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# Unparalleled in Polymer Coatings and Adhesives Technology

#### Development of conducting adhesive materials for microelectronic applications

Electrically and/or thermally conducting adhesive materials are classified into two categories depending on their conduction modes: isotropic and anisotropic materials. Silver-particle filled epoxy is the most common example of the class of isotropic materials which are conductive in all directions. This material has been long used in the electronic applications as a die-bonding material, where its good thermal conduction rather than its electrical conduction property is utilized. The silver-filled epoxy material has several limitations for high performance electrical interconnections, such as low electrical conductivity, increase in contact resistance during thermal exposure, low joint strength, corrosion issue due to silver migration, difficulty in rework, and so forth. The anisotropic conducting material provides electrical and/or thermal conduction only in one direction. An anisotropic conducting film (ACF) is used for interconnecting TAB mounted chips to a liquid crystal display panel, where fine pitch interconnection and low temperature assembly are required. In this paper, a brief review of the state-of-art conducting adhesive technology is provided. Subsequently, development of new conducting adhesive materials is presented for several different applications, which include high temperature materials for ceramic substrates, and low temperature materials for organic substrates.

Key words: Electrically conducting adhesives, Pb-free solders, silver-filled epoxy, isotropic materials, thermoplastic resins, tin-coated copper fillers, metallurgical bonds, BiSn-coated copper particles, contact resistance, joint strength

## INTRODUCTION

Most electrical conductors used in electronic devices are made of metals, such as copper, aluminum, gold, silver, lead/tin alloys, molybdenum and others. Solder connection technology using lead/tin alloys plays a key role in various levels of electronic packaging,1,2 such as flip-chip connection (or C4), solder-ball connection in ball-grid arrays (BGA), and IC package assembly to a printed circuit board (PCB). Solder joints produced in the electronic packages serve critically as electrical interconnections as well as mechanical/physical connections. When either of the functions is not achieved, the solder joint is considered to have failed, which can often threaten a shutdown of the whole electronic system.

In order to overcome the limitations of the silver-filled epoxy materials, several new formulations have been developed recently for various applications. To meet the reworkability requirement in high performance applications, such as in a multichip module (MCM), a reworkable thermoplastic resin has been incorporated with a proper solvent and silver particles.15 Solvent removal from the thermoplastic resin has been carefully controlled during the reflow cycle. Another reworkable thermoplastic conductive paste has also been reported for a fine-pitch flip-chip application." Here, by loading up the fine silver particles more than 40% in volume, a high electrical conductivity better than that of the Pb-Sn eutectic solder has been achieved.

A new class of conductive adhesive materials has been developed by replacing silver particles with other conducting particles, such as solder particles,23 a mixture of solder and copper,13,24 tin-coated copper,16,25 silver-coated copper,26 and others.27 A solder/ polymer composite paste material has been developed by mixing solder powder particles, thermoplastic polymer resin in a volatile solvent, and a fluxing agent.23 Upon reflow, an oxide-free, partially coalesced solder connection is obtained, which is polymer strengthened and reworkable at a low reflow temperature or in the presence of polymer solvent. A hybrid of solder and conductive adhesive joining technologies has been developed to exploit the advantages of both.13 This new conductive adhesive is a mixture of a solder powder, a metal powder of high melting point such as copper, a fluxing agent, a polymer resin, and others. Here, the electrical connection is established through transient liquid phase sintering (TLPS) among metal and solder powder as well as to the conducting pads. A promising result has been reported with the SMT joints made of the TLPS conductive paste in terms of electrical conductivity, impact strength, and reliability, which are substantially better than those of the conventional conductive adhesives.24 Another improvement has been reported with the high conductivity Pb-free conducting materials made of a conducting filler powder coated with a low melting point metal, a thermoplastic polymer resin, and other minor

organic additives.25,27 Similar to the TLPS conductive paste, these high conductivity Pb-free conducting materials do also provide metallurgical bonding between adjacent filler particles, and between the filler particles and the contact pads to be joined, in addition to the adhesive bonding from the polymer matrix. Another interesting variation of copper-based conductive adhesive has been developed by using silver-coated copper powder as a filler material.26 This conductive adhesive however shows a significant increase in contact resistance during thermal cycling and heat/ humidity exposure. Hence, further improvement is required before it can be used for high performance applications. In the following, development of the high conductivity Pb-free conducting materials is further described for two different applications; one for high temperature applications with ceramic substrates, and another for love temperature with organic substrates.

This new electrically conducting adhesive material consists of a conducting filler powder coated with a low melting point metal, a thermoplastic polymer resin, and other minor organic additives. A conducting filler powder is selected from the group consisting of Au, Cu, Ag, Al, Pd and Pt. The filler particles are coated with low melting point, nontoxic metals which can be fused to achieve metallurgical bonding between adjacent filler particles, and between the particles and the contact surfaces that are joined using the adhesive material. The coating layer is selected from the group of fusible metals, such as Bi, In, Sn, Sb, Zn, and their alloys. The polymeric material is selected from the group consisting of polyimide, siloxane, polyimide-siloxane, polyester, phenoxy, styrene allyl alcohol, and others. The relative amount of filler powder added to the polymer matrix varies according to the applications. To insure uniform dispersion of the ingredients, the mixture is processed in a three-roll shear mill. The viscosity is also controlled by adjusting the volume fraction of the filler powder as well as the amount of other additives. Since the present conducting adhesive is primarily based on particle-particle and particle-pad metallurgical bonds, the critical volume fraction of the filler material required to achieve an acceptable conductivity level is much less than the conventional silver-epoxy adhesive, which relies on physical contact and percolation mechanism among the filler particles. As an example, a new electrically conducting adhesive introduced for the high temperature applications is discussed here.ls.zs This is made of tin-coated copper powder filler, a thermoplastic polyimide-siloxane resin, and other additives. This material is a good candidate in replacing the high temperature solder joints, such as controlled collapse chip connections (C4) and solder ball connection (SBC) to a ceramic substrate. Figure 1 shows schematically an electrical connection between two surfaces formed with this conducting adhesive. The conducting copper particles coated with a thin layer of tin are dispersed uniformly in the matrix of a polyimide-siloxane resin. During the joining process, the conducting particles come into contact with each other to form metallurgical bond among the particles as well as to the surfaces by melting the tin layer. The interfacial reaction between the tin layer and copper powder has also been investigated by the method of differential scanning calorimetry (DSC) to understand the joining kinetics and intermetallic formation.28 The metallurgical bond among the conducting particles provides better electrical conduction and higher mechanical strength of the joint. Table I summarizes the electrical resistance values and mechanical strength of the model joints formed with this high temperature Sn/Cu conducting adhesive material. The electrical resistance value of the Pb/Sn solder joint serves as a reference for comparison. The resistance of the silver-epoxy joint is about 50% higher than that of the Pb/Sn. The joint resistance of the new Sn/Cu adhesive with a high filler loading shows even a lower resistance than that of the Pb/Sn solder joint. The resistance of the Sn/Cu adhesive with a medium loading is close to that of the Pb/Sn. Average shear strength of the model joints made with the present Pb-free, Sn/Cu conducting adhesive material is compared with those of other joints in Table I. As expected, the Pb/Sn solder joint shows the highest joint strength. The joint shear strength of the Sn/Cu adhesive materials varies according to the level of the filler loading, but in an opposite way, as the electrical resistance of the joints does. The joint strength of the Sn/Cu adhesive materials decreases as the level of the filler loading increases. In general, the Pb-free, Sn/Cu adhesive material demonstrates a better joint strength than the silver-epoxy material, and for a low loading formulation it shows a joint strength very close to that of the Pb/Sn solder joint. A few reliability tests conducted so far with the Sn/Cu adhesive have shown promising results for the applications of direct chip attach and discrete device attachment to a ceramic substrate.

Low temperature adhesive materials are made of conducting copper powder coated with a thin layer of low melting point, Pb-free metals selected from Sn, In, Bi, Sb, Zn and their alloys. The conducting particles are mixed with an environmentally-safe fluxing agent, and dispersed in the matrix of thermoplastic or thermosetting polymers. Here, we present one example of low temperature adhesive materials containing conducting copper powder coated with a thin layer of BiSn alloys whose melting points are below 200 deg C. This conducting filler particles of a few micron in diameter are mixed with a thermoplastic polymer and a fluxing agent to formulate a

low temperature conducting adhesive, denoted as LT/Cu. In order to characterize the electrical and mechanical properties of the low temperature conductive adhesive material, model joint samples are made by joining two "Lshaped" copper coupons, as described previously.25 The model joint samples are bonded at 188 deg C with a pressure of 25 psi by using the LT/Cu adhesive as listed in Table I. The reduction of the bonding temperature from 250 deg C to 188 deg C is therefore achieved by replacing tin-coated copper powder with the BiSn-coated copper. This low bond temperature is even lower than the reflow temperature of solder paste, 215 deg C. commonly practiced in SMT soldering. Electrical and mechanical properties of the model joints made of the LT/Cu paste are measured as described previously,25 listed in Table I. The average values of contact resistance of the LT/Cu samples exhibit slightly higher than those of the Sn/Cu ones. But the joint strength of the LT/Cu samples demonstrate higher values than those of the Sn/Cu. Table II compares several salient properties of the low temperature conducting adhesive, LT/Cu, with those of other conducting materials, such as silverfilled epoxy, tin-lead solder paste of 63%Sn-37%Pb eutectic composition, and tin-coated copper conducting adhesive denoted by Sn/Cu. The properties listed for the Sn/Cu adhesive cover three different formulations discussed previously, namely, low, medium and high loading of the filler material, while those listed for the LT/Cu cover only for one formulation, that is, the medium loading. Bulk resistivity values of Sn/Cu and LT/Cu are obtained from the electrical measurement with the "2L" model joint samples as discussed previously.27 The contact resistance listed in Table II is estimated by multiplying a nominal joint area with its total resistance value. The joint strength value is obtained by dividing the average fracture force by its nominal joint area. The contact resistance and bulk resistivity of LT/Cu are slightly inferior to those of Sn/Cu, while the joint strength of LT/Cu is somewhat better than that of Sn/Cu. This is attributed to the better adhesion properties of the new low cost polymer resin (LCP) used in formulating the new LT/Cu adhesive. The electrical and mechanical properties of the new electrically conducting adhesives, Sn/Cu and LT/Cu, are significantly better than those of the commercial silver-filled epoxy, and are also comparable to those of the solder joint.

In summary, a brief review of the state-of art conducting adhesive technology is provided including silver-filled epoxy materials, reworkable thermoplastic adhesives, and copper-based conducting adhesive materials. Subsequently, two examples of the new high conductivity Pb-free conducting materials are presented for two different applications; tin-coated copper-based adhesive for the high temperature applications for ceramic substrates, and BiSn-coated copper-based adhesive for organic substrates. The copper conducting filler particles with a low melting point coating such as BiSn alloys enable assembly at a temperature lower than that used for SMT soldering. The low melting point coating material provides metallurgical bond among the conducting particles as well as to the substrate, which leads to an enhanced electrical and mechanical properties of the joints. A low cost thermoplastic polymer is also incorporated in the new formulations.

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