Pb-free Component Finishes

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Abstract

Tin-lead is used as the primary electronic interconnection material in solder pastes, printed wiring board (PWB) coatings, and as a finish on the external leads of electronic components such as surface mount and through hole devices. Impending restrictions on the use of lead (Pb) has resulted in a search for alternatives to Sn-Pb solder in the three aforementioned areas of electronic interconnection. While research and development of both Pb-free solder pastes and Pb-free circuit board coatings has been substantial, to date minimal data has been published on producing a Pb-free finish on the external leads of components.

In order to create a truly environmentally safe Pb-free electronic assembly it is required that Pb-free materials be used throughout the interconnection. As with solder pastes and circuit board coatings, several options exist for creating a Pb-free component finish. The component finish need not necessarily duplicate the selected solder paste composition; the main requirement is that it be entirely compatible with the Pb-free solder paste material set. To date, most research on Pb-free solder paste materials has identified binary, tertiary, and quaternary alloys of tin with additions of trace metals such as silver, copper, and/or bismuth as the most promising to replace Sn-Pb. This paper will introduce a number of Pb-free component finishes such as nickel/palladium, pure tin, tin-bismuth, tin-silver, and tin-copper. Solderability performance will be demonstrated with both Pb-containing and Pb-free solders, and other important deposit properties will be presented.

INUDSTRY DIRECTION

The global trend towards providing lead (Pb)-free electronic materials, driven by both legislation and market forces, is now well established[1-4]. Extensive activities are underway in both industry and academia to identify alternatives to Pb for the various aspects of Sn-Pb solder electronic assemblies, namely, printed wiring board (PWB) coatings, solder paste, and component finishes. Available Pb-free PWB coatings are well known (electroless nickel/immersion gold, organic solderability preservatives, electroless silver, electroless tin, etc.). In the area of Pb-free solder pastes, the National Center for Manufacturing Sciences (NCMS) published the results of their four-year Lead Free Solder Project in 1997[5] which identified Sn-Bi, Sn-Ag, and Sn-Ag-Bi as the Pb-free alloys most likely to replace Sn-Pb. More recently, solder pastes consisting of a tertiary Sn-Ag-Cu alloy have been identified as most promising[6], and industry consortia NEMI has formally endorsed a Sn(95.4%)-Ag(3.9%)-Cu(0.7%) solder paste as a standardized Pb-free paste for reflow applications[7]. For the solder paste portion of electronics assembly, the selection of Pb-free materials has been given clear direction.

For electronic components, Sn-Pb has been used as an external lead finish since the 1970s. In 1989, Texas Instruments developed a multilayer palladium (Pd) component finish[8], commonly known today as "NiPd" whereby Sn-Pb was eliminated from the package and a Pb-free component finish was therefore created. However, the component industry has been relatively slow to adopt NiPd finishes on a mass production scale, primarily due to lingering technical issues (ductility, solderability, corrosion) and, more significantly, cost concerns as the price of Pd metal has exceeded US$700 per tr. oz.

A true need exists for a functional, cost-effective Pb-free solder coating which can replace Sn-Pb on the external leads of components. The component finish must be fully compatible with the solder paste materials. As mentioned previously, Sn-Ag-Cu, Sn-Bi, and Sn-Ag, have thus far been identified as promising Pb-free solder paste materials, therefore, Pb-free solder component finishes which are compatible with these materials were investigated, namely, Sn-Bi, Sn, Sn-Ag, and Sn-Cu.

MELTING POINT

The melting points of the various Pb-free component finishes under consideration vary widely as shown in Table 1. Sn-Bi is the only finish which has a melting point in the range of Sn-Pb eutectic and this is the main reason Bi-containing Pb-free solders were selected in the earlier Pb-free studies. However, Sn-Bi forms a low-melting point Sn-Bi-Pb phase if Pb is introduced. This leads to reduced solder joint reliability (fatigue/cracking during thermal cycling; fillet lifting of through-hole devices)[9] if Sn-Bi solder is contaminated with Pb, which is to be expected especially in the early years of transition to Pb-free. For this and other reasons, non-Bi containing Pb-free solders have taken precedence. However, in order to utilize the non-Bi Pb-free alternatives much higher reflow temperatures will be required during board assembly operations. Figure 1 is an example of a Pb-free reflow temperature profile, showing peak reflow temperatures of 255-260°C. Such high temperatures will obviously have a detrimental impact on the other materials of construction, particularly the organic materials such as the PWB laminate material and the molding compounds used in packaging of the device. All of these material sets need to undergo significant modification to meet the requirements of Pb-free.

Due to these challenges, two alternative approaches towards Pb-free implementation in industry have emerged: (1) a two-phase approach whereby Bi-containing Pb-free solders are utilized in a temporary Phase I period to enable the continued use of existing organic electronic materials, while non-Bi Pb-free solders are transitioned to in Phase II, providing extended time for organic materials development; (2) a single phase approach whereby the non-Bi containing solders are implemented up-front along with the high Tg organic materials in a single stage conversion process. Approach (1) appears to be most popular in Japan, as the Pb-free roadmaps of most Japanese electronics companies call for Sn-Bi solders in the early years to be followed by Sn-Ag-Cu solders in later years[10]. This is likely due to the accelerated timing of the Pb-free implementation plans in Japan.

Electronic companies in other parts of the world seem to favor Approach (2), perhaps so as to minimize the effort and expense required for Pb-free materials conversions. Given this situation, an electronic component finish supply strategy that satisfies both approaches is needed.

TIN-BISMUTH

For low melting point applications, we electroplated deposits of 95Sn/5Bi from a methane sulfonate electrolyte on 14-lead SOICs composed of Olin 194 base material. Plating parameters are shown in Table 2. Deposits were tested by wetting balance according to the solderability test parameters shown in Table 3. Wetting balance results compared to the other finishes tested are shown in Table 4. The surface morphology of 90Sn/10Bi by SEM at 2000X magnification is shown in Figure 2. Composition stability of the Sn-Bi deposits is illustrated in Figure 3. Codeposited carbon contents of this deposit are shown in Table 5.

Fifty 44-L PLCC components were plated with the Sn-Bi 95-5 deposit over Olin C151 base material. These samples showed no evidence of cracking at 2000X magnification after forming in a J-bend configuration. No whisker growth was observed after 6 months of storage on the formed or unformed units.

As mentioned previously, one of the critical limitations of Sn-Bi as a component finish is its incompatibility with Sn-Pb solder due to the formation of a low melting point Sn-Bi-Pb phase. Therefore, Sn-Bi can generally only be used where control over the entire assembly process is maintained to avoid incompatibility issues.

PURE TIN

For high melting point applications, tin is one type of Pb-free material which has excellent wetting properties, is non-toxic, is easy to electroplate, and has reasonable cost. However, pure tin has historically been restricted in its application as a component finish due to the "tin whisker" problem: dendritic growths or "whiskers" of tin can form during storage of the component which can bridge leads and cause short circuits (Figure 4). The mechanisms of tin whisker formation have never been fully elucidated, however, critical deposit factors affecting whisker formation are reported to be stress, thickness, grain size, intermetallic compound formation, storage temperature, and alloying tin with other metals. Although an industry standard whisker test has yet to be developed, it is generally widely accepted that pure, unalloyed tin deposits can never be truly "whisker-free". However, a fundamental understanding of the relationships between the physical properties of the tin deposit and whisker formation can lead to optimized conditions which will minimize whisker growth. While a detailed discussion on whisker formation is beyond the scope of this paper and will be the subject of a future publication, it is widely believed that large, well polygonized grain sizes will minimize whisker formation due to the lower level of microstress this structure imparts to the deposit. We electroplated deposits of Sn from a methane sulfonate electrolyte plating process specifically formulated to produce low stress, well polygonized, large grains as illustrated in Figure 5. 100-L PQFPs composed of Olin 7025 base material were plated according to the parameters shown in Table 2 and the deposits were tested by wetting balance according to the solderability test parameters shown in Table 3. Wetting balance results with Sn-Pb and Sn-Ag-Cu solder compared to the other finishes tested are shown in Table 4. Codeposited carbon contents of this deposit are shown in Table 5.

Fifty 44-L PLCC components were plated with the large-grain Sn deposit over Olin C151 base material. These samples showed no evidence of cracking at 2000X magnification after forming in a J-bend configuration. No whisker growth was observed after 3 months of storage on the formed or unformed units.

TIN-SILVER

In terms of electroplating process formulation, the potential difference between Sn and Ag is very large, as shown in Table 6. As can be seen, Ag is a much more noble metal compared to Sn, and therefore to obtain Sn-Ag deposits containing low percentages of Ag complexing agents must be used in solution, which complicates waste treatment. Cost, security, and inventory concerns also arise when dealing with precious metals.

Notwithstanding its limitations, Sn-Ag has very desirable mechanical and solderability properties, therefore, we electroplated deposits of 97Sn/3Ag from a proprietary electrolyte on 14-lead SOICs composed of Olin 194 base material. Plating parameters are shown in Table 2. Deposits were tested by wetting balance for solderability performance using the test parameters shown in Table 3. Wetting balance results compared to the other finishes tested are shown in Table 4. SEM photomicrographs of the Sn-Ag deposit are shown in Figure 6.

TIN-COPPER

Sn-Cu is yet another option for a Pb-free component finish, and at least one communications networks provider has publicly announced the qualification of an entire Pb-free assembly process based on Sn-Cu [11]. Careful control of deposit composition is required when electroplating Sn-Cu due to large variations in melting point vs. Cu content.

We electroplated deposits of 99Sn/1Cu from a proprietary patent-pending electrolyte on 14-lead SOICs composed of Olin 194 base material. Plating parameters are shown in Table 2. Deposits were tested by wetting balance according to the solderability test parameters shown in Table 3. Wetting balance results with Sn-Pb and Sn-Ag-Cu solder compared to the other finishes tested are shown in Table 4. The surface morphology of 99Sn/1Cu by SEM at 2000X magnification is shown in Figure 7. Figure VVV shows the effect of current density and process temperature on Sn-Cu deposit composition. Codeposited carbon contents of this deposit are shown in Table 5.

Fifty 44-L PLCC components were plated with the 99/1 Sn/Cu deposit over Olin C151 base material. These samples showed no evidence of cracking at 2000X magnification after forming in a J-bend configuration. No whisker growth was observed after 6 months of storage on the formed or unformed units.

DISCUSSION

Solderability of the 95Sn/5Bi, the low-stress tin, the 97Sn/3Ag, and the 99Sn/1Cu deposits plated from our processes in Sn-Pb solder were comparable to the industry standard 90Sn/10Pb deposit as demonstrated by the similar zero cross times for these finishes in Table 4. Solderability of the Sn and Sn-Cu deposits in the Sn-Ag-Cu solder was comparable as zero cross time was less than one second and solder wetting observed at 10X magnification exhibited greater than 95% coverage under all conditions tested.

Surface morphology of the 95Sn/5Bi, the 97Sn/3Ag, and the 99Sn/1Cu deposits plated from our processes were comparable to the industry standard 90Sn/10Pb deposit as demonstrated by the SEM photomicrographs in Figures 2 & 6 while the low-stress pure tin deposit possesses the desired well polygonized large grained surface morphology demonstrated in Figure 5. Maintaining suitable surface morphology is important in order to obtain the necessary component finish characteristics such as appearance, hardness, ductility, and stress. Forming of plated PLCC units in production assembly equipment exhibited no cracking of any of the component finishes tested, indicating deposit ductility is excellent.

Recognizing the fact that the requirement for Sn-Bi component finishes is relatively short term, and the issues facing Sn-Ag will take additional time to resolve, it is believed that pure tin and Sn-Cu will be the leading Pb-free component finishes for the IC industry today. As tin plating is relatively well understood in industry today, the Sn-Cu component finish was subjected to additional characterization testing.

Surface analysis of the Sn-Cu deposit by Auger and X-ray photoelectron spectroscopy (XPS) analysis was performed. The Auger surface map shown in Figure 7 shows that Cu is uniformly dispersed throughout the deposit. The XPS spectrum at a 1 μm deposit depth (Figure 8) demonstrates that Cu is present as metallic Cu. This data is important because it demonstrates that the Sn-Cu is deposited as an alloy and that Sn-Cu intermetallic compounds are not formed in the as-plated condition. X-ray diffraction (XRD) studies on the Sn-Cu deposit indicate that the preferred orientation is <211>. This is important because reflowed tin deposits also exhibit a strong <211> orientation. As reflowed tin is known to be free of tin whisker growth, the data suggests that Sn-Cu deposits from our process will have minimal whisker growth.

CONCLUSION

Metallic and non-metallic coatings on printed wiring boards meet established standards for providing a Pb-free finish. For the board assembly operation, Bi-containing solders may be used as in interim solution in certain applications while Sn-Ag-Cu appears to be gaining acceptance as the industry standard for Pb-free solder paste materials. Any Pb-free component finish selected must be compatible with the Pb-free materials used on PWBs and in the solder paste. The final selection of a Pb-free component finish will be dictated by end user requirements, compatibility issues, and application.

We have developed Sn-Bi, Sn, Sn-Ag and Sn-Cu plating processes to meet this range of requirements, in addition to offering NiPd plating processes. The properties of the deposits resulting from our processes have been demonstrated to exhibit solderability performance, surface morphology, ductility, and whisker growth formation equivalent to Sn-Pb. The Pb-free solder plating processes demonstrated in this paper will satisfy upcoming industry requirements for Pb-free external lead finishes on electronic components. Sn and Sn-Cu appear to be the most promising Pb-free component finishes for satisfying the majority of electronic device metallization applications.

References

1. European Draft Directive on Waste from Electrical and Electronic Equipment, 3rd Rev., July 1999
2. US House of Representatives Bill HR 2479
3. US Senate Bill S-729, Lead Reduction Act.
4. Japanese Ministry of Health and Welfare/MITI Recycling Bill, in force from April 2001.
5. NCMS report 0401RE96, "Lead Free Solder Project Final Report," August 1997
6. "Get a Jump on the Lead Ban", Christopher Rhodes, IPC, *SMT,* August 1999 issue
7. "Lead-free Project Focuses on Electronics Assemblies", E. Bradley, J. Bath, G. Whitten, S. Chada, *Advanced Packaging,* Feb. 2000, pp. 34-42
8. European Patent Application No. 89302939.7, Texas Instruments, 3/23/89
9. "An Overview of Lead-free Alloy Selection Trends by Worldwide Region," C. Bastecki, IPCWorks, Oct. 1999, International Summit on Lead-free Electronics Assemblies
10. "Research and Devlopments for Lead-Free Soldering in Japan," K. Suganuma, , IPCWorks, Oct. 1999, International Summit on Lead-free Electronics Assemblies
11. IEC/Nortel Press Release, May 29, 1997, Newark, NY

Table 1 ***Melting Point of Sn-Pb and Pb-free Component Finish Materials***		
Material	**Eutectic Composition**	**Melting Pt °C**
Sn-Pb	63Sn/37Pb	183°C
Sn	NA	232°C
Sn-Bi	42Sn/58Bi	138°C
Sn-Ag	96.5Sn/ 3.5 Ag	221°C
Sn-Cu	99.3Sn/ 0.7Cu	227°C

Table 2 ***Plating Parameters for the Pb-free Component Finishes***					
Process	Sn-Pb	Sn	Sn-Bi	Sn-Ag	Sn-Cu
Sn content	40 g/l	50 g/l	55 g/l	40 g/l	60 g/l
Alloying element content	4 g/l	NA	7 g/l	1 g/l	1 g/l
Acid content	200 ml/l	200 ml/l	200 ml/l	100 ml/l	200 ml/l
Additive	105 ml/l	115 ml/l	100 ml/l	100+50 ml/l	115 ml/l
Temperature	40°C	40°C	45°C	45°C	45°C
Current Density	20 A/dm^2	20 A/dm^2	15 A/dm^2	10 A/dm^2	20 A/dm^2

Table 3 ***Solderability Test Parameters***	
Solder temperature	245°C – Sn/Pb 260°C – Sn/Ag/Cu
Immersion Depth	0.2 mm
Immersion Time	5 seconds
Immersion Rate	5 mm/sec
Flux	Rosin, non-activated
Deposit Conditions	As plated Steam Aged 8 hrs Heat Aged 16 hrs/155°C

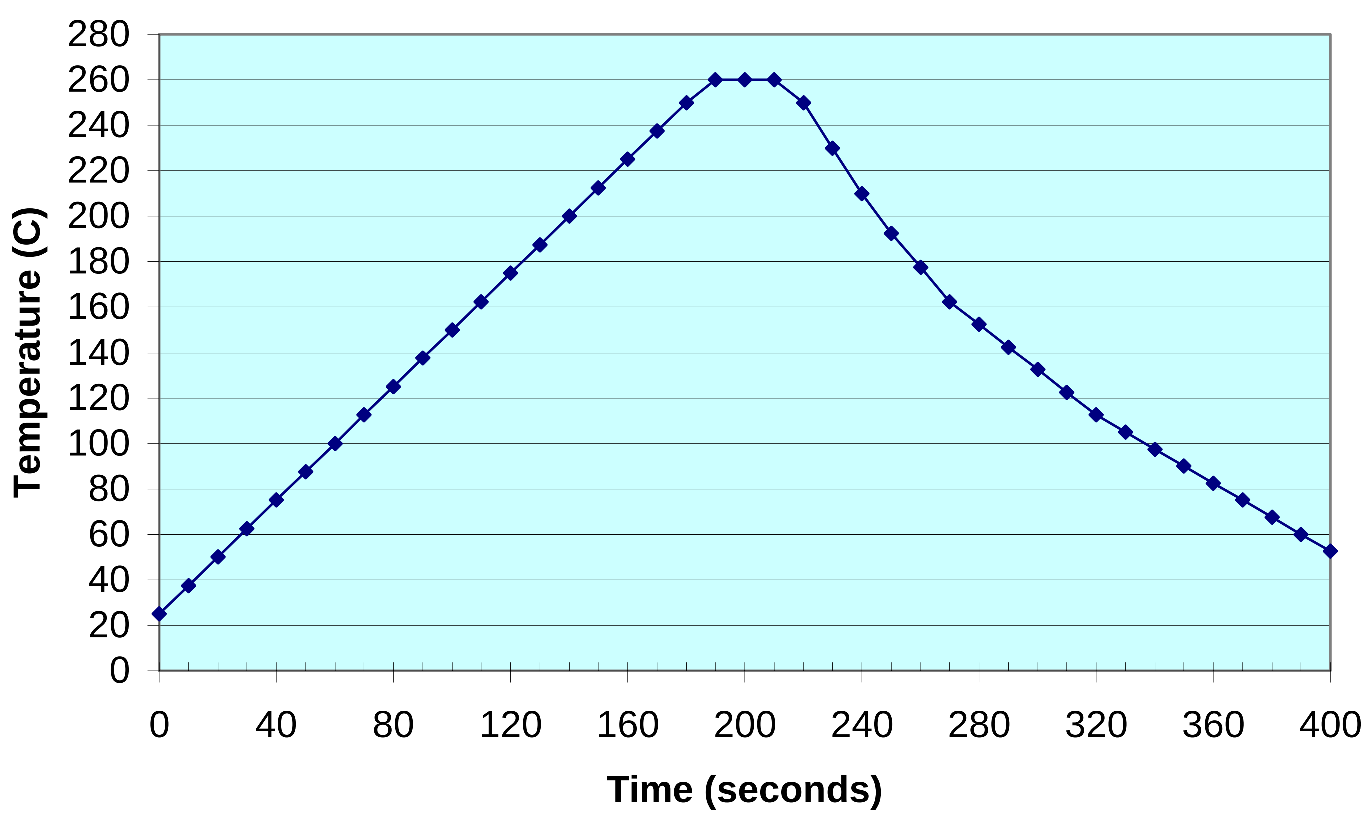
Table 4 ***Solderability Test Results***			
Component Finish/ Solder Type	Aging Condition	Zero Cross Time (sec)	% Coverage (Visual)
Sn-Pb 90-10 Sn/Pb	As plated	0.29	>95%
Sn-Pb 90-10 Sn/Pb	Steam Aged	0.46	>95%
Sn-Pb 90-10 Sn/Pb	Heat Aged	0.32	>95%
Sn Sn/Pb	As plated	0.01	>95%
Sn Sn/Pb	Steam Aged	0.38	>95%
Sn Sn/Pb	Heat Aged	0.94	>95%
Sn Sn/Ag/Cu	As plated	0.16	>95%
Sn Sn/Ag/Cu	Steam Aged	0.21	>95%
Sn Sn/Ag/Cu	Heat Aged	0.35	>95%
Sn-Bi 90-10 Sn/Pb	As plated	0.32	>95%
Sn-Bi 90-10 Sn/Pb	Steam Aged	0.18	>95%
Sn-Bi 90-10 Sn/Pb	Heat Aged	0.25	>95%
Sn-Bi 90-10 Sn/Ag/Cu	As plated	0.40	>95%
Sn-Bi 90-10 Sn/Ag/Cu	Steam Aged	0.20	>95%
Sn-Bi 90-10 Sn/Ag/Cu	Heat Aged	0.20	>95%
Sn-Ag 97-3 Sn/Pb	As plated	0.42	>95%
Sn-Ag 97-3 Sn/Pb	Steam Aged	0.54	>95%
Sn-Ag 97-3 Sn/Pb	Heat Aged	0.53	>95%
Sn-Cu 99-1 Sn/Pb	As plated	0.39	>95%
Sn-Cu 99-1 Sn/Pb	Steam Aged	0.83	>95%
Sn-Cu 99-1 Sn/Pb	Heat Aged	0.79	>95%
Sn-Cu 99-1 Sn/Ag/Cu	As plated	0.20	>95%
Sn-Cu 99-1 Sn/Ag/Cu	Steam Aged	0.40	>95%
Sn-Cu 99-1 Sn/Ag/Cu	Heat Aged	0.39	>95%

Table 5 ***Codeposited Carbon Content of Pb-free Component Finish Materials***		
Material	**Current Density**	**% Codep.**

	(A/dm^2)	Carbon
Sn	15	0.0024
Sn-Bi	15	0.0063
Sn-Cu	20	0.0048

Table 6 ***Electrochemical Potential Series***	
$Ag^{1+} \rightarrow Ag^{0}$	0.7996 V
$Sn^{2+} \rightarrow Sn^{0}$	- 0.1375 V
$Sn^{4+} \rightarrow Sn^{0}$	- 0.9450 V

Figure 1 - Pb-free Component Reflow Temp. Profile



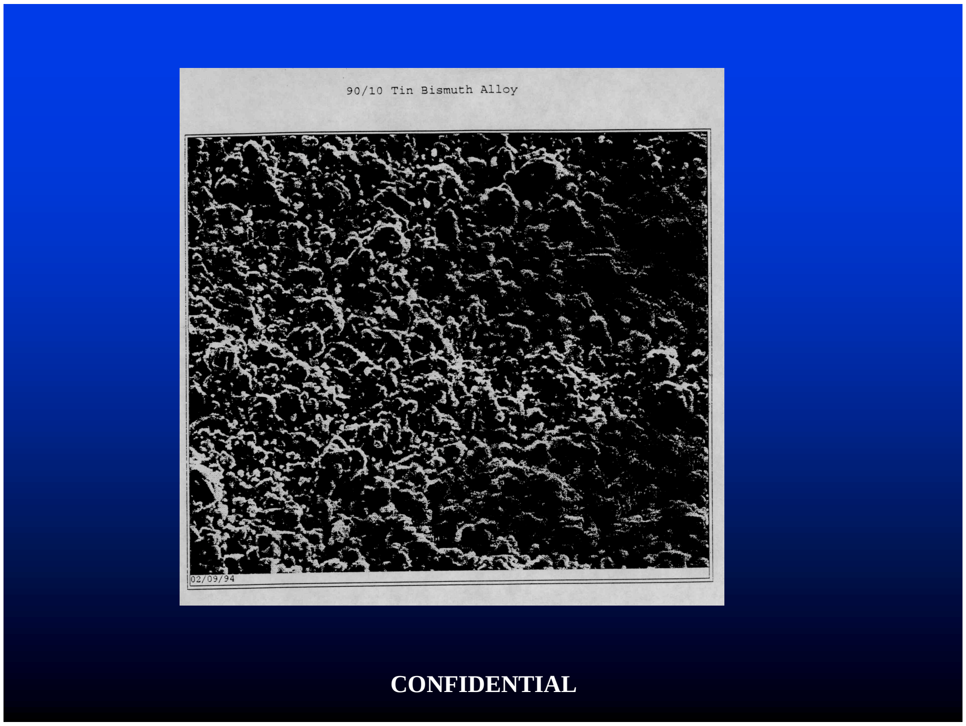
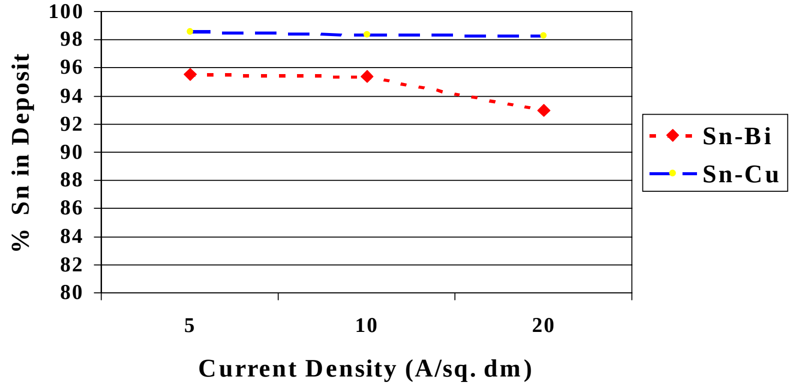


Figure 2 – Sn/Bi deposit surface morphology

Figure 3
Sn-Bi and Sn-Cu Deposit Composition vs. CD



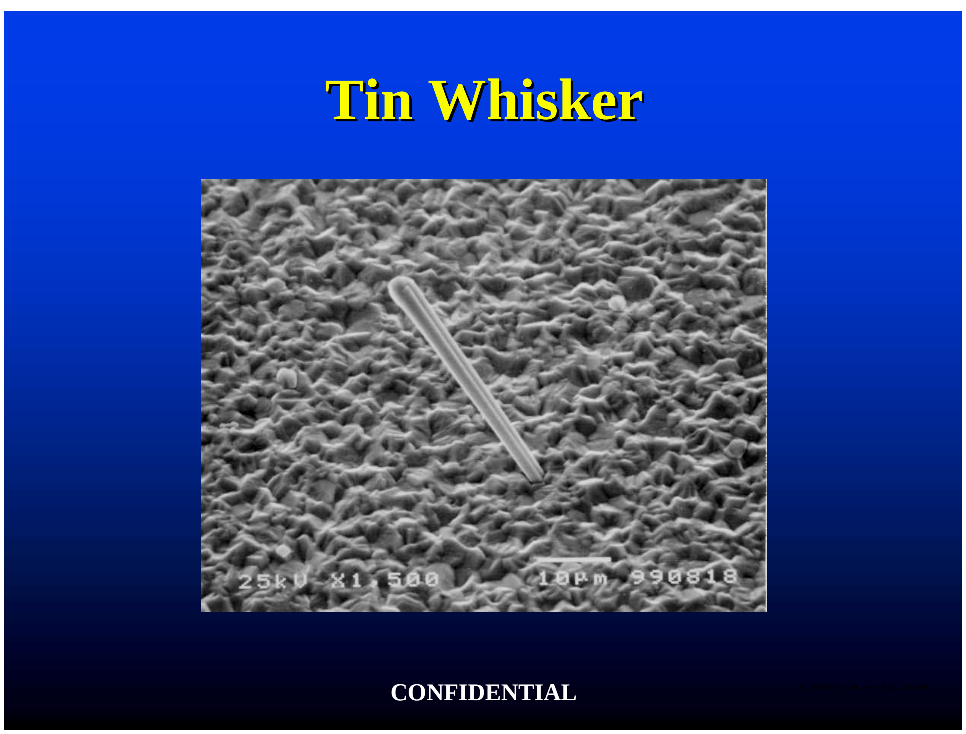


Figure 4 – Tin Whisker

Figure 5 – Low stress tin process well polygonized large grain size

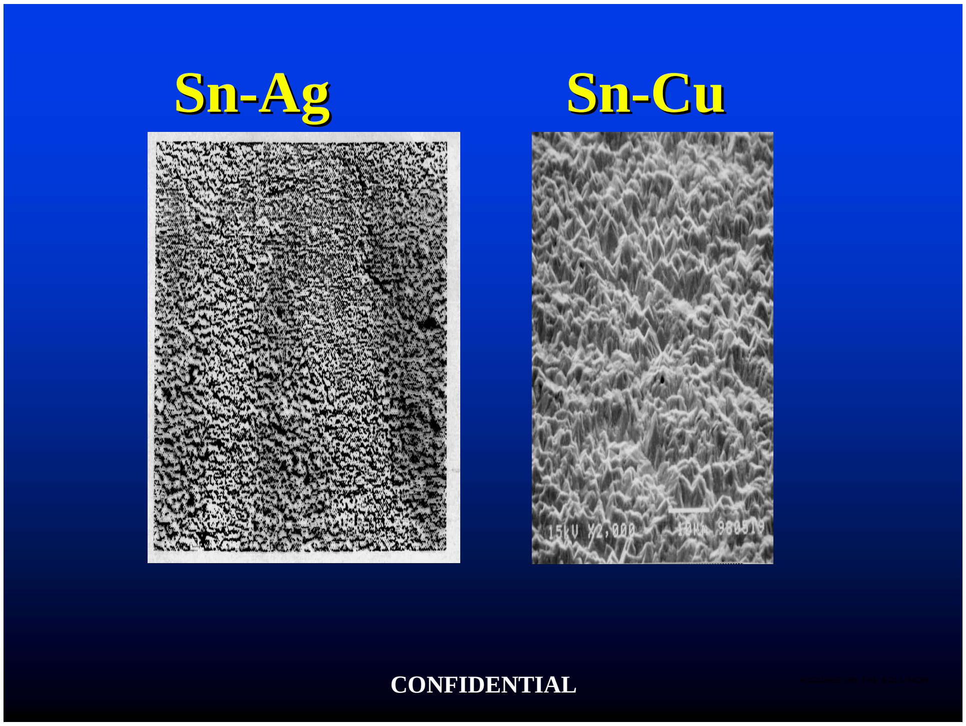
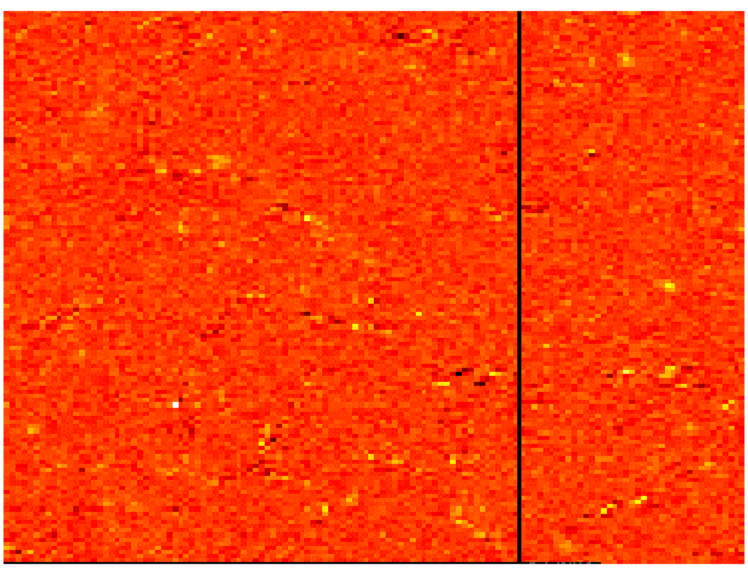


Figure 6: Sn-Ag (L) and Sn-Cu (Rt) SEM Surface Morphology (2000X)

Figure 7 – Sn-Cu Auger Map for Cu



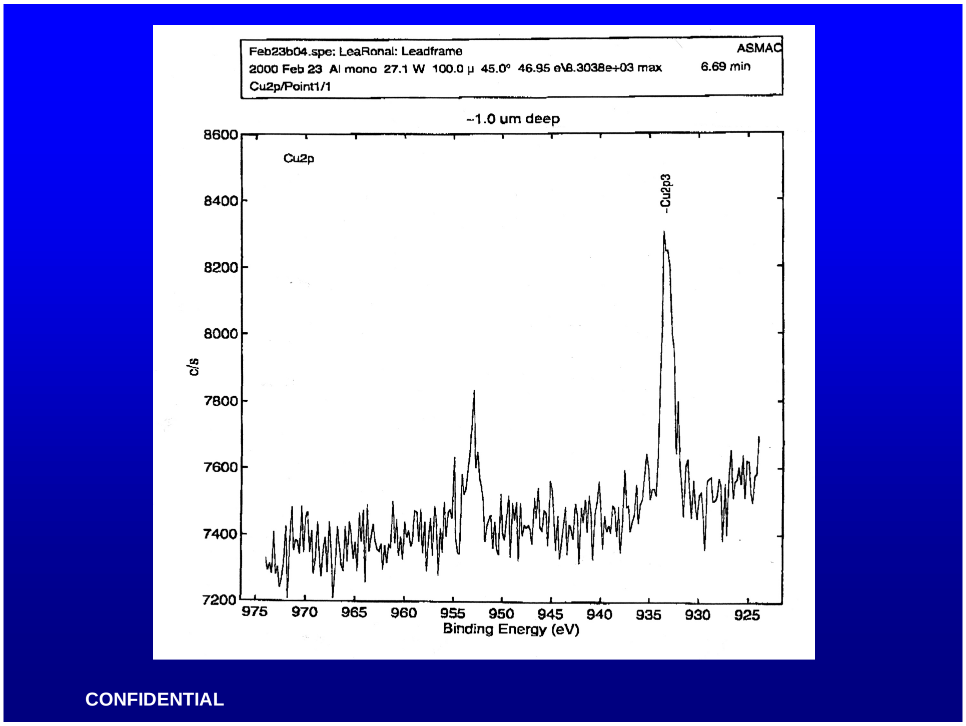


Figure 8 - Sn-Cu XPS spectrum for Cu