications [5]. Although its higher price, a comparison with others lead-free solders, as Zn-Sn and bismuth alloys, indicates that Au-Sn presents a superior fatigue resistance [2]. In addition, its comparatively low eutectic temperature of 278 °C, relative to other hard solders such as Au-Ge and Au-Si, makes it ideally suited for temperature sensitive applications [1]. Conventionally, most Au-Sn alloys are deposited either as solder preforms or via vacuum deposition techniques, such as sputtering or evaporation [2, 5]. The disadvantages of those techniques are: difficult alignment, poor thickness control, easy oxidation (preforms), and the required expensive equipments (vacuum deposition). An alternative technique, which combines the process control capability with the relatively low cost of preforms, is the electrodeposition.

Electrodeposition of an alloy solder can be done either sequentially, using separate Au and Sn baths, or simultaneously from a single bath. An electroplating process for simultaneously depositing Au-Sn alloys from non-cyanide baths has been developed by Sun and Ivey [6] and Funaoka et al. [7]. An advantage of these co-electrodeposition processes is that Sn oxide formation, which can occur during sequential electrodeposition, can be prevented. However, one of the main challenges of depositing Au-Sn alloys is the plating bath stability, once baths currently have a useful lifetime of 2 or 3 days. Keeping Au and Sn separated in two different solutions can extend the lifetime of the bath. The mixture can be done just before use with the reducing agent, increasing the stability to 12 months [8].

The use of sulfite as a complexing agent for gold plating baths is common in studies of cyanide-free baths. The Au¹⁺-sulfite bath is unstable, justified by a disproportional reaction from Au³⁺ and metallic Au, which cause the bath decomposition spontaneously on standing by condition [9, 10]. This instability can be overcame if all the gold ions are complexed, and the use of ammonium citrate, which complex gold ions in the forms Au(NH₃)₂⁺ (K = 27mol L⁻¹ [11]) and Au(NH₃)₄³⁺ (K = 30mol L⁻¹ [11]), contributes to stabilizes the bath.

The production of colloidal gold is undesirable in gold plating since particles tend to be included in the deposit and promote the formation of nodules. The concentration of Au^{1+} is therefore dependent on both, the amount of free sulfite and also on the magnitude of the stability constant of Au¹⁺, and tends to increase as the pH is lowered [9].

The addition of sulfite in a gold solution also reduces the deposit thickness and roughness. It occurs because the deposition of a metal from a complexed ion requires more energy to promote the nucleation of the film [12].

Others additives are usually found in electrodeposition baths to increase the bath stability or improve some deposits characteristics. The L-ascorbic acid used in Au-Sn baths prevents Sn hydrolysis [6], and it also acts as reducing agent of Au [13]. Ammonium citrate is used to prevent Au hydrolysis [6], as buffer [6] and as complexing agent of Sn and Au [11, 14].

The tin deposition from Sn^{2+} salt occurs from acid baths. The deposition of tin from a chloride-only solution results in non-uniform deposits with poor adherence. The addition of organic additives improves the deposit quality, but is usually difficult to control its reproducibility. However, the addition of only ammonium citrate to the stannous chloride bath complexes the Sn^{2+} and results in flat, uniform and with good adherence deposits [15].

The gold-tin alloy deposition is possible, although the redox potentials are different, because of diminishing of the Au deposition potential, by the gold complex, to a value close to the Sn. Accordingly, the composition of the alloy is dependent on the applied potential. The study of the gold-tin bath is going to define the potentials and the compositions of the alloy.

In this paper, we present the study of a noncyanide Au-Sn bath with good stability to obtain potentiostatically deposited Au-Sn alloys. In addition, Au-Sn bath speciation was also investigated through a program for chemical equilibrium simulation (CHEAQS Pro) and the electrochemical reactions were obtained with the aid of Cyclic Voltammetry (CV). Also, Rutherford Backscattering Spectroscopy (RBS) was used to determine the deposits composition and thickness with SIMNRA 6.04 [16].

2. Au-Sn BATH SPECIATION SIMULATION

In this analysis, the equilibrium activities of gold and tin complexes were calculated using the CHEAQS Pro 2008.1 [17]. This is a general-purpose program for solving chemical equilibria in aqueous solution. The stability constants for the bath parts were included in its library to perform the calculations. These stability constants were adopted from the literature [9, 11, 13, 14, 16-19] and the simulation results, as well as cyclic voltammetry, were used to establish the possible electrochemical reaction.

From bath speciation simulation, activity of each ion in solution was obtained. Activity defines the

availability of an ion as its concentration multiplied by the activity coefficient [20] and can be explained taking into account that the ions present in an electrolytic solution interact with each other, and this interaction changes the availability of the ions to participate in a given electrochemical reaction. From this point of view, the bath concentrations of the ions do not reflect the real reactivity of them. Based on the obtained activity, oxidation and reduction potentials were obtained with the aid of the Nernst equation [20] in order to compare to the values as extracted from cyclic voltammetry (CV).

3. EXPERIMENTAL DETAILS

Solutions were prepared from chemicals of analytical grade or better, and Milli-Q deionized water (18.2 M Ω cm), using potassium tetrachloroaurate (III) (KAuCl₄), sodium sulfite anhydrous (Na₂SO₃), ammonium citrate ((NH₄)₂HC₆H₅O₇), L-ascorbic acid (H₂C₆H₆O₆), and stannous chloride (SnCl₂ . 2 H₂O). All solutions were fresh, and agitated using a stirrer.

The Na₂SO₃, added to the KAuCl₄ bath, complexes Au³⁺ ions, and reduces it to Au¹⁺ by forming AuSO₃⁻ (K = 12.3mol L⁻¹ [9]) and Au(SO₃)₂³⁻ (K = 26.8mol L⁻¹ [9]) species, and changes the bath color from yellow to colorless . The formation of the complexes is guaranteed by adding the reagents in the following sequence: gold solution (KAuCl₄, Na₂SO₃ and L-ascorbic acid), tin solution (ammonium citrate, SnCl₂), then, these two solutions were mixed.

The pH was measured using pH tapes. All the experiments were performed at room temperature $(25^{\circ}C \pm 2^{\circ}C)$.

The working electrode (or cathode) employed in the electrodepositions was a metalized Si wafers with evaporated Ti and Au layers, 17.5 and 122.8 nm thick, respectively. Ti was deposited in order to promote Au adherence onto Si and Au was used as starting surface due to its high electrochemical oxidation potential (E^0 > 1000 mV_{SHE}, the standard hydrogen electrode), which prevents the bath contamination with foreign materials when inserted in the bath. The area of the electrode exposed to the solution was 1x1 cm², delimited with an insulate tape (Scotch, 3M).

Electrochemical studies and film deposition were made using a potentiostat (PGSTAT302N, Autolab) in the three-electrode configuration. The reference electrode was a silver-silver chloride electrode (Ag/AgCl, E = $0.210 V_{SHE}$). The cyclic voltammetry was recorded using a Pt planar electrode from BAS as working electrode.

Potential ranged during the cyclic voltammetry from 200 to $-1000 \text{ mV}_{Ag/AgCl}$, cycled at 50 mV s⁻¹. The electrodeposition processes were limited in 30 min, during constant agitation. This study included baths with different concentration of ammonium citrate (200, 150, 100, 50 g L⁻¹), L-ascorbic acid (30, 15, 7.5, 3.75 g L⁻¹), SnCl₂ (2.5, 5, 10, 20 g L⁻¹), and Na₂SO₃ (120, 90, 60, 30g L⁻¹). Potentiostatic electrodepositions were performed at $-400, -500, -600, \text{ and } -700 \text{ mV}_{Ag/AgCl}$.

The simulations of RBS spectra considered the initial thicknesses of silicon, titanium, and gold from the working electrode.

4. RESULTS AND DISCUSSION

The pH of the gold-tin baths was around 5.0 and remained at this value due the high concentration of ammonium citrate. The pH of the KAuCl₄-only solution was 3.0. If Na₂SO₃ is added to the KAuCl₄ solution, pH was increased to around 9.0 and, by adding L-ascorbic acid to the KAuCl₄-Na₂SO₃ solutions, pH was about 7.0. Also for SnCl₂-only solution, pH was around 2.0. As a result, it is possible to infer that the KAuCl₄-Na₂SO₃ solution presented higher pH due to sulfide, which produces a weakly OH-species in water medium (hydrolysis).

A. Cyclic Voltammetry and Simulation

Figure 1 shows the cyclic voltammogram of a typical Au-Sn bath, a bath containing KAuCl₄ (5 g L⁻¹), S_nCl_2 (5 g L⁻¹), ammonium citrate (200 g L⁻¹), sodium sulfite (60 g L⁻¹), and L-ascorbic acid (15 g L⁻¹), at 50 mV s⁻¹, and using Pt working electrode. It was noteworthy that the reduction peak corresponds to both depositions of gold and tin, indicated by an arrow labeled cathodic peak (centered at -700 mV_{Ag/AgCl}, with start at -450 mV_{Ag/AgCl}). The reduction potential for Au¹⁺ (simulated activity of 3.974 10⁻²⁷ mol L⁻¹), cal-



Figure 1. Cyclic voltammogram from a bath containing KAuCl₄ (5 g L⁻¹), SnCl₂ (5g L⁻¹), ammonium citrate (200 g L⁻¹), sodium sulfite (60 g L⁻¹), and L-ascorbic acid (15 g L⁻¹), at 50 mV s⁻¹, and using Pt working electrode.

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culated through Nernst equations for AuCl₂- (E⁰ = 1150 mV_{NHE}) was -460 mV_{Ag/AgCl}, which is very close to the reduction start point obtained from CV. The complexation with sulfite and ammonium changes extends the reduction in a large negative range from -450 to -900 mV_{Ag/AgCl}, centered at -700 mV_{Ag/AgCl} [21]. In addition, the reduction of Sn²⁺ occurs at a potential close to that of Au¹⁺. Using Nernst equation, the reduction potential was -407 mV_{Ag/AgCl} for Sn²⁺ (simulated activity of 9.795 10⁻³ mol L⁻¹) with E⁰ of -137.5 mV_{NHE}. As the Sn²⁺ is also complexed (in the form Sn(C₆H₅O₇)⁻, K = 7.65mol L⁻¹ [14]), its reduction potential possibly follow the same behavior of Au¹⁺.

The oxidation peak can be observed centered at $-128 \text{ mV}_{Ag/AgCl}$ arrow labeled anodic peak, probably due to the oxidation of L-ascorbic acid.

The changes occurred at the electrode surface during oxidation moved the reduction peak slightly to a higher potential at the second cycle (from -700 to $-680 \text{ mV}_{Ag/AgCl}$). The electrode surface became dark gray, corresponding to the deposition of gold-tin alloy. Reduction of hydrogen was verified to occur for potentials higher than $-870 \text{ mV}_{Ag/AgCl}$ in the voltammogram, but no visible bubbles formation was observed.

During the cyclic voltammetry, it was also observed the formation of a brown powder at the electrode surface. This powder, known as a colloidal gold [13, 22, 23], occurred because of the reduction of gold close to the electrode surface, but not close enough to be incorporated in the electrodeposited film. The exchange current rate was possibly sufficiently high that the reduced gold was not incorporated in the film. A similar phenomenon was observed in literature [24]. The observed color corroborates that the composition of the powder may be mainly gold. The colloidal formation should be prevented during the electrodeposition processes, in order to avoid the lost of material, bath degradation, and the incorporation of reduced gold at the film, degrading its density and homogeneity.

A new bath was prepared, removing the SnCl₂, and a cyclic voltammetry was done to confirm if the colloidal formation occurred because of the gold. Again, it was observed the colloidal formation.

The simulation of ionic Au species in the goldtin bath suggests that precipitation of gold may occur spontaneously in bath, for all concentrations studied, as showed in figure 2. This fact can be explained as follows: the addition of ammonium citrate or ascorbic acid to the bath increase the activity of $Au(NH_3)_{2^+}$, due to the disproportion in NH_3 - Au^{1+} equilibrium. Similarly, $AuCl_2$ - activity is increased with the addition of $SnCl_2$, and all Au species have their activity increased (not shown). On the other hand, addition of Na_2SO_3 induced a decrease of all Au species activi-



Figure 2. Simulations of Au species in Au-Sn baths, changing concentration of (a) ammonium citrate (50 to 200 g L⁻¹), (b) L-ascorbic acid (3.8 to 30 g L⁻¹), (c) SnCl₂ (2.5 to 20 g L⁻¹), and (d) Na₂SO₃ (30 to 120 g L⁻¹), using CHEAQS Pro.

ties, due to the disproportion in Au¹⁺ complexes equilibrium, which favors the reduction of Au species. All the thickness and percentage of tin obtained are shown at table I.

Figure 4 shows the influence of ammonium cit-

The simulation of ionic Sn species in the goldtin bath, showed in figure 3, indicated that the predominant species in the Au-Sn bath are SnCl-, Sn²⁺ and SnCl_{2(aq)}. The increase in ammonium citrate concentration increases the relative activity of these Sn species, while slight increase can be observed with the increase of L-ascorbic concentration. The increase of the SnCl₂ concentration, however, decrease the relative amount of SnCl⁺ and Sn²⁺, and increase activity of SnCl_{2(aq)} more than the others reagents. Finally, the increase of the Na₂SO₃ concentration presents an opposite action compared to the increase of the SnCl₂ concentration, increasing the activity of SnCl⁺ and Sn²⁺ and decreasing the activity of SnCl_{2(aq)}.

B. RBS Study of Deposits' Composition

Potentiostatic electrodepositions were carried out based on the cyclic voltammetry. As shown, it was identified the contribution of each reagent of the bath to the deposit characteristics. The potential suitable for potentiostatic electrodeposition was defined considering the middle point between the minimum and maximum value of current achieved in the cyclic voltammogram of the corresponding solution during reduction ($-500 \text{ mV}_{Ag/AgCl}$). rate concentration in the gold-tin alloy deposited during 30 min. Maximum areal concentration (see table I) was achieved when the concentration of ammonium citrate was 150 g L⁻¹, and the maximum tin atomic percentage was achieved for 100 g L⁻¹. The lower conof ammonium centration citrate $(50 \text{ g } \text{L}^{-1})$ reduces both the thickness and the relative amount of tin in the alloy, as indicated. The colloidal formation was only observed for 200 g L⁻¹ of ammonium citrate. The addition of ammonium citrate is important as a buffer agent, and also due to the formation of complex Au1+ with ammonium, which decreases its exchange current (i_0) , and produces deposits thinner and less rough, as inferred from RBS in figure 4. However, the citrate presence presents an unwanted effect if the concentration is high. The contribution of citrate in the formation of colloidal gold was already identified [23], and it seems to occur for concentration over 150 g L⁻¹.

Figure 5 shows the influence of L-ascorbic acid concentration in the gold-tin alloy deposited during 30 min. Maximum areal concentration and atomic percentage (see table I) of tin were achieved when the concentration of L-ascorbic acid was 3.8 g L⁻¹, however the deposit presented a non-uniform interface between the



Figure 3. Simulations of Sn species in Au-Sn baths, changing concentration of (a) ammonium citrate (50 to 200 g L⁻¹), (b) L-ascorbic acid (3.8 to 30 g L⁻¹), (c) SnCl₂ (2.5 to 20 g L⁻¹), and (d) Na₂SO₃ (30 to 120 g L⁻¹), using CHEAQS Pro.

deposit and the electrode that can be seen in the RBS profile, indicated by the arrow labeled deposit alectrode interface. The increase of the L-ascorbic acid concentration decreases this effect, and also the thickness and atomic percentage of tin. The presence of L-ascorbic acid in this solution decreases the reduction of hydrogen, due to the ascorbate strong adsorbition on the electrode surface [25]. The non-uniform interface at low concentration seems to be because of the less adsorption of the ascorbate at the electrode surface.

Another evaluated parameter was the influence of the concentration of the $SnCl_2$ in the bath and the tin amount in the alloy. The results are presented in figure 6. No colloidal formation was observed for concentrations above 10 g L⁻¹. From the speciation simulations, the increase of $SnCl_2$ concentration increases the presence of Cl⁻ in the bath, which complex the Au¹⁺ and prevents the formation of colloidal Au. The increase of $SnCl_2$ concentration in the bath slightly increases the concentration of tin in the deposit. At 2.5 g L⁻¹ of $SnCl_2$, the deposit-electrode interface also presents a non-uniform interface. The non-uniform interface at low concentration seems to be due to the less adsorption of the chloride at the electrode surface [26].

Following, Na₂SO₃ was evaluated to identify the influence of its concentration in the bath, and the results are presented in figure 7. No colloidal formation was observed for concentrations of 30, 90 and 120 g L⁻¹. Also, from the speciation simulation, higher values of Na₂SO₃ (90 and 120 g L⁻¹) increased the presence of

 SO_3^{2-} in the bath, which complex the Au¹⁺ and prevent the formation of colloidal Au, similarly as Cl⁻. In contrast, the lower concentration (30 g L⁻¹) do not present a clear effect responsible of avoiding colloidal Au formation. In

TABLE I. Areal concentration and relative concentration of tin related to the ammonium citrate, L-ascorbic acid, $SnCl_2$, Na_2SO_3 concentrations, and potential of deposition.

	Concentration (g L ⁻¹)	Areal (10 ¹⁵ at . cm ⁻²)	at.% Sn at. % Sn	Colloidal Au
Ammonium				
citrate	50	515	1	No
	100	1710	12	No
	150	2050	8	No
	200	920	8	Yes
L-ascorbic				
acid	3.8	2600	16	Yes
	7.6	2110	11	Yes
	15	920	8	Yes
	30	1580	5	Yes
SnCl ₂	2.5	1490	10	Yes
-	5	920	8	Yes
	10	3780	11	No
	20	2330	14	No
Na ₂ SO ₃	30	3250	10	No
	60	920	8	Yes
	90	1470	6	No
	120	2100	2	No
	mV _{Ag/AgCI}	Areal	at.% Sn	Colloidal
	5 0	concentration		Au
		(101º at. cm²²)		
Potential	-400	990	3	No
	-500	920	8	Yes
	-600	1700	8	Yes
	-700	1500	14	Yes

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Figure 4. RBS spectra of samples electrodeposited in tin-gold baths containing 200 g L⁻¹, 150 g L⁻¹, 100 gl⁻¹ and 50 g L⁻¹ of ammonium citrate, KAuCl₄ (5 g L⁻¹), SnCl₂ (5 g L⁻¹), L-ascorbic acid (15 g L⁻¹) and Na₂SO₃ (60 g L⁻¹), at –500 mV_{Ag/AgCl}, during 30 minutes.



Figure 6. RBS spectra of samples electrodeposited in tin-gold baths containing 2.5 g L⁻¹, 5 g L⁻¹, 10 g L⁻¹ and 20 g L⁻¹ of SnCl₂ (5 g L⁻¹), ammonium citrate (150 g L⁻¹), L-ascorbic acid (15 g L⁻¹) and Na₂SO₃ (60 g L⁻¹), at –500 mV_{Aq/AqCl} during 30 minutes.

this case, simulations showed the lowest ionic strength (Fi) if compared with other concentrations (2.58, 2.77, 2.96, L⁻¹,respectively to 30, 60, 90, 120mol L⁻¹ of Na₂ SO₃), which means decrease in the diffusion of ionic species to the electrode-solution interface. This effect could avoid the formation of colloidal gold, although the deposit became non-uniform and porous. The increase in Na₂SO₃ concentration decreases the concentration of tin incorporated at the deposit. This effect should be related to the complexation of SO₃²⁻, indicated in the following reaction [18]:

 $SO_3^{2-} + 2 OH^- = SO_4^{2-} + H_2O + 2e^-, E_{red}^0 = -0.93 V_H$

The last evaluated parameter was the deposition potential. Considering the cyclic voltammogram of the deposition bath, shown in figure 1, it was defi-



Figure 5. RBS spectra of samples electrodeposited in tin-gold baths containing 30 g L⁻¹, 15 g L⁻¹, 7.6 g L⁻¹ and 3.8 g L⁻¹ of L-ascorbic acid, KAuCl₄ (5 g L⁻¹), ammonium citrate (150 g L⁻¹), SnCl₂ (5 g L⁻¹) and Na₂SO₃ (60 g L⁻¹), at -500 mV_{Ag/AgCl}, during 30 minutes.



Figure 7. RBS spectra of samples electrodeposited in tin-gold baths containing 30 g L⁻¹, 60 g L⁻¹, 90 g L⁻¹ and 120 g L⁻¹ of Na₂SO₃, KAuCl₄ (5 g L⁻¹), SnCl₂ (5 g L⁻¹), ammonium citrate (150 g L⁻¹), and L-ascorbic acid (15 g L⁻¹) at -500 mV_{Ag/AgCl} during 30 minutes.

ned potentials in the regions where the deposition occurs. The deposition potentials chosen were -400, -500, -600 and $-700 \text{ mV}_{Ag/AgCl}$. Then, with the aid of RBS, it was evaluated the thickness and alloy composition of the obtained films for fixed potentials (figure 8). The results are also presented in table I.

Only the depositions at $-400 \text{ mV}_{Ag/AgCl}$ did not result in colloidal Au formation, due to the low current achieved, which means surface limited reaction. The atomic percentage of tin increase with the potential increase, and this is because the lower addition of gold in the deposit and more colloidal gold formation. The deposits obtained in -600 and -700 mV_{Ag/AgCl} presented a non-uniform interface between the deposit and the electrode that can be seen in the RBS profiles, indicated by arrows labeled Deposit electrode interface.



Figure 8. RBS spectra of samples electrodeposited at -400 mV_{Ag/AgCl}, -500 mV_{Ag/AgCl}, -600 mV_{Ag/AgCl}, and -700 mV_{Ag/AgCl} in tin-gold baths containing KAuCl₄ (5 g L⁻¹), SnCl₂ (5 g L⁻¹), ammonium citrate (200 g L⁻¹), L-ascorbic acid (15 g L⁻¹) and Na₂SO₃ (60 g L⁻¹), during 30 minutes.

5. CONCLUSIONS

We presented the study of a non-cyanide Au-Sn bath to obtain a potentiostatically deposited Au-Sn alloy. The formation of colloidal gold was verified during the cyclic voltammogram and some electrodepositions. The spontaneous reduction of gold was predicted during the simulation of the bath, however, the bath presented good stability during electrodepositions for 50 to 150 g L-1 of ammonium citrate, 10 and 20 g L⁻¹ of SnCl₂, 30, 90 and 120 g L⁻¹ of Na_2SO_3 (deposited at -500 mV_{Ag/AgCl}) and deposition potential at -400 mV. L-ascorbic acid concentration, among the values studied, did not prevent colloidal gold formation. The amount of tin incorporated at the deposits obtained are limited between 2 and 16 atomic %. It was possible to change deposits thickness and the percentage of tin incorporated by varying the deposition potential. As a result, potentiostatic electrodeposition of Au-Sn alloys from a non-cyanide bath for soldering were obtained, with best condition (no colloidal formation and highest atomic percentage of tin) for the bath containing 200 g L⁻¹ ammonium citrate, 15 g L⁻¹ L-ascorbic acid, 20 g L⁻¹ of SnCl₂, 60 g L⁻¹ of NaSO₃, 5 g L⁻¹ KAuCl₄, electrodeposited at $-500 \text{ mV}_{\text{Ag/AgCl}}$.

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