Non-Cyanide Electrolytes for Gold Plating – A Review

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Nowadays, the cyanide and ferrous cyanide solutions are used in practice for gold plating. The traditional baths employed for soft gold as well as hard gold plating contain the cyanide complex, $[Au(CN)_2]^-$, as the source of gold, which release free cyanide ions during the plating. Those compounds are very toxic, and formation and maintenance of cyanide baths is expensive and risky for technical personnel; also, they attack photoresists used to delineate circuit patterns and bonding pads. Due to this reason, and especially in modern time, there is a trend of using the electrolytes without content of cyanides. These electrolytes are mainly based on some organic compounds. This article is an overview of the non-cyanide electrolytes for gold plating introduced into practice or only tested in the laboratory. The large number of investigated complexes fulfils the coating quality requests, but there are problems related to their stability. Decorative gold plating obtained from classic cyanide electrolyte and an electrolyte based on mercaptotriazole have shown similar characteristics such as microhardness, surface roughness, visual appearance and adhesion. At the same time, this bath remained stable in a period of at least nine months.

1. INTRODUCTION

The history of gold deposition began in the early nineteenth century when many art objects were electroplated with gold. It has been traced to the early work of Brugnatelli in 1805 [1]. Gold electroplating formulations based on the double salt gold potassium cyanide was patented in 1840. Since then, many types of gold formulations have been produced to meet the market requirements. Due to the changing trends in fashion, the application of certain colours or shades of the electroplated gold can only last for about forty years [2, 3]. The electronics industry began its development in the 1940's and 1950's; during this period, platters faced new demands for deposits with different properties,

required for decorative plating. The modification of the gold deposits physical properties was required by electronics manufacturers. The electronics manufacturers required that the physical properties of the gold deposits be modified. They were interested in the conductivity, contact resistance, corrosion resistance, electrical as well as physical wear resistance, and the hardness and purity of the deposits. Since the properties of the electroplated gold films are influenced by the incorporation of impurities or inclusion of other metallic or non-metallic constituents, both electroplated soft and hard gold being used in the electronics industry faced no exception. This has led to the development of more gold and gold alloy baths [3-6]. Gold plating was not only limited for decorative applications with the beginning of the electronics era. Nonetheless, the use of gold for decorative applications still contributes to about ten percent of present-day gold plated items [5].

The motives behind the use of electroplated gold changed dramatically in the mid-twentieth century when the emerging electronics industry required special-purpose electrical connections. The electronics industry consumed 5,330,000 troy ounces in 1994. Figure 1 shows the growth in the use of gold in the electronics industry by year. The use of electroplated gold in a variety of different functions in the electronics industry has led to (1) many advances in fundamental understanding of the electrodeposition process and (2) new electroplating technologies over the past 25 years. Electrochemically deposited gold has satisfied many of the demands of the electronics industry. Gold has the third best electrical and thermal conductivity of all metals at room temperature. Also it has high ductility and excellent wear resistance, which are important for electrical contacts [7].
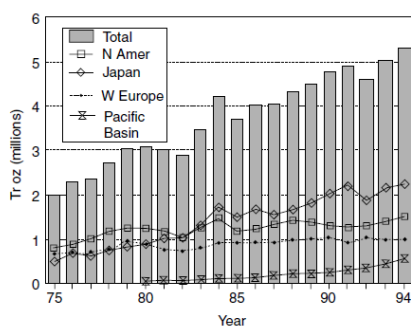

Figure 1. Gold demand in the electronics industry for Japan, North America, Western Europe, and the Pacific Basin (not Japan) [7]

Electrodeposition of gold is not a new process, but has been widely used in the automotive industries, biomedical processes and electronics industries such as in computers, telecommunications, aerospace applications, *etc* [8-18]. The combination of excellent electrical conductivity and high corrosion resistance has led to its widespread use as a standard material for interconnects, bond pads, contacts, as well as conductors, electrodes, and other passive components. Depending on the use, most micro fabricated gold can be classified as hard or soft gold [6].

Hard gold is mainly used in connectors or jewellery, where wear is a concern [18], but also as a contact material for electrical connectors and printed circuit boards (PCBs), relays and switches, which should be resistant to mechanical wear whilst having a low electrical contact resistance [11, 12 and 6].

Hard gold alloys are particularly employed in those fields of industry where the contact is subjected to wear by the making and breaking of connections. In general, hard gold is obtained by codepositing gold with metals such as nickel, cobalt and iron as hardening agents [6, 19]. Inclusion of these materials considerably alters the properties of the deposit, giving a significant rise in hardness and wear resistance [20-22]. The presence of impurities also reduces the tendency of the gold layer to weld by friction, which makes this material very attractive for connectors and contact applications [17].

Soft gold is used where ductility, conductivity and purity are a priority, such as optoelectronics devices, high frequency components, x-ray masks and bond pads. Soft gold is usually plated from solutions containing thallium, arsenic, pyridinium and other compounds [23].

Soft gold, on the other hand, is used for electronic packaging, such as fabrication of interconnects in integrated circuits (ICs), or forming connections to external devices, using tape automated bumping (TAB) or chip-on-glass (COG) and chip-on-flex (COF) techniques [8-16]. The key process in all these technologies is gold wafer bumping. In addition to its use in connecting driver ICs to flat panel displays, gold bumping is also used for high density of I/O (input/output) connections and many packaging applications [11]. Soft gold deposits have also been used to fabricate X-ray masks and three-dimensional microstructures by the Lithographie Galvanoformung Abformung (LIGA) process, which are useful in micro-electro-mechanical systems (MEMS) [14-16]. In the optoelectronics industry, gold is used to fabricate interconnects and transmission lines [17].

A larger number of plating baths for the electrodeposition of soft gold have been developed [12, 24-27], but not all are suitable for through-mask plating applications, which is illustrated in Figure 2. An essential requirement is that the plating bath shows good compatibility with the photoresists material, otherwise the size and shape of the plated structures will be compromised [10, 17, and 28]. Most positive resists are soluble in alkaline solutions so that it is important that the pH is maintained below 9.5, and ideally a bath of near neutral pH should be used [12, 25]. In high volume wafer plating it is also essential that the plating baths are capable of long-term stable operation and are not prone to decomposition [9].
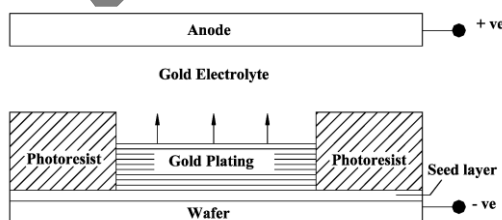

Figure 2. Illustration of gold bump plating by through-mask plating [29]

2. CHEMICAL PROPERTIES OF GOLD AND GOLD COMPLEXES

Gold is always electrodeposited from aqueous solutions of gold complexes, knowledge of the characteristics of these complexes and in particular their stabilities are fundamental to any consideration of the electrodeposition of gold. Gold is classified, with Cu and Ag, in group IB of the periodic table and has a single s electron outside a completed d shell. Despite the similarity of these

metals in electronic structures and ionization potentials, there are many important differences in their redox chemistry. Much of the chemistry of gold and its compounds, especially its behaviour in aqueous solution, can be related to its relatively high electronegativity, i.e. the tendency to attract bonding electrons. Gold is very stable, as indicated by its lack of reactivity in air and in a majority of aqueous solutions, including strong acids [30].

Gold is also the most noble of metals; it is the only metal that is not attacked by either oxygen or sulfur at any temperature [31]. The stability of gold is reduced in the presence of certain complexing ligands, such as cyanide, halides, thiourea and thiocyanate by formation of stable complexes. As a result, gold can be dissolved in relatively mild oxidizing solutions, e.g. aerated aqueous cyanide solutions. This unique behaviour allows gold to be extracted very selectively from ores [32].

Gold compounds exist almost exclusively in the Au(I) and the Au(III) oxidation states, although complexes of Au(IV) are known, and several Au(II) complexes have been identified in solutions. However, neither of the simple aquated ions Au^+ nor Au^{3+} occurs in the free state to any significant extent. Gold compounds usually exist as complexes formed by covalent bonding between a central Au^+ and Au^{3+} cation and a number of ligands, which may either be ions such as Cl^-, Br^-, I^-, OH^-, CN^-, SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, or uncharged molecules such as NH_3, H_2O, $(NH_2)_2CS$, etc. Ions, which can form stable complexes with gold (I) are listed in Table 1 and for gold(III) in Table 2 [33].

Table 1. Stability constants (β) and standard reduction potentials (E^0) for Au(I) species

Au(I) species	Log β	E^0 (V) vs. NHE	Reference
$Au(CN)_2^-$	38.7	-0.595	[34]
$Au(CyS^*)_2^{5-}$	31.1	-0.144	[35]
$Au(S_2O_3)(SO_3)_2^{5-}$	30.8		[36]
$Au(S_2O_3)(SO_3)^{3-}$	27.1		[36]
$Au(SO_3)_2^{3-}$	26.8	0.111	[37]
$Au(S_2O_3)_2^{3-}$	26.1	0.153	[34]
$Au(th^{**})_2^+$	22.2	0.380	[34]
$Au(OH)_2^-$	21.9	0.400	[35]
$AuOH$	20.1	0.506	[35]
$Au(NH_3)_2^+$	19.2	0.563	[34]
AuI_2^-	18.9	0.578	[34]
$Au(SCN)_2^-$	17.5	0.662	[34]
$AuBr_2^-$	12.4	0.960	[34]
$AuCl_2^-$	9.2	1.154	[34]
Au^+		1.695	[34]

* CyS-cysteinate ion
**th-thiourea

Table 2. Stability constants (β) for Au(III) species [22]

Au(III) Complexes	log β
$Au(CN)_4^-$	56
$Au(OH)_4^-$	55
AuI_4^-	47
$Au(SCN)_4^-$	42
$AuBr_4^-$	32
$AuCl_4^-$	26
$Au(SO_4)_2^-$	6

The stability constants of Au(I) and Au(III) complexes are important properties when electrodeposition of gold from these complexes is considered, since they determine the distribution of various forms of gold ions, such as free metal and complexed ions, which become available for discharge at the cathode. The stability constants of the complexes between gold ions and the ligands as well as the concentration of the ligands are the factors which determine whether the gold ions can be reduced from its complexed form during the process of electrodeposition [3].

Traditionally, gold has been plated from gold cyanide electrolytes, where (Au$^+$) is ligated with cyanide (CN$^-$). The cyanide bath is exceptionally stable with the stability constant of AuCN being 10^{38} [38]. However, due to concerns about safety and disposal of process waste, there is growing concern regarding the use of cyanide based processes [33].

Gold exists primarily in the 1$^+$ and 3$^+$ oxidation states. Electroplating baths formulated from Au(III) complexes are relatively rare [24, 26]. Firstly it should be noted that aurous ion, Au(I), is not stable in aqueous solution and is prone to disproportionation [17, 12, 9, 27] to form metallic gold or undergo hydrolysis to form AuOH [34, 35]. For this reason, all gold plating processes are formulated from Au(I) complexes and deposition typically takes place by direct electroreduction of the complexed species. The aurous ion complexes with a large range of ligands, forming linear complexes with a preferred coordination of 2, but some 3 and 4 coordinate species are also known [9, 27]. If the formation of complexes involving the aurous ion and a ligand, L, is written as:

$$Au^+ + xL^{n-} \Leftrightarrow AuL_x^{(xn-1)-} \tag{1}$$

the overall stability constant, β, can be defined as:

$$\beta = \left[AuL_x^{(xn-1)-}\right] / \left[Au^+\right]\left[L^{n-}\right]^x \tag{2}$$

Some of the most common Au(I) complexes along with their stability constants and standard reduction potentials are shown in Table 1. The magnitude of the stability constant is particularly

important as it gives an indication of how stable the complex is likely to be and it also affects the electrochemical characteristics. For example, the standard electrode potential of the gold complex shifts to increasingly more negative potentials as the stability constants increases (see Table 1) [33].

Despite the importance of the stability constant in establishing the chemical and electrochemical properties of the plating solution, there is relatively little data regarding the stability of many gold complexes [35]. There are also some large discrepancies in stability constants obtained from different literature sources. For example, a value of log β ≈10 is commonly assumed [9, 12, 24, 25, 27] for the $Au(SO_3)_2^{3-}$ complex but recently it was shown that the available experimental data indicates a much higher value of log β≈27 and the observed characteristics of sulfite baths are more consistent with the latter value [9, 36, 37, 39]. The values given in Table 1 reflect what we believe to be the most consistent and reliable values, although considerable uncertainties remain for some species. In many cases, direct measurements of stability constants have not been possible and approximate values have been inferred by a variety of indirect methods. For example, it is possible to estimate the stability constants of complexes based upon the linear free energy relationship between Au(I) complexes and those of other metals with a d10 electron configuration such as Cu(I), Ag(I) and Hg(II) [36, 34-35]. Similar linear relationships also exist between Au(III) and Au(I) complexes and this has enabled the prediction of log β values where experimental data is not available [35, 40-42].

The Au(I) cyanide complex is by far the most important for electrodeposition. However, there are several shortcomings to the use of $[Au(CN)_2]^-$ which have stimulated the investigation and commercialization of other gold complexes in plating baths [43]. The stability of the gold cyanide complex causes the reduction potential to occur at very negative potentials, resulting in the coreduction of hydrogen ions, which lowers the plating efficiency and makes the development of electroless plating baths difficult [43]. The release of free cyanide during the reduction of $[Au(CN)_2]^-$ can be incompatible with positive photoresists used in the microelectronics industry [23, 29]. It has also been found that the residual stress of the plated gold can be controlled in non-cyanide baths [14, 44]. Low-stress deposits are of particular interest for X-ray lithography masks because they must be thin, flat, and made from high-atomic-number elements. Lastly, the health and safety of workers and the environmental impact of the wide-scale use of cyanide are a concern.

The chemistry of gold(III) complexes is far less developed than the corresponding gold(I) complexes. Gold(III) gives stable complexes with C, N, P, S, or even O-donor ligands. Organometallic chemistry is very important because many compounds have been prepared starting from organometallic gold(III) precursors. The stability constants of Au(III) shown in Table 2 are important because Au(III) can also be used as the source of gold in baths in place of Au(I), and Au(III) can also be formed at the anode during plating through the oxidation of Au(I) [7].

3. PLATING PROCESSES

Figure 3 illustrates the process of electrodeposition using an electrolyte containing a complex metal ion. Within the *Helmholtz* double layer, the co-ordinated positive metal ion in its ligand field is

attracted towards the cathode surface. The distribution of ligands around the metal is distorted in this region. The negatively charged complex ion becomes polarised in the electric field of the cathode, thus the ligand ions are freed and the metal is then deposited onto the cathode [18, 24]. Finally, within the Helmholtz layer the complex breaks up. Its component ligand ions or molecules are freed and the metal cation is deposited as metal atom on cathode [24].
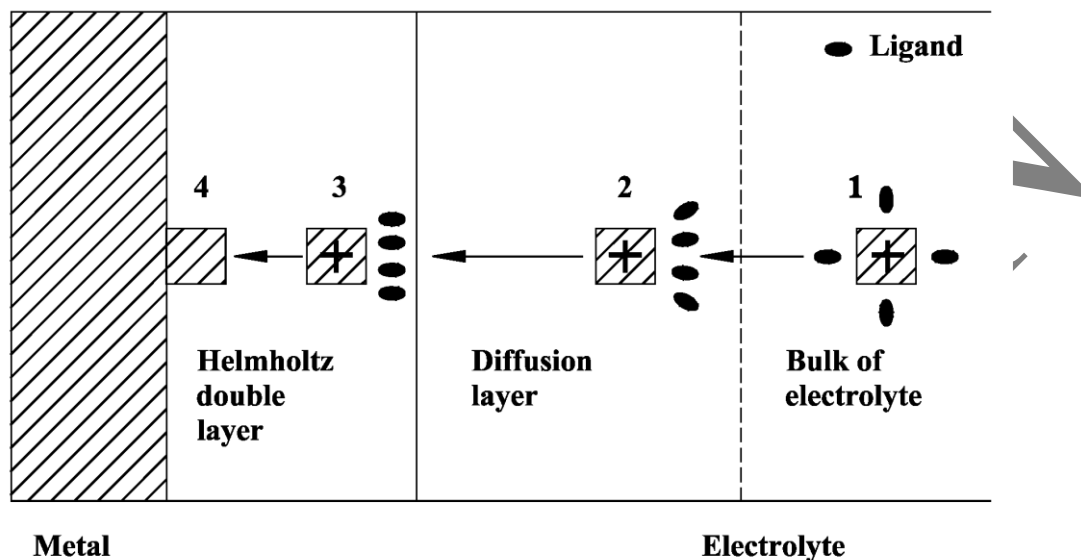

Figure 3. Schematic diagram of gold deposition process [24]

In general, the principal reaction for gold electrodeposition [24] from a plating bath containing cyanide, sulfite or thiosulfate as the complexant with monovalent gold ions is:

$$[Au(I)L]_{complex} + e^- \leftrightarrow Au + L \tag{3}$$

For a homogeneous reversible reaction, the law of mass action dictates that:

$$\frac{[Au(I)L]_{complex}}{[Au^+][L]} = \beta \tag{4}$$

where [Au], [complex] and [Au(I)-complex] are the concentrations of gold ion, complex ion and gold complex in the solution. The constant, β known as the stability constant, is a measure of the strength of the complexant. Since the disproportionation of gold in solution is controlled by the concentration of gold complex, knowledge of the stability constant of the complex is essential for the determination of the bath stability [24].

Nowadays, the cyanide and ferrous cyanide solutions are used in practice for gold plating. Those compounds are very toxic, and formation and maintenance of cyanide baths is expensive and risky for technical personnel. Due to this reason, and especially nowadays, there is a trend of using the

electrolytes without content of cyanides. Content of those electrolytes is mainly based on some organic compounds. However, their usage has not found the satisfied industry use due to the low constant stability that is demonstrated by complex destruction and extraction the elementary gold from electrolyte.

4. CLASIFICATION 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 Figure 3 illustrates this classification [25].
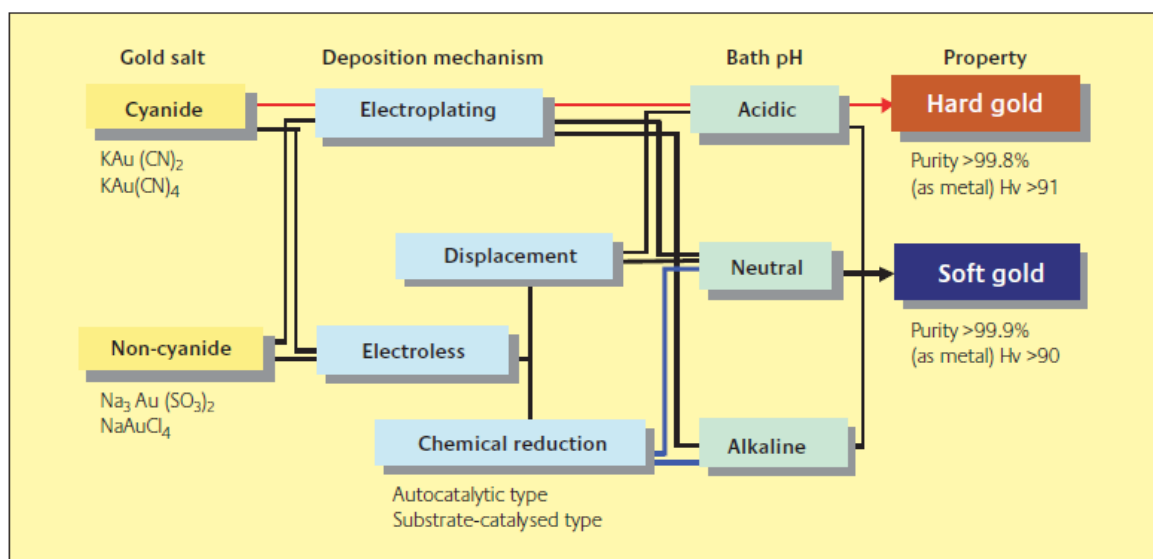

Figure 4. Classification of gold plating [25]

The electrolytic cyanide-type baths include those operated at acidic, neutral, or alkaline pHs, and they can deposit either hard gold or soft gold. Non-cyanide type baths can be operated only at neutral or alkaline pHs 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.

This paper reviews currently available non-cyanide electrolytes for gold plating:
1.   Sulfite bath
2.   Thiosulfate bath
3.   Mixed sulfite-thiosulfate bath
4.   Thiourea bath

5. Ascorbic Acid Bath
6. Baths Containing No Additional Reducing Agent
7. Au(I) thiomalate bath
8. Other baths
9. Bath based on mercaptotriazole

4.1 Sulfite bath

The use of a gold sulfite complex for gold plating has been known since 1842 [44] and it is still the gold complex most commonly used to prepare non-cyanide baths. Gold sulfite baths traditionally attracted attention because of their ability to produce smooth, bright, and ductile pure gold deposits with good microthrowing power. Gold alloy deposits of low or high carat with high ductility can also be produced more readily with sulfite baths than with cyanide baths [44, 26].

For microelectronic and optoelectronic applications, sulfite based baths possess a number of important advantages over cyanide processes. For example, they tend to have better throwing power than cyanide baths, and this can result in better bump thickness uniformity across the wafer [9]. In general, gold bumps deposited from sulfite baths have excellent shape, uniform height and low surface roughness and do not exhibit under-plating [33].

Most importantly, they are non-toxic and the requirements for handling and disposal are much lower than for cyanide baths. The stability constant of $\left[Au(SO_3)_2\right]^{3-}$ is, however, 10^{11} times lower than for the corresponding cyanide complex (Table 1) but gold sulfite baths still possess relatively high stability, particularly under alkaline conditions [9]. Their compatibility with most photoresists is also good, and as long as the pH is maintained below 10, dissolution and delamination of the photoresists is not observed [9, 17, 28, 38]. In order to satisfy the requirements of resist compatibility and bath stability most commercial gold sulfite processes are operated in the pH range 9 to 10.

In the sulfite-based bath, gold exists in the form of $\left[Au(SO_3)_2\right]^{3-}$. On standing, the excess sulfite in solution tends to decompose spontaneously to form gold and sulfite ions:

$$Au(SO_3)_2^{3-} \leftrightarrow Au^+ + 2SO_2^{3-} \tag{5}$$
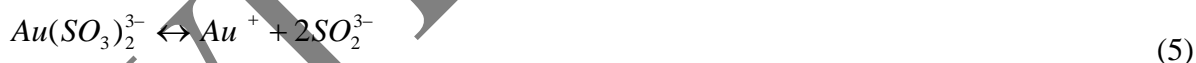
A precipitate of metallic gold is formed by the following disproportionation reaction:

$$3Au^+ \rightarrow 2Au^0 + Au^{3+} \tag{6}$$

The sulfite ion itself can also decompose according to reaction 7, which forms hydroxyl ions. This equilibrium is pH dependent.

$$SO_2^{3-} + H_2O \leftrightarrow SO_2 + 2OH^- \tag{7}$$

At a pH of 7.0, the equilibrium of sulfurous acid in reaction 7 starts to shift to the right, thereby releasing SO_2.

A second reaction is the cathodic reduction of sulfite to dithionite, $S_2O_4^{2-}$, which can lead to a chemical reduction of gold ions to metallic gold [45].

To suppress the bath instability resulting from this reaction, all commercially available sulfite baths contain proprietary stabilizing additives [12].

To counteract these stability problems, many Au (I) sulfite baths described in the literature are operated at pH ≥ 8.0 [7, 9, 15, 16, 44]. This means that problems can still arise when photoresists, which are soluble in alkaline solutions, are used. While the dissolution of these resists is slower, under milder alkaline conditions (as compared to cyanide electrolytes), significant organic contamination of the plating bath can occur as the plating process continues. This can affect deposit hardness, stress and morphology as well as make the process control difficult. Since conventional positive photoresists are unstable in alkaline pHs, it is desirable to use an electrolyte that can be operated at a neutral or acidic pH to minimise the interaction between the resist and the plating bath, whilst having better stability [39, 45].

Commercially available sulfite baths have addressed this problem by incorporating proprietary stabilising additives.

Since the initial work of Horkans and Romankiw [46] a large number of papers demonstrating the suitability of gold sulfite baths for fabricating microelectronics, optoelectronics and MEMS devices have appeared. In general, good results were reported in these studies, but a perceived weakness [12, 24-27, 38] of the sulfite baths is that they are unstable under neutral or acidic conditions necessary for optimum resist compatibility. A number of approaches have been presented to allow sulfite baths to operate at lower pH, and traditionally this has involved the addition of stabilising agents to the bath. The use of these additives is undesirable from the process control point of view, but a number of sulfite processes have been developed which can operate stably at near neutral pH [33].

The addition of an amine such as ethylenediamine is well known to stabilize the bath through the formation of a mixed gold complex [26, 44], which also makes it possible to operate the bath in lower pH range of 5 to 8, rather than pH>8 for the bath containing no amine. Mason [45] as well as Honma and Kagaya [47] found that the addition of 2,2'-dipyridine suppresses the disproportionation reaction to a large extent, presumably through the formation of its complex with Au⁺. No adverse effect was observed on hardness or surface morphology. Morrissey [48] 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 photoresists. However, from the environmental context, using such organic additives can cause waste disposal problems. Reuse of electrolytes, thereby, compromise the long term sustainability of the process [18].

The use of bath additives to modify or enhance the properties of the electrodeposited gold has also been investigated. For example, arsenic has traditionally been used as a brightener in gold sulfite baths and it also has a strong influence on deposit hardness, microstructure and stress [9, 46, 49]. Similarly, thallium is often employed as a grain refiner and its influence on hardness and stress has also been investigated [14, 15]. The influence of the plating conditions on deposit stress has also been explored in a number of papers. It appears that by careful manipulation of the current density,

temperature and concentration of additives it is possible to deposit gold with essentially zero stress [14, 15].

Sulfite baths are usually formulated from sodium or potassium salts but ammonium gold sulfite baths have also been developed [27, 28, and 49]. These baths have been mainly used for electroforming (e.g. dental) applications but Simon [50] has recently shown their suitability for wafer plating applications. Deposits from ammonium sulfite bath had excellent characteristics (e.g. low hardness, stress and roughness) even in the absence of additives. In addition, the bath could be operated stably at a pH of 6 -7 without requiring the use of stabilising agents. Despite the long history of gold sulfite baths, there is little agreement regarding the electrodeposition mechanism. The simplest scheme involving direct one electron reduction of the $[Au(SO_3)_2]^{3-}$ -complex seems to only occur at low overpotentials or at high pH (i.e. > 9) [47, 51]. At lower pH a variety of different mechanisms have been proposed [51, 52], usually involving a series of coupled chemical and electrochemical steps. Subsequent Raman [53] and electrochemical measurements [54] have shown the importance of adsorbed species and the formation of passivating sulfur films on the gold deposition process.

Bath composition and operating conditions for a sulfite bath are shown in Table 3.

Table 3. Sulfite bath composition and operating conditions [55]

| Bath constituent	
$(NH_4)_3\{Au(SO_3)_2\}$	$[Au^+]=10$ g/dm^3
pH	9.5
Temperature	40^0C
Current density	0.15-0.5 A/dm²
Agitation	Magnetic stirring

The addition of As^{3+} improves the brightness of the gold deposit, but it is known to increase its hardness if the bath is operated at an alkaline pH [45, 48]. With the acidic bath of Morrissey, the addition of As^{3+} improves the brightness without increasing the hardness.

Watanabe *et al.* [8] tested sulfite electrolytes containing cerium ions to improve the smoothness and softness of the gold films for the formation of microbumps. They also investigated whether the inclusion of conductive salts such as sulfuric acid and boric acids improved deposit smoothness. They reported that the addition of heavy metal ions such as thallium and arsenic were effective in improving the topology of deposited gold, but these additives are highly toxic which makes them unsustainable in the long term [55].

As a second course of action, ammonium sulfite baths, which operate in the pH range 6.0 to 8.0, have also been developed. These baths are useful alternatives to the commonly used sodium sulfite electrolyte [50].

4.2 Thiosulfate bath

The electrodeposition of gold from an Au(I)-thiosulfate complex has been known since as early as 1913. [26], but it has never been used for making a practical plating bath. The stability constant of the $\left[Au(S_2O_3)_2\right]^{3-}$ -complex is equal to 10^{26} [57]. In contrast to the sulfite and cyanide baths, little attention has been paid to the development of gold thiosulfate plating processes [12, 25-27]. This is somewhat surprising given the potentially low toxicity of a thiosulfate bath and the relatively high stability of the $\left[Au(S_2O_3)_2\right]^{3-}$ -complex, but presumably has arisen because the inherent instability of the thiosulfate anion with respect to disproportionation [12, 25, 27]. The $S_2O_2^{3-}$ - ion is relatively stable at low concentrations and high pH, but under acid or neutral conditions it can readily disproportionate to form colloidal sulfur [58]. Depending on the conditions, a number of decomposition reactions are possible, but the disproportionation can be represented simply as:

$$S_2O_3^{2-} \leftrightarrow S^0 + SO_3^{2-} \tag{8}$$
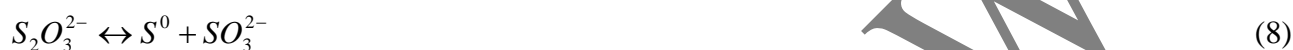
At neutral or mildly acidic conditions, pH ≈ 6.0, protonation of excess $S_2O_3^{2-}$ forms HSO_3^- and colloidal sulfur; this hinders its industrial exploitation:

$$H^+ + S_2O_3^{2-} \leftrightarrow S^0 + HSO_3^- \tag{9}$$

At still lower pH values, the HSO_3^- ion combines with a second proton and yields H_2SO_3 which eventually leads to the evolution of sulfur dioxide. It is clear that reactions 8 and 9 impede the use of thiosulfate-based electrolytes for gold deposition [29].

The preparation of a stable bath typically requires the formulation of an electrolyte containing a low concentration of free $S_2O_3^{2-}$, operation at a pH > 9 [57] or the use of stabilisers such as sulfinic acids [27]. Despite these limitations, there have been a few attempts to develop gold thiosulfate plating processes. For example, Wang et al. [58] have proposed a non-cyanide plating bath which contains thiosulfate and iodide as complexing agents and which operates at pH of 9.3. Given the much larger stability constant for the former species it is expected that the $Au(SO_3)_2^{3-}$ species predominates and indeed the authors found no evidence for complexation of Au(I) with iodide ions. The optimised gold thiosulfate bath produced semi-bright, smooth and uniform gold deposits with a current efficiency approaching 100% at current densities of 1–5mA/cm^2. The suitability of this thiosulfate for through-mask plating was also demonstrated.

Sullivan and Kohl [43] studied the reduction of the $Au(SO_3)_2^{3-}$ complex in a solution containing a citrate buffer, excess potassium chloride and operating at a pH of 6.4. The thermodynamic and kinetic properties of the complex were determined, but no attempt was made to examine deposit properties or examine its suitability for through-mask plating applications. The authors suggest that gold deposition takes place by a direct one electron reduction of the $Au(S_2O_3)_2^{3-}$ complex, but others

[59] have proposed a mechanism involving the loss of one $S_2O_3^{2-}$ ligand in a preceding chemical step followed by direct reduction of the $AuS_2O_3^-$-species.

4.3 Mixed sulfite-thiosulfate bath

The non-cyanide 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, Pauradier and Gadet [56], as well as Alymore and Muir [57], investigated the possibility of electroplating soft gold from a bath containing the two ligands. It was found that the mixed ligand bath is highly stable even without the addition of any stabilizer [61-63]. The composition and operating conditions of the mixed ligand electroplating bath proposed by Kato and Okinaka are given in Table 4 [25].

Table 4. Composition and operating conditions of Au(l) thiosulfate-sulfite electroplating bath [25]

Bath constituent	mol/l
NaAuCl$_4$·2H$_2$O	0.06
Na$_2$SO$_3$	0.42
Na$_2$S$_2$O$_3$·2H$_2$O	0.42 (Variable 0.42-1.26)
Na$_2$HPO$_4$	0.30
pH	6.0
Temperature	60°C
Current density	5mA/cm^2

Crucially, mixed sulfite-thiosulfate bath could be operated at near neutral or slightly acidic conditions which make it compatible with essentially all photoresists materials. The enhanced stability of the mixed bath was attributed to the formation of gold thiosulfate or mixed sulfite-thiosulfate complexes with large stability constants. The decomposition of thiosulfate in the bath was minimised by the presence of a large amount of excess sulfite. This tends to drive the equilibrium in reaction (8) to the left thereby minimising the formation of colloidal sulfur in the bath [23].

Osaka and coworkers [23] investigated the possibility of electroplating soft gold from a thiosulfate-sulfite mixed ligand bath, specifically for application to the formation of microbumps on silicon wafers. Optimized bath compositions and operating conditions are listed in Table 5 together with the hardness values of the gold deposits obtained. This bath is operated at a slightly acidic pH of 6.0 and at a mildly elevated temperature of 60°C. It is highly stable, and there is no need to add any stabilizer to suppress spontaneous decomposition. The gold plated under optimal conditions has a Vickers hardness of approximately 80 kg/mm^2 in the as-deposited state, which decreases to 50 kg/mm^2 upon annealing at 350°C for only 30 min [12].

The deposit hardness could be controlled by changing the relative amounts of sulfite or thiosulfate in the bath, the use of additives such as thallium, or by annealing. The influence of sulfur inclusion on the deposit morphology and hardness was investigated in detail. The addition of thallium ions, in the form of Tl_2SO_4, as a grain refiner was found to decrease hardness and improve surface morphology of the gold deposit [29].

Table 5. Compositions and operating conditions of gold(I) thiosulfate-sulfite mixed ligand bath and Vickers hardness of electroplated soft gold [12]

	With Tl^+	Without Tl^+
$NaAuCl_4\cdot2H_2O$	0.06M	0.06M
Na_2SO_3	0.42	1.1-1.4[*]
$Na_2S_2O_3\cdot5H_2O$	0.42	1.1-1.4[*]
Na_2HPO_4	0.30	0.30
Tl^+ (added as Tl_2SO_4)	5ppm	
pH	6.0	6.0
Temperature (°C)	60°C	60°C
Current density (A/dm^2)		
Agitation	mild	mild
Deposit hardness (kg/mm^2)		
As deposits	88	87-88
After annealing at 350°C	52	45-60

[*] $[Na_2SO_3]:[Na_2S_2O_3]=1:1$

The improved bath offered soft gold deposits under safe, neutral, low temperature and stable plating conditions. However, there are some problems with this electrolyte. Toxicity of thallium (human poison; lethal dose approximately 0.1 mg/m^3) is of concern [64-65]. The inclusion of Tl^+ affects adversely the bonding of gold wires to the plated structure [66]. Finally, the thallium content in the electrolyte needs close monitoring during process operation.

In the initial study [23] of gold deposition from the mixed ligand system, five variables were found to affect the hardness as well as the sulfur content of the deposit. They are: current density, bath temperature, pH, the addition of thallium ions, and the total ligand concentration ($[S_2O_3]^{2-} to [SO_3]^{2-}$).

It was 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. It was found that the sulfur content decrease with increasing total ligand concentration ($[S_2O_3]^{2-} + [SO_3]^{2-}$), where the ratio of $[S_2O_3]^{2-}$ to $[SO_3]^{2-}$ was kept constant at unity. This rather unexpected finding demanded a detailed study of the mechanism of sulfur inclusion and chemical identification of the sulfur-containing species responsible for the included sulfur [12].
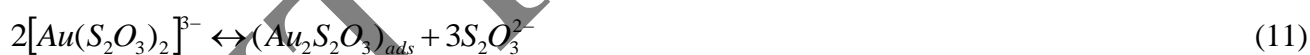
The study [12] showed that thiosulfate was the main source of sulfur inclusion, and it was considered possible that either one or both of the following two reactions could lead to the inclusion of sulfur:

(a) $S_2O_3^{2-} \leftrightarrow S + SO_3^{2-}$ or   (8)

(b) $S_2O_3^{2-} + 6H^+ + 4e^- \leftrightarrow 2S + 3H_2O$ (10)

A thiosulfate compound is considered in two forms: $NaAu(S_2O_3)$ or $Au_2S_2O_3$.

The distinction between (8) and (10) was made by comparing the results of sulfur analyses performed by a combustion method in an oxygen atmosphere or a nitrogen atmosphere. Because the method measures sulfur in the form of SO_2 produced by combustion of the sample, elemental sulfur can be determined only in an atmosphere containing oxygen and not in pure nitrogen. Experimentally, identical results were found in both pure oxygen and pure nitrogen: 110 and 115 ppm for deposits plated in the mixed ligand bath, and 180 and 190 ppm for deposits produced in the bath containing thiosulfate alone. Based on these results, it was concluded that elemental sulfur is not the form of sulfur included in the gold. The compound $NaAu(S_2O_3)$ is known to be a slightly soluble compound [12, 29].

Based on these experimental results, the possibility of elemental sulfur being the form of sulfur inclusion was excluded. On the other hand, if compound $NaAu(S_2O_3)$ 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, this compound accounts for, at most, only 10% of the entire amount of sulfur included in the gold. These findings led to the assumption that a major portion of the sulfur included in the gold exists in the form of $Au_2S_2O_3$. This species is likely to be in an adsorbed state on the cathode surface according to equation (11) below:

$$2\left[Au(S_2O_3)_2\right]^{3-} \leftrightarrow (Au_2S_2O_3)_{ads} + 3S_2O_3^{2-}$$ (11)

$$(Au_2S_2O_3)_{ads} + 2e^- \leftrightarrow 2Au + S_2O_3^{2-}$$ (12)

$$\left[Au(S_2O_3)_2\right]^{3-} + e^- \leftrightarrow Au + 2S_2O_3^{2-}$$ (13)

Reaction (11) is followed by the electrochemical reduction (12) of $\left[Au(S_2O_3)_2\right]^{3-}_{ads}$ to deposit gold with the overall reaction given by (13). According to this mechanism, the formation of the adsorbed species by reaction (11), and hence the sulfur inclusion, should be more favourable at lower free $S_2O_3^{2-}$ concentrations. At very high $S_2O_3^{2-}$ concentrations the gold deposition is believed to take place directly from the bulk species, $\left[Au(S_2O_3)_2\right]^{3-}$ via reaction (13) 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 [63].

Based on the mixed ligand electrolyte of Osaka, a group of authors at Newcastle University has developed an electrolyte for soft gold electrodeposition which has attempted to eliminate Na_2HPO_4 and Tl^+. Table 6 shows the formulation of gold electrolytes used by Osaka and Newcastle group [29].

Table 6. Comparison of composition of gold thiosulfate-sulfite electrolyte used by Osaka and Newcastle group [29]

Chemical	Composition	
	Osaka	Newcastle
$NaAuCl_4$	0.06M	-
$HAuCl_4$	-	0.05M
Na_2SO_3	0.42M	0.42M
$Na_2S_2O_3$	0.42M	0.42M
Na_2HPO_4	0.30M	-
Tl_2SO_4	5-30ppm	-

Roy [18] prepared solution by first dissolving both thiosulfate and sulfite complexes together (0.42 M Na_2SO_3 and 0.42 M $Na_2S_2O_3$) with deionised water. It was found that Na_2SO_3 acted as a buffer and maintained the pH of the solution; if it were not added at the same time as $Na_2S_2O_3$, the solution pH decreased rapidly leading to sulfur precipitation. Thereafter, 0.05 M $HAuCl_4$ was added slowly to the solution containing the mixed ligand by means of a burette in order to avoid any rapid changes in pH. It was necessary to stir the solution as well as monitor the pH throughout the preparation process. If this method was not followed, the pH of the solution decreased rapidly, precipitating $S°$ and releasing SO_2.

UV-visible spectroscopy analysis was carried out to determine the gold complex in solution. The experiments revealed that Au(I) was complexed with thiosulfate no evidence of a mixed complex was found [29]. Based on his own results, Liew proposed an alternative view of the system [66]. He believes that the monovalent gold ion (Au (I)) is complexed by thiosulfate which has a relatively high stability constant:

$$2\left[Au(S_2O_3)_2\right]^{3-} \leftrightarrow Au_2S_2O_3 + 3S_2O_3^{2-} \tag{14}$$

The sulfite ligand, on the other hand, simply maintains a high level of bisulfite ions in the solution under neutral or mildly acidic conditions, which shifts the equilibrium between the thiosulfate, sulfur and bisulfite ions in eqn. 15 towards the left, making the formation of sulfur less favourable.

$$H^+ + (S_2O_3)^{2-} \leftrightarrow (HSO_3)^- \tag{15}$$

This means that gold is stabilised by the formation of $\left[Au(S_2O_3)_2\right]^{3-}$ ions and precipitation of sulfur is avoided by excess $(HSO_3)^-$. In this regard, the electrolyte constituents work in 'synergy'.

The use of this electrolyte was tested at the site of an industrial partner, where degradation in a sulfite electrolyte was observed typically after plating 20–25 wafers. Stability of the bath was monitored by depositing a total of 30 wafers in a flow cell over 2 weeks [68]. In these experiments, there was no apparent degradation or physical change in the electrolyte. Table 7 summaries the performance of the electrolyte during industrial tests. In these experiments the process conditions for both the thiosulfate-sulfite and sulfite electrolyte were the same. The electrolyte pH remained near-neutral (pH 7.4) throughout the two weeks and the process remained stable during the entire period. The plating solution remained colourless and clear, showing no signs of precipitation [29].

Table 7. Summary of sulfite and thiosulfate-sulfite electrolyte performances during industrial tests [29]

	Sulfite	Thiosulfate-sulfite (Newcastle)
pH	9.5±0.1/stable	7.4±0.1/stable
Current efficiency	98.2%	98.9%
Cell potential	1.3V	0.7V
Resist compatibility	Poor Speckled pits found on resist surface	Good No changes in physical appearance of resist
Electrolyte stability	Average Signs of bath decomposition as colour changed to purple	Good No apparent degradation or precipitation
Hardness	Soft	Soft
Uniformity	Average	Average
Roughness	Smooth	Rougher

After plating, each wafer was inspected for signs of dissolution, cracking or delamination of the photoresists. Figure 5 shows no observable physical change of the resist on the wafer after electrodeposition from the thiosulfate-sulfite bath, which suggests that there was no significant interaction between the resist and the bath. Current efficiency of the gold deposition was determined gravimetrically from a series of plating experiments and the average current efficiency obtained was 98.9%, which was slightly higher than the sulfite electrolyte [68].

The hardness of gold deposited from the thiosulfate-sulfite bath at three different current densities was compared to that of samples plated from the sulfite bath. Deposits obtained had hardness values in the range of 0.7 to 0.9 GPa, which are softer than the sulfite deposits (*ca*. 0.95 to 1.20 GPa) [29].

Gold deposits from the plating electrolyte were bright and adherent. The plated structures, examined by scanning electron microscopy showed good reproduction of the photoresists mould. The

gold structures achieved had straight side-walls with top planar surface and exhibit a columnar microstructure, similar to the deposits obtained from the electrolyte by Osaka and the sulfite bath [29].

Roughness of deposited gold was found to be in the range of 200–250nm, which is higher than the average deposits obtained from sulfite electrolytes [69]. Other properties such as thickness uniformity and stress of the plated structure were also investigated and were found to be compatible within the requirements for a wide range of micro and opto-electronic applications [68].
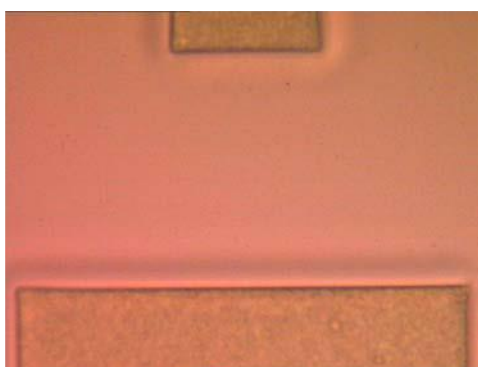

Figure 5. SEM image of resist after deposition from modified gold thiosulfate-sulfite solution, pH 7.4 at 3.5 mA/cm^2 [29]

Table 8. Comparison of acid cyanide and thiosulfate-sulfite gold plating electrolytes for soft gold deposition [29]

Chemical properties of plating bath	Acid cyanide	Thiosulfate-sulfite (Newcastle)
Toxicity	Potentially toxic	Non-toxic
Operating bath pH	pH 5.0 (acidic)	pH 7.4 (near-neutral)
Bath stability	Best stability	Stable
Waste disposal	Gold recovery possible and CN⁻ is converted to CO_3^{2-}	Possibility of gold recovery by electrowinning
Resist compatibility	Penetrates and delaminates organic photoresists, which leads to 'underplating'	No significant attack on photoresists
Ease of bath preparation	Fairly difficult	Fairly difficult
Relative electrolyte cost	Controlled by the price of gold	Controlled by the price of gold
Physical properties of deposited gold Microstructure	Underplating may lead to shape change of gold bumps, causing loss of device performance	Straight side-walled gold bumps formed and good reproduction of photoresists mould
Brightness	Bright	Bright
Hardness	1.0 GPa (65 °C) 1.7 GPa (25°C)	0.7–0.9 GPa (55 °C)
Roughness	Fine-grained	Slightly rough ~ 200nm
Anode products	Carbonate (non-toxic)	Sulfate (easily rendered non-toxic)

The mixed thiosulfate-sulfite electrolyte also has advantage over the acid-cyanide solution. Comparison of the chemical and physical properties is listed in Table 8. It is clear that for soft gold deposition purposes, the thiosulfate-sulfite electrolyte is a better alternative from hardness and resist-compatibility point of view, and offers competitive process chemistry.

4.4 Thiourea bath

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi, Ltd. [25, 61, and 70]. Basic and improved versions of the bath composition and operating conditions are shown in Table 9. In this system thiourea has been shown to undergo complex chemical reactions through the formation of a radical intermediate, $(NH)(NH_2)CS$, 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, $(NH_2)_2CSO_2$, which appears to be responsible for bath instability. Hydroquinone appearing as an additional component of the bath (see Table 9) 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.

Table 9. Basic and improved thiourea baths [25, 71]

Bath constituent	Basic bath	Improved bath
$NaAuCl_4 \cdot 2H_2O$ (mol/dm^3)	0.0125	0.0125
$Na_2S_2O_3 \cdot 5H_2O$ (mol/dm^3)	0.1	0.1
Na_2SO_3 (mol/dm^3)	0.4	0.4
$Na_2B_4O_7 \cdot 10H_2O$ (mol/dm^3)	0.13	0.13
Thiourea (mol/dm^3)	0.033	0.033
Hydroquinone (mol/dm^3)	-	0.002
pH	9.0	8.0
Temperature (^{0}C)	80	70
Bath life with load (h)	12	50
Bath life without load	60 [h]	> 1 month
Plating rate (μm/h)	0.8	1.2

4.5. Ascorbic Acid Bath

In the studies [23, 62] authors developed a thiosulfate-sulfite mixed ligand bath with ascorbic acid as the reducing agent. The compositions of the basic bath and an improved bath are shown in Table 10. The possibility of developing these baths was initially investigated based on the 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.

Table 10. Basic and improved ascorbic acid baths [70]

Bath constituent	Standard bath	Improved bath
$NaAuCl_4 \cdot 2H_2O$ (mol/dm^3)	0.0125	
$Na_3Au(SO_3)_2$ (mol/dm^3)	-	0.01
$Na_2S_2O_3 \cdot 5H_2O$ (mol/dm^3)	0.1	0.1
Na_2SO_3 (mol/dm^3)	0.1	0.4
NH_4Cl (mol/dm^3)	0.05	-
K_2HPO_4 (mol/dm^3)	-	0.1
Sodium L-ascorbate (mol/dm^3)	0.2	0.1
Additive	-	trace
pH	6,0	7.2
Temperature (^{0}C)	60	60
Bath life	<8 [h]	6 months
Plating rate (μm/h)	1.2-1.5	0.8-1.1

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 photoresists technique. These findings led to the development of an improved bath which is stable for the period of five metal turnovers 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 [25].

4.6. Baths Containing No Additional Reducing Agent

Krulik and Mandich [68] 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.

Sato [71] as well as Leblanc [72] and collaborators studied the reaction mechanism of this system in detail. The bath composition and operating conditions used in these investigations are listed in Table 11, which are similar to those of the autocatalytic bath listed in Table 10 except that the reducing agent (ascorbic acid) was excluded.

Table 11. Bath composition and operating conditions of no additional reducing agent bath [25]

Bath constituent	
$NaAuCl_4 \cdot 2H_2O$ (mol/dm^3)	0.01
Na_2SO_3 (mol/dm^3)	0.32
$Na_2S_2O_3 \cdot 5H_2O$ (mol/dm^3)	0.08
Na_2HPO_4 (mol/dm^3)	0.05
K_2HPO_4 (mol/dm^3)	0.32
pH	9.0
Temperature (^{0}C)	60
Agitation	Mechanical Stirrer

From the experimental results above, the following conclusions were drawn: the gold deposition from the mixed ligand bath containing no added reducing agent proceeds by two different reactions occurring simultaneously, that is, substrate-catalysed reaction (80-90%) with sulfite ion as the reducing agent and galvanic displacement reaction with the nickel substrate (10-20%) and no autocatalytic gold deposition takes place in this bath [25, 72, 73].

4.7. Au(I) thiomalate bath

Gold thiomalate complex is used in the plating baths in the form of NaAu(I) thiomalate ($C_4H_4AuNaO_4S$ or $C_4H_3AuNa_2O_4S$). Basic characteristics of this complex are its high stability and the fact that plays an important role in obtaining Au-Sn alloys [26]. Significant use of gold thiomalate is in medicine for the treatment of rheumatoid arthritis [74]. Figure 8 shows the structural formula of sodium gold thiomalate [75].
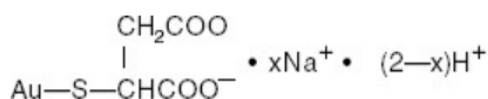
$$\begin{array}{c} CH_2COO \\ | \\ Au-S-CHCOO^- \end{array} \cdot \ xNa^+ \cdot \ (2-x)H^+$$

Figure 8. Structural formula of sodium gold thiomalate [74]

4.8 Other baths

Some of the complexes shown in Table 1 might serve as the basis for gold plating baths. In practice, however, solutions containing halide, ammonia, hydroxide, thiocyanate and hydroxide

ligands have all been found to be unsuitable due to a combination of poor deposit properties, instability or toxicity [26, 27]. In the late 1970s an alternative non-cyanide gold bath based on a nitrosulfito complex was proposed [73]. This bath was formulated around the $[Au(SO_3)_2(NO_2)]^{4-}$ - complex and was considered to be more stable than traditional sulfite baths. The nitro-sulfito bath was found to have a high current efficiency (> 90%) and throwing power and could be used to produce thick, smooth, low stress deposits with a relatively low hardness. However, this bath has not been widely used and has not been applied in microelectronic, optoelectronic or micro-system applications [33].

Gold plating baths based on complexes between Au(I) and mercapto-alkylsulfonic acid ligands such as 2-mercaptoethanoic acid (MES), 3-mercapto-propanoic acids (MPS) and 2,3-dimercaptopropane-1-sulfonic acid (DMPS) have also been developed [27]. The stability constants of $[Au(MES)_2]^{2-}$ and $[Au(MPS)_2]^{2-}$ have not been measured, but based on a comparison with related gold mercapto complexes [9] values of log β≈30 can be expected. This is comparable to sulfite and thiosulfate complexes of Au(I) but is lower than for cyanide. Similarly, DMPS is known to form a 1:1 complex with Au(I) with a stability constant of log β= 45.5 [56].These baths are non-toxic and stable under mild alkaline conditions, but the current efficiency is relatively low (< 40%). The resulting deposits are smooth and ductile, but their suitability for typical through-mask plating applications has not yet been investigated [25].

More recently, gold plating baths employing hydantoin ligands have been proposed [74]. These ligands are nontoxic and form stable complexes with both Au(I) and Au(IIII). For example, Au(I) complexes with 1-methylhydantoin (MH) to form the species $[Au(MH)_2]_2^+$, while 5,5-dimethylhydantoin (DMH) complexes with Au(III) to form $[Au(DMH)_2]_4^-$ [70]. Stability constants of logβ=17.0 $[Au(MH)_2]_2^+$ and logβ= 1.7 $[Au(DMH)_2]_4^-$ have been determined for these species [71]. Under optimum plating conditions (i.e. 60°C and pH = 8) the current efficiency is close to 100% and the deposits are smooth, uniform, dense and have high solderability [77]. Thallium has also been used to reduce the grain size and increase the brightness of deposits obtained from the DMH bath [78].

4.9. Bath based on mercaptotriazole

The organic gold complex based on mercaptotriazole was investigated in Mining and Metallurgy Institute Bor and Technical faculty in Bor, Serbia [78-83]. Electrolyte was stable for nine months without visible signs of degradation and precipitation of elementary gold. Detailed investigations were carried out in order to determine the optimum conditions for obtaining quality decorative gold plating from this electrolyte and to compare it with the quality of gold plating obtained from the classic cyanide electrolyte.

In the first stages of experimental investigations, in the aim of detailed comparison of bath composition and operating conditions polarization curves were recorded and determined the limiting current densities for electrolyte based on mercaptotriazole (without and with additives) and classic cyanide electrolyte (AUROCIN DPB-trade mark). Based on recorded polarization curves for gold complex with mercaptotriazole with various gold concentrations without additives it was concluded

that limiting current density increases with an increase of gold ion concentration in electrolyte ($0.07 A/dm^2$ for $C_{Au}=3 g/dm^3$ to $0.01 A/dm^2$ for $C_{Au}=1 g/dm^3$), as well as in cyanide baths, and that the values of limiting current densities are lower regarding to cyanide of baths. Polarization curves for solution with $C_{Au}= 2.5 g/dm^3$ without additives and solution of the same concentration with various concentration of TC EHC additive show that the presence of the additive even in the lowest investigate concentration ($0.03 g/dm^3$) significantly decreases limiting current density, while further increase in concentration practically has no effect on value of limit current density [79, 26]. Bath composition and operating conditions of electrolyte based on mercaptotriazole are shown in Table 12 [80-83].

Table 12. Bath composition and operating conditions of electrolyte based on mercaptotriazole [79]

Bath constituent	Au-mercaptotriazole
Gold concentration (g/dm^3)	2.5
pH	9
Temperature (°C)	22
Time (s)	105
Cathode current density (A/dm^2)	1
Current intensity (A)	0.12
Voltage (V)	3.5

Table 13. Optimal parameters of the deposition of decorative gold coatings and measured values of coating thickness, surface roughness and microhardness

	Cyanide electrolyte AUROCIN DPB	Gold complex based on mercaptotriazole Au-MT
Gold concentration (g/dm^3)	1.5	2.5
Cathode current density (A/dm^2)	1	1
Temperature (°C)	20	20
pH	9	9
Concentration of additives	AUROCIN DPB additive 1 – (20 g/dm^3) AUROCIN DPB additive 2 – (4 ml/dm^3)	-
Thickness b (μm)	0.08	0.08
Surface roughness R_a (μm)	0.052	0.066
Microhardness HK (MPa)	740	660
SEM	Good adhesion	Good adhesion

Table 13 shows optimal working parameters for a cyanide bath and a bath with mercaptotriazole and measured values of coating thickness, surface roughness, microhardness and adhesion.

Experimental investigations proved that the quality of decorative gold plating obtained from gold based organic complex of mercaptotriazole satisfies all the requirements of decorative gold plating, where current density effect on appearance and thickness of coating is far lower than in classic cyanide bath. The most important advantage of this electrolyte is ecologic, where gold could be regenerated by simple settling with hydrogen peroxide when sulfur is precipitated.

5. CONCLUSION

This article provides an overview of the electrolytes used for soft gold electrodeposition. The traditional gold plating baths containing $KAu(CN)_2$ as the source of gold 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 photoresists and other materials used in the packaging of high density circuits. The developed non-cyanide electrolytes have been compared with the traditional ones. 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 systems containing both thiosulfate and sulfite have been more stable baths for both electroplating and electroless plating, the latter including both autocatalytic and substrate-catalyzed processes. Experimental investigations showed that the quality of decorative gold platting, obtained from gold based organic complex of mercaptotriazole satisfy all the requirements of decorative gold plating; at the same time current density effect on appearance and thickness of coating is lower than in classic cyanide bath.

References

1. G. Langbein and W. T. Brannt, *Electroplating of Metal*, 4th ed., Henry Carey Baird and Co., Philadelphia, (1902) 3
2. L. B. Hunt, *Gold Bull.* 6(1) (1873) 16
3. C. Wan Ngah, Ph.D. Thesis, Universiti Sains Islam Malaysia (2004)
4. R. Duva and D. G. Foulke, *Plating* 55 (1968) 1056
5. A. Blair, *Gold Bull.* 14(4) (1981) 167

6. Y. Okinaka and M. Hoshino, *Gold Bull.* 31(1) (1998) 3
7. Paul A. Kohl, *Modern Electroplating*, Chapter 4, Joan Wiley&Sons Hoboken, Ontario, Canada (2010) 115
8. H. Watanabe, S. Hayashi and H. Honma, *J. Electrochem. Soc.* 146(2) (1999) 574
9. A. Gemmler, W. Keller, H. Ritcher and K. Ruess, *Plat. Surf. Finish.* 81(8) (1994) 52
10. J. Traut, J. Wright and J. Williams, *Plat. Surf. Finish.* 77(9) (1990) 49
11. J. Jasper and D. Shiels, *Europ. Semicond.* 22(7) (2000) 86
12. Y. Okinaka, *Gold. Bull.*, 33(4) (2000) 117
13. I. R. Christie and B. P. Cameron, *Gold Bull.* 27(1) (1994) 12
14. W. J. Daukler, D. J. Resnick, W. A. Johnson and A. W. Yanof, *Microelectron. Eng.* 23 (1994) 235
15. W. Chu, M. L. Schattenburg and H. I. Smith, *Microelectron. Eng.* 17 (1992) 223
16. A. Maner, S. Harsch and W. Ehrfeld, *Plat. Surf. Finish.* 75 (1998) 60
17. K. Kosaki, M. Matsuoka, Y. Seiwa, S. Orisaka, K. Nishitani and M. Otsubo, Proceedings of the First Symposium on Electrochemical Microfabrication, Pennington, NJ (1992) 317
18. S. Roy, *ECS Trans.* 16 (36) (2009) 67
19. W. Sun and D. G. Ivey, *Mater. Scien. and Engineer.* B65 (1999) 111
20. Y. Okinaka and S. Nakahara, *J. Electrochem.Soc.* 123(9) (1976) 1284
21. T. E. Dinan and H. Y. Cheh, *J. Electrochem. Soc.* 139(2) (1992) 410
22. Y. Cheh and R. Sard, *J. Electrochem. Soc.* 118(11) (1971) 1737
23. T. Osaka, A. Kodera, T. Misato, T. Homma and Y. Okinaka, *J. Electrochem.Soc.* 144 (1997) 3462
24. P. Wilkinson, *Gold Bull.* 19 (1986) 75
25. M. Kato and Y. Okinaka, *Gold Bull.* 37(1-2) (2004) 37
26. W. S. Rapson and T Groenewald, *Gold Usage*, Academic Press, London, (1978)
27. J. Simon and W. Kuhn, Proceedings of the AESF Technical Conference SUR/FIN, '99, American Electroplaters and Surface Finishers Society, (1999) 373
28. E. Smallbrugge, B. Jacobs, S. Falcone, E.J. Geluk and F. Karouta, Proceedings Symposium IEEE/LEOS, (2000)
29. M. J. Liew, S. Roy and K. Scott, *Green Chem.* 5 (2003) 376
30. X.Wang, N. Issaev and J. G. Osteryoung, *J. Electrochem. Soc.* 144 (1997)
31. R. J. Puddephatt, *The chemistry of gold*, Elsevier Science Ltd, US, (1978)
32. J. Marsden, I. Hause, *Chemistry of gold extraction*, Society for Mining Metallurgy & Exploration, New York, (1992)
33. T. A. Green, *Gold Bull.* 40(2) (2007) 105
34. A. J. Bard, J. Jordan and R. Parsons Editors, *Standard Potentials in Aqueous Solutions*, Marcel Dekker, New York, (1985)
35. D. Vlassopoulos, S. A. Wood and A. Mucci, *Geochim. et Cosmochim. Acta.* 54 (1990) 1575
36. W. Perera, G. Senanayake and M. .J. Nicol, *Inorg. Chim. Acta.* 358 (2005) 2183
37. J. G. Webster, *Geochim. et Cosmochim. Acta.* 50 (1986) 1837
38. H. Honma and K. Hagiwara, *J. Electrochem. Soc.* 142 (1995) 81
39. T. A. Green and S. Roy, J. *Electrochem. Soc.* 153 (2006) C157 D.
40. N. P. Finkelstein and R. D. Hancock, *Gold Bull.* 7 (1974) 72
41. G. Senanayake, *Miner. Enginee.* 17 (2004) 785
42. M. Pourbaix, *Atlas of Electrochemical Equilibra in Aqueous Solutions*, Pergamon, New York, 1966
43. A. M. Sullivan and P. A. Kohl, *J. Electrochem. Soc.* 144 (1997) 1686
44. W. J. Dauksher, D. J. Resnick, W. A. Johnson, and A.W. Yanof, *Microelectron. Eng.* 23 (1994) 235
45. D. Mason, *Plat. Surf. Finish.* 73(5) (1986) 20
46. J. Horkans and L.T. Romankiw, *J. Electrochem. Soc.* 124 (1977) 1499
47. H. Honma and Y. Kagaya, *J. Electrochem. Soc.*, 1993, 140, L135
48. R.J. Morrissey, *Plat. Surf. Finish.* 80(4) (1993) 75

49. J.J. Kelly, N. Yang, T. Headley and J. Hachman, *J. Electrochem. Soc.* 150 (2003) C445
50. J. Simon, W. Zilske and F. Simon, International Flip Chip, Ball Grid Array, TAB and Advanced Packaging Symposium, (1995) 275
51. J. - P. Derivaz, A. Resin and S. Losi, *Surf. Technol.* 5 (1977) 369
52. N. Shirai, S. Yoshimura, E. Sato and N. Kubota, Hyomen Gijutsu, *J. Surface Finish. Soc. Japan*, 39(1989) 543
53. A. Fanigliulo and B. Bozzini, *Trans. Inst. Metal Finish.* 80 (2002) 132
54. G. Baltrunas, A. Valiuniene and R. Valiunas, *Polish J. Chem.* 77 (2003) 1819
55. W. Kuhl, W. Zilske, *Patent* 6165342 (2000)
56. J. Pouradier and M.C. Gadet, *J. Chim. Phys.* 66 (1964) 109
57. M. G. Alymore and D. M. Muir, *Minerals Engineer.* 14 (2001) 135
58. X. Wang, N. Issaev, and J. G. Osteryoung, *J. Electrochem. Soc.* 145 (1998) 974
59. M. Kato, N. Niikura, H. Hoshino and I. Ohno, *J. Surf. Finish. Soc*. Japan, 1991, 42, 729
60. 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
61. M. Kato, Y. Yazawa and Y. Okinaka, Proceedings AESF Technical Conference, SUR/FIN '95, American Electroplaters and Surface Finishers Society, (1995) 805
62. T. Osaka, A. Kodera, T. Misato, T. Homma and Y. Okinaka, J. *Electrochem. Soc.* 144 (1997) 3462
63. T. Osaka, M. Kato, J. Sato, K. Yoshizawa, T. Homma, Y. Okinaka and O. Yoshioka, *J. Electrochem. Soc.* 148 (2001) C659
64. R. J. Lewis Sr., *Rapid Guide to Hazardous Chemicals in the Workplace*, 4th Ed., John Wiley & Sons, Inc., USA (2000)
65. D. W. Endicott, H. K. James and F. Nobel, *Plat. Surf. Finish.* 69(8) (1981) 58
66. M. J. Liew, Novel Gold Electrodeposition Process for Micro and Opto Electronics, PhD Thesis, University of Newcastle upon Tyne, (2002)
67. T. A. Green, S. Roy and M. J. Liew, *J. Electrochem. Soc.*, 150 (2003) C101
68. G.A. Krulik and N.V. Mandich, *U.S. Patent* (1993) 5
69. T. Inoue, S. Ando, J. Ushio, H. Okudaira, H. Takehara, T. Ohta, H. Yamamoto and H. Yokono, *J. Surf. Finish. Soc. Japan* 49 (2000) 1298
70. M. Kato, J. Sato, H. Otani, T. Homma, Y. Okinaka, T. Osaka and O. Yoshioka, *J. Electrochem. Soc.* 149 (2002) C164
71. J. Sato, M. Kato, H. Otani, T. Homma, Y. Okinaka, T. Osaka and O. Yoshioka, *J. Electrochem. Soc.* 149 (2002) C168
72. D. J. Leblanc, Ph.D. Thesis, McMaster University (1996)
73. Shaw III, C. F. "Gold-Based Medicinal Agents". *Chemical Reviews* 99 (9): (1999) 2589–600
74. P. Hydes and H. Middleton, *Gold Bull.* 12 (1979) 90
75. Y. Ohtani, K. Sugawara, K. Nemoto, A. Shiozawa, A. Yamaguchi, K. Oyaizu and M. Yuasa, *J. Surface Finish. Soc. Japan* 55 (2004) 933
76. Y. Ohtani, T. Saito, K. Sugawara, A. Shiozawa, A. Yamaguchi, K. Oyaizu and M. Yuasa, *J. Surface Finish. Soc. Japan* 56 (2005) 479
77. Y. Ohtani, K. Sugawara, K. Nemoto, A. Shiozawa, A. Yamaguchi, K. Oyaizu and M. Yuasa, *J. Surface Finish. Soc. Japan* 57 (2006) 167
78. S. Dimitrijevic, M. Rajcic-Vujasinovic, R. Jancic-Hajneman, D. Trifunovic, J. Bajat, V. Trujic, S. Alagic, International Scientific and Profesional Meeting Eco-Ist'12, (2012) 194
79. S.Dimitrijevic, V. Trujic, M. Rajcic-Vujasinovic, D.Trifunovic, Lj. Stamenkovic, 40th International October Conference on Mining and Metallurgy, (2008) 458
80. S.Dimitrijevic, V. Trujic, M. Rajcic-Vujasinovic, 13th International Research TMT, (2009) 893
81. S. Dimitrijevic, V. Trujic, M. Rajcic-Vujasinovic, 14th International Research TMT, (2010) 669

82. S. Dimitrijevic, V. Trujic, M. Rajcic-Vujasinovic, 42th International October Conference on Mining and Metallurgy, Proceedings, (2010) 294

83. S. Dimitrijevic, M. Rajcic-Vujasinovic, V. Grekulovic, S. Alagic, V. Trujic, *Electrochim. Acta* - accepted