Effects of glass on densification and interfacial bonding of LTCC co-fired Ag electrode

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Abstract. In this paper, the effects of particle size and content of glass additive on the sintering densification, interfacial bonding and electrical properties of silver electrode of LTCC were investigated. The particle size of glass powder would mainly affect the densification rate of electrode film and the uniformity of glass phase distribution. The content of glass played a key role in the density of electrode film, the distribution of glass phase and the interface bonding. When the relative content of glass was low, the glass phase could not wet the silver powder effectively. Thus, the silver film was not dense and the interfacial adhesion was weak. When the relative content was too high, there would be too much glass phase at the surface and interior of the electrode film, which would increase the silver film resistance. By adjusting the particle size and relative content of glass, the co-firing compatibility of LTCC and thick film silver electrode could be better realized. When the content of glass additive was 1.0 wt%, the sintered film illustrated the optimum performance of densified microstructure and low sheet resistance of 1.32 mΩ/sq.

1. Introduction
Recently, with the rapid development of electronic information and intelligent manufacturing industry, the integration, intelligence and reliability of devices have become the critical factors in circuit design and packaging[1, 2]. LTCC (Low temperature co-fired ceramic) technology integrates dielectric materials (capacitors, substrate materials), magnetic dielectric materials (inductors), conductive and resistive materials in the form of laminated co-firing, which can achieve high integration density, multi-function and high reliability packaging[3]. Therefore, LTCC technology has become one of the main means of packaging and integration of passive devices and hybrid circuits[4, 5].

LTCC material is critical for LTCC technology. At present, lead borosilicate glass/Al₂O₃ system of Dupont is commonly used for LTCC substrate material with its easily-controlled sintering process and stable dielectric properties. In order to achieve the high-frequency and high-speed transmission of circuit signals and reduce the energy loss, Ag is often used as the wiring electrode owing to its high conductivity[6]. However, due to the differences between the physical properties of LTCC substrate material and thick film silver conductor, defects such as warping, cracking, porosity and Ag diffusion in the electrode film can be easily occurred during the co-firing process of the two materials[7-10], which affects the reliability of the device. This has become the main obstacle in the application of LTCC technology.

Several attempts have been made to solve these problems in which the main technical approach is to realize the co-firing matching of Ag electrode and LTCC substrate. The co-firing densification of
Ag electrode film has been adjusted by changing the composition of glass phase\cite{11-13}, glass particle size\cite{14}, relative content\cite{15-17}, silver powder morphology and particle size\cite{17, 18}, sintering temperature and process\cite{19-21}. However, research on the effect of Pb-B-Si-O (lead borosilicate) glass particle size and content on film densification, interfacial bonding and microstructure change has not been systematically conducted, and the role of glass phase in the process of film densification and interfacial bonding is still not clear.

In this article, based on the lead borosilicate glass/Al$_2$O$_3$ substrate system, the effect of glass additives on the sintering densification process and interface microstructure of silver electrode film was discussed by changing the particle size and relative content of glass.

2. Experimental procedures

2.1. Preparation of glass additives

The glass additives for co-fired silver paste were prepared by conventional melt-quenching method. The composition of the glass is shown in Table 1. The raw materials were uniformly mixed by ball milling for 4 h, dried, and melted in a high temperature resistance furnace at 1400 °C for 2 h. The high temperature glass melt was quenched quickly into DI water to obtain glass frits. The glass frits, agate balls and ethanol were put into the agate jar at a ratio of 1:3:2, milled at the speed of 1000 rpm. The received suspension was dried in the oven at 90 °C for 8 hours.

| Glass | PbO  | SiO$_2$ | B$_2$O$_3$ | Al$_2$O$_3$ | CaO  | Others |
|-------|------|---------|------------|------------|------|--------|
| G1    | 29.06| 39.12   | 10.04      | 7.97       | 4.38 | 9.43   |

Table 1 Compositions of glass additive (wt%)

In order to obtain a series of glass powders with different particle sizes, glasses were milled at different time durations. The glass powders milled for 2 h, 4 h, 8 h, 16 h and 24 h were named as G1-1, G1-2, G1-3, G1-4, G1-5, respectively. The micro-morphology and particle size distribution of glass powders were characterized by scanning electron microscopy (SEM, JEOL JSM-7900F, Japan) and laser particle size analyzer (OMIEC, LS908A, United Kingdom). The surface area of glass powders were identified by surface area & pore size analyzer (Quantachrome, NOVA 2200e, America). The sintering shrinkage behavior of glass were measured by a dilatometer (Netzsch DIL 402C, Germany). The image of the sintering process were performed by hot-stage microscopy (HSM, Hesse EM301, Germany).

As illustrated in Fig. 1, the particle size of the powder decreases with the extension of ball milling time. However, the morphology of the powder shows irregular shape, and when the particle size is small, some particles were agglomerated in Fig. 1(d) and (e). The median particle size (D$_{50}$) and
distribution of the glass powders obtained with different milling time is shown in Fig. 2. It can be seen that the two particle size distribution peaks of G1-4 and G1-5 are caused by the agglomeration of particles. Besides, it can be seen from Table 2 that the specific surface area increases gradually with the decrease of particle size.

![Fig. 2. The particle size distributions of glass powder](image)

| Glass | G1-1 | G1-2 | G1-3 | G1-4 | G1-5 |
|-------|------|------|------|------|------|
| BET surface area | 2.85 | 5.48 | 7.46 | 8.54 | 10.53 |

### 2.2. Preparation of silver paste

![Fig. 3. The micro-morphology of Ag powder](image)

Table 3 Composition of silver paste (wt%)

| Component | Silver powder | Glass powder | Organic carrier | Modifier |
|-----------|---------------|--------------|----------------|----------|
| Paste     | 85            | 1            | 13.5           | 0.5      |

The conductive silver paste is composed of silver powder as functional phase, glass powder as additives, organic carrier and organic modifier. After being weighed according to the composition shown in Table 3, the raw materials were put into the mixing tank after being preliminary mixed, and the silver paste mixture produced employing the planetary gravity mixer. In order to make the silver powder and glass powder distributed in the organic carrier more uniformly and stably, the silver paste mixture was rolled through a three-roller, and the distance between the rollers was gradually reduced (100-5 μm). The silver conductor paste was obtained to be suitable for screen printing.

The functional silver powder was an analogous spherical powder with a particle size of 0.7-0.9 μm and specific surface area of 0.52 m²/g. And its microstructure being shown in Fig. 3. In the procedure of studying the effects of the content of glass additives, the solid content was maintained at 86 wt% (the total mass fraction of silver powder and glass powder), and the relative content of glass was changed to 0.5 wt%, 1.0 wt%, 2.0 wt% and 4.0 wt%.

### 2.3. Silver thick film electrode preparation and characterization

The silver electrode layer for LTCC was fabricated by thick film printing. First of all, the silver paste
forms a conductive pattern on the surface of the ceramic green tape by screen printing. Then the volatile solvent in the film was removed by drying at 70 °C for 30 min. Secondly, the green tapes were laminated at 70 °C/20 MPa for 5 min and the thickness of the stack was 3-6 layers. The samples in the sintering furnace were heated to 450 °C for 2 h to remove the organic components in the green tape and Ag layer, then raised up to 875 °C and held for 15 min. Then, the co-fired samples were obtained after cooling with the furnace. The sintering densification, microstructures and electrode diffusion were characterized by a field emission gun scanning electron microscopy (SEM) in secondary electron (SE) mode, back scattered electron (BSE) mode and energy dispersive X-ray spectroscopy (EDS). The sheet resistances of the film were measured by digital DC resistance tester (SB2231, China).

3. Results and discussion

3.1. Effects of glass particle size on sintering densification of electrode film

![Graphs showing sintering shrinkage behavior](image)

Fig. 4. Sintering shrinkage behavior of glass powders with different particle sizes (a) sintering shrinkage curve and (b) sintering shrinkage rate curve

| Glass | G1-1      | G1-2      | G1-3      | G1-4      | G1-5      |
|-------|-----------|-----------|-----------|-----------|-----------|
| $T_s$ | 583.3°C   | 579.9°C   | 572.0°C   | 569.7°C   | 563.4°C   |
| $T_{max}$ | 614.5°C | 609.2°C   | 604.5°C   | 598.9°C   | 594.3°C   |

Fig. 4 shows the variation of sintering shrinkage and shrinkage rate with temperature of different glass powders. The characteristic temperatures are described in Table 4, in which $T_s$ is the glass softening point and $T_{max}$ is the peak temperature of the maximum sintering shrinkage rate. With the decrease of the particle size, the initial shrinkage temperature of the glass decreases, the temperature of $T_s$ and $T_{max}$ are decreased, and the sintering shrinkage increases rapidly after being softened. The smaller particle size means larger specific surface area and higher surface energy, which provides a greater driving force during the sintering process.

The sintering of the silver film is a solid-state sintering process, but the glass additive can introduce the liquid phase sintering. Therefore, glass phase as the sintering additive will significantly affect the sintering densification process. As shown in Fig. 5, with the decrease of the glass particle size, the surface structure of the silver films changes from rough and non-uniform distribution to flat and densified structure, and then convert to the surface with porous morphology. The main reason is that the particle size of the glass powder is large ($D_{50} > 2.84 \mu m$) and the glass melts and flows at a high temperature during the sintering process. Glass phases can not effectively wet the silver powder and enter the gap between the silver powders, thereby the accumulation of more glass phase on the surface of the film. As the particle size decreases, the melting flow temperature of the glass decreases, the glass phase flowed better to enter the gap of the silver powders, which can be uniformly dispersed at the interface of Ag/LTCC to form an effective interface bonding promote the densification of the film.
However, the present study found that the surface pores increased obviously when the particle size was smaller ($D_{50} < 1.79 \mu m$).

In order to observe the change of the surface microstructure of the sintered film more clearly, the secondary electron imaging with high morphology contrast was used. The glass additive with large particle size of $D_{50} > 2.84 \mu m$ will cause the segregation of glass phase and concave and convex structures on the surface, and the latter is due to the variation of sintering shrinkage at different position. Conversely, for the glass additive with small particle size of $D_{50} < 1.79 \mu m$, the glass phase flows more easily into the gap and promotes the rapid densification process of the silver powder. which is earlier than the sintering densification of the ceramic green tapes, and the gas barrier layer is formed after the densification of the silver layer. As a result, there is no quasi-continuous pore channel to release the gas produced from the sintering densification of ceramic green tapes. When the gas accumulated, a "gas pin" is formed under pressure to break through the molten glass layer, so the needle hole is formed on the surface of the silver film. The glass particle size is smaller, and the sintering densification of the silver layer is earlier than LTCC green tapes, leading to the more obvious "gas pin" phenomenon and the formation of porous structure at the later stage of sintering.

![Fig. 5. BSE-SEM and SE-SEM images of the films with different size glasses (a, f) G1-1, (b, g) G1-2, (c, h) G1-3, (d, i) G1-4 and (e, j) G1-5](image)

![Fig. 6. BSE-SEM cross-sectional micrographs of sintered films (a) G1-1, (b) G1-2, (c) G1-3, (d) G1-4 and (e) G1-5](image)

Detailed information of the cross-sectional microstructure of silver thick film is shown in Fig. 6. The bright white region is corresponding to the silver layer, the bottom is the co-fired ceramic layer, the gray region in the silver layer is the glass phase, and the dark black region is the hole. Consistent with the above conclusions, the glass powders with large particle size ($D_{50} > 2.84 \mu m$) have poor fluidity, resulting in the agglomeration and uneven distribution of glass phase in the film. With the
decrease of glass particle size, the residual glass phase decreases obviously and distributes uniformly. In addition, more glass melt will flow along the pores between silver particles to the interface between silver and LTCC substrate materials under gravity. But if the particle size of the powder is too small ($D_{50} < 1.79 \, \mu m$), the film could be densified rapidly and the gas formed by the sintering densification of the ceramic green tape is difficult to discharge, which will form "gas pin" and punctured pores in the interface with the gas pressure increasing.

In summary, the change of the particle size of the glass powder will affect the uniformity of the distribution of the glass phase in the interior and surface of the film. This will also change the densification state of the film. It would affect the interface bonding between the film and the substrate material inevitably. When the particle size of glass powder is too large ($D_{50} > 2.84 \, \mu m$), the distribution of glass phase is uneven and it will be easy to form glass phase aggregation. The surface appears concave and convex structure, and the roughness is increased. When the particle size of the powder is too small ($D_{50} < 1.79 \, \mu m$), the softening point is reduced and make it easy to fill the silver powder gap, which promotes the rapid densification of the film and closes the pore channel in the silver powder. The gas produced by the densification of the ceramic green tape will lead to punctured pores, which affects the interface bonding and electrical properties of the film. Only by adding appropriate particle size of glass powder ($1.79 \, \mu m < D_{50} < 2.84 \, \mu m$), the electrode film with uniform density and good interface bonding can be obtained.

3.2. Effects of content of glass on sintering densification and interfacial bonding of electrode film

![Fig. 7. Variation of relative projected area and average contact angle of G1 glass on Al$_2$O$_3$ substrate](image)

Fig. 7. Variation of relative projected area and average contact angle of G1 glass on Al$_2$O$_3$ substrate

G1 glass powder with a particle size of $D_{50} = 2.48 \, \mu m$ was selected as an additive to investigate the effect of relative content of glass additive on the Ag electrode film. Fig. 7 presents the sintering shrinkage process of G1 glass. The relative area of G1 glass decreases with the shrinkage process, and the average contact angle between G1 glass and Al$_2$O$_3$ substrate increases at first and then decreases rapidly. As shown in Fig. 8, the hot-stage microscopy (HSM) images at different characteristic temperatures reflects this change more clearly. When $T < T_{DT}$ (deformation temperature), G1 glass can still maintain the cube shape. As the temperature rises to $T_{ST}$ (sphere temperature), owing to the surface tension and gravity, the glass shape changes to sphere and the contact angle increases. As the temperature continues to increase to $T = T_{HT}$ (hemisphere temperature), G1 glass begins to wet with the substrate. Finally, the temperature reaches $T_{FT}$ (flowing temperature), G1 glass spreads on the surface of the Al$_2$O$_3$ substrate, and the average contact angle decreases to 48.5°. Owing to the good wetting
properties of G1 glass and Al₂O₃ ceramics, it is very easy to form a good wetting combination when the glass phase flows to the interface of Ag/ceramic substrate.

Fig. 9. BSE-SEM surface micrographs (illustration for SE-SEM images) of sintered films (a) 0.5 wt%, (b) 1.0 wt%, (c) 2.0 wt% and (d) 4.0 wt%

Fig. 9 shows the surface microstructure of silver electrode film with different content of glass additives. When the content of glass is low (0.5 wt%), there are many pores on the surface of the film, which is attributed to that the glass additives is too small to wet the silver powder effectively after liquefaction, and the produced capillarity is not enough to drive the film to achieve complete densification. With the increase of the content of glass, the effects of liquid phase sintering is enhanced, the particles are closely arranged, and the pores are reduced. However, when the relative content is more than 2.0 wt%, though the film has a high densification degree, the glass phase appears surplus and accumulates on the surface of the film, which would increases the resistance of the silver electrode. The main reason is that when the temperature rises to the sintering temperature of the green tape, the densification and volume contraction of the ceramic layer produces compressive stress and discharges gas at the same time. Under the double effect, the amount of migration of the low viscosity glass melt with good fluidity to the surface of the film is increased, resulting in the accumulation of glass phase.

Fig. 10. BSE-SEM surface micrograph and EDS images of film adding 4.0 wt% G1-glass (a) BSE micrograph, (b) Ag element, (c) Pb element, (d) Si element, (e) B element, (f) Al element, (g) Ca element and (h) O element

The BSE-SEM and EDS images of silver electrode film with 4.0 wt% G1-glass are illustrated in Fig. 10. The BSE-SEM images of film presents bright and dark phases distinctly. The EDS images show that the brighter region is silver grain, and the darker region is mainly the aggregation of glass-
forming phases such as PbO, SiO₂ and Al₂O₃. The uneven distribution of glass phase will hinder the contact between silver grains and damage the conductive structure to a certain extent.

![Fig. 11. SE/BSE-SEM surface micrographs adding 4.0 wt% G1-glass (a, b) film surface and (c, d) film surface after HF etching](image)

![Fig. 12. BSE-SEM cross-sectional micrographs of sintered films (a) 0.5 wt%, (b) 1.0 wt%, (c) 2.0 wt% and (d) 4.0 wt%](image)

Fig. 11 shows the surface micrographs of silver electrode film before and after HF etching. In order to clarify the distribution of the glass phase on the surface, the glass phase on the surface of the electrode film was etched by 5.0 wt% HF solution. The glass phase is mainly attached to the surface of silver grains. Therefore, if the glass phase is abundant, it will mainly accumulate on the silver conductor surface, which will greatly affect the chemical plating and bonding properties in the next conductor process.

It can be seen from Fig. 12 that with the increase of relative content of glass, the tiny pores in the film gradually disappear, and the densification degree of the sintered film increases significantly. However, when too much glass is added (> 2.0 wt%), more residual glass phase will appear. The silver layer containing glass melt cause the silver powder to rearrange and form a densified structure. When the glass content is high, more glass melt is produced, and the densification rate of is fast. In the later stage of sintering, the silver particles densify and sink, part of the glass melt migrate to the surface of the film, and the others can not migrate to the interface area in time and remain in the Ag electrode film.
3.3. Effects of content of glass on electrode diffusion

Fig. 13 presents the elements distribution in the cross section of silver electrode prepared with different relative contents of glass additives. It can be seen that the Ag element in the thick film electrode does not diffuse to the substrate, which shows a good co-firing compatibility.

3.4. Electrical properties

As shown in Fig. 14, with the decrease of glass particle size, the sheet resistance of the film decreases at first and then increases. When the content of glass in the silver paste increases, the sheet resistance of the electrode film decreases and then increases rapidly. To obtain a silver electrode film with dense and excellent electrical properties, the relative content of glass additives should be controlled between 0.5 wt% and 2.0 wt%.

4. Conclusions

In this work, we found that the glass particle size of glass additives would mainly affect the uniformity of glass phase dispersion in the interior and surface of the thick film. When the glass particle size is large, the glass phase distribution is uneven, which is easy to produce glass phase aggregation. And too small particle size of glass would cause the rapid densification of the film and block the pore channels in the silver powder, so the surface is suffers from porous defects. Different content of glass
in the silver paste will determine the densification of the electrode film, the distribution of the glass phase and the interface bonding. The glass with low content could not wet the silver powder effectively, which is not enough to drive the silver powder to form a dense structure. The glass content is too high, too much residual glass phase in the internal and surface of the conductor film, resulting in the deterioration of electrical properties. When the glass particle size is in the range of 1.79 μm ~ 2.84 μm, and the relative content is between 0.5 wt% and 2.0 wt%, a dense and uniform silver electrode film with excellent performance and high reliability can be obtained.

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References
[1] H. Zhu, H. Gu, Y. Dong, W. Bian, Q. Zhang, Performance of borosilicate glass/Ba₃(VO₄)₂ ceramic composites and chemical stability with Ag electrodes, Journal of the European Ceramic Society 40(10) (2020) 3600-3607.
[2] F. Wang, W. Zhang, X. Chen, H. Mao, Z. Liu, S. Bai, Low temperature sintering and characterization of La₂O₃-B₂O₃-CaO glass-ceramic/LaBO₃ composites for LTCC application, Journal of the European Ceramic Society 40(6) (2020) 2382-2389.
[3] L.E. Khoong, Y.M. Tan, Y.C. Lam, Overview on fabrication of three-dimensional structures in multi-layer ceramic substrate, Journal of the European Ceramic Society 30(10) (2010) 1973-1987.
[4] D.K. Kharbanda, P.K. Khanna, Design and development of LTCC based package for 3-axis packaging of MEMS sensors, IEEE, 2017.
[5] M. Ihle, S. Ziesche, C. Zech, B. Baumann, Compact LTCC Packaging and Printing Technologies for Sub–THz Modules, 2018 7th Electronic System-Integration Technology Conference (ESTC), 2018, pp. 1-4.
[6] S.B. Rane, T. Seth, G.J. Phatak, D.P. Amalnerkar, B.K. Das, Influence of surfactants treatment on silver powder and its thick films, Materials Letters 57(20) (2003) 3096-3100.
[7] J.-H. Jean, C.-R. Chang, Cofiring Kinetics and Mechanisms of an Ag-Metalized Ceramic-Filled Glass Electronic Package, Journal of the American Ceramic Society 80(12) (2005) 3084-3092.
[8] M. Gruber, I. Kraleva, P. Supancic, R. Danzer, R. Bermejo, A novel approach to assess the mechanical reliability of thin, ceramic-based multilayer architectures, Journal of the European Ceramic Society 40(14) (2020) 4727-4736.
[9] C.-S. Hsi, Y.-R. Chen, H.-I. Hsiang, Diffusivity of silver ions in the low temperature co-fired ceramic (LTCC) substrates, Journal of Materials Science 46(13) (2011) 4695-4700.
[10] M.S. Ma, Z.F. Liu, F.Q. Zhang, F. Liu, Y.X. Li, Suppression of Silver Diffusion in Borosilicate Glass-Based Low-Temperature Cofired Ceramics by Copper Oxide Addition, Journal of the American Ceramic Society 99(7) (2016) 2402-2407.
[11] Q. Sun, Y. Qi, M.Y. Li, H.B. Xu, Y.F. Li, Synthesis of PVZ glass and its improvement on mechanical and electrical properties of low temperature sintered silver paste, Journal of Materials Science-Materials in Electronics 31(10) (2020) 8086-8098.
[12] S.P. Wu, Q.Y. Zhao, L.Q. Zheng, X.H. Ding, Behaviors of ZnO-doped silver thick film and silver grain growth mechanism, Solid State Sciences 13(3) (2011) 548-552.
[13] J. Qin, W.J. Zhang, S.X. Bai, Z.F. Liu, Effect of Pb-Te-O glasses on Ag thick-film contact in crystalline silicon solar cells, Solar Energy Materials and Solar Cells 144 (2016) 256-263.
[14] J.H. Kim, H.Y. Koo, Y.N. Ko, Y.C. Kang, Characteristics of Bi-based glass frit having similar mean size and morphology to those of silver powders at high firing temperatures, Journal of Alloys and Compounds 497(1) (2010) 259-266.
[15] J. Bangali, S. Rane, G. Phatak, S. Gangal, Silver thick film pastes for low temperature co-fired
ceramics: impact of glass frit variation, Soldering & Surface Mount Technology 20(3) (2008) 41-46.

[16] S.A. Ketkar, G.G. Umarji, G.J. Phatak, T. Seth, U.P. Mulik, D.P. Amalnerkar, Glass frit content - Property co-relation in thick films of photoimageable silver conductor paste, Materials Science and Engineering B-Solid State Materials for Advanced Technology 132(1-2) (2006) 197-203.

[17] S.S. Yao, J.J. Xing, J.F. Zhang, S.H. Xiong, Y.X. Yang, X. Yuan, H.B. Li, H. Tong, Microscopic investigation on sintering mechanism of electronic silver paste and its effect on electrical conductivity of sintered electrodes, Journal of Materials Science-Materials in Electronics 29(21) (2018) 18540-18546.

[18] A. Okada, T. Ogihara, The Effect of Particle Size on Sintering of Conductive Silver Paste in Electrode for LTCC, Transactions of the Materials Research Society of Japan 34(1) (2009) 121-124.

[19] Y.-C. Lin, J.-H. Jean, Constrained Sintering of Silver Circuit Paste, Journal of the American Ceramic Society 87(2) (2004) 187-191.

[20] A. Pietrikova, T. Girasek, J. Durišin, K. Saksl, Pressureless Silver Sintering in Power Application, 2018 International Conference on Diagnostics in Electrical Engineering (Diagnostika), 2018, pp. 1-4.

[21] S. Qi, R. Zuo, Z. Ma, Densification kinetics and anisotropic microstructure evolution in LTCC films constrained by rigid substrate, Ceramics International 42(2, Part B) (2016) 3388-3396.