Gold Electrodeposition for Microelectronic, Optoelectronic and Microsystem Applications

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Abstract

The electrodeposition of gold is a key technology in the fabrication of many microelectronic, optoelectronic and microsystem devices. In this review, we examine some recent applications, and consider the suitability of various gold plating systems for device fabrication. The properties of gold cyanide and sulfite baths and their limitations are considered first. This is followed by an analysis of the latest generation of non-cyanide baths, including the thiosulfate, sulfite-thiosulfate and ammonium gold systems. Plating baths containing mercapto-alkylsulfonic acid and hydantoin ligands are also briefly discussed. Finally an analysis of the stability of gold plating baths is presented.

1 Introduction

The deposition of gold has numerous applications in microelectronic, optoelectronic and microsystem technologies [1-3]. The use of gold in these industries arises primarily because of its excellent corrosion resistance, solderability and bondability and its high electrical and thermal conductivity. Moreover, gold can be readily deposited using a variety of techniques including physical vapour deposition (PVD) such as sputtering and evaporation and also electrodeposition methods such as electro and electro-less plating. In many instances the use of electrodeposition techniques are preferred because of their relatively low-cost and potentially higher deposition rate and film thickness compared to PVD methods. In addition, electrodeposition can be performed with relatively simple and inexpensive equipment and the processes are typically operated under near-ambient conditions of pressure and temperature.

In the micro-electronics industry, the electrodeposition of gold has been traditionally used to metallise contact pads on semiconductor integrated circuits (ICs) to allow electrical interconnects to package terminals using gold or aluminium wire bonding [2,3]. In such applications, the high bondability and corrosion resistance of gold ensure that wire bonds can be made with very high reliability. Electrodeposition is also extensively to fabricate gold-plated contacts on devices, for example, edge connectors on printed circuit boards [2,3]. For such applications it is necessary to electrodeposit gold with a high hardness and wear resistance and with a low contact resistance.

Since the 1980s there has been a trend away from wire bonding to more advanced packaging and interconnect technologies which allow a higher number of I/O (input output) connections between ICs and external devices to be made [1]. An early example of this technology is tape automated bonding (TAB) - also known as tape carrier packaging (TCP) [1,4,5]. In this technique, high density I/O connections are facilitated by the electrodeposition of gold bumps on to the contacts pads of the IC device. This process is done at wafer level with all bumps on the wafer being formed simultaneously. The IC is then mounted on to a flexible polymer tape containing repeated metallised interconnection patterns. After alignment, the tape interconnect pads are attached to the gold bumps by thermo-compression bonding. In this manner a large number of high reliability interconnects can be formed simultaneously. Gold wafer bumping is now an established packaging technology for ICs which require a high number of I/O connections [1,4]. For example, interconnects between liquid crystal displays (LCDs) and their associated driver ICs are usually performed using TCP and related methods such as chip-on-glass (COG) and chip-on-film (COF) techniques [5].

In addition to its use in the silicon-based microelectronics industry, gold plating has also been extensively used in the

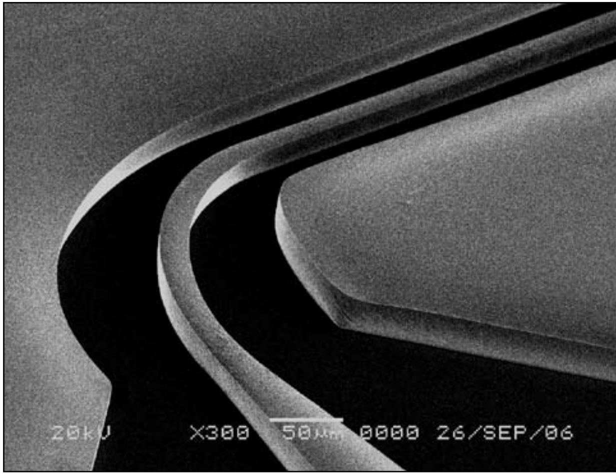


Figure 1

SEM micrographs of gold electrode structures plated on to a lithium niobate wafer from a commercial sulfite bath. The thickness of the gold is 35 μm and the width of the central electrode in the straight region is 15 μm

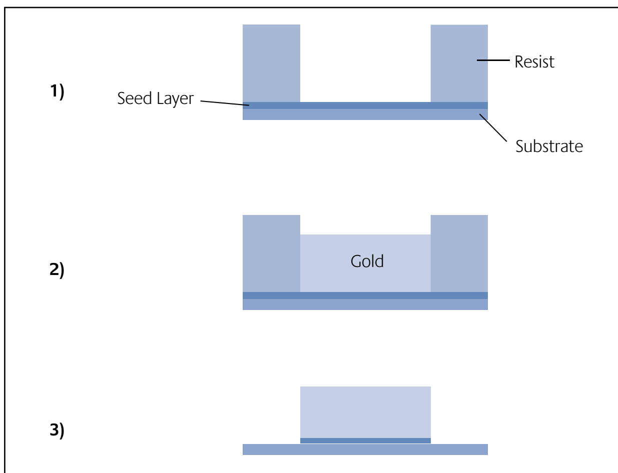


Figure 2

Overview of fabrication steps for through-mask plating. 1) Seed layer deposition and photoresist patterning; 2) gold electroplating; 3) photoresist removal and seed layer etching

fabrication of III-V semiconductor devices and optoelectronic components [6-9]. For example, in the manufacture of gallium arsenide ICs, gold electrodeposition is used extensively to fabricate air-bridge interconnections [6], heat sinks [7] and also for via filling and back-side metallisation of wafers [8]. In the optoelectronics industry, gold is used to fabricate interconnects and transmission lines, such as in the fabrication of lithium niobate optical modulators [9]. Figure 1, for example, shows a typical gold coplanar-waveguide RF electrode structure electroplated on to a lithium niobate wafer. The packaging and assembly of optoelectronic components has also made extensive use of gold plating technology. For example, electrodeposited gold and eutectic gold-tin bumps have been used to mount optoelectronic devices such as high-power LEDs, PIN diodes and indium phosphide laser dies using flip chip and TAB processes [10].

In the emerging field of micro-electromechanical systems (MEMs) technologies gold electrodeposition is frequently used to form electrical connections, structural layers, electrodes and bond pads on devices. It is also used to fabricate absorbers for x-ray masks for use in the LIGA microfabrication process [11,12]. One representative example of the use of gold plating in MEMS is the deposition of gold to fabricate flexible, implantable electrode arrays [13,14]. In such applications, the electrodes and associated interconnects must have low resistance, good mechanical properties and excellent biocompatibility [13]. These properties are readily achieved by gold electro-deposition, although in practice the electrode arrays may be coated with a thin layer of other materials (e.g. Pt and IrO_2) to improve their stability and performance [14].

The majority of the applications mentioned above require patterned electrodeposition of gold using the so-called 'through-mask' plating technique [1,15]. In this process, the wafer substrate is typically covered with a conductive 'seed' layer which acts as the plating base and an underlying adhesion or barrier layer. Typically these metal seed layers are deposited using sputtering or evaporation. The substrate is then patterned with a photoresist, and gold is selectively electroplated into the resist-free areas. Following plating of the structures to the desired height (typically 5 – 30 μm) the photoresist mask is stripped and the metal plating base is removed by wet etching. This process is shown schematically in Figure 2. The use of this through-mask technique enables small features with high aspect ratios to be formed and has important advantage over alternative microfabrication methods such as lift-off or etching [15].

In all applications it is desirable to electrodeposit gold structures which are ductile, with low stress and hardness and good dimensional tolerances. For wafer bumping applications it is important that the bumps are coplanar and of consistent height and have low hardness and surface roughness, otherwise the reliability of interconnects may be reduced [4,16]. A low deposit stress is also desirable otherwise adhesion to the substrate may be compromised, and it is essential in LIGA fabrication to avoid distortion of the mask [11,12]. In micro-wave and RF applications [7,9] it is important the electrical conductivity of the gold transmission line is high and surface roughness is low in order to minimise signal attenuation.

The extent to which these desirable properties can be obtained depends largely on the characteristics of the plating process. The present review will therefore examine the use of various gold electroplating processes which can be use to fabricate gold structures on wafers suitable for various microelectronic, optoelectronic and micro-system applications. The emphasis is on the patterned electrodeposition of soft gold of high thickness and aspect ratio. The electrodeposition of hard gold and the use of electro-less gold plating in microelectronics have been reviewed elsewhere [3,17-19] and will not be discussed here.

Table 1

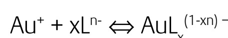
Stability constants, β, and standard reduction potentials, E^0, for Au(I) species. Note that 'th' represents thiourea, while 'CyS' denotes the cysteinate ion

Au(I) species	log β	E^0 (V) vs NHE	Reference
$Au(CN)_2^-$	38.7	-0.595	[23]
$Au(CyS)_2^{3-}$	31.1	-0.144	[28]
$Au(S_2O_3)(SO_3)_2^{5-}$	30.8		[51]
$Au(S_2O_3)(SO_3)^{3-}$	27.1		[51]
$Au(SO_3)_2^{3-}$	26.8	0.111	[25]
$Au(S_2O_3)_2^{3-}$	26.1	0.153	[23]
$Au(th)_2^+$	22.2	0.380	[23]
$Au(OH)_2^-$	21.9	0.400	[22]
AuOH	20.1	0.506	[22]
$Au(NH_3)_2^+$	19.2	0.563	[23]
AuI_2^-	18.9	0.578	[23]
$Au(SCN)_2^-$	17.5	0.662	[23]
$AuBr_2^-$	12.4	0.960	[23]
$AuCl_2^-$	9.2	1.154	[23]
Au^+		1.695	[23]

2 Plating processes

A larger number of plating baths for the electrodeposition of soft gold have been developed [17-21], but not all are suitable for through-mask plating applications. An essential requirement is that the plating bath shows good compatibility with the photoresist material, otherwise the size and shape of the plated structures will be compromised [4,6,8]. Most positive resist 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 [18,19]. In high-volume wafer plating it is also essential that the plating baths is capable of long-term stable operation and is not prone to decomposition [16]. As will be discussed later, a number of plating baths have issues relating to resist compatibility and/or long-term stability.

Before reviewing specific plating processes, it is useful to review some fundamental aspects of the aqueous solution chemistry of gold. This will concentrate mainly on Au(I) species as electroplating baths formulated from Au(IIII) complexes are relatively rare [17,20]. Firstly it should be noted that aurous ion, Au(I), is not stable in aqueous solution and is prone to disproportionate [6,16,18,21] to form metallic gold or undergo hydrolysis to form AuOH [22]. For this reason, all gold plating processes are formulated from Au(I) complexes and deposition typically takes place by direct electro-reduction 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 [20,21]. If the formation of complexes involving the aurous ion and a ligand, L, is written as:



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

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

$$\beta_x = [AuL_x^{(1-xn)-}] / [Au^+] [L^{n-}]^x$$

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).

Despite the importance of the stability constant in establishing the chemical and electrochemical properties of the plating solution there is relatively little data [23] regarding the stability of many gold complexes. There are also some large discrepancies in stability constants obtained from different literature sources. For example, a value of log $\beta_2 \approx 10$ is commonly assumed [16-21] for the $Au(SO_3)_2^{3-}$ complex but we have recently shown [24] that the available experimental data [20,25,26] indicates a much higher value of log $\beta_2 \approx 27$ and the observed characteristics of sulfite baths are more consistent with the latter value. 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 d^{10} electron configuration such as Cu(I), Ag(I) and Hg(II) [27-29]. 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 [28,29].

2.1 Cyanide bath

The use of cyanide baths in gold plating has a long history and it is a relatively mature and well understood process [17,20,21]. Soft gold can be deposited from cyanide baths under alkaline, neutral or acid solutions and the deposition rate is typically higher than for most non-cyanide gold processes. Cyanide baths also have a long life and due to the strength of the cyanide complex, $Au(CN)_2^-$, (Table 1) they are resistant to disproportionation, hydrolysis, oxidation and ligand substitution reactions that may cause instability or decomposition. Cyanide is also cheap, and its gold salts can be easily manufactured.

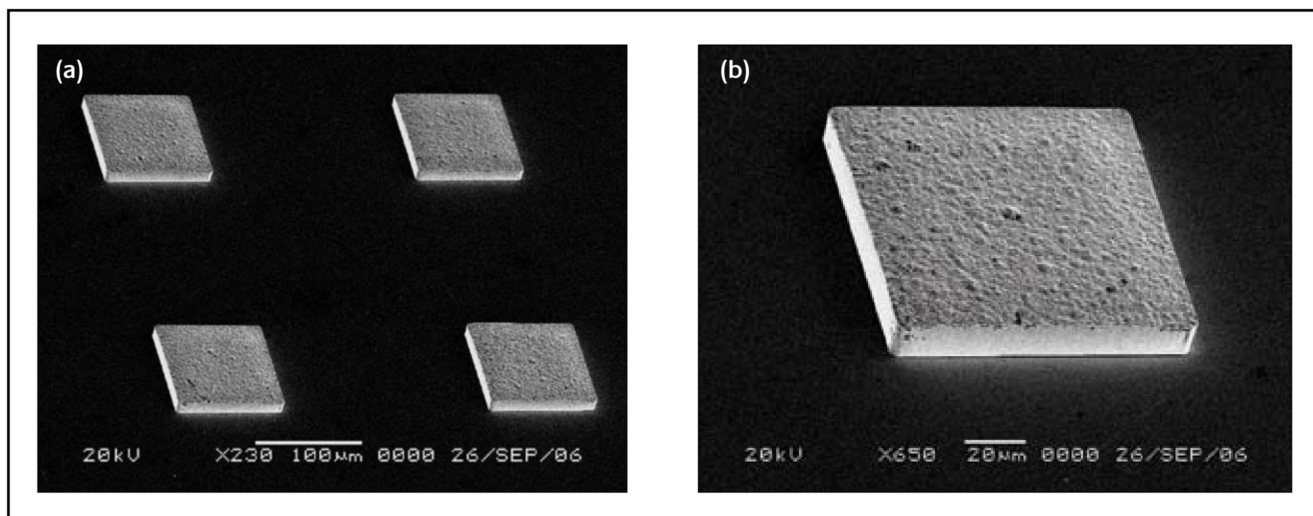


Figure 3

a) SEM image of an array of gold test bumps electroplated on to a silicon wafer from a sulfite bath. The thickness of the plated gold is approximately 15 µm. (b) SEM image of a single 100 × 100 µm gold bump. Note the excellent shape, uniform height, and low surface roughness of the bump

The main problem with the use of cyanide baths are their poor compatibility with many standard positive photoresists. A commonly encountered defect is extraneous plating underneath the photoresist layer ('under-plating') which is highly undesirable in most applications [4,6,8,30]. It is generally believed [31] that this effect arises because of a local increase in the solution pH at the photoresist-gold interface during the electrodeposition process, resulting in partial lifting and dissolution of the resist. Poor control of the dimensional tolerances and distorted bump features have also been observed during plating from a cyanide bath [32]. This was attributed to the reaction of free cyanide ions in the plating solution with a carbonyl group of the dissolution inhibitor in the photoresist to form cyanohydrin. The other principal disadvantage of cyanide is its high toxicity. The health and safety issues associated with the use and disposal of cyanide baths is another reason why they are seldom used in microelectronic, optoelectronic and micro-system industries.

2.2 Sulfite bath

Gold sulfite baths have traditionally been used because of their ability to produce thick gold electrodeposits which are smooth, bright, ductile and have low stress [8,16-19,30]. 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 [16]. In general, gold bumps deposited from sulfite baths have excellent shape, uniform height and low surface roughness and do not exhibit under-plating (Figure 3).

Most importantly, they are non-toxic and the requirements for handling and disposal are much lower than for cyanide baths. The stability constant of $Au(SO_3)_2^{3-}$ 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 [16]. Their compatibility with most photo-resists is also good, and as long as the pH is maintained below 10 dissolution and delamination of the photoresist is not observed [6,8,16,30]. 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.

Since the initial work of Romankiw [33] 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 [17-21,30] 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 undesirable from the point of view of process control but a number of sulfite processes have been developed which can operate stably a near neutral pH. For example, the addition of organic amines such ethylene diammine allows sulfite baths to be operated at a pH range of 5–8, and this stabilisation has been attributed to the formation of mixed sulphite amine complexes [20]. Similarly, Morrissey [34] has also developed a gold sulfite bath which is stable to a pH of 4.5 using polyamines and aromatic nitro compounds as additives. More recently, a gold sulfite bath operable at pH = 8 has been reported [30] using 2,2'-dipyridyl as a stabiliser.

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 [16,34,35]. Similarly, thallium is often employed as a grain

refiner and its influence on hardness and stress has also been investigated [11,12]. The influence of the plating conditions on deposit stress has also been explored in a number of papers. It appears that by careful manipulation the current density, temperature and concentration of additives it is possible to deposit gold with essentially zero stress [11,12]. Pulse plating has also been used to influence deposit characteristics. Some workers have reported no improvement using pulse plating [33] but others [34,35] have observed enhanced deposits properties relative to DC plating.

Sulfite baths are usually formulated from sodium or potassium salts but ammonium gold sulfite baths have also been developed [8,36,37]. These baths have been mainly used for electroforming (e.g. dental) applications but Simon [36] 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. However, despite their considerable potential, ammonium gold sulfite baths have not yet found wide use.

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 over-potentials or at high pH (i.e. > 9) [33,38]. At lower pH a variety of different mechanisms have been proposed [38,39], usually involving a series of coupled chemical and electrochemical steps. Subsequent Raman [40] and electrochemical measurements [26] have shown the importance of adsorbed species and the formation of passivating sulphur films on the gold deposition process. It is clear that the overall mechanism is quite complex and further studies are required.

2.3 Thiosulfate bath

In contrast to the sulfite and cyanide baths, there has been little attention paid to the development of gold thiosulfate plating processes [18-21]. This is somewhat surprising given the potentially low toxicity of a thiosulfate bath and the relatively high stability of the $Au(S_2O_3)_2^{3}$ complex, but presumably has arisen because the inherent instability of the thiosulfate anion with respect to disproportionation [18,19,21]. The $S_2O_3^{2-}$ ion is relative stable at low concentrations and high pH, but under acid or neutral condition it can readily disproportionate to form colloidal sulphur [41]. Depending on the conditions, a number of decomposition reactions are possible, but the disproportionation can be represented simply as:

$$S_2O_3^{2-} \Leftrightarrow S_2O_3^{2-} + S \qquad (1)$$

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 [41] or the use of stabilisers such as sulfinic acids [21].

Despite these limitations, there have been a few attempts to develop gold thiosulfate plating processes. For example, Osteryoung [42] has 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 – 5 mA cm^{-2}. The suitability of this thiosulfate for through-mask plating was also demonstrated.

More recently, 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 [42] 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.

2.4 Mixed sulfite-thiosulfate bath

Issues relating to the stability and performance of sulfite and thiosulfate baths have ultimately led to the development of a 'mixed' sulfite-thiosulfate bath [18,19]. This was originally developed for electro-less plating applications [44,45] but a version suitable for electroplating was subsequently developed [46]. It was found that mixed sulfite bath had higher stability than either the pure sulfite or thiosulfate baths, and did not require the use of stabilisers. Crucially, it could be operated at near neutral or slightly acidic conditions which make it compatible with essentially all photoresist 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 1 to the left thereby minimising the formation of colloidal sulfur in the bath [41].

The mixed bath used by Osaka [46] contained 0.05 M $HAuCl_4$, 0.42 M Na_2SO_3, 0.42 M $Na_2S_2O_3$ and 0.30 M Na_2HPO_4 and typically operated at a pH of 6 - 7. It was found that this bath was suitable for depositing micro-bumps on patterned silicon wafers and did not result in any degradation of the photoresist or extraneous deposition of gold. The resulting gold bumps were smooth, coplanar and had a hardness (typically 50 - 80 HVN) suitable for TAB/TCP bonding. The deposit hardness could be controlled

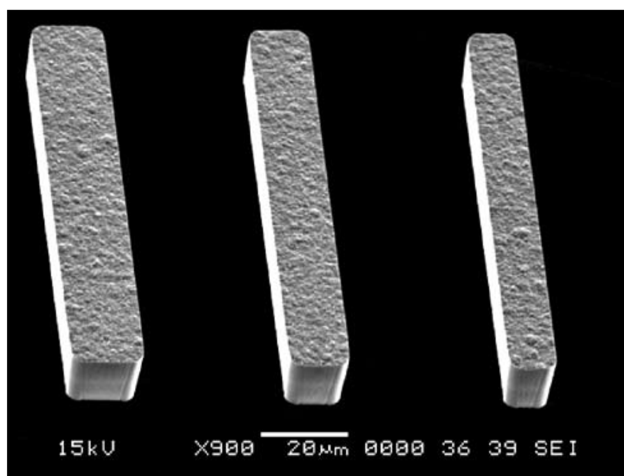


Figure 4

SEM image of gold test structures deposited from a mixed sulfite-thiosulfate plating bath. Nominal widths of the gold lines are 6, 9 and 12 μm

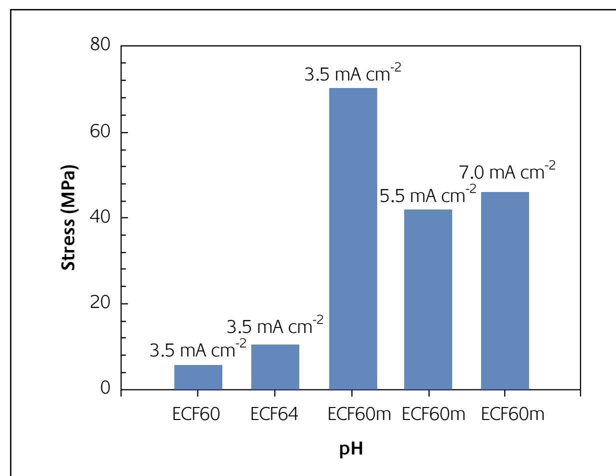


Figure 5

Measured deposit stress for 15 μm thick gold films electroplated from sulfite (ECF60), ammonium sulfite (ECF64) and sulfite-thiosulfate (ECF60m) plating baths. In all cases the stress is tensile

by changing the relative amounts of sulfite or thiosulfate in the bath, the use of additives such as thallium, or by annealing. In a subsequent paper [47] the influence of sulfur inclusion on the deposit morphology and hardness was investigated in detail.

More recently, we examined in detail the suitability of the mixed bath for optoelectronic and microelectronic applications [48]. Using a sulfite-thiosulfate bath of similar composition and pH we found that it was highly stable and had excellent photoresist compatibility. At typical operating current densities of 1 – 5 mA cm^{-2} the current efficiency was close to 100%. Under optimum conditions, the bath produced uniform gold bumps with low stress, roughness and hardness and with good dimensional tolerances. Figure 4 shows an array of gold bump test structures that were electrodeposited from the mixed bath. Figure 5 shows a comparison of the stress obtained from the mixed bath compared to commercially available sulfite and ammonium sulfite baths. In general, the mixed bath produced deposit which had comparable or better characteristics than those obtained from pure sulfite baths, although there was some evidence that the adhesion to the substrate was marginally worse [48]. Brown [49] recently compared the performance of sulfite and a mixed sulfite-thiosulfate baths and also found that the former had better adhesion.

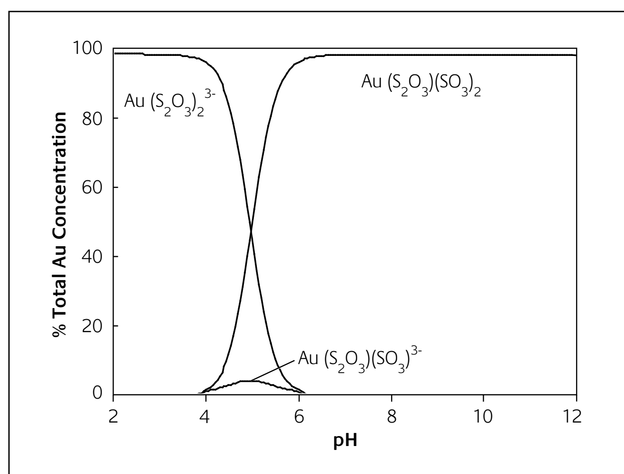


Figure 6

Concentration of dominant Au(I) complexes as a function of pH in a sulfite-thiosulfate bath containing 0.05 M $HAuCl_4$, 0.42 M Na_2SO_3 and 0.42 M $Na_2S_2O_3$. The stability constants in Table 1 were used in these calculations

Despite the good plating performance of the sulfite-thiosulfate baths there is some uncertainty regarding the relevant solution chemistry. Based upon initial polarisation measurements it was proposed [44] that the main electroactive species in the mixed bath was $Au(S_2O_3)_2^{3-}$, however, subsequent experiments [45] indicated the possible formation of mixed sulfite-thiosulfate Au(I) complexes. The evidence for the existence of these mixed complexes was largely circumstantial but subsequent ion chromatography measurements [50] support the existence of the $Au(S_2O_3)(SO_3)^{3-}$ species. Recent potentiometric and Raman studies have indicated the presence of $Au(S_2O_3)(SO_3)^{3-}$ and $Au(S_2O_3)(SO_3)_2^{5-}$ in solution and their stability constants have also been estimated [51].

Using this data, we have recently analysed the speciation in such mixed baths [24]. It was found that the dominant species at neutral or basic are mixed complexes of the form $Au(S_2O_3)(SO_3)^{3-}$ and $Au(S_2O_3)(SO_3)_2^{5}$ and the thiosulfate complex, $Au(S_2O_3)_2^{3-}$, is only dominant under acidic conditions. Figure 6 shows the concentration of these various complexes as a function of pH of the bath. The electrodeposition mechanism from the mixed baths has not been examined in detail, but presumably will involve direction reduction of one or more of the complexes.

2.5 Other baths

Since Au(I) forms compounds with many other ligands, it might be envisaged that some of the complexes shown in

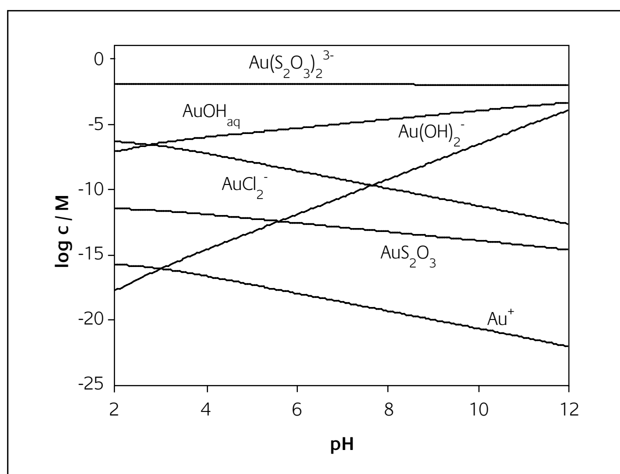


Figure 7

Distribution of Au(I) species as a function of pH in a thiosulfate plating solution containing 0.01 M $Na_3Au(S_2O_3)_2$ and 1.25 M KCl

Table 1 might serve as the basis for gold plating baths. In practice, however, solutions containing halide, ammonia, hydroxide, thiocyanate, thiourea and hydroxide ligands have all been found to be unsuitable due to a combination of poor deposit properties, instability or toxicity [20,21]. In the late 1970s an alternative non-cyanide gold bath based on a nitro-sulfito complex was proposed [52]. 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.

Gold plating baths based on complexes between Au(I) and mercapto-alkylsulfonic acid ligands such as 2-mercapto-ethanoic acid (MES), 3-mercapto-propanoic acids (MPS) and 2,3-dimercaptopropane-1-sulfonic acid (DMPS) have also been developed [21]. The stability constant of $Au(MES)_2^{2-}$ and $Au(MPS)_2^{2-}$ have not been measured, but based on a comparison with related gold mercapto complexes [28] values of $\log \beta_2 \approx 30$ 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 $\log \beta_1 = 45.5$ [53].These baths are non-toxic and stable under weakly alkaline conditions, but the current density 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.

More recently, gold plating baths employing hydantoin ligands have been proposed [54-56]. These ligands are non-toxic and form stable complexes with both Au(I) and Au(IIII). For example, Au(I) complexes with 1-methylhydantoin (MH) to form the species $Au(MH)_2^+$, while 5,5-dimethylhydantoin (DMH) complexes with Au(III) to form $Au(DMH)_4^-$ [54]. Stability constants of $\log \beta_2 = 17.0$ ($Au(MH)_2^+$) and $\log \beta_2 = 21.7$ ($Au(DMH)_4^-$) have been determined for these species [55]. 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 [54]. Thallium has also been used to reduce the grain size and increase the brightness of deposits obtained from the DMH bath [56].

2.6 Bath stability

A significant problem with many gold plating baths is their poor stability. It has already been noted that the cyanide baths are highly stable, but non-cyanide baths show varying degrees of instability which can make their use in a production environment difficult. The instability of many free-standing gold plating solutions usually manifests itself in the formation of colloidal gold, and this is typically attributed [6,18,19,30,57] to the disproportionation of uncomplexed Au(I) ions in the solution:

$$3Au^+ \Leftrightarrow 2Au + Au^{3+} \quad (2)$$

The formation of colloidal gold is undesirable in gold plating as the particles tend to increase surface roughness and promote the formation of nodules and other defects [16]. The surface of the gold particles can induce additional autocatalytic deposition of gold, so that the decomposition of the bath is accelerated [6]. In extreme cases extraneous gold deposition on surfaces of the plating cell can also occur.

Recently we have performed a speciation analysis of a number of Au(I) baths containing sulfite and thiosulfate as ligands and showed that the concentration of Au^+ is typically extremely low and it is therefore unlikely that observed instability can arise from reaction 2, even though thermodynamically it is very favourable [24]. It is more probable that colloidal gold is formed from the disproportionation of other unstable Au(I) complexes present in solution. For example, Table 2 indicates the equilibrium constant, K_d, for the disproportionation of various Au(I) species calculated from available thermodynamic data [23,29,58]. It can be seen that the stability of complexes with respect to disproportionation increases in the order: $CN^- > SO_3^{2-} > S_2O_3^{2-} > OH^- > SCN^- > I^- > Br^- > Cl^- > NH_3$. Baths containing, halide, hydroxide or ammonia ligands are therefore particularly prone to disproportionation while those containing cyanide, sulfite and thiosulfate are likely to be stable. Note, however, that this is only a thermodynamic prediction of instability and in practice the rate of disproportionation may be so slow that the baths are usable for short periods of time [29].

Figure 7 represents the results of speciation calculations [24] for a gold thiosulfate bath [43]. The dominant species is $Au(S_2O_3)_2^{3-}$ and according to Table 2 this species is stable with respect to disproportionation. However, other Au(I) species such as $AuCl_2^-$, AuOH and $Au(OH)_2^-$ are also present at lower concentrations, and these species can undergo

Table 2

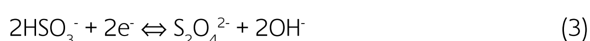
Disproportionation equilibrium constants, K_d, for various Au(I) species. Values denoted with † were calculated from the standard electrode potentials of the relevant Au(I) and Au(III) complex [24]

Disproportionation reaction	K_d	Ref.
$3Au(NH_3)_2^+ \Leftrightarrow 2Au + Au(NH_3)_4^{3+} + 2NH_3$	10^{12}	[58]
$3Au^+ \Leftrightarrow 2\ Au + Au^{3+}$	$10^{9.9}$	†
$3AuCl_2^- \Leftrightarrow 2Au + AuCl_4$- $+ 2Cl^-$	$10^{7.7}$	[58]
$3AuBr_2^- \Leftrightarrow 2Au + AuBr_4^- + 2Br^-$	$10^{5.3}$	[58]
$AuOH \Leftrightarrow Au + 0.25O_2 + 0.5H_2$	$10^{1.2}$	[29]
$3AuI_2^- \Leftrightarrow 2Au + AuI_4^- + 2I^-$	$10^{0.9}$	†
$3Au(SCN)_2^- \Leftrightarrow 2Au + Au(SCN)_4^- + 2SCN^-$	$10^{0.3}$	[58]
$Au(OH)_2^- \Leftrightarrow Au + OH^- + 0.25O_2 + 0.5H_2O$	$10^{-0.2}$	[29]
$3Au(S_2O_3)_2^{3-} \Leftrightarrow 2Au + Au(S_2O_3)_4^{5-} + 2S_2O_3^{2-}$	$\sim 10^{-8}$	†
$3Au(SO_3)_2^{3-} \Leftrightarrow 2Au + Au(SO_3)_4^{5-} + 2SO_3^{2-}$	$\sim 10^{-8}$	†
$3Au(CN)_2^- \Leftrightarrow 2Au + Au(CN)_4^- + 2CN^-$	$\sim 10^{-21}$	†

disproportionation to form colloidal gold. Moreover, the total concentration of these species might prove a useful tool in predicting the relative stability of baths. It was found, for example, that higher stability of sulfite-thiosulfate baths compared to pure sulfite baths could be rationalised in terms of the lower concentration of disproportionating species in the former system. Such an analysis can also be used to understand why sulfite and thiosulfate baths tend to be more stable at high pH and with higher concentration of complexing agents.

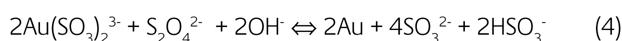
Other modes of solution decomposition have also been identified. For example, the oxidation of ligands (e.g. sulfite to sulfate) will tend to increase the concentration of other less stable Au(I) species and reduce overall bath stability [16]. Similarly, various hydrolysis, ligand exchange and protonation reactions can lead to the formation of unstable gold species which may adversely affect the stability of the plating bath [29]. Finally, the photosensitivity of gold compounds is well known [59] and prolonged exposure to UV light can also induce decomposition of gold plating solutions.

The stability of Au(I) baths during electrodeposition can also be limited by the formation of colloidal gold. It is generally thought [16,17,36] that the instability of sulfite containing baths is due to the cathodic reduction of bisulfite ions to form dithionite ions:



$$2HSO_3^- + 2e^- \Leftrightarrow S_2O_4^{2-} + 2OH^- \quad (3)$$

which occurs in parallel to the main reduction of the gold complex. For gold sulfite baths at pH > 9 the current efficiency of the deposition process is essentially 100% and the gold reduction reaction dominates. However, at lower pH and high current densities the current efficiency is found to decrease indicating a larger contribution from reaction 3 [30,49,55]. The dithionite species is a strong reducing agent and can directly reduce many Au complexes to form colloidal gold, for example [16,17]:



$$2Au(SO_3)_2^{3-} + S_2O_4^{2-} + 2OH^- \Leftrightarrow 2Au + 4SO_3^{2-} + 2HSO_3^- \quad (4)$$

The bisulfite ion is typically only a significant species at pH < 9 [24] and this suggests a reason why gold sulfite solution at relatively high pH tends to be more stable than those at low pH. At pH > 9 excess sulfite is entirely in the form of SO_3^{2-} and it is known that, under alkaline conditions, the reduction of SO_3^{2-} to $S_2O_4^{2-}$ cannot be attained [23]. In addition, the reduction potential of the bisulfite ion shift to more cathodic potentials as the pH is increased [54] so that increased alkalinity will also tend to favour the reduction of the Au(I) complex.

The improved stability of the sulfite-thiosulfite and thiosulfite baths compared to sulfite baths under electrodeposition conditions can also be rationalised in terms of the formation of dithionite. In the case of the mixed sulfite-thiosulfite bath, reduction of the gold complex occurs at a less cathodic potential than for sulfite [49] so that, at the same pH and current density, there is considerably less dithionite formation. For this reason it is possible to operate the mixed bath at higher current densities and lower pH without forming dithionite. Finally, the gold thiosulfate bath is not prone to this form of instability simply because it does not contain any bisulfite species.

The decomposition of gold plating solution can be conveniently monitored by characteristic UV-visible absorption peak at around 313 nm [30] and a plasmon band at 500 – 600 nm arising from the formation of colloidal gold [60]. The former peak has been assigned to an Au(III) complex [30] but we have recently shown [24] that it is more likely that this peak arises from the dithionite ion which absorbs at 315 nm [61]. In order to reduce the concentration of dithionite, a number of bath additives can be employed. For example, if strong oxidising agents such as picric acid, ferricyanide or 2,2'-dipyridyl are added to the solution, dithionite will tend to react with these species in preference to any gold complex [16,17,30]. However, the use of such stabilisers makes process control more difficult and it is preferable to make suitable adjustments to the bath chemistry, pH and current density in order to minimise the formation of dithionite.

3.0 Conclusions

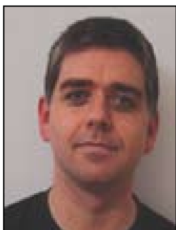
The unique properties of gold make it an essential material for the fabrication of a wide range of microelectronics, micro-system and optoelectronics components. Currently the main use for electrodeposited gold is in microelectronic packaging, but it is anticipated that its use in optoelectronic and microsystem markets will also increase substantially in the near future. In addition, recent requirements for lead-free components may substantially increase the use of gold in many packaging applications. The deposition of gold using through-

mask plating will continue to be an important metallisation process, particularly when thick films with high aspect ratios are required. A necessary requirement for this technology will be the continued development of plating baths which are robust, environmentally friendly and capable of producing high quality deposits. Traditional gold cyanide baths have proven to be unsuitable for such applications, mainly due to their poor resist compatibility and toxicity. The sulfite bath has addressed many of the issues associated with cyanide processes – it is relatively stable, non-toxic and is widely used in industry. There are, however, still some issues which require attention. For example, sulfite baths often require the use of additives to obtain desirable deposit properties and stabilisers to ensure satisfactory operation at low pH.

The latest generation of non-cyanide baths offers some significant improvements over existing sulfite baths. For example, the mixed sulfite-thiosulfate bath can operate stably at near neutral pH and good deposit properties can be obtained even in the absence of additives. The ammonium gold sulfite bath offers similar advantages, and is capable of producing deposits of comparable quality to existing sulfite baths. Baths containing hydantoin or mercapto-alkylsulfonic acid ligands also show considerable potential, although they require further evaluation. Despite the advantages of these new baths their use has been largely restricted to academic environments, but their wide-spread use in industry should be realised in the near future.

One perceived problem with most non-cyanide baths is their poor stability. However, many aspects of bath stability are now understood, and it is possible to design baths which can be operated stably over a wide range of conditions. In particular, speciation analysis has proven a useful tool for evaluating the stability of baths and understanding the action of various stabilisers. The ultimate aim of such approaches is to develop baths which produce high quality deposits without the need for stabiliser or additives.

About the authors



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