Rare Metal Materials and Engineering
Volume 49, Issue 5, May 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(5): 1526-1532.

ARTICLE

Effect of the Silver with Different Morphologies on the Performance of Electrically Conductive Adhesives

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Abstract: The morphology of silver fillers, the surface lubricants of the silver fillers, the composition of the resin matrix, and curing procedures will affect the performance of electrically conductive adhesives (ECAs). The morphology of silver fillers is a crucial factor. The effect of silver with different morphologies on the performance of ECAs under the same conditions was studied. Silver flakes, silver spheres and silver wires were prepared and treated with glutaric acid to eliminate the effects of other factors. Then, these silver particles were used as conductive fillers and composited with epoxy resin to prepare ECAs. The thermal degradation, electrical conduction properties, mechanical properties and storage stability of ECAs were investigated. The results show that the ECAs filled with silver wires exhibit the lowest electrical resistivity and percolation threshold and the best mechanical properties as well as good storage stability compared to the other ECAs under the same conditions. The ECAs filled with silver flakes show better electrical conduction properties and storage stability but poorer mechanical properties than the ECAs filled with silver spheres.

Key words: morphology of silver; electrically conductive adhesives; silver wires; silver flakes; silver spheres

Electrically conductive adhesives (ECAs) are used as replacements for the traditional eutectic SnPb solder alloys in electronic packaging and interconnect applications, such as die attachments, multilayer printed circuits and surface mount technology. However, compared with mature soldering technology, ECA technology has some limitations, such as relatively low electrical and thermal conductivity, unstable contact resistance and poor impact strength[1,2]. To improve these properties, many works have been performed, such as using silver nanowires as conductive fillers[3,4], introducing carbon materials[5-7], removing or changing the surface lubricants of silver particles[8,9] and using hybrid resins and fillers[10]. The formulation, material design and process should be optimized and developed to enhance reliable performance[11]. ECAs are mainly composed of a polymer matrix (epoxy, silicone, cyanate ester, polyurethane, etc.) and electrically conductive fillers (silver (Ag), gold (Au), nickel (Ni), copper (Cu), etc.). Silver-filled epoxy composites are widely used conductive adhesives, in which the epoxy resins wet and bond to almost all surfaces, showing high performance, whereas the silver offers advantages of high conductivity and conductivity stability[12]. Research shows that the morphology of silver fillers is a crucial factor affecting the performance of ECAs. Huang-wu Chiang et al. reported the influence of silver flakes, silver dendrites and silver nanosized particles used as conductive fillers on the electrical conduction properties of ECAs[13]. Y. H. Wang et al. studied the resistivity and shear strength of ECAs filled with silver nanowires[14]. In addition to the morphology of the silver fillers, the composition of the matrix, surface lubricants of the silver fillers and curing procedures will also affect the performance of ECAs. S. Khairul Anuar et al. reported the effect of epoxy systems on the properties of ECAs[15]. Ling Wang et al. introduced short-chain difunctional acids with various structures in situ to replace the commonly used surfactant stearic acid on the silver filler surface to improve the electrical conductivity of ECAs. Oxalic acid, phthalic acid and cis-hexahydrophthalic acid deteriorated the electrical conductivity of ECAs, whereas the electrical conductivity was

Received date: May 05, 2019
Foundation item: GDAS'Special Project of Science and Technology Development (2017GDASCX-0850, 2017GDASCX-0705)
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significantly improved with the use of succinic acid and adipic acid[16]. Xiong Nana et al. studied the influence of curing procedures on the electrical properties of epoxy-based isotropic conductive adhesives[17]. However, only a few studies on how the shape of silver fillers affects the properties of ECAs under the same conditions have been published thus far.

In this study, we purchased silver flakes and silver spheres and synthesized silver wires in our lab. Then, these silver particles were treated in the same way to minimize other factors affecting the properties. ECAs filled with silver flakes, silver spheres and silver wires were prepared. The thermal degradation, electrical properties, mechanical properties and storage stability of the ECAs were characterized.

1 Experiment

A commercial epoxy resin (CYD 128) was purchased from SINOPEC Baling Company. Triethanolamine (98%) was used as the hardener, supplied by Aladdin Biochemical Technology Co. LTD. Acetone, silver nitrate and ethylene glycol were purchased from Guangzhou Chemical Reagent Factory. Sodium sulfide ($Na_2S·9H_2O$) was purchased from Tianjin Fuchen Chemical Reagents Factory. Poly (vinylpyrrolidone) (PVP K30) was purchased from Shanghai Boao Biotechnology Co. LTD. Glutaric acid (99%) was purchased from Aladdin Biochemical Technology Co. Ltd. All chemical reagents were of analytical grade and used as received without further treatment. Silver flakes were purchased from Guangzhou Hongwu Materials Technology Co. Ltd. Silver spheres were purchased from Nangong City Pingyuan Alloy Material Co. Ltd. Silver wires were synthesized in our laboratory according to Ref. [18]. All silver particles were treated with glutaric acid[19] before being added to the polymer matrix.

Epoxy resin, triethanolamine and acetone with a mass ratio of 1:0.15:0.02 were placed into a small beaker with stirring. The mixture and silver particles were poured into a three-roll grinder and mixed 15 times to uniformly disperse the fillers in the matrix. Two strips of polyimide tape were applied parallel to each other on a precleaned glass slide with a gap of 5 mm between them. Then, the composite mixtures were poured into the gap and leveled with a scraping blade. Finally, the ECAs were cured at 200 °C for 30 min.

The morphologies of the silver particles and composites were studied by field emission scanning electron microcopy (SEM, JEOL JSM-7001F). X-ray diffraction (XRD) patterns of the silver particles were recorded by a powder X-ray diffractometer (PANalytical X'Pert3) using Cu Kα radiation (40 kV and 40 mA). XRD data were collected at room temperature using Cu Kα (λ=0.154 18 nm) X-rays. A scanning rate of 0.2°/s and a 2θ range of 10°~90° were used. Energy dispersive X-ray spectroscopy was used to analyze the quantitative element contents of carbon and silver on the surface of the silver fillers (EDS, Oxford Inca 400). Raman spectra were obtained using a Raman spectrometer (H. J. Y LabRAM Aramis). The 633 nm line of the He-Ne laser was used for experiments. The slit was set to 100 μm. The thermal properties of the ECAs were characterized by thermogravimetric analysis (TGA Q50) under nitrogen. The temperature was increased from 30 to 700 °C at a heating rate of 10 °C/min.

The resistivity of the ECAs was measured using a four-point probe meter (DMR-1C, Nanjing Daming Instrument Co. Ltd). The resistivity (ρ) was calculated using Eq. (1):

$$\rho=Rd \quad (1)$$

where R and d denote the sheet resistance and thickness of the sample, respectively. The thickness of the cured samples was measured with a micrometer gauge. The average sheet resistance and thickness of the sample were estimated from measurements at five points on the sample surface. Three parallel samples were prepared for each ECA. We considered the samples to be not conductive when the resistivity could not be read because the value was out of range of the meter.

The ECA samples for the lap shear strength test were prepared according to the National Standard of the People's Republic of China GB7124-2008 (EQV ISO 4587:2003). In accordance with the standard, the adhesive was used to bond two panels of stainless steel, with dimensions of (1.6 ±0.1) mm thick, (25±0.25) mm wide and (100±0.25) mm long, and the bonding part on the sample was B=12.5±0.25 mm in width and L=(25±0.25) mm in length. The prepared sample was cured at 200 °C for 30 min. The panels were pulled apart by an electronic universal testing machine (MTS, CMT4204) at a pull rate of 5 mm/min. Five parallel samples were prepared for each ECA. The lap shear strength (τ) was calculated using Eq. (2):

$$\tau=F/(BL) \quad (2)$$

where F is the force applied to break apart the bonded panels, B is the width of the bonded area and L is the length of the bonded area.

The storage stability of the ECAs was elucidated by measuring their resistivity after storage at –20 °C for 3, 6 and 10 m.

2 Results and Discussion

2.1 Characterization of silver particles

The XRD patterns of the silver particles are shown in Fig. 1. Five diffraction peaks are observed at 2θ values of 38°, 44°, 64°, 77° and 81°, which are indexed to the (111), (200), (220), (311) and (222) planes of pure face-centered-cubic (fcc) silver crystals, respectively. The lattice constant calculated from these XRD patterns is 0.408 65 nm, which is close to the reported value (a=0.408 65 nm, JCPDS file 04-0783).

Fig.2 presents the morphology of the silver particles. The SEM images show that the silver wires (Fig.2a) have a

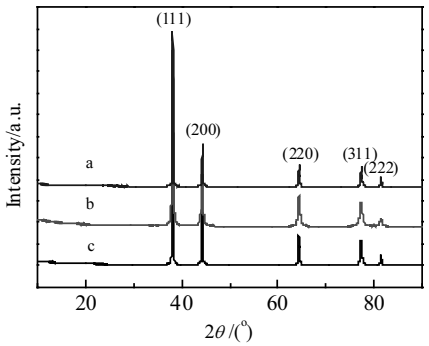

Fig.1 XRD patterns of silver wires (a), silver flakes (b) and silver spheres (c)

diameter of approximately 1 μm, the silver flakes (Fig.2b) have a diameter of approximately 1 μm and the silver spheres (Fig.2c) have a diameter of approximately 1 μm.

The lubricants of the silver particle surfaces are nonconductive, and ECAs are believed to become conductive only after this layer has been removed[8]. Different surface treatments of silver particles for ECAs can affect the conduction properties[20-23]. Therefore, we treated all silver particles with glutaric acid before adding them to the polymer matrix to eliminate the effect of the lubricants. All modified silver particles show similar Raman spectra, as shown in Fig.3. The bands at 2931, 1639, and 1401 cm^{-1} in the three spectra are assigned to C-H stretching, C=O stretching, and C-H flexural vibration, respectively. The strong band at 238 cm^{-1}

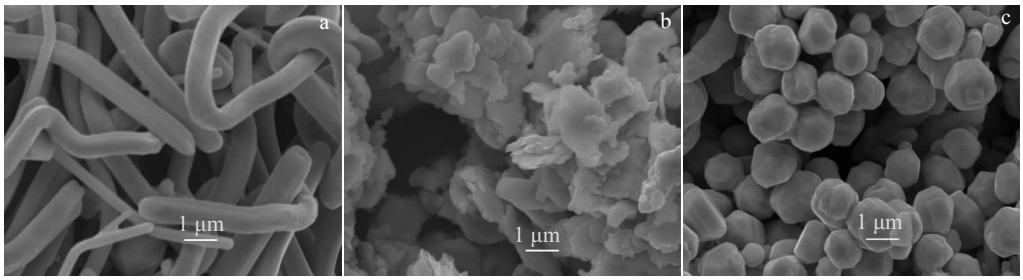

Fig.2 SEM images of silver wires (a), silver flakes (b) and silver spheres (c)

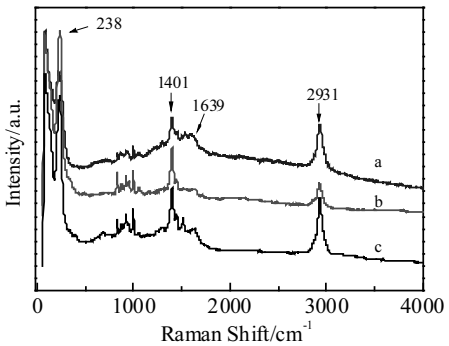

Fig.3 Raman spectra for glutaric acid adsorbed on silver wires (a), silver flakes (b) and silver spheres (c)

is ascribed to COO-Ag vibration[19]. This strong peak near 230 cm^{-1} was reported by Moskovits and Suh and attributed to COO-Ag vibration[24]. The Raman results demonstrate that the surface chemical composition of all silver particles is similar. The glutaric acid was absorbed on the silver wire, silver flake and silver sphere surfaces after treatment.

EDS was used to detect the quantitative element contents of the silver particles after treatment with glutaric acid[9]. As shown in Table 1, the silver wires contain 2.0 wt% carbon and 96.9 wt% silver, the silver flakes contain 2.1 wt% carbon and 96.5 wt% silver, and the silver spheres contain 2.0 wt% carbon and 97.1 wt% silver. The carbon and silver contents of the three silver particles are similar, indicating that the amounts of glutaric acid absorbed on the surfaces of the silver particles are similar.

2.2 Properties of ECAs

The TGA curves of the ECAs are shown in Fig. 4. All samples lose mass at 250~430 °C, which should be the decomposition temperature interval of epoxy resin. This interval is not affected by the shape of the silver fillers. The residual mass of

Table 1 Quantitative element contents of silver particles after treatment (wt%)

Element	Silver wires	Silver flakes	Silver spheres
Ag	96.9(±0.2)	96.5(±0.1)	97.1(±0.1)
C	2.0(±0.1)	2.1(±0.1)	2.0(±0.1)

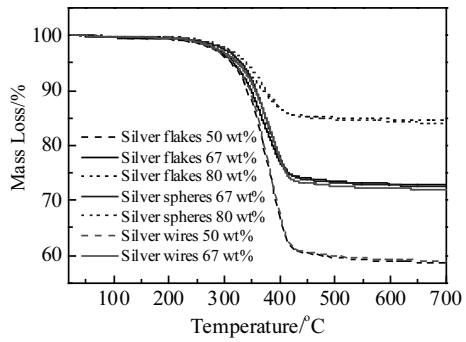

Fig.4 TGA curves of ECAs

the ECAs with the same silver contents are similar. This result demonstrates that the conductive filler contents of the ECAs are as expected.

The electrical resistivity of the as-made ECAs is shown in Table 2. The electrical resistivity decreases with increasing silver content. At 67 wt% silver loading, the ECAs filled with silver wires show the lowest electrical resistivity of approximately 6.36×10^{-4} Ω·cm, followed by that of the ECAs filled with silver flakes of approximately 7.89×10^{-4} Ω·cm. The ECAs filled with silver spheres are non-electrically conductive. This result indicates that ECAs filled with silver wires show the best electrical conductivity at the same silver content. The ECAs filled with silver spheres at 67 wt% loading are non-electrically conductive. The ECAs filled with silver flakes at 67 wt% loading show electrical conductivity, and the electrical resistivity is 7.89×10^{-4} Ω·cm, but the ECAs filled with silver flakes at 50 wt% loading are non-electrically conductive. The ECAs filled with silver wires at a 33 wt% loading still show electrical conductivity, and the electrical resistivity is 8.5×10^{-2} Ω·cm. No conductivity can be observed below a critical value, known as the percolation threshold[25,26]. The results show that the percolation threshold of the ECAs filled with silver wires is the lowest among the three types of silver particles, followed by the silver flakes and silver spheres.

Fig.5 presents cross-section SEM images of the ECAs after curing. The silver particles are randomly distributed in the resin matrix. The distribution of silver particles becomes denser with increasing silver loading. The silver particles contact each other and form conductive networks more easily when the filler distribution is denser. Therefore, the electrical resistivity decreases with increasing silver content. The silver wires exhibit zigzag shapes (Fig. 6a).These shapes make them intertwine with each other to form a conductive

Table 2 Resistivity of ECAs (Ω·cm)

Ag loading	33 wt%	50 wt%	67 wt%	73 wt%	80 wt%
Silver wires	8.5×10^{-2} ($\pm2.15\times10^{-2}$)	3.74×10^{-3} ($\pm0.87\times10^{-3}$)	6.36×10^{-4} ($\pm0.27\times10^{-4}$)		
Silver flakes		Nonconductive	7.89×10^{-4} ($\pm0.11\times10^{-4}$)	4.83×10^{-4} ($\pm0.10\times10^{-4}$)	1.94×10^{-4} ($\pm0.07\times10^{-4}$)
Silver spheres			Nonconductive	1.17×10^{-3} ($\pm0.05\times10^{-3}$)	9.13×10^{-4} ($\pm0.30\times10^{-4}$)

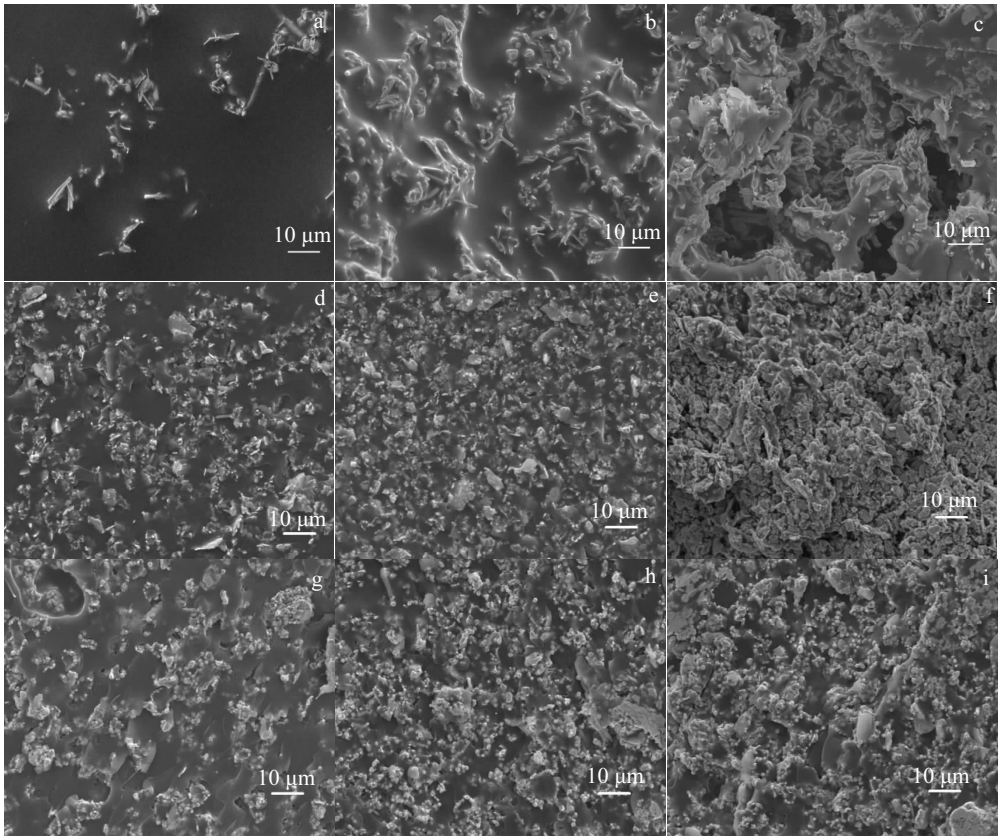

Fig.5 Cross-section SEM images of ECAs after curing: (a) wires 33 wt%, (b) wires 50 wt%, (c) wires 67 wt%, (d) flakes 50 wt%, (e) flakes 67 wt%, (f) flakes 80 wt%, (g) spheres 67 wt%, (h) spheres 73 wt%, and (i) spheres 80 wt%

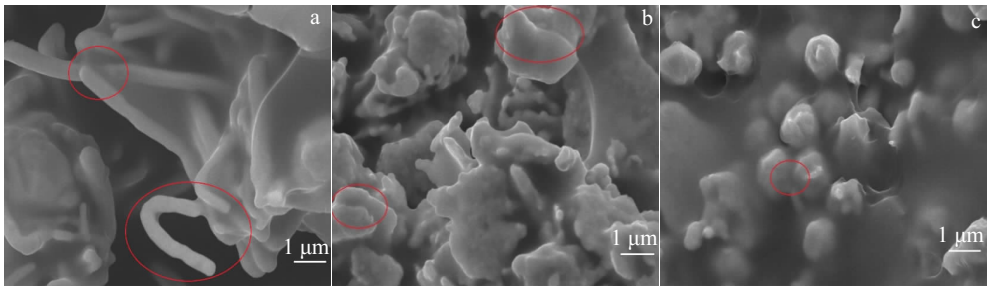

Fig.6 Cross-section SEM images of ECAs after curing: (a) cured ECA filled with 67 wt% silver wires, (b) cured ECA filled with 80 wt% silver flakes, (c) cured ECA filled with 80 wt% silver spheres

pathway. Compared to the other morphologies, the wires can contact other wires at a relatively far distance. Easy formation of a conductive network and the tunneling effect might be reasons why a low resistivity and a low percolation threshold are achieved for ECAs[27,28]. Therefore, ECAs filled with silver wires show the lowest percolation threshold and electrical resistivity. The diameters of the silver flakes and silver spheres are approximately 1 μm. At the same mass, the number of flakes is greater than that of spheres (Fig. 5), and thus, flakes have a higher chance to contact each other. Moreover, the silver flakes form a conductive network by overlapping neighboring flakes, and the silver spheres form limited point contacts (Fig. 6b and Fig. 6c). Therefore, ECAs filled with silver flakes exhibit better electrical conduction properties than ECAs filled with silver spheres.

ECAs provide not only electrical connections but also mechanical support. Therefore, the adhesion strength is another crucial parameter of ECAs. The lap shear strength is chiefly related to the strength of adhesion between the adhesive and the surfaces of the test sample[29]. Fig. 7 shows the lap shear strengths of ECAs filled with different electrically conductive fillers. ECAs filled with silver wires show the highest lap shear strength, followed by ECAs filled with silver spheres and ECAs filled with silver flakes. The dispersion, filler-matrix interface interaction and processing conditions are crucial to the mechanical properties[30]. Silver wires with a fiber-like shape can more easily contact the resin and be wetted by the resin and do not break the continuity of the resin matrix[2]. Therefore, ECAs filled with silver wires show the best mechanical properties. The silver flakes overlap with each other, forming clusters. According to van der Waals's force, the interactions within a cluster are too weak, leading to worse mechanical properties of the ECAs[31]. Consequently, ECAs filled with silver flakes show the lowest lap shear strength.

To study the storage stability of the ECAs with different electrically conductive fillers, the resistivity of the ECAs was measured after storage at -20 °C for 3, 6 and 10 m(month). The results are shown in Table 3. The resistivities of the ECAs filled with silver wires and of the ECAs filled with silver flakes show little change after storage for 6 m, but the resistivity of the ECAs filled with silver spheres increases significantly after storage for 3 m. This result demonstrates that ECAs filled with silver wires and ECAs filled with

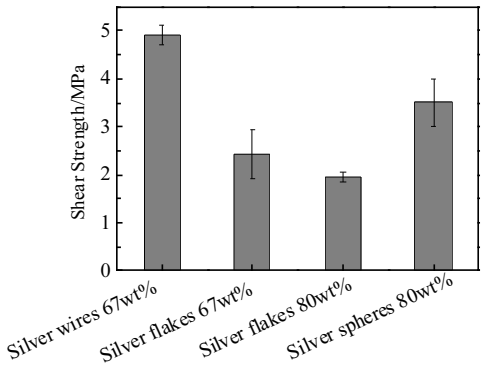

Fig.7 Lap shear strengths of ECAs

Table 3 Resistivities of ECAs after storage at –20 °C for 3, 6 and 10 m (Ω·cm)

	Initial	3 m	6 m	10 m
Silver wires 67 wt%	6.36×10^{-4} ($\pm0.27\times10^{-4}$)	6.49×10^{-4} ($\pm0.17\times10^{-4}$)	8.01×10^{-4} ($\pm0.16\times10^{-4}$)	1.03×10^{-3} ($\pm0.02\times10^{-3}$)
Silver flakes 67 wt%	7.89×10^{-4} ($\pm0.11\times10^{-4}$)	8.27×10^{-4} ($\pm0.10\times10^{-4}$)	8.40×10^{-4} ($\pm0.05\times10^{-4}$)	1.31×10^{-3} ($\pm0.30\times10^{-3}$)
Silver flakes 80 wt%	1.94×10^{-4} ($\pm0.07\times10^{-4}$)	1.83×10^{-4} ($\pm0.10\times10^{-4}$)	1.81×10^{-4} ($\pm0.07\times10^{-4}$)	1.67×10^{-4} ($\pm0.04\times10^{-4}$)
Silver spheres 80 wt%	9.13×10^{-4} ($\pm0.30\times10^{-4}$)	4.82×10^{-3} ($\pm2.10\times10^{-3}$)	2.07×10^{-2} ($\pm1.01\times10^{-2}$)	1.41×10^{-1} ($\pm1.00\times10^{-1}$)

silver flakes have excellent storage stability, and ECAs filled with silver spheres show poorer storage stability than the two other ECAs.

3 Conclusions

1) The morphology of conductive fillers is a crucial factor affecting the properties of ECAs.

2) ECAs filled with silver wires show the lowest electrical resistivity and percolation threshold and the best mechanical properties compared to ECAs filled with silver flakes or spheres as well as good storage stability.

3) ECAs filled with silver flakes show better electrical conduction properties and storage stability but poorer mechanical properties than ECAs filled with silver spheres.

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不同形貌的银对导电胶性能的影响

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摘 要：银的形貌、银表面的润滑剂、树脂基体的组成及固化过程都对导电胶（ECAs）的性能有影响。其中银的形貌是一个关键因素。作者在相同条件下研究了不同形貌的银对导电胶性能的影响。采用戊二酸处理了银片、银球和银线以消除其它因素的影响，然后这些银粒子被用做导电填料与环氧树脂复合制备导电胶。研究了所制备的导电胶的热降解性能、导电性能、机械性能和贮存稳定性。结果显示，在相同条件下银线制备的导电胶具有最低电阻率和渗流阈值、最好的机械性能以及较好的贮存稳定性，银片制备的导电胶导电性能和贮存稳定性比用银球制备的导电胶好，但机械性能比用银球制备的导电胶差。

关键词：银的形貌；导电胶；银线；银片；银球

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