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Lead-Free Solder Bumping Technologies

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Abstract

Electroplated pure tin and tin alloys such as Sn99.3Cu0.7%, Sn98%Bi2% and Sn96.5%Ag3.5% have been identified as viable drop-in replacements to tin-lead solder. High melting point tin alloys such as Pb97%Sn3% and Au80%Sn20% are also required by the electronics industry for flip chip applications. Capabilities of the commercial pure tin bumping chemistries will be discussed and demonstrated.

However, commercially feasible plating systems for lead-free tin alloys have yet to be developed. The major difficulty in plating tin alloys comes from the large difference in standard deposition potential of tin and the alloying metals that result in poor alloy control and immersion of alloying metals on tin parts and anodes. Enthone Inc. has developed new processes that allow robust and reliable electroplating of these alloys. We also studied the effect of plating parameters (current density, agitation, temperature, etc.) and alloy composition on the materials properties of deposited alloys such as voiding, bump height uniformity across a wafer, reflowability, phase composition, structure, hardness and melting temperature. A few defect types specific to bump plating and ways to overcome them will be discussed. Recommendation will be made on utilization of specific finishes for different electronic applications.

Introduction

One of the ways for interconnecting and packaging an integrated circuit without the use of wire-bonds or leads is to use flip chip technology. It offers a number of advantages over conventional wire bonding technologies such as high number of interconnections per unit area, faster speed of interconnection, lower power consumption, smaller board area with smaller footprint and light weight packages. Electroplated wafer bumping offers many advantages for high pin count and fine pitch advanced packages that are widely applied in high end, high performance circuits. For instance, the yield loss due to defects is the lowest among competing technologies such as stencil or solder paste printing. Bumped wafers using the electroplated process is forecast to reach a capacity of over 6 millions of 200mm-equivalent wafers this year, and will increase two-fold in the year 2005 to over 12 millions.[1]

Alternative technologies are currently available for wafer bumping such as microball mounting, evaporating, stencil and paste printing. The cost of the microball mounting will increase and the speed of the process will diminish sharply as the bump density on a chip increases. The main issue of evaporative technologies is high cost, especially for low alpha processes, as well an inability to deposit metals with low vapor pressure like tin. Stencil and paste printing are highly versatile methods and allow straightforward deposition of multielemented alloys. However, this method usually requires relatively large pad and pitch size (ca. 250 μm), suffers from voiding caused by large amounts of flux and generally decreasing yield with reduction in pitch size. Electroplating offers some unique alternatives to these processes such as tight pitch size (35 μm has been demonstrated recently by Fujitsu), high yields (less than < 3 ppm loss), low voiding, very low cost and theoretical ability to plate very small features with high aspect ratio (true leveling). Reliable electroplating on 300 mm wafers has been reported recently with lead–tin and lead free solders by Unitive, Inc.

Global implementation of lead-free initiatives requires the development of electroplated tin or tin alloys, which have properties to become drop-in replacement for tin-lead solder. Current technologies use high lead high melting point alloys such as Pb95%Sn5% % (m_p = 315 °C), Pb97%Sn3% % (m_p = 320 °C), eutectic Au80%Sn20% (m_p = 278 °C), as well as conventional eutectic Pb37%Sn63%, (m_p=183 °C). Lead metal for flip chip application is currently exempted from “WEEE” and “RoHS” directives for lack of alternatives but that status is likely to change. Therefore, there is a need for electroplated lead free solders for flip-chip applications.

Electroplated pure tin as well as tin alloys such as Sn99.3%Cu0.7% and Sn98%Bi2% were identified as feasible alternative to replace tin-lead.[1] Plating of tin-silver, tin-zinc or tertiary alloys of the above metals, such as Sn-Ag-Cu, for example, is possible but is not practical due to cost, complexity, poor alloy control and environmental issues. Therefore we limit our discussion of lead free alternatives to pure tin, eutectic Sn99.3%Cu0.7% and Sn98%Bi2% alloys. From electroplating point of view pure tin is the cheapest and simplest way of wafer bumping as compared to its alloys. The main industry concern with pure tin deposits is formation of filaments or “whiskers” that can shorten a circuit. Fortunately, new wafer bumping chemistries do not need to be completely "whisker-free" because of the relatively large pitch and high bump thickness, which masks effects of intermetallic compounds formation and stress buildup. IMC formation and stress buildup induced by them are believed to be key contributors to whisker formation. Also, plated bumps are reflowed a number of times, which reduces the stress even further. Both tin-copper and tin-bismuth alloys were believed at some point to be whisker free. In fact, our experience is that electroplated tin alloys do not differ significantly from pure tin in terms of whisker performance. It is the cocktail of organic additives as well as nature of the substrate and other factors, which ultimately lead to stress formation over time that mostly affects whisker propensity. Nevertheless, because eutectic tin-copper and Sn98%Bi2% alloys have relatively low melting point of *ca*. 227 °C (vs. 232 °C for pure tin) desired in some applications, as well as good solderability and mechanical strength they have produced in the industry.

Although electroplating of tin alloys has been known for many years (see examples in refs. 2-5) it was a difficult process. The major difficulty in plating tin alloys comes from the large difference in standard deposition potential of tin and the alloying metal. This problem was traditionally overcome by adding a complex agent that would change the nature of the electrodeposition reaction from simple metal ion reduction to reduction of the metal complex with equilibrium redox potential close to that of tin (II) ions. This method usually allows very good control of the plating process and properties of the deposit. However, most of the known complex agents are environmentally unfavorable and currently are in process of being banned for use. An alternative way of depositing tin alloys takes advantage of metal-specific additives, which can significantly slow down or completely inhibit reduction current of alloying element in the certain range of potentials due to metal-specific adsorption of additives on a surface. This method makes the process environmentally friendly, reduces immersion deposition on tin and provides good control of alloy composition in a wide operating window.

Previous work on codeposition of Sn and Bi mainly focused on formation of the alloy with up to 0.4 %Bi, which is beneficial in preventing the harmful phase transformation of pure tin from α-phase to β-phase at temperatures below 13 °C. Plating baths of this type were typically sulfuric acid based and utilized different organic additives to produce tin alloy with desirable properties. The complexity of these baths also became a major shortcoming because sometimes over five organic additives were required to stabilize the composition of the deposited alloy and to obtain good surface morphology. Also, there is some concern of accidental formation of very low melting point bismuth-lead alloys.

Commercial codeposition of Sn and Cu is mainly known as bronze plating. In this process high copper content alloy is formed. However most of the known bronze plating chemistries can not be used for wafer bumping of SnCu alloys required by electronic industry. The purpose of this work was to utilize our experience in high-speed tin and tin alloys methanesulfonate chemistries to study the feasibility of low speed lead free wafer bumping processes. The desirable lead free processes should be environmentally friendly, dendrite free, have low immersion rates, produce low void bumps at high yield and be robust and practical for manufacturing operations. In addition to the requirement for lead free solders listed above new lead free deposits have to operate at relatively low current densities (2-40 mA/cm^2) and provide relatively uniform bump height distribution (15% variation across 200 mm wafer is considered acceptable). They should also have good solder joint strength and ability to pass multiple reflows.

In this paper we describe several lead free electroplating alternatives for flip-chip applications and compare them with existing electroplating lead-tin processes.

Results and Discussion

Existing Lead-Tin Technologies and Their Limitations

Electrodeposition potentials of tin and lead are very close to each other. For this reason plating of tin-lead alloys of different composition is relatively straightforward. Electrodeposition of the high melting point Pb97%Sn3% alloy is often used for flip-chip applications. Electroplating baths for tin–lead solder with different amount of lead are well known and have been extensively used in plating industry. However, there are some new and unique requirements for baths used for wafer bumping as compared to more conventional plating processes. For example, patterns of solution agitation in fountain plate are quite different from those in either rack or barrel or reel to reel applications. Also, complicated geometry and ever decreasing aspect ratio mandates usage of higher throwing power baths at low current densities (2-40 mA/cm^2) with subsequent lower metal concentration and longer plating time. Typical bath compositions used for Pb97%Sn3% bump plating as well as for some lead free bump chemistries are summarized in Table 1. Quick analysis of the data in Table 1 suggests that generally lower metal and higher organic additive concentrations are required in order to produce smooth, uniform and reflowable bumps as compared with parameters used in high current density plating of leadframes and/or connectors.

Table 1 - Typical Composition of the Solutions for Tin Alloy Bump Plating

Composition, g/l and operating parameters	**Sn3%Pb97,%**	**Sn100,%**	**Sn98%Bi2,%**	**Sn99.3%Cu0.7,%**	**Sn100%, High CD**
Tin metal as SnMSA, g/L	5.5	20	20	30	80
Pb metal as PbMSA, g/L	20				
Bi metal as BiMSA, g/L			6		
Cu metal as Cu MSA, g/L				0.3	
MSA, mL/L	115	150	150	150	200
Wetting agent, g/L	3.6	12	10	6	6
Grain refiner, g/L	0.1	0.2	1	0.1	0.5
Antioxidant, g/L	1	1	1	2	1
Current density, ASF	1-50	1-50	1-50	1-50	50-500
Temperature range, °C	20-60	20-55	20-50	20-35	20-60

We will examine one representative tin lead process in more details and show its strengths and limitations. In particular, we will discuss how variations in additive concentrations and other plating parameters affect properties of the plated bumps. Figure 1 shows how current density changes as a function of applied voltage at two different plating conditions. Curve 1 shows voltammogram obtained on rotating disk electrode (RDE) at 500 RPM while curve 2 was obtained on bump patterned wafer with nickel-vanadium based pads. (Nickel-vanadium alloy is common under bump metallization (UBM) layer because it is a good diffusion barrier and it is easily wetted by solder). High agitation conditions used to obtain curve 1 lead to lower voltage (potential) required to achieve a desired current. Tin deposition starts approximately at – 0.6 V vs. Ag/AgCl electrode, becomes massive at ca. – 0.8 V and does not reach a diffusion limit. At potentials more negative than – 1.2 V reduction of hydrogen ions begins to take off, "stealing" some of the current. On a nickel-vanadium based pads tin deposition starts at somewhat lower (more negative) potential, ca. – 0.8 V, curve 2 in Figure 1. Hydrogen evolution becomes important at potentials negative of –1.2 V. Therefore, the desired range of potentials in lead-tin plating is between – 0.8 and - 1.2 V vs. AgCl and between 5 and 30 mA/cm^2. As a bump height grows in size so does its surface area. Therefore, in order to keep current density relatively the same across the height of the bump an adjustment (increase) in applied current is required with time. Current density used in the very beginning of plating process will determine alloy composition right on the surface of the substrate and, therefore, will affect adhesion properties and result in formation or absence of (un)desired intermetallic compounds. Current density used in the middle of the process will largely affect voids formation. Current density used at the very end of the plating process will determine elemental surface composition and surface morphology of the bump. Surface composition and morphology will, in turn, affect surface oxidation rate and therefore, reflowability and corrosion resistance at all subsequent processing steps. In view of this it is very important to choose optimal current density recipe. This current density vs. time profile will depend on the size of the pad, as well as on photoresist and total bump thickness.

Figure 2 shows typical surface morphology of the deposited Pb97%Sn3% bumps as viewed by SEM. Grains have polygonal shape and are about 5-10 μm in size. After the photoresist strip bumps have mushroom-like appearance (see cross section in Figure 3) due to overplating but assume more spherical shape after reflow. A smooth surface shown in Figure 2 is essential for multiple bump reflowability. Figure 4 shows preferential suppression of tin achieved by changing concentrations of one surfactant. In fact, by manipulating concentrations of two surfactants in the formulation and metal levels essentially any alloy composition could be achieved, from pure tin to pure lead. However, as shown in next paragraph, even existing lead-tin chemistries might have some flaws when it comes down to plating smaller and smaller features. Therefore, transition from a lead rich alloy to a lead free one is not as simple as changing metal and additives concentrations in lead-tin baths.

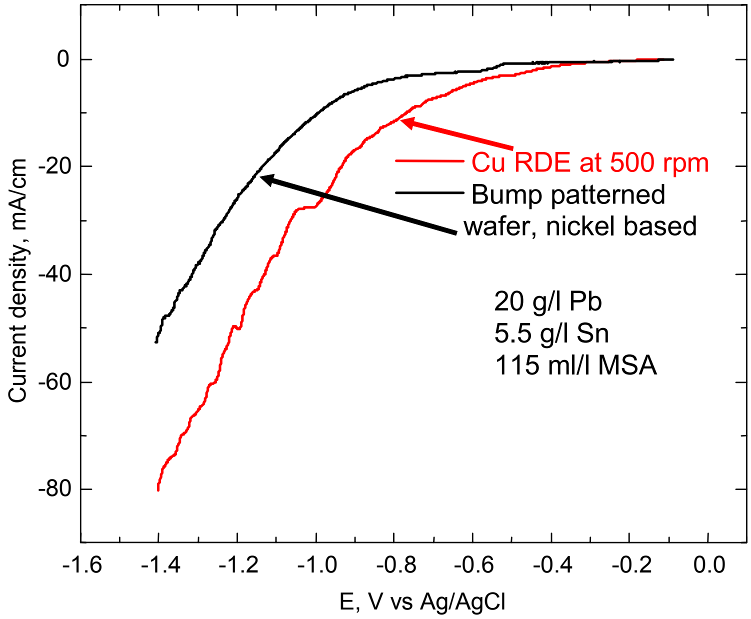


Figure 1 - Current vs. Voltage Curve in Electrodeposition of Lead-Tin Alloy at two different conditions

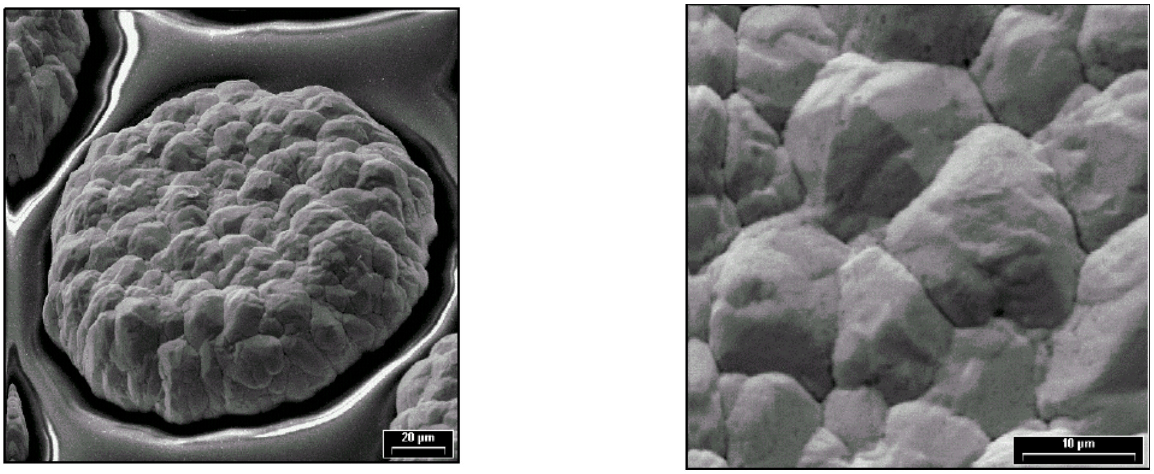


Figure 2 - SEM Images of Electroplated Lead-Tin Deposit

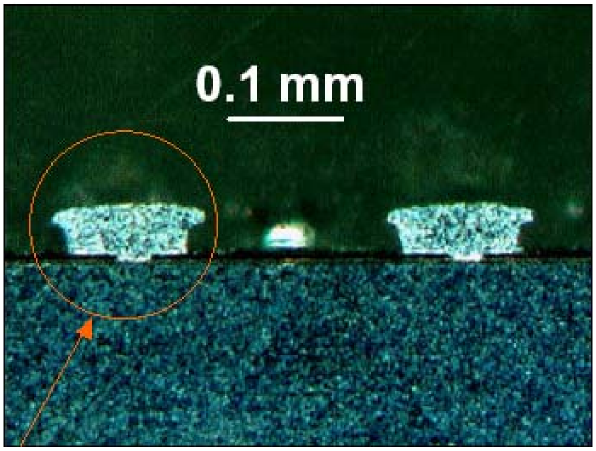


Figure 3 - Cross Sections of the Plated PbSn Bumps as Viewed by SEM

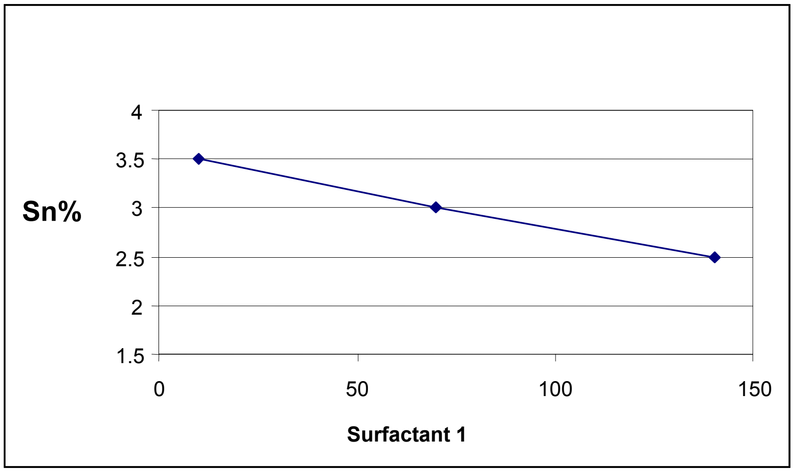


Figure 4 - Amount of Codeposited Tin as a Function of Surfactant Concentration

One of the drawbacks of the bump electroplating is relatively long plating time as compared with other competing technologies for wafer bumping. However, with constant decrease in bump size and height it becomes less and less of a problem. As the aspect ratio of the feature becomes larger due to circuits miniaturization it becomes increasingly more difficult to plate low void tin-lead balls with high yield. One of the problems is poor agitation into the pads. When diffusion rate of the metal ions into the plated feature is not fast enough to carry on applied current the observed bias (voltage) shifts negative and additional cathodic reactions like hydrogen evolution will take place. Hydrogen evolution results in tiny hydrogen bubbles trapped between pads and electrolyte solution, which subsequently insulate the surface and causes no deposition at some (usually central) areas of the pads or void formation throughout the bump height. In the former case, it could result in round "hole" in the middle of the bump. This round hole in usually goes all the way to bare nickel-vanadium substrate. No organic or inorganic residues were detected on the surface of nickel-vanadium substrate. No defects were found in the UBM thickness layer either. Since agitation in the fountain plater is the best in the central and middle parts of the wafer, we would expect most defects to manifest themselves at the edges of the wafer. Indeed, clear radial distribution of the defects across the 200 mm wafer was observed. About 99% of the defects are situated in the outer two dies of the wafer. As expected, frequency of the defects is also a strong function of the flow rate: the faster the rate the less defects are observed. Formation of bubbles also depends on many other factors like photoresist thickness, electrodeposition potential at the pad and the nature of the substrate. As the thickness of photoresist goes down from 25 to 10 μm, defect frequency drops down by two orders of magnitude. Nickel-vanadium substrate is known to have very low hydrogen overpotential meaning that hydrogen gas evolution will begin at the potentials theoretically predicted by Nernst equation (around -0.23 V vs. Ag/AgCl electrode), that is, nickel-vanadium has essentially zero overpotential. As seen in Figure 1, massive lead-tin deposition takes place in the range of potentials much more negative than – 0.23 V. So, one would expect that hydrogen evolution would take on the nickel-vanadium substrate. However, lead and tin metals have some of the highest hydrogen overpotential values (ca. – 0.5 V). This means that there will be no hydrogen gas bubble formation on lead or tin even at the potentials significantly more negative than those predicted by Nernst equation. Therefore, if one could deposit just few monolayers of tin or lead on a bare nickel-vanadium surface, theoretically there should be no hydrogen gas formation at the deposition potentials for lead and tin or consequent current densities. Indeed, modification of the current recipe incorporating very small current density in the very first few seconds of the plating process dramatically decreases the number of the observed defects. In conclusion, we have showed that as the final diameter of the desired bump decreases as a result of circuit's miniaturization, appropriate changes in the electroplating technologies also have to be made.

Yet another issue is accumulation of organic breakdown products in the aged baths. These by-products apparently adsorb on the metal surface and shift deposition potential down to the region where hydrogen evolution is strong even on lead-tin surface, Figure 6. The net effect is again insulation of the surface of the bump from the liquid solution and formation the hole in the middle of the bump. We have shown that even existing lead tin wafer bumping technologies are not flawless when it comes to plating smaller and smaller features.

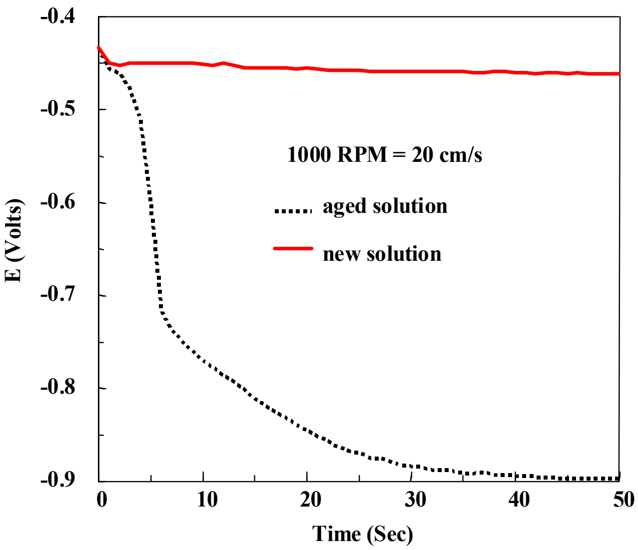


Figure 5 - Potential of the First Stage of Electrodeposition as a Function of Bath Age

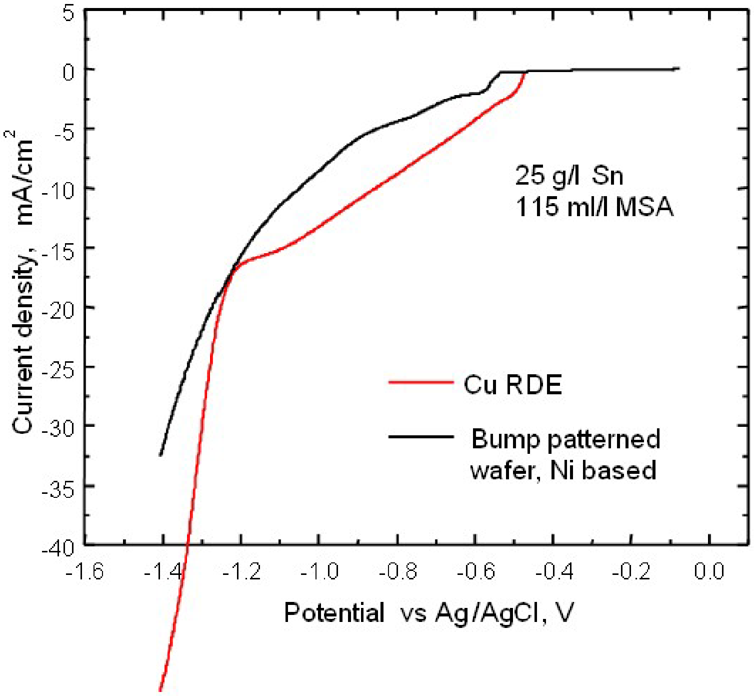


Figure 6 - Current vs. Potential Curves for Electrodeposition of Pure Tin

Lead Free Pure Tin Processes

Elimination of lead from lead tin alloys is not a straightforward process. For example, lead acts as a grain refiner in lead tin alloys, which leads to formation of relatively smooth bumps and therefore good reflowability. We have studied four different pure tin chemistries for their suitability to wafer bumping. The idea was to find an (organic) grain refiner or surfactant, which would allow production of smooth pure tin bumps. The obvious advantages of pure tin chemistries vs. tin alloys are simplicity and low cost. As mentioned before, whisker issues, which could be critical in connector and leadframes applications, are not as important in bump plating, at the present thickness and pitch size.

Electrodeposition of pure tin was studied electrochemically and results are shown in Figure 7. Exactly he same cocktail of organic additives was used as that used for lead-tin deposition described above. Just like in the case of lead-tin alloy better agitation on RDE lead to lower (more positive) electrodeposition potentials as compared to plating directly on patterned wafer. Massive tin electrodeposition commenced at ca. – 0.48 V on RDE vs. – 0.58 V on wafer pads, reflecting the fact that more negative potential is needed for wafer pads as compared to RDE. (Surfaces of both copper RDE and nickel-vanadium wafer pads are already covered by pure tin at these potentials so electrodeposition takes place essentially on pure tin in both cases.) Also, total metal concentration for data shown in Figures 1 and 7 was the same at 25 g/L (20 g/L of lead and 5 g/l of tin in the case of lead-tin alloy). Comparison of Figures 1 and 7 shows that in both cases current does not reach diffusion controlled limit, and at relatively negative potentials, current due to hydrogen evolution becomes significant as compared to current due to tin deposition. Electrochemical data obtained for pure tin and lead tin depositions on bumped wafer are overlaid in Figure 7 and are essentially the same within experimental error. This is not surprising because electrodeposition potentials of lead and tin in additive free solutions essentially coincide. However, as shown later, elimination of lead from the deposit is not as simple as removing lead ions from the solution. A number of material properties (like surface tension) of the deposit change dramatically as one switches from lead tin to pure tin, and this is usually highly affected by the nature of the organic additives present in the bath. For these reasons we studied four different chemistries for applicability to wafer bumping.

Bumps were plated in EEJA fountain plating tool at flow rates of 15-18 liters/minute with no diffuser present and on a 200 mm bump patterned wafers with nickel-vanadium alloy as pads substrate. Special current densities sequence was used in order to keep effective current density relatively the same as mushroom-like bumps grow in size. All bumps were plated ca. 45 μm thick in about 32 minutes. Surface morphology of the bumps plated out of four different chemistries was examined by SEM and is shown in Figures 8-10.

First, chemistry A discussed in previous section for plating lead tin alloy was modified and bumps were plated at different concentrations of organic additives. Figure 8 clearly shows that as a concentration of one additive (necessarily to provide smooth surface) increased, plated bumps started to show larger and more frequent defects in the middle of the bump. The hole in the middle goes all the way down to the substrate and is attributed to the hydrogen bubble formation as described above for lead–tin process. This process was therefore deemed unsuitable for pure tin plating. Next, a variation of methanesulfonic acid based high-speed chemistry B was adjusted for bump plating. Figure 9 (top) shows no surface defects (at all concentrations studied) but rather rough bump surface. As a result the bumps plated from this chemistry were not easily reflowable. Figure 9, bottom, shows optical image of the bump plated from yet another methanesulfonic acid based chemistry C. Again, rough and grainy bump surface created reflow problems. At last, chemistry D (Figure 10) provided smooth and reflective surface across the range of current densities and was chosen for further characterization. The cross section of the bump as viewed by SEM is shown on Figure 11 at three different magnifications. The diameter of the top of the mushroom is ca. 120 μm. The bump height uniformity across 200 mm wafer was less than 10% (48 μm in the center and 45 μm at the edges of the wafer). Figure 12 shows bump height profile before reflow as measured by white light interferometer (Zygo New View 200). Slight dip in the middle of the otherwise flat bump is likely an artifact as judged by cross sections of the as plated bumps (Figure 11).

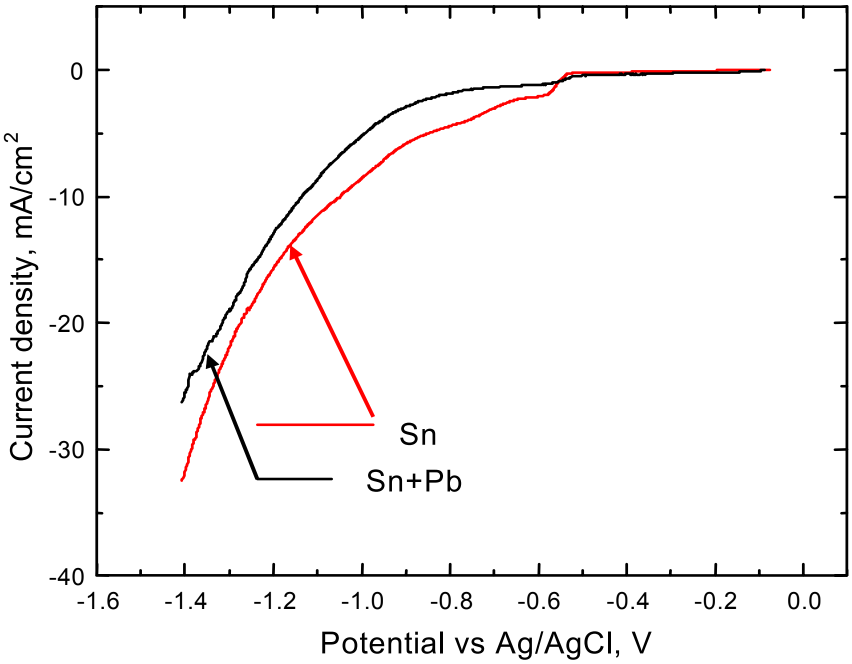


Figure 7 - Current vs. Potential for Curves for Pure Tin vs. Lead-Tin (97/3) are Compared

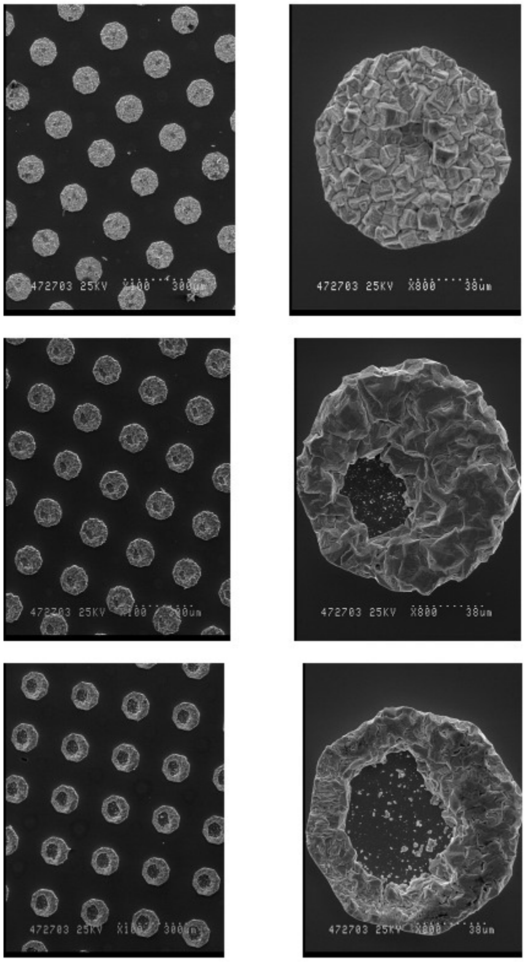


Figure 8 - Bump Morphology of Pure tin Chemistry A;Top: Recommended Amound of Additives Middle; Doubled Amount of Additives; Bottom: Additives Tripled

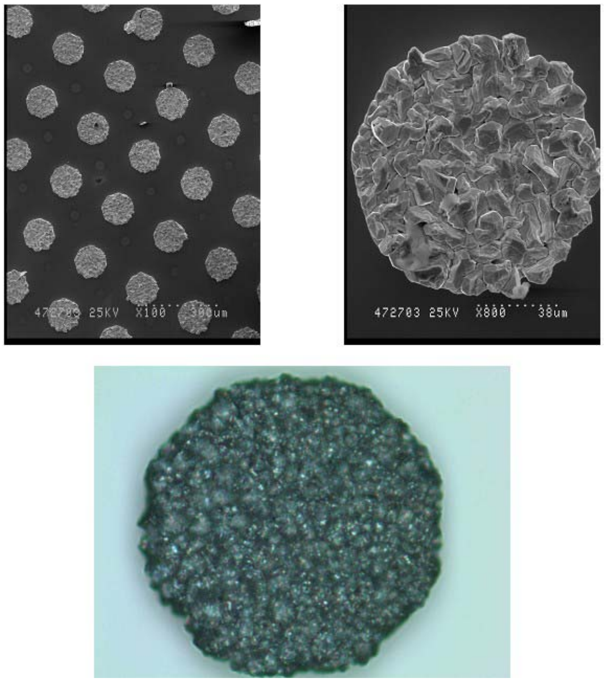


Figure 9 - SEM Images of the Bump Surfaces Produced from of Chemistry B (top) and C (bottom)

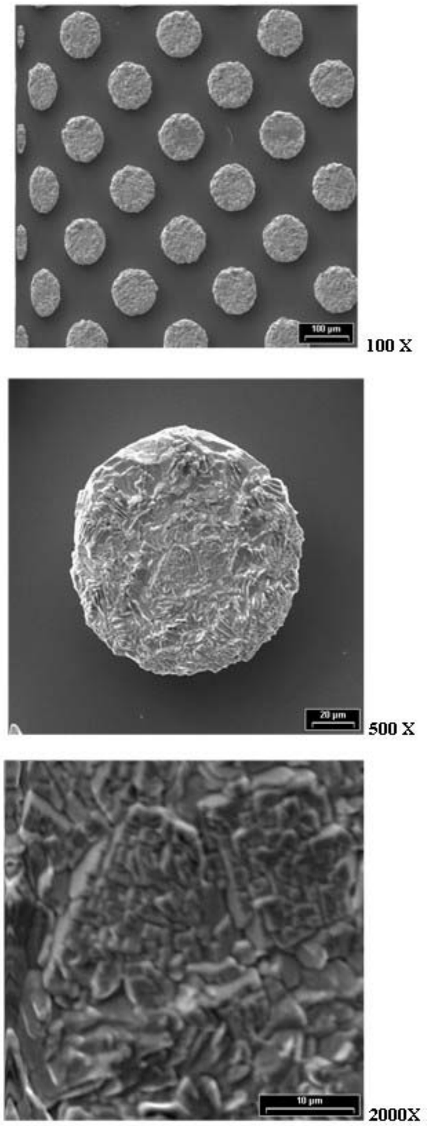


Figure 10 - Bump Morphology of the Pure Tin Chemistry D at Three Different Magnifications

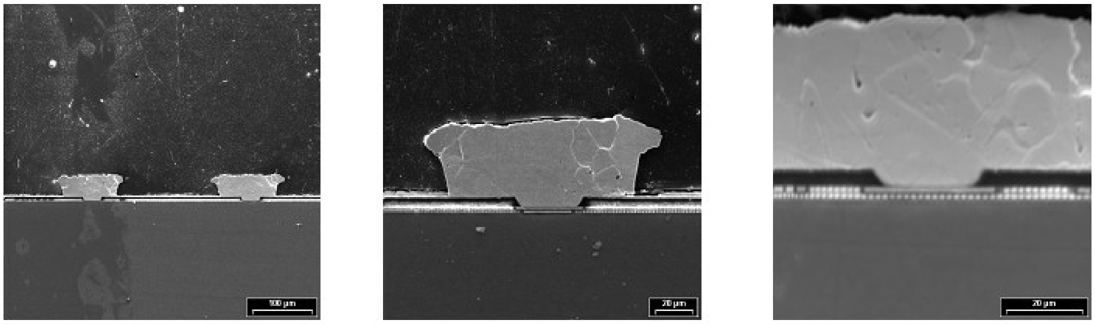


Figure 11 - Cross Section of the Bumps from Chemistry D after Photoresist Strip at Three Different Magnifications

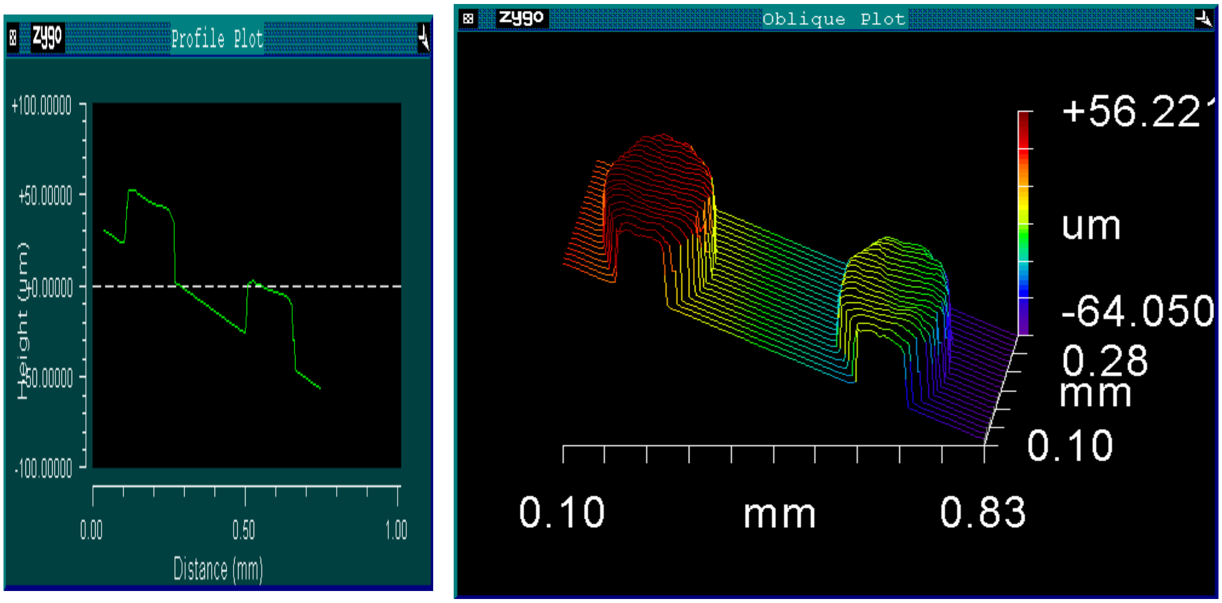


Figure 12 - Bump Height Profile from Pure Tin Chemistry D

One of the wafers plated from chemistry D wafers was diced and reflowed in convection reflow oven (OmniFlo 7) in nitrogen atmosphere (670-690 ppm oxygen) with the following heating profiles: 44 s at 200°C, 13 s at 240°C and peak temperature of 244.4°C. This profile was not optimized for pure tin deposit but rather copied from the one used for tin-lead deposits reflow. No flux was used in the process. SEM images of reflowed pure tin balls are shown on Figure 13. After reflow the diameter of the mushroom decreased but the ball height increased slightly. Reflowed balls are not perfect spheres probably because no flux was utilized and temperature profile was not optimized. Large variations in reflowability were found using different types of reflow ovens. It should be noted that it is much more difficult to reflow pure tin vs. tin-lead into perfect spheres because of the large differences in the surface tension between pure tin and lead-tin alloys. Wafer was subsequently diced and pieces of reflowed wafer were further characterized for voiding by x-ray tomography. Voiding in bumps results from formation and entrapment of hydrogen gas and/or plating solution. Typical images produced by this tomograph are shown in Figure 14. The results of the voiding analysis performed are listed in Table 2. Overall, all tin bumps have very low voided areas. Bumps at the edges of a wafer tend to have higher voided volumes than the ones in the center, probably due to better solution agitation in the central and middle areas.

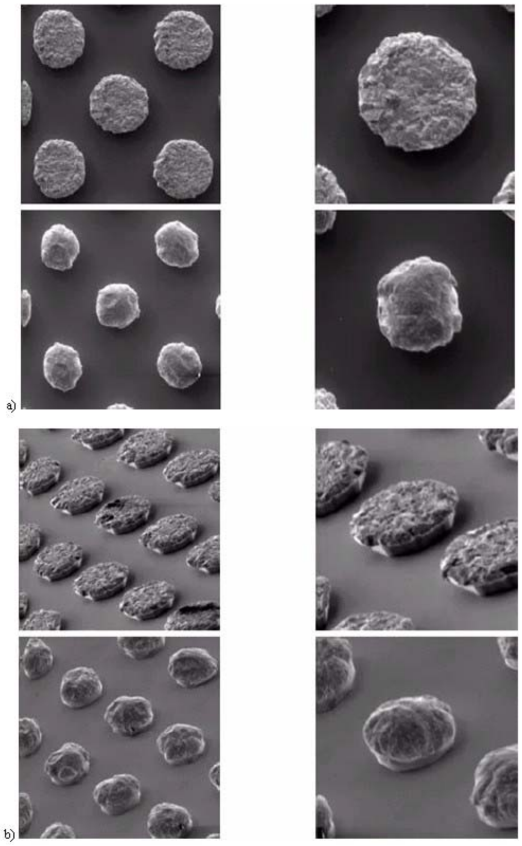
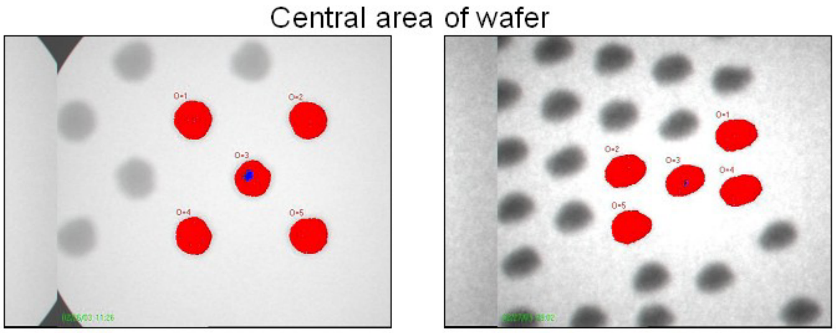
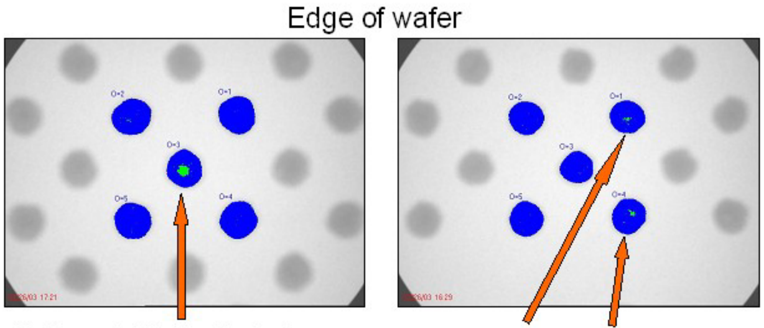


Figure 13 - SEM View of the Bumps from Chemistry D Before and After Reflow a) Right Angle SEM View; Top Row as Plated, Second Row After Reflow b) 60° Angle SEM View, Top Row as Plated, Second Row After Reflow



Void area: 7.52% (Max.) in the bump
Top view

The same bumps on a tilted image
Tilted 38 degrees



Void area: 9.43% (Max.) in the bump
Top view

Void areas: 2.01% and 2.36% in the bumps
Top view

Figure 14 - Voids in Bumps Plated from Pure Tin Chemistry D - Example of X-ray Images: Blue-Analyzed Bumps, Green-Voids

Table 2 - Voiding Types and Volumes Across the Wafer

Standard/Spec. 7095	Center	Edges
Sample size (number of bumps)	65	65
Total voids area / total bumps area (%)	0.36	0.95
Bumps in Class III: void area in each bump < 9.00%	65	64
Bumps in Class II: void area in each bump ≥ 9.00% and < 20.25%	0	1
Bumps in Class I: void area in each bump ≥ 20.25% and < 36.00%	0	0
Maximum void area in each bump (%)	7.52	9.43

Lead Free Tin Alloys: Tin-Copper

Tin copper bath developed for high current density plating of leadframes and connectors was described elsewhere.[8] Additive levels of the high-speed tin copper bath were modified to provide the best performance as judged by bump roughness and thickness distribution across the wafer and are shown in Table 1. Metal levels were also modified to meet the current density requirement common in bump plating. Nickel-vanadium layer over copper UBM is required to prevent excessive formation of tin-copper intermetallic compounds when plating tin rich alloys such as tin both tin-copper and tin-bismuth described in this paper. SEM images of the plated tin copper bump before reflow are shown on Figure 15. The bumps are very smooth and have fine grain structure. The content of the copper in alloy was found to be relatively stable across the wafer. Similar small variations in copper content of the deposit and as functions of current density and agitation was reported in reference 8. The best (lowest) bump roughness was achieved at the highest current density used (ca. 90 mA/cm^2). The bump height uniformity across 200 mm wafer was again less than 10% (48 μm in the middle area of the wafer, 47 μm at the edges and 42 μm in the center). The deposition rate was found to be linear with current density. The highest deposition rate was measured to be ca. 4.2 μm/min at 90 mA/cm^2, which is very close to the limited current density of a bath containing ca. 20 g/L of tin metal.

A disadvantage of SnCu bath is low level of copper metal in the solution, which requires constant monitoring in order to keep the alloy composition constant. According to Sn-Cu phase diagram, slight increase in codeposited copper percentage from 0.7 to 5% leads to significant jump in melting temperature of the alloy from 227 °C to ca. 380 °C. This could also be considered an advantage if a high melting point alloy is required. SnCu baths are also known to be prone to Sn(II) to Sn(IV) oxidation which is catalyzed by a number of transition metals including copper. A mixture of antioxidants was required in order to obtain chemistry stable over the course of few months. In the wafer bumping industry this problem could be alleviated relatively easily. Due to small amount of the solution in the tool and compact tool geometry it is feasible to perform plating under nitrogen flow. Yet another problem in tin alloy plating is formation of immersion layer of more noble metal (copper in this case) on tin anodes and other surfaces. The rate of this immersion was found to be highly dependent on the metal surface and decreased in the following order: stainless steel>>Sn>Ni. Employing an ion selective membrane over the anode could minimize this immersion deposition. Overall, plating of eutectic SnCu bumps is possible but complicated.

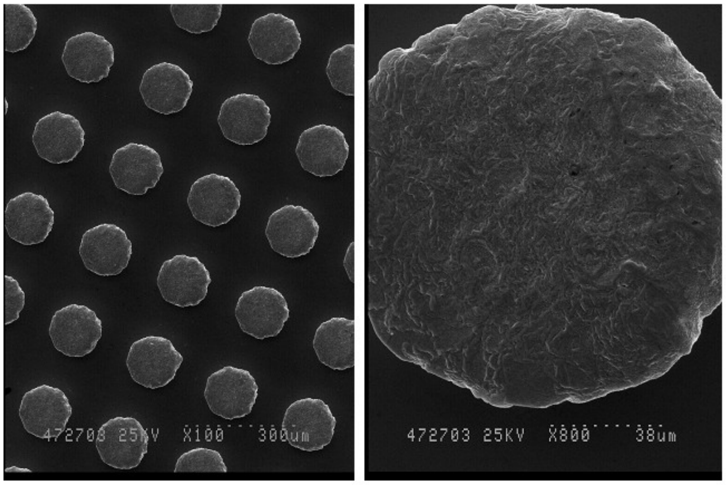


Figure 15 - Sn99.3%Cu0.7% Solder Bumps Plated on Patterned Silicon Wafer

Lead Free Tin Alloys: Tin-Bismut

Tin bismuth bath developed for high current density plating of leadframes and connectors was described previously.[8] Additive and metal levels in the bath were optimized similar to the case of tin-copper bath. The SEM images of the plated bumps are shown in Figure 16, at three different magnifications and as a function of additive concentration: "normal" in the top row and optimized (doubled) in the bottom row (latter are also shown in Table 2). The content of the bismuth in alloy was found to be relatively stable across the wafer but with larger variation as compared to tin copper bath described above. Similar small variations in bismuth content of the deposit and as functions of current density and agitation was observed.[8] As mentioned before, higher additive concentrations were generally required in all tin and tin alloys bump chemistries as compared to high-speed conditions. Plated bumps were reflowed in a pattern similar to pure tin or tin copper deposits. The rate of bismuth immersion deposition was higher than in the case of tin copper bath and followed similar pattern of reactivity: stainless steel>>Sn>Ni>glass. Again, employing ion selective membrane over anode could help minimizing the problem. Tin bismuth bath was dramatically more stable with respect to tin (II) to tin (IV) oxidation than tin copper bath and essentially the same as pure tin or tin lead baths.

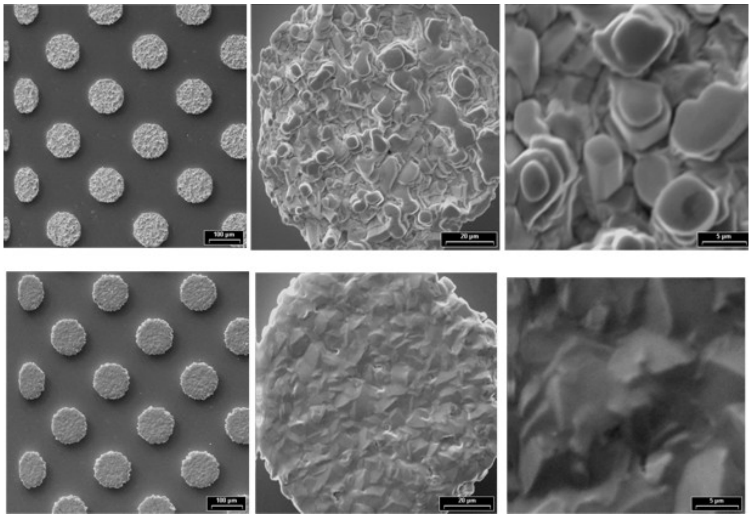


Figure 16 - Sn98%Bi2% Solder Bumps Plated on Pattern Silicon Wafer at Three Different Magnifications - Low Additive Concentrations (top row) and Double Additive Concentration (bottom row)

Conclusions

Existing lead-tin electroplating technology was studied and showed its strength and weaknesses. Few different pure tin chemistries were evaluated for wafer bumping applications and benchmarked against common lead tin processes. One of the chemistries was found superior to others in terms of defect formation and bump roughness. Plated pure tin bumps were compact and dendrite free, bump heights are uniform, bump reflowed at 245°C without using flux. Very low voiding was found by x-ray tomography after reflow.

While both tin copper and tin bismuth plating is possible, pure tin chemistries appear to be most practical. Tin copper bath suffer from accelerated stannous tin oxidation while tin bismuth chemistry is prone to immersion deposition on the anodes as well as on the different surfaces of tool itself. Since the codepositing metal levels in the bath are low, frequent bath replenishment is required. Alloy control in both cases could be achieved but it adds complications to the process. For the above reasons we believe that pure tin rather than tin alloys will be a deposit of choice, al least for electroplated deposits. However, tin copper process might still be a process of choice for some specialized applications given its unusual melting point properties as illustrated by phase diagram.

References

1. J.J. Lee, Press Release, ASE Group.
2. E. Bradley, K. Snowdown, and R. Gedney, "Lead-free Update", *Circuits Assembly,* December 1999, p.31.
3. H. Nawafune, K. Ikeda, K. Shiba, S. Mizumoto, T. Takeuchi and K. Aoki*, Hyomen Gijutsu* (1999), 50 (10), 923-927.
4. M. Fukuda, K. Hirakawa, and Y. Matsumoto, *Hyomen Gijutsu* (1999), 50(12), 1125-1129.
5. T. Kondo, K. Obata, T. Takeuchi, and S. Masaki, *Plat. Surf. Finish.* (1998), 85(2), 51-55.
6. S.A. Maksimenko, V.N. Kudrjavtsev, K.M. Tutina, A.N Popov and R. A. Gerasimov, *Soviet Electrochemistry* (1990) 26 (12) 1375-1532.
7. C. Fan, Y. Zhang and J. Abys, in *AESF Proceedings*, Nashville, 2001.
8. O. Khaselev, I.S. Zavarine, C. Xu, C. Fan, Y. Zhang, and J. Abys Proceedings of the APEX 2003 Conference.