Tin Whisker Studies—Experimentation & Mechanistic Understanding

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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.

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Introduction

Much has been written about tin whisker growth formation in recent years, and intense industry activity is currently focussed on this phenomenon. At least two international industry consortia have undertaken extensive whisker projects in recent months (Soldertec/ITRI – UK; NEMI – USA). 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 affects on tin whisker growth.

Alloying 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.

Experiment

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.

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

Whisker growth test conditions used are provided in Table II.

Table I – Electroplating Solution Conditions

Parameter	Soln I	Soln II	Soln III	Soln IV
Sn conc.	65 g/l	65 g/l	65 g/l	40 g/l
Alloying element conc.	None	~1% Cu in deposit	None	None
Acid Type	MSA	MSA	MSA	Non-MSA
Acid conc.	200 g/l	200 g/l	200 g/l	150 ml/l
Additive Type	Conv.	Conv	Lg. Grain	Tech. EP
Additive Conc	65 ml/l	100 ml/l	55 ml/l	70 ml/l
Current Density	200 ASF	200 ASF	200 ASF	200 ASF

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 in a cut strip plating machine* to a thickness of 5-15 µm on a common industry lead frame substrate (Olin C194). SEM photomicrographs of the deposits produced from each of the solutions type I through IV are provided in Figures 1 through 4. "Conventional" additive type means one in which a conventional fine-grained matte deposit is produced as shown in Figure 1. "Large grain" additive is defined as an additive system producing grain sizes in the range of 3-8 µm diameter as shown in Figure 3. A new type of organic additive system** was used with the proprietary non-MSA electrolyte as shown in Figure 4. An industry control matte 90-10 Sn-Pb deposit SEM photomicrograph is shown for comparison purposes in Figure 5.

Deposits were then subjected to the conditions listed in Table II. 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 III below.

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	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	1 year+3 months	No

* Technic SP-800, Plainview, NY
** Tech. EP, Providence, RI

Figures 6 through 9 show SEM photomicrographs of 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-III) all produced tin whiskers within one month when aged at 55°C, 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 to +150°C 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 has not formed whiskers after over one year of room temperature aging.

Discussion

The results demonstrate that an alloying element added to a tin deposit, in this case 1% co-deposited copper, has 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 operation the copper immersed onto the anodes and plated parts when the current was turned off, and the solution was unstable. There appears 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 form 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, or when subjected to 1000 cycles of –55 to +150°C, 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, 4, 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 is due to the formation of copper-tin intermetallic compounds, due to diffusion of copper from the base material and 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.

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 IV below. These results were obtained for 10 microns pure tin deposit over a brass substrate:

Table IV

Solution Used to Electroplate Deposit	Substrate	Stress Level As Plated	Stress Level After Aging	Aging Condition	Reference
MSA Tin	Cu	11 MPa Tensile	8 MPa Compressive	7 days RT	Lee B.Z. & Lee D.N., 1998 Acta Metallurgica
MSA Tin	Cu	4 MPa Compressive	13.4 MPa Compressive	15 months RT	Chen, et al, "Understanding Whisker Phenomenon Pt II" AESF SUR/FIN 2001
MSA Tin	Ni-plated Cu	NA	14 MPa Tensile	3 months RT	Chen, et al, "Understanding Whisker Phenomenon Pt II" AESF SUR/FIN 2001
Organic Additive Non-MSA Tin	Cu	18.7 MPa Tensile	14.9 MPa Tensile	3 months RT	Internal Technic Testing*
Organic Additive Non-MSA Tin	Cu	18.7 MPa Tensile	11.2 MPa Tensile	3 months 55°C bake	Internal Technic Testing*

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 V below:

Table V - XRD Comparison

Deposit Type	Preferred crystal orientation
MSA Tin [6, 7]	<211>
Non-MSA Tin [6, 7]	<220>
Tin-lead 60-40 [8]	<220>, <200>
Tin-silver 97-3 [8]	<220>
Reflowed Tin [7,8]	<220>, <321>

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 Figures 4 and 5).

Conclusions

The results from our whisker growth studies indicate that several methods popularly believed to inhibit tin whisker growth, namely 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. 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, US Patents 6,183,619; 6,248,228; 6,251,253; & 6,179,985, granted to Technic Inc., Jan.-June 2001.
2. *ibid*
3. Y. Zhang, "Understanding Whisker Phenomenon – Part I, Growth Kinetics", Proceedings of APEX Conference, Jan. 2002.
4. Chen Xu, "Understanding Whisker Phenomenon – Part II, Competitive Mechanisms", Proceedings of APEX Conference, Jan. 2002
5. Toben, M., et. al., "Tin Whiskers in Electrodeposits: An Overview of Mechanisms That Drive Their Growth"; Proceedings of AESF SUR/FIN 2001 Conference, June 2001.Internal Technic data, obtained from a Siemens D5000 **È/È** DiffractometerData provided by ST Microelectronics - Corporate Package Development; Grenoble, France and Agrate, Italy.Data provided by Dr. Ing Max Schloetter Co., Geislingen, Germany.

Figure 1
Surface Morphology of tin deposit produced from Solution I

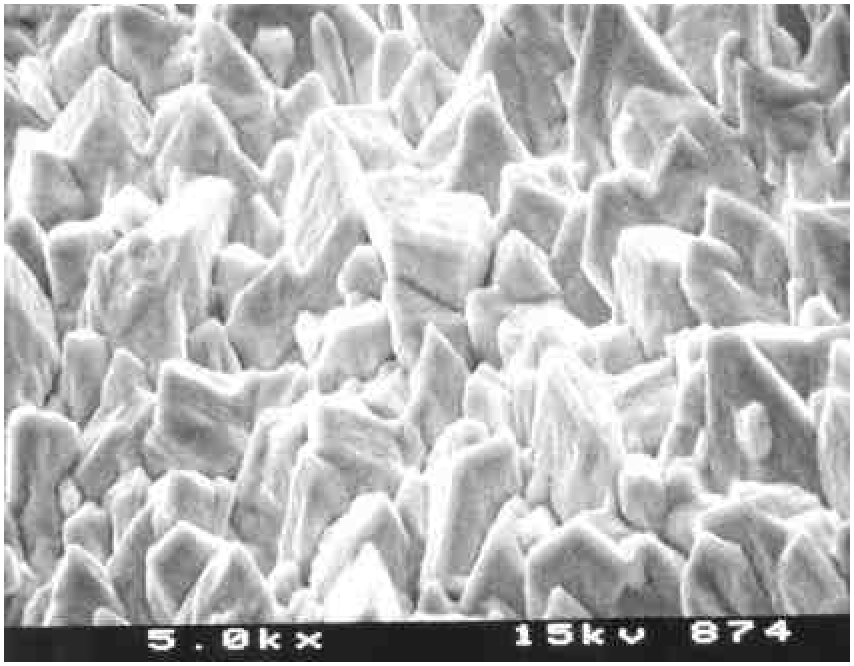

Figure 2
Surface Morphology of tin-copper deposit produced from Solution II

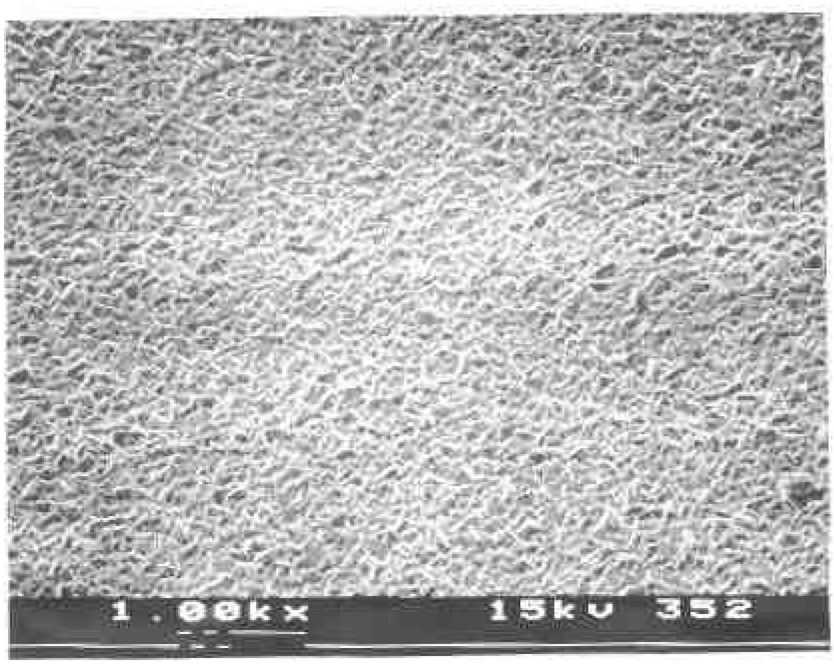

Figure 3
Surface Morphology of tin deposit produced from Solution III

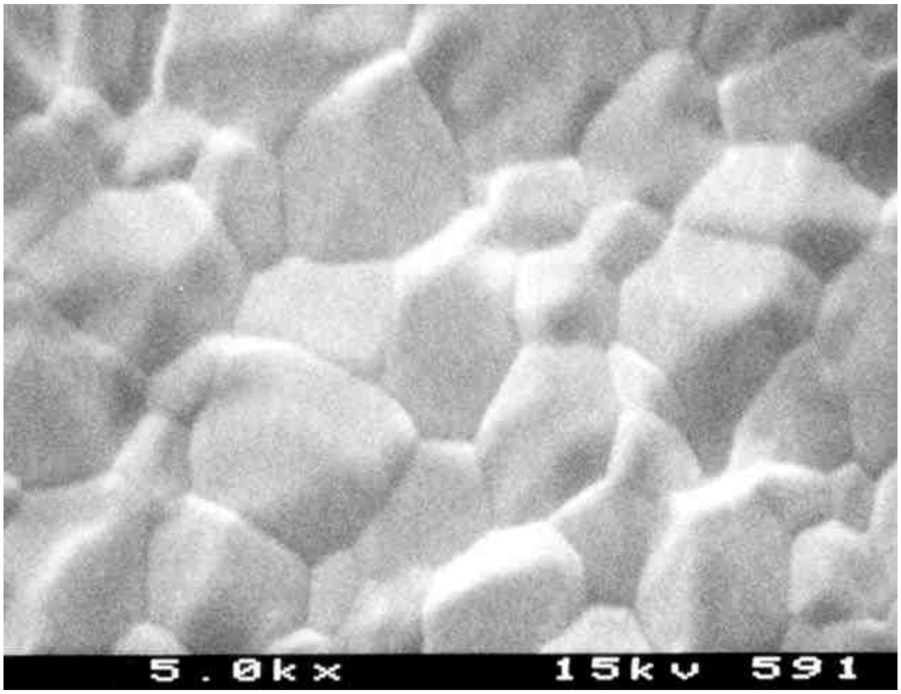

Figure 4
Surface Morphology of tin deposit produced from Solution IV

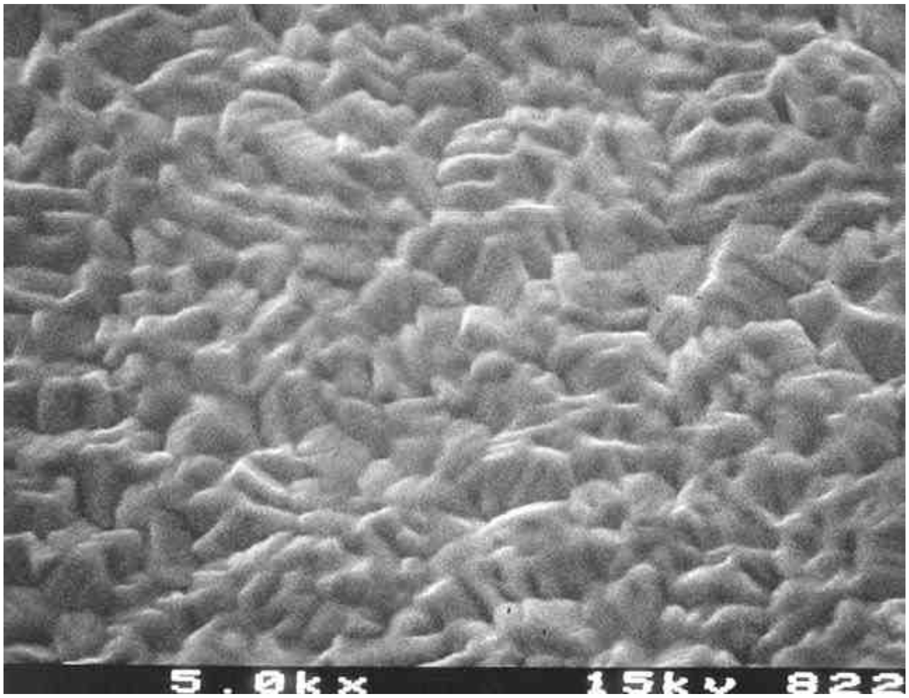

Figure 5
Surface Morphology of 90-10 tin-lead deposit (control)

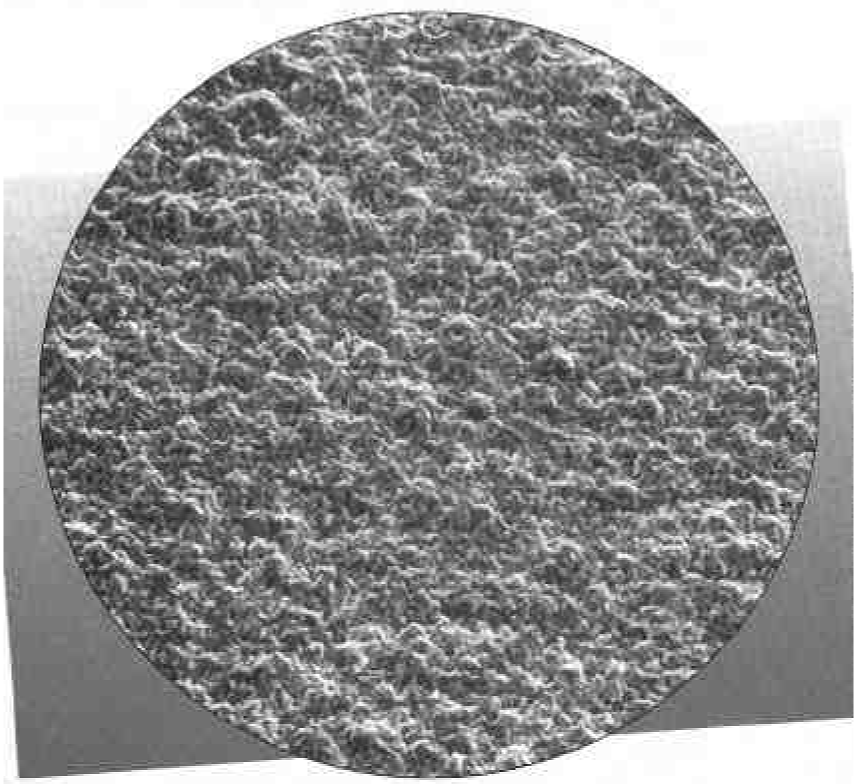

Figure 6
Tin Whiskers Observed on Deposit I

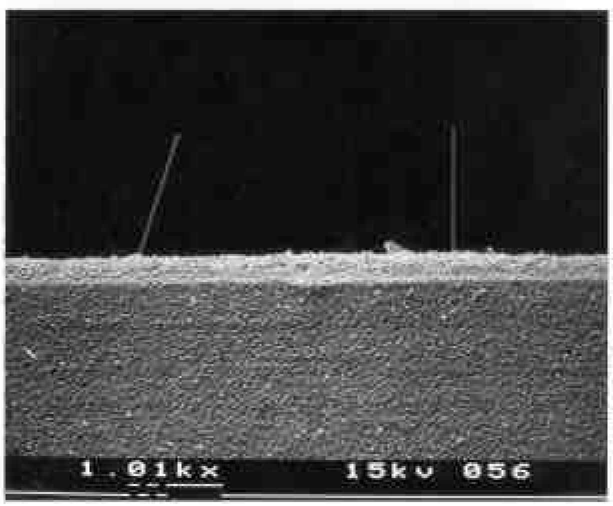

Figure 7
Tin Whiskers Observed on Deposit II

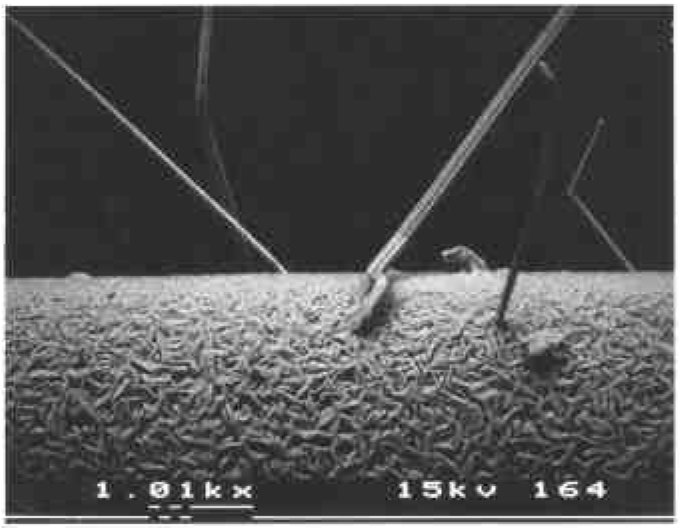

Figure 8
Tin Whiskers Observed on Deposit III

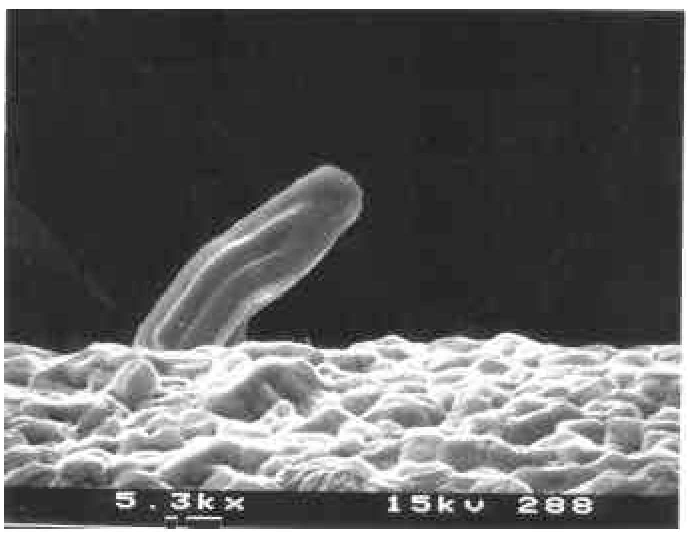

Figure 9
No Tin Whiskers Observed on Deposit IV