Silver Electrodeposition from Thiosulfate Solutions

by S. Sriveeraraghavan, R.M. Krishnan and S.R. Natarajan
Central Electrochemical Research Institute, Karaikudi, India

INTRODUCTION

Pollution considerations have been an impetus for development of noncyanide electroplating processes. Though most silver plating has been and continues to be carried out from cyanide solutions, efforts have been made by different workers to develop cyanide-free silver solutions. Cyanide continues to be used due to the fact that, as yet, no complex as stable as the double cyanide silver complex has been identified. It was, however, possible for the authors to work out suitable strike and plating solutions for electrodeposition of silver. The silver plating solutions identified have high conductivity with adequate throwing power. The deposits are smooth and have good adherence to copper substrates.

Silver is usually electrodeposited from cyanide electrolytes because of their high conductivity and throwing power and the high stability of the silver complex present in them. Table I[1] gives the stability constants of various silver complexes reported in the literature. The cyanide silver complex has the greatest stability. A number of electrolytes have, however, been examined by different workers for their ability to deposit silver as indicated in Table II.[2]

Table I. Stability Constants of Silver Complexes

Complex Ion	Logarithm of Stability Constant
$Ag(CN)_2$ (cyanide)	21.1
$Ag(CH_4N_4S)_3$	13.5
AgI_4^{3-} (iodide)	13.4
$Ag(S_2O_3)_2$ (thiosulfate	12.5
$Ag(SCN)_4$ (thiocyanate)	11.2
$Ag(SO_3)_2$ (sulphite)	8.4
$AgBr_4^{3-}$ (bromide)	8.3
$Ag(en)_2$ (ethylene diamine)	7.4
$Ag(NH_3)_2^+$ (ammonia)	6.5
$AgCl_4$ (chloride)	5.7

On consideration of cost and freedom from toxicity, the thiosulfate bath offered promise and thus an investigation was conducted. This paper is a result of the studies performed.

Table II. Noncyanide Baths Reported in Literature

No.	Bath		Operating Conditions
1	Silver sulfate	30 g/L	2 A/dm^2
	Ammonia (25%)	75 cc/L	Room temperature
	Potassium iodide	600 g/L	
	Sodium pyrophosphate	60 g/L	
2	Silver nitrate	30-40 g/L	0.5-3.0 A/dm^2
	Potassium iodide	300-400 g/L	Up to 40°C
	Polyethylene polyamine	10-100 g/L	
3	Silver iodide	40-80 g/L	0.5-3.0 A/dm^2
	Sodium iodide	400-600 g/L	Room temperature
	Polyvinyl alcohol	0.5-2.0 g/L	
	Sodium thiosulfate	1.2 g/L	
4	Silver nitrate	35 g/L	0.5-1.5 A/dm^2
	Ammonium sulfate	150 g/L	Up to 30°C
	Citric acid	4 g/L	pH 10-10.6
	Ferric sulfate	0.4-3.0 g/L	
	Ammonia	2-50 ml/L	
5	Silver nitrate	20-30 g/L	
	Sodium pyrophosphate	20-25 g/L	0.8-1.1 A/dm^2
	Ammonia (1.25%)	60-100 ml/L	Room temperature
	Sodium nitrite	40-70 g/L	
	Ammonium sulfate	40-70 g/L	

EXPERIMENTAL

PRELIMINARY EXPERIMENTS:

Different solutions were prepared by precipitating silver as silver chloride and then dissolving the latter in an excess of sodium thiosulfate before the addition of other constituents. In the preliminary experiments silver from silver nitrate solution was precipitated as iodide, sulfate, thiocyanate, succinate, citrate, carbonate, oxalate, thiosulfate or bromide. The solutions obtained by dissolving the same in an excess of sodium thiosulfate were examined for their plating characteristics. Further experiments were carried out only with the thiosulfate solution, as it was found to give rise to better quality deposits with good corrosion of the silver anodes.

STUDIES ON BATH STABILITY:

As the bath was stored, silver sulfide formed gradually and in an increasing quantity. The possibility of suppressing, or at least retarding, the formation of silver sulfide was examined by introducing potassium metabisulfite in different quantities to different thiosulfate based silver solutions.

Silver plating was carried out on 7.5 x 2.5 cm specimens of copper substrates.

PRETREATMENTS:

As only loosely adherent deposits were initially obtained on copper substrates the usefulness of each of the following pretreatments was investigated:

1. Immersion in a diluted thiosulfate based solution.
2. Striking silver in a 10 times diluted plating bath for a short time at a high current density.
3. Dips in solutions of ammonium thiocyanate at different concentrations, at room temperature.
4. Application of an electrolytic nickel layer as a preplate.

SOLUTION CONDUCTIVITY:

Solution conductivity is an important aspect in plating, especially as it is related to the voltage necessary for operating a bath. Therefore values of conductivities of various thiosulfate based baths with 20, 30 and 50 g/L silver, 500 g/L sodium thiosulfate and 30 g/L potassium metabisulfite, were measured and compared with those of the conventional cyanide bath, making use of a conductivity bridge. The conductivities of both distilled and double distilled water were also measured. Experiments were also carried out on the throwing power of each of the two selected solutions and the microhardness of deposits from them.

Table III. Preliminary Experiments

No.		Composition g/L	Remarks
1	Silver as carbonate Ammonium thiosulfate Sodium thiosulfate	25 15 200	Sodium carbonate was used for precipitating silver; the bath turned black. Spongy deposit at 0.5 A/dm^2
2	Silver as carbonate Ammonium thiosulfate Sodium thiosulfate	25 15 200	Sodium bicarbonate was used for precipitation of silver; bath turned black. Mat white, but nonadherent deposit
3	Silver oxalate Sodium thiosulfate	50 300	Silver was precipitated with sodium oxalate; the bath turned black
4	Silver thiocyanate Sodium thiosulfate	50 300	Silver was precipitated with sodium thiocyanate; the bath turned black
5	Silver citrate Sodium thiosulfate	50 300	Silver was precipitated with dilute sodium hydroxide and citric acid was then added; the bath turned black
6	Silver succinate Sodium thiosulfate	50 300	Silver succinate was produced by treating precipitated silver hydroxide with succinic acid
7	Silver bormate Sodium thiosulfate	50 300	Poor solubility of silver bromate
8	Silver nitrate Ethylene diamine Sodium thiosulfate	30 500 300	Bath turned black
9	Silver as chloride Sodium thiosulfate	300 300	Silver was precipitated as chloride with silver nitrate and potassium chloride. Bath was clear for 2 days
10	Silver as chloride Sodium thiosulfate Sodium acetate	32 300 40	Precipitated silver chloride was used
11	Silver as chloride Sodium thiosulfate Ammonium chloride	32 300 40	"
12	Silver as chloride Sodium thiosulfate Ammonium carbonate	32 300 40	"

Table IV. Effect of Substrate Pretreatment on Adhesion

No.	Pretreatment	Remarks
1	Degrease, electroclean, acid dip	Nonadherent
2	Striking in 10 times diluted silver bath	"
3	Anodic treatment in the plating bath for 10 minutes at 0.01 A/dm^2	"
4	Cathodic treatment in 5% ammonium thiocyanate	"
5	Anodic treatment in 5% ammonium thiocyanate	"
6	Dip in 10% ammonium thiocyanate at 30°C for 3 minutes	Adherent
7	Dip in 10% ammonium thiocyanate at 30°C for 5 minutes	"
8	Dip in 5% ammonium thiocyanate at 30°C for 10 minutes	Nonadherent
9	Dip in 10% ammonium thiocyanate for 10 minutes	Adherent
10	Dip in 10% ammonium thiocyanate solution for 15 minutes	"
11	Degrease dip in 10% ammonium thiocyanate for 10 minutes	Nonadherent
12	Anodic treatment in 10% ammonium thiocyanate at 0.012 A/dm^2 for 10 minutes	"
13	Anodic treatment in 10% ammonium thiocyanate at 0.16 A/dm^2	"
14	Anodic treatment in 300 g/L $Na_2S_2O_3$ at 0.012 A/dm^2 for 10 minutes	"
15	Anodic treatment in 300 g/L $Na_2S_2O_3$ at 0.2 A/dm^2 for 10 minutes	"
16	Anodic treatment in dilute solution of thiosulfate solution for 1 minute	"
17	Degrease, strike in dilute thiosulfate silver bath at 0.2 A/dm^2 for 10 minutes	"

Note: Pretreatment No. 11 on nickel plated copper.

RESULTS AND DISCUSSION

The results of preliminary experiments on different thiosulfate based solutions are given in Table III. Out of 12 compositions investigated, only the bath composed of silver chloride and sodium thiosulfate was found to be fairly stable. In the case of other baths, there was a tendency for silver to precipitate; in addition, deposits were nonadherent or of poor appearance even at low current densities.

As the silver chloride and sodium thiosulfate bath appeared to be better in terms of stability and performance, further investigations were carried out with the same type of solutions without and with potassium metabisulfite as a stabilizer, for collecting data on their deposition characteristics.

PRETREATMENTS:

The result of different pretreatments attempted with a view to preventing formation of loosely adherent deposits, are given in Table IV. It may be noted that a dip in 10% ammonium thiocya-

Table V. Conductivities of Thiosulfate Silver Baths at 25°C

Bath	Conductivity (mho-cm)
Distilled water	1.65×10^{-5}
Double distilled water	0.85×10^{-5}
Bath 1	1.00×10^{-1}
Bath 2	1.05×10^{-1}
Bath 3	1.10×10^{-1}
Bath 4	1.10×10^{-1}
Bath 5	1.40×10^{-1}

Bath 1	Ag content	20 g/L
	$Na_2S_2O_3$	300 g/L
	$K_2S_2O_5$	30 g/L
Bath 2	Ag content	20 g/L
	$Na_2S_2O_3$	500 g/L
	$K_2S_2O_5$	30 g/L
Bath 3	Ag content	30 g/L
	$Na_2S_2O_3$	500 g/L
	$K_2S_2O_5$	30 g/L
Bath 4	Ag content	50 g/L
	$Na_2S_2O_3$	500 g/L
	$K_2S_2O_5$	30 g/L
Bath 5	Ag content	29 g/L
	NaCN	70 g/L
	Na_2CO_3	45 g/L

nate at 30°C for 3 minutes, helps produce an adherent deposit of silver on copper without producing an immersion deposit. This is obviously due to formation of a thin brown colored layer of copper thiocyanate which minimizes the tendency of the substrate to dissolve, though slightly, and hence give rise to immersion deposition of silver. A small loss of substrate copper, increasing with the duration of immersion, was observed.

As far as an undercoat of nickel was concerned, it was found that an anodic treatment of the nickel plated surface specimen in a 300 g/L sodium thiosulfate 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.

SOLUTION CONDUCTIVITY:

It is observed from Table V that the conductivities of the thiosulfate based baths containing 20, 30, and 50 g/L silver (Baths 2, 3 and 4) (1.1 x 10^{-1}mho-cm) are only slightly less than that of the cyanide bath (1.4 x 10^{-1}mho-cm).

BATHS SELECTED:

The results obtained led to the selection of the following two compositions for further studies:

	Bath 1	*Bath 2*
Silver as chloride, g/L	30	50
Sodium thiosulfite, g/L	500	500
Potassium metabisulfite, g/L	30	30

The baths were found to be stable for several months without deterioration and could be operated at room temperature in the current density range of 0.5 to 1.25 A/dm^2 with a cathode current efficiency of about 100% which tended to decrease at higher current densities such as 1.5 A/dm^2 with the efficiency going down to 67%.

The throwing power of each of the two baths was found to be good, ranging from 58 to 75% for a current density of 0.5 A/dm^2 and from 81% for 0.75 A/dm^2.

The Vickers microhardness of deposits was found to be between 60 and 63 kg/mm^2 being slightly lower than in the case of those from cyanide baths and thus enabling easier buffing.

CONCLUSION

With many factors in its favor, such as good throwing power, good conductivity, high current efficiency, adequate deposit hardness and adequate bath stability, the thiosulfate bath deserves to be examined at least for those applications, where the use of a cyanide solution is undesirable. **MF**

References

1. Rolf Ludwig, Interfinish, Pt II (1976), p 687.
2. F.A. Lowenheim (Ed.), "Modern Electroplating," New York, 3rd Edition, John Wiley and Sons, Inc., 1974.
3. RM. Krishnan et al, Bull. Electrochem, 2 (3), 257 (1986).