Tin Whisker Studies-Experimentation & Mechanistic Understanding

by Rob Schetty*

Much has been written and speculated about the mechanism and formation of tin whisker growth, and numerous variables have been identified as contributing towards whisker growth. Many of these variables are outside the realm of control of the plating operation. The ideal situation for addressing the tin whisker growth issue would be to develop a plating bath chemistry that is as robust as possible in terms of minimizing whisker growth, given a wide variety of external factors. This paper examines the influence of several variables of the electroplating chemistry on tin whisker growth, and seeks to provide an enhanced mechanistic understanding of the fundamental deposit characteristics that affect whisker formation, and more importantly, how to control these characteristics in a production plating application.

Much has been written about tin whisker growth formation in recent years, and intense industry activity is currently focused on this phenomenon. At least two international industry consortia have undertaken extensive whisker projects in the last year. Numerous factors related to the substrate, deposit and aging conditions have been identified as being responsible for tin whisker formation. This paper will examine several factors in the electroplating process and their effects on tin whisker growth.

Alloying certain elements in tin deposits are widely believed to inhibit or eliminate tin whisker growth. We examined the effect of copper additions to a pure tin deposit. In addition, we studied the effect of the type of electrolyte/organic additive type used to electroplate pure tin and its effect on whisker growth.

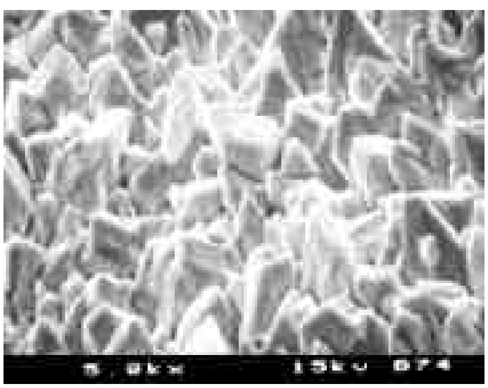

Fig. 1—Surface morphology of a tin deposit produced from Solution I.

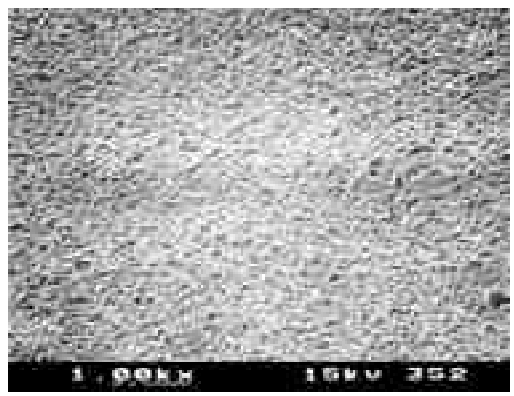

Fig. 2—Surface morphology of a tin-copper deposit produced from Solution II.

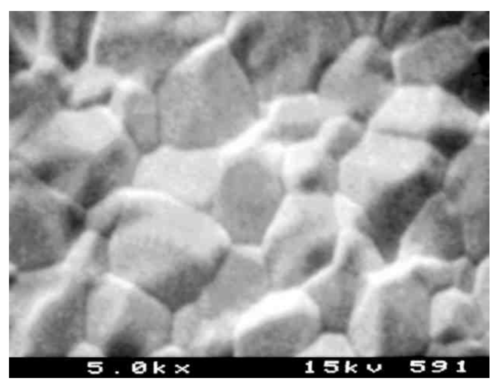

Fig. 3—Surface morphology of a tin deposit produced from Solution III.

Nuts & Bolts: What This Paper Means to You

Much has been written and speculated about the mechanism and formation of tin whisker growth, and many factors have been identified as causes. Many of the causes lie beyond just the plating operation. The ideal situation would be to have a bath that is as robust as possible in terms of minimizing whisker growth. This paper examines the influence of several variables of the electroplating chemistry on tin whisker growth, and how to control them in production. The results show that a number of approaches currently in vogue are not necessarily the cure-alls that they are cracked up to be.

*Corresponding Author:
Mr. Rob Schetty
Technic Advanced Technology Division Technic, Inc.
III East Ames Court
Plainview, NY 11803
E-mail: rschetty@technic.com

Experimental

Most if not all tin/tin alloy deposits plated in the electronics industry today are deposited from an electrolyte based upon methane sulfonic acid (MSA). MSA, combined with the metals of interest and the proprietary organic additives, impart the specific deposit properties. Recently, a novel, proprietary non-MSA acid type for electroplating tin and its alloys was developed.[1] This electrolyte is known to have specific advantages such as increased stannous tin ion stability, lower corrosivity, increased current density range and reduced cost vs. MSA-containing solutions.[2] We examined tin whisker growth from both MSA-containing and non-MSA containing electrolytes, combined with specific organic additives.

Table 1
Electroplating Solution Conditions

Parameter	Solution I	Solution II	Solution III	Solution IV
Tin concentration	65 g/L	65 g/L	65 g/L	40 g/L
Alloy element concentration	None	~1% Copper in deposit	None	None
Acid type	MSA	MSA	MSA	Non-MSA
Acid concentration	200 g/L	200 g/L	200 g/L	150 g/L
Additive type	Conventional	Conventional	Large grain	Proprietary*
Additive concentration	65 mL/L	100 mL/L	55 mL/L	70 mL/L
Current density, A/dm²	21.5	21.5	21.5	21.5
Current density, A/ft²	200	200	200	200

** Technistan EP, Technic, Inc., Providence, RI.*

The electroplating process conditions used in this experiment are listed in Table 1. The whisker growth test conditions used are provided in Table 2.

Deposits were electroplated in the solutions listed in Table 1 in a cut strip plating machine** to a thickness of 5 to 15 μm (197 to 591 μ-in.) on a common industry lead frame substrate. Scanning electron photomicrographs of the deposits produced from each of the solutions type I through IV are provided in Figs. 1 through 4. "Conventional" additive type means one in which a conventional fine-grained matte deposit is produced as shown in Fig. 1. "Large grain" additive is defined as an additive system producing grain sizes in the range of 3 to 8 μm (118 to 315 μ-in.) diameter as shown in Fig. 3. A new type of organic additive system*** was used with the proprietary non-MSA electrolyte as shown in Fig. 4. An industry control matte 90:10 tin-lead deposit SEM photo is shown for comparison in Fig. 5.

Deposits were then subjected to the conditions listed in Table 2. Whisker growth was periodically observed (typically monthly) by SEM at 2000-5000X magnification.

Results

Whisker growth results for the various solutions and whisker test conditions are shown in Table 3. Figures 6 through 9 show SEM photos of the typical whiskers observed.

Comparing the results for whisker test Type A, the deposits from the conventional MSA pure tin, the MSA tin-copper and the "large grain" MSA pure tin (Solutions I through III) all produced tin whiskers within one month when aged at 55°C (131°F), whereas the deposits from the non-MSA pure tin solution (Solution IV) has not exhibited whisker growth after twelve months of aging. This test is ongoing.

For deposits subjected to thermal cycling at -55°C to +150°C (-67°F to +302°F) for 1000 cycles, the large grain MSA pure tin deposit produced tin whiskers while the deposit produced from the non-MSA pure tin solution did not.

When subjected to room temperature aging in an office environment, all deposits except that produced by the non-MSA solution produced tin whiskers within one to three months. The tin deposit produced from the non-MSA solution had not formed whiskers after over one year of room temperature aging.

*** Technic SP-800, Technic Advanced Technology Div., Plainview, NY.*
**** Technistan EP, Technic, Inc., Providence, RI.*

Discussion

The results demonstrate that an alloying element added to a tin deposit, in this case 1% co-deposited copper, had little to no effect on inhibiting tin whisker growth. Tin-copper deposits demonstrated no appreciable advantage in terms of minimizing whisker growth and in fact the opposite appeared to be the case as copper seemed to accelerate whisker growth. In addition, during the plating opera-

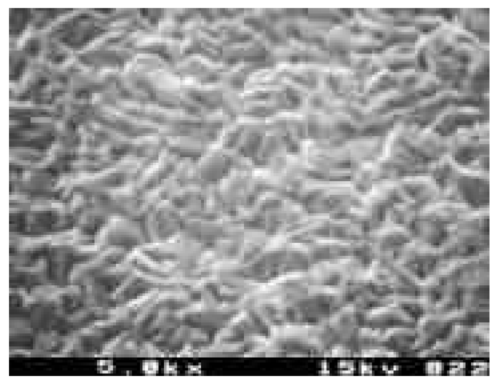

Fig. 4—Surface morphology of a tin deposit produced from Solution IV.

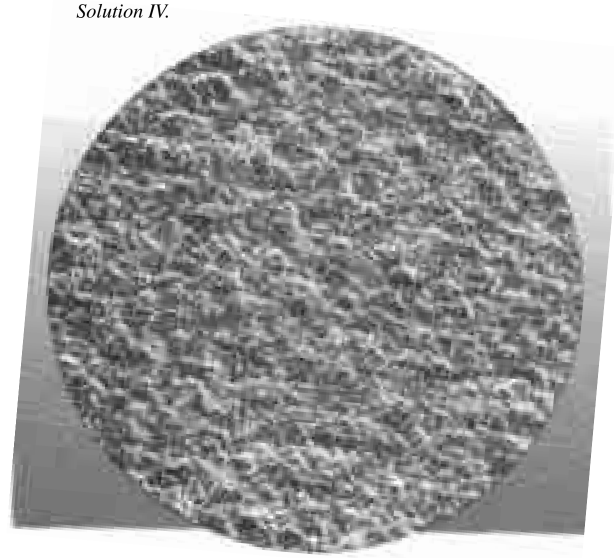

Fig. 5—Surface morphology of a 90:10 tin-lead deposit (control).

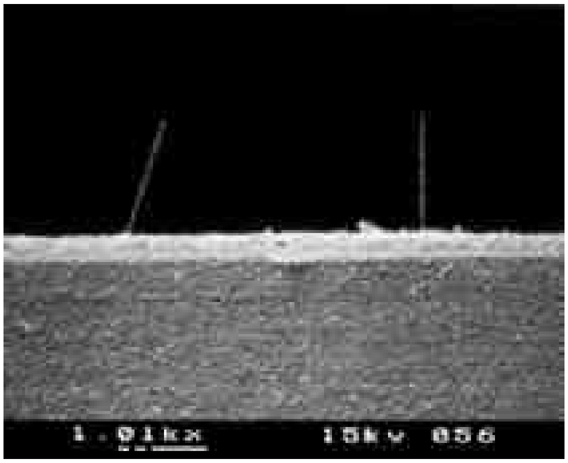

Fig. 6—Tin whiskers observed on Deposit I.

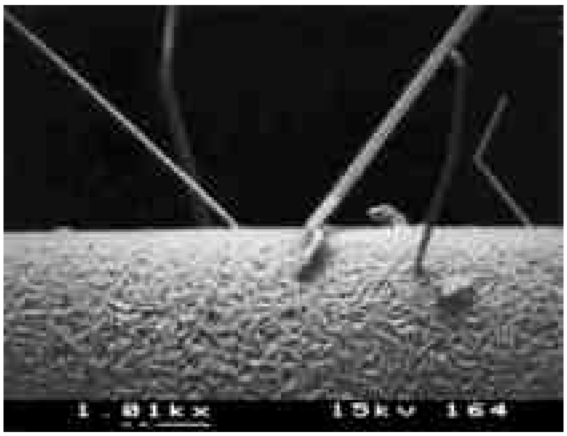

Fig. 7—Tin whiskers observed on Deposit II.

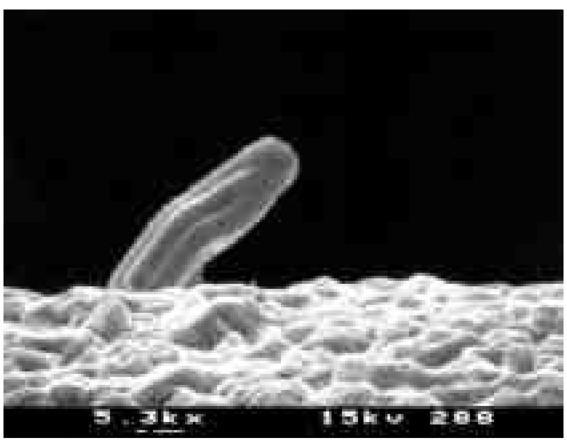

Fig. 8—Tin whiskers observed on Deposit III.

Fig. 9—No tin whiskers observed on Deposit IV.

Table 2
Whisker Test Type & Deposit Aging Conditions

Type	Conditions
A	Dry bake: 55°C (131°F)
B	Thermal cycle: -65°C to +150°F (-85°F to +302°F)
C	20 - 25°C (68 - 77°F); 40—60% relative humidity

Table 3
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	1 month	Yes
IV	A	12 months	No
III	B	1000 cycles	Yes
IV	B	1000 cycles	No
I	C	3 months	Yes
II	C	1 month	Yes
III	C	3 months	Yes
IV	C	15 months	No

tion the copper immersion-coated the anodes and plated parts when the current was turned off, and the solution was unstable. There appeared to be no benefit in selecting a tin-copper alloy process for semiconductor component lead finishing.

The results also demonstrate that there appears to be little to no benefit in selecting a "large grain" pure tin deposit. Although highly touted in recent years as a cure-all to the tin whisker problem, the results in this experiment and others demonstrate that tin whiskers formed at approximately an equivalent rate and magnitude from solutions which utilize "large grain size" producing plating bath additives vs. "conventional" additives.

The most significant factor in terms of whisker formation emerging from this study is the effect of acid/additive type. In all cases, tin deposits produced from the proprietary non-MSA acid/organic additive combination produced the least amount of tin whiskers compared to tin or tin-copper deposits produced from MSA-containing electrolytes. Tin deposits plated from the non-MSA solution did not form tin whiskers when aged for over nine months continuously at 55°C (131°F), or when subjected to 1000 cycles of -55°C to +150°C (-67°F to +302°F), or when aged at room temperature for one year. This combination of acid/additive type appears to offer a significant advantage in terms of tin whisker formation.

In order to better understand the mechanism behind this whisker growth minimization phenomenon, the deposit of concern was subjected to additional testing.

Recent publications[3-5] have indicated that tin deposited over copper/copper alloy substrates in the as-plated condition generally start out with no or slightly low compressive stress but during deposit aging compressive stress increases significantly. It is theorized that this increase in compressive stress arises from the formation of copper-tin intermetallic compounds, due to diffusion of copper from the base material. Furthermore, this compressive stress provides the driving force for tin whisker formation. It is important to point out that the tin plating processes utilized in these studies were based on MSA.

Table 4
Internal Stress Levels for Various Tin Electrodeposits

Electroplating Solution Used	Substrate	Stress Level, As Plated	Stress Level, After Aging	Aging Condition	Reference
MSA Tin	Cu	11 MPa (1600 psi) (tensile)	8 MPa (1160 psi) (compressive)	7 days RT	6
MSA Tin	Cu	4 MPa (580 psi) (compressive)	8 MPa (1940 psi) (compressive)	15 months RT	4
MSA Tin	Ni-plated Cu	N.A.	14 MPa (2030 psi) (tensile)	3 months RT	4
Non-MSA Tin with Organic Additive	Cu	18.7 MPa (2710 psi) (tensile)	14.9 MPa (2160 psi) (tensile)	3 months RT	Internal Technic Testing
Non-MSA Tin with Organic Additive	Cu	18.7 MPa (2710 psi) (tensile)	11.2 MPa (1620 psi) (tensile)	3 months 55°C;131°F bake	Internal Technic Testing

Table 5
X-ray Diffraction Comparison

Deposit type	Preferred crystal orientation
MSA Tin[7,8]	<211>
Non-MSA Tin[7,8]	<220>
Tin-lead, 60/40[9]	<220>,<200>
Tin-silver, 97/3[9]	<220>
Reflowed tin[8,9]	<220>,<321>

In contrast, the stress results for tin deposits produced from the non-MSA electrolyte do not show an increase in compressive stress over time as shown in Table 4. These results were obtained for 10 μm (394 μ-in.) of pure tin over a brass substrate.

Further insight into the mechanistic behavior of this system can be found by examining the preferred crystal orientation of the deposits by X-ray-diffraction (XRD) as shown in Table 5. As these results indicate, tin deposits produced from the MSA electrolyte and the non-MSA electrolyte possess radically different preferred crystal orientations, <211> vs. <220> respectively, which may help to explain their fundamentally different tin whisker growth behavior. The tin deposits from the non-MSA process have a <220> preferred crystal orientation which it shares in common with other known "non-whiskering" deposits such as tin-lead, tin-silver and reflowed tin.

An examination of the surface morphology indicates that the tin deposit produced from the non-MSA process also has a surface morphology which is very similar to that of tin-lead which is widely believed to be non-whiskering (see Figs. 4 and 5).

Conclusions

The results from our whisker growth studies indicate that several methods popularly believed to inhibit tin whisker growth, namely the addition of an alloying element such as copper and utilization of a tin plating process additive which produces a large grain size, are not at all effective, under the specific set of plating conditions described here. In our tests, the most significant factor affecting tin whisker growth was the type of electrolyte utilized to deposit the tin. We identified a specific proprietary non-MSA acid and additive combination which did not generate tin whiskers when subjected to several whisker tests common in the industry today. Further investigation into the metallurgical characteristics of the tin deposit produced from this process reveal that compressive stresses are not built up over time as is common with other systems, and furthermore, the deposit shares a common preferred crystal orientation with other non-whiskering deposits.

It appears that the unique metallurgical properties of the deposit obtained from the non-MSA electrolyte are responsible for its minimal whisker growth characteristics. Further work is ongoing to characterize this deposit.

References

1. H. Gilman, *et al.*, U.S. patents 6,183,619; 6,248,228; 6,251,253; and 6,179,985 (2001).
2. *ibid.*
3. Y. Zhang, *Proc. APEX Conference 2002*, IPC, Northbrook, IL, 2002.
4. X. Chen, *Proc. APEX Conference 2002*, IPC, Northbrook, IL, 2002.
5. M. Toben, *et al.*, *Proc. AESF SUR/FIN 2001*, AESF, Orlando, FL, (2001).
6. B.Z. Lee & D.N. Lee, *Acta Mat.*, **46** (10), 3701 (1998).
7. Internal Technic Data.
8. Data provided by ST Microelectronics, Corporate Package Development, Grenoble, France and Agrate, Italy.
9. Data provided by Dr.-Ing. Max Schloetter Co., Geislingen, Germany.

About the Author

Rob Schetty is a VP for Technic, where he has responsibility for worldwide plating chemical sales, marketing and technology implementation for the Technic Advanced Technology Division. Rob received his Bachelor of Science degree in chemical engineering from the University of Pennsylvania. He has been with Technic for several years and prior to that he spent 15 years in various positions at other suppliers, including R&D, a multi-year assignment in Asia, and various senior management positions. Rob has expertise in many aspects of electronics manufacturing and holds multiple patents related to electronics plating. In addition, he has published over 20 papers related to electronic and industrial metals plating.