Electrical Conduction Models for Isotropically Conductive Adhesive Joints

Li Li, *Member, IEEE*, and James E. Morris, *Senior Member, IEEE*

***Abstract*— An electrical conduction model for silver filled isotropically conductive adhesives (ICA) was developed. The model combines the microscopic resistance of the bulk silver particles and the contact between silver flakes with the macroscale resistor network calculation by percolation theory. The resistivities of the composites were calculated by resistor network simulations considering both contact effects and particle size effects. Three different types of film typically exist on the silver surface: residual organic films; tarnish films; and a thin epoxy layer. The contact resistance between silver flakes can be due to a constriction resistance, to the tunneling resistance through insulating films, or to the resistance of more conductive layers. The constriction resistance is produced by the restriction of the current flow by small contact spots and is controlled by the actual contact spot area (metallic contact), which is dependent on the contact force between flakes. The tunneling resistance is caused by the very thin layer which may reside on the silver flakes between the metallic contact spots, and is dependent on a barrier film thickness and potential. Oxide and sulfide tarnish films are typically degenerate semiconductors.**

Two- and three-dimensional (2-D and 3-D) computer simulations were performed to predict the effects of particle sizes, shapes, and distribution on the percolation conduction thresholds and cluster sizes. The model predicts that the percolation threshold decreases with broad particle size distributions and high aspect ratio particles. The effective resistivity of the adhesive depends on the thickness dimension of the adhesive pad geometry, with very thin layers resulting in high percolation thresholds and high resistivities. Resistivity does not change with the pad thicknesses greater than a certain thickness level. Silver flake orientation on the surface increases the resistivity of the conductive adhesive pads, but in the same magnitude range. The resistivities of the materials are controlled by silver flake sizes and the nature of the contacts.

***Index Terms*— Conduction model, electrical conductive adhesives, percolation.**

I. Introduction

THE ELECTRICAL resistivity of the conductive adhesive does not depend only on the volumetric silver concentrations as predicted by percolation theory (which is limited in its applicability to the matrix sites occupied by spherical particles) [1], [2], but also on the adhesive cure kinetics, silver flake sizes, distributions, orientations, and microscopic flake contact effects. The silver filled epoxies studied are not conductive unless they are subjected to thermal cure [3], [4]. Therefore, contact resistances between the flakes must be considered in the electrical conduction mechanism of the composite system. Percolation theory assumes metallic conduction between particles, i.e., electrons will travel along continuous chains formed by metallic particles in contact, and does not consider the finite resistance of tunneling conduction across the insulating gaps which interrupt particle-to-particle contacts or constriction resistance caused by the small contact area. Large contact pressures may enlarge the metallic contact spots area by elastic and plastic deformation and also potentially break the organic and tarnish films to produce fresh metallic contacts. The decomposition of the acid insulating layer during the thermal cure will also contribute to the conduction development. The resistivity decreases during thermal cure and with successive heating and cooling cycles [3] can be explained by the changes from an insulating gap between flakes to high resistance tunneling dominated conduction, and finally to metallic conduction after cure.

The purpose of this conduction model study is to provide guidelines for design and process rules for isotropically conductive adhesives (ICA) materials by relating the physical and processing properties of the material to the electrical performance of adhesive joints, and to get a better fundamental understanding of the conduction mechanisms in the composite system.

Computer simulations were used to generate random or partially oriented silver flake distributed structures based on experimental observations of the adhesive joints and particulate geometries. Conduction networks were developed and the computer identified the macroscopic scale contact types and the percolation conduction network clusters. The resistivity of the composite is calculated by solving Kirchoff's current equation at each site in the matrix and the percolation threshold is obtained from the resistivity versus filler volume percentage curves. Microscopic scale contact effects, such as pressure dependent contact resistance between flakes, tunnel conduction through an insulating polymer film (or other absorbed films), a conductive metal oxide film, broken contacts, and decomposition of the organic insulating coating during temperature changes were derived analytically based on assumptions. Thermal and residual stress development during cure is considered in the microscopic contact effects. Computer models combining the microscopic analytical contact resistance model with the macroscopic silver flake percolation network, and with geometric and orientation effects included, give the resistance range of adhesives based on some simplified assumptions.

II. Numerical Simulation and Resistivity Calculation

The details of the theoretical and numerical model approaches, as well as the microscopic conduction models of

Manuscript received June 3, 1996; revised December 3, 1996.

L. Li is with the Motorola Semiconductor Products Sector, Tempe, AZ 85284 USA.

J. E. Morris is with the Department of Electrical Engineering, State University of New York at Binghamton, Binghamton, NY 13902-6000 USA.

Publisher Item Identifier S 1070-9886(97)01694-6.

1070–9886/97$10.00 © 1997 IEEE

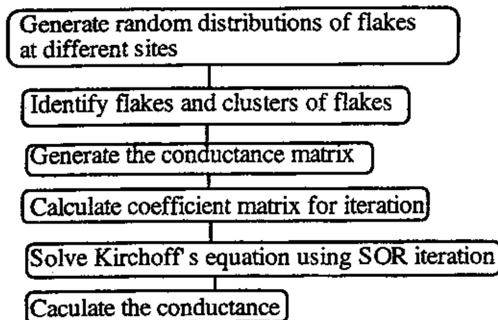


Fig. 1. The simplified flow chart for the simulation model.

the flake contacts, have been discussed in our earlier paper [5]. Resistivities of the composite matrices were calculated by solving the linear equations of Kirchoff's rules with computer iterations [6].

To calculate the resistance of the percolation cluster, also called a "random resistor network," Kirchoff's rules gives the system of coupled linear equations for the voltages at every site

$$I_i = \sum_j (V_j - V_i)\sigma_{ij} \tag{1}$$

where V_i is the voltage at site i, I_i is the net external current going into the site i (nonzero only at the external terminals, and zero on all other sites) and σ_{ij} is the conductance of the connection between the nearest neighbor sites i and j.

The computer simulation program first generates the random occupied sites for the silver flakes in a matrix. The program then counts and identifies the percolation clusters, and gives the common cluster identification number and calculates the number of flakes in these particular sites. Each cluster is checked to see if there is connection between the top and bottom electrodes. If any two sites at opposite electrodes have the same cluster identification number, the sample is determined to percolate in the direction perpendicular to the electrodes. These properties are generated according to the specified filler volume percentage. The resistor networks are established after the continuous percolation clusters are identified. The resistivity of the system is calculated by a program which solves the resistor network equations by iteration and finite difference numerical methods [4].

The silver flake resistivity is 1.67×10^{-6} Ω-cm, with the epoxy assumed to be 5×10^{11} Ω-cm, and contact resistances are calculated (constriction and tunneling resistances) dependent on the contact forces [7]. The simplified flow chart of the model development is shown in Fig. 1. The two-dimensional (2-D) calculation results show that particles with distributed sizes have a lower resistivity transition point, and also lower resistivity. Particles with broad size distributions have the same effects [5].

Three-dimensional (3-D) conduction model simulations were conducted to include the contact resistance effects between the silver flakes. The matrix sizes in the simulation program represent the adhesive pad sizes and thicknesses of the bonding in the adhesive joints. The silver flake is treated as a rectangular shaped particle. The random distribution of the flakes in the matrix is limited by the regular mesh directions, and is actually orientated only in the x, y, and z directions. The resistivity calculation was performed by solving Kirchoff's current equation at each site. The iterative method was used with the applied voltage boundary condition on the top and bottom planes. The potential at each node was solved with the known conductances at each site and contact by the current equations [4]. Silver flake dimensions consist of several cubic mesh units depending on the size defined. The interfaces with the epoxy matrix, another silver flake, or within the same flake were identified by the program, and the appropriate conductance of the epoxy, contact, or silver is then used in the current equation. Contact resistance was used in the calculation if the program identified one particle in contact with its neighbor particles. The thicknesses of the adhesive joints after bonding and cure are around 10–30 μm [8]. One unit mesh size in the simulation corresponds to 1 μm in real adhesive joint dimension, i.e., a $2 \times 2 \times 1$ particle size is actually a $2\,\mu\text{m} \times 2\,\mu\text{m} \times 1\,\mu\text{m}$ filler. The $60 \times 60 \times 30$ matrix dimension size is a $60\,\mu\text{m} \times 60\,\mu\text{m} \times 30\,\mu\text{m}$ adhesive pad; the actual pad area in real applications is normally larger than $60\,\mu\text{m} \times 60\,\mu\text{m}$, except the very fine pitch applications for flip chip bumps. The matrix dimension is limited by the hardware calculation speed and memory capability. However, the dimensions used in these simulations are well above the particle sizes, and we can assume the general simulation trend is similar for larger pads.

Fig. 2(a) shows the resistivity of the material versus filler volume percentage for a matrix size $60 \times 60 \times 20$ with filler particle sizes $2 \times 2 \times 1$ and $4 \times 4 \times 1$. The resistivities of silver and of the epoxy matrix are the same as used in the 2-D model, and the contact resistance between the particles is assumed to be $0.24\,\Omega$ in this case. Contact resistance [5] is calculated by

$$\begin{aligned} R_{contact} &= R_c + R_t \\ &= \frac{\rho}{2a} + \frac{\eta}{A_c} \end{aligned} \tag{2}$$

assuming the constriction resistance, R_c, is the dominant term and ignoring the tunneling resistance, R_t, term for the fully cured materials. The contact size of 70 nm in diameter from the TEM investigations [8] is used for the calculation. The resistivity of the system changes with the contact resistance, and this effect will be discussed later. The resistivity versus filler volume percentage curve has a lower percolation threshold for the $4 \times 4 \times 1$ particle size ($V_c = 29\%$ for random size distribution and 32% for monosized particles) than that for the $2 \times 2 \times 1$ particle size ($V_c = 34\%$ for random sizes and 37% for monosized particles). The random size distributions generated in the simulations include different percentages of particle sizes less or equal to the size indicated (such as $2 \times 2 \times 1$, random), and Fig. 2(c) shows the details of the percentages of these particles sizes. This indicates that the high aspect ratio particles will have a lower percolation threshold, and this is one reason to use the flake fillers. Fig. 2(b) shows the percolation curves for a $60 \times 60 \times 30$ matrix with $2 \times 2 \times 1$ and $2 \times 2 \times 2$ particles of monosize and random size distributions. The random size filler has a lower percolation threshold than that of the monosized particles

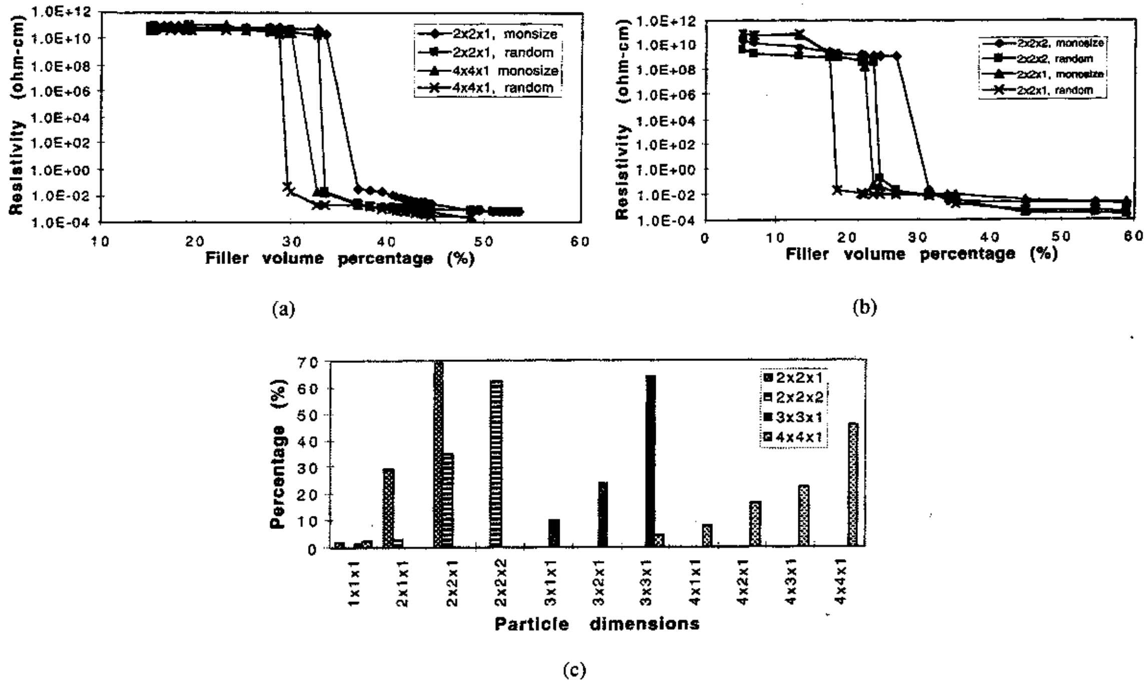


Fig. 2. Resistivity versus filler volume percentage in the 3-D simulations: (a) Matrix $60 \times 60 \times 20$, (b) matrix $60 \times 60 \times 30$, and (c) percentages of the particles sizes for the random particle size distributions.

again. This is consistent with the experimental results by other investigators [9], [10]. The broad size fillers are easier to form a percolation network because the small particles can fill the interstices between large particles. The same particle shape effects as shown in Fig. 2(a) can be found here: the higher aspect ratio filler system has a lower percolation threshold.

The percolation threshold also depends on the thickness of the material. For the same monosized particle size $2 \times 2 \times 1$, the $60 \times 60 \times 20$ matrix has a higher V_c at 35% compared to V_c at 24% obtained from the $60 \times 60 \times 30$ matrix. The percolation conduction network may be cut in the Z-dimension if the matrix thickness is too thin, and more fillers are needed to form the continuous "backbone" in the system. Clearly from the 2-D simulation results discussed in our earlier paper [5], the percolation threshold in the 2-D network is much higher than that of the 3-D results. The resistivity dependence of the thickness of the joint after the percolation threshold for a 60×60 area with 36% $2 \times 2 \times 2$ and $2 \times 2 \times 1$ random size particles is shown in Fig. 3. The resistivities decrease with the increased matrix thicknesses. The thinner adhesive layer has a larger increase in resistivity, and the resistivity does not change much after the adhesive thickness is larger than certain thickness value (about ten times the flake dimensions). This phenomenon has been observed in our preliminary studies [11] and by other investigators [12]. (50 μm thick screen printed samples had a higher resistivity than 0.9 and 1.6 mm thick stenciled printed samples (much larger than the ten times the flake dimensions) [11].

Because of the finite matrix dimension used, the random number generator cannot assure a perfect random distribution. The reproducibility of the model results were tested with different random seeds. Fig. 4(a) shows the resistivity versus filler volume percentage with five random seed generators for

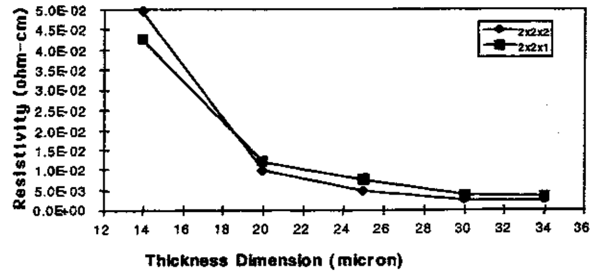
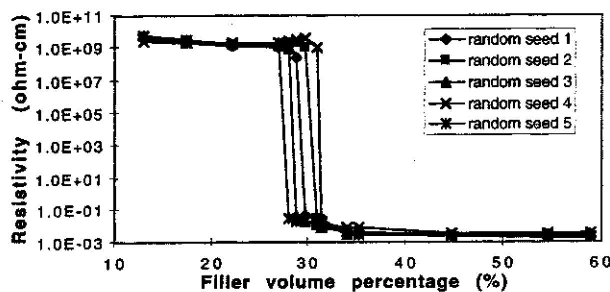


Fig. 3. Resistivity versus adhesive pad thickness for a 60×60 matrix area at 36% filler volume percentage for random distributed particles.

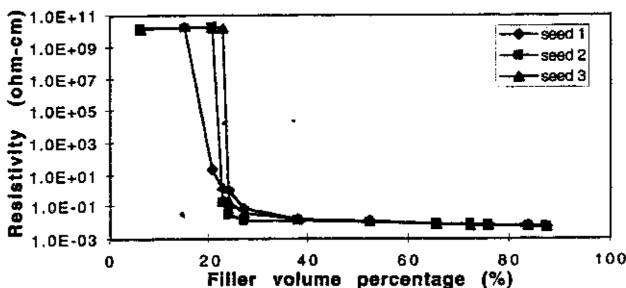
a $60 \times 60 \times 30$ matrix filled with $2 \times 2 \times 2$ monosized particles. The resistivity does not change by different random seeds below and above the percolation threshold, but it is more sensitive around the percolation threshold, representing the relative dispersion in these parameters in physical systems. The percolation threshold, V_c, is spread over the range of 27–32%, and this indicates the accuracy of the model simulation with different random seeds. Fig. 4(b) is another case for the $60 \times 60 \times 30$ matrix filled with random $4 \times 4 \times 1$ particles. In this case the percolation thresholds vary from 18–24%, and the resistivities below and after the percolation threshold are in the same range for different random seeds.

III. Silver Flake Orientation Effects

Silver flake alignments on the surfaces were observed in the bulk adhesives and their joints from the microstructural studies [8], [11]. The resistivity of the adhesive pad is calculated by the computer simulation by arranging the particle orientation on the top and bottom layers of the matrix structure. The 3-D FORTRAN program [4], which considers the particle

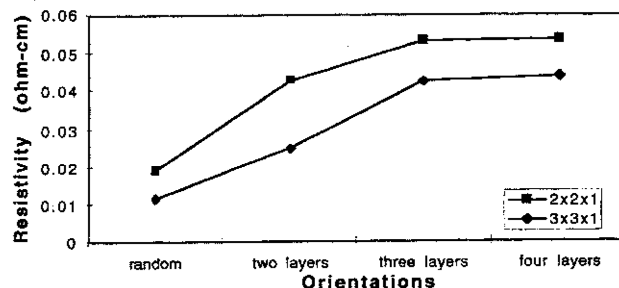


(a)

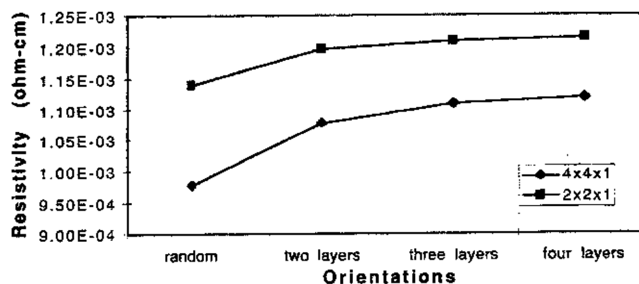


(b)

Fig. 4. Resistivity versus filler volume percentage with different random seeds for a $60 \times 60 \times 30$ matrix: (a) $2 \times 2 \times 2$ monosized particles and (b) $4 \times 4 \times 1$ random fillers.



(a)



(b)

Fig. 5. Resistivity versus particle orientations: (a) A $60 \times 60 \times 30$ matrix with 31% monosized fillers and (b) a $72 \times 72 \times 30$ matrix with 40% random size particles.

alignment effects, is based on the 3-D conduction model program with the additional consideration of the orientation effects.

Fig. 5(a) is the simulation result for a $60 \times 60 \times 30$ matrix filled with 31% $2\times2\times1$ and $3\times3\times1$ monosized particles. The resistivities increase with the particle orientation in one layer on the top and bottom planes, and then increase slowly for the two layer alignment, and nearly saturate for the three layer flake alignment. Fig. 5(b) shows similar results for a $72\times72\times 30$ matrix filled with 40% $4 \times 4 \times 1$ and $2 \times 2 \times 1$ random size particles. The resistivity value is lower here because of the higher filler percentage above the percolation threshold. Overall, the silver flake orientation structure increases the resistivity of adhesive pad in the direction perpendicular to the alignment layer, but within the same order of magnitude. The model simulation results show that conductivity of the adhesive joint is not changed dramatically by the silver flake alignment or orientation effects. The mechanical adhesion strength is more likely to be degraded by the silver flake orientations on the joint surface, which reveal less adhesive layer or area for the mechanical bonding between the two adherent surfaces. This may contribute to the issues of the poor adhesion and shock strength of the adhesive joints compared to solder joints [8].

IV. Contact Resistance Effects on Resistivity

The contact resistance of 0.24 Ω was used in the above simulation cases; it was selected to represent the value for the cured adhesive assuming the constriction resistance to be the main contribution of the contact resistance. During the adhesive thermal cure process, the contact resistance between silver flakes is the main factor controlling the resistivity change of the adhesives. The contact resistance experiences several stages of physical and magnitude change in the curing process. Even though the filler volume percentage is already above the percolation threshold before cure, the resistivity of the conductive adhesives is still high (106 Ω-cm). The contact resistance before cure is mainly contributed by the insulating gaps between the flakes caused by the uncured polymer, by organic insulating layers covered on the surfaces, or by any tarnish film existing on the flake surfaces. The contact resistance is governed by (2) with both constriction and tunneling terms, but is dominated by the larger tunneling resistance term. The constriction resistance term is calculated to be 0.167 Ω while the tunneling resistance is 3821 Ω with $\eta = 0.3\times10^{-6}$ Ω-cm^2 for a 1 nm gap thickness [13] and a 100 nm contact diameter. The tunneling resistance per cm^2(η) is exponentially dependent on the insulating film thickness,and is similarly sensitive to potential barrier height and shape [4].

Fig. 6 shows the contact resistance effect on the resistivity of a $60\times60\times30$ matrix for $2\times2\times2$ and $2\times2\times1$ monosized fillers at 31% volume percentage. The model here assumes the contact resistance and contact force are the same for any of the two silver flake contacts, which is independent of the particle size and distribution; only the contact area is changed by the contact forces. The resistivity increases several orders of magnitude with the increases in contact resistance even beyond the percolation threshold. The experimental results of the conduction development [3], [4] show orders of magnitude drop of the resistivities of the conductive adhesives during cure. This is closely related to the conduction mechanism change from the (insulating) tunneling resistance to dominance

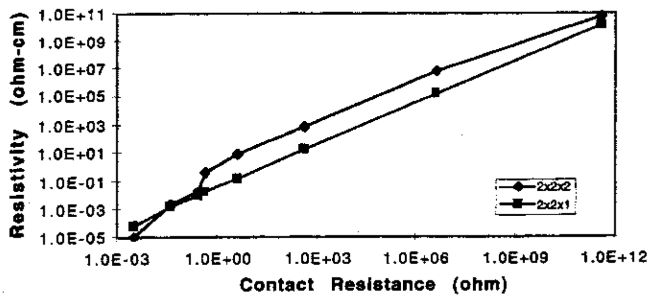


Fig. 6. Resistivity versus contact resistance for a 60 × 60 × 30 matrix with monosized fillers.

by metallic resistance. The physical process is related to the decomposition of the acid layers and breakage of the soft tarnish films in the silver flake contacts. Continued small scale resistivity decreases are accompanied by the enlargement of the contact area by the contact force induced by the curing or cooling process. Large flake fillers possibly have larger contact areas as compared to small flakes. The silver contact dimensions of Adhesive A [4], [8], which has a flake size less than 0.5 μm, range from 50–100 nm as observed by TEM, and the constriction resistances are calculated to be 0.334 Ω and 0.167 Ω. The 0.5 μm diameter silver particle resistance is approximately two orders of magnitude smaller than the constriction resistance. Therefore the conduction is restricted by the constriction resistance for Adhesive A, assuming the metallic contact (no tunneling resistance term) for the completely cured materials.

As is usually the case in solid-state physics, the temperature dependence of resistivity (TCR) provides a good means for investigating the conduction process in the heterogeneous materials [14]. The experimental TCR result discussed for Adhesive A is $1.8 \times 10^{-3}/°C$ [4]. The smaller constriction dimensions, such as 50–100 nm for Adhesive A, are on the order of electron mean free paths, give a high resistance and a lower TCR. Other conduction mechanisms such as tunneling and the degenerate semiconducting conduction may also exist besides the metallic conduction [15]. The smaller the filler particles are, the larger the numbers of contacts involved in the material for the same filler volume percentage. The conduction mechanisms associated with these contact effects are expected to be more important than the silver conduction through the submicron particles. Adhesive B has a measured TCR value at $2.4 \times 10^{-3}/°C$ [4], [8]. Adhesive B has a bimodal flake size distribution, with the larger flake size ranging from 2–6 μm and another class less than 0.5 μm [4], [8]. The constriction resistance is determined by the contact area between the metal filler particles. The contact dimension could be larger than the 50–100 nm range for the larger particles. The calculated constriction resistance is in the same magnitude as that of the silver particles, assuming a contact size around 500 nm for 6 μm diameter flakes. In this case, constriction and silver conduction will have similar contributions to the resistivity. However, Adhesive B contains lots of smaller size particles as well, which have a dominant constriction resistance, and also possible zero and negative TCR conduction mechanisms. Adhesive C has flakes from 3–8 μm and less than 1 μm particles, and the TCR is measured to be $2.9 \times 10^{-3}/°C$ [4], [8]. The small particle size group will have a lower TCR, while the larger size particles possibly have a TCR closer to silver's. In our preliminary studies [11], all the adhesives have measured TCR's very close to silver's. These adhesives have larger silver flake sizes of 10–15 μm. The contact area between these larger flakes will be larger as well, the constriction resistance is in turn smaller than the silver metal particle resistance. Metallic conduction through the silver flake is expected to be the dominant resistance mechanism.

V. Conclusion

An electrical conduction model was developed by understanding the microscopic conduction between the silver flake particles and macroscale conduction explained by the percolation theory. The contact resistances between the silver particles were considered. The contact pressure and force applied on the silver flake contacts have very important effects on the contact resistance. The material hardness, pressure between particles and particle contact sizes are important parameters controlling the contact resistance. These will all decrease the contact resistance between the particles and hence reduce the resistivity of the conductive adhesives. The decomposition of the acid insulating layer during the thermal cure will contribute to one or more linkages in the critical cluster "backbone" paths.

The resistivities of the composites were calculated by resistor network simulations considering the contact effects and particle size effects. Very thin layers result in high percolation thresholds and high resistivities. After a certain thickness level, resistivity does not change with the pad thickness. Silver flake orientation on the surface increases the resistivity of the conductive adhesive pads, but in the same magnitude range. The resistivities of the materials are controlled by the contact nature and silver flake sizes. During the thermal cure process, contact resistance changes from insulating to tunneling, and finally to metallic contact.

TCR's of the materials are dependent on the silver particle sizes and distributions. For the very small fillers (<0.5 μm), small constriction dimensions induce lower TCR's. Other zero and negative TCR conduction mechanisms may exist (tunneling or semiconducting). For the bimodal silver filler size (3–8 μm, and <1 μm), such as Adhesives B and C, constriction and silver metallic conduction as well as the other TCR mechanisms associated with the smaller range of particles coexist. For the larger silver fillers (10–15 μm), the silver metal conduction mechanism will be the dominant component of resistance.

References

[1] E. Pike and C. H. Seager, "Percolation and conductivity: A computer study I and II," *Phys. Rev. B*, vol. 10, no. 4, pp. 1421–1434, 1435–1446, Aug. 1974.

[2] S. Kirkpatrick, "Percolation and conduction," *Rev. Modern Phys.*, vol. 45, no. 4, pp. 574–588, 1973.

[3] D. Klosterman and L. Li, "Conduction and microstructure development in Ag filled epoxies," in *Proc. Int. Sem. Conductive Adhesive Electron. Packag.*, Eindhoven, The Netherlands, Sept. 5, 1995, pp. 5–15.

[4] L. Li, "Basic and applied studies of electrically conductive adhesives," Ph.D. dissertation, State University of New York at Binghamton, 1995.
[5] L. Li and J. E. Morris, "Electrical conduction models for isotropically conductive adhesives," in *Proc. Int. Sem. Conductive Adhesive Electron. Packag.*, Eindhoven, The Netherlands, Sept. 5, 1995, pp. 35–44.
[6] G. D. Smith, *Numerical Solution of Partial Differential Equations: Finite Difference Methods*, 3rd ed. Oxford, U.K.: Clarendon, 1985.
[7] N. Vittal, R. C. Aiyer, C. R. Aiyer, M. S. Setty, S. D. Phadke, and R. N. Karekar, "Formulation of silver loaded manganite based thermistor paste and application of percolation theory for sudden transition in conductance," *J. Appl. Phys.*, vol. 64, no. 10, pp. 5244–5248, Nov. 1988.
[8] L. Li, J. E. Morris, J. Liu, Z. Lai, L. Ljungkrona, and C. Li, "Reliability and failure mechanism of isotropically conductive adhesives joints," in *Proc. 45th IEEE Electron. Comp., Technol. Conf.*, Las Vegas, NV, May 1995, pp. 114–120.
[9] J. P. Reboul, "Ionic polarization and electronic conduction in carbon-black-filled poly-vinylchoride," *J. Appl. Phys.*, vol. 46, no. 7, p. 2961, 1975.
[10] S. S. Sastry, G. Satyanandam, T. F. S. Raj, and R. Vasanthakumari, "Effect of fillers on electrical properties of epoxy composites," *J. Appl. Polym. Sci.*, vol. 36, pp. 1607–1615, 1988.
[11] L. Li, C. Lizzul, H. Kim, I. Sacolik, and J. E. Morris, "Electrical, structural and processing properties of electrically conductive adhesives," *IEEE Trans. Comp., Hybrids, Manufact. Technol.*, vol. 16, pp. 843–851, Dec. 1993.
[12] G. R. Ruschau, S. Yoshikawa, and R. E. Newnham, "Percolation constraints in the use of conductor-filled polymers for interconnects," in *Proc. 42nd IEEE Electron. Comp. Technol. Conf.*, May 18–20, 1992, pp. 481–486.
[13] ——, "Resistivities of conductive composites," *J. Appl. Phys.*, vol. 72, no. 3, pp. 953–959, Aug. 1992.
[14] L. Nicodemo, L. Nicolais, G. Romeo, and E. Scafora, "Temperature effect on the electrical resistivity of metal/polymer composites," *Polym. Eng. Sci.*, vol. 18, no. 4, pp. 293–298, Mar. 1978.
[15] F. Carmona and C. Mouney, "Temperature-dependent resistivity and conduction mechanism in carbon particle-filled polymers," *J. Mater. Sci.*, vol. 27, pp. 1322–1326, 1992.

Li Li (M'95) received the B.S. and M.S. degrees in material science and engineering from the University of Science and Technology, Beijing, China, and the Ph.D. degree in electrical engineering from the State University of New York at Binghamton, Binghamton, NY.

She is currently a Process Development Engineer at Motorola Advanced Interconnect Systems Laboratory, Tempe, AZ, working on low cost flip chip interconnect. She worked at Motorola CMRC during the summer of 1994 on advanced flip chip on board encapsulant materials. She worked on conductive adhesive research as a Research Associate at IVF, Sweden, in October and November 1994, and at Motorola from January to June 1995.

Dr. Li is the first Motorola-IEEE/CPMT Graduate Fellowship Winner for research in electronic packaging.

James E. Morris (SM'82), for a photograph and biography, see this issue, p. 2.