New Electrically Conductive Adhesives (ECAs) for Flexible Interconnect Applications

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Abstract

By blending flexible epoxy with rigid epoxy or using epoxies with different chain lengths, the mechanical properties of the resulting polymer matrices could be tuned to meet different requirements. With the introduction of nanoparticles into the formulation, better electrical properties of the resulting flexible ECAs (FECAs) have been achieved via particle-particle interface enhancement. Moreover, adhesion strength of FECAs on a Au surface has been significantly improved by using conjugated difunctional molecules. With optimized material properties of FECAs, device level test indicated that the FECAs can be used for flexible electronics. In addition, conductive thin films with certain transparency have been developed using Ag-coated glass fiber as filler.

Introduction

With the increasing concern of toxicity of lead, considerable efforts have been devoted to the development of two lead-free alternatives, lead-free solders and polymer-based electrically conductive adhesives (ECAs). However, high processing temperature of lead-free solders significantly limits their applications in organic/polymer packaged components and low-cost organic printed circuit boards. Electrically conductive adhesive, as a promising alternative to tin-lead solder has drawn much attention as an environmentally friendly solution for lead-free interconnects due to the advantages of environmental friendliness, mild processing conditions, fewer processing steps, and especially the fine pitch interconnect capability due to the availability of nano-sized conductive fillers (Figure 1). Therefore, ECAs have been widely used in bonding the flex circuit of a glass LCD display to the mating of conducting electrode traces onto a PCB, or attaching a component lead to a matching pad on a thermally-sensitive printed circuit board, etc. [1-6]

In recent years, intense effort has been devoted to the fabrication and formulation of flexible electronic materials (substrate, interconnect etc) to address the dramatically increasing need for high performance, highly compact and portable devices. [7, 8] Those flexible materials offer significant advantages of low profile, light weight and high-density electronic packaging, attractive for the current and emerging applications in microelectronics. [8] In particular, flexible interconnects allows for highly integrated systems on flexible substrate materials and the development of more compact end-products.

Typically, rigid epoxy resins (such as bisphenol A) are used as polymer matrices for ECAs to provide chemical bonding, excellent mechanical properties and adhesion strengths. However, with the popularity of flexible electronics, there are some limitations when using these rigid ECAs as interconnects, especially under highly mechanical bending conditions. Moreover, the internal stress generated by the thermal curing of rigid epoxy resins tends to cause the reliability problems. Compared with tin-lead solders, the main disadvantages for polymer composites are the high electrical resistivity and poor reliability. Therefore, to improve the joint reliability and allow their wide applications in flexible electronics, it is critical to make the flexible interconnect with high adhesive strength and low resistance.

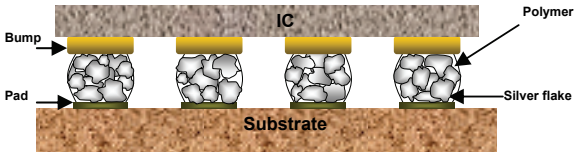
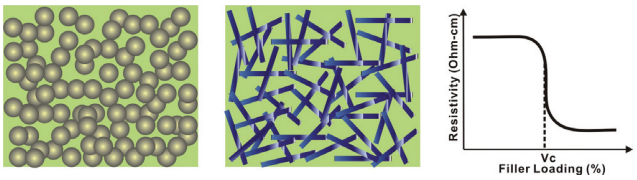


Figure 1 Schematic illustrations of isotropically conductive adhesive (ICA) in flip-chip bonding interconnections.

In addition to flexibility, we aim at developing transparent FECA with good electrical conductivity for transparent conductive coatings. Generally, a lower filler loading is required to achieve the transparency in a composite, since most conductive fillers tend to block the light. However, a relatively high loading level is needed for ECAs to achieve the electrical conductivity. At low filler concentrations, electrically conductive particles/fibers are dispersed within the polymer matrix as isolated fillers. Above certain filler concentrations, conductive particles contact with each other and form a three-dimensional conductive network (Figure 2 (a)). This critical concentration is known as a percolation threshold (V_c), at which the resistivity of the composite drops dramatically (Figure 2 (c)). The volume fraction of the conductive fillers in an isotropically conductive adhesive (ICA) should be equal to or higher than the critical volume fraction to achieve desirable conductivity. One possibility to address the conflicting requirements for making transparent and conductive composites is to use the high-aspect-ratio highly electrically conductive fillers and prevent the aggregation of fillers in the polymer matrix (Figure 2 (b)). Carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWNTs), are a promising candidate for the development of transparent and conductive films and it has been extensively studied in the recent years. [9-11] However, high cost of CNTs, aggregation of CNTs, purification of CNTs and lack of mass production of SWNTs could be the factors that limit their applications. [9]



(a) (b) (c)

Figure 2 Schematic illustrations of conductivity establishment for polymer composites with (a) spherical fillers, (b) high aspect ratio fillers (fiber/wire) and (c) percolation threshold (V_c) in a resistivity vs. filler loading plot.

Previously, we have reported tuned physical properties of polymer matrices by blending of flexible epoxy with rigid epoxy. In this paper, we will further study (1) the effect of epoxies with different lengths on the physical properties of polymer matrices, (2) introduction of Ag nanoparticles into the formulation to improve the electrical properties, (3) the feasibility of the developed flexible ECAs for flexible electronics, (4) the development of conductive thin films with a certain transparency using low-cost Ag-coated glass fibers as fillers.

Experimental

A diglycidyl ether of bisphenol-F (DGEBF) epoxy resin and a flexible epoxy were used as matrix resins. An anhydride type hardener was employed as a cross-linker. Two types of silver flakes donated by Ferro Corporation were incorporated into the ECA formulations.

The resistivity of ECAs was calculated from the bulk resistance of the specimen with specific dimensions. Two strips of an adhesive tape were applied onto a pre-cleaned glass slide with a gap of 6.62 mm between these two strips. The conductive adhesive paste was then printed on the glass slide, and then the tapes were removed after curing. The bulk resistance (R) of this ECA strip was measured as well as the size of the specimen. The bulk resistivity, ρ, was calculated using Equation 1:

$$\rho = \frac{t \times w}{l} \times R \qquad (1)$$

where l, w, t are the length, width and thickness of the sample, respectively.

The specimens were exposed to the condition of 85 ^{o}C/85% RH (in a temperature and humidity chamber from Lunaire Environmental, model EO932W-4).

Dynamic mechanical properties of cured conductive adhesives were investigated using a dynamic mechanical analyzer (DMA) from TA Instruments, model 2980, with a film tension clamp. After a sample was mounted on the clamp, the temperature was raised from 25 ^{o}C to 200 ^{o}C at a heating rate of 3 ^{o}C /min. The samples were studied under an oscillation mode with a frequency of 1 Hz.

Coefficients of thermal expansion (CTEs) and glass transition temperatures (T_gs) of polymer matrices were measured with a thermomechnical analyzer (TMA) from TA Instruments, model 2940. An expansion probe was used and a static force applied on this probe was set to 0.050 N. Temperature was ramped from 25 ^{o}C to 250 ^{o}C at a heating rate of 5 ^{o}C/min. The dimension change with temperature was recorded. [12, 13]

The morphology of the polymer composites was studied by field emission scanning electron microscopy (SEM, JEOL 1530).

For the adhesion study, a die shear tester (Dage series 4000) was utilized, with a configuration shown in Figure 3. The size of the silicon die was 2 mm by 2 mm.

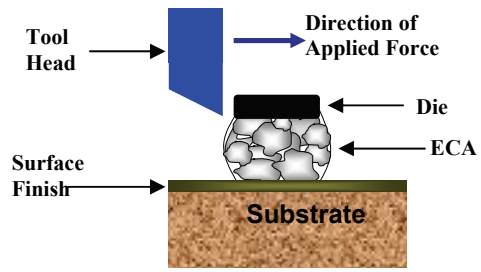


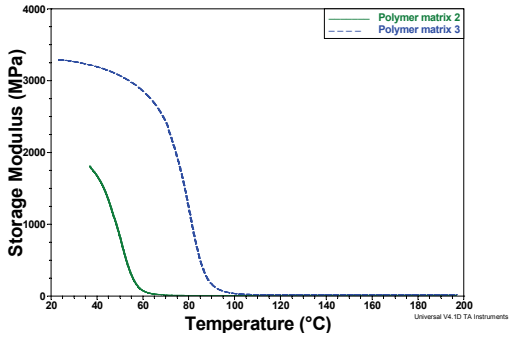
Figure 3 Schematic illustration of die shear test.

Results and Discussion

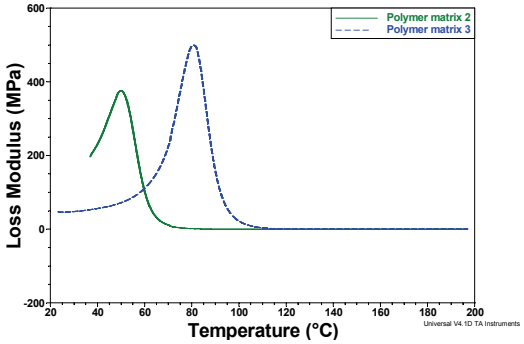
Mechanical Properties of Polymer Matrices

We have reported flexible ECAs which consist of a mixture of a flexible epoxy and a typical rigid epoxy and silver flakes. [14] Various ratios of these two epoxies were studied to combine the advantages of their flexibility, adhesion, shrinkage of different epoxies. By tuning the ratios of epoxies and fillers, the elastic modulus, T_g, adhesion strength, electrical conductivity and impact strength can be modified accordingly to meet the requirements for different applications. In this study, we further demonstrated new flexible ECAs with epoxies of different chain lengths. By changing the chain lengths between two epoxide groups of flexible epoxy, the cross-link density will be further tuned and thus allow the material properties such as storage modulus, loss modulus and T_g can be further tuned accordingly for different applications. Figure 4 shows the change of storage modulus and loss modulus of the polymer matrix as a function of temperature. The storage modulus and loss modulus of polymer matrices are in the range of 2-3 GPa and 50-200 MPa, respectively.

Figure 5 shows CTE of polymer matrices with different ratios of the flexible epoxy to rigid one. By changing their ratios or using epoxies with different chain lengths, the CTE of polymer matrices can be tuned in a certain range. If the ratio of flexible epoxy to rigid epoxy is 50:50, the CTE of cured polymer matrices is about 70 ppm/^{o}C while it is about 81 ppm/^{o}C for the polymer matrices resulting from 70:30. Tuning the CTE of interconnect materials is crucial for flexible electronics since the CTE mismatch will cause thermomechanical stress and lead to the poor reliability of the joint. In short, by either blending the flexible epoxy with rigid epoxy or using epoxies with different chain lengths, the resulting polymer matrices could be widely tuned to meet the different requirements.



(a)



(b)

Figure 4 Changes of (a) storage modulus and (b) loss modulus of epoxy resins with different chain lengths.

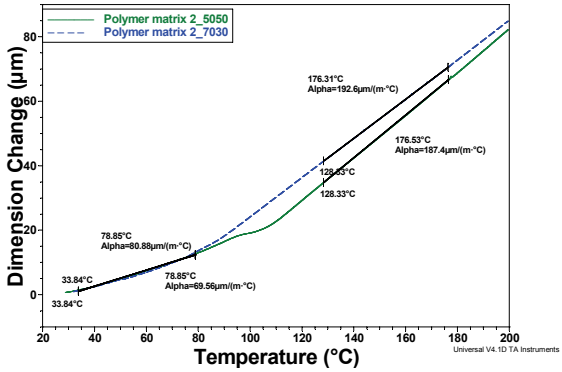


Figure 5 Dimension changes of polymer matrices with different ratios of flexible epoxy to rigid epoxy.

Electrical Properties of ECAs with Ag Nanoparticles

The cure shrinkage plays a very important role during conductivity establishment in a conductive adhesive. It has been discovered that an ICA with higher cure shrinkage generally shows a better electrical conductivity due to more intimate contact between conductive fillers. However, for flexible ECAs, it was found that with increasing the amount of the flexible epoxy in the ECA formulations, there was less shrinkage after cure but the electrical conductivity was higher with more flexible ECAs. In order to further improve the electrical conductivity, Ag nanoparticles were introduced. Due to the high reactivity of Ag nanoparticles, the sintering between silver nanoparticles and silver flakes and among silver nanoparticles would form the metallurgical bonds and decrease the contact resistance among those conductive fillers leading to the dramatic reduction in the electrical contact resistance. [15, 16] Figure 6 shows the SEM image of ECAs using a flexible polymer matrix. The surface of Ag flakes is rough as it sintered with Ag nanoparticles. With the introduction of Ag nanoparticles, bulk resistivity of ECA could be further reduced and it was also confirmed that ECAs with the flexible polymer matrix have higher conductivity than that of the rigid one. More importantly, the possible sintering/interface diffusion between ECAs and metal pads could significantly reduce the joint resistance.

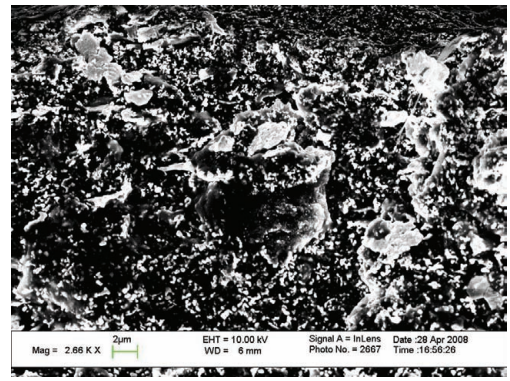


Figure 6 SEM images of flexible ECAs with the introduction of silver nanoparticles.

Adhesion Strength of ECAs on Metal Surface

The adhesion strength of ECAs on different substrates is crucial for interconnect applications. FECAs with different ratios of flexible and rigid epoxy were formulated and the die shear strengths of the FECAs on glass, polyimide and gold substrates have been reported by our research group. [14] Typically with the increase in the content of the flexible epoxy, the adhesion strength continuously decreases. Comparing the adhesion strength of FECAs on various substrates, the adhesion strength of FECAs on Au was the lowest when using the same resin formulation. In order to enhance the adhesion strength, silane coupling agents have been widely used. Depending on the surface properties of the substrate, coupling agents containing different functional groups are available for selection such as thiol, carboxylic acid, amine and epoxide groups. The thiol group has a strong affinity to the Au surface. [17-19] In particular, conjugated molecules have a smaller band gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and possess delocalized π-electrons that can contribute to the electrical conduction. [20] The adhesion strengths of FECA on a Au surface with di-functional conjugated SAM treatment were measured for the formulation of 50 wt% and 70 wt% flexible epoxy, respectively. As shown in Figure 7, with the treatment, the adhesion strength of FECA on a Au substrate was significantly enhanced. The di-functional molecules that can strongly bind the Au surface and react with epoxy resins allow the formation of strong interface between Au surface and epoxy leading to the improved adhesion strength.

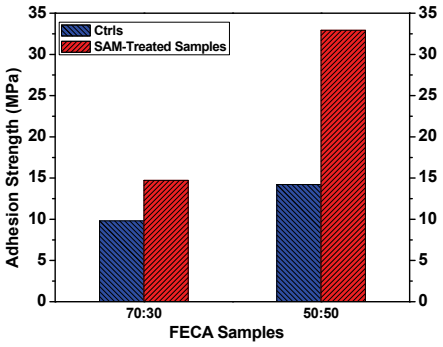


Figure 7 Adhesion strengths of FECA on Au surface with and without coupling agent.

In order to confirm that the flexible ECAs can be used for flexible interconnection, a device level test has been done. The lighting chips were assembled on the Ni/Au surface on a flexible polyimide substrate using the flexible ECAs. With a power supply, light emission without flickering as-assembled was observed for our samples while commercial polyurethane ECAs shows flickering during substrate rolling/bending. This indicates that the electrical/mechanical properties of our flexible interconnect materials are excellent for flexible electronics.

Transparency

High-aspect-ratio conductive fillers are more favorable to achieve percolation at a much lower filler loading. In order to develop ECAs with high conductivity and high transparency, the key factors such as electrical conductivity of the fillers, the aspect ratio of the fillers, the wettability of the fillers by epoxy resins have to be explored. Micron-sized silver-coated glass fibers were employed in this study owing to its low cost, lightweight and availability. With the increase in the filler loading, bulk resistivity of ECAs was decreased. Figure 8 shows the coating of the substrate with 50 μm-thick ECAs with 35 wt% Ag-coated glass fibers. The electrical conductivity of the film is about several tens of S/cm. The key issues for the preparation of transparent and flexible ECAs are the proper dispersion of conductive fillers and prevent the unfavorable aggregation of conductive fillers. From this point of view, the flexible epoxy with silver nanowires (as shown in Figure 9) may have advantages to enhance the dispersion and reduce the scattering. Moreover, with Ag nanowires, the sample could be made much thinner to achieve better transparency. Further studies of ECAs filled with Ag nanowires for the development of transparent and flexible ECAs are needed.

Figure 8 Coating of the substrate with 50 μm-thick ECAs with 35 wt% Ag-coated glass fibers (in the marked area).

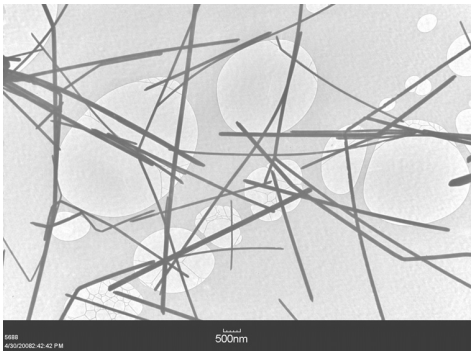


Figure 9 Transmission electron micrograph of silver nanowires synthesized in our lab.

Conclusions

A variety of FECAs have been formulated to provide a wide range of electrical and mechanical properties. By tuning the ratios of flexible and rigid epoxies or using epoxy resins with different chain lengths, the electrical and mechanical properties can be modified accordingly to satisfy the requirements for different applications. In particular, good flexibility, high electrical conductivity, and good reliability could be achieved for the flexible interconnect. The adhesion strength of FECA can be significantly enhanced with treatment of di-functional SAM molecules. Additionally, relatively high electrical conductivity of an ECA thin film with a certain transparency has been achieved. The flexible ECAs developed will have promising applications in large scale flexible printed electronics such as flat panel displays, solar cells, etc.

Acknowledgments

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