Research Square

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Tuning the Electrical Resistivity of Conductive Silver Paste Prepared by Blending Multi-Morphologies and Micro-Nanometers Silver Powder

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Abstract

As an important interconnection material in electronics, conductive silver paste has attract much research interest in chip packaging and printed circuit board due to its predominant properties like high conductivity and flexible interconnection. In this paper, the silver nanoparticles, the silver sphere particles and flake silver powder are fabricated by various methods. Different proportions of silver powder are selected to prepare micro-silver paste and mn silver paste (fabricated by silver nanoparticles : sphere particles : flake silver powder=1:1:1). Compared to traditional silver paste (containing 80wt% silver), the electrical resistivity of micro-silver paste containing 66.67wt% silver and cured at 200℃ for 45min in air is about (3.31±0.73)×10^{-5}Ω·cm when the ratio of sphere particle to flake silver powder is 1:1, the resistance of silver paste doesn't also increase dramatically after bending ten times. The addition of nano-silver particles can reduce the resistivity in lower temperature curing. The folding endurance of mn silver paste is comparable to that of micro-silver paste with sphere : flake=1:1.

1. Introduction

Recently, with the rapid development of micro-chip packaging and flexible printed circuit board, conditional electronic interconnection materials have been unable to meet the rising requirements in IC package and solar cell. As a key conductive material for the fabrication of electronic components, conductive silver pastes have attracted extensive attention[1]. Silver paste is composed of conductive filler, binder phase, solvent and other auxiliary agents. According to the different binder phase, the silver paste can be divided into polymer type silver conductive paste and sintering type silver conductive paste.[2] The Ag paste has excellent electrical conductivity, good thermal conductivity, high tensile strength (170 MPa) and Young's modulus (74 GPa).[3–6] Due to small size effect and surface effect, low temperature sintering can be achieved by adding Ag nanoparticles(Ag NPs)[7]. In addition, the conductive silver slurry can realize flexible interconnection[8]. Because of the above excellent performance, conductive silver paste is widely used in solar cells, flexible printed circuit boards, radio frequency identification system (RFID), electromagnetic shielding, membrane switches and other devices[9–13].

At present, the bottleneck of Ag paste is how to decrease the resistivity and reduce the cost. The conductive mechanism of metal-filled conductive paste is the result of the percolation theory, tunneling theory and field emission theory[14–16]. The resistance of paste including three parts, that is, where is the intrinsic resistance in the packing, is the contact resistance between particles, and is the tunneling resistance. Point contact is formed between spherical powder fillers, while surface contact and line contact are formed between sheet powder fillers.[17] Adding appropriate spherical silver nanoparticles into the flake silver matrix can maximize the contact area and fill the gap between the conductive phase particles. In this way the number of conductive network is increasing, leading to the rising of electrical conductivity. Liu C[18] synthesized the Ag paste by using 2μm Ag micron-flakes and 20 nm Ag NPs, which has good conductivity of 3.673×10^{-5}Ω·cm. Jung[19] found that the mixed silver paste composed of Ag NPs and micron silver sheets had good adhesion and flexibility, when the content of silver flake is 50%, the performance of silver paste is the best. In addition, the choice of organic carrier also affects the

conductivity of the silver paste. The residues of organic carrier are inevitable in the real sintering process, so the effective resistivity of Ag paste after curing is controlled not only by the resistivity of the silver powder but also by the resistivity of the organic carrier[20]. Therefore, the dielectric constant should be considered when selecting organic solvents. At the same time, the volatilization temperature of organic carrier will affect the removal of organic.

There are two strategies to reduce the cost of conductive silver paste. One is to reduce the filling ratio of silver powder. The high price of silver powder determines the high cost of silver paste.[21] However, reducing the mass percentage of silver powder may result in a decrease in electrical conductivity. Cai-Fu Li[22] prepared silver paste with high conductivity by mixing silver sheets and liquid poly(dimethylsiloxane) (PDMS). The lowest resistivity is about 8.7×10^{-5} Ω·cm when the Ag plate load reaches 91%, but is only 3.7×10^{-4}Ωcm when the Ag plate mass percentage is reduced to 80%. Another way is to use more micron silver sheets in the mixed slurry.[23] In industry, the Ag sheets is generally prepared by ball milling method, which is simple to operate and low cost. The third is to use organic carriers with simple composition and low cost, such as epoxy resin, ethyl cellulose, ethanol, ethylene glycol, polyvinyl alcohol, hexanol and other organic solvents that can be volatilized at low temperature.[24]

In this study, we synthesis the nano-silver particle and flake silver powder in two ways and purchase silver sphere particle (average diameter:1μm). We fabricate micro-silver paste and mn-silver paste containing 66wt% silver by blending multi-morphologies and micro-nanometers silver powder successfully. Rheological properties of silver paste were tested. The effects of curing time and curing temperature on the conductivity, pencil hardness and adhesion of the silver paste were studied. The objective is to establish a correlation between the resistivity and the proportion ratio of multi-morphologic silver powder, we also aim to explore a new way to fabricate high conductivity, low-cost silver paste.

2. Experimental

2.1 Materials

Silver nitrate (AgNO3, Sinopharm Group Chemical Reagent Co. Ltd), 1-Hexanol (C6H14O, Runhui Biotechnology Co. Ltd), Ethylene glycol (EG, Sinopharm Group Chemical Reagent Co. Ltd), Polyethylene glycol (PEG, Tianjin Guangfu Fine Chemical Research Institute), Stearic acid (C18H36O2, Sinopharm Group Chemical Reagent Co. Ltd), Commercial globular silver powder (Changsha Titd mental powder Co. Ltd), Polyvinylpyrrolidone (PVP, K88-96, Aladdin industrial Co., Ltd), The average molecular weight of the PVP polymer used was 1300,000.

The Ag NPs (average diameter:50nm) are prepared by chemical reduction procedure: First, 10g $AgNO_3$ was dissolved in 50ml EG as precursor solution, 150ml EG (reducing agent), 100ml PEG(reducing agent) and 20g PVP(protective agent) were mixed as reduction solution. Then the precursor solution was poured into the reaction solution and stirred at 160℃ for 30min. Finally, the precipitation was centrifuged and

washed several times with ethanol and dried at room temperature. The micro-silver flakes used in this work were fabricated by high energy ball milling.

2.2 Sample preparation

First, 1g PVP was dissolved in 20ml 1-Hexanol as organic solvent. Then, silver powder and organic solvent with a weight ratio of 2:1 were pre-mixed and rolled at least four times. Meanwhile, the four samples were prepared by the same method, marked #1, #2, #3 and #4, respectively. As shown in Table 1. Finally, those silver pastes were screen printed on a 0.075mm thick polyimide (PI) substrate to form a 60mm×0.6mm line, as shown in Fig. 1 and then those patterns were cured in muffle furnace at different temperature and time in air.

Table 1
Various silver pastes proportions

Label	spherical Ag powders	Micro-silver flakes	Nano-silver particle	Organic solvent
#1	1	1		1
#2	2	1		1.5
#3	1	2		1.5
#4	1	1	1	1.5

2.3 Measurements and characterization

The rheological property of silver paste is performed using a rotary rheometer (AR2000EX, USA), equipped with a tablet of 40mm. The specific surface area of silver powder is determined by automatic specific surface analyzer (Monosorb, USA). The morphology of silver powder and microstructure of silver paste after curing were observed with a field-emission scanning electron microscopy (SEM, FEI Quanta FEG 250). X-ray diffraction (XRD) test was performed using fully automatic X-ray diffractometer (D/max 2550 VB). DC low resistance tester was executed to measure resistance of silver paste after curing.

3. Result And Discussion

3.1 Characterization of silver powder

The size and morphology of silver powder used in this work are shown in **Figure.2.** It can be seen that the average particle size of spherical silver powder is 1μm. The morphology of flake silver powder is irregular and the average size is 4μm. The average size of nano-silver powder is 50nm. The specific surface area of three kinds of silver powder is measured, as shown in **Table.1**. It can be seen that the specific surface area of flake silver powder is 1.85m^2/g, 3 times larger than that of spherical silver powder, which is beneficial to improve the electrical conductivity.

In order to identify the crystallinity of silver powder, X-ray diffraction pattern is performed, as shown in Fig. 3. It can be seen that the peak is exactly consistent with the diffraction of silver powder. This indicates that the crystallinity of the centrifuged nano-silver powder is very high with seldom impurities.

3.2 The steady-state rheology property of silver paste

In order to measure the rheology behavior of silver paste, the steady-state rheology test is compared and analyzed, as shown in Figure.4. It is easy to tell that the viscosity of silver paste decrease with increasing shear rate, gradually. The initial viscosity decreases from 153.1Pa·s in #3 sample to 38.14Pa·s in #2 sample, gradually. This is mainly due to the poor fluidity of flake silver powder compared with spherical silver powder. When the silver paste flows, the spherical particles are rolling, the friction is small, its liquidity is good. The friction between the flake particles is large, its liquidity is poor. The more flake silver powder, the worse the liquidity is. Flake silver powder too much or too little can affect the fluidity of paste and the viscosity of silver paste prepared by sphere: flake = 1:1 is moderate.

3.3 Curing morphology

In order to study the cause of resistivity change, the morphologies of silver paste cured at multiple temperatures is observed by scanning electron microscopy, as shown in Figure.5. It can be seen that spherical silver particle is evenly distributed in the pores between flake silver. Sintering neck is generated and porosity is increased with temperature rising, which also explains why the resistivity drops as the temperature rises.

Figure.6 shows that the SEM image of micro-silver paste with spherical : flake = 1:1 cured at different time. It can be seen that the number of sintering neck is gradually increased with the extension of curing time. The porosity of silver paste is first increasing from 16–24% when curing time is from 15min to 60min and then increases no longer, because the organic volatilization in the silver paste can produce a lot of pores, with curing time extends, the organic has evaporated almost when curing time is 60min, the porosity is at its maximum. Porosity of silver paste does not change due to temperature unchanged after 60min.

Figure.7 shows that the SEM image of mn silver paste cured at multiple temperatures. It can be seen that nano-silver particles dispersed well at low temperature (< 150℃) due to low surface activity and ultrasonic vibration. But when the temperature exceeds 150℃, the surface activity of silver nanoparticles increased and they begin to aggregate and grow together.

3.4 Electrical resistivity

Figure.7 shows that electrical resistivity of silver paste after curing under different conditions. Electrical resistivity of micro-silver paste cured at multiple temperatures is shown in Figure.7 (a). Rising the temperature lead to a decrease in the average electrical resistivity and tend to stable gradually. Electrical resistivity of #1 sample is significantly lower than that of other two samples cured at 175℃ and reach $5.61\times10^{-5}\Omega\cdot$cm after curing at 200℃ and then falling slowly. Figure.7 (b) shows that electrical resistivity of micro-silver paste cured at different time. Extending the curing time result in a decrease in the average

electrical resistivity first decline from 15min to 45min, then increase at 60min and descend after 60min again. Figure.7 (c) shows that electrical resistivity of mn silver paste. It can be seen that the addition of nano-silver particle reduced the resistivity of micro-silver paste. The resistivity of mn silver paste cured at 100℃ reached to $3.4\times10^{-4}\Omega\cdot$cm, which is lower than that of micro-silver paste cured at 150℃. However, the resistivity of mn silver paste cured above 150℃ is higher than that of micro-silver paste cured at the same temperature. Figure.7 (d) shows that the resistivity of mn silver paste cured at different time. Extending the curing time is beneficial to the reduction of electrical resistivity.

The present results indicate that the variation of resistivity of micro-silver paste is as follow: as the temperature rises, the sintering neck is generated between particles, gradually. The connection between particles changes from physical contact to chemical contact, as shown in Fig. 5, resistivity of silver paste decreases obviously. The silver paste line first shrink 45min ago, the distance between particles is dominant. The contact area increases, resistivity of silver paste decreases. At the same time, organic volatilization in the silver paste produced more and more pores. Porosity of silver paste reaches the maximum when curing time reaches 60min, the resistivity of silver paste is controlled by porosity and increases slightly. When curing time exceeds 60min, sintering neck is dominant, the increase in the number of sintering neck leads to the decrease in resistivity.

The addition of nano-silver particles reduced the resistivity at low temperature curing, but the effect is not obvious at high temperature. It is mainly because the nanoparticle could disperse well at low temperature due to low surface activity and ultrasonic vibration, while the temperature is above 150℃, the surface activity of silver nanoparticles increased and agglomerated together. The agglomeration of silver nanoparticles results in the decrease of contact area and the increase of resistivity.

3.5 Mechanical properties

3.5.1 Pencil hardness

Pencil hardness of silver paste cured at multiple temperatures is shown in Table 2. Rising the temperature results in an increase in the pencil hardness of the silver paste. This is due to the emergence of sintering neck, which makes the connections between particles tighter. The more number of spherical silver powder, the poor the pencil hardness of silver paste after curing at the same temperature is. Because of the real contact area of spherical silver powder is smaller comparing with flake powder.

Table 2
specific surface area of silver powder

	Spherical silver	Flake silver	Nano-silver
Specific surface area(m^2/g)	0.55	1.85	11.40

Table 3
Pencil hardness of silver paste cured at different temperature

Temperature	150℃	175℃	200℃	225℃	250℃
Sphere : flake = 1:1	B	HB	2H	3H	5H
Sphere : flake = 1:2	B	H	2H	4H	5H
Sphere : flake = 2:1	6B	B	2H	3H	4H

Adhesion level of silver paste cured at different temperature is shown in Table 3. The adhesion level of silver paste after curing decreases with temperature rising. Because as the temperature rising, the amount of organic solvent decreases, the adhesion level falls. The change of adhesion level of different silver paste at the same temperature is consistent with the hardness of pencil.

Table 4
Adhesion level of different silver paste cured at different temperature

Temperature	150℃	175℃	200℃	225℃	250℃
Sphere : flake = 1:1	5B	4B	4B	3B	B
Sphere : flake = 1:2	5B	5B	5B	4B	3B
Sphere : flake = 2:1	5B	4B	3B	B	B

Figure.9 shows that variation of electrical resistance of two kinds of silver paste with folding times. It can be seen that after folding for 10 times, the resistivity of the silver paste with sphere : flake = 1:1 and sphere : flake : nano = 1:1:1 increases sharply until it breaks off, so the folding endurance of two kinds of silver paste is the good.

Conclusion

In summary, micro-silver paste and mn silver paste were prepared by blending multi-morphologies and micro-nanometers silver powder. The effects of silver proportion, curing time and curing temperature on the conductivity, pencil hardness and adhesion of the silver paste were studied. The specific conclusions are as follows:

1. Nano-silver particles are synthesized by one step aqueous-phase reduction reaction. Flake silver powder is fabricated by high energy ball milling. Micro-silver paste and mn silver paste containing 66.67wt% silver are prepared by blending the proportion of these silver powders, which saves cost compared to traditional silver paste with a content of 80wt%.
2. The resistivity of silver paste decreases with the increase of temperature, gradually. The resistivity of micro-silver paste with sphere : flake=1:1 cured at 200℃ for 45min in air is about (3.31±0.73)×10^{-}

^{5}Ω·cm. The resistivity of silver paste first drops before 45min, then slightly increases at 60min, and finally decreases.

3. The addition of nano-silver particles can reduce the resistivity in low temperature. The prepared two kinds of conductive silver paste exhibited low resistivity and excellent durability in terms of folding endurance. The resistance of silver paste with sphere : flake : nano=1:1:1 does not change abruptly after bending ten times.

Declarations

The authors declare that they have no conflicts of interest to this work.

Author contribution

Xiao Liu[#] and Siyuan Wu[#] contributed equally to this manuscript. Baishan Chen performed scanning electron microscopy. Xiao Liu and Siyuan Wu carried out X-Ray Diffraction tests (XRD) and other experiments. Siwei Tang, Wensheng Liu, Yufeng Huang and Yunzhu Ma participated in analyses of results; Siwei Tang, Wensheng Liu and Yunzhu Ma supervised the experiments and discussions, assisted in analyses of results; Xiao Liu, Siyuan Wu and Siwei Tang wrote the paper. All authors reviewed the manuscript, and contributed to the analyses, and writing of the manuscript.

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