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A High Reliability, Stress-free Copper Deposit for FPC, Polyimide and Rigid-Flex

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Abstract
Today's wide variety of laminate materials and specialized dielectric choices pose a challenge for process engineering. In particular, smooth surfaces, such as polyimide, flex circuit substrates and rigid-flex constructions with window cut-outs, can be a challenge for electroless copper and plating processes. Conventional electroless copper systems often required pre-treatments with hazardous chemicals or have a small process window to achieve a uniform coverage without blistering. To overcome the challenge of metallizing smooth surfaces, a new stress-free electroless copper was developed to serve this important sector of the printed circuit industry.

Introduction

As the thermal, physical, chemical and electrical properties of PCBs have advanced so too have the substrates of construction. With a wide variety of substrates available, it is becoming increasing difficult to accommodate these new substrates in current manufacturing processes (1). Polyimide resins (PI), for example, provide exceptional thermal and chemical stability but remain challenging with industry standard processes. In particular, electroless copper deposition, the most commonly used method of metallizing a nonconductive substrate, is susceptible to blistering or peeling due to the low adhesion of the copper film to the substrate. Typically, electroless copper films require mechanical anchoring to provide adhesion to a substrate to prevent blistering. A roughened surface is commonly created with a chemical or plasma etch process to help create anchoring sites. Conventional chemical etches, which were primarily designed for epoxy substrates, are generally ineffective at activating PI substrates (2). Plasma etching, which is effective at etching PI, is still insufficient to prevent peeling and blistering (3). Some manufacturing processes have resorted to using an alkaline solution containing hydrazine (4). While this can be effective at improving adhesion of electroless copper films, hydrazine is extremely hazardous and challenging to handle safely. In addition, many material types, such as those that contain adhesive bonding layers, are incompatible with strong alkaline solutions.

Due to the fact that most surface treatments are ineffective, or not practical or compatible in some situations, it is critical that the electroless copper process provides a significantly wide processing window to alleviate blistering defects and accommodate a variety of substrate types. The most common commercially available electroless copper plating solutions are not designed to meet these requirements. It is known that blistering and peeling of the copper deposit is also a function of the internal stress and strain of the deposit and that additives can be included in an electroless copper solution that affect the properties of the resulting electroless copper deposits (5-7). However, inclusion of additives may affect PCB reliability and careful selection is necessary. In this study, we evaluate select additives in an electroless copper system for their influence on the deposit stress and, ultimately, their effect on the reliability of a PCB by thermal shock and Interconnect Stress Test (IST).

Experimental

Electroless copper plating solutions comprised of 0.03 M copper sulfate, 0.15 M formaldehyde, 0.08 M metal chelator, 0.1-0.3 M sodium hydroxide and select stress reducing additives were used for electroless copper metallization. The substrates were activated with palladium prior to electroless copper metallization. 1 to 2 microns of electroless copper was deposited onto the substrates of interest. The substrate was also processed through the aforementioned solution to increase chemical byproducts of the electroless copper reaction, represented by an increase in specific gravity, from a specific gravity of 1.03 to 1.10. These solutions were evaluated at various points within this range. PI substrates were used for blister evaluation.

Internal stress was evaluated using a production spiral contractometer with a 0.15mm nickel and teflon coated spiral per ASTM B 636-84 (2001).

A 1.57 mm thick interconnect defect (ICD) solder shock coupon comprised of 8 layers of alternating 1 oz. and ½ oz. copper and 1.02 mm plated through holes (PTH) was used for evaluation. The substrate of construction was an epoxy FR-4 with a 180°C glass transition temperature (T_g). After electroless copper metallization these coupons were electroplated in a commercially available sulfuric acid based copper plating solution to increase the total copper deposit thickness to 28-30 microns prior to ten thermal shocks at 288°C for 10 seconds each in accordance with IPC-TM-650 2.4.13f. Cross sectional evaluation was performed on seven PTHs per coupon.

Reliability was also evaluated using an IST testing system. IST coupon design GM40001A with a thickness of 3.18 mm comprised of 14 ½ oz. copper layers was used for evaluation. The coupon was constructed using the same substrate as the ICD coupon and contained 0.25 mm and 0.38 mm PTHs and 0.15 mm micro vias (MV). All coupons were precycled at 260°C six times to simulate the assembly process. The IST equipment was set to cycle between 25°C and 150°C (PTH) or 25°C to 190°C (MV) with 3 minutes of heating and 2 minutes of cooling. Coupons were tested for 1000 cycles or to failure defined as a 10% increase in resistance. Failure mode was evaluated and documented. This coupon is comprised of two circuits, S1 being PTH and S2 being MV, with S1 being evaluated first followed by S2. These IST coupons were electroplated in a commercially available sulfuric acid based copper plating solution to increase the total copper deposit thickness to 28-30 microns. A picture of the IST coupon is shown in figure 1.

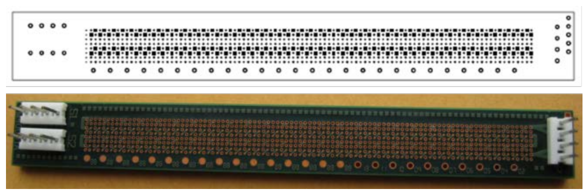

Figure 1. GM40001A

Results and Discussion

The effect of the additives on the electroless copper deposit was first evaluated using PI substrates that historically have been problematic for electroless copper processing. These materials are all PI substrates found commonly in the manufacturing of flexible PCBs. Comparative studies were visually performed with and without the additives to determine their effectiveness at reducing or eliminating blistering and peeling of the copper deposit. Figure 2 and 3 represent materials that have shown poor coverage on an additive free electroless copper solution. With the addition of the additives a significant improvement is observed.

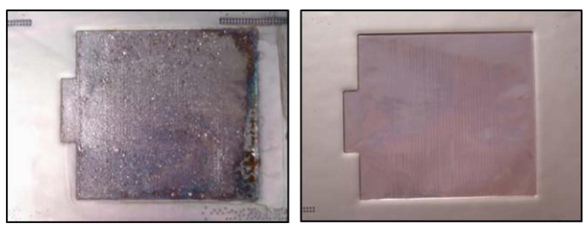

Figure 2. Sequentially laminated Rigid-Flex PI window cut-outs exposed to electroless copper processing. Electroless copper (left) and electroless copper with stress reducing additives (right)

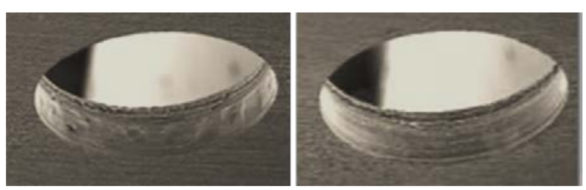

Figure 3. Flexible PI PTH. Electroless copper (left) and electroless copper with stress reducing additives (right)

The reduction of blistering is attributed to reduced internal stress of the copper deposit. Additives included in the electroless copper solution effect the stress of the resulting electroless copper deposit. Electroless copper deposits normally exhibit compressive stress and tend to lift, or blister, off of smooth surfaces that lack mechanical anchoring sites. With the proper selection of additives the stress of the deposit can be significantly reduced.

Deposit stress can be measured in a number of ways. A common method in the electroplating industry is through the use of a spiral contractometer. The copper deposits of four electroless copper solutions containing different additives were evaluated using a production spiral contractometer. Figure 4 indicates that internal stress of the deposit is significantly affected by additives. Typical electroless copper solutions utilized in PCB manufacturing are similar to Electroless B and C and D. With the addition of select stress reducing additives, labeled Electroless A, the stress of the deposit is reduced significantly.

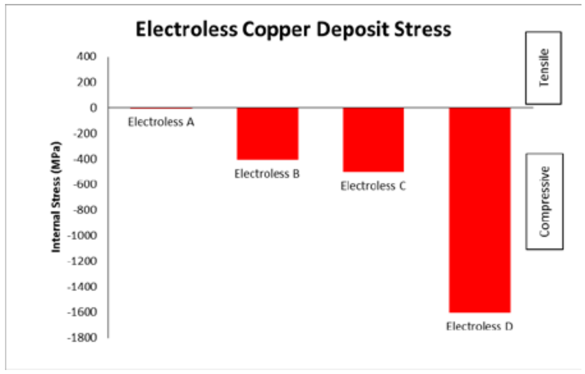

Figure 4. Electroless copper deposit stresses measured by spiral contractometer. Additives in the electroless copper solution have a significant influence on the resulting deposit stress.

Electroless copper solutions containing additives from Electroless A in Figure 4 were evaluated further to determine the influence on PCB reliability. Specifically, the resulting copper deposit's reliability was evaluated on interconnects within multilayer PCBs when exposed to thermal stress. The substrate was processed through these solutions and replenished accordingly with chemical components to maintain consistent operating conditions. Operating in this way allows the solution to increase in electroless copper byproducts, such as formate, sulfate, additives, etc., similar to how commercial electroless copper systems are operated. In general, electroless copper solutions are controlled by analysis of the main chemical components as well as the specific gravity of the solution. As electroless copper solutions increase in specific gravity, undesired properties, such as solution instability, deposit defects, and byproduct formation, become more pronounced. Ultimately, these properties can affect the reliability of the copper deposit.

ICD solder shock test coupons were processed through these solutions at various specific gravity levels and evaluated accordingly. In all situations there were no ICDs encountered. Each data point in figure 5 represents 12 interconnects evaluated in 7 PTHs for a total of 84 opportunities per data point. In total, approximately 4500 interconnects were evaluated.

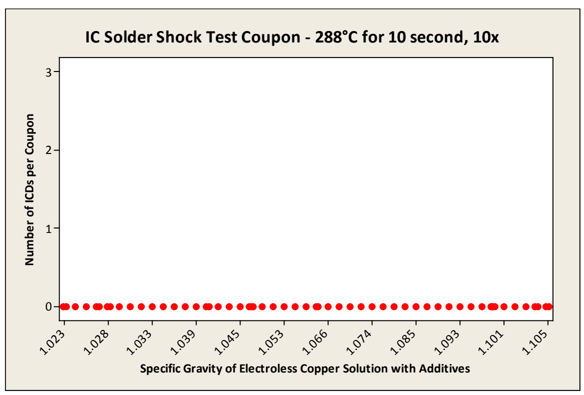

Figure 5. 10x Solder Shock test from a bath specific gravity of 1.02 – 1.10.

IST coupons were also evaluated after processing through the electroless copper solutions with stress reducing additives. Table 1 shows the results of each test according to specific gravity and deposit thickness. Test coupon outcomes are reported as cycles to failure and results listed as power, sense or accept. Coupons that reached 1000 cycles received an accept result. Failure before 1000 cycles was initially determined by the IST system to be on the power or sense circuit. In general, a failure in the power circuit can indicate a failure at the copper barrel/interlayer interface which is of primary interest when evaluating an electroless copper deposits interconnect reliability. A failure in the sense circuit is typically attributed to a failure in the PTH copper plating, i.e. a barrel crack. However, in both cases cross section evaluation is necessary to confirm failure mode.

Table 1. IST GM40001A Results.

Specific Gravity	Electroless Copper Deposit Thickness (µm)	S1 Result	S1 Cycles	S2 Result	S2 Cycles
1.060	1.55	Sense	880	Accept	1000
1.060	1.55	Accept	1000	Accept	1000
1.060	1.55	Accept	1000	Accept	1000
1.060	1.55	Accept	1000	Accept	1000
1.060	1.55	Accept	1000	Accept	1000
1.090	2.03	Accept	1000	Accept	1000
1.090	2.03	Sense	985	Accept	1000
1.090	2.03	Accept	1000	Accept	1000
1.090	2.03	Accept	1000	Accept	1000
1.090	2.03	Accept	1000	Accept	1000
1.040	1.50	Sense	486	Accept	1000
1.040	1.50	Accept	1000	Accept	1000
1.040	1.50	Sense	586	Accept	1000
1.040	1.50	Accept	1000	Accept	1000
1.040	1.50	Accept	1000	Accept	1000
1.040	1.50	Accept	1000	Accept	1000
1.092	1.73	Accept	1000	Accept	1000
1.092	1.73	Accept	1000	Accept	1000
1.092	1.73	Sense	768	Accept	1000
1.092	1.73	Sense	999	Accept	1000
1.092	1.73	Sense	649	Accept	1000
1.070	1.23	Sense	966	Accept	1000
1.070	1.23	Accept	1000	Accept	1000
1.070	1.23	Accept	1000	Accept	1000
1.070	1.23	Sense	653	Accept	1000
1.070	1.23	Sense	864	Accept	1000
1.070	1.23	Sense	938	Accept	1000
1.100	1.32	Accept	1000	Accept	1000
1.100	1.32	Accept	1000	Accept	1000
1.100	1.32	Accept	1000	Accept	1000
1.100	1.32	Accept	1000	Accept	1000
1.100	1.32	Accept	1000	Accept	1000
1.070	1.18	Accept	1000	Accept	1000
1.070	1.18	Accept	1000	Accept	1000
1.070	1.18	Accept	1000	Accept	1000
1.070	1.18	Accept	1000	Accept	1000
1.070	1.18	Accept	1000	Accept	1000
1.075	0.94	Accept	1000	Accept	1000
1.075	0.94	Accept	1000	Accept	1000
1.075	0.94	Accept	1000	Accept	1000
1.075	0.94	Accept	1000	Accept	1000
1.075	0.94	Accept	1000	Accept	1000
1.075	0.94	Accept	1000	Accept	1000
1.100	1.14	Accept	1000	Accept	1000
1.100	1.14	Accept	1000	Accept	1000
1.100	1.14	Accept	1000	Accept	1000
1.100	1.14	Accept	1000	Accept	1000
1.100	1.14	Accept	1000	Accept	1000

As mentioned previously, all IST coupons that failed to reach 1000 cycles were evaluated by cross section to determine the root cause of failure. In all instances, the failure was attributed to cracking of the copper plating, or barrel cracks, as shown in figure 6. There were no failures attributable to the electroless copper deposit or ICDs.

Figure 6. Examples of IST sense circuit failures identified by cross section evaluation as copper plating cracks.

Next, Life Data Regression Analysis was performed with the two predictors, specific gravity and deposit thickness, to determine their effect on IST cycles to failure. The data was fit using a Weibull distribution. In both cases, the two factors were not statistically significant at $\alpha = 0.05$. Since the two factors were not significant, the results were pooled together and fitted to a Weibull distribution shown in figure 7. The results were then compared to historical data of electroless copper without stress reducing additives and similar coupon construction. The comparison is shown in figure 8. Note that the historical IST data was performed at a lower preconditioning temperature of 230°C. It is generally accepted that preconditioning at higher temperatures is a more critical test with regard to IST failure.

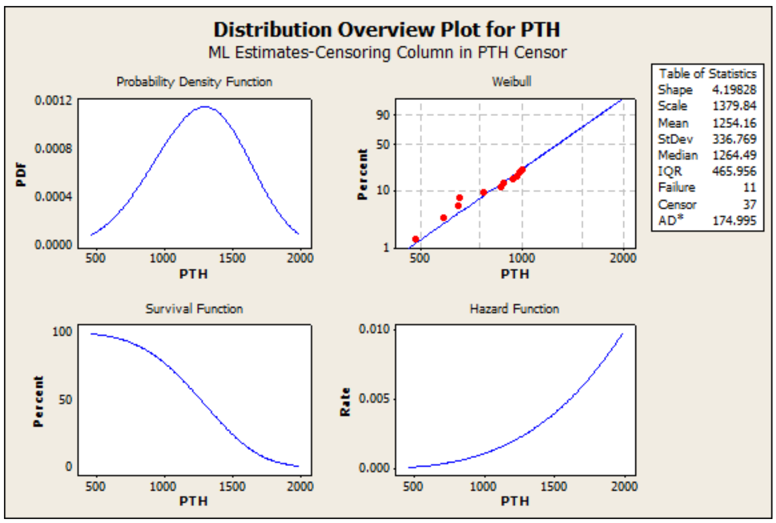

Figure 7. Distribution overview plot of all IST coupons based on cycles to failure. The data was right censored at 1000 cycles.

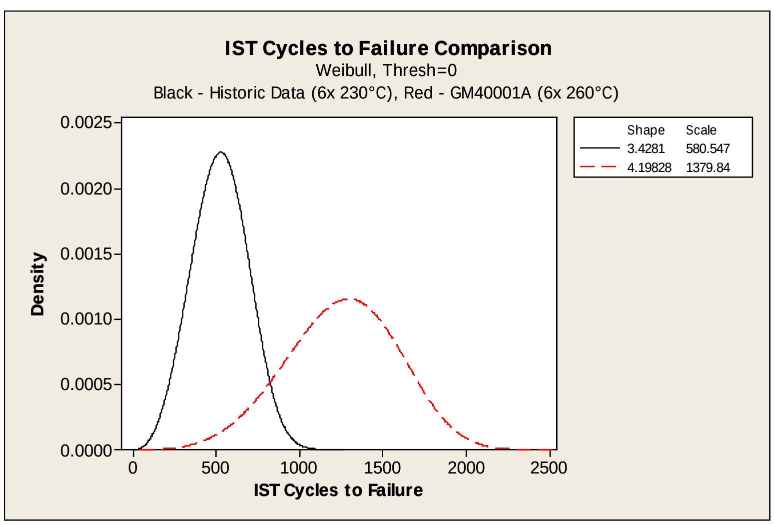

Figure 8. Comparison of IST cycles to failure of the PTH with (red) and without (black) stress reducing additives.

The additives had no negative effects on interconnect reliability of the electroless copper deposit when compared to historical data of an electroless copper solution without stress reducing additives. Next, the S2 circuit, which contained the MVs, was evaluated. After 1000 cycles there were no defects present at any parameters evaluated. A cross section is shown in figure 9. No additional evaluation was necessary. Due to the IST coupon design and test parameters used in this study, the S2 circuit has already experience up to 1000 cycles during testing of the S1 circuit. Therefore, the S2 circuits have experienced up to 2000 cycles of heating and cooling.

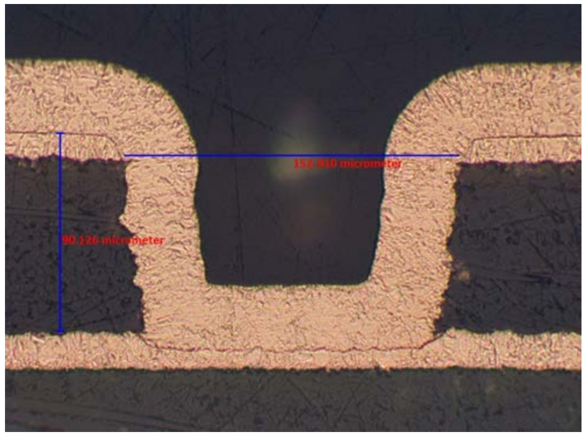

Figure 9. Cross section of an IST coupon MV after 1000 cycles.

Conclusions

Select additives can be added to an electroless copper solution which decrease the stress of an electroless copper deposit. The reduced stress allows for a blister free copper deposit on smooth, difficult to metallize substrates such as PI. These additives showed no adverse effects on the interconnect reliability of the resulting copper deposit when exposed to thermal stress as evaluated by solder shock and IST.

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