Reliability Studies of an Isotropic Electrically Conductive Adhesive

James E. Morris (j.e.morris@ieee.org)
Department of Electrical and Computer Engineering, Portland State University, Oregon, USA
Falk Anderssohn (fanderssohn@hotmail.com)
Department of Electrical Engineering, Dresden University of Technology, Germany
Santosh Kudtarkar (santoshkudtarkar@hotmail.com)
Department of Electrical Engineering, State University of New York at Binghamton, U.S.A.
Enrico Loos (enrico.loos@physik.tu-chemnitz.de)
Department of Physics, Chemnitz University of Technology, Germany

Abstract

ICA reliability continues to be a source of concern for widespread practical implementations in commercial products. In addition, there is still much to be understood in the basic principles of how such materials function. This paper includes contributions in both areas, in further understanding of ICA size effects, in the interpretation of the beneficial effects of vacuum treatments before curing, with additional drop test data, and with critical comments on common electrical test techniques.

Introduction

The mainstream response to the no-Pb requirements emerging from worldwide environmental concerns has been the development of no-Pb solder alloys. However, for flip-chips, the significantly higher process temperatures exacerbate the thermomechanical stress problems that already pose the greatest problem for flip-chip reliability. Electrically conductive adhesives (ECAs) are viable alternatives, including both isotropic and anisotropic (ICAs & ACAs) [1].

Recent work in the ICA field has greatly expanded the community's understanding of both fundamental operational physics and failure modes [2-4]. In general, it is understood that electronic conduction through the two-phase metal-polymer matrix takes place by percolation along chains of metallic particles, but there is no universal conclusion with regard to the conduction mechanism between particles. The bulk resistivity of the well-cured material remains essentially stable under 85/85 testing, but contacts fail by galvanic corrosion of different contact and ICA metals. (The ICA metal is usually silver.) Thermomechanical cycling of ICA-based flip-chip interconnect shows it to be more robust than solders in this area, but lack of impact resistance remains the Achilles' heel of the technology. Mechanical adhesion and electrical conductivities of commercial materials are generally quite satisfactory, and similar to those of solders (although usually somewhat lower.)

A series of projects were undertaken to continue previous work in impact resistance [5], and the effects of vacuum on adhesion [6]. New work was begun on the demonstration of size effects in ICA contacts, on the use of silver contacts to avoid galvanic corrosion with silver loaded epoxies, and on the improvement of electrical test vehicle design to avoid current crowding. A theoretical comparison is also made of the high frequency performances of ICAs and solders.

An ICA contact pad cannot be relied upon to display the manufacturer's specified bulk resistivity. There are two opposing non-ideal effects that come into play. The widely observed layering effect at ICA surfaces will contribute to a higher effective resistivity. It is not yet determined whether this effect is due to surface tension or to squeegee drag effects, but its universality suggests the former. It is also not certain whether a similar effect occurs at the substrate surface. In addition, the resistivity of the ICA interconnect pad should decrease as the thickness decreases towards the percolation coherence length, where the meandering percolation paths begin to be intersected by the contact planes [7]. The electrical resistivity can be determined as a function of thickness if one begins with a thick contact (many times the coherence length) and successively thins it down, layer by layer.

In past work on plasma cleaning of contact pads, it was observed that adhesion was improved by exposure of the ICA to vacuum prior to curing [6]. It was obvious from visual inspection of bubble craters on the exposed surface that the effect must be correlated with out-gassing. It was postulated that out-gassing early in the curing process produces bubbles at the ICA-substrate interface, which decrease the overall adhesion strength. The initial plan was to compare bubble counts at the substrate interface for joints cured with and without the vacuum treatment.

In the course of the vacuum study, it was recognized from some initial data that spurious results were attributable to current crowding effects. This observation led to the re-design of some test structures, especially for 4-point measurements on ICA tracks on PWB circuit boards, for the galvanic corrosion experiment below.

The final application of ICA-interconnected chips will often be in high frequency digital systems. To this end, there have been several comparisons of the high frequency performances of ICAs and ACAs with solder. The general conclusion is usually that there is no significant difference, but usually the experiment is dominated by the transmission line effects anyway, and not by the ECA. Nevertheless, for ICAs one would expect that both would be controlled by skin effect at very high frequencies [7], and both would indeed be similar. A simple calculation makes the point.

Recent work has demonstrated that ICA impact resistance is limited by the mechanical loss modulus, and that conventional commercial materials cannot be expected to pass the ad hoc NMSRC drop test standard. Nevertheless, a previous study reported much better drop test data for the Ablebond 8175 ICA used here, than others had obtained [5]. The results were open to criticism, however, on the grounds that they were obtained by printing a large area of paste, and pressing the component leads down into it. (This technique is also used by other groups.) The effect is that some paste squeezes up between the leads, and can conceivably provide additional support to the leads. Leads were observed to bend, without detaching. The current experiments were intended to duplicate the earlier results, if possible, with individual pads, and also to determine whether there were any changes in the ICA resistances prior to detachment by impact failure.

Materials & Preparation

Adhesive Material: The conductive adhesive used for this research work was the isotropic conductive adhesive Ablebond 8175 manufactured by Ablestik. This is a silver-flake filled conductive adhesive with a silver content of about 70Wt%. The adhesive is thermosetting and designed as a solder replacement in microelectronic connections.

Table 1: Ablebond 8175

Property	**Values**
Viscosity @ 25°C	55,000 cps
Work Life @ 25°C	2 weeks
Cure Condition	1 hour @ 150°C
Cure Option	1/2 hour @ 175°C
Volume Resistivity	$5*10^{-4}$ ohm-cm
Glass Transition Temperature (T_g)	90°C
Coefficient of Thermal Expansion	Below T_g 55ppm/°C
	Above T_g 200ppm/°C
Thermal Conductivity	3.20W/mK@ 121°C

Curing: The curing was done in a Heller six-zone circulating hot air reflow oven with the profile of Figure 1, which includes a preheating period for out-gassing. The cure temperature and the belt speed selected for Ablebond 8175 is 178 °C @ 6 cm/min for the drop test samples, but 152°C @ 3cm/min for the others.

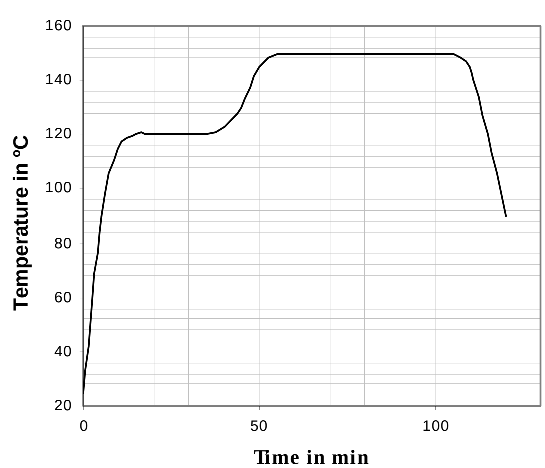

Figure 1: Temperature profile while curing

Electrical Measurements

Current Crowding: There are some special problems to be solved in setting up measurement systems for very low resistances, such as ICA interconnections. Lead resistances are often comparable, and mandate the use of 4-point or Kelvin-probe techniques. Consider the case in Figure 2(a), where the copper contact lines are actually the track on a prototyping PWB. 30μΩ was measured to the left of the ICA, and 90μΩ to the right, instead of the expected value around 50μΩ, due to the current crowding shown. The problem lies in the thickness of the copper track, which leads to track resistance comparable to or greater than the ICA resistance. The solution is to replace the PWB track with a copper strap, as shown in Figure 2(b).

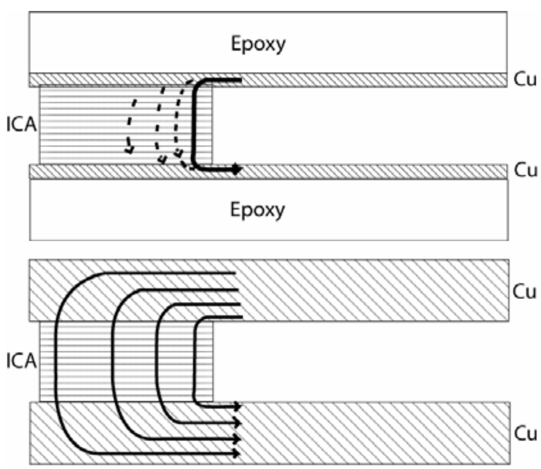

Figure 4: (a) Crowding (b)Equally distributed

Four-Point Measurements: Once again, the problem illustrated in Figure 3(a) for a 4-point measurement along an ICA track is due to the dimensions of the PWB copper line. But the issue this time is the opposite, i.e. that even the thin Cu track can short out a significant part of the ICA, due to the low (comparable) thickness of the printed ICA track. Now the voltage sense measurement across the two center electrodes will include interface potentials. The problem can be minimized (but not cured) by minimizing the sense lead/track dimensions, either thickness or width or both, as in Figure 3(b), but the cure requires the complete removal of the sense leads from the current path., as in Figure 3(c).

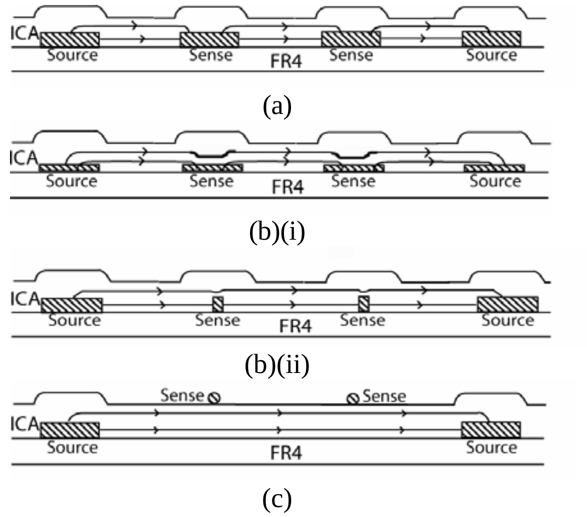

Figure 3: 4-point measurement using ICA track across proto-board current lines (a) Sense lines short ICA (b)(i) thinned contacts (b)(ii) trimmed contacts (c) Surface point contacts

High Frequency Effects: In modeling high frequency responses, it has been shown that skin effect dominates the equivalent circuit of the ICA. Current is confined to a surface depth δ at frequency f, where

$$\delta = \rho / \sqrt{\pi \mu f} \ ,$$

ρ is the dc resistivity, μ is the permeability. The skin effect resistance is then given (in Ω/square) by $R_S = \rho/\delta$, and the associated internal inductive reactance $X_{INT} = \omega L_{INT} = R_S$. The total reactance is $\omega(L_{INT} + L_{EXT})$, where L_{EXT} is typically dominant in an ICA/solder lead joint geometry.

Some assumptions must be made before the data can be applied to a given solder or ICA contact joint geometry. Assume a joint 2mm x 2mm and 100μm thick. L_{EXT} can be calculated from various approximate formulae, but scaling experimentally measured values to this geometry gives $L_{EXT} \approx 4$pH. Similarly, we can assume $\rho_{ICA} \approx 20\rho_{Ag}$ at dc. Skin effect does not become evident until the skin depth is comparable to the c/s dimensions of the sample, and until then $L_{INT} = \mu_0 / 4\pi$ (H/m). Figure 4 illustrates the variations of resistance and reactance with frequency for the solder and ICA cases, with two different assumptions for the ICA. In one (the expected) it is assumed that high frequency capacitive coupling between particles effectively includes them all in one percolating cluster, so the overall dimensions are used. In the other, a single percolation path about 10μm square is assumed. The point is that there is little difference expected between the ICA and solder cases with respect to high frequency behavior.

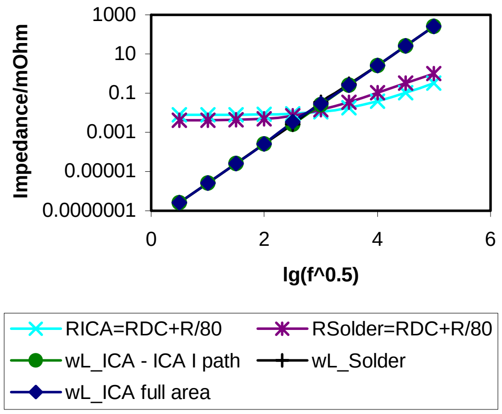

Figure 4: Comparison of R_s and X versus frequency for solder and ICA joints

Size Effects on Resistivity

Objectives and Expectations: This investigation looks at the resistance as a function of the thickness of an ICA pad. The initial shape was cubic with a thickness around 100 times the maximum particle size of the silver fillers Later we will vary width and length within the same range. An important point to consider is the percolation threshold of the Ablebond 8175 and its correlation with the resistance. Starting with the initial $1mm^3$ ICA sample, the thickness is steadily reduced by polishing away the exposed surface.

For a concentration of silver fillers much higher than the percolation threshold, a trend of resistance, R(h), with pad thickness, h, similar to Figure 5 can be expected. It can be divided into three parts, which refer to the following effects as h is reduced:

- Steep drop from the initial height value, providing evidence for the assumption that the metal particles align with the surface, caused by the surface tension of the printed adhesive.
- Reduction with thickness for constant resistivity.
- Faster decrease of resistance as the percolation threshold decreases at thicknesses on the order of the coherence length.
- Possible resistivity increase at very low thickness due to alignment at the substrate.

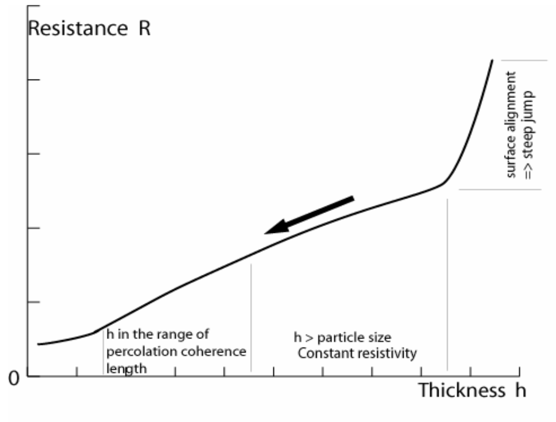

Figure 5: Anticipated variation of R(h).

Process of Sample Preparation &Assembly

The following process steps were used to prepare the samples:

- Cut Cu coated circuit board (30x25mm).
- Cut mask. to same size as the circuit board
- Punch square hole into mask. (10x10mm)
- Mask, Print and Cure ICA
- Cut the samples using a diamond saw.

Reproducible measurements require:

- 4-point measurement to eliminate contact and other resistances.
- Homogeneous current density in the ICA.

To provide these requirements the apparatus shown in Figure 6 was used, with a mercury contact, which is:

- Fluid at room temperature
- Electrically conductive
- with High surface tension
- and Low viscosity

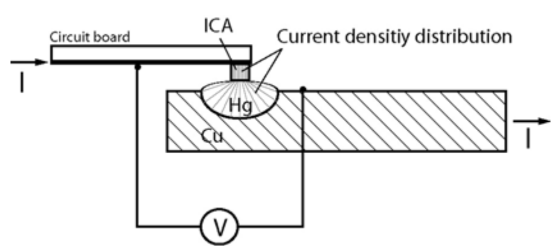

Figure 6: Measurement schematic

The geometry assures that the Hg drop is held in place. Taking into account the orders of magnitude of the resistivities of the conducting materials the geometry shown in Figure 6 can provide a nearly homogenous current distribution, because the resistivity of copper is two orders of magnitude lower than either the ICA's or mercury's.

The advantages of using mercury as a contact material are:

- Good electrical contact, and
- Hg does not wet the sample material because of its high surface tension, which makes detachment easier for the reduction of thickness.

But, there are also problems to deal with:

- Poisonous; requires working under a hood with rubber gloves and laboratory clothes.
- The Hg drop has to be renewed, or at least freed from the oxide layer that appears within the first couple of hours.

The probes are applied as shown in Figure 6. A constant current was applied and each measurement value of the voltage was recorded before decreasing the ICA thickness by abrading with fine sanding paper. The dimensions of the ICA cube were measured with a digital micrometer.

<u>Results:</u> Values are compensated for:

- Resistance of the copper of the circuit board
- Contact resistance between copper and ICA
- ICA to mercury contact resistance
- Resistance of the mercury ball
- Contact resistance Hg to Cu block

Figures 7 and 8 show the results for several single samples. Each resistance is scaled to a cross-section area of one square millimeter (Figure 9) and the resistivity was calculated (Figure 10). Figure 11 compares some curves with the unity-slope line expected for constant resistivity.

<u>Conclusions:</u> It can be seen immediately that the measured values are strongly scattered and therefore the verification of the expected effects is difficult.

The very high slope at the beginning of each sample's experiment provides clear evidence for alignment effects, despite the scatter of the measurement values. Figure 10 strongly indicates particle alignment on the substrate. The mean resistivity ($13.2x10^{-4}\Omega cm$).is twice the manufacturer's specification ($5x10^{-4}\Omega cm$).

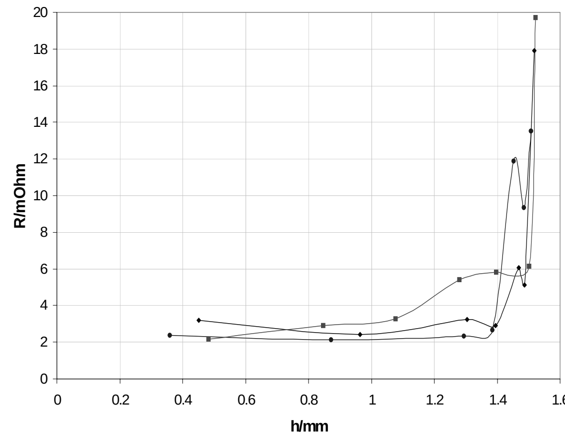

Figure 7: Sample group 1. Resistance as a function of thickness of the ICA cube. Each curve refers to a single sample.

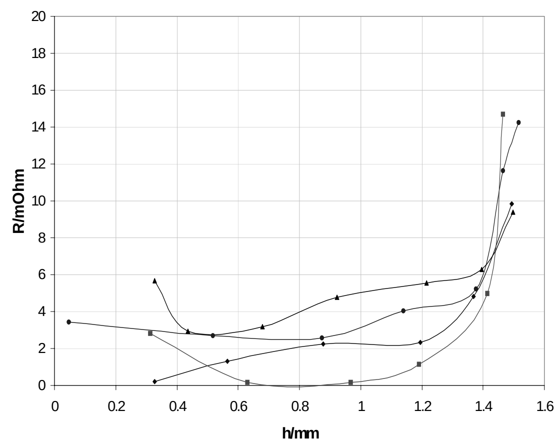

Figure 8: Sample group 2. Resistance as a function of thickness of the ICA cube. Each curve refers to a single sample.

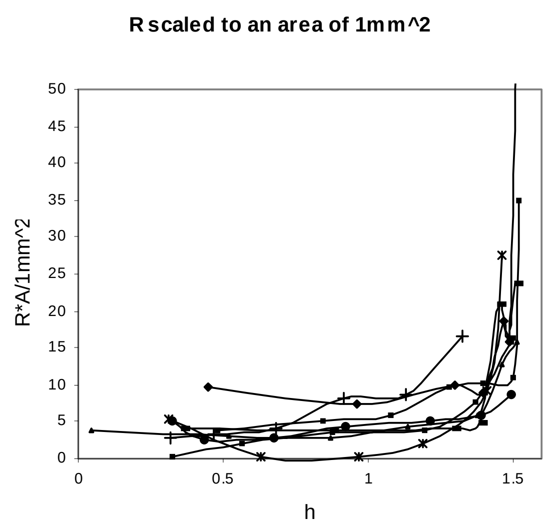

Figure 9: Resistance as a function of the thickness for all samples scaled to a cross section area of $1mm^2$.

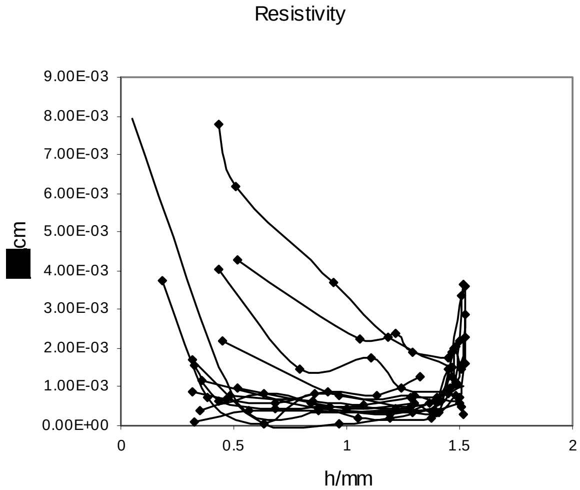

Figure 10: Resistivity as a function of the thickness.

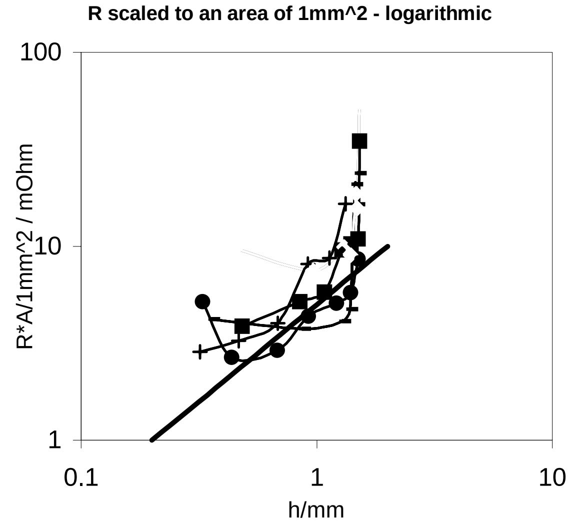

Figure 11: Resistance shown in logarithmic scale including the line of slope for constant resistivity bulk effect

Vacuum Effects

Sample Assembly & Test: Two 20x1.5cm strips of 1mm copper sheet metal were glued together by conductive adhesive in such way that there was an overlap of 1cm. The two strips were kept at a specified separation by small spacer strips in between them. These stripes were pressed together and held in place until after the curing process by a specially made clamping mechanism. After curing the sample was cut in a linear precision saw into 4mm wide pieces. These samples were then cleaned from any residual adhesive to accomplish reproducible adhesive areas. he ICA is placed between two partly overlapping parallel copper strips from solid 1mm thick copper sheet metal rather than just copper plated circuit board, since the resistivity of the copper is not negligibly small in comparison to the conductive adhesive.

For the same reason the four point measurement frequently implemented by a cross-shaped sample geometry was not used since this geometry does not guarantee even current distribution over the whole contact area due to current crowding.

The adhesive was cured for 1 hour at 150°C, without pre-heat. Half the samples were vacuum treated before curing and slicing. They were subjected to a vacuum of about 10mbar for 20 minutes. After this procedure they were treated the same way as the other samples. Measurements of all dimensions of the adhesive joints were recorded. For the width and length a micrometer screw was used. The ICA-thickness was measured optically with a CCD-camera with the appendant measurement equipment. From these values the area of the joint was calculated.

Resistance Measurement: Because of the very low resistance of the ICA-joint a standard micro-ohm-meter could not be used. Instead a digital current source with a current of 1A and a 6-digit multimeter was used. For resistance measurement the four-point method was used to eliminate influences of the contacts or the copper strips on the resistance. The current was supplied to the two protruding copper ends of the sample. The voltage drop over the ICA-joint was directly measured on each side of the joint.

Pull Test The pull test was done using a vise to hold one end of the sample and a clamp on the other end to attach the force gauge. The gauge used was a AccuForce Digital Force Gauge. The maximum value of the force (at breakage) was recorded.

Pull Test Results: For the pull test, 15-20 samples of the vacuum treated and normal sample groups with ICA layer thicknesses of about 0.6mm were used. Already during the sample manufacturing it was notable that about twice as many samples of the non-vacuum treated group broke during grinding and other steps within the manufacturing process. This first impression was confirmed by the conducted pull test with these two different sample groups.

	No vacuum	Vacuum
Average Strength	160 N	235 N
Standard Deviation	108 N	56 N

From these values can be seen that the pull test strength for the vacuum treated samples is over 40% higher than for the non-treated samples. From the standard deviation values can be seen that the variation of the strength of the joint is nearly twice as high for the untreated samples. From these results, some conclusion about the reliability and reproducibility of the joint strength can be made.

It is not absolutely sure if this difference in pull test strength is related to bubbles adhering to the ICA-copper-surface since the vacuum treated samples still show some bubbles, but it is certainly consistent with the hypothesis. The more dominant failure mechanism for the vacuum treated sample is breakage of the adhesive joint itself (cohesive failure) whereas adhesive-copper-interfacial (adhesive) failure dominated for the untreated samples.

Resistance Results: Since the contact resistance seems to be very small in comparison to the bulk resistance of the ICA-sample and the tolerances in the experiment it was not possible to isolate the contact resistance of the Copper-ICA-Interface. Even though the manufacturing process of the samples and the samples themselves were quite accurate and reproducible, the results of the resistance measurement had considerable scatter. To keep the results representative 26 samples of each, the vacuum treated and untreated samples were made.

	No vacuum	Vacuum
Average Resistivity	$4.22 \cdot 10^{-3}\,\Omega cm$	$2.92 \cdot 10^{-3}\,\Omega cm$
Std Dev'n	$3.29 \cdot 10^{-3}\,\Omega cm$	$1.53 \cdot 10^{-3}\,\Omega cm$

From this result it can be seen that the resistance seems to decrease by 30% under vacuum treatment. The strong scattering was not explainable by the tolerances of the sample and the measurement procedure. Under vacuum influence this scattering effect however decreased by about 50%. The figures are similar to the adhesive strength data scatter, and may indicate similar reductions in bubble densities in the bulk.

Conclusion: Application of vacuum to the ICA seems to lower its bulk resistivity. Also the deviation of the individual samples seems to decrease when this technique is used. This can contribute to more predictable and therefore more reliable ICA joints. The shear strength of the joints also increases noticeably after the vacuum treatment. The deviation of the pull test strength values was lower for the samples exposed to the vacuum. The increase in shear strength and decrease in resistivity seem to be connected to each other. The different failure mechanisms for both groups of samples during the pull test suggest higher adhesion between the ICA and the copper after the vacuum treatment. The idea of bubbles causing higher resistance and lower shear strength could not be confirmed absolutely, but is consistent with the data Bubbles were still visible within the adhesive and at the ICA-copper-interface after the vacuum treatment (Figure 12.)

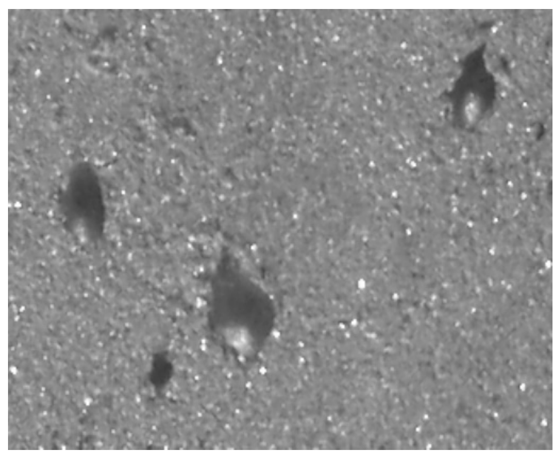

Figure 12: Bubbles on the ICA-Copper-Interface of a vacuum treated sample

Drop Tests

Test Materials and Test Devices:

Three chips were selected for the experiment:

- SOIC (Small Outline Integrated Circuit – SO28GT-7.6mm gull-wing)

– PLCC (Plastic Leaded Chip Carrier- PLCC68T J-lead) and
– QFP (Quad Flat Pack 160T25-3.9 J-lead)

The chips are daisy-chained to test for ICA resistance changes between drops. Daisy-chain circuitry was milled into Cu-clad FR4 boards. Components are manually mounted using the printer's vacuum tweezers. After curing the drop tests were performed on the boards after a time period of 24 hours.

Results and Discussion: The PLCC package failed a 36 inch drop test after 5 drops and the QFP failed after 8 drops.

For the SOIC package the drop test was performed in two orientations as shown below in Figure 13.

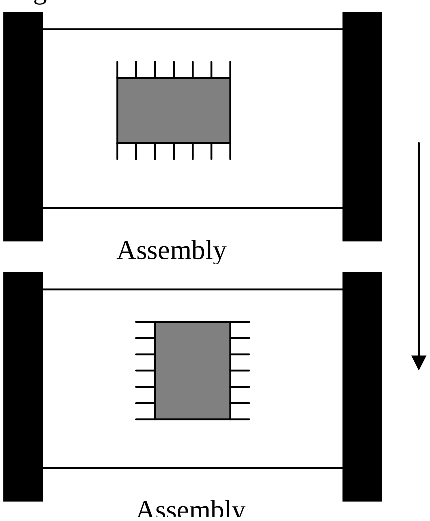

Figure 19: Orthogonal ass

Assembly 1 took 6 drops and Assembly 2 took 4 drops to fail the 36-inch drop test.

After each drop test was performed, the resistance of the adhesive joints was measured. Even after the drop test failed and the chip was detached from the board, the chips were not electrically damaged, even though some of the chip leads were slightly bent.

It is very critical for the adhesive to absorb mechanical energy [8]. The curing temperature selected here was at the high end of the specified range, and the adhesive joints seemed brittle, causing failure during drop tests. Better prior results were obtained with the lower cure temperature [5].

References

[1] S. Norlyng, Advancing Microelectronics, July/August 2001, 28-32.

[2] Li Li & J. E. Morris, Int. J. Microelectronic Packaging, 1(3) 1998, pp. 159-175.

[
3] J. Liu & J. E. Morris, Proc. 1999 Workshop on Polymeric Materials in Microelectronics & Photonics (POLY'99,) Paris, Dec 1999, 259-281.

[4] J. E. Morris, Proc. 3rd Microelec. Materials Conference, Berlin April 2000, 181-186.

[5] S. MacDavitt & J. E. Morris, Proc. Adhesives 2000, Helsinki, 221-224.

[6] S. Probsthain & J. E. Morris, Proc. Adhesives 2000, Helsinki, 41-45.

[7] J. E. Morris, Chapter 3 in "Electrically Conductive Adhesives: A Comprehensive Review" J. Liu editor, Electrochemical Press, UK, (1999) 37-77.

[8] Q. Tong, S. Vona, R. Kuder & D. Shenfield, Proc. Adhesives'98, Binghamton, NY, 272-277.