Z-Axis Anisotropic Electrically Conducting Polymer-Matrix Composite Film

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A z-axis anisotropic electrically conducting polymer-matrix composite film was developed. It comprised 25 volume percent copper coated polyether sulfone particles and a polyimidesiloxane matrix. Each particle protruded from both sides of the film and provided a conducting path along the z-axis. A z-axis pressure of 40 kPa resulted in a z-axis electrical resistivity of 2 $\Omega \cdot cm$ for the overall film (i.e., 0.5 $\Omega \cdot cm$ for a conducting path); subsequent pressure removal caused the resistivity to rise to 7 $\Omega \cdot cm$ only. The film exhibited negligible stress relaxation and a low modulus of 1.67 GPa.

1 Introduction

Solders in electrical connections are as old as the electronics industry itself. They are used extensively for both die attach and wire bonding in different levels of electronic packaging. One of the key advantages of soldering when compared to traditional thermosetting adhesive bonding is that soldering is a reversible process and thus allows the joint to be reworkable. Because of the mismatched coefficients of thermal expansion (CTE) between the die and the substrate that are joined with solder, the reliability of soldered joints has become a primary problem in electronics. Moreover, soldering is limiting the wiring pitch density [1–3]; typical soldering is limited to a pitch density corresponding to a wire spacing of more than 6 mils. In addition to the thermal fatigue and limited pitch size of solder joints, chemical pollution is another problem because environmentally hazardous fluxing and defluxing chemicals are needed during the soldering process.

Increasingly important in electronic packaging are the use of an array of solder bumps for chip-to-substrate connections and the use of surface-mount rather than through-hole devices. In these applications, a z-axis conducting film (a film that is electrically conducting along its short (z) dimension and electrically insulating in all other directions) can serve to replace an array of solder joints, thus saving much processing cost and making the interconnection easily separable. The z-axis conductor may be in the form of a resilient film (for a separable connector) or an adhesive film, depending on the polymer used. In the elastomeric (silicone-matrix) conductive separable interconnection material developed by AT&T Bell Laboratories [4], conducting columns made by magnetic alignment of conductor particles are distributed in an irregular manner throughout a polymer sheet with the columns oriented in the z-direction of the sheet. In one particular material, the distance between the conducting columns of thickness of 400 μm is about 180 μm. By applying and maintaining a constant pressure, the film conducts along the z-direction only. Because of the large dimension and the required pressure, this particular film is limited to be used in printed wiring board connectors, device testing connectors and thermal interface materials.

State of the art z-axis electrically conducting films of two types have been developed by 3M Corp. [5, 6]. One type involves metal particles totally embedded as a single layer in a polymer matrix, which, during assembly, melts, flows, and becomes much thinner. This allows the metal particles to be almost uncovered and causes the polymer matrix to essentially vanish, and the film to be not reusable. The other type involves clusters of metal-coated polymer particles embedded in a polymer matrix, such that each cluster extends across the whole thickness of the film. Each cluster, presumably made by magnetic alignment of the metal (nickel)-coated polymer particles, serves as a conducting path in the z-axis; there is no need for the polymer film to recede in order to expose the ends of each conducting path. The first type is attractive in its capability for a high conducting path density, since there is only one conducting particle per path. However, it suffers in that the film is not reusable. The second type is attractive in its reusability, but it suffers from a low conducting path density, since there are quite a few (e.g., 12) conducting particles per conducting path. In this work, the advantages of these two types are combined and manifested in a new type of z-axis film in which there is only one conducting particle per path and the polymer film does not need to recede due to the fact that each particle extends across the whole thickness of the film. Thus, the new z-axis film is reusable and capable of a high conducting path density. In order to realize this new z-axis film technology, a method to coat thermoplastic particles with metal was developed, though this process is not described in this paper due to its proprietary nature.

Another z-axis conductive interconnector material was developed by AIT, Inc. [7], but due to the proprietary nature of the technology, information about the material or the processing method was not available at all. Due to the proprietary and infant nature of the z-axis film technology, there is much room for further research.

In this paper, a newly developed z-axis electrically conductive film is described. It can be used as an adhesive film or a resilient film. It is comprised of metal coated thermoplastic (in contrast to the thermoset particles of $3M$) polymer particles and a thermoplastic matrix. The thermoplastic particles can easily be deformed under pressure, thereby resulting in easy formation (requiring little stress) of a good electrical contact. The fine metal-coated polymer particles were uniformly and randomly distributed in a single layer such that the adjacent particles did not touch one another in the x-y plane, thereby forming an electrically conductive path in the z-direction only. The particle protruded out of both sides of the film. Due to the presence of only one particle per conducting path, this work provided a film capable of a high conducting path density. The in-plane electrical resistivity exceeded 10^{10} $\Omega \cdot cm$; the z-axis resistivity was 2
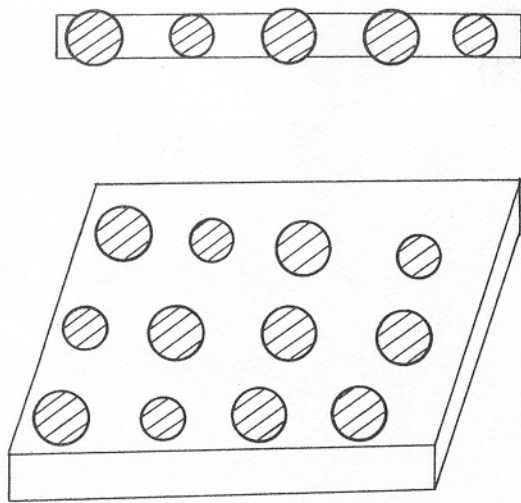
Fig. 1 A schematic of the z-axis conductive film of this work

$\Omega \cdot cm$. The thickness of the film was determined by the size of the metal-coated polymer particles. It could be as thin as 50 μm and only a small amount of pressure (~ 1 kPa) was necessary to obtain a good electrical contact. A schematic of this z-axis film is shown in Fig. 1. Because the conducting particles were uniformly distributed in the x-y plane, the volume fraction of the conducting particles in the film could be as high as 25 percent. Therefore, this novel z-axis conductive film can be used as a high density (about 50 μm between adjacent conducting particles or 10^4 conducting paths per cm^2) interconnection to replace traditional solder arrays.

2 Materials Preparation and Characterization

2.1 Metal-Coated Polymer Particles. The polymer used to form the particles was polyether sulfone (PES, ICI Victrex 4100P), a thermoplastic. PES is an engineering polymer with good mechanical properties and chemical resistance. The properties of this polymer are shown in Table 1. Before coating, a proprietary surface treatment was necessary in order to achieve good bonding between the coating and the polymer particle.

After the surface treatment, copper coating was first performed by electroless plating using a copper sulphate electrolyte. In order to form a continuous electrically conductive layer, an electroplating process was used after the electroless plating. Fig. 2 shows a single Cu-coated PES particle at different magnifications. The copper, though grainy, was macroscopically uniform on the surface of the polymer particle. The final average thickness of the coating layer was about 2 μm, as observed on a polished section under the SEM and shown in Fig. 3 at two different magnifications. After sieving, the coated particles were of two size classes: 50–100 μm, and 100–150 μm.

The reasons for using PES to produce the conductive particles are that small particle size PES was available and that surface treated PES could be easily coated by electroless plating.

Table 1 Properties of polyether sulfone (PES) polymer

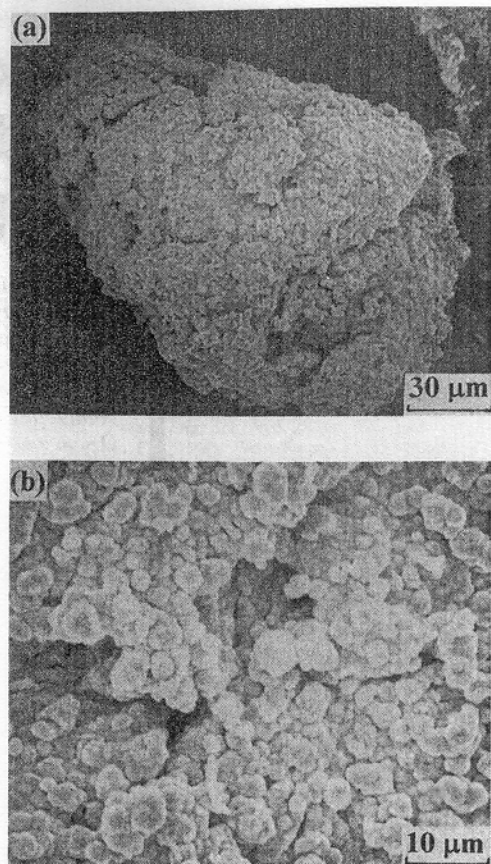|	
T_g	220–222°C
Density	1.37 g/cm³
Particle size (as received)	100–150 μm
Tensile strength	46 ± 1 MPa
Tensile modulus	2.64 ± 0.19 GPa
Elongation at break	(3.1 0.3) %
Electrical resistivity	>10^{10} Ω.cm
Coefficient of thermal expansion	55 × 10^{-6}/K

Fig. 2 SEM photographs of a Cu-coated PES particle
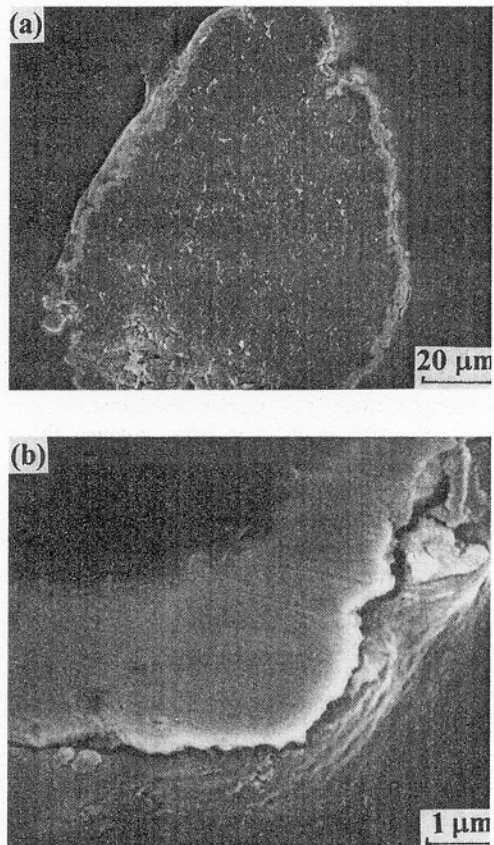
Fig. 3 Polished cross section of a Cu-coated PES particle

Table 2   Properties of polyimidesiloxane (PISO) polymer

T_g	240°C
Density	1.25 g/cm³
Tensile strength	40 ± 3 MPa
Tensile modulus	2.2 ± 0.17 GPa
Elongation at break	(2.4 ± 0.25) %
Electrical resistivity	>10^{10} Ω.cm
Thermal conductivity	0.143 W/m.K
Coefficient of thermal expansion (30–100°C)	101.5 × 10^{-6}/K

2.2   Polymer Solution.   Polyimidesiloxane (PISO) (Occidental Chemical Co., SIM-2030MO) was chosen as the matrix of the film. The PISO polymer is a copolymer of imide and siloxane. Because of the presence of siloxane in the polymer, PISO exhibits good ductility, low modulus and good thermal stability. It also has attractive dielectric properties and processing conditions [8, 9]. Its typical properties are shown in Table 2. The PISO was dissolved in an *n*-methyl-2-pyrrolidone (NMP) solvent. The PISO content of the solution was 25 wt.%. The PISO content of the solution was determined by the required thickness of the film.

2.3   Sample Preparation.   The copper coated polymer particles, and the liquid PISO polymer, were mixed before casting. The Doctor Blade Method was used for casting the film after the slurry had been made bubble free by vacuum. The cast film was dried in an air circulated furnace at 250°C for 4–8 h and was then cut into different shapes for electrical and mechanical testing.

The content of the copper-coated polymer particles was determined by the required electrically conducting column density. Each column contained one particle. The coated particle content was approximately controlled at 25 vol.% of the composite film. As each particle protruded from both sides of the film, the film area covered by the particles was less than 25 percent.

2.4   Electrical Resistivity versus Pressure.   The electrical resistivity of the film was measured by using the four-probe method (Fig. 4). For measuring the resistivity in the *z*-axis, silver paint was applied to the test area (10 mm diameter) on both sides of the film and three films were stacked with copper cylinders (10 mm diameter, 10 mm height) in between (Fig. 4(*a*)), such that the four copper cylinders were lined up with the test area on each of the three *z*-axis films. The two current probes were applied to the outer pair of copper plates; the two voltage probes were applied to the inner pair of copper plates. The *z*-axis resistivity (ρ) was calculated from the equation

$$\rho = (V/I)\pi r^2/d,$$

where *d* is the film thickness, *r* is 5 mm, *V* is the measured voltage, and *I* is the measured current. For measuring the resistivity in the *y*-direction, silver paint was applied along the perimeters of four parallel *y-z* planes (Fig. 4(*b*)). The two current probes were applied to the outer pair of *y-z* planes; the two voltage probes were applied to the inner pair of *y-z* planes. Because the *z*-axis electrical resistivity was pressure dependent, the measurement was carried out under different *z*-axis pressures during pressure increase and subsequent pressure decrease. The electrical resistivity in both directions, namely the *z*-axis direction and the in-plane direction, were separately measured under different *z*-axis pressures.

2.5   Mechanical Testing.   A Perkin-Elmer Dynamic Mechanical Analyzer (DMA-7) with a film extension fixture was used for measuring the in-plane (*x-y*) dynamic tensile modulus at different temperatures. The scanned temperature rate was 2°C/min and a helium purge gas was used in order to obtain a uniform temperature distribution in the furnace. The 2.4 MPa static stress and 2.0 MPa dynamic stress were applied. The frequency was 1 Hz.
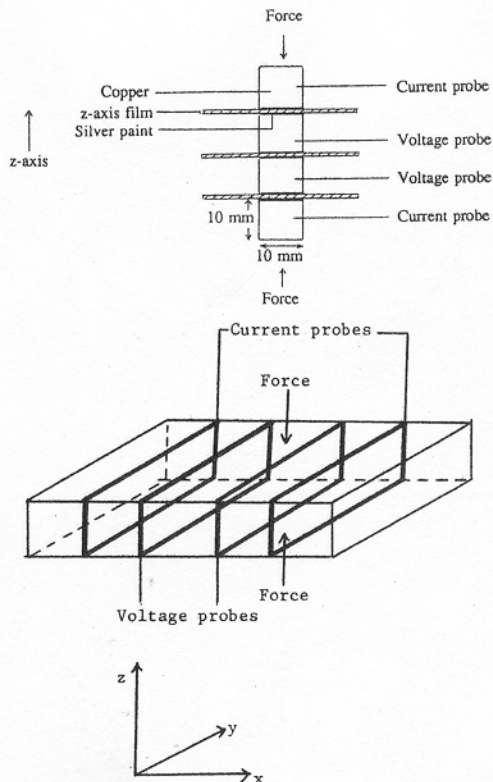

Fig. 4   Schematic illustration of method for measuring the electrical resistivity: (*a*) *z*-axis; (*b*) *y*-axis

3   Results and Discussion

3.1   Electrical Resistivity.   The electrical resistivity of the film as a function of increasing pressure along the *z*-axis is illustrated in Fig. 5. Samples 1 and 2 were composite films containing 25 vol.% 100–150 μm Cu-coated PES particles. Sample 3 was a film containing 25 vol.% 50–100 μm Cu-coated particles. The electrical resistivity in the *z*-direction dropped sharply with pressure. When the contact pressure reached about 40 kPa, the lowest electrical resistivity (2 Ω·cm) was attained.

The film's *z*-axis resistivity (ρ) is related to the resistivity (ρ_s) within a conducting path:
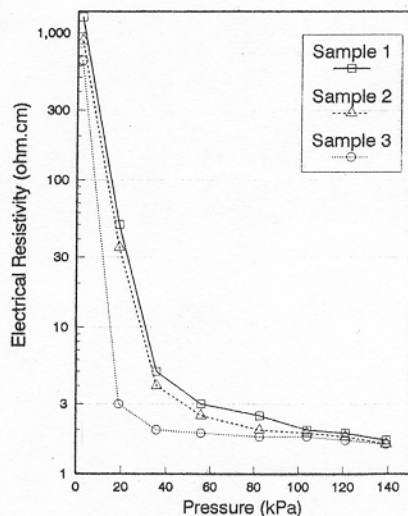

Fig. 5   Electrical resistivity of the *z*-axis film along the *z*-direction versus increasing pressure
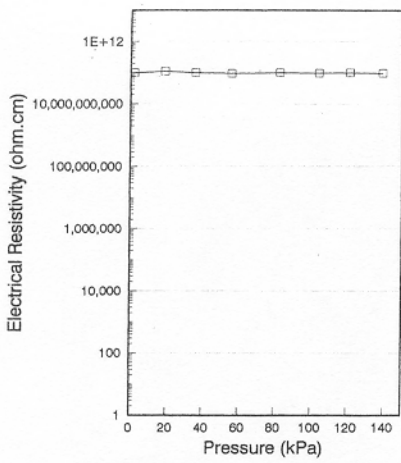
Fig. 6 Electrical resistivity of the z-axis film in the in-plane direction versus increasing pressure

$$\frac{1}{\rho} = \frac{f_s}{\rho_s} + \frac{f_s}{\rho_s} + \cdots = \frac{nf_s}{\rho_s}$$

where f_s is the volume fraction of one conducting path, and n is the number of conducting paths. Since $nf_s = 0.25$, and $\rho = 2 \, \Omega \cdot \text{cm}$,

$$\rho_s = nf_s\rho = 0.25 \, (2\Omega \cdot \text{cm}) = 0.5 \, \Omega \cdot \text{cm}.$$

The electrical resistivity of the film in the in-plane direction remained constant at a high value as the pressure changed, as shown in Fig. 6. Because of the high electrical resistivity in the in-plane direction compared to the z-direction, this film was indeed electrically anisotropic.

Figure 7 shows the variation of the resistivity of the film containing 25 vol.% 50–100 μm Cu-coated PES particles in the z-axis direction upon pressure application and subsequent release. It can be seen that the resistivity was not completely reversible upon pressure release. The resistivity only returned to 7 $\Omega \cdot$ cm, even at zero pressure. This is mainly because the large conducting particles became flat under the pressure, thereby resulting in more conducting paths as the smaller conducting particles started to contribute to the conduction. This low resistivity after pressure release is attractive for maintaining good electrical contact in the z-axis after pressure release.
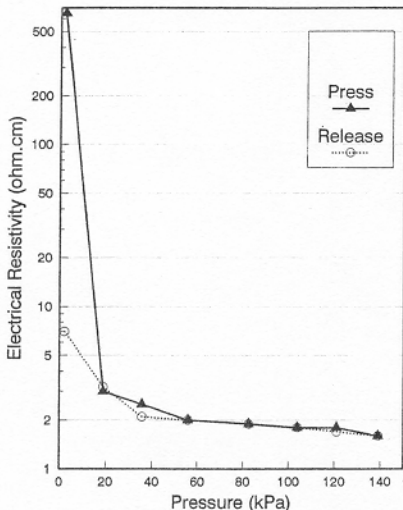

Fig. 7 Variation of the resistivity of the film in the z-axis upon pressure increase and subsequent release
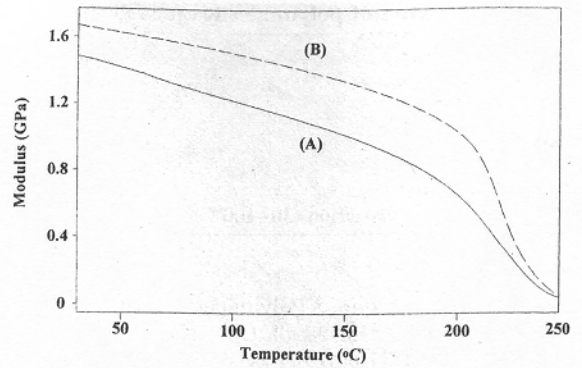

Fig. 8 Dynamic tensile modulus (x-y) of the film versus temperature: (A) pure polymer film; (B) The z-axis conducting film

Each conducting path can be approximated as a copper cylindrical wall with the polymer matrix within the cylinder. The cylinder has outside diameter (d_1) 75 μm, inside diameter (d_2) 71 μm, height 75 μm, and wall thickness 2 μm. The electrical resistivity ρ_s of each conducting path, as calculated by using the Rule of Mixtures, is $1.5 \times 10^{-5} \, \Omega \cdot$ cm, which is much lower than the measured value of 0.5 $\Omega \cdot$ cm. The calculation procedure uses the equation

$$\frac{1}{\rho_s} = \frac{f_c}{\rho_c} + \frac{f_p}{\rho_p},$$

or

$$\frac{1}{\rho_s} \approx \frac{f_c}{\rho_c},$$

where c refers to the conducting particles, and p refers to the polymer matrix. The resistivity of copper is

$$\rho_c = 1.6 \times 10^{-6} \, \Omega \cdot \text{cm}.$$

The volume fraction of copper is

$$f_c = \frac{d_1^2 - d_2^2}{d_1^2} = \frac{75^2 - 71^2}{75^2} = 0.104.$$

Hence,

$$\rho_s = \frac{\rho_c}{f_c} = \frac{1.6 \times 10^{-6}}{0.104} \, \Omega \cdot \text{cm} = 1.5 \times 10^{-5} \, \Omega \cdot \text{cm}.$$

One of the reasons for the difference is related to the quality of the copper coating. A continuous film of average thickness 2 μm was assumed in the calculation. However, there may be a certain degree of discontinuity in the coated layer, thereby resulting in high electrical resistivity for the conducting particles themselves. Another reason is that the copper layer may have undergone a certain degree of oxidation during the film fabrication, which resulted in a higher resistivity than ideal copper. Although the conducting path density of the film was 10^3 per cm^2, some of the paths may not contribute to the z-axis conduction, thereby causing the measured value per conducting path to be yet higher.

3.2 Stress Relaxation. The stress relaxation curve of the z-axis film containing 25 vol.% of 50–100 μm Cu-coated PES particles was obtained at a constant strain of 10 percent, which yielded a z-axis compressive modulus of 10 GPa. The stress only changed slightly with time—from 0.95 MPa at time zero to 0.93 MPa at seven days.

3.3 Thermomechanical Properties. The tensile modulus (x-y) versus temperature is shown in Fig. 8. Curve A is for the polymer film and Curve B is for the z-axis conducting film
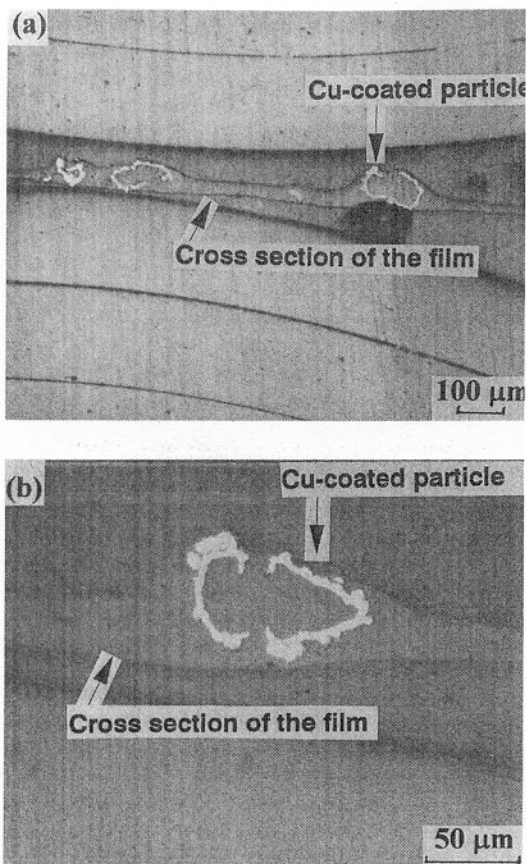
Fig. 9 Optical microscope photographs of the cross section of the z-axis conducting film

containing 25 vol.% 50–100 μm Cu-coated PES particles. It can be seen that the moduli of the composites were similar to that of the neat polymer film, even though the composite film contained the metal-coated polymer particles. The low modulus of the conducting film is helpful for restraining the thermal stress.

3.4 Structure of the z-Axis Conducting Film. The polished cross section of the z-axis conducting film containing Cu-coated particles of size of 50–100 μm is shown in Fig. 9. The bright shell is the copper coating on a PES particle; the thin layer (as marked) is the cross section of the film; the remaining area is the mounting material. It can be seen that the thickness of the film can be as small as 50 μm. Each Cu-coated PES particle extended across the thickness of the film to form an electrically conducting path along the z-axis. As the observed cross section of a conducting particle is not perfectly spherical and the distribution of particles is not perfectly uniform, future improvements are required for practical application. The simplifying assumptions used for modeling in this work may cause considerable deviation.

Although this study used PES as the polymer particles, numerous other thermoplastic polymers are possible, such as polyetherimide (PEI), polyamideimide (PAI), polyphenylene sulfide (PPS), and polyetheretherketone (PEEK), etc. Although

rubber particles have good deformability, the large shrinkage under pressure may cause either cracking of the conducting coating layer or delamination of the metal-coated layer with the rubber particles. This may result in insufficient reliability and reusability of this kind of conducting film. Although this study used PISO as the polymer matrix, numerous other thermoplastics are possible, such as polyimide (PI), silicone (SI), and polybenzocyclobutene (PBC), etc.

4 Conclusion

The z-axis conducting film is a new technology for replacing traditional solder arrays in electronic packaging. Made from 25 vol.% Cu-coated PES particles and a PISO (SIM-2030MO) polymer matrix, the film was electrically conducting in the z-axis only. By applying a pressure of 40 kPa, an electrical resistivity of 2 $\Omega \cdot$ cm was reached along the z-axis while the film was electrically insulating in the in-plane direction. The resistivity remained low (i.e., 7 $\Omega \cdot$ cm) after subsequent pressure release. The electrical resistivity of each conducting path was 0.5 $\Omega \cdot$ cm. In addition, the film exhibited negligible stress relaxation and a low dynamic tensile modulus of 1.67 GPa at room temperature.

Even though several kinds of z-axis conducting film had been previously reported [4–7], they all had different applications in electronic packaging. The film made from this work probably provided a higher area coverage of the conducting particles and was probably easier to make. Therefore, it can be used as a reusable z-axis conducting film with a high conducting path density in electronic packaging. It is also possible to make a film of yet higher packing density ($>10^4$ conducting paths per cm^2) than what is described here by using finer conducting particles. The Cu-coated thermoplastic particles in this work are more easily deformed under pressure than most thermoset particles, thereby allowing easier formation (requiring less pressure) of a good electrical contact. In order to reduce the thickness of the film and to further increase the conducting path density, a technology other than the Doctor Blade method may be pursued. Furthermore, other coating methods, such as chemical vapor deposition (CVD), may be used to possibly improve the quality of the coating, thereby reducing the thickness of the metal layer, the particle size, as well as the weight of the film.

5 References

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