

Conductivity Mechanisms of Isotropic Conductive Adhesives (ICA's)

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Abstract—Isotropic conductive adhesives (ICA's) are usually composites of adhesive resins with conductive fillers (mainly silver flakes). The adhesive pastes before cure usually have low electrical conductivity. The conductive adhesives become highly conductive only after the adhesives are cured and solidified. The mechanisms of conductivity achievement in conductive adhesives were discussed. Experiments were carefully designed in order to determine the roles of adhesive shrinkage and silver (Ag) flake lubricant removal on adhesive conductivity achievement during cure. The conductivity establishment of the selected adhesive pastes and the cure shrinkage of the corresponding adhesive resins during cure were studied. Then conductivity developments of some metallic fillers and ICA pastes with external pressures were studied by using a specially designed test device. In addition, conductivity, resin cure shrinkage, and Ag flake lubricant behavior of an ICA which was cured at room temperature (25 °C) were investigated. Based on the results, it was found that cure shrinkage of the resin, rather than lubricant removal, was the prerequisite for conductivity development of conductive adhesives. In addition, an explanation of how cure shrinkage could cause conductivity achievement of conductive adhesives during cure was proposed in this paper.

Index Terms—Conductivity establishment, mechanism, shrinkage, isotropic conductive adhesives.

I. INTRODUCTION

THERE has been considerable effort to develop isotropic conductive adhesives (ICA's) for electronics applications during the past few years even though conductive adhesives have been used for decades in the areas such as die attach, hybrid, and display assembly. At the same time, a great deal of research work has been conducted in the effort to replace lead-based solders in microelectronics applications mainly due to toxicity and environmental incompatibility of the lead in tin-lead solders [1]–[6].

In general, conductive adhesive pastes are formulated by mixing polymeric resins (such as epoxies, silicones, and polyimides) and metallic fillers. The most popular fillers are silver (Ag) flakes that generally have a thin layer of organic lubricant on their surface to improve their dispersity. In general, conductive adhesive pastes have high resistance before cure. The adhesives can achieve high conductivity after they are cured [7]–[8]. However, the conduction mechanism for

isotropic conductive adhesive is still not fully understood. It was suggested that the conductivity establishment during thermal cure was the result of removal of the lubricant and that matrix shrinkage did not play a significant role either in the development or in the final value of conductivity [7]. However, there was not enough evidence to support this hypothesis in this paper. In other literature, the effects of compressive force induced by cure shrinkage on conductivity were also mentioned [9], [10]. Again, no strong evidence was provided. The purpose of this study is to elucidate the roles of cure shrinkage and lubricant removal in conductivity achievement and conductivity mechanism of ICA's.

II. EXPERIMENTAL

A. Materials Preparations

Two silver flakes with an organic lubricant layer on their surfaces and a silver powder without a lubricant were purchased from Degussa Corporation. A blank silver powder (without lubricant) was purchased from Chemet Corporation. A commercial ICA, ICA-A, was used in the study of conductivity establishment during cure.

A bisphenol F type epoxy resin, RSL1738, was purchased from Shell Chemical Company. 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZCN), from Sikoku Chemical Company, was employed as the hardener. Methanol, tetrahydrofuran, and diethylene glycol butyl ether were purchased from Aldrich Chemical Company. All of the chemicals were used as received.

B. Apparatus and Experimental Procedures

1) *Conductivity Development During Cure*: The test device for this study is depicted in Fig. 1. Two copper strips were bonded onto a glass slide. Two strips of a tape were placed onto the slide with a 0.1 inch distance between them. The conductive adhesive pastes and Ag flakes were spread between the gap by a doctor blade. After the tape strips were removed, the specimen was then placed on a hot plate. The resistance change of the samples during the heating was measured from the two copper strips by a Keithley 2000 multimeter. Temperature of the glass slide surface was monitored with a type K thermocouple thermometer (model 650, Omega Engineering, Inc.).

2) *Cure Shrinkage Measurements Using a Thermomechanical Analyzer (TMA)*: Dimension change of an ICA paste during thermal cure was measured using a thermomechanical analyzer from TA Instruments, model 2940. The measurement setup is shown in Fig. 2. Microscope cover glass, which was

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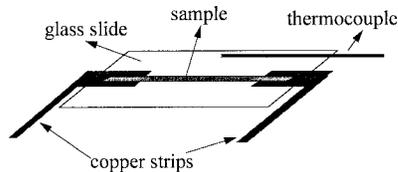


Fig. 1. Test device for conductivity achievement during heating.

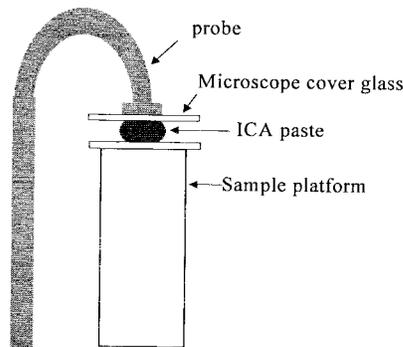


Fig. 2. Measurement setup of dimension changes using a TMA.

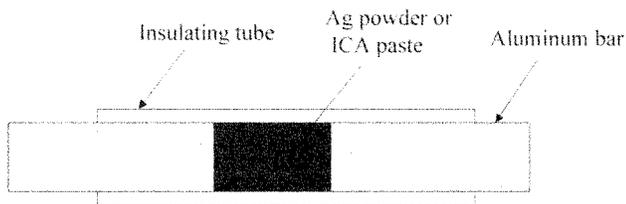


Fig. 3. Test device for conductivity change with external pressures.

about 0.15 mm thick, was used as sample holders. A piece of cover glass with the proper size was placed on the sample platform of the TMA first. A small amount of the ICA paste was placed on this cover glass, and then another piece of cover glass was placed on the ICA paste. The sample was cured in the TMA and dimension change during cure of this specimen was recorded. A macroexpansion probe was employed, and the static force of the probe was kept at a low level (0.01 Newton) to ensure that the adhesive paste was not squeezed out during heating. The heating rate was 5 °C per minute. Although it was difficult to convert the dimension change of ICA samples into shrinkage in this case, dimension changes were still a practical indication of cure shrinkage of the ICA. Therefore, dimension change of samples during cure was used to represent cure shrinkage.

3) *Conductivity Development of Silver (Ag) Powders and ICA Pastes with External Pressures:* The test device for this study is shown in Fig. 3. This test vehicle consisted of an insulating tube with a 3/8 inch inner diameter and two aluminum (Al) bars with a 3/8 inch diameter. Ag powders or ICA pastes were placed in the tube. Then pressure was applied to the powders or pastes through these two Al bars with a RIMAC press (purchased from Rinck-Mcilwaine-Inc.). The resistance change was measured from the Al bars with the Keithley multimeter.

4) *Conductivity Achievement of a Conductive Adhesive:* A conductive adhesive was formulated with an epoxy resin (RSL 1738), a hardener (2E4MZCN), and a Ag flake. Weight ratio

of the epoxy to the hardener is 94 to 6, and the loading of the Ag flake is 80 weight percent. This adhesive was cured at 25 °C for one week and solidified. Bulk resistance of the cured sample was measured using the Keithley multimeter with a four-point probe. Bulk resistivity was calculated based on the bulk resistance. These measurement setup and calculation method can be found elsewhere [8].

5) *Lubricant Behavior of the Ag Flake:* In order to simulate the Ag flake lubricant behavior in the above conductive adhesive during cure, two samples were prepared. One sample contained the Ag flake and the epoxy. The other sample contained the Ag flake and 6 wt% 2E4MZCN methanol solution, respectively. These samples were also kept at 25 °C for one week, and then the mixtures were washed with tetrahydrofuran three times to remove the epoxy and hardener. After drying under vacuum at room temperature, the treated Ag flakes were studied by a differential scanning calorimeter (DSC) from TA Instruments, Model 2920. Exothermic peak areas (ΔH , J/g) of the DSC curves were used to estimate the amounts of lubricants [11].

III. RESULTS AND DISCUSSION

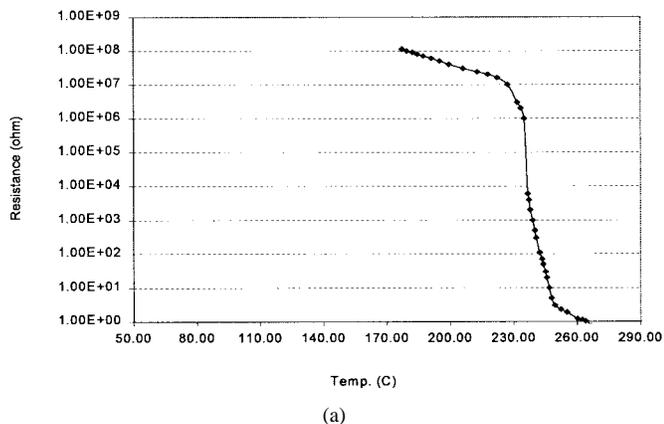
A. Conductivity Achievement of ICA's During Cure

The resistance change with temperatures of a Ag flake and an Ag flake-filled ICA, ICA-A, was tested using the device in Fig. 1. Results are shown in Fig. 4. Both samples showed very high resistance before heating. However, their resistance decreased dramatically above certain temperatures (T_{cond}). As can be seen in the figure, the T_{cond} of the Ag flake (230 °C) is much higher than that of the adhesive (130 °C). These results indicate that the epoxy resin lowered the T_{cond} . T_{cond} of the Ag flake is consistent with the onset of lubricant decomposition of the Ag flake lubricant from our previous DSC study, which is shown in Fig. 5. Also, it was found that the Ag particles agglomerated together after heating. This may be caused by the removal of the lubricant on the Ag flake at high temperature. Without any external pressure, Ag flakes can become conductive after the lubricants decomposed.

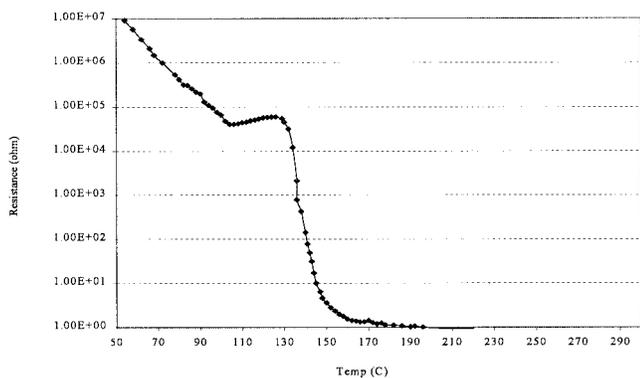
For the ICA, its T_{cond} (130 °C) is much lower than the onset of decomposition temperature of the Ag flake lubricant (approximately 230 °C). Therefore, at the T_{cond} of this ICA, the lubricant certainly did not decompose. The lubricant was either:

- 1) dissolved and/or reacted with the epoxy resin;
- 2) remained on the Ag flake surface after cure.

During the cure of the ICA, the epoxy resin shrinks. Therefore, the Ag flakes in the adhesive would experience a compressive stress caused by resin shrinkage. This compressive stress would make the Ag flake particles closer and improve adhesive conductivity [9], [10]. The dimension changes with heating of this ICA and the sample holder (microscope cover glass) were studied using a thermomechanical analyzer. The results are shown in Fig. 6. From this Figure, the cover glass did not have obvious dimension change, but the ICA showed significant dimension decrease (cure shrinkage) at the same temperature range as the T_{cond} of the ICA.



(a)



(b)

Fig. 4. Resistance change during heating of (a) an Ag flake and (b) an ICA.

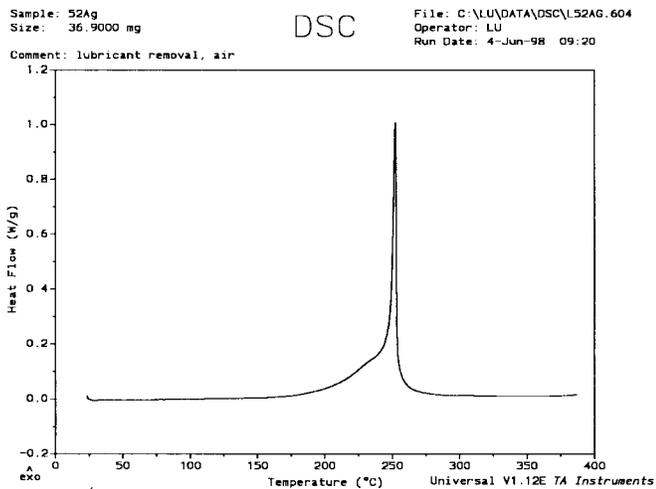


Fig. 5. DSC curve of a Ag flake in air.

This study indicates that resin cure shrinkage plays a very important role during conductivity establishment of a conductive adhesive. However, at this point, the possibility that the dissolution of the Ag flake lubricants by the resin at the T_{cond} of the ICA also causes conductivity development could not be eliminated.

B. Conductivity Development of Ag Powders and ICA Pastes with External Pressures

A thin layer of insulating organic lubricant resulting from Ag flake production remains on Ag flakes [12]. Our previous

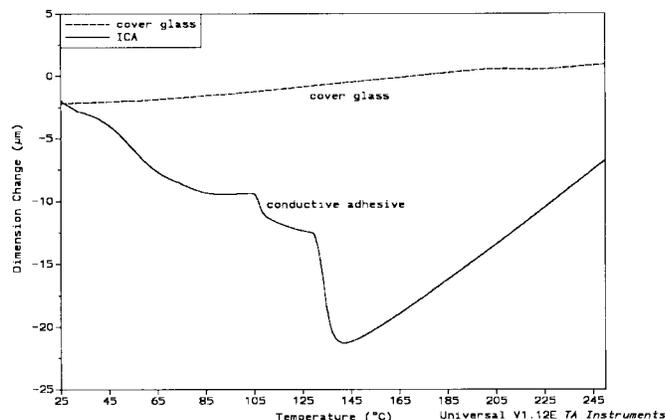


Fig. 6. Dimension changes of an ICA measured using a TMA.

study indicated that this lubricant layer was a salt formed between the fatty acid lubricant and the Ag flake surface [13]. It was believed that the low conductivity of ICA pastes was caused by this layer [7]. The purpose of this study is to simulate the Ag flake behaviors caused by resin cure shrinkage in the ICA formulations by investigating the relationship between conductivity of Ag flakes and external pressures.

Two commercially lubricated Ag flakes (Ag A and B), both of which have lubricants and a Ag powder without lubricant (Ag C), were tested. The results are shown in Fig. 7. The Ag particles were packed very loosely in the tube of the test device at the initial stage when they were first placed into the tube. After applying a very small force through the bars, the Ag particles were packed more densely and low resistance values were obtained. The resistance decreased only slightly with further increase in external pressures. These tests were done at room temperature, therefore, the lubricants of the Ag flakes were not thermally removed. Also, under these low pressures, the lubricants were not mechanically removed either. The fact that blank Ag powder (Ag C) showed similar resistance behavior to these two Ag flakes suggests that lubricants do not affect electrical conductivity significantly in this case. Therefore, the conductivity establishments of these Ag particles were the result of intimate contacts between the Ag particles caused by the small external pressures. The results demonstrated that the conductivity of the Ag flakes could be achieved just by applying very small pressures to the material without lubricant removal. The result also implies that adhesive pastes might achieve conductivity just by resin cure shrinkage.

In addition, conductivity establishment of an ICA paste with external pressure was also studied using this test device. Due to slight mismatch between the aluminum bars and the tube, some resin leaked out between the Al bars and the tube. By using this test vehicle, it was found that the ICA paste became conductive above certain pressure. The conductivity development of the ICA paste was probably due to closer contact of the Ag flakes after some of the resin was squeezed out. This experiment was repeated after the test device had been modified. The modified test device had perfect match between the tube and bars so no resin leakage was found under pressures. It was observed the ICA remained highly insulating with external pressure. This

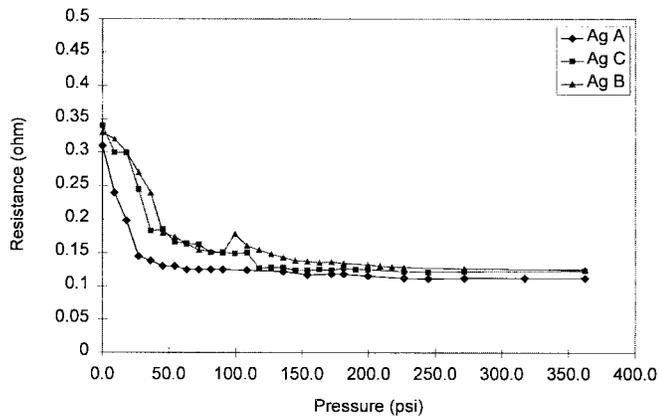


Fig. 7. Resistance changes of some Ag particles with external pressures.

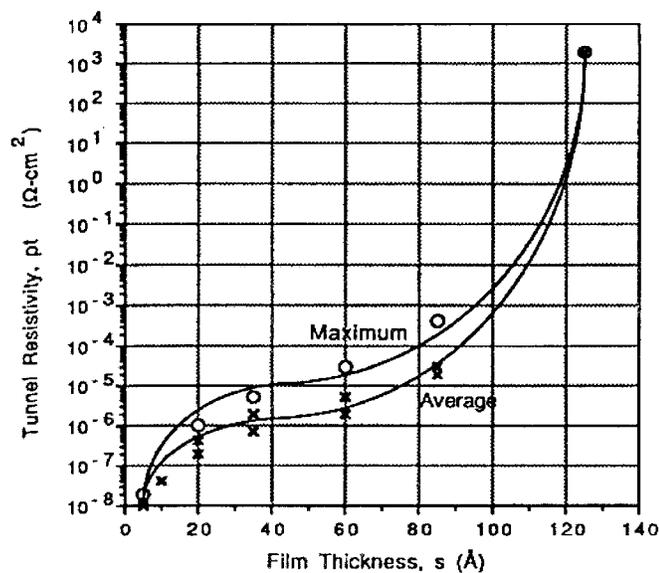


Fig. 8. Tunnel resistivity for thin films as a functions of film thickness [10].

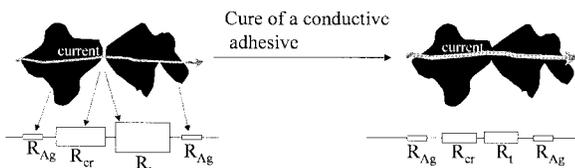


Fig. 9. Change of a particle-particle contact resistance due to the more intimate contact between two Ag flakes caused by shrinkage of the polymeric matrix. (R_{Ag} -bulk resistance of Ag).

was probably because the ICA paste was not compressible (no shrinkage) and the Ag flakes were not brought closer even though an external pressure was applied. This study further proved that ICA pastes could not become conductive unless the Ag particles are pushed closer together.

C. Conductivity Achievement of a Conductive Adhesive and the Lubricant Behavior of the Ag Flake

A Ag flake-filled conductive adhesive was cured at 25 °C in order to ensure that the lubricant was not thermally removed after cure. The resistivity of the adhesive before cure was

TABLE I
 ΔH VALUES OF Ag FLAKES

Ag flakes	Average ΔH (J/g)	Standard Deviation
Recovered from epoxy	50.0	0.4
Recovered from 2E4MZ-CN methanol solution	46.6	0.5
Untreated	48.4	0.8

beyond the measurement limits of the multimeter. After cure, the resistivity changed to 4×10^{-3} ohm-cm. Because the ICA was cured at room temperature, the lubricant on the Ag flakes was not thermally removed. Therefore the conductivity was either due to dissolution of the insulating lubricant layer by the resin or intimate contact between the Ag flakes caused by the resin cure shrinkage.

The shrinkage of the resin part of this adhesive was calculated from the densities of the uncured and cured resin. The densities of the resin before cure and after cure were measured with a gravity bottle. An ether, diethylene glycol butyl ether, was used as the medium in the density measurement of the cured resin. Assuming no significant weight change during the cure of the resin, resin cure shrinkage can be calculated using the following equation:

$$\text{Shrinkage} = \frac{1/d_e - 1/d_s}{1/d_e} \times 100$$

where d_e is the density of the uncured resin and d_s is the density of the cured resin. Based on the above equation, the resin cure shrinkage of this adhesive was 3.42%.

In order to find out if the Ag flake lubricant remained on the Ag flake surfaces after the adhesive was cured at room temperature (25 °C), another parallel experiment was conducted. Two samples were prepared: one contained the same Ag flake with the epoxy resin (RSL1837) and the other contained the Ag flake and 6 wt.% hardener (2E4MZCN) methanol solution. Methanol was used as a solvent because it would not remove the Ag flake lubricants [11]. The mixtures were kept at 25 °C for the same period of time as the cure time of the ICA. Then, the mixtures were washed with tetrahydrofuran (THF) three times to remove the resin and hardener. Previous study showed that THF also did not wash away the lubricants [11]. After drying at room temperature and under vacuum, the recovered Ag flakes were studied by DSC in an air atmosphere and compared with the same Ag flake which was just washed three times with THF. The peak area (ΔH , J/g) of the exothermic peak in the DSC curves of the Ag flakes were used to estimate the amount of the lubricants semi-quantitatively [11]. For each Ag flake, three samples were studied. The average ΔH and standard deviation for each of the Ag flakes are given in Table I.

As can be seen from above table, ΔH values of the recovered Ag flakes are the same as that of the original Ag flake within experimental error. The result indicates that the Ag flake lubricant was not removed after being exposed to the epoxy or hardener under the cure condition of the ICA, a week at room temperature. The result suggested that the lubricant remained on the Ag flake surfaces after the ICA was cured at room temperature for a week. Therefore, high

conductivity of this conductive adhesive was achieved only through resin cure shrinkage. It can be concluded from this experiment that conductivity of ICA's can be achieved just by resin cure shrinkage even though lubricant removal may contribute to the high conductivity [11]. Therefore, lubricant removal is not a prerequisite for conductivity achievement.

In a conductive composite, once filler loading reaches the percolation threshold, a significant number of percolated linkages are formed. Each percolated linkage should be thought as a series of resistors, with each particle and each particle-particle contact contributing to the total resistance in the linkage. There are two important contributions to the particle-particle contact resistance: a constriction resistance and a tunneling resistance. Constriction resistance $R_{cr} = \rho_i/d$, where ρ_i is the intrinsic filler resistivity and d is the diameter of the contact spot. For particles with a layer of thin film coated on their surfaces, if the thickness of the film is on the order of 100 Å or less, quantum-mechanical tunneling can occur, resulting in lower resistivities [9]. Tunneling resistance $R_t = \rho_t/a$, where ρ_t is the tunneling resistivity and a is the contact area. The resistivity of the film is not a factor in tunneling, so that organics, polymers, and oxides will have similar tunneling resistivities for similar thicknesses. The dependence of tunneling resistivities on the insulating film thickness can be described by a general tunneling curve (shown in Fig. 8) [9]. The particle-particle contact resistance is the sum of these two separate effects, $R_c = \rho_i/d + \rho_t/a$. In general, the tunneling resistance term dominates R_c .

Before cure, in an ICA formulation, a thin layer of epoxy resin cover each Ag particle surface besides the lubricant layer even though theoretically the particle should contact each other according to percolation theory. Each percolated linkage has high total resistance, and thus the ICA has high resistance before cure. When the ICA cures, the resin shrinks and compresses the particles bringing all the particles closer together. Therefore, the insulating film thickness is decreased, and thus tunneling resistivity decreases dramatically. Also, particle-particle contact area, a , and contact diameter, d , increase after cure. The increases of a and d cause R_{cr} and R_t both to decrease. Therefore, the total contact resistance, R_c , decreases. A schematic explanation is given in Fig. 9.

IV. CONCLUSION

ICA's become highly conductive only after they are cured and solidified. ICA pastes can achieve high conductivity through resin cure shrinkage alone. Therefore, resin cure shrinkage rather than lubricant removal is the prerequisite for conductivity achievement of ICA's even though lubricant removal may contribute to conductivity.

The resin probably compresses and causes Ag flakes to contact more intimately with the resin shrinkage during a thermal cure. The decrease of distance between the flakes caused the dramatic drop of particle-particle contact resistance. Thus, the total resistance of a percolation linkage decreased dramatically during a thermal cure.

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C. P. Wong (SM'87-F'92), for a photograph and biography, see this issue, p. 201.