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Preparation and performance of Ag-coated Cu flakes filled epoxy as electrically conductive adhesives

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Abstract

A low-cost and high performance Ag-coated Cu flakes filled epoxy was prepared as electrically conductive adhesives (ECAs) for light emitting diode (LED) packaging. As-prepared ECAs consisted of bisphenol-F-epoxy resin, micro-sized Ag-coated Cu flakes and other additives. The ECAs with content of 70 wt % Ag-coated Cu flakes pre-modified by silane coupling agent (SCA) exhibited much lower bulk resistivity ($8.4*10^{-3}$ Ωcm) than that of ECA filled with 70 wt % Ag-coated Cu flakes without SCA modification ($1.6*10^{-1}$ Ωcm). An appropriate content of diluent (below 20 wt %) was beneficial for the flakes' regular dispersion in resin, which enhanced the electrical conductivity ($10^{-4} \sim -10^{-5}$ Ωcm) and mechanical strength (>14 Mpa) of ECAs.

Keywords: Electrically conductive adhesives (ECAs); Ag-coated Cu flakes; Light emitting diode (LED); Silane coupling agent (SCA); Diluent

Background

In recent years, Light Emitting Diode (LED) has rapidly developed to high power and high brightness for illumination due to its small size, low-energy consumption and other advantages [1-3]. The electrically conductive adhesive (ECA) is usually used for LED packaging, which requires high electrical conductivity, thermal conductivity and mechanical properties. Electrically conductive adhesives are composed of polymer binder (epoxy resin, phenolic, polyurethane, silicon, etc.), and conductive filler (gold, silver, copper, carbon black, graphene, etc.) [4-7]. The polymer binders provide mechanical strength, and the conductive fillers provide electrical and thermal conduction. ECAs require fewer processing steps, lower processing temperature, and they are environmental friendly and energy damping compared to traditional solders [8,9].

The Ag-filled ECAs are the most mature product in commercial market due to its excellent electrical and thermal conductive property. However, because of the high price of Ag, great attentions and efforts have been made to reduce the costs of ECAs [10,11]. Cu has the most comparable property to Ag but it is easily oxidized and corroded. Ag coated Cu materials have been developed to hinder the Cu oxidation, whilst maintain the excellent electrical and thermal conductivity [11,12]. Generally, high filler loadings are needed to get better electrical and thermal conductive performance. However, too high filler loading will deteriorate the mechanical property. Therefore, it is

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still a challenge for the preparation of ECAs with a high electrical and thermal conductivity without adversely affecting the mechanical properties.

Herein, we successfully prepared Ag-coated Cu flakes filled ECAs and investigated the effect of adhesive composition on the performance.

Methods

Materials

Ag-coated Cu flakes were provided by Shenzhen Jinchuanyu Science and Techonlogy Company. Reactive diluent, JD350 and silane coupling agent (SCA), KH570 were provided by Shenzhen Jiadida Chemical Company. Non-reactive diluent, Diisobutyl phthalate (DIBP) were purchased from Sinopharm Chemical Reagent Company. The bisphenol-F-epoxy resin, curing agent, Methylhexahydrophthalic anhydride (MeHHPA) and catalyst, 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN) were purchased from Shell Chemical Company. All chemicals were analytical grade and used as received without further treatment.

Treatment of the Ag-coated Cu flakes

The Ag-coated Cu flakes were added into a mixed solution of ethanol and KH570, then ultrasonic treatment for more than 1 h, and the powder were received by filtration, and then rinsed with ethanol to remove remnants of KH570. The powders were dried in a vacuum oven at room-temperature for 24 h.

Preparation of Ag-coated Cu flakes filled ECAs

The resin, diluent, curing agent, coupling agent, and catalyst were mixed using Speed-Mixer (DAC 600 Mixer Range, FlackTek) in a specific ratio (100:50:120:3:7) at a speed of 2500 rpm for 5 min until all ingredients were evenly dispersed. Then micro-sized Ag-coated Cu flakes were added into the viscous polymer matrix and the matrix was stirred in the same rotational procedure as above. Finally, the different formulated adhesives were thermal cured at 150 and 180°C for other properties test.

Characterization and performance measurements

Scanning electron micrographs (SEM) and energy-dispersive X-ray spectroscopic (EDS) were performed on FEI Nova NanoSEM450 instrument.

Liquid ECAs were manually printed flatly onto a glass substrate by a small scraper to form stripe of 6 mm *75 mm. Then they were cured at different temperature for 2 h and cooled down to room temperature in oven. The bulk resistivity was calculated by

$$\rho = R \cdot \frac{w \times t}{1}$$

Where ρ (Ωcm) is the bulk resistivity, R (Ω) is the bulk resistance which measured by a Keithley 2000 multimeter, w (cm), t (cm) and l (cm) are the width, thickness and length of the silver-epoxy resin conductive adhesive stripes respectively. Each ECAs sample was tested at five different positions, and the averages were determined.

The shear strength of the ECAs was determined by binding two steel panels, and the binding area with width and length of 20 mm and 12 mm respectively. The steel panel was acid-etched before bonding with the ECAs. Then they were cured at different

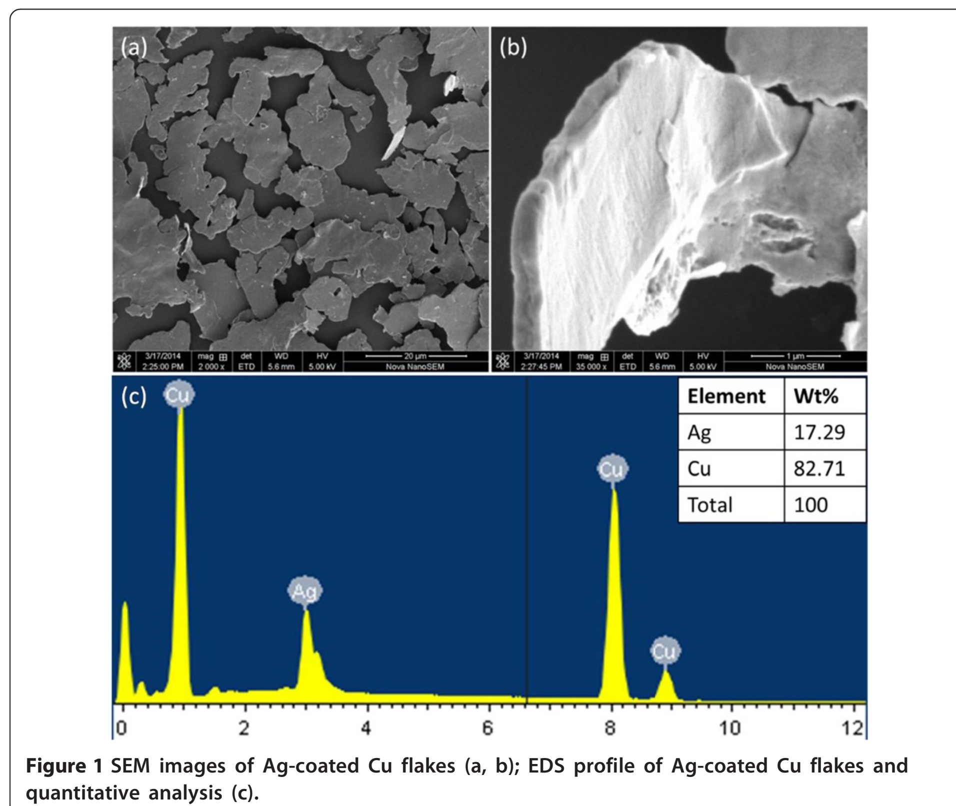
temperatures for 2 h and cooled down to room temperature in oven. The shear strength was calculated by

$$\tau = \frac{P}{B * L}.$$

Where τ (MPa) is shear strength, P (N) is measured with an electronic universal testing machine at pull rate of 5 mm/min, B (mm) and L (mm) are the binding width adn length respectively. Each ECAs sample was tested five times, and the averages were determined.

Results and discussion

Figure 1 showed the SEM images of the Ag-coated Cu flakes. The Ag-coated Cu flakes were random shape with about 5 ~ 20 um edge length (Figure 1(a)) and ~250 nm thickness (Figure 1(b)). To determine the composition of the Ag-coated Cu flakes, EDS was performed (Figure 1(c)). Only Ag and Cu peaks were observed in the spectrum, suggesting that the samples were not oxidized, and the Ag concentration in Ag-coated Cu flakes was 17.3 wt %. The electricity properties of the ECAs filled with 70 wt % Ag-coated Cu flakes untreated and modified by SCA were presented in Figure 2. The result indicated that the bulk resistivity decreased drastically from $1.6*10^{-1}$ Ωcm to $8.4*10^{-3}$ Ωcm after the Ag coated Cu flakes modified by SCA. The electrical conductivity of ECAs with Ag-coated Cu flakes modified by SCA was improved greatly compared with that of ECAs added SCA in the prepared paste. The longtime ultrasonic treatment increased the SCA coating effects on the surface of fillers. The effective coating of SCA



Element	Wt%
Ag	17.29
Cu	82.71
Total	100

Figure 1 SEM images of Ag-coated Cu flakes (a, b); EDS profile of Ag-coated Cu flakes and quantitative analysis (c).

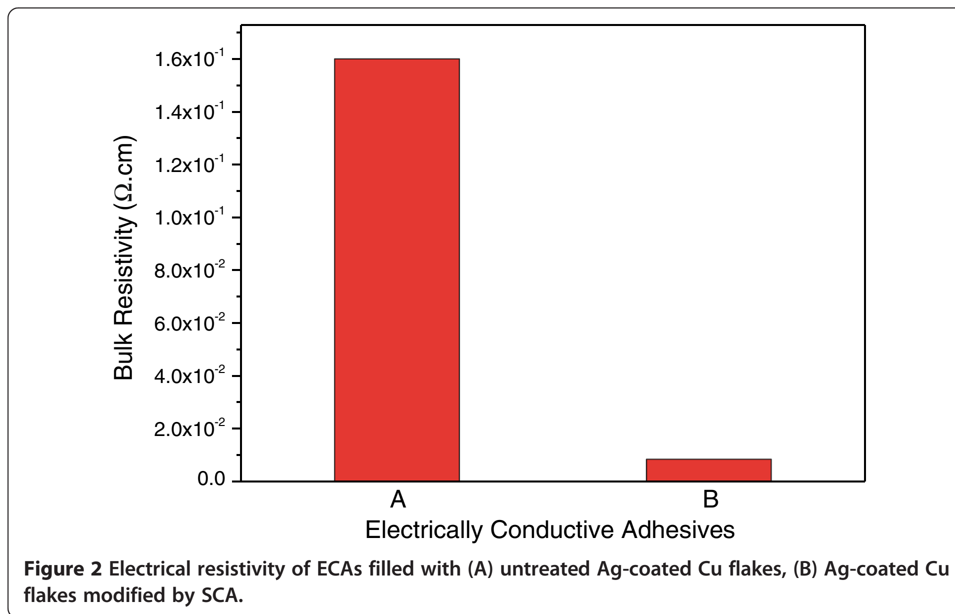


Figure 2 Electrical resistivity of ECAs filled with (A) untreated Ag-coated Cu flakes, (B) Ag-coated Cu flakes modified by SCA.

would benefit for Ag-coated Cu flakes' wettability and dispersity in resin. SCA is usually used for improving inorganic fillers' dispersion in polymer, because of their two different functional groups, one attached to polymer and the other attracted to fillers [13-15]. The SCA functioned as molecular bridges here at the interface of polymer binder and Ag coated Cu fillers, resulting in the formation of covalent chemical bonds across the interface.

Diisobutyl phthalate (DIBP) was used as a non-reactive diluent added in the ECAs to improve the viscosity. Figure 3 showed the electrical properties of the ECAs filled with 80 wt % Ag-coated Cu flakes cured at 150°C and 180°C as a function of the composition of the diluent. The ECAs cured at 180°C showed lower bulk resistivity than that cured

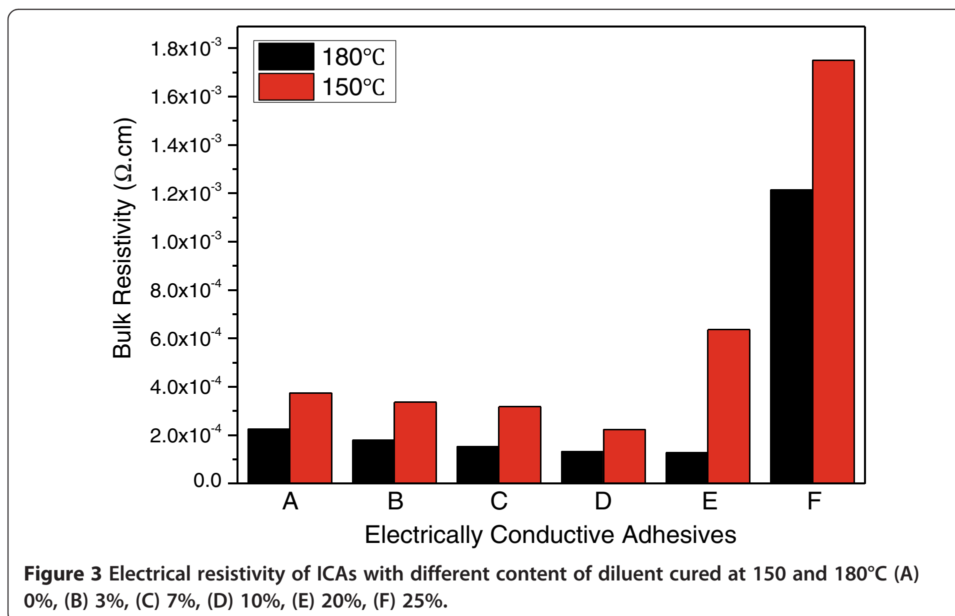


Figure 3 Electrical resistivity of ICAs with different content of diluent cured at 150 and 180°C (A) 0%, (B) 3%, (C) 7%, (D) 10%, (E) 20%, (F) 25%.

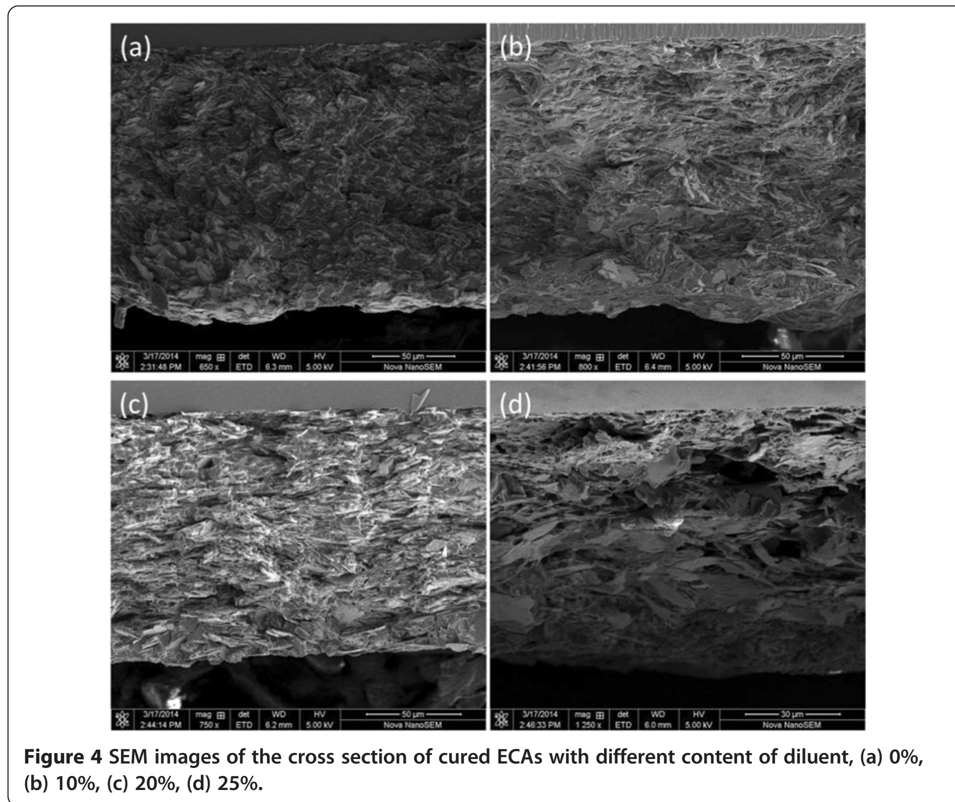


Figure 4 **SEM images of the cross section of cured ECAs with different content of diluent, (a) 0%, (b) 10%, (c) 20%, (d) 25%.**

at 150°C. The bulk resistivity of the ECAs decreased with increasing content of DIBP within certain limits, but the change was tiny. The ECAs with addition of 20 wt % of DIBP exhibited lowest bulk resistivity of $1.27*10^{-4}$ Ωcm, which decreased 56% than ECAs without diluent ($2.25*10^{-4}$ Ωcm). However the bulk resistivity obviously increased to $1.21*10^{-3}$ Ωcm with higher content of DIBP (25 wt %). The diluent might be helpful for the dispersion of Ag-coated Cu flakes in the resin during the mixing

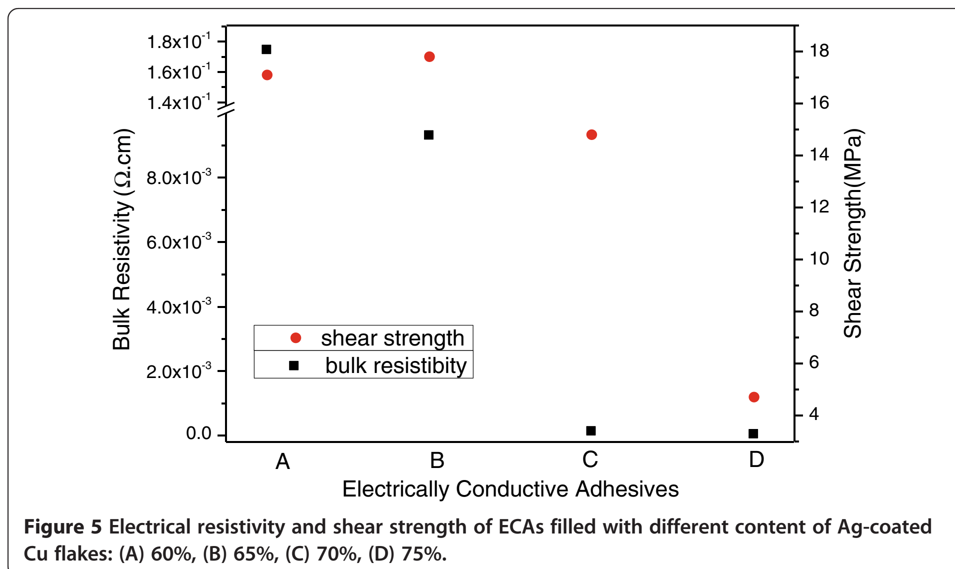


Figure 5 **Electrical resistivity and shear strength of ECAs filled with different content of Ag-coated Cu flakes: (A) 60%, (B) 65%, (C) 70%, (D) 75%.**

process. As the non-reactive diluent was evaporated after being cured, and then higher electrical, thermal conductive and fillers-contained ECAs were obtained. Figure 4 showed the SEM images of the cross section of cured ECAs with different content of diluent. It could be found that the Ag-coated Cu flakes dispersed in resin in all directions (Figure 4a), the disorder distribution resulted to the dot-to-dot contact between flakes. The addition of DIBP contributed to low viscosity, and the disorganized Ag-coated Cu flakes changed to regular and dispersed in horizontal direction (Figure 4c) due to its own gravity, and emerged more and more face-to-face contact between flakes. While the too much diluent, a large number of gap in ECAs was emerged (Figure 4d) due to the evaluation of diluent. The resistance of the ECAs resulted from materials intrinsic and the constriction resistance of fillers. The flakes' horizontal direction dispersion in ECAs contributed to the face-to-face contact between fillers, the large contact area leaded to high electrical conductivity.

Figure 5 showed the electrical resistivity and shear strength of ECAs filled with different content of Ag-coated Cu flakes. The rheological property of ECAs was influenced with the high content filler, In order to improve the dispersion of Ag-coated Cu flakes, the DIBP was added in ECAs-(B, C, D) with proportions of 1.5%, 3.2%, 10% respectively. The ECAs-A exhibited low electrically property due to insufficient filler amount, the electrical conductive network was not formed in ECAs. More physical contact between fillers increased with the higher loading of filler, and the bulk resistivity decreased dramatically down to the lowest of $6.2*10^{-5}$ Ωcm. The value was comparable to that of commercial Ag-filled ECAs ($10^{-4} \sim 10^{-5}$ Ωcm). The mechanical property is the other crucial factor that dictates the suitability of the ECAs to be applied in LED packaging. Besides ECA-D showed relatively low shear strength about 4.7 MPa, the rest of the ECAs in this paper possessed comparable shear strength from 14.8 ~ 17.8 MPa.

Conclusions

In summary, the electrical conductivity of ECAs was improved remarkably by the filler treated with SCA. A proper amount of non-reactive diluent could reduce the viscosity, and benefit for the flakes' regular dispersion. The electrical conductivity and mechanical strength was enhanced due to the face-to-face between fillers. The Ag-coated Cu flakes filled ECAs might be applied in LED packaging.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

HMR carried out the experiments and presented the first draft of the paper as the fisrt author. KZ, YM and CP provided guidance for the experiments, XZF, RS conceived original ideas and helped to draft the manuscript. All authors read and approved the manuscript.

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