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The Chemistry and Properties of a Newly Developed Immersion Silver Coating for PWB

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To meet the emerging requirement of eliminating lead from electronics, the printed wiring board (PWB) industry is migrating from hot-air-leveled SnPb solder to alternative final finishes. A thin layer (2-3 microinches) of silver coating on copper has proven to be solderable for up to one year, and to withstand the higher temperature excursions encountered when using lead–free solders. A new improved process capable of a wide range of thickness is needed to meet current and future applications beyond solderability, such as pressfit and long term contact resistance. There is a perception that silver thickness alone determines application success. This paper describes a new immersion silver process and the resulting coating properties in tarnish resistance, solderability, surface insulation resistance and electromigration resistance.

Introduction

Immersion silver has received a great deal of interest in recent years as the alternative final finish of choice to HASL for many OEMs in the telecommunications, computer, automotive and consumer electronics industries. As the popularity of immersion silver has grown, a number of proprietary plating formulations have emerged from the supplier base since the original immersion silver process was introduced to the industry circa 1996.[1] There have been numerous studies exploring the capabilities and advantages of the immersion silver plating processes currently available in the marketplace0[2,3]. One distinction among the various chemistries available has been "thick" vs "thin" immersion silver coatings. Fundamental differences in the surface preparation and plating processes influence the performance of the various immersion silver coatings, thus resulting in different performance characteristics that are independent of the silver thickness as measured by X-ray fluorescence (XRF). Recognizing the difference in coating performance, IPC Committee 4-14 has adopted two separate thickness requirements for immersion silver.[4] This paper introduces a new plating process with a fast deposition rate that does not compromise the performance at low thickness. As an example, the paper shows that at a given silver thickness, the tarnish resistance is different for silver coatings plated from two different processes. Because the deposit characteristics vary from process to process, the silver thickness requirements to ensure reliable performance at assembly and beyond should not be applied generically to all immersion silver processes, but should be considered individually.

Experimental

Plating

A commercial process (Process A) known for fast deposition and thick silver was used as a benchmark for the newly developed process (Process B). For each process, samples were prepared through cleaning, etching, pre-dip and plating steps as per manufacturers' recommended procedures.

To encompass the various hydrodynamic conditions from production lines, plating was conducted at three agitation conditions: stagnant, mild agitation and regular agitation (estimated linear speeds of 0, 1.6 and 3.2 cm/s). Samples were plated for different lengths of time to generate a wide range of silver thickness. Panels of laminated copper (3 cm x 5 cm) were plated to determined silver thickness, coating uniformity and tarnish resistance. Wetting balance and surface insulation resistance (SIR) coupons were also plated for the intended tests. The silver coating thickness was measured by using a CMI 900 X-ray Fluorescence System from Oxford Instruments.

Tarnishing Tests

The tarnish resistance was evaluated by two tests, i.e., the humidity test of 85°C/85% relative humidity (RH) and a hydrogen sulfide test. The latter was specially designed to reveal porosity by modifying the Western Electric corrosion test (Manufacturing Standard 17000, Section 1310, Issue 1, June 1982). In this work, 1 ml of ammonium sulfide (reagent grade 20 wt% ammonium sulfide) was added to 100 ml deionized water in a 2-liter clean desiccator and the solution was gently agitated to have a uniform mixture. The samples were placed on a holder, and then put on a clean and dry porcelain supporter in the desiccator above the ammonium sulfide solution at 24±4°C. The desiccator was capped for 2 minutes. After the test, the samples were removed from the desiccator for visual and microscopical examination.

Surface Analysis

The Auger electron measurements were carried out with a Physical Electronics Model 600 Scanning Auger Microprobe, which was equipped with a LaB6 filament and a single pass cylinder mirror analyzer (CMA). The beam energy used was 3 KeV and the beam size was about ~5 µm at the largest objective aperture used in the experiments. The sampling depth was about 40Å for a metallic substrate at an electron energy of 400 eV. The system was also equipped with a differentially pumped ion gun for the sample cleaning and depth profile analysis. The sputtering rate was about 5.4 nm/min, calibrated by using a SiO2 film on Si.

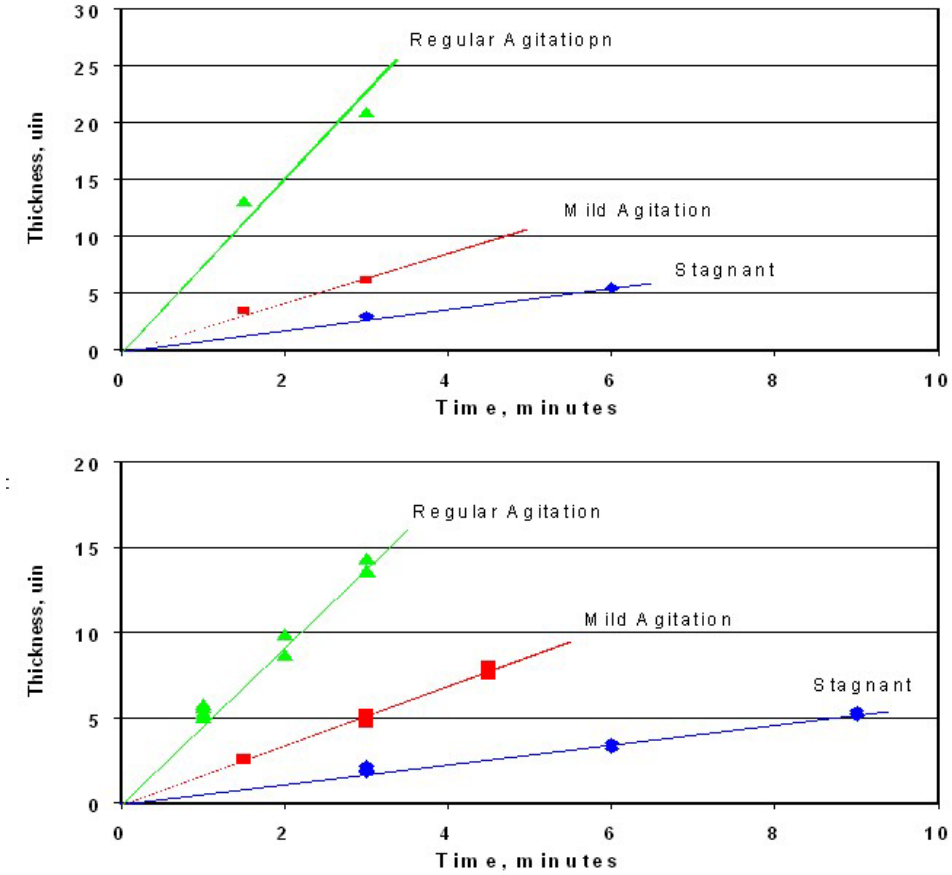

Figure 1 - Silver Thickness for Process A (top), and for Process B (bottom)

Solderability by Wetting Balance

The solderability was evaluated by a wetting balance test. The coupons plated with silver were environmentally aged at 85°C/ 85%RH for 24 hours before the wetting balance test. Some coupons were treated with up to five reflow cycles prior to the test. The reflow was conducted in air by using a BTU TRS combination IR/forced convection reflow oven with a Pb-free temperature profile, i.e., T_{peak} = 262°C. The wetting balance test was conducted per IPC/EIA J-STD-003A section 4.3.1[5] by using a "Robotic Process Systems" Automated Wetting Balance Tester with SLS 65 C (alcohol based, 2.2% solid, no-clean) flux and SnPb (63%Sn) solder.

Surface Insulation Resistance/ Electromigration tests

An IPC-25-B comb pattern (0.0125-inch space) was used for the SIR and electromigration tests. To accentuate the possibility of electromigration of a thick silver finish, three thickness of 6, 12 and 20 µin (as measured on the large land area of the comb) were tested. Twelve measurements (four on each of the three combs) were taken for each material tested. The coupons were exposed to 85°C/85% RH without bias for 96 hours for the SIR test. At the end of the SIR test, a 10-volt bias was applied for 500 hours for the electromigration test. The resistance was measured under a 100-volt bias.

Results and Discussion

Silver Coatings vs Plating Conditions

Figures 1A and 1B show the silver thickness as a function of plating time and agitation conditions for Process A and B, respectively. Under the recommended operating conditions for the chemistries, Process A is about 50% faster than Process B.

For both processes, the thickness increases linearly with time under a given agitation condition within the various plating duration. They also show that the silver thickness or the deposition rate increases with agitation. The mechanisms for both processes is the displacement reaction between the silver ions in solution and the copper metal on the PWB:

$$2Ag^{+} + Cu^{0} = 2Ag^{0} + Cu^{+2}$$

The agitation dependence suggests that the reaction is controlled by the cathodic reaction, e.g., reduction of silver ions.

Figure 2 shows the SEM photomicrographs of silver coatings of various thickness from the two processes. The coating morphology remains unchanged as the thickness increases for both processes. The silver from Process B appears to have a finer grain structure, which was confirmed by X-ray diffraction.

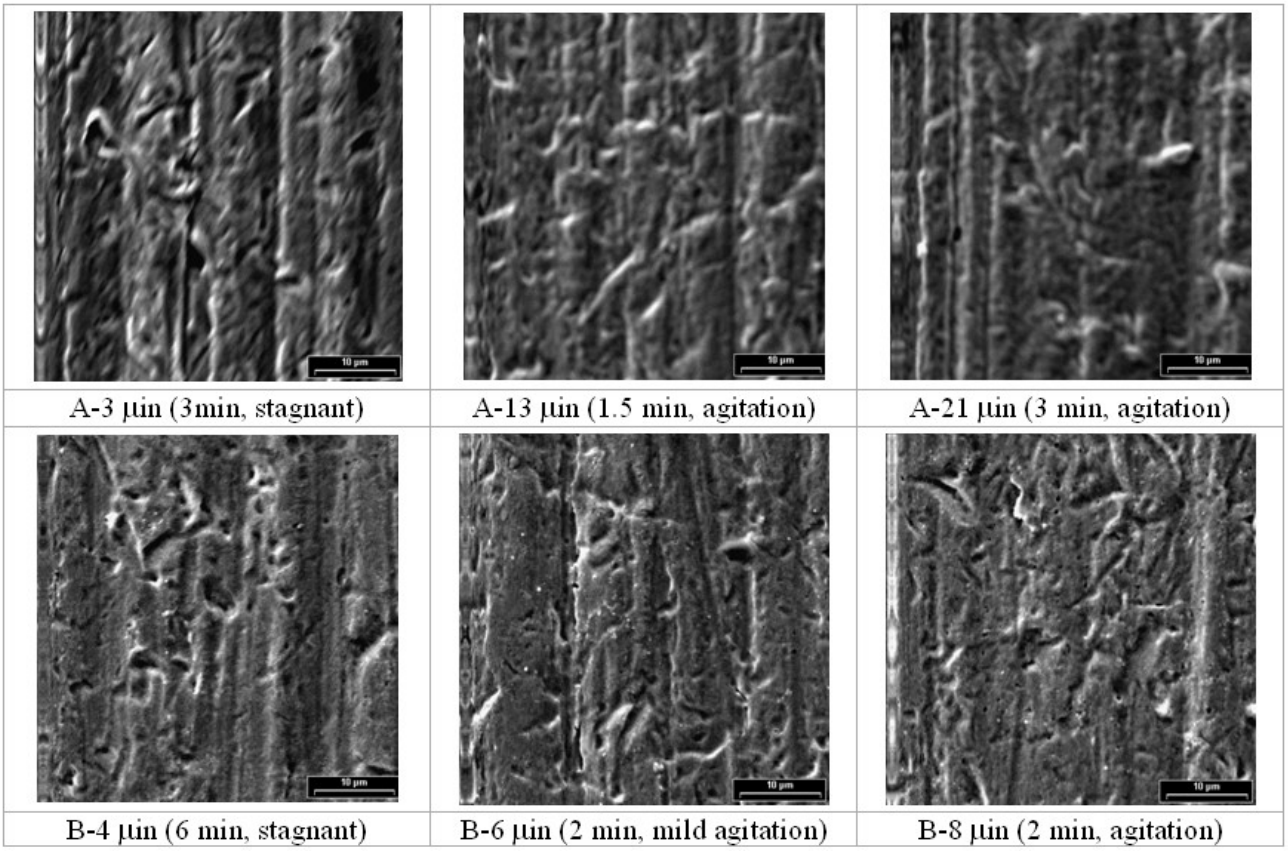

Figure 2 - SEM Photomicrographs of Silver Coated from Process A (top) and Process B (bottom)

Tarnish Resistance

Figure 3 shows the test panels after being exposed to 85°C/85%RH for 24 hours. It can be seen that the silver coating is heavily tarnished at thickness below 6 µin for Process A, while the silver coating is only slightly tarnished for all thickness from Process B. Figure 4 shows the test panels after the hydrogen sulfide test. Again, it is clear that the degree of tarnishing decreases as the silver thickness increases, and the silver from Process B outperforms that from Process A at the comparable thickness. It is evident that the areas with scratches are more prone to tarnishing for both processes.

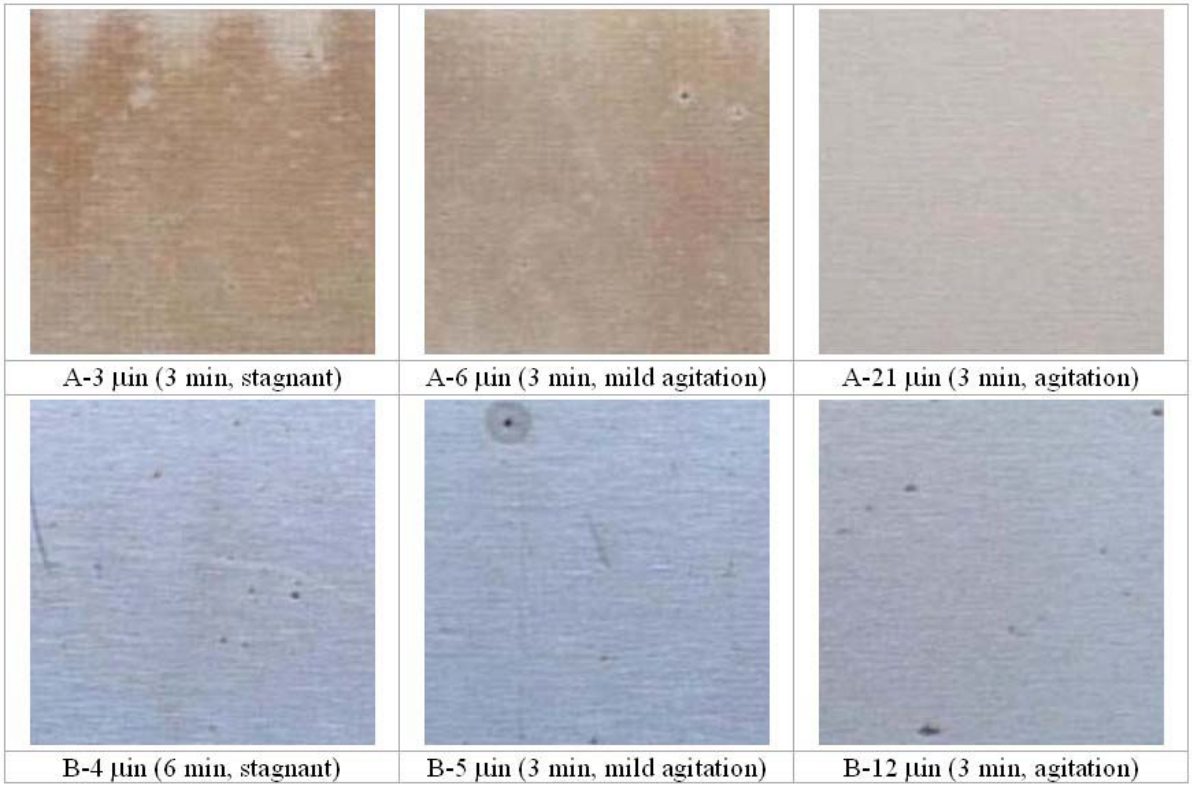

Figure 3 - Appearance of Samples after 24 Hour Exposure to the Humidity Test for Silver Coated from Process A (top) and Process B (bottom)

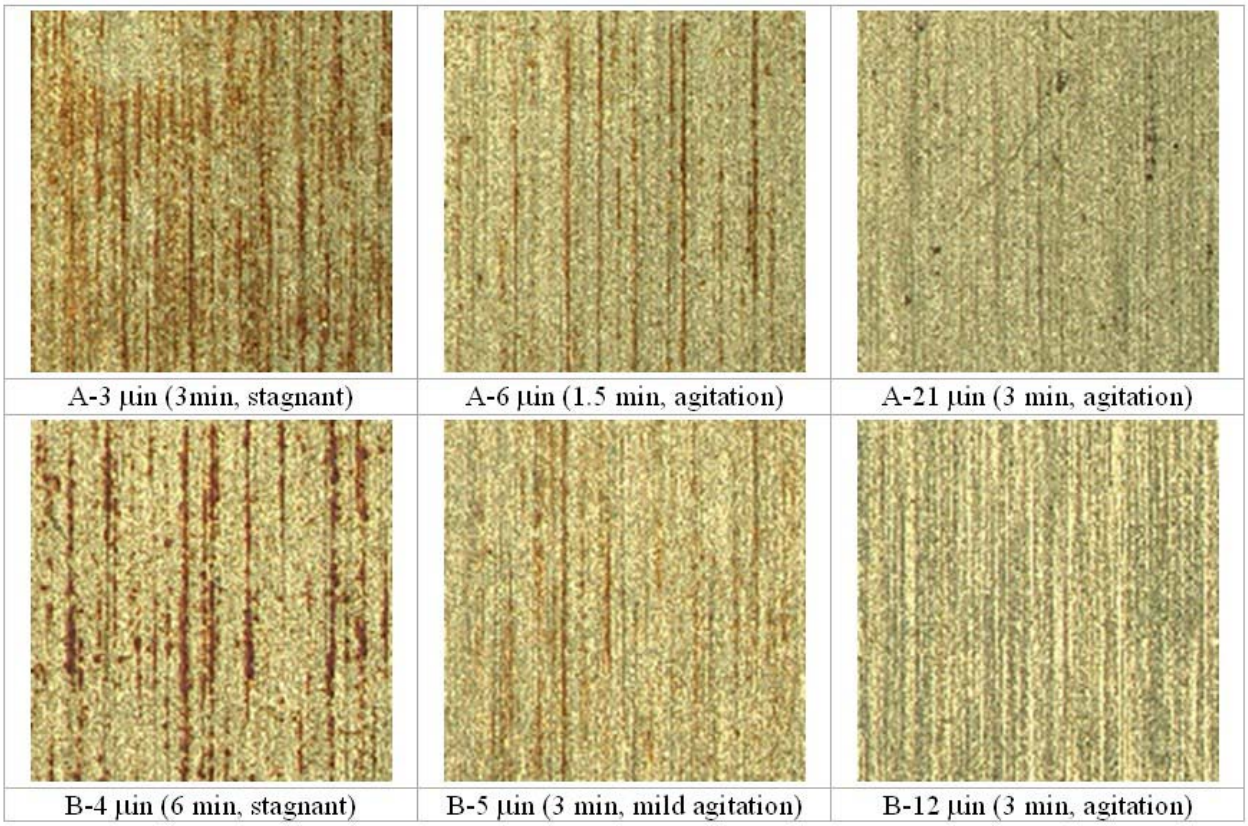

Figure 4 - Appearance of Samples after 2 Minute Exposure to the Hydrogen Sulfide Test for Silver Coated from Process A (top) and Process B (bottom)

Figure 5 shows the Auger electron surface analysis for the silver from Process A, i.e., 3.4 μin after the humidity test and 13 μin after the hydrogen sulfide test. In both cases, the surface is covered with C, O and Cu and a very small amount of silver.

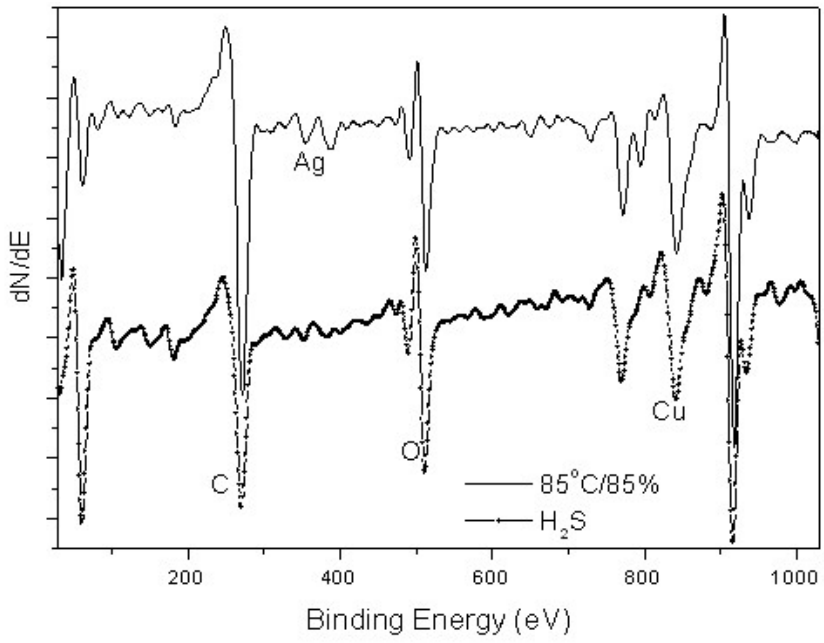

Figure 5 - Auger Surface Analysis of 3.4 μin Silver from PROCESS A after the Humidity Test (top), and 13 μin Silver from Process A after Hydrogen Sulfide Test (bottom)

Figure 6 shows the Auger depth profile of the 3.4 μin sample from humidity test. On the surface, there are about 63 atomic % Cu, 34% O and 2-3% Ag. The relative amounts of Cu and O suggest that copper exist as Cu_2O on the surface. The profile also shows inter-diffusion between copper and silver. Because of the low solubility of copper in silver, the diffusion of copper is unlikely through the bulk of silver grains, but via the grain boundaries and/or the pores in the silver. When a PWB is exposed to an atmosphere that is corrosive to both copper substrate and silver deposit, the atmosphere penetrates through the defects, such as pores and grain boundaries in the silver coating, and attacks the copper underneath. Thus, the tarnishing resistance depends not only on the thickness of silver but also on the porosity and structure of the silver deposit.

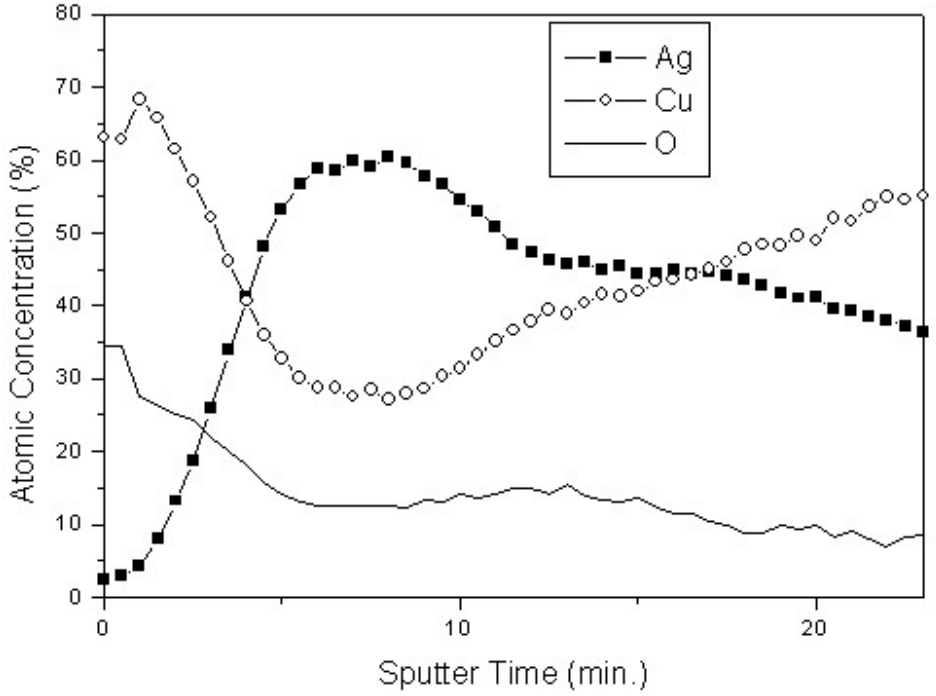

Figure 6 - Auger Depth Profile of the 3.4 μin Silver from Process A after 24-Hour Exposure to Humidity Test

Solderability of Silver from Process B

The results of wetting balance tests of nine silver coatings in the thickness range of 2.8 to 12.3 µin produced from various operating conditions are summarized in Table 1. The results include the parameters of "time to zero buoyancy" (T_o), "wetting force at two seconds from start of test" (F_2), "wetting force at five seconds from start of test" (F_5), "maximum wetting force" (F_{max}), and "time to 2/3 of the maximum wetting force" ($T_{2/3max}$).

Table 1 - Results of wetting balance tests for Process B samples aged for 24 hours in 85 °C/85%RH (0X), and followed by five times reflow treatment (5X)

Plating	Agitation	No			Mild			Regular		
	Time (min)	3	6	9	1.5	3	4.5	1	2	3
	Ag (µin)	2.8	5.2	7.9	3.8	6.6	10.3	5.5	9.5	12.3
Reflow 0X	T_o (sec)	0	0	0	0	0	0.5	0.5	0.41	0.47
	F_2 (µN/mm)	248	243	229	244	248	253	204	247	235
	F_5(µN/mm)	252	243	247	254	242	255	208	272	240
	F_{max}(µN/mm)	254	253	256	260	252	256	229	285	250
	$T_{2/3max}$ (sec)	0.82	0.85	0.90	0.80	0.84	0.91	1.00	0.90	0.84
Reflow 5X	T_o (sec)	0.88	0.81	0.91	0.77	0.69	0.73	**1.2**	0.62	0.84
	F_2 (µN/mm)	151	178	168	170	199	218	**69**	244	154
	F_5(µN/mm)	173	193	200	198	210	225	**100**	230	237
	F_{max}(µN/mm)	182	202	200	211	212	225	**119**	249	237
	$T_{2/3max}$ (sec)	1.60	1.40	1.60	1.60	1.30	1.20	**2.60**	1.10	1.10

After being conditioned in 85°C/85% RH for 24 hours, all nine coatings, regardless of the thickness and plating conditions, remain tarnish-free and demonstrate excellent solderability, i.e., T_o < 1 second, and F_2 > 200 µN/mm. The solderability is relatively independent of the thickness and the plating conditions over the range studied. This result agrees with the findings by IPC committee 4-14 that "2 µin is an acceptable lower limit for immersion silver where solderability is the only functionality".[6] Furthermore, wetting occurs instantaneously (T_o = 0) for thinner coatings, but takes about 0.5 second for thicker coatings.

After five reflow treatments, except for one sample plated for one minute with regular agitation, the eight other samples still demonstrate good solderability, T_o < 1. The effect of multiple Pb-free reflow thermal excursions is exemplified in Figure 7. In general, as the number of reflows increases, T_o gradually increases and the wetting forces (F_2, F_5 and F_{max}) slightly decrease. The good solderability exhibited by the samples of 2.8 and 3.6 µin silver suggests that the minimum thickness of 7.2 µin (0.18 µm) to preserve solderability found by Sirtori et al.[7] is process specific and should not be applied generically to all immersion silver processes.

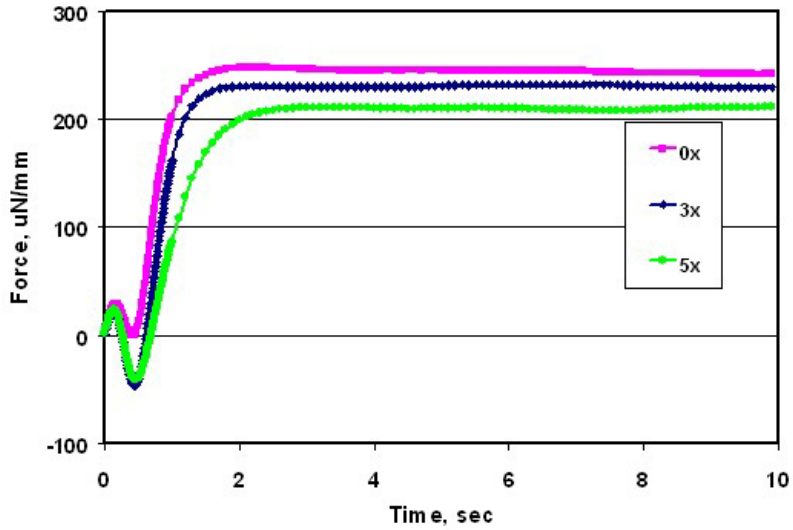

Figure 7 - Effect of Reflow on Wetting Balance Curve of Silver Plated from Process B (6.5 µin at Mild Agitation for 3 Minutes)

SIR and Electromigration of Silver from Process B

Figure 8 shows the box-whisker plots of surface insulation resistance measured after 96-hour exposure to 85°C/85%RH. For the three silver thicknesses (6, 12 and 20 μin) tested, the individual resistance is in the range of 4×10^9 to 2×10^{10} ohms (4-20 Gohms), independent of the silver thickness, and comparable to that of the bare copper.

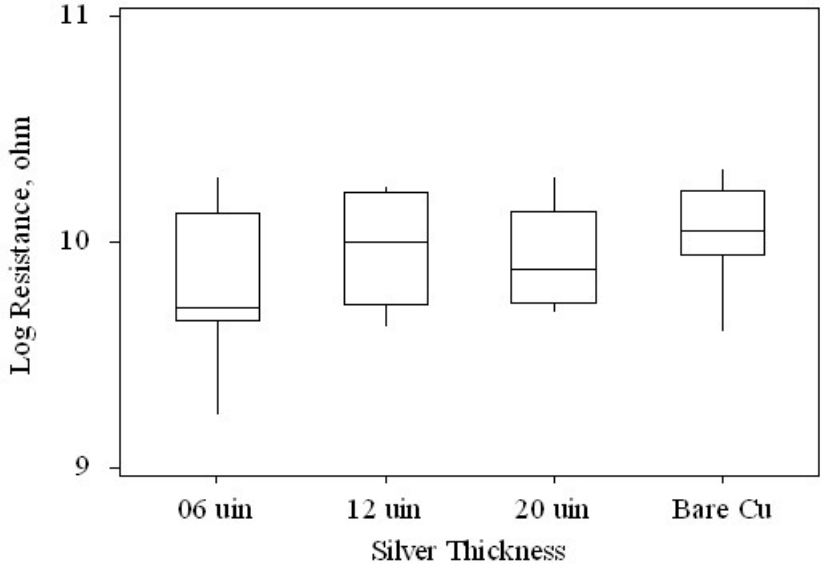

Figure 8 - Box-Whisker Plot of SIR for Silver Plated from Process B (Measured after 96 Hour Exposure to 85°C/85%RH)

The temperature and humidity dependence of the surface insulation resistance can be described by an empirical equation:[8]

$$R = R_o e^{-b \times RH} e^{E_a/kT}$$

where R_o is a material constant, b constant, RH relative humidity in %, E_a activation energy in eV, κ Boltzmann constant, and T absolute temperature in K. In a separated study, E_a was found to be 0.893 eV for both the "thin" silver and OSP type finishes on the same substrate used in the study. Thus, by using this empirical equation, the surface insulation resistance at 35°C/85%RH is estimated as about 1000 Gohms (10^{12} ohm), 50 times of the required 20 Gohms as specified by BellCore (GR-78-CORE) for the 35°C/85%RH aging condition.

Figure 9 shows the box-whisker plots of surface insulation resistance after 500-hour exposure to 85°C/85%RH under a 10-volt bias. The resistance measured on the three silver thicknesses is about 10 Gohms (10^{10} ohms), greater than the values measured at the beginning of the test as shown in Figure 8. No evidence of electromigration was found upon examination of the samples.

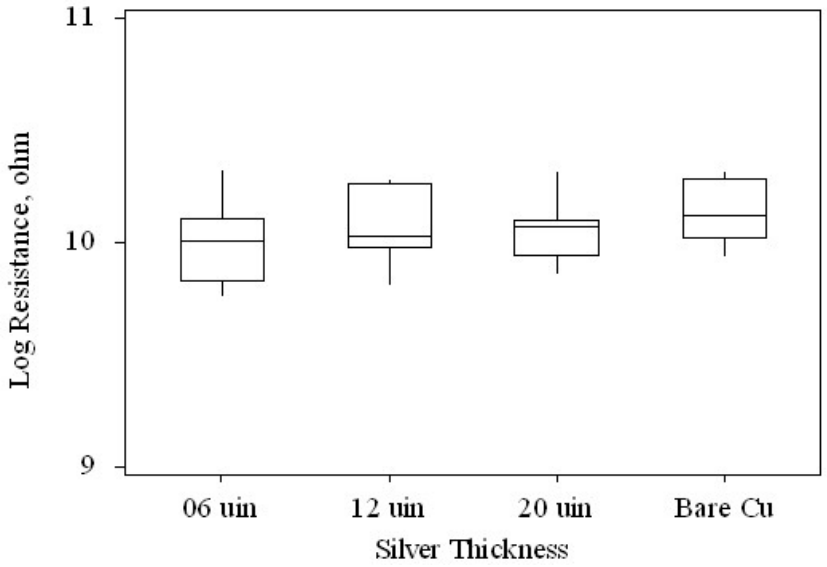

Figure 9 - Box-Whisker Plot of Electro-Migration Resistance for Silver Plated from Process B (Measured after 500 Hour Exposure to 85°C/85%RH under a 10-V bias)

Conclusions

1) For both Processes A and B silver deposition depends on the hydrodynamic conditions. While the deposition rate increases with agitation, the coating morphology remains unchanged.
2) Silver coating tarnishes in both the humidity and the H_2S tests as a result of Cu_2O formation on the surface.
3) The minimum thickness of immersion silver that is required to provide an adequate tarnish resistance and to preserve the solderability depends on the plating process/chemistry.
4) From Process B, 2-3 μin (0.07 μm) silver can preserve the solderability after 24 hours exposure to 85°C/85%RH plus five Pb-free reflows.
5) From Process B, silver up to 20 μin (0.5 μm) shows good surface insulation resistance and electromigration resistance.

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