

THIOSULPHATE BATHS FOR SILVER PLATING

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ABSTRACT

Electroplating silver from thiosulphate solutions has received increasing attention recently because of the emphasis on pollution-free processes. This paper reports the results of studies for identifying suitable compositions for silver plating. Different aspects encompassing stability, conductivity, cathode current efficiency, deposition-rate and throwing power of solutions as well as deposit properties like appearance, microhardness and adhesion were examined. The preplating sequence for improving deposit adhesion was also investigated. The studies enabled identification of two methods of pretreatment and production of sound deposits with good adhesion to copper and nickel plated copper specimens.

Key words:

INTRODUCTION

Presently we are in the middle of a new generation of silver plating processes. As a result of the escalating cost of gold, silver is under investigation as a potential substitute for gold, particularly in the semiconductor field. The recognition of the need for pollution control is also highly felt nowadays and this has intensified efforts to formulate noncyanide compositions as a substitute for cyanide based solutions for electroplating.

There have been a number of attempts in the recent years in discovering noncyanide silver complexes for the electrodeposition process. Table I lists the most important complexes and their stability constants [1]. In the choice of a complex of practical value, the most important landmarks are in regard to: (i) iodide electrolyte (ii) silver nitrate-ammonium sulphate electrolytes and (iii) thiosulphate electrolytes.

Table I: Stability constants of Silver Complexes

Complex Ion	Logarithm of Stability Constant
Ag (CN) ₂ (cyanide)	21.1
Ag (CH ₄ N ₂ S) ₃	13.5
AgI ₄ ³⁻ (Iodide)	13.4
Ag (S ₂ O ₃) ₂ ³⁻ (thiosulphate)	12.5
Ag (SCN) ₄ ³⁻ (thiocyanate)	11.2
Ag (SO ₃) ₂ ³⁻ (sulphite)	8.4
AgBr ₄ ⁺ (bromide)	8.3
Ag (en) ₂ ⁺ (ethylenediamine)	7.4
Ag (NH ₃) ₂ ⁺ (ammonia)	6.5
AgCl ₄ ³⁻ (Chloride)	5.7

Table II gives some of the compositions of electrolytes based upon iodide and ammonia complexes as published [2]. Most of the compositions containing silver thiosulphate complex are covered under patents. It was therefore considered worthwhile by the authors to undertake investigations and this paper presents a report on the work done. Solution characteristics, namely, current efficiency, rate of deposition and throwing power, and deposit properties like appearance, microhardness and adhesion were studied. Procedures were also worked out for preparation of the plating solution and for pretreatment of copper substrates.

Table II: Silver plating solutions based on iodide and ammonia complexes

Bath composition	Cathodic current density, temp. etc.
1. Silver sulphate 30 g/l Ammonia (25%) 75 cc/l Potassium iodide 600 g/l Sodium pyrophosphate 60 g/l	2 A.dm ⁻² room temperature
2. Silver nitrate 30-40 g/l Potassium iodide 300-400 g/l Polyethylene, polyamine 10-100 g/l	0.5-3.0 A/dm ⁻² upto 40°C
3. Silver iodide 40-80 g/l Sodium iodide 400-600 g/l Polyvinyl alcohol 0.5-2.0 g/l Sodium thiosulphate 1-2 g/l	0.5-3.0 A/dm ⁻² room temperature
4. Silver nitrate 35 g/l Ammonium sulphate 150 g/l Citric acid 4 g/l Ferric sulphate 0.4-3.0 g/l Ammonia 2-50 ml/l	0.5-1.5 A/dm ⁻² pH 10-10.6 upto 30°C
5. Silver nitrate 20-30 g/l Sodium pyrophosphate 20-25 g/l Ammonia (1.25%) 60-100 ml Sodium nitrite 40-70 g/l Ammonium sulphate 40-70 g/l	0.8-1.1 A/dm ⁻² room temperature

EXPERIMENTAL

Preparation of the bath

A number of experiments were necessary for identifying suitable compositions for plating. The tendency of a thiosulphate solution containing silver to precipitate black silver sulphide created a need for including a suitable stabilizer, like potassium metabisulphite. The majority of the experiments were performed with solutions I and II the compositions of which were selected on the basis of preliminary experiments.

Solution I

Silver as chloride	50 g/l
Sodium thiosulphate	500 g/l
Potassium metabisulphite	30 g/l

Solution II

Silver as chloride	30 g/l
Sodium thiosulphate	500 g/l
Potassium metabisulphite	30 g/l

Silver chloride was precipitated from silver nitrate and potassium chloride and was dissolved in sodium thiosulphate solution. Potassium metabisulphite was then added and the solution volume made up as required.

Effects of variation of concentrations of the constituents

Different quantities of silver chloride were prepared and the precipitated compound (silver 10-50 g/l) dissolved in an excess of sodium thiosulphate (500 g/l), with the addition of 30 g/l potassium metabisulphite. Silver deposition was carried out from these solutions at different current densities, stirring being resorted to especially when plating at a current density higher than 0.5 A.dm⁻². In order to fix the range of sodium thiosulphate for production of acceptable deposits with adequate solution stability, solutions containing 50 g/l silver as silver chloride, 30 g/l potassium metabisulphite and 100-600 g/l sodium thiosulphate were used for silver plating.

Potassium metabisulphite being the constituent added for improving solution stability it was considered worthwhile to fix its permissible concentration range giving rise to sound deposits. Solutions with 30-50 g/l silver as silver chloride, 500 g/l sodium thiosulphate and 0-50 g/l potassium metabisulphite were studied.

Studies on preplating treatments

The conventional preplating treatment with a striking solution was not effective in producing adherent silver deposits from the plating solution. Various preplating treatments were therefore examined and the useful life of the pretreatment solutions was also investigated. The following sequence was employed for obtaining 50 μm thick silver deposits on copper:

- i) Degrease ii) electroclean iii) preplate treatment like striking in 10 times diluted bath or anodic treatment in the plating bath cathodic/anodic immersion treatment in ammonium thiocyanate solution and iv) silver plate.

Deposits adherence was tested qualitatively by bending the plated specimens. As the conventional preplating treatment was not also effective in producing adherent silver deposits on nickel plated surfaces, silver was deposited on nickel plated copper substrates for qualitatively studying the deposit adhesion. The following pretreatment was investigated for its usefulness:

- i) degrease ii) electroclean iii) pretreatments such as immersion/anodic treatment in 10% ammonium thiocyanate solution, anodic processing in sodium thiosulphate solution at different current densities, anodically treating in dilute silver thiosulphate bath, or the earlier treatment followed by strike in the same solution iv) strike with silver in the silver strike solution for 1 minute at 0.16 A.dm⁻² at room temperature and v) silver plating in the bath proper.

Studies with Solution I

Effect of current density

Current efficiency experiments were carried out at different current densities with copper substrates of 12.5 cm² exposed area and subjected to preplating treatments as explained earlier. Mechanical stirring was employed when plating was carried out at current densities higher than 0.5 A.dm⁻²

Deposit hardness

The silver deposits were electropolished in a solution of the following solution before testing them for microhardness:

Sodium cyanide	10 g/l
Potassium ferrocyanide	100 g/l
Applied voltage	2.5 V
Time	1 minute
Cathode	Graphite

The microhardness values were measured by the Vicker's method of indentation using a Russian made π MT-3 Microscope Hardness Meter at a load of 5 g.

Studies with Solution II

The current efficiency experiments were performed at different current densities with copper specimens of 12.5 cm² area after taking them through a suitable pretreatment as described earlier.

Throwing power

This was determined for each of the two baths employing the Haring-Blum cell and Field's formula.

Porosity

The porosity of the silver deposits obtained from both the baths was determined by the electrographic method, with a filter paper of 25 x 25 mm size dipped in a 5% potassium nitrate solution at 2.5 V for a duration of one minute.

Effects of temperature and pH

These were also studied by varying the temperature and pH of solutions I and II separately and carrying out silver deposition.

RESULTS AND DISCUSSION

Preparation of the bath

The bath composition finally recommended in this paper had been found to keep well without any decomposition for more than seven months. It was earlier found, however, that solutions prepared making use of soluble silver salts had a noticeable tendency to decompose and hence a proper method of solution preparation involving the use of an insoluble silver compound and a stabilizer was necessary. It was also found that with potassium metabisulphite as an ingredient good solution stability could be achieved. Any large change of pH or temperature of solution decreases its stability markedly.

Effect of variation of silver concentration

With an increase in silver concentration there is a possibility of the stability of the bath being slightly affected for a given thiosulphate concentration but better deposits are obtained. Acceptable deposits can be produced even at high current densities up to 1.5 A.dm⁻² with solution agitation. Solutions with low silver contents permit only low current density operation, rough or spongy deposits being produced at normal current densities (Table III). Generally solution agitation e.g. by means of a magnetic stirrer improves the quality of silver deposits. Silver chloride equivalent to 10-15 g/l silver concentration was used for preparation of the plating bath. Increased quantities of silver chloride dissolve in sodium thiosulphate only slowly and with intensive stirring.

Table III: Effect of silver concentration on the stability and performance of bath

Composition	Observations
1. Silver as chloride 10/20 g/l Sodium thiosulphate 500 g/l Potassium metabisulphite 30 g/l	Stable; the low silver content did not permit production of sound deposits even at low current densities
2. Silver as chloride 30/40/50 g/l Sodium thiosulphate 500 g/l Potassium metabisulphite 30 g/l	Stable; current densities up to 0.77/1.00/1.50 A.dm ⁻² respectively with stirring could be used.

Effect of variation of sodium thiosulphate concentration

An increase in concentration of thiosulphate causes silver chloride to dissolve more easily. On considerations of solution stability, the sodium thiosulphate concentration was fixed at 500 g/l (Table IV).

Table IV: Effect of sodium thiosulphate on bath stability and performance

Composition	Remarks
1. Silver as chloride 30 g/l Sodium thiosulphate 100/200/ 300 g/l, Potassium metabisulphite 30 g/l	Silver chloride did not dissolve completely
2. Silver as chloride 30 g/l Sodium thiosulphate 400/500/ 600 g/l, Potassium metabisulphite 30 g/l	Sound deposits were obtained, with stability and plating characteristics improving successively with this salt addition

Effect of potassium metabisulphite

The initial experiments on preparation of the bath established the usefulness of this compound as a stabilizer. An increase in concentration of this salt, increases the stability of the bath. A minimum concentration of 20 g/l potassium metabisulphite is essential for good bath stability; solutions containing not less than 20 g/l of this compound are undecomposed even after 6 months of preparation (Table V)

Table V: Effect of potassium metabisulphite on bath stability

Composition	Remarks
1. Silver as chloride 30 g/l Sodium thiosulphate 500 g/l Potassium metabisulphite 0 g/l	Highly unstable
2. Silver as chloride 30 g/l Sodium thiosulphate 500 g/l Potassium metabisulphite 10/20 g/l	Stable for 1 month/ more than 3 months respectively
3. Silver as chloride 30 g/l Sodium thiosulphate 500 g/l Potassium metabisulphite 30/40/50 g/l	Stable for more than 7 months

Preplating treatments

Experiments on alternative methods of pretreatment showed a dip in 10% ammonium thiocyanate to be helpful in obtaining adherent silver deposits. The improved deposit adhesion is obviously due to formation of a brown colored thin layer of copper thiocyanate which minimise the tendency of the substrate to dissolve, though slightly, and hence permit immersion deposition of silver. There is also a small loss of substrate copper which increases with duration of treatment in thiocyanate solution (Table VI). As far as an undercoat of nickel was concerned it was found that an anodic treatment of the nickel plated specimen in a 300 g/l sodium thiosulphate solution with a silver content one tenth of that in the bath, and a cathodic strike in the same solution were necessary to produce an adherent silver deposit.

Table VI: Effect of duration of immersion of copper substrates on metal loss and adhesion of silver deposit

Duration (min)	Copper weight loss [g. dm ⁻²]	Remarks
1	No loss	Deposit not adherent
3-10	"	Adherent deposit
15	0.0004	"
30	0.0005	"
60	0.0006	"
75	0.0008	"
75	0.0017	"

Effect of current density

With Solution I, an increase in current density (c.d.) up to 1.25 A.dm⁻² does not have much influence on the current efficiency which ranges 96-98% (Table VII). When however the current density is increased to 1.5 A.dm⁻² it becomes difficult to obtain coherent deposits without stirring and the

current efficiency is only 67%. In the case of Solution II, an increase of current density does not alter the current efficiency from near 100% (Table VIII) in the c.d. range 0.25-0.5 A.dm⁻²

Table VII: Current efficiencies of bath I at different current densities and corresponding deposit hardness values

Current density A.dm ⁻²	Current efficiency (%)	Microhardness kg. mm ⁻² (Vickers)
0.50	98.5	53
0.75	95.7	58
1.00	96.7	56
1.25	96.4	50
1.50	67.0	--

Table VIII: Current efficiencies of bath II at different current densities and corresponding deposit hardness values

Current density in (A.dm ⁻²)	Current efficiency (%)	Hardness kg. mm ⁻² (Vickers)
0.25	99.5	63
0.50	100.0	63
0.75	97.2	60
1.00	65.0	--

Microhardness

The microhardness of the deposit is also not affected much with current density. The deposits have a microhardness of the order of 55 and 60 kg.mm⁻² respectively from baths I and II which are considerably lower than in the case of deposits from cyanide solutions. Thus deposits from thiosulphate baths are more easily buffable than conventional deposits.

Throwing power

The throwing power (nearly 60%) of Solution I at normal current densities, is also acceptably adequate (Table IX). An increase in either pH or temperature of this bath does not help in further improvement of deposits.

In the case of Solution II, the throwing power is 75-81% at current densities of 0.5-0.75 A.dm⁻² and is 15-20% higher than for the more concentrated bath, as can normally be expected (Table IX).

Table IX: Throwing power of baths I and II

Current density (A.dm ⁻²)	Throwing power (%)	
	Bath I	Bath II
0.50	57.6	75.4
0.75	61.8	81.4

Porosity

Results of the porosity measurement carried out with Solution II are given in Table X. A silver deposit of not less than 15 μm thickness is found to be nonporous.

Table X: Porosity of silver deposits from Bath II

Thickness of silver deposit (μm)	Number of pores per dm ²
5	Highly porous
10	16 pores
15/20/25	No pores

If any black silver sulphide precipitate is formed, it may be filtered off and treated with a solution of sodium hypochlorite, to obtain silver chloride and the latter, after thorough washing redissolved in the plating solution.

CONCLUSIONS

Excellent silver deposits can be obtained from solutions of composition and operating parameters as below:

	Solution I	Solution II
Silver as chloride, g/l	50	30
Sodium thiosulphate, g/l	500	500
Potassium metabisulphite, g/l	30	30
Temperature	Room	Room
Cathodic current density A.dm ⁻²	0.5-1.25	0.25-0.75
pH	4-4.5	4-4.5

REFERENCES

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