

Preparation and Optimization of Pyrophosphate Bath for Copper Electroplating of Microwave Components

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ABSTRACT

The principles of copper deposition from pyrophosphate electrolytes have been explained. Based on these principles, a method of preparation of plating bath from basic constituents has been described. It was found that copper pyrophosphate is precipitated from solutions of copper sulphate and potassium pyrophosphate at a pH of 5.0. For maximum efficiency, copper pyrophosphate has to be dissolved in potassium pyrophosphate in a weight ratio of 1 : 4 or a total P_2O_7 : Cu ratio of 7.5 : 1. By using optimum values of anode : cathode area, 2.5, pH , 5.0, temperature, 55°C and a cathode current density of 0.8 A/dm^2 , bright, adherent copper electroplates were deposited on electroless copper plated Al_2O_3 substrates employed in microwave components.

1. INTRODUCTION

Copper plating is required on hybrid microwave integrated circuit components for providing a highly conducting layer on ceramics and plastics substrates. These substrates are previously plated with thin metallic films by vacuum methods or electroless techniques. The electrodeposited coating must adhere well to the underlying substrate.

The conventional copper plating baths consist of copper sulphate-sulphuric acid (pH : 0.3–2.0) or copper cyanide-sodium cyanide (pH : 12.0). The acid fluoborate baths (pH : 0.2) are used less frequently. These acidic baths are highly corrosive for plating of delicate IC components, while the alkaline cyanide baths pose the problems

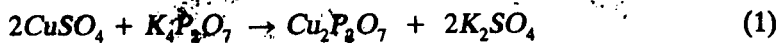
of environmental disposal. The need for a non-corrosive and non-toxic electro-plating bath thus becomes inevitable.

The weakly alkaline pyrophosphate bath (pH : 8-9) provides an attractive choice. The bath is known to produce bright, fine grained, smooth deposits of low internal stresses, has a high throwing power and is already popular for plating through holes of the PCBs². Unfortunately the indigenous sources of this bath are irregular. This situation has forced many platers to import these formulations. The purpose of the present investigation is to understand the principles of copper deposition from pyrophosphate electrolytes and thereby optimize the quantities of bath ingredients to enable it to be prepared from the indigenously available constituents.

2. PRINCIPLES

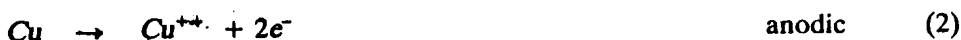
Copper forms complex anions such as $CuP_2O_7^{2-}$, $Cu_2P_2O_7^{6-}$ and cations such as $Cu_4P_2O_7^+$ with pyrophosphate. However, the pH ranges of formation of these complex ions are not precisely known.

On adding a solution of potassium pyrophosphate, $K_4P_2O_7$ to a solution of copper sulphate, $CuSO_4 \cdot 5H_2O$, a precipitate of copper pyrophosphate, $Cu_2P_2O_7 \cdot 3H_2O$ is produced according to the reaction,



The precipitated copper pyrophosphate can be dissolved in solutions containing different quantities of potassium pyrophosphate. By carrying out electrolysis of these solutions containing different weight ratios of $P_2O_7 : Cu$, the most optimum ratio giving a highly adherent copper deposit with maximum efficiency can be determined.

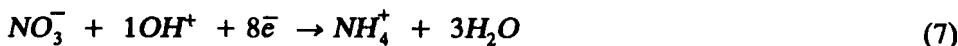
The complex prepared as above dissociates giving Cu^{++} and $P_2O_7^{4-}$ ions. On electrolysis using copper anodes, the main electrode reactions are,



Besides, there are products of water decomposition arising from



The hydrogen gas formed causes cathode polarisation leading to a decrease in plating rate. To prevent this, NO_3^- ions are added in form ammonium nitrate, NH_4NO_3 , which acts as



NH_4^+ increases the anode corrosion and acts as a grain refiner for the deposits.

After long plating periods, pyrophosphate hydrolyses to orthophosphate as



This decreases the throwing power as well as ductility of the deposits. Orthophosphate also forms, if the bath is acidified below $\text{pH} 7$ or is heated to $>60^\circ\text{C}$. Its concentration should not exceed 100 g/l , in which case the bath has to be discarded.

Besides nitrates, iodides, bromides, oxalates, thiourea, dextrin, glycerol, formalin, citrates and sachharin have all been used as additives. However, the disadvantages of organic additives is the accumulation of degradation products in the bath necessitating their removal by continuous filtration.

3. EXPERIMENTAL

120 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (A.R) is dissolved in 700 ml distilled water contained in a one litre beaker. 200 ml of 100 g potassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7$ was also prepared. The latter was added to former with continuous stirring. A precipitate of copper pyrophosphate formed. The addition was continued till the precipitation was complete, as evidenced by taking an aliquot of the supernatant liquor and mixing it with $\text{K}_4\text{P}_2\text{O}_7$ solution to check for unreacted copper. The pH after complete precipitation was 5.0 . Any excess of $\text{K}_4\text{P}_2\text{O}_7$ solution was avoided, as the same redissolved the precipitate. The volume of pyrophosphate solution thus consumed was 160 ml .

The precipitate was allowed to settle and the upper liquor containing K_2SO_4 was removed by decantation. It was washed by adding further quantities of distilled water. Washing was continued, till the copper liquor was free from SO_4 impurities. (Tested with dil BaCl_2 solution). Thereafter, it was filtered, dried at 110°C for 3 hrs . cooled and weighed.

A 300 ml of plating bath was made by dissolving 30 g of copper pyrophosphate prepared above, 85 g of $\text{K}_4\text{P}_2\text{O}_7$ and 4 g of $\text{NH}_4 \text{NO}_3$. This had a pH of 9.5 , which was adjusted to 8.0 by adding pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$. It was then filtered, taken in a 500 ml beaker and heated to 55°C on a thermostatically controlled hot plate-cum-magnetic stirrer.

The electroless copper plated Al_2O_3 substrates ($2 \times 1 \text{ inch}$, 25 mm thick) were electroplated. The plating jig consisted of two identical electrolytic grade copper anodes ($2 \times 2.5 \text{ inch}$, 5 mm thick), fitted vertically at a distance of 2.5 inch by screwing to a perspex plate ($4 \times 4 \text{ inch}$, 5 mm thick). The substrate was fixed in a copper rod holder and held in the middle of these two anodes. The plating was carried out at a constant current of 0.2 A for 2.5 hrs . The quantity of copper deposited was found out by weighing the substrate before and after plating.

The adhesivity of electroplated copper was qualitatively tested by using the conventional Scotch tape.

Likewise, five more baths each containing 30 g of copper pyrophosphate, 4 g of H_2NO_3 but different quantities of $\text{K}_4\text{P}_2\text{O}_7$ were prepared and the substrates were electroplated under identical conditions. These results are presented in Table 1.

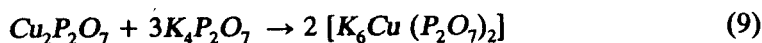
Table 1. Effect of $\text{P}_2\text{O}_7 : \text{Cu}$ ratio on performance of copper pyrophosphate electroplating baths

Bath No.	$\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (g)	$\text{K}_4\text{P}_2\text{O}_7$ (g)	$\text{P}_2\text{O}_7 : \text{Cu}$	C (Amp)	V (Volt)	Cu plated (g)	Adhesivity	Remarks
	30	85	5.54	0.2	0.2	0.086	poor	non-uniform deposit, anodes black
	30	105	6.52	0.2	0.2	0.217	excellent	bright uniform deposit, anodes pink
3.	30	125	7.50	0.2	0.2 for 0.5 hr 0.3 for 2 hrs	0.215	excellent	bright uniform deposit, anodes bright
4.	30	145	8.47	0.2	0.3 for 1 hr 0.2 for 1.5 hrs	0.219	good	-do-
	30	165	8.45	0.2	0.4 for 0.5 hr 0.3 for 2 hrs	0.250	poor	-do-
	30	185	10.42	0.2	0.5 for 0.25 hr 0.4 for 2.25 hrs	0.239	poor	-do-

4. RESULTS AND DISCUSSION

The quantity of $\text{K}_4\text{P}_2\text{O}_7$ required for complete precipitation was 80 g and the weight of $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ produced was 82 g. If reaction (1) is valid, the expected yield of $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ should be 85 g. However, the difference of 3 g might be attributed to the losses during washings. As mentioned under section 3, this reaction is complete at $\text{pH} : 5.0$.

It will be evident from Table 1 that $\text{Cu}_2\text{P}_2\text{O}_7$ dissolves in $\text{K}_4\text{P}_2\text{O}_7$ for a weight ratio of $\text{P}_2\text{O}_7 : \text{Cu} = 5.5$. This value corresponds to the formation of a hexavalent anion viz, $\text{Cu}(\text{P}_2\text{O}_7)^{6-}$, which results from the dissociation of the complex produced as per the reaction,



It is also seen that the weight of copper deposited per unit quantity of electricity is minimum for the above bath No. 1. Besides, the anodes were black possibly due to formation of cupric oxides causing a decrease in anode efficiency. As the $\text{P}_2\text{O}_7 : \text{Cu}$ ratio increased to 6.5 for bath 2, the quantity of copper deposited also increased more than two folds. Still, the anodes were pink indicating the formation of cuprous oxide. However, for the ratio of 7.5 although the weight of copper decreased a little, the anodes corroded brightly. This occurs at nearly 100 per cent anode efficiency and renders the bath economical, since it does not become necessary to replenish the

expensive pyrophosphate salt. The adhesivity of copper electroplate was meeting the specification laid down for subsequent processing of the plated substrates.

5. CONCLUSIONS

- (i) Copper pyrophosphate can be produced by mixing a solution of copper sulphate with a solution of potassium pyrophosphate in a mole ratio of 1 : 1.
- (ii) Copper pyrophosphate can be dissolved in excess potassium pyrophosphate in a weight ratio of 1 : 4 or a P_2O_7 : Cu ratio of 7.5 : 1.
- (iii) By using a cathodic current density of 0.8 A/dm^2 , temperature 55°C and pH , 8.0, highly adherent bright copper coatings have been obtained on electroless copper plated Al_2O_3 substrates.

ACKNOWLEDGEMENT

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