Electroless Gold for Micro and Macro Electronic Applications

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Traditionally pure gold deposits for electronic applications have always been electroplated, although very thin pure gold deposits have been available as "immersion" deposits up to 0.1 µm maximum. During the last few years the requirements to produce a bondable pure gold with a thickness of up to 2.0 microns on complex and difficult substrates has developed. This paper will describe a new non cyanide process for the electroless gold plating of PCB's, DCB's and Hybrid type products. The process operation conditions and results obtained will be described in detail.

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Electroless Gold Plating

INTRODUCTION

Electroless Plating. (1)

Electroless plating processes deposit a uniform thickness of metal onto parts by chemical reduction (no current is required). This allows complex parts to be plated evenly and completely, even over sharp edges and deep recesses. Electroless Nickel (Ni/P) and Electroless Copper processes are the most widely used in the market. They are both "autocatalytic" (self-cataysing), in that they will continue to plate onto their own deposits after the substrate has been completely covered. They can usually be plated to substantial thicknesses unlike the traditional "Immersion" deposits.

In recent years electroless systems using precious metals have been developed to meet the requirements of the Electronics Industry where more complex designs have limited the use of the more traditional techniques. Electrolytic methods were found to be difficult due to the need for interconnection and immersion techniques limited due to insufficient thicknesses achieved. Immersion plating is sometimes referred to as electroless plating. This is incorrect. The mechanism is chemical displacement…..the substrate metal acts as a reducing agent to displace metal ions from their solutions and coat the surface. Plating only occurs when the substrate metal has a lower oxidation potential than the metal in solution and continues only as long as the substrate metal is exposed. Plating will proceed through the pores in the deposit to build the deposit but at the same time dissolving the basis metal. Eventually the coating builds up to its maximum thickness where the plating rate is so slow to have effectively stopped.

For Example Nickel will not deposit onto copper, it requires a promoter (often Pd).

Gold will deposit onto nickel. Maximum thickness 0.25 microns, typically 0.1 micron.

Gold Plating. (2)

Gold is one of the most noble metals and is counted among those metals with the best electrical properties. These combined features make gold a logical choice for electronic circuitry and interconnection applications. It's only restriction in use being it's high price.

Much of the development and technology associated with gold recently has been related to minimising this cost of gold deposition . Significant reductions in the use of gold for electronic contacts and semi-conductor devices have been achieved whist maintaining performance. Significant reductions in the amount of gold used has been achieved over the years by the use of,

a) Reducing the minimum gold thickness.
b) Improvement in the distribution of the gold deposit.
c) The greater use of selectively plating techniques.

It is with this last area (selective plating) we are to consider here as it could be said that electroless plating is a selective technique where with the use of a mask (or not) the electroless plating can be applied only to the area required.

With the continued growth in the electronics market the need for gold plating has increased in terms of numbers of components plated and newer techniques to plate this gold particularly in the microelectronics market have become evident.

Classically cyanide systems have been tried using borohydride or dimethylamineborohydride (3,4,&5) as the reducing agent. These baths were autocatalytic and met the requirement of producing a pure soft bondable gold. Unfortunately often the photoresists used with the process were not stable in these baths due to the cyanide present and the alkalinity of the bath.

Gold salts other than cyanide have been investigated . They include gold sulphite, gold thiosulphate, gold thiomalate, gold chloride and gold phosphate. Of these the most extensive development work has been with the sulphite gold. Okinaka and Hoshimo reported in the Gold Bulletin 1998 (6) on the various types of gold process (non-cyanide) available.

It was reported that the non-cyanide type baths described were not considered to be stable enough to have practical applications. Baths containing both Sulphite and Thiosulphate were reported to be more stable and baths containing Thiourea (7, 8 & 9), ascorbic acid (10,11 & 12), hypophosphite (13) or Hydrazine (14) as the reducing agent have been developed. Okinaka and Hishino (6)gave details of examples and operating conditions. See table IV

Devices to be thermally bonded require a pure gold deposit (usually greater than 99.9%) with a freedom form porosity. This paper will therefore describe a new non-cyanide pure gold process capable of producing deposits deposits up to 3 microns from an electroless bath.

Features of The Electroless Gold

Non cyanide	-	Neutral bath solution
Long bath life	-	Continual use and replenishment
Lemon yellow and matt deposits	-	Fine grain size
Low hardness	-	Uniform thickness
Good bondability	-	Not sensitive to photo resist

APPLICATIONS

Printed Circuits	Glass printed circuit

P-BGA	Tape carrier package T-BGA
Ceramics and glass board	Circuits on silicon wafers

THE ELECTROLESS GOLD SOLUTION

The Electroless Gold Solution is non-cyanide type electroless plating solution based on Sodium Gold Sulphite.

The Electroless Gold Solution is specially designed to obtain thick and uniform gold film on complicated patterns.

The Electroless Gold Solution is self-catalytic and contains reducing agents.

The Electroless Gold Solution has high plating rate.

The Electroless Gold Solution has long bath life and gold can be replenished during continual use.

The pH Electroless Gold Solution is around 7.0 and therefore the solution is mild for the substrate.

The Electroless Gold Solution is suitable for surface treatment of electronic parts especially for the photo-resist coated parts with high mounting density.

SUBSTRATES FOR GOLD PLATING

Precious metals such as Pt, Pd, Rh and Au can be plated directly with the Electroless Gold.

Base metals which are pre-coated with an Immersion type gold can be plated. Electroless Ni-P plating deposits are most suitable for Electroless Gold plating following Immersion Gold pre-plating.

Note: Thickness and adhesion depends on the kind of substrate and pre-treatment.

PLANT & EQUIPMENT

As with all electroless systems due to their activity care should be taken when determining the plant and equipment to be used.

1) Tank Design.

Polypropylene with a very smooth surface is acceptable. Roughening of the surface should be avoided at all costs as this can promote the deposition of gold. Glass lined or enamel lined materials along with acrylic resin and smooth polypropylene are recommended.

2) Filtration.

As with other electroless systems filtration is important to maintain the stability of the bath as well as for the usual reasons of keeping the bath free from particles. Especially important in microelectronic devices.

A one micron filter should be used for this application filtering usually twice a day. It is not usual to filter during plating.

3) Agitation.

3.1.) In order to maintain the solution stability air should be bubbled through the solution during plating. This air bubbling is usual also during the heating of the solution and during the cooling down. Weak air bubbling is recommended and it will increase the solution life. Obviously the air bubbling should be kept away from direct impingement on the parts to be plated.

3.2.) Moderate agitation will also be required to maintain the solution temperature. A continuous circulation system is not recommended as gold can deposits can build up in the pump. Heating:
Indirect heating is recommended. Mechanical agitation is therefore preferred including of the parts to be plated.

4) Heating.

Indirect heating is recommended. Direct heating can lead to deposits around the heater. If a direct heater has to be used then this should be a Teflon sheathed type with a wide heating area, therefore avoiding local hot areas.

5) Cooling Equipment.

For batch plating cooling equipment is not required. However for continuous plating this may be required.

OPERATING CONDITIONS.

The bath is operated as per Table 1.

1) Temperature.

The bath should be kept below 80^{o}C in order to avoid decomposition of the solution. The bath is recommended to operate at 70^{o}C. It can be seen clearly from Table 2,3 & 4 how plating speed increases with temperature.

2) pH.

The pH should be kept in the range 6.0-7.5 in order to maintain solution stability. The pH is adjusted with Sodium Hydroxide to increase the pH and Sulphurous Acid to decrease the pH.

3) Specific Area.

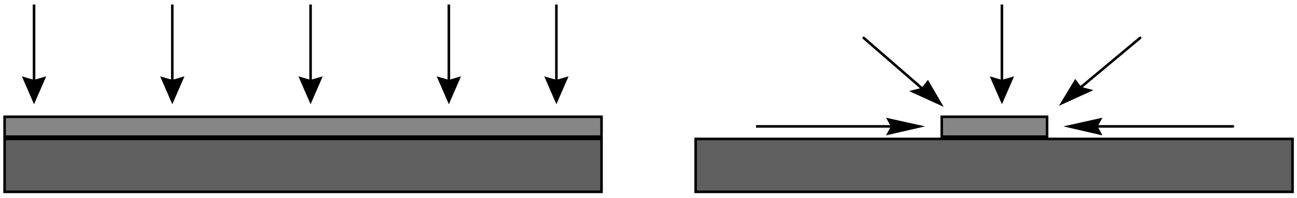
As per Table 1, this is quire wide. However care should be taken in order not to overload the bath and reduce the gold content significantly during plating. If this happens the plating rate can reduce, see tables 2, 3 & 4.

4) Stabiliser Effect.

It has been noticed when plating circuitry with a large variation of land areas that some distribution effects can be seen. This effect is caused by the effect of the stabiliser. In comparisons, smaller land areas can be over stabilised due to excessive stabiliser effect. This can lead to differences in the plating rate, hence overall thickness. Therefore control of the stabiliser is important for the type of work to be plated.

principle:

stabilizer concentration:



5) Gold Content.

This needs to be maintained to achieve a consistent plating rate and therefore final thickness.

6) Reducer Content.

This also must be maintained within its range to ensure the plating rate is consistent.

MAKE-UP

Example on the make up conditions for 10 litres.

Before making up, clean a tank, container, filter and other equipment sufficiently with demineralised water to ensure a good thorough cleansing has occurred..

1) Pour 5 litres of Make-up Solution into the container. This solution will contain the gold complex.

2) Pour 5 litres of Make-up Solution R into the container with stirring. This solution will contain the reducer complex.

It is normal for electroless solutions to be supplied as a two part system keeping the gold complex and the reducer separate in their concentrated form. Mixing together only occurs in the diluted form.

3) Keep stirring and mix enough.

4) Start air-blowing into the made up solution with the air bubbler.

5) Heat the solution to set temperature.

6) Check the pH. (Gold concentration is 4.0 g/l and pH is around 7.0).

MAINTENANCE OF SOLUTION

1) **Gold Concentration and Reducer Concentration.**

Maintenance of gold concentration of the Electroless Gold is most important for keeping the deposition rate and stability.

10 ml of Gold Replenisher is used corresponding to 1 gram of gold.

10 ml of Reducer Solution is added at the same time of gold replenishment.

For exact replenishment, periodical analysis of gold and other components is important.

2) **Temperature**

Temperature is an important factor to obtain the constant deposition rate. Keep the temperature shown on table 1.

Below 60°C, deposition rate of gold tends to decrease and above 80°C the solution tends to degenerate.

3) **pH**

Increase with Sodium Hydroxide

Decrease with Sulphurous Acid.

4) **Specific Area**

As specific area decreases, deposition rate of gold increases but stability of solution decreases.

5) **Filtration**

Filtration is needed periodically.

TREATMENT PROCESSES

For ENIG

Acid clean → Water rinse → Chemical etching → Water rinse → Acid → Water rinse

Pd activator → Water rinse → Acid → Water rinse → Electroless nickel plating

Water rinse → Immersion gold plating → Water rinse → Hot water rinse → Dry

For BGA and other electroless applications

Acid clean → Water rinse → Chemical etching → Water rinse → Acid → Water rinse

Pd activator → Water rinse → Acid → Water rinse → Electroless nickel plating

Water rinse → Immersion gold plating → Water rinse → Electroless gold plating

Water rinse → Hot water rinse → Dry

Other Applications.

Substrate (PCB, BGA) → Acidic degreasing → 10% H_2SO_4 dipping → Soft chemical etching →

10% H_2SO_4 dipping → Activating → Accelerating → Electroless Nickel → Immersion Gold →

Electroless Gold.

Note: Nickel deposits should not be plated with Electroless Gold directly.

RESULTS FROM PRODUCTION.

Thicknesses of up to 3 microns have been achieved consistently in production. At above three microns the plating rate slowed substantially.

The plating rate was directly influenced by Temperature. The higher the Temperature the higher the plating rate. See tables 2, 3 & 4.

Solderability trials were carried out with the thinner gold deposits and found to be acceptable both before and after life testing (steam ageing etc.).

Of course much of the requirement to plate thick gold is related to the need to wire bond to the deposit. Bonding trials were conducted as per Table 7 and the results shown in Tables 8 and 9. Bonding was and is satisfactory.

CONCLUSIONS.

This new non cyanide system is workable system and is currently being used in production. It will produce deposits up to 3 microns with satisfactory bonding. It can be used for thinner deposits if solderability is the requirement. The process can be replenished (see Table 6).

Future work will look at developing the process to achieve greater thicknesses, faster plating rates (without losing stability) and increasing the bath life (no of turnovers).

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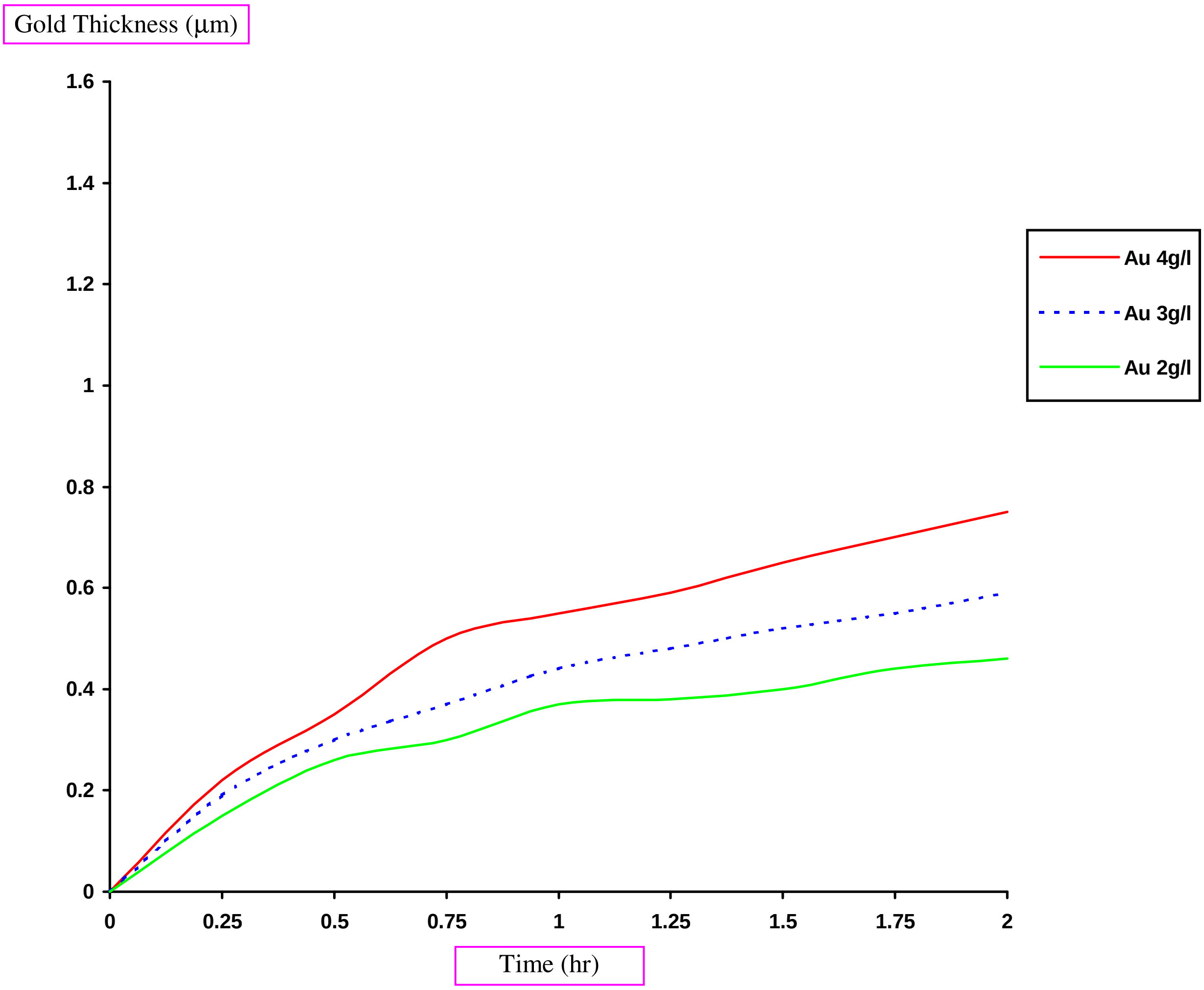
TABLE 1

OPERATING CONDITIONS

DESCRIPTION	RANGE	OPTIMUM
Gold Content	3.0 - 4.5 g/l	4.0 g/l
Temperature	65 - 75°C	70°C
Reducer	15 - 30 mls/litre	25 mls/litre
pH	6.0 - 8.0	7.0
Agitation	moderate – weak	moderate
Air-blowing	mild bubbling	
Specific Area	0.1 - 4 dm^2/L	1 - 2 dm^2/L
Plating Rate	0.7 - 1.0 µm/hr	

Note: Plating Rate depends on substrates and plating conditions.

TABLE 2



Effect of Plating Time on Gold Thickness

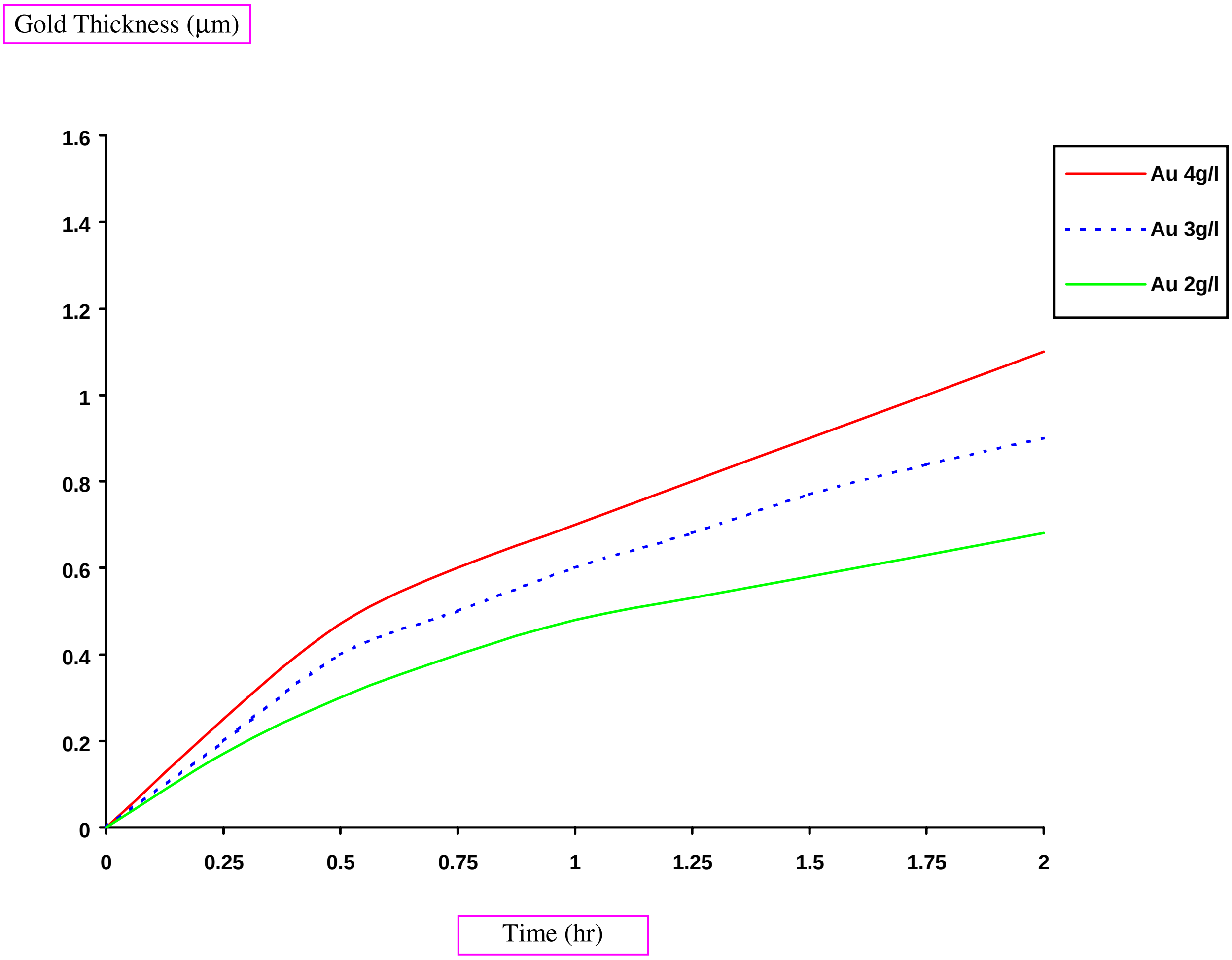
Operating Condition:

pH : 7.0

Temperature : 65°C

Agitation : Medium

TABLE 3



Effect of Plating Time on Gold Thickness

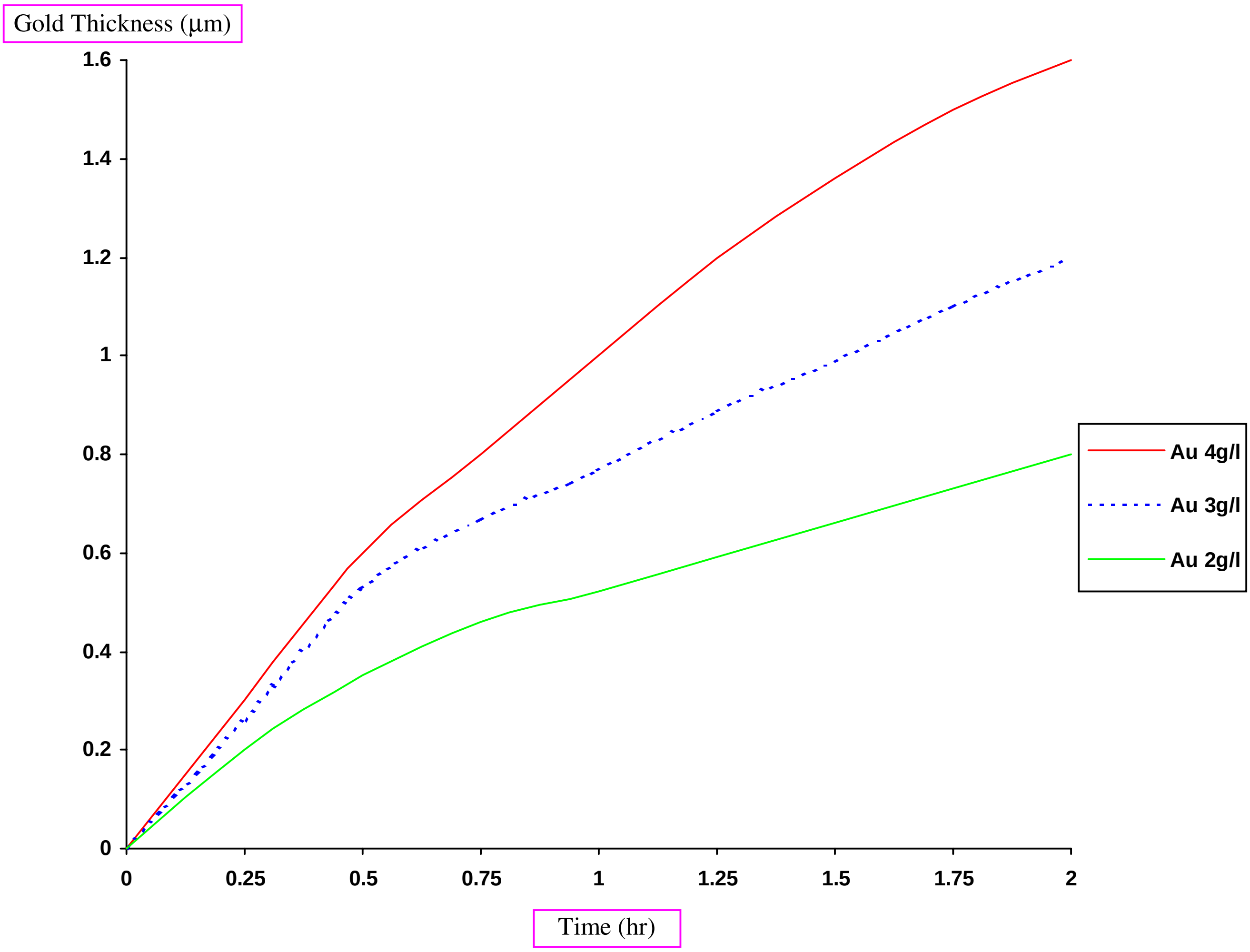
Operating Condition:

pH : 7.0

Temperature : 70°C

Agitation : Medium

TABLE 4



Effect of Plating Time on Gold Thickness

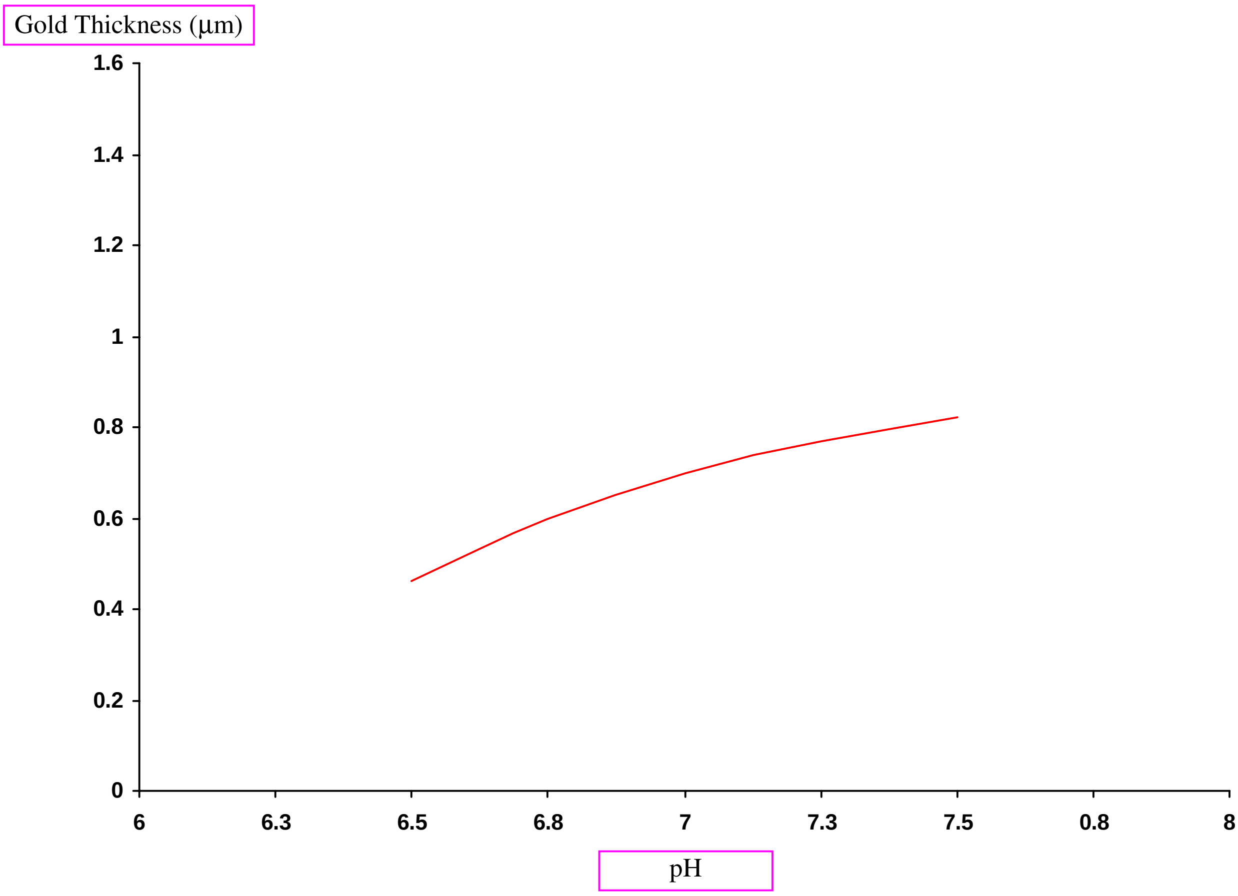
Operating Condition:

pH : 7.0

Temperature : 75°C

Agitation : Medium

TABLE 5

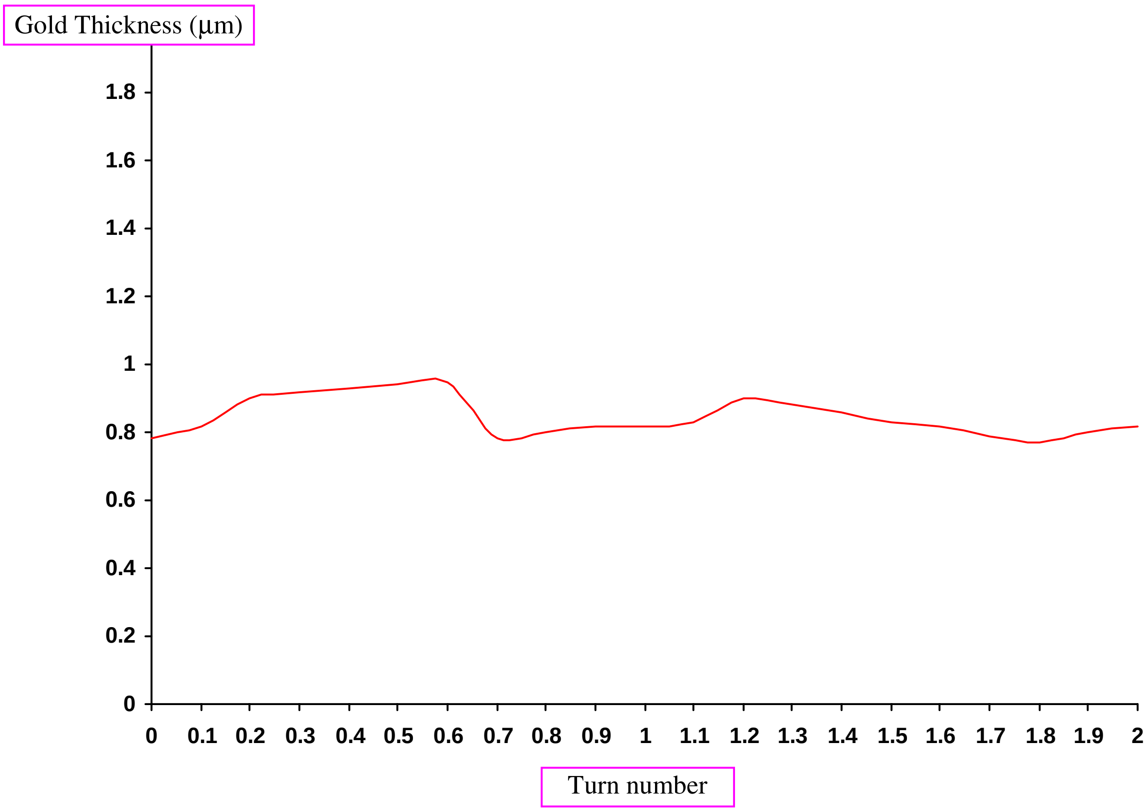


Effect of pH on Gold Thickness

Operating Condition:

Au content	:	4.0 g/l
Time	:	1 hr
Temperature	:	70°C
Agitation	:	Medium

TABLE 6



Replenishment Test

Operating Condition:

Solution	:	Au: 4g/l, pH: 7.0, V: 1 litre)
Plating sample	:	Pcb
Plating temp.	:	70°C
Plating time	:	1 hour

TABLE 7

Evaluation Process

Wire Bonding (100 Pieces) • Center Pull Strength test (100 Pieces)

Bonding condition

Machine : Wirebonde SWB-FA-UTC-43 (SHINKAWA)

Au Wire : SR Type F25 µm

Capillary : Ceramics normal Type (Microswis)

Condition

Bond load ; 1 st = 50 , 2nd =100 (gf)

Bonding time ; 1st = 20, 2nd = 20 (ms)

Wire ; Au wire F25µm

Stage Temp. ; 140 (?)

Shape of loop ; long

High of loop ; 120µm

Length of loop ; 5.0mm

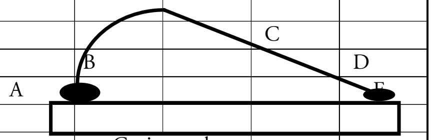
Center Pull strength test condition

Machine : Wirebonde SWB-FA-UTC-43 (SHINKAWA)

Condition

Pull Speed : 500µm

Center Pull Strength test

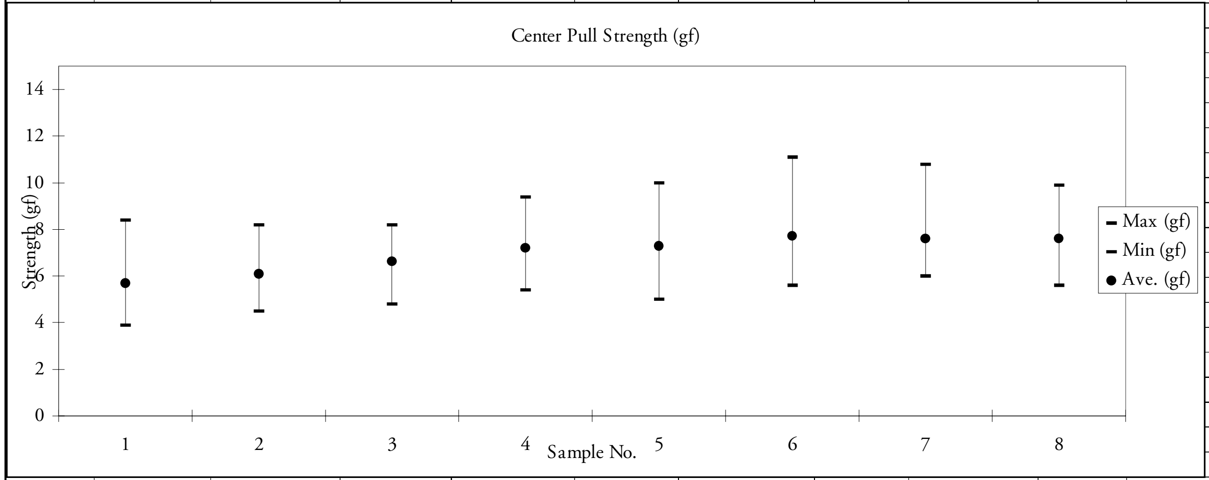


Cutting mode

TABLE 8

Electroless GOLD PLATING PROCESS

Wire Bondabilty

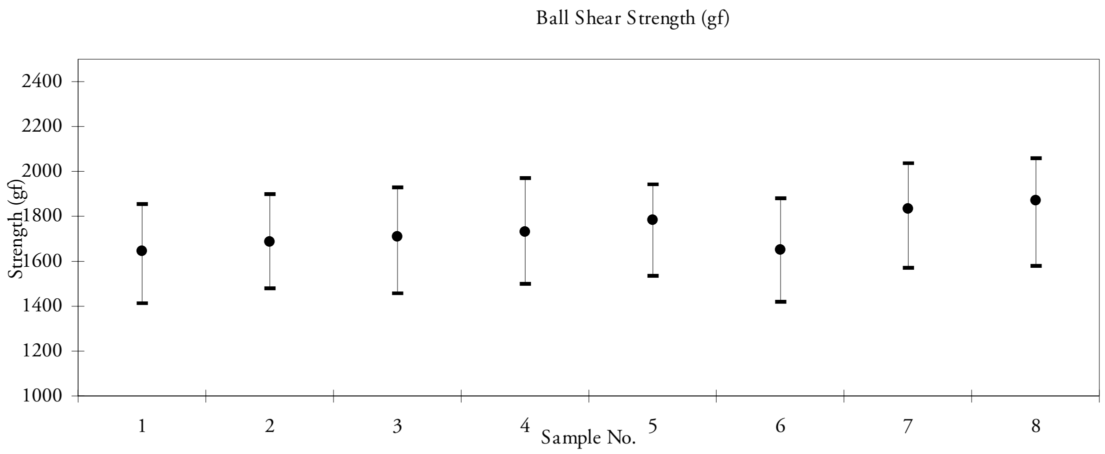


Sample	Ni Plating	Au Thickness	Center-Pull Strength n = 100			
		(µm)	Max (gf)	Min (gf)	Ave. (gf)	Cutting mode
1	3.0µm	0.05	8.4	3.9	5.7	B mode
2	3.0µm	0.1	8.2	4.5	6.1	B mode
3	3.0µm	0.2	8.2	4.8	6.62	B mode
4	3.0µm	0.3	9.4	5.4	7.2	B mode
5	3.0µm	0.5	10	5	7.3	B mode
6	2.0µm	0.3	11.1	5.6	7.7	B mode
7	5.0µm	0.3	10.8	6	7.6	B mode
8	10.0µm	0.3	9.9	5.6	7.6	B mode

TABLE 9

Electroless GOLD PLATING PROCESS

Ball Shear Strength



Sample	Ni Plating	Au Thickness	Ball Share Strength n = 20			
		(µm)	Max (gf)	Min (gf)	Ave. (gf)	Main Cutting mode
1	3.0µm	0.05	1855	1413	1645	C-2 mode
2	3.0µm	0.1	1899	1480	1688	B mode
3	3.0µm	0.2	1928	1457	1710	B mode
4	3.0µm	0.3	1971	1500	1732	B mode
5	3.0µm	0.5	1942	1536	1783	B mode
6	2.0µm	0.3	1880	1420	1652	C-2 mode
7	5.0µm	0.3	2036	1572	1833	B mode
8	10.0µm	0.3	2058	1580	1870	B mode

	Reducing Agent				
Bath Constituent	Thiourea	Ascorbic Acid		Hypophosphite	Hydrazine
	(8)	(11)	(15)	(13)	(14)
$NaAuCl_4$	0.005-0.025M	0.01M		0.0025M	
$Na_3Au(SO_3)_2$			0.006M		
$(NH_4)_3AU(SO_3)_2$					0.01M
Na_2 EDTA					0.25
Na_2SO_3	0.04-0.2	0.8-0.32	0.1	0.05	
$Na_2S_2O_3$	0.2-0.6	0.08-0.32	0.1	0.05	0.063
$Na_2B_4O_7$	0.066-0.13				
Na_2HPO_4		0.05-0.2			
NH_4Cl			0.05		
Boric Acid				0.16	
K Tartrate					0.13
Hydroquinone	0.0018-0.018				
Metacaptobenzothiazole		Trace			
Stabiliser			0.1-100 ppm		
Dimethylamine					0.067
2-Chloromethylquinoline					10 ppm
Tl_2SO_4					3 ppm
Reducing Agent	0.0013-0.013	0.05-0.2	0.25	0.075	0.36
pH	7.5-8.5	7.5	6.0	7.5	6.5
Temperature	60-90 ^{o}C	60^{o} C	60^{o} C	70^{o} C	60^{o} C