Electroless Gold Plating Using L-cysteine as Reducing Agent & its Deposition Mechanism

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Electroless gold plating was studied in a solution containing a mercaptosuccinic acid complex, with L-cysteine used as a reducing agent. This process contains no cyanides while operating at a neutral pH. The autocatalytic process produced a smooth, dull-to-lustrous gold film. Even at nickel contamination levels up to 100 ppm, the bath neither decomposed nor developed an indication of turbidity. A study of the deposition mechanism for this bath is also given in this paper.

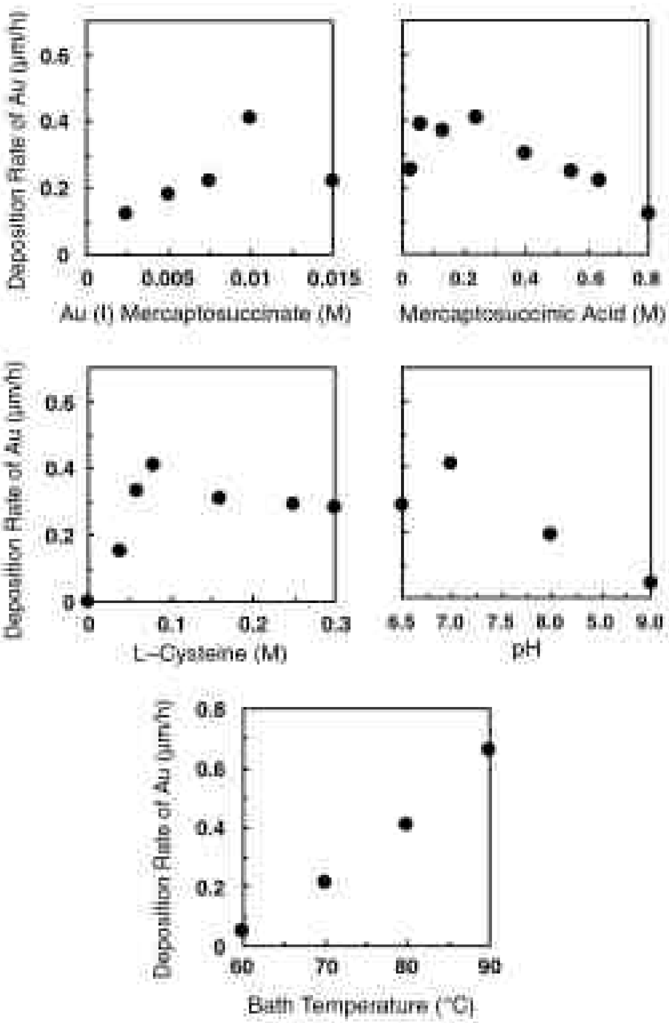

Fig. 1—Effects of bath components and plating conditions on the deposition rate.

Gold deposits have excellent physical properties, including electrical conductivity and solderability. In terms of chemical properties they exhibit excellent resistance to acid and other chemicals. Consequently, gold plating is used in connectors on printed circuit boards, ceramic IC packages and semiconductor devices. The gold electroplating process has been primarily used in such electronic applications. The current trend is toward packing more and more circuit elements in smaller and smaller spaces. Accordingly, it has become very difficult to plate the gold on such electronic parts by electroplating. Because the electroplating process lacks uniformity of current distribution, it is difficult to obtain uniform thicknesses on such complicated shapes. Such problems call for the use of electroless gold plating.

The electroless gold plating bath most commonly used to date has a high pH, with potassium dicyanoaurate(I) used as the metal salt, potassium cyanide as the complexing agent and DMAB as the reducing agent.[1] The gold film obtained from such a bath generally satisfies the requirements for the electronic parts referred to above. As a result, the cyanide type bath is still in widespread use. The cyanide bath, however, is highly toxic, leading to concerns about the working environment. Operation at such a high pH, moreover, can erode the resist used for masking. Furthermore, the bath is highly sensitive to nickel contamination. Given all of this, a stable and neutral electroless gold bath has long been desired. A cyanide-free bath has been reported by Ushio,[2] Katoh[3] and Shindoh, et al.[4] Their baths used gold sulfite or thiosulfate as chelating agents, and amine borane, thiourea or ascorbic acid as reducing agents.

Nuts & Bolts: What This Paper Means to You

This work represents progress toward a cyanide-free, neutral electroless gold plating solution. This process involves a solution containing a mercaptosuccinic acid complex, with L-cysteine used as a reducing agent. The autocatalytic process produced a smooth, dull-to-lustrous gold film. Even at nickel contamination levels up to 100 ppm, the bath neither decomposed nor developed an indication of turbidity. A study of the deposition mechanism for this bath is also given in this paper.

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Table 1
Basic Bath Composition & Plating Conditions

Au(I) Mercaptosuccinate	0.01 mol/L
Mercaptosuccinic acid	0.27 mol/L
L-cysteine	0.08 mol/L
Potassium dihydrogen phosphate	0.15 mol/L
pH @ 25°C (78°F)	7.0
Temperature	80°C (176°F)
pH adjustment	KOH

We have studied an electroless gold plating bath with ethanethiols used as complexing and reducing agents. An electroless gold plating process with mercaptosuccinic acid (MS) as a complexing agent and L-cysteine or 2-aminoethanethiol as a reducing agent has shown excellent stability, allowing gold to deposit autocatalytically even at neutral pH.[5,6] This bath, moreover, was not observed to decompose or to decrease the deposition rate remarkably when subject to nickel contamination above 100 ppm.

The work reported here was intended to establish the plating bath composition and operating conditions that permitted autocatalytic gold deposition with this process chemistry. We also studied the gold deposition mechanism, using colorimetry, DC-polarography and potential scanning methods.

Experimental

Deposition Rate & Surface Morphology

Table 1 shows the basic plating bath composition and operating conditions. Auric mercaptosuccinate (I) was used as the metal salt. Mercaptosuccinic acid and L-cysteine were used as complexing and reducing agents, respectively. Both were commercially available, special-class reagents. Potassium dihydrogenphosphate was used as a buffer while the pH was adjusted with potassium hydroxide. The choice of a chelating agent was based on the theory of hard and soft acids and bases.[7] In other words, Au^+, which is a soft Lewis acid, readily forms coordination compounds with the soft Lewis bases, R_2S, RSH and RS^-.

The plating substrate (10 x 10 x 0.5 mm; 0.39 in. x 0.39 in. x 20 mil) employed was a gold plate degreased by cathodic electrolysis. The deposition rate was based on the weight change before and after plating, i.e., after immersion in the electroless gold plating bath for a specified time. The surface morphology of the deposit was examined with a scanning electron microscope (SEM).

Deposition Mechanism Study

A Double-beam spectrometer[**] was used to colorimetrically determine the complex composition of auric mercaptosuccinate.

In order to clarify the electroless plating deposition mechanism, it is generally necessary to measure the rate at which the metal is deposited, the rate at which hydrogen gas is generated and the rate at which the reducing agent is oxidized. In such a bath as reported here, where ethanethiols are applied as both complexing and reducing agents however, it is difficult to separate and estimate them. The gold deposition mechanism, therefore, was electrochemically studied by DC-polarographic and potential-scanning methods. In DC-polarography, a dropping mercury electrode[***] was used as the working electrode and a mercury pool was used as the counter-electrode, with a silver-silver chloride electrode (3.3 mol/L KCl) applied as a reference electrode.

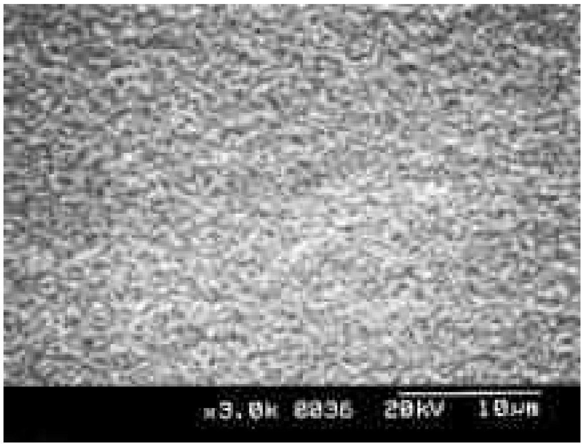

Fig. 2—Surface morphology of a thick gold film (2 μm; 79 μ-in.).

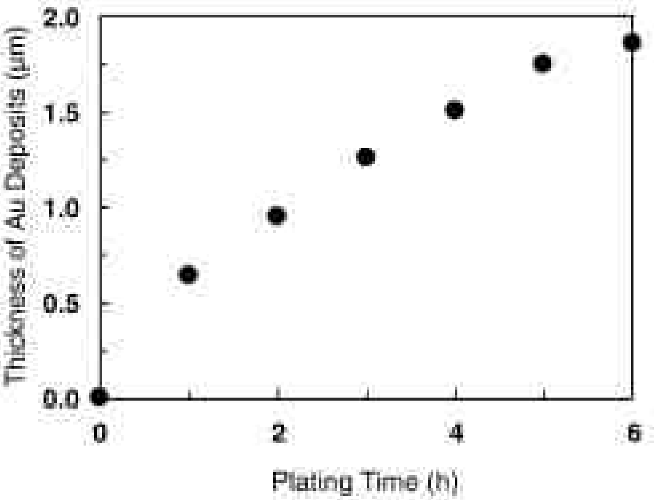

Fig. 3—Relation between plating time and gold deposit thickness.

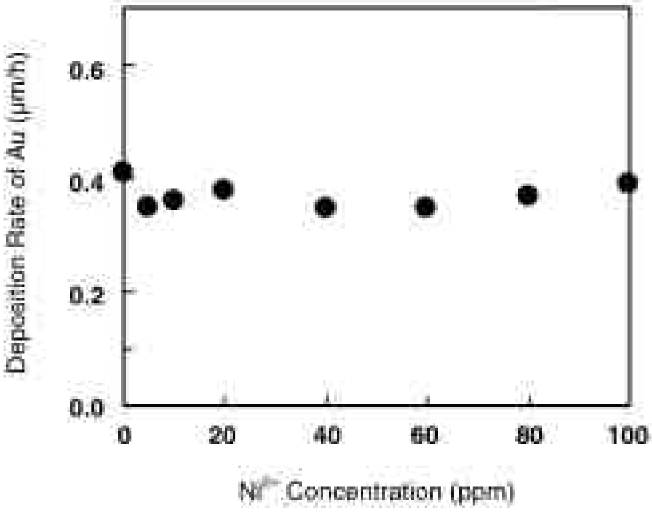

Fig. 4—Effect of nickel ion concentration on the deposition rate.

An electrochemical measurement system[****] was used to determine the polarization curves by the potential scanning method, with a scanning rate of 10 mV/s. The working electrode was a platinum disc electrode embedded in a Teflon holder. Whenever a polarization curve was run, the bath (25°C; 77°F) which had L-cysteine removed from the bath (Table 1) was used after electroplating

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[**] *Model U-2000A, Hitachi, Ltd., Tokyo, Japan.*

[***] *C. Uyemura & Co., Ltd., Osaka, Japan.*

[****] *Model HZ-3000, Hokuto Denko Corporation, Tokyo, Japan.*

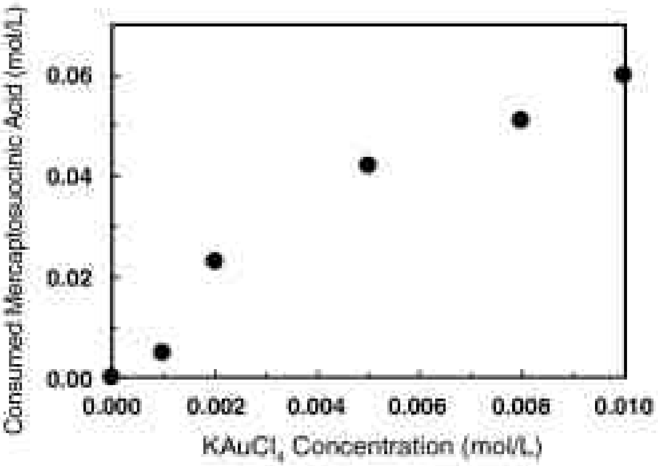


Fig. 5—Relation between KAuCl$_4$ concentration and consumption of mercaptosuccinic acid.

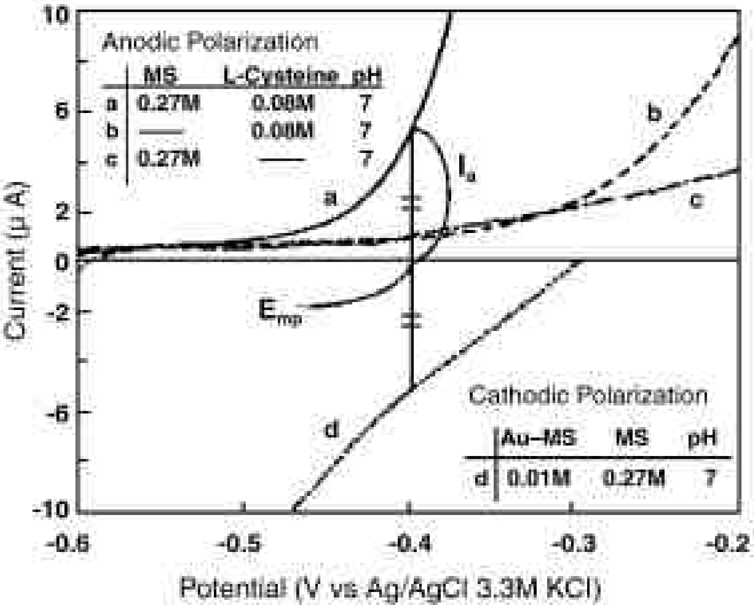


Fig. 6—Anodic and cathodic polarization of the gold electrode at 80°C (176°F).

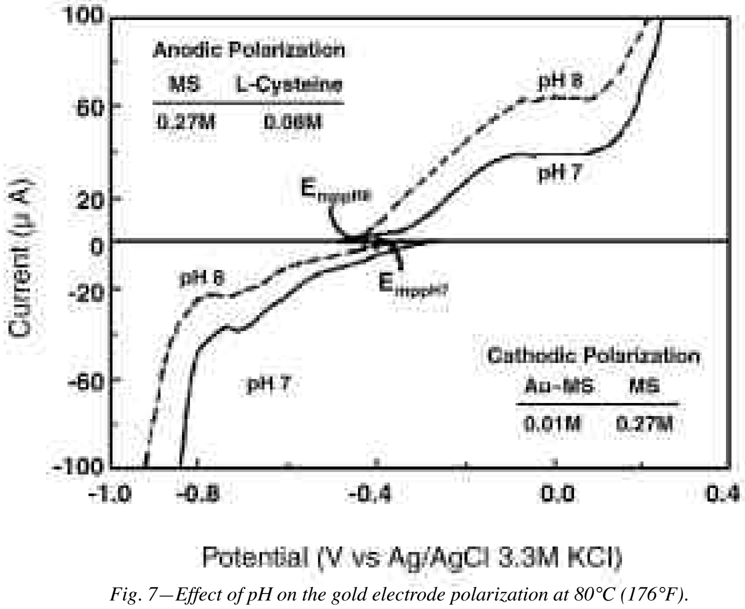


Fig. 7—Effect of pH on the gold electrode polarization at 80°C (176°F).

with gold to a thickness of 5 μm (0.2 mil). The counterelectrode was a platinum wire and a silver-silver chloride electrode (3.3 mol/L KCl) was used as the reference electrode. Unless otherwise specified, any electrode potential referred cited here relates to a potential referenced to that electrode.

In order to determine a local anodic polarization curve, a solution based on the plating bath composition was prepared without the metal salt (auric mercaptosuccinate (I)). The MS and L-cysteine contained in the bath, moreover, are derivatives from an ethanethiol. To make certain of their action as reducing agents, therefore, these ethanethiol derivatives had their local anodic polarization curves determined using their respective single-component solutions. In order to determine the local cathodic polarization curve, a solution was prepared without the reducing agent (L-cysteine).

Results & Discussion

Effect of Various Bath Components On the Deposition Rate

Figure 1 shows the deposition rates obtained when a variety of factors in the plating bath were varied under the plating conditions shown in Table 1. The factors that were found to affect the deposition rate significantly include the concentrations of gold (I) salt, L-cysteine, the pH and the bath temperature. With gold (I) salt, MS and L-cysteine concentrations of 0.01, 0.27 and 0.08 mol/L, respectively, the deposition rate was found to reach a maximum. The pH was found to be quite significant; the deposition rate decreased above pH 7.0. In addition, the deposition rate increased coupled with a rise in bath temperature. No gold deposited from the bath without L-cysteine. From this, it may be concluded that in this bath, MS and L-cysteine acted, respectively, as the complexing and reducing agents.

Figure 2 depicts the surface morphology of a 2-μm (79 μ-in.) thick gold film, obtained from this basic plating bath. The film was found to be smooth and fine-grained, with good adhesion to the gold substrate.

Figure 3 shows the relation between plating time and plated film thickness. As the plating time increased, a larger incremental amount of gold was found to deposit. From this, we conclude that the plating bath was an autocatalytic electroless plating process. Even after plating for seven hours or more, the plating bath was found neither to turn turbid nor to spontaneously deposit gold, showing its excellent stability.

Figure 4 shows the effect of nickel ion concentration on the deposition rate. A cyanide-based plating process would decompose with only a small amount of nickel contamination. The electroless gold plating bath reported here however, did not decompose even at a nickel concentration of 100 ppm. However, the deposition rate did decrease slightly. Plating could be sustained over long periods of time. It should be noted however, that this bath is susceptible to copper contamination. Even 2 ppm of copper caused the bath to decompose. It is necessary, therefore, when working with copper substrates, to treat the surface in such a way as to avoid copper dissolution.

A copper substrate that had been electroplated with 2 μm (79 μ-in.) of semibright nickel was used as a substrate for electroless gold plating. As a result, a number of pinholes were formed and copper dissolved through the pinholes. Consequently, the bath decomposed in a short time. If however, after the nickel electroplating, however, the base was plated with a 2 μm (79 μ-in.) layer of electroless nickel-phosphorus, the copper dissolution could be suppressed. This was verified by high-frequency plasma emission spectrographic analysis. The bath was found to remain stable over many hours.

Deposition Mechanisms

Determining the Complex of Auric Mercaptosuccinate by Colorimetry

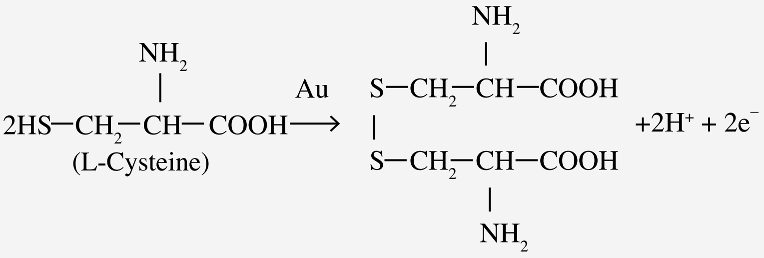
A yellow potassium tetrachloroaurate (III) aqueous solution (containing 0.01M as aurate(III), having an absorption peak at 310 nm, was found to change from yellow to colorless, with a brown tone intervening, when 0.03M or more of MS was added. A smaller amount of MS added, however, was found to generate a brown sediment, along with reduced Au(III) . These findings suggested that auric ions exist as a complex of Au(I)-MS.

Polarographic Studies

In order to clarify the mechanism whereby gold deposits from the auric mercaptosuccinate, it is necessary to know how gold ions and MS co-exist in solution. Accordingly, a bath was prepared by adding MS solution, at its plating bath composition of 0.27 mol/L, to the potassium tetrachloroaurate (III) at various concentrations (0.001 thru 0.01 mol/L). With this bath, DC-polarography was used to determine the limit current caused by oxidation of MS. The MS concentration in the bath was estimated from the result,[8] shown in Fig. 5. In this estimation, a linear relation (r = 0.993) was observed between the MS concentration and the limiting current at -0.20V. Therefore, this relation was used as a calibration curve. The potassium tetrachloroaurate (III), at concentrations of 0.001, 0.005 and 0.01 mol/L, showed limiting currents of 77.3, 65.3 and 60.0 μA, respectively. Thus, the limiting current was observed to decrease, as the aurate concentration increased. From these results, it may be concluded that the MS consumption increased in the Au(III) to Au(I) reduction while raising the percentage of Au(I) in the bath. As a result, auric ions exist in the form of Au(I) in the electroless gold plating bath.

Table 2
Basic Bath Composition & Plating Conditions

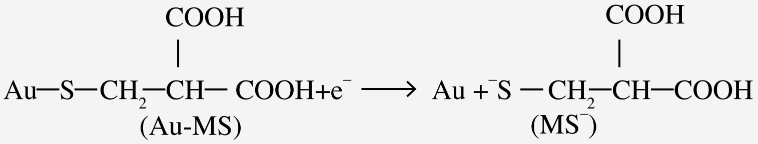
Local Anode Reaction



$$2HS-CH_2-\overset{NH_2}{\overset{|}{CH}}-COOH \xrightarrow{Au} \begin{array}{l} S-CH_2-\overset{NH_2}{\overset{|}{CH}}-COOH \\ | \\ S-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH \end{array} +2H^+ + 2e^-$$

(L-Cysteine)

Local Cathode Reaction



$$Au-S-CH_2-\overset{COOH}{\overset{|}{CH}}-COOH+e^- \longrightarrow Au + {}^-S-CH_2-\overset{COOH}{\overset{|}{CH}}-COOH$$

(Au-MS) (MS$^-$)

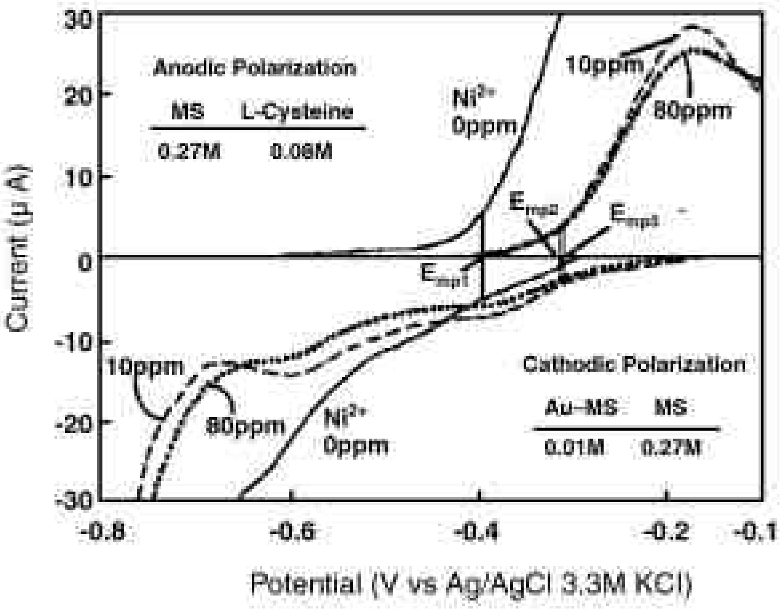


Fig. 8—Effect of nickel concentration on the gold electrode polarization at 80°C (176°F).

Potential Scanning Polarization Studies

Figure 6 shows the local anodic/cathodic polarization curves via the potential scanning studies. Curves a, b and c, respectively, represent the anodic polarization of an MS/L-cysteine solution mixture, a single L-cysteine solution and a single MS solution. Curve d relates to the cathodic polarization of an auric mercaptosuccinate(I)/MS solution mixture . In Fig. 6, the mixed electrode potential (E_{mp}) obtained from polarization curves a and d was found to be around -0.4V. This value closely agreed with the -0.39V, equilibrium electrode potential in the basic plating bath.

At E_{mp}, an anodic current was present not only in the single L-cysteine solution but also in the MS solution. This supports the polarographic and colorimetric findings. That is, MS is a complexing agent, and at the same time, it is acting as a reducing agent from Au(III) to Au (I).

Based on the reaction

$$Au^+ + e^- \leftrightarrows Au,$$

therefore, we obtained a deposition rate of 0.61 μm/h from the current I_a (5.0 μA) at E_{mp}, which closely agreed with the deposition rate in the basic plating bath of 0.66 μm/h. At E_{mp}, however, the sum of the respective currents in the individual single solutions of MS and L-cysteine would not always equal the current for the MS + L-cysteine solution mixture. Thus we could not verify that an anodic current was generated at the mixed electrode potential.

From the results of the colorimetry, DC-polarography and potential scanning studies, it may be concluded that the gold deposition reaction is based on the mechanism shown in Table 2. Here, L-cysteine oxidizes autocatalytically into L-cysteine on the surface of gold. The electrons supplied, coupled with such a reaction, cause Au(I) to be reduced to Au(0).

Figure 7 shows the effects of pH on the local anodic/cathodic polarization curves. In the anodic polarization curve of the MS + L-cysteine solution mixture, an increase in pH caused the equilibrium electrode potential to be shifted to the base, resulting in a larger oxidizing current.

In the cathodic polarization curve of the auric mercaptosuccinate (I) + MS solution mixture, an increase in pH caused the equilibrium electrode potential to be shifted to the base. As a result, gold deposition was suppressed. At pH 7 and pH 8, E_{mp} was found to be around -0.40V to -0.44V. The currents were 5.0 and 3.2 μA, respectively. The deposition rates calculated from those currents were found to agree with the values actually measured at pH 7 and pH 8.

Figure 8 shows the effect of nickel contamination on the anodic/cathodic polarization curves. In the basic bath, anodic current began to flow at an applied potential of around -0.6V. With nickel ions added, however, the anodic current began at a potential about 0.2V more noble. From the cathodic polarization curve, nickel contamination caused the cathodic current to start flowing at a more noble potential. The current coupled with an increased anodic/cathodic polarization around the mixed electrode potential was found to decrease with an increase in nickel contamination. The deposition rates calculated from the current values at their respective mixed electrode potentials (E_{mp1} thru E_{mp3}) were in good agreement with the values actually measured. Therefore, the decrease in actual plating rate of the bath to which nickel ions were added arose from the suppression of reactions at both local anode and cathode at the mixed electrode potential.

Conclusion

In the electroless gold plating bath with mercaptosuccinic acid and L-cysteine used as complexing and reducing agents, respectively, the gold film deposited autocatalytically. We established the optimum bath composition and plating conditions. At the same time, colorimetry, DC-polarography and potential scanning methods were used to study the form in which the gold ions existed, as well as the deposition mechanism. As a result, we came to the following conclusions:

1. The mercaptosuccinate/L-cysteine allows electroless plating from a stable cyanide-free bath at a neutral pH. A fine-grained gold film could be produced. The bath was also resistant to nickel contamination at levels of 100 ppm or greater.
2. Mercaptosuccinic acid acts as a reducing agent from Au(III) to Au(I); it is also a chelating agent. Gold deposition results from Au(I) reduction, coupled with the oxidation of L-cysteine.

   Local anode reaction:

   $$2\text{ L-cysteine} \xrightarrow{(Au)} 2\text{L-cysteine} + 2H^+ + 2e^-$$

   Local cathode reaction:

   $$\text{Au(I)-MS} + e^- \rightarrow \text{Au(0)} + \text{MS}^-$$

3. The mixed electrode potential (E_{mp}) obtained from local anodic/cathodic polarization curves agreed with the equilibrium electrode potential in the plating bath. The deposition rate calculated from the current at E_{mp}, moreover, was found to be in good agreement with the actual measured value. Thus, we confirmed that the mixed electrode potential theory holds in this electroless gold plating bath.

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