

THE EFFECT OF LEAD CONTENT AND SURFACE ROUGHNESS ON WETTING AND SPREADING OF LOW-LEAD AND NO-LEAD SOLDERS ON COPPER-CLAD FR-4 LAMINATES*

Joel O. Stevenson,
John L. Roberts, Rick N. Davidson, Fred G. Yost, and F. Michael Hosking
Materials and Process Sciences Center
Sandia National Laboratories
Albuquerque, NM

RECEIVED

FEB 10 1997

OSTI

MASTER

ABSTRACT

Environmental and health concerns pertaining to lead have encouraged research into low-lead alloys for electronic soldering. The development of solder alloys containing lower amounts of lead than Sn/Pb eutectic (37 wt.% lead), but possessing similar properties, is an industry-wide goal. To determine the wettability of low-lead solders, 21 alloys each of Sn/Ag and Sn/Cu eutectic (containing 0 to 10 wt.% lead and/or indium) were tested on as-received copper-clad FR-4. Contact angles for the alloys ranged from 12.5 to 38.9° and area of spread measurements ranged from 5.2 to 17.3 mm² compared with 5 to 15° and ~19 mm², respectively, for Sn/Pb eutectic. Alloys with 8 to 10 wt.% lead showed contact angles and areas of spread similar to Sn/Pb eutectic under similar conditions. The best results on the as-received substrates, compared to the Sn/Pb eutectic, were obtained from the Sn/Ag eutectic with 10 wt.% lead.

The very low-lead (less than 10 wt.% lead) and lead-free alloys, however, failed to achieve the performance level of eutectic Sn/Pb solders. A desire to improve the spreading of very low-lead and lead-free solders provided the impetus for our efforts to produce "engineered" rough surfaces. In an attempt to improve the wettability and spreading behavior of very low-lead and lead-free alloys, the very low-lead and lead-free members of the Sn/Ag system were tested on roughened copper-clad FR-4. Every alloy in the test suite demonstrated improvement in area of spread on the roughened substrates. The best results on the roughened substrates, compared to the Sn/Pb eutectic, were obtained from the Sn/Ag eutectic with 8 wt.% lead.

The effects of surface roughness on the wettability and flow behavior of solder alloys has provided insight into surface morphologies that lead to improved solderability. Roughness characterizations using optical interferometry and scanning electron microscopy will be discussed. Area of spread measurements performed on these roughened substrates show that very low-lead and lead-free solders can also be made to wet and spread on a level similar to Sn/Pb eutectic under similar conditions through the use of engineered rough surfaces.

INTRODUCTION

Certain products containing lead have probable links to human illnesses. Ingestion or inhalation of even small amounts of lead can result in learning and behavioral disorders. Although the electronic industry may be exempted from proposed legislation to tax or ban lead-containing products, thereby allowing the continued use of lead in solder alloys, the electronic soldering business may have to face the financial hardship of a heavy tax.

Recent work on the development of alternative Pb-free solders has produced several alloys that only partially meet the requirements of electronics soldering technologies (Lee, et al., 1994; Miller, et al., 1994; McCormack, et al., 1994). These alloys are rich in Sn and contain various elements including Ag, Cu, In, and Bi. Many of these alloys display useful characteristics such as lower melting temperatures. These alloying elements also possess disadvantageous properties that must be considered. For example, excess Bi segregates to interfaces such as grain and cell boundaries and can cause embrittlement (McCormack and Jin, 1994). Zn is susceptible to corrosion and possesses very high oxidizing potential that can significantly accelerate solder drossing (Hondros and McLean, 1974). Indium is very expensive and accelerates solder joint oxidation, especially in moist environments (Konetzki, et al., 1990). Most alloy ingredients are, therefore, generally added in small amounts. Industrial experience indicates that, realistically, no more than 18% Bi and 3 to 6% In can be added to any solder alloy. Few practical Pb-free alloy candidates exist that can serve as a drop-in replacement for traditional Sn/Pb alloys. That is, no candidate alloy melts and wets component surfaces in the same temperature-time profile as the Sn/Pb system.

For this work, two groups of 21 solder alloys each were made. One group is based on the Sn/Ag eutectic composition and the other on the Sn/Cu eutectic composition. Both Pb and In were added to these eutectic compositions in 2 wt.% increments, up to 10 wt.%. The melting behavior of these alloys was investigated with differential scanning calorimetry (DSC). The wetting behavior of the alloys was assessed through measurements of the equilibrium contact angle and area of spread on as-received copper-clad FR-4 substrates.

HH
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

* This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The wetting behavior of the very low-lead and lead-free Sn/Ag alloys was also assessed through area of spread measurements on roughened copper-clad FR-4 substrates.

From these measurements, we show that it may be possible to produce solder alloys that behave like Pb-containing solder, but with only a fraction of the Pb content. The use of such alloys will obviate any need to modify existing manufacturing processes. We also discuss results with roughened substrates that demonstrate that very low-lead and lead-free alloys may be made to behave in a manner similar to Sn/Pb eutectic. This etching technology is compatible with existing printed wiring board (PWB) manufacturing technologies.

BACKGROUND/HISTORY

Rough surfaces and their implication for wettability have been studied by many researchers (Ref. 7-16). These studies established the importance of surface roughness in wetting phenomena. Work by Wenzel described surface conditions necessary for wetting (Wenzel, 1936). Wenzel developed a relationship showing that increases in roughness produce decreased contact angles between wetting liquid and solid substrate. This result has been investigated for years in an effort to understand wetting behavior on rough surfaces.

Researchers have determined that an additional driving force exists for wetting on rough or grooved surfaces, namely, flow into open channel capillaries (Romero and Yost, 1995; Yost, et al., 1995). Liquid solder flows into the open channels by capillary action. Solder flow within these V-shaped grooves is dependent on the orientation and physical dimensions of the grooves. Plated copper inherently possess some degree of open capillary roughness that encourages solder flow. This roughness can be enhanced using chemical etchants, thereby improving wettability.

An industry-wide desire for improved solder joint manufacturability and reliability has provided the impetus for our efforts to produce "engineered" rough surfaces. Conventional Sn/Pb solders exhibit very good area of spread and low contact angles. However, recent efforts to reduce or eliminate Pb have produced solders with low area of spread and high contact angles. Wenzel's equations encouraged us to view surface roughness as a process variable that can be utilized to improve wettability by increasing area of spread and decreasing contact angle.

Surface roughness can be enhanced in a variety of ways. Electroplating can increase the surface roughness of copper substrates (Yost, et al., 1995). Electrochemical etching also has the potential for increasing surface roughness. A literature search uncovered numerous chemical etches for copper (Ref. 17-35). The referenced applications are myriad and do not necessarily seek increased surface roughness. Applications include manufacture of semiconductor devices and printed circuit boards, dissimilar materials joining, microjoining, diffusion welding, and ultrasonic welding.

Sandia National Laboratories has recently completed a Cooperative Research and Development Agreement (CRADA) with consortium members of the National Center for Manufacturing Sciences (NCMS) to develop fundamental generic technology in PWB materials and surface finishes.

The effects of surface roughness on the wettability and solderability behavior of several types of copper board finishes were investigated to gain insight into surface morphologies that lead to improved solderability (Stevenson, et al., 1995). Initial testing with six chemical etches demonstrated that surface roughness can be greatly enhanced through chemical etching. Noticeable improvements in solder wettability were observed to accompany increases in roughness. Scanning electron micrographs of representative test surfaces from this study are shown in Figures 1a - 1h to demonstrate the diversity of surfaces that can be obtained through chemical etching of copper surfaces.

The FeCl_3/HCl etch (Figure 1f) produced the largest roughness gains observed on the electroplated copper substrate. Figure 1g illustrates the enhanced degree of roughness that can be obtained through increased etching time. The $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch (Figure 1h) produced the largest roughness gains observed on the electroless-plated copper substrate.

In a follow-up study on a Ball Grid Array Test Vehicle (BGATV) substrate, a 10% HCl baseline pretreatment and two chloride-based etching solutions were evaluated for their copper roughening ability (Hosking, et al., 1996; Hosking, et al., 1996). Different FeCl_3 and CuCl_2 concentrations (127, 253, and 380 g/liter) were investigated. Hydrogen peroxide (H_2O_2) was added to the CuCl_2 solutions to accentuate the etch process. The peroxide is an oxidizer and promotes preferential etching by the CuCl_2 through an iterative reoxidation and etch process. A third etching procedure used a sequential CuCl_2 and FeCl_3 dual etch. The BGATV is a series of copper pads and lines of various sizes and widths deposited on a circuit board. 63Sn-37Pb solder paste is stenciled onto the round pad areas and RMA flux is brushed onto the exposed copper surfaces. The BGATV is then passed through a solder reflow machine (N_2 cover) at 9 inches per minute where a series of hot plates melt the solder paste in a controlled manner. The objective is to induce solder flow down the lines from the pads, completely filling the interior of each pattern.

Roughness results for the BGATV copper samples are detailed in Table I. Area path (R_p), maximum peak-to-valley (R_t), root-mean-square (R_q), and arithmetic mean (R_a) roughness values were compiled from optical profilometry traces for each etch condition. Since it was difficult to interpret the peak-based metrics (R_t , R_q , and R_a) due to the somewhat rippled surface produced by the underlying FR-4 laminate layers, experimental analysis concentrated on the normalized surface area metric, R_p , although the other roughness parameters exhibited similar measured trends. R_p is determined by dividing the measured 3D surface area by the 2D projected measurement area. This provides a good reflection of the roughness ratio in Wenzel's equation, which depends on the mean square slope of a surface, rather than its amplitude (Yost, et al., 1995). While R_p is not mean square slope, the two metrics convey similar information. This normalized parameter is consequently more characteristic of general surface roughness, as compared to the localized nature of the other roughness parameters.

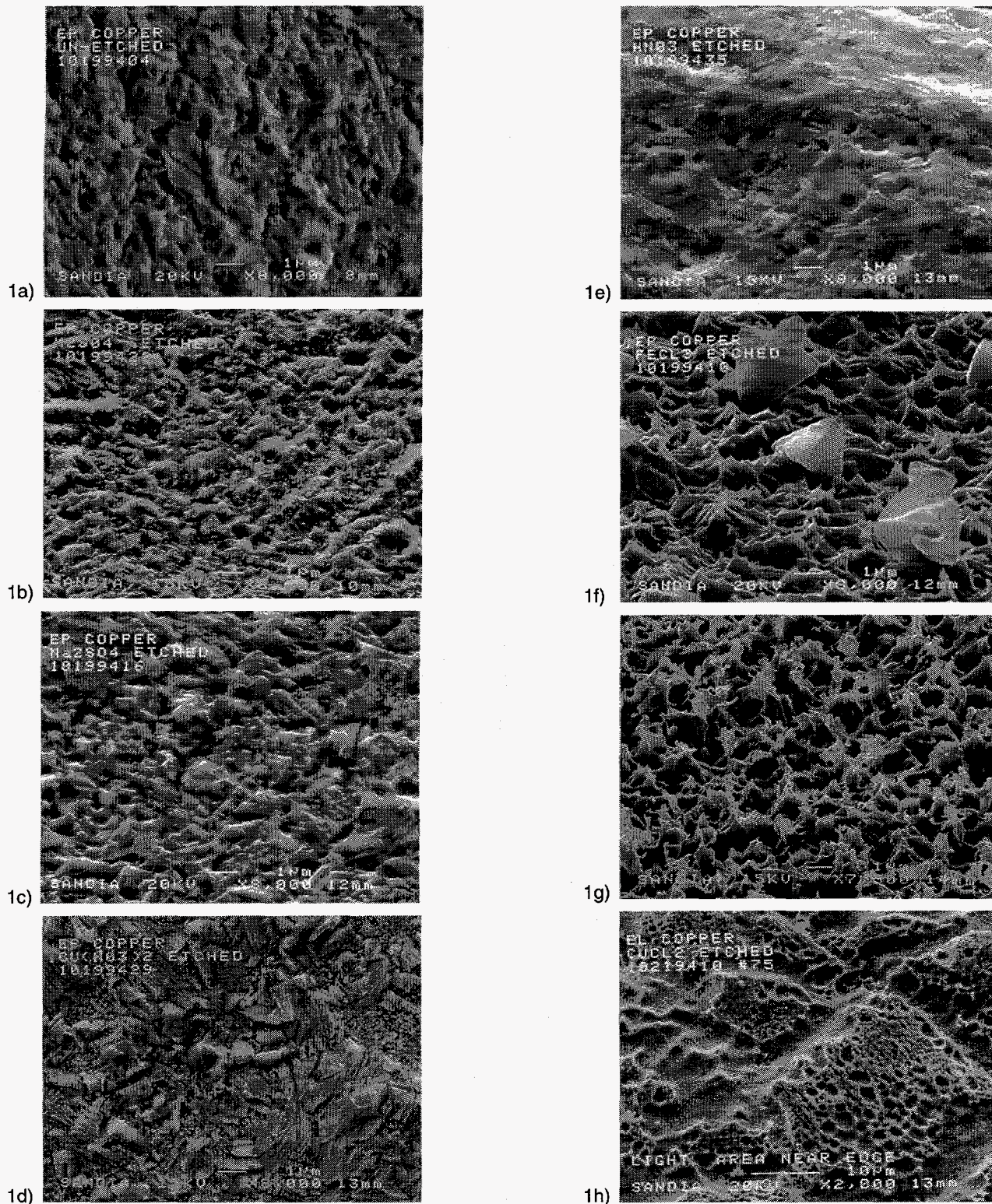


Figure 1. SEM's of test surfaces. 60 sec etches and electroplated FR-4 Cu except as noted. Micrographs a - f at 8000X magnification with 1 μ m fiduciary marks. Micrograph g at 7500X mag with 1 μ m fiduciary mark. Micrograph h at 2000X mag with 10 μ m fiduciary mark. a) Unetched b) H_2SO_4/H_2O_2 c) $Na_2SO_4/H_2SO_4/H_2O_2$ d) $HNO_3/Cu(NO_3)_2$ e) HNO_3/H_2SO_4 f) $FeCl_3/HCl$ g) $FeCl_3/HCl$ (90 sec) h) $CuCl_2/H_2O_2/HCl$ (electroless-plated FR-4 Cu)

Table I: Optical Profilometry Measurements on Baseline and Etched BGATV Surfaces

Surface Treatment & Time	Area Path Index R_{p-} ($\mu\text{m}^2/\mu\text{m}^2$)	Peak-to-Valley R_{T-} (μm)	RMS R_{Q-} (nm)	Arithmetic Mean R_{A-} (nm)
Baseline, 10% HCl	1.768 ± 0.102	4.6 ± 0.2	405.1 ± 21.8	311.6 ± 16.9
FeCl ₃ (127 g)*, 30 s	2.453 ± 0.053	7.1 ± 1.5	727.0 ± 214.4	553.6 ± 183.1
FeCl ₃ (127 g)*, 120 s	3.101 ± 0.201	10.0 ± 1.5	1073.3 ± 319.6	806.6 ± 255.3
FeCl ₃ (253 g)*, 75 s	2.564 ± 0.039	7.7 ± 2.0	673.6 ± 140.6	508.4 ± 88.1
FeCl ₃ (380 g)*, 30 s	2.375 ± 0.197	5.7 ± 1.1	555.6 ± 37.7	435.4 ± 27.5
FeCl ₃ (380 g)*, 120 s	2.541 ± 0.071	7.8 ± 0.7	842.5 ± 164.5	666.3 ± 131.9
CuCl ₂ (127 g) + H ₂ O ₂ (7 ml)*, 30 s	2.486 ± 0.166	7.7 ± 1.1	752.8 ± 209.7	556.0 ± 108.2
CuCl ₂ (127 g) + H ₂ O ₂ (7 ml)*, 120 s	2.657 ± 0.064	9.1 ± 2.2	787.0 ± 60.6	602.9 ± 37.8
CuCl ₂ (253 g) + H ₂ O ₂ (14 ml)*, 75 s	2.518 ± 0.073	5.4 ± 0.8	606.1 ± 114.2	479.3 ± 98.9
CuCl ₂ (380 g) + H ₂ O ₂ (21 ml)*, 30 s	1.783 ± 0.299	5.2 ± 0.8	475.8 ± 142.3	368.4 ± 130.9
CuCl ₂ (380 g) + H ₂ O ₂ (21 ml)*, 120 s	2.155 ± 0.275	5.6 ± 0.7	591.1 ± 156.6	455.3 ± 127.8
CuCl ₂ (253 g) + H ₂ O ₂ (14 ml)*, 30 s followed by FeCl ₃ (253 g)*, 30 s	3.062 ± 0.113	9.8 ± 2.9	1207.7 ± 248.6	930.7 ± 197.4

80X Magnification

* (per liter of 50 vol.% HCl stock solution)

As seen in Table I, the FeCl₃/HCl etch produced the largest roughness gains on BGATV substrates. Three-dimensional images of the roughness data and their peak-to-valley ranges are presented in Figure 2. The 10% HCl baseline condition did exhibit a certain degree of roughness (Figure 2a). The FeCl₃/HCl etch generally produced a relatively homogeneous surface topography with uniform, moderate scale peaks and valleys, as shown in Figure 2b. The CuCl₂/H₂O₂/HCl etch yielded a more heterogeneous surface, with high peaks along the trace edges and deep, broad valleys over the remaining surface area. The dual etch process produced the most interesting results, yielding a bimodal topography consisting of generally uniform peaks and valleys with deeper interconnected grooves. This "grooved" topography is believed to be caused by preferential etching along the copper grain boundaries (Figure 2c) and is common to most chemical etching processes (Fradkov, 1994). Under controlled conditions, the "grooved" pattern can enhance solder flow. If overetched, however, wider "grooves" with a shallow slope can inhibit flow.

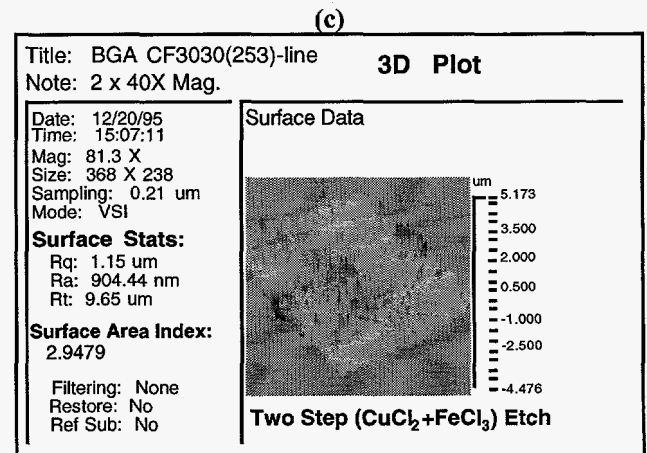
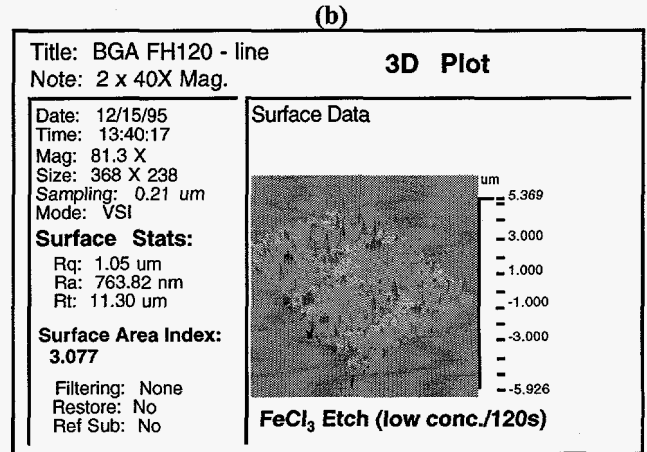
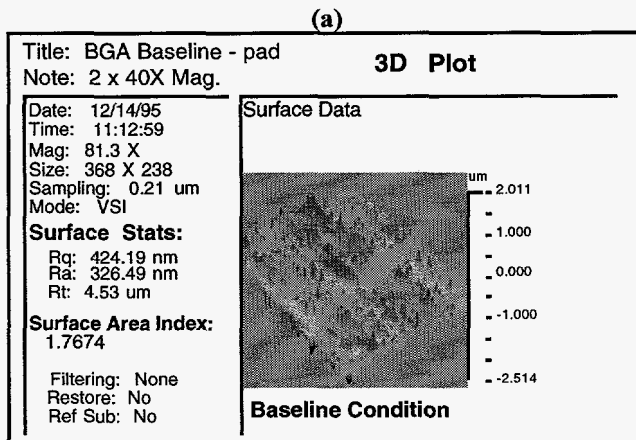


Figure 2: Mapped surface topography of (a) baseline, (b) FeCl₃/HCl (127 g/liter, 120 sec), and (c) dual CuCl₂/H₂O₂/HCl and FeCl₃/HCl etched BGATVs.

EXPERIMENTAL PROCEDURE

The compositions of the experimental alloys are given in Tables II and III. Bulk solder alloy samples were produced from commercially pure elemental metals weighed to the nearest milligram and then sealed in a quartz glass tube. The tube was evacuated and backfilled to atmospheric pressure with argon three times. The tube was evacuated a fourth time, backfilled with argon to 15 to 20 inches Hg vacuum, and sealed. This series of backfills was done to ensure that the amount of O₂ in the tube is minimized. The sealed tubes were placed in a furnace at 1100°C for 24 hours and then quenched in room temperature water. Ten milligram solder spheres were produced from the bulk solder spheres by reflowing in a glass dish with RMA flux. DSC analysis was performed on the solder spheres to measure onset temperature, T_o, at a heating rate of 10°C per minute. The onset temperature is defined by the intersection of a line tangent to the point of greatest heat flow and a line connecting points at the beginning and end of the phase change event.

Copper-clad FR-4 coupons were used to evaluate solder surface wetting. A process temperature of 240°C was chosen because it is approximately 20°C above the T_o of over 90% of the alloys. Verification of the FR-4 surface temperature process maximum of 240°C was determined by soldering a thermocouple to a sample substrate with a high temperature solder (95% Pb, 5% Sn). A parametric time/temperature study was performed using a sample coupon to determine both the time delay and the surface steady state temperature for various preset hot plate temperatures. It was found that 240°C was achieved at a hot plate temperature of 270°C. Insulative properties of the FR-4 board do not allow the surface temperature to exceed the process temperature of 240°C throughout the duration of the experiment.

An FR-4 coupon was lightly fluxed with a 50 vol.% (equal parts by volume) mixture of isopropyl alcohol and rosin-based mildly activated (RMA) flux and placed on a hot plate. When the coupon reached the appropriate temperature, the coupon was slightly reflowed. This caused a decrease in substrate temperature of between 5 and 10°C. The substrate was allowed to reheat to process temperature (~10 sec). A solder sphere was placed on the substrate and melted in less than four seconds. The solder drop was left on the substrate for a total of one minute and the substrate removed from the hot plate and allowed to cool to room temperature. A total of 124

soldered samples were made in this manner. On the as-received substrates, two soldered samples were produced for each of the 42 solder alloys (21 Sn/Ag and 21 Sn/Cu). On the roughened substrates, two samples were produced for Sn/Ag alloys 1 to 20. Terminal area of spread and contact angle measurements were made with a video analysis system. Contact angle measurements were performed on the as-received substrates only.

The rough surfaces for the current work were produced using the FeCl₃/HCl etchant. The etchant was formulated by mixing a 50 vol.% HCl stock solution with 253 g FeCl₃ per liter of stock solution. Samples were rinsed in ethanol and deionized water prior to immersion in the etchant bath. Samples were etched for 75 seconds and rinsed in dilute HCl and deionized water.

Non-contact profilometry was used to measure the roughness of the etched surfaces and map their topography. The instrument, manufactured by WYKO Corp., uses a white light interferometer source to measure the degree of fringe modulation or coherence. The system is capable of profiling surfaces with root-mean-square roughness ranging from 1 Å to over 20 µm and with steps over 100 µm. Surface area, arithmetic average, root-mean-square, and maximum peak-to-valley roughness measurements are typical outputs available with this technology. ASME 846.1 describes quantitative parameters used to characterize surfaces from measured profiles (ASME, 1992). Parameters are typically profile-amplitude sensitive, profile-wavelength sensitive, or sensitive to both amplitude and wavelength.

Baseline roughness measurements were made on the as-received test coupons before conducting the etching experiments. Similar measurements were performed after etching. The measurement area was approximately 58 µm x 77 µm. The copper-clad FR-4 coupons used in this study were sectioned from conventionally fabricated PWB materials. The test coupon consisted of a 3/8" diameter copper pad patterned on a 1" X 1/2" rectangular piece of PWB substrate. The nominal Cu thickness was 17 µm (0.5 oz. Cu). The substrate was a single-sided, 0.060" (1.52 mm) thick, epoxy resin/fiberglass-reinforced laminate (FR-4) board. The test coupons were sectioned from the same BGATV used in previous studies (Hosking, et al., 1996; Hosking, et al., 1996).

Table II. Compositions of the Sn/Ag based low-lead solder alloys (balance Sn).

Alloy #	wt.% Ag	wt.% Pb	wt.% In	Alloy #	wt.% Ag	wt.% Pb	wt.% In	Alloy #	wt.% Ag	wt.% Pb	wt.% In
1	3.50	0.00	0.00	8	3.29	2.00	4.00	15	3.22	8.00	0.00
2	3.43	0.00	2.00	9	3.29	4.00	2.00	16	3.15	0.00	10.00
3	3.43	2.00	0.00	10	3.29	6.00	0.00	17	3.15	2.00	8.00
4	3.36	0.00	4.00	11	3.22	0.00	8.00	18	3.15	4.00	6.00
5	3.36	2.00	2.00	12	3.22	2.00	6.00	19	3.15	6.00	4.00
6	3.36	4.00	0.00	13	3.22	4.00	4.00	20	3.15	8.00	2.00
7	3.29	0.00	6.00	14	3.22	6.00	2.00	21	3.15	10.00	0.00

Table III. Compositions of the Sn/Cu based low-lead solder alloys (balance Sn).

Alloy #	wt.% Cu	wt.% Pb	wt.% In	Alloy #	wt.% Cu	wt.% Pb	wt.% In	Alloy #	wt.% Cu	wt.% Pb	wt.% In
1	0.90	0.00	0.00	8	0.85	2.00	4.00	15	0.83	8.00	0.00
2	0.88	0.00	2.00	9	0.85	4.00	2.00	16	0.81	0.00	10.00
3	0.88	2.00	0.00	10	0.85	6.00	0.00	17	0.81	2.00	8.00
4	0.86	0.00	4.00	11	0.83	0.00	8.00	18	0.81	4.00	6.00
5	0.86	2.00	2.00	12	0.83	2.00	6.00	19	0.81	6.00	4.00
6	0.86	4.00	0.00	13	0.83	4.00	4.00	20	0.81	8.00	2.00
7	0.85	0.00	6.00	14	0.83	6.00	2.00	21	0.81	10.00	0.00

RESULTS & DISCUSSION

Onset Temperature

The onset temperature, T_0 , is used as a measure of the melting temperature of an alloy. Only a single DSC measurement is made for each of the forty-two alloys. Each of the Sn/Ag and Sn/Cu alloys that contained Pb exhibit evidence of the Sn/Pb eutectic reaction at approximately 183°C. The DSC traces also show that the onset temperatures of the experimental Sn/Ag and Sn/Cu eutectic compositions are very close to the onset temperatures of the true eutectic compositions. The eutectic compositions from this experiment have onset temperatures of 223°C and 228°C for Sn/Ag and Sn/Cu, respectively. The addition of Pb to both the Sn/Ag and Sn/Cu binary eutectic systems provides a significant decrease in T_0 . This effect is clearly seen in Figure 3 and Figure 4. Although most of these low-lead alloys do not exhibit onset temperatures under 200°C, a number of them are just over this desired limit and a few from the Sn/Ag system do provide onset temperatures below 200°C. The alloys exhibiting temperatures below 200°C compare favorably to Sn/Pb eutectic solder with a eutectic temperature of 183°C. The addition of In and Pb to the base eutectic systems provide an almost identical drop in T_0 (about 30°C) for both systems.

Comparing the alloys with only lead and indium additions and ignoring the mixed alloys in the center of the composition triangle, it can be seen that the Sn/Ag system gives better results overall and that lead decreases T_0 slightly more than indium. These trends can be seen by comparing the results in Figure 3 and Figure 4. This may be simply due to the fact that the Sn/Ag eutectic has a lower eutectic temperature than Sn/Cu and that indium has a lower melting temperature than lead (157°C versus 327°C). If a lower T_0 is the desired solder property, then the Sn/Ag eutectic based alloys will give slightly better results than the Sn/Cu system. The alloys inside the composition triangle follow the general trend that onset temperature decreases with increasing total concentration of Pb and In. The Sn/Ag and Sn/Cu systems attain minimum onset temperatures of 195° and 200°C, respectively, at 4 wt.% In and 6 wt.% Pb. Clearly, this is an optimum mixture of Pb and In in the two eutectic systems, within the composition studied, to produce a minimum T_0 .

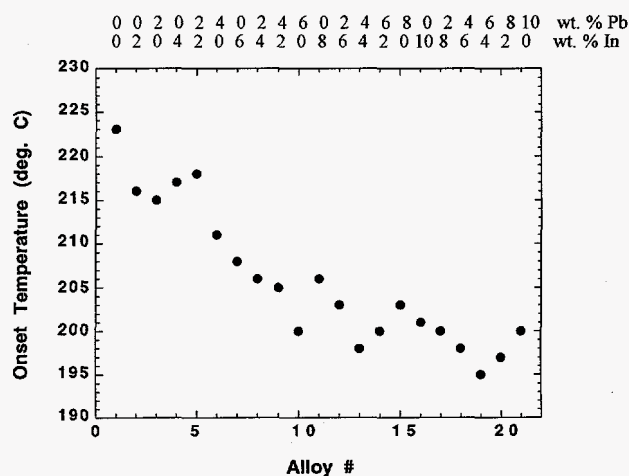


Figure 3. Measured onset temperatures of the low-Pb Sn/Ag eutectic alloys. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

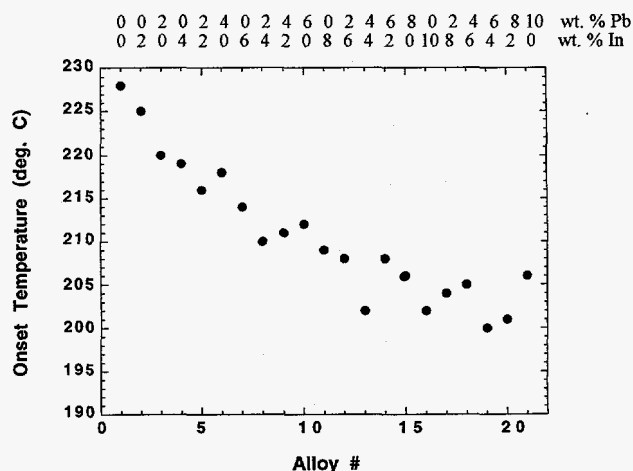


Figure 4. Measured onset temperatures of the low-Pb Sn/Cu eutectic alloys. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

Contact Angle

Contact angle, θ , was measured after the solder had reached quasi-equilibrium (no visible motion of the wetting line for at least 45 seconds) and cooled to room temperature. A quasi-equilibrium state is defined because it is difficult to determine when complete thermodynamic equilibrium has been achieved since slow solder spreading can persist for long periods of time. Solders near the Sn/Pb eutectic composition typically produce contact angles of about 5 to 15° depending on temperature and flux type. The cosine of the contact angle is the important thermodynamic quantity defined by Young's equation and thus should be the compared quantity (Murray and Darvell, 1990). Plots of $\cos(\theta)$ for the low-Pb solder alloys are given in Figure 5 and Figure 6. These single data points are obtained from the average of 16 measurements (eight per sessile drop from two repetitions each).

$\cos(\theta)$ values cover a range from 0.78 to 0.98 for the Sn/Ag alloys and 0.78 to 0.96 for the Sn/Cu alloys. Most of the solder alloys exhibit $\cos(\theta)$ values that are considered good to very good (>0.87 to >0.97 , respectively, which correspond to $<30^\circ$ and $<15^\circ$) with less than half of the total alloys exhibiting values of $\cos(\theta) < 0.87$. It is evident that the addition of Pb and In to the two binary eutectic alloys significantly increases the value of $\cos(\theta)$. Comparing the data, one sees that alloys along the Pb ternary leg (alloys 1, 3, 6, 10, 15, 21) produce larger $\cos(\theta)$ values than most of the other alloy combinations.

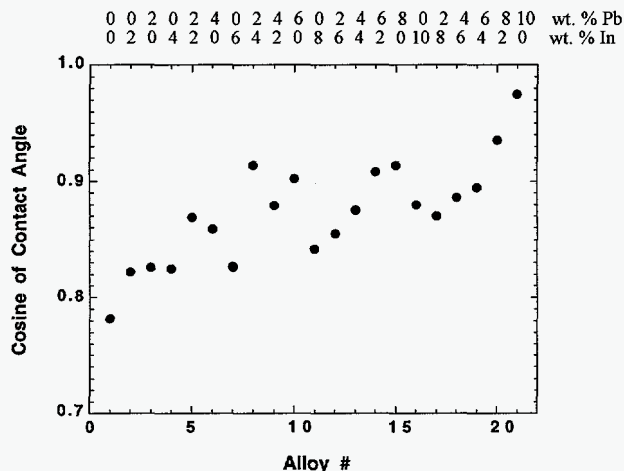


Figure 5. Cosine of the measured contact angles of the low-Pb Sn/Ag eutectic alloys on as-received substrates. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

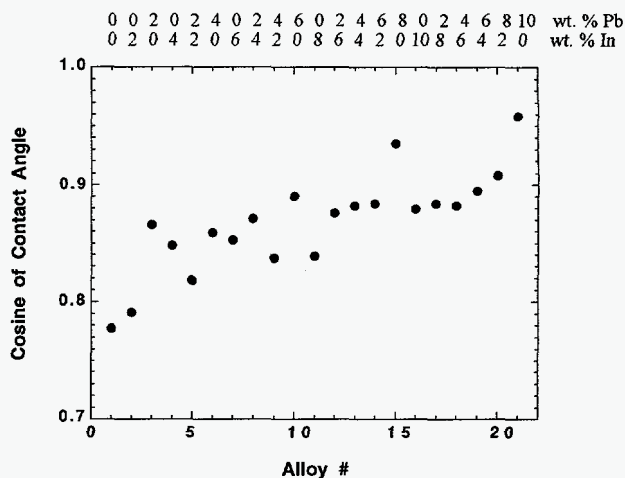


Figure 6. Cosine of the measured contact angles of the low-Pb Sn/Cu eutectic alloys on as-received substrates. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

Terminal Area of Spread

Terminal area of spread measurements were taken after the specimens had come to quasi-equilibrium and cooled to room temperature. The terminal area of spread, A_T , is the planar area of the substrate covered by the sessile drop. A solder that spreads more with a fixed volume is considered favorable and is said to exhibit better solderability. A typical A_T for Sn/Pb eutectic solder is $\sim 19 \text{ mm}^2$. On the as-received substrates, the Sn/Ag alloys exhibited a maximum A_T of 17.3 mm^2 and a minimum of 5.7 mm^2 , whereas the upper and lower limits for the Sn/Cu alloys were 10.3 mm^2 and 5.2 mm^2 , respectively. A_T data on these as-received substrates is shown in Figure 7 and Figure 8. The data points are the average of two measurements on each of the solder alloys.

Along the Pb ternary leg (alloys 1, 3, 6, 10, 15, 21) there is less than a 50% increase in A_T for either the Sn/Ag or Sn/Cu until the Pb content reaches approximately 8 wt.%. Up to this point, there is a slight but steady increase in A_T that does not extend beyond 9 mm^2 . At higher levels of Pb, A_T continues to increase for the Sn/Ag system while the Sn/Cu system plateaus at around 10 mm^2 at 8 wt.% Pb. The increase in area of spread obtained from the alloys with addition of In only or the mixed Pb/In alloys are of minor significance, though an argument might be made for a general trend that A_T increases slightly with increasing total concentration of Pb and In. Although In produces a reasonable decrease in T_0 and θ of a given alloy, it has a very small effect on A_T . As observed with onset temperatures and contact angles, the area of spread numbers for the Sn/Ag system are slightly better than the Sn/Cu system with the same level of Pb addition. Again, comparing the effects of additions of only Pb or In to the system, one can see that the results are generally very similar, however, the Sn/Ag solder at 10 wt.% Pb shows more pronounced spreading than the corresponding Sn/Cu solder.

Since the Sn/Ag system performed slightly better than the Sn/Cu system with the same level of Pb addition, rough surfaces were explored using the Sn/Ag system only. The goal was to use engineered rough surfaces to raise the A_T for the very low-Pb and no-Pb alloys (alloys 1 to 20) to values approaching as-received alloy 21 (10 wt.% Pb). To this end, 40 etched substrates (2 trials each of 20 alloys) were prepared and A_T measurements again performed. On these roughened substrates, Sn/Ag alloys 1 to 20 exhibited a maximum area of spread of 75.1 mm² and a minimum of 12.5 mm². The A_T data on these roughened substrates are shown in Figure 9. The data points are the average of two measurements on each of the solder alloys. The A_T data on the roughened substrates are again shown in Figure 10 for comparison with the as-received Sn/Ag alloy 21 data.

Figures 9 and 10 show that the A_T values are greatly enhanced on the roughened surfaces. The spreading behavior of many of the members of the roughened alloy set 1 to 20 greatly exceed the spreading of alloy 21 on as-received substrates. Representative scanning electron micrographs of the two surfaces, as-received and roughened, are shown in Figure 11. Figure 12 displays representative three-dimensional optical images of as-received and roughened surfaces.

An in-depth analysis of wetting trends on the roughened substrates is complicated by the rather large range of spreading values between trials. Once again, however, A_T generally increases with Pb content along the Pb ternary leg (alloys 1, 3, 6, 10, 15). Although the exact role of Pb and In content in the spreading behavior of the alloys on rough surfaces is inconclusive due to the large variation in behavior between trials, it is clear that spreading is improved by rough surfaces. Without exception, the 40 roughened coupons exhibited enhanced spreading over their as-received counterparts. Of particular interest, several of the roughened substrate no-lead alloys (1, 2, 7, 11) have spreading values that exceed the baseline 10 wt.% Pb as-received substrate.

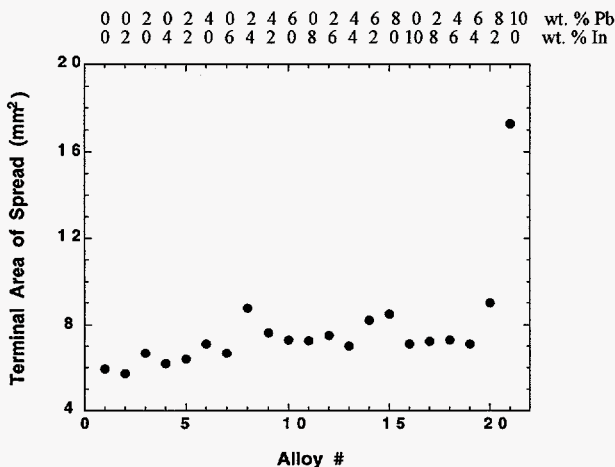


Figure 7. Measured terminal areas of spread for the low-Pb Sn/Ag eutectic alloys on as-received substrates. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

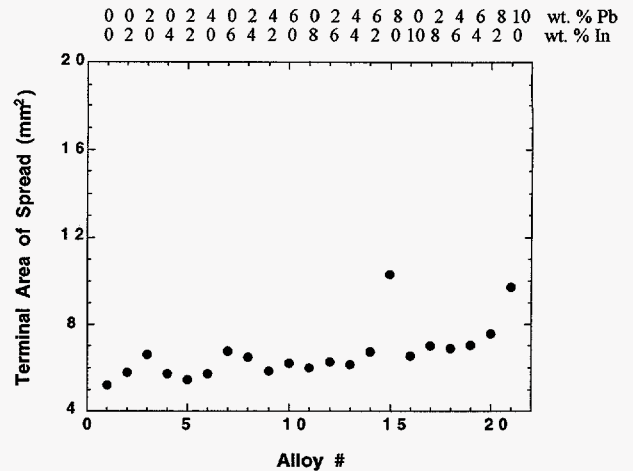


Figure 8. Measured terminal areas of spread for the low-Pb Sn/Cu eutectic alloys on as-received substrates. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

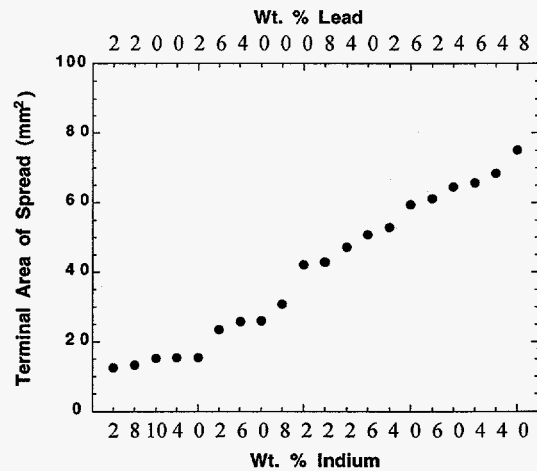


Figure 9. Measured terminal areas of spread for the low-Pb Sn/Ag eutectic alloys on roughened substrates. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

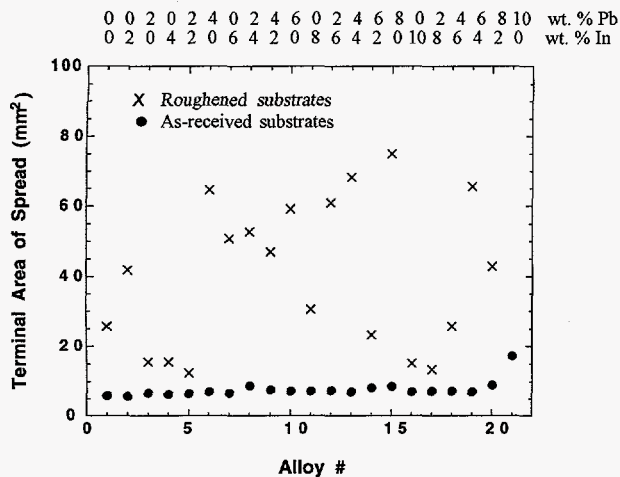


Figure 10. Measured terminal areas of spread for the low-Pb Sn/Ag eutectic alloys on as-received and roughened substrates. Solder alloy compositions are the binary eutectic with the indicated additions of Pb and In.

Title: EL Baseline - FR4

Note: 2 x 40X Mag. (unetched)

3D Plot

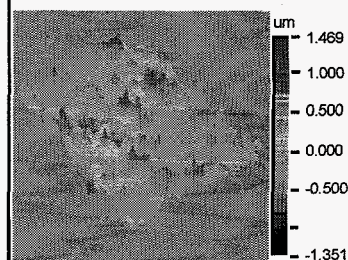
Date: 02/12/96
 Time: 12:38:15
 Mag: 81.3 X
 Size: 368 X 238
 Sampling: 0.21 um
 Mode: VSI

Surface Stats:
 Rq: 363.93 nm
 Ra: 292.47 nm
 Rt: 2.82 um

Terms Removed:
 Tilt

Filtering: None
 Restore: No
 Ref Sub: No

Surface Data



Title: BGA FH75(253) - line

Note: 2 x 40X Mag.

3D Plot

Date: 12/15/95
 Time: 14:44:09
 Mag: 81.3 X
 Size: 368 X 238
 Sampling: 0.21 um
 Mode: VSI

Surface Stats:
 Rq: 660.67 nm
 Ra: 507.25 nm
 Rt: 7.90 um

Terms Removed:
 Tilt

Filtering: None
 Restore: No
 Ref Sub: No

Surface Data

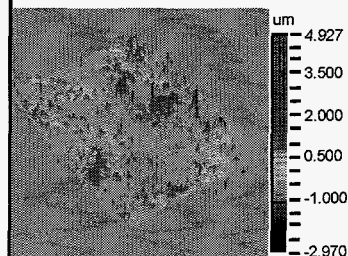
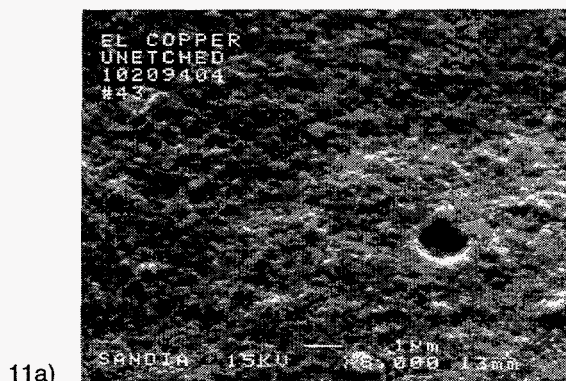
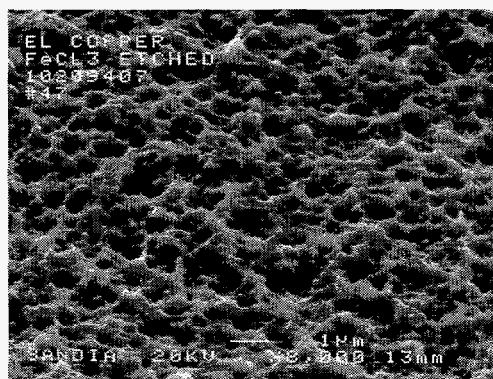


Figure 12. Mapped surface topography of a) Unetched baseline b) FeCl₃/HCl etched (253 g/liter, 75 sec).



11a)



11b)

Figure 11. SEM's of copper surfaces at high magnification. Micrographs at 8000X magnification with 1 μm fiduciary marks. a) As-received (i.e. unetched) b) FeCl₃/HCl etched

SUMMARY & CONCLUSIONS

These results show that it is possible to reduce lead use without sacrificing solderability. A 67% reduction in the amount of lead in a solder alloy can still provide acceptable solderability, when compared to Sn/Pb eutectic solder, with no more than a 20°C increase in onset temperature. As demonstrated in this investigation, if further reductions in lead content are desired, rough surfaces may be engineered to provide the required level of wettability. Physically rougher surfaces were produced through chemical etching of FR-4 copper. Noticeable improvements in wettability/solderability of very low-lead Sn/Ag solder alloys were observed on these roughened substrates. These results demonstrate the importance of surface roughness on solder flow.

Both the Sn/Ag and Sn/Cu systems follow the same trends of decreased onset temperature and contact angle and increased area of spread with higher levels of In and Pb. The Sn/Ag based alloys with over 8 wt.% Pb more closely match the solderability characteristics of Sn/Pb eutectic, while the

Sn/Cu based alloys provide a slightly higher melting point with decreased solderability. Clearly, the most beneficial effects, decreased contact angle and increased area of spread, come from the addition of 8 to 10 wt.% Pb. However, alloys with less than the prescribed 8 to 10 wt.% Pb can provide excellent wetting through the use of engineered rough surfaces.

This investigation clearly demonstrates the importance of roughness on solder wettability, regardless of the method used to create a distinctive surface topography. The desire for low-lead and possibly no-lead solder alloys has made this issue particularly timely. Controlling the solder wetting and flow response by engineering the physical properties of the surface should yield more robust processes. Another important outcome of the study was the recognition of the significance of the baseline surface conditions prior to solder processing. For example, surface roughness is typically ignored as a process variable at the board level. This is usually not a problem with "older" PWB technology, since the processing windows are larger. With more advanced technology, however, the materials and processing limits have shrunk and are less forgiving. As a consequence, the roughness parameter can no longer be treated as a constant. The essential point is to clearly understand the significant effect that roughness can have on solder spreading.

ACKNOWLEDGMENTS

The authors wish to thank Terry Gulinger and Darrel Frear for their critical review of the manuscript. The authors also acknowledge Paul Vianco for technical insight into solder fundamentals. The authors acknowledge Ed O'Toole, Cindy Hernandez, and Gary Zender for the solder alloy spreading experiments, BGATV wetting experiments, and SEM, respectively. We thank Dipesh Goel for assistance with SEM photos. Technical comments from the NCMS PWB Surface Finishes Team were also valuable. This work was performed under CRADA No. 01030B at Sandia National Laboratories supported by the U.S. Department of Energy under contract DE-AC04-94AL85000. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy.

REFERENCES

- Lee, N. C., Slattery, J. A., Sovinsky, J. R., Artaki, I., and Vianco, P. T., 1994, Sandia National Laboratories Publication SAND94-1542C.
- Miller, C. M., Anderson, I. E., and Smith, J. F., 1994, *J. Electronic Materials*, Vol. 23, No. 7, pp. 595-601.
- McCormack, M., Jin, S., and Chen, H. S., 1994, *J. Electronic Materials*, Vol. 23, No. 7, pp. 687-690.
- McCormack, M. and Jin, S., 1994, *J. Electronic Materials*, Vol. 23, No. 7, pp. 635-640.
- Hondros, E. D. and McLean, D., 1974, *Philos. Mag. A*, Vol. 29, No. 4, pp. 771-795.
- Konetzki, R. A., Zhang, M. X., Sluzewski, D. A., and Chang, Y. A., 1990, *J. Elect. Packaging*, Vol. 112, pp. 175-178.
- Wenzel, R. N., 1936, *Ind. Eng. Chem.*, **28**, 988.
- Parker, E. R. and Smoluchowski, R., 1994, *Trans. ASM*, **35**, 362.
- Shuttleworth, R. and Bailey, G. L. J., 1948, *Disc. Faraday Soc.*, **3**, 16.
- Goryunov, Y. V., 1964, *Russ. Chem. Rev.*, **33**, 467.
- Johnson, R. E. and Dettre, R. H., 1964, *Contact Angle, Wettability, and Adhesion* (edited by R. F. Gould). Advances in Chemistry Series 43, American Chemical Soc., Wash., D.C.
- Hitchcock, S. J., Carroll, N. T., and Nicholas, M. J., 1981, *J. Mater. Sci.*, **16**, 714.
- Nicholas, M. G. and Crispin, R. M., 1986, *J. Mater. Sci.*, **21**, 522.
- Cazabat, A. M. and Cohen Stuart, M. A., 1986, *J. Phys. Chem.*, **90**, 5845.
- Romero, L. and Yost, F. G., Submitted 1995, *J. Fluid Mech.*
- Yost, F.G., Michael, J. R., and Eisenmann, E. T., 1995, *Acta Metall. Mater.*, **43**, 299.
- Tench, D. M. and Anderson, D. P., 1993, "Uniform Solder Coating on Roughened Substrate", Rockwell International Corp., US Patent 5178965.
- Nelson, N. J., 1984, "Process and Structure for Etching Copper", PSI Star Inc., US Patent 4451327.
- King, E. B., 1972, "Continuous Redox Process for Dissolving Copper from Substrates", Southern California Chemical Co. Inc., US Patent 3705061.
- Tokyo Shibaura Dairi KK, 1984, "Diffusion Bonding of Copper to Ceramic Substrates for Semiconductor Module", European Patent 115158-A2.
- Ling, J. and Albright, C. E., 1984, "The Influence of Atmospheric Contamination on Copper to Copper Ultrasonic Cleaning", *Proceedings of 34th Electronics Components Conference, CHMT/EIA Conference*, New Orleans, LA, IEEE, 84CH2030-5, 209-218.
- Kauczor, E., 1978, "Preparation of Test Pieces for Macroscopic Examination", *Praktiker*, **30**, 5 82-84.
- Moore, J. T., 1976, "Continuous Ammoniacal Etches", *Electroplat. Met. Finish.*, **29(5)**, 6-8.
- Beyer, S. J. and Lukes, R. M., 1974, "Regeneration of Ferric Chloride Copper Etching Solutions", General Electric Co., US Patent 3794571.
- Douglas, M. A., 1992, "Copper Dry Etch Process Using Organic and Amine Radicals", Texas Instruments, US Patent 5100499.
- Caruana, A. and Rainer, H., 1991, "Process for Etching Work Pieces Using Copper Tetramine Complex", DuPont E. I. de Nemours and Co., US Patent 5076885.
- Brock, A. J. and Pryor, M. J., 1990, "Process for Etching Copper Base Materials Using Peroxydisulfuric Acid and Halide", Olin Corp., US Patent 4973380.
- Martens, P. A. and Nelson, N. J., 1990, "Copper Etching Process and Product with Controlled Nitrous Acid Reaction", PSI Star Inc., US Patent 4927700.
- Barnett, D. J., Battey, J. F., and Nelson, N. J., 1988, "Copper Etching Process and Product Using Liquid Etchant", PSI Star Inc., US Patent 4767662.
- Nelson, N. J., 1986, "Copper Etching Process and Solution", PSI Star Inc., US Patent 4632727.
- McGowan, W. M., 1985, "Solution and Process for Treating Copper and Copper Alloys", Lea Manuf. Co., US Patent 4510018.
- Katsutoshi, I. and Akira, M., 1976, "Etching Solutions for Copper and Copper Alloys", Tokai Electrochemical Co., US Patent 3939089 and US Patent 3936332.
- Winfried, E. and Alfred, R., 1975, "Process and Apparatus for Etching Copper and Copper Alloys", Hoellmueller Hans Maschinenbau, US Patent 3880685.
- Nelson, N. J., 1984, "Process for Etching an Aluminum-Copper Alloy with Chlorine", PSI Star Inc., US Patent 4468284.
- Chiang, J., 1974, "Process of Etching Copper Circuits", FMC Corp., US Patent 3844857 and US Patent 3837945.
- Stevenson, J. O., Hosking, F. M., Gulinger, T. R., Yost, F. G., and Sorensen, N. R., 1995, "Inspection of Chemically Roughened Copper Surfaces...", *Conf. Proc. 28th Annual International Metallographic Society Convention*, Albuquerque, NM.
- Hosking, F. M., Stevenson, J. O., and Yost, F. G., Submitted 1996, "Capillary Solder Flow on Chemically Roughened PWB Surfaces", *Journal of Electronic Packaging and Production*.
- Hosking, F. M., Stevenson, J. O., and Hernandez, C. L., 1996, "Parametric Study on the Solderability of Etched PWB Copper", *Conf. Proc. Surface Mount International Conference* (Surface Mount Technology Association), San Jose, CA.
- Fradkov, V. E., 1994, *Scripta Metall. et Mat.*, **30(12)**, 1599-1603.
- ASME 846.1 85, 1992, American Society of Mechanical Engineers.
- Murray, M. D. and Darvell, B. W., 1990, *J. Phys. D: Appl. Phys.*, Vol. 23, pp. 1150-1155.