Electrodeposition, Growth Morphology & Melting Characteristics of Gold-Tin Eutectic Alloys

G. Holmbom, J.A. Abys, H.K. Straschil & M. Svensson

Eutectic Au-Sn (80/20 percent by weight) solders have good electrical and heat conducting properties, as well as superior thermal fatigue strength as compared to other material used in microelectronics assembly, such as SnPb-solders and conducting epoxies. A chemistry has been developed to electroplate high quality Au-Sn deposits and to characterize the coatings in terms of alloy and phase composition, structure, and melting characteristics. An operating window and the long-term stability of the plating process have been established.

The production of microelectronics devices includes the delicate task of choosing a technique for mounting the chip to its carrier. This can be done either by using conductive adhesives or by soldering (*e.g.*, Sn-Pb or In-based solders). An excellent alternative is eutectic gold-tin solder (80/20 percent by weight, Fig. 1). It has a high thermal fatigue strength and excellent electrical and heat-conducting properties, compared to the Sn-Pb solders.[1-4] Combined with other solders, a wide range of melting points for hierarchical bonding can be obtained.

Metallurgical gold-tin *preforms* is a method of application that suffers from a number of disadvantages. The handling and alignment of thousands of preforms is problematic and requires expensive "pick and place" robotics. For many applications, the preforms are thicker than required, which can cause bridging and shortages for fine-pitch applications. In addition, when the dimensions of the bond areas decrease below 100 μm through the introduction of the flip-chip concept, dealing with preforms becomes impractical.

Alternatively, electrodeposition is a one-step batch operation that offers efficient materials usage and limited capital investment. The process offers some challenges, however, because control of the composition of the alloy is critical. The
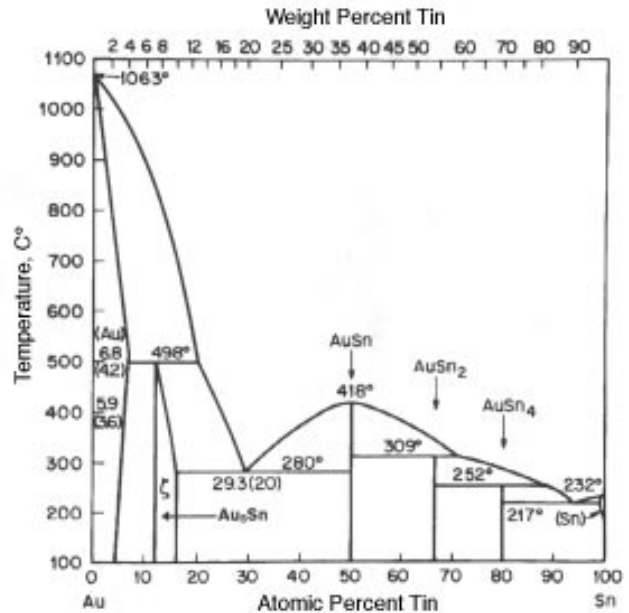

Fig. 1—Equilibrium phase diagram of the binary Au-Sn alloy. Alloys with composition at the eutectic point at 71 atomic % Au (80 % by weight) are used for soldering purposes.

melting point of the alloy rises rapidly with increasing Au content as a result of the steepness of the liquidus line on the gold-rich side of the eutectic point (Fig. 1) and, consequently, the properties of the solder change. Reflow does not occur at 280 °C as expected, but at higher temperatures (*e.g.*, at ~13 percent Sn by weight, 498 °C).

In many available Au-Sn plating baths, the Sn content in the electrolyte decreases with time. It has been observed that Sn-rich agglomerates form, reducing the available amount of
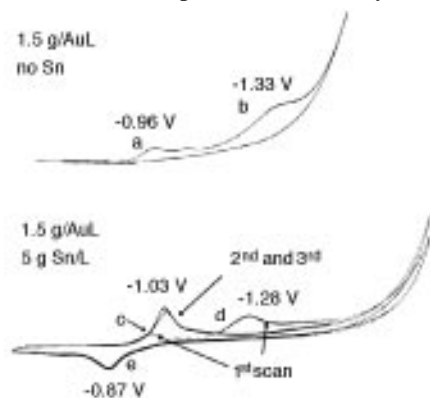

Fig. 2—Cyclic voltammograms obtained from electrolytes with composition as in Table 1. The upper voltammogram, original scan from -0.6 to -1.5 V with 1.5 g Au/L without Sn, shows reduction characteristics of the Au component (a and b); the lower voltammogram, scanned from -0.6 V to -1.8 V with 1.5 g Au and 5 g Sn/L shows reduction of the Au component (c and d) and oxidation of the Sn component (e) as well as depolarization (f) from alloying of the electrode.
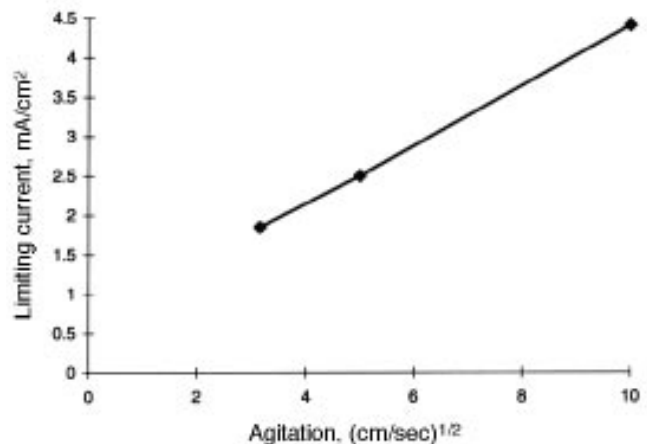

Fig. 3—Limiting current densities for Au in gold-tin plating bath on a rotating disk electrode at 40 °C, pH 11.5 and [Au] = 1.5 g/L.
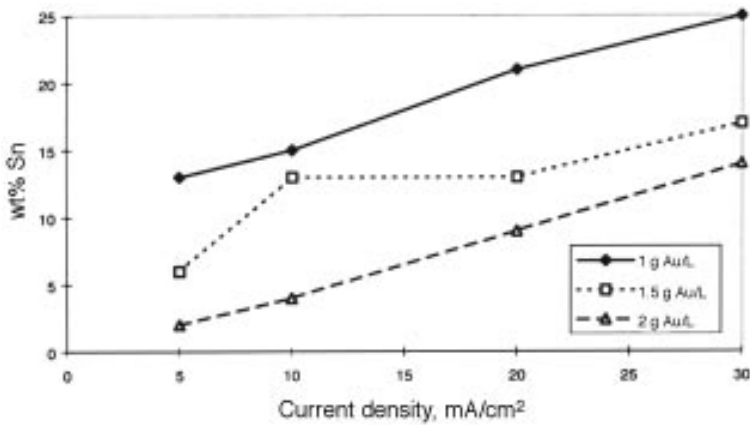
Fig. 4—Effect of Au(CN)$_2^-$ concentration and current density on Au-Sn alloy composition. Increased Au(CN)$_2^-$ concentration in bath and decreased current density reduces Sn content in alloy.
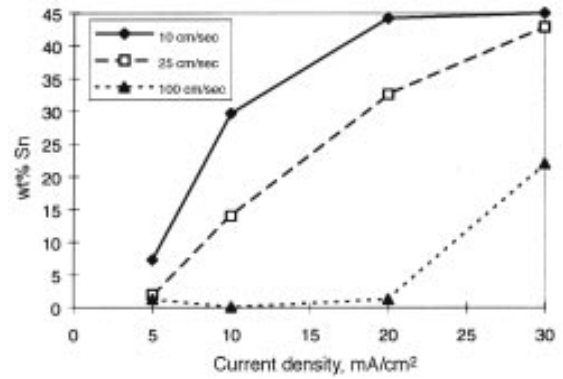

Fig. 5—Effect of solution agitation on deposit alloy composition. Increased agitation reduces Sn content in alloy.
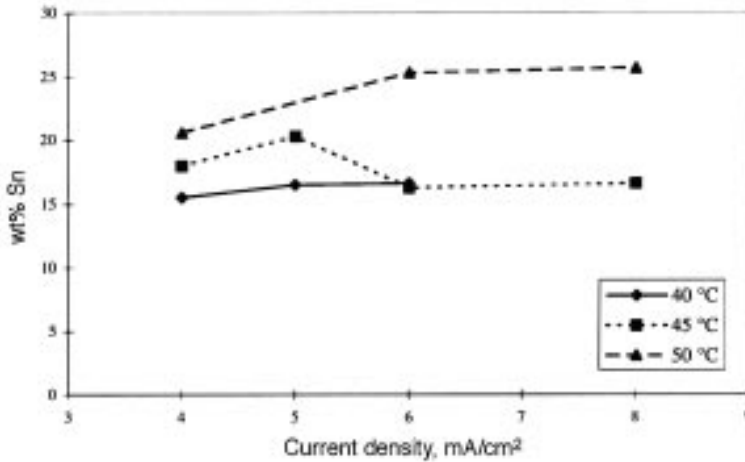

Fig. 6—Effect of bath temperature on deposit alloy composition. Increased temperature reduces Sn content in alloy.
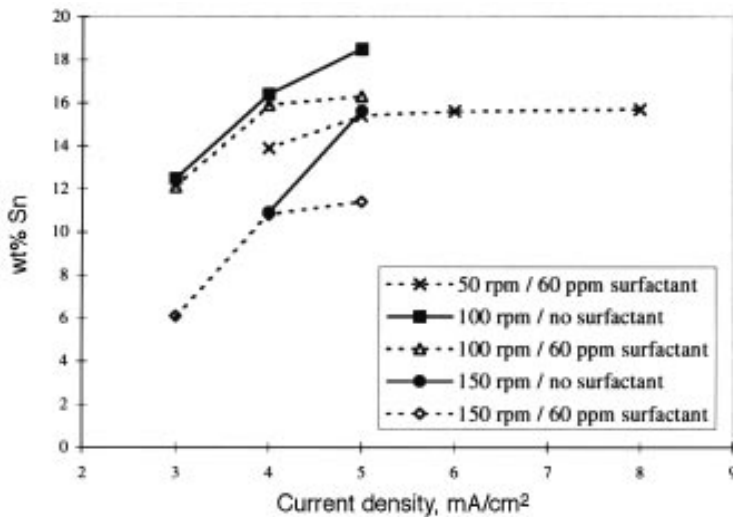

Fig. 7—Effect of addition of a pitting preventing additive. For a limited range of current densities, it appears as though the alloy composition can be stabilized at low agitation.

A process has been developed that can plate eutectic gold-tin alloys reproducibly under production conditions. The plating chemistry was characterized by cyclic voltammetry. The melting characteristics, chemical and phase composition, and microstructure were characterized. Operating parameters and the effect of variation of these are reported herein. Data are included for long-term operation of this plating solution at deposition rates suitable for wafer processing.

Experimental Procedure

Cyclic voltammetry was conducted on gold rotating disk electrodes at temperatures from 25 to 60 °C and agitation from 0 to 1000 rpm. The counter-electrode was platinized titanium mesh and a saturated calomel electrode was used as the reference.

The plated samples were prepared from solutions as listed in Table 1. The cathodes were copper foil, rotating cylinder electrodes. The deposits were prepared under conditions described in Table 2, and were also used for long-term bath performance monitoring by plating approximately 8 μm of gold-tin eutectic coatings on a metallized (100 nm Ti - 200 nm Pt - 50 nm Au) 4-in. silicon wafer.

The properties of the plated alloys were characterized as follows: The chemical composition was measured by atomic absorption spectroscopy (AA). The phase analysis and microstructure investigation were done by X-ray diffraction (XRD) and transmission electron microscopy/electron diffraction (TEM/SAD), also utilizing EDS. The melting point and reflow characteristics were analyzed by differential scanning calorimetry (DSC).

Results & Discussion
Electrochemical Characterization
The electrochemical reactions were characterized using standard cyclic voltammetry. The voltammetry was performed in an electrolyte containing 1.5 g/L Au and at an electrolyte temperature of 40 °C. The reduction process of the dicyanoaurate ion, Au(CN)$_2^-$, can either be from direct reduction of dicyanoaurate ion or from an adsorbed intermediate.[7] The adsorbed intermediate is formed and reduced at about -0.96 V (peak a in Fig. 2) while

Sn and so reducing the Sn content in the deposits. A pyrophosphate formulation was developed by Kubota et al.[5,6] This has proven to be stable, although the Sn-pyrophosphate has a limited solubility. This bath also produces eutectic alloys. The authors are not familiar with the long-term stability of this process.
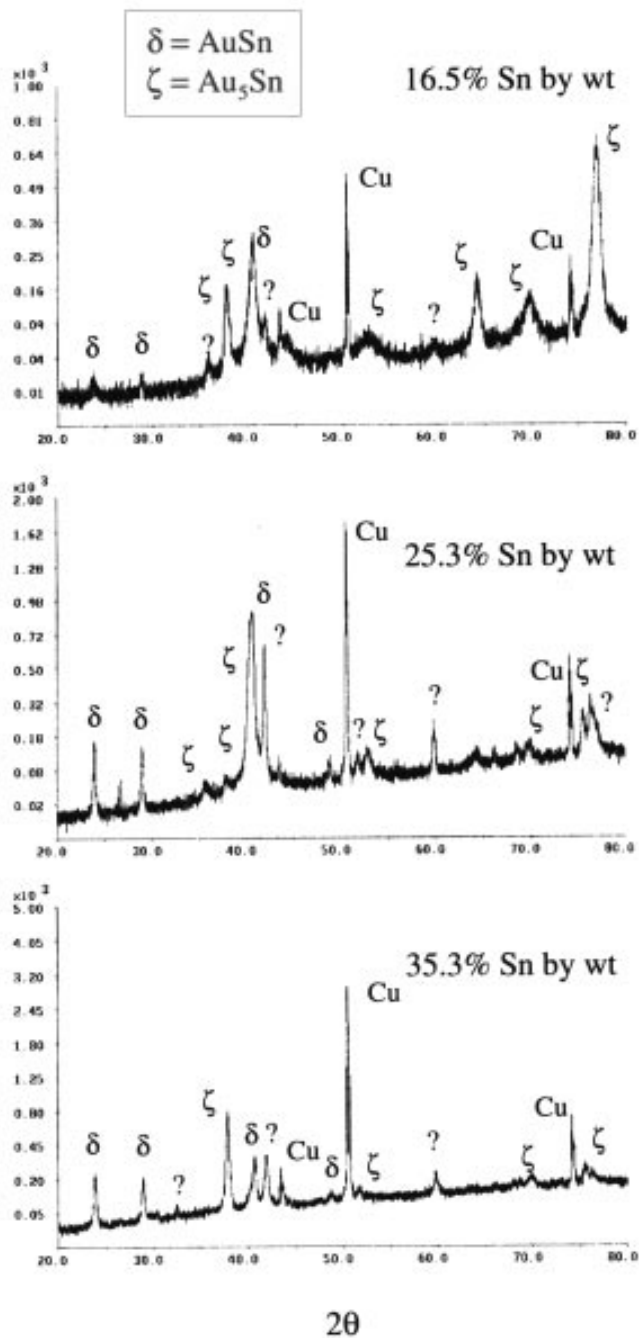
δ = AuSn
ζ = Au₅Sn

Fig. 8—X-ray diffractograms of electrodeposited gold-tin alloys with Sn content of 16, 25 and 35% by weight. The z and d-phases are identified.

Table 1
Electrolyte Composition for Gold-Tin Deposition

Bath constituent	Concentration, g/L	
	Range	Optimal
Au metal in the form of $Au(CN)_2^-$	0.5-15	2
Sn metal in the form of SnO_3^{-2}	5-30	20
PO_4^{-3}	20-50	40
CO_3^{-2}	10-30	20
CN^-	20-50	40
Proprietary additive	20-100 ppm	60 ppm
pH	10-11	10.5

Table 2
Operating Conditions for Au-Sn Alloy Plating Chemistry

	Range	Optimal
Temperature	40-50 °C	45 °C
Current Density	5-15 mA/cm²	8 mA/cm²
Agitation	5-10 cm/sec	7.5 cm/sec
Current Efficiency	40-70 %	55 %
Plating rate	6-11 μm/hr	9 μm/hr

the direct reduction occurs at about -1.3 V vs. SCE (b in Fig. 2). These results agree well with what has been reported by Bard.[7] The reduction potential is only slightly affected by temperature. The effect of agitation on limiting current density for reduction of $Au(CN)_2^-$ is shown in Fig. 3.

Cyclic voltammetry of a bath containing Au (1.5 g/L) and Sn (5 g/L) shows a reduction behavior similar to that of the pure Au bath on a virgin Au electrode (see Fig. 2: peaks c and d). When performing scans in the positive direction from -1.8 V to -0.6 V, however, an oxidation process is observed at -0.87 V, which was not observed for the pure Au system. This indicates oxidation of Sn that was deposited at low potentials. In addition, when the electrode surface was alloyed by Sn, the reduction of Au^+ occurred at -1.03 V. The reduction of stannate, SnO_3^{-2} could not be observed because of the presence of the hydrogen reduction wave. A minor shoulder at about -1.5 V, however, indicated possible Sn^{+4} reduction at this potential.

Alloy Deposit Control

The influence of the current density, the ratio of the metallic species in the electrolyte ($Sn^{+4}:Au^+$), the temperature, and the solution agitation on the composition of the deposits, have been studied. The effect of a proprietary additive utilized to provide a uniform coverage was also studied. An operating window for production of Au-Sn eutectic alloys has been established.

Figure 4 shows the effect of the metallic species ratio, at different current densities, on the deposit composition. The alloy composition is sensitive to the amount of $Au(CN)_2^-$ in the electrolyte; the Sn content is increased by reducing the $Au(CN)_2^-$ content. It can also be observed that the Sn content is increased by increasing current density. The solution agitation affects the composition, as illustrated in Fig. 5 and the effect of temperature is illustrated in Fig. 6. The Sn content is reduced by increased agitation, as well as by increased temperature.

A number of the above observations can be explained by elementary electrochemistry. The $Au(CN)_2^-$ ions are reduced at a more positive reduction potential than the SnO_3^{-2} ions. From cyclic voltammetry (see discussion above), it is appar-

ent that the diffusion limiting current for $Au(CN)_2^-$ has to be exceeded for the deposition of Sn to begin. Consequently, during alloy deposition, the partial current for Au deposition is constant and only the partial current for Sn is affected by variation in the total applied current. Thereby, the deposition of Au is favored under conditions where the total applied current is close to the $Au(CN)_2^-$ diffusion limiting current density (*i.e.*, at low current densities) or when the diffusion limiting current density for $Au(CN)_2^-$ is increased by, for example, increased solution agitation or increased temperature.

To avoid pitting during alloy deposition, an additive was used in the electrolyte. The effect of this additive on the alloy composition is illustrated in Fig. 7. It appears that the additive stabilizes the alloy composition, at least for a limited range of current densities at low agitation.

Crystal Structure & Microstructure

The crystal structure was studied to determine whether the alloy was a true eutectic containing the ζ (Au_5Sn) and δ (AuSn) phases rather than any of the other possible phases present in the AuSn system, as shown in Fig. 1. The possible existence of other phases, such as Au or $AuSn_4$ would most likely affect the melting characteristics upon reflow of the solder alloy.

The crystal structure was evaluated by XRD and by TEM/SAD. The 80/20 eutectic gold-tin alloy is a two-phase material consisting of ζ-phase (Au_5Sn) and δ-phase (AuSn), as can be seen in Fig. 1. For alloys with Sn content lower than 4.2 percent by weight, only a gold fcc phase is expected. In a composition range from 10 to 37 percent, the ζ- and δ-phases are expected, while for deposits with Sn content above 37 percent, AuSn and $AuSn_2$ are expected, and above 55 percent, $AuSn_4$ is also expected.

In Fig. 8, X-ray diffractograms from electrodeposited alloys with compositions of 16, 25 and 35 percent Sn by weight are shown. Both the ζ- and the δ-phases are clearly identified. There are, however, peaks shifted in position, indicating either stresses or defects in the ζ-phase or, possibly, the existence of a gold fcc phase. Electron diffraction (TEM/SAD) confirms the existence of the ζ- and the δ-phases but does not support the existence of a gold fcc phase.

The ratio of the ζ- to the δ-phase is reduced when the Sn content of the alloy is increased. Figure 9 depicts a qualitative perspective of the growing fraction of the δ-phase in a composition range from 16 to 35 percent Sn by weight in the gold-tin alloy. The ratio was taken as the peak height of the sum of the (100) and (101) δ-phase reflections to the (300) and (306) ζ-reflections.

In the electrodeposited dual phase alloys, the ζ- and δ-phases exist as 100 to 150 nm large grains, as illustrated in Fig. 10. In the δ-phase grains, no defects are observed by TEM and the corresponding SAD patterns are sharp, con-
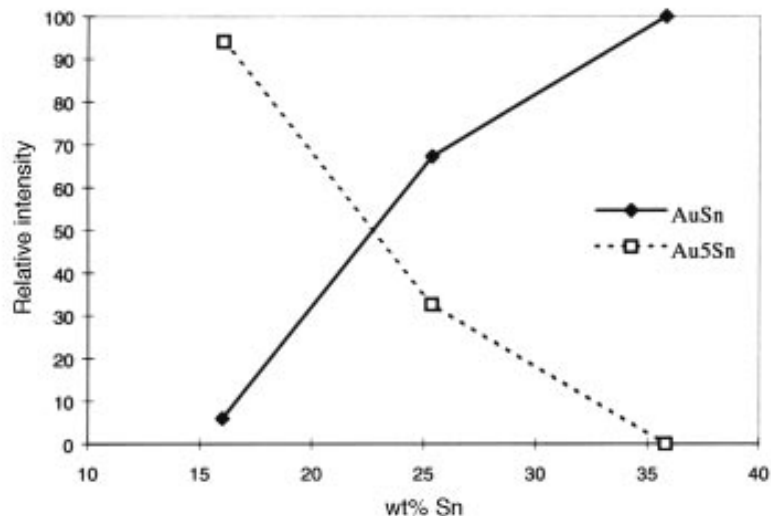

Fig. 9—Ratio of z (AuSn) to d-phase (Au$_5$Sn) of electrodeposited gold-tin alloys at 16, 25 and 35% Sn by weight. The ratio was calculated as the sum of the peak heights of (100) and (101) d-phase peaks to the sum of the (300) and (306) z-phase peaks. The fraction of d-phase increases with increasing Sn content as expected.
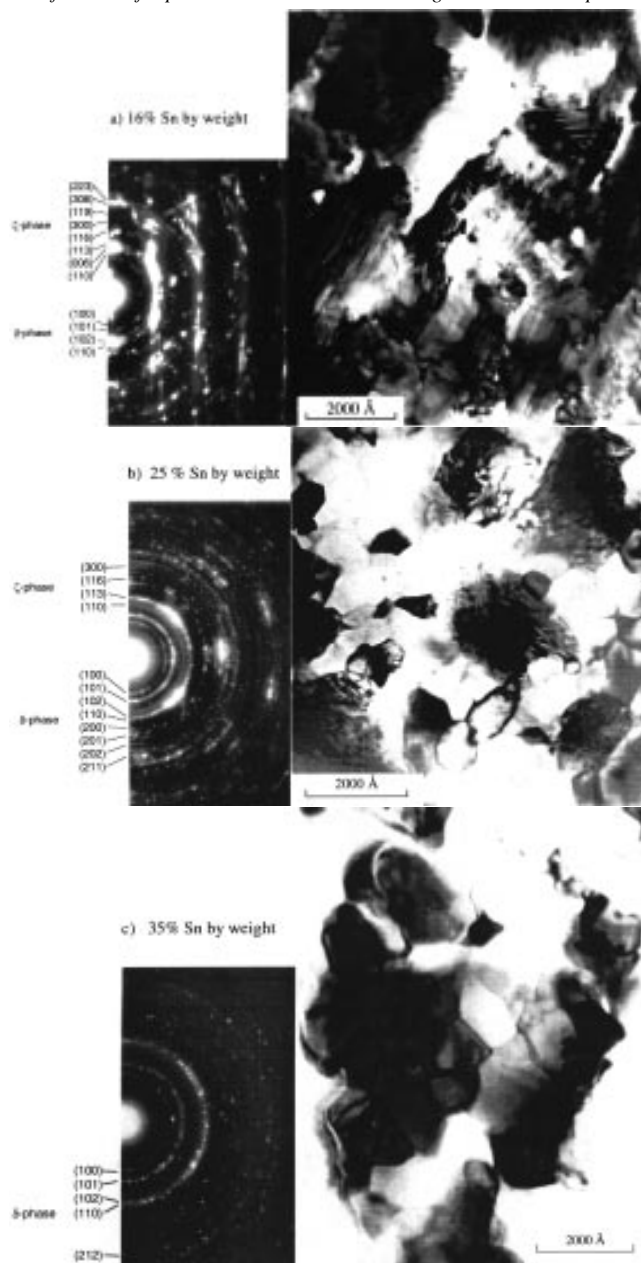

Fig. 10—TEM micrographs showing the microstructure of electrodeposited gold-tin alloys of (a) 16, (b) 25 and (c) 35 % Sn by weight, respectively: (a) both the z and the d-phases are seen. The z-grains dominate and contain lamellar features as well as streaks in the SAD patterns, while the d-phase grains appear with only few defects; (b) only a small number of d-grains are observed. The lamellar features and the streaks can be seen; (c) mainly low-defect z-grains are observed.
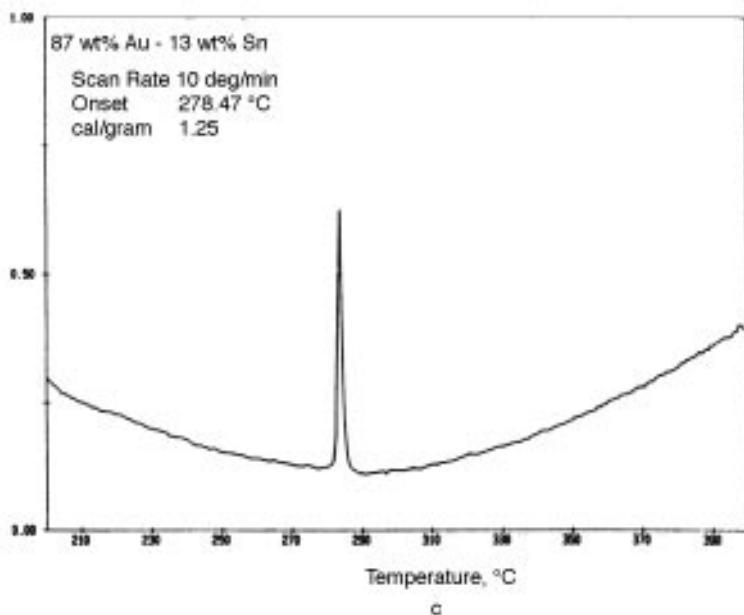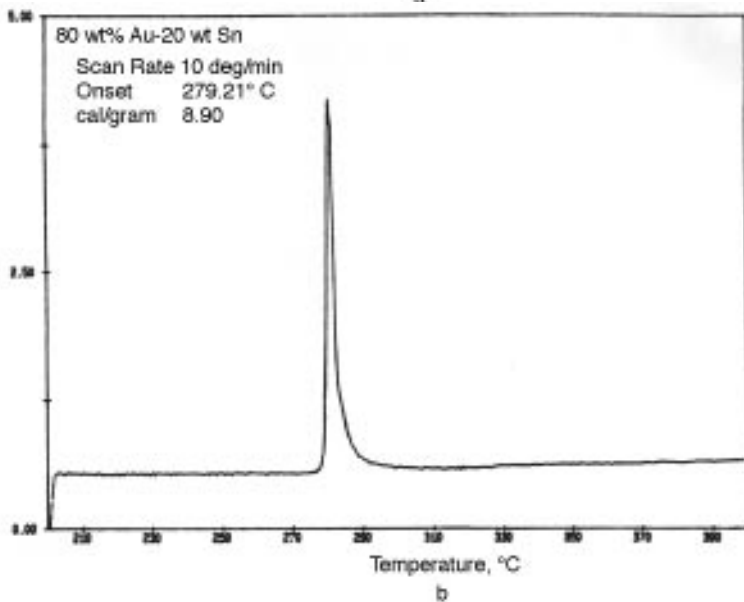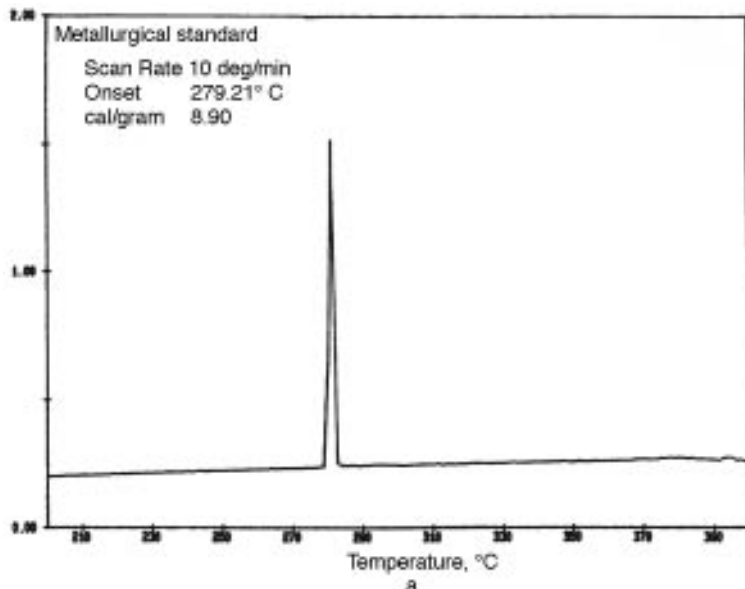
Fig. 11—DSC graphs showing melting characteristics of gold-tin alloys: (a) a metallurgical 80/20 Au-Sn standard is shown; (b) a plated 80/20 sample; (c) - (f) scans from plated alloys with Sn contents of 13 (c), 24 (d), 36 (e), and 57% by weight (f).

firming a relatively distortion-free grain structure. The ζ-phase grains, however, contain numerous lamellas, and streaks are observed in the SAD patterns (see Fig. 10). This indicates the presence of stacking faults or twins in this phase, and is the reason for the broadening and the streaks in the ζ-phase peaks in the selected area diffraction patterns of Fig. 10a.

Melting Characteristics
The melting point and reflow characteristics were studied by DSC. As a reference, gold-tin preforms were used, as illustrated in Figs. 11 and 12. The heat of fusion for the eutectic melting of metallurgical preforms was about 33 J/g. This compares to deposited alloys of eutectic or near-eutectic composition, as shown in Figs. 11a and b. The heat of fusion data are within 60 percent of the preform data for alloys with composition ranging from about 19 to 25 percent Sn by weight, as illustrated in Fig. 12.

For off-eutectic composition alloys, the DSC data look quite different, as illustrated in Fig. 11c-f. For Au-rich alloys, no endothermal reactions are observed up to 420 °C. For alloys at 13 percent Sn, an endothermal reaction is observed at 280 °C, indicating a minor melting reaction, leaving a substantial amount of unmelted material behind. For Sn-rich alloys just below 50 atomic percent (= 36 percent by weight) Sn, in addition to the eutectic melting at 280 °C, a second reaction is observed, peaking at 418 °C, indicating melting of the δ-phase. For alloys with Sn content around 57 percent, two endothermal reactions are observed, one at 252 °C, indicating melting of the $AuSn_4$, and one at 309°C, indicating melting of $AuSn_2$-phases.

Stability & Reproducibility Of the Deposition Process
To evaluate the long-term stability of the process and electrolyte, first, the electrolyte composition and the operating parameters had to be fixed. From the earlier results, it was concluded that to obtain reproducible results, the optimal bath composition is as shown in Table 1, and the optimal operating conditions are described in Table 2. The deposited material has a dark golden brown to gray appearance and a low density. As illustrated by Fig. 13, this can be explained by the roughness of the surface. The shiny silver appearance normally associated with 80/20 gold-tin eutectic is obtained upon reflow of the solder in a non-oxidizing atmosphere (see Fig. 13). A volume contraction of about 40 percent is observed because of the porous nature of the plated material.

The uniformity of the deposit thickness was confirmed by plating the full surface of a 4-in. silicon wafer, then etching away all material except an array of rectangular boxes distributed uniformly in a 2 1/2-in. square in the center of the wafer. Sixty-four measurements of the step height gave an average plated thickness of 5.59 μm and a standard deviation of 0.72 μm. This implies that

the current distribution over the surface of the wafer does not vary enough to affect the composition of the alloy coating locally. Analytical data supporting this are given below.

A functional test of the composition is the melting behavior of the deposited material. This can be done conveniently by using differential scanning calorimetry (DSC). Figures 11 and 12 exemplify DSC graphs for various compositions of Au-Sn alloys. The graphs contain information on both temperature and heat content for the phase transitions observed as endothermal reactions. It is clear from Fig. 12, that the heat content for the eutectic melting reaction depends on the alloy composition and that it is gradually reduced when moving away from the eutectic 80/20 composition. There is a scatter in the plot observed, even for metallurgical preform samples. One source for this is experimental errors. More importantly, the melting behavior of Au-Sn is quite complex. As seen in Fig. 10, the Au-Sn alloy is a two-phase material composed of the ζ (Au$_5$Sn) and δ (AuSn) phases. These two phases are segregated into domains of variable size. The SEM images of Fig. 13 indicate that the growth is porous and columnar and, from the characteristics of the melted material (Fig. 13d), it can be assumed that the individual columns may be single-phase domains. The melting characteristics therefore involve not only the heat of fusion, but also contributions from energy changes connected with interdiffusion of these materials. This contribution would be influenced by the physical properties of the material, such as the size of the grains and the domains. Regardless of this complication, it is observed that the plated samples showing a heat of transition greater than 21 J/g show a composition within the range of 19 to 24 percent Sn by weight suitable for eutectic bonding.

The porous structure shown in Fig. 13 appears to be in contrast to a dense structure, as observed by TEM in Fig. 10. However, it was not possible to obtain any TEM samples from the mid- or upper section of the coating, but only close to the substrate, where the coating has sufficient density.

To check the uniformity of the deposited material across a wafer, 17 DSC determinations were made from a plated 4-in. wafer. Samples were taken along an axis of the wafer, as well as the edges where the greatest current density variation would be expected. For the 10 samples taken around the edge of the wafer, the heat of transition varied between 23.7 and 32.0 J/g, while the seven interior samples varied between 29.0 and 31.4 J/g. All areas of the wafer were within the desired control range for alloy composition.

Figure 14 shows the variation in heat of transition data reflecting the compositional variations as a function of the plating bath age. Sample plating runs were done about every 0.1 bath turnover and the performance was checked by DSC. All samples having a heat of transition greater than 21 J/g
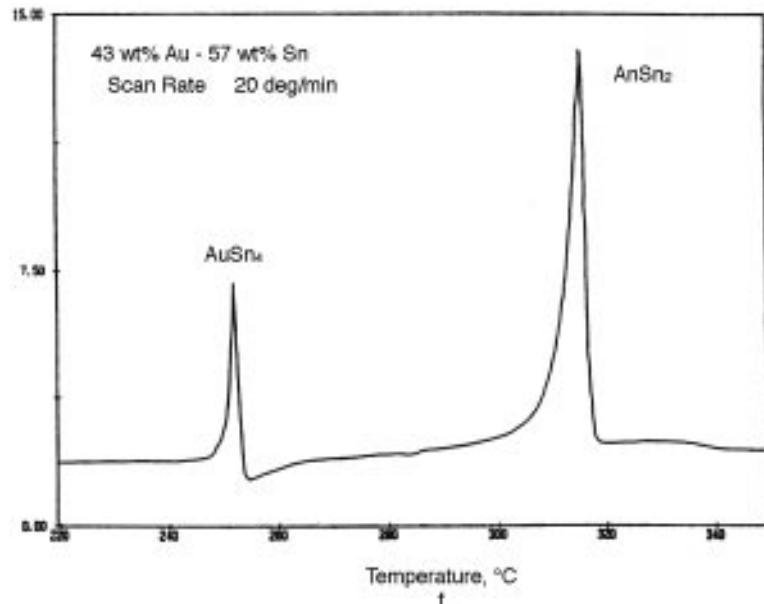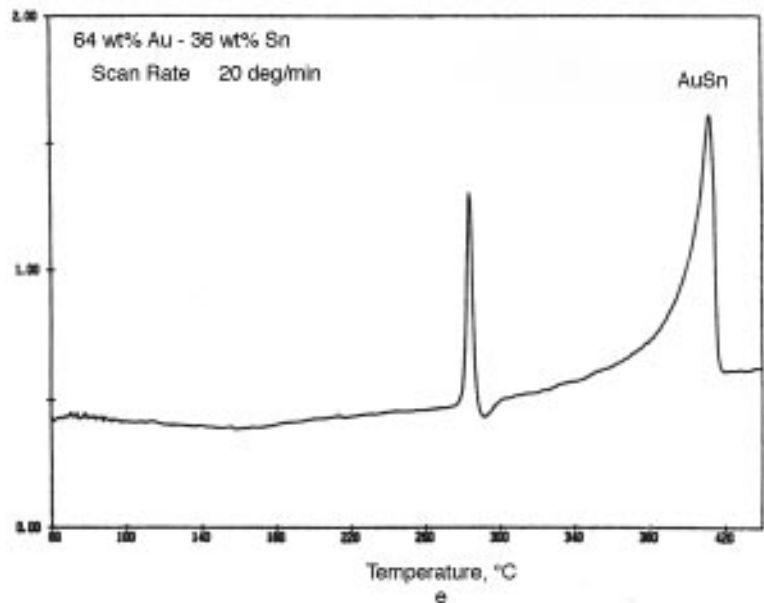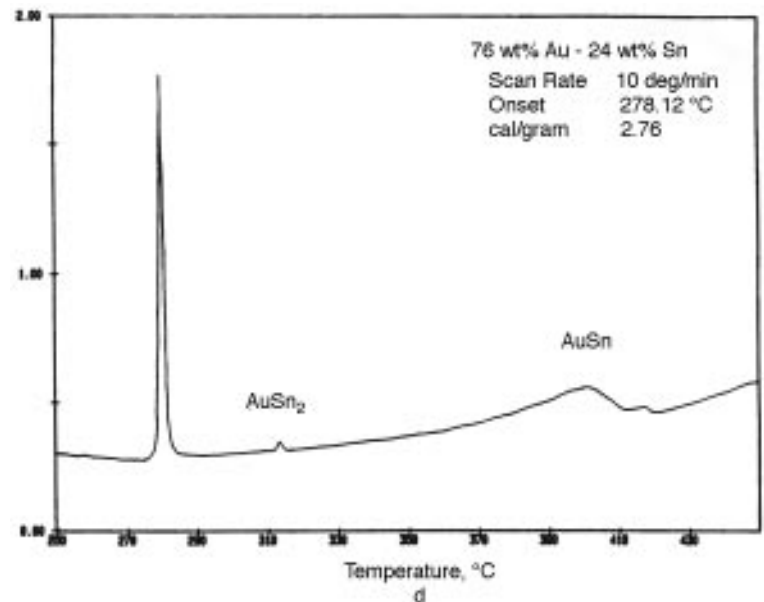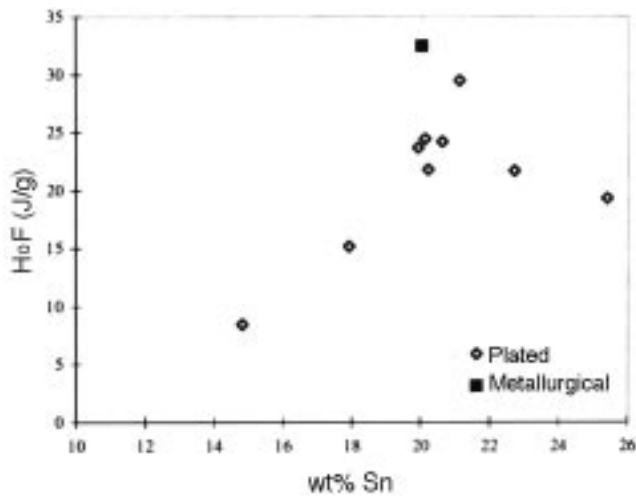

Fig. 11 (continued)

Fig. 12—Heat of fusion data obtained by DSC of eutectic preform and of eutectic or near-eutectic electrodeposited gold-tin alloys.
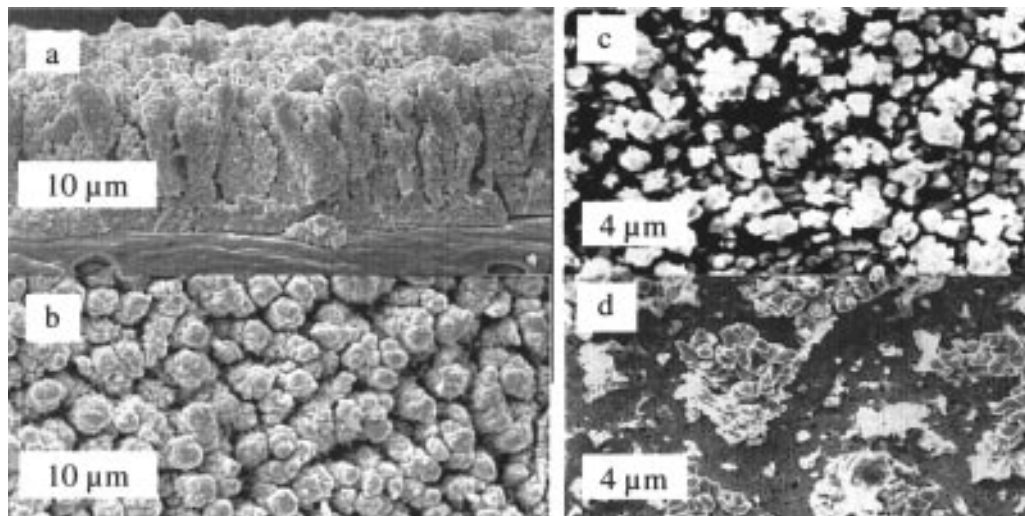

Fig. 13—SEM images showing structure of the porous plated Au-Sn alloy in cross section (a) and top view (b). During reflow, the deposit melts partly. Part (c) shows the deposit before and (d) after reflow.
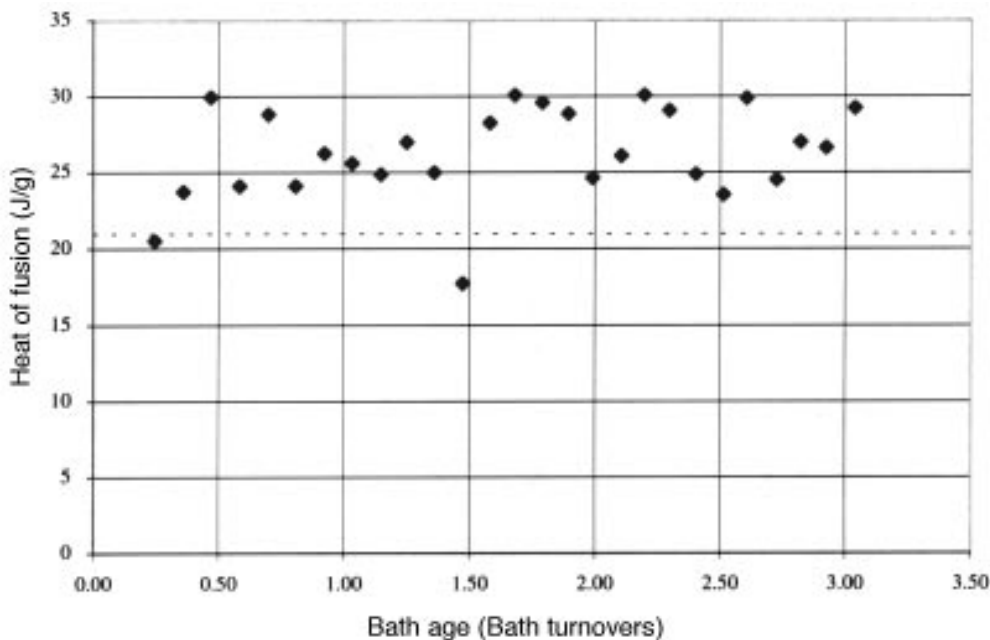

Fig. 14—Heat of fusion of the eutectic reaction at 280 °C as a function of bath age. The low value at ~1.5 BTO was a result of allowing the pH to drift out of control. The dotted line represents the minimum heat of fusion to allow good eutectic bonding.

correspond to compositions within the control range. The exceptional point near 1.5 bath turnovers is a result of allowing the pH of the bath to drift out of control.

Summary

This study can be summarized as follows:

1. Gold-tin alloys can be plated from a slightly alkaline bath with good reproducibility and composition control, exhibiting material properties useful as a 280 °C eutectic solder.

2. The alloy deposits with the Au reduction at about -1.0 V on the alloy surface, which is depolarized compared to a pure Au surface, where the reduction occurs at -1.3 V. The Sn deposition is shown to be reversible through an oxidation reaction at -0.85 V.

3. The composition of the gold-tin alloy is sensitive to current density and agitation, as well as gold concentration and bath temperature. Operating windows, however, can be defined by careful control of the pH (by ±0.1 unit) and by bringing the current distribution and the hydrodynamic conditions under control.

4. The plated gold-tin alloy is crystallographically similar to the bulk material with respect to phase composition. The eutectic alloy consists of a Au_5Sn (ζ) and a AuSn (δ) phase. The grain structure of the plated alloy shows grain sizes of 100 to 150 nm. The ζ-phase grains appear defect-free, while the δ-phase grains contain lamellar defects, probably a result of stacking faults or twins.

5. The melting characteristics of the plated alloy indicates good agreement with the bulk material. Heat of fusion data of plated alloys are within 60 percent of preform data within a composition range of 19 to 24 percent Sn by weight.

6. The long-term stability of the process has been evaluated up to an age of three bath turnovers. No significant change in heat of fusion data was observed.

References
1. C. Wright, *IEEE Trans. Parts, Hybrids, Pack.*, **PHP-13,** 202 (1977).
2. D.D. Zimmerman, *Solid State Technol.,* 44 (1972).
3. D.R. Olsen & H.M. Berg, *IEEE Comp., Hybrids, Manufact.,* **CHMT-2**, 257 (1979).
4. G. Matijasevic & C.C. Lee, *J. Electron. Mater.,* **18**, 327 (1989).
5. N. Kubota, T. Horikoshi & E. Sato, *J. Met. Fin. Soc. Japan.,* **34**, 37 (1983).
6. N. Kubota, T. Horikoshi & E. Sato, *Plat. and Surf. Fin.,* **71**, 46 (March 1984).
7. A.J. Bard, *Encyclopedia of Electrochemistry of the Elements*, Vol. IV, Marcel Dekker, Inc., New York and Basel.

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