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Study on the mechanism of forming silver nanoparticles on micron-scale flake silver powder

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Abstract

Due to the high conductivity and stability of silver, silver ink has been widely used in the field of printed electronics. However, since mechanical strain would cause the contact between key particles to be broken. Recently, higher requirements have been put on the bending resistance of silver paste. In this experiment, by preparing Ag NPs: Ag Flakes composite materials of 20:80 and 30:70 respectively, a new method for preparing stable modified flake silver powder is proposed, and the attachment and growth methods of Ag NPs reduced on micron flake silver powder is discussed. Flake silver powder, dispersant and reducing agent are added to the silver-ammonia complex, and the nano-silver particles are reduced on the flake silver powder by controlling the reaction conditions. When Ag⁺: Ag Flakes in the solution is 30:70, there is a clear interface between the silver particles and the silver flakes, and the size distribution range is between 10 and 100 nm; when Ag⁺: Ag Flakes is 20:80, the distance between the nano-silver particles and the silver plate crystal plane is about 0.222 nm and 0.260 nm, these spacings represent the (1–12) and (004) planes of Ag, respectively. The reduced silver particles grow on the surface of the silver sheet, the size is about 5 ~ 60 nm, and form a sheet-point combination of shaped silver powder, which can be used to make conductive silver paste with cost and performance competitiveness. The reaction can be completed at room temperature (5 ~ 25 °C) and atmospheric pressure (80 ~ 100 kPa), the operation is simple, the reaction time is short, and it has a positive effect on the commercial production of printable highly conductive silver paste.

1. Introduction

With the rapid development of today’s electronic functional devices, electronic products have put forward low-cost, high-performance requirements for the production process, and the preparation of novel printable conductive materials also faces new challenges [1–6]. Among them, the widely used conductive silver paste also puts forward higher requirements for the preparation of new type of silver powder [7–11].

At present, the advantages of micron-level flake silver in its excellent conductive performance and low cost are often used as the main conductive filler in commercial conductive silver paste, which can effectively reduce the amount of contact between the particles in the slurry at low curing temperature, thereby reducing contact resistance [12, 13]. When discrete metallic silver particles form a printable silver conductor, a continuous 3D conductive penetration network must be established. Generally, micron-sized metal particles are mixed with a non-conductive binder or polymer matrix to obtain a printed conductive paste, which promotes the cohesive force of the conductive film and its adhesion to the underlying substrate during the subsequent heating and curing process.

Studies have shown that the addition of highly conductive nanoparticles to micron-particles silver ink can further effectively reduce contact resistance [14–16]. Meng Y et al used nano Ag₂O particles to decorate the silver ink prepared by Ag flake silver, sintered at 150 °C without using organic materials with limited shelf life, and prepared silver ink with high conductivity [17]. Nanoparticles have a relatively high surface energy, the melting point will be significantly reduced under the effect of nano-effects. These effects could further reduce the
sintering temperature of conductive inks to metallize them at low temperatures, and then provide lower resistance between particles [18]. On this basis, if the nano silver is directly modified on the surface of the flake silver powder, Ag NPs can be better connected with the Ag flake during the sintering process of this paste. When the nanoparticles are combined with the silver flakes in the form of metal bonds, the interface energy and defects can be greatly reduced, and the curing conditions of the silver paste can be further reduced.

In recent studies, silver complexes have attracted much attention as a new silver conductive paste prepared from silver precursors [19, 20]. Vaseem M et al developed a silver-ethyamine-ethanolamine-formate-complex based transparent and stable ink, 17 wt% of this ink was printed and sintered on a variety of substrates with uniform surface morphology and excellent adhesion, and its performance remained after five months [6]. Inspired by it, we tried to use the classic Tollens reagent as the silver precursor-silver-ammonia complex, and carefully observed the nanoparticles’ attachment and growth on silver after reduction. The preliminary research has been explored, and in view of the feasibility of this method, we have made some improvements to the experiment [21]. The reaction equation is as follows equations (1)–(3):

\[
2\text{AgNO}_3 + 2\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{AgO} \downarrow + \text{H}_2 + 2\text{NH}_4\text{NO}_3
\] (1)

\[
\text{AgO} + 4\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow 2[\text{Ag(NH}_3)_2]\text{OH}
\] (2)

Then, sodium borohydride was used to reduce Ag⁺ to silver nanoparticles from this complex:

\[
[\text{Ag(NO}_3)_2]\text{OH} + \text{NaBH}_4 \rightarrow 4\text{Ag} \downarrow + \text{NaBH}_2(\text{OH})_2 + 8\text{NH}_3 + 2\text{H}_2\text{O}
\] (3)

2. Experiment

2.1. Materials

Silver nitrate(AgNO₃), ammonia(NH₄·H₂O) were purchased from Sinopharm Group, sodium borohydride(NaBH₄), lauric acid was obtained from Aladdin, silver tablets(FAg-6501) were from Sino-Platinum Metals.

2.2. Preparation of silver flakes/Ag NPs

First, 0.3147 g and 0.472 g of silver nitrate was dissolved in 50 ml of deionized water respectively. Then, 0.8 g and 0.7 g micron grade Ag flakes, 0.75 ml concentrated ammonia water and 0.375 g lauric acid was dispersed in 50 ml deionized water. Next, these two solutions were sonicated for 30 min to make them fully mixed. 1.4 ml of 0.5 mol l⁻¹ NaBH₄ water solution was slowly added dropwise to the micronized Ag-flakes. After the dropwise addition was completed, it was stirred well to obtain a black colloid. Then 20% (V/V) phosphoric acid was added to the silver colloid to adjust the pH to 4 ~ 6. The precipitate was left standing for 10 h, and the precipitate was washed three times and dried at 70 °C to obtain composite materials with m_{Ag NPs}: m_{Ag Flakes} of 20:80 and 30:70, respectively. A comparison was made unmodified silver flakes and Ag NPs synthesized without adding flake Ag.

2.3. Characterization method

Scanning electron microscope(SEM) was used to observe the morphology of silver powder, and the composition of silver powder was obtained by EDS spectroscopy. Transmission electron microscopy(TEM) was used to obtain more magnification morphology information, and the growth direction of Ag NPs crystals on silver sheets was calculated.

3. Results and discussion

A simple method was first used to prepare a low-cost silver-ammonia complex as a precursor, and the chemical reduction method was used to directly synthesize Ag NPs on the surface of Ag flakes. According to figure 1(a), the size of the original flake silver is about 3 μm, and the surface is flat and smooth. After the reduction reaction is completed, it can be observed that many fine particles are evenly dispersed on the surface of the Ag flakes, proving that the nanoparticles have successfully attached to the silver flakes, as shown in figure 1(b). Figure 1(c) shows the Ag NPs synthesized without adding silver flakes. It can be seen that the agglomeration phenomenon, the particle size is generally between 30 ~ 80 nm. Figure 1(d) shows the TEM photo of a single piece of silver after modification of Ag NPs. Gray nano-silver particles can be observed around the black Ag flake.

Figure 2 shows the EDS spectrum of Ag NPs attached and grown on a silver sheet under electron microscope. The Ag element is the highest peak at three points, occupying the absolute main proportion. It proves that this method succeeds in attaching Ag NPs to the flake silver without introducing impurities.
By comparing the two samples of m\textsubscript{Ag NPs} : m\textsubscript{Ag Flakes} at 20:80 and 30:70 as shown in figure 3, it can be seen in figure 3(a) that a large number of Ag NPs are deposited on the silver flakes, and a large number of free nanoparticles are not seen; in figure 3(c), the Ag NPs deposited on the silver flakes were significantly reduced, and a large number of agglomerated free nano silver particles appeared. In terms of size, the sample size in figure 3(b) is about 5 \sim 60 \text{ nm}, while the sample size in figure 3(d) is about 10 \sim 100 \text{ nm}.

It can be seen in table 1 that the specific surface area and pore volume of the sample with 20:80 m\textsubscript{Ag NPs} : m\textsubscript{Ag Flakes} are significantly lower than the original flake silver, while the sample with 30:70 m\textsubscript{Ag NPs} : m\textsubscript{Ag Flakes} is between the former two. This is because when the ratio of m\textsubscript{Ag NPs} : m\textsubscript{Ag Flakes} is 20:80, Ag NPs has no obvious agglomeration, and the specific surface area and pore volume will be significantly reduced. In the sample with m\textsubscript{Ag NPs} : m\textsubscript{Ag Flakes} of 30:70, Ag NPs agglomerates seriously, the specific surface area and pore volume will increase relatively.
Therefore, as the proportion of Ag NPs increases, the deposited nanoparticles decrease and the free and agglomerated particles increase significantly, and the size of the nanoparticles also increases significantly.

Figure 4 shows the experimental process and the simulation effect before precipitation. In the meantime, the generated nano silver particles will be coated by the surfactant lauric acid in the system to prevent the unlimited growth of nano silver particles, thereby forming a stable colloidal system. In the preparation stage, the main forms of lauric acid in the ammonia solution are ammonium laurate ($C_{11}H_{23}COONH_4$) and laurate anion ($C_{11}H_{23}COO^−$), both of which have good solubility in water, and the nano silver colloid formed at this time is quite stable; When the pH of the system is lowered from 4 to 6, the laurate anion becomes lauric acid, and the solubility of lauric acid in water is very small, so the colloidal equilibrium system is broken, and the silver nanoparticles will precipitate together with the lauric acid.

Figure 5 focuses on describing the growth of nanoparticles on flake silver.

Figures 5(a), (b) are TEM with $m_{Ag\,NPs}:m_{Ag\,Flakes}$ of 20:80 and 30:70 respectively. There is no obvious boundary between the nanoparticles and the silver flake matrix in figure 5(a), and the obvious interface can be seen in figure 5(b), marked as Boundary1, 2. It is inferred that the nanoparticles in the two samples have different attachment methods.

Using the HRTEM image provided in figure 5(c), we can gain a deeper understanding of the microstructure and crystallinity of Ag NP in the prepared $m_{Ag\,NPs}:m_{Ag\,Flakes}$ at 20:80. The marked interplanar crystal spacings are about 0.222 nm and 0.260 nm, and these spacings represent the (1−12) and (004) planes of Ag, respectively. The results show that the crystalline Ag NP has been deposited on the Ag flakes by the precipitation method. At the same time, the nano-silver particles and the flake silver powder have the same crystal lattice orientation on both sides of the grain boundary, indicating that there are nano-silver particles grown directly from the flake silver powder.

Nanomaterials have a relatively high surface energy due to their size. At the same time, due to the high diffusion rate of nanomaterials, when two clean interfaces are close together, they will automatically diffuse to

| Table 1. The specific surface and pore volume of the original silver powder and the modified Ag Flakes. |
|-------------------------------------------------|-----------------|-----------------|
| Specifi Surface (m$^2$ g$^{-1}$) | Ag Flakes | $m_{Ag\,NPs}:m_{Ag\,Flakes} = 20:80$ | $m_{Ag\,NPs}:m_{Ag\,Flakes} = 30:70$ |
| Pore Volume (ml g$^{-1}$) | 0.0158 | 0.0062 | 0.0331 |
| 2.0219 | 0.6261 | 1.1752 |

Therefore, as the proportion of Ag NPs increases, the deposited nanoparticles decrease and the free and agglomerated particles increase significantly, and the size of the nanoparticles also increases significantly.

Figure 3. Characterization of Ag NPs attached to the silver sheet: (a), (b) Ag NPs: Ag Flakes is 20:80; (c), (d) Ag NPs: Ag Flakes is 30:70.
form a metal bond [22]. The formation of this kind of silver particles with a narrow size distribution range is divided into two stages: first, the nucleus is formed in the supersaturated solution, and further grows through the diffusion mechanism, and then these primary particles aggregate to form secondary particles. Under alkaline conditions, the primary particles are more likely to aggregate together, resulting in the formation of spherical secondary particles [21].

As shown in figure 5(d), there are two ways to attach Ag NPs to silver flakes: At first, some Ag\(^+\) nucleates on a part of the silver flake surface, and grows and penetrates into the silver flake under the action of diffusion (point 1); while the remaining Ag\(^+\) nucleates uniformly (point 2) and aggregates with the silver particles that nucleate first (point 1). They diffuse into contact with the nucleated silver particles (point 1) on the silver sheet and form aggregates. In the presence of surfactant lauric acid colloid, the degree of aggregation of primary particles is limited, resulting in the size of silver particles being controlled to irregularly shaped nanoscale size (<100 nm). In these composite Ag particles formed by diffusion, a fairly stable metal bond is formed at the interface. This self-directional attachment is the key to nanomaterials [23], which can greatly reduce the interface energy and defects and make this interconnected composite material. And there are only few defects, and the interface resistance between nano-silver and flake silver is small. These conditions are very important for later curing of silver paste into circuits [24].

In addition, during the process of making silver paste and curing, nano-silver particles can form sinter between other silver flakes in contact with it. And the interface resistance is much smaller than the contact resistance of the physical contact between the pieces of silver. Nano silver as a conductive channel between two flake silver powders can improve the conductivity of the printed circuit. The argument in this regard will be reflected in the follow-up research.

4. Conclusion

In summary, a new type of Ag NP-modified sheet silver chemical synthesis method has been developed, and the attachment method of Ag NP on the silver sheet has been discussed, which provides theoretical support for the subsequent preparation of flexible and highly conductive printed bodies. In this method, we use a simple and controllable method to reduce Ag\(^+\) in the silver ammonia complex to nano-scale Ag particles. When \(m_{Ag\,NPs}\cdot m_{Ag\,Flakes}\) is 20:80, the distance between the mark and the crystal plane is about 0.222 nm and 0.260 nm. These spacings represent the (1–12) and (004) planes of Ag respectively; and when \(m_{Ag\,NPs}\cdot m_{Ag\,Flakes}\) is 30:70, due to the increase of Ag\(^+\), the reduced Ag NPs agglomerated seriously. The clean flake silver relies on its high surface
energy to cause the Ag\(^+\) near it to be first reduced. These first reduced Ag NPs act as nucleation points and grow into nanoparticles on the surface of the flake silver powder. In addition, some free Ag\(^+\) in the solution is in contact with the nano silver on the surface of the flake silver powder and forms a metal bond under the action of diffusion. As an excellent surfactant, lauric acid is in a colloidal state in the aqueous solution, which can wrap Ag NPs to prevent its unlimited growth, and strictly control the reduced silver particles to the size requirements of nanomaterials (<100 nm). The interfacial composite silver powder has fewer defects at the interface, which provides excellent innate advantages for the subsequent preparation of silver conductive paste.

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**Figure 5.** Characterization of Ag NPs growth on silver flakes: (a), (b) m\(_{\text{Ag NPs}}\):m\(_{\text{Ag flakes}}\) 20:80, 30:70 TEM; (c), (d) nano-silver particles grown on flake silver-HRTEM.
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