Isotropic Conductive Adhesive Interconnect Technology in Electronics Packaging Applications

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Abstract

This paper is intended to provide an initial resource for researchers and practitioners entering the isotropic conductive adhesive (ICA) field, but may also prove useful to those with prior experience. It presents an historical overview of the issues confronted in ICA development and use in various electronics packaging applications in place of soldering technology.

1. Introduction

Electrically Conductive adhesives (ECAs) have been used for electronics packaging applications for decades in hybrid, die-attach and display assembly. There are two primary categories of ECAs: anisotropic conductive adhesive (ACA) and ICAs. While toxicity and environmental issues with tin-lead solders triggered initial ECA interest, it has been other advantages which continue to drive research for both flip-chip and surface mount technology (SMT). ICAs are also used extensively in die-attach, for small passive chip attachment in automotive electronics, and in RFID tags, for both antenna and chip connections.

The references presented here are organized by topic to provide an easy introduction to the field of ICA research with both historical and current perspectives.

2. ICA Technology

ICAs have been developed as possible candidates for replacement of traditional tin/lead (Sn/Pb) solder for electronic interconnect applications. ICAs have advantages of low processing temperature, elimination of lead, no-flux, no-clean and simple processing [1, 2].

The ICA consists of a two-phase mixture of metal conductor and polymer (epoxy) adhesive. The metal contact is typically a bimodal distribution of silver (Ag) flakes and powder (Figures 1 and 2). ICA resistivity drops dramatically (Figure 3) when the metallic content exceeds the “percolation threshold”.

Ten years ago or more, the focus in ICA studies was already on empirical reliability data, e.g. resistance stability and adhesion shear tests [3], humidity effects [4] and other thermal testing [5, 6], usually with comparisons to solder’s properties and an environmentally aware manufacturing focus [7]. The emphasis in most of the references below will be on explanations and improvement of these early results.

3. Technology Reviews

There are a few review papers in print and these are intended to introduce ICAs to newcomers to the field, Reference [8], concentrates on established background principles, while [9] offers a more comprehensive technology review, updated in [10]. The most complete sources of information are the dedicated book [11] and an on-line course [12] at www.cpmt.org.

Figure 1 ICA bi-modal filler distribution (Ag flakes & powder), with surface layering evident.

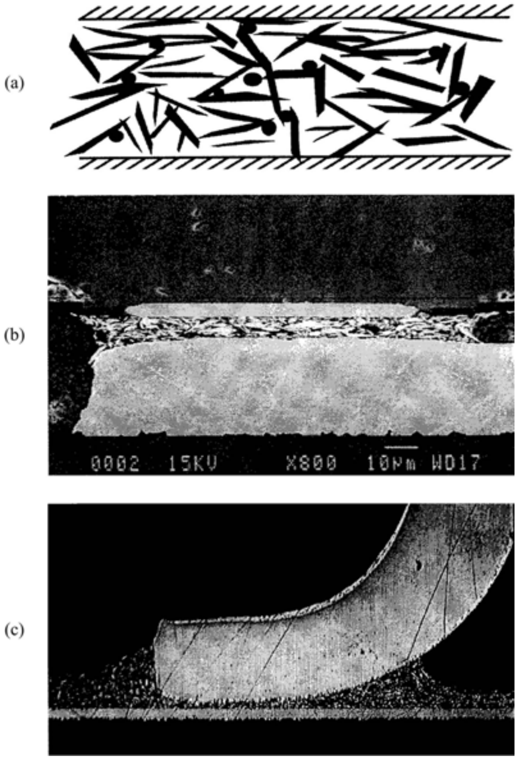

Figure 2 ICA contact joints: (a) schematic, (b) flip-chip on FR-4, (c) SMT on FR-4.

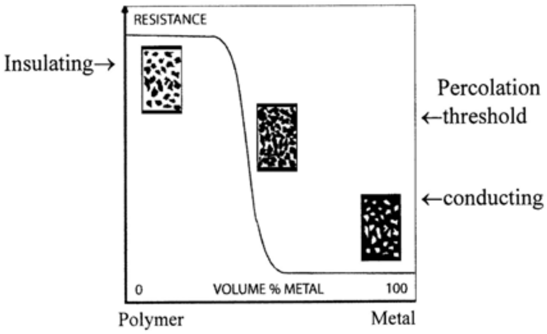

Figure 3 Percolation threshold.

4. Electrical Properties

A. Percolation

As the proportion of metal in the ICA polymer matrix is increased, the resistance drops only slightly until the "percolation threshed" is reached, when the first continuous metal path is established through the composite material [13].

The primary concepts of electrical conduction in ICAs are covered in reference [13], especially the application of percolation theory, which is well developed for the elementary system of uniform conducting spheres (or cubes) in a perfectly insulating medium [14].

B. Structure

The electrical resistance includes contributions form the metallic flakes and from the contact resistances between particles and at the contacts. Metallic resistance can dominate [15].

The efficiency of bi-modal particle distributions has been demonstrated to reduce the percolation threshold [16] and either flakes or powders can be used for the smaller particles [15].

C. Size effect

Existing models confirm the effects of surface layering at a qualitative level [17], and size effects [18, 19], i.e. the increase and decrease in effective conductivity respectively for limited ICA sample dimensions parallel and perpendicular to current flow.

At low thicknesses, the track flakes are all layered, but as thickness increases, the proportion of internal disorder increases [20]. However, application of pressure during cure may force all the flakes into alignment [21].

Reference [22] shows the resistance of a z-axis contact as it is mechanically thinned. A sharp drop in resistivity corresponds to the removal of the aligned surface layer.

D. Modeling

For ICAs, there have been some superficial efforts at structural modeling in the past, and as a result, comparisons of electrical models with experiment were either strictly qualitative [1, 2] or subject to parameter adjustment to achieve a fit.

For ten micron diameter flakes one micron thick, and micron-sized smaller particles, the electron mean free path (mfp) is not going to be reduced significantly from the bulk value, and no accounting is needed for size effects in the particles. (Note that this would not apply to the nano-particle ICA variant [23], where the mfp is limited by the particle dimensions.) But the nature of the surface could be important for the assessment of mfp limitation for constriction resistance, (with rough surfaces limiting the mfp by random "diffuse" scattering, and with "specular" reflections from smooth surfaces having no such mfp effect.

Li et al [17] published electrical conduction models for silver filled isotropically conductive adhesives, combining the microscopic resistance of the bulk silver particles and the contact between silver flakes with the macroscale resistor network calculation by percolation theory. The model predicts that the resistivity decrease with the stress developed during the cure process of the conductive adhesives and with particle size distributions [24].

Recently, a dynamic model of the effects of compression has demonstrated flake alignment quite dramatically [25]. As the structure fills up, this process becomes more and more time consuming. A potential energy technique has proved effective [26] in reducing computation time, but the most recent advances have been by the use of compression algorithms applied to initially well separated particles [25, 27, 28].

Electrical modeling requires the addition of the conduction processes discussed below to each of the elements: intra-particle, inter-particle, and contact, with the structural model itself providing the percolation component. Existing models confirm the effects of surface layering at a qualitative level [17], and bimodal size effects [17, 18, 26, 29].

Molecular dynamics (MD) simulations demonstrate the coalescence of Ag nanoparticles, and their deposition on a gold substrate at various temperatures from 400K to 1,000 K using the embedded atom method [30].

E. Measurement

Contact resistance can be isolated from the bulk composite resistivity by the combination of three-terminal measurement with the more common four-terminal [22, 31].

Finite geometries can lead to errors, however, if care is not exercised. The same sort of problem can be experienced with z-axis samples (and with ACA testing) due to finite track resistances comparable to the sample's [22, 32].

F. High frequency effects

In 2000, Shimada et al [33] reported work on the electrical characterization of ICAs. Current capacity measurements are shown and other electrical properties, such as inductance, capacitance, and resistance, by both LCR meter and four-point probe measurements both in the direct current (DC) and alternating current (AC) ranges of the ICAs.

Li et al [15] showed that the ICA high frequency behavior is fully attributable to skin effect in the metal filler.

The high-frequency ICA data of Li et al [15] have been extended by Wu et al [34] and by Dernevik et al [35, 36]. Li and Wu focused mainly on the MHz region, and

Dernevik on the GHz region. Wu reported that ICA joints can change their high frequency properties during bending.

At frequencies where skin effect is dominant, the lower resistance advantage enjoyed by solder at DC disappears, as the effective cross-sectional area shrinks with the skin depth for solder and ICA alike [37]. The essential point is that there is no noticeable high-frequency performance difference between ICAs and solder [38].

G. Noise

Electrical noise measurements are also often a useful diagnostic tool, and there is noise data in the literature [39, 40], but as is often the case, the interpretation is ambiguous.

5. Mechanical Properties: Adhesion

Published ICA adhesive and shear strengths are on the same order as those of solder, usually a little less [41], occasionally higher [42], but anyway adequate [43].

Brief exposure to vacuum prior to cure visibly decreases ICA paste volume as gas escapes from the surface, but the more practical technique is a pre-cure heat soak, e.g. for about 20~30 minutes at 100~120 ^{o}C, which achieves the same result and marked reliability improvement [44, 45].

In the SMT application, however, the thermoplastic properties of the polymer lead to the accumulation of plastic strain, which initiates cracking [45].

Morris and Probsthain published a paper [44] where they studied mechanical and electrical properties comparable to solder's. The effects of varying plasma process time and applied power on adhesion and electrical performance of ICA-connections are described.

Plasma cleaning of the adherent surfaces would seem to be a logical step, but so far preliminary data shows no improvement in adhesive strength with either Ar or O_2 plasma treatments, despite the demonstrated removal of organic contaminants and oxides [35, 37]. Wolter et al [42, 46] have demonstrated that it is the polar component of surface energy which is increased by plasma treatments. Experimental studies consistently show that the mechanical component of adhesion dominates [47, 48], with best results from surface roughening, (which may be accomplished by high-energy plasmas.) (A simple NCA shows good electrical stability, provided the contact surfaces are roughened [20].)

A conducting polymer interface layer can promote ICA adhesion [49]. Keil et al [50] improved adhesive strengths by structuring the contact pad so a proportion of the ICA contacts the FR-4 epoxy surface rather than metal. Interfacial and bulk fracture mechanisms have been studied by Gupta et al [51].

6. Thermal Properties

The thermal performance of an adhesively assembled chip is of vital interest as power dissipation in the chip increases. Sihlbom et al have simulated power dissipations for both ICA and ACA flip-chip joints [52].

7. Metallic Filler

The most popular filler material for ICAs is silver, Ag, because it is not as expensive as Au, and has superior conductivity and chemical stability. In addition, it is easy to precipitate into a wide range of controllable sizes and shapes, and silver oxides show high conductivity [53-57].

In addition, nickel can be used as stable conductive fillers. Generally, isotropic nickel adhesives show both higher filler resistance and contact resistance than silver-based product. It is also hard to fabricate into optimized geometries because of its hardness and malleability [55].

Marshall reported on copper-based conductive polymers [58]. Copper has had a limited success due to its tendency to form a non-conductive oxide surface layer.

A. Surface lubricant

The flakes require lubrication, so typically stearic acid (soap) is added, to resist the tendency to “clump” together.

Lu et al [59, 60] reported on the characteristics of silver flake lubricants for electrically conductive adhesives, with the first [59] studying the chemical nature of the lubricant layer, interaction between the lubricant layer and silver flakes, and thermal behavior of the lubricants during heating, and the second [60] reporting the thermal decomposition behavior of the lubricant.

Wong has achieved reduction of overall resistance by replacing the traditional stearic acid with shorter chain alternatives [61-63]. Silver is typically tarnished, and presumably would oxidize within the polymer, even if initially “clean” but it is not clear what effect the surface lubricants identified on flake surfaces [64] would have on this process.

Benson, on the other hand, has shown that the lubricant breaks down during cure, and leaves a carbon residue on the flake surface [65], which is expected to control the inter-particle resistance.

B. Low melting point alloys (LMPA) & fusible filler

Kim et al published a paper [66] on a hybrid of solder and conductive adhesive joining technology using new ICAs with fusible filler particles. The purpose of this paper was to develop an assembly process to form metallurgical interconnection, not only between the fusible filler, but also between the fusible filler and the conducting pads.

There have also been materials reported using low melting point alloys, or Sn-coated Ag particles [67-69]. The intent is for the particles to form metallurgical bonds during the polymer cure, to achieve lower contact resistances. The greater rigidity of the metallic network could be a problem if the contacts fracture under mechanical stress, but apparently the Sn inhibits Ag migration [69].

Self-alignment is a critical component to the success and reliability of solder attachment of area-array flip chips, and the absence of a similar surface-tension driven property in ICAs in widely seen as an impediment to their adoption for this role. Wu et al [70, 71] coaxed a minimal ICA self-alignment effect from an LMPA content

C. Nanoparticles

Kottaus et al [56] reported the study of isotropically conductive bonding filled with aggregates of nano-size Ag particles as highly porous aggregate conductive filler. The goal was to decrease the metal loading to improve the mechanical performance for specified electrical properties. It has been shown that it is possible to decrease the total metal loading with good electrical conductivity using a bimodal filler distribution [72], but that the nanoparticles increase resistivity for given total filler content, due to mean free path limits and increased numbers of contacts.

Reference [73] shows the thermal behavior of silver nanoparticles with respect to the sintering reaction. Surface changes of the particles during sintering and crystal structure variation are addressed as well.

Ye at al [74] observed ~50 nm diameter contacts between nanoparticles. Similar contacts have been observed between micron-scaled ICA particles [75].

The addition of carbon nanotubes to the Ag-flake/epoxy mix [76] lower percolation threshold, as expected, and may be more effective than Ag nano-particles.

8. Polymer Materials

A. Polymers selection

Isotropically conductive adhesive formulations usually include epoxy resin as the polymeric matrix. Although it has superior adhesion capability, one of its drawbacks is its tendency to absorb moisture.

In [77-79], Wong's group describes a thermoplastic ICA with improved conductivity. Water may accumulate at the interface of the ICA and contact pad, and cause contact resistance degradation. In this study, an alternative thermoplastic polymer matrix with low moisture absorption is used in the ICA formulation, with polyarylene ether (PAE-2), which has extremely low moisture absorption (0.279 wt%). Poor adhesion was the main mechanism for unstable contact resistance, and two methods of adhesion improvement were evaluated in [79]. One is to use coupling agents and the other is to blend the thermoplastic with epoxy. Both methods showed promise in improving the contact resistance stability of the PAE-2 based ICA, but adhesion again really correlates with surface roughness.

In 2004, Li and Wong published a paper [80] about a liquid diepoxide re-workable epoxy resin for ICAs. The diepoxide may provide good mechanical properties, low moisture up-take, and an appropriate decomposition temperature that allows individual removal of bad components without damaging the board and its surroundings. Silicones have also been widely used.

B. Curing

In 1998, Klosterman et al published a paper [24] focused on the influence of cure on resistivity, joint resistance and reliability. Novel analytical methods were developed to define the cure conditions that produce optimum electrical properties and stability.

The cure process has been modeled successfully by very simple mathematical expressions [31, 81], which do however require accurately determined parameters from experimental differential scanning calorimetry (DSC) data.

In 2000, Lu et al [82, 83] correlated the effects of shrinkage with ICA conductivity during cure. The ICA cured non-isothermally by a temperature increase from 30 to 250 ^{o}C, and its heat flow, storage modulus, dimension change and electrical conductivity were studied with a differential scanning calorimeter (DSC), rheometer, thermomechanical analyzer (TMA) and electrical multimeter.

It seems that the electrical resistance of the joint is related to the curing degree, especially for non-noble metal surfaces. Contact resistance vs. curing time for an epoxy conductive adhesive cured at 150 ^{o}C, and following 1000 hours of damp heat treatment at 85 ^{o}C, 85%RH is shown in [84]. The corresponding curing degree varies between 65% and 90%, determined by DSC. Below a critical curing degree (77% for one adhesive), the electrical resistance of the joint increases significantly, because an incompletely cured epoxy can absorb a significant amount of moisture, which in turn causes oxidation/hydration of the Sn37Pb bonding surface and less crosslinking/shrinking of the polymeric matrix [85].

Wu et al [86] have studied ICA viscoelastic properties, and conclude as a result that stable structures require a low temperature cure, followed by a stabilization ramp to higher levels.

At full cure conditions, however, the electrical resistance and the mechanical strength of conductive adhesives are also guaranteed [87].

The feasibility of variable frequency microwave cure of ICAs has been demonstrated [88, 89].

9. Reliability

A. Mechanical cycling

To understand the degradation mechanisms, Mo et al [90] focused on the electrical performance of a commercial ICA joint under mechanical loading. To gain insight into the electrical degradation mechanism, finite-element modeling (FEM) was executed, and the effects of mechanical loading on the initial intimate interaction among silver fillers were analyzed.

Polymer creep coefficients are much higher than solders. Therefore, it is not surprising that ICAs out-perform solder on mechanical cycling tests by an order of magnitude [91]. However, thermal cycling results do not show similar benefits [92], possibly due to the Ag/epoxy interfacial fracture suggested by initial wear observations [21].

B. Contact resistance and galvanic corrosion

It is the contact resistance that has been shown to be the source of electrical reliability problems [93-95], with galvanic corrosion between dissimilar metals at the contact interfaces [96-98].

With this understanding of the process, it was shown that resistance drift could be inhibited by the addition of corrosion inhibitors, oxygen scavengers, and/or sacrificial anode material to the polymer matrix [99-101]. For example, in [102], Lu and Wong studied mixtures of an epoxide-modified polyurethane resin with a bisphenol-F type epoxy resin and a corrosion inhibitor. Moisture can be minimized with anhydride-cured epoxies [103].

Moisture effects on the polymer degradation in conductive adhesives have been studied by Khoo and Liu [104], and moisture distribution within the joint has been modeled by Dudek et al [105] for viscoelastic modeling of thermal cycling failure.

C. Drop test

The drop test failure rate has been a problem, leading to the widespread adoption of the NCMS (National Center for Manufacturing Science) criteria as a de facto standard [1]. When one examines drop test survival data, the success rate correlates with the (imaginary) dissipation modulus rather than with adhesive strength [106-108]. One way to design materials with high dissipation modulus is to select polymers with glass transition temperature T_g below the operating range, i.e. below room temperature, in general [109]. The addition of carbon fibers to the ICA is also helpful [50].

There is an improvement in drop test results for a commercial ICA with the addition of a pre-cure heat soak to the processing schedule [110].

D. High current

In a dc study of three ICAs, Morris et al [37] found that high current failure correlated directly with temperature rise, which in turn correlated with the joint resistance, and hence to intenal power dissipation. Kotthaus et al [111] reached a similar conclusion.

E. Ag migration

There have been concerns about possible failures due to surface migration of Ag. Sancaktar et al have recently correlated electromigration with Ag surface pitting [112].

There also appears to be a field threshold, and moisture is a requisite, but systematic study is required to establish the boundaries to the effect [113]. In addition, the diffusion and clustering of metals in polymers is well established [111, 114, 115].

Ag migration is evident in un-cured material [37], and it has been suggested that commercial additives to the polymer seal the silver surface, defeating migration tendencies.

10. Environmental Properties

The environmental impact of ECAs has been studied by several research groups. Segerberg et al [116] compared use of conductive adhesive joining with soldering for SMT applications and concluded that the relative environmental load of the conductive adhesives is dependent on the mining condition of silver. Westphal et al [117] concluded in their study that conductive adhesives are generally better in terms of environmental loading compared to solder.

More work is needed to clarify environmental pros and cons, particularly, since environmental concerns have been an ICA technology driver.

11. Miscellaneous

There are various novel approaches to the improvement of electrical connectivity at a given metal content, including magnetic alignment of nickel filler rods [118], the use of polymer particles to force z-axis alignment of flakes [119], and electric fields [37].

Vanfleteren et al [120] worked on low temperature flip-chip processing using ICA and NCA for flexible display applications. They developed a new ICA/NCA flip-chip technology, based on the no-flow underfill soldered flip-chip technology, which eliminates the drawbacks of the conventional ICA flip-chip technology.

Conclusions

Earlier versions of this paper were presented at ISSE'05, Vienna and HDP'05, Shanghai. We welcome comments, and suggestions for significant references we may have missed, before final Journal publication.

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