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Electrodeposition of Gold and Gold Alloys for bonding
In MEMS

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1. Gold and Gold Alloy in Microelectromechanical System

The development of microelectromechanical systems (MEMS) industry gave inputs to investigate new materials due to importance of thin films. Most of the electronic devices fabricated in MEMS use materials such as silicon and many other thin films, which are not well characterized regarding their electrical properties relevant to MEMS application. Little research has been conducted on microscale gold, because it has not been considered earlier as an engineering material[1].

Thin gold films are used in many MEMS devices because of high electrical conductivity. Some of the applications include radio-frequency (RF) MEMS which can operate at gigahertz frequencies, allowing for large bandwidth and extremely high signal-to-noise ratios and in inertial MEMS to increase mass of proof-mass for achieving higher sensitivity in MEMS accelerometers. These films can also be used in variable capacitor, chemical and biological sensors, optical detectors etc.

Some basic requirements for Au films used in MEMS applications are as follows[2]:

1. High conductivity.
2. Film–substrate adhesion should be strong enough to prevent cracking, delamination and spallation.
3. Residual stress developed should be minimum to prevent deformation of MEMS structure.
4. Films should be stable within a wide range of temperature (from below zero to several hundred degree Celsius).
5. Films should be resistant to surface wears, corrosion and oxidation.

1.1 Electrodeposition of Gold and Gold Alloys in MEMS.

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. It has high ductility and excellent wear resistance, which are important for electrical contacts. The inertness of gold prevents the formation of insulating surface oxides (as compared to metals like aluminum), so insulating surface oxide does not form on its surface. Gold is an excellent metal for wire bonding integrated circuits (ICs). Gold wires can be bonded to pure, soft gold pads by thermocompression bonding (300–400°C at high pressure to form a weld) or thermosonic bonding (150–200°C with ultrasonic energy to form a weld)[3].

Electroplating is an electrodeposition process for producing a dense, uniform, and adherent coating, usually of metal or alloys, upon a surface by the act of electric current. The coating produced is usually for decorative and/or protective purposes, or enhancing specific properties of the surface [4]. The surface can be conductors, such as metal, or nonconductors, such as plastics. Electroplating products are widely used for many industries, such as automobile, ship, air space, machinery, electronics, jewelry, defense, and toy industries. The core part of the electroplating process is the electrolytic cell (electroplating unit). In the electrolytic cell (electroplating unit) a current is passed through a bath containing electrolyte, the anode, and the cathode. In industrial production, pretreatment and post-treatment steps are usually needed as well [5].

The electrodeposition of pure gold is an enabling technology for wafer bump and wirebonding interconnect applications. Most conventional pure gold electroplating processes used in the electronics industry are cyanide based [6]. Due to the toxicity of the free cyanide formed during electrolysis, as well as cyanide's incompatibility with positive photoresists, sulfite-based gold processes have been the traditional alternative for wafer applications. However, traditional sulfite-based processes have suffered from issues with solution stability and the necessity for annealing to achieve the desired deposit hardness.

Soft gold electroplating is mainly used for wire bond and surface mount applications, which involve a large number of bump bonds on a chip. The gold should be soft enough so that the bumps can be easily deformed to accommodate small variations in thickness. Cyanide based electrolytes are the most extensively used in the industry. The gold (I) cyanide complex $\text{Au}(\text{CN})_2^-$ has a stability constant of 10^{39} , which makes the solution very stable, and shifts the standard reduction potential of gold (I) from 1.71V to -0.61V (SHE). However, in recent years, the health and safety concerns regarding the use of cyanide have overwhelmed the benefits it brings. In addition, free cyanide containing solutions can be incompatible with positive photoresists used in the microelectronics industry because they attack the interface between the resist film and the substrate, lifting the resist and depositing extraneous gold under the resist. Therefore, the demand for cyanide-free gold electroplating processes has increased significantly [6].

The workpiece to be plated is the cathode (negative terminal). The anode, however, can be one of the two types: sacrificial anode (dissolvable anode) and permanent anode (inert anode). The sacrificial anodes are made of the metal that is to be deposited. The permanent anodes can only complete the electrical circuit, but cannot provide a source of fresh metal to replace what has been

removed from the solution by deposition at the cathode. Platinum and carbon are usually used as inert anodes. Electrolyte is the electrical conductor in which current is carried by ions rather than by free electrons (as in a metal). Electrolyte completes an electric circuit between two electrodes [7]. Upon application of electric current, the positive ions in the electrolyte will move toward the cathode and the negatively charged ions toward the anode. This migration of ions through the electrolyte constitutes the electric current in that part of the circuit. The migration of electrons into the anode through the wiring and an electric generator and then back to the cathode constitutes the current in the external circuit. The metallic ions of the salt in the electrolyte carry a positive charge and are thus attracted to the cathode. When they reach the negatively charged workpiece, it provides electrons to reduce those positively charged ions to metallic form, and then the metal atoms will be deposited onto the surface of the negatively charged workpiece.

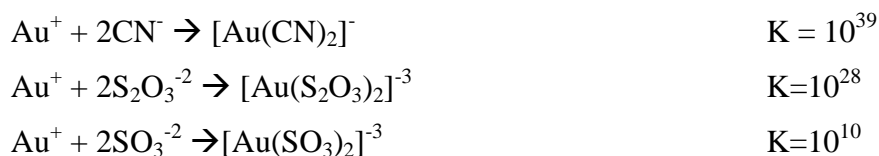
Electrodeposition or electrochemical deposition (of metals or alloys) involves the reduction of metal ions from electrolytes. At the cathode, electrons are supplied to cations, which migrate to the anode. In its simplest form, the reaction in aqueous medium at the cathode follows the equation [5]:



with a corresponding anode reaction. At the anode, electrons are supplied to the anions, which migrate to the anode. The anode material can be either a sacrificial anode or an inert anode. For the sacrificial anode, the anode reaction is [5]:



Gold exists primarily in the +1 and +3 oxidation states. The standard potential versus the normal hydrogen electrode (N.H.E) for a variety of Au(I) and Au(III) complexes is given in Table 1.1 [3]. The most important ion for electrodeposition is $[Au(CN)_2]^{-}$. The stability of the Au(I) cyanide complex is reflected in the shift of the reduction potential for Au(I) from 1.71V (aqua complex) to -0.611V (cyanide complex). The stability constant for $[Au(CN)_2]^{-}$ is 10^{39} . Two other gold complexes are of interest for electrodeposition, gold sulfite ($K=10^{10}$) and gold thiosulfate ($K=10^{28}$) [3].



The potentials for the reduction of Au(III) to Au and Au(III) to Au(I) 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 [3].

Half Reactions	Potential
Au(I) → Au	
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	1.71–1.85
$\text{AuCl}_2^- + \text{e}^- \rightarrow \text{Au} + 2\text{Cl}^-$	1.15
$\text{AuBr}_2^- + \text{e}^- \rightarrow \text{Au} + 2\text{Br}^-$	0.96
$\text{AuI}_2^- + \text{e}^- \rightarrow \text{Au} + 2\text{I}^-$	0.58
$[\text{Au}(\text{SCN})_2]^- + \text{e}^- \rightarrow \text{Au} + 2\text{SCN}^-$	0.66
$[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-} + \text{e}^- \rightarrow \text{Au} + 2\text{S}_2\text{O}_3^{2-}$	0.15
$[\text{Au}(\text{CN})_2]^- + \text{e}^- \rightarrow \text{Au} + 2\text{CN}^-$	-0.61
Au(III) → Au	
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.71–1.85
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	1.0
$\text{AuBr}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Br}^-$	0.85
$[\text{AuI}_4]^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{I}^-$	0.56
$[\text{Au}(\text{SCN})_4]^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{SCN}^-$	0.64
Au(III) → Au(I)	
$\text{Au}^{3+} + 2\text{e}^- \rightarrow \text{Au}^+$	1.40
$[\text{AuCl}_4]^- + 2\text{e}^- \rightarrow [\text{AuCl}_2]^- + 2\text{Cl}^-$	0.92
$[\text{AuBr}_4]^- + 2\text{e}^- \rightarrow [\text{AuBr}_2]^- + 2\text{Br}^-$	0.80
$[\text{AuI}_4]^- + 2\text{e}^- \rightarrow [\text{AuI}_2]^- + 2\text{I}^-$	0.55
$[\text{Au}(\text{SCN})_4]^- + 3\text{e}^- \rightarrow [\text{Au}(\text{SCN})_2]^- + 2\text{SCN}^-$	0.62

Table 1.1: Standard Reduction Potentials for Gold Ions (V vs. NHE)

Gold film is a polycrystalline film. The microstructural characteristics of polycrystalline films control their properties, performance, and reliability in applications in wide variety of electronic, magnetic, photonic, chemical, and micromechanical devices and systems. Gold films have columnar structure. The knowledge of diffusion process operating in gold film is important for application and design of microelectronic devices, fabrication and reliability of the thin-film package. Adhesion of gold film on silicon is poor, so a layer of chromium (Cr) is used before gold deposition, which enhances the adhesion of the film with substrate. Owing to this discrete layer of Cr, gold film has poor thermal stability because of the natural tendency of Cr to diffuse to the film surface at higher temperatures [1]. Besides Cr diffusion the other main factor controlling the resistance of the film is its grain structure, which in turn is controlled by the deposition parameters like current density, electrolyte temperature, thickness of deposited gold film and the annealing temperature. The variation of stress and resistivity of electroplated gold film with various deposition

parameters such as current density, deposition temperature of the electrolyte, thickness of the gold film and annealing temperature.

Gold-tin eutectic alloy solders are commonly used for microelectronic device packaging, because of their excellent combination of mechanical and thermal properties. The industry standard contains 70 at% gold and has a eutectic temperature of 280°C [8]. A possible alternative could be the Sn-rich eutectic composition that is present in the gold-tin system (Figure 1.1). The second eutectic exists at 6.8 at% Au and a temperature of 217°C. This composition may also be a candidate Pb-free solder for microelectronic applications.

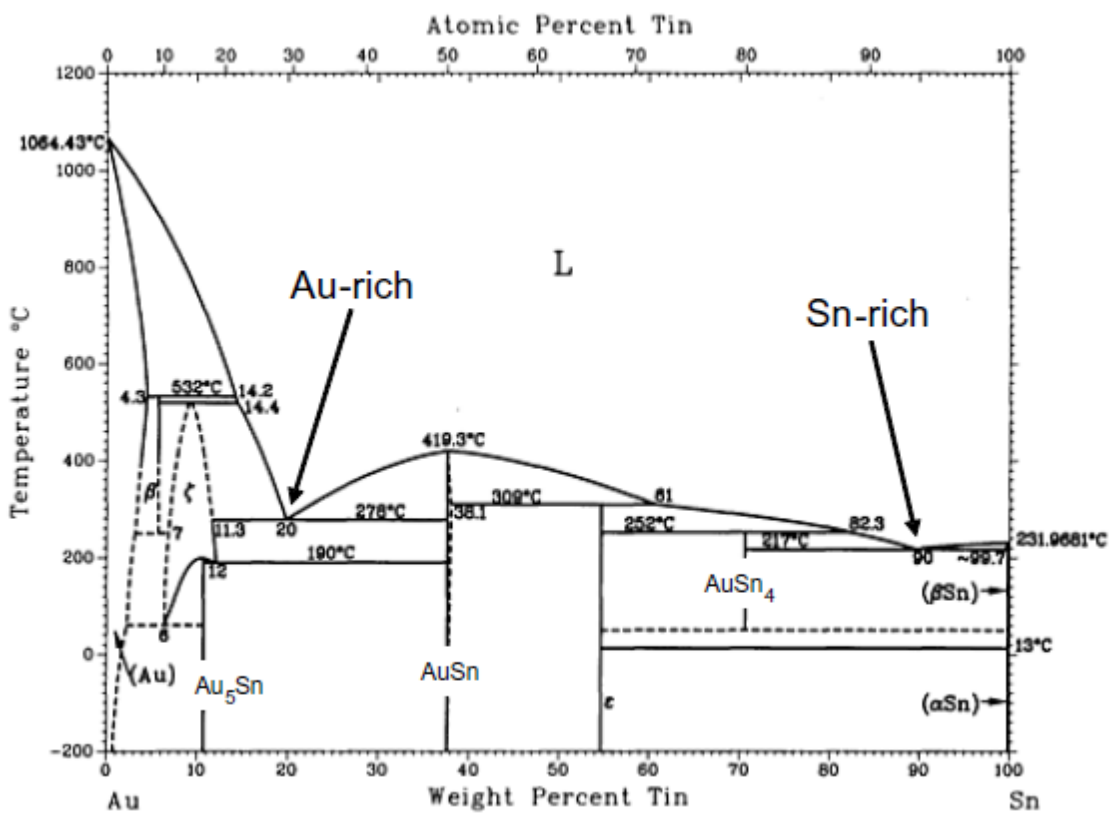


Figure 1.1: Au-Sn binary phase diagram [9]

According to Lee and Chuang [10], the Sn-rich eutectic has suitable properties to be used for packaging applications, and its use would significantly reduce material costs. Department of Chemical and Materials Engineering in University of Alberta has developed a simple solution for the electrodeposition of Sn; this solution consists of tin chloride and tri-ammonium citrate. Gold particles (submicron size) can be added to this solution to form a suspension, which can be used to electrodeposit Sn-rich, Au-Sn eutectic solder films, with uniform thickness and composition [8].

The films in this study were deposited onto Pt metalized silicon wafers from the aforementioned Sn solution with suspended Au particles, using a pulse plating power supply.

The Au particles are incorporated between the Sn grains. Solder joint integrity is dependent on the formation and distribution of brittle intermetallic phases. As such, Sn rich solder films were aged and/or reflowed to study intermetallic formation. After aging or reflow, the two eutectic phases form in the film [8]. The study will focus on the effects of plating conditions on the morphology and composition of Sn rich, Sn-Au solder films and intermetallic formation during aging and reflow.

The residual stress of gold films deposited on silicon wafers is important for microsystems and microelectromechanical systems (MEMSs). Gold is an excellent structural and contact material for MEMSs because it is difficult to oxidize. The residual stress of gold films annealed at different temperatures plated from a neutral-pH cyanide bath was measured. Recrystallization of the gold occurs at high temperature, which relieves the stress due to mismatch of the coefficient of thermal expansion (CTE) between the gold and the silicon substrate. Normally, the gold achieves a stress neutral point at the highest temperature. The CTE mismatch between the metal and the substrate caused tensile stress in the gold during cooldown. Stresses on the order of 50, 200, and 350 MPa were observed at anneal temperatures of 100, 250, and 400°C [11].

Residual stress is a particular problem for free-standing gold structures where flatness is desired, such as in X-ray lithography masks. The stress films deposited from a neutral pH cyanide bath was found to be 50 MPa tensile whereas the addition of 25 ppm arsenic changes the stress to 30 MPa compressive. Pulsed current reduced the stress to <5 MPa compressive. In other applications, the stress gradient in gold films deposited at different conditions was used to build precise-curvature cantilever beams for microswitches [12].

It has also been found that the residual stress of the plated gold can be controlled in non-cyanide baths. 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 [3].

2. TYPICAL DIRECT CURRENT (DC) PLATING BATHS:

The cyanide-based baths are divided into three classifications [3];

1. The Alkaline Gold Cyanide Bath (pH>8.5)
 2. Acidic, buffered baths (pH between 1.8 and 6)
 3. Neutral, buffered gold cyanide bath (pH between 6 and 8.5)
- The fourth group of baths, noncyanide plating baths.

Gold readily forms alloys with other metals during the deposition process substrate onto substrate which it was plated. Gold or its alloy deposits become hard or soft, dull or bright, depending on the impurities and deposition conditions.

The materials of plated gold in use for this purpose can be classified into two categories: soft gold and hard gold. Soft gold is used for metalizing bonding pads and fabricating micro bumps on silicon IC chips and ceramic packaging boards, while hard gold is used as a contact material on electrical connectors, printed circuit boards, and mechanical relays. Electrolytic methods are available for plating both soft gold and hard gold.

Electroplated hard gold is the most commonly used contact material for high reliability electrical connectors and relays. The major factor determining the hardness of this material is its small grain size. On the other hand, with the recent advances in miniaturization of electronic components and devices, dimensions of electrical contact areas are expected to reach, and may become even smaller than, the grain size of the hard gold that is 20–30 nm. When this ultimate miniaturization is realized, the bulk hardness and the resistance to mechanical wear of the hard gold will no longer be retained. To meet the requirement of this trend, we considered it meaningful to have available a technology of electroplating an amorphous gold or gold alloy, because physical properties of amorphous materials in general are known to be independent of their size or physical dimensions.

The properties of hard-gold films of such small dimensions are expected to deviate significantly from those of bulk hard gold. On the other hand, mechanical properties of amorphous metals and alloys in general are known to be independent of their size because of the absence of crystal grains in such materials. Thus, to be prepared for the future need of an amorphous electrical contact

material. Investigation on the possibility of electroplating amorphous Au–Ni alloy from a bath prepared by adding a gold salt into a bath that is already known to deposit an amorphous alloy such as Ni–W. This approach was successful in developing a process to electroplate amorphous Au–Ni alloy with a hardness value greater than twice that of the conventional hard gold without adversely affecting the electrical contact resistance. Using a similar approach, we also developed a process for electroplating amorphous Au–Co alloy films.

At $\text{pH} < 8$, the predominate form of cyanide is $\text{HCN}(\text{g})$, which evolves as a gaseous product. HCN gas is highly toxic, and its evolution from plating baths is a health concern. Appropriate ventilation is required for all cyanide baths. The presence of significant concentrations of free cyanide in the bath, such as in the case of alkaline baths, is also a health risk because accidental cyanide ingestion or injection can occur [3].

The presence of free cyanide in the bath is a major consideration in the selection of the anode and metal ion replenishment method. In the presence of free cyanide, gold metal can be used as a consumable anode because it can be electrochemically oxidized forming the gold cyanide complex. In the absence of free cyanide, gold is not oxidized to any appreciable extent, so it acts like an inert electrode. The ramifications of this will be included for each bath [3].

2.1. Alkaline Cyanide Baths

Alkaline cyanide baths operate at high pH and with an excess of free cyanide. Potassium cyanide is generally used as a source of the free cyanide in these baths. Since there is appreciable free cyanide present, the cyanide released during the deposition reaction does not significantly alter the cyanide concentration in the bath. Thus the Nernstian shifts in the reduction potential of Au(I) cyanide due to accumulation of free cyanide (even in the vicinity of the electrode surface) do not occur [3].

Cathode: $[\text{Au}(\text{CN})_2]^- + \text{e}^- \rightarrow \text{Au} + 2\text{CN}^-$

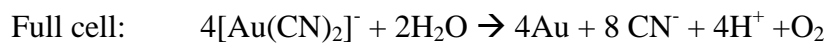
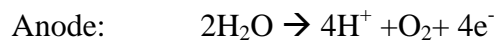
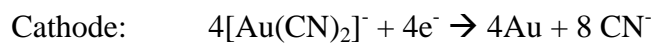
Anode: $\text{Au} + 2\text{CN}^- \rightarrow [\text{Au}(\text{CN})_2]^- + \text{e}^-$

Full cell: No change to plating solution

The main changes are appeared in the bath due to oxidation or reduction side reactions, drag-out of plating salts, and drag-in of water or impurities. The free cyanide promotes the corrosion of the gold anode (forming $[\text{Au}(\text{CN})_2]^-$), increases the throwing power, and improves the conductivity. Free

cyanide also retards the codeposition of some metals because the stability of their cyanide complexes shifts their reduction potential to values more negative than those used during deposition. The absorption of atmospheric carbon dioxide increases the concentration of carbonate in the solution as a result of the reaction between cyanide and CO₂. The carbonate can help to stabilize the pH and improve throwing power slightly [3].

Nonsoluble, dimensionally stable anodes, like platinized titanium or stainless steel, are sometimes used. Oxygen gas and hydrogen ions are the dominant products at the insoluble, dimensionally stable anodes,



The hydrogen ions produced in anode equation and shown in equation of full cell for the full cell can either be neutralized by hydroxide (lowering the pH of the solution) or form HCN (g) and evolve from the bath as a gas depending on the operating pH. Thus the pH and the gold cyanide ion concentration of the bath will drop as current is passed, as shown by the two half reactions. Both these effects must be reversed through the addition of plating salts and KOH. The addition of KOH and KAu(CN)₂ as a replenishment for the right-hand side of full cell equation will result in the accumulation of KCN (in the form of K⁺ and CN⁻ until the KCN solubility product is reached) in the bath. The buildup of KCN is somewhat mitigated by drag-out. An insoluble anode is convenient because the cathode current distribution is reproducible and consistent over long periods of time. Also the anode does not have to be replaced as it corrodes. Thus, anode maintenance is replaced by bath maintenance [KOH and KAu(CN)₂ additions]. The cathodic current efficiency for the deposition of the metal from alkaline baths can be as high as 90–100% with adequate gold content in the bath and sufficient agitation [13].

2.2. Acid Cyanide Baths

The nonalkaline, cyanide-based baths contain other metals and normally use a citrate buffer. They are operated around pH 4. Low-pH buffered baths were consumed in wide application throughout the electronics industry for contact surfaces, corrosion protection, bonding surfaces, and special electroforming. The pH of the baths allows the use of photoresist and other polymers.

Anodes in these baths are usually platinized titanium, gold, or gold-plated platinized titanium [3]. The gold-plated electrodes are found not to dissolve readily at low current densities because of the low free-cyanide concentration. This, however, is not the case at high current densities and low solution volume where appreciable transient concentrations of free cyanide can build up and lead to the oxidation and dissolution of a pure gold anode [3]. Stainless steel and carbon anodes are found to introduce contamination, and their use is discouraged. The use of insoluble anodes requires that plating salts be added to the bath to replenish the gold content [e.g., $\text{KAu}(\text{CN})_2$] and maintain pH control. Although K^+ removal and pH control can be accomplished by an ion exchange method, drag-out and salt addition are the usual method of bath maintenance [14].

The codeposition of other metals with gold is easily compatible with acid cyanide baths, resulting in marked changes in the physical properties (especially hardness) of the deposits. Hard gold is a great milestone for electronic components where low contact resistance, pore-free deposits, wear resistance, and chemical inertness are functional requirements. Such applications include the multiple-insertion electrical contacts found on printed wiring board contacts or spring contacts [3].

Bright, hard deposits can be produced from alkaline and acid cyanide baths containing cobalt, nickel, indium, silver, arsenic, or cadmium.

A typical range of concentrations is given below [13]:

$\text{KAu}(\text{CN})_2$	12- 15 gL^{-1}
Citric Acid	90-115 gL^{-1}
Cobalt (added as acetate or sulfate)	0.07- 0.1 gL^{-1}
pH (adjust with KOH)	3.6-4.7
Temperature	40-65° C

To establish the proper pH, KOH is added to the bath. A concentration of 50 gL^{-1} KOH will produce a bath of about pH 4.0. Baths that produce pure gold deposits often operate at close to 100% current efficiency [13]. The high current density used in high-speed baths can produce a temporary buildup of free cyanide in the bath that may lead to the corrosion of a gold anode or even the slow oxidation of a platinum anode. It has also been found that $[\text{Au}(\text{CN})_4]^-$ can be formed at the anode, especially under high current and high cobalt concentrations at a platinum anode.

One of the limiting factors for the current density is the rise in pH in the vicinity of the electrode during the reduction process, through either gold deposition or hydrogen gas production [3].

At higher pH or higher temperature, the cobalt and carbon contents of the deposit decrease. An increase in pH above 5.5 virtually eliminates the cobalt from the deposit. This increase demonstrates the ability of acid cyanide baths for codeposit metals with gold. Lower current densities (smaller rate of consumption of protons at the cathode) or higher mass transport (higher rate of delivery of protons from the solution) will mitigate the rise in pH in the electrode boundary layer during deposition. Thus the higher the solution agitation, the greater is the allowable current density. The cobalt or nickel ions are known to codeposit in the gold in at least two different forms, the cyano complex and as a substitutional alloy. The increase in hardness is due to the grain refining effect of the codeposited cyanocomplex. The porosity of the deposited gold also decreases with higher mass transport and lower current density.

2.3. Neutral Cyanide Baths

Nonalkaline baths exhibit a wider range of physical and chemical properties than possible at higher pH [3]. The hardness is the result of a reduction in the grain size of the gold caused by the codeposit increasing the rate of grain nucleation. It was also noted that the amount of codeposited metal (e.g., cobalt or nickel) decreased to nearly zero at $\text{pH} > 5.5$. Although the metals used to harden gold are not readily codeposited from neutral pH baths, it has been found that hard gold (as well as soft gold) can be formed in neutral baths by the careful selection of the plating parameters without the use of additives. In the neutral baths the gold salt used is the same as in alkaline and acid baths, $\text{KAu}(\text{CN})_2$. The neutral pH and absence of free cyanide make these formulations the preferred ones for use with photoresist and other polymeric materials.

The neutral baths produce pure, soft gold at relatively low current densities, typically $2\text{--}5 \text{ mA cm}^{-2}$ and $60\text{--}70^\circ\text{C}$. The phosphate salts serve only as the supporting electrolyte and pH control, so that strict control of their concentration is not critical. The phosphate buffer can be used for acid, neutral, or basic conditions with pH adjustment carried out by the addition of KOH or H_3PO_4 . Control of pH, temperature, and gold concentration is critically important.

Additive-free hard gold (AFHG) can be produced from neutral baths using phosphate. The advantages of AFHG baths over metal hardened baths are [15];

1. No need to control additive concentration
2. High current efficiency
3. Greater tolerance for heavy metal impurities due to the insolubility of many metal phosphates
4. High ductility and thermally stable contact resistance for electronic components.

However, AFHG baths are highly susceptible to bath contamination. Small amounts of impurities, such as nickel, cobalt, or iron ions, can cause large changes to the physical properties deposited from the bath. It can be difficult to clean the plating bath of the unexpected impurities. The AFHG bath was shown to have superior tensile strength, total elongation (high ductility), and more stable contact resistance than comparable deposits from a cobalt-hardened acid bath. However, a small increase in contact resistance was found when the deposit was heated to $>100^{\circ}\text{C}$ due to the surface segregation of AuCN [16].

The use of a gold anode is usually an unacceptable solution to the Au(III) problem because of the anode maintenance and changing cathodic current distribution as the anode corrodes and changes shape. The buildup of Au(III) is somewhat mitigated by the dilution effects due to drag-out. Other possible solutions to the Au(III) problem are to use a $\text{RuO}_2/\text{TiO}_2$ (often called dimensionally stable anode, DSA), adjust the current density to correct for the lower current efficiency, or chemically treat the Au(III) by reduction (e.g., hydrazine) or removal (activated carbon).

2.4. Noncyanide Baths

The Au(I) cyanide complex is by far the most important for electrodeposition. However, there are several approaches for the use of $[\text{Au}(\text{CN})_2]^-$ which have stimulated the investigation and commercialization of other gold complexes in plating baths. 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. The release of free cyanide during the reduction of $[\text{Au}(\text{CN})_2]^-$ can be incompatible with positive photoresists used in the microelectronics industry. The operating parameters of commercial gold sulfite baths have been presented with special attention given to the effect of plating temperature and current density on residual stress in the deposited metal. Lastly, the health and safety of workers and the environmental impact of the wide-scale use of cyanide are

a concern. But, Alkaline sulfite baths can also be used without the use of thallium, which itself is a health hazard [3].

Although Au(I) sulfite has been used in commercial baths, the complex is susceptible to disproportionation, forming Au(III) and metallic gold. This spontaneous decomposition of the bath has led commercial baths to use proprietary stabilizing additives. The gold sulfite complex $\text{Au}(\text{SO}_3)_2^{-3}$ is the most common alternative to cyanide. This complex has a stability constant of 10^{10} , much less than that of the gold cyanide complex. Gold (I) sulfite is came across some problems particularly at $\text{pH} < 7$ where sulfite transforms to bisulfite. Therefore, stability is always an issue for sulfite-based gold electroplating solutions, and stabilizing additives are usually necessary. Gold (I) thiosulfate has a stability constant which is between that of Au(I) sulfite and Au(I) cyanide. Gold (I) thiosulfate complex $\text{Au}(\text{S}_2\text{O}_3)_2^{-3}$ is another alternative to cyanide. Its stability constant (10^{28}) is between cyanide and sulfite complexes and it is stable in weakly acidic solutions. However, thiosulfate ions themselves are not stable without the presence of free sulfite. They undergo disproportionation and produce sulfite ions and free sulfur, which precipitates.

The Au(I) thiosulfate complex is stable in weakly acidic solutions because of the low bath stability for thiosulfate. The dominant species in mixed-complex baths, $\text{S}_2\text{O}_2^{-3}$ and $\text{S}_2\text{O}_2^{-3}$, at neutral or basic conditions have been reported to be $\text{Au}(\text{S}_2\text{O}_3)(\text{SO}_3)^{-3}$ [17]. The thiosulfate-only complex is dominant at low pH. The existence of the mixed ion complex was suggested in previous studies based on the deposition potential. It was also reported that the results from the sulfide-only bath are consistent with a higher stability constant (10^{27}), rather than the commonly assumed value of 10^{10} [16].

The effect of mixed thiosulfate–sulfite electrolytes produce soft gold deposits suitable for forming gold “bumps” on ICs and in electronic interconnections. The Vickers hardness of the electrodeposited gold was 80 kg mm^{-2} in the as-deposited state and 50 kg mm^{-2} after annealing. The optimum bath with thallium was composed of the following formulation [16]:

$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$	0.06 M
Na_2SO_3	0.42 M
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.42 M
Na_2HPO_4	0.03 M
TI^+ (added as TI_2SO_4)	0.03 M

pH	6
Temperature	60°C
Current density	5mAcm ⁻²

The mixed sulfide–thiosulfate plating bath was used to produce soft gold deposits for gold bumps and wire-bonding applications. Bright gold deposits were obtained at a cathodic deposition efficiency (current efficiency) of greater than 99%. The purity of the gold deposits was greater than 99.99% and had a hardness between 60 and 80 Knoop. The bath composition is as follows [3]:

Gold as metal	10 g L ⁻¹
Sulfide	70 g L ⁻¹
Thiosulfate	70 g L ⁻¹
Additives	10 g L ⁻¹
pH	5
Temperature	50°C

The deposition of gold from the iodide–thiosulfate bath suggests that the chemical reaction preceding the electron transfer step is the dissociation of the $[\text{Au}(\text{S}_2\text{O}_3)_2]^{-3}$ to form $[\text{Au}(\text{S}_2\text{O}_3)_2]^{-}$ and $\text{S}_2\text{O}_3^{-2}$.

In each of the studies involving a mixed-thiosulfate bath (sulfite–thiosulfate and iodide–thiosulfate), it was observed that the mixed-salt gold complex is more stable and harder to reduce than either of the single-salt complexes. That is, the Au(I) sulfite–thiosulfate complex is reduced at potentials more negative than either the Au(I) sulfite or Au(I) thiosulfate complex.

Electroplating of soft gold is generally carried out with a bath containing $\text{KAu}(\text{CN})_2$ in a phosphate buffer of pH 7 at a mildly elevated temperature. It does not contain free cyanide ions initially, but they are generated at the cathode surface as a result of the gold deposition reaction. The cyanide ions are partly converted into HCN, which escape into the atmosphere, and partly remain in the bath. The presence of free cyanide is undesirable not only for its toxicity but also for its incompatibility with photoresists used to delineate circuit patterns through which the gold is to be plated. Cyanide attacks the interface between the substrate and the photoresist, lifting the latter and depositing extraneous gold under the photoresist. To avoid these problems, an Au(I) sulfite bath is used instead. However, the sulfite bath easily undergoes a disproportionation reaction to form

Au(III) and metallic Au because of the relatively low stability of the Au(I) sulfite complex, causing the bath to decompose spontaneously on standing, unless a suitable stabilizer is added to the bath. All commercially available Au(I) sulfite baths contain proprietary stabilizing additives.

In contrast, the Au(I) thiosulfate–sulfite mixed ligand bath we developed is highly stable and requires no stabilizing additive. We selected this system in view of the fact that it is used successfully for formulating non-cyanide gold plating baths yielding good bath stability and deposit properties.

3. ELECTROLYTIC METAL DEPOSITION

There are three types of electrolytic metal deposition processes: direct current electrodeposition, pulse plating, and laser-induced metal deposition.

3.1. Direct Current Electrodeposition

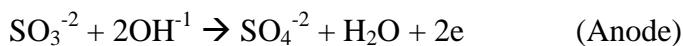
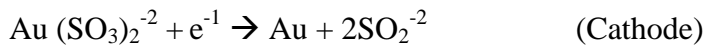
In the direct current (DC) electrodeposition, the current source is. A power source in the form of a battery or rectifier (which converts alternating current electricity to regulated low-voltage DC current) provides the necessary current [7].

Electroplating is performed in a plating unit. Electrodes, immersed in the electroplating bath (electrolyte), are connected to the output of a DC current source. The workpiece is to be plated acts as a negatively charged cathode. The positively charged anode(s) completes the electric circuit. This type of circuit arrangement directs electrons (negative charge carriers) into a path from the power supply (rectifier) to the cathode (the workpiece to be plated).

The geometric shape and contour of a workpiece to be plated affect the thickness of the deposited layer. In general, workpieces with sharp corners and features will tend to have thicker deposits on the outside corners and thinner ones in the recessed areas. The cause of this difference in the resulting layer thickness is that the DC current flows more densely to sharp edges than to the less accessible recessed areas. In other words, the current distribution is not uniform [5].

3.2. Pulse Plating

Electrodeposition using pulsed currents is known as pulse plating. The pulsed currents can be unipolar (on–off) or bipolar (current reversal). Pulses can be used along or be superimposed on a DC feed. By using the bipolar pulse, metal deposition occurs in the cathodic pulse period, with a limited amount of metal being redissolved in the anodic period. This repeated deposition and partial redissolution could improve the morphology and the physical properties of the deposit. The replacement of a direct by a pulsed current in the electrodeposition of gold has a marked effect in improving the mechanical properties of the deposits and in reducing their internal stresses. For many applications in the electronics industry pulse plating therefore offers considerable advantages [5].



The structure and surface roughness of gold and gold alloy deposits can be influenced by periodically reversed or pulsed current. Apparently the need for a high conductivity gold electrodeposit for integrated circuitry initiated the development of a pulse plating unit which supplied an on-off D.C. pulse with on- and off-times in the millisecond range and operated with current peaks up to 8 A. In general the on- and off-times were in the range of 1:10. The advantages claimed for the pulse plating of gold were [19]:

1. A substantial increase in rate of deposition.
2. Less danger of hydrogen embrittlement.
3. A reduction in the need for additives.
4. A lower level of impurities from the electrolyte.

Pulse plating of gold in the production of semiconductor devices seems to be a procedure which is comparable to vacuum deposition but much more convenient and rapid, especially for experimental purposes.

Cheh has done theoretical calculations and experimental measurements which clearly show that for phosphate, citrate and cyanide gold electrolytes the limiting current density is higher in pulse than in D.C. plating because of the higher concentration of gold ions in the diffusion layer, although the

limiting overall plating rate is lower. According to Cheh this increase in the limiting current density might be the reason for the improved physical properties by yielding a different type of structure in the deposit [20]. Pulse plating markedly affects the properties of the deposit and its fine gold deposits produce a dense fine-grained structure with about half the resistivity of normal D.C. plated layers. The fact that pulse plated deposits have the lowest porosity of all gold films deposited by various methods was attributed by Rehrig to the densely packed continuous fine grained structure with barely visible grain boundaries. It is shown at Figure 3.1. [21].

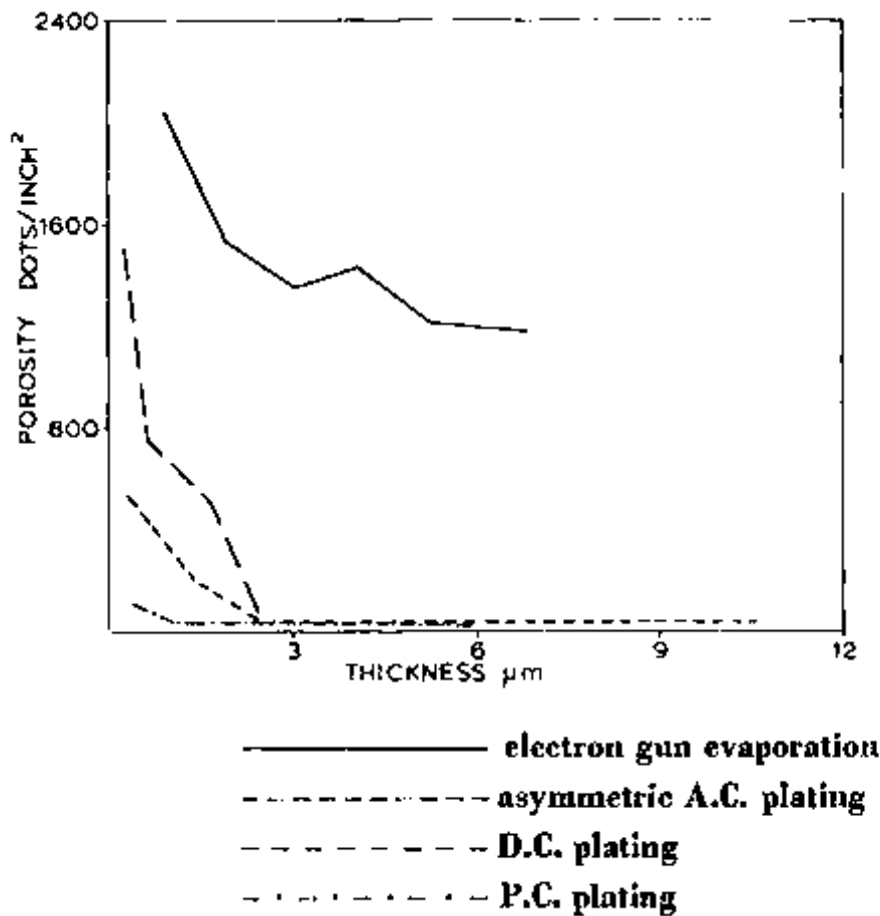


Figure 3.1: Relationship between porosity and thickness of various types of gold films according to Rehrig [21].

The very small grain size and the high purity also serve to explain the difference in tensile strength and elongation observed by Lendvay and Raub and shown in Figure 3.2 [19]. In the as-deposited condition fine-grained deposits gave a tensile strength about 25 percent higher than with D.C. plated deposits. D.C. plated deposits show a slight increase in tensile strength after heat treatment at 100°C, which is followed by a continuous decrease at higher temperatures, while elongation rose

more or less steadily. The increase at 100°C is very likely due to the beginning of decomposition of incorporated impurities. Pulse plated deposits with lower impurity concentrations do not show any hardening effect. As one might expect from a purer metal, its tensile strength also decreases much more rapidly during heating.

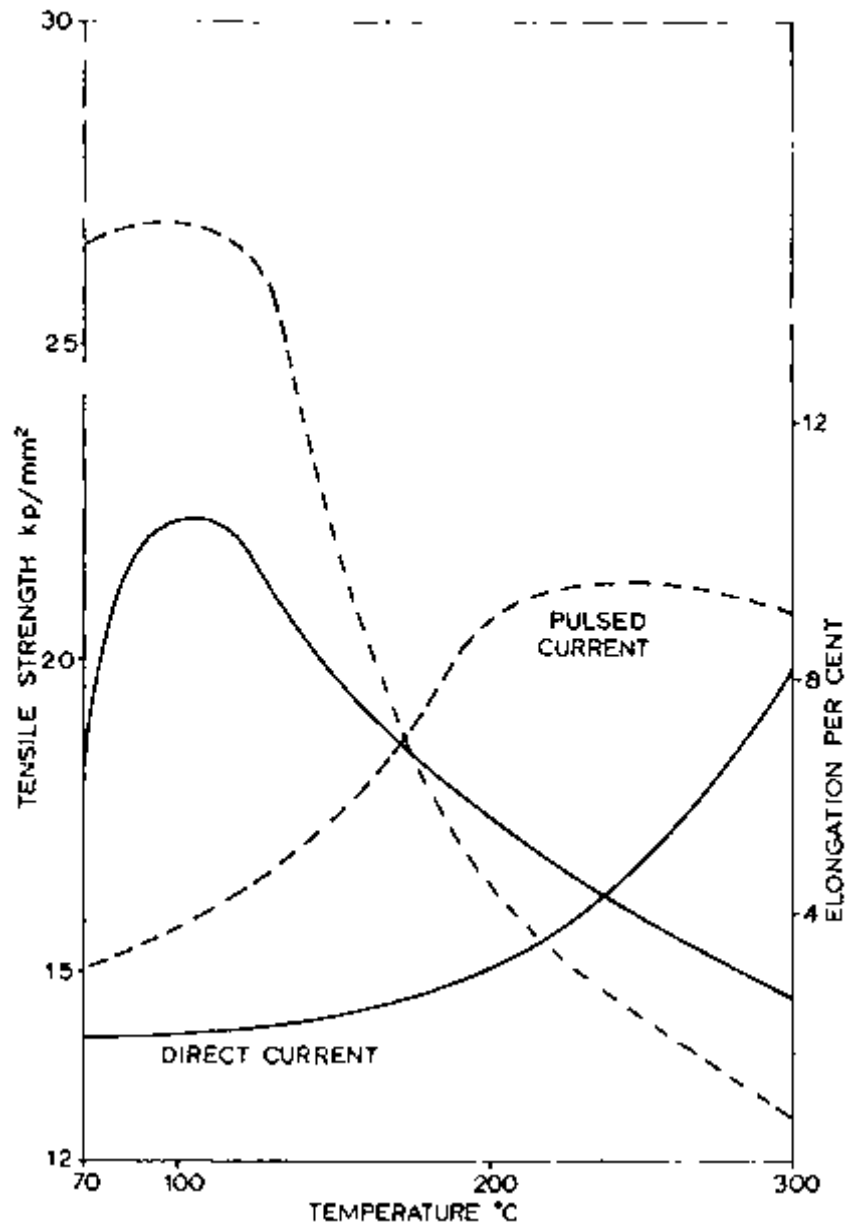


Figure 3.2: Tensile strength and elongation of pulsed current and direct current plated deposits from a phosphate gold solution [19].

3.3. Laser-Induced Metal Deposition

In laser-induced metal deposition, a focused laser beam is used to accelerate the metal deposition. Experiments have shown that the deposition rate can be increased by 1000 times [7]. The plating equipment mainly consists of a laser head with focusing optics and the electrolytic cell. The focused laser beam can pass through a hole in the anode through the electrolyte and impinge on the cathode surfaces.

4. ELECTROLYTE

Different metals may need different types of electrolyte. Types of electrolytes include water solutions of acids, bases, or metal salts, certain pure liquids, and molten salts. Gases may act as electrolytes under conditions of high temperature or low pressure. In addition to metal salts, electrodeposition electrolytes usually contain a number of additives for various purposes. Some agents are used to increase electrolyte conductivity (supporting electrolytes). Others may be used for increasing bath stability (stabilizers), activating the surface (surfactants or wetting agents), improving leveling or metal distribution (leveling agents), or optimizing the chemical, physical, or technology properties of the coating. These coating properties include corrosion resistance, brightness or reflectivity, hardness, mechanical strength, ductility, internal stress, wear resistance, or solderability [7].

The properties of electrolyte are usually characterized by electrolytic conductance, covering power, macrothrowing power, and microthrowing power [18]. Inorganic and organic salts, acids or alkalis can be used to increase the electrolytic conductance. The conductivity of an electrolyte is a function of the degree of dissociation, the mobility of the individual ions, the temperature and viscosity, and the electrolyte composition.

Covering power describes that how electrodeposition electrolyte can cover the entire surface of a workpiece being plated, with desired uniform thickness. Covering power is influenced by the nature of the substrate surface, the electrolyte composition, the temperature and viscosity, and the current density. Macrothrowing power predicts the ability of an electrolyte to lay down as nearly as possible a uniformly thick deposit across the surface of a workpiece [5]. A good covering power is a prerequisite for good macrothrowing power. Other factors that affect macrothrowing power include

the current distribution and current density, electrolyte composition, electrolytic conductance, and electrolyte agitation.

Microthrowing power indicates that how metal electrodeposition occurs at the outer plane of the substrate or at the base of valleys or cracks. Microthrowing power can be improved by activating the surfaces at the base of valleys or cracks to promote electrodeposition there, while inhibiting the outer surfaces by using inhibitors preferentially. In many cases, microthrowing power is inversely related to macrothrowing power [5].

4.1. ELECTROLYTE ADDITIVES

Electrodeposition electrolytes usually contain various other species. Thus both inorganic and organic salts, acids or alkalis will be added to increase electrolyte conductivity. Other species, both organic or inorganic, may be added for specific purposes, for example, to increase bath stability, or improve leveling or metal distribution, or to optimize the chemical, physical or technological properties of the deposited metal (corrosion resistance, brightness or reflectivity, hardness, mechanical strength, ductility, internal stress, wear-resistance or solderability) [7].

In working with such additives, it should be recognised that they are often effective over only a defined concentration range, and should their concentrations fall outside this range, all kinds of problem can arise either in the deposition processor the deposit properties.

There are three principal types of additives associated with high purity gold electrolytes: Complexing agents, grain refiners and hardening agents. Complexing agents such as pyrophosphate ion, organophosphorus compounds and polyphosphates are added to reduce the activity of metallic impurities in the solution by forming stable complexes and hence minimizing codeposition. Organic chelating agents such as EDTA and related compounds are also used. Relatively small amounts of base metals are used for providing grain refinement. These additives also provide smoothing and semi-brightening of the deposit, while not being codeposited to a significant extent. In neutral solutions, arsenic and thallium have been used. Some additives such as alums and hydrazine sulfate have been claimed to harden the electrodeposit without being codeposited.

Use of heavy metal ions in trace quantities (parts per million) in gold electroplating solutions, induces a marked cathodic depolarization which extends the range of current densities over which smooth, fine grained deposits can be obtained. In slightly alkaline phosphate electrolytes the most

effective additives comprise the family of elements Hg, Ti, Pb and Bi, which lie immediately adjacent to gold in the periodic table.

They exhibit a strong tendency to form an adsorbed monolayer on gold and platinum electrodes. This is done at potentials positive to those at which their cathodic deposition as bulk metals would begin, i.e. at under potentials. Deposits obtained with these additives have a very fine and highly uniform grain size. The various heavy metal ions have a brightening effectiveness which is in the order $\text{I} > \text{Pb} > \text{Bi} > \text{Hg}$. This is the inverse order of their electron work functions (the amount of energy required to lift an electron out of a lattice). The postulated mechanism for this performance is that the elements form an adsorbed monolayer on the surface of the gold. This lowers its work function and thereby lowers its deposition potential so that deposition then occurs at under potentials.

Carriers' are compounds of large molecular weight which, in the presence of small numbers of chloride ions, will move the start of the curve towards the right, increasing the voltage needed to produce the desired current. This gives a deposit with a tighter grain structure, and improves plating distribution and throwing power.

'Brighteners' are disulphide compounds with a low molecular weight that reduce the effect of the carrier by increasing the current. They have a key role in determining the physical properties of the deposit, in particular tensile strength and percentage elongation.

'Levellers' are a class of aromatic compound that are absorbed preferentially at high current areas, suppressing the plating locally, and allowing the thickness in areas of lower current density to 'catch up'.

The electrodeposition of metal coatings in industrial metal finishing is usually based on aqueous electrolytes, known in the industry as electrodeposition baths or simply, baths. Their primary constituent is the metal salt of the metal to be deposited, then in most cases an acid or alkali to promote conduction. In some cases the bath is buffered. In addition, there will be additives to promote the electrodeposition process or optimize the deposit properties [7].

4.1.1. Brightening agents

In metal finishing, bright or highly reflective surfaces (the terms are usually synonymous) can be of both decorative and functional importance, if for no other reason that bright surfaces require less mechanical finishing, after plating, if indeed any at all.

Defining brightness or reflectivity of a surface as the extent to which incident light is reflected, it follows that surface roughness and unevenness are antithetical to good reflectance. Reflective surfaces are characterized by a crystallite size at the surface of less than $0.3 \mu\text{m}^2$. Thus, highly reflective deposits are found under conditions where fine-grained deposits are formed. To achieve this, it is long-established practice to add metallic or organic compounds, known as brighteners or brightening agents. Their use is based on empiricism, there being no certain means of predicting their effects. In the same way, selecting the most appropriate such compound(s) will usually be based on trial-and-error.

Two different types of brightener are recognized, the first being brightener carriers, the second, brightener additives [7].

Addition of brightener carriers, also known as primary brighteners or Class I brighteners, leads to a significant grain refining action in the deposited metal. While this greatly increases the brightness of the metal, it will not impart a mirror-finish or anything close to this. Among the best-known brighteners of this type are;

- sulfonamides
- sulfonimides
- benzenesulfonic acids (mono-, di- or trisulfonic acids)
- naphthalenesulfonic acids (mono-, di- or trisulfonic acids)
- alkylsulfonic acids
- sulfinic acids
- arylsulfonesulfonates.

These primary brighteners are essential components of a complete brightening system, in that they reinforce the efficacy of Class II or secondary brighteners, the latter being rarely used without the former. Class II brighteners, even at very low concentrations, impart a near-mirror finish to the deposited metal. The most important of these are listed in Table 4.1.

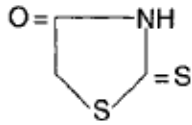
Designation	Structural formula
Thiourea	$\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$
Acylthiourea	$\begin{array}{c} \text{O} \qquad \qquad \text{S} \\ \qquad \qquad \\ \text{R}-\text{C}-\text{NH}-\text{C}-\text{NH}_2 \end{array}$
Mercaptoalkylsulfonic acid	$\text{HS}-\text{C}_n\text{H}_{2n}-\text{SO}_3\text{H}$
Bis-(sulfoalkyl)-disulfide	$[\text{S}-\text{C}_n\text{H}_{2n}-\text{SO}_3\text{H}]_2$
Thiocarboxylic acid amide	$\begin{array}{c} \text{S} \\ \\ \text{R} \text{ > } \text{N}-\text{C}-\text{S}-\text{C}_n\text{H}_{2n}-\text{SO}_3 \\ \\ \text{R}' \end{array}$
Thiocarbazono	$\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{N}-\text{C}-\text{O} \end{array}$
Thiosemicarbazone	$\begin{array}{c} \text{S} \\ \\ \text{R} \text{ > } \text{C}=\text{N}-\text{NH}-\text{C}-\text{NH}_2 \\ \\ \text{R}' \end{array}$
Thiohydantoin	

Table 4.1: Some commonly used brighteners.

Out of a very large number of potential Class II brighteners, only a few are used in practice, largely because many such species are highly effective in their brightening action, they can adversely affect process or deposit properties in other ways. In order to minimize this, secondary brighteners are usually employed with a primary brightener in a combination known for the compatibility and synergy of both.

A number of electrolytes form bright deposits only in a comparatively narrow temperature and current density operating window. Figure 4.1 shows this for chromium deposition.

As Figure 4.1 shows at any given temperature, a range of current densities exists, within which bright deposits can be formed. Alternatively, at any given current density, there is range of temperatures in which the same is true. Figure 4.1 is valid only for a particular chromium electrolyte system, and depending on concentrations of species used, and the catalyst, similar diagrams can be drawn, though the general shape of these is similar. At a given temperature, the widest possible range of operating current densities is desirable, especially when items of complex

geometry or with deep profiles are involved, as in such cases, there will be marked variations in current density at different locations on the work, An approach such as that shown in Figure 4.2 is essential in ensuring that bright deposits are formed over the entire surface, however complex this might be.

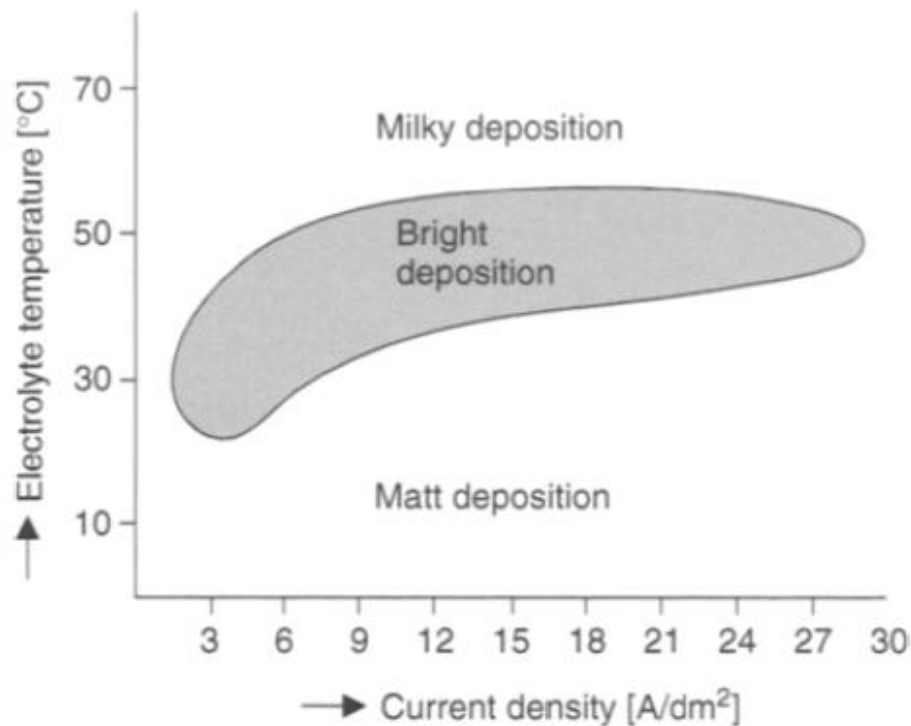


Figure 4.2: Operating window for bright chromium deposition as function of deposition temperature and current density.

There are many theories to explain the brightening action of this class of additive. Most probably, the effect is due to a controlling effect, and perhaps a rate-limiting action, on the electrocrystallization step. Such theories link with the accepted mechanism for metal electrodeposition, based on a nucleation and growth at a series of centers. From the growth nuclei, grains develop with a range of sizes and orientations.

It is assumed that the brighteners are preferentially adsorbed on the developing growth peaks, thereby inhibiting further growth at these points. Having no alternative, the electrocrystallisation is forced to continue in the valleys rather than the peaks, whereby a levelling action results. The end result is a smooth and shiny surface. It follows that brightening is associated with a levelling action as well.

4.1.2. Levelling agents

Either before or after electroplating, it may be necessary for the work to be mechanically finished, using grinding, then polishing stages, and these can significantly add to the overall cost, especially when the deposited metal is hard, for example, hard chromium. Such kind of these additives is not necessary for the gold due to its mechanical and physical properties. Levelling agents can act to smooth pre-existing irregularities in the surface, such as pits or scratches and thus, they compensate for poor surface quality of incoming work.

The levelling action of an electrolyte, that is to say its ability to form a smoother surface than that of the original substrate, is defined as 'levelling power'.

By levelling action is implied the deposition of a greater thickness of metal in the depths of a groove than at its outer edge. This can be quantitatively expressed as:

$$E = \frac{d_t - d}{R_z} \cdot 100\%$$

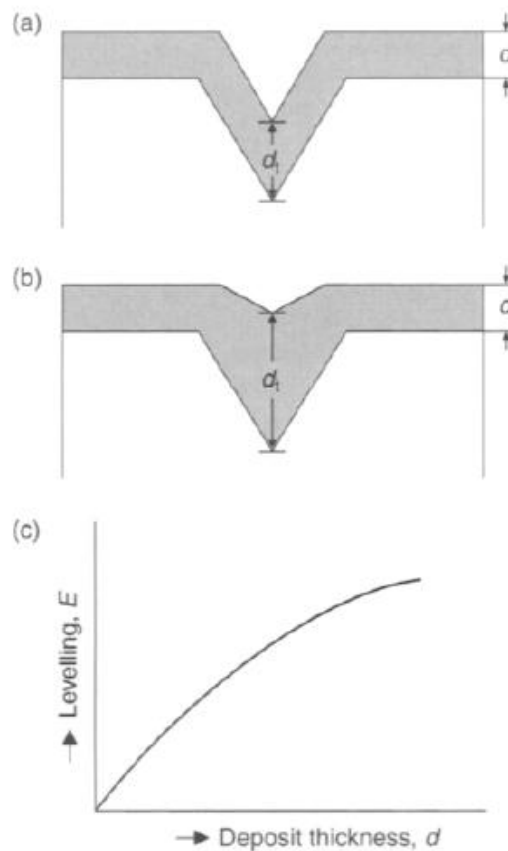


Figure 4.3: Illustration of levelling action: (a) geometric levelling; (b) true levelling; (c) levelling as function of deposit thickness [7].

E is the levelling effect, d_t the deposit thickness at the base of the groove, d the overall deposit thickness and R_z the roughness of the substrate.

A distinction is made between geometric and true levelling. In the former case, the key factor is that the deposit is thicker at the bottom of a groove than at the edge (Figure 4.3a). The effect is measured in terms of the geometry and shape of the groove. The hallmark of true levelling is a higher metal deposition rate in the groove than at the adjacent areas (Figure 4.3b) and this results when the so-called levelling agents or levellers are added to the electrolyte. The manner in which these additives work is by restricting the rate of metal deposition, but only at those locations where they are freely supplied, specifically at peaks and edges. The levelling action of such species can vary quite widely, apart from which it is usually temperature dependant and can often be enhanced by work movement or solution agitation. Levelling action is a function of deposit thickness and increases as thickness increases (Figure 4.3c).

4.1.3. Surfactants (wetting agents)

Plating baths will usually contain wetting agents, also known as surfactants. These are characterized by their asymmetry and dipolar nature. They have a hydrophilic ('water loving') 'head' and a hydrophobic ('water-repellent') 'tail'. Surfactants can be 'anionic', 'cationic' or 'non-ionic' depending on the charge at the hydrophilic end. The polar hydrophilic radicals are typically-COO- or-SO₃ groupings, while the hydrophobic part of the molecule might be a non-polar aliphatic long-chain hydrocarbon. Non-ionic surfactants are themselves uncharged, acquiring their charge from ions present in aqueous solution [7].

Wetting agents are surface-active species, that is, they act by accumulating at a surface or interface. At an air-electrolyte interface, they are oriented with hydrophilic head into solution, the hydrophobic tail to the air-side. In this way they reduce the surface tension of a liquid. Anionic or non-ionic surfactants are most often used. The lowering of surface tension facilitates the release of gas bubbles adhering to the work surface, whether these be cathodically evolved hydrogen or trapped air. Where such bubbles adhere to the surface, their shielding action results in little electrodeposition occurring and they can be the cause of pitting or deposit porosity. In addition to the prevention of pits or pores in the deposit is the main purpose of wetting agents or surfactants.

Addition of surface-active agents also results in the following:

- certain organic compounds, insoluble or poorly soluble in water can be solubilised or their distribution in solution made more uniform;
- coagulation and sedimentation of suspended solid matter as dirt in solution which would otherwise lead to rough or porous deposits, is reduced;
- crystal growth is inhibited and a brightening action of the deposit results;
- draining of adherent electrolyte, on withdrawing the work from solution is improved, drag-out losses are reduced.

In aqueous electrodeposition solutions using surface additives is extremely important owing to significant effects on the growth and structure of deposits. The striking effects of additive agents on electrocrystallization in low concentrations (ranging from a few milligrams per liter to a few percent) point to their adsorption on high energy surface areas where it causes an inhibiting effect on the most active growth sites. There are three principal types of additives associated with high purity gold electrolytes: grain refiners, complexing agents, and hardening agents. Additives act as grain refiners and levelers because of their effects on the structure of the electrical double layer on the surface and electrode kinetics. A large number of mechanisms have suggested to explain behavior of additives such as blocking the surface, changes in Helmholtz potential, complex formation including induced adsorption and ion bridging, ion pairing, changes in interfacial tension and filming of the electrode, hydrogen evolution effects, hydrogen absorption, anomalous codeposition and the effect on intermediates .

It has long been known that the formation of crystals depends sensitively on the presence of additives and impurities. It was found that soluble, as well as insoluble additives could affect crystallization. Moreover, the foreign of foreign atoms can influence the mutual binding energy and thus the nucleation probability. Addition of foreign elements is one of the methods for the control of nucleation.

Proper additives can accelerate or decelerate crystal growth and affect the size, shape and the robustness of the crystals. The influence of additives on the growth of gold single crystals and also the possible growth of complex crystals was investigated. Additives were mixed with the silica gel before the gelling process; their concentration, about 20 mM, was 10-times lower than that of the HAuCl_4 component [23].

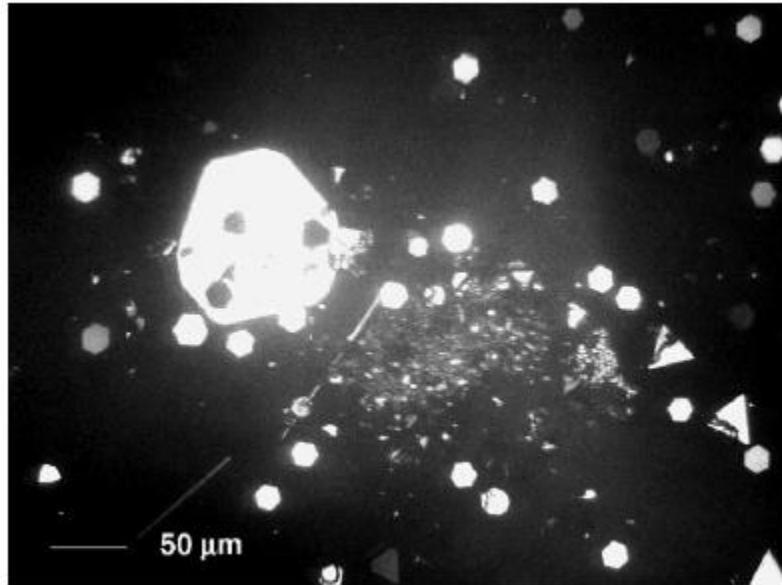


Figure 4.4: Digital camera photo of the hexagonal gold microcrystals preferential growth after addition of $\text{Pd}(\text{CH}_3\text{COO})_2$ to the silica gel [23].

Because of the specific gold reaction that occurs on the anode which leads to the formation of the microcrystals, complex crystals were not observed. However at the same time it was found that the presence of additives such a copper sulfate, palladium acetate or chromium oxide in the gel affects the crystal growth. For example, in the presence of palladium acetate, the crystals preferentially grew into hexagonal shapes with similar sizes of about $20\mu\text{m}$ (Figure 5.4). Hexagonal crystals make up about 10-15% of all crystals when no additives are present; this increased in the presence of palladium acetate to 85-90%.

Acetic acid reversibly adsorbs on the Au crystal surface, and acts as an inhibiting agent to reduce crystal growth. The surface free energy of the equilibrium crystal must have a minimum value. Due to the adsorption of additive molecules, the surface tension and the ledge tension change and affect the equilibrium form of the crystal. It is assumed this leads to the growth of relatively small hexagonal crystals of similar size.

On the other hand, addition of copper sulfate to the gel produced a harvest of big crystals with diameters in the range of hundreds of microns and with high-quality surfaces [23]. A possible explanation for this behavior is that the ledge tension decreases as a result of sulfate adsorption on the surface of gold. Adsorption would lead to a change in the shape of the nuclei and also the mean

step separation for spiral growth, resulting in the formation of more kink positions and an increase in crystal growth rate.

Other additives such as chromium oxide caused the growth of gold crystals in vertical lines in the space between the anode and the cathode. We attribute this to an increase in the stability of the $[\text{AuCl}_2]^-$ complex which slowly disproportionates further from the anode and forms crystals in the central region of the cell.

Cysteine (2-amino3-mercaptopropanoic acid) is an organic material which can make complex with gold ions. These complexes can deposit Au particles on the cathode surface separately and cause grain refining. The oxygen reduction on gold nanoparticles which are deposited from 1 mM solution with cysteine additive is eight times higher than that on the gold bulk deposit at -0.8 V potential. This behavior can be attributed to increase of effective surface area by decreasing nanoparticles size. Cysteine was found as an appropriate agent to refine gold nanoparticles due to increase of nucleation sites and improve kinetic parameters without considerable change in the purity of deposits. Particle size considerations in the presence of cysteine indicated that the gold nanoparticles are uniformly distributed in the range of 10–40 nm. Improved catalytic properties of gold nanoparticles can be obtained when their effective surface area is increased. It is established that oxygen reduction on refined gold nanoparticle deposits is eight times greater than that on conventional gold deposits [22].

Chloride solution with cysteine additive was used as electrolyte in gold nanoparticles electrodeposition. Atomic Force Microscope was used to evaluate the effect of cysteine on the morphology and topography of gold nanoparticles.

Further investigation of additives on the nucleation and growth of gold single microcrystals will provide valuable information for the preparation of a variety of single crystals.

The electroplated Au films were obtained from the bath consisting of a mixture:

$0.05\text{M KAu}(\text{CN})_2 + 0.25\text{M } (\text{NH}_4)\text{H}_2\text{HPO}_4 + 0.40\text{M } (\text{NH}_4)_2\text{HHPO}_4$ without and with additives of surfactants, namely 10 mg/l oxyethylendiphosphoric acid (H_4OEtDP) + 0.75 mg/l

cyanethilendiamine (CyEn) at 60-70 °C and pH 5.6. The deposition was performed at the cathodic current densities 0.2 to 0.7 A/dm² on the brass substrate using Pt anode [24].

Properties	Samples, deposited from phosphate baths at current densities, A dm ⁻²					
	without additives			with additives of H ₄ OEtDP and CyEn		
	0.2	0.3	0.5	0.2	0.3	0.5
Rate of deposition, μm hour ⁻¹	13	13	12	13	16	15
Porosity, number porous per cm ²	2	5	7	–	–	1

Table 4.1. Comparative properties of the gold coatings produced at different condition of electrolysis

In order to reduce the porosity of film the effect of some surfactants was studied. The positive effect of composition additives (H₄OEtDP and CyEn) is revealed. The optimal composition of surfactants is: 10 mg/l H₄OEtDP and 0.75 mg/lCyEn. The gold films obtained from phosphoric acid bath with additives are light, fine-crystalline, well-adherent to the brass substrate. Adding of these specific surfactants almost excludes the pores in electroplated film. Simultaneously the gold electrodeposition rate increases at higher current densities 0.3 – 0.5 A/dm² due to reducing the hydrogen evolution rate (Table 4.1). Moreover, the adding of these surfactants enable to obtain Au films (at 0.5A/dm²) that possess the excellent microhardness. In our opinion, the increase of microhardness is resulted by the grain size decrease with increasing cathodic current density.

So, the adding of H₄OEtDP and CyEn to the phosphoric gilding bath expands the range of current densities up to 0.6 A/dm². Properties of the obtained films are reasonable for microelectronics application.

The gold sulfite complex Au(SO₃)₂⁻³ is the most common alternative to cyanide. This complex has a stability constant of 10¹⁰, much less than that of the gold cyanide complex. Consequently, it is susceptible to disproportionation resulting in the formation of Au (III) and metallic gold, especially at pH less than 7, where sulfite protonates to form bisulfite. Therefore, stability is always an issue for sulfite-based gold electroplating solutions, and stabilizing additives are usually necessary.

The effect of temperature, pH, sulfite concentration, gold concentration and additive concentration play on the achievable range for current density range. Temperature has the strongest effect on the current density range, which increases with increasing temperature. The current density range can also be increased by raising the pH and gold concentration, or decreasing the sulfite concentration, however is not significantly affected by the additive concentration [25].

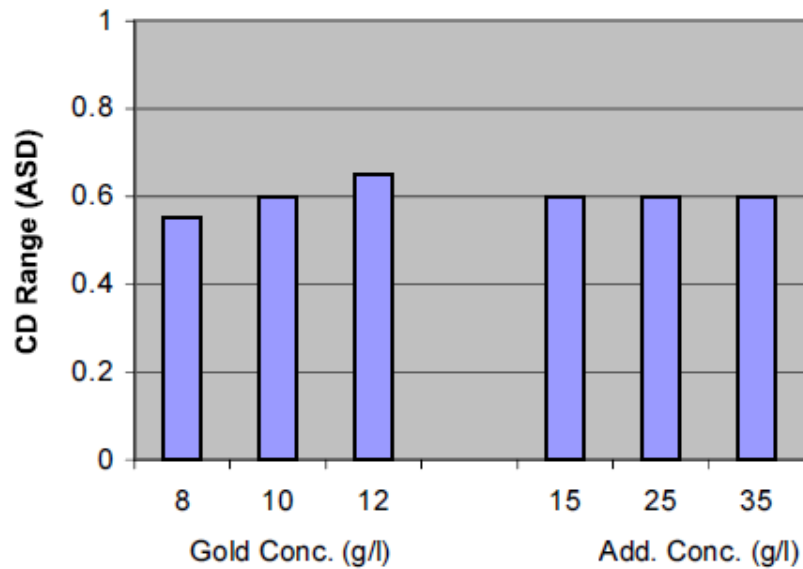


Figure 4.5: The effects of gold and additive concentrations on the plating current density range [25].

The presence of ammonia in the copper–ammonia–thiosulfate system is essential as it stabilizes copper (II) and reduces its rate of reaction with thiosulfate. The gold oxidation polarisation curve obtained for ammonium, potassium, and sodium thiosulfate solutions using a polished pure solid gold electrode are shown in Figure 4.6. It is immediately obvious that gold oxidises much more readily in ammonium and potassium thiosulfate solutions than sodium thiosulfate solutions [26].

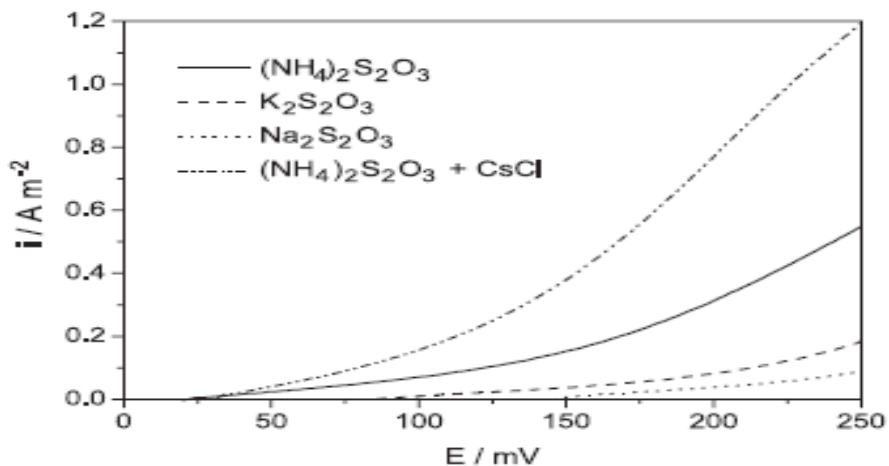


Figure 4.6: Linear sweep voltammograms showing the gold oxidation half reaction in either 0.2 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, $\text{K}_2\text{S}_2\text{O}_3$, or $\text{Na}_2\text{S}_2\text{O}_3$. Also shown is the polarization curve obtained for 0.2 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ with 0.05 M CsCl added [26].

The cations such as potassium, which are higher in atomic mass and less hydrated compared with sodium, are more likely to be adsorbed onto the gold surface. It is known that the ion pair dissociation constants for the alkali metal ions with thiosulfate ions decrease in the sequence of $\text{Na} > \text{K} > \text{Rb} > \text{Cs}$. Therefore, one would expect that K^+ is more likely to form an ion pair with gold thiosulfate or thiosulfate than Na^+ . An additional experiment was also carried out where 0.05 M caesium chloride was added to an ammonium thiosulfate solution, and it can be seen from Figure 4.6 that the most active polarisation curve was obtained in this instance. This result is consistent with the presence of the heavy alkali metals giving rise to a higher rate of gold oxidation in thiosulfate solutions. In practical terms, it should be apparent that the gold leaching reaction would occur more readily in ammonium thiosulfate solutions than in sodium thiosulfate solutions.

It has been shown that the presence of ammonium ions dramatically enhance the oxidation of gold in thiosulfate solution (Figure 4.6). Therefore, the effect of alkyl ammonium ions on the oxidation of gold was also studied. The polarisation curve for the oxidation of gold in sodium thiosulfate solutions in the presence of 0.05 M alkyl ammonium chloride was obtained using the pure solid gold disc, and these are shown in Fig. 6. It is clear that the addition of mono-methyl and di-methyl ammonium ions also enhance the gold oxidation half reaction, although the effect is not as pronounced as for ammonium ions. It can also be seen from Figure 4.7 that the gold oxidation reaction is actually hindered in the presence of tri-methyl ammonium ions. A similar result was observed for the tetra-methyl ammonium ion. It would appear that in the case where tri-methyl and tetra-methyl ammonium ions are present in the thiosulfate solutions, the decrease in the gold

oxidation rate could be attributed to the coverage of the gold surface with the adsorbed ions, since the degree of adsorption of alkyl ammonium ions increases as the number of alkyl groups increase.

In order to achieve higher gold leach rates in thiosulfate solutions using oxidants other than copper (II), the gold oxidation half reaction needs to be improved. Therefore, the effect of additives, such as potassium ethyl xanthate (PEX) and thiourea (TU) on the gold oxidation reaction was studied. Using the standard electrochemical techniques, it is difficult to interpret the data in the presence of either xanthate or thiourea, as both these species can be oxidized.

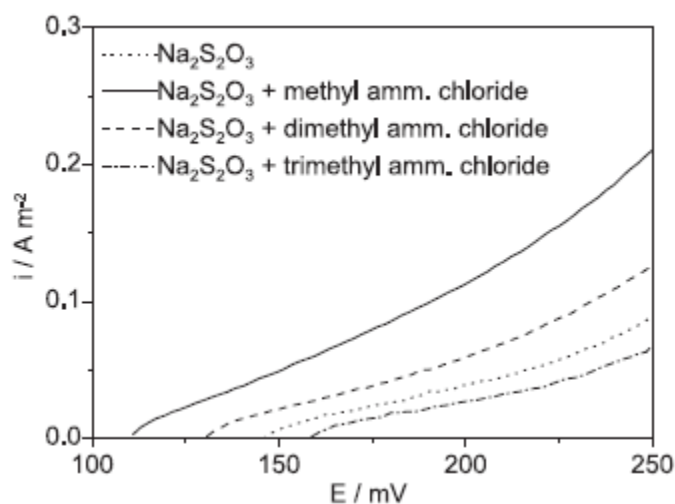


Figure 4.7: Linear sweep voltammograms showing the oxidation of gold in 0.2 M sodium thiosulfate in the presence of 0.05 M alkyl ammonium chloride [26].

The polarisation curves are shown in Figure 4.8 for ammonium thiosulfate solutions containing 5 mM of either xanthate or thiourea. It should be clear that the addition of 5 mM of thiourea is extremely beneficial to oxidation of gold in thiosulfate solutions, with the current rapidly increasing as the potential is increased above 125 mV. This type of polarization curve is typical of active dissolution processes, such as the oxidation of copper or silver in thiosulfate solutions. It is not possible that the gold thiourea complex is being formed in this instance, since an experiment conducted with 10 mM thiourea and 0.2 M ammonium sulfate did not result in any gold oxidation in the potential region 0–300 mV. In comparison, the addition of potassium ethyl xanthate is shown in Figure 4.8 to completely block the oxidation of gold, with no gold oxidation being observed within a wide potential range. It is worth noting that both xanthate and thiourea are used as surface

modifiers in many different processes, and hence one could attribute the effects shown in Figure 4.8 to the adsorption of these species onto the gold surface in the thiosulfate solutions.

An important point to note is that thiourea is considered a potential carcinogen, and hence its use as an additive may be restricted. A qualitative description of the results is shown in Table 4.2. These additives were chosen because they are either known to adsorb readily on metal surfaces, and/or they have characteristics which are similar to thiourea. It can be seen that most of the additives actually resulted in passivation of the gold surface. However, the presence of thioacetamide was found to have a similar effect to thiourea in dramatically improving the gold oxidation half reaction.

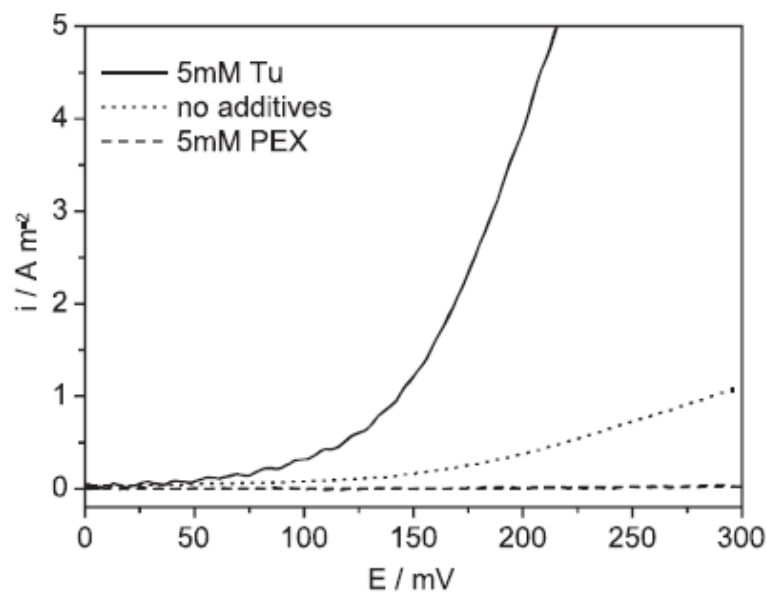


Figure 4.8: Linear sweep voltammograms showing the effect of thiourea and potassium ethyl xanthane on the gold oxidation half reaction in 0.2 M ammonium thiosulfate [26].

It should be apparent that the leaching of gold in solutions containing thiourea is likely to be much more rapid than leaching in the absence of thiourea. The effect of thiourea concentration on the gold oxidation half reaction was investigated and Figure 5.9 shows the current density for gold oxidation at various thiourea concentrations. At any potential, the gold oxidation half reaction is slower at lower thiourea concentrations. However, the improvement of the gold oxidation observed is significant even at the lower thiourea concentrations. In general, it is recommended that thiourea concentration greater than 5 mM should be maintained in order to achieve appreciable gold oxidation rates.

Effect of additives on the gold oxidation half reaction	
Additive	Characteristic of the gold oxidation half reaction
Potassium ethyl xanthate	completely passive
Thiourea	much more active
Thioacetamide	similar effect to thiourea
Thioglycolic acid	completely passive
Pyridine	completely passive
Sulphanilamide	more active but only in the absence of O ₂
Sulphinic acid	completely passive
Sodium di-ethyl dithiocarbamate (NaEDC)	completely passive
Imidazole	completely passive
Mercaptobenzothiazole	completely passive

The concentration of additive was 5 mM, with exception of Mercaptobenzothiazole, which was saturated due to its low solubility.

Table 4.2. Effect of additives on the gold oxidation half reaction [26].

The presence of thiourea significantly improves the oxidation of gold in ammonium thiosulfate solutions. So can the ammonium ions be removed when thiourea is present? Thus, experiments were performed to determine the current density for gold oxidation within the potential range from 0 to 300 mV. The polarization curves are shown in Figure 4.9. It is immediately obvious that the presence of thiourea also enhances the gold oxidation in sodium thiosulfate solutions.

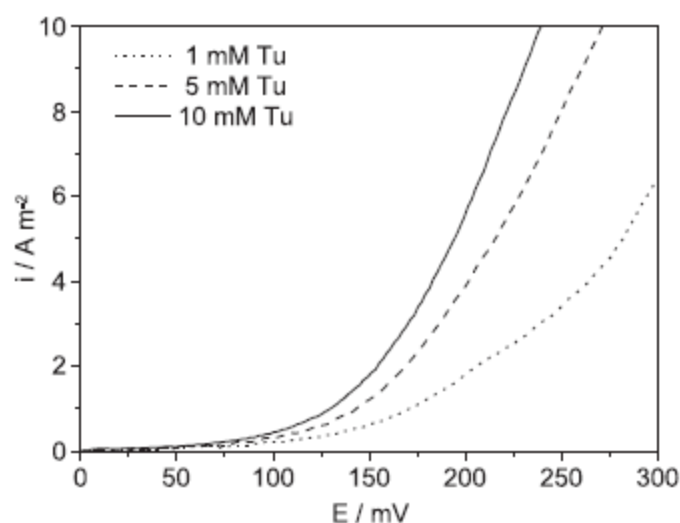


Figure 4.9: Linear sweep voltammograms showing the effect of thiourea concentration on the gold oxidation half reaction in 0.2 M ammonium thiosulfate [26].

The addition of caesium ions also increased the reactivity of the gold. The effect of additives such as thiourea and potassium ethyl xanthate was also investigated, and it was found that the addition of xanthate resulted in the complete passivation of the gold surface. However, the presence of small amounts of thiourea substantially improves the oxidation of gold in thiosulfate solutions. This effect was more pronounced in ammonium thiosulfate solutions than in sodium thiosulfate solutions.

5. SURFACE PREPARATION

Gold plating is often the last step in a long series of processing steps, making it immediately suspect when difficulties are encountered. However, in many cases the problems that appear at the gold plating step are due to the cleaning and preparation processes preceding gold deposition. Poor, incomplete, or inappropriate cleaning can result in inadequate gold deposits. While problems do occur in the gold plating process, only a good engineering evaluation of the defective deposits can elucidate the failure mechanism.

Workpieces to be plated may be put through a variety of pretreating processes, including surface cleaning, surface modification, and rinsing [18]. A schematic data flow of a typical electroplating plant, including surface treatment and waste treatment, is depicted in Figure 5.1.

The purpose of surface pretreatment is to remove contaminants, such as dust and films, from the substrate surface. The surface contamination can be extrinsic, composed of organic debris and mineral dust from the environment or preceding processes. It can also be intrinsic, such as a native oxide layer. Contaminants and films interfere with bonding, which can cause poor adhesion and even prevent deposition. Therefore, surface pretreatment is important to ensure plating quality. Most (metal) surface treatment operations have three basic steps: surface cleaning, surface treatment, and rinsing.

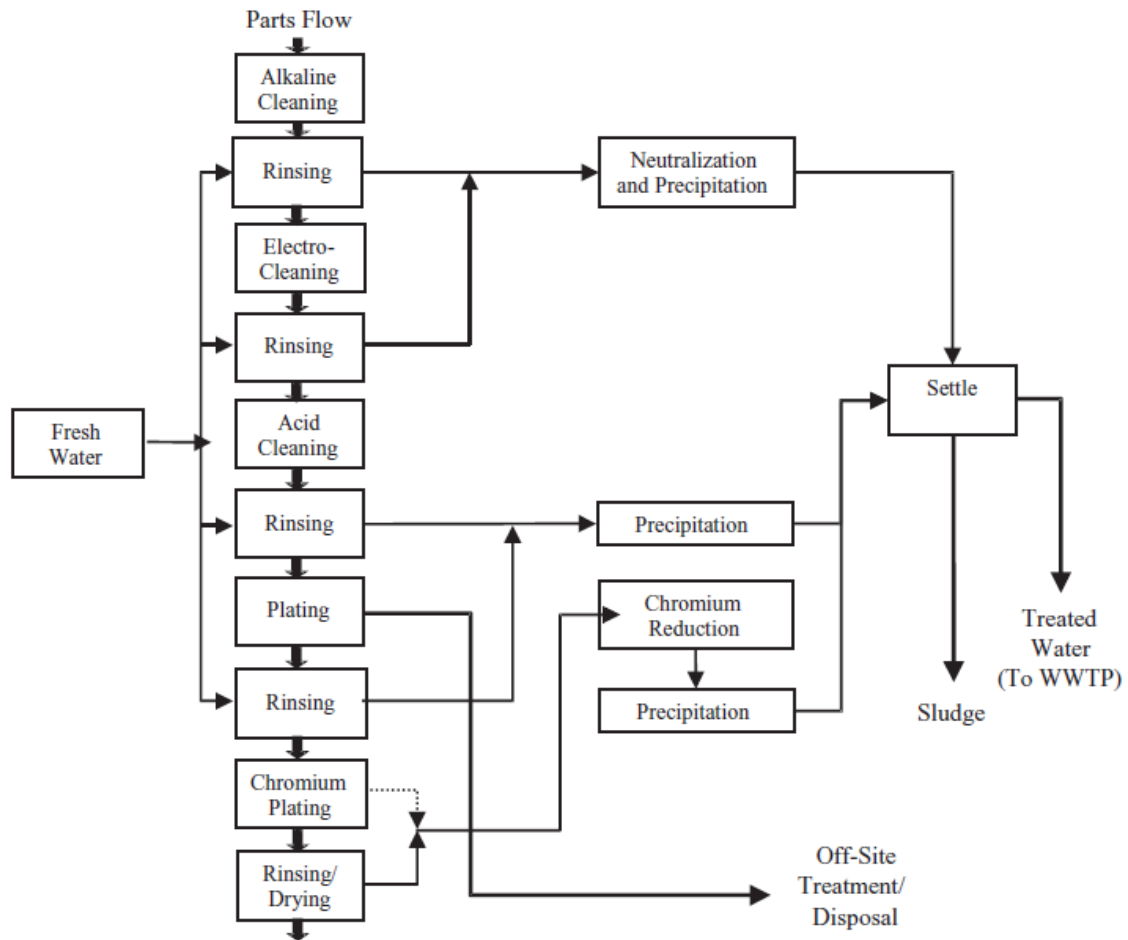


Figure 5.1: Process data flow of a typical electroplating plant [18].

5.1. Surface Cleaning

Cleaning methods should be able to minimize substrate damage while removing the contaminants, dust, film, and/or debris. Cleaning processes are based on two approaches: Chemical approach and Mechanical approach.

5.1.1. Chemical Approaches

A chemical approach usually includes solvent degreasing, alkaline cleaning, (soak cleaning), and acid cleaning (acid pickling).

5.1.1.1. Solvent Degreasing: Contaminants consist of oils and grease of various types, waxes, and miscellaneous organic materials. These contaminants can be removed by appropriate organic solvents, either by dipping the workpieces in the solvent or by vapor decreasing.

5.1.1.2. Alkaline Cleaning: Workpieces are immersed in tanks of hot alkaline cleaning solutions to remove dirt and solid soil. A special type of alkaline cleaning is electrocleaning. In electrocleaning, the workpiece can be either the cathode (namely direct cleaning) or the anode (reverse cleaning). Electrocleaning adds to the chemical action of the cleaner the mechanical action caused by plentiful gas evolution at the surface of the workpiece.

5.1.1.3. Acid Cleaning: Acid cleaning can move heavy scale, heat-treat scale, oxide, and the like. The most commonly used acids include sulfuric and hydrochloric. Pickling can also be combined with current to be more effective.

5.1.2. Mechanical Approaches

Mechanical preparations include polishing, buffing, and some variations. Polishing is to remove small amounts of metal by means of abrasives. It produces a surface that is free of the larger imperfections left by grinding, and is a preliminary to buffing. Buffing is similar to polishing, but uses finer abrasives to remove very little metal. Buffing can produce an extremely smooth surface.

5.2. Surface Modification

Surface modification includes change in surface attributes, such as application of (metal) layer(s) and/or hardening.

5.2.1. Rinsing

In wet plating, when workpieces are transferred from one treating solution to another, or when they leave the final treating solution, they carry some of the solution in which it has been immersed. This solution is called drag-out. In most cases, this residue solution should be removed from the workpieces surface by rinsing before the workpieces enter the next step in sequence, or come out of the final processing solution. The dirty rinse water will be sent to the wastewater treatment facilities before being discharged to a public sewage system [5].

Copper, brass, and silver parts are easily plated once cleaned. The normal practice may require degreasing in an alkaline spray or soak or by a solvent vapor degreaser. A copper part may require a bright dip (10% sulfuric acid in water) to remove the native oxide. Beryllium copper spring material or castings should be carefully cleaned by a 15-min soak in boiling NaCN and NaOH solution (38 g NaCN, 38 g NaOH, and 1 L H₂O) followed by a water rinse and bright dip and final rinse. Other procedures use a dip in 60% by volume H₂SO₄ at 50°C for 30 s followed by a water rinse.

Nickel parts must be activated before gold plating or the plate may peel. Activation can be accomplished by a dip in warm 1 : 1 HCl in water. It is very important not to allow the nickel parts to dry after activation before gold plating. Nickel alloys like Kovar can be cleaned by soaking for many minutes in hot 18% HCl. The oxide-free surface is prepared for plating by bright dipping for several seconds in 1 : 3 nitric acid–acetic acid with 15 mL HCl per liter of solution at 70°C. Kovar can be first plated with Woods or Watts nickel before gold plating or to gold strike the nickel alloy directly at high current in a low-gold-content bath followed by normal gold plating [3].

Gold plating onto aluminum and aluminum alloys has become more common, particularly for electronics and space applications. The surface is first degreased, such as in trichloroethylene vapors, followed by alkaline cleaning in trisodium orthophosphate (Na₃PO₄, 12 g L⁻¹; H₂O, 25 g L⁻¹; and Na₂CO₃, 20 g L⁻¹) at 60°C for 2–3 min. After water rinsing, the aluminum surface is cleaned in a mixed-acid solution (sulfuric acid, 10 mL L⁻¹; hydrofluoric acid (40%), 12.5 mL L⁻¹, and nitric acid, 255 mL L⁻¹) for 2–3 min. A zinc displacement deposition process can precede the electroless nickel underlayer (nickel sulfate, 30 g L⁻¹; zinc sulfate, 40 g L⁻¹; sodium hydroxide, 106 g L⁻¹; potassium cyanide, 10 g L⁻¹; potassium bitartrate, 40 g L⁻¹; copper sulfate, 5 g L⁻¹; and ferric chloride, 2 g L⁻¹) for 1 min. The first zinc layer is stripped in 50% nitric acid followed by a second zinc layer by immersion for 30 s. Extreme caution should be practiced when handling hydrofluoric acid and potassium cyanide, especially when the cyanide is in the same vicinity as acids.

Gold films are widely used in MEMS applications because of its excellent physicochemical stability, low resistivity, and high reflectivity for infrared radiation. However, adhesion onto silicon has been problematic. A two-step electrodeposition process was found to give growth directly onto a silicon surface. After stripping the surface oxide from the silicon, gold is plated and annealed and then a final coating of gold is plated. The current density of the initial gold plate is critical.

The adhesion of gold directly to glass is very difficult. An ion beam mixing process has been used to produce gold films directly bonded to glass. An Au–C bilayer film was deposited on glass followed by ion beam “mixing” caused by the Xe^+ ion implantation. The ion implantation process provides for atomic mixing of the thin layer with the glass. A thicker film of gold could then be deposited. Excellent adhesion of the gold film on glass was obtained.

Thin electroplated gold wires were bonded to hydrogen silsesquioxane glass by a transfer process using imprint lithography. The transfer process first produced thin gold wires on silicon from AuCN^{-4} immersion plating onto silicon. Silicon serves as the reducing agent for gold deposition. The plating bath contained free fluoride to dissolve the oxidized silicon. The lack of adhesion of the gold wire onto the silicon surface allows easy release and transfer onto the glass.

The direct thermocompression bonding of plated gold surfaces was used to achieve MEMS packaging. Two silicon wafers were bonded together at a pressure of 2.5 MPa and temperature of 320°C . The gold film produced on the side walls of via holes was used for bonding to two parts together, providing a hermetic seal for the MEMS package.

Service requirements may need an underplate between the base metal and the gold electroplate. Specifications for gold plated copper parts exposed to temperatures $> 60^\circ\text{C}$ often require an intervening nickel-plated barrier to prevent copper–gold interdiffusion and subsequent copper bleed through to the surface. The barrier may be 5–10 μm of low-stress nickel, like that plated from a sulfamate bath. Gold plating on zinc-based alloys should have at least 8 μm of nickel over 8 μm of copper. Tin or lead should have 8 μm of nickel over 2 μm of copper.

The use of a gold strike is common before the deposition of a thick gold plate. The thickness of a gold strike may be 0.02–0.25 μm , depending on the thickness and requirements of the full gold thickness. A gold strike bath is usually a dilute version of a normal gold plating bath. A high current density is used to overcome activation control of the plating process. A large fraction of the gold cyanide ions at the electrode surface are reduced to gold at a high nucleation rate. Thus a uniform deposit is formed over the electrode surface compensating for inhomogeneities across it, which may have created problems under normal gold plating conditions. The gold strike surface has increased adhesion and porosity, and less contamination is dragged into the main plating bath. A typical strike bath would have 0.8 g L^{-1} gold versus 8 g L^{-1} and current densities 2–10 times higher than the conventional bath.

5.2.2 High-Speed Strip Plating

There has been extensive use of high-speed plating as well as selective plating in the semiconductor industry since around 1970 [3]. In particular, reducing cost and materials in the reel-to-reel electroplating of electrical connectors has led to many innovations in high-speed plating. Reel-to-reel plating of connectors includes facilities for cleaning and preparation of parts, strike plating, and transport of parts and chemicals. The sequence of the processes is similar to those in batch plating; however, size, space, and time limitations have stimulated a fine tuning of the processes, which makes their review worthwhile. The strip plating process for electrical connectors is composed of the following processes: (1) ultrasonic clean, (2) electropolish, (3) acid dip, (4) nickel plate, (5) gold strike, (6) hard gold plate, (7) hot rinse, and (8) dry. Cleaning is limited to non-foaming solutions because of the need for rapid recirculation of the liquid from a reservoir tank. Ultrasonic agitation speeds up the cleaning process by dislodging the contaminants from the surface through cavitation. Electropolishing is an anodic process where metal dissolves (cleaning and deburring) in proportion to the anode current density. Copper alloys used for electrical connectors electropolish well in 1 : 1 phosphoric acid in water. Current densities as high as 4000 mAcm^{-2} can be used to accommodate high-speed processing with small electroplating cells. A major problem in electropolishing is the deposition of copper powder at the cathode, which must be removed periodically to avoid cell shorting. While it is desirable to have the electrodes in close proximity to reduce solution heating and voltage, wider spacing (e.g., 1.5 cm) is necessary to mitigate cell shorting from powdery copper loosely adherent to the cathode. The copper phosphate residue can be removed by a hot-water rinse followed by a rinse in 10% sulfuric acid (by volume) at 60°C . The nickel underplate (0.14 mm) can be from a nickel sulfate or nickel sulfamate bath.

	Gold Strike	High-Speed Bath
$\text{KAu}(\text{CN})_2$	4 gL^{-1}	44 gL^{-1}
K_2HPO_4	120 gL^{-1}	—
KH_2PO_4	30 gL^{-1}	100 gL^{-1}
KOH	—	28 gL^{-1}
Temperature	65°C	40°C
pH	7.0	7.0

Figure 5.2: The AFHG baths used in reel-to-reel gold strike.

The current density for the gold strike is 30 mA cm^{-2} . The hardness of the final deposit is achieved by producing small grains, which is the result of high current density at low temperature. The hardness of the gold plated from the high speed bath given above is 180 KHN_{25} for current densities

between 150 and 250 mAcm⁻². The hardness drops off at lower current densities, to 150 KHN₂₅ for 100 mAcm⁻², and 125 KHN₂₅ at 50mAcm⁻². Others have used even higher current densities (800–2000 mA cm⁻²), although the conditions are different. A final hot rinse and drying complete the strip plating process. The plating process can be accomplished in relatively short-length plating cells (18 in. long) with insoluble anodes that allow precise placement of the hardware in an attempt to selectively plate the gold only on the functional area of the connectors. Although a majority of the gold can be deposited on the contact area of connectors, it is extremely difficult to prevent some plating on nonfunctional areas immersed in the plating bath. Laser-assisted plating has been shown to assist in the selective plating process. Laser processes have been developed to improve the selectivity of the deposition process. The direct irradiation by a pulsed laser has been shown to cause extremely rapid surface heating, increasing the agitation and deposition rate. It also increases the interdiffusion of the deposited atoms. Lasers have also been used in a patterning technique where the whole component was coated with an insulator, such as glycol phthalate, paraffin wax, or photoresist, and an yttrium–aluminum–garnet (YAG) laser was used to burn off the material in small areas which were then plated [27]. One problem is the precise alignment of the laser to the part either in a moving or a step-and-repeat process.

6. GOLD AND GOLD ALLOY BONDING IN MEMS

Several practical micromachining techniques in silicon have emerged from recent research. However, the complexity of the micromechanical systems that would potentially benefit from these developments often exceeds the performance limits of these technologies when applied to a single wafer. Silicon wafer-to-wafer bonding offers the designer of such a system an extra degree of flexibility to trade-off single-wafer concentrated complexity for multi-wafer solutions. Wafer-to-wafer bonding has been used in applications such as power devices and has been particularly successful in integrated silicon sensors.

The main advantage of wafer-to-wafer bonding in the application is that it enables the separate fabrication of the sensor wafer and the wafer in which the active readout electronics is integrated, until the very last processing step. The sensor wafer can, therefore, be designed for maximum performance of the sensing element, without jeopardizing the performance of integrated active devices; the compatibility is not impaired. Moreover, the separation also allows for the use of different specialized foundries for processing of the sensor wafer and the readout wafer. Assembly can take place afterwards using relatively simple equipment, so that the batch fabrication advantage

of the silicon technology is maintained. This approach, however, makes low-temperature wafer-to-wafer bonding and through-wafer interconnect mandatory [28].

Wafer-to-wafer bonding has the potential to overcome many of problems that are not overcome by single wafer technologies. Individual wafers can be subjected to relatively simple bulk and/or surface micromachining steps and can subsequently be combined to realize a complex micromechanical function. The electronic circuits can, in principle, be integrated in any of the wafers, which further improves the design flexibility. As dicing and packaging take place after bonding, the micromechanical devices can be designed to be less prone to breaking during fabrication that would otherwise result from the reduced integrity of the individual bulk-micromachined wafer(s).

Wafer-to-wafer bonding processes for microstructure fabrication processes have an impact in packaging and structure design. Processes are categorized into direct bonds, anodic bonds, and bonds with intermediate layers. Micromachining encompasses a broad range of technologies anchored in the core technology of microlithographic pattern transfer. A large fraction of the micromachining technologies are specific to the silicon material system principally due to the origins of the field, namely, the silicon integrated circuit (IC) industry. In the silicon micromachining field, there have been two dominant fabrication methods, broadly classified as bulk micromachining (etching deep features into a wafer) and surface micromachining (depositing, patterning, and selective etching of films on a wafer) [29]. Fundamentally, both of these techniques rely on some form of etching or material removal. A complementary, additive, micromachining technology is the wafer-to-wafer bonding of patterned substrates, often simultaneously involving alignment of the substrates.

These wafer-to-wafer bonds were performed at low temperatures (less than 450°C) and involved either field-assisted silicon-to-glass bonding (anodic bonding) or a eutectic bond between silicon wafers using a gold thin film. The advantage of the low temperatures of these bonds was that wafers with common IC metals such as Al could withstand this temperature without degradation. These bonding methods offer the advantage in some circumstances of being high-temperature stable bonds, thus permitting a wide range of subsequent processes. The emergence of these techniques has catalyzed a great deal of activity in wafer-to-wafer bonding for a range of applications.

The wafer-to-wafer bond illustrated in Figure 6.1., is a thin-film glass frit bond. The pressure sensor has been fabricated using bulk micromachining and thin-film processes for the piezoresistors. In the case of a gauge pressure sensor, the lower wafer is etched to form an inlet port, and thus the role of the lower wafer bond reverts from that of a vacuum seal to a first-level pressure inlet manifold. In either case, the primary function of the wafer bonding is to effect a package function.

Particularly in the sensors industry, that packaging can be a dominant component in the final manufactured cost of a device. By achieving package function at the wafer level, it is possible to realize tremendous overall savings in cost since this enables the packaging of a multitude of sensors or actuators simultaneously, eliminating costly individual chip-packaging steps.

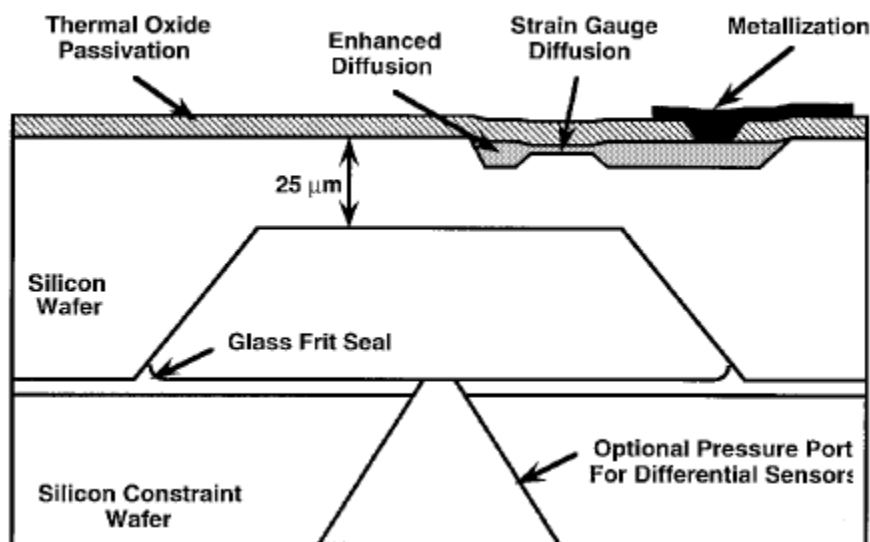


Figure 6.1: A Motorola pressure sensor using glass frit wafer bonding for packaging.

Another example of the use of wafer bonding in the manufacture of pressure sensors is shown in Figure 6.2. Here, the pressure sensor is formed by a high-temperature silicon direct bond, followed by thinning of a wafer and fabrication of the piezoresistors. In comparison with the conventional bulk micromachined pressure sensor of Figure 6.1, this pressure sensor has several interesting features that are enabled by the wafer bonding. The wafer bonding produces a reference cavity for the absolute pressure sensor as in the previous case; however, the cavity depth can be made considerably smaller (1–10 μm) as compared to the bulk micromachined devices ($\sim 500 \mu\text{m}$). The benefit of this is that the lower surface of the sealed cavity can function as an overpressure stop. In the event of a large pressure, the sensing membrane can be designed to “bottom out” against the

cavity lower surface, preventing catastrophic failure of the pressure sensor. There are several other noteworthy advantages of this device.

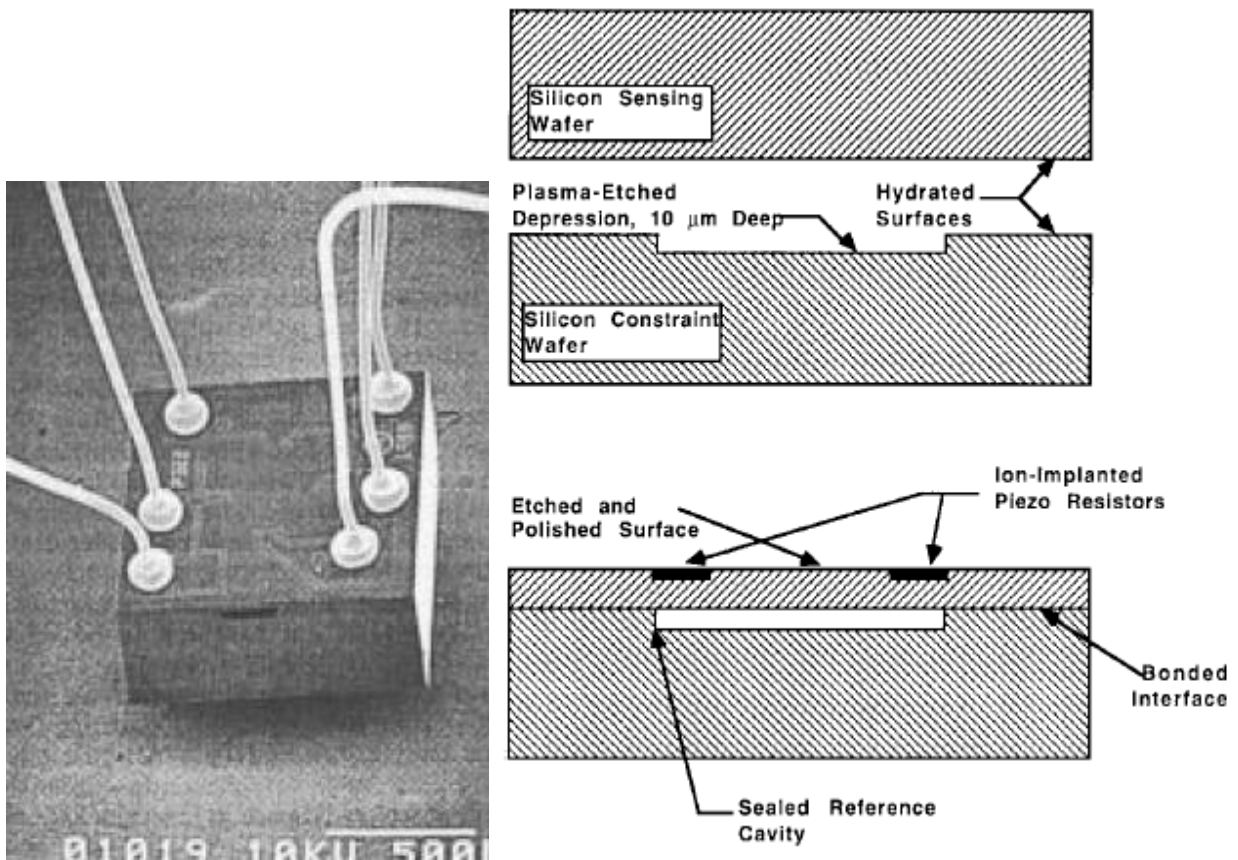


Figure 6.2: A silicon wafer-bonded pressure sensor. Die photo (Left). Cross section of process (Right).

A multitude of other interesting examples of sensors built using wafer bonding exist. One noteworthy early example is that of an accelerometer in which the bonding not only defines the critical mechanical flexures in the device but also is used to implement overacceleration stops for the proof mass. This greatly enhances the manufacturability and packaging of the device.

6.1. Categories of Wafer-to-Wafer Bonding

The types of wafer bonding that are most commonly employed in microstructure fabrication can be placed in three categories:

6.1.1. Direct Bonds

Wafers are directly contacted without the assistance of significant pressure or any intermediate layers or fields. These bonding schemes rely on the tendency for smooth surfaces to adhere, and always utilize some form of thermal cycling after the contacting to increase the bond strength. The maximum temperature of the anneal defines the bonding as being low temperature (450 °C) or high temperature (800 °C) [29].

6.1.2. Anodic Bonds

The wafers are contacted and the bond is completed by application of an electric field at temperatures in the range of 300–450 C. The bond is typically performed between a sodium-bearing glass wafer and a silicon wafer [29].

6.1.3. Intermediate-Layer Bonds

This category includes all bonding mechanisms that require an intermediate layer to promote the wafer bond. This could include eutectic bonds, polymers, solders, or thermocompression bonds. Many of these wafer-level bonds are a scale-up of bonds that have been routinely performed at the die level in the packaging of IC's.

Intermediate bonding is the bonding of two silicon wafers using an intermediate layer; a polymer glue, a soft glass or gold beyond the eutectic temperature of the Au-Si binary system. The special property of the silicide-based bond is the good electrical contact between the two bonded wafers. There is the gold-silicon hard solder that has already been frequently used for silicon die bonding to a substrate. The silicon-gold binary system reveals the most dramatic reduction of the melting temperature. As shown in Figure 6.3, the melting temperature is reduced from 1063 °C at pure gold to 363 °C, whereby 19 at.% silicon is dissolved in the eutectic silicon-gold compound. Eutectic die bonding is often used in industry. An Au/Si compound with 19 at.% Si is used as a substrate and heated up to a temperature slightly above the eutectic temperature (dashed line in Figure 6.3). This Au/Si substrate acts as a solder and consumes silicon from the die after it is brought into direct contact. Silicon is dissolved until the saturation composition is reached (X, in the Figure 6.3). Upon cooling a reliable bond was obtained. An extension of this technique is the micron bump bonding, in which multi-electrode contacts can be made between a die and the Si/Au substrate [28]. Although this technique has so far only been used in die bonding, it can in principle also be employed for silicon wafer-to-wafer bonding with gold as an intermediate layer.

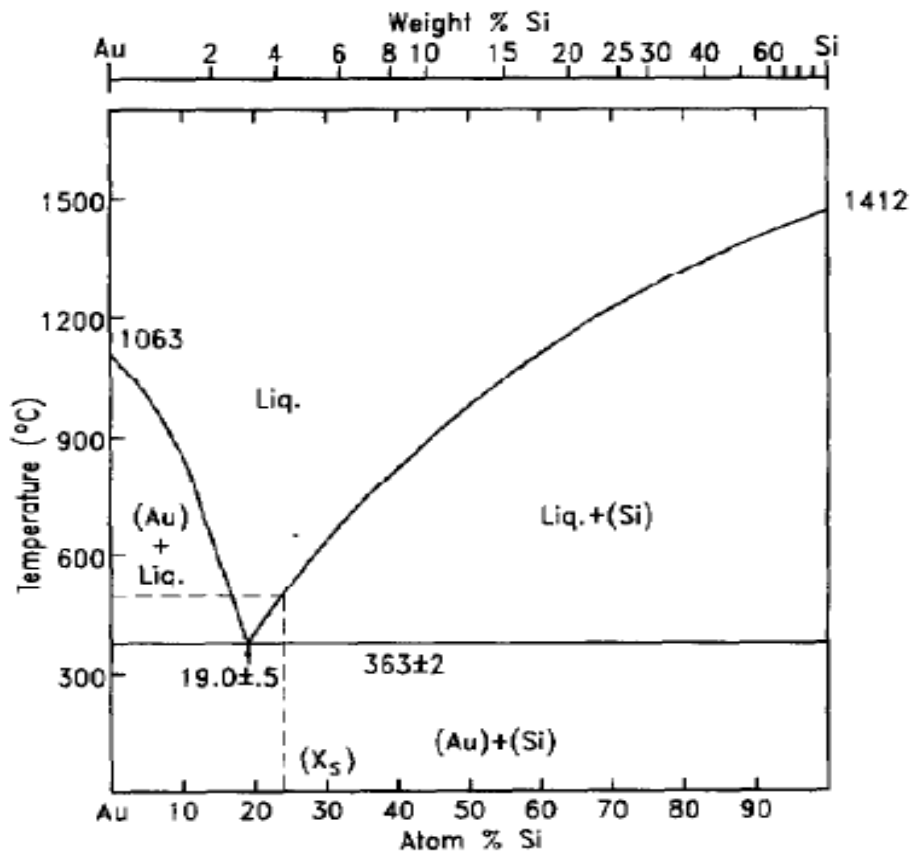


Figure 6.3: Silicon-gold phase diagram [28].

Problems associated with gold eutectic bonding are the long-term drift in sealed-cavity devices and the possible trap formation halfway to the bandgap. Contamination of silicon with gold would result in a severe reduction of the minority carrier lifetime in integrated active devices. Under normal conditions silicon dissolves in the flowing gold and not vice versa, so there is, in principle, no gold doping of the wafer. Experiments have demonstrated the suitability of the eutectic low-temperature wafer-to-wafer bonding for multi-wafer smart sensors, the compatibility with techniques for through-wafer interconnect and the functional integrity of the bonded device. The sealing performance needs to be demonstrated using an endurance test on an integrated pressure sensor. Smart micromechanical sensors and actuators can be fabricated with electronic and/or micromechanical functions distributed over various wafers, due to the low-temperature processing and the implementation of through-wafer interconnect. The area consumption required for bonding (sealing) and etching of through holes makes the technique less-suitable for high-density wafer-scale integration, but it is of great promise in smart sensors, where up to 10 leads is usually sufficient.

Silicon microstructures can be sealed together by Eutectic Bonding. For instance, it is possible to bond bare silicon against Au covered silicon, or Au covered silicon against Au covered silicon. Another alternative is to use a Au/Si preform with a composition close to the eutectic concentration. The eutectic temperature for Au/Si is 363 degrees Celsius, which is well below the critical temperature for Al metallized components. In addition Au is a quite commonly used thin film material. These are reasons to prefer the Au/Si choice, but the eutectic sealing can also be performed with other materials [30].

The major problem with the eutectic bonding is to obtain complete bonding of large areas. Even native oxides prevent the bonding to take place. To reduce this problem the native oxide on the silicon should be removed before Au deposition, for instance by backsputtering. In addition some mechanical motion could be required during bonding to enhance the alloying process.

Eutectic Bonding by a Au/Sn preform has been reported to introduce substantial mounting stress in piezo-resistive sensors causing long term drift due to relaxation of the built-in stress. The materials usable for eutectic bonding of metallized silicon components are quite ductile, and this is a probable disadvantage resulting in long term mechanical drift.

Silicon wafer bonding has been used to fabricate surface-micromachining-like structures for a variety of sensors and actuators. Figure 6.4 illustrates the process. We begin by joining two silicon wafers, a device wafer containing an etch-stop layer and a handle wafer containing etched cavities, using wafer bonding. The bulk of the device wafer is then thinned to produce a wafer with sealed cavities which looks virtually identical to an unprocessed wafer. At this point the bonded and thinned structure can be returned to a standard IC facility for electronics fabrication. Following circuit processing, low-temperature back-end processes are performed to functionalize the sensors. The process has two significant features. First, the mechanical layer which results from this process has reliable, reproduceable mechanical properties. Second, the electronics integration strategy is compatible with standard IC processes and equipment [31].

Modification to the thinning process is to achieve electrical isolation of the mechanical layer from the substrate. presented in the future. Thinning methods are critically important in wafer bonded micromachining processes since the thickness tolerance of the mechanical parts will be defined by this step. We described an electrochemical thinning process that produces a n-type mechanical layer

on a n-type substrate. However, electrical isolation is important for a class of structures built in this technology (accelerometers and gyroscopes, for example).

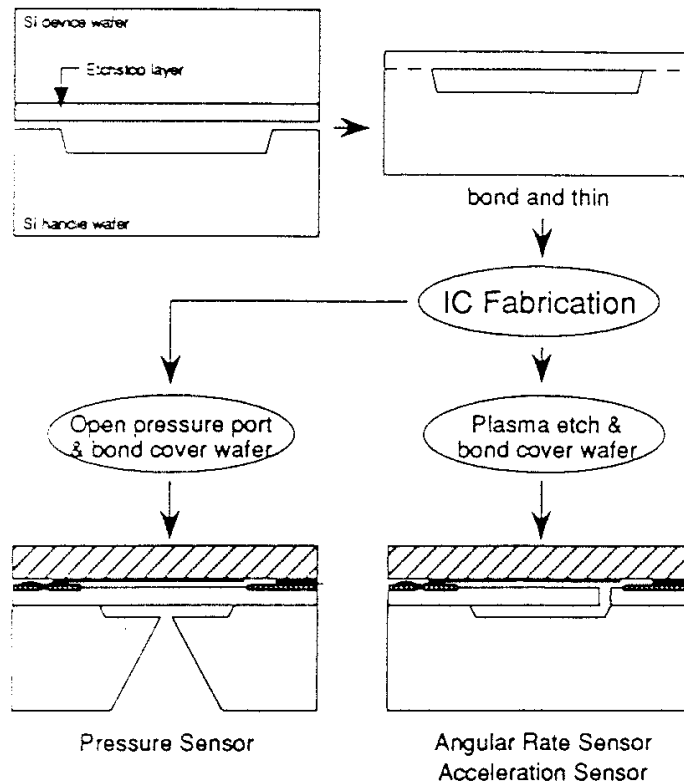
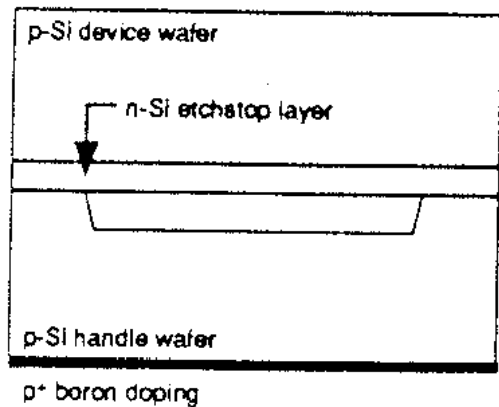


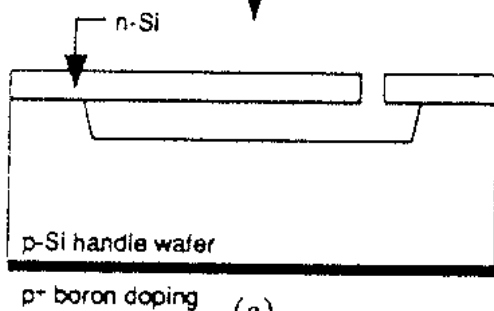
Figure 6.4: MIT wafer-bonded integrated sensor process [31].

Two technical approaches are either to use a buried chemical etch-stop (p++ doping or oxide) and bonding to an oxide coated substrate wafer (dielectric-isolation) or to use a junction electrochemical etch-stop and a p-type substrate wafer (junction-isolation) as illustrated in Figure 6.5. Electrochemical etch-stop methods are known to produce high quality mechanical structures, but the layers are most conveniently formed by silicon-silicon bonding, where the lower wafer provides an accessible electrical connection during the etch-stop process. This process thus precludes electrical isolation of the mechanical parts from the substrate.

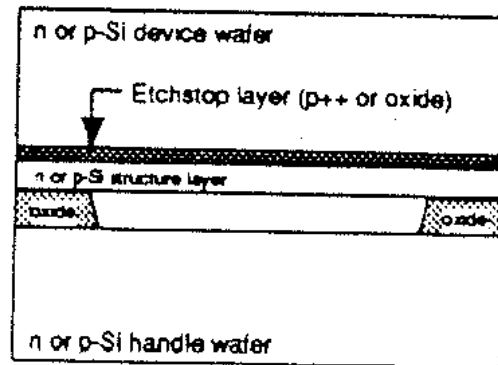
Junction-Isolation



Electrochemical
Etchback
Pattern for
mechanical structures



Dielectric-Isolation



Etch back and form
mechanical structures

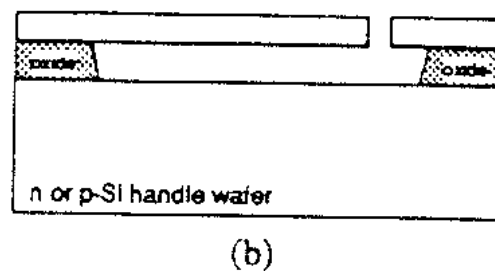


Figure 6.5: Sealed cavity processes for electrical isolation of the mechanical parts from substrate.

A second important feature of the integrated process is the ability to fabricate these parts using a completely dry release process. A resist-mask is used for device patterning followed by a Si plasma etch to pattern the mechanical structure and a plasma etch to remove the -resist-With this dry release method, large suspended plates have been successfully fabricated as tuning fork tines for the gyroscopes and the proof masses for the accelerometers.

In the process of piezo-resistive pressure sensor packaging, a simple thermo-compression bonding setup has been fabricated to achieve the wire bonding interconnection of a silicon chip with printed circuit board. An annealed gold wire is joined onto a pad surface with a needle-like chisel under a force of 0.5–1.5 N/point. The temperature of the substrate was maintained in the range of 150–200°C and the temperature of the chisel was fixed at around 150°C during wire bonding operation. The tensile strength of the wire bonding was measured with a bonding tester by the destructive-pulling experiment and was found to be at the average of 132 mN/mm² [32]. The microstructure of

the bonding point was examined by scanning electron microscopy. The interface of the thermo-compression bonding was shown to possess an acceptable level of reliability for a micro-electromechanical system (MEMS)-based device. The results showed that this setup can be easily operated for fabrication and is suitable for fabricating not only low-cost pressure sensors, but also other

6.2. Wirebonding

Wirebonding is an electrical interconnection technique using thin wire and a combination of heat, pressure and/or ultrasonic energy. Wire bonding is a solid phase welding process, where the two metallic materials (wire and pad surface) are brought into intimate contact. Once the surfaces are in intimate contact, electron sharing or interdiffusion of atoms takes place, resulting in the formation of wirebond. In wirebonding process, bonding force can lead to material deformation, breaking up contamination layer and smoothing out surface asperity, which can be enhanced by the application of ultrasonic energy. Heat can accelerate Interatomic diffusion, thus the bond formation [33].

Wirebonding process begins by firmly attaching the backside of a chip to a chip carrier using either an organic conductive adhesive or a solder (Die Attach). The wires then are welded using a special bonding tool (capillary or wedge). Depending on bonding agent (heat and ultrasonic energy), the bonding process can be defined to three major processes: thermocompression bonding (T/C), ultrasonic bonding (U/S), and thermosonic bonding (T/S), as shown in Table 6.1.

Wirebonding	Pressure	Temperature	Ultrasonic energy	Wire
Thermocompression	High	300-500 °C	No	Au
Ultrasonic	Low	25 °C	Yes	Au, Al
Thermosonic	Low	100-150 °C	Yes	Au

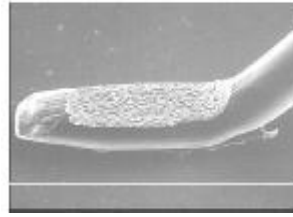
Table 6.1. Three wirebonding processes [33].

There are two basic forms of wire bond: ball bond and wedge bond, the corresponding bonding technique, bonding tool and materials are listed in Table 6.2. Currently, thermosonic gold ball bonding is the most widely used bonding technique, primarily because it is faster than ultrasonic aluminum bonding. Once the ball bond is made on the device, the wire may be moved in any

direction without stress on the wire, which greatly facilitates automatic wire bonding, as the movement need only be in the x and y directions.



Ball Bond



Wedge Bond

Figure 6.6: Two basic forms of wire bond [33].

Wirebond	Bonding technique	Bonding tool	Wire	Pad	Speed
Ball bond	T/C	Capillary	Au	Al,Au	10 wires/sec (T/S)
Wedge bond	T/S, U/S	Wedge	Au, Al	Al,Au	4 wires/sec

Table 6.2. Wire bond formation [33].

In this technique, wire is passed through a hollow capillary, and an electronic-flame-off system (EFO) is used to melt a small portion of the wire extending beneath the capillary. The surface tension of the molten metal forms a spherical shape, or ball, as the wire material solidifies. The ball is pressed to the bonding pad on the die with sufficient force to cause plastic deformation and atomic interdiffusion of the wire and the underlying metallization, which ensure the intimate contact between the two metal surfaces and form the first bond (ball bond). The capillary is then raised and repositioned over the second bond site on the substrate, a precisely shaped wire connection called a wire loop is thus created as the wire goes. Deforming the wire against the bonding pad makes the second bond (wedge bond or stitch bond), having a crescent or fishtail shape made by the imprint of the capillary's outer geometry. Then the wire clamp is closed, and the capillary ascends once again, breaking the wire just above the wedge, an exact wire length is left for EFO to form a new ball to begin bonding the next wire. Ball bonding is generally used in thermocompression (T/C) or thermosonic bonding (T/S) process. This technique requires a high temperature ranging from 100°C to 500°C depending on bonding process. Heat is generated during the manufacturing process either by a heated capillary feeding the wire or by a heated pedestal on which the assembly is placed or by both depending on the bonding purpose and materials. Relatively small gold wire (< 75 μ m) is mostly used in this technique because of its easy deformation under pressure at elevated temperature, its resistance to oxide formation, and its ball formability during a flame-off or

electronic discharge cutting process. Ball bonding is generally used in application where the pad pitch is greater than 100 μm . However, the application of the pitches with 50 μm has been reported.

Wedge bonding is named based on the shape of its bonding tool. In this technique, the wire is fed at an angle usually 30-60° from the horizontal bonding surface through a hole in the back of a bonding wedge. Normally, forward bonding is preferred, i.e. the first bond is made to the die and the second is made to the substrate. The reason is that it can be far less susceptible to edge shorts between the wire and die. By descending the wedge onto the IC bond pad, the wire is pinned against the pad surface and an U/S or T/S bond is performed. Next, the wedge rises and executes a motion to create a desired loop shape. At the second bond location, the wedge descends, making a second bond. During the loop formation, the movement of the axis of the bonding wedge feed hole must be aligned with the center line of the first bond, so that the wire can be fed freely through the hole in the wedge. Several methods can be used to end the wire after the second bond. For small wires (<75 μm), clamps can be used to break the wire while machine bonding force is maintained on the second bond (clamp tear), or the clamps remains stationary and the bonding tool raises off the second bond to tear the wire (table tear). The clamp tear process offers a slightly higher yield and reliability than the table tear process due to the force maintained on the second bond during the clamp tear motion. The clamp tear process also offers a light speed advantage over the table tear process due to fewer required table motions. However, the table tear process, with a higher wire feed angle capability and stationary clamp, has the potential to provide slightly more clearance from package obstructions such as a bond shelf or pin grid. For large bonding wires (>75 μm), other methods can be used such as a cutting blade or the placement of the wire into a channel in the wedge for wire termination. As the wedge ascends, the clamped wire is fed under it to begin bonding the next wire.

Wedge bonding technique can be used for both aluminum wire and gold wire bonding applications. The principle difference between the two processes is that the aluminum wire is bonded in an ultrasonic bonding process at room temperature, whereas gold wire wedge bonding is performed through a thermosonic bonding process with heating up to 150°C. A considerable advantage of the wedge bonding is that it can be designed and manufactured to very small dimensions, down to 50 μm pitch. However, factors based on machine rotational movements make the overall speed of the process less than thermosonic ball bonding. Aluminum ultrasonic bonding is the most common wedge bonding process because of the low cost and the low working temperature. The main

advantage for gold wire wedge bonding is the possibility to avoid the need of hermetic packaging after bonding due to the inert properties of the gold. In addition, a wedge bond will give a smaller footprint than a ball bond, which specially benefits the microwave devices with small pads that require a gold wire junction.

A Multi Chip Modules, abbreviated “MCM”, is described as a package combining multiple ICs into a single system-level unit. The resulting module is capable of handling an entire function. An MCM can in many ways be looked upon as a single component containing several components connected to do some function. The components are normally mounted un-encapsulated on a substrate where the bare dies are connected to the surface by wire bonding, tape bonding or flip-chip. The module is then personated by some kind of plastic moulding. The module is then mounted on the PCB in the same way as any other QFP or BGA component.

Deposited MCMs are MCMs where the conducting layers are deposited on some sort of carrier, usually ceramic but also on silicon. The metal deposition is normally done by sputtering or evaporation in vacuum. After the deposition process the metallized surface is patterned by applying a photosensitive resist that after exposing and developing function as an etch resist. All metal not covered by the resist is removed. After the patterning of one layer, a dielectric coating can be applied. For organic dielectrics this are often done by spinning or spraying, whereas non-organic dielectrics are deposited by Chemical Vapour Deposition (CVD). Holes in the dielectric are opened by a similar photolithographic process and new layers can be added.

6.2.1. Wirebonding on SBU

The MCM-L and MCM-Flex have significantly softer dielectrics than most other MCM technologies. This means that a careful design of the bond pad and careful specification of the metallization system. Also the bonding process is important.

- Gold thickness on the substrate is defined by the type of bond process used and the bond strength.
- Secondary metal finishes may be required to provide a rigid bonding surface at high temperature
- The substrate Tg is critical in determining the bond strength and reliability. If the wire bonding process takes the board above the Tg, then localized deformation and sinking of the bond pad area will occur.

Wire bonding typically requires between 100 and 1250 nm of soft gold on the bond pad. For thin layers (100–200 nm) immersion gold can be used. This process is self-limiting, and gold is plated on all exposed surfaces, after the solder mask has been applied. Once a complete gold coverage of the surface is achieved, the plating process stops. Immersion gold is the least expensive gold finish available. This coating is commonly used for ordinary surface mount assembly, and provides excellent solderability and coplanarity without a significant cost increase compared to other finishes. This means that the same finish can be used for both wirebonding and soldering.

If higher gold thickness is needed (500–1000 nm) for gold wire bonding, electroless gold can be used. The electroless process means that all exposed metal surfaces will be plated. The process will continue as long as it is immersed into the plating bath. However, this amount of gold will have a negative effect on the solder, causing a brittle joint.

If thicker gold is needed, electroplating has to be used. Electroplated gold is selectively added onto the metal surfaces that are included in the external electrical circuit. This means that all wire bonding pads must be connected together in a bus. The electroplating is a more costly process, and the required bussing can cause some design (layout) problems.

The gold thickness influences the wire bond pull strength. A study by McDermott is shown in Table 6.3 below. In this study a 25 μm gold wire has been bonded onto different gold surfaces. In all cases a 5 μm nickel layer underneath the gold.

Gold finish	Thickness [nm]	Average Bond Strength [g]	Standart Deviation [g]
Immersion Gold	110	8,01	1,31
Immersion Gold	125	9,60	1,30
Electroless Gold	530	9,77	1,66
Electroless Gold	900	9,93	1,24

Table 6.3. A study by McDermott

6.3. Classic Thin Films

Classic thin-film hybrid technology is an example of a technique that fall into this technology [34]. This technology is based on one thin gold signal layer on top of an alumina substrate. Crossovers are made by wire bonding. The backside of the substrate can be gold coated for the use as a ground plane.

Advantages

- Narrow lines possible.
- Low dielectric loss tangent ($\gg 0.0001$)
- Resistors and small capacitors can be integrated in the wiring
- Trimming of resistors is possible
- Very good thermal performance, depending on the substrate ($\lambda \sim 30\text{-}200 \text{ W/mK}$)

Disadvantages

- One layer may cause routing problems.
- Long bond wires for crossovers may be too inductive for some applications.
- 50 ohm lines will be as wide as the thickness of the substrate.
- High dielectric constant ($\sim 7\text{-}10$)
- Medium cost

6.4. Gold wire:

Gold wire is used extensively for thermocompression bonding and thermosonic bonding. In producing the gold bonding wires, surface finish and surface cleanliness are the critical issues to ensure the formation of a strong bond and to prevent clogging of bonding capillaries. Pure gold can usually be drawn to produce an adequate breaking strength (ultimate tensile strength of the wire) and proper elongation (ratio of the increase in wire length at rupture to the initial wire length given as a percentage) for use as bond wire.

Ultra pure gold is very soft, therefore small amounts of impurities such as 5-10 ppm by weight of Be or 30-100 ppm by weight of Cu are added to make the gold wire workable [34]. Be-doped wire is stronger than Cu-doped wire by about 10-20% under most conditions, thus advantageous for

automated thermosonic bonding where high-speed capillary movements generate higher stresses than in slow or manual bonders.

6.5. Metallurgical systems

In wirebonding process, different pad metallizations are used, depending to the production requirements. Therefore, different metallurgical systems can be formed with different reliability behaviours. The typical metallurgical systems are [34]:

Au-Au system

Gold wire bonded to a gold bond pad is extremely reliable because the bond is not subject to interface corrosion, intermetallic formation, or other bond-degrading conditions. Even a poorly welded gold-gold bond will increase in strength with time and temperature. Gold wire welds best with heat although cold ultrasonic Au-Au wire bonds can be made. Either thermocompression or thermosonic bonds are easily and reliably made. Thermocompression bondability, however, is strongly affected by surface contamination.

Au-Al system

Au-Al welding system is the most commonly used in wirebonding process. However, this bonding system can easily lead to formation of Au-Al intermetallic compounds and associated Kirkendall voids. The formation can be accelerated with the temperature and time of the operational life. There are five intermetallic compounds that are all colored: Au_5Al_2 (tan), Au_4Al (tan), Au_2Al (metallic gray), AuAl (white), and AuAl_2 (deep purple). AuAl_2 can initially form in the interface between gold and aluminum during bonding process even at room temperature and could transform to other Au-Al compounds depending on the temperature, time and bonding configurations. Therefore, this system often presents a problem in reliability of the bonds.

Au-Cu system

Bonding gold wires to bare copper lead frames can cause the formation of three ductile intermetallic phases (Cu_3Au , AuCu , and Au_3Cu) with overall activation energies of 0.8 to 1 eV. The formation of these intermetallic compounds can decrease the bond strength at higher temperatures (200-325°C) as a result of Kirkendall voiding. The degradation is apparently dependent on the microstructure, weld quality, and impurity content of the copper. Cleanliness of the bonding surface is extremely important to ensure good bondability and reliability in Cu-Au systems. In addition, if polymer

material is used for die attach, the polymer must be cured in an inert atmosphere to prevent oxidation.

Au-Ag system

The Au-Ag wire bond-system is very reliable for very long times at high temperatures. This bond system does not form intermetallic compounds and does not exhibit interface corrosion. Gold-wire bonds to silverplated lead frames have been successfully used in high production for many years. Bondability problems can be caused by contaminants like sulfur. Thermosonic Au-Ag bonding is usually performed at high temperature (approximately 250°C) which dissociates thin silver-sulfide films thus increases bondability of silver.

7. EXPERIMENTS

Soft gold for electronics or other applications can be obtained by controlling the structure by metal additions into the electrolyte and also by electrodeposition with very short current pulses and long off times. Soft gold is obtained from baths containing a small quantity of thallium ions as an additive, while hard gold is obtained from similar baths with nickel ions as an alternative additive. Thallium is not deposited, but affects strongly the adsorption phenomena at the gold cathodic surface. Normal metal ions addition gives soft gold deposits, while inert metal addition give hard gold layers. The main influence of normal metal addition is a decrease in the cathodic voltage during deposition, with decrease in inhibition condition coming from complexant interaction with the cathodic surface. A similar effect can be obtained with pulsed current, when the voltage increase is limited, favouring the capacitance charging with respect to the faradaic discharge. In these conditions, lateral growth prevails with respect to outgrowth, which becomes predominant in inhibition conditions. Cyanide and sulphite gold baths show a similar behaviour with respect to inhibition phenomena by complexant at surfaces.

8.1 Experimental Section

The silicon substrates wafers coated by sputtering with a gold thin layer on titanium. Before applying electrodeposition, all substrates were degreased with acetone and rinsed with distilled water. The electrolyte was prepared from some certain quantity chemicals and distilled water. The electrolyte had the following composition: for the study of additives, $\text{KAu}(\text{CN})_2$ 0,04M, $\text{K}_2\text{C}_2\text{O}_4$ 0,5M, KH_2PO_4 0,123M and K_2HPO_4 0,057M. To this electrolyte, were added Ni^{+2} 15 ppm from a

nickel sulphamate, or Tl^+ 40 ppm from a thallium chloride solution and the results were compared with those obtained from the bath without additions. In some tests, a commercial gold sulphite electrolyte was used. Platinised titanium mesh was used as the anode.

The solution composition and operating conditions are shown in Table 7.1. The bath electrokinetic behavior was controlled by cyclic voltammetry on a gold plated electrode. So as to obtain the voltage transients during steady state electrodeposition, apply the secondary current pulse (SCP) technique.

Current was supplied to the cell as well as power in galvanostatic mode (AMEL 550). The current density was 1 mA cm^{-2} . All electrochemical tests were performed in prismatic Pyrex cells including about 300 mL of solution; hydrodynamic conditions and current distribution were fully characterised. Electrochemical measurements were performed in a three-electrode configuration, utilising a measuring cell with an SCE reference electrode in connection to the working electrode with a lateral channel Piontelli probe (mean distance of lateral slit from surface $30 \text{ }\mu\text{m}$). No ohmic corrections were made, because of the Piontelli probe. All substrates were electrodeposited thick enough to obtain a crystallographic orientation imposed by the electrolyte. Potentiodynamic runs were performed on electrodes previously coated (about $3 \text{ }\mu\text{m}$) in the same electrodeposition bath, with scan rate 0.1 mV s^{-1} .

Electrolyte Au	Electrolyte AuNi	Electrolyte AuTI	Operating Parameters
$KAu(CN)_2$ 0.04M $K_2C_2O_4$ 0.4M KH_2PO_4 0.123M K_2HPO_4 0.057M	Electrolyte Au + 15 ppm Ni	Electrolyte Au + 40 ppm TI	pH 6.8 Deposition time: 100 s or 4h Current density: 1 mA cm^{-2} Substrate: Au/Ti sputtered Si wafer Anode: Platinum (Pt)

Table 7.1. Composition and operation conditions for Au, Au-Ni and Au-TI electroplating solutions

The screened coulomb potential method is related to a voltage relaxation technique, as well as short current pulses superimposed on the metal cathode during electrodeposition. Four effects are considered for the evaluation of the voltage increase:

1. If ohmic drop happens at less than one nanosecond, this quantity of the drop is not important for the voltage $\eta(t)$ increase.
2. The capacitance current related to the nature and amount of electroactive species adsorbed at the electrode.

$$i_c = C_{ads} \exp(\eta/B_t) d\eta/dt$$

C_{ads} , adsorption pseudocapacitance, determines the slope of the voltage.

B_t : Transient Tafel slope

3. Current is applied for the faradaic reaction

$$i_F = i_D \exp(\eta/B_t)$$

i_D : Deposition current density and it reaches a steady state within a few milliseconds.

4. At the adsorbed layer, the change of concentrations occurs in the second run and introduced with τ as a transition time constant respect to a Sand type behavior. The pulse current density;

$$i_P = i_C + i_F$$

The equation of the overvoltage transient;

$$\eta(t) = B_t \ln [i_P / i_D - (i_P / i_D - 1) \exp(-i_D t / B_t / C_{ADS})] + (RT / z / F) t^{1/2} / \tau$$

The composition was measured by EDS analysis. Thickness and morphology were investigated by means of laser profilometry (UBM Microfocus) and SEM (Cambridge Stereoscan 360). The surface Dimension of the surface features was obtained by image analysis software. The phase structure and the texture of the deposits were determined by X-ray diffractometry with Cu K_α radiation and a powder goniometer (Philips PW1830). Gold deposit structure was measured by SEM and AFM also with using XRD and we obtain a thickness around 10 μm . Gold deposition was compared respect to thermal analysis records and we obtain very different grain size and defects presence considering metal additives (Ni or TI) or without metal additives. We obtain different curves and they identify different mechanical behavior.

7.2. Experimental Results

7.2.1. Effect of TI^+ and Ni^{+2} on electrokinetics and structure of gold coating from cyanide baths

Figure 7.1 depicts the relation between voltage relation and time that is duration of gold or gold alloy electrodeposition in the cyanide-oxalate-phosphate bath. If we compare to different baths,

different cathodic voltage increase are obtained during the electrodeposition of gold. In Tl-added electrolyte, cathodic voltage increase occurs more than 100 mV with respect to the other electrolytes which is additive-free or Ni added. Deposition voltage is more stable in the case of no additives or Ni-added bath. Voltage changes during electrodeposition as a result of uncontrolled inhibition phenomena.

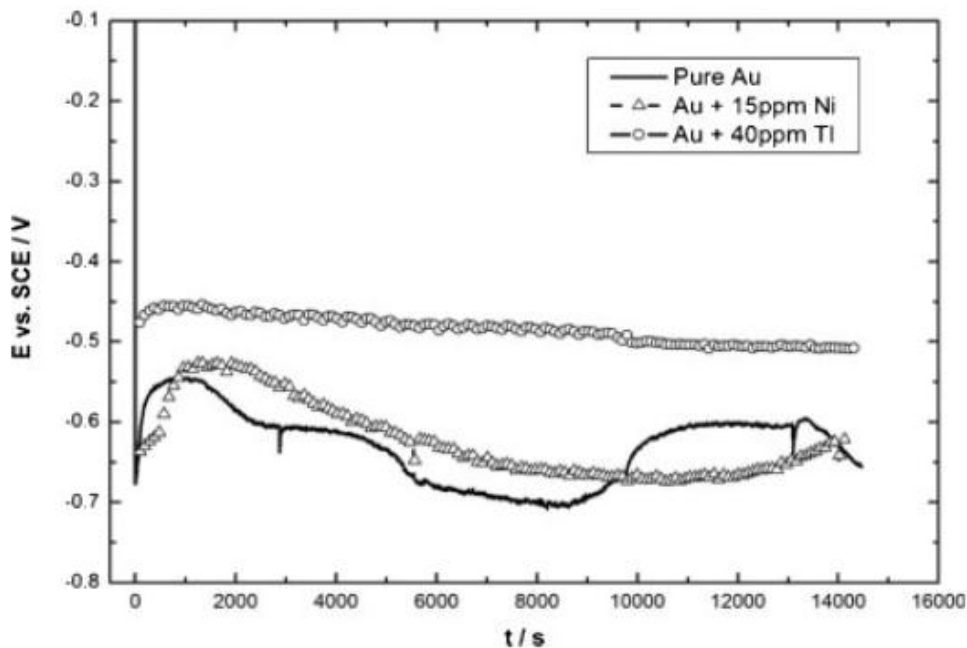


Figure 7.1. Cathodic voltage variation with time during electrodeposition of gold and gold alloys, Au-Ni and Au-Ti

If we see the cyclic voltammetry graph (Figure 7.2), we obtain very different behavior for the Tl additive bath, no additive and Ni additive. The maximum peak reaches to 0.75 V which is related to gold deposition, but other two solutions one of them occurs at about 1.08 V and the other occurs at 0.33 V.

SCP curves related with these three solutions are shown in Figure 7.3 give the transient parameters and reported in Table 7.2. The transient Tafel parameter is very low for the AuTl bath, intermediate for the Au bath and $>RT/F$, high for the AuNi bath and in the range of $2RT/F$ (typical of hydrogen discharge). The adsorption pseudocapacitance is very high for AuTl and much less for Au or AuNi. We can obtain that adsorbed layer's modification dedicates to diffusion of discharging species during the pulse.

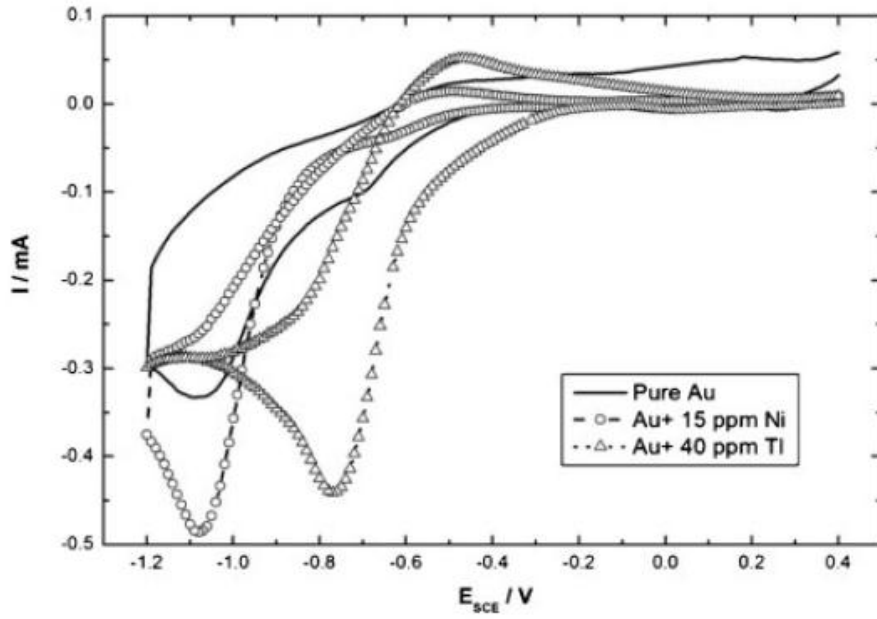


Figure 7.2: Cyclic voltammetry obtained from Au, Au-Ni and Au-Tl electroplating solutions.

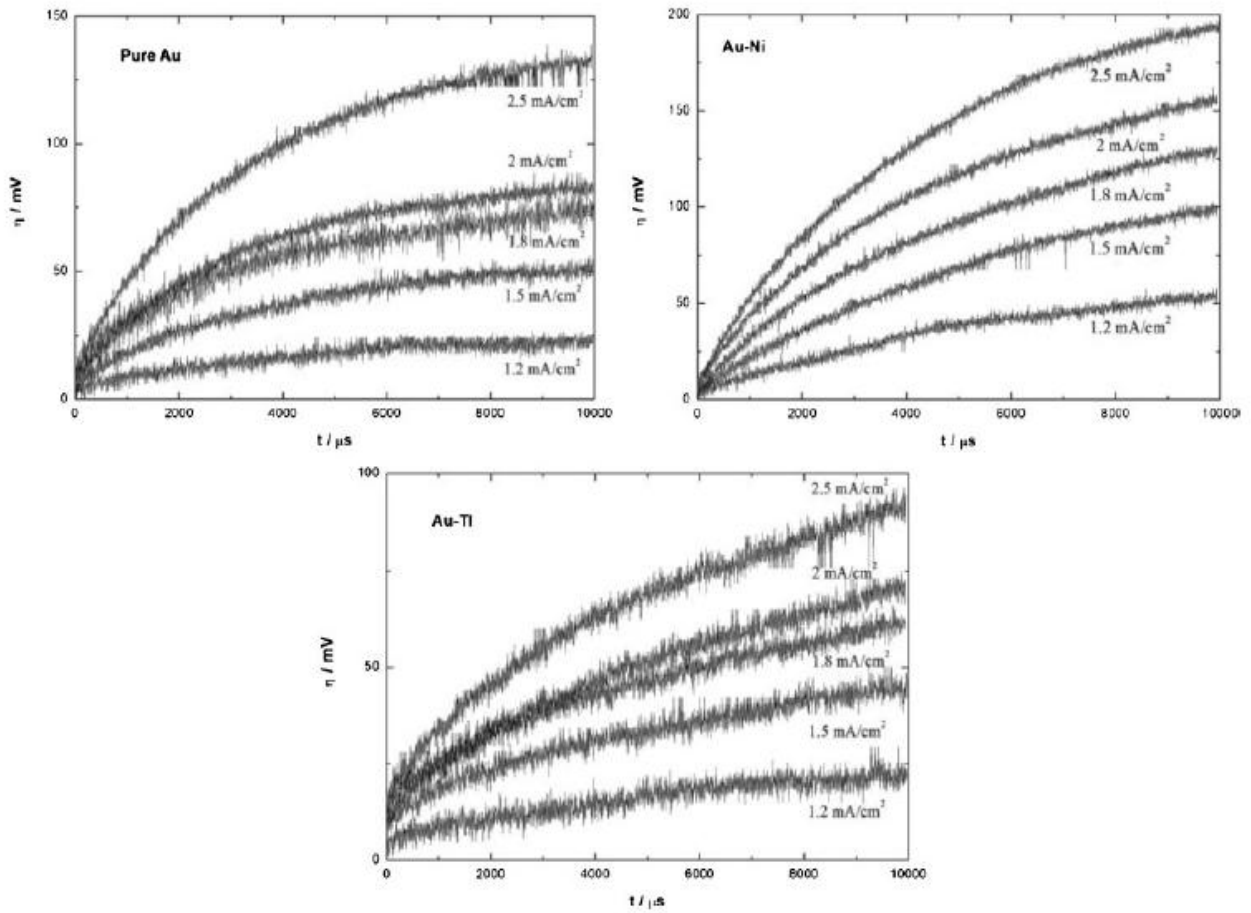


Figure 7.3: Secondary current pulses obtained from Au, Au-Ni and Au-Tl surfaces after 1 hour of deposition

The diffusion coefficient is higher for AuTl rather than pure Au and AuNi at Figure 7.4. After 100s gold deposition the surface layer surfaces behave differently with respect to pure gold bath, Ni ions additives bath and Tl ions additives bath and this behavior is shown in Figure 7.5. Additives affect the nucleation of the gold layers; Ni⁺² ions additive decreases the grain size, while Tl⁺ ions additive increases the grain size.

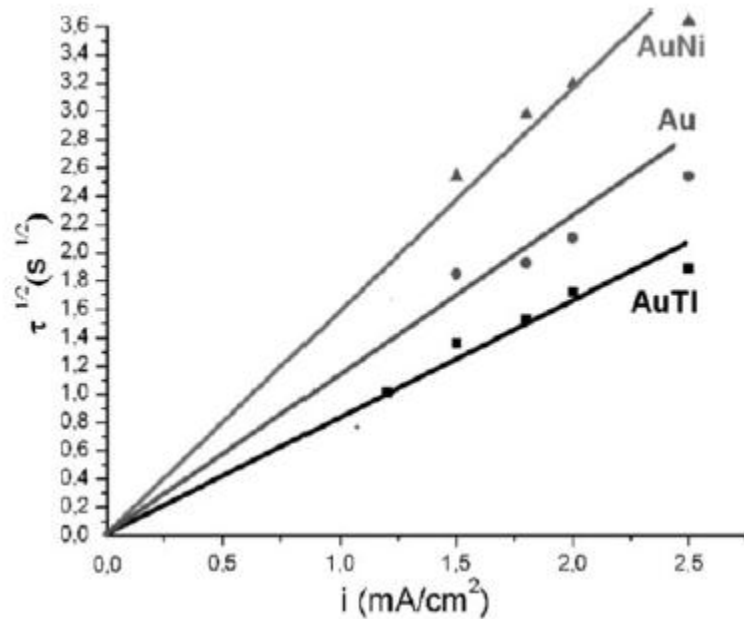


Figure 7.4: Variation of transition time as function of current density in Au, Au-Ni and Au-Tl electroplating solutions

Solution	$B_t/mV \text{ dec}^{-1}$	$C_{ADS}/\mu F \text{ cm}^{-2}$	$RT/(zF)$	τ/s
Au	75	45	80-250	0.25-0.55
AuNi	125	46	140-220	0.10-0.22
AuTl	25	140	200-350	0.4-2.0

Table 7.2 SCP parameters obtained after deposition of 1h with Au, Au-Ni and Au-Tl electroplating solutions

After 4 hour deposition time, 10 μm thickness is obtained with applying a current 1 $mA \text{ cm}^{-2}$. Figure 7.6 shows the surface after experiments. Table 7.3 presents the parameters of thickness, microhardness, elastic modulus and roughness.

Solution	Thickness/ μm	HV	E/GPa	Ra/nm
Au	6.0	128	76	86
Au+Ni	8.2	140	76	34
Au+Ti	9.0	86	77	129

Table 7.3 Thickness, hardness, elasticity modulus and surface roughness for the Au, Au-Ni and Au-Ti coating surfaces after 4h of deposition at 1 Ma cm^{-2} .

The hardness of soft AuTi is lower than Au and hard AuNi. Each elastic modulus is nearly constant and the roughness of AuTi is greater than values of Au and AuNi. XRD patterns show a decrease in the peak enlargement at middle height for AuTi with respect to Au and AuNi, and an increase in the preferred orientation (111) for AuTi, while AuNi shows a strong (110) preferred orientation.

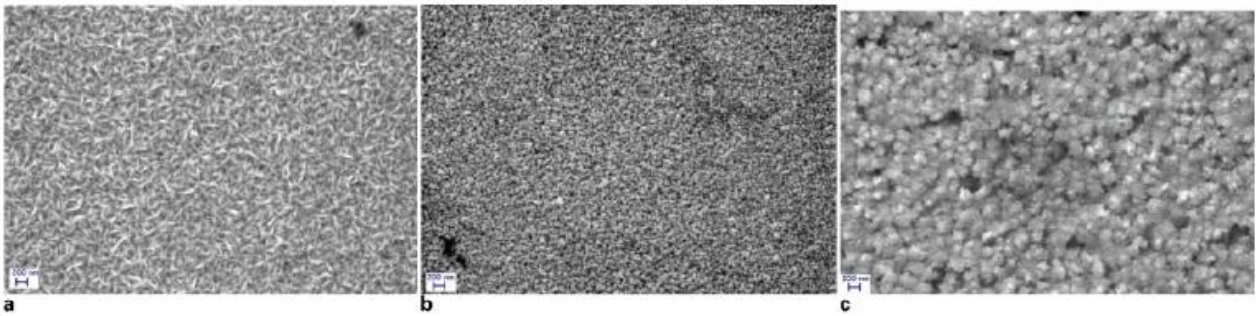


Figure 7.5: a)Au, b)Au-Ni and c) Au-Ti electrodeposited surfaces after 100 s of deposition at 1 mA cm^{-2} on Au/Ti plated Si wafer

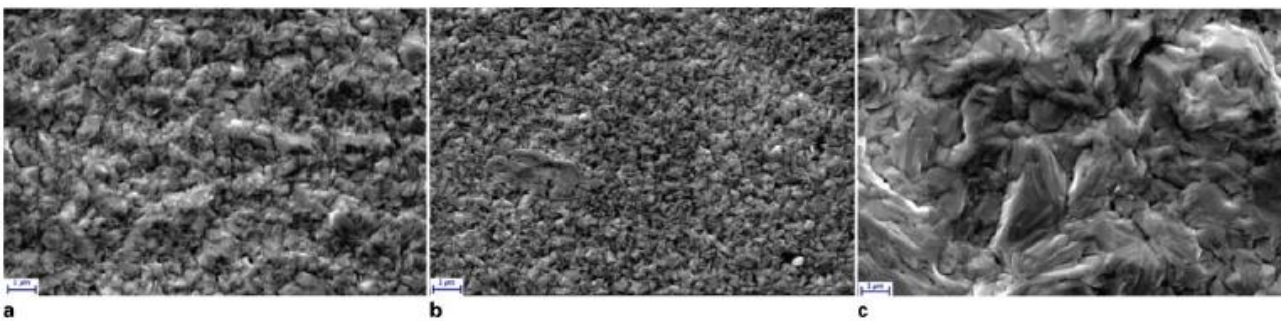


Figure 7.6: a)Au, b)Au-Ni and c) Au-Ti electrodeposited surfaces after 4h of deposition at 1 mA cm^{-2}

7.2.2. Effect of very short pulse time of deposition on structure of gold layers from sulphite bath:

A commercial gold sulphite based electrolyte was used for direct and pulse plating on sputtered gold substrates and it contains 10 g L^{-1} gold and the other supplementary compounds $\text{Au}(\text{S}_2\text{O}_3)_2^{-3}$ 0.05M , Na_2SO_3 0.4M and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. During the direct plating, current density was applied 4 mA cm^{-2} for 35 minutes. Besides, pulse plating was performed for 60 minutes with $t_{\text{ON}} = 0.1 \text{ ms}$ at $i_p = 400 \text{ mA cm}^{-2}$ and $t_{\text{OFF}} = 100 \text{ ms}$ at zero current. Other plating conditions: room temperature and pH 6.8.

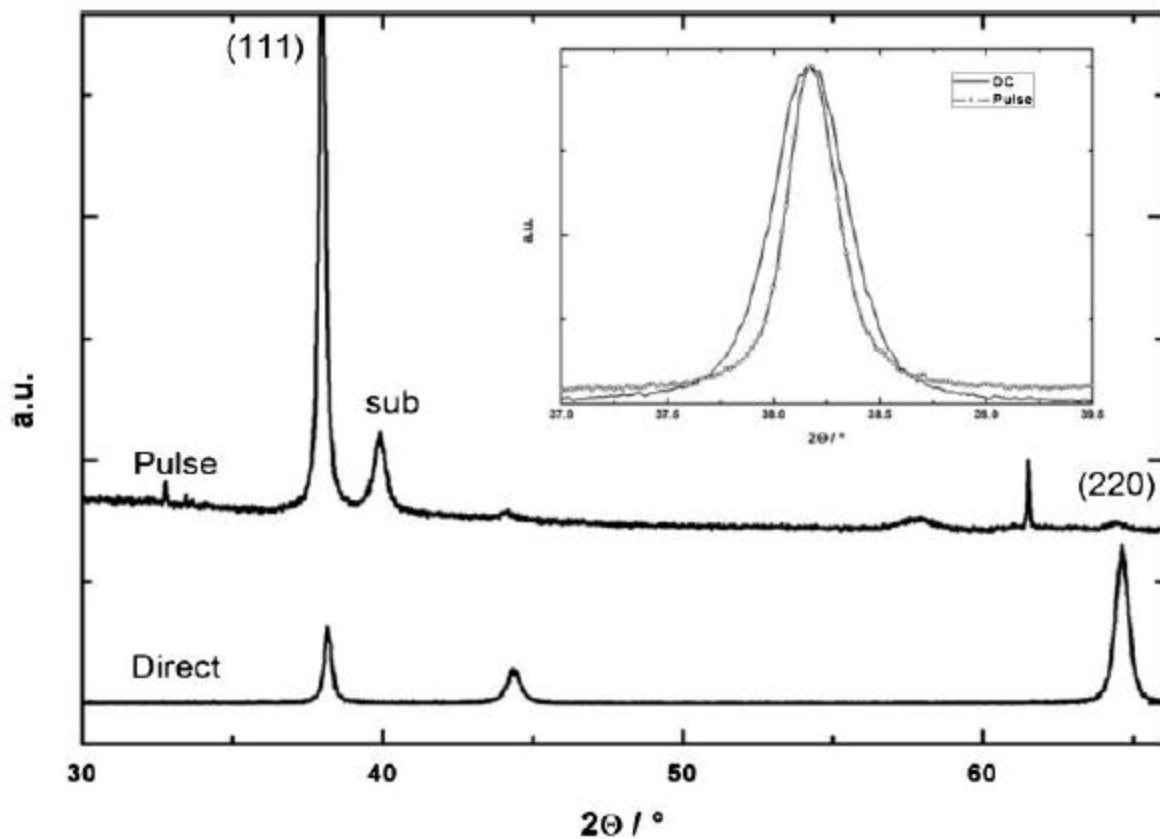


Figure 7.7: XRD patterns of Au deposited with direct or pulsed current from sulphite bath and comparison of (111) peak

Figure 7.7 shows the XRD patterns of the two samples, with a higher half width full maximum for directly electroplated gold and an almost half value for the pulse plated deposits. Pulse plating also induces a strong preferential orientation along the (111) plane, while directly plated gold is characterised by a more intense XRD peak for the (220) plane. Figure 7.8 shows the surface of the electrodeposited gold layer obtained with direct or continuous current.

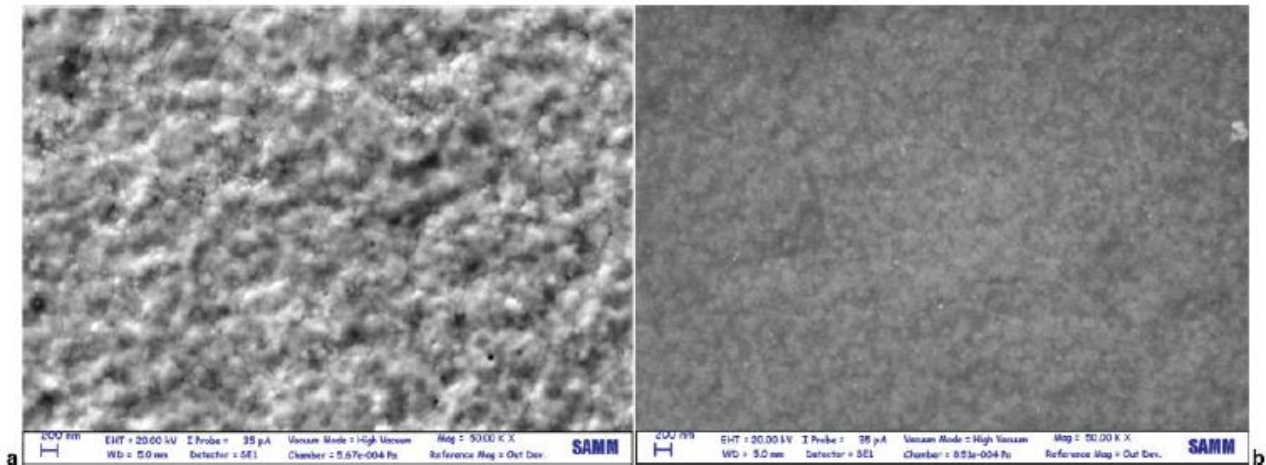


Figure 7.8: Surface of Au deposited with a) direct or b) pulsed current from sulphite bath.

8. CONCLUSION:

During my study, I tried to understand behavior of gold and gold alloy electrodeposition in micro electromechanical systems (MEMS) with searching previous experiments and sources. First, the advantages and disadvantages of this plating process were investigated. Pure gold is so expensive therefore, reduction of the gold quantity on the substrate was aimed for the commercial demands with respect to its desired properties. Au, Ag, Ni, Cr generally were used in the replace of huge amount of gold.

Electrolytes that are used in the gold electrodeposition process, were investigated. Due to the good compability with the photoresist materials and its bath stability, sulfite baths were used. Also in the condition of the laboratory and in the terms of human health, non-cyanide baths were chosen during the experiments.

Gold electrodeposition occurs in strongly complex solutions of cyanides or thiosulphates–sulphites. The effects of temperature and laboratory conditions must be thought and experiments should be obtained in strongly inhibited conditions. Applied current densities were evaluated in terms of physical and chemical features of deposited material. Generally for DC plating, current density, in the window chosen between $0,5 \text{ mA cm}^{-2}$ and 5 mA cm^{-2} , were applied to observe the its effects on the stress, adsorption, growth mechanism, constituents distribution of deposited gold alloy.

Additives were studied and the effect of metal ion additives on the structure and morphology of gold deposited from cyanide or sulphite baths was confirmed by the present results: Ni^{+2} decreases grain size, increases hardness and favours outgrowth; Tl^{+} increases grain size, decreases hardness and favours lateral growth. One of the most important results in the study is the decrease in the cathodic overvoltage during the deposition in the presence of Tl^{+} .

Some important results have been achieved: it is possible to obtain soft gold deposits without additives, but by controlling the current pulses. If the current pulse is in the range of tenths of milliseconds, the capacitance current prevails and the voltage increase at the cathode is limited. As a consequence, the grain size of the gold deposit becomes larger, with fewer defects and smoother morphology.

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