The Development of a Non-Silver-Based Conductive Adhesive for Use in Flip-Switch Technology

Table of Contents

List of Illustrations and Tables

2.0 List of Parameters, Abbreviations, and Symbols

Notation	*Explanation*
η	Viscosity (Nsm^2 or cPs; $10^{-3}Nsm^2=1cPs$)
R	Electrical resistance (Ohms)
R_s	Sample resistance (Ohms)
R_c	Contact resistance (Ohms)
Ω	Ohm, Unit of electrical resistance
W_f	Weight fraction (%)
V_f	Volume fraction (%)
L	Length (cm)
t	Thickness (cm)
A_c	Cross sectional area (thickness·width, cm^2)
$\rho_e(A)$	Electrical resistivity (Ω-cm) for A
$\sigma_e(A)$	Electrical conductivity - tensor and scalar (Siemens/cm) for A
$\rho_m(A)$	Mass density for A (g/cm^3)
V	Electric potential difference (volts, V)
I	Electric current (amps, A)
J, J	Electric Current density - vector and magnitude ($amps/cm^2$)
E, E	Electric Field - vector and magnitude (volts/cm)
g	Acceleration of gravity (9.81 m/s^2)
v_t	Terminal velocity of falling sphere (m/s)
SEM	Scanning Electron Microscopy
RCPS	Random Close-Packed Spheres
oz.	Ounce, British (28.4g)

4.x Resistivity Measurement of Zn, Ag Conductive Epoxy Samples

Samples for resistivity measurements were sectioned to a precise geometry (see figure 4.y), measured with a micrometer. The surface "skin" layer, present only for the Ag-based sample, was removed with methanol prior to sectioning. After sectioning, the linear four-terminal resistances were measured for each sample across the length (see Appendix 1). The resistance of such a section is given by $R = \rho_e L / A_c$, where ρ_e is the electrical resistivity, L is the length, and A_c is the cross-sectional area of the sample (note $A_c = W \cdot t$), which was then used to calculate the resistivity.
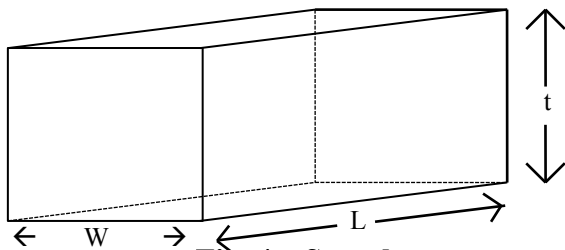
Fig. 4.y Sample geometry used for resistivity measurements.

Lead placement was at the extremes of the length to avoid current distribution effects in the resistance measurement. In addition, metal bars of Cu and Al were measured to gauge the accuracy of the technique; resistivities were measured to within 25-50% of quoted values (Iwasa, p. 394). Only two samples were sufficiently conductive to allow resistivity measurements (see table 4.1).

Metal Data (10μm flake)			Epoxy Data (all Epotek)	Resistivity (ρ_e, Ω-cm)
Type	V_f	W_f	Type	4-terminal

Ag[*]	71%	24%	301	$\sim 10^5 \pm 50\%$
Zn	72%	34%	301-2	$\sim 10^4 \pm 25\%$

Table 4.1: Samples used for resistivity measurements. [*] Section measured was the section mixed with methanol.

Similar measurements were attempted for a sample with 60% volume fraction Cu powder; however, the resistance was greater than the measurable range, 20MΩ. From this, however, we can deduce that the resistivity is *at least* greater than $\sim 10^7 \Omega$-cm.

5.0 Discussion

5.1 Epoxy Viscosity and Mix Kinetics

Cu-based samples:

Analysis of mixing and post-cure cross-sectional analysis showed that for the Cu based samples, a large degree of settling occurred, as well as the formation of a thin "skin" of Cu particles on the surface of the sample. For a simple viscous liquid, the settling properties of solid spheres is primarily a function of viscosity (η) and particle radius (r). (Poirier and Geiger, p. 71) SEM analysis of the starting Cu powders used showed a non-negligible distribution of sizes for both the 3-10μm and 10-20μm powder, with largely spherical particles. Further, some sub-micron powder was present in both powders. To illustrate the problems that arise with settling, we will develop a simple model for estimating the settling distance vs. time of the Cu spheres.

First, we assume that the viscosity of the epoxy is largely constant for the time regime of interest; this limits us to the early-cure stages where little cross-linking has occurred. Second, since most samples were cured overnight at room temperature, we will assume a 24 hour cure

cycle, and that the early-cure stage is approximately 2-4 hours long (*i.e.* viscosity changes little for the first 2-4 hours). Falling spheres in a viscous liquid (viscosity η, mass density $\rho_m(epoxy)$) under only the influence of gravity achieve a terminal velocity of (Poirier and Geiger, p. 71)

$$V_t = 2R^2[\rho_m(epoxy)-\rho_m(Cu)]/9\eta \qquad\qquad (9.1)$$

for laminar flow. Since distance settled $=V_t*$ time, we see that for the most viscous epoxy used (~5000 cPs) 20μm spheres will settle more than 1mm in only 15 minutes – well before the epoxy has set sufficiently to trap the spheres. However, for 3μm spheres, it takes nearly 10 hours for the same distance of settling – long after the epoxy has set and trapped the spheres. For 10μm spheres, which are present in both powders, the time to settle ~1mm is roughly 1 hour, presumably before the epoxy has cured sufficiently. Thus, this crude model indicates that, for either powder used, some of the spheres will settle rapidly, before the epoxy cures, and some will not settle noticeably before setting occurs due to the presence of a range of particle sizes. This large degree of settling explains not only the large amount of sediment found in the samples (due to the larger particles) but also the "skin" found on the samples (due to the very small particles). Note that for the lower viscosity epoxies, the settling time is shorter.

The above model is quite crude; however, it is meant to deal only with the early-cure stages of the epoxy, and is used only to show *qualitatively* that particle segregation is significant for spherical particles, especially with a range of particle sizes. However, this indicates that for a true suspension of Cu spheres, the epoxy pre-cure viscosity must be prohibitively high as to make mixing quite difficult. It is also interesting to note that even the Cu-rich portion on the bottom of

the sample was not conductive, even though the volume fraction was presumably quite high there. Possible reasons for this will be discussed presently.

Ag- and Zn-based samples:

For the Ag and Zn samples, 10μm flake particles were used. No settling was observed in the cross-sectional analysis or during mixing. However, in both cases, a "skin" was formed at the top surface of the sample. For these samples, the above model does not apply, as it applies only to spheres. Qualitatively, we may state that the skin must be formed by smaller flakes, which settle more slowly. The presence of small flakes, as well as a distribution of other sizes, is supported by the SEM micrographs of the Zn and Ag flake. Further, since no significant degree of settling was observed, this indicates that the flakes tend to settle more slowly than their spherical counterparts. This is quite obvious to anyone who has ever tossed coins and pebbles into a fountain; the shape anisotropy of the coin (similar to a flake) allows it to sink much more slowly than the pebble (somewhat spherical). Thus, a more homogenous suspension is formed for flakes than for similarly sized spheres.

5.2 Contact Resistance and Volume Fraction

Figure 5.1 shows metal volume fraction vs. weight fraction for the three metals used (assuming that ρ_m(epoxy)=1.4g/cm^3), with experimental data points included. For the Cu samples, no conductive samples were obtained with as high as 60% volume fraction Cu. For Ag and Zn samples, some conductivity was observed at as low as 25-30% volume fraction. Like the settling characteristics, this is also attributable to the shape anisotropy of the Ag and Zn flake

compared with the Cu spherical powder. Some insight as to why the geometrical effects evidently play such a large role can be gained by considering the random close packing of spheres. For the random close-packed spheres the average solid volume fraction of V_f=63%, with an average of 8.5 contacts per sphere, and an average separation of 2-2.3R. (Allen and Thomas, p. **) From fig. 5.1, the Cu sample with highest volume fraction (~60%) is quite close to the RCPS limit, and yet did not conduct. Looking at the optical micrographs (fig. X.x) obtained, it is easy to see that this is attributable to the small number and small area of physical contacts between spheres. The SEM micrographs show a large number of spheres are quite close together, but most spheres or groups of spheres have space between them. Since these samples are just under the RCPS limit, the average separation can be expected to be >2R . For micron-sized particles, even a gap of 0.1R is too little to allow current flow between adjacent spheres. Further, even for touching spheres, the area of contact is quite small , likely << $(0.5\mu m)^2$. With such a small contact area, the resistivity would be quite large *even if the RCPS limit was reached.* Thus, the spherical powder used is unsuitable for forming low-resistive conductive paths in a non-conductive matrix, even near the RCPS limit. As discussed in the background, the presence of a distribution of sizes of spheres alters the packing fraction and allows for more contacts; however, this does not change the nature of the sphere contact.

For the Ag and Zn flake, however, slightly conductive samples were obtained for 25-30% volume fractions, when Cu samples of similar volume fraction and higher did not conduct. This also is largely due to the shape anisotropy of the flakes, which enhances connectivity between flakes. As a simple comparison, imagine two boxes, one with coins and one with paper clips, both with similar area fractions covering the box bottom. Now shake the boxes, and observe the

contact between particles in the two boxes. Coins have only point contact, with a maximum of about 6 contacts per coin. The paper clips, however, can connect along much longer surfaces and form a pseudo-networked structure with edge-edge, surface-surface, and edge-surface contacts. This is similar to the flake vs. sphere contact in the epoxy-metal composites; spheres have about 8.5 contacts per sphere, but only point contacts (which are highly resistive). The flakes, however, can form much larger contact areas and form a conductive path much easier (and with much lower resistance) at lower volume fractions. Flakes tend to conglomerate to form a pseudo-network of filaments, while the spheres tend to approach the RCPS-type structure with increasing volume fraction, which is inherently less conductive due to point-only contact. Thus, the critical volume fraction for conductivity is inherently lower for flakes. For spheres, it appears that even near RCPS or "cement" type packing conductivity is not achieved, suggesting that the contact resistance cannot be overcome in that system even when near the highest possible volume fraction. The possible presence of an oxide or sulfide layer on the particle surface may cause further problems, however, and this will be discussed shortly.
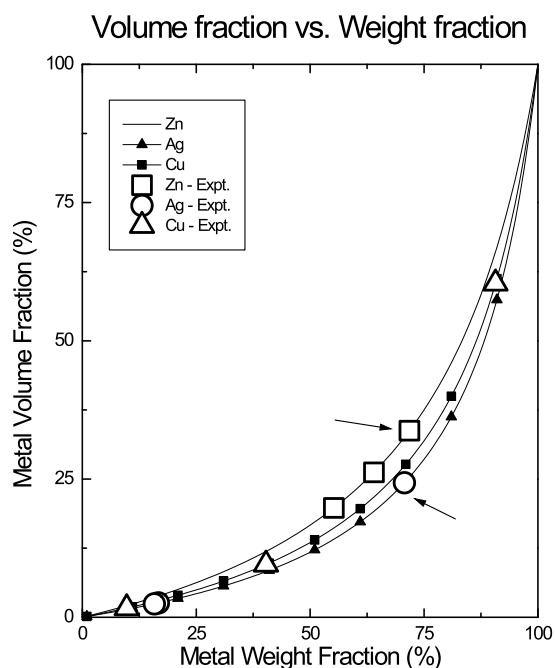
Fig. 5.1: Metal volume fraction vs. weight fraction. Arrows refer to conductive samples used for resistivity measurements.

5.3 Effects of oxide or sulfide layers on contact resistance.

Copper spherical powder was ruled out after initial work when even very high volume fractions (up to 60% Cu) were non-conductive. This was attributed mainly to contact resistance between spheres (see 5.2); however, contact resistance between spheres has two primary components. First, as discussed in section 5.2, there is the obvious geometrical problem of tangential or near-tangential contact, which creates a high contact resistance. Second, however, there is the metal surface chemistry. For Cu, it is known that the exposure of Cu metal to air tends to form an oxide or sulfide layer, while Zn tends to form primarily an oxide layer. For Ag, however, exposure to air tends to form a sulfide layer (Ag_2S) – commonly known as "silver

tarnish." It is also known that for Zn, only a surface layer of oxide is formed. (Dean, 6.69-6.106; Daintith, 59-60,198, 237)

The presence or absence of these oxide or sulfide layers can significantly change the contact resistance between metal particles. For flakes or spheres, a highly insulating oxide or sulfide layer on the particle surface will inhibit current flow. If sufficiently thick, an insulating layer could inhibit current flow altogether. Thus, determining the surface chemistry of the metal particles to be used is of extreme importance. For one of the samples, the Cu powder washed in a weak citric acid solution to remove any oxide. The resulting solution after washing showed a light blue color, and after several days (when much of the solution had evaporated) a blue precipitate was found at the bottom of the beaker. This is characteristic of nearly all Cu(II) compounds, which tend to be blue in solution (Daintith, 59-60). Both CuO and $CuSO_4$, the most likely surface layers to be formed, are blue in solution and form blue crystals on precipitation. CuO_2, another likely candidate, can be ruled out due to its water insolubility. Since citric acid is used to etch the Cu oxides, the presence of a sulfate layer (or at least sulfate in the solution) can be ruled out. Further, it is known that the primary corrosion mechanism of pure Cu in air is the oxide (simply due to the relative abundance of oxygen). Thus, it can be determined that the *primary* surface layer on the Cu powder was CuO. The amount of precipitate which was formed after drying the citric acid-copper oxide solution was estimated at no less than 10% of the total volume of Cu powder weighed; thus, a large amount of oxide was formed on the powder surface. This is most likely due simply to air exposure; the laser-atomization process is done in an inert atmosphere, which should not have caused any excessive oxide layer to form during processing.

The excessive amount of oxide found on the Cu powder, as well as its spherical shape, can easily explain the absence of conductivity even in Cu-epoxy samples up to V_f=60%. CuO is a highly insulating compound; even a few tens of nanometers of such an oxide can effectively prevent the flow of current at the low current levels relevant to this system (Wolf, pp. 1-10). This also effectively rules out using Cu flake instead of spherical powder. Given the much greater surface area (and therefore reactivity) of Cu flake vs. Cu powder, any problems related to surface oxide would be magnified greatly.

The Ag flake, the only commonly used metal particle in present conductive adhesives, has a much smaller problem with surface layers, as expected. Silver tends to form Ag_2S in air, known as "silver tarnish." Silver oxide is typically only formed by reaction with ozone or other more reactive oxygen species, not in air. Though this sulfide surface layer readily forms on Ag in air, especially when in the highly reactive flake form, the kinetics of the surface are much slower than for most oxide surface layers (as anyone who owns silverware knows; thick tarnish buildup forms only over a relatively long period of time when compared to typical oxides). This is in part due simply to the relative abundance of oxygen when compared to sulfur or sulfur-containing compounds in the atmosphere. Thus, the contact resistance of Ag particle will be significantly different than for Cu particles, since the primary surface layer is the somewhat conductive sulfide and not the oxide (though the conductivity is still quite high). Combining the higher conductivity of Ag_2S with its slower kinetics of formation, it is not unreasonable that the surface contact with Ag flake should be much better than for even Cu flake. When geometrical considerations taken into account, the Ag flake is far superior to Cu flake or Cu spherical powder.

As for Zn flake, similar problems to Cu powder are expected. Zn flake is highly reactive, especially in the micron-size range. ZnO is, however, semiconducting (as is ZnS; Y.M. Chiang *et al*, 226) while CuO is insulating. Further, since the depth of ZnO formation is limited to the surface (Daintith, 237) the contact resistance with Zn flake should not be significantly different than with Ag, possibly better. This is somewhat borne out by the fact that Zn-epoxy samples were conductive at V_f=33%. However, a Zn-based sample did not conduct at V_f=26%, while a Ag-based sample conducted at V_f=25%. This is most likely caused by four factors: 1) the resistivity of pure Zn is approximately three times that of Ag, 2) the exact details of the surface chemistry (*e.g.* thickness of surface layer, conductivity) are not known at this time, 3) the conductivity of the 25% volume fraction Ag sample was one order of magnitude higher than the 33% volume fraction Zn sample, suggesting that an Ag sample at 33% volume fraction may have similar conductivity, and 4) the volume fractions are similar enough that experimental differences in mixing and the use of different epoxies in the two cases makes it uncertain whether these points lie outside the experimental error. At the present time, however, Zn looks like an attractive alternative to Ag in many respects.

5.4 Conductivity measurements

The conductivity measurements on bulk sections of the Zn and Ag based samples indicate that the critical volume fraction for *noticeable* conductivity (*i.e.* in the 10^6 Ω-cm range with the equipment used) is in the 25-35% metal volume fraction range for flake. As mentioned, no significantly conducting Cu spherical powder samples were found, even near 60% Cu volume fraction. The bulk conductivity of the two Ag and Zn samples measured, however, is quite high.

Compared with competing products (in the 10^{-3}-10^{-4} Ω-cm range), with similar volume fractions of metal flake, the conductivity is 7-8 orders of magnitude higher. This can be explained primarily by mixing techniques, and to a lesser degree, porosity.

The presence of a thin "skin" of metal particles has already been discussed (section 5.1); even in flake based samples, some segregation was observed. Cross sectional analysis of the conductive samples (optically) indicates a largely homogeneous mixture, even at the surface. This is most likely due to the larger volume fraction of metal flake, which slows further the segregation and settling process (due to increased viscosity and sphere "clumping" and collision). However, a section of the Ag-based sample was mixed with methanol prior to curing. The section mixed with methanol showed a much better surface finish (smooth, uniform surface) compared to the section without methanol. The section with methanol also had a thin surface "skin" approximately 0.1mm thick which was highly conductive, with the bulk appearing largely homogeneous (from the cross sectional analysis). This surface layer evidently had a much higher conductivity than the bulk, even when compared to the bulk region with methanol.

The presence of the surface layer in the methanol-mixed region can be explained by the simple settling model presented in section 5.1. The methanol lowered the viscosity of the epoxy during the early cure stages, allowing some of the smaller flakes to "float" at the top of the mix, resulting in a higher volume fraction of Ag flake there. Also, the presence of the methanol during mixing and the resulting lower viscosity allowed more homogeneous mixing throughout the sample, shown by the lower porosity, evidenced during cross-sectional analysis. Thus, the methanol-mixed region showed generally more homogeneous mixing on the whole, but also exhibited a thin "skin" of Ag flakes not observed in the region mixed without methanol. This is

further shown by the fact that the section mixed without methanol was essentially non-conductive, on the surface or in the bulk, while the section with methanol was conductive in the bulk and even more so on the surface.

The effect of the methanol on the porosity, homogeneity, and conductivity reveals the importance of pre-cure mixing on the cured conductive adhesive. Epotek 410E, when mixed, has the consistency of a "creamy paste" whereas the mixed samples prepared in this work without methanol exhibited some clumping, and were quite viscous. The samples mixed with methanol appeared "creamy" quite similar to the 410E and were generally much more homogeneous. However, the 410E did not show a conductive "skin" like the methanol mixed samples, and were much more conductive throughout. By use of a different solvent or by varying the amount of solvent mixed in, the mixing characteristics of the 410 could likely be duplicated. This is based on an analysis of the conductive "skin" formed on the methanol-mixed Ag flake sample, presented below.

Resistance measurements of the conductive skin, based on a two terminal technique (see Appendix 1) indicated a much lower resistivity in that section of the sample. This portion of the sample was removed with methanol before sectioning in order to obtain a bulk measurement. However, an unwashed portion of the methanol-mixed region was subsequently measured by a two-terminal technique. No sectioning was necessary, since preliminary estimates of the "skin" conductivity placed it several orders of magnitude below that of the bulk. Thus, only a vanishing amount of current is expected to flow through the bulk region, and the resistance measured should be confined almost entirely to the surface. Surface layer thickness was estimated at

0.1mm. Resitances of approximately 0.1 ohm[1] or less were measured for a 1mm X 0.2mm area of the skin. This gives a resistivity of roughly 2mΩ-cm, nearly that of the 410E (quoted as 0.2 mΩ-cm) and similar to other products (*e.g.* SPI silver epoxy, quoted as 0.5-7 mΩ-cm). Though the measurement performed was quite crude, it indicates that the surface resistivity for the methanol-mixed Ag sample was several orders of magnitude below the bulk resistivity, and possibly quite close to competing products.

Based on surface and bulk resistivity measurements, if the methanol-aided mixing process could be perfected, a bulk conductivity similar to the surface conductivity (and that of the Epotek and SPI products) could be achieved with Ag based, and quite possibly Zn based conductive adhesives. Further, the methanol-mixing process seems to aid in reducing porosity.

5.4 Strength

Since sufficiently conducting samples were not prepared, the strength of the resulting product was not assessed. Epotek 410E quotes a lap shear strength (Al to Al) of 1000psi at 20°C. This is not far from the quoted strength of the non-conductive (*i.e.* no metal filler) Epotek epoxies. Thus, it seems that the metal particles used do not aid the mechanical properties significantly in this case. Furthermore, for the desired applications (*e.g.* flip-switch technology) strength should be more than adequate for any of the epoxies used, with or without metal filler (see Appendix 2 for epoxy data sheets).

The issue of strength brings to light other possible applications, however. Many steel-filled epoxies are now on the market (*e.g.* Fas-Weld, QuikSteel), designed primarily for

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[1] The lower limit of measurement with the equipment used was roughly 0.1Ω. The reading of 0.1Ω measured thus gives only an upper limit.

applications where welding or soldering is impractical or difficult (such as in automobiles and underwater applications). Though these epoxies are non-conductive, many of the issues addressed in this work translate directly to these products (such as mixing, porosity, and segregation). See Appendix 3 for "QuickSteel" property list.

5.5 Review of Cost Analysis

Based on preliminary results with Zn based conductive epoxy samples and an analysis of the surface layer chemistry with Zn, Zn flake appears to be an attractive alternative to Ag based conductive epoxies. Zn flake is about 1/20 the cost per weight of Ag flake, which means large savings in materials costs. For the Epotek 410E, it was determined that the weight fraction Ag was 70%. Alfa Aesar quotes Ag flake (10μm) at $1400/kg (or $1.4/g); assuming this cost, for 1 oz of Ag based epoxy (28.4g), the cost of Ag alone is $27.8 per oz. Since the total cost of the 410E is $46 per oz, roughly $17 per oz is attributable to processing, *etc*. Using Zn in place of Ag at the same volume fraction (23.7%), which corresponds to a 61%wt for Zn, the materials cost of Zn is only $0.91 per oz. Thus, based on *materials cost alone*, a competing Zn based product could be as much as ~$25 per oz cheaper, assuming similar specifications could be met with the Zn based product (which is not clear at this time). This analysis does not consider the reduced cost of buying the metal flake in bulk, which would possibly alter the savings estimate. Also, processing costs are assumed to be similar in both cases.

However, despite the enormous savings which could be had using Zn in place of Ag, there are other costs to consider. Ag flake, if inhaled, can cause serious liver damage. This requires numerous safety protocols be followed in the manufacture of Ag based epoxies. However, Zn

powder is combustible, even explosive, for small (micron sized) flake suspended in air[2]. This creates many hazards, requiring that adequate safety measures be taken, at no small cost. Whether the cost of these safety measures would offset any financial gain from using Zn powder is not immediately assessable, but must be considered for Zn to be considered a competing filler for conductive epoxies. Still, this problem is encountered in many areas of processing and manufacturing (some materials similarly combustible include CoffeeMate® non-dairy coffee creamer, Al powder, grain dust, and flour – all common products), and is surmountable. The safety issue should not be taken lightly, but it may not be a fatal point for Zn use.[3]

5.6 Miscellaneous

Vacuum curing:

Several samples were cured in a vacuum oven, some at elevated temperature for a few hours, and one at room temperature overnight. Vacuum curing was conceived in order to reduce porosity by outgassing the sample. During the early cure stages, vacuum outgassing would presumably remove trapped gasses and reduce the resulting porosity. However, problems resulted. First, the samples cured at elevated temperatures showed an anomalous degree of porosity; the sample essentially formed an epoxy foam. This is attributed to the relatively slow outgassing rate of the epoxy mixture. Crosslinking occurred too early in the outgassing stage, and trapped gas could not escape due to the increased viscosity, resulting in a foam structure. Second, the sample cured overnight at room temperature did in fact show reduced porosity, evidenced by cross-sectional analysis. In that case, degassing of the sample is mostly complete before the cure

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[2] The Zn flake is explosive when in air; a mass of powder in a jar is not explosive, only the "aerosol" portion.

[3] After all, Zn flake is not nitroglycerin; if adequate safety measures are taken, Zn flake is harmless as an explosive.

progresses very far, and the foaming does not take place. Though relatively few trials with vacuum curing were done, this illustrates some potential problems with vacuum curing. Careful outgassing must be performed before curing has progressed too far. Curing at room temperature overnight seems to help reduce porosity, but to cure at elevated temperatures the cure must not proceed to quickly. Degassing before heating may be the most reasonable, but in any case there is a compromise between the slow degassing and the cure kinetics to even lower porosity to the level achievable by curing in atmosphere. Still, if controlled properly, vacuum curing can reduce porosity of the conductive epoxies.

As for the impact of porosity, it is obvious that porosity will increase the resistivity of these adhesives and also reduce strength. However, based on a cross sectional analysis of samples prepared, porosity is mainly a mixing issue; if properly mixed, porosity can be made almost negligible. Vacuum curing will further reduce remaining porosity, but is unlikely to be viable in most commercial applications of these products.

Processing and Prototype Design

6.1 Processing Design

The process leading to a conductive adhesive based on suspended metal particles is rather simple in principle. The final prototypes fabricated consisted of an epoxy matrix of Epotek 301 or 301-2 (see Appendix 2 for properties) in which Ag flake ($10\mu m$) or Zn flake (-325 mesh; ~1-$44\mu m$) was suspended. Epoxy was weighed and mixed, then metal flake was mixed in and hand stirred to a homogenous suspension. Samples of 1-5g epoxy were typically used. The epoxy-metal suspensions spread on a glass plate or in a petri dish and then cured either 1) in air, 24+ hours, 2) in vacuum, $\sim25°C$, and 3) in vacuum, $65°C$. Preparations were made for curing in plexiglass molds, whose design has previously been described. Details of specific processes are described in section 3.

6.2 Prototype design

Samples for inital conductivity characterization by a two-terminal technique (by testing resistance of a bulk section of the sample; see Appendix 1) were cured either on glass plates or in petri dishes, and were not sectioned. The samples (3) used for four-terminal resistivity measurements (see Appendix 1) were sectioned from those samples which exhibited some degree of conductivity. Sectioning was performed with a razor blade, to dimensions of approximately 0.5mm x 1mm x 2mm. Exact dimensions were determined in each case with a micrometer. The four-terminal resistivity measurements are described in Appendix 1, and the sample geometry in section 4.

7.0 Conclusions

7.1 Cu as a conductive filler

Based on a falling-sphere model of the Cu spherical powder in uncured epoxy and corrosion characteristics of Cu, it must be ruled out as a conductive filler. Even near the RCPS limit of sphere packing, and with a wide range of different sizes of spheres, Cu based samples showed no significant conductivity. The surface layer formed in air is primarily a non-conductive oxide, essentially ruling out good conductive contact between flakes. Further, Cu flake is approximately as expensive as Ag flake; thus, nothing can be gained by using Cu even in flake form.

7.2 Zn as a conductive filler

On the other hand, Zn is readily available in flake form, and is a small fraction of the cost of Ag flake. Zn tends to form a semiconducting oxide in air, which lends itself to reasonable good contact resistance between flakes. Though the resistivity of Zn is approximately three times higher than Cu or Ag, it is expected that contact resistance will largely dominate the resistivity of the resulting conductive adhesive, such that this difference will not be a fatal point for Zn. Conducting samples were prepared using Zn, and with improved mixing techniques (possibly using methanol or another solvent), it may be able to compete with Ag on a strictly performance basis with drastic cost savings. However, Zn in flake form is rather volatile – it is combustible and somewhat explosive when suspended in air. For any process using Zn flake, adequate safety measures must be undertaken during processing (not simply a one-time investment in safety

equipment). Though Ag flake is relatively toxic to humans, that is more easily surmounted. If Zn flake based products could be shown to have adequate performance, further cost analysis based on the inclusion of adequate safety equipment must be performed to see if the potential profits from switching to Zn could be realized. Essentially, it must be assessed if it is possible 1) to make a competing product with comparable volume resistivity, and 2) to ensure that the safety costs of handling Zn flake are not in excess of the gains made by using Zn powder for Zn based conductive adhesives to be a viable competing product.

7.3 Existing Ag based products

Ag flake has been found to a good, perhaps the best, choice for a conductive adhesive based on 1) Ag is readily available in flake form, 2) Ag does not form a seriously detrimental surface layer to prohibit good contact resistance, and 3) pure Ag has a very low bulk resistivity. In fact, the only possible detriments for using Ag are its high cost and its relative toxicity to humans in flake form. Though the toxicity creates some additional safety requirements for processing, such problems are easily surmounted (*e.g.* use of respirators, gloves, and other safety gear as well as fume hoods) and would be necessary for any metal flake used. The high cost of Ag, estimated to account for well more than 50% of the total product cost (as much as $28 of the $46 per oz can be attributed to Ag alone), is a serious detriment, especially if it is to be used in large scale processing and fabrication like flip-chip technology. However, at the current time, it is not clear whether Zn (the only likely alternative) based conductive adhesives can achieve the low resistivities that the Ag-based products can (as low as $10^{-4}\Omega$-cm), or whether added safety-related costs would prohibit the use of Zn.

7.4 Processing

The main issue yet to be solved with processing is that of mixing. Methanol (or solvent) aided mixing increases homogeneity, decreases porosity, and thus decreases resistivity. However, the solvent-aided mixing has yet to be perfected. Good conductivity in samples prepared thusly has been confined to the surface. Bulk conductivity was enhanced, but inadequately. Porosity was indeed improved, and the resulting surface finish was greatly improved. It is believed that perfecting the solvent-aided mixing process can yield epoxies with good conductivity not confined to the surface, but the process parameters need to be further investigated (such as proportion of solvent to epoxy used, and evaporation characteristics of solvent during epoxy cure).

Vacuum curing of the epoxy also presents a somewhat attractive method of reducing porosity. Critical factors include degassing time, curing time, and curing temperature. Whether or not vacuum curing is viable for commercial use of these products must be determined on a situation by situation basis, but it is unlikely to be viable in most cases.

Appendix 1: Conductivity, Resistivity and Four-Terminal Resistance Measurements[4]

The movement of electric charges, resulting in an electric current, is driven by an electric field (E). In most materials, the induced current density (J, typically in A/cm^2) is given by

$$\mathbf{J}=\sigma_e\mathbf{E} \tag{A1}$$

where σ_e is the conductivity of the sample. The value of the conductivity depends on the material in question intrinsically as well as extrinsic factors, such as microstructure, impurities, *etc*. The conductivity also generally depends on parameters such as temperature, pressure, magnetic field, *etc*., but it does not in general depend on the electric field. Given that **J** and **E** are vectors, mathematically σ_e must be a second-rank tensor. Physically, this means that **J** is not necessarily in the direction of **E**; *i.e.* a material may have an anisotropic conductivity. In the present case, since the samples in question are presumed to be homogenous mixtures of metal particles and epoxy, the conduction can be assumed to be isotropic. In that case, σ can be viewed as a scalar quantity, and also we need only consider the magnitudes of **J** and **E**. (Allen and Thomas; Purcell)

Equ. (A1) is an expression of Ohm's law, an empirical generalization derived from experiment, not a general theorem. In any material, for sufficiently large electric field, Ohm's law will fail; in some materials, "non-Ohmic" behavior can occur at relatively low fields. However, in the present case (and in a wide range of materials) it is sufficient to consider eqn. (A1) to be

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[4] Unreferenced sections of this appendix are based on one of the author's (P.L.) experience in this area.

essentially correct, as well as considering σ_e to be a scalar quantity. Taking a sample as in fig. 4.y, with electric field (magnitude E) applied along the length, we have a current density (magnitude J) induced in the same direction along the length. Relating J and E to the measurable quantities I (current) and V (voltage), we have $J=I/A_c$, and $E=V/L$. Using eqn. (A1), and its counterpart $R=V/I$, we arrive at $\sigma_e=L/A_cR$. This calculation involves an implicit assumption, *viz.* uniform current density. (Purcell) This assumption may not always be justified for conductive adhesives, since the metal particles tend to form narrow conductive channels; however, macroscopically there should be little deviation given the relative size of the channels and the samples used.

Quite often, the resistivity (ρ_e) is used in place of the scalar conductivity; it is given by $\rho_e=\sigma_e^{-1}$. Thus, the resistivity of a sample with the geometry of fig. 4.y has

$$\rho_e=A_cR/L. \tag{A2}$$

In practice, measuring the resistance of a sample accurately presents some difficulties. One difficulty encountered is that of the leads. Measuring voltage and current of a sample requires that conductive probes, or leads, be attached to the sample in question. Leads must be of a highly conductive material (often Au or Ag for precision applications), and must be attached as to minimize current distribution effects. In the case of fig. 4.y, this could be accomplished by plating the ends of the sample with a highly conductive material and attaching probes to the ends. If the leads are highly resistive, or their placement encourages non-uniform current distribution, inaccurate results may be measured. In addition, the contact between the leads and the sample may be non-negligible cause inaccuracies (by inducing further voltage drop). Thus, the leads

must make good contact to the sample, they must have a high conductivity relative to the sample, and they must be strategically placed.

One way of surmounting these problems is to use a four-terminal resistance measurement. The simplest possible resistance measurement consists of two probes. A current is passed between the two leads, and the voltage induced measured across the same two leads. Obviously, this would include any contact resistance as well as the sample resistance (fig. A1).
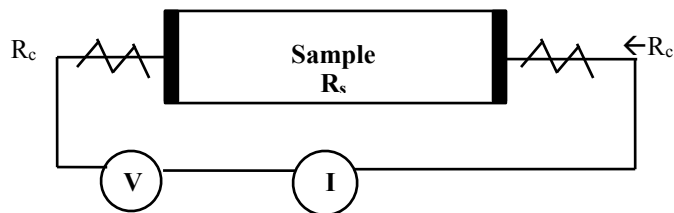

Figure A1: Two terminal measurement geometry.

Thus, for the two-terminal geometry depicted in fig. A1, the measured resistance will be R_s+2R_c. If contact resistance (R_c) is sufficiently small, then the difference between the measured resistance and the sample resistance (R_s) is also small. However, the contact resistance can often dominate the measurement, for high resistance samples as well as low resistance samples. In this case, the contact resistance must be eliminated, which can be accomplished *via* a four-terminal resistance measurement.

The four-terminal technique essentially utilizes the high impedance of a voltmeter to exclude contact resistance. Instead of using one lead on either end of the sample, two leads are attached on each side; one for current and one for voltage. The current is passed through the sample *via* the current leads, and the voltage measured by *separate* voltage leads (see fig. A2). Since the voltmeter has a high impedance (often $>>10^6\Omega$), essentially zero current flows through

it. Thus, the voltage drop measured by the voltmeter is only that of the sample, effectively excluding contact resistance.
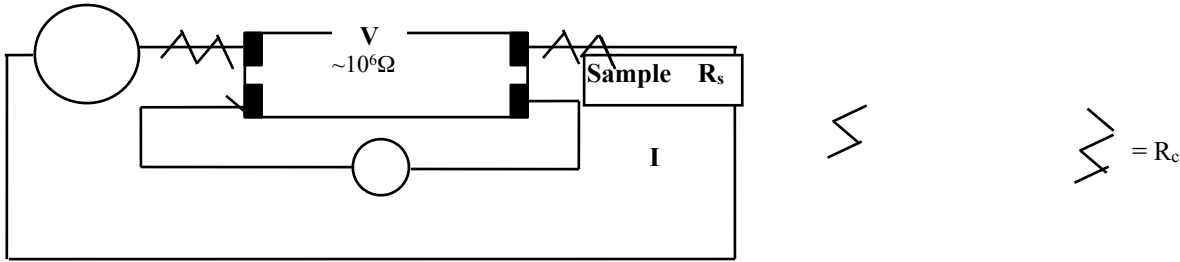

Figure A2: Four-terminal van der Pauw geometry

The four-terminal technique is widely used whenever precise measurements are required. The geometry shown above, where the leads are placed in a roughly square arrangement, is known as the van der Pauw method. Using this method requires that additional corrections be made for current distribution effects; the resistivity is not simply given by eqn (A2). An alternative geometry is shown below, where leads are placed linearly.
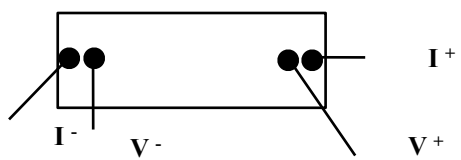
Figure A3: Four terminal linear geometry.

In the present case, the linear geometry was used to simplify post-measurement analysis.

Appendix 2: Epoxy Data Sheets.

Appendix 3: Quick-Steel Data Sheet

Data for CarGo QuickSteel (P.O. Box 1567, Conroe, Tx, 77305. (409) 539-1555)

Volume Resistivity	$5 \times 10^{15}\Omega$-cm
Dielectric Strength `	400 volts/mil @ 0.12m
Density	1.9 g/cm^3
Compression strength	18 000 psi
Tensile Strength	6 000 psi
Modulus of Elasticity	6×10^5 psi
Shear Strength	800 psi
Izod Impact	0.03 fr. Lb./in a notch
Hardness (Shore D)	85
Maximum Temperature	500°F

Two parts in one epoxy. Twist off desired amount, knead to uniform color. Hardening begins within 2 minutes. Can be drilled, filed, tapped, machined, etc. after 1 hour. For underwater use, hold forcefully onto substrate until adhesion begins to take effect.

Appendix 4: Mathcad Worksheets used for various calculations.

Simple model of sphere settling in Cu based conductive adhesives

$i := 1 .. 5$

1=Ag, 2=Cu, 3=Zn, 4=epoxy alone, 5=Epotek 410E; relevant materials

$$\rho_1 := 10.5 \frac{gm}{cm^3}$$

$$\rho_2 := 8.96 \frac{gm}{cm^3}$$

$$\rho_3 := 7 \cdot \frac{gm}{cm^3}$$

$$\rho_4 := 1.4 \frac{gm}{cm^3}$$

densities of materials 1-4 in g/cm^3
Wm = weight of metal mixed in; We = weight of epoxy mixed in, pt a+b

$wf := 0.01, 0.02 .. 1$

metal weight fraction measured; wf= wm/(we+wm)

$\eta := 0.1 \cdot newton \cdot sec \cdot m^2, 0.2 \cdot newton \cdot sec \cdot m^2 .. 5 \cdot newton \cdot sec \cdot m^2$

pre-cure mixed viscosity in Nms^2

$R := 1 \cdot 10^{-6} \cdot m, 2 \cdot 10^{-6} \cdot m .. 50 \cdot 10^{-6} \cdot m$

spherical particle radius in m

$g := 9.81 \cdot m \cdot sec^{-2}$

acceleration of gravity

$$Vt(R, i, \eta) := \frac{2 \cdot R^2 \cdot \left(\rho_4 - \rho_i\right) \cdot g}{9 \cdot \eta}$$

Assuming constant viscosity, distance terminal velocity
of settling spheres

$t := 0 \cdot min, 5 \cdot min .. 4 \cdot hr$

$d(R, i, \eta, t) := Vt(R, i, \eta) \cdot t$

Lets say viscosity is largely unchanged over the first 4 hours of a 24 hour cure; after that, viscosity is large enough to prevent settling. If we want particles to settle less than a distance d . . .

$d\left(20 \cdot 10^{-6} \cdot m, 2, 5 \cdot newton \cdot sec \cdot m^{-2}, 15 \cdot min\right) = -1.187 \cdot 10^{-3} \cdot m$

$d\left(3 \cdot 10^{-6} \cdot m, 2, 5 \cdot newton \cdot sec \cdot m^{-2}, 10 \cdot hr\right) = -1.068 \cdot 10^{-3} \cdot m$

so, even for a epoxy with viscosity of 5000 cPs, the 20 micron spheres settle more than 1mm in only 15min! For the 3 micron spheres, it takes nearly 10 hours for the same amount of settling.

given distribution of sizes, this leads to a huge degree of segregation!

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