Research of microscale silver particle paste on Al₂O₃, pre-dried dielectric layer and pre-fired dielectric layer substrate by a co-firing process

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Abstract

In this paper, the silver paste was prepared by highly dispersed spherical silver powders with an average particle size of 0.85 μm. The silver conductive thick films were printed on Al₂O₃ and dielectric layer by screen-printing, the dielectric layer had been heat-treated differently, one was dried, the other fired. The corresponding sintering behaviors, electrical and mechanical properties of silver films were investigated systematically. Besides, we made a chip resistor to test performance. The results show that the silver conducting film on fired dielectric is compact, uniform and defect-free, the resistivity and adhesion are 2.54 μΩ·cm and 20.3 N mm⁻² respectively. With the increase of sintering times, the conductivity of silver films on the fired dielectric layer increases first and then decreases, while the adhesion increases continuously. We proposed that the diffusion quantity of glasses from the dielectric layer to the surface was the key step in the period of the properties of silver films. The silver film on the fired dielectric layer has better applications in the high current chip resistors.

1. Introduction

The rapidly developing wireless industry requires high-performance materials to build a low loss, high thermally and portability stable integrated packages for active and passive components such as conductors, resistors, capacitors, thermistors, semiconductors, etc [1–3]. The electronic systems have demanded electronic functional components in terms of size, weight, reliability and safety, and the more efficient microelectronic packaging [4]. Low temperature co-fired glass–ceramics technology has been referred to as a key technology for advanced packaging with widely successful applications owing to simply achieving highly reliable and miniature modules [5–8]. However, the mechanical and electrical properties of thick film conducting system may be affected due to the requirement of physical and chemical compatibility between the conductive layer and insulating layer with different material fabricated, especially at high temperature for a long time co-firing processes.

Currently, silver paste is available commercially for co-fired applications because of the lowest electrical resistance and thermodynamically stable [9–12]. However, more scholars pay more attention to dielectric properties of ceramic [13–15], no extensive reports are available on the research of conductive thick film on co-fired modules. It must be noted that the differential shrinkage mismatch and densification rate of the components in the insulating substrate may cause defects of the conductive thick film on the surface, such as warping, fracture, concave or convex. About the electrical properties of LTCC Bangali [16] reported the glass frit percentage used for the formulation of paste was equally responsible for the warping or cambering of co-fired ceramic. Fang Zhang [17] successfully prepared copper pastes for co-firing, their copper powder coated with glass. Therefore, the thermal coefficient of expansion of the co-fired substrate and binder used in paste should be matched [18].

In this study, ceramic will be replaced by glass thick-film with screen-printing. We further analyzed the matching problem between the dielectric layer and the conductive silver layer. The highly dispersed spherical
silver powder with an average particle size of 0.85µm was used to prepare silver paste. The silver conductive thick films were printed on Al₂O₃ and dielectric film by screen-printing. The dielectric layer had been heat-treated differently, one was dried, the other fired. We compared the conductivity and adhesion of silver films on the dielectric layer and Al₂O₃ substance. The microstructure of thick film and silver diffusion range were investigated. The influence of silver film repeated sintering was also discussed. Finally, we made a chip resistor to test performance.

2. Experimental

2.1. Materials
The raw materials used for the synthesis of organic vehicle have been listed as follows, including terpineol (CP, China Pharmaceutical Group Chemical Reagents Co., Ltd), diethylene glycol monobutyl ether acetate (98%, Aladdin), 2,2,4-trimethyl-1,3-pentanediol isobutyrate (99%, Aladdin), ethylcellulose (45–55mPa.s, Aladdin), Triton X-10 (AR, Mclean) and polyamide wax. Figure 1 shows the SEM images of the Ag and glass particles, the Ag powder with an average particle size of 0.85µm, and the morphology of silver particles is spherical. The glass powder is an irregular column with an average particle size of 1.0µm, its transition temperature is 610 °C.

2.2. Paste preparation
The appropriate amounts of terpineol, diethylene glycol monobutyl ether acetate, 2,2,4-trimethyl-1,3-pentanediol isobutyrate, ethylcellulose, Triton X-10, and polyamide wax acetate were well mixed by heating in a water bath with 70 °C to synthesize organic vehicle. The Ag powder, glass frits and organic vehicle were carefully mixed in a mixer so that all the solid materials adequately get wetted and dispersed in the vehicle, the mass ratio of Ag powder, glass frits and the organic vehicle was 80:3:17. Then the paste was ground by three roll milling and this process was repeated until the dispersion under 5um.

The dielectric paste was commercially available from the Selectech Group (Shenzhen, China), the transition temperature of glass (Tg) is 620 °C.

2.3. Sintering and characterization
First, thin dielectric films were deposited on the Al₂O₃ substrate by the screen printing method. Then leveling and drying, get dried dielectric film. Finally, these dried films were sintered by muffle furnace in the air to prepare for the fired dielectric film. The silver paste was printed on Al₂O₃(TA), dried dielectric film(TB) and fired dielectric film(TC) with an area of 2 cm × 2 cm(Electrical resistivity test) and 2 mm × 2 mm(Adhesion measurement), respectively, the whole printing process was shown in figure 2. Silver paste sintering process was the same as that of dielectric paste, a single firing profile was maintained for all the firing steps, which was displayed in figure 3, the screen-printed patterns were allowed to settle for 20 min, then dried at 120 °C in air, the removal of organic binder takes place at 400 °C and the sintering of the film was carried out at 850 °C with dwell of 10 min where frit and metal reactions occurred simultaneously.

The morphology of Ag and glass particles, the surface of the dried dielectric film and sintered dielectric film were observed by SEM. The surface and cross-section morphological characteristics of fired silver films were also observed by SEM equipped with Energy Dispersion Spectrum (EDS, JSM-7600F) accessory. The thermal
characterization of glass frits was carried out with a term analyzer (NETZSCHSTA 409 PC/PG). The electrical resistances of silver films were measured by the 4-point probe method (RTS-8, Guangzhou 4-point tech). The adhesion of silver film was tested using a tensiometer (HF-500, HBO).

3. Results and discussion

3.1. Morphology of the dielectric film after different heat treatment

Figure 4 TB shows the surface SEM image of the dried dielectric film, the organic solvent evaporated completely after drying, leaving only organic thickeners and glass powders, the surface of the dried dielectric film is coarse, poriferous and of lax structure. While the TC is dense without pores, due to organic matter evaporate completely and glass frits would melted and agglomerated after sintering.
3.2. The conductivity of the silver film

Figure 5 shows the electrical resistivity of silver films on TA, TB, and TC. The conductivity of silver films between on TA and TB have a minor difference, the electrical resistivity is 2.87 \( \mu \Omega \cdot \text{cm} \) and 2.90 \( \mu \Omega \cdot \text{cm} \) respectively, and the electrical resistivity of the silver film on TC is the best, just 2.54 \( \mu \Omega \cdot \text{cm} \).

To examine how the dielectric layer influences the contact formation, SEM and EDS were used to analyze the silver distribution of contact interface. The conductivity of silver film mainly depend on the connection of silver powders into a complete conductive circuit to guide the electronic transmission. The main factors affecting the conductivity of silver film are the internal resistance of silver powder, the contact resistance and the tunneling resistance, beside the silver is an excellent conductive material so that the contact resistance of powder and the through resistance are main troubles affecting the conductivity of silver film. It is seen from figure 6 TA(a,b) that uneven and rough surface morphology with a large number of holes was observed on the surface of the silver film on alumina, suggesting great contact resistance would exhibit high resistivity. On the other hand, the surface of the silver film on the dielectric layer appears to be smooth has been displayed in figure 6 TC(a).

Figure 6 TB(a) shows the micro-surface of the silver film appears as obvious bulges, which will lead to a reliability concern involving the circuit breaker between conductors, no found in figure 6 TC(a). For further investigation, the structure of thick films was observed by high-resolution images. The microstructure of silver films on dried/sintered dielectric layer after co-firing at 850 \( ^\circ \text{C} \) was shown in figures 6TB(b) and TC(b), respectively. All surface are dense, the main difference between the two is that TB(b) appears so many filaments on the surface and TC(b) is normal silver film. As a known, the molten glass from silver paste wetted and wrapped silver powder to enhance the mass diffusion at the sintering temperature on the heat resistant substrate [19, 20]. Therefore, it is a common phenomenon that holes happen on silver film due to silver paste sintering performance. We proposed
that the internal stress existing in the dielectric layer sintering process favored the silver electrode became dense. For silver films on TB and TC, we speculated that the filaments were the glass overflowed from the dielectric layer during the sintering process because the sintering reaction of dried dielectric film with powder state was more intense, this point had been proved from the silver film surface of EDS, the silver content of TA, TB, and TC are 75.90 wt%, 68.52 wt%, and 74.65 wt% respectively. Or in other words, the number of glass content of TB becomes more. The problem is that excessive glass diffusion leads to tunneling resistivity was increased to reduce the conductivity of silver film.

3.3. The adhesion of the silver film
Figure 7 presents the adhesion of the silver film joints bonded with the different substrate. It is obvious that the adhesion of the joints prepared silver film on Al₂O₃ is very low, 14.6 N mm⁻². On the other hand, the joints fabricated with the dielectric layer to the co-firing process has much higher adhesion. Moreover, the silver film
on pre-dried dielectric layer joints bonded is the highest adhesion, 29.8 N mm\(^{-2}\). And the adhesion of the silver layer on pre-sintered dielectric layer is also up to 20.3 N mm\(^{-2}\).

The cross-sectional SEM microstructure and EDS of the silver film on TA, TB, and TC were observed in figure 8. Conductive thick films connect with substrate closely, no gap at the junction as shown by circles in figures 8 TA(a), TB(a) and TC(a). The thickness of the silver layer is about 8um. However, we found an interesting question, the EDS testing show that the distribution of silver element in the boundary is different between TA, TB, and TC. On the alumina substrate, silver falls precipitously, it indicated that the boundary between the silver layer and alumina substrate was clear. However, figure 8 TB(b) shows that the content of silver first decrease slowly and then fall quickly from silver layer to Al\(_2\)O\(_3\), suggesting that a litter silver precipitated into dielectric layer while did not diffused to the alumina substrate. The EDS of silver with a continuous downward trend in dielectric layer was displayed in figure 8 TC(b) clearly, because more silver had diffused to the whole dielectric layer, and the diffusion amount of silver powders was more than that of silver film on TB, which may caused package failure of the dielectric layer.

As shown in figures 6 and 8 that the ratio of silver and glass of the silver layer on TA, TB and TC are different. As it is known to all, the adhesion of the silver layer is determined by the bonding ability between glass and substrate \[21\]. During the high-temperature bonding process, the partially melted glass liquid in the dielectric layer is refluxed upward along with the silver powder particles and silver powders deposited by gravity which results in a silver-glass mixing layer, leading to a greatly increased joint strength. For TB, the dried dielectric film has so many pores on the surface that more silver powders were deposited in the medium layer, while the dense pre-fired dielectric film prevent the diffusion of silver powder. Moreover, the molten glass flows more violently on account of sintering with powder state. Therefore, as shown in figure 8, when the co-firing process was used, the TB and TC of joint clearly showed the complex glass silver entangled network structure contacted interface between dense sintered particles and substrate.

### 3.4. Effect of multiple sintering on the properties of silver films on TC

Figure 9 shows the electrical resistivity and adhesion of silver films on TC from sintering once to five times. Clearly, the resistivity of silver films on TC decreases first and then increases with the number of repeated firing, the behavior of the electrical resistivity of silver films on TC decreases to its minimum value of 2.43 m\(\Omega\)·cm after the third sintering, the adhesion of the silver layer on the dielectric layer increases linearly with the sintering times. The adhesion reached 24.9 N mm\(^{-2}\) after the fifth sintering.

Figure 10 presents the SEM micrographs of the sintering surfaces of the Ag grids with different sintering times. The results show that silver film with the number of firing under 3 displays smoother and denser surface morphology. In addition, it can be seen that the size of the silver particles grew up with the sintering times increases, leading to more effective densification and contributing the reduction of contact resistance, so the resistivity of the Ag film reduces to 2.43m\(\Omega\)·cm shown in figure 9. We believed that the molten glass from the dielectric layer can fully wet the silver particles, which could effectively promoted the growth of silver powders. However, it can be clearly seen in figure 11 TC(4,5) that much larger filaments were distributed on the surface, it’s probably because excessive glasses diffused from the dielectric layer. Meanwhile, the appearance of glass filaments on the surface of silver films gradually extended until the blurring grain boundary of silver with more
Figure 8. SEM and EDS images of the cross section of Ag paste printed on Al₂O₃ (TA), pre-dried dielectric layer (TB) and pre-fired dielectric layer (TC).

Figure 9. The electrical resistivity and adhesion of silver films on pre-fired dielectric layer (TC) with repeated sinterings.
sintering, which broke down the electrical conductivity of the conductive thick film. For the adhesion of silver films, in a word, more sintering times, more reverse osmosis glass, will bring stronger shear strength.

4. Preparation and testing of the chip resistance device

The silver film can be used for the preparation of high current chip resistance devices with fault-free and high conductivity, so the silver film on TC was used to make 40 A chip resistor after packaging. The main test project

Figure 10. SEM images of the surface of silver films on pre-fired dielectric layer(TC) with repeated sintering.

Figure 11. Statistics of 20 groups of resistance data figure 12 Relationship between resistance and fusing time.
is as follows: Collect the resistance and distribution standard deviation of chip resistor; test the fusing performance of chip resistors at 3.5 times of rated current (In); test the stability of the device at In for 6 h. The above results are shown in table 1. The rule requirement about fusing time for fused chip resistor is under 5 s; The rule requirement about the stability of the chip resistor is Case Temperature under 95 °C and resistance value variance rate under 1%. The total number of samples in this experiment is 20.

Figure 11 shows 20 sets of resistance data, the range of resistance value distribution from 646 mΩ to 664 mΩ, the average resistance of silver finger on TC is 653.25 mΩ with standard deviation(std) is 4.82. Figure 12 presents the resistance has a linear relation with the fusing time. Clearly, high resistance can gather more heat at the same time and current condition, so shorter fusing time. In addition, it also illustrates that our devices have no defects.

Figure 13 shows the x-ray diagrams of the front side of the device before and after breaking, the narrow part in the middle is the fusing part of the chip resistor, the fusing part will be completely disconnected to form an open circuit for protecting the power devices after passing 3.5 In. Finally, the case temperature of the resistance device was 54 °C and resistance was reduced by 0.59%, which is standard in such experiments.

| Appearance of silver layer | Resistance (mΩ) | Std of resistance | Fusing time (ms) | Stability at In for 6 h |
|----------------------------|-----------------|------------------|-----------------|------------------------|
| TC-Ag                      | 653.25          | 4.82             | 262.5           | Resistance (mΩ) Case Temperature(°C) |
| Bright color, no defect on the surface | 649.38          | 54               |

Figure 12. Relationship between resistance and fusing time.

Figure 13. The X-ray diagrams of the silver film on pre-fired dielectric layer before(A) and after(B) fusing.
5. Conclusion

In summary, the conductivity and adhesion of the silver film on the dielectric layer are better than that of alumina. However, it’s found that the co-firing of silver paste mixed with the dried dielectric layer is easy to make the glass reverse osmosis from the dielectric layer at 850 °C, which is harmful to the conductivity of silver films. The good news is that the pre-sintered dielectric layer can greatly reduce the glass reverse osmosis and enhance the compact degree of the silver layer. The silver paste print on the sintered dielectric layer was successfully used to prepare high current chip resistors.

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