

Deconstructing the Myth of Percolation in Electrically Conductive Adhesives and Its Implications

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Abstract

The modern emphasis on green technologies has caused the electronics industry to seek alternative solutions to lead-based interconnections. Electrically conductive adhesive (ECAs) composed of metallic fillers within a polymer matrix have received the majority of the interest in lead-free interconnect technology. However, ECAs are still unable to meet the demands of high performance consumer electronics.

Previous research recognized a critical filler concentration where there is a dramatic increase in conductivity, followed by a plateau. Researchers have labeled this transition as evidence of a percolation, implying a continuous interconnected metallic network. Our work comprised of a series of "proof of concept" type experiments deconstructs the myth of percolation and emphasize the functional role of the polymer matrix. From a theoretical standpoint direct metal to metal contact is not feasible since silver particles coated with short chain acids are easily wet by the polymer matrix. Assembly conducted under low mechanical stresses is unable to displace the adsorbed surfactant to form metallic contact. Moreover, preparation of a high K epoxy (Dielectric Constant ~ 5.5), Co(III) acetylacetonates (Co(III) AcAcs) doped diglycidyl ether of bisphenol F had unstable conductivities orders of magnitude lower than the control samples; under similar applied DC. Dielectric constant has a minimal effect if metal to metal contact is the dominant charge transport mechanism. However, tunneling through materials with high dielectric constant impedes the tunneling efficiency.

We clearly demonstrate that charge transport at the interface occurs via secondary conductivity pathways, dominated by thermally assisted tunneling mechanisms. The importance of these secondary conductivity mechanisms is highly dependent on the particle-thin film dielectric interaction. This revolutionary discovery provides a new approach for scientists and engineers to improve the performance of electrically conductive adhesives through the incorporation of electrically functional matrix materials.

Introduction

The semiconductor industry has made considerable strides within the past decades but integration and interconnection of components into electronic systems has remained essentially unchanged. Lead (Pb) based alloys, eutectic tin-lead (Sn/Pb) solders have been the de facto interconnect material used for power, ground and signal transmission for the semiconductor industry. However, toxicological and environmental concerns associated with lead based interconnects have caused manufactures to seek alternative interconnect materials.

To date, efforts to produce alternative interconnect materials have focused on two alternatives: Lead-free solders

and electrically conductive adhesives (ECAs). Most lead free solders contain Sn because it is inexpensive and melts at relatively low temperatures (232°C). However, the melting temperature (T_m) is high when compared with conventional Pb based solders ($T_m=183^{\circ}\text{C}$). The ability to processes electronics at temperatures $<150^{\circ}\text{C}$ will increase long term reliability. Although some lower temperature Lead-free solders are available, like Indium/Tin (Sn/In $T_m=120^{\circ}\text{C}$), Tin/Bismuth (Sn/Bi $T_m=138^{\circ}\text{C}$), and Tin/Zinc/Silver/Aluminum/Gallium (Sn/Zn/Ag/Al/Ga $T_m=189^{\circ}\text{C}$), their properties and processability are still of concern [1]. On the other hand, polymer-based composite systems like ECAs are the ideal green interconnect alternative to lead-containing solder interconnects. Compared to metallic solder technology, ECAs offer numerous advantages, such as environmental friendliness (elimination of lead usage and flux cleaning), mild processing conditions, fewer processing steps (reducing processing cost), and fine pitch capability [2-3]. Polymer-based ECAs offer the advantage that they can be processed at $T<150^{\circ}\text{C}$, temperatures significantly lower than metallic solders. The full scale integration of polymer based ECAs with low temperature processability would dramatically reduce the carbon footprint of the semiconductor industry.

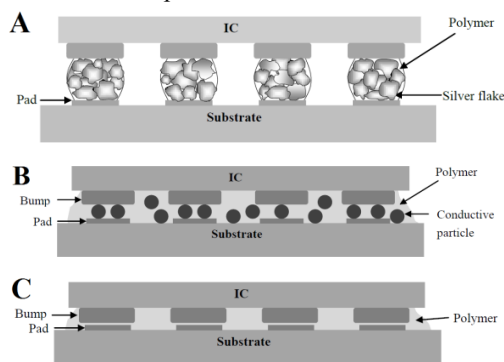


Figure 1. Schematic drawing of (a) isotropic conductive adhesive (b) anisotropic conductive adhesive (c) non-conductive adhesive

ECAs have been commonly classified into three categories: isotropically conductive adhesives (ICA), anisotropically conductive adhesives (ACA) and non-conducting adhesives (NCA). ICA generally have high metallic filler loadings >80 wt%. The high filler loading in ICAs creates an interconnected network unconfined by directionality (Figure 1a). ACAs (Figure 1b) have reduced metallic filler loadings ($<5-10$ wt%) to avoid formation of a "percolated" network (Figure 2). The reduced metallic filler loading in ACAs limit conduction to only the $-z$ direction. NCA (Figure 1c), unlike ICA and ACA, does not contain any

conductive particles, instead an organic adhesive is used to bond the bump to the pad under an applied pressure (1-500 MPa) and elevated temperatures ($T \sim 150^\circ\text{C}$). It has been claimed that conductivity in NCA results from the formation of metallic contact spots (bump-pad) in the inherently rough surfaces[4].

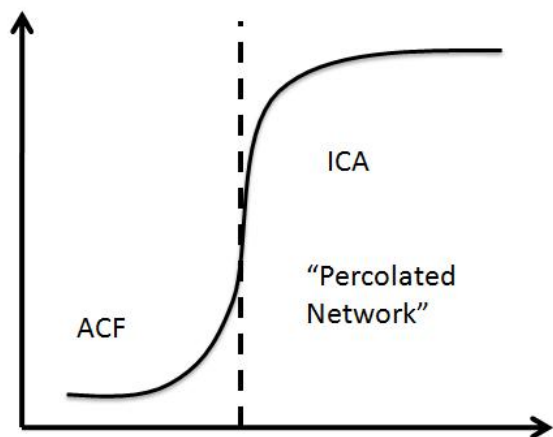


Figure 2. Schematic drawing of a percolated network

These simple descriptions of the conductive pathways in ECA, despite being intuitively correct, are lacking justification. These descriptions beg the question, are these conduction pathways the result of a metallic interface? Questions regarding the interfacial phenomenon have been largely ignored due to their inherent complexity. Modern characterization techniques are unable to probe composite interfaces with the sub-nanometer scale resolution necessary to confirm the presence of a metallic interface.

It is essential for understanding and future developments that we are able to accurately describe the particle and joint interconnectivity within ECA. Furthermore, we must understand how the interfacial properties of the particles, bumps and pads affect the interconnect performance.

We deconstruct the myth of percolation and present a new approach to conceptualize ECA in terms of metallic islands isolated by nanometer to sub-nanometer dielectric barriers. This new understanding will prove paramount in our ability to engineer ECA capable of full scale integration into future high performance electronics.

Experimental Methods

Two proof of concept type experiments were used to deconstruct the myth of percolation: 1. Theoretical analysis of the interfacial properties of the composite. 2. Study of the dielectric constant effects on conduction in ICA.

Theoretical reconceptualization of the filler interface

Thermogravimetric analysis was conducted using a Q5000 (TA Instruments). Ag flakes (Ferro Corporation) were heated

to 150°C at a rate of $10^\circ\text{C}/\text{min}$, the flakes were held isothermally for 1 hour concluding with a ramp up to 300°C at a rate of $5^\circ\text{C}/\text{min}$. Differential Scanning Calorimetry (DSC) Q2000 (TA Instruments) was conducted isothermally at 150°C for 1 hour, followed by a temperature ramp at a rate of $5^\circ\text{C}/\text{min}$ up to 300°C . The silver flake interactions were conceptualized by considering the forces that result due to deformations in the adsorbed monolayer upon close approach. The Hertz model and the Shull correction factor were used to qualitatively describe the surface forces between approaching Ag flakes.

Effect of matrix dielectric on electrical conductivity

Diglycidyl ether of bisphenol-F (DGEBF, Shell Chemical Company) (Epon 862) was doped with Cobalt (III) Acetylacetonate (CoAcAc) (98% Sigma Aldrich) at concentrations of 2.5 and 5 wt%. CoAcAc was dissolved in DGEBF at 80°C for >7 hours, until the CoAcAc was completely dissolved. Curing agent, hexahydro-4-methylphthalic anhydride (HMPA, Lindau Chemicals) and catalyst 1-cyanoethyl-2-ethyl-4-methylimidazole (Imidazole) (2E4MZ-CN, Shikoku Chemicals Corporation) was added to the epoxy solution at room temperature. ECA was prepared by dispersing a bimodal mixture of silver flakes in the epoxy formulation in a 4(Ag):1(epoxy) ratio by weight; as described in Table I. Two strips of Kapton tape (Dupont) were applied onto pre-cleaned glass slides. Epoxy formulations were printed onto glass slides. Following thermal cure at 150°C for 1 hour, bulk resistance was measured using a Keithley 2000(Keithley Instruments Inc.) multimeter; using the four wire method. The width and length of the specimen was measured using a digital caliper (VWR). The thickness of the sample was measured by Heidenhain (thickness measuring equipment, ND 281B, Germany). The bulk resistivity was calculated using Equation 1 where l , w and t are the length, width and thickness respectively:

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

The dielectric constants of the prepared epoxies were determined using a dielectric analyzer TA Instruments model 2970, using a single surface remote sensor at room temperature immediately following curing at 150°C . The cure kinetics of the epoxy systems formulated was determined using a differential scanning calorimeter TA Instruments model Q2000 at a ramp rate of $5^\circ\text{C}/\text{min}$ up to a maximum temperature of 250°C .

Results and Discussion

Theoretical reconceptualization of the filler interface

DSC on silver flakes coated with stearic acid determined the desorption temperature to be 185.5°C , significantly greater than the ECA curing temperature of 150°C (Figure 3a).

Table I. Epoxy Formulations

Experiment	Epoxy Used	Epoxy/HMPA/Imidazole	Co(III) ACAC	Silver A	Silver B	Cure Temperature/Time
Dielectric Effect control	862	20	0	40	40	150°C / 1 Hr
Dielectric Effect 2.5 wt%	862	17.5	2.5	40	40	150°C / 1 Hr
Dielectric Effect 5 wt%	862	15	5	40	40	150°C / 1 Hr

Isothermal DSC confirmed that there is no desorption during the curing process (Figure 3B). TGA did show some evidence of weight loss at 150 °C; however this is likely to correspond to weakly adsorbed organics or water on the surface of the Ag flakes. The desorption of the surfactant is evident by the peak at 189.5°C, similar to the desorption peak temperature found with DSC. The positive weight gain seen in the TGA is likely the result of oxidation following desorption. If the weight loss at 150°C is correlated to desorption, the rate of desorption is slow. Since the imidazole based cure used in the epoxy system reacts quickly, gelation occurs prior to significant desorption of surfactants. Desorption following polymeric gelation will not affect the ECA morphology. Thus we must assume that the surfactants remain on the surface of the silver flakes following the curing process.

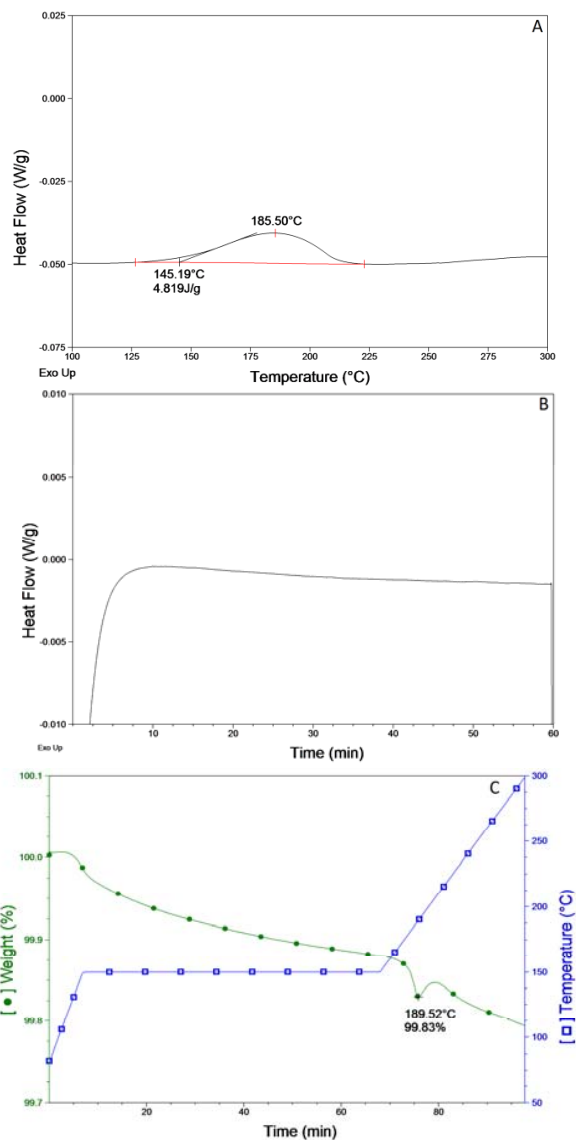


Figure 3. Characterization of surfactant desorption A.)DSC 5 °C/min to 250 °C B)DSC isothermal 150 °C for 1 hour C. TGA isothermal 150°C ramp from 150 °C to 300 °C at 5°C/min

These adsorbed surfactants are essential to obtain highly conductive ECA. The surface adsorbed surfactants act as a lubricant, stabilizing the particle dispersion and preventing aggregation. Silver flakes dispersions stabilized with stearic acid surfactants were stable for >3 months without any noticeable sedimentation or aggregation. Without surface treatment of silver flakes ECA formulations are unstable and inhomogeneous. Thus, because of the existence of a thin layer of adsorbed surfactant on the surface of the silver flakes, the interactions between two silver flakes can be visualized as shown in Figure 4A.

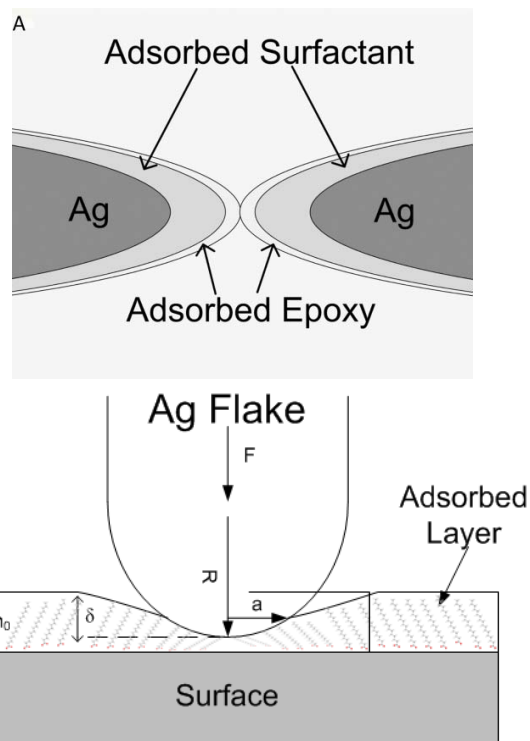


Figure 4 (a) Schematic diagram of interface between two silver flakes on close approach. (b) Diagram of particle interaction with chemically adsorbed Stearic acid.

The silver flakes will be coated with a surfactant layer ~2.3 nm thick and a layer of physically adsorbed epoxy. The thickness of the physically adsorbed epoxy layer is dependent on its molecular length, conformation and surface interactions. Upon close approach of particles during printing, the surfactant and surface adsorbed epoxy must deform to form metallurgical contact. Under the assumption that the silver particles are not deformed during the printing process, the deformation of the surfactant layer can be modeled by the Hertz theory (Figure 4b)[5]. The Hertz theory relates the contact area with the force through the bulk modulus of elasticity of a penetrating sphere of radius R onto a planar surface. For simplicity we will assume that the adsorbed layer is a homogenous elastomer with thickness h. Therefore, silver flake on close approach will cause an indentation (δ) in the monolayer proportional to the contact area.

$$\delta = \frac{a^2}{R} \quad (2)$$

The indentation of the surfactant molecules can be related to the applied force through the bulk modulus (K_{bulk}):

$$K_{bulk} = \frac{3E}{2(1-\nu)^2} \quad (3)$$

$$F = K_{bulk} R^{1/2} \delta^{3/2} \quad (4)$$

The applied force causes a distribution in the normal stress ($p(r)$) of the adsorbed layer along the radius of the penetrating particle:

$$p(r) = \frac{3K_{bulk}a}{2\pi R} \left(1 - \left(\frac{r}{a}\right)^2\right)^{1/2} \quad (5)$$

The yield stress of the adsorbed layer perpendicular to the loading axis is defined from the point where the sphere starts penetrating into the adsorbed layer:

$$\sigma_{y\perp} = \frac{3F_y}{2\pi a_y^2} \quad (6)$$

Upon indentation, the adsorbed layer will act to distribute the stress. This effect is incorporated through the Shull correction factor for indentation [6].

$$\delta = \delta_H \left(0.4 + 0.6 \exp\left(-\frac{1.8a}{h_0}\right)\right) \quad (7)$$

$$F = F_H \left(1 + 0.15 \left(\frac{a}{h_0}\right)^3\right) \quad (8)$$

ECA formulations are significantly more complex than the simplified model above, however the aforementioned model provides a novel perspective and insight into the interfacial forces. Both the Hertz model and the Shull correction factors assume a non-interacting, low viscosity, frictionless medium. Experimental determination of the repulsive force of adsorbed surfactants in aqueous solutions, using atomic force microscopy has shown the repulsion force to vary between 1-15 nN (~2.5-37.5 MPa) [7]. The variation in repulsion force is a direct result of the molecular length of the adsorbed layer and dispersion stability. The models represented only accounts for the interaction when one of the surfaces is treated; interactions with two surfactant modified surfaces are exceedingly more complex. Furthermore, secondary relaxation mechanisms of the epoxy which acts as the solvent and large frictional forces at the interface add an additional degree of complexity. Since all these effects serve to increase the particle-particle repulsion, this model can be used to define the minimum possible force needed to cause direct metallic contact. A more complex and descriptive model is needed to quantitatively understand the surface forces in ECA. However, since the required force to cause deformation in the adsorbed surfactant is well in excess of the applied force during screen printing, formation of a metallic interface is infeasible. This implies that a thin dielectric layer exists between the silver flakes. Thus secondary charge transport mechanisms dominate charge transport at the interface. These secondary conduction mechanisms consist of tunneling and hopping electron transport mechanisms. The statistical

probability of these tunneling/hopping mechanisms control the macro scale conductivity of ECAs.

Effect of matrix dielectric on electrical conductivity

DEA determined that the concentration of CoAcAc and the dielectric constant of the epoxy are directly correlated. This increase in dielectric constant upon doping with CoAcAc is due to highly polarizable bonds in the AcAc structure. It was found that the dielectric constant of the undoped epoxy and 2.5 wt% CoAcAc epoxy was ~3.1 and ~4.2 respectively. The epoxy doped with 5 wt% CoAcAc has been shown to have a dielectric constant of ~5.5 [8].

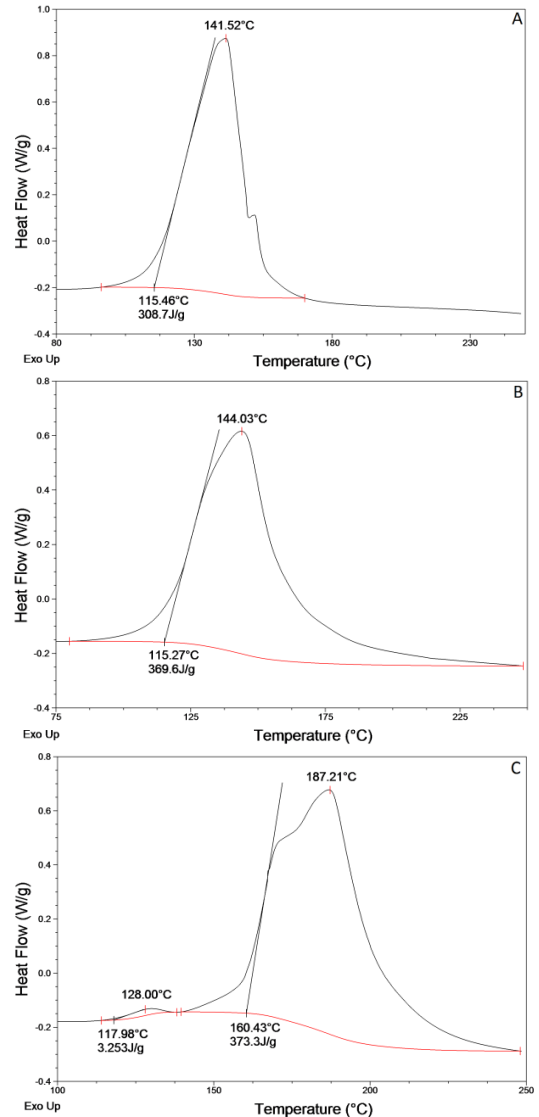


Figure 5. DSC of (a) 862 Imidazole cured (b) 862 doped with 5 wt% CoAcAc (c) 862 CoAcAc cure

DSC confirmed that the cure mechanism was unaltered by the addition of the CoAcAc, a latent catalyst. Comparison of the curing profile for undoped and doped epoxies shows that the enthalpy of reaction and onset temperature was unchanged by the addition of the CoAcAc (Figure 5a-b). DSC of CoAcAc cured epoxy was found to have an onset temperature 160.43 °C, ~45°C higher than both the doped and undoped

epoxies (Figure 5c). Thus, the CoAcAc doping played an insignificant role in the cure mechanism.

The conductivity measurements on epoxies formulated as described in Table I are shown in Figure 6. ECA prepared with the undoped epoxy was found to have an average resistivity of $9.71 \times 10^{-4} \pm 3.37 \times 10^{-4} \Omega \cdot \text{cm}$. The CoAcAc doped ECA was found to have a resistivity directly correlated with the doping concentration/dielectric constant. The resistivity of the ECA doped with 2.5 wt% and 5 wt% CoAcAc had average resistivities of $2.24 \times 10^{-3} \pm 7.09 \times 10^{-4} \Omega \cdot \text{cm}$ and $1.56 \pm 0.52 \Omega \cdot \text{cm}$ respectively. If the silver flakes are in direct metallic contact dielectric constant of the epoxy should have no effect on the DC resistivity. However, tunneling probability is inversely correlated to the polarizability of the tunneling medium [9]. Thus, tunneling must play a significant role in the conduction pathway. If a percolated network of metallurgical interconnected particles existed, the alterations to the tunneling probability would have a minimal effect on the bulk resistivity. The orders of magnitude dependence of the bulk resistivity on tunneling probability confirms that a percolated metallic network does not exist.

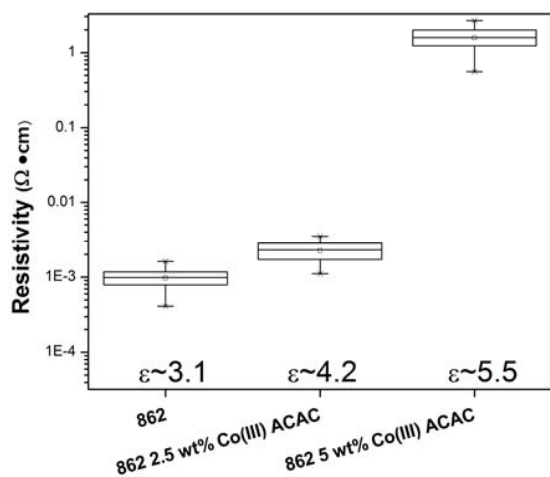


Figure 6. Box plot of the correlation between resistivity and dielectric constant

Outlook and Perspective

The evidence confirming that a percolated metallic network does not exist in electrically conductive adhesives is not unexpected. Over the past 15 years, results in literature have described phenomenon that could only be explained by a system consisting of small metallic islands separated by nanometer to sub-nanometer dielectric. However, previous literature has failed to deduce that their results imply that a percolated network does not exist.

Recently, Zhang et al showed that it is capable to produce highly conductive ECAs with low temperature sintering (150-180 °C) of silver nanoparticles [10]. The sintering process hinged on the ability to decompose the organic surfactants at the surface prior to gelation. The decomposition of the surfactant leads to direct metal contact between the silver flakes, enabling the sintering of nanoparticles at the interface.

It is widely accepted in literature that treating the surface with self-assembled monolayers (SAMs) tunes the work function at the metallic interface [11-12]. Tuning the work

function using thiol based SAMs has been proven to reduce both contact and bulk resistivity [2, 13-16]. The incorporation of SAMs, typically ~1 nm in length, could only alter the electrical properties if they persist following curing at the interface. Thus, nanoscale tunneling junctions have a significant contribution to the bulk resistivity.

Furthermore, it is commonly accepted that the thermal coefficient of resistance (TCR) of ECA is positive [17]. However, it is significantly less positive than the bulk metal [17]. The positive TCR associated with all pure metals is the result of scattering of electrons due to thermal vibrations. Other inhomogeneities that effect scattering are stress fields, impurity atoms and coherency mismatches. All of these effects increase the scattering probability and are temperature independent. The only known effect that can cause a negative shift in the TCR from pure metal are thermally activated transport processes (tunneling and hopping). Thus, the deviation seen in the TCR can be correlated qualitatively to the significance and probability of tunneling events in ECA. Once again we confirm that secondary electron transport mechanisms (tunneling and hopping) are more important than assumed by the conventional theories of ECA.

Conclusions

We clearly show through a series of proof of concept type experiments that existence of a directly interconnected percolated metallic network is infeasible. Through application of the Hertz model and the Shull correction factor it was theorized that strong repulsive forces at the interface will prohibit direct metallic interaction. Experiments on doped epoxies with varying dielectric constants determined that the dielectric constant and bulk resistivity are directly correlated; implying that tunneling and hopping mechanism dominate electron transport between the metallic flakes.

This new conceptualization of ECA in terms of isolated metallic islands separated by nanometer to sub-nanometer dielectrics will shift the focus of research. Future research in ECA will focus on the electrical properties of the dielectric rather than solely focusing on its mechanical and adhesive properties. This new insight provides a springboard for the study of functional dielectric materials that can facilitate secondary charge transport between isolated metallic particles, enabling the production of low cost, high performance, green ECAs.

Acknowledgments

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