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Sintering behavior of silver conductive thick film with frit in information display

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Abstract A silver conductive thick film with a frit was examined for its potential applications in the plasma display panel industry. A low melting glass frit (firing temperature, less than 600 °C) was used in the conductive thick film for this work. The thermal behavior of the silver, frit and mixing powder was studied using hot stage microscopy. During the sintering of the silver conductive thick film with the frit, the frit melted, which was followed by accelerated densification. However, the increase in spreading rate with frit affected the microstructure, which has 1.9% porosity and the geometry of the silver conductive thick film. These results suggest that the content of the frit, firing temperature and the thermal properties of the frit in the silver conductive thick film influence the level of shrinkage, conductivity, and shape of the thick film.

Keywords Silver powder · Shrinkage · Thick film · Bulk resistivity · Frit

1 Introduction

Various electrode materials have been developed for many applications in the electronic industry [1–3]. Recently, silver has been used as the main conductive component in a conductive thick film material due to its extremely low resistivity and the lowest cost among the noble metals [4, 5]. However, the silver conductive thick film has been mainly studied in silver with the sintering behaviors being examined at around 850 °C [1–5]. Many methods have been developed to prepare silver powder, including the chemical reduction of silver ions in an aqueous solution with or without stabilizing agents [4, 5]. A paste made from a silver conductive thick film contains silver powder, frit and vehicle. The silver powders provide the conducting phase. The frits (oxide glasses) promote the sintering of the silver powders during firing and enable the binding of the metal film to the substrate. The organic phases disperse the metal powder and binder components to impart the desired rheological properties to the paste [5]. The technology for realizing conductive thick films is of considerable importance in the manufacture of various electronic devices, such as hybrid integrated circuits, multilayer ceramic capacitors and displays [1–9].

In the PDP (plasma display panel) industry, silver conductive thick films are used in bus and address electrodes. The electrode in a PDP is formed using a photolithographic method with firing at 550 or 580 °C due to the strain temperature of the substrate [10–12]. The paste for a silver thick film for PDP has been examined using a silver powder and vehicle for photolithographic methods [10]. However, there have been few studies on silver conductive thick film containing the frit at low temperatures (<600 °C). The frit improves the sintering of the silver conductive thick film but affects the film through the stress caused by rapid densification [13].

The aim of this study was to obtain the primary results for a silver conductive thick film of PDP and to understand the sintering behavior of a silver conductive thick film containing a frit. The Bi_2O_3–B_2O_3–ZnO glass system is mainly used as glass frit in a silver conductive thick film on account of its low viscosity at firing temperature (580 °C).

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2 Experimental procedure

The raw materials for the glass frit were Bi_2O_3, H_3BO_3, SiO_2, $BaCO_3$, Al_2O_3 and ZnO, which have high purity (Aldrich, USA). The batch ($37Bi_2O_3$–$19B_2O_3$–40ZnO–4(SiO_2–Al_2O_3–BaO) in mol%) was melted in an alumina crucible at 1200 °C for 30 min. The glass melt was poured quickly and quenched on a metal roller and pulverized in a planetary mill for 24 h. For the preparation of bulk specimens, the melted glass from a furnace was poured into a graphite mould and heated to 10 °C above the glass transition temperature. The mould was then moved back into the furnace to anneal the glass for 1 h, and furnace cooled.

Spherical silver (Y60613C, Daejoo Co., Korea) powder was used in these experiments. Table 1 shows the silver powder basic properties and frit. The (x) glass powder and ($1-x$) Ag powder (x=0.1 and 0.2 wt.%) were mixed using a ball mill for 24 h and then dried. The mixture powder and Ag powder were combined with the vehicle for the paste using a three-rolls mill for 1 h and then coated on an alumina substrate with a die coater. The thick film was dried in an IR oven for 30 min and sintered at 580 °C for 30 min.

The glass transition temperature (T_g), the dilatometric softening point (T_d) and the shrinkage of the frit were determined using a dilatometer (L75HS, Linseis, Selb, Germany). The coefficient of thermal expansion (CTE) of the glass was examined at temperatures ranging from 30 to 250 °C by the dilatometer. The particle size of the frit was determined using a particle size analyzer (PSA, Mastersizer 2000, Malvern, UK). The microstructure of the samples was examined using scanning electron microscopy (SEM, HITACHI, Tokyo, Japan). The level of pellet (3 mm in diameter and 3 mm in height) shrinkage was measured using hot stage microscopy (Okdu Co., Seoul, Korea). The bulk resistivity of the thick silver film was examined using a Hall-effect measurement system (EGK, Korea).

3 Results and discussion

The glass composition of this experiment was determined in a previous study [14]. The glass-forming region of the

Table 1 Distribution of the particle size, specific surface area and density of the silver and frit.

Properties		Silver	Frit
Distribution of particle size (μm)	D_{10}	0.6	0.14
	D_{50}	1.6	0.18
	D_{90}	2.6	0.23
	Mean	1.8	0.19
Specific surface area (m^2/g)		0.78	13.9
Density (g/cm^3)		5.1	7.1

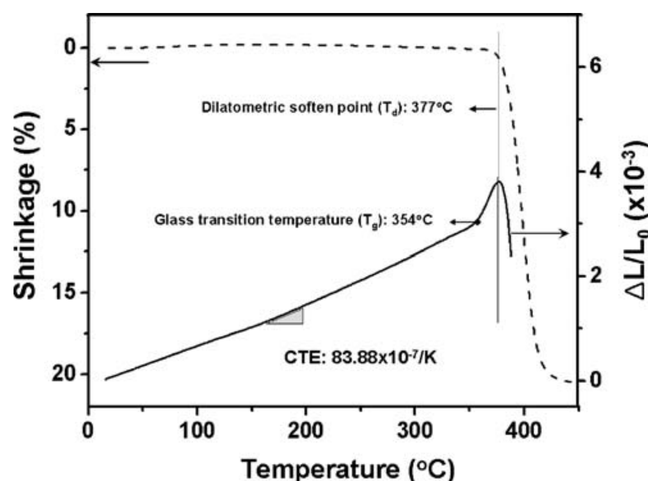

Fig. 1 Shrinkage of the frit and liner expansion of the bulk glass with increasing temperature (heating rate: 10 °C/min)

Bi_2O_3–B_2O_3–ZnO ternary system is dependent on the B_2O_3 concentration in the range of 20–80 mol%. The ternary system forms glasses in the wide range of the B_2O_3 contents, playing a role as a glass former. The phase diagram shows that the liquidus temperature is <700 °C in the Bi_2O_3–B_2O_3–ZnO ternary system and there is a eutectic point [14]. This suggests that the Bi_2O_3–B_2O_3–ZnO ternary system can easily form glasses near the eutectic point. The experimental glass composition had a low melting point that was near the eutectic point, thereby causing the frit to be wetted at a low firing temperature (<580 °C).

The glass transition temperature (T_g) of the experimental glass was found to be 354 °C, and the dilatometic softening point (T_d) and the starting point of shrinkage occurred at 377 °C in Fig. 1. After shrinkage had started, the level of frit shrinkage increased dynamically up to 423 °C and leveled off thereafter. In view of the glass properties, such as T_g and T_d, the glass composition is suitable for enhancing the sinterability of the composites (Ag and frit). Considering that the linear shrinkage of the glass powder well packed is 13–15% [15], the 7% shrinkage shown in Fig. 1 is related to the dimension of the initial green body. Furthermore, the coefficient of thermal expansion (CTE) of the glass was approximately 83×10^{-7}/K, which is similar to the CTE of the glass substrate (85×10^{-7}/K), which in PDP [12].

Based on Fig. 2(a), the silver conductive thick film appears to be getting the densification with grain growth at 580 °C. Therefore, the microstructure of the pure silver conductive thick film suggests the final stage of sintering after firing at 580 °C [16]. Spherical type pores were found in the microstructure between the grain boundaries [Fig. 2(b)], and the porosity of the pure silver conductive thick film was 12.6%. As shown in Fig. 2(b), the grain size increased five times that of the silver powder (d_{50}=1.6 μm). The silver powder appears to be sintered by grain boundary

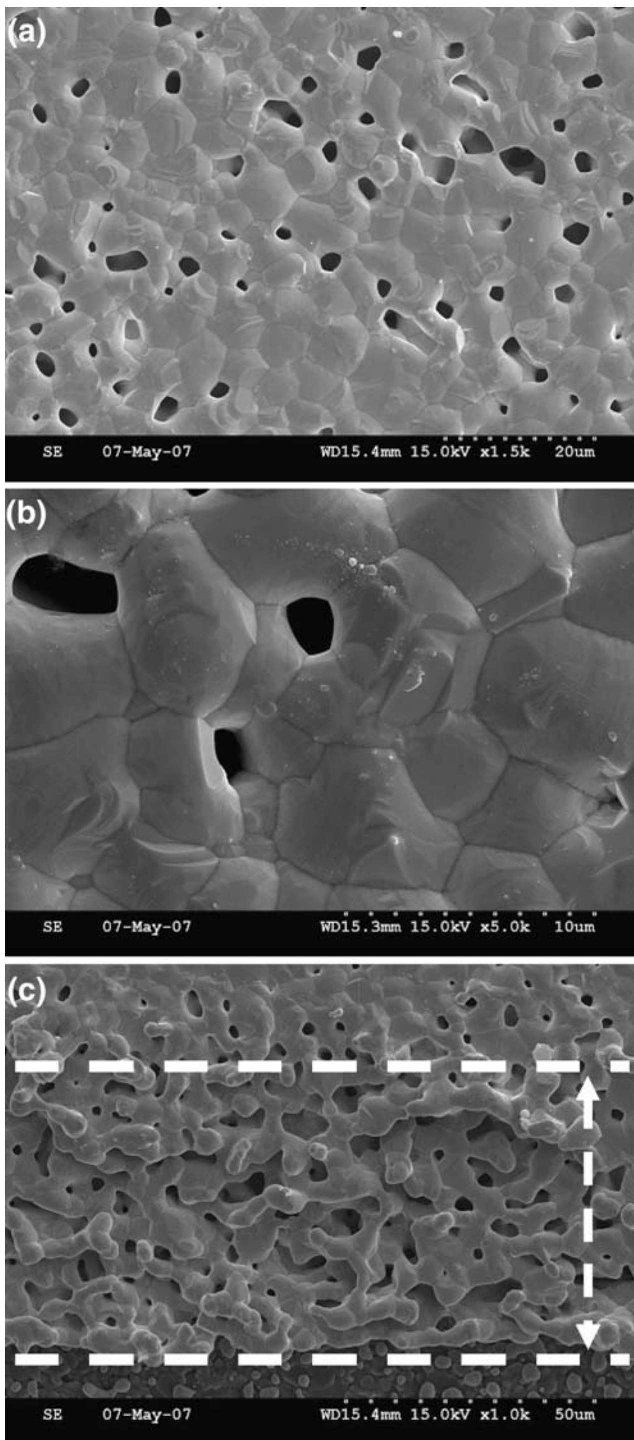

Fig. 2 Microstructure of the Ag conductive thick film (**a**), high magnification of (**a**) region (**b**), and the edge of thick film (the total thickness of film is 20 μm) (**c**) fired at 580 °C for 30 min

self diffusion [17, 18]. Figure 2(c) shows that the shape of the thick film was terminated at the edge of the thick film through the densification and interface of the substrate. Therefore, the pure silver thick film was formed with weak layers in the vertical direction.

A comparison of Figs. 2(a) and 3(a) show that the addition of 10 wt.% frit in the silver conductive thick film contributed to the high densification, and had only 1.9% porosity. Furthermore, each silver powder was connected by the melted frit, as shown in Fig. 3(b). Therefore, the silver powder was sintered with the liquid glass phase. If

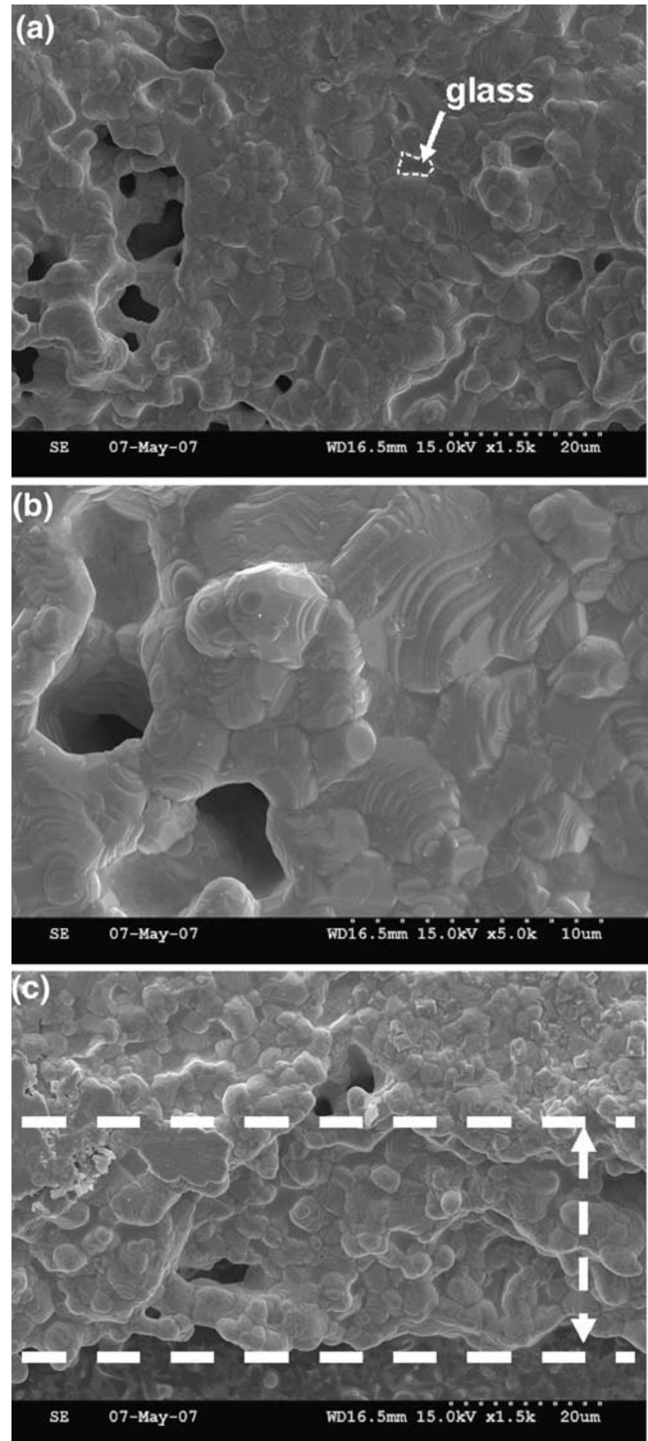

Fig. 3 Microstructure of the 90Ag+10frit (wt.%) conductive thick film (**a**), high magnification of (**a**) region (**b**) and the edge of thick film (**c**) after firing at 580 °C for 30 min

the frit becomes liquid, chemical reactions such as the migration of silver into the liquid frit would occur slowly on the surface of the silver. However, the melted frit without a chemical reaction flows into the bottom of the thick film and generates a number of pores in the matrix. It is believed that the silver conductive thick film contains 90 wt.% Ag and 10 wt.% frit was stretched in the horizontal direction by the viscous flow of the melted frit and contracted in the vertical direction in Fig. 3(c).

As shown in Figs. 2 and 3, the silver conductive thick film with or without the frit showed a significantly different microstructure. Moreover, the resistivity of the conductive thick film was dependent on the film microstructure [8, 9]. Therefore, the silver conductive thick films had a different bulk resistivity, as shown in Table 2. This indicates that a lower porosity reduces the resistivity and excess frit content increases the resistivity. The 20 wt.% frit contents in the silver conductive thick film had a higher bulk resistivity than the film containing 10 wt.% frit. Many researchers have reported that the silver particles in silver conductive thick film are immersed in the glass pool and are not connected by the addition of >10 wt.% of the frit, which is similar to the results reported in this study [8, 9].

As shown in Fig. 4(a), the changed volume of the frit decreased dynamically at 390 °C. The change in volume matched the dilatometer results (linear change) of the frit. The changed volume of the frit was highest at 420 °C, which remained constant at higher temperatures. The level of densification of the frit reached the theoretical density after 420 °C. However, above 460 °C, the pellet of the frit showed viscous flow. It was changed with the area in the side of the pellet, spreading the pellet on the substrate. The spreading rate of the molten frit was −0.18%/°C or −1.8%/min at temperatures ranging from 465 to 540 °C.

At 600 °C, the changed volume of the pellet, which consisted of pure silver powder, was the lowest, as shown in Fig. 4(a,b). On the other hand, a pellet of the mixture of the silver powder and frit shrank in a linear manner at 390 °C with no further shrinkage at 500 °C. It is believed that high densification of the pellet can be achieved with the presence of a liquid phase. Unfortunately, the liquid was expended at temperatures higher than 540 °C, as a result of the pellet swelling with the liquid flow of the frit. Therefore, excess molten frit penetrates the silver skeletal into the bottom of the pellet as a result of the liquid flow. A comparison of the changed volume of the pellet and the microstructure of the thick film revealed that the excess melted frit causes the production of pores on the surface of the silver conductive thick film. Moreover, a glass rich region forms at the bottom of the silver conductive thick film. Fortunately, the porosity of the silver conductive thick film with or without the frit corresponds to the changed volume of the pellets above 500 °C. Hence, a 12.6% volume change in the pure silver and 1.9% in the mixture powder can be attributed to the porosity of the thick pure silver film and mixture powder, respectively [Fig. 4(b)].

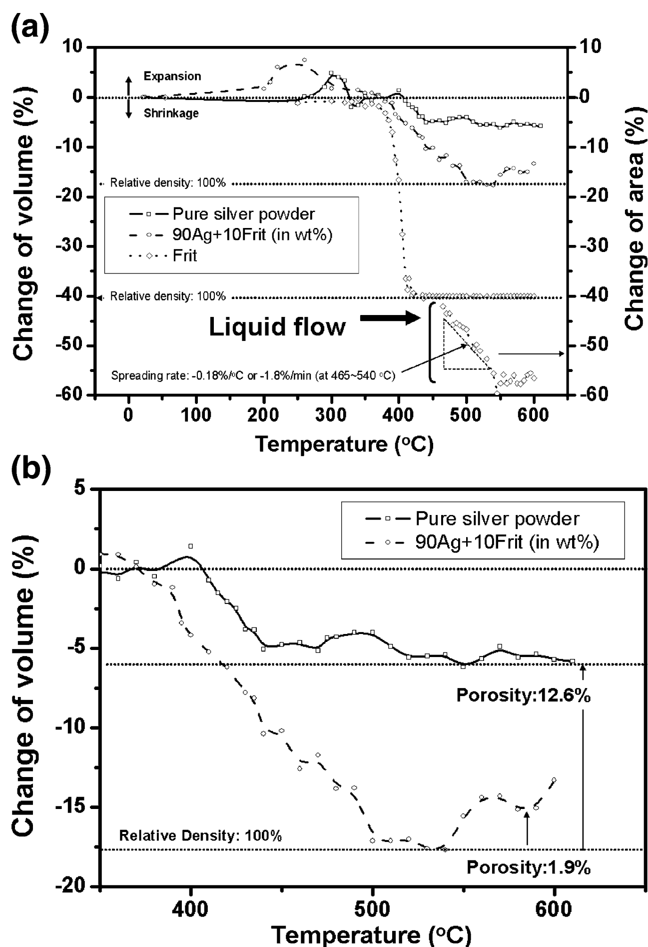

Fig. 4 (**a**) Densification profiles of the frit, pure silver powder and mixture powders (90Ag powder and 10frit (in wt.%)) using hot stage microscopy. For the frit, the variation in volume is constant 420 °C but a change of area is detectable down to 600 °C. (**b**) Densification profiles of the pure silver powder and mixture powders (90Ag powder and 10frit (in wt.%))

The pure silver powder, mixture of silver and frit expanded at temperatures ranging from 200 to 350 °C, as shown in Fig. 4(a). It is believed that the expansion in the range is the result of the evaporation of moisture and impurities around the powders.

Based on these results, the silver conductive thick film should be considered with the content of the frit and the

Table 2 Bulk resistivity and porosity of the thick films consisted of Ag powder, 90Ag+10frit and 80Ag+20frit after firing at 580 °C for 30 min.

Samples	Ag powder	90Ag+10frit (wt.%)	80Ag+20frit (wt.%)
Bulk resistivity ($\times 10^{-3}$ Ω·cm)	1.68	0.36	0.42
Porosity (%)	12.6	1.9	0

firing temperature. Therefore, controlling the content of the frit is related to the densification and the bulk resistivity in silver conductive thick film. Moreover, if the addition of 10wt% frit is used in the silver conductive thick film, it should be fired at between 500~540 °C. Therefore, the frit should be considered for accelerating densification but does not require high temperatures for firing.

4 Conclusion

The microstructure of the silver conductive thick film with or without a frit fired at 580 °C for 30 min was dominated by pores and the viscous flow of the molten residual frit. The addition of the frit in the silver conductive thick film affected the production of pores, its shapes and the bulk resistivity. The frit composition needs to be considered in a silver conductive thick film with the thermal properties, such as T_g, T_s, CTE, and the degree of densification.

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