The Qualification of a Pure Tin Plating Process as a Lead Free Finish for I.C. Packaging

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Abstract

ST Malta is currently using electrodeposited 85/15 tin lead as a solderable finish for component lead-frames. With the drive towards lead-free electronics ST needed to evaluate and approve an appropriate lead-free finish. Pure tin was selected as the most desirable finish. This paper will describe trials carried out with a new pure tin process (Rohm and Haas Electronic Materials Solderon^{TM} ST-300(1)). The evaluation was conducted in a production Meco magazine-to-magazine plating machine in the ST Malta facility. A variety of lead-frame substrates was evaluated and deposits produced were subjected to the same tests as standard production. Since whiskering is of particular concern for pure tin deposits, extensive whisker tests were undertaken.

The results obtained for the pure tin finish were very similar to those obtained with the standard tin/lead finish. No whiskering was found on any of the substrates. The trials concluded that the new pure tin process provides an ideal lead-free finish for semiconductor lead-frames. The process was found to be reliable, robust and a suitable drop-in replacement to the current tin/lead process.

Introduction

With the date for the introduction of legislation (2,3) requiring lead-free electronics now fixed as July 1 2006 many companies are vigorously searching for lead free coatings for use on components. To date, the standard finish for semi-conductor lead frames has been 85/15 tin/lead. Rohm and Haas Electronic Materials, as a developer of plating solutions, and ST Microelectronics, as an IC packaging company, are ideal partners to cooperate in a project to evaluate a new pure tin process for lead frame applications. Rohm and Haas have studied extensively alternatives to tin/lead and published a number of papers in this field (4,5,6,7). None of the alloyed alternatives (tin/silver, tin/bismuth or tin/copper) have substantial benefits over pure tin and each of the alloyed alternatives has its own drawbacks. Whiskering is a major concern to potential users of pure tin deposits and the new process was specifically designed to produce a deposit with a combination of crystal plane orientations that will ensure minimum whisker risk (8). Thus, pure tin has been demonstrated to be equivalent to tin/lead and this cooperation between Rohm and Haas Electronic Materials and ST Microelectronics will show that this can also be realised on a production scale. The main objective of this exercise is to qualify a lead-free plating process at ST Microelectronics Malta and to demonstrate world-class process capability in terms of quality and reliability in comparison with standard tin/lead production.

General

The plating was carried out on MECO strip to strip plating machine (type EDL/EPL 2400 strips/hour and S/No.93-1-0046). The machine was cleaned for one week using sodium hydroxide and hydrogen peroxide solution to ensure removal of lead residues and neutralised with dilute methane sulphonic acid prior to installation of the pure tin process. The plated samples were produced over a one-week period during August 2002. The packages used for the trial were as shown in Table 1.

Table 1 – Packages Used In The Trials

Type	Package	Alloy	Pitch count	Stamped/Etched	Specification limits
SMD	TQFP 10x10	C7025	64L	Stamped	7-20 µm
SMD	PQFP 28x28	C7025	208L	Etched	7-20 µm
THD	PDIP	C194	32L	Stamped	7-20 µm
THD	FLEXIWATT	KFC	25L	Stamped	7-20 µm
SMD	PLCC	C151	44L	Stamped	7-20 µm

The plating solution was made and operated as shown in Tables 2 and 3.

Table 2 - Bath Make-up

Chemicals Required	Volume
Deionised Water	580 ml
Tin Concentrate 300 g/l	170 ml
Acid Concentrate	150 ml
Additive	80 ml
Antioxidant	10 ml
Deionised water	to make one litre

Table 3 - Bath Operating Parameters

Parameter	Range	Optimum
Tin (II)	40 - 60 g/l	50 g/l
Total Acid	200 - 300 ml/l	250 ml/l
Temperature	40 - 50°C	45°C
Additive	50 - 110 ml/l	80 ml/l
Antioxidant	5 - 20 ml/l	10 ml/l
Cathode Current Density	5 - 25 A/dm^2	15 A/dm^2
Agitation	Vigorous solution coupled with cathode movement	
Anode Current Density	0.1 - 5.0 A/dm^2 (anode to cathode ratio is relatively unimportant)	
Anodes	Tin slabs in titanium baskets.	
Deposition rate	ca. 7.5 microns/minute under optimum conditions	

The process sequence for the pure tin plating trials was as shown in Table 4.

Table 4 – Process Sequence

No.	Process / Product	Make-up	Temp. (°C)	Tank Volume	Current Density (A/dm²)	Cell Length (m)	Total Current (A)	Agitation	Remarks
1	Deflasher	50% v/v	45	500 L	15-25	5.7	400	Normal	Pt/Ti Cathodic
2	Cleaner	50 g/l (+35 g/l NaOH)	40	150 L	5	1.5	50	Normal	Stainless steel Anodic
4	Microetch	75 g/l (+ 60 ml/l H_2SO_4)	35	150 L		0.9		Normal	
5	Activation	Acid 200 ml/l	30	85 L	5				Pt/Ti Cathodic
6	Solderon^{TM} ST-300	As per data sheet	45	600 L	15-30	6	400-600	240 L/minute	4 cells 4 x 1.5 m
7	Neutralisation	Make-up Salt, 5g/l	60			0.8		Normal	
8	Belt stripper	As per data sheet	30		20			Normal	Anodic/ cathodic

Measurement Criteria

The following measurement criteria were used: -

- Visual appearance
- Crystal Structure
- Adhesion
- Ductility
- Thickness Distribution
- Whisker test
- Solderability
- Wettability

Appearance was assessed visually and by optical microscopy at 50x magnification. Crystal structure and topography were determined by focused ion beam (FIB) spectroscopy and scanning electron microscopy (SEM).

Adhesion and ductility were measured by standard “trim and form” techniques.

Thickness distribution was determined by X-ray fluorescence measurements at specific locations across the lead frames.

Degree of whiskering was observed after storage at ambient temperature, dry heat at 55°C, heating at 60°C/93%RH and thermal cycling testing (one set with 500 cycles –35°C/+125°C and another set with 1500 cycles –55°C/+85°C with 7 minutes plateau at each temperature).

Solderability was determined by traditional dip and look methods and wettability was measured using a wetting balance. Solderability and wettability were measured in the as plated condition, after dry baking and after controlled temperature/humidity ageing at 85°C/85%RH. Both tin-lead solder and tin-silver-copper solder were used in every case.

Methods and Results

Appearance

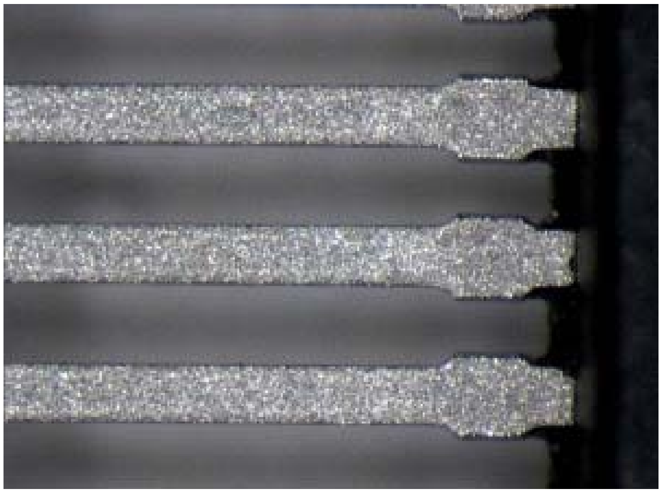

Figure 1 - Optical Microscopy (50X)

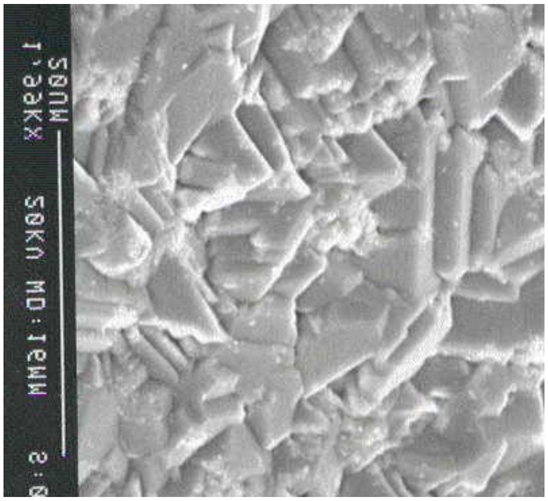

Figure 2 - SEM

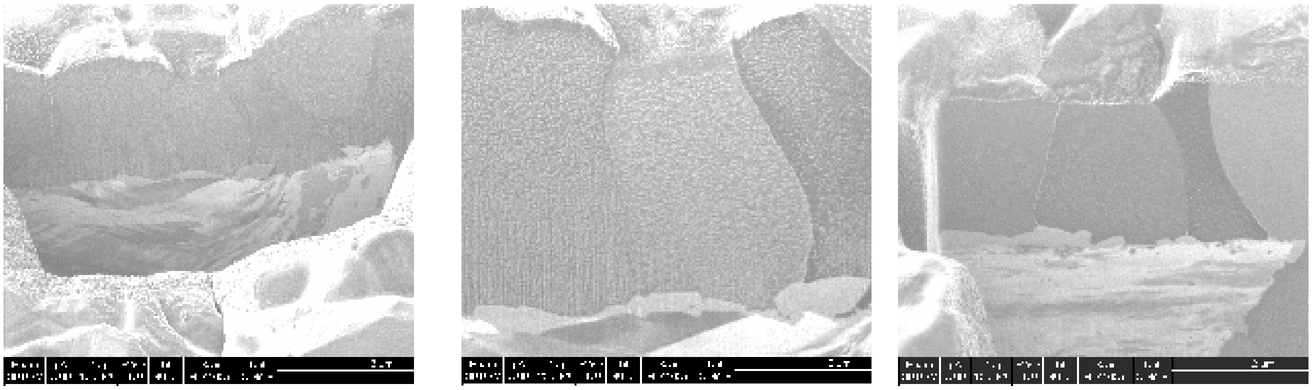

Figure 3 – FIB Images

No discoloration was observed after storage of plated packages for 3 months under ambient conditions.

Trim and Form

No difference in performance was seen between the new pure tin process and traditional tin/lead plating. No dust formation was observed and there was no cracking in the region of the bend. All devices passed a simple adhesive-tape adhesion test.

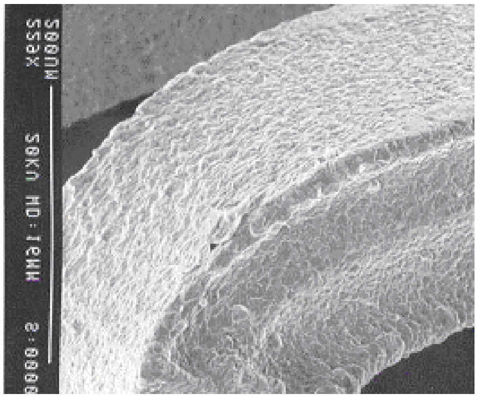

Figure 4 – Appearance after trim and form

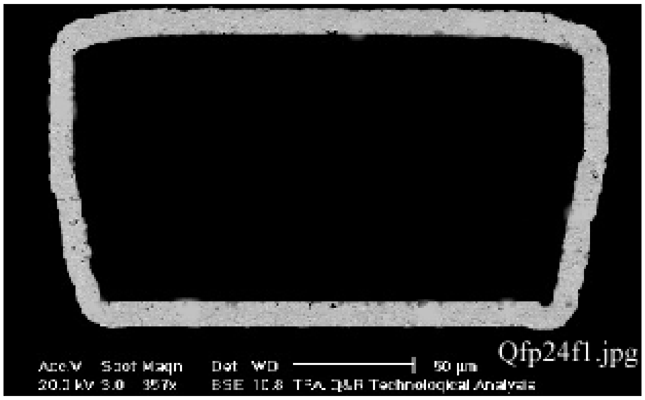

Figure 5 – Lead cross-section to examine plating thickness uniformity

Thickness Distribution

Thickness (in microns) was measured using calibrated X-ray fluorescence. The results are presented in Table 5.

Table 5 – Deposit Thickness Distribution

Position	**PQFP**	**FW**	**PLCC**	**PDIP**	**TQFP**	**Mean**
Left	9.86	11.13	10.65	10.62	10.34	
Top	10.45	10.51	8.63	11.08	8.97	
Middle	11.33	10.55	9.98	13.15	10.54	
Middle	9.41	11.25	10.48	12.89	10.64	
Bottom	11.53	10.41	11.07	11.84	9.73	
Right	9.51	10.45	10.14	10.73	10.96	
Mean	10.348	10.717	10.158	11.718	10.197	
Sigma	0.836	0.339	0.769	1.002	0.663	**0.722**
Cp	**2.592**	**6.391**	**2.818**	**2.162**	**3.268**	**3.446**
Cpk	1.335	3.655	1.369	1.570	1.607	**1.907**

Average Cp and Cpk values for all packages were greater than 1.67. A recent stringent specification for automotive devices requires a process capability with Cpk>1.67. No measurements were found to lie outside the thickness specification range of 7-20µm. Metal thickness distribution could be further optimised with fine adjustment of machine shields in future trials.

Solderability

Solderability was measured under the following conditions:

1) After 8 hours ageing at 85°C/85%RH
2) After 16 hours dry baking at 150°C.

The technique used was a 10 second dip in Alpha 100 non active flux (type ROL0) followed by molten solder as follows: tin/lead (63/37) and tin/silver/copper (96/3.5/0.5) – through hole devices 5 seconds at 245°C for both solders and surface mount devices 3 seconds at 245°C for tin/silver/copper and 5 seconds at 220°C for tin/lead. The results from the solderability testing are summarised in Table 6.

Inference from the Solderability Results

All parts passed the solderability testing at 100% rate for all devices, all testing conditions and all ageing conditions. This test is very critical because pure tin is well known to be susceptible to failures after high temperature/high humidity ageing and dipping into low-temperature solder. This is due to the higher oxidation rate and higher melting point of pure tin compared to tin-lead.

Wettability

The standard wettability test was performed on a Metronelec Menisco ST-50 wetting balance using 63/37 tin/lead solder at 235°C with Alpha 100 non active flux (type ROL0). Lead free soldering was carried out with same wetting balance but using a 96/3.5/0.5 Sn/Ag/Cu solder pot at 245°C also using Alpha 100 flux. Wettability tests were carried out on non-aged devices and devices that were either aged at 85°C/85%RH for 4 hrs or dry heat aged at 150°C for 16 hrs. Comparative testing of parts that have undergone ageing is considered to be more important and to predict more accurately use in service, since it may be several months before production parts are assembled by a customer. The tests were more severe than our process requirements, since we control finished parts to have zero cross-time of less than 3s and to reach a force of greater than 0.1mN/mm at 5s. The I.C.s at finishing are either directly packed or could undergo a bake typically for 12 hours at 125°C.

Figures 6, 7 and 8 show typical wetting force curves which compare results from standard tin-lead parts with those from parts plated in the new pure tin process. The pure tin wettability is seen to be initially slower than that for the standard tin/lead plating, because of the higher melting point of pure tin and the rougher surface morphology, but the final force reached is higher, indicating a higher degree of wetting incorporating a larger volume of solder being drawn which should yield a stronger final joint. This could be due to the rough surface holding a larger amount of flux. A new process is currently under evaluation which has been developed specifically to have a smoother surface (finer grain) to address the issue of wetting speed and improve resistance to ageing effects.

Solderability and wettability are complimentary in terms of performance assessment.

Table 6 – Solderability Test Results

Package	Ageing	Solder	Temperature, °C	Time, seconds	Result
TQFP 10X10	85°C/85%RH	SnPb	220	5	10/10
TQFP 10X10	85°C/85%RH	SnAgCu	245	3	10/10
TQFP 10X10	Dry Bake	SnPb	220	5	10/10
TQFP 10X10	Dry Bake	SnAgCu	245	3	10/10
PQFP28X28	85°C/85%RH	SnPb	220	5	10/10
PQFP28X28	85°C/85%RH	SnAgCu	245	3	10/10
PQFP28X28	Dry Bake	SnPb	220	5	10/10
PQFP28X28	Dry Bake	SnAgCu	245	3	10/10
PLCC 44L	85°C/85%RH	SnPb	220	5	10/10
PLCC 44L	85°C/85%RH	SnAgCu	245	3	10/10
PLCC 44L	Dry Bake	SnPb	220	5	10/10
PLCC 44L	Dry Bake	SnAgCu	245	3	10/10
PDIP32L	85°C/85%RH	SnPb	245	5	10/10
PDIP32L	85°C/85%RH	SnAgCu	245	5	10/10
PDIP32L	Dry Bake	SnPb	245	5	10/10
PDIP32L	Dry Bake	SnAgCu	245	5	10/10
FW 25L	85°C/85%RH	SnPb	245	5	10/10
FW 25L	85°C/85%RH	SnAgCu	245	5	10/10
FW 25L	Dry Bake	SnPb	245	5	10/10
FW 25L	Dry Bake	SnAgCu	245	5	10/10

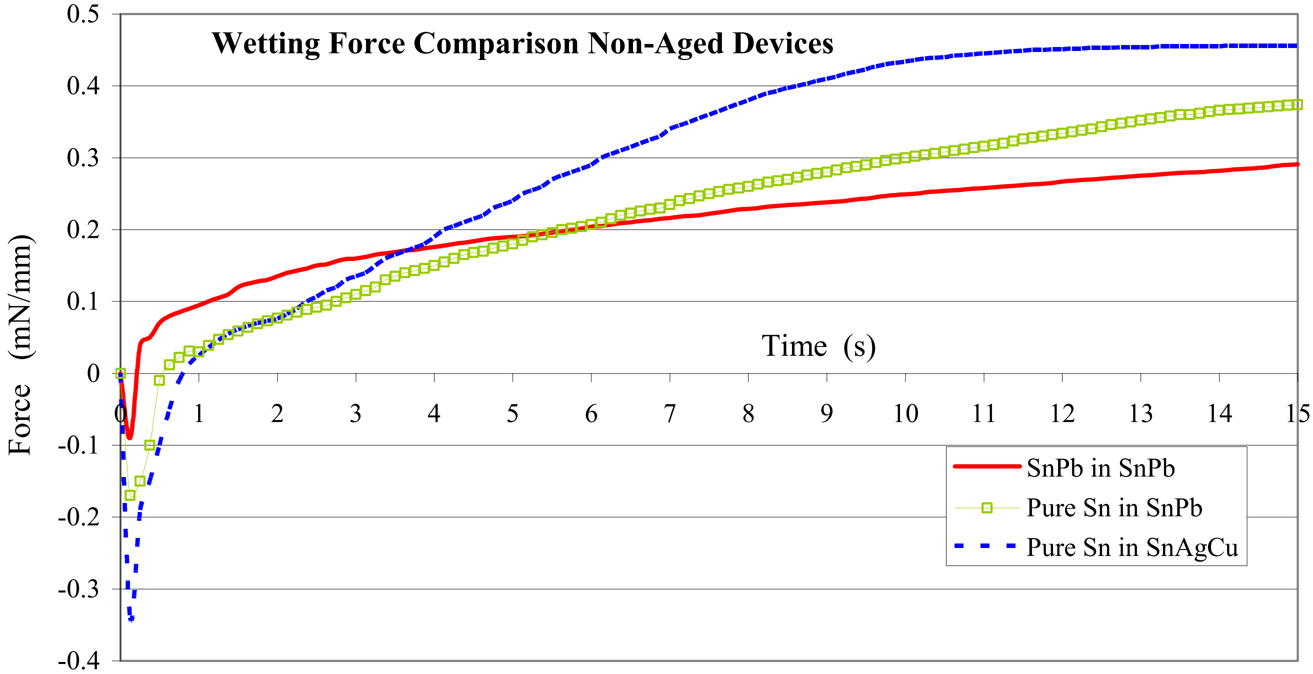

Figure 6 – Comparison of Wetting Force Curves (Non-Aged)

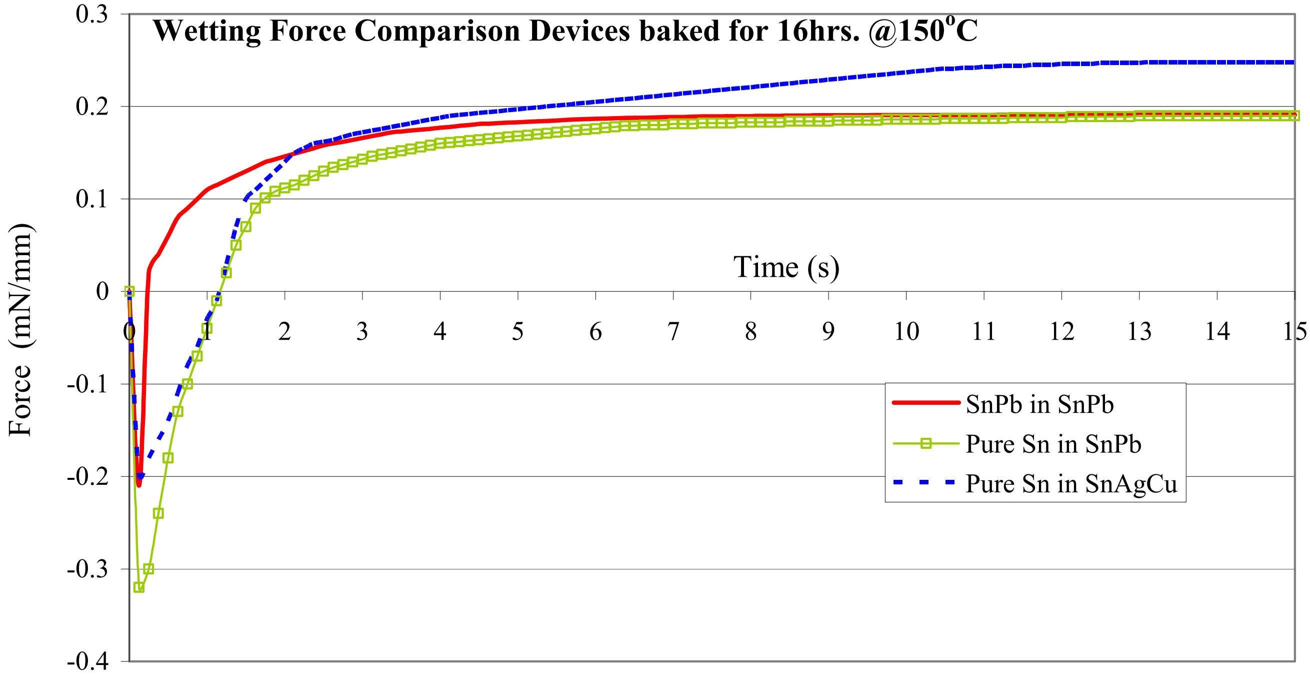

Figure 7 – Comparison of Wetting Force Curves (Baked Devices)

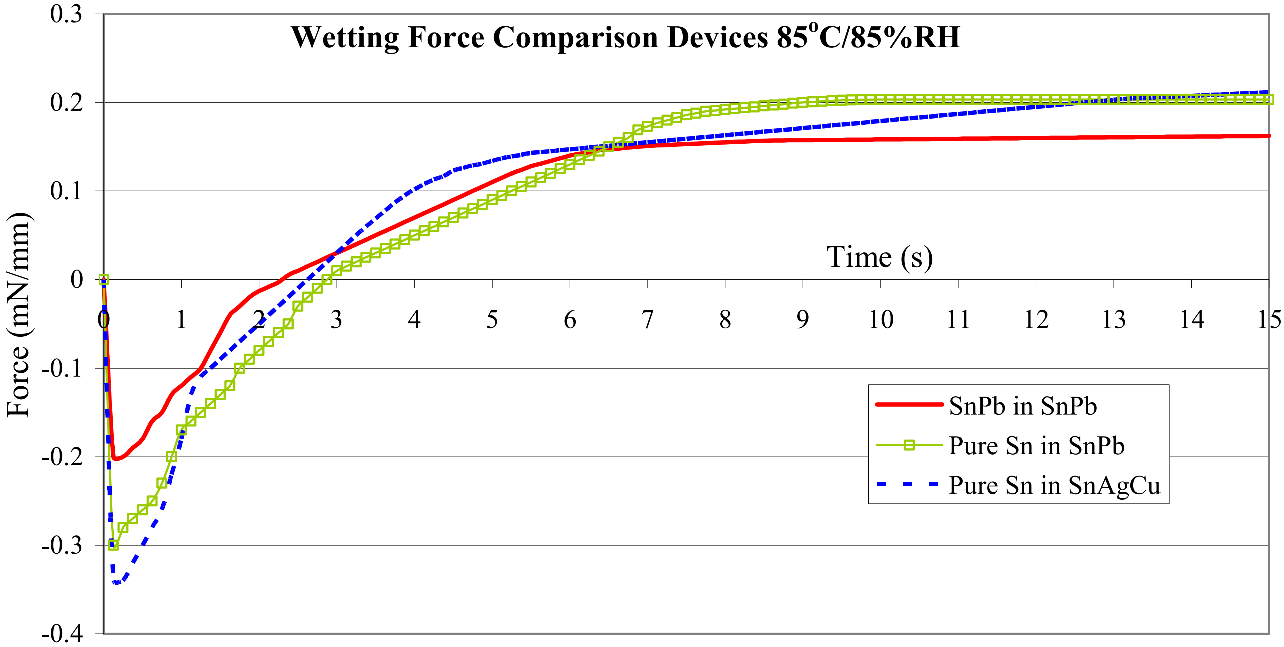

Figure 8 – Comparison of Wetting Force Curves (High Humidity Aged Devices)

Whisker Test Experiments

Inspection for whiskers was carried out on formed devices as follows:-

1) Ambient storage for 2 years.
2) Storage at 55°C (dry heat) for 6 months.
3) Storage at 60°C and 93%RH for 6 months.
4) 500 thermal cycles (-35°C to +125°C, 7 minutes at each temperature).
5) 1500 thermal cycles (-55°C to +85°C, 7 minutes at each temperature).

Samples size was approximately 40 devices and inspection was initially carried out at 50X magnification and any dubious devices were re-inspected at 200-500X using an optical microscope or SEM.

Additional inspection was carried out on uncropped leadframes stored under ambient conditions.

The length of any projections was measured but no whiskers were observed for the new pure tin process even after very close inspection. Results are summarised in Table 7.

Table 7 – Whisker Test Results

	Failure Rate: # failed units/total units							
	Dry Heat, 55 ± 2°C		**Ambient (≈ 23°C/60%RH) and Hot/High Humidity (60°C/93%RH)**				**Thermal Cycles**	
							(-35°C to +125°C)	**(-55°C to +85°C)**
Storage Time:	**2 months**	**6 months**	**2 months**	**6 months**	**1 year**	**2 years**	**500 cycles**	**1500 cycles**
PLCC 44L	0/29	0/29	0/10	0/10	0/10	0/10	0/10	0/10
DIP 32L	0/32	0/32	0/10	0/10	0/10	0/10	0/10	0/10
FW 25L	0/34	0/34	0/10	0/10	0/10	0/10	0/10	0/10
TQFP 10x10	0/30	0/30	0/10	0/10	0/10	0/10	0/10	0/10
PQFP 28x28	0/48	0/48	0/10	0/10	0/10	0/10	0/10	0/10

During the lead-free evaluation in Malta a number of pure tin processes from different suppliers were evaluated. Post-baking was not included in this investigation and it is interesting to note that in this series of trials ST-300 did not exhibit any whiskers at the upper edge of frames after storage under ambient conditions. A plating thickness of 4 µm was found at this upper edge of the frame for all suppliers. The longest whisker found for one supplier was 30-40 µm, a second supplier had 15 µm whiskers in this region and a third supplier 12 µm. ST-300 had no whiskers in this region even though the thickness on that area of the lead-frame was also ca. 4 µm.

Although the whiskers that were found would not automatically disqualify any of the processes since no whiskers were found on the critical lead area of the frame it does indicate that some processes are less robust than others in terms of whisker resistance. When post baking is used the specification of a maximum whisker length of 50 µm after 2 years storage under ambient conditions can easily be achieved without being dependent on a particular tin plating process. ST Microelectronics has adopted a post-bake of 1 hour at 150°C as an extra guarantee to customers that deposits are whisker free (See Table 8).

Tin Whisker Minimisation

Whisker Mechanism

Tin whiskers form as result as copper combining with tin and forming an intermetallic compound (both Cu_6Sn_5 and Cu_3Sn species are present). As the copper diffuses through the grain boundaries of the tin coating it forms IMC and this creates a compressive stress and it is the relief of this stress that produces whisker growth. At room temperature, the predominating diffusing species is Cu_6Sn_5 and it is a volume change that produces the stress. In tin/lead deposits, lead in the grain boundaries prevents diffusion and thus stress build up and whiskering. Alternatives to lead e.g. silver copper and bismuth, in small quantities, are not as efficient as lead in this regard.

There are a number of countermeasures that can be used to prevent whisker formation in pure tin coatings. Annealing the deposit at 150°C for one hour removes stress from the tin coating and produces a uniformly thick intermetallic coating that acts as a barrier against further diffusion. Alternatively several different undercoats (nickel, copper or silver) can be used as diffusion barriers. Nickel readily prevents copper diffusion. Nickel itself also forms an intermetallic compound with tin but this IMC does not create the same stresses since the volume change associated with NiSn is much smaller and in fact this stress is tensile which is beneficial. A copper undercoat with a crystal orientation (220) prevents whiskering whereas one with (111) orientation actually promotes whisker growth. A silver undercoat prevents whiskering since silver forms a stable intermetallic compound with the tin as Ag_3Sn causing no compressive stress inside the deposit.

A study at ST Malta confirmed the benefits of a nickel underlayer. However there are several process disadvantages. These include the need to modify the machine to plate the nickel in-line and keep the surface active; stripping of nickel from the stainless steel carrier belt is difficult and results in flaking of the plated layer from the belt. Nickel being a hard and brittle material, is prone to cracking and may pose a hazard in exposing the copper substrate after the trim and form process. Furthermore the inclusion of an extra process necessitates additional process control.

Increasing tin thickness also reduces tin whiskering since quantity of IMC formed is independent of thickness so the greater the deposit thickness the smaller the proportion of IMC and thus lower stress and less whiskering.

Etching the substrate heavily can also reduce whisker formation. Removing the surface layer that is damaged by rolling reduces stress and an etched surface produces a more uniform intermetallic compound and it is a heterogeneous IMC layer that causes whiskering.

ST Malta carried out a designed experiment to verify some of these mechanistic concepts and the results are presented at the end of this section.

Modifying the properties of the tin coating is also a method that can be used to control whisker growth.

The first generation low whiskering tin processes were designed to be large grain size. Extremely fine-grained bright pure tin is historically renowned for being particularly prone to whiskering, the reason being that the many grain boundaries offer many opportunities for grain boundary diffusion and high compressive stress. Large grain pure tin processes are columnar and have a grain size of 10-15 microns. As a result of the reduced grain boundary density, diffusion is reduced and reduced stress build up minimises whisker growth.

The new process is a second generation pure tin process and in addition to being large grain it has a combination of crystal orientations that minimise whisker growth under the harshest condition

It is the interaction of the individual crystal orientations with one another that is the important factor. It has been established from examination of the X-ray diffraction patterns of numerous tin coatings that there is a correlation between the angles between the crystal planes and the tendency for the deposit to grow whiskers. It has been found that coatings with large angles between the crystal planes have a low tendency to grow whiskers whereas deposits with small interplanar angles are more prone to whisker growth. The grain boundary between two crystal lattices contains a high density of vacancies and imperfections. The greater the number of vacancies, the more pathways there are for tin to self-diffuse without stress build up. Therefore smaller angles result in narrower grain boundaries with fewer vacancies and fewer pathways for tin to move and hence build up in stress and whisker growth. It has been found empirically that angles smaller than 22° are deemed to be critical (in fact there is a critical range of 5-22°). In practice electrodeposits contain a variety of crystal orientations and to predict whisker performance it is important to calculate the percentage of critical angles as compared to the total possible number of angles.

The predominant orientations of the deposits from the new process are 101, 211, 112, and 312. This combination of orientations has 7% of angles in the critical range. This low percentage explains the good whiskering performance of ST-300. A typical matt pure tin process with a high tendency for whiskering may have a texture of 431, 321, and 211 orientations and this combination has 65% of angles smaller than 22°.

Designed Experiment Details

The low whiskering propensity of the deposits from the new process has been demonstrated above, but it was considered appropriate to investigate in more detail the practical factors which might promote or suppress whisker formation. This was done in a designed experiment with frame type, deposit thickness, surface etching and post-plate baking as the control variables. The pure tin deposits were applied to copper-alloy lead frames. The design of the experiment and the results obtained are provided in Table 8.

From these results it can be clearly concluded that :

1) PDIP frames are more prone to whiskers (due to the presence of zinc in the alloy).
2) Post baking completely suppresses whiskering at any thickness and any etching condition.
3) Good etching completely suppresses whiskering. No whiskers are seen on leads where there is good etching, even at low thickness and with no post baking.
4) Low thickness tends to produce more whiskering. No whiskers are seen at >6um deposit thickness. (Frame edges would have lower thickness and can produce whiskers at these points only).
5) Whiskers are completely under control if these 3 precautions are taken, but post-baking is the most important since this treatment completely reaches all points of the device and forms a very stable IMC.

Table 8 – Results from the Designed Experiment on Whisker Suppression

Frame Type	Thickness, µm	Pre-plate Etching	Post-plate Baking	Whiskers on Leads	Whiskers on Frame Edge	Time
PDIP 32L	1.5	No	Yes	No	No	3 weeks
PDIP 32L	4	No	Yes	No	No	3 weeks
PDIP 32L	6	No	Yes	No	No	3 weeks
PDIP 32L	7	No	Yes	No	No	3 weeks
PDIP 32L	8	No	Yes	No	No	3 weeks
PDIP 32L	1.5	No	No	Few, 10-20µm	Few, 10-20µm	3 weeks
PDIP 32L	4	No	No	Heavy, 20-50µm	Heavy, 20-50µm	3 weeks
PDIP 32L	6	No	No	No	Few, 10-20µm	3 weeks
PDIP 32L	7	No	No	No	Few, 10-20µm	3 weeks
PDIP 32L	8	No	No	No	Few, 10-20µm	3 weeks
PDIP 32L	2.5	No	No	Heavy, 20-50µm	Heavy, 20-50µm	3 months
PDIP 32L	2.5	Yes	No	No	Few, 10-15µm	3 months
PDIP 32L	5	Yes	No	No	No	3 months
PDIP 32L	10	No	No	No	Heavy, 30-50µm	3 months
PDIP 40L	10	Yes	No	No	No	8 months
PDIP 42L	10	Yes	No	No	No	8 months
PDIP 56L*	12	Yes	No	No	Few, 10-15µm	8 months
PLCC 44L	2.5	Yes	No	No	No	8 months
PLCC 44L	5	Yes	No	No	No	8 months
PLCC 44L	7.5	Yes	No	No	No	8 months
PLCC 44L	10	Yes	No	No	No	8 months
FW 25L	2.5	Yes	No	No	No	8 months
FW 25L	5	Yes	No	No	No	8 months
FW 25L	7.5	Yes	No	No	No	8 months
FW 25L	10	Yes	No	No	No	8 months
FW 25L	10	Yes	Yes	No	No	8 months
TQFP 10x10	2.5	No	No	Few, 10-15µm	Many, 10-15µm	3 months
TQFP 10x10	2.5	No	Yes	No	No	3 months
TQFP 10x10	10	No	No	No	Few, 10-15µm	3 months
TQFP 10x10	10	No	Yes	No	No	3 months
TQFP 10x10	10	Yes	Yes	No	No	3 months
TQFP 20x20	10	Yes	Yes	No	No	3 months
PQFP 28x28	12	Yes	No	No	No	8 months

*This sample has short whiskers at the frame edge because the frame edge was masked by the carrier belt and so there was no etching and low deposit thickness in this region.

Conclusions

These trials demonstrated that the new pure tin process would meet all the requirements of ST Microelectronics for lead-free plating the outer leads of IC packaging devices.

Results equivalent to standard tin/lead production were obtained for characteristics such as freedom from whiskering, solderability after ageing and ductility.

The new pure tin-plating solution gave equivalent results to a corresponding tin/lead electrolyte and could therefore be considered a drop-in replacement.

References

(1) Solderon^{TM} ST-300, proprietary process of Rohm and Haas Electronic Materials., L.L.C., Packaging & Finishing Technologies Division, Freeport, NY, USA.
(2) EC Directive on Waste Electrical and Electronic Equipment (WEEE Directive).
(3) EC Directive on Restriction of Hazardous Materials (RHS Directive).
(4) K.J. Whitlaw & J.N. Crosby, “An Empirical Study Into Whisker-Growth of Tin & Tin Alloy Electrodeposits”, SURFIN 2002, Chicago, IL, June 2002.
(5) K.J. Whitlaw & J.N. Crosby, “An Investigation into Methods for Minimising Tin Whisker Growth”, SURFIN 2003, Milwaukee, WI, June 2003.
(6) A. Egli, W. Zhang, J. Heber, F. Schwager, M. Toben, “Where Crystal Planes Meet: Contribution to the Understanding of the Tin Whisker Growth Process”, IPC Annual Meeting, New Orleans, LA, November 2002.
(7) W. Zhang, A. Egli, F. Schwager and N. Brown, “Investigation of Sn-Cu Intermetallic Compounds by AFM: New Aspects of the Role of Intermetallic Compounds in Whisker Formation”, NEMI Tin Whisker Workshop/54th ECTC, Las Vegas, June 2004.
(8) K.J. Whitlaw, A. Egli & M. Toben, “Preventing Whiskers in Electrodeposited Tin for Semiconductor Lead Frame Applications”, Circuit World (2004), 30(2), 20-24.