Electrodeposited Tin Properties & Their Effect on Component Finish Reliability

Phil Fusco
(Technic Inc./USA)

Electrodeposited Tin Properties & Their Effect on Component Finish Reliability

Rob Schetty
Technic Advanced Technology Division, Plainview NY USA

ABSTRACT

As the European Community's Directive on the Restriction of Hazardous Substances in Electrical and Electronic Equipment banning lead (Pb) in electronics products will take effect on July 1, 2006, most electronics manufacturers will be commencing with volume production of Pb-free components by the middle of 2004. Electrodeposited pure tin finishes on electronic components are a leading contender to replace the industry standard tin-lead. Commensurate with this shift will be a somewhat steep learning curve as manufacturers adapt a variety of equipment and processes to contend with the issues surrounding this critical, industry-wide material conversion.

Since the electrodeposited finish directly influences the critical reliability characteristics of the component itself, the nature of the Pb-free component finish must be well characterized and understood. Only through a thorough examination of the attributes of the electroplated tin deposit can critical decisions be made regarding component finish reliability. This paper investigates the properties of electrodeposited tin that may have an effect on component reliability, namely, grain structure (size and shape), oxide formation, tin whisker formation, and solderability. Data will be presented from laboratory and production settings, with the objective being to enable manufacturers to draw their own conclusions regarding previously established perceptions and misconceptions about electrodeposited tin properties.

Tin Whisker Growth – Background

Many publications have been written on the tin whisker phenomenon recently, and much more information is available on this subject than there was just a few years ago. In particular, recent papers have focused more on the practical implications of the tin electroplating process and the ensuing tin electrodeposit as opposed to the more academic papers of the past which focused more on fundamental mechanisms. In the mid-1990's it was espoused that a "large, polygonal" grain (namely, 3-8 µm diameter) of the tin deposit was beneficial for whisker growth. After this theory was introduced, many plating process suppliers rushed to produce their own version of "large grain tin" deposits which were allegedly "whisker-free" or resistant to whisker growth and in fact nearly all commercially available tin plating solutions which claim to have resistance to tin whisker growth today are based on this principle. We decided to examine the effect of tin grain size and shape on tin whisker growth through the following experiments.

Tin Whisker Growth – Experimentation

We examined tin whisker growth from several matte tin plating electrolytes combined with specific organic additives.

Electroplating process conditions used in this experiment are listed in Table I.

Table I – Electroplating Solution Conditions

Parameter	Soln I	Soln II	Soln III
Sn conc.	65 g/l	65 g/l	40 g/l
Acid Type	MSA	MSA	Mixed Acid
Acid conc.	200 g/l	200 g/l	100 ml/l
Additive Type	Fine grain matte	Lg. Grain matte	Fine grain matte
Grain size	2-4 µm	3-8 µm	1-2 µm
Additive(s) Conc	65 ml/l	55 ml/l	60 ml/l
Current Density	200 ASF	200 ASF	200 ASF

Whisker growth test conditions utilized are provided in Table II.

Table II – Whisker Test Type: Deposit Aging Conditions	
Type	**Condition**
A	55°C, dry bake
B	Temp Cycling, -65 to +150°C
C	20-25°C, 40-60% RH

Deposits were electroplated in the solutions listed in Table I to a thickness of 5-15 μm on a common lead frame industry prepared substrate (Olin C194). SEM photomicrographs of the deposits produced from each of the solutions type I through III are provided in Figures 1 through 3. Deposits were then subjected to the whisker test conditions listed in Table II. Whisker growth was periodically observed (once per month) by SEM at 2000-5000X magnification, and photomicrographs were taken of any unusual or suspicious growths observed.

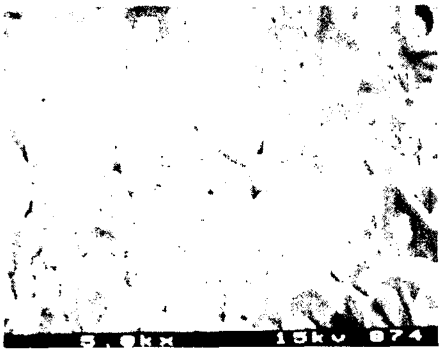

Fig 1 – Grain structure of tin deposit produced from Solution I

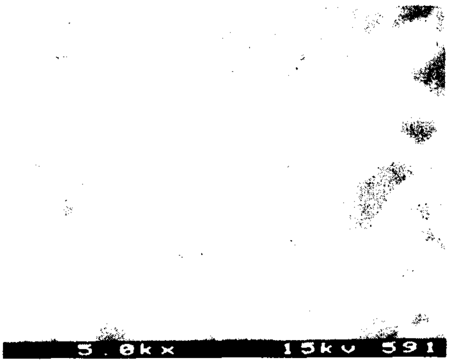

Fig 2 – Grain structure of tin deposit produced from Solution II

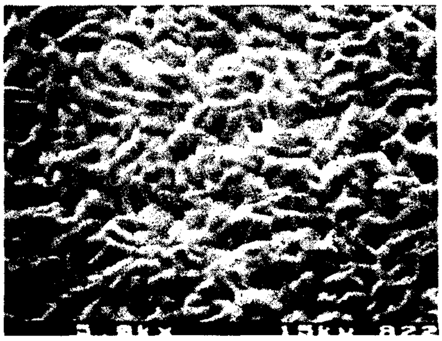

Fig 3 – Grain structure of tin deposit produced from Solution III

Results

Whisker growth results for the various solutions and whisker test conditions are shown in Table III below and in Figures 4 & 5.

Table III – Whisker Test Results			
Deposit Type	**Whisker Test Type**	**Whisker Test Duration**	**Tin Whiskers Observed*?**
I	A	1 month	Yes
II	A	1 month	Yes
III	A	2 years +	No
II	B	1000 cycles	Yes
III	B	1000 cycles	No
I	C	3 months	Yes
II	C	3 months	Yes
III	C	2 years +	No

*defined as growths > 5 μm in length satisfying the NEMI tin whisker definition

Fig 4 - Tin Whiskers Observed on Deposit I

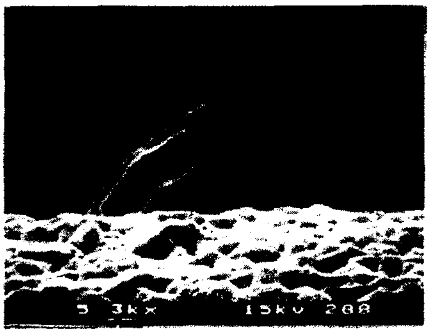

Fig 5 - Tin Whiskers Observed on Deposit II

Comparing the results for whisker test type A, the deposits from Solution (I) ("small grain" MSA matte tin) and Solution (II) ("large grain" MSA matte tin) both produced tin whisker growth within one month when aged at 55°C, whereas the deposits from the Solution (III) (fine grained "mixed acid" tin) did not. For deposits subjected to thermal cycling at –65 to +150°C for 1000 cycles, deposits from Solution (II) produced tin whiskers while the deposit produced from Solution (III) did not (Note: deposits from Solution (I) were not subjected to this whisker test). Finally, when subjected to room temperature aging in an office environment, all deposits except that produced by Solution (III) produced tin whiskers within one to three months. The tin deposit produced from Solution (III) has not formed whiskers after more than two years of room temperature aging.

Discussion

These results lead to the conclusion that tin grain size and shape is not at all a good predictor for tin whisker growth propensity of the tin deposit. The reportedly whisker resistant "large grain" tin produced tin whiskers under most of the conditions tested, while a "fine grain" tin deposit did not. Obviously there are other forces at work.

Since the time that the "large grain" tin deposit theory was advocated, additional studies have focused in more detail on other characteristics of the tin deposit, and several other properties of the deposit have been found to significantly affect tin whisker growth properties, specifically internal stress and crystal orientation. Examining the same deposits used in our whisker tests above by X-ray diffraction (XRD) produced the following results:

Deposit	Stress	PreferredCrystal Orientation(s)
Solution (I)	-8.8 MPa	<321>, <211>
Solution (II)	-11.2 MPa	<321>, <211>
Solution (III)	+18 MPa	<220>, <200>

The stress and crystal orientation data reveals significant differences between the three deposits tested, namely deposits from Solutions (I) and (II) had a compressive stress level while the deposit from Solution (III) had a tensile stress level, and the preferred crystal orientations of the deposits from Solutions (I) and (II) were similar to each other and very different from the crystal orientations from the deposit plated from Solution (III).

Recent whisker mechanistic understanding has concluded definitively that compressive stress is the driving force for the tin whisker growth phenomenon. Specifically, if there is no compressive stress present in the tin deposit, tin whiskers will never be observed. Additionally, there is evidence that preferred crystal orientation of the tin deposit plays an important secondary role regarding tin whisker growth propensity [1,2,3,4]. With this new information backed by much evidence and data behind it, it can be observed that the effect of the tin grain size and structure may in fact have very little to do with tin whisker growth propensity. Our experiments showed that a large grain tin deposit with a compressive stress level and a particular preferred crystal orientation did produce significant tin whisker growth under a variety of whisker test conditions. Conversely, a fine grain matte tin deposit with a tensile stress level and an alternative preferred crystal orientation did not form significant tin whisker growth under the same conditions. By eliminating the driving force for tin whisker growth (compressive stress), aided possibly by specific crystal orientations in the deposit, we can see that the effect of tin grain diameter on whisker growth was minimal.

In this author's opinion, the theory leading to the conclusion that a large grain structure will minimize tin whisker growth evolved from several misconceptions, one of them related to co-deposited carbon content in the tin deposit since increased levels of co-deposited carbon in the tin deposit are believed to enhance tin whisker growth propensity. The carbon content of the deposit is determined directly by the chemistry used to electrodeposit the tin, namely, the electrolyte and the proprietary organic additives contained therein. In most tin electroplating processes, as the co-deposited carbon is increased in the deposit, the tin grain diameter becomes smaller. This may have led to the misconception that in order to minimize co-deposited carbon, one must maximize the tin grain size. This is simply not true. With proper optimization of tin plating electrolyte and organic additive technology, it is possible to obtain a small diameter "fine grain" matte tin deposit while at the same time maintaining a low co-deposited carbon content. The co-deposited carbon content of the deposits from the three solutions we tested were all less than 100 ppm, and specifically the co-deposited carbon content of the deposit from Solution (III) was 68 ppm.

Tin Grain Diameter and Other Deposit Properties

Since our studies determined that tin grain diameter has little to no influence on tin whisker growth relative to other factors, we decided to examine the effect of tin grain diameter on other tin deposit properties, specifically, oxide resistance and solderability.

Experiment

In this experiment, deposits were plated from two of the three matte tin plating solutions used in the previous section (i.e., Solutions (II) and (III)) and an additional plating solution was added to produce a bright tin deposit (Solution IV). These solutions were prepared according to the conditions outlined in Table IV below:

Table IV – Electroplating Solution Conditions

Parameter	Soln II	Soln III	Soln IV
Sn conc.	65 g/l	40 g/l	60 g/l
Acid Type	MSA	Mixed Acid	Mixed Acid
Acid conc.	200 g/l	100 ml/l	100 ml/l
Additive Type	Lg. Grain matte	Fine grain matte	Bright
Grain size	3-8 μm	1-2 μm	<1 μm
Additive(s) Conc	55 ml/l	60 ml/l	80 ml/l
Current Density	200 ASF	200 ASF	150 ASF

Deposits were electroplated in the solutions listed above to a thickness of 8-12 μm on a common lead frame industry prepared substrate (Olin C194) and then subjected to a variety of thermal conditioning as listed in Table V:

Table V – Thermal Conditioning

Condition	Duration
Natural Aging	2 months
"Stress Relief Bake"	150°C / 1 hr
Oven Bake	150°C / 16 hrs
Bake + Steam Age	150°C / 16 hrs + 8 hrs steam aging

After conditioning, the deposits were evaluated for solderability performance by wetting balance and for quantitative oxide thickness level determination by SERA[5] as per the parameters outlined in Tables VI & VII.

Table VI - Wetting Balance Parameters

Model	Kester KWB 1000
Test Method	IPC-JEDEC J-STD-002B
Insertion speed	25.4 mm/sec (strip type)
Dip time	3-5 sec
Dip depth	0.5-1.0 mm
Sn-Pb	solder at 215-220°C
R-type	non-activated flux
Note: 3 units tested at each condition	

Table VII - SERA Parameters

Model	QC-100
Applied Current	0.603 μA
Gasket Diameter	0.160 cm
Current Density	15-60 μA/cm2
Surface Area Measured	0.0201 cm2
Sampling Frequency	1.0 sec
Electrolyte	Borax Buffer

Results

Wetting balance results for the severely thermally conditioned samples (16 hrs bake at 150 deg. C + 8 hrs. steam aging) are shown in Figures 6, 7, and 8 and are summarized in Figure 9. SERA results are summarized in Figure 10 and select SERA curves for the severely thermally conditioned samples are shown in Figures 11, 12, and 13.

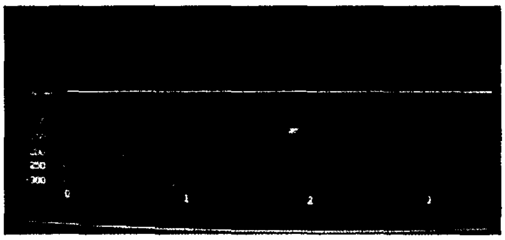

Fig 6 –Conventional Large Grain Tin Deposit
Deposit baked 16 hrs/150°C + 8 hrs steam age
Sn/Pb solder dip, 215°C, 3 sec.
ZCT: never reached; Max force: ~-75µN/mm

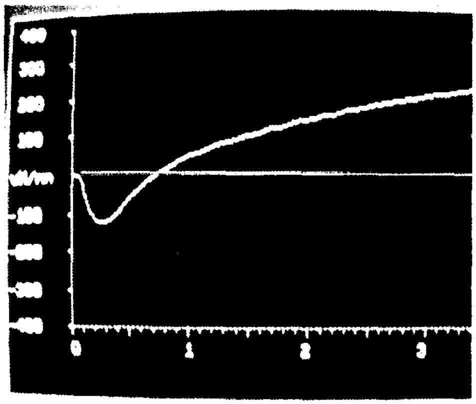

Fig 7 – Bright Tin Deposit
Deposit baked 16 hr/150°C + 8 hrs steam age
Sn/Pb solder dip, 215°C, 3 sec.
ZCT: ~0.7 sec. Max force: >200 µN/mm

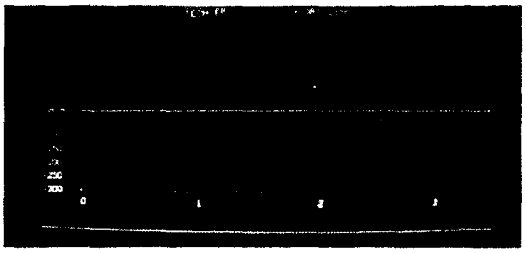

Fig 8 - Fine Grain Matte Tin Deposit
Deposit baked 16 hr/150°C + 8 hrs steam age
Sn/Pb solder dip, 215°C, 3 sec. ZCT: ~0.75 sec. Max force: ~+125µN/mm

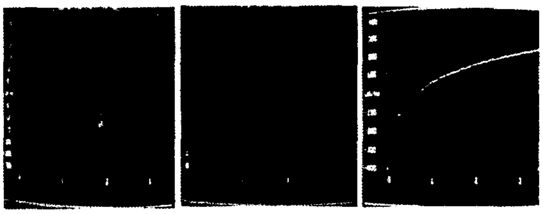

Fig 9 – Wetting Balance Performance vs. Grain Size
(l to r: large grain/matte tin; fine grain/matte tin; bright tin)

Deposit Type	Aging Condition	Total Oxide Thickness (Å)
Lg. Grain Matte Tin	60 days RT	50
Fine Grained Matte Tin	60 days RT	31
Bright Tin	60 days RT	NA
Lg. Grain Matte Tin	Bake 150°C/1 hr	45
Fine Grained Matte Tin	Bake 150°C/1 hr	32
Lg. Grain Matte Tin	Bake 150°C/16 hrs	63
Fine Grained Matte Tin	Bake 150°C/16 hrs	35
Bright Tin	Bake 150°C/16 hrs	32
Lg. Grain Matte Tin	Bake 150°C/16 hrs + 8 hrs steam aging	122
Fine Grained Matte Tin	Bake 150°C/16 hrs + 8 hrs steam aging	78
Bright Tin	Bake 150°C/16 hrs + 8 hrs steam aging	43

Fig 10 – Oxide Thickness vs Tin Deposit Grain Size
SERA Results Summary Chart

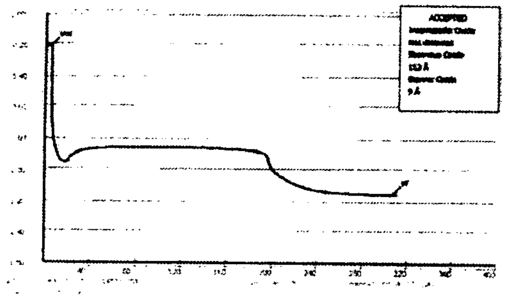

Fig 11 – SERA Results
Large Grain Matte Tin after bake 150°C, 16 hrs + 8 hrs steam aging
Total oxide = 122 Å; SnO = 113 / SnO_2 = 9

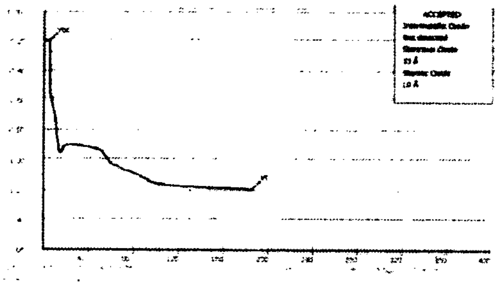

Fig 12 – SERA Results
Bright Tin after bake 150°C, 16 hrs + 8 hrs steam aging
Total oxide = 43 Å; SnO = 33 / SnO_2 = 10

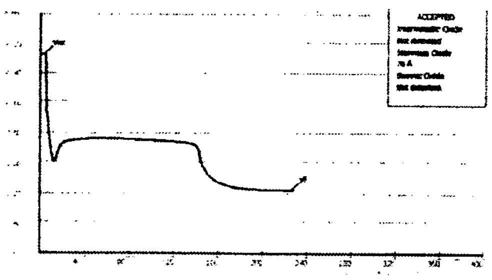

Fig 13 – SERA Results
Fine grain matte tin after bake 150°C, 16 hrs + 8 hrs steam aging
Total oxide = 78 Å; SnO = 78 / SnO_2 = 0

Discussion

Some very interesting trends emerge from this data. Firstly in terms of wetting balance performance, it can be observed that the large grain matte tin performs very poorly after severe thermal conditioning (16 hrs bake at 150 deg. C + 8 hrs. steam aging), with negative wetting throughout the duration of the test as shown in Figure 6. In contrast, the bright tin deposit performs extremely well after the same severe thermal conditioning procedures as shown in Figure 7. The wetting balance performance of the fine grain matte tin deposit after severe thermal conditioning (Figure 8) approaches the wetting balance performance of the bright tin but is an order of magnitude improvement compared to the large grain matte tin deposit. A comparison of all three wetting balance curves together bears this out (Figure 9).

The SERA analysis sheds light on determining why the above wetting balance performance trends were observed, and in addition provides some additional important information on this subject. First from Figure 10 it can be seen that the amount of oxide on the surface of the matte tin deposits after the "stress relief bake" of one hour at 150 °C is roughly equivalent to that after aging 60 days at room temperature. This means the implementation of a post-plating stress relief bake is equivalent to approximately two months of storage at room temperature. The implication is that the stress relief bake, which will be a commonly implemented industry tin whisker mitigation technique, effectively shortens the component shelf life by two months.

In terms of the grain size comparison, the data clearly indicates that the amount of oxide present on the surface of the tin deposit is inversely proportional to the grain size at equivalent sets of thermal conditioning. The bright tin deposit with its extremely small grain diameter exhibited approximately half the amount of oxide growth on the surface compared to the large grain matte tin deposit at any given set of thermal conditions. It is obvious that oxide resistance is directly related to grain size. The fine grain matte tin deposit approached the oxide resistance of the bright deposit and exhibited significantly reduced oxide layer thicknesses compared to the large grain matte tin deposit at any given set of thermal conditions.

In terms of explaining these results, the answer may be due to surface roughness and the available area for oxygen penetration - the large grain matte tin deposit with its acicular, rough structure and large grain diameter has a large surface area with significantly increased potential reaction sites for oxide formation compared to the fine grain matte tin or bright tin deposits which are relatively smooth.

Armed with the oxide layer thickness data, it is straightforward to see why the wetting balance performance exhibited the trends previously described: the large grain matte tin deposit is very prone to oxide formation and the level of oxide generated during severe thermal conditioning is sufficient to result in the very poor wetting balance behavior observed. In contrast, the bright tin and the fine grain matte tin deposits with their small grain diameters are very resistant to oxide formation and therefore with minimal oxides on the surface, the wetting balance performance is superior. The benefit of the fine grain matte tin is that it is also low in co-deposited carbon content and is whisker resistant as reported previously, whereas the bright tin deposit would not meet the industry requirements for co-deposited carbon and tin whisker growth.

Final Conclusions

We have demonstrated that other properties of the tin deposit, namely internal stress levels and crystal orientation, are much more significant factors affecting tin whisker growth than grain size of the tin deposit. Any claims that a tin deposit that possesses a large grain structure will be whisker-resistant without regard for the other more important deposit properties is misguided. We have demonstrated that a whisker-resistant matte tin deposit with a small grain diameter (1-2 μm) and low co-deposited carbon content is possible.

Furthermore with regard to oxide resistance and solderability performance of matte tin deposits, this data has convincingly demonstrated several severe detrimental effects of using a large grain tin deposit. A clear correlation has been identified between tin grain diameter, oxide resistance capability, and wetting balance solderability performance and that is: smaller tin grain diameter = improved oxide resistance capability = improved solderability performance. As end-user thermal conditioning requirements continue to become more severe and solderability requirements continue to become more stringent and the industry seeks to implement additional thermal exposures such as the "post-plating bake" for tin whisker mitigation, the process window for solderability performance of tin deposits is becoming increasingly narrow. This paper has demonstrated that through the use of a fine grain matte tin deposit that solderability process window can be opened significantly.

References:

1. R Schetty, "Whisker Growth Studies", *Proc. of the IPC Annual Meeting.*, Sept., 2001.
2. A.Egli, W. Zhang, J. Heber, F. Schwater, and M. Toben, "Where Crystal Planes Meet: Contribution to the Understanding of the Whisker Growth Process", *IPC Annual Meeting*, pp. S08-3-1 to S-8-3-5, Nov. 2002.
3. R. Schetty, "Tin Whisker Growth & the Metallurgical Properties of Electrodeposited Tin", *The Proc. of the IPC/JEDEC Conf.*, May 2002.
4. W.J. Choi, T.Y. Lee, and K.N. Tu, "Structure and Kinetics of Sn Whisker Growth on Pb-free Solder Finish", *Proc. IEEE Elec. Comp. & Tech. Conf.*, pp. 628-633, 2002.
5. ECI Technology, E. Rutherford, NJ, USA.