Regeneration of Electroless Copper Baths

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INTRODUCTION

It is possible to reactivate a spent electroless copper bath by replenishing the consumed ingredients and recycling the complexing agent and alkali already in the solution. This is feasible because the reaction products neither accelerate nor poison the copper deposition reaction.

Electroless copper baths use copper (II) sulfate as the source of copper ions and formaldehyde as the reducing agent. The baths are operated above pH 10 with sodium hydroxide and sodium carbonate providing the alkalinity. A complexing or chelating agent holds the copper in solution and stabilizes the bath. A stabilizer such as thiourea or mercaptobenzothiazole (MBT) is required to further control the deposition rate and stabilize the bath.[1-2] The reaction for copper deposition is:

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + H_2 + 2H_2O + 2HCOO^- \quad (1)$$

For each mole of copper deposited, two moles of formaldehyde and four moles of alkali are consumed. In practice, more formaldehyde and alkali are required,[3] indicating that side reactions take place.

The disproportionation of formaldehyde with alkali to form methanol and formate ions also consumes HCHO and OH^-:

$$2\,HCHO + OH^- \rightarrow CH_3OH + HCOO^- \quad (2)$$

The deposited copper surface becomes relatively rough because of the carry-over of palladium from the activation bath and copper particles acting as nuclei. Finally, spontaneous decomposition takes place and the bath must be discarded; however, appreciable amounts of complexing agent and alkali remain in the bath. The most expensive and concentrated ingredient of the bath, the complexing agent, potassium sodium tartrate, does not participate in the deposition reaction, as shown in equation 1.

Table I. Composition of Concentrated and Dilute Electroless Copper Baths

Ingredients	*Concentrated Bath*		*Dilute Bath*	
	g/L	moles/L	g/L	moles/L
$CuSO_4 \cdot 5H_2O$	30	0.12	5	0.02
NaK tartrate	100	0.48	20	0.1
NaOH	50	1.25	4	0.1
Na_2CO_3	30	0.28	5	0.05
HCHO, 37%	30 ml/L	0.4	10 ml/L	0.13
Stabilizer, thiourea		5 ppm		5 ppm

EXPERIMENTAL

A concentrated and a dilute electroless copper bath[4-6] were prepared with the compositions shown in Table I. These baths gave a smooth and bright copper deposit on $PdCl_2$-$SnCl_2$ catalytic activated articles.[7] The baths were used until most of the copper was depleted. This could easily be seen by the fading color of the blue cupric complex ion.

The first step in recycling the baths is to add 5 g/L of granular activated charcoal to absorb the stabilizer. Because the stabilizer is depleted and copper particles are present, a spontaneous reaction takes place: copper deposits on the container walls or separates as a granular precipitate. After 24 hours, the solution becomes crystal clear. The supernatant liquid is then filtered into a clean container for bath regeneration.

To reactivate the baths, 4 ppm of stabilizer is added and the pH is adjusted to 11 by using 40 wt% NaOH stock solution. A stock solution of 25 wt% $CuSO_4 \cdot 5H_2O$ is used to replenish the baths. The copper sulfate stock solution is added with constant stirring. Development of a deep blue color indicates cupric complexes have formed. Finally, 10 ml/L formaldehyde is added and the bath is again ready for copper deposition.

These baths can be regenerated more than six times and show excellent stability. The deposit is a highly uniform and bright copper.

DISCUSSION

An electroless copper bath must be discarded after a single use. Replacing the depleted chemicals allows the bath to be reused, provided the reaction products do not interfere with the deposition reaction.

In general, a bath becomes out of control when an excess of copper particles is suspended in the solution or when the stabilizer decomposes. Organic compound containments may also lead to an unstable bath. Granular activated charcoal treatment can remove the stabilizer and organic contaminants from the solution. This accelerates spontaneous deposition of copper particles which, along with other granular precipitates, can be filtered out easily. Carbon treatment and filtration are common steps in a plating line, thus costs should not be increased.

The quantity of complexing agent in a bath is usually more than two times the number of moles required to form cupric complexes. The concentration is essentially unchanged before and after use except for minor drag-out. It was found in this work that one of the reaction products, $HCOO^-$, is also an excellent complexing agent. The presence of formate ion further stabilizes a bath and yields a bright copper deposit. Accordingly, less stabilizer should be used after each regeneration. The recommended stabilizer replenishment is 3 to 4 ppm.

Organic stabilizers such as thiourea, MBT or aromatic nitro compounds[8] are preferred in these baths because they can be extracted by activated charcoal treatment. Their amount must be precisely controlled and not exceed 5 ppm after a regeneration.

Stock solutions of copper sulfate and sodium hydroxide were prepared at their solubility saturation limit. This requires that only a few milliliters of the stock solution be added in order to avoid a rapid increase in the bath volume. If a dilute stock solution is used, then there is a risk of rapidly increasing bath volume after each regeneration. The ingredient concentrations decrease as bath volume increases. Finally, a dilution limit is reached and the complexing agent must be replenished. This will happen when the bath volume has been doubled by a few recycles. MF

References

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Biography

Philip Yan is a senior research scientist at ARCO Solar, Inc., in Chatsworth, CA, where he investigates various aspects of photovoltaic technology. He holds a PhD in applied chemistry from Boston University.