J Mater Sci (2011) 46:4695–4700
DOI 10.1007/s10853-011-5377-z

Diffusivity of silver ions in the low temperature co-fired ceramic (LTCC) substrates

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Received: 13 November 2010 / Accepted: 7 February 2011 / Published online: 16 February 2011
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Abstract Diffusion of silver inner-electrode occurred during sintering of commercial low temperature co-fired glass ceramic substrate made the dielectric surface become light yellow. The samples added with silicon oxide (SiO_2) powder, however, maintained white color. Silicon-oxide powder was used to modified the sintering behavior and inhibit the silver ions diffusion for the LTCC ceramics. The alumina particles in the LTCC substrates could be regarded as the diffusion barrier of silver ions. The activation energy for silver ions diffusion in the LTCC substrates was 101 kJ/mol. When 5 wt% SiO_2 powder was added into the LTCC substrate, the diffusion activation energy of silver ions became 145 kJ/mol. At sintering temperature of 1180 K, the diffusion coefficient of silver ion in the LTCC ceramic substrates with and without additional SiO_2 were 8.88×10^{-13} cm^2/s and 1.08×10^{-12} cm^2/s, respectively.

Introduction

In recent years, low temperature co-fired ceramic (LTCC) substrates integrated with passive devices have been used extensively for high-density packaging module [1–3] and high-performance wireless components [4]. High-conductivity metals, such as Cu and Ag have been widely used as inner-electrode materials in the LTCC components and modules. Since it can be sintered without atmosphere control, Ag metal and its alloy have been considered as high effective inner-electrode materials in the LTCC manufacturing. Adhesion and shrinkage match between the electrode and substrate, camber behavior of the sintered modules, and diffusion of silver ion during sintering are three major issues for the metallization of LTCC components and modules. Camber behavior of multilayer structure co-firing with Ag paste has been intensive studied by Jean and co-workers [5, 6]. Diffusion of Ag ions in the high-glass content LTCC substrates was considered to influence of reliability and performance of the LTCC modules on the subjects of increasing leakage current and decreasing insulation resistance [7]. Although migration of silver ions in various electronic components and hybrid electronics were investigated early [8, 9], the diffusion of silver ions in the high-glass content LTCC substrate was seldom reported. Reaction kinetic and mechanism between silver electrodes and ceramic-filled glass substrates [10], silver diffusion and microstructure development in the LTCC system [11] were previously investigated.

In this study, diffusion kinetics of silver ions in a commercial LTCC substrate was investigated. Silica powder was used as an additive for the LTCC substrate in order to inhibit the diffusion of Ag ions in the substrates.

Experimental procedure

LTCC substrates were prepared using commercial powder of ceramic-filled glass (alumina-filled Si–Ba–B–Al-Ti–Ca glass) and the same powder added with 5 wt% reagent-grade amorphous silica. The powders mixed with organic binder (B-73305, Ferro, San Narcos, CA, USA) at 50:50 ratio were ball-milled using high-purity alumina balls

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before tape-cast to desired thickness. Silver conducting paste (Ag8985, Shoei Co., Japan) was printed on the green tape and dried at 130 °C for 30 min. The printed green tapes were laminated at 60 °C under pressure of 20 MPa for 3 min in an isostatic pressing chamber. The laminated sample, then, was diced as chips with size of 2.24 × 1.36 × 1.1 mm^3. The diced samples were heated to 450 °C with a 10 °C/h heating rate for binder burnout before co-firing was conducted at temperatures between 1050 and 1180 vK for 15–120 min by a heating rate of 4 °C/min. The samples were cut perpendicular to substrate surface along the longitude of the conducting layer. Cross-section samples were then polished using diamond films to 1 μm surface roughness before etching with diluted 3 % HF + HCl solution. Analysis of microstructure was performed with scanning electron microscopy (SEM, JEOL 5600, Tokyo, Japan). Inter-diffusion between Ag and LTCC substrate was examined using energy dispersive X-ray spectroscopy (EDS, 6587, Oxford, England) equipped with SEM. Crystalline phases of the co-fired resistors were determined by X-ray diffractometry (XRD) using X-2000 (Scintag, CA, USA). Raman spectrum measurements were performed at room temperature with a resolution of about 0.5 cm^{-1}, and the signals were recorded by a Jobin–Yvon LabRAM HR micro-Raman spectrometer equipped with a liquid-nitrogen-cooled CCD. The 40 mW output of the 514.5-nm Ar^+ ion laser was used as the excitation source.

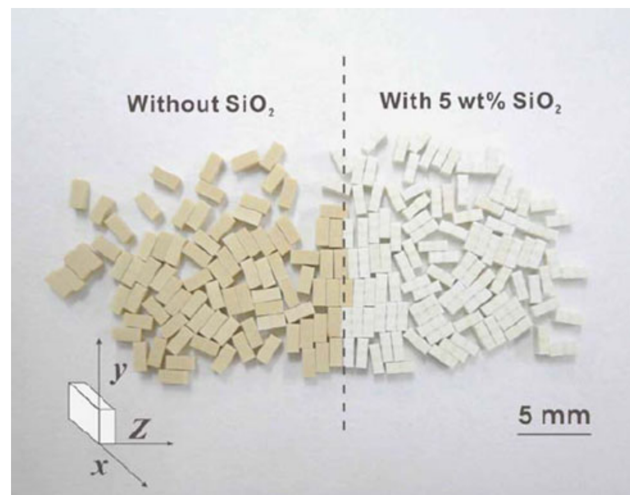

Fig. 1 Morphologies of silver metalized LTCC chips with (*right side*) and without (*left side*) SiO_2 addition, the chips were aligned in *y* direction

Results and discussions

Diffusion of silver inner-electrode occurred during sintering of LTCC substrate made the dielectric surface become light brown, the left side samples shown in Fig. 1. It appears that adding SiO_2 to the LTCC substrate, the right side samples shown in Fig. 1, has effectively reduced silver diffusion into the LTCC substrate, leading to its surface maintained white in color.

Single layer LTCC tape without SiO_2, sintered at 1150 K for 30 min, had shrinkage of 23, 23, and 12% on the length, width and thick directions. When 5 wt% SiO_2 was added to the LTCC substrate, the shrinkage of the LTCC single layer tape on the length and width direction reduced to 20%, its shrinkage on the perpendicular direction increased to 14%. In addition of SiO_2 increased the viscosity of the glassy phase in the materials and also increased the sintering temperature of LTCC materials [12]. Higher viscosity of glassy phase resulted from the addition of SiO_2 made the substrate had lower shrinkage in the planar directions (*x* and *y* directions), and increased the shrinkage in the thickness (*z*) direction. The single layer LTCC tapes with and without SiO_2 addition had similar volume shrinkage of about 47%.

During sintering, the multilayer LTCC chips had different shrinkage ratios with different directions, as listed in Table 1. The shrinkage on the *z* direction had largest shrinkage among three directions of the chips with and without SiO_2 addition. Owing to constraint sintering resulted from the difference of the shrinkage behavior between the inner-silver electrode and LTCC materials during sintering, the chip's shrinkage on the *x* and *y* directions were about half of the single layer LTCC tape, and hence made the shrinkage of the chip on the *z* direction was larger than that of the LTCC single layer tape. When the chips were sintered at temperatures between 1050 and 1180 K, the shrinkages of the multilayer chips without SiO_2 addition on the *x* and *y* directions were around 10.5–13.5 and the shrinkage on the *z* direction was about 17–18%. When 5 wt% SiO_2 was added to the LTCC tape, the chips' shrinkages on the *x* and *y* directions were between 7 and 11%, which were lower than the chips without SiO_2 addition. The shrinkage of the SiO_2 added chips on the *z* direction was about double values of that of the chips without SiO_2 addition, which had shrinkage around 31–33.5%. The volumes of chips without SiO_2 added shrunk about 33–37% after sintering, the chips with SiO_2 added, however, had volume decreasing 41–45%. From the microstructures observation results, the dielectric layer in the chip without SiO_2 addition had higher porosity than the dielectric layer in the SiO_2 added chip, as shown in Fig. 2.

In the previous investigation [12], LTCC material with SiO_2 addition had two shrinkage stages, and the temperature difference between first and second shrinkage stage

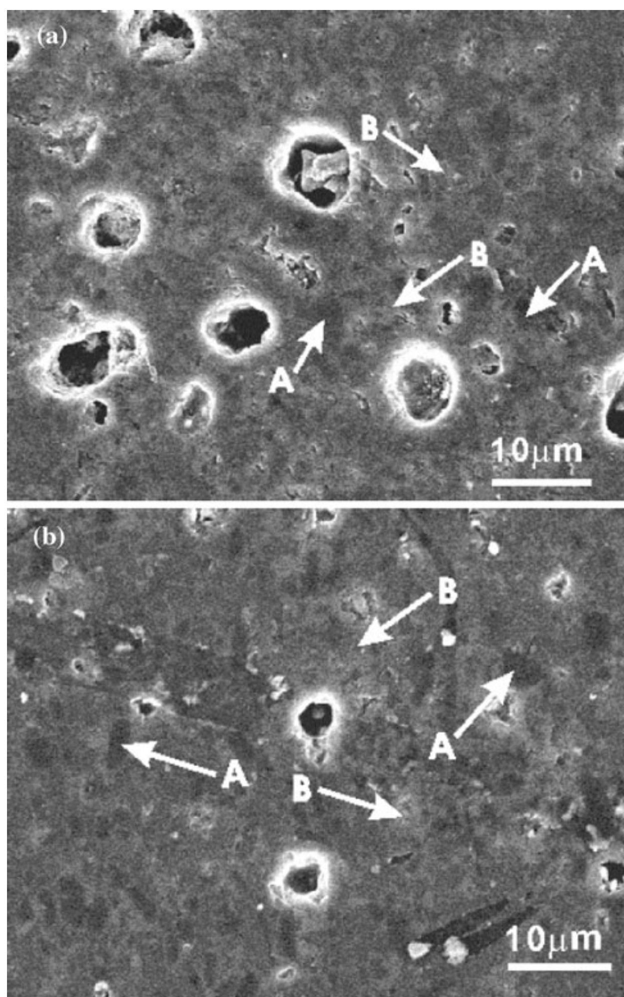

Fig. 2 Microstructures of LTCC chips **a** without and **b** with SiO_2 additions sintered at temperature 1150 K for 30 min

was about 100 K. There was only one stage shrinkage behavior of the LTCC material without SiO_2 addition. The pores in the SiO_2 added chips remained open after first stage shrinkage, the pore continuously shrunk before second stage shrinkage occurred. The constrained sintering effects in the SiO_2 added chips were more evident than that in the chips without SiO_2 addition, which resulted in the x and y direction shrinkages of former chip were smaller than the latter. Therefore, the SiO_2 added chips continuously shrunk in z direction after first stage shrinkage, leading to the shrinkage in z direction was much higher than that of LTCC chips without adding SiO_2. When the chips were sintered at temperature between 1050 and 1150 K, the shrinkages for the chips with or without SiO_2 additions increased with increasing the sintering temperature or time. The SiO_2 added chips reached second stage shrinkage when they were sintered at temperature higher than 1050 K. After sintering at temperature of 1180 K, the chips with or without SiO_2 addition had lower shrinkage than those were sintered at 1150 K, which may be because of the dissolution of alumina in the glass.

Alumina was the only crystalline phase presented in the X-ray diffraction pattern for LTCC tape sintered at 1180 K (Chen and Hsi unpublished paper). Dark and gray areas were observed from the SEM micrographs, dark areas were pointed by "A" and grey areas were pointed by "B" in Fig. 2. The dark areas in the microstructure were identified as high-aluminum contented phases under EDS analysis, where were considered as the locations of alumina phase. The gray areas contained Al_2O_3, SiO_2, BaO, and CaO as major compositions. The gray area in the chips without SiO_2 addition had higher Al_2O_3 and CaO contents than those of the SiO_2 added chips.

Silver atoms were detected from the grey areas in the chips with or without SiO_2 added, their contents increased with increasing sintering temperature, as shown in Fig. 3. The gray areas in the chips without SiO_2 addition had silver content in the range of 2.76–3.36 wt%. The silver contents in the gray phases of SiO_2 added chips, however, were lower than 1.59 wt%. Figure 4 illustrates Raman spectra collected from chips with and without SiO_2 addition, and LTCC sintered tape sintered at 1100 K for 30 min. Three bands at 445, 510, and 605 cm^{-1} were clearly observed for all the samples, however, an additional band at 240 cm^{-1} was solely found at the chip without SiO_2 added. The band at 240 cm^{-1} related to the Ag–O phonons, which was of similar frequency in the Raman spectrum of $\delta_s(AgO_2)$ of the distorted square-planar '$Ag^{III}O_4$' unit of AgO structure [13, 14]. Silver ion in the chip without SiO_2 addition formed Ag–O bond in the glassy phase of the chip. The light brown appeared on the surface of the chip without SiO_2 addition, therefore, was because of the formation of Ag–O bonds in the chip. When the silver content was higher than 2.5 wt% as detected from the sintered chips without the addition of SiO_2, the Ag–O bonds formed and the chips turned light brown color. When the silver contents were lower than 1.5 wt% as those measured from SiO_2 added chips, Ag–O bond was not found in the chips and it appeared as white color.

Silver concentration profiles in the LTCC dielectric layer perpendicular to the direction of sliver electrode layer of chips without SiO_2 addition sintered at 1050, 1100, 1150, and 1180 K for 30 min are shown in Fig. 5a. The diffusion process can be assessed as undimentional diffusion into a semi-infinite medium from a constant surface concentration of silver, $Cs_{(Ag)}$. The concentration of silver ions in LTCC substrates were calculated by the Fick's second law, as the follows:

$$C_{Ag}(x,t)/Cs_{(Ag)} = 1 - \mathrm{erf}\left[x \Big/ 2\left(D_{Ag}t\right)^{0.5}\right] \quad (1)$$

Table 1 Shrinkage of LTCC chips in *x* (length), *y* (width), and *z* (thickness) directions during sintering

Sintering temperature (K)	Sintering time (min)	Shrinkage (%)					
		Without SiO_2			With 5 wt% SiO_2		
		Length	Width	Thickness	Length	Width	Thickness
1050	15	12.49	10.86	17.03	9.61	7.67	32.51
	30	12.76	11.24	17.31	9.89	7.98	32.82
	60	12.81	11.57	17.57	10.29	8.16	33.03
	120	13.06	11.81	18.01	10.58	8.37	33.42
1100	15	12.74	11.03	17.31	9.86	7.91	32.7
	30	12.87	11.36	17.52	10	8.07	33.09
	60	13.09	11.78	17.89	10.37	8.28	33.37
	120	13.29	12.01	18.11	10.66	8.57	33.68
1150	15	12.81	11.47	17.48	9.90	8.15	32.7
	30	12.94	11.59	17.69	10.24	8.23	32.94
	60	13.35	11.79	17.94	10.59	8.49	33.28
	120	13.67	12.19	18.32	10.78	8.77	33.54
1180	15	12.75	11.19	17.24	9.41	7.94	32.34
	30	12.51	10.98	16.97	9.01	7.9	32.07
	60	12.21	10.66	16.39	8.76	7.72	31.76
	120	11.93	10.49	16.09	8.48	7.24	31.39

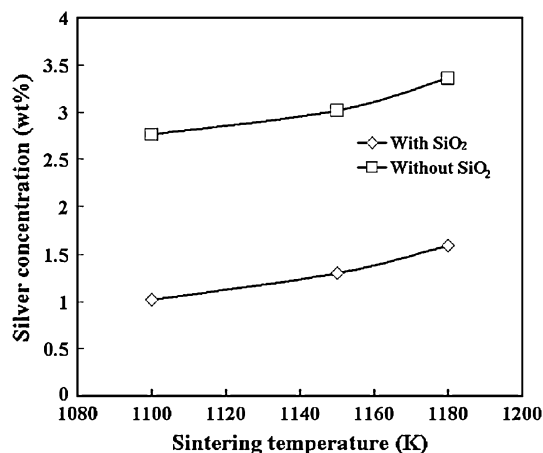

Fig. 3 Silver concentrations of the dielectric in the chips with and without SiO_2 addition

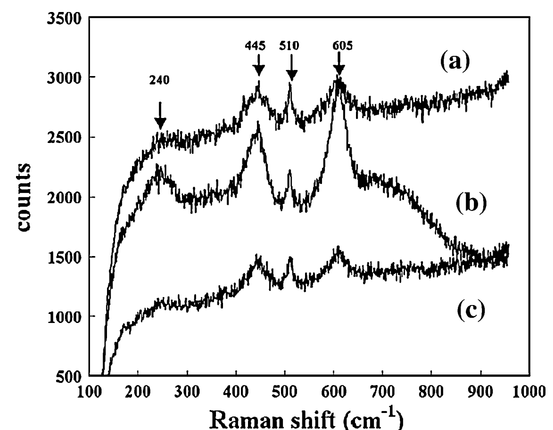

Fig. 4 Raman spectra for **a** LTCC sintered tape, **b** without SiO_2 added chip, and **c** with SiO_2 added chip

where $C_{Ag}(x, t)$ is the concentration of silver ions measured at distance *x* from the interface of sliver layer for a given period of time, $Cs_{(Ag)}$ is equal to 100% for silver electrode, and D_{Ag} is the diffusion coefficient of silver ion, the erf in Eq. 1 stands for error function [15]. The value of $C_{Ag}(x, t)$/$Cs_{(Ag)}$ ratio was directly calculated from the EPMA measurement of sample. The diffusivities of silver ions in the LTCC materials were calculated from the silver concentration profiles shown in Fig. 6 by Eq. 1. It is found that the average diffusivities of silver ions were 3.01×10^{-13} cm^2/s at 1050 K, 4.19×10^{-13} cm^2/s at 1100 K, 8.71×10^{-13} cm^2/s at 1150 K, and 1.08×10^{-12} cm^2/s at 1180 K. These results were higher than previous report [10], which might be because of the different glass type used and alumina content in this study. There was only 5 wt% alumina content for the LTCC material used in the previous report, but the alumina content for the LTCC material used in this study was ~40%. Alumina grains can be considered as diffusion barriers for silver ions in the LTCC chip, the true diffusion path of silver ions were longer than that directly measured from the cross-section of the chips. Calculated from the silver concentration profile of the SiO_2 added dielectric layer, as indicated in Fig. 5b, the diffusivities of silver ions in the chip were 9.87×10^{-14} cm^2/s at 1050 K, 2.59×10^{-13} cm^2/s at

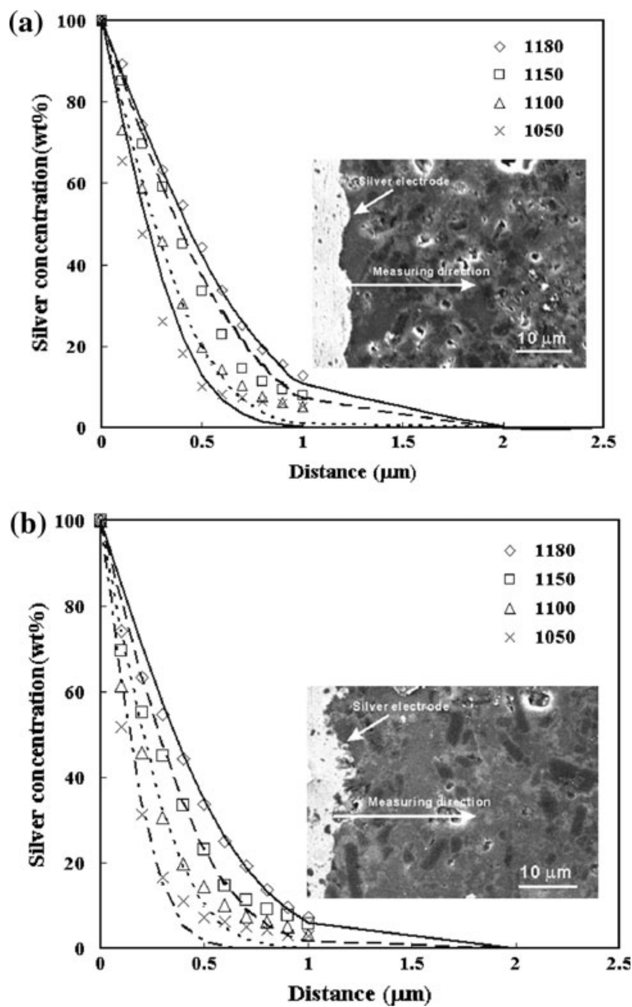

Fig. 5 Silver-concentration profiles of dielectric measuring from Ag/LTCC interface of **a** Chips without SiO_2 addition and **b** chips with 5 wt% SiO_2 addition. The samples were sintered at temperature of 1050, 1100, 1150, and 1180 K for 30 min

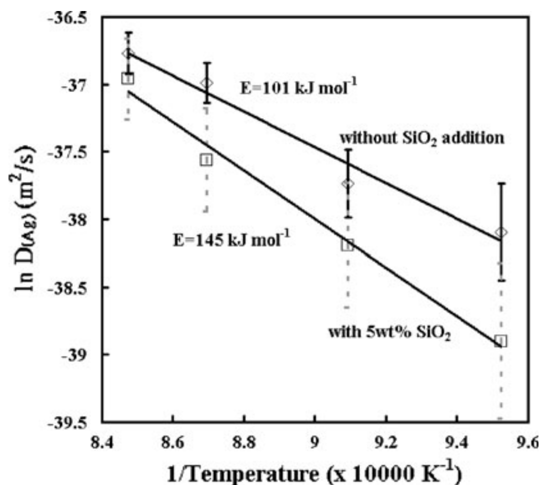

Fig. 6 Logarithm of Ag diffusivity ($\ln(D_{Ag})$) as a function of reciprocal temperature ($1/T$)

1100 K, 4.87×10^{-13} cm^2/s at 1150 K, and 8.88×10^{-13} cm^2/s at 1180 K. The diffusivities of silver ions in the SiO_2 added LTCC dielectric layers were about one order lower than those in the LTCC dielectric layers without SiO_2 additions.

Summarizing the diffusion coefficients for all temperatures investigated, an Arrhenius plot was obtained as shown in Fig. 6. The activation energy (E) of silver ion in the LTCC dielectric material can be calculated by the Arrhenius equation:

$$D = D_0 \exp(-Q_d/RT) \quad (2)$$

where D_0 is a temperature-independent pre-exponential (m^2/s), Q_d is the activation energy for diffusion, R is the gas constant, 8.31 J/mol-K. The diffusion activation energy of silver ions in the LTCC dielectric layer of the chip determined from the slope of Arrhenius plot was 101 kJ/mol. The diffusion activation energy of silver ions in the SiO_2 added LTCC dielectric layer was 145 kJ/mol. The diffusion activation energies of silver ions measured in this study were much higher than those of silver ions in glasses [10], which may be because of high-alumina content (~40 wt%) in the LTCC materials used in this study. The increase in the viscosity of glassy phase in the LTCC dielectric material because of the addition of SiO_2 would be considered as the major factor to decrease the diffusivity of silver ions, and to increase the activation energy of silver ions in the LTCC dielectric material.

Conclusions

In this study, the authors demonstrate an easy method to decrease the diffusivity of silver ions in LTCC dielectric materials by adding 5 wt% SiO_2 to the dielectric raw materials. This process effectively improved the coloring LTCC chips by decreasing the silver ions content in the glassy phase of dielectric. The increase in the viscosity of glassy phase in the LTCC dielectric material because of the addition of SiO_2 may decrease the diffusivity of silver ions, and increase the activation energy of silver ions in the LTCC dielectric material. Alumina grains in the LTCC dielectric layer can behave as diffusion barriers of silver ions in the dielectric layer, which reduced the diffusivity and increased the diffusion activation energy of silver ions in the dielectric layer.

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