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ARTICLE

# Preparation of Silver Pastes with High Electrical Conductivity After Folding

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**Abstract:** The influence of Ag flake size on the electrical conductivity of silver pastes before and after folding was investigated. The low-temperature curing conductive silver pastes with good electrical conductivity after folding were fabricated using Ag flake with different flake sizes. Then the silver pastes were screen-printed on the polyimide substrate and sintered at 140 °C to form the circuits. The electrical resistivity of the printed circuits was detected by micro-ohmmeter. In order to measure the flexibility of Ag circuits, the variance of electrical resistivity of Ag circuits was detected after they were folded. The surface morphology of the folded Ag circuits was observed by the scanning electron microscopy. The conductive mechanism was analyzed. The results show that the small Ag flakes can act as the bridge between the unconnected flakes and fill the gaps after the circuits are folded, which forms the conductive networks, thereby improving the electrical conductivity after folding.

**Key words:** conductive silver paste; Ag flake; electrical conductivity

In recent years, the conductive silver paste has been widely studied as a very important conductive functional material to prepare the advanced electronic components and devices[1]. The low-temperature curing conductive silver paste is mainly composed of polymer resins and silver particles, which has been widely used in the flat-panel displays[2], radio-frequency identification tags[3,4], antennas, sensors, and electronic packaging[5,6] due to its good properties.

The polymer resins provide physical and mechanical properties and the silver particles transfer electricity due to their low electrical resistivity[7]. The morphology and size of silver particles play a significant role in the physical properties and printing effects of the silver paste[8]. Currently, most of the silver pastes are made of the spherical micron silver powder with a relatively high electrical resistivity. In order to reduce the electrical resistivity of the silver paste, the Ag flakes and the spherical silver particles are mixed to improve the electrical conductivity[9]. Wang et al[10] used Ag nanowires and micro-sized Ag flakes and obtained a silver paste with the electrical resistivity of $10^{-6}$ Ω·m. The connection between the spherical silver powders in the silver paste is primarily the point contact, whereas that between Ag flakes is mainly the line contact and surface contact. The volume conductivity of silver pastes prepared by large Ag flakes is larger than that by small spherical silver powder at the same mass because of the larger contact area between the Ag flakes[11]. However, it is also found the nano-sized silver particles have a positive influence on the electrical conductivity. Lee et al[12] indicated that near the percolation threshold, the addition of nano-sized silver particles can decrease the electrical resistivity by forming a conductive path. Chiang et al[8] used the silver flakes, silver dendrites, and nano-sized silver powders to reduce the percolation threshold, because the nano-sized silver particles could fill the gaps between the silver flakes.

Although the silver paste prepared by Ag flakes has a low electrical resistivity, it is still difficult for Ag flakes to pass through the mesh during the screen-printing process, due to its large size[13]. Besides, it is found that the silver paste with the large-sized Ag flakes has excellent electrical conductivity but it nearly loses the electrical conductivity after it is folded. However, the silver paste with the small-sized Ag flakes

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shows the opposite situation. The flexibility is important for the applications including the flexible-printed circuits, touch-screen panels, and membrane keyboards. Various methods have been implied to improve the flexibility of the conductive components, such as using polymer substrates, adding agents to the pastes, and applying the surface coatings[14-16]. Park et al[17] focused on the mechanical properties of screen-printed silver circuits with different contents of silver flakes, and found that the best flexibility of the screen-printed silver circuits can be achieved by containing 50wt% silver flakes. Liu et al[18] investigated the synergistic effect of silver nanowire with graphene oxide, and found that the drawn conductive traces possess high electrical conductivity and remarkable foldability simultaneously. Liu et al[19] investigated the effects of the molecular weight of the resin on the performance of silver paste, and found that the flexural resistance has no direct relationship with the molecular weight of the polyester resin. Araki et al[14] studied the influence of different sintering temperatures on the flexibility of screen-printed Ag circuits on the polyimide (PI) film, and found that the flexibility is decreased because the consolidation of the Ag nanoparticles becomes faster with increasing the sintering temperature. Generally, the electrical properties of circuits are poor whereas the flexibility of circuits is good. Therefore, the flexural resistance is often evaluated through the resistance change and plays a vital role in the practical application of flexible-printed circuits.

For the flexible electronic applications, it is important to improve both their electrical conductivity and the flexibility. In this research, a series of silver pastes with Ag flakes of different sizes were prepared to achieve the high electrical conductivity after folding. The silver pastes were screen-printed on the flexible PI substrate. The effects of the silver flake size on the silver paste properties, including the electrical resistivity and the electrical conductivity after folding, were investigated.

## 1 Experiment

Polyester resin, polymethyl methacrylate (PMMA), and thermoplastic polyurethanes (TPU) were used as the binder phase. Polyamide wax was the additive material, acting as the suspending agent. Dibasic ester (DBE) was used as the solvent. Four types of Ag flake (Zhongxin New Materials Co., Ltd) were used as the conductive materials in this research: the micro-sized Ag flake of 10, 5, 3 μm in length and the nano-sized Ag flake of 200 nm in length.

The binder was dissolved in the solvent and stirred uniformly at room temperature. The mass fraction of the binder and the solvent was 9.5wt% and 42wt%, respectively. The mass ratio of polyester resin: TPU: PMMA=1: 0.6: 0.3 in the binder phase. Then, 0.5wt% polyamide wax was added into the solution to obtain the organic carrier. Finally, the commercial silver flake and the organic carrier were mixed and well ground to prepare the silver pastes. The mass fraction of silver flake was 48wt%. The mass fraction of each filler in the silver paste composite is listed in Table 1. Eight silver pastes with Ag flake of different sizes were prepared and their related data are shown in Table 2.

The silver pastes were screen-printed with a line-shape of 80 mm× 0.7 mm on the PI substrate, as shown in Fig. 1, and then sintered in an ambient atmosphere at 140 °C for 30 min. The thickness of silver film was measured by a step profiler (Kosaka ET200, Japan). The resistance $R$ of the screen-printed line was measured by Suzhou Jingge Electronic GOM-801H DC micro-ohmmeter. The electrical resistivity $\rho$ was calculated by Eq.(1), as follows:

$$\rho = Rhw/l \times 100\% \tag{1}$$

where $h$, $w$, $l$ are the thickness, width, and length of the line, respectively. Then, the substrate film was folded for 10 times with the pressing of 2 kg for 1 min during each folding, as shown in Fig. 2. Then the resistance of the screen-printed circuits was measured again to calculate the folding change rate $\varphi$ by Eq.(2), as follows:

$$\varphi = (R_2 - R_1)/R_1 \times 100\% \tag{2}$$

where $R_1$ and $R_2$ are the resistance before and after folding, respectively.

The surface and cross-section morphologies of the screen-printed circuits were observed by scanning electron microscopy (SEM, JEOL, Japan, model JSM-5610LV). The

**Table 1 Composition of filler in silver paste (wt%)**

| Polyester resin | TPU | PMMA | DBE | Polyamide wax | Ag flake |
|---|---|---|---|---|---|
| 5.0 | 3.0 | 1.5 | 42.0 | 0.5 | 48.0 |

**Table 2 Silver pastes with the combination of different Ag flakes**

| Specimen | Content of Ag flake/wt% | | | | Thickness/μm | Electrical resistivity/Ω |
|---|---|---|---|---|---|---|
| | 10 μm | 5 μm | 3 μm | 200 nm | | |
| Paste-1 | 100 | 0 | 0 | 0 | 5.6 | 5.84 |
| Paste-2 | 0 | 100 | 0 | 0 | 6.4 | 9.03 |
| Paste-3 | 0 | 0 | 100 | 0 | 6.5 | 41.9 |
| Paste-4 | 80 | 20 | 0 | 0 | 5.8 | 5.52 |
| Paste-5 | 60 | 40 | 0 | 0 | 6.2 | 3.08 |
| Paste-6 | 50 | 50 | 0 | 0 | 5.5 | 9.26 |
| Paste-7 | 60 | 20 | 20 | 0 | 6.2 | 4.54 |
| Paste-8 | 60 | 20 | 10 | 10 | 6.5 | 4.26 |

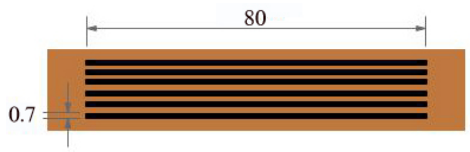


Fig.1 Schematic diagram of silver paste lines on PI substrate

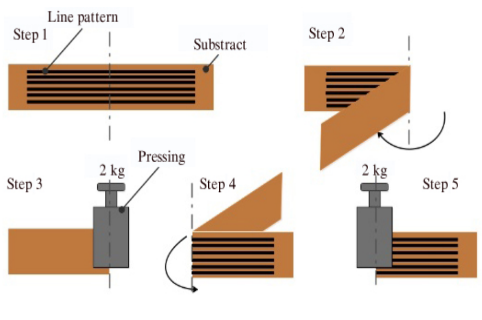


Fig.2 Schematic diagram of folding process

size distribution and porosity of the silver paste surface were measured by field emission SEM coupled with image analyzer and the Brunauer-Emmett-Teller (BET) method.

## 2 Results and Discussion

### 2.1 Silver pastes prepared with single Ag flake

The morphologies and size distributions of the silver pastes on the screen-printed circuits are shown in Fig. 3. It is clear that the Ag flakes in Paste-1 and Paste-2 specimens are flat on the silver paste surface. As shown in Fig.4, the Ag flakes are layer-aligned on the substrate, forming a good conductive path. The thickness of the film is 5~7 μm. However, on the surface of Paste-3 specimen, the agglomeration phenomenon and a serious pore structure can be observed (Fig. 3c). With decreasing the flake size from micro scale to the nano scale, the surface energy is increased, resulting in the Ag flake aggregation.

The electrical resistivity and the folding change rate of the silver pastes prepared by Ag flakes of different sizes are shown in Fig. 5. The Paste-1 specimen shows a relatively low electrical resistivity ($2.87\times10^{-7}$ Ω·m). With decreasing the silver size, the electrical resistivity is increased. The electrical resistivity of Paste-3 specimen is $23.86\times10^{-7}$ Ω·m, which is about eight times larger than that of Paste-1. Therefore, the larger the size of the Ag flake, the shorter the conductivity distance. The surface of Paste-1 specimen is mainly composed of large Ag flakes of 10 μm in length which are orderly arranged in the organic polymer, forming a good conductive path. However, a great number of small Ag flakes can be observed in the Paste-3 specimen, which weakens the free electron conduction. The porosity of the silver paste surfaces of Paste-1, Paste-2, and Paste-3 is 35.73%, 49.05%, and 59.02%, respectively. The surface porosity is increased with decreasing the flake size, resulting in the significant increment in resistance. In brief, the aggregation of Ag flakes and pores in Paste-3 specimen are harmful for the free electron conduction, which leads to the deterioration of electrical conductivity.

As shown in Fig. 5, the folding change rate indicates a different tendency compared with the electrical conductivity variance. After folding, the Paste-1 specimen nearly loses its electrical conductivity and the Paste-2 specimen shows a relatively good electrical conductivity. The initial folding change rate of Paste-1 specimen is 100%, proving that the electrical conductivity of the silver paste with large Ag flakes is seriously destroyed by folding. With decreasing the flake size from 10 μm to 5 μm, the electrical conductivity of Paste-2

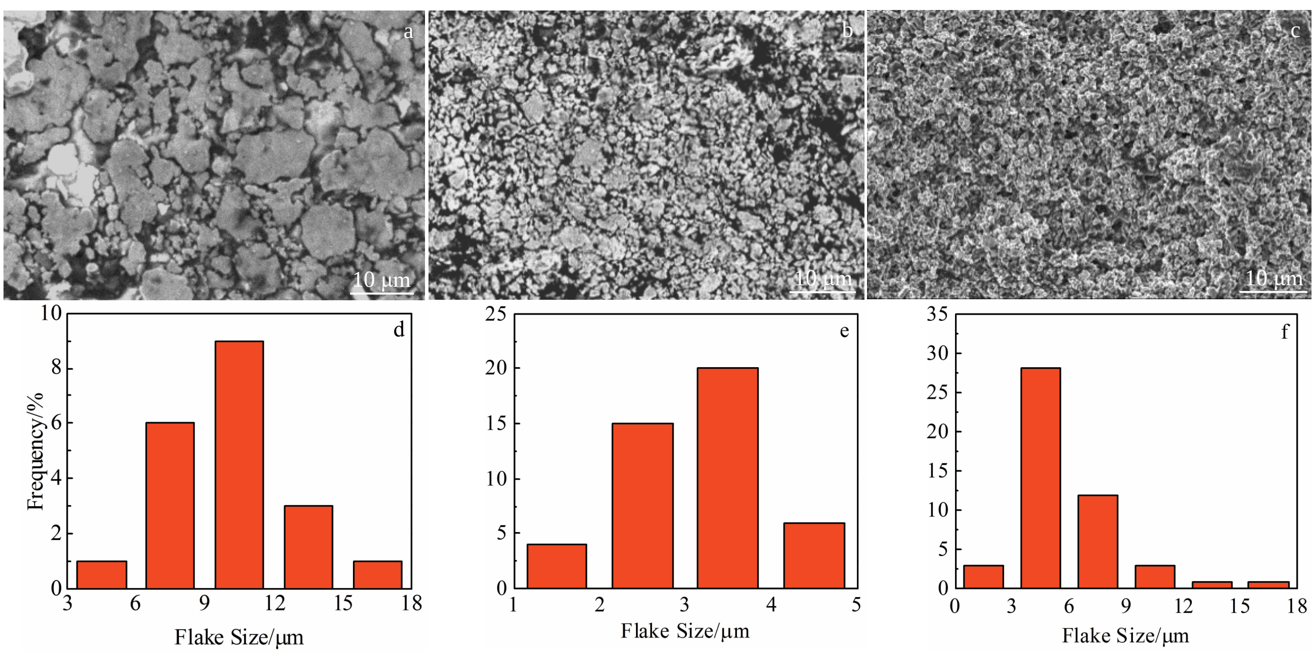


Fig.3 Surface morphologies (a~c) and flake size distributions (d~f) of Paste-1 (a, d), Paste-2 (b, e), and Paste-3 (c, f) specimens

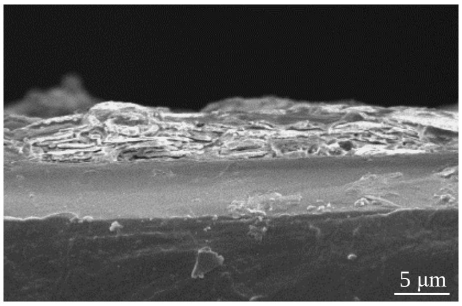


Fig.4 Cross-section morphology of Paste-1 specimen

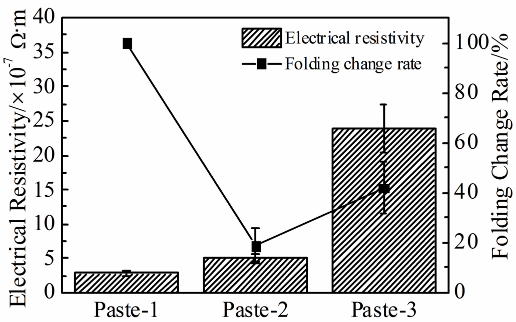


Fig.5 Electrical resistivity and folding change rate of Paste-1, Paste-2, and Paste-3 specimens

specimen is ameliorated. With further decreasing the flake size from 5 μm to 3 μm, the electrical conductivity becomes worse again due to the flake aggregation.

### 2.2 Silver pastes prepared with different Ag flakes

#### 2.2.1 Electrical resistivity

According to the electrical resistivity results, the Paste-1 specimen shows the best electrical conductivity, whereas the Paste-2 specimen shows the best electrical conductivity based on the folding change rate results. Therefore, the Ag flakes of 10 and 5 μm in length are both selected to prepare the mixed silver pastes for the optimized properties of folding change rate and electrical conductivity, and the detailed components of specimens are listed in Table 2.

The electrical resistivity of the mixed silver pastes with Ag flakes of 10 and 5 μm in length are shown in Fig.6. It can be seen that with increasing the content of Ag flakes of 5 μm in length, the electrical resistivity is gradually decreased. The minimum electrical resistivity of about $1.689\times10^{-7}$ Ω·m can be achieved for Paste-5 specimen when the Ag flakes of 5 μm account for 40wt%. Then the electrical resistivity is increased with further increasing the content of the Ag flakes of 5 μm. The surface morphology and flake size distribution of Paste-5 specimen are shown in Fig.7. The surface of Paste-5 specimen is composed of not only the large Ag flakes, but also the small Ag flakes which can fill the gaps between the large Ag flakes. The porosity of Paste-5 specimen is calculated as 31.10%, which is lower than that of Paste-1 (35.73%) and Paste-2 (49.05%) specimens. Therefore, it can be inferred that the addition of small Ag flakes with a specific content into the

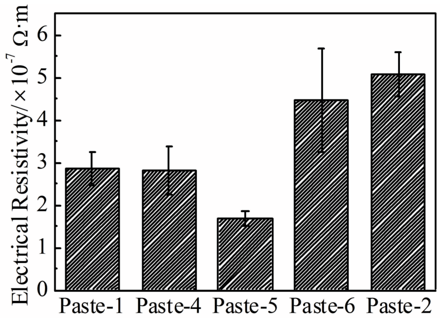


Fig.6 Electrical resistivity of mixed silver pastes with Ag flakes of 10 and 5 μm in length

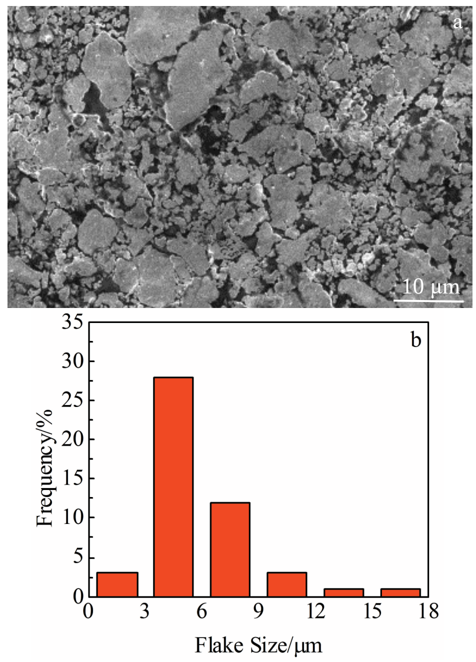


Fig.7 Surface morphology (a) and flake size distribution (b) of Paste-5 specimen

large Ag flakes is beneficial to the improvement in electrical conductivity due to the reduction in porosity of the silver pastes, as shown in Fig.8. The addition of small Ag flakes can build a conductive network through the original unconnected large Ag flakes, thereby decreasing the electrical resistivity of the silver paste composites. The increase in electrical resistivity of Paste-6 specimen is due to the increase of contact resistance caused by the numerous small Ag flakes.

#### 2.2.2 Electrical conductivity after folding

Fig.9 shows the folding change rate of mixed silver pastes, which is regularly decreased with increasing the content of Ag flakes of 5 μm, indicating that the small Ag flakes have a positive effect on the folding change rate.

Fig. 10 shows SEM surface morphologies of the silver pastes after folding. It should be noted that rough cracks of 10 μm in width exist on the surface of Paste-1 specimen after folding, which are mainly caused by the drop of large Ag

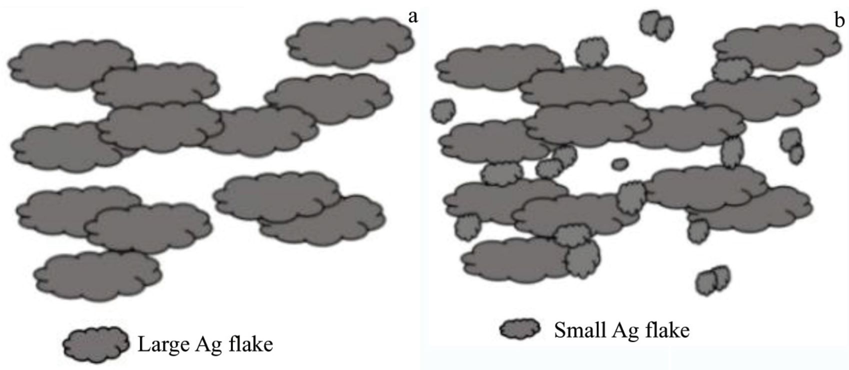


Fig.8 Schematic diagrams of before (a) and after (b) adding small Ag flakes for improvement in electrical conductivity of silver paste

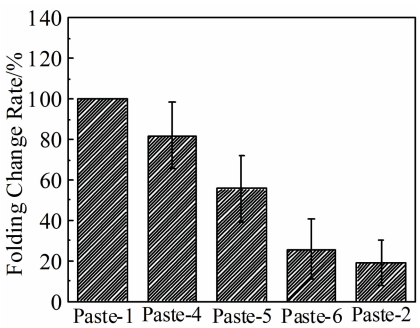


Fig.9 Folding change rate of mixed silver pastes with Ag flakes of 10 and 5 μm in length

flakes. The cracks can also be observed on the surface of Paste-2 and Paste-5 specimens, whereas the cracks of Paste-2 specimen are relatively narrow (width of 2 μm). Thus, the electrical resistivity of Paste-2 specimen has little change after folding. Meanwhile, it can be observed that the cracks on the surface of Paste-5 specimen is filled by some small Ag flakes, as indicated by the arrow in Fig. 10c. The schematic diagram of adding small Ag flakes to improve the electrical conductivity of silver paste after folding is shown in Fig.11. Some small Ag flakes can act as the bridges to connect big flakes, thereby ensuring the effective connection after folding. These results indicate that adding small Ag flakes to the large Ag flakes is a good choice to decrease the folding change rate.

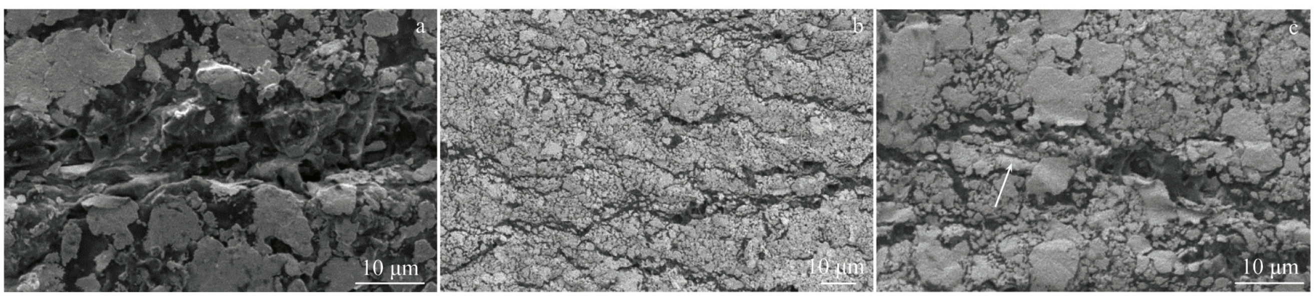


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Fig.10 SEM surface morphologies of different silver pastes after folding: (a) Paste-1, (b) Paste-2, and (c) Paste-5

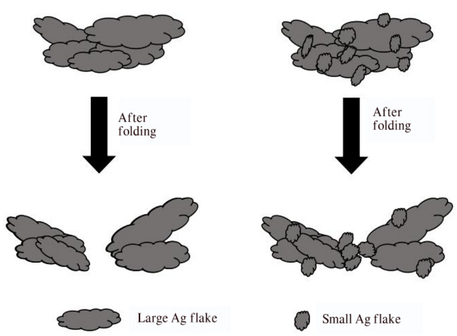


Fig.11 Schematic diagram of adding small Ag flakes for improvement in electrical conductivity of silver paste after folding

## 2.3 Addition of small Ag flakes

The silver pastes with large Ag flakes have good electrical conductivity because of the relatively short conductive path. The silver pastes with small Ag flakes have good electrical conductivity after folding because small Ag flakes can well fill the cracks. The Paste-5 specimen shows the optimal electrical conductivity before and after folding. So the further improvement of reducing Ag flake size of silver pastes was conducted based on Paste-5 specimen, i.e., Paste-7 and Paste-8 specimens were prepared. Fig. 12 shows the morphology of silver paste of 200 nm in size, and the aggregation phenomenon can be observed when the silver paste size is 100~200 nm. Fig. 13 presents the electrical resistivity and folding change rate of Paste-5, Paste-7, and Paste-8 specimens. It is indicated that after adding a certain number of small Ag flakes, the electrical conductivity of silver paste after folding is improved and the low electrical resistivity retains. The electrical resistivity and folding change rate are $2.43\times10^{-7}$

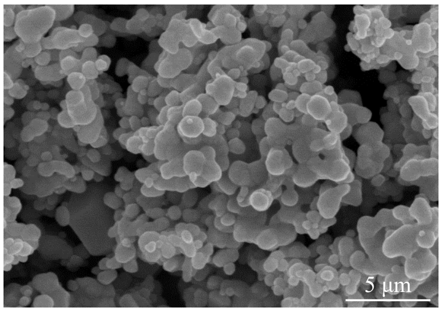


Fig.12 Morphology of silver paste of 200 nm in size

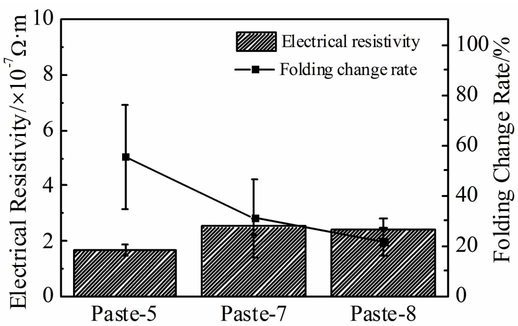


Fig.13 Electrical resistivity and folding change rate of Paste-5, Paste-7, and Paste-8 specimens

Ω·m and 21.8%, respectively, which are better than the results in other researches (the common electrical resistivity is on the order of $10^{-6}$ Ω·m[17]).

## 3 Conclusions

1) The electrical resistivity of silver pastes is decreased with increasing the Ag flake size due to smaller porosity and larger connect area between Ag flakes. The silver pastes prepared by large Ag flakes show bad electrical conductivity after folding because of the formation of rough cracks.

2) The optimal properties of electrical conductivity and folding endurance are achieved for the mixed Ag pastes with 60wt% Ag flakes of 10 μm and 40wt% Ag flakes of 5 μm.

3) The conductive mechanism is that the small Ag flakes can act as the bridge and fill the gaps between the unconnected large Ag flakes after folding, which forms the conductive networks to improve the electrical conductivity and folding endurance.

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# 耐折高导电性银浆的制备

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**摘　要：**研究了银片粒径对折叠前后银浆电导率的影响。采用不同粒径的片状银制备了具有良好导电性能的低温固化耐折导电银浆料，将银浆网印在聚酰亚胺基板上，在140 ℃下烧结形成网印电路。用微欧姆计检测了印刷电路的电阻率，对印刷银电路折叠前后的电阻变化进行了检测，并用扫描电镜对其表面形貌进行了研究，分析了导电机理。结果表明，小片Ag作为未连接薄片之间的桥梁，在折叠后填补了空白，形成导电网络，提高了折叠后的银浆导电性能。

**关键词：**导电银浆；片状银；导电性

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