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Elemental distribution near the interfaces between cordierite–spodumene glass-ceramic substrates and cofired Ag/Pd electrodes

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Abstract

Multilayer glass-ceramic substrates containing β-spodumene and α-cordierite were cofired with Ag/Pd electrodes. The elemental distribution near the interface between substrate and electrode was investigated. The MgO-containing substrates with the cofired Ag/Pd electrodes revealed a four-layer structure with abnormal Ag-, Bi-, and Mg-distributions near the electrode-substrate interface when 85Ag/15Pd electrode was used. This phenomenon disappeared when 70Ag/30Pd was used. It is thought that the existence of Bi_2O_3 in the electrode and MgO in the substrate might be responsible for this anomaly. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: D. Cordierite; D. Glass-ceramics; E. Substrates; E. Electrodes; Spodumene

1. Introduction

Several efforts have been made on developing multilayer ceramic substrates to replace conventional alumina substrates for high-performance LSI packaging [1]. To fulfill high speed signal-propagation requirements, the substrate should have a low dielectric constant. For avoiding damage to the semiconductor due to thermal stress, the coefficient of thermal expansion (CTE) of the substrate material should be near that of Si (30×10^{-7} K^{-1}). In addition, a low sintering temperature (<1000°C) of the substrate material is required, to enable cofiring with low-resistance metals such as copper, silver, or gold.

Several glass-ceramic materials have the potential to meet substrate goals [1–4]. The crystalline phases are α-cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), β-spodumene ($Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$), anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), or celsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$). Among them, cordierite glass-ceramics in the system $MgO–Al_2O_3–SiO_2$ also are increasingly used in applications where thermal shock resistance is important [5]. Spodumene glass-ceramics in the system $Li_2O–Al_2O_3–SiO_2$ are also important for cooktop panels, stove windows, cookware, and some precision parts [6], because of their low and even negative CTE [7].

In the present study, multilayer glass-ceramic substrates containing β-spodumene and α-cordierite were cofired with Ag/Pd electrodes. The elemental distribution near the interface between substrate and electrode was investigated.

2. Experimental procedure

Three glass compositions were used for the glass-ceramic substrates (wt%): x M + (100-x) L, where $x=0$, 80, and 100, and M and L denote $MgO-Al_2O_3-SiO_2$ and $Li_2O-Al_2O_3-SiO_2$ compositions, respectively (see Table 1). Well-mixed, dried powders containing appropriate amounts of reagent-grade Li_2CO_3, Al_2O_3, SiO_2, B_2O_3, and H_3PO_4 were melted in a Pt crucible for 4 h at 1550–1600°C. The melts were quenched into frit form by being poured into deionized water. The dried frits were crushed in an alumina-lined mortar grinder until the powder passed through 100 mesh. The crushed glass powders were then milled for 72 h in yttria-stablized zirconia-lined mills containing yttria-stablized zirconia balls and alcohol. The resulting slurries were dried and screened (60 mesh). The average particle sizes for the resulting glass powders were measured with a particle-size analyzer and were in the range of 2–2.5 μm.

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Table 1
Compositions of M and L

Composition (wt%)						
	Li_2O	MgO	Al_2O_3	SiO_2	B_2O_3	P_2O_5
M		23.75	20.90	50.35	2.5	2.5
L	7.65		26.02	61.33	2.5	2.5

The green samples with disk or sheet form were prepared. The disk samples were uniaxially dry-pressed in a 10 mm diameter steel die lubricated with a thin layer of stearic acid. Slurries consisting of glass powder and organic vehicles (solvent, plasticizer, and binder) were mixed by ball-milling and cast into green sheets (thickness~0.1 mm) by a tape casting process. The green sheets were then cut into 30×30 mm squares, followed by screen printing Ag/Pd conductor paste (85/15 and 70/30, Shoei Chemical Inc., Tokyo, Japan). The metallized green sheets were then laminated together at 80–85°C for 30 min under 17 MPa pressure. The green samples were sintered at typically 925°C for 2–4 h.

Phase identification of the fired samples was conducted by X-ray diffraction (XRD) analysis. The fired samples were polished and then coated with a thin film of carbon for the electron probe microanalysis (EPMA).

3. Results and discussion

At first, the crystalline phases formed in disk samples were investigated. The XRD patterns for 100M and 100L samples fired at 900–950°C for 1–4 h showed α-cordierite (α-C) and β-spodumene (β-S), respectively. The XRD patterns for 80M20L sample fired at 800–950°C for 15–240 min are shown in Fig. 1. It can be seen that the sample fired at 800°C for 15 min was still amorphous. A high quartz s.s. (h-Q) with Li_2O-Al_2O_3-SiO_2 composition crystallized when the fired time was prolonged to 60 min. The h-Q phase begins to transform into β-S when the sample was fired at 900°C for 30 min, and α-C crystallized from glass when the firing time was prolonged to 240 min. The α-C amount obviously increased when the sample was fired at 925–950°C for 240 min. The h-Q to β-S phase transformation was nearly complete when the sample was fired at 950°C for 240 min.

In the present study, the glass powders were obtained by quenching the melt to form a single (Li_2O, MgO)-Al_2O_3-SiO_2 glass. We have also prepared the 80M20L glass powder by mixing 100M and 100L glass powders in the 80:20 ratio. The glass–ceramics were then obtained by sintering the mixed glass powders. It was found that the XRD patterns of the fired samples were quite the same whether mixed glasses or single glass of average composition was used.

According to Fig. 1, a large amount of α-C has formed in the 80M20L sample fired at 925°C for 240 min. Thus, the substrates in the following study were fired at this temperature. For the 100M, 100L, and 80M20L substrates, it was found that the XRD patterns were quite the same as those for the disk samples. For the 80M20L sample, the measured coefficient of thermal expansion and dielectric constant at 1 MHz was 23×10^{-7} K^{-1} and 5.5, being suitable for substrate application.

Fig. 2(a) shows the cross-sectional secondary electron image (SEI) of the 80M20L substrate cofired at 925°C for 4 h with 85Ag/15Pd conductor. It can be seen that the conductor region reveals a four-layer structure (denoted as A, B_1, B_2, and C). The enlarged micrograph of the conductor region is shown in Fig. 2(b). The elemental distributions (Ag, Pd, and Bi: from the conductor; Mg, Al, and Si: from the substrate) are also shown in Fig. 2(a). It can be seen that Pd, Al, and Si

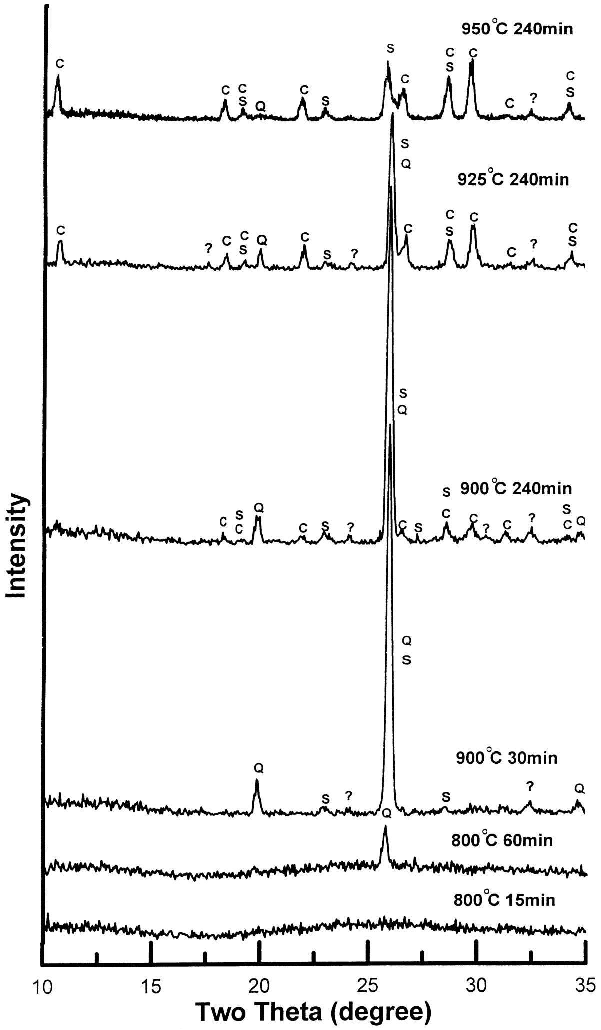

Fig. 1. XRD patterns of the 80M20L disk samples fired at 800–950°C for 15–240 min (Q: h-Q s.s., S: β-S, C: α-C).

have distributions which are normally observed in a diffusion system. However, the distributions of Ag, Bi, and Mg are striking. In the central conductor region (layer A), strong intensity of Ag can be seen. Layer B_1 and, especially, layer B_2 are almost lacking of Ag. However, a segregation of Ag in layer C occurred. It is also noted that Bi (from conductor) did not strongly concentrate in the central layer A, while a strong Bi-segregation is seen in layers B_1 and B_2. For the elements from the substrate, Mg also shows a segregation in layers B_1 and B_2. Namely, layers B_1 and B_2 exhibit Bi- and Mg-segregation, and are deficient in Ag. Layer C shows a local Ag-segregation.

Fig. 3(a) and (b) shows the cross-sectional SEI and elemental distribution of the 100L substrate cofired at 925°C for 2 h with 85Ag/15Pd and 70Ag/30Pd conductors, respectively. The porous region near the conductor is possibly formed by the mismatch in densification rate between substrate and conductor. It can be seen that, unlike in the 80M20L substrate, the

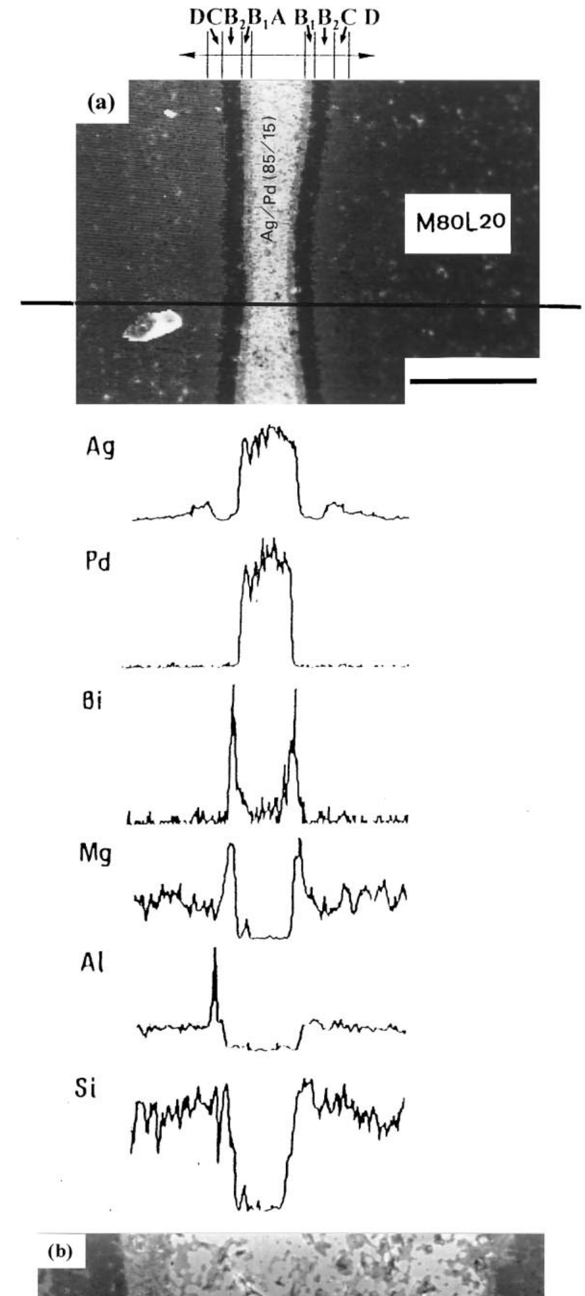

Fig. 2. (a) Cross-sectional SEI and corresponding elemental distribution of the 80M20L substrate cofired at 925°C for 4 h with 85Ag/15Pd conductor (bar = 100 μm). (b) Enlarged micrograph (bar = 10 μm).

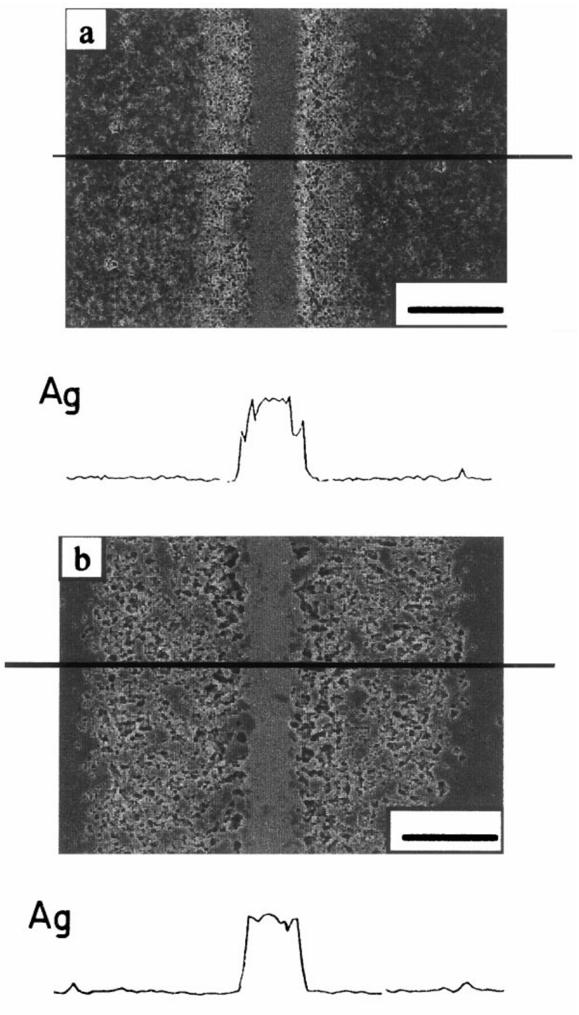

Fig. 3. Cross-sectional SEI and corresponding elemental distribution of the 100L substrate cofired at 925°C for 2 h with (a) 85Ag/15Pd and (b) 70Ag/30Pd conductor (bar = 25 μm).

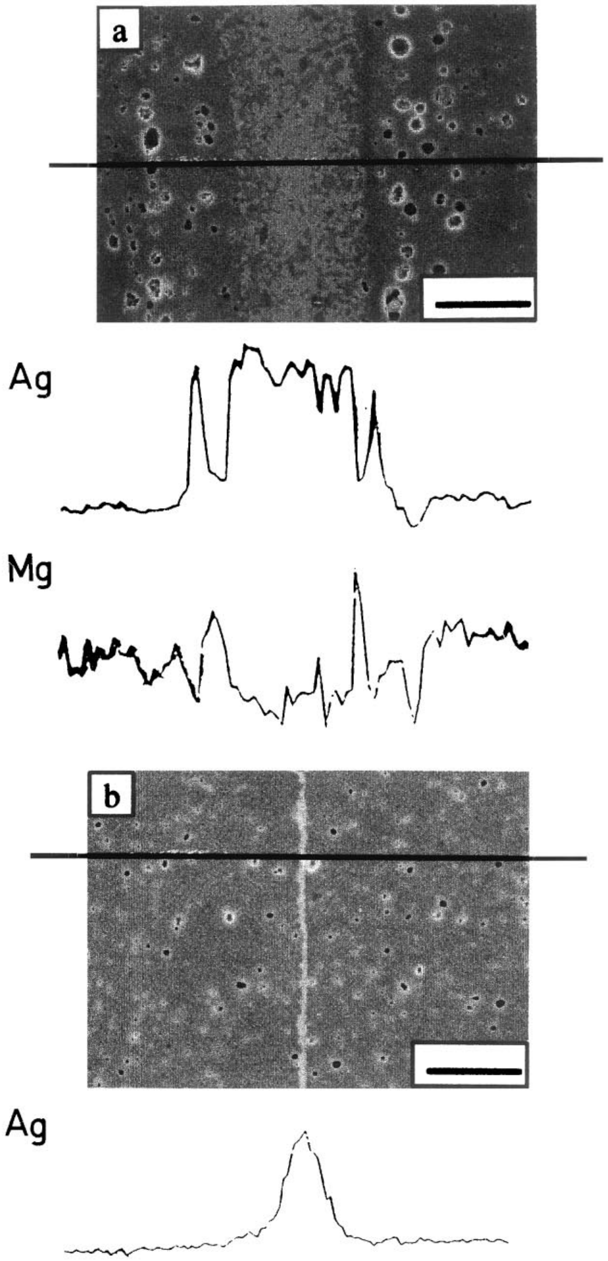

Fig. 4. Cross-sectional SEI and corresponding elemental distribution of the 100M substrate cofired at 925°C for 2 h with (a) 85Ag/15Pd and (b) 70Ag/30Pd conductor (bar = 25 μm).

four-layer structure disappeared and Ag was only distributed in the central conductor region. The level of Bi is too low to be detected. Other elements have distributions which are usually observed in a diffusion system.

Fig. 4(a) and (b) shows the cross-sectional SEI and the elemental distribution of the 100M substrate cofired at 925°C for 2 h with 85Ag/15Pd and 70Ag/30Pd conductors, respectively. For the 85Ag/15Pd electrode, the anomaly in Ag- and Mg-distributions are similar to those observed in 80M20L substrate (Fig. 2), except that the level of Bi is too low to be detected. However, for the 70Ag/30Pd conductor, the elements did not show any abnormal segregation, similar to those observed in 100L substrate [Fig. 3(a) and (b)].

According to Fig. 2 (for 80M20L) and Fig. 3 (for 100L), it is concluded that, when the MgO-free substrate was cofired with Ag/Pd conductors, the anomaly in elemental distributions disappeared, no matter what Ag/Pd-electrode composition was used. It seems that the existence of MgO in the substrate should be one of the factors responsible for the anomaly. According to Fig. 2 (for 80M20L) and Fig. 4 (for 100M), it is concluded that, for the MgO-containing substrates, the anomaly in elemental distribution occurred when 85Ag/15Pd electrode was used, and disappeared when 70Ag/30Pd was used. In addition to the difference in Ag/Pd ratio, the as-received 85Ag/15Pd paste contains Bi_2O_3 while 70Ag/30Pd is Bi_2O_3-free. It is thus suggested that the existence of Bi_2O_3 could be another factor responsible for the anomaly.

The local segregations of Ag in layer C and Mg and Bi in layers B_1 and B_2 possibly implied an uphill nature of diffusion, which can sometimes be observed in a system with multicomponent diffusion. Another possibility for the anomaly is that, according to the similar distributions of Mg and Bi, layers B_1 and B_2 might be formed by compound formation between Mg and Bi, thus ejecting Ag to form layer C.

4. Conclusions

(1). The crystalline phases formed in the substrates sintered at 925°C for 2–4 h were α-cordierite and/or β-spodumene, depending on the parent glass composition. The substrate containing both cordierite and spodumene has a thermal expansion coefficient of 23×10^{-7} K^{-1} and dielectric constant of about 5.5.
(2). The MgO-containing substrates with the cofired Ag/Pd electrodes revealed a four-layer structure with abnormal Ag-, Bi-, and Mg-distribution near the electrode–substrate interface when 85Ag/15Pd electrode was used. This phenomenon disappeared when 70Ag/30Pd was used. It is thought that the existence of Bi_2O_3 in electrode and MgO in substrate might be responsible for the anomaly.
(3). The local segregations of Ag, Mg, and Bi possibly implied an uphill nature of diffusion or caused by compound formation between Mg and Bi.

Acknowledgements

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