

Tech Talk

Fine Lines in High Yield (Part CXLV)

Staying Out of Trouble in Gold Electro-plating

Karl H. Dietz (for CircuiTree Magazine, October, 2007)



Karl Dietz is the manager at DuPont's Electronic Materials Laboratory, Research Triangle Park, NC. His responsibilities include application studies for printed circuit materials. Karl has 35 years of experience in a variety of R&D, manufacturing and quality control functions and holds a PhD. in organic chemistry from the University of Frankfurt, Germany. If you would like to participate in the exchange or if you have any questions, Karl Dietz can be reached at 919-248-5248, fax: (919) 248-5132, or via e-mail <Karl.h.dietz@usa.dupont.com>.

Several gold plating processes are being practiced in PWB fabrication: there is ENIG (electroless nickel, immersion gold), electroless gold which allows thicker gold deposits than ENIG, and there are gold electroplating processes. The most common electroplating process is acid potassium gold cyanide. Since there is the potential for HCN release from the gold cyanide bath at a low pH, other cyanide-free processes have been looked at such as the sodium gold sulfite process (Ref. 1) which is run at a pH of 6 to 7, but it has not been adopted in PWB fabrication because the plating bath is harsh in the dry film resist and the bath releases SO₂ at a pH of less than 5. The acid potassium gold cyanide bath can be run safely in the pH range of 3.5 to 5.0 (Ref. 2). Below a pH of 3.1 there is the danger of HCN evolution. In the specified plating pH range it is possible to co-deposit small amounts of other metals that impart desirable properties, such as cobalt to harden the gold deposit. Gold baths are typically run with DC current, however good results are also reported with pulse plating (Ref. 3).

The theoretical amount (100% plating efficiency) is calculated by inserting the equivalent weight for gold of 196.967 in the second equation, converting seconds into minutes, which results in a theoretical amount of 123 mg per Amp-minute. The actual plating efficiency is then calculated by dividing the actual amount plated into the theoretical amount.

% Efficiency	=	$\frac{\text{Actual Amount Plated} \times 100\%}{\text{Theoretical Amount}}$
Theoretical Amount (wt. of deposit in grams)	=	$\frac{(\text{Equiv. Wt.}) \times \text{Amps} \times \text{Time (sec)}}{96,500}$

Figure 1: Actual and Theoretical Plating Efficiency

Good chemical resistance is needed in a gold plating film, and the resist needs to be thick enough to conform to an already circuitized surface for selective gold plating. This added thickness can enhance the chemical resistance in diffusion limited chemical attacks. As mentioned above, gold baths are notoriously inefficient, especially when run at low gold concentrations. This leads to high hydrogen evolution at the cathode with a correspondingly high level of localized hydroxide ions (Ref. 4). This will of course raise the pH in the vicinity of the resist, acting like a stripper, causing the resist to lift, a problem which we

tend to fight by improving agitation to dissipate the hydroxide ions quickly. However, the resist formulation has to be reasonably hydrophobic and capable of withstanding an elevated pH. This is why alkaline etch resists have a good chance of performing well as gold plating resists. This failure mechanism for aqueous processable resists that contain carboxylic acid groups is plausible: John Deuber (Reference 5) points out that solvent processable resists which don't have carboxylic acid functions did behave well in gold baths and it was with the advent of aqueous processable resists that resist break-down became a problem that had to be overcome by reformulating the traditional cobalt-gold baths to minimize the occurrence of this defect. The

Parameter	Property
Gold Content (as potassium gold cyanide)	0.5 -2.0 Troy oz/ gal
pH	3.5 - 5.0
Conductivity Enhancing Salts	Vendor Specific
Temperature	70 - 120 °F (21 - 49 °C)
Current Density	10 ASF
Anodes	Platinized Titanium
Agitation	Vigorous Solution Movement
Filtration	Continuous
Plating Efficiency	30 - 70%

Table 1 gives the characteristics of a typical gold cyanide plating process.

Notable is the low plating efficiency which is usually blamed for the most common defect originating in gold plating namely "resist break-down", a misnomer for resist lifting that leads to underplating.

The actual plating efficiency should be monitored and corrective measures need to be taken if the plating efficiency is at the low end of the acceptable range. Such measures are discussed later. The actual efficiency of the gold bath can be calculated as shown in Figure 1.



The miracles of science™



resist's propensity to lift is also aggravated by internal stresses at the resist copper interface. Consider that cyanide-gold complexes are stable in the range of approximately pH 3.5 - 6, and that many gold baths are therefore run in the pH range of 4 to 5. Further consider that the pK_a of the carboxylic acid functions in the binder of the resist is around 5, which means that at a pH of 5, given sufficient time, half of the acid groups will eventually convert to a salt in the gold plating environment. This in turn means, that the resist will swell considerably as the salt formation is accompanied by hydration, and considerable strain results at the resist/copper interface, ultimately leading to resist lifting. To assure resist survival under these demanding conditions we want to select a fairly hydrophobic resist to minimize the diffusion of hydrated ions into the resist. The trade-off in this selection is typically a slower strip speed.

The root cause of resist failure in gold plating may be a weakening of the resist due to attack in the preceding nickel plating but it becomes noticeable only after gold plating. Sulfamate nickel baths seem to be more benign than Watts nickel. This behavior is often attributed to the higher temperature of the Watts bath. Another explanation points to the faster diffusion rate into the resist of smaller ions, such as chloride. The nickel chloride in the Watts bath facilitates the anode corrosion. In the sulfamate bath, nickel bromide serves this function. The chloride ion of the Watts bath is smaller than the bromide ion (and much smaller than the sulfamate ion) and could therefore explain a faster penetration of the resist that leads to swelling and stresses. In line with this explanation is the observation that fluoride ions that are smaller than chloride are even more damaging to the resist. This is why fluoborate tin/lead baths have boric acid added to shift the equilibrium between fluoborate and free fluoride and borate in the direction of fluoborate which lowers the fluoride concentration.

To minimize resist lifting (break-down) defects we need to run the gold bath at a relatively high plating efficiency. Higher gold concentration in the plating bath has this effect as shown in Figure 2. However there is a reluctance to go to high gold concentrations because of the higher initial cost of the bath (of course there is no higher gold consumption for a given job, just the initial cost of the bath).

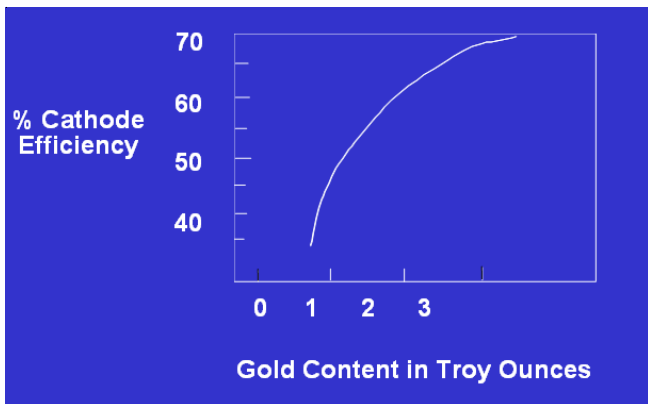


Figure 2: Plating Efficiency vs Gold Concentration

Plating efficiency also increases with lower current density as shown in Figure 3

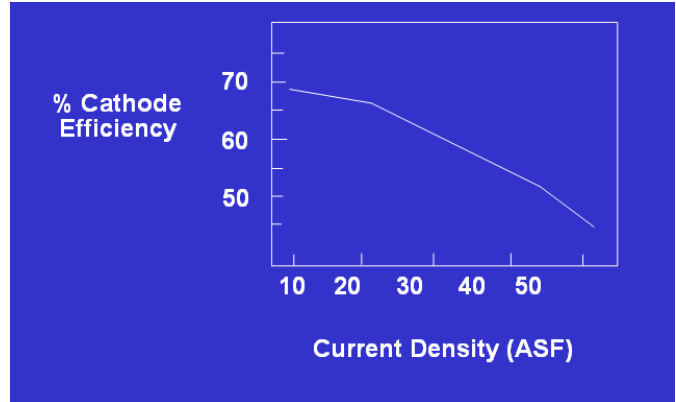


Figure 3: Plating Efficiency vs Current Density

Plating efficiency is also increased as we increase pH (see Figure 4; also Ref. 5)

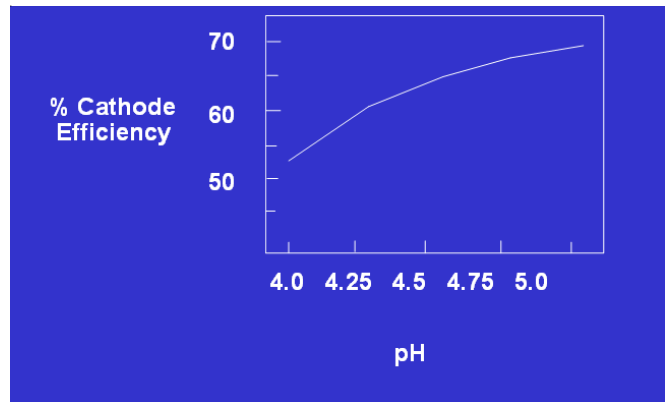


Figure 4: Plating Efficiency vs pH

Last not least, plating efficiency also increases with higher temperature (see Figure 5)

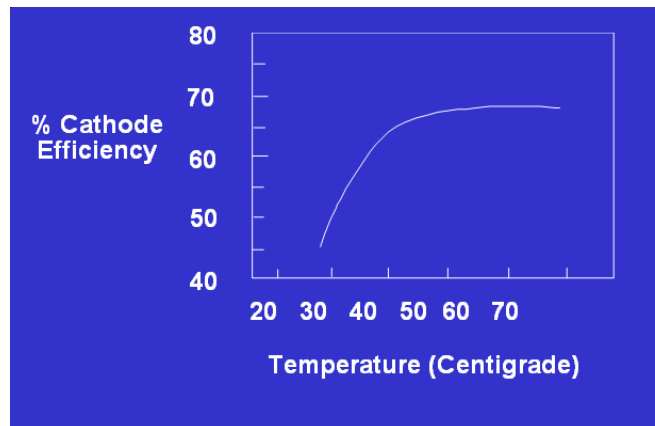



Figure 5: Plating Efficiency vs Temperature



To toughen the gold plating resist and enhance its chance of survival in the gold bath, a post-development bake, typically 15-20 minutes at 150 °F (65 °C), is often practiced but results vary. Higher lamination temperature is also often employed: the “board (laminator) exit temperature” recommendation for outer layer gold plating is typically 48 – 55 °C (120 – 130 °F) compared to 43 – 55 °C (110 – 130 °F) for other outer layers. For selective gold plating where the dry film resist has to adhere to the soldermask surface, a matte soldermask surface is preferred over a glossy surface for better adhesion. If the soldermask is not inherently matte, the soldermask surface may be pumice treated to increase the micro-roughness.

There are two types of gold baths we should distinguish: so called “hard” gold and “soft” gold. The hard gold is used as a gold “strike” (thin plating) prior to deep gold plating, or it might be used for plating electrical contact areas. Gold deposit thicknesses are in the range of 5 to 25 micro-inches, plating conditions are typically 100 – 110 °F (38 – 43 °C), pH 3.5 - 5.0, and 2 – 5 ASF. Soft gold baths are usually used for deep gold (full pattern plating). Soft gold baths tend to have better plating efficiencies than hard gold baths, yet they are harsher on the resist because of the longer immersion time, higher pH (4.5 – 7.0), higher temperatures (100 – 140 °F), and higher current densities (5 – 10 ASF).

A curious defect, that has been observed in gold contact plating, is described in Reference 6. A purple-colored stain is observed on the laminate between gold plated contacts. This stain was identified as “Purple of Cassius”, a colloidal gold colorant used for glass staining and named after the 1700th century Dutch alchemist who first observed it when he added stannic acid to a very dilute solution of gold. The most likely scenario that leads to this laminate stain is the swelling of the epoxy e.g. by the glycol ethers used in the desmear swell & etch, the retention of tin from the HASL process in the porous laminate surface, the oxidation of the tin to stannic acid in the oxidative environment of tin/lead stripping, the formation of the insoluble beta-form of the stannic acid that survives post-solder strip rinses, and finds its way into the gold bath where it forms the gold colloid Purple of Cassius on the laminate. This colloidal gold is not just a cosmetic blemish but may lead to high resistance shorts.

References

1. A Versatile Non-Cyanide Gold Plating System, Ronald J. Morrissey, Plating & Surface Finishing, April 1993, pg. 75
2. Gold Plating, Alan Blair, Plating & Surface Finishing, August 1995, pg. 60
3. Gold Deposits Obtained by Pulse Plating, Plating & Surface Finishing, December 1990, pg. 71
4. Fine Lines in High Yields, (Part XLII): All-Purpose versus Specialty Photoresists, Karl H. Dietz, Circuitree Magazine, February 1999, pg. 60
5. Gold Plating with Aqueous Resists, John Deuber, PC Fab, April, 1989, pg. 93
6. “The Purple of Cassius”: A Recurrent Gold Finger, Tab-plating Problem, K. Minten and J. Messer, Circuit World, Vol. 19 No. 1, 1992, pg.44