Lead-Free Plating for Semiconductor Devices
Production Qualification & Implementation

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Lead (Pb) in electronic products has become increasingly regulated because of concerns about its impact on health and the environment. For example, the European Union has enacted a phase-out and complete ban on lead in electronic products by mid-2006. In view of this, the semiconductor industry is urgently required to study new materials to replace lead in their products, including solder plating materials for integrated circuit packages.

This paper presents the findings of a series of experiments by a major global integrated device manufacturer to evaluate various commercial lead-free plating alternatives, including tin, tin-copper and tin-bismuth products. Three different IC package types (TSOP 48, PLCC 32 and S0IC44) were used in both off line and in a production environment to evaluate solderability aspects including plating thickness, ionic impurity, morphology grade, solder whisker growth, solderability (tests under steam-age and bake conditions) and lead pull tests of mounted packages. Since no lead-free plating standards of quality were available at the time of the study, normal solder plating standards were used as a reference.

Initial experiments revealed solderability issues (especially poor morphology grades and whiskering with both tin-bismuth and tin-copper materials). Tin plating looked the most promising material. Tin and tin-bismuth plating were further investigated in production processes to attempt to eliminate the initial quality issues, and to develop, fine-tune and optimize the plating process.

The extensive experiments of this study of lead-free plating has yielded a great amount of information pertaining to the different chemistries of the different plating types, has identified a number of production concerns, and suggests process parameters for tin and tin-bismuth plating types that makes these materials viable replacements for tin-lead plating.

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Introduction

Tin/Lead solder mixture at a weight ratio of Sn/Pb 85/15% is widely used in solder plating processes of IC (Integrated Circuit) manufacturers. It has been the preferred lead finish for peripheral lead packages due to its high reliability under different operating conditions, and it is readily available and inexpensive.

Alternative lead-free solder plating materials currently being proposed in the market include pure tin (100% Sn),tin-copper (Sn-0.7Cu),tin-bismuth (Sn-3Bi),tin–silver (Sn-3.5Ag), and pre-plated frames (Ni/Pd or µPPF).

This study focused on evaluating the plating quality and developing reliable process parameters for the pure tin, tin-bismuth, and tin-copper lead-free solder plating alternatives.

Tin–silver is constrained by high cost, plating chemical instability, limiting process window, the difficulty and complexity of wastewater treatment .The pre-plated frame were not considered practical and viable alternatives worth studying at this stage, due to their high cost, ease to crack after Trim & Form and their reputation for solderability issues.

The methodology of the study of the 3 selected lead-free solder plating alternative involved 2 phases:

Phase 1: A preliminary study of the impact on solderability and solder quality of the lead-free plating alternatives, and selection for further manufacturability study in production.

Phase 2: Manufacturability study in production.

Phase 1: Preliminary Study

A preliminary study of the 3 lead-free solder plating materials—Pure tin (Sn), tin-copper (Sn/Cu), and tin-bismuth (Sn/Bi)—in pilot line experiments was carried out to study characteristics of the materials and evaluate of solderability and solder quality issues, including thickness, composition, grain structure (morphology), whisker, visual inspection of after plating and trim & form, and solderability test (after 8 hours of steam-aging,245C solder pot).

The experiments were carried out on C194 stamped leadframes of package types PL32, SO44 and TS48M. All of the samples passed the tests, except for the tin-copper plated samples, where 100 % whisker growth was observed just 2 weeks after plating. Consequently, this material was dropped for further manufacturability studies.

Phase 2: Manufacturability Study

Pure tin (Sn) and tin-bismuth (Sn/Bi) products from 2 different manufacturers (in this paper referred to as vendor A and vendor B.) were further evaluated in production mode (using strip-to-strip plating on solder plating systems at a UPH of 1,000-1,050 strips per hour—*Refer to* Table 1: Test Vehicle in Production Mode).

Table 1: Test Vehicle in Production Mode

Package Samples: SO44, PL32, TS48M

Lead-Free Solder Material	Vendor	Leadframe Material	Plating Acid Type
Pure Tin	A	C-194 STAMPED	Mixed Acid
	B	C-194 STAMPED	MSA
Tin-Bismuth	A	C-194	MSA
	B	C-194	MSA

Table 2: Plating Thickness Results

Vendor	Plating type	Package	S.S. (Reading)	Thickness (micro inch)		
				Min.	Mean	Max.
A	Pure Tin (Mix Acid)	PL32	15	363.7	440.5	485.9
		SO44	15	362.7	435.5	519.2
		TS48M	15	324	435.8	521.2
B	Pure Tin (MSA)	PL32	15	429.3	443.1	471.9
		SO44	15	337	449.1	509.7
		TS48M	15	403	440.1	483.6
A	Sn/Bi	PL32	15	388.6	427.23	464.5
		SO44	15	369	440.95	506.5
		TS48M	15	384	421.18	456.51
B	Sn/Bi	PL32	15	392.3	442	484.8
		SO44	15	403.5	442.4	506.1
		TS48M	15	343.6	437.1	495.7

1. Thickness & Composition Evaluation

Thickness and composition of 15 samples of each of the experiment package types were measured using a Seiko X-Ray Fluorescent Thickness Measurement machine (XRF). The criteria called for an average thickness of 400-450 micro inches. The result showed that the lead-free plating chemistries achieved acceptable thickness control—*Refer to* Table 2: Plating Thickness Results.

The target deposition of Bi in Sn/Bi lead-free solder plating was 1-2.5 %. Pure tin deposition is expected to be 100 % (no impurities). Both pure tin and tin/bismuth achieved the desired ranges—*Refer to* Table3: Plating Composition Results.

Table 3: Plating Composition Results

Vendor	Plating type	Package	S.S. (Reading)	Composition (%Sn)		
				Min.	Mean	Max.
A	Pure Tin	PL32	15	100	100	100
	(Mix Acid)	SO44	15	100	100	100
		TS48M	15	100	100	100
B	Pure Tin	PL32	15	100	100	100
	(MSA)	SO44	15	100	100	100
		TS48M	15	100	100	100
A	Sn/Bi [1]	PL32	15	97.57	98.37	98.5
		SO44	15	97.8	98.6	98.85
		TS48M	15	97.84	97.9	98.2
B	Sn/Bi	PL32	15	98.56	98.89	98.9
		SO44	15	98.75	98.89	98.9
		TS48M	15	98.46	98.68	98.95

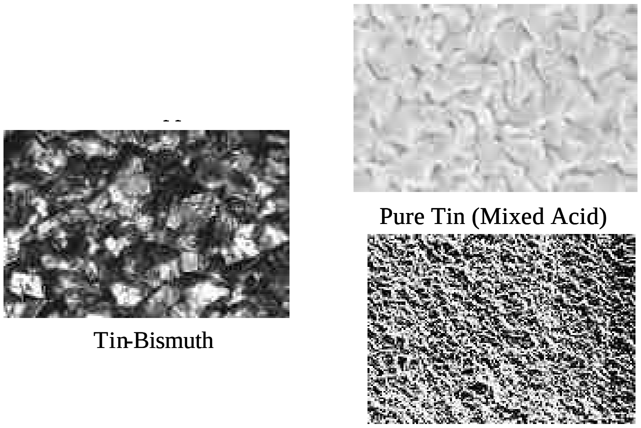
[1] Sn/Bi composition spec. range is 97.5 -99.0% Sn

2. *Visual Inspection after Plating and after Trim & Form*

After plating, 500 samples of each of the experiment package types were inspected for solder coverage issues. Both pure tin and tin-bismuth materials showed satisfactory solder coverage, with no plating quality issues observed. After trim & form, 100 units of each package type were sampled for visual inspection. Here too all results passed the criteria of the inspection. No plated layer crack or scraping was observed.

3. *Grain Structure (Morphology)*

Grain structure of the lead-free plated parts was evaluated using a SEM (Scanning Electron Microscope) at 2000X. Grain structure was compared against existing standards of current tin/lead solder, which we define as 'worm-like' in grain structure. None of the lead-free solder plating materials met this standard (*Refer to* Figure 1: Morphology Grades Vendor A Plating Chemicals , and Figure 2: Morphology Grades Vendor B), and further study in production mode was required to optimize chemical concentration and other plating parameters to control the morphology of the lead-free solder plating materials under investigation.

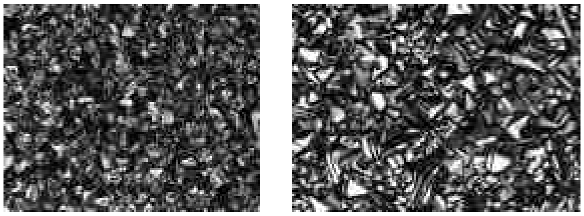


Pure Tin (Mixed Acid)

Tin-Bismuth

Tin-Lead

Figure 1: Morphology Grades Vendor A Plating Chemicals



Tin- Bismuth

Pure tin (MSA)

Figure 2: Morphology Grades Vendor B Plating Chemicals

4. Solderability Test (Dip and Look)

The solderability test involved inspection and evaluation of solder coverage of the soldered units after applying Kester 145 Flux and dipping them in solder pot (Sn63/Pb37 and Sn/3.8Ag), pot temperature: 245 +/- 5 °C). Prior to solderability testing, different groups of samples (5 units/test/package type) were preconditioned in a steam-age chamber and baking oven under different condition. All samples of all lead-free plating types were passed at all test conditions.

Table 4: Preconditioning Conditions Matrix

Test condition	Steam age (Hrs.)	Baking (°C.)	Baking Time (Hrs.)
1	0	0	0
2	8	0	0
3	16	0	0
4	0	125	8
5	8	125	8
6	0	150	4
7	8	150	4
8	0	150	8
9	8	150	8

5. SMT Test

SMT (Surface Mount Technology) tests are carried out to evaluate the joint of the device on a PCB. This study used both standard (Sn63/Pb37) solder paste and a lead-free solder paste (Sn95.5/Ag4.0/Cu0.5) to evaluate the surface mount joint of the devices solder plated with lead-free materials. The reflow profile was as per NEMI recommendations, with a peak reflow temperature of 255 +5/-0 °C. The samples were steam-age preconditioned for 8 hours prior to lead pull testing (50 leads/lot) and the wetting ability (area) was also evaluated against standard SMT wetting criteria. The combined results of the lead pull test and the post oven inspection are shown in Table 5: Lead Pull Test Results and Table 6: Post–Reflow Oven Inspection Result.

Table 5: Lead Pull Test Results

Package	***Paste Type***	**Lead Pull Test**				
		Sn/Pb	**Vendor A**		**Vendor B**	
			Sn	**Sn-Bi**	**Sn**	**Sn-Bi**
PL32	Sn/Pb	Pass	Pass	Pass	Pass	Pass
	Sn/Ag/Cu	Pass	Pass	Pass	Fail	Fail
SO44	Sn/Pb	Pass	Pass	Pass	Pass	Pass
	Sn/Ag/Cu	Pass	Pass	Pass	Pass	Pass
TS48M	Sn/Pb	Pass	Pass	Pass	Pass	Fail
	Sn/Ag/Cu	Pass	Pass	Pass	Pass	Pass

Table 6: Post-Reflow Oven Inspection Results

Pkg.	**Paste Type**	**Sn/Pb**	**Vendor A**		**Vendor B**	
			Sn	**Sn-Bi**	**Sn**	**Sn-Bi**
PL32	Sn/Pb	Pass	Pass	Pass	Pass	Pass
	Sn/Ag/Cu	Pass	Pass	Pass	Pass	Pass
SO44	Sn/Pb	Pass	Pass	Pass	Pass	Pass
	Sn/Ag/Cu	Pass	Pass	Pass	Pass	Pass
TS48	Sn/Pb	Pass	Pass	Non-wetting (2/240 leads)	Pass	Dewetting (2/240 leads)
	Sn/Ag/Cu	Pass	Pass	Non-wetting (2/240 leads)	Pass	Dewetting (2/240 leads)

6. *Whisker Test*

The lead-free samples were stored in various conditions to observe whisker growth—*Refer to*

Table 7: Whisker Growth Storage Conditions. No whisker growth was observed on any of the samples stored under all conditions. The samples were checked under 10-40x microscope (20 samples/test run) and SEM (2000x, 2 samples/test run)

Table 7: Whisker Growth Storage Conditions

Condition	Storage Condition
1	Temp. cycle (-65 to 150°C) 1000 cycles
2	SPP (121°C, 2 atm, 100%RH) 168 hrs.
3	SPP (121°C, 2 atm, 100%RH) 500 hrs.
4	Storage at 50-55°C, high % RH, 6 months
5	Leave in 20-25°C, 40-65% RH, 2 months
6	Leave in 20-25°C, 40-65% RH, 4 months
7	Leave in 20-25°C, 40-65% RH, 6 months
8	Leave in 20-25°C, 40-65% RH, 8 months
9	Leave in 20-25°C, 40-65% RH, 12 months
10	Store in dry pack, 6 months

7. *Tin Deposit Properties and Tin Whisker Growth*

In previous publications [4-7] the beneficial effects of producing a tensile-stressed tin layer to minimize tin whisker growth has been demonstrated. Additionally in these same publications the potential significance of preferred crystal orientation in the tin deposit and its relationship to tin whisker growth propensity was uncovered. As an additional exercise here the quantitative stress and preferred crystal orientation measurements of the tin deposits produced in the production plating line at AMD were examined by x-ray diffraction (XRD) and compared to previously obtained results from laboratory testing. XRD measurements were taken approximately three months after deposits were plated and stored in a non-humidity controlled, room temperature environment. The XRD results are summarized below:

Table 8: XRD Results

Tin Plating Solution	Stress (MPa)	Preferred crystal orientation(s)
Vendor A	+ 1.0 MPa (tensile)	<332>, <112>, <101>
Vendor B	- 0.6 MPa (compressive)	<332>, <112>, <101>
Vendor C	- 0.9 MPa (compressive)	<112>, <332>, <101>

8. *Discussion*

From the XRD results in Table 8, one can see that only one tin deposit (Vendor A tin) produced a tensile stress in the tin layer after approximately three months storage. This reproduces results obtained in laboratory testing with this same tin electrodeposit as previously reported[4-6]. This result is significant because it indicates that the laboratory results which resulted from the theoretical background and development of this process are in fact fully reproduced and duplicated in real-life production environment.

In terms of the preferred crystal orientation results above, the results are equally interesting and deserve some further discussion. Electroplated tin deposits are poly-crystals. From the crystal growth perspective, internal stress can be generated if the crystal lattice of the deposited metal as well as its growth direction do not follow certain preferred orientations. During the deposition process, the first few atomic layers are characterized as epitaxial; the crystal lattice of the coating tends to match that of the substrate. However, as layers build, the epitaxial behavior may change to a structure dictated by the electrolyte and additive composition.

In addition, during the deposition process, if the growth direction of the tin coating is completely random, the growth rate would be the same in all the crystallographic facets. However, in practice, the growth directions of the tin crystals are not completely random, they usually exhibit one or more preferred orientations. This means that the growth of the tin grains with the preferred orientation is kinetically more favored (i.e., more stable) compared with other directions. In other words, other orientations eventually are replaced by this preferred orientation during the nucleation and crystal growth process.

As we know, whisker growth is a phenomenon which is driven by compressive stress in the tin coating. However, if the deposit crystal lattice is orderly and desirable, there will be less stress to initiate whisker growth. Therefore, the growth of whiskers requires the existence of imperfect grains and lattice defects that result in dislocations of the grains. In practice, there are always some crystal defects generated during deposition; however these defects do not necessarily have the crystallographic orientation to influence deposit growth. In the Vendor A tin plating process, the organic additives preferably suppress certain crystal growth directions, and concurrently, facilitate the crystal growth in other directions.

It has been reported [4-9] that when tin coatings possess certain preferred crystal orientations, the whisker growth propensity is greatly reduced even under the most rigorous accelerated whisker test conditions when compared with tin deposits that do not contain these preferred orientations. Examples of such “beneficial” preferred crystal orientations include <220>, <200>, <420> and others. Similarly, it has been identified that when tin deposits possess certain other types of “detrimental” preferred crystal orientations the whisker growth propensity is increased. Examples of such “detrimental” preferred crystal orientations include <321> and <211>, and others.

We theorize that a tin deposit which contains the “beneficial” preferred crystal orientations, or alternately a tin deposit which lacks the “detrimental” preferred crystal orientations, will have a lower propensity toward tin whisker growth. Conversely, a tin deposit which lacks the “beneficial” preferred crystal orientations that we have identified, or alternately a tin deposit which contains the “detrimental” preferred crystal orientations, will have a higher propensity toward tin whisker growth. Several independent studies have recently confirmed these findings, including a recent synchrotron radiation micro-diffraction study of tin whiskers in which researchers found that the tin whisker growth direction is <100> and the tin deposit which produced the whiskers had a preferred orientation of <321 > [10].

The Vendor A tin plating process has been shown in laboratory experiments to produce tin deposits which consistently contain the “beneficial” preferred crystal orientations and/or in which the “detrimental” preferred crystal orientations are minimized. Reviewing the XRD results obtained in Table 8, one can see that the Vendor A tin deposit does not contain the “detrimental” preferred crystal orientations mentioned above, again confirming in a production environment the results previously obtained in a laboratory setting. Interestingly, the three tin deposits generated in production for this study did not contain the “detrimental” preferred crystal orientations.

It is important to point out at this juncture that although preferred crystal orientation may be a significant secondary factor for explaining the tin whisker growth phenomenon, deposit stress is still the primary factor and more specifically, compressive stress in the deposit remains the primary driving force for tin whisker growth. Tin whiskers cannot form without the presence of compressive stress in the tin layer.

In terms of predicting risk of long term whisker formation during storage, Vendor A tin would have the lowest risk of whisker growth due to the tensile stress level present in the tin layer while Vendor B and Vendor C tin would have a much higher risk of whisker growth due to the compressive stress levels present in those deposits. Vendor C tin may have a slightly higher risk of whisker formation since its compressive stress level is higher than Vendor B tin.

Independent confirmation of the minimal whisker growth tendencies of the Vendor A tin production-plated components has recently been reported [11]. In this detailed study, the effect of plating chemistry type and tin deposit thickness on whisker growth was examined. The tin whisker growth properties of tin deposits produced from “Supplier A sulfate chemistry” (i.e., Vendor A in the current study) and from several alternate methane sulfonic acid (MSA) based tin plating chemistries were evaluated as were deposit thicknesses. As illustrated in Figure 1 and Figure 2 below, the clear benefits of the Vendor A tin in terms of minimizing whisker growth was demonstrated.

Matte Tin MSA
TC –55°C to +85°C, 500 cycles
1000X magnification

Matte Tin – Mixed Acid
TC –55°C to +85°C, 500 cycles
1500X magnification

I. Boguslavsky, P. Bush, "NEMI Tin Whisker Test Group – Phase 2 DOE Results", Proceedings from IPC Annual Meeting, Nov. 2002, New Orleans, LA, USA.

Figure 3: Effect of Electrolyte Type on Tin Whisker Growth

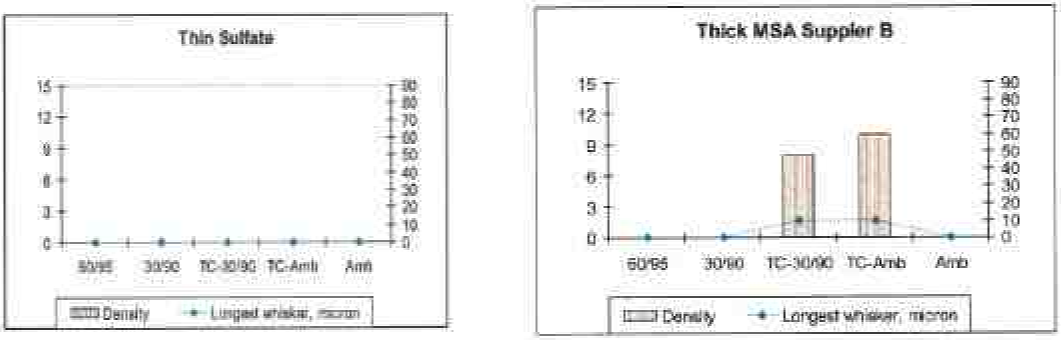


Figure 4: Effect of Bath Chemistry

9. Conclusion

From the evaluations of the lead-free solder plating materials studied, we can conclude that:

1. Solder thickness and composition can generally be well controlled with both pure tin and tin-bismuth.

2. No plating quality issues (cracking, whiskering, etc.) were observed with both pure tin and tin–bismuth after plating and trim& form.

3. No solderability issues were observed with both lead-free plating solutions at 245°C., and under various preconditioning conditions.

4. Of the 2 lead-free plating materials, the SMT test results inferred that pure tin(mixed acid) was the more compatible material with lead-free pastes.

5. No whisker growth was observed with both pure tin and tin-bismuth up to 12 months storage after plating. Further study of the life of the materials is ongoing. Target up to 24 months storage.

6. Tin/Bismuth(Sn/Bi) :

   -Tin/Bismuth plating is very difficult to strip off from the belt and units.

   -Bi immersion to Cu leadframes , stainless steel conveyor belt and immersion in the heaters of the machines are observed.

   -Bi content in the solution drops rapidly. The chemical concentration is difficult to control.

7. Adopting universal whisker growth testing methodologies and standards would be very much desired.

   As a conclusion, this study would recommend pure tin (mixed acid) to be the most promising lead-free solder plating alternative.

10. Future Work

The authors of this paper are continuing long-term studies on manufacturability and compatible with various types of lead-free paste of the lead-free alternatives that were the subject of this study, as well as the phenomenon of whisker growth. Also underway are reliability studies to determine the predictable life of these lead-free solder plating alternatives, as well as the potential impact of these materials and related processes on the environment, health and safety.

11. References

1. Dr. Manfred Jordan, *The Electrodeposit of Tin and its Alloy* , Eugen G. Leuze Publishers, 1995.

2. Rob Schetty, “Advancements in Pb-free Processing Technology,” Technic Pb-free Seminar 2001, pp.3-38.

3. Marc.Dittes, “Green Packages-Requirements, Materials, Results,” 3rd.Electronics Packaging Technology Conference, pp.1-5.

4. R. Schetty, “Whisker Growth Studies”, Proceedings of IPC Annual Meeting, Session V, Paper B, October 2001, Orlando, FL, USA.

5. R. Schetty, “Tin Whisker Growth and the Metallurgical Properties of Electrodeposited Tin”, Proceedings of IPC/JEDEC meeting, pp. 137-161, May 2002, San Jose, CA USA.

6. R. Schetty, “Tin Whisker Studies – Experimentation & Mechanistic Understanding”, Proceedings of AESF SUR/FIN Conference, June 2002, Chicago, IL, USA.

7. R. Schetty, K. Hwang, Y. Zhang, “Whisker Growth – the Substrate Effect and Beyond”, Proceedings of IEEE/CALCE Conference, January 2003, Shenzen, China.

8. A. Egli, et al, “Where Crystal Planes Meet – Contribution to the Understanding of the Tin Whisker Growth Process”, Proceedings of IPC Annual Meeting, Nov. 2002, New Orleans, LA, USA.

9. J. Lee, et al, “Whisker Formation Study of Lead-Free Plated Packages”, Proceedings of IPC/JEDEC Pb-free Conference, Taipei, Taiwan, Dec. 2002.

10. W. J. Choi, T. Y. Lee, K. N. Tu, N. Tamura, R. S. Celestre, A. A. MacDowell, Y. Y. Bong, L. Nguyen, and G. T. T. Sheng, "Structure and Kinetics of Sn Whisker Growth on Pb-free Solder Finish", 52nd Electronic Component & Technology Conference Proceedings (IEEE Catalog number 02CH3734-5), San Diego, CA, 628-633 (2002).

11. I. Boguslavsky, P. Bush, “NEMI Tin Whisker Test Group – Phase 2 DOE Results”, Proceedings from IPC Annual Meeting, Nov. 2002, New Orleans, LA, USA.