

Some Recent Developments in Non-Cyanide Gold Plating for Electronics Applications

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The plated gold being used by the electronics industry can be broadly classified into two categories: soft gold and hard gold. Soft gold is used for circuit metallization and for bonding semiconductor chips, while hard gold is indispensable as the contact material on electrical connectors, electromechanical relays, and printed circuit boards. The traditional baths from which to plate soft gold as well as hard gold contain the cyanide complex, $[\text{Au}(\text{CN})_2]$, as the source of gold, which liberates free cyanide ions during the plating. The free cyanide is not only highly toxic but also attacks photoresists used to delineate circuit patterns and bonding pads. For these reasons, non-cyanide baths are in use to plate soft gold, whereas hard gold can be plated only from cyanide baths at present. In this presentation, the current status of both electrolytic and electroless non-cyanide processes for plating soft gold will be reviewed.

1 Introduction

In the electronics industry, gold plating is widely used to prepare the surfaces of electrical contacts and wire bonding pads of semiconductor devices by taking advantage of the characteristics of high electrical conductivity, high reliability, and high corrosion resistance of gold. In recent years, with the rapid progress of electronic devices, the development of “high density packaging technology” has become essential, and the gold-plating technology is expected to be compatible with this trend and capable of preserving the high reliability under the new circumstances.

The traditional cyanide-type gold plating bath containing potassium cyanoaurate(I), $\text{KAu}(\text{CN})_2$, as the source of gold, has been in use for both electrolytic and electroless plating. The cyanide bath has a long, successful history of being highly stable and capable of yielding gold films with excellent physical properties. However, the cyanide bath has problems of toxicity and suffers from the tendency of attacking the positive photo resist film which is used to delineate circuit patterns.

Therefore, non-cyanide baths using $\text{Au}(\text{I})$ -sulfite complex have been in use. Since the line density of circuit patterns is increased with the necessity of incorporating electrically isolated patterns in many applications, the demand for electroless plating has been increasing in recent years. In particular, because of the toxicity and material compatibility problems associated with the cyanide bath, the need for a practical non-cyanide electroless gold plating bath has been increasing. To meet this demand, non-cyanide electroless baths using a gold salt such as NaAuCl_4 or $\text{Na}_3\text{Au}(\text{SO}_3)_2$ were developed in the past. However, those non-cyanide baths developed before 1990 generally suffered from insufficient bath stability for routine practical use, and their applications were limited in scope.

This paper reviews currently available electrolytic as well as electroless gold plating processes utilizing gold complexes other than the cyanide compound with emphasis on the extremely stable system containing both sulfite and thiosulfate as complexing agents for $\text{Au}(\text{I})$. The description will be focused particularly on the new autocatalytic electroless gold plating bath and the substrate-catalyzed electroless bath, both of which we have developed using mixtures of thiosulfate and sulfite as complexing agents for $\text{Au}(\text{I})$.

2 Classification of Gold Plating Baths

Gold plating baths can be classified into various categories depending on the gold salt used, the reaction mechanism, bath pH, and properties of the deposit obtained. The diagram shown in Fig.1 illustrates this classification.

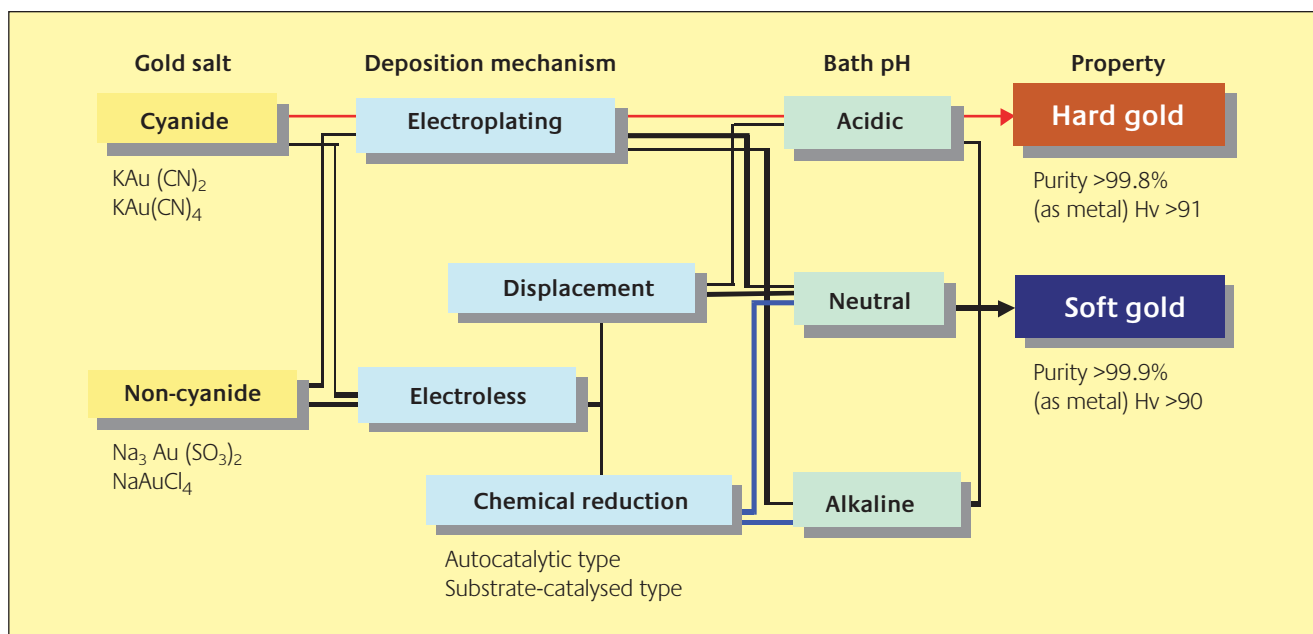


Figure 1
Classification of gold plating

The electrolytic cyanide-type baths include those operated at acidic, neutral, or alkaline pH's, and they can deposit either hard gold or soft gold. On the other hand, non-cyanide type baths can be operated only at neutral or alkaline pH's by either an electrolytic or electroless mechanism, but the baths presently available can deposit soft gold only. Hard gold can be deposited only from a cyanide-type electroplating bath at present, and neither a cyanide-type electroless hard gold plating bath nor a non-cyanide type electrolytic or electroless hard gold plating bath has yet been developed to the authors' knowledge.

3 Sulfite Baths

3.1 Electroplating – The use of gold(I) sulfite complex, $[\text{Au}(\text{SO}_3)_2]^{3-}$, for electroplating gold has been known since 1842(1). Gold(I)-sulfite complex has been in use for many years as the source of gold in commercial non-cyanide, electrolytic gold plating baths. The sulfite bath without stabilizing additives suffers from instability caused by the low stability constant of the sulfite complex itself, which is approximately equal to 10^{10} as compared to 10^{39} for the cyanide complex, $[\text{Au}(\text{CN})_2]^-$. Because of the low stability constant, Au^+ ions are formed more readily from the sulfite complex than from the cyanide complex, and these ions undergo the disproportionation reaction, $2\text{Au}^+ \rightleftharpoons \text{Au}(0) + \text{Au}^{3+}$, forming a precipitate of metallic gold. To suppress this reaction, all commercially available sulfite baths contain proprietary stabilizing additive(s). The addition of a

polyamine such as ethylenediamine is known to stabilize the sulfite bath through the formation of a mixed ligand gold complex (1,2), which also makes it possible to operate the bath in a lower pH range of 5 to 8, rather than >8 for the bath containing no amine. Morrissey(3) found that simultaneous addition of ethylenediamine and nitrobenzene stabilizes the bath to such an extent that the bath can be operated at a pH as low as 4.0 to 6.5. The ability of the bath to function in the low pH range is significant because it enhances the compatibility with photo resists. More recently, 2,2'-bipyridine has been shown to stabilize the sulfite bath, presumably because it forms a complex with Au^+ . (4)

3.2 Electroless Plating – The gold(I) sulfite complex has also been used to formulate electroless gold plating baths. Conventional reducing agents for electroless plating such as hypophosphite, formaldehyde, hydrazine, borohydride, and DMAB have been investigated for use with the sulfite complex (5-8). More recently, less common reducing agents such as thiourea and its derivatives have been used successfully(9). These systems require the addition of a stabilizer for practical use. For example, EDTA, triethanolamine, and NTA (nitrilotriacetic acid) have been reported to serve as the stabilizer(10, 11). These additives may form mixed ligand complexes of Au(I) with sulfite as ethylenediamine does.

4 Thiosulfate Baths

4.1 Electroplating – The electroplating of gold from Au(I) thiosulfate complex has been known since as early as 1913

(2), but it has never been used for making a practical bath. In view of the fact that the stability constant of $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ is equal to 10^{26} , which is orders of magnitude greater than that of the sulfite complex, the thiosulfate complex might be expected to be a viable alternative to the sulfite complex. The reason why the thiosulfate complex has not been used successfully for making a practical bath seems to be the instability of thiosulfate ion itself with respect to its disproportionation reaction: $\text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{S} + \text{SO}_3^{2-}$.

Recently, an electrolytic gold plating bath using Au(I) thiosulfate complex and containing iodide ions as an additive has been reported. In this system, metallic gold is used as the anode, which dissolves into the bath during the plating to maintain the Au(I) concentration constant (12).

4.2 Electroless Plating – Prior to 1994, thiosulfate was used as a single complexing agent for Au(I) only in a galvanic displacement (“immersion”) bath (13) and in an electroplating bath (14), while in 1994 Sullivan, Patel and Kohl (15) utilized the Au(I) thiosulfate complex to formulate an autocatalytic bath using ascorbic acid as the reducing agent. This bath was operated at a pH between 6.4 and 9.2 at room temperature. In this system the accumulation of free $\text{S}_2\text{O}_3^{2-}$ ions produced by the reduction of $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ decreases the plating rate. Sullivan and Kohl (16) found that the periodic addition of H_2O_2 removes the excess $\text{S}_2\text{O}_3^{2-}$ ions to maintain a constant plating rate. However, this bath has only a short life (<2 hr) and hence needs to be improved to make it useful for industrial applications.

5 Thiosulfate-Sulfite Mixed Ligand Bath

5.1 Electroplating – The noncyanide baths described above containing either sulfite or thiosulfate as a sole complexing agent appear to be of limited use because of insufficient stability of the systems. In view of the prior successful development of electroless gold plating baths containing both thiosulfate and sulfite (17,18), which will be described in the subsequent section, the present authors and collaborators investigated the possibility of electroplating soft gold from a bath containing the two ligands (19). It was found that the mixed ligand bath is highly stable even without the addition of any stabilizer. The composition and operating conditions of the mixed ligand electroplating bath are given in Table 1.

To plate pure soft gold useful for electronics applications, it is important to operate the bath under the conditions which minimize the sulfur content. The gold deposit from this bath showed a hardness of $H_v = 80$, which could be decreased to $H_v = 50$ by the addition of TI^+ ion in the bath and by annealing the deposit for 30 minutes at 350°C . It was

Table 1

Composition and operating conditions of Au(I) thiosulfate-sulfite electroplating bath

Bath constituents	mol/l
$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	0.06
Na_2SO_3	0.42
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.42 (Variable 0.42-1.26)
Na_2HPO_4	0.30
pH	6.0
Temperature	60°C
Current density	$5\text{mA} \cdot \text{cm}^{-2}$

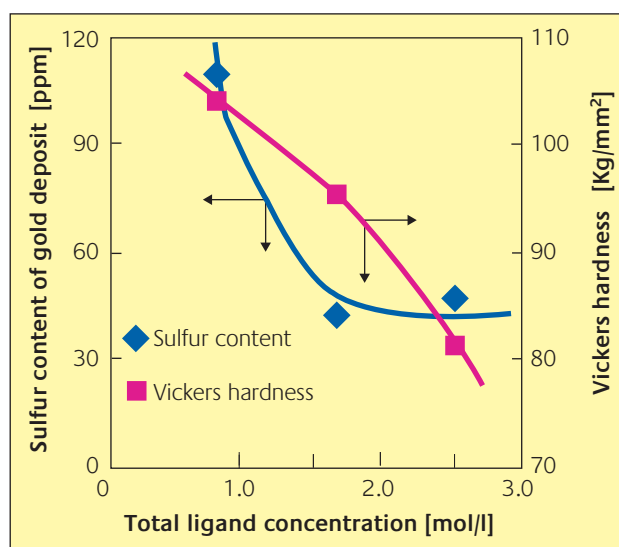


Figure 2

Effect of total ligand concentration ($[\text{SO}_3^{2-}] + [\text{S}_2\text{O}_3^{2-}]$) on sulfur content and hardness of gold deposited from the gold(I) thiosulfate-sulfite bath ($[\text{SO}_3^{2-}] = [\text{S}_2\text{O}_3^{2-}]$)

found that the gold deposit obtained from this bath contains sulfur as an impurity element, and that the hardness increases with increasing sulfur content of the deposit. Surprisingly, however, as shown in Fig. 2, the sulfur content was found to decrease with increasing total ligand concentration ($[\text{S}_2\text{O}_3^{2-}] + [\text{SO}_3^{2-}]$), where the ratio of $[\text{S}_2\text{O}_3^{2-}]$ to $[\text{SO}_3^{2-}]$ was kept constant at unity. This rather unexpected finding prompted us to conduct a detailed study of the mechanism of sulfur inclusion and to chemically identify the sulfur-containing species responsible for the included sulfur.

The study showed that thiosulfate was the main source of sulfur inclusion, and it was considered possible that either one or both of the following two reactions could lead to the inclusion of sulfur:

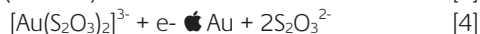
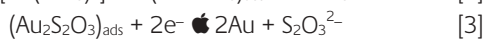
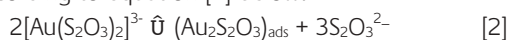
1. Elemental sulfur formed as a result of reaction [1]:



Thiosulfate compound: (a) $\text{NaAu}(\text{S}_2\text{O}_3)$ or (b) $\text{Au}_2\text{S}_2\text{O}_3$

If reaction [1] were responsible for the sulfur inclusion, the formation and hence the inclusion of elemental sulfur would

be favored by lowering the bath pH and by increasing the concentration of free thiosulfate ions. However, exactly the opposite pH effect was actually observed, and also the observed effect of thiosulfate concentration was exactly opposite to the effect predicted by reaction [1]. Based on these experimental results, the possibility of elemental sulfur being the form of sulfur inclusion was excluded. On the other hand, if compound (a), $\text{NaAu}(\text{S}_2\text{O}_3)$, is the only source of sulfur, the formula predicts that the atomic ratio of Na to S included in the gold should be equal to 1 : 2, whereas experimentally the atomic ratio was found to be as small as 0.1 : 2. Thus, compound (a) accounts for, at most, only 10% of the entire amount of sulfur included in the gold. These findings led us to the assumption that a major portion of the sulfur included in the gold exists in the form of $\text{Au}_2\text{S}_2\text{O}_3$. This species is likely to be in an adsorbed state on the cathode surface according to equation [2] below:



Reaction [2] is followed by the electrochemical reduction [3] of $(\text{Au}_2\text{S}_2\text{O}_3)_{\text{ads}}$ to deposit gold with the overall reaction given by [4]. According to this mechanism, the formation of the adsorbed species by reaction [2], and hence the sulfur inclusion, should be more favorable at lower free $\text{S}_2\text{O}_3^{2-}$ concentrations. At very high $\text{S}_2\text{O}_3^{2-}$ concentrations the gold deposition is believed to take place directly from the bulk species, $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$, via reaction [4] without going through the formation of the adsorbed intermediate. Thus, the above mechanism explains the experimental result that the smaller amount of sulfur is included in the gold at higher free thiosulfate concentrations (20).

It has been demonstrated that this highly stable bath is suitable for fabricating microbumps through a patterned photo resist without any degradation of the photo resist or any extraneous deposition of gold. Green *et al.* (21) reported that this type of bath yielded satisfactory results in their evaluations.

5.2 Electroless Plating – Autocatalytic gold plating baths containing both thiosulfate and sulfite with thiourea or ascorbic acid as the reducing agent were first developed in 1987-1988 (17,18). Those baths have since been greatly improved and they are now commercially available for large scale operations. As is the case with any autocatalytic baths, the selection of a suitable stabilizer is the key to successful long-term use of those baths. In the thiourea bath, hydroquinone acts as a stabilizer as well as a recycling agent for thiourea, while in the ascorbic acid bath, a minute amount of 2-mercaptobenzothiazole (MBT) serves as a stabilizer.

Following the initial development, the thiosulfate-sulfite mixed ligand system has been investigated quite actively. The

baths using hydrazine (22,23) and sodium hypophosphite (24) as the reducing agent were developed. More recently, it was reported that the deposition of gold in the thiosulfate-sulfite mixed ligand system takes place autocatalytically even without adding any reducing agent (25). The present authors and collaborators have since conducted a detailed study on this aspect, which led to the conclusion that the bath without any added reducing agent functions as a substrate-catalyzed system rather than an autocatalytic system. A description of this study will be included below.

5.2.1 Thiourea bath

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi, Ltd. (17,25). Basic and improved versions of the bath composition and operating conditions are shown in Table 2. In this system thiourea has been shown to undergo complex chemical reactions through the formation of a radical intermediate, $(\text{NH})(\text{NH}_2)\text{CS}\cdot$, to form final products including urea, a major product, and dicyandiamide. This radical intermediate is believed to react with dissolved oxygen in the bath to form formamidine sulfinic acid, $(\text{NH}_2)_2\text{CSO}_2$, which appears to be responsible for bath instability. Hydroquinone appearing as an additional component of the bath (see Table 2) reacts quickly with the radical intermediate before it produces the undesirable compound. It is also significant that the reaction between hydroquinone and the radical intermediate regenerates thiourea. Thus hydroquinone acts as a stabilizer as well as a recycling agent for thiourea.

5.2.2 Ascorbic Acid Bath

The present authors and collaborators developed a thiosulfate-sulfite mixed ligand bath with ascorbic acid as the reducing agent (18,27). The compositions of the basic bath and an improved bath are shown in Table 3. The possibility of developing these baths was initially investigated based on the

Table 2

Basic and improved thiourea baths (26)

		Basic bath	Improved Bath
$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	mol/L	0.0125	0.0125
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	mol/L	0.1	0.1
Na_2SO_3	mol/L	0.4	0.4
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	mol/L	0.13	0.13
Thiourea	mol/L	0.033	0.033
Hydroquinone	mol/L	none	0.002
pH		9.0	8.0
Temp.	°C	80	70
Bath life with load		12hr	50hr
Bath life without load		60hr	> 1 month
Plating rate	$\mu\text{m h}^{-1}$	0.8	1.2

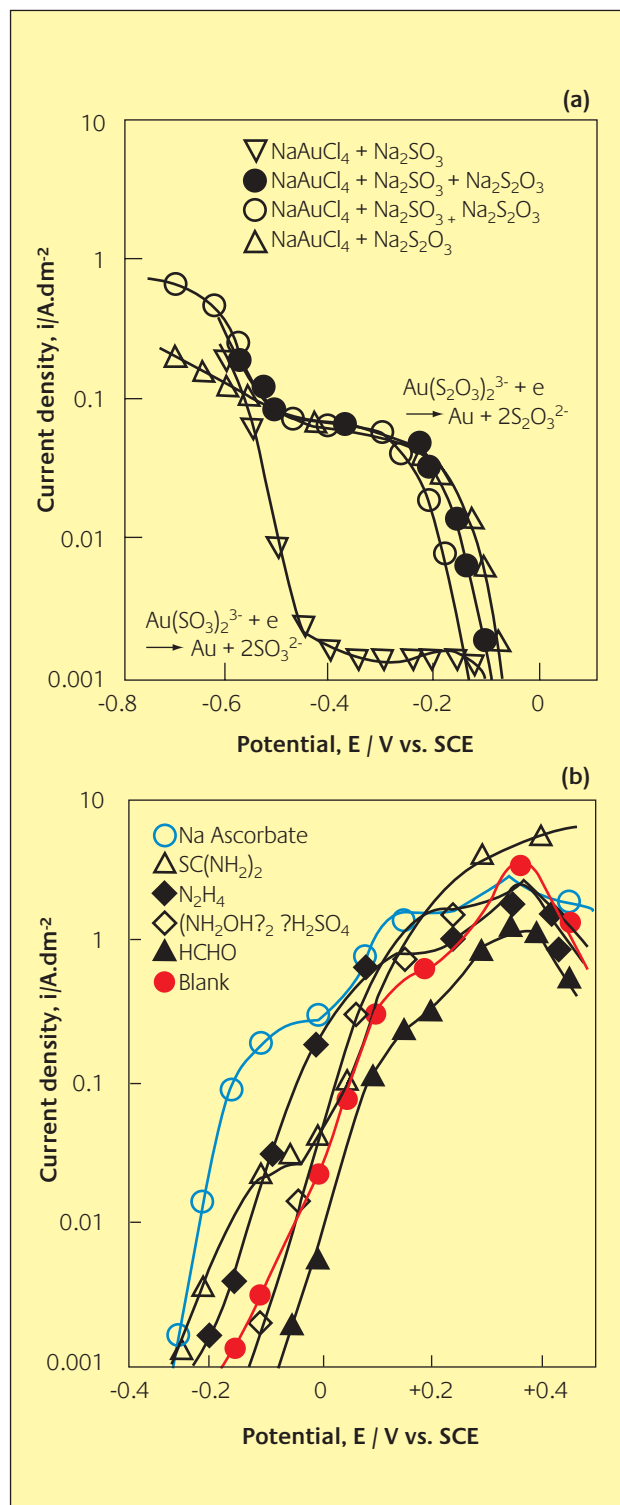
Table 3

Basic and improved ascorbic acid baths (27)

		Bath A Standard Bath	Bath B Improved Bath
NaAuCl ₄ • 2H ₂ O	mol/L	0.0125	–
Na ₃ Au(SO ₃) ₂	mol/L	–	0.01
Na ₂ S ₂ O ₃ • 5H ₂ O	mol/L	0.1	0.1
Na ₂ SO ₃	mol/L	0.1	0.4
NH ₄ Cl	mol/L	0.05	–
K ₂ HPO ₄	mol/L	–	0.1
Sodium L-ascorbate	mol/L	0.2	0.1
Additive		–	trace
pH		6.0	7.2
Temp.	°C	60	60
Bath life		<8hr	6 months
Plating rate	μm h ⁻¹	1.2-1.5	0.8-1.1

well-known mixed potential theory combined with partial polarization curves measured at a gold electrode. This investigation showed that the thiosulfate-sulfite mixed ligand system gives a practical deposition rate and a high stability compared with the baths containing thiosulfate alone or sulfite alone, and that, amongst the many reducing agents tested, only ascorbic acid, hydrazine and thiourea can serve as the practical reducing agent for the autocatalytic deposition of gold. Figure 3(a) shows the partial cathodic polarization curves, while partial anodic polarization curves are shown in Fig. 3(b). As a consequence of evaluation of the bath stability, deposition rate, and deposit appearance, ascorbic acid was selected as the most suitable reducing agent for this bath.

With the aim of improving and controlling the bath stability, a simple and sensitive device using visible light irradiation was developed and employed to evaluate effects of various bath stabilizing additives. As a result of this study, improvements were achieved in the bath stability, the selectivity in the plating of patterned substrates, and in the plating rate. Heterocyclic mercapto compounds such as mercaptobenzothiazole (MBT) were found to be especially effective for improving the bath stability while maintaining the plating rate at an acceptable level. It has also been shown that increasing the sulfite concentration improves the bath stability, and that the addition of excess sulfite helps prevent extraneous gold deposition from occurring on the surface of ceramic substrates with a circuit pattern delineated by using a conventional photo resist technique. These findings led to the development of an improved bath which is stable for the period of five metal turnovers (5MTO) with periodic replenishment of main bath constituents and with a proper control of bath contamination. Currently, the improved bath is in large-scale commercial operation for plating contact terminals of printed circuit boards.

**Figure 3**

(a) Cathodic polarization curves for gold deposition from various mixture of $NaAuCl_4$, Na_2SO_3 , and $Na_2S_2O_3$
 Bath comp. : 0.2M Na_2SO_3 + 0.01M $NaAuCl_4$ + 0.1M NH_4Cl + xM $Na_2S_2O_3$,
 x : ∇ , \bullet , \circ ; 0.1, \triangle ; 0.1 (in the absence of $Na_2S_2O_3$), \circ ; 0.4, WE: Au,
 pH6.0, 60°C
 (b) Anodic polarization curves of various reducing agents in basic bath
 Bath comp. : 0.2M Na_2SO_3 + 0.1M NH_4Cl + 0.1M $Na_2S_2O_3$ + 0.1M
 reducing agent, WE: Au, pH6.0, 60°C

5.2.3 Baths Containing No Additional Reducing Agent

Kruklik and Mandich (25) reported that the Au(I) thiosulfate-sulfite mixed ligand system functions as an autocatalytic bath in the absence of any conventional reducing agent. They believed that the thiosulfate-sulfite mixture itself is a reducing agent system, and that sulfite functions as the main reducing agent in this bath.

The present authors and collaborators studied the reaction mechanism of this system in detail (28,29). The bath composition and operating conditions used in this investigation are listed in Table 4, which are similar to those of the autocatalytic bath listed in Table 3 except that the reducing agent (ascorbic acid) was excluded. Figure 4 compares the two substrates, electroless NiB film and pure gold sheet, for the variation of gold deposit thickness with plating time. It is seen that gold deposition took place only on NiB and not on the gold sheet. This result clearly shows that the gold deposition from this bath is not, even partially, autocatalytic. Figure 5 compares the calculated and actual thicknesses of the gold deposit produced in the bath of Table 4 with those of the gold film deposited in a commercial galvanic displacement (immersion) bath. It is seen that for the latter bath, the gold thickness calculated from the amount of dissolved nickel agrees well with the thickness of gold actually achieved as expected. On the other hand, for the bath under investigation, the gold thickness calculated from the amount of dissolved nickel is only about 20% of the actual gold thickness determined. Thus, the galvanic displacement reaction accounts for only 20% of the total deposit thickness, and therefore there must be another mechanism which accounts for the remaining 80% of the deposited gold. This additional mechanism is attributed to the catalytic activity of the substrate nickel. It was considered possible that either thiosulfate or sulfite (or both) could serve as the reducing agent(s) in this substrate-catalyzed reaction. Therefore, split cell experiments and polarization measurements were performed to identify the species serving as the reducing agent. The results of these experiments showed conclusively that sulfite ions, not thiosulfate ions, serve as the reducing agent in the substrate-catalyzed gold deposition reaction.

From all of the experimental results described above, the following conclusions were drawn: (1) The gold deposition from the mixed ligand bath containing no added reducing agent proceeds by two different reactions occurring simultaneously, that is, substrate-catalyzed reaction (80-90%) with sulfite ion as the reducing agent and galvanic displacement reaction with the nickel substrate (10-20%). (2) No autocatalytic gold deposition takes place in this bath. This mechanism is illustrated schematically in Fig. 6.

In view of the interest in the substrate catalytic mechanism from the practical viewpoint, further investigations were carried out to understand effects of

Table 4

Bath composition and operating conditions of no additional reducing agent bath

Bath constituents	mol/l
NaAuCl ₄ •2H ₂ O	0.01
Na ₂ SO ₃	0.32
Na ₂ S ₂ O ₃ •5H ₂ O	0.08
Na ₂ HPO ₄	0.32
pH	9.0
Temp.	60°C
Agitation	Mechanical Stirrer

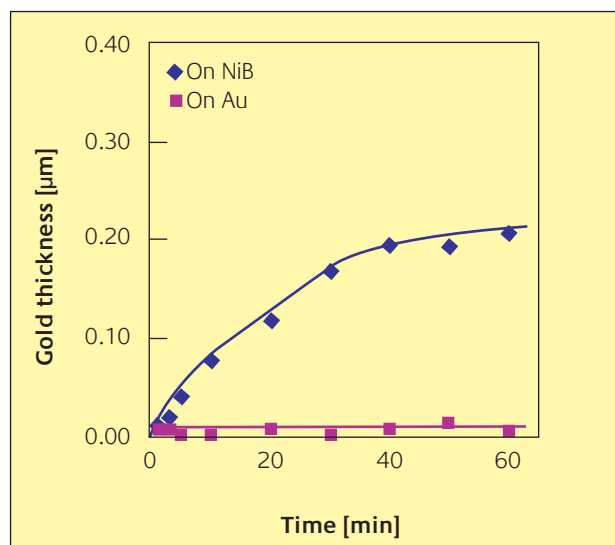


Figure 4

Effect of substrate material on the variation of gold thickness with plating time

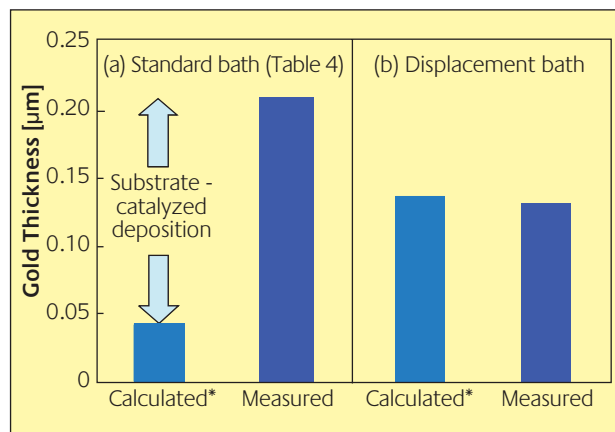


Figure 5

Comparison between calculated and measured deposit thicknesses for (a) standard bath and (b) galvanic displacement bath

(*Calculated from amount of dissolved Ni²⁺, Plating time: 60min.)

substrate material and pretreatment on the characteristics of the gold film obtained and to determine effects of plating variables on the porosity of the film. Among the various Ni

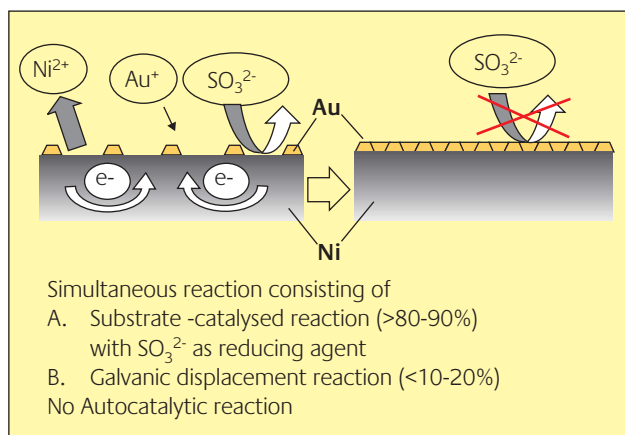


Figure 6
 Mechanism of electroless gold deposition on nickel from thiosulfate-sulfite bath, no additional reducing agent bath

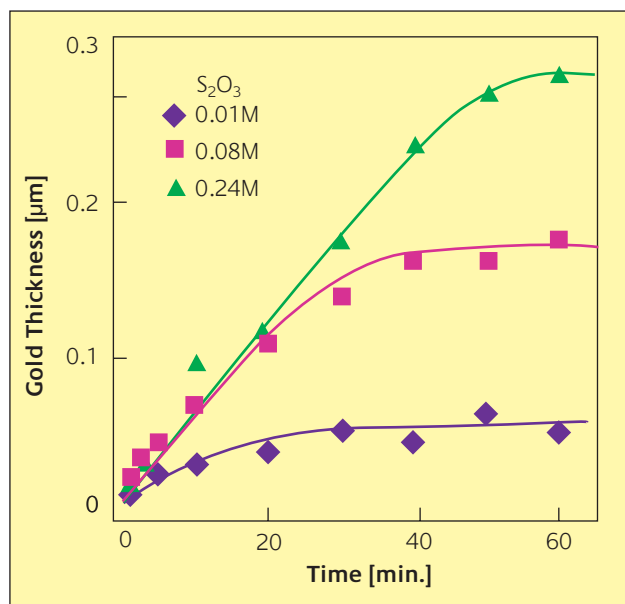


Figure 7
 Gold thickness vs. plating time at different thiosulfate concentrations (Mixed ligand bath with no additional reducing agent)
 Substrate: Ni-P(P:4.7wt%), Pre-treatment:0.5M Na_2SO_3 , 1s, 60°C

substrates investigated, the low P-content (4.7 wt% P) electroless Ni-P pretreated with 0.1M Na_2SO_3 was found to be most suitable for producing very uniform, adherent gold films. Figure 7 shows the variation of gold thickness with plating time on the low P-content Ni-P substrate at three different thiosulfate concentrations. It is seen that the gold thickness reaches a maximum constant value after approximately 60 min of plating at all thiosulfate concentrations, and that the maximum thickness obtainable increases with increasing thiosulfate concentration. Attempts were made to obtain corresponding data on electroless Ni-B substrates, but no satisfactory gold films could be reproducibly produced even on those substrates pretreated with various solutions.

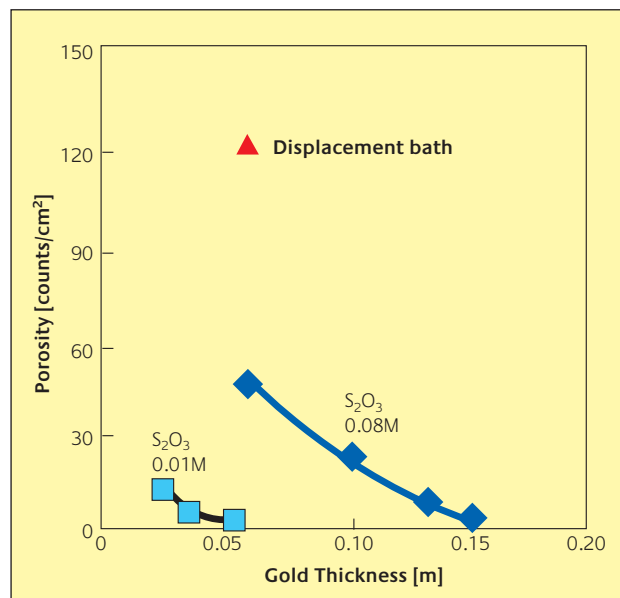


Figure 8
 Variation of porosity with thickness of gold films deposited at two different thiosulfate concentrations (mixed ligand bath with no additional reducing agent) Substrate: Ni-P (P:4.7wt%)

Figure 8 presents quantitative porosity data plotted against the thickness of gold films produced in the baths containing 0.01M and 0.08M thiosulfate. At the higher thiosulfate concentration, the maximum gold thickness obtained was greater; nevertheless, the porosity was also significantly greater. This was rather unexpected, but the remarkable fact is that an essentially pore-free gold film was produced at the thickness as small as 0.04 µm when the thiosulfate concentration was 0.01M. For comparison, the porosity of the film formed by galvanic displacement is also indicated in Fig. 8. The significantly greater porosity of this film is apparent. These results clearly demonstrate the superiority of the substrate-catalyzed process for preparing gold films with a low porosity. Such gold films have been shown to be suitable for use in conjunction with gold wire bonding in the semiconductor packaging technology.

6 Concluding Remarks

The traditional gold plating baths containing $\text{KAu}(\text{CN})_2$ as the source of gold in neutral or mildly acidic media have served well for many years in the past for various applications in the electronics industry. In recent years, however, disadvantages of the cyanide system have become more apparent not only because of the greater consciousness about the use of toxic materials, but also because of the incompatibility of cyanide with photo resists and other materials used in the packaging of high density circuits. This is particularly evident for the

plating of pure soft gold. Non-cyanide baths using Au(I)-sulfite or Au(I)-thiosulfate as the source of gold have been available for both electrolytic and electroless plating of soft gold, but those compounds, when used alone, are not sufficiently stable. On the other hand, the mixed ligand system containing both thiosulfate and sulfite have been shown recently to be capable of providing much more stable baths for both electroplating and electroless plating, the latter including both autocatalytic and substrate-catalyzed processes. The characteristics of the mixed ligand system have now been thoroughly investigated and well understood. The authors anticipate that the application of this non-cyanide system will keep expanding in the future.

Finally, it should be noted that the hard gold, which is being used widely in the connector, mechanical relay, and printed circuit board industries, presently can be plated only from cyanide-based baths. Furthermore, no electroless hard gold baths are currently available. Development of new systems to fill these gaps can be anticipated in the future.

About the Authors

Dr. Masaru Kato is employed by Kanto Chemical Co., Inc., Japan, a major producer of reagent chemicals and high purity chemicals for the electronics industry. He received his Bachelor of Engineering degree in applied chemistry from Tohoku University, Sendai, and a Doctor of Engineering degree from Waseda University, Tokyo, Japan. He is a Group manager at the company's central research Laboratory. He has been actively involved in the development of gold plating, especially electroless gold plating for the past fifteen years. His research interests include the electrochemistry of deposition and etching of metals. Dr. Okinaka has been involved in the R & D of the electrolytic and electroless plating of metals, primarily gold and copper, for electronics applications for more than 35 years. After retirement from AT&T Bell Laboratories, USA in 1990, he was a Visiting Professor at Waseda University, Tokyo, Japan until 1996, where he continues to participate actively in research as a Visiting Research Scientist. He also serves as a Technical Consultant for Kanto Chemical Co.

References

- 1 "Gold Plating Technology", ed. F.H. Reid and W. Goldie, Electrochemical Publications, Ltd., Ayr, Scotland, 1974
- 2 W.S. Rapson and T. Groenewald, "Gold Usage", Academic Press, Inc., New York, 1978
- 3 R.J. Morrissey, *Plating and Surface Finish.*, 1993, **80**(4), 75
- 4 H. Honma and Y. Kagaya, *J. Electrochem. Soc.*, 1993, **140**, L135

- 5 F. Richter, R. Gesemann, L. Gierth and E. Hoyer, German Patent, 1981 DD150762
- 6 R. Gesemann, F. Richter, L. Gierth, U. Bechtloff and E. Hoyer, German Patent, 1983 DD160283
- 7 R. Gesemann, F. Richter, L. Gierth, E. Hoyer and J. Hartung, German Patent, 1983 DD160284
- 8 F. Richter, R. Gesemann, L. Gierth and E. Hoyer, German Patent, 1986, DD240915
- 9 Y. Sato, T. Osawa, K. Kaieda and K. Kobayakawa, *Plating and Surface Finish.*, 1994, **81**(9), 74
- 10 F. Richter, R. Gesemann, L. Gierth and E. Hoyer, German Patent, 1989, DD268484
- 11 Y. Shindo and H. Honma, *Proceedings of 84th Conference of Surface Finishers Society of Japan*, 1991, 163
- 12 X. Wang, N. Issaev and J.G. Osteryoung, *J. Electrochem. Soc.*, 1998, **145**, 974
- 13 B. Michael and J. Barbara, German Patent, 1987, DE2803147
- 14 L. Rolf and C. Josif, German Patent, 1967, DE2445537
- 15 A. Sullivan, A. Patel and P.A. Kohl, *Proceedings of the AESF Technical Conference SUR/FIN'94*, American Electroplaters and Surface Finishers Society, 1994, 595
- 16 A. Sullivan and P.A. Kohl, *J. Electrochem. Soc.*, 1995, **142**, 2250
- 17 M. Kato, N. Niikura, H. Hoshino and I. Ohno, *J. Surf. Finish. Soc. Japan*, 1991, **42**, 729
- 18 T. Inoue, S. Ando, H. Okudaira, J. Ushio, A. Tomizawa, H. Takehara, T. Shimazaki, H. Yamamoto and H. Yokono, *Proceedings of the 45th IEEE Electronic Components Technology Conference*, 1995, 1059
- 19 T. Osaka, A. Koderia, T. Misato, T. Homma, Y. Okinaka and O. Yoshioka, *J. Electrochem. Soc.*, 1997, **144**, 3462
- 20 T. Osaka, M. Kato, J. Sato, K. Yoshizawa, T. Homma, Y. Okinaka and O. Yoshioka, *J. Electrochem. Soc.*, 2001, **148**, C659
- 21 T.A. Green, M.-J. Liew and S. Roy, *J. Electrochem. Soc.*, 2003, **150**, C104
- 22 K. Shiokawa, T. Kudo, and N. Asaoka, *Kokai Tokkyo Koho* (Japanese Patent Disclosures) 1991, 3-215677
- 23 M. Hiratuka, M. Kurashina, H. Nawahune, *Journal of JIEP*, 2002, **5**(1), 72
- 24 M. Paunovic and C. Sambucetti, *Proceedings of the Symposium on Electrochemically Deposited Thin Films, The Electrochemical Society, Inc.*, 1994, **PV94-31**, 34
- 25 G.A. Krulik and N.V. Mandich, *U.S. Patent*, 1993, 5,232,491
- 26 T. Inoue, S. Ando, J. Ushio, H. Okudaira, H. Takehara, T. Ohta, H. Yamamoto and H. Yokono, *J. Surf. Finish. Soc. Japan*, 2000, **49**, 1298
- 27 M. Kato, Y. Yazawa and Y. Okinaka, *Proceedings of the AESF Technical Conference, 'SUR/FIN'95'*, 1995, 805
- 28 M. Kato, J. Sato, H. Otani, T. Homma, Y. Okinaka, T. Osaka and O. Yoshioka, *J. Electrochem. Soc.*, 2002, **149**, C164
- 29 J. Sato, M. Kato, H. Otani, T. Homma, Y. Okinaka, T. Osaka and O. Yoshioka, *J. Electrochem. Soc.*, 2002, **149**, C168