Future Developments in Electrically Conductive Adhesives Technology

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Abstract

The paper identifies numerous areas for research investment in the field of ECAs, primarily ICAs. While some of these are proposals for direct technological development, most are specifications for pure research studies, with the contention that technological development follows understanding.

1 Introduction

Electrically conductive adhesive (ECA) technologies are winning acceptance in the marketplace for solder replacement for both flip-chip attachment and surface mount technology (SMT) applications. The technology drivers are typically low temperature processing, environmental concerns, fine pitch capabilities, and even superior reliability. Most research in the field to date has been focussed on solving specific problems, some of which are mentioned below, but with most of these now understood, and with potential solutions in sight, research efforts will begin to address some new objectives. These can be classified as:

(a) The systematic measurement and tabulation of materials properties, (data for design),
(b) The study of fundamental properties and mechanisms, including
(c) The simulation of structure/property relationships, which validate that understanding,
(d) The identification and development of new applications of the materials, and, of course,
(e) The continued application of the knowledge so acquired to specific problem-solving.

This paper will concentrate on the application of research to isotropic conductive adhesives (ICAs), with a brief mention of anisotropic conductive adhesives (ACAs), including anisotropic conductive film (ACF), sometimes termed "z-axis" film (ZAF). ICAs typically consist of a bi-modal distribution of silver flakes and smaller particles in an epoxy adhesive.

Commercial materials typically achieve electrical resistivities on the order of $10^{-4}\ \Omega$.cm, about 1½ orders greater than that of pure silver. These are quite adequate for solder replacement. The mechanical adhesive strengths cited in the literature tend to vary, but are typically less than but similar to solder's. The adoption of ICAs for solder replacement would be much more widespread if it were not for their disappointing performance in drop tests. However, basic research has identified the drop test problem to lie not with lack of adhesive strength, but to be due to the low epoxy loss modulus. With the problem understood, the cure is inevitable with time. Similarly, reliability issues with the electrode interface are now understood to be due to electrochemical corrosion, explaining the well-known instability of the silver-based ICAs with Ni or Sn/Pb interfaces, and the superior performance of Au and Pd coatings. Finally, in this brief review of recent work, it must be pointed out that all no-Pb candidates for adoption as a standard Sn/Pb solder replacement have higher processing temperatures than Sn/Pb, which already presents major reliability problems due to thermo-mechanical stress.

Much of this past work is summarized in [1], and the reader is directed to the references cited therein for the original work being discussed here.

2 Electrical Properties

2.1 Inter-flake conduction

The fundamental mechanism of electrical conduction between flakes remains an unanswered question. ICA conduction is an example of a percolation system, which in some materials can account for all the resistance. Direct observation of some contacts, however, clearly indicates a significant constriction resistance component. But the main question relates to the surface condition of the flake. Is the sandwiched material insulating polymer, or organic lubricant, or degenerate semiconducting silver oxide? In the first case certainly, and the second possibly, conduction would be by electron tunneling, which is exceptionally sensitive to very minor variations in surface condition and gap width (and hence curing conditions.)

The inter-particulate contact areas observed (~7nm diameter) lead to estimated degrees of current concentration which would lead to significant localized heating effects at high currents. Epoxy degradation at high currents has been correlated with measured ICA surface temperatures, possibly from just such a heat source. Of course, current crowding can also lead to electromigration failures over longer times, even with negligible Joule heating. Assume that $10A/mm^2$ is concentrated by percolation to $100A/mm^2$ in the Ag conductors, and again at the $100nm^2$ inter-particle contacts to $10^8A/cm^2$ by the concentration from $1\mu m^2$ particle dimensions. This is more than enough to initiate electromigration, but only if there is metal-to-metal contact.

2.2 Model percolation

Quantitative theory is validated by successful simulation. Work progresses on modeling electrical properties, but realistic representations of the system require substantial memory, and efficient random particle placement algorithms.

3 Thermal Properties

Very little attention has been paid to thermal ICA properties, and the solder interconnect to be replaced very often plays a significant role in the thermal dissipation of the chip package. In general, the ICA thermal resistance will be greater than the solder's, but the ratio will be less than the electrical resistance ratio, due to the epoxy's thermal properties. The thermal modeling problem (beyond trivial idealizations) will be more difficult than the electrical, due to the epoxy contribution. The simplest part of this research program will be the actual experimental measurements, but these are more difficult than the corresponding electrical measurements.

The other thermal research issues are measurement of the thermal coefficient of expansion (TCE), and probably the plausibility of TCE reduction by fillers, e.g. silica as employed in underfills and ACAs.

4 Mechanical Properties

4.1 Adhesion

Initial attempts at the improvement of ICA adhesion by plasma treatment of the electrode surface were unsuccessful, but show recent promise. Demonstrated removal of both oxide and organic contaminants had no measurable effect. Higher energy ion bombardments might have a roughening effect on the surface.

4.2 Fusible link systems

The "fusible link" systems fall somewhere between the ICA and ACA. The concept is that a low resistance metal such as Cu is coated with a low melting point metal such as Sn, which fuses the metallic conducting system together. One of the ICA advantages over solder is higher compliance, but this advantage may not carry over to these materials.

4.3 Internal movement:

There is evidence that the metallic components of the percolation system move relative to each other during thermal cycling. Hysteresis in resistance-temperature plots is interpreted in terms of "make-and-break" amongst the percolation paths, and initial resistance decreases in thermal cycling is attributed to "initial wear." This is an issue for compliance modeling.

4.4 Mechanical Measurements

As ICAs gain acceptance as solder alternatives, users will need a range of materials data for reliability lifetime estimates and design. When process windows become more robust and properties more predictable, this data will eventually be supplied by the manufacturer. Parameters include:

- Thermal coefficient of expansion
- Compliance
- Creep

Young’s modulus
Fracture strength
Viscoelastic properties

Loss modulus
Fatigue failure
etc.

4.5 Mechanical Modeling

The ICA is a composite material, and much research has been performed on the modeling of the mechanical properties of composites. The ICA is more difficult than many other composites, due to the filler concentration and geometries. The material properties to be modeled are listed above.

5 Materials Development

5.1 Impact resistance

Drop test results have been dramatically improved by the use of high loss modulus epoxies, with glass transition temperatures T_g below room temperature. But above T_g such materials typically have high TCE, and the ICA resistivity may suffer from relaxed mechanical properties, so the search is on for new suitable materials, whether with low T_g or otherwise.

5.2 Self-alignment

For flip-chip attachment, solder's self-alignment capability provides a unique advantage for fine pitch applications. This is not regarded as a major problem for ICA attachment at present with state-of-art placement accuracy, but could be in the future as I/O increases require tighter tolerances. There is no fundamental reason why a polymer cannot be designed to provide the same capability, but the problem might be the high filler content.

5.3 Structural Control

The ICA design goal is a material with minimum resistivity (high metallic content) and maximum adhesion (high epoxy content.) The assumption is that the distribution of the filler particles within the epoxy is random, but in practice layering effects may order some proportion of the flakes perpendicular to current flow. It would be beneficial to be able to align the metallic filler along the direction of current flow, and three approaches have been taken to this problem. (a) Ni rods may be ordered in a magnetic field, achieving nearly an order reduction in interconnect resistance. But Ni has a higher resistivity than Ag, and has a high resistivity oxide, so there is no overall benefit. A modification is proposed here, to use Au or Ag coated Ni rods, to avoid the oxide surface contact problem. (b) Adapting the principle to Ag, an electric field applied prior to cure reduces joint resistance by about 50%, which is probably not worth the extra processing complication. It is not certain whether this is an alignment effect, or some result of internal Ag migration, so the study is ongoing. (c) Mechanical ordering has been attempted by the insertion of spherical thermoset beads, which constrain the flakes to wrap around them. Adhesion was improved, but not electrical conductance. An advance on the technique is proposed here to use coated beads.

6 Novel Applications

One spin-off from early ICA materials development has been the availability of materials for micro-via fill when the need developed. So one should watch for other potential new technologies that might benefit from the ECA concept. In the SMT area, there is such a potential application to “imprint” boards, where Cu interconnect channels are manufactured by a press, and direct physical masking for etch resist [2]. Similarly, the development of the “micro-claw” concept for chip interconnect offers new opportunities [3]. It has also been proposed that printed ICA could be used for "build-up" circuitry on a substrate, using the flake alignment phenomenon now to lower the effective resistivity along the substrate surface, as for RF ID-tag antennas.

7 Processing Issues

7.1 Flake alignment

The flake alignment issue has been mentioned above. In an ICA, the surface flakes are invariably aligned along the surface, which is an undesirable effect for effective conduction perpendicular to the surface. It has been supposed that the effect might be the consequence of squeegee drag during printing, but it is apparently also observed with syringe dispensation, and its discovery inside an air bubble argues for an origin in surface tension. If sufficient pressure is applied during processing that the ICA flows outwards (as for no-flow underfill, or an ACA), the pressure flow aligns the flakes parallel to the substrate throughout the material.

7.2 Under-cure effects

The specification of a cure schedule that will guarantee a complete cure has been a problem in the past. Incompletely cured polymers do not display the expected mechanical properties, and absorb water much more readily than the ideally cured material. In the ICA context, that would lead to increased likelihood of corrosion failure. The development of a cure monitor would assist in the control of the process window. Such a monitor would work much the same as a solder paste impedance spectroscopy system.

7.3 Fine pitch limits

Much is made of the fine-pitch capability of the ICA versus solder, but there is little performance data to confirm the point, or to establish fine pitch limits and identify the limiting material factors.

7.4 Reproducibility

Quite apart from processing parameter variations, a random variation in electrical properties (and others) can be expected from the size effect that accompanies percolation phenomena. Starting with the percolation resistivity of an infinite cubic sample, the threshold is decreased for shortened samples, and increased for lengthened geometries. Furthermore, the threshold is reduced for small samples (defined in terms of the filler particulate size.) But the issue at point here is that the dispersion in the resistivity increases as the sample size decreases, as would be expected for any statistical system.

8 Reliability Issues

8.1 Corrosion

Major resistance increases under 85/85 testing have been identified as the result of electrochemical corrosion at the contacts. The process requires the presence of water, and of electrochemically dissimilar metals, so Ag-based ICAs require noble metal electrode finishes for stability. Clearly, the combination of Ag flakes with Ag contacts would be much more stable still, and would remove the need for the addition of corrosion inhibitors and oxygen scavengers to the polymer mix.

8.2 Intermetallics

Interfacial reliability problems can often be traced to the inter-diffusion of dissimilar metals across the interface, with the formation of Kirkendall voids and brittle inter-metallic alloys. Both can lead to increased resistance and to fracture, particularly under fatigue testing. The problem is avoided by the use of like metals on both sides of the interface, arguing again for investigation of the Ag/Ag system, or other alternatives.

8.3 Silver migration

A consequence of the proposal above would be the need for a fundamental study of the phenomenon or problem of Ag migration. The literature suggests that there is a voltage (or field) threshold to the effect. It is clearly inhibited by appropriate polymer choices, but the fundamental basis of this process is not established in the literature. The unique combination of Ag and its oxide's conductivities gives the Ag/Ag system special advantages, which make such a study of the primary perceived problem essential.

9 Environmental Issues

No-Pb legislation was an early technology driver for ICA development, but as for no-Pb solders, the objective has become specifically the development of alternative materials with no Pb. The broader environmental goal must be kept in mind at all times, or the no-Pb solutions may turn out to be all too temporary! It is essential to investigate the full environmental impact of all such proposed material, and in the immediate case it is not clear that the substitution of of Ag for Pb is much of an advance. More study is required here to compare toxicities of some of the no-Pb technologies being developed.

10 Anisotropic Conductive Adhesives (ACAs)

The discussion has been limited to ICA technologies by time and space. However, a couple of random observations are in order. (The ICA size effect relates the critical percolation threshold to both the sample geometry and size, as mentioned above. The ACA can be regarded as a limiting case of the ICA, where the sample thickness has been reduced to the filler dimension, so the percolation threshold tends to zero.)

There has recently been a spurt of electrical modeling from various groups, covering both the solid sphere (typically Ni with softer electrodes) and coated polymer sphere variants, with both finite element and analytical approaches. The models can be extended yet, with the inclusion of more realistic electrode contact areas, variable coating thickness under deformation, etc. [4]

There has been a great deal of emphasis on the drop test for ICAs, but no comparable impact resistance data exists for ACAs. The increased polymer contact area on the electrodes is expected to increase the ACA adhesive strength in comparison to the ICA's, but the primary result of the impact resistance studies on ICAs is that survival correlates with the loss modulus, and not at all with adhesion. So why is there no impact problem with ACAs?

11 Summary and Conclusion

The paper has covered a wide range of potential research areas in ICAs, covering the range of research from the purely technological through to basic. The contention is that technological development follows basic understanding.

References

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