Using Novel Materials to Enhance the Efficiency of Conductive Polymer

Cheng Yang[1], Matthew M. F. Yuen[2], Bing Xu[1]
[1]Department of Chemistry, The Hong Kong University of Science and Technology
[2]Department of Mechanical Engineering, The Hong Kong University of Science and Technology
Email: yangch@ust.hk, meymf@ust.hk, chbingxu@ust.hk Tel: +852-2358-8814

Abstract

Conductive polymers have a vast market in integrated circuits (IC) and microsystems packaging to enhance mechanical, thermal, electrical performance, and cost effectiveness[1]. Isotropically conductive adhesives (ICAs) have been explored for attaching encapsulated surface mount components on rigid and flexible printed circuits [2]. However, the practical use of conductive adhesives in surface mount applications is limited because of the weak electric conductivity. Jiang et al [3] used nano-sized silver particles as a candidate for conducting filers in order to reduce the sintering temperature, but the contact resistance is still high. Some groups [4, 5] studied a series of methods such as using carboxylic acid group containing chemicals as surfactants to enhance the conductivity of ICAs in a variety of conditions, but because the micron-sized silver fillers have a high sintering temperature, the enhancement in conductivity is still limited.

In order to further improve the conductivity of ICAs and minimize the cost, we experimented on a series of materials for silver surface pretreatment. We noticed an about 20 times improvement in conductivity of the modified ICA than the control sample (75% silver content in all samples). The volume resistivity of the optimum formulation reached the level of 10^{-6} Ω·cm. We also analyzed the adhesion strength and thermal property of the modified ICA material. The study indicated that both the electrical properties and the mechanical property were improved without negatively affecting the other physical properties, and they are both remain stable after subjecting to the 85°C and 85% relative humidity conditioning test.

Introduction

Silver filled isotropic conductive adhesives (ICAs) are widely applied as interconnect materials in liquid crystal display (LCD), smart card applications, flip-chip assembly, chip scale package (CSP) and ball grid array (BGA) applications in replacement of solder. They have numerous advantages, such as environmental friendliness, mild processing conditions (enabling the use of heat-sensitive and low-cost components and substrates), reduced processing steps (lowering down the cost), low stress on the substrates, and fine pitch interconnect capability (enabling the miniaturization of electronic devices) [6-11]. Typically, micron-sized silver flakes are dispersed in a resin matrix to form ICA, the polymer resin provides mechanical interconnection and the conductive fillers provide electrical conductivity. For spherical particles the percolation threshold of the silver network in the polymeric matrix is about 16% to 30% by volume [12]. Higher aspect ratio of the silver filler helps to lower the percolation threshold. Consequently, silver flakes are more often used in these applications than spherical silver particles. Nevertheless, the percolation threshold of silver flakes remains quite high (about 20 % by volume). Therefore, typical polymer based conductive formulations have very high silver loading (70-85 wt%).

The volume resistivity of a typical ICA formulation is about 10^{-4} Ω·cm [13], which still remains about 2 orders higher than the resistivity of native silver metal (1.59×10^{-6} Ω·cm). Maximizing the percolation efficiency to a reasonable level is an interesting topic. One simple way to increase the electrical conductivity of the ICA is to increase the content of silver fillers in the ICA formulation. However, excessive filler loading degrades the mechanical property of the ICAs and increases the material cost. Moreover, the consequent high viscosity of the ICAs can potentially result in other problems such as generating voids and difficulties in processing etc. After all, improving the conductivity and maintaining the mechanical properties of the ICA has been the main issue for the study in this area.

During the past few years, there have been increasing interests in the studies of surface modification of conductive fillers [3, 4, 14]. The overall resistance is the sum of the resistance of fillers and the contact resistance between filler and pads. Decreasing the contact resistance of the fillers is an efficient way to improve the overall conductivity. Using the low sintering temperature of silver nanoparticles to achieve better bonding between adjacent filler particles has been studied [3]. However, the increased number of nanoparticles actually increases the isotropic property of the composite ICA, hence increases the percolation threshold of the filler concentration in a bulk composite adhesive. Meanwhile, using nano-sized filler particles increases the surface contact area between the filler and the resin matrix. This would increase the viscosity of the ICA paste, which is also a potential problem for ICA processing. Therefore, it is urgent and important to find a surface chemistry strategy to improve the electric percolation of the ICAs without interfering the mechanical property and viscosity.

In this paper, we studied the surface modification of commercial silver microflakes (fillers) (with the diameter from about 3 to 30 μm) using a series of new materials and characterized the properties of the modified ICA samples. We studied the volume resistivity of the ICA samples using four-point probe tester and the adhesion strength of the ICA samples in a lap shear test; we also studied the thermal expansion property (CTE) of the ICA samples and the differential scanning calorimetry (DSC) result of the modified silver microflakes. We noticed an about 20 times improvement in conductivity of the ICA compared with the control sample (both contain 75 wt% silver). Before aging, the modified ICA showed 56% higher in adhesion strength than the control ICA; after aging, the modified ICA still

showed 69% higher in the adhesion strength to the copper substrate. We also characterized the morphology of the ICA samples under electron microscope (TEM and SEM). The contact resistance and adhesion strength of the ICA undergone 85°C and 85% relative humidity (RH) test was found stable with respect to aging time. The improved wetting between the filler and resin matrix also results in the improvement of mechanical property. Different from the previous studies, there is no evidence that the improved percolation is because of a lowered sintering temperature; there is no additional smaller particles getting involved either. The exploration of the working mechanism is still undergoing but the possible reason may be related with the improved anti-oxidizing property of the silver fillers and the wettability with resins.

Experimental

Materials and Preparations

Silver microflakes were obtained from Sichuan Changcheng Jinyin Jinglian Factory, China, with the dimension from 3 to 30 μm. Ethanol was used as the solvent for surface modification for the silver microflakes. The surface-modified silver microflakes were filtered and dried in vacuum before mixing with resins. A bisphenol-A type EPON 828 (Shell) epoxy resin and an anhydride type hardener of methyltetrahydrophthalic anhydride (MTHPA, Lindau Chemicals) were employed as matrix resin and crosslinker, respectively. The ratio of epoxy to hardener was 1:0.85 based on the epoxide equivalent weight (EEW) of the epoxy resin and the hydroxyl equivalent weight (HEW) of the hardener. The catalyst is 2-ethyl, 4-methyl imidazole and the concentration of the catalyst was 1 part per hundred parts resin. The silver microflakes were pretreated by the surface treatment chemicals in ethanol and dried in vacuum. Then the silver microflakes and the resins were thoroughly mixed for 30 minutes before cured at 150°C for 15 minutes in a memmert oven. Some ICA samples were conditioned in a TERCHY MHU-150L humidity chamber (85°C /85%RH) to test the reliability of the samples.

Characterizations

Measurement of volume resistivity

The ICA samples were screen-printed onto a PET film and cured in a Memmert oven at 150°C for 15 minutes. A Surface Profile System (Alpha-Step 200) was used to analyze the profile of the cured ICAs. A Jandel Four-point Probe tester was used to measure the volume resistivity of the ICA samples.

Electron microscope (EM) micrographs of the ICAs

A JEOL 6700 field emission scanning electron microscopy (FESEM) was used to study the cross section of the ICA samples; the surface of the samples was ground before testings. The accelerated voltage was 8 kV.

A JEOL 2010 transmission microscopy (TEM) was used to study the cross sections of the ICA samples, the samples were cut into thin cross sections with the thickness of 80 nm on a *Leica Ultracut R* ultramicrotome machine before TEM analysis.

Adhesion strength analysis

The test to determine the strength properties of adhesive in shear was carried out on an INSTRON 5567 tensile tester. The ICA is bonded between two panels of bare copper with dimensions 20.0 mm thickness, 10 ± 0.05 mm width and 40 ± 0.05 mm length (scheme 1). The surfaces of the panels were etched by using glacial acetic acid prior to bonding the adhesive to be tested. The adhesive was applied between etched panels and clamped with a 15 ± 0.1 mm overlap, giving a bonding area of 150 mm^2. To control the thickness, two pieces of 200 μm diameter glass fibers were used as spacers. The two fibers were placed in the adhesive between the panels and the thickness was double-checked using a caliper. After curing, the cooled panels were pulled apart by an INSTRON Machine at a pulling rate of 1.3 mm/min using a pair of numeric crossheads. Two groups of specimens were prepared for the test. In each group 20 bar pairs were prepared for each kind of ICA. One group was tested after left for 24 hours at room temperature after cure. The other group was tested after the samples were conditioned at 85°C/85%RH for 168 hours. The measurement method refers to ISO 4587-1979, and the adhesion strength value can be obtained by $s = f / a$, where s is the adhesion strength (MPa), f the pulling force at failure (N) and a the joint area (mm^2).

Coefficients of thermal expansions measurements

Coefficients of thermal expansions (CTEs) and glass transition temperatures (T_gs) of the ICA samples were measured on a thermomechanical analyzer (TMA), model: Mettler Toledo TMA/ SDTA840. Temperature was ramped from 30°C to 250°C at a heating rate of 10°C/min. The dimension change with temperature was recorded. The slope of the straight line before the T_g was the CTE of the sample.

DSC measurements of the modified silver flakes

The heat flow of the modified silver flake samples (about 5 mg) were tested on a TA Q1000 Differential scanning calorimeter (DSC). Some of the silver flake samples underwent the surface pretreatment of chemical A. The samples were protected by nitrogen and the temperature ramped from 30°C to 280°C at a heating rate of 5°C/min.

Results and Discussions

Effects of surface pretreatment on electrical conductivity of the ICAs

We tried three different chemicals (chemical A, B, and C) for the surface modification of the silver flakes. These chemicals have similar functionalities which are reactive towards the filler material. Figure 1 shows a series of studies of the volume resistivities of the surface modified ICA samples. The volume resistivities of all samples were tested 24 hours after cure, except for those indicated elsewhere. In Figure 1 (A), the volume resistivity varies according to the chemical A weight percentage variation in the silver flakes. At 0.2% loading of the chemical A to silver flakes, the volume resistivity of the ICA sample shows the lowest volume resistivity (5.8×10^{-6} Ω·cm), which is about 20 times decrement. However, at 0.05% loading the volume resistivity of the ICA is in the range of

10^{-4} Ω·cm, which is in the same scale of the control ICA sample. At a higher chemical A pretreatment level, further increasing the chemical A content increases the volume resistivity. For example, at 5% the volume resistivity is 3.6 x 10^{-5} Ω·cm, which indicates, a higher level of chemical A results in an inferior percolation performance. From this figure, 0.2% of chemical loading in silver flakes is the optimum condition. Figure 1 (B) shows the volume resistivity of the ICA samples with the silver surface modification using different chemicals. Chemical A, chemical B, and chemical C all have similar functionality towards silver. At the same silver loading (75 wt%) the volume resistivity of the ICA samples varies a lot. Chemical A shows the lowest resistivity and chemical C shows the highest. But the three chemicals show improved electrical percolation compared with the control sample, which possesses only the native silver flakes. We further analyzed the reliability of this 0.2% chemical A pretreatment ICA sample. In a 168 hours 85°C/85%RH aging test, the volume resistivity of the ICA sample was measured (Figure 1 (C)). The ICA specimens were collected and tested at every 24 hours interval, and the volume resistivity variation was recorded. There is a slight decrease of volume resistivity after 2 days and after 4 days the resistivity touches the bottom. Finally, the resistivity of the ICA rises to about its original level at day seven. The overall variation is in the range of 20%. This aging test shows that the chemical A treatment does not significantly affect the reliability in its electrical conductivity. Figure 2 shows the photographic images of the ICA samples which were screen-printed on a PET film. The width of each of the seven bars is 2 ± 0.1 mm, and the thickness is about 20 ± 3 μm (measured on an Alpha-Step 200 Surface Profile System). There is minor difference in color of the modified ICA sample and the control.

Micro-morphology of the modified ICA samples

In order to further study the interface interaction between the modified silver fillers and the resin matrix, we studied the micro-morphology in the cross sections of the cured ICA samples. The samples were analyzed on a JEOL 2010F TEM, and the thickness of each sample was carefully controlled at 80 nm via ultramicrotomy. Figure 3 (A) shows the interface of the 0.2% chemical A pretreated silver flakes in an ICA sample. From the inset image, we can clearly notice the adjacent two silver flakes merge together. The HRTEM image shows the coherent connection between the crystal lattices of two adjacent silver flakes. This shows the possibility for the atomic connection between the adjacent silver flakes after the surface modification. From the same image, there is no observable chemical A leftovers at the silver surface. Besides TEM analysis, we also studied the bulk modified ICA samples (0.2% chemical a treatment for the silver flakes) via scanning electron microscopy (SEM). Figure 3 (B) shows the SEM image of the ground surface of the cross section of the modified ICA sample. Without any agglomerations, the silver flakes are well-dispersed in the resin matrix.

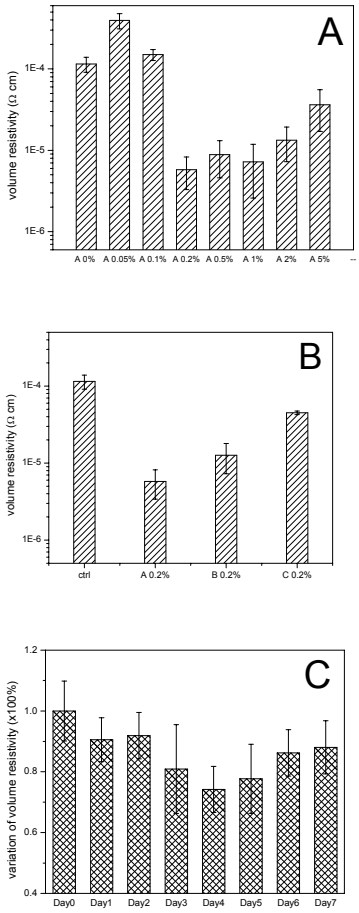


Figure 1. Volume resistivity of the ICAs in different conditions. (A) volume resistivity of the ICAs with 75 wt% silver filler loadings. (x-axis shows the chemical A content to silver flakes.) (B)Volume resistivity of the ICAs with 75 wt% silver filler loadings (x-axis shows the chemical A, B, C and control sample). (C) Volume resistivity change of the ICA with 75 wt% silver filler loading (chemical A content is 0.2 wt% to silver) in an 85°C/85%RH aging test.

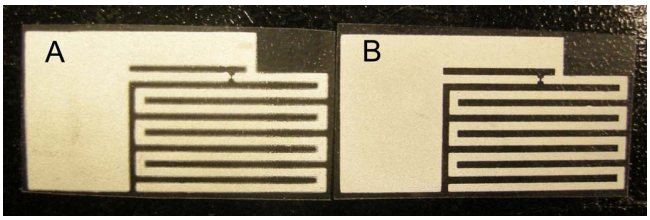


Figure 2. Photographic images of the screen-printed ICA samples. (A) 0.2 wt% chemical A modified silver in its ICA formulation (75 wt% silver); (B) control sample (bare silver) in its ICA formulation (75 wt% silver).

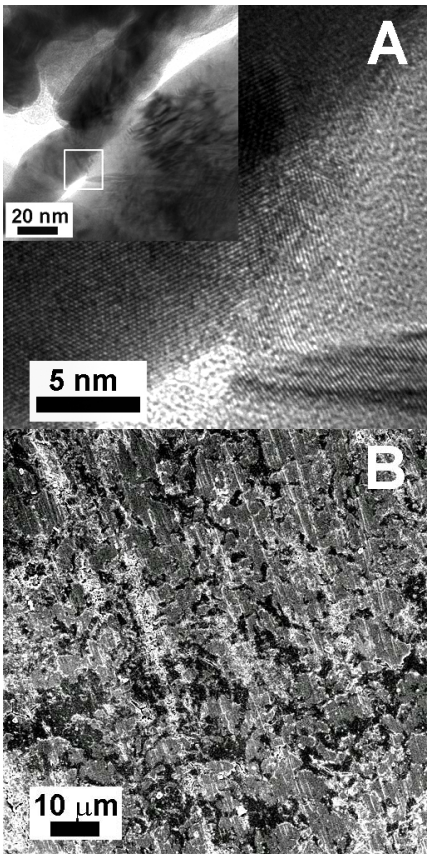
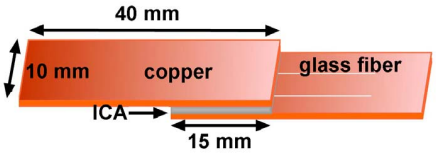


Figure 3. (A) A HRTEM image of the chemical A modified (0.2%) silver flakes in the ICA samples. The white square in the inset image shows the magnified part of the image. (B) SEM image of the cross section profile of the same sample.

Adhesion strength measurement

Besides providing electrical interconnection, ICAs also provides mechanical support. Adhesion strength of ICAs is a critical parameter of the ICAs. We carried out the adhesion strength measurement on smooth copper panel substrates and tested the ICA's adhesion reliability (scheme 1). Each ICA formulation was tested and the average of the adhesion strength of these specimens is reported (Figure 4). As shown in this figure, the lap shear strength of both ICAs decreased about 30% after aging. Before aging, the adhesion strength of the modified ICA shows 56% higher than the control ICA (0% chemical A pretreatment); after aging, the modified ICA still shows 69% higher in the adhesion strength to copper panel. This improvement can be attributed to the improved adhesion between matrix and fillers and the transmission of mechanical energy (tensile stress, impact energy, etc.) from the resin matrix to the fillers. This result shows that the interfacial activity of chemical A in increasing the strength of (chemical) bonding between the fillers and the matrix. Figure 5 shows the SEM images of the cohesive fails for tensile strength test samples after the lap shear test. As shown in the figure, the morphology of the fractured surface of lap shear specimens do not show much difference from each other. They are both smooth and the adhesion failure occurs between the specimen panel and the adhesive.



Scheme 1. A schematic illustration of a lap shear test specimen. The ICA is filled in between and the thickness of the ICA is 200 μm (controlled by the glass fibers).

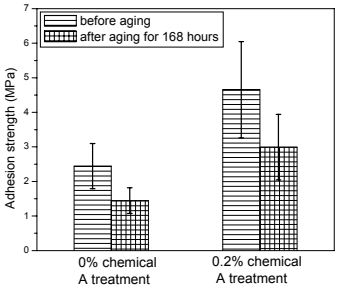


Figure 4. Adhesion strength test in the 85°C/85%RH aging test of the ICA samples with 0.2% chemical A treated silver flakes.

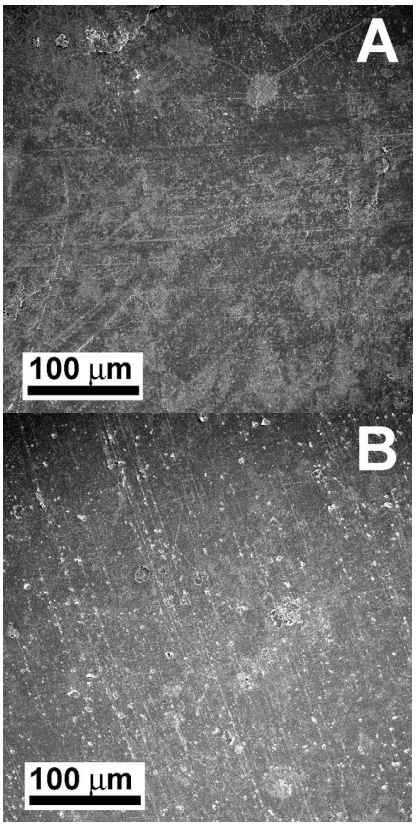


Figure 5. SEM images of the lap shear fracture surface (without aging). (A) control sample, (B) ICA samples with 0.2% chemical A treated silver flakes (magnification: 250x).

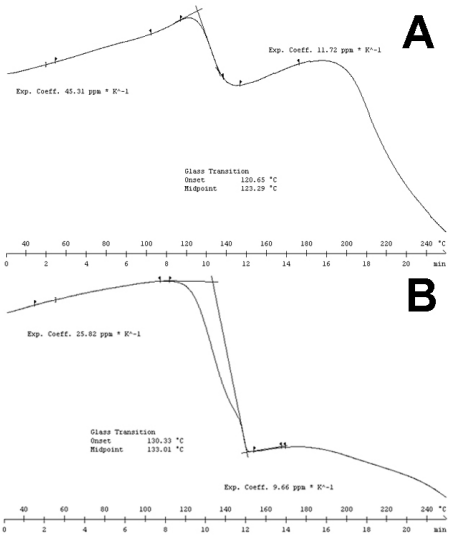


Figure 6. Thermal expansion curves from the CTE analysis of fully-cured ICA samples (A) control sample (without surface modification of silver); (B) ICA sample with 0.2% chemical A surface treatment of silver.

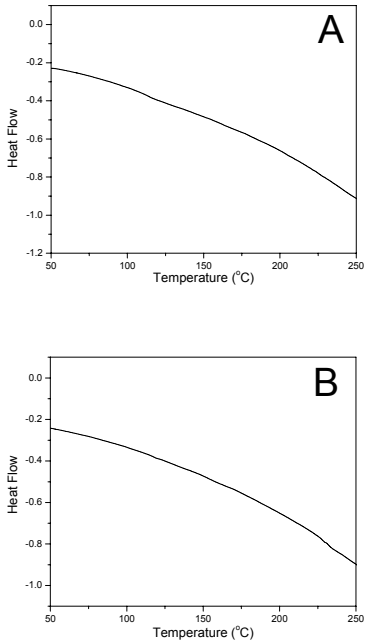


Figure 7. DSC heat flow curves of the silver flake samples. (A) Control sample (without silver surface pretreatment); (B) 0.2% chemical A pretreatment.

Thermal analysis of the ICA samples

CTE analysis of the modified ICA samples was carried out on a thermomechanical analyzer (TMA). Temperature was ramped from 30°C to 250°C at a heating rate of 10°C/min. The dimension change with temperature was recorded. In Figure 6 (A), the expansion coefficient of the control sample was recorded 45.3 ppm·k^{-1}, and the expansion coefficient of the surface modified ICA showed 25.8 ppm·k^{-1}. Meanwhile, there is a slight increment in the glass transition temperature (T_g). The T_g of the modified ICA shows 130.0°C, which is about 10°C increase than the T_g of the control sample. The T_g and CTE in both modified ICA and control sample are in good condition for electronic packaging applications.

The heat flow of the native and modified silver flake sample (about 5 mg) were tested on a TA Q1000 Differential scanning calorimeter (DSC). The heat flow curve of the control sample (figure 7(A)) was very smooth and there is no observable heat flow peak in the range from 50 to 250°C. Comparable to the control sample, the silver flakes with 0.2% chemical A pretreatment shows a very smooth curve, indicating no sintering or other phase transition processes noticeable.

From the above data, excellent conductivity and mechanical property can be achieved via a simple surface modification of the silver flakes. This is a general strategy that can be applied in parallel with different treatment methods, such as adding polymeric latex as filling additives to lower the percolation threshold of the composite adhesive [15]. The strategy is efficient in lowering the contact resistance between the adjacent silver fillers, hence to lower the overall percolation threshold. Further explorations in this area are in progress.

Conclusion

In this study, we present a novel surface modification approach of silver fillers and studied the effects on both electrical conductivity and mechanical property of ICAs. Different from the other studies ever reported, the improved electrical percolation is not related to the sintering effect of small particles. Since the surface treatment does not introduce any major morphological change of the fillers and there are no nano sized silver fillers involved, this technique only changes the viscosity of the paste marginally. It is found that adding different amount of the chemical A on the filler surface has different effect on the conductivity of the ICAs. We observed a 20 times decrement in volume resistivity at 0.2 wt% of the chemical A treatment for the silver flakes. At this surface coupling level, we noticed the adhesion strength of the ICA to copper is also improved. The reliability of the modified ICA is excellent since there is no significant decrement in both mechanical property and electrical conductivity after a 168 hours aging test at 85°C/85%RH. The volume resistivity retains about 6 x 10^{-6} Ω·cm and the adhesion strength retains about 4.7 MPa. SEM analysis of the interface between the ICA and copper substrate revealed a strong adhesion/bonding between the filler and the matrix with the addition of chemical A. Further study on the application of this chemical in ICA is recommended.

Acknowledgements:

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