Hybrid silver pastes with synergistic effect of multi-scale silver fillers and the application in flexible circuits

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Abstract

Silver circuits prepared by new hybrid pastes exhibit high electrical conductivity and mechanical properties, which are ideal for modern flexible electronics. Herein, the hybrid silver pastes composed of different silver nanoparticle content (0, 10, 20, 30 wt%), micron-sized silver flakes and epoxy-based binders were prepared. The corresponding electrical conductivity and bending resistance of the screen-printed silver circuits were studied. The experimental results demonstrated that the synergistic effect of micro-size silver flakes and nanoparticles can greatly improve the electrical conductivity and bending resistance of flexible circuits. Specifically, the silver circuits with 46 wt% micro-size silver flakes and 20 wt% silver nanoparticles incorporation exhibit a lower electrical resistivity of $8.1 \times 10^{-3} \Omega \cdot \text{cm}$. Moreover, 10 wt% silver nanoparticles can be applied to significantly reduce the resistance change of flexible circuit, indicating a superior bending property. Our designed hybrid silver pastes with excellent performance might enable valuable applications in advanced electronic devices.

1. Introduction

Flexible integrated circuits are essential for future wearable electronic devices, strain sensors, flexible displays and antennas, etc. [1–3]. Direct printing conductive materials on flexible substrates by screen printing is efficient, cost-effective and environmental-friendly to fabricate flexible circuits [4–9]. Among conductive materials, conductive composites composed of conductive fillers and organic additives are of vital importance. Silver has been widely used as printing ink due to its superior conductivity, and the typical organic silver compounds or silver nanoparticle pastes have been reported in screen printing silver conductors [10–14]. To form printed silver conductors by discrete metal particles, a 3D continuous conductive percolation network should be established. Sintering silver particles together by high temperature treatment is an effective method to reduce the contact resistance and total resistivity of printed conductive silver paste [15]. However, regarding flexible electronic products, polymer based flexible substrates are usually heat-sensitive. For example, the long-term working temperature of commercial polyimide (PI) film is less than 250 °C, which is far lower than the melting point of silver metal. To overcome this temperature limitation, the development of high-performance low-temperature curable silver pastes have drawn considerable research interests during the past decade, which can be processed at low curing temperature (far below the melting temperature of silver and polymer substrate) to achieve good conductivity and bending property [16, 17].

For preparing low-temperature conductive silver pastes, the metal particles are usually mixed with polymer matrix or adhesive to promote the cohesion and adhesion of the silver film, in an attempt to obtain interconnected silver particles to form a conductive network [18, 19]. The micro-sized silver flakes are usually used as the main conductive filler of commercial low-temperature curing conductive silver pastes. However, its sheet stacking is not adequately tight, which can lead to relatively high contact resistance [20]. The synergistic effect of multi-scale functional fillers in hybrid silver pastes can significantly reduce the contact resistance, thereby increasing the electrical conductivity. For stretchable circuits, it is also critical to achieve adequate high
Table 1. Detailed compositions and designations of the silver pastes.

| Designations       | Micro-sized silver flakes (wt%) | Silver nanoparticles (wt%) | Epoxy (wt%) | KH-560 (wt%) | Organic vehicle (wt%) |
|--------------------|---------------------------------|-----------------------------|-------------|--------------|----------------------|
| 66% Ag flake       | 66                              | 0                           | 5           | 4            | 25                   |
| 56% Ag flake/10% Ag NP | 56                             | 10                          | 5           | 4            | 25                   |
| 46% Ag flake/20% Ag NP | 46                             | 20                          | 5           | 4            | 25                   |
| 36% Ag flake/30% Ag NP | 36                             | 30                          | 5           | 4            | 25                   |
interfacial adhesion to bear large repeated mechanical stress with minimum electrical resistance increase [21, 22]. However, the bending resistance of low temperature hybrid silver pastes used in flexible circuits has been rarely studied in literature.

In this work, we have explored a novel silver paste consisting of micro-sized silver flakes, silver nanoparticles and organic components. The different morphology and particle size of silver powder were adopted to optimize the electrical conductivity of low-temperature curing conductive silver paste. The effects of silver nanoparticles on the volume resistivity and bending resistance of silver paste were also systematically investigated. The synergistic effect of the micro-sized silver flakes and silver nanoparticles can significantly improve the resistance of the silver circuit after series of bending tests, demonstrating its great potential in the application of flexible electronics.

2. Experimental

2.1. Materials
The micro-sized silver flakes (purity ≥99.5%, with lateral size of 5 μm) and silver nanoparticles (purity ≥99.5%, with diameter of 500 nm) were obtained from Chengdu Tianfu Metal Powder, China. Dibasic esters DBE, ethyl cellulose dibutyl phthalate and 3-Glycidoxypropyltrimethoxy silane (KH560) were purchased from Sinopharm Chemical Reagents Co., Ltd. Epoxy resin (bisphenol A, PT-7016) was supplied by Nantong Xingchen Synthetic Material Co., Ltd.

2.2. Silver paste preparation
First, the hybrid silver pastes combining with the micro-sized silver flakes and silver nanoparticles, were added in epoxy and organic vehicle comprising thickening agent (ethyl cellulose) and dispersing agent (dibasic esters DBE). Then, the mixtures were dispersed by high-speed homogenizer at 1000 rpm for 5 min. Afterwards, a 3-roll-mill machine was used to disperse the powder particles homogeneously in the paste. The final low-temperature conductive silver paste was obtained by vacuuming.

The paste is composed of silver components and organic vehicle. Among them, silver particles are distributed in the network structure composed of polymers in organic vehicle to reduce the settlement caused by the agglomeration of metal particles, so that it has high stability. At the same time, the rheological agent in the organic carrier makes the paste have rheological properties. With the acceleration of printing speed, the viscosity of the paste decreases, so that the paste can be smoothly printed to the substrate surface through wire mesh. The detailed compositions and designations of the silver pastes prepared in this study are listed in table 1.

The screen printing method is to use the squeegee to pass the specific paste through the screen mesh, and then use the tension of the screen to separate the screen from the substrate, so as to directly print the required graphics on the substrate, which is simple and fast. The as-prepared silver pastes with wet film thickness of 30 ~ 40 μm was coated on PI substrate through screen printing method using an automatic printing machine (PHP-1212B, Shanghai Hoting Screen printing equipment CO., Ltd.) The screen printer setup parameters (snap off distance 1mm, speed 180 mm s⁻¹), resin squeegee details (size 30 cm × 50 mm × 9 mm, hardness 75, printing angle 45°), and screen details (mesh count 325 mesh, wire diameter 28 μm, mesh thickness 30 μm and screen tension 30 N) are set. The flexible silver circuits of PI substrates coated with silver paste were dried at 100 °C in oven for 15 min, and finally were sintered at 220 °C for 120 min.
2.3. Material characterization

The volume resistivity of the silver circuits was measured using a LCR tester (TH283, Changzhou Tonghui Electronic CO., Ltd). Specifically, the silver wire with a line width of 1 mm and a total length of 100 mm was obtained by screen printing for electrical Test. To obtain the averaged resistance of silver wire, five replicated tests were performed for each sample. The volume resistivity of silver circuit have been calculated using the following equation:

$$\rho_v = R \times h \times 10^{-4}$$

where $\rho_v$ is the volume resistivity ($\Omega \cdot \text{cm}$), $R$ is the resistance ($\Omega$), $h$ is the thickness of silver circuit ($\mu\text{m}$).

To investigate the mechanical flexibility and stability of the printed silver circuits, the silver circuits were bent 10–50 times. In order to carry out the bending experiment, we pasted one end of PI to the surface of copper bar (1mm radius) [23], then curled the PI substrate clockwise, and stayed at the end for 30 s after all crimping. Then it returns to the flat state, and then it is processed in the same way in the counterclockwise direction. Such a group is counted as a cycle. The schematic diagram of the bending experiment is illustrated in figure 1. The change of volume resistivity $\Delta R = R/ R_0$ is used to characterize the bending resistance of silver circuit, where $R$ is the resistance value after multiple bending, and $R_0$ is the original resistance value.

The microstructures of the silver films were examined by a scanning electronic microscope (Quanta 200, FEI, USA). Adhesion tests of silver circuits were measured with reference of GB/T 9286–98. Briefly, the PI substrate covered with silver electrode was cutted by a hundred grid knife to form a grid pattern. Each sample is cut 5 times in the vertical direction, respectively. Secondly, the 3M600 adhesive tape was firmly pasted on the cut silver electrode, and then quickly torn off at the minimum angle. The adhesion grade was obtained by observing the exfoliation of the silver electrode through a magnifying glass.

3. Results and discussion

In this study, the effect of the silver nanoparticles content on the electrical resistivity of hybrid silver pastes has been studied by mixing 0 wt%, 10 wt%, 20 wt% and 30 wt% silver nanoparticles with the same content of micro-size silver flakes in hybrid silver pastes, as shown in figure 2. With increasing the content of silver nanoparticles, the electrical resistivity of the silver pastes decreases in the beginning, and then increases. The resistivity of silver circuit decreases from $8.8 \times 10^{-5} \Omega \cdot \text{cm}$ to $8 \times 10^{-5} \Omega \cdot \text{cm}$ with 20 wt% silver nanoparticle incorporation. However, with the addition of 30 wt% silver nanoparticles, the conductivity of the silver pastes is significantly deteriorated with the electrical resistivity increasing to $9.7 \times 10^{-5} \Omega \cdot \text{cm}$. After adding 40% silver nanoparticles, it was found that the conductivity deteriorated further and the resistance increased to $9.9 \times 10^{-5} \Omega \cdot \text{cm}$.

Figure 3 shows the SEM images of silver pastes surface with different silver nanoparticles content. Figure 3(a) illustrates the surface of silver paste without addition of silver nanoparticles, and it can be seen that the micro-sized silver flakes overlap each other to form an interconnected network, forming paths for electron transport. Figures 3(b)–(d) demonstrate the silver pastes surface obtained by adding 10 wt%, 20 wt% and 30
wt% silver nanoparticles, respectively. The nanoparticles are homogeneously distributed in the entire hybrid silver pastes, both on the surface and interstitial in the micro-size silver flakes. The silver nanoparticles act as a bridge to connect the flakes together, which can greatly improve the quality of the interface, thereby reducing the contact resistance and improving the conductivity of the silver paste. Comparing higher magnification micrographs inset figures 3(c) and (d), it can be observed that the accumulation of excess silver nanoparticles (30 wt%) can result in obvious agglomeration, which is adverse to the connection between silver flakes and leads to the deterioration of conductivity.

To further explain the effect of silver nanoparticles on the electrical resistivity of silver pastes, the cross sections of silver pastes with different amount of nanoparticles incorporation were investigated, as shown in figure 4. The low-density silver paste is stacked by micro-sized silver flakes, with a large number of holes. With the addition of silver nanoparticles, the micropores among silver flakes are filled, and the density of silver pastes has been improved, as illustrated in figures 4(b) and (c). Figure 4(d) displays the SEM image of the silver pastes with 30 wt% silver nanoparticles. The excess of sphere-like nanoparticle accumulation leads to the poor connection between silver flakes, resulting in the destruction of the conductive network. The silver nanoparticles can improve the contact between the silver flakes, therefore the appropriate composition is of vital importance for the conductivity of the silver pastes. Combining the electrical measurement and micromorphology analysis of the silver pastes, it can be concluded that the silver paste with 20 wt% silver nanoparticles addition possess the most superior conductivity.

Apart from directly affecting the conductivity of the printed silver circuit, the content of silver nanoparticles also affects the elasticity of mechanical bending. The bending resistance of printed circuits is critical in flexible electronic products. The silver pastes have been coated onto PI substrate through screen printing method to fabricate silver circuits. The prepared silver circuits were bent 10 to 50 times, respectively, and the electrical resistivity was tested to evaluate the mechanical flexibility and stability of the silver pastes, as provided in figure 5. Figures 5(a)–(c) show the relationship between the electrical resistivity of the silver circuits with different silver nanoparticles content (10 wt%, 20 wt%, 30 wt%) and the number of bending cycles, compared with the circuit without silver nanoparticle addition. It can be seen that the circuit made of silver flakes exhibits the lowest flexibility and the most inferior bending durability, and the electrical resistivity increases rapidly with increasing
Figure 4. SEM image of cross section of hybrid silver pastes with various silver nanoparticles contents (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%.

Figure 5. Variation of electrical resistance of hybrid silver pastes with various silver nanoparticles (Ag NP) contents (a) 10 wt%, (b) 20 wt%, (c) 30 wt% under different bending cycles, (d) The $R/R_0$ values of serial hybrid silver pastes.
bending cycles. This can be due to the mechanical-strain caused silver flake separation with consequent inferior contact between the flakes during the bending process, thus destroying the continuity of the conductive network. It can also be seen that the addition of silver nanoparticles can improve the flexibility and the bending durability, but the excessive content can deteriorate the electrical conductivity. As shown in figure 5(d), the combination of 10 wt% silver nanoparticles and 56 wt% micro-size silver flakes possess the smallest $R/R_0$ value, indicating the superior flexibility and bending durability.
The fatigue behavior of flexible silver circuits depends largely on the microstructure of the silver film. Therefore, we compared the micro morphology of the silver circuits with 0 wt% – 20 wt% silver nanoparticles addition after 50 bending cycles, as shown in figures 6(a)–(d). The green arrow in figure 6 indicates the bending direction of the silver circuits. The silver circuit without silver nanoparticles exhibit obvious microcracks after 50 bending cycles, as marked by the red arrow in figure 6(a). These microcracks are perpendicular to the bending direction and extend to the periphery like an umbrella, which leads to a rapid increase in the electrical resistivity of the silver circuit. In comparison, the hybrid silver pastes compose of micro-sized silver flakes and silver nanoparticles. Because the nanoparticles act as a bridge between silver flakes, the number of contact points between adjacent flakes can be increased, and the integrity of the conductive network after the bending cycle can be consequently improved. Therefore, compared with the circuit fabricated by pure micro-size silver flakes, the hybrid silver circuits exhibit no obvious microcracks, as shown in figures 6(b)–(d). However, when the content reaches more than 20%, on the one hand, the agglomeration of nanoparticles is enhanced, on the other hand, there are fewer residual pores, and the improvement of bending performance of AgNP is not obvious. So, the silver traces with 20% and 30% AgNP having almost same electrical performance during bending test.

Figure 7 illustrates the synergy of multi-scale fillers on the bending characteristics of flexible circuit. The electrical resistance of the printed silver circuits composed of only micro-size silver flakes can increase significantly after multiple bending, which can be attributed to the cracking and separation of the silver flakes during bending process, as shown in figure 7(a). However, as for flexible circuits made of hybrid silver pastes in figure 7(b), the integrated silver nanoparticle can fill in among the silver flakes, which reduces the contact resistance between the fillers, thereby improving the circuit flexibility.

The adhesion strength of hybrid silver pastes has also been examined to evaluate the bonding between the silver pastes and flexible substrate, as listed in table 2. Based on the morphology of the peeling surface, the adhesion strength level can be divided into 0B ~ 5B level, with level 5B indicating no peeling. It can be seen from table 2 that the adhesion grade of all the silver pastes (after 50 bending cycles) in this study can reach 5B level, which means the different ratio of micro-size silver flakes and silver nanoparticles shows no effect on the adhesion of the silver pastes. Figure 8 illustrates the typical surface morphology of hybrid silver pastes on PI substrate before and after grid test. It can observe that no obvious exfoliation of silver layer after series of tests can be obtained.
4. Conclusions

In summary, the effect of silver nanoparticle content on electrical conductivity and bending resistance of low-temperature curing silver pastes was systematically investigated. The nanoparticles can fill the gap between the micro flakes and act as the bridge to enhance the network conductivity. The electrical conductivity of the circuits increases firstly and then decreases with the increasing of silver nanoparticles content. The silver circuits with 20 wt% silver nanoparticles incorporation show the lowest electrical resistivity of $8.1 \times 10^{-3} \Omega \cdot \text{cm}$. In addition, the nanoparticles can also inhibit the microcracks growth of silver circuit after bending cycles. 10 wt% silver nanoparticles can significantly reduce the change of resistance of flexible circuits. Our designed hybrid silver pastes with excellent performance might enable valuable applications in advanced electronic devices.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest/Competing interests

Authors declare no conflict of interest in this research work.

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