

**STUDIES ON FORMULATIONS FOR GOLD
ALLOY PLATING BATH TO PRODUCE
DIFFERENT SHADES OF ELECTRODEPOSITS**

by

CHE WAN ZANARIAH BTE CHE WAN NGAH

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ABBREVIATIONS

ΔE^*	Delta E
μm	Micrometer
ANOVA	Analysis of variance
CCD	Central composite design
DOE	Design of experiment
FFD	Fractional factorial design
g L^{-1}	Gram per liter
JCPDS	Joint Committee on Powder Diffraction Standard
mg	Milligram
min	Minute
ml	Milliliter
nm	Nanometer
OFAT	One factor at the time
PGC	Potassium gold cyanide
RSM	Response surface method
SRA	Spectral reflectance accessories
UV	Ultra Violet
vs.	Versus

**KAJIAN FORMULASI LARUTAN PENGELEKTROSADURAN ALOI EMAS
UNTUK MENGHASILKAN LAPISAN ENAPSADUR DENGAN WARNA
YANG BERBEZA**

ABSTRAK

Kajian untuk memformulasi larutan pengelektrosaduran aloi emas secara sistematik telah dilakukan dengan menggunakan kaedah rekabentuk eksperimen. Rekabentuk eksperimen separa faktor telah dijalankan untuk mengenalpasti kesan kehadiran logam argentum, palladium, nikel dan indium yang digunakan sebagai agen penambah di dalam larutan pengelektrosaduran terhadap warna enapsadur yang diperolehi. Warna panel Hull yang telah disadurkan dianalisa dengan menggunakan Spektrofotometer ultralembayung yang dilengkapi dengan aksesori pembalikan spektrum. Warna tersebut dinilai secara kuantitatif dengan menggunakan kaedah pengukuran warna yang berasaskan kepada skala warna yang seragam atau lebih dikenali sebagai sistem CIELAB. Kaedah ini mengambil kira perbezaan warna di antara dua spesimen yang mempunyai koordinat warna yang tersendiri (L_1^* , a_1^* , b_1^* , dan L_2^* , a_2^* , b_2^*) dan dilaporkan sebagai ΔE^* .

Perbezaan warna (color tolerance) yang dibenarkan terdapat pada panel Hull pula ditentukan dengan membina rajah kawalan (control chart) dan nilai had atas sebesar 5.37 telah diperolehi. Ini bermakna jika ΔE^* yang dikira di antara dua lokasi pengukuran pada satu panel Hull atau di antara dua panel Hull yang berbeza adalah kurang atau sama dengan 5.37, maka warna kedua-dua lokasi atau kedua-dua panel tersebut dianggap masih berada dalam julat perbezaan yang dibenarkan. Perbezaan warna yang diceraap ini juga dinilai secara statistik untuk menentukan samada

penambahan sesuatu logam dalam larutan pengelektrosaduran memberikan perubahan warna yang signifikan pada enapsadur. Penambahan logam argentum serta gabungan logam argentum dan palladium ke dalam larutan pengelektrosaduran telah memberikan tiga warna enapsadur yang signifikan terhadap warna seperti keemasan, seperti warna logam argentum dan seperti warna aloi tembaga. Manakala penambahan logam nikel didapati telah memberikan warna enapsadur yang signifikan terhadap platinum piawai. Prosedur pengoptimuman yang dijalankan ke atas penambahan gabungan logam nikel dan indium ke dalam larutan pengelektrosaduran telah menunjukkan kehadiran warna enapsadur yang hampir serupa dengan warna 2N-18 Yellow aloi emas karat yang komersil. Penambahan logam palladium pula menghasilkan enapsadur yang mempunyai warna yang berbeza dari warna emas tanpa sebarang respon yang signifikan terhadap analisa warna yang dilakukan, manakala penambahan indium langsung tidak menunjukkan perubahan warna yang ketara berbanding warna emas.

Corak keluk pemantulan yang dicerap pada sesuatu panel Hull pula merupakan identiti bagi enapsadur yang diperolehi dari larutan pengelektrosaduran tertentu. Enapsadur yang tidak mempunyai sebarang logam penambah menunjukkan corak pemantulan yang seiras dengan corak pemantulan yang ditunjukkan oleh piawai emas. Keluk pemantulan juga dipengaruhi oleh sifat kekasaran permukaan yang dianalisa di mana permukaan yang mempunyai nilai R_a yang rendah akan memberikan pantulan yang lebih tinggi.

Analisis EDAX pula membuktikan bahawa aloi binari Au-Ag, Au-Pd dan Au-Ni serta aloi ternari Au-Ag-Pd dan Au-Ni-In telah berjaya diaplikasikan. Penyelidikan ke atas lapisan enapsadur yang terpilih menunjukkan saiz struktur kristal yang terbentuk adalah amat kecil iaitu dalam julat pengukuran nanometer di antara 4.48 hingga 50.05 nm. Rupabentuk struktur pula berbeza beza bergantung kepada jenis logam yang

terenap bersama emas. Imej SEM menunjukkan kebanyakan lapisan enapsadur yang mengandungi logam argentum, palladium dan nikel secara berasingan serta enapsadur yang mengandungi gabungan logam argentum-palladium dan nikel-indium menunjukkan kehadiran struktur 'globular' menandakan bahawa ianya adalah permukaan yang rata. Manakala imej AFM pula menunjukkan topografi permukaan yang lebih jelas dengan kehadiran struktur yang lebih tersusun seperti bongkah kecil yang terherot serta kehadiran struktur 'jurang' pada sesetengah sampel yang dianalisa. Kehadiran planar Au (111) juga dikesan pada semua sampel yang dianalisa strukturnya dengan teknik XRD menunjukkan pemendapan enapsadur yang selari dengan struktur Cu (111) yang digunakan sebagai substrat.

ABSTRACT

The systematic studies on formulations for gold alloy plating baths were conducted by employing experimental design. The fractional factorial design method was used to identify the effect of silver, palladium, nickel, and indium additions in the electroplating solutions on the shades of the electrodeposited gold films produced. The color of the electrodeposited Hull cell panels were analyzed using a spectrophotometer UV equipped with spectral reflectance accessories. Color quantification for the electrodeposited gold films produced was conducted by employing a uniform color scale known as CIELAB. The system facilitates the measurement of the difference between two color specimens (L_1^* , a_1^* , b_1^* , and L_2^* , a_2^* , b_2^*) and the color difference evaluated was reported as ΔE^* .

Color tolerance was determined by employing control charts where the values of ΔE^* up to 5.37 between any measured locations or between any two electroplated Hull cell panels is still considered to be within the acceptable process limit. The differences in color were statistically evaluated to find out whether the additions of each metal to the electroplating solutions has any significant effect on the shades of the electrodeposits produced. The addition of silver and combination of silver-palladium in the electroplating solutions has produced three different shades of electrodeposits, which gave significant response against the standard gold, brass and silver. Nickel addition to the electroplating solution has produced electrodeposits which gave significant response toward platinum standard. Also, optimization procedure conducted on the combination of nickel-indium additions to the electroplating solutions reveal gold deposits with a color close to 2N-18 Yellow commercial carat gold. While addition of palladium give a different color to that of gold with no significant color

response recorded. Conversely the addition of indium to the electroplating solution does not give any significant color changes.

The reflectance pattern observed from a Hull cell panel becomes the fingerprint representing the bath origin. Reflectance curves for electrodeposited gold film without the presence of any metal inclusions is similar to the one given by gold standard. The reflectance is also affected by the surface roughness of the samples analyzed where the surface having smaller roughness (R_a) always reflects higher compared to the one with a bigger value.

EDAX analyses proved that the formations of binary Au-Ag, Au-Pd, Au-Ni and ternary Au-Ag-Pd, Au-Ni-In gold electrodeposited gold alloys were successfully developed in this study. Investigations conducted on selected samples also shows that the sizes of the crystal structures developed on the surface are very small with R_a values ranging between 4.48 to 50.05 nm. The features of the surface structures also depend on the types of metal inclusions in the deposits. SEM micrographs of the gold deposits containing only silver, only palladium and only nickel or combinations of silver-palladium and combinations of nickel-indium inclusions in the deposits can only give an indication of a very smooth surfaces with the majority of them displaying some globular growth features. Conversely with AFM imaging the transition from a faceted pyramidal-like island features to a morphology displaying distorted square structures stacked up in terraces and ridge features for certain samples can be clearly seen. XRD analysis also indicates the presence of Au (111) growth direction in all samples analyzed indicating that (111) planes of gold grow parallel to the copper (111) planes used as a substrate.

CHAPTER 1 INTRODUCTION

1.1 Brief history and development of gold plating

The history of gold deposition began in the early nineteenth century when many art objects were electroplated with gold. Gold electroplating formulations based on the double salt gold potassium cyanide was patented in 1840, since then many types of gold formulations have been produced to meet the market requirements. Due to the changing trends in fashion, the application of certain colors or shades of the electroplated gold can only last for about twenty or thirty years (Hunt, 1973, 1991; Weisberg, 1974a, b, 1993, 1997). The electronics industry began its development in the 1940's and 1950's; during this period platers were exposed to new demands for deposits with different properties that had been required for decorative plating. The electronics manufacturers required that the physical properties of the gold deposits be modified. They were interested in the conductivity, contact resistance, corrosion resistance, electrical as well as physical wear resistance, and the hardness and purity of the deposits. Since the properties of the electroplated gold films are influenced by the incorporation of impurities or inclusion of other metallic or non-metallic constituents, both electroplated soft and hard gold being used in the electronics industry faced no exception. This has led to the development of more gold and gold alloy baths (Foulke, 1974a; Weisberg, 1997; Blair, 2000; Okinaka, 2000). Gold plating was not only limited for decorative applications with the beginning of the electronics era. Nonetheless, the use of gold for decorative applications still contributes to about ten percent of present-day gold plated items (Blair, 2000).

1.2 Gold electroplating formulations

There are many electroplating systems in the market for depositing pure gold and gold alloys onto gold jewelry and onto base metals for decorative applications. There are also many others for technical applications such as electrical contacts and connectors, where the coating properties must have a certain technical performance. Generally there are eight classes of gold electroplate that are included in most of today's gold plating industries as listed in Table 1.1. These gold plating solutions covers five general groups as listed in Table 1.2 (Weisberg, 1993).

1.3 Fundamentals of metal deposition

Metal deposition is very important from the practical point of view because it is the basis of the electroplating, electrowinning, electrorefining and electrogalvanizing industries. It is also of fundamental interest since the deposition of a metal constitutes a model electrochemical system. The processes of metal deposition from vapor and from solution have many features in common. Both involve transport of metal atoms (ions) from the fluid phase to the surface, incorporation on to the surface, aggregation, and accumulation of a crystalline deposit. Vapor deposition is simpler due to the absence of a solvent and no electron transfer reaction at the metal-fluid interface is required. Deposition of metal at the metal-solution interface is also referred as electrocrystallization (Lyons Jr. 1974; Bard and Faulkner, 1980; Ritchie *et al.* 1999). There are three types of electrochemical processes for the deposition of metals from the solution, which are electroplating, immersion plating and electroless plating.

Table 1.1. General classes of gold electroplate used in gold plating industries
(Weisberg, 1993).

Class A	Decorative 24K gold flash, rack and barrel
Class B	Decorative gold alloy flash, rack and barrel
Class C	Decorative gold alloy heavy, rack. These deposits may be either C-1 karat color or C-2 karat assay
Class D	Industrial/electronic high purity soft gold, rack, barrel and selective
Class E	Industrial/electronic hard bright heavy 99.5% gold, rack, barrel and selective.
Class F	Industrial/electronic gold alloy heavy, rack and selective
Class G	Refinishing, repair and general. Pure and bright alloy, rack and selective brush
Class H	Miscellaneous, including electroforming of gold and gold alloys, statuary and architectural, etc.

Table 1.2. General groups of gold and gold alloy plating solutions (Weisberg, 1993).

Group 1	Alkaline gold cyanide (pH >10), for gold and gold alloy plating. Class A, B, C, D, occasionally F and G, and H
Group 2	Neutral gold cyanide (pH 6 - 9), for high purity gold plating. Class D and G
Group 3	Acid gold cyanide (pH 3.5 - 5), for bright hard gold and gold alloy plating. Occasionally Class B, C, E, F, and G
Group 4	Non-Cyanide, generally sulfite, for gold and gold alloy plating. Occasionally Class A, B, C, D, F, G, and H
Group 5	Miscellaneous

1.3.1 Electroplating process

The objective of an electroplating process is to prepare a deposit, which adheres well to the substrate and has the required mechanical, chemical and physical properties. The principal components used in an electroplating process are shown schematically in Figure 1.1. The item to be coated is connected to the negative pole of a direct current source and this is the cathode. The anode usually consists of a plate or rod of the metal to be coated which is connected to the positive pole of the direct current source. The current causes the anode to dissolve; this compensates for the loss from solution of metal ions that are deposited on the part to be coated. The object to be plated is made the cathode in an electrolyte bath containing a metal ion M^{n+} and the reaction at the cathode is as follows:



In general cases, M^{n+} may be a simple ion such as a hydrated Cu^{2+} or it may be a metal complex such as $[Au(CN)_2]^{-}$. The preferred anode reaction is the dissolution of the same metal to its precursor in the solution which is as follows:



Where subscript A and C denote anode and cathode respectively.

In an ideal case, metal M is simply transferred from the anode (A) to cathode (C), and the electrolysis condition are controlled in such a way that the current efficiencies of reaction [1.1] and [1.2] are the same and the concentration of M^{n+} in the bath remains constant. In a few cases, the metal ion has to be added as a solid salt and then an inert anode is employed. The anode reaction is then oxygen evolution (Pletcher and Walsh, 1993; Corti, 2002).

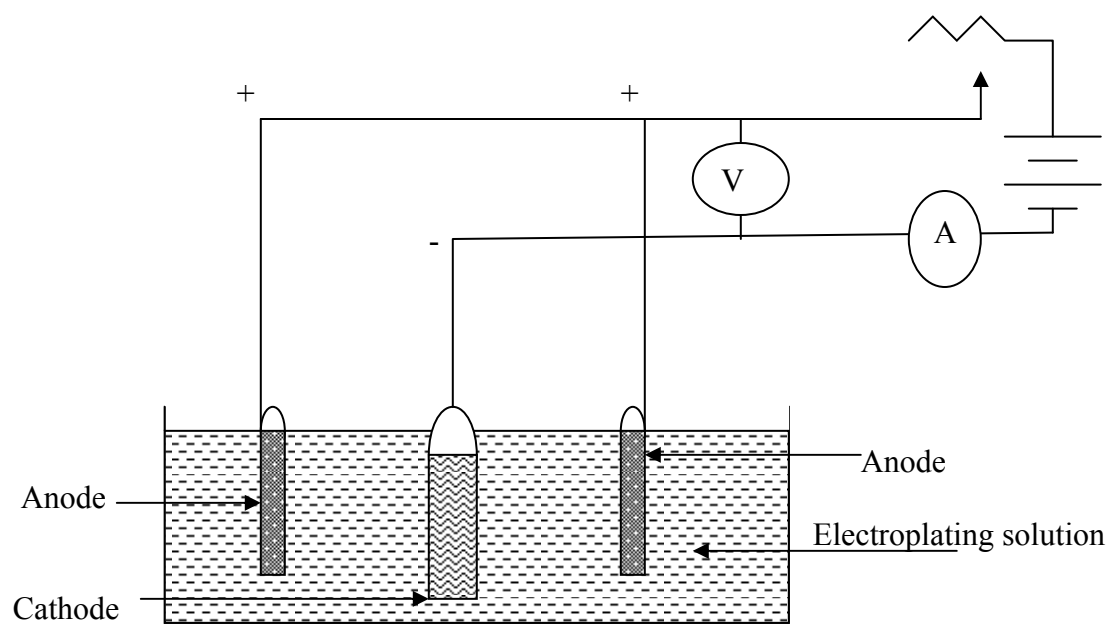


Figure 1.1. Schematic of electrochemical plating cell.

Electroplating is the only method by which metals with high melting points such as copper, nickel, chromium, silver, gold, platinum and rhodium can be deposited. Electroplated deposits have a fine structure and often have very valuable properties such as high hardness, high reflectivity etc. A great advantage of electroplating is that the thickness of the layer can be controlled to a fraction of a micron (Mohler, 1951).

1.3.2 Immersion deposition

This process is also called cementation or displacement deposition. The substrate is less noble than the metal in the solution; simple displacement occurs as the substrate metal M dissolves, the overall process is as follows:



M will deposit onto M_1 at a declining rate and often this type of deposit is porous with poor adhesion. The process will continue until the substrate is eventually covered with M and there is no more surface available for deposition to take place. This process does not require any reducing agent in the solution. The electrons are furnished by the substrate itself and immersion deposition ceases as soon as the substrate is completely covered by the coating (Parker, 1974).

1.3.3 Electroless deposition.

Electroless deposition is also referred to as deposition of metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy to be deposited. The process provides a continuous buildup of a metal or alloy coating on a suitable substrate by simple immersion in an appropriate aqueous solution. A chemical reducing agent 'R' in

the solution supplies the electrons for the reactions as shown in equation [1.5], where the reactions occur only on a ‘catalytic’ surface. The overall process is shown in equation [1.6].



The deposition of the metal is autocatalytic; once nucleation has occurred, further reaction is a favorable process and the deposition process will occur at a fast rate on the growing deposit (Lamouche *et al.* 1987; Iacovangelo and Zarnach, 1991; Iacovangelo, 1991; Lowenheim, 1995).

1.4 Chemical considerations of the electroplating bath.

Plating baths are normally composed of several chemicals where each of it serves one or more functions. Generally, these chemicals are a metal salt which provides the metal ions to be deposited and anions which form complexes with ions of the depositing metal and will also assist with anode dissolution. Many metals salts are rather poor conductors, where their ions are said to have low mobility. Therefore, to increase the conductivity, conducting salts are normally added to the plating bath. Phosphates, carbonates and citrates are commonly used as buffering and conducting agents for gold plating baths. In alkaline gold sulphite baths, metals such as Cd, Ti, Mo, W, Pb, Zn, Fe, In, Ni, Co, Sn, Cu, Mn and V as well as semi-metals such as Sb, As, Se and Te in various concentrations have been used as brightening additives (Foulke, 1974b, c; Lowenheim, 1995; Sun and Ivey, 1999).

Parameters such as metal content in the bath, temperature, rate of agitation, current density and pH should be optimized or modified to meet a specific goal. This means that plating baths should be continually maintained at optimum conditions to ensure the high quality of the deposit produced. Bath chemistry usually changes as the plating process proceeds, particularly rapidly in electroless plating and high speed electroplating with relatively small volumes and insoluble anodes. Therefore, in addition to the usual maintenance of metal ion concentration, pH and additives, baths must be treated periodically to remove or modify undesirable constituents such as impurities or degraded additives. Usually activated carbon is used for the removal of organic impurities or additives (Ostrow and Nobel, 1974).

1.5 Chemical properties of gold and its complexes

Since gold is always electrodeposited from aqueous solutions of gold complexes, knowledge of the characteristics of these complexes and in particular their stabilities are fundamental to any consideration of the electrodeposition of gold. Gold is classified, with Cu and Ag, in group IB of the periodic table and has a single s electron outside a completed d shell. Despite the similarity of these metals in electronic structures and ionization potentials, there are many important differences in their redox chemistry. Much of the chemistry of gold and its compounds, especially its behavior in aqueous solution, can be related to its relatively high electronegativity, i.e. the tendency to attract bonding electrons. Gold is very stable, as indicated by its lack of reactivity in air and in a majority of aqueous solutions, including strong acids (Wang, 1997). Gold is also the most noble of metals, it is the only metal that is not attacked by either oxygen or sulfur at any temperature (Puddephatt, 1978). The stability of gold is reduced in the presence of certain

complexing ligands, such as cyanide, halides, thiourea and thiocyanate by formation of stable complexes. As a result, gold can be dissolved in relatively mild oxidizing solutions, e.g. aerated aqueous cyanide solutions. This unique behaviour allows gold to be extracted very selectively from ores (Marsden and House, 1992).

Gold compounds exist almost exclusively in the Au(I) and the Au(III) oxidation states, although complexes of Au(IV) are known, and several Au(II) complexes have been identified in solutions. However, neither of the simple aquated ions Au^+ nor Au^{3+} occur in the free state to any significant extent. Gold compounds usually exist as complexes formed by covalent bonding between a central Au^+ and Au^{3+} cation and a number of ligands, which may either be ions such as Cl^- , Br^- , I^- , OH^- , CN^- , SCN^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, or uncharged molecules such as NH_3 , H_2O , Ph_3P , $(\text{NH}_2)_2\text{CS}$, etc. Ions, which can form stable complexes with gold, are listed in Table 1.3. Their stability constants show that some complexing ligands form more stable complexes with Au(I) and others with Au(III) (Puddhepat, 1978; Yannoupoulus, 1991; Marsden and House, 1992; Guan and Han, 1995). The stability constants of Au(I) and Au(III) complexes are important properties when electrodeposition of gold from these complexes is considered, since they determine the distribution of various forms of gold ions, such as free metal and complexed ions, which become available for discharge at the cathode. The stability constants of the complexes between gold ions and the ligands as well as the concentration of the ligands are the factors which determine whether the gold ions can be reduced from its complexed form during the process of electrodeposition.

Table 1.3. Stability constant β for selected Au(I) dan Au(III) complexes (Marsden and House, 1992; Wang, 1997).

Au(I)		Au(III)	
Complex	β	Complex	β
$\text{Au}(\text{CN})_2^-$	2×10^{38}	$\text{Au}(\text{CN})_4^-$	$\sim 10^{56}$
AuS^-	$\sim 10^{40}$	$\text{Au}(\text{OH})_4^-$	$\sim 10^{55}$
$\text{Au}(\text{SO}_3)_2^{3-}$	$\sim 10^{30}$	AuI_4^-	5×10^{47}
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	5×10^{25}	$\text{Au}(\text{SCN})_4^-$	10^{42}
$\text{Au}[\text{SC}(\text{NH}_2)_2]^{2+}$	$\sim 10^{25}$	AuBr_4^-	10^{32}
$\text{Au}(\text{OH})_2^-$	$\sim 10^{21}$	AuCl_4^-	10^{26}
AuI_2^-	4×10^{19}	$\text{Au}(\text{SO}_4)_2^-$	$\sim 10^6$
$\text{Au}(\text{SCN})_2^-$	1.3×10^{17}		
AuBr_2^-	10^{12}		
AuCl_2^-	10^9		
$\text{Au}(\text{NH}_3)_2^+$	1.4×10^{18}		

\sim * Approximate value

Table 1.4 shows the standard reduction potentials for the selected gold ions and their complexed ions. It shows that standard reduction potentials for reduction of Au(I) and Au(III) from their complexes are more negative than that from free Au^+ and Au^{3+} . The negative value of E° for $\text{Au}(\text{CN})_2^-$ explains why this complex is very stable in electroplating solutions. This also gives it the ability to codeposit gold with base metals. (Marsden and House, 1992; Wang, 1998). Gold is usually plated from cyanide solutions. The deposits produced from these types of solutions have a more fine-grained structure than those obtained from hydrochloric acid solutions, which are ordinarily used for gold refining. Gold is also plated from solutions prepared by dissolving the gold salt (gold chloride or fulminating gold) in potassium ferrocyanide (Puddephatt, 1978).

1.5.1 Electrochemical aspects of the gold deposition from gold complexes

For a metal M in contact with a solution of its ions, M^{n+} , deposition of the metal can be expressed by the reaction;



The reduction potential, E is given by the Nernst equation

$$E = E^\circ_{n/0} - \frac{RT}{nF} \ln \frac{(M)}{(M^{n+})} \quad [1.8]$$

Where R is the gas constant, T absolute temperature, $E^\circ_{n/0}$ is standard reduction potential and F is Faraday constant. If the convention is adopted that the activity of the solid phase (M) is unity and if it is assumed that, under the conditions of deposition of gold, the concentration $[M^{n+}]$ is equivalent to the activity (M^{n+}), the equation reduces to

$$E = E^\circ_{n/0} + \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad [1.9]$$

Table 1.4. Standard reduction potentials for selected gold ions and their complex ions
(Marsden and House, 1992).

Half-reaction	E^0 / V
Au (I)/ Au (0)	
$\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}$	+1.71
$\text{AuCl}_2^- + \text{e}^- \rightleftharpoons \text{Au} + 2\text{Cl}^-$	+1.154
$\text{AuBr}_2^- + \text{e}^- \rightleftharpoons \text{Au} + 2\text{Br}^-$	+0.96
$\text{AuI}_2^- + \text{e}^- \rightleftharpoons \text{Au} + 2\text{I}^-$	+0.578
$\text{AuI (s)} + \text{e}^- \rightleftharpoons \text{Au} + \text{I}^-$	+0.53
$\text{Au(CN)}_2^- + \text{e}^- \rightleftharpoons \text{Au} + 2\text{CN}^-$	-0.611
$\text{Au(SCN)}_2^- + \text{e}^- \rightleftharpoons \text{Au} + 2\text{SCN}^-$	+0.662
$\text{Au(S}_2\text{O}_3)_2^{3-} + \text{e}^- \rightleftharpoons \text{Au} + 2\text{S}_2\text{O}_3^{2-}$	+0.153
$\text{Au[CS(NH}_2)_2]_2^+ + \text{e}^- \rightleftharpoons \text{Au} + 2\text{CS(NH}_2)_2$	+0.38
$\text{AuOH} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{Au} + \text{H}_2\text{O}$	+2.33
Au(III)/ Au(0)	
$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$	+1.52
$\text{AuCl}_4^- + 3\text{e}^- \rightleftharpoons \text{Au} + 4\text{Cl}^-$	+1.002
$\text{AuBr}_4^- + 3\text{e}^- \rightleftharpoons \text{Au} + 4\text{Br}^-$	+0.854
$\text{AuI}_4^- + 3\text{e}^- \rightleftharpoons \text{Au} + 4\text{I}^-$	+0.56
$\text{Au(SCN)}_4^- + 3\text{e}^- \rightleftharpoons \text{Au} + 4\text{SCN}^-$	+0.636
$\text{Au}_2\text{O}_3 + 6\text{e}^- \rightleftharpoons 2\text{Au} + 3\text{H}_2\text{O}$	+1.51
$\text{A(OH)}_3 + 3\text{H}^+ + \text{e}^- \rightleftharpoons \text{Au} + 3\text{H}_2\text{O}$	+1.45

If these relationships are applied to the deposition of gold from free Au^+ and Au^{3+} ions, then at 25°C for the reaction of $\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}$,

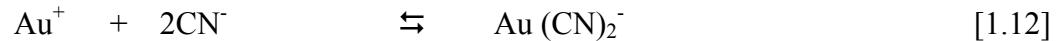
$$E = E^{\circ}_{1/0} + 0.0591 \log [\text{Au}^+] \quad [1.10]$$

For the reaction $\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$

$$E = E^{\circ}_{3/0} + 0.0197 \log [\text{Au}^{3+}] \quad [1.11]$$

As indicated by equations [1.9] and [1.10], the E values for the reduction Au^+ and Au^{3+} depend not only on the E° values for these ions but also upon the values of $[\text{Au}^+]$ and $[\text{Au}^{3+}]$. Complexing agents will affect $[\text{Au}^+]$ and $[\text{Au}^{3+}]$ and therefore can modify the conditions under which gold is deposited from the plating bath (Bard and Faulkner, 1980; Yannopoulos, 1991; Marsden and House, 1992; Wang, 1997).

When cyanides are added to the Au^+ solutions, Au^+ ion forms complexes shown by the following equation:



This is a linear complex and is the most stable formed by Au(I), where its stability constant in aqueous solution has been estimated as 10^{39} . The potassium salt $\text{K}[\text{Au}(\text{CN})_2]$ which is known as Potassium Gold Cyanide (PGC), is the most commonly used in gold electroplating and can be prepared by dissolving gold powder in potassium cyanide (KCN) solution in the presence of air. The other alternative for preparing this salt is by the electrolytic method based on dissolution of a pure gold anode in aqueous potassium cyanide solution. When the solution of colorless $\text{K}[\text{Au}(\text{CN})_2]$ is treated with 2M HCl and heated to boil, decomposition occurs and lemon yellow colored AuCN will be crystallized from the solution (Puddephatt, 1978).

1.6 The applications of gold electroplating

1.6.1 Industrial/ Electronic gold plating

Electroplated gold used in the electronics industry can be broadly classified into two categories: soft gold and hard gold. Soft gold is used mainly in the fabrication and packaging of semiconductor devices and is generally plated from cyanide baths with the addition of a small amount of Tl^+ , Pb^{2+} or As^{3+} ions (Douglas, 2002). Hard gold are widely used as contact materials on electrical connectors and printed circuit boards. In these applications, wear resistance and electrical contact resistance are the properties of primary concern. These baths contain complexed cobalt or nickel in small quantities, to improve hardness and brightness of the deposit (Nakahara and Okinaka, 1980).

1.6.2 Decorative gold plating

The decorative properties of gold deposits are superior compared to other metal deposits (Puddephatt, 1978). Gold has a high chemical resistance; it dissolves only in aqua regia or in a mixture of hydrochloric and chromic acids. Gold unlike silver does not become tarnished, because it does not react with hydrogen sulfide or with any other sulfur-containing agent. A great advantage of electrolytically obtained gold deposits is that their hue can be varied greatly by adding other metals to the solution or to the anodes, which are then codeposited with gold. It is obvious that gold deposits are used mainly for decorative purposes, particularly if the surface has to remain attractive and bright for a long time (Mohler, 1951).

Today's decorative gold plating processes are applied with varying thickness to a very wide range of consumer products such as watchcases and bands, plumbing fixtures,

writing instruments, jewelry, eyeglass frames, cigarette lighters, fashion accessories and lighting fixtures. Most costume jewelry that are marked “gold flash” or left unmarked, is plated with two to four micro inches of gold over bright nickel with the plating time of 5 to 30 seconds.

Watch cases, watch bands and writing instruments are often plated to thickness of 2 to 5 microns (80 to 200 microinches). The watch industry often uses duplex gold by first applying a thick deposit of alloy gold followed by hard acid gold deposit of up to 0.5 microns (20 microinches). This final layer of gold also provides the final color. Plumbing, bathroom and kitchen accessories usually fall into two segments. Those that are plated with gold to the thickness ranging from a minimum of 0.5 microns to 3 microns or more (20 microinches to 120 microinches) are marketed to the luxury markets. The other utilizes flash deposits of 0.075 microns to 0.125 microns (3 to 5 microinches), followed by a topcoat, either clear powder coat or electrophoretically applied lacquers. Fashion jewelry typically uses deposits ranging in thickness from a flash of 0.075 microns to 2.5 microns or more (3 to 100 microinches) of hard gold deposit. The recommended trade practice rules for the jewelry industry require that this deposit be called gold flash or gold wash. In order to be called gold electroplate, it is necessary to have a minimum thickness of seven to thirty microinches, while gold deposits over 100 microinches are considered as “heavy gold electroplate” (Weisberg, 1997; Douglas, 2002).

1.7 Introduction to colored gold plating

Gold can be colored to various colors and this can be achieved metallurgically by alloying gold with two, three, four or even more elements. The same can be achieved

electrochemically. However, the difficulties in controlling the composition and inclusion can multiply almost exponentially as the number of alloy constituents increase (Lowenheim, 1995). Almost all conventional colored carat golds are based on gold-silver-copper alloys. The three metals have the same crystal structure (face cubic centered, FCC) and so are compatible with each other over a large range of compositions. Pure (24 carat) gold is a deep yellow color of an orange shade of yellow and is very soft and malleable. The colored carat gold alloys range in gold content from 8 to 22 carats (33.3% to 91.6% gold) and can be obtained in a range of color shades: green shades of yellow, pale yellow, yellow, deep yellow, pink/rose and red. There are also white gold and even unusual colored gold such as purple gold. They all have different mechanical properties such as strength, hardness and malleability (ductility) and so alloys can be heat treated to maximize strength and hardness. Likewise, the electroplating of gold alloys has been established in the metal finishing industry and typical baths have been described elsewhere (Duffy, 1981; Dettke, 1991; Lowenheim, 1995; LeaRonal, 1997). The problem of codepositing two (or more) metals in the form of alloys does not differ from that of depositing a single metal. However, in practice finding conditions for the deposition of an alloy in the form of an adherent, coherent, and useful deposit is not easy. Two basic conditions that are useful in codepositing two metals are: first, at least one of the metals must be capable of being independently deposited alone; and second, their deposition potential must be fairly close together. This is due to the fact that there is only one potential at a time at any electrode, therefore, for two metals to codeposit simultaneously at an electrode, they must take place at the same potential. To achieve this, the conditions must be arranged so that the more

electronegative (less noble) potential of the less noble metal can be reached without using an excessive current density.

Alloy plating is employed to deposit two or more metals simultaneously. This method is used in a variety of applications, because the produced plating can vary in many respects, including color and physical properties, depending on the ratios of the deposited metals. For two or more metals to be deposited simultaneously and for the deposit ratio among the metals to be the same through a wide current-density range, various substances are added to keep the electrodeposition potentials of different metals as close to each other as possible. As a result, the solution composition is complicated. The table of standard electrode potential (Table 1.5) is a rough guide for deciding whether two metals can be co-deposited from simple salt solutions. The table of electrode potentials can be used to predict the alloy plating possibilities, thus metals that are close together in the table are in general easier to codeposit than metals that are far apart (Lowenheim, 1995).

In colored gold electroplating, only thin “flash” coatings are normally deposited, and the amount of gold used represents only a very small percentage of the total amount consumed in electroplating. These types of gold baths are formulated with less than 4 grams per liter of gold and are normally operated at high temperatures to achieve bright deposits. The color of the gold alloy deposits are very much dependent on the composition of the electrolyte, the operating current density (voltage) and the degree of agitation (Weisberg, 1993). Therefore, to achieve a certain color, all operating conditions should be controlled as closely as possible (Foulke, 1974c). Too low a current density tends to favor the deposition of gold and causes the alloy to become richer, too high a current density at first favors the alloys and pales out the color while further raising the current density

Table 1.5. Standard oxidation electrode potential for selected metals (Marsden, and House, 1992; Lowenheim, 1995).

Electrode	Potential, V	Electrode	Potential, V
$\text{Li} \rightleftharpoons \text{Li}^+ + \text{e}^-$	-3.045	$\text{Co} \rightleftharpoons \text{Co}^{++} + 2\text{e}^-$	-0.277
$\text{Rb} \rightleftharpoons \text{Rb}^+ + \text{e}^-$	-2.93	$\text{Ni} \rightleftharpoons \text{Ni}^{++} + 2\text{e}^-$	-0.25
$\text{K} \rightleftharpoons \text{K}^+ + \text{e}^-$	-2.924	$\text{Sn} \rightleftharpoons \text{Sn}^{++} + 2\text{e}^-$	-0.136
$\text{Ba} \rightleftharpoons \text{Ba}^{++} + 2\text{e}^-$	-2.90	$\text{Pb} \rightleftharpoons \text{Pb}^{++} + 2\text{e}^-$	-0.126
$\text{Sr} \rightleftharpoons \text{Sr}^{++} + 2\text{e}^-$	-2.90	$\text{Fe} \rightleftharpoons \text{Fe}^{3+} + 3\text{e}^-$	-0.040
$\text{Ca} \rightleftharpoons \text{Ca}^{++} + 2\text{e}^-$	-2.87	$\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$	0.0000
$\text{Na} \rightleftharpoons \text{Na}^{++} + 2\text{e}^-$	-2.175	$\text{Sb} \rightleftharpoons \text{Sb}^{3+} + 3\text{e}^-$	+0.150
$\text{Mg} \rightleftharpoons \text{Mg}^{++} + 2\text{e}^-$	-2.37	$\text{Bi} \rightleftharpoons \text{Bi}^{3+} + 3\text{e}^-$	+0.20
$\text{Al} \rightleftharpoons \text{Al}^{3+} + 3\text{e}^-$	-1.67	$\text{As} \rightleftharpoons \text{As}^{3+} + 3\text{e}^-$	+0.30
$\text{Mn} \rightleftharpoons \text{Mn}^{++} + 2\text{e}^-$	-1.18	$\text{Cu} \rightleftharpoons \text{Cu}^{++} + 2\text{e}^-$	+0.34
$\text{Zn} \rightleftharpoons \text{Zn}^{++} + 2\text{e}^-$	-0.762	$4\text{OH}^- \rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	+0.401
$\text{Cr} \rightleftharpoons \text{Cr}^{3+} + 3\text{e}^-$	-0.74	$\text{Cu} \rightleftharpoons \text{Cu}^+ + \text{e}^-$	+0.52
$\text{Cr} \rightleftharpoons \text{Cr}^{++} + 2\text{e}^-$	-0.56	$2\text{Hg} \rightleftharpoons \text{Hg}_2^{++} + 2\text{e}^-$	+0.789
$\text{Fe} \rightleftharpoons \text{Fe}^{++} + 2\text{e}^-$	-0.441	$\text{Ag} \rightleftharpoons \text{Ag}^+ + \text{e}^-$	+0.799
$\text{Cd} \rightleftharpoons \text{Cd}^{++} + 2\text{e}^-$	-0.402	$\text{Pd} \rightleftharpoons \text{Pd}^{++} + 2\text{e}^-$	+0.987
$\text{In} \rightleftharpoons \text{In}^{3+} + 3\text{e}^-$	-0.34	$\text{Au} \rightleftharpoons \text{Au}^{3+} + 3\text{e}^-$	+1.50
$\text{Tl} \rightleftharpoons \text{Tl}^+ + \text{e}^-$	-0.336	$\text{Au} \rightleftharpoons \text{Au}^+ + \text{e}^-$	+1.68

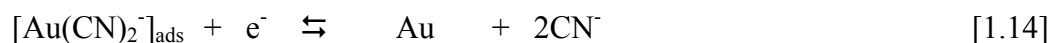
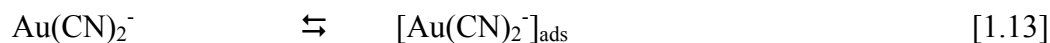
causes the development of pink or orange or red tones to the deposits. The effect of temperature is similar to current density. Low temperatures favor the gold yellow and higher temperatures favor the alloy colors. Temperatures over 70°C should be avoided, except in the rose gold, because of the rapid breakdown of cyanide and the darkening of the color.

Gold plating solution containing copper is very sensitive to changes in free cyanide content. Low cyanide causes an increase in the pink or red shades and high cyanide significantly increases the yellow by holding back the copper. It is rarely necessary to adjust the pH of a gold or gold alloy bath. They are usually buffered between 10 to 11. Only pink or rose or red gold are favored by higher readings (Weisberg, 1993). In addition, there are other factors that will alter the color of the deposits, for example the surface finish of the basis metal will also affect the apparent color of the deposit. The color of the basis metal could also alter the color of the gold deposit by adding its color to the gold until the deposits are sufficiently thick to obscure the base. Various gold formulations of different shades with and without metals addition in the electroplating bath have been reported by many researchers and the list of commercially available gold plating formulations is attached in the Appendix I (Foulke, 1974a, b, e, f; Duffy, 1981; Dettke, 1991; LeaRonal, 1997; Weisberg, 1997).

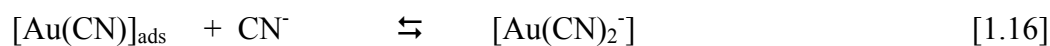
1.8 Gold electrodeposition process

The technology for gold plating processes from various electrolytes is quite well developed and is briefly reviewed here. The deposition of gold from Au(I) cyanide complex in alkaline cyanide (pH = 12.2) is believed to occur both by direct reduction of

Au(CN)_2^- and by the formation of an intermediate (MacArthur, 1972). The electrochemical reaction, which takes place during the reduction from alkaline solution occurs at the cathode as follows:



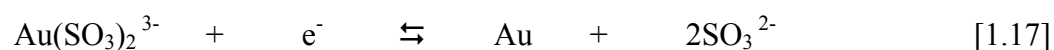
The oxidation reaction at the anode is



Cathro and Koch (1964) used potentiostatic and galvanostatic measurements on gold oxidation in an alkaline cyanide electrolyte. They concluded that gold was oxidized to $[\text{Au(CN)}_2^-]_{\text{ads}}$ at potential less than - 0.6V (SCE reference) and became passive in the potentials range - 0.6 to - 0.3V through the formation of gold oxide or basic cyanide. In 1972, MacArthur used voltammetric and galvanostatic techniques to study the gold reduction in the alkaline cyanide solution and postulated a two-reduction pathway. One reduction pathway at low over potentials involved $(\text{AuCN})_{\text{ads}}$ as the reactive species. The other, at high over potentials involves a direct charge transfer to soluble Au(CN)_2^- . In 1976 McIntyre and Peck reported their investigation of gold deposition in the presence of heavy metal ions including lead and thallium and this is where the electrodeposition of gold alloy has been investigated, however they only limited their research to the polarization study. Eisenmann (1978) also studied gold alloy deposition where he focused on the kinetics of gold deposition from two commercial hard gold baths and soft gold baths containing lead ions.

Besides cyanide containing baths, gold chloride electrolytes have also been used in the early days of gold plating, however today they are employed almost exclusively in the electrochemical refining of gold (Sun and Ivey, 1999). The mechanism of the deposition of gold from solution of Au(II) square planar complexes was studied by Watt and Cunningham (1963). They reported that the deposition from potassium Au(II) chloride, bromide and cyanide occurs with approximately 100% current efficiency from undissociated complexes. Investigations of the cathodic behavior of Au in chloride solutions have shown that the quality of the cathode deposit is strongly influenced by the relative amounts of Au(I) and Au(III) in the solution. The reduction of Au(III) chloride to metal can be expected to involve the formation of Au(I) as an intermediate species. Under plating conditions, Au will be deposited from both Au(III) and Au(I) species (Yannopoulos, 1991; Marsden and House 1992;).

Gold is also electroplated from the Au(I) sulphite complex as shown in the following reaction.



The sulphite complex is less stable than the cyanide complex but it has the advantage of being less toxic. The sulphite baths are also capable of producing deposits with a wide range of properties through suitable manipulation of plating conditions and bath composition (Horkans and Romankiw, 1971; Foulke, 1974a, b, c; d, e, f, g; Morrissey, 1993, 2000; Honma and Kagaya, 1993; Wang *et al.* 1996, 1998). The gold sulphite complex ($\text{Na}_3\text{Au}(\text{SO}_3)_2$) is the only viable gold plating solution that is cyanide free. However, these alkaline solutions work best if preceded by a cyanide-based gold strike (Blair, 2000). Nakahara and Okinaka (1981) has studied the deposition of gold in additive

free hard gold formulations and they reported that AuCN has also been codeposited, bringing about a grain refining effect and resulting the increase in hardness.

The most stable complexes of Au(I) and Au(III) are those that are formed with the cyanide ion. It is therefore not surprising that the majority of industrially important processes involving gold in solution are based on the use of cyanide. A number of studies on gold dissolution in concentrated cyanide solutions have also been done (Cathro and Koch, 1964; Kirk *et al.* 1978). Although the cyanide-containing baths are toxic, but they also have been associated with having the widest color range. The formulations based on potassium gold cyanide, free potassium cyanide and coloring additives are extremely versatile, offering flash coats, thin and thick deposits. Alloy deposits are often used in duplex gold systems and electroforming. This has made the cyanide system more suitable than the other system when it comes to decorative plating which requires a wide color range. However, as improvements have been made in other systems, the future use for alkaline cyanide gold will mostly limited to alloys, duplex systems, and electroforming (Foulke, 1974a; Douglas, 2002).

Much of the earlier work on gold electroplating processes was conducted to study their electrochemical behavior in various media. Even the microstructure properties in various types of applications and situation have been studied in detail. For example Cheh and Sard (1971) had used the galvanostatic techniques to study the electrochemical and structural aspects of gold deposition from dilute cyanide, citrates and phosphates buffered plating solutions and found that the alkaline cyanide system showed the greatest tendency to form an outward growth morphology consisting of fine features termed spikes that are responsible for the characteristic brown appearance of deposits plated under a wide variety

of conditions. He also initiated the reflectivity measurements on gold deposits and found that the index of reflectivity (R_s) correlates reasonably with deposit morphology in most cases. Since then there has been no publications concerning optical properties of the electrodeposited gold alloy films. In 1974, Reinheimer studied the contaminations of carbonaceous material in the gold deposits plated from pure phosphate and citrate buffered KAu(CN)_2 solutions and concluded that an increase of the bath temperature results in a lower carbon content. Rao and Weil (1980) studied the initial stage of epitaxial electrocrystallization of gold from an additive free alkaline sulfite solution on polycrystalline copper and silver substrates. Later, in 1981 Holmbom and Jacobson compared the nucleation and initial growth of pulse plated gold versus direct current plated gold electroplated from equivalent conditions. The mechanisms of how cobalt, nickel, lead and thallium affect the grain size of the electrodeposited gold were studied by Bindra *et al.* (1989) where the degree of grain growth during deposition of the films was found to correlate with the hardness of the films deposited in the presence of cobalt and the softness of the films deposited in the presence of lead.

The most striking feature of developments in the electroplating field for the past two decades has been the growth in the use of gold plating for industrial applications, a growth directly related to the rapid development in the electronics and telecommunications over the same period. Decorative gold plating has also developed side by side with the industrial gold plating. Information about the chemical and electrochemical behaviors of the gold ions has provided the scientific basis to optimize plating conditions and to control plating processes. A few reports on studies of the effect of incorporated or inclusions of metallic and non metallic material to the physical and morphological properties of the