Gold Plating Technologies Using "Sulphite Systems"

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Despite a sometimes bad press, sulphite gold systems have been with us for some while. Their use in "wafer" manufacture has been well documented. This paper will present a short historical resume, current production applications, and then feature fully the newly developed electroless systems and ammonium based electrolytic systems. Both technical and decorative functions will be described.

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Introduction

Over recent years applications for sulphite systems have been re-evaluated for sometimes environmental reasons and sometimes application reasons. This paper will describe the historical information, current applications and new formulations to meet the increased requirements for sulphite systems.

General information.

There are only a few complexes of gold, which are suitable for the commercial use in gold plating. The most important being the cyanide complex of gold(I). This complex has been the subject of many papers over many years and no doubt will continue its domination for some time. Other gold complexes such as thiomalate and thiosulphate have also been evaluated but with little commercial success. (1)

Gold plating baths based on the trivalent gold complex do have some commercial value for specific applications but as of yet only in limited numbers.

Therefore the other most widely used and useful complex is the sulphite gold (I) complex. The use of the gold sulphite complex for gold plating has been known since 1842 (2) and is still the mostly widely used complex to prepare non-cyanide baths. Gold sulphite baths are popular due to their ability to produce smooth, bright and ductile pure gold deposits.

In the sulphite bath, gold exists in the form $[Au(SO_3)_2]^{3-}$. The stability constant of this complex is approximately equal to 10^{10} (3) which is orders of magnitude smaller than the cyanide complex $[AuCN_2]^-$ at 10^{39} (4).

Dissociation of the gold(I) sulphite complex occurs by the reaction;

$$Au(SO_3)_2^{3-} \Leftrightarrow Au^+ + 2SO_2^{3-}$$

For this reason the complex can tend to decompose spontaneously to form a precipitate of metallic gold from the following reaction;

$$2Au^+ \rightarrow Au(0) + Au^{3+} \quad (5)$$

The formation of the diothionate ion $S_2O_4^{2-}$ which is a powerful reducing agent leads to a gradual reduction of the gold complex to metallic gold. Below pH 4.7 the sulphite ion breaks down

To suppress instability resulting from this reaction all sulphite baths contain stabilising additives. The addition of an amine such as ethylenediamine is well known for this use. The reduction of the gold complex between pH 4.7 and 8.0 can be decreased considerably by strengthening the sulphite complex with ethylenediamine or by an oxiding agent such as picric acid. These oxidising agents react with the diothionate at a faster rate than the gold sulphite complex. However the use of these additives can make the bath difficult to control and therefore not as completely effective.

Additives such as Arsenic, Thallium or Antimony are often added as brightening reagents but they do change the hardness and ductility of the deposits.

Range of electrolytes available.

Available for many years, non-cyanide SULPHITE systems have been used in a wide variety of applications. Their soft bright deposits and good throwing power of the baths have made for many interesting applications. Examples are

Hybrid Circuits.

Bump plating of gold pads.

High reflectivity optical devises.

Spectacles.

Under Bump Metalisation for Wafers .

Electroless gold plating for wire bonding.

Traditionally most of the formulations for these applications have been based on either Potassium Gold Sulphite and Sodium Gold Sulphite. In particular Sodium Gold Sulphite based solutions are widely used for the gold plating of bumps for wire bonding as well as for plating of circuitry (See pictures 1 & 2). Solutions based on Potassium Gold Sulphite have also been used for circuitry and for high reflectivity optical electronic devices. Formulations based on Potassium Gold Sulphite have also been used to give a range of colour golds. Yellow – Pink – White etc.

Formulations. A list of the types of formulations for electronic applications can be found in table 1 together with the **operating conditions.**

Formulations. A list of the types of formulations for decorative applications can be found in table 2 together with the **operating conditions.**

New applications.

General

As mentioned above, in recent years applications for sulphite systems have been re-evaluated for sometimes environmental reasons and sometimes application reasons. Requirements from these process have become more stringent both from the hazardous nature and from the capabilities of the deposit. Below will be discussed the new processes available for a number of applications.

Wafer applications.

In recent years the application of Sodium Gold Sulphite based systems for UBM (under bump metalisation) and electroless gold plating of wafer pads has increased significantly. In this application the gold is first applied as an immersion deposit over electroless nickel plated aluminium pads. Further plating using an electroless gold process to produce thicknesses of up to 3 microns can then be applied. (6)

Formulations. A list of the types of formulations can be found in table 3.

Operating conditions. The operating conditions of these types of baths can be found in table 4.

Electrocoping for dental crowns.

Electrolysis has been used in dentistry and the dental laboratories for many years.. The use of electroformed gold copings as the core of fixed oral prosthesis was first introduced by O.W.Rogers in 1961 (7). The process had several drawbacks, not least the use of a cyanide electrolyte therefore posing a potential health hazard. In the late 70s (8)Wismann developed an electrolytic system using a cyanide free electrolyte but large expensive equipment was required. In the 80s much smaller systems were developed and introduced to the market. (9)

Formulations. A list of the types of formulations and operating conditions can be found in table 5.

New applications using Ammonium Gold Sulphite systems.

A New Dental Electrocoping Solution.

As mentioned above the potential for producing gold crowns had been realised some years ago. The use of sulphite systems increased dramatically with the introduction of systems based on Ammonium Gold Sulphite as the internal stress of the deposit from these solutions was found to be less stressed than that produced from Sodium and Potassium Gold Sulphite systems. (See Table 6,7 & 8).

Solutions based on Ammonium Gold Sulphite containing various additives, metallic, semi metal and organic, have been patented over the last few years. The addition of the various additives is to achieve grain refined deposits giving a semi bright appearance.

The information below will describe a new process that enables a semi bright, low stress deposit up to 250 microns thick, suitable for an electroformed crown (electrocoping) without the addition of any of the above or co-deposited additives. The formulation of the bath is simple and so is the operation. The key is in the purity and manufacturing of the ammonium gold sulphite together with the bath formulation – and the equipment used. The solution is supplied as a ready-to-use semi-bright gold plating solution and the deposit will be a lustrous low stressed deposit when plated under the optimum conditions.

Application. The plastic mould of the crown is first connected to a conductive wire and the complete assembly is coated with an air drying silver conductive coating. Complete coverage from the area to be plated to the conductive wire is essential for good conductivity to the crown area, Plating times are usually around 5 hours and after plating the mould is removed leaving the formed crown with the coating of silver on the inside. This silver coating is then removed with a solution of nitric acid. (See pictures 3 & 4)

Formulation.

Ammonium Gold Sulphite (100g/l)	16.5g/l
Ammonium Sulphite	100g/l
Conducting Salt	40g/l
Additive	10g/l

Operating Conditions.

Gold Concentration.	15-16.5g/l.	Depending on the Unit used
Sulphite Concentration	100g/l free sulphite minimum	
pH	9.1	
Temperature	50ºC	
Current Density	$1 A/dm^2$	
	$10 A/ft^2$	

Deposit Density 19.3 g/cc semi bright low stress

Deposition speed At $1.0 A/dm^2$ 200 microns will be produced in 5hrs

Note: During electrocoping the overall efficiency may fall to between 90-98% depending on the ultimate thickness of deposit.

A New System for the Electronic Market (Based on Ammonium Gold Sulphite).

In similarity to the dental bath this process does not contain any additives. The deposit produced is a pure gold deposit with a hardness value of 80-90HV.

The solution is supplied as a ready-to-use semi-bright gold plating solution and the deposit will be a lustrous low stressed deposit when plated under the optimum conditions.

Operating Conditions.

	Range	Optimum
Gold Content	8-12g/l	10g/l
Free Sulphite	80-120g/l	100g/l
pH	7.8 – 9.0	8.0
Temperature	40-50ºC	45ºC
Current Density	0.1-0.5 A/dm^2 1-5 A/ft^2	

Deposit Density 19.3 g/cc semi bright low stress

Deposition speed	At 0.3 A/dm^2. 1 micron Au in	5.25 minutes
	At 0.2 A/dm^2. 1 micron Au in	7.9 minutes
	(assuming 100% cathode efficiency *i.e.* 122 mg/amp.min.)	

The stress in the deposit when measured using the panel contractometer is seen to be much lower than deposits from solutions based on Potassium Gold Sulphite. This method measures the stress across a test panel as it is plated to thickness. This improvement in stress is due to the purity of the ammonium gold sulphite produced and the lack of additives in the process. (See Table 9)

Equipment.

Unplasticised PVC, polypropylene or polyethylene are recommended materials for tank fabrication. PTFE sheath immersion heaters are recommended and should be used in conjunction with a suitable thermostat.

Constant filtration through a 5 micron polypropylene filter is recommended. Care should be taken to avoid aerating the bath, by keeping delivery line below solution level.

The rectifier employed should be equipped with an ammeter, voltmeter and an infinitely variable current control; the inclusion of an amp-minute meter is highly advantageous.

Control of the bath.

Gold content and free sulphite need to be maintained at or above the minimum levels as quoted in the operating conditions.

The pH of the process is normally stable therefore should not need to be checked regularly. However it must not be allowed to fall below pH 8.0. Should adjustment be necessary Ammonium Hydroxide Solution (50% w/v) is added to raise the pH.

A New System for the Bump Plating of Wafers (Based on Ammonium Gold Sulphite).

Described below is a new solution based on Ammonium Gold Sulphite for the plating of gold bumps onto wafers. Pads of between 50 x 50 microns and 100 x 100 microns have been plated using this system up to 25 microns. The bath does contain bismuth as a grain refining additive. It will produce a fine grained deposit with sheer walls and a density = 19.3g/cc, semi bright, low stress.

Operating Conditions.

	Range	Optimum
Gold Content	8-12g/l	10g/l
Free Sulphite	80-120g/l	100g/l
Complexing Agent		50g/l
Additive (Bi)		10mg/l
pH	6.7 – 7.5	7.0
Temperature	45-55ºC	50ºC
Current Density	0.5 A/dm^2 5 A/ft^2	

Deposit Density 19.3 g/cc semi bright low stress

Deposition speed 1 micron in 3 minutes.

Deposit Characteristics

Hardness HV 50-70

Purity 99.99%

Bonding test with 25 micron wire OK

Pull test (Kulicke & Soffa) OK.

New Decorative "Colour Golds" based on Ammonium Gold Sulphite.

A range of golds based on Ammonium Gold Sulphite for gilding with original colours have been developed over recent years. There have been produced in response to the market's requirement to have original colours. Gold deposits with a colouring of pink, green and blue have been developed. The basis of the bath is Ammonium Gold Sulphite with additions containing copper, cadmium and silver either singularly or in combination. (See Table 10)

Conclusions.

Solutions based on "non cyanide", therefore sulphite, are gaining more importance as the perception towards more environmentally friendly processes gains momentum. New applications are also being found where the unique properties of the sulphite process, particularly based on Ammonium Gold Sulphite, meets the requirement of an ever changing market.

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Table 1

	Type A	Type B	Type C	Type D	Type E	Type F	Type G
Basis	Potassium	Potassium	Sodium	Sodium	Sodium	Sodium	Sodium
Gold Conc	10g/l	10g/l	10g/l	10g/l	10g/l	10g/l	10g/l
Sulphite Conc	35g/l	35g/l	30g/l	30g/l	30g/l	30g/l	30g/l
Temperature	55°C	55°C	52°C	45°C	65°C	50°C	60°C
pH	9.5	9.5	7.3	7.2	7.2	7.2	7.8
Density	9°Be	9°Be	12°Be	18°Be	18°Be	12°Be	12°Be
Additive	No	Yes	Yes	Yes	Yes	Yes	Yes
Type	None	Arsenic	Thallium	Thallium	Thallium	Arsenic	Thallium
Concentration	0	50 mg/l	15 mg/l	15-30mg/l	15 mg/l	15 mg/l	15 mg/l
CD A/dm2	0.1 - 0.3	0.1 - 0.3	0.1-1.0	0.1-1.0	0.4-0.6	0.1-0.5	0.4-0.6
Brightness	Matt	Bright	Semi	Bright	Matt	Matt	Semi
	Reflective		Bright				Bright
Application (s)	Pattern	Pattern	Pattern	Pattern	Bump	Pattern	Bump
	Plating	Plating	Plating	Plating		Plating	
			Bump		Heat Sink	Heat Sink	Heat Sink
Purity	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%	99.99%
Hardness (1)	60 - 100	140	90-95		90-95		90-95
Hardness (2)			50-60		50-60		50-60

1) Hardness as plated. 2) Hardness annealed. Hardness KVH (10gm)

Table 2

Colour	Yellow	Pink	White
Basis	Potassium	Potassium	Potassium
Gold Conc	10g/l	10g/l	10g/l
Sulphite Conc	35g/l	30g/l	30g/l
Palladium	No	Yes	Yes
Copper	No	Yes	Yes
Wetting Agent	No	No	Yes
Temperature	55°C	60°C	60°C
PH	9.5	9.5	9.5
Density	9°Be	12°Be	12°Be
Additive	Yes	Yes	Yes
Type	Arsenic	Arsenic	Arsenic
Concentration	50 mg/l	50 mg/l	50 mg/l
CD A/dm2	0.1 - 0.3	0.25-1.25	0.25-1.25
Brightness	Bright	Bright	Bright
Carat	24ct	20ct	20ct
Harndess HV (20g)	140	350	350

Table 3

	Reducing Agent	Reducing Agent	Reducing Agent	Reducing Agent	Reducing Agent
Bath	Thiourea	Ascorbic Acid		Hypophosphite	Hydrazine
	(10)	(11)	(12)	(13)	(14)
Constituents	0.005-0.25M	0.01M		0.0025M	
$NaAuCl_4$			0.006M		
$Na_3Au(SO_3)_2$					0.01M
$(NH_4)_3AU(SO_3)_2$					
Na_2 EDTA					0.025M
Na_2SO_3	0.04-0.2M	0.08-0.32M	0.1M	0.05M	
$Na_2S_2O_3$	0.2-0.6M	0.08-0.32M	0.1M	0.05M	0.063M
$Na_2B_4O_7$	0.066-.13M				
Na_2HPO_4		0.05-02M			
NH_4Cl			0.05M		
Boric Acid				0.16M	
K Tartrate					0.13M
Hydroquinone	0.0018-0.018M				
Metacaptobenzothiazole		Trace			
Stabiliser			01-100ppm		
Dimethylamine					0.067M
2-Chloromethylquinoline					10ppm
Tl_2SO_4					3ppm
Reducing Agent	0.0013-0.013M	0.05-0.2M	0.25M	0.075M	0.36M
pH	7.5-8.5	7.5	6.0	7.5	6.5
Temperature	60-90°C	60°C	60°C	70°C	60°C

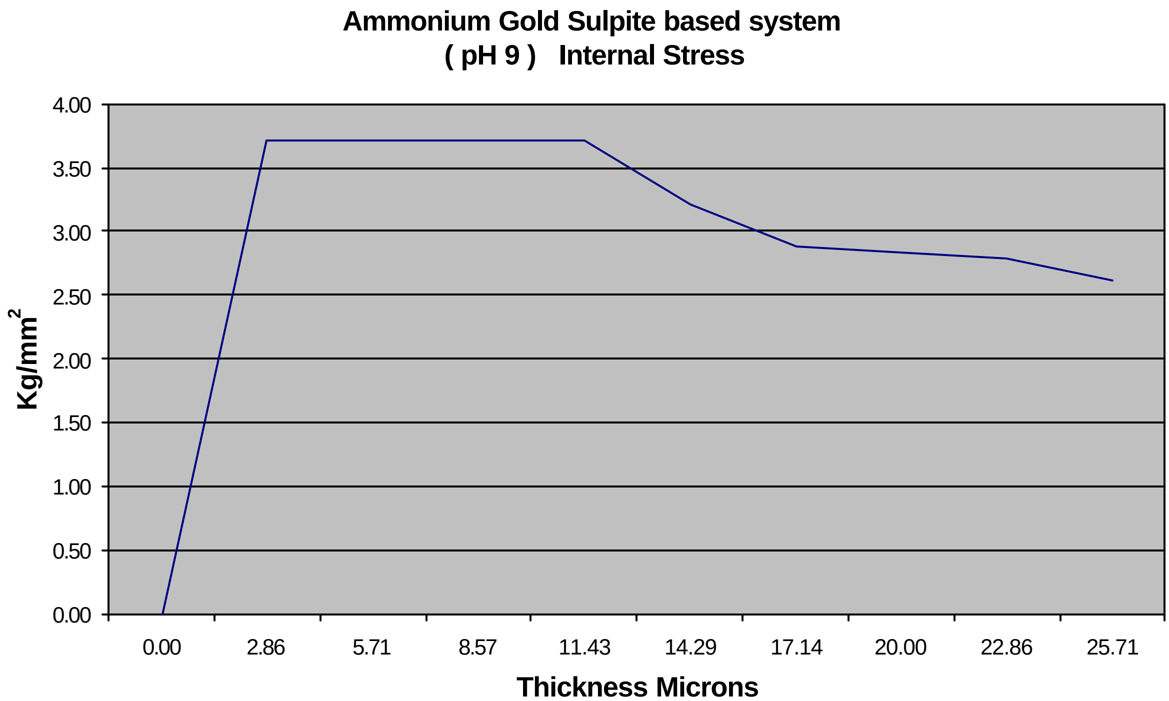
Table 4

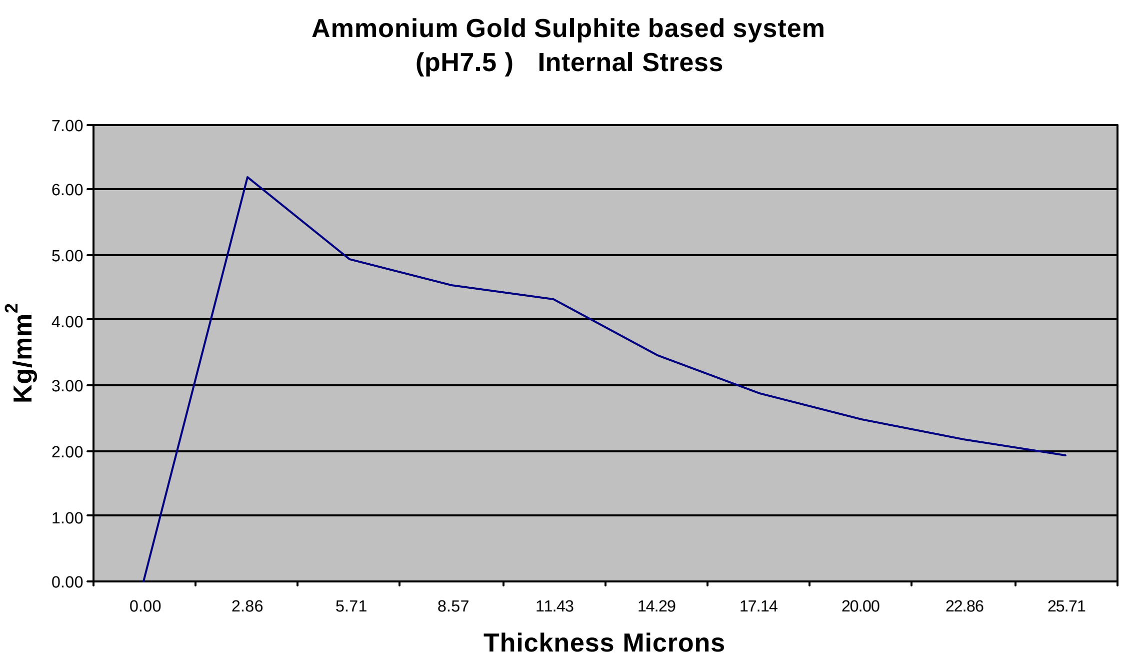
	Immersion Gold Cyanide Free	Electroless Gold Cyanide Free	Electroless Gold Cyanide Free
Application	Wafer UBM	Packaging	Wafer
		Wafer	Bonding
Basis	Sodium	Sodium	Sodium
Gold Conc	3.0 g/l	4.0 g/l	3.4 g/l
Range	0.5 - 3.0 g/l		3.0 - 4.5 g/l
Temperature	65°C	65°C	70°C
Range	65-80°C		65-75°C
Additive	Yes	Yes	Yes
pH	7.0	7.0	7.0
Range	6.0 - 8.0	6.0 - 8.0	6.0 - 8.0
Specific Area	0.1- 4 dm2/l	0.1- 4 dm2/l	0.1- 4 dm2/l
Agitation	Weak	Moderate	Moderate
		plus mild air	plus mild air
Plating Rate	0.01 µm/min	0.7 µm to	0.7 µm to
		1.0 µm/hr	1.0 µm/hr
		Max 3-4 µm	Max 3-4 µm
Turnovers	Depending on usage	2X	2X

Table 5

Basis	Ammonium	Ammonium	Ammonium	Ammonium
Gold as complex	10g/l	15g/l	15g/l	8g/l
Palladium as complex				2g/l
Ammonium Sulphite Solution 34%	40 ml/l	20 ml/l	10ml/l	100ml/l
Ammonium Sulphate	40g/l	20g/l	80g/l	20g/l
Ammonium Hydrogen Phosphate	20g/l	20g/l		No
Ammonium Tartrate	100mg/l	120mg/l		
EDTA	50mg/l	50mg/l		
Organic Additive (1)	100mg/l	80mg/l		No
Organic Additive (2)		100mg/l	300mg/l	
Organic Additive (3)			60g/l	40g/l
Organic Additive (4)			160mg/l	
Organic Additive (5)				10mg/l
Organic Additive (6)				0.5-2g/l
Glycin				5g/l
Copper Additive	40mg/l	50mg/l	80mg/l	125mg/l
Temperature	55-65°C	60-65°C	50-60°C	55-58°C
pH	7.5 - 8.0	7.5	8.0 -9.0	7.8
CD A/dm2	0.5 A/dm2	0.4 A/dm2	0.4-0.6A/dm2	0.3-0.6A/dm2

Table 6 & 7


Ammonium Gold Sulpite based system
(pH 9) Internal Stress
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Kg/mm2
0.00
2.86
5.71
8.57
11.43
14.29
17.14
20.00
22.86
25.71
Thickness Microns


Ammonium Gold Sulphite based system
(pH7.5) Internal Stress
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6.00
5.00
4.00
3.00
2.00
1.00
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Kg/mm2
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2.86
5.71
8.57
11.43
14.29
17.14
20.00
22.86
25.71
Thickness Microns

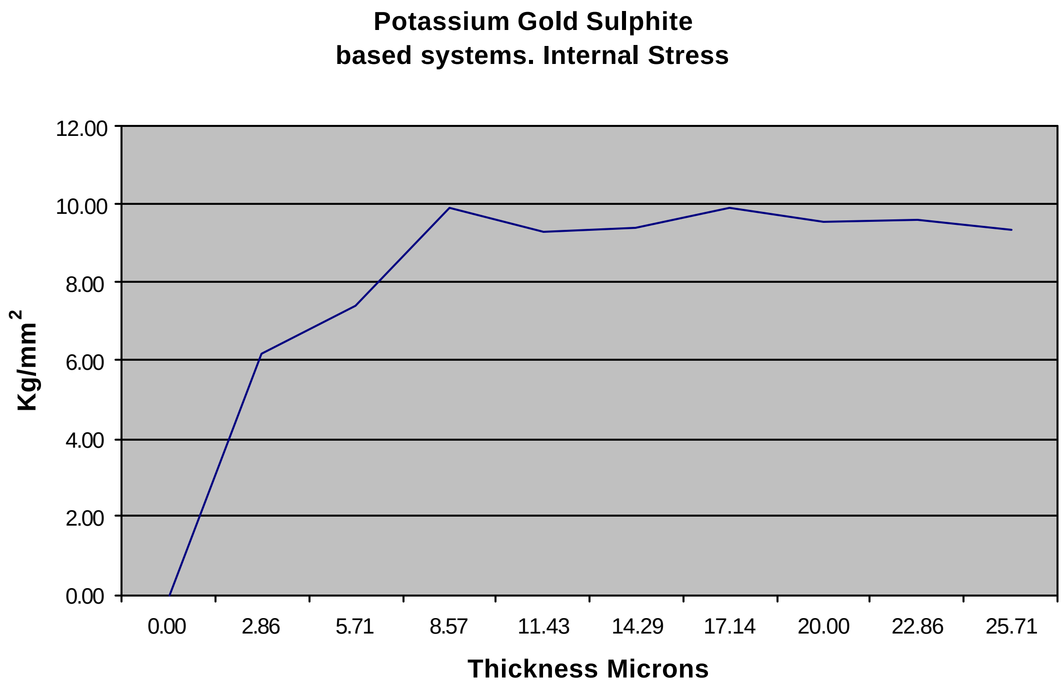
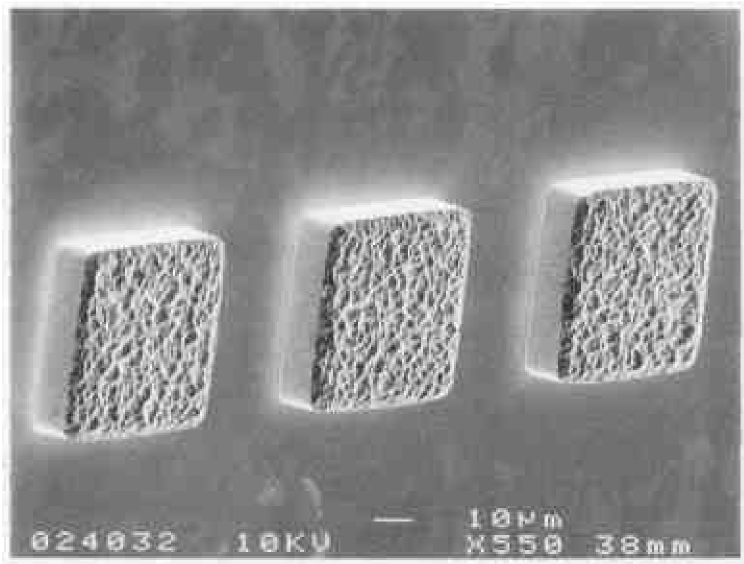

Potassium Gold Sulphite
based systems. Internal Stress
Kg/mm2
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00
2.86
5.71
8.57
11.43
14.29
17.14
20.00
22.86
25.71
Thickness Microns

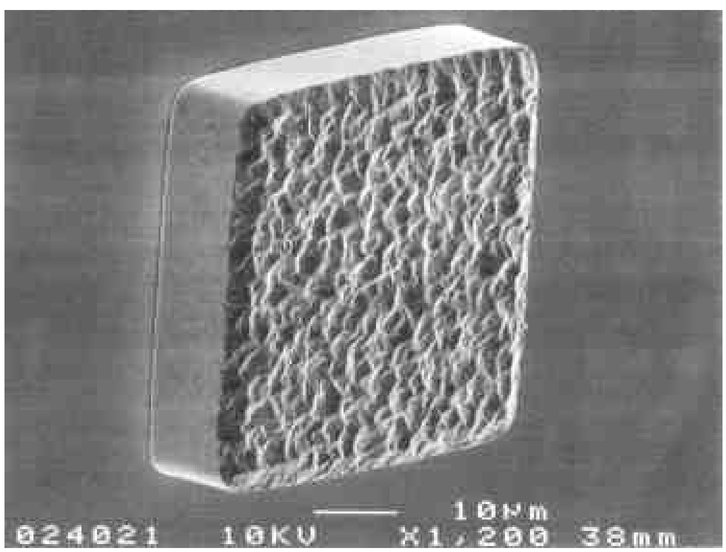
Table 10

Colour	Yellow/Gold	Rose	Grey Roe	Grey	White	Green
Basis	Potassium	Potassium	Potassium	Potassium	Potassium	Potassium
Or	Ammonium	Ammonium	Ammonium	Ammonium	Ammonium	Ammonium
Gold Conc	1g/l	1g/l	1g/l	1g/l	1g/l	1g/l
Sulphite Conc	30g/l	30g/l	30g/l	30g/l	30g/l	30g/l
Palladium	0 g/l	50 mg/l	100 mg/l	150 mg/l	200 mg/l	100 mg/l
Cadmium	No	No	No	No	No	Yes
Wetting Agent	No	No	No	No	No	No
Temperature	40°C	40°C	40°C	45°C	50°C	45°C
PH	10.5	10.5	10.5	10.5	10.5	10.5
Density	8°Be	8°Be	8°Be	8°Be	8°Be	8°Be
Additive (As)	No	No	No	No	No	No
CD A/dm2	0.3 - 1.5	0.3 - 1.5	0.3 - 1.5	0.3 - 1.5	0.3 - 1.5	0.3 - 1.5
Brightness	Bright	Bright	Bright	Bright	Bright	Bright
Carat	24ct	23ct	22ct	21ct	21ct	22ct
Harndess HV (25g)	160	190	220	250	300	250

Picture 1). Gold plated bumps



Picture 2. Gold Plated Bump



Pictures of the stages in the electrocoping process.