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PZT thick films on LTCC substrates with an interposed alumina barrier layer

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Abstract

PZT thick films ($PbZr_{0.53}Ti_{0.47}O_3$ with the addition of 6% PbO and 2% $Pb_5Ge_3O_{11}$) with a low sintering temperature were printed and fired on LTCC substrates (951, Du Pont), covered with an alumina barrier layer. The electrical characteristics (remanent polarisation, coercive field, dielectric constant and dielectric loss) of these PZT thick films, together with sets prepared on "unprotected" LTCC substrates and on alumina substrates were compared. Whereas the electrical characteristics of the films on LTCC substrates deteriorated significantly due to interactions between the LTCC substrates and the PZT layers the values obtained for the LTCC/alumina barrier structures were comparable with those on ceramic alumina substrates.

Keywords: $Pb(Zr,Ti)O_3$; Films; Al_2O_3

1. Introduction

Piezoelectric ceramics are used in a wide range of sensors, actuators and transducers that are important in diverse fields such as industrial process control, environmental monitoring, communications, information systems, and medical instrumentation. Thick-film technology, i.e., the deposition of thick-film pastes by screen printing, on ceramics, primarily alumina substrates, is a relatively simple and convenient method for producing layers with a thickness of up to 100 μm. The characteristics of thick-film ferroelectrics are similar to those of bulk materials.[1–4] The compositions of piezoelectric thick films are almost exclusively based on $Pb(Zr_{1-x}Ti_x)O_3$, referred to as PZT. The processing temperatures required to obtain dense PZT ceramics are around 1200 °C; this is too high for most of the relevant substrates and is also not compatible with thick-film technology. To achieve processing temperatures between 800 and 900 °C the basic compositions need to be modified with additives that form liquid phases at these temperatures. The sintering temperature can be lowered with mixtures of low-melting oxides, e.g. $Pb_5Ge_3O_{11}$,[5–7] Cu_2O–PbO,[8–10] Li_2CO_3–Bi_2O_3,[10–12] Bi_2O_3–ZnO.[13]

Ceramic multi-chip modules (MCM-Cs) are defined as multilayer substrates with buried conductor lines as well as other passive components. For an overview of passive integrated components in MCMs, see for example, the work of Dziedzic and Golonka.[14]

Low-temperature co-fired ceramic (LTCC) materials, which are sintered at the temperatures typically used for thick-film processing, i.e., around 850 °C, are widely used for the production of MCM-Cs, especially for telecommunications and automotive applications. The main required characteristic is that the LTCC tape must sinter to a dense and non-porous layer when fired at around 850 °C. Therefore, it has to contain a low-melting-point glass phase.[15,16]

For some applications, for example, integrated sensors or micro-actuators, piezo $Pb(Zr,Ti)O_3$ (PZT) thick films, either

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on surface of LTCC substrate or embedded within multilayer LTCC structures, would be of interest. It is interesting to note that while there are many papers on passive components, either on or buried within LTCC structures, there are sparse data on piezo materials. Hrovat et al.[17] studied PZT thick films that were fired on the top of green LTCC tapes. Their results showed significantly degradation of the ferroelectric characteristics due to interactions between the PZT and LTCC materials during firing. Thelemann et al.[18] reported the construction of a micro-pump that was driven by a piezo-electric layer printed and fired on the surface of the pre-fired MCM.

For compatibility with LTCC materials PZT thick films that are sintered at relatively low temperatures, at about 850 °C or less, would be of interest. The aim of this work was to study the compatibility between LTCC 951 tapes (Du Pont) and screen-printed PZT paste as well as to investigate the electrical characteristics of the PZT layers. The green Du Pont LTCC 951 tape is a mixture of alumina, glass and organic vehicle. During firing, the anorthite ($(Na,Ca)(Al,Si)_4O_8$) phase crystallizes.[17]

The aim was to study electrical characteristics of PZT thick films with low firing temperature printed and fired on LTCC substrates. As preliminary experiments indicated that due to the interaction between the printed PZT layers and the LTCC substrates during firing the electrical characteristics deteriorate significantly,[17,19] a barrier layer was interposed. The barrier layer was based on alumina with the addition of the low-melting-point lead germanate as a sintering aid.

2. Experimental

PZT 53/47 powder ($PbZr_{0.53}Ti_{0.47}O_3$) with an excess of 6 mol% PbO was prepared by mixed-oxide synthesis at 900 °C for 1 h from high-purity PbO (litharge) 99.9% (Fluka), ZrO_2 99% (Tosoh), and TiO_2 99% (Fluka). To this was added 2 wt.% of lead germanate, with the composition $Pb_5Ge_3O_{11}$ (melting point 738 °C) as a sintering aid. The lead germanate (PGO) was also prepared by mixed-oxide synthesis from PbO and GeO_2 99% (Ventron) at 700 °C. After synthesis, both compositions were ball milled in acetone for 1 h and dried. The material for the barrier layer was similarly prepared, i.e., by mixing a fine-grained alumina A-16 (Alcoa) and 6 wt. % of pre-reacted PGO. Thick-film pastes were prepared from the PZT (2% PGO) and Al_2O_3 (6% PGO) and an organic vehicle.

The LTCC substrates (Du Pont, 951) were made by laminating three layers of LTCC tape at 70 °C and at a pressure of 20 MPa. The thickness of the green tape was 200 μm, and dimension of test structures was 25 mm × 25 mm. The thick-film structure was prepared by first printing twice a barrier layer (alumina mixed with PGO) on LTCC substrates and firing at 850 °C. On this structure a gold thick film conductor (Remex 3243) was printed and fired at 850 °C. Over this the PZT film was printed six times with intermediate drying and fired at 800 °C for 8 h. The thickness of fired LTCC substrates was 510 μm. The thicknesses of the PZT film, gold electrode and barrier layer after the thermal treatment, estimated from micrograph cross sections, was around 50 μm, 10 μm and 40 μm, respectively.

For the electrical measurements gold electrodes were sputtered onto the PZT films. The values of the remanent polarisation and the coercive field were determined from ferroelectric hysteresis curves measured with an Aixact TF Analyser 2000 at 50 Hz. The real and the imaginary parts of the complex dielectric constant were measured with an HP 4284 A Precision LCR Meter at 1 kHz.

For the microstructural investigation the samples were mounted in epoxy in a cross-sectional orientation and then cut and polished using standard metallographic techniques. A JEOL JSM 5800 scanning electron microscope (SEM) equipped with an ISIS 300 energy-dispersive X-ray (EDS) analyzer was used for the overall micro-structural and compositional analyses. EDS spectra were quantified using the ZAF (Z—atomic number correction, A—absorption correction, and F—fluorescence correction) method and a virtual standard package library. The library contains pre-recorded standard element profiles under the same experimental conditions.

3. Results and discussion

In Table 1 the electrical parameters, i.e. remanent polarisation P_r, coercive field E_c, dielectric constant ε' and dielectric loss $\tan\delta$, of the LTCC/barrier/Au/PZT structures are presented. The electrical characteristics of these structures are compared to the characteristics of similar structures printed on fired LTCC substrates and alumina substrates, all fired at 800 °C.[7,19] The hysteresis loops of the PZT films on the alumina substrates and on the LTCC substrates with or without barrier layers are shown in Fig. 1. The hysteresis loop of a PZT thick film on LTCC/alumina/barrier substrate is denoted "LTCC/Barr".

The electrical characteristics of the samples that were fired on the LTCC substrates without an alumina barrier deteriorated due to interactions between the LTCC substrate and the PZT layer. The remanent polarisation and the dielectric constant are significantly lower than those of the PZT layers on alumina substrates. The relatively low dielectric constant indicates the formation of phases with a low permittivity.[11] On the other hand, the characteristics of the PZT thick films fired on LTCC substrates with barrier layers are more similar to the characteristics of the films on alumina substrates. The dielectric constant and the remanent polarisation are similar, but the

Table 1
Electrical parameters of Au/PZT structures on LTCC and alumina

Structure	P_r (μC/cm^2)	E_c (kV/cm)	ε'	$\tan\delta$
LTCC/barrier	26	56	550	0.04
LTCC[19]	4.4	120	280	0.02
Alumina[7]	29	25	780	0.03

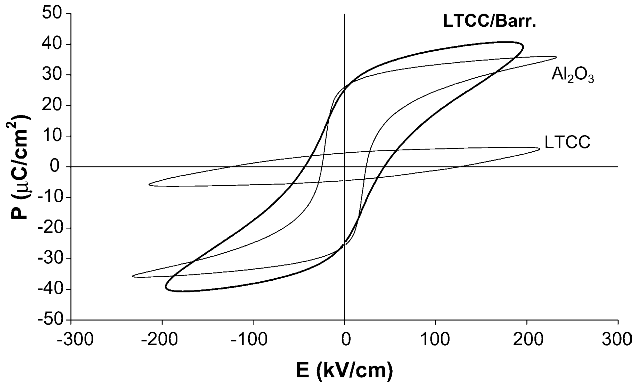

Fig. 1. Hysteresis loops of PZT thick films on sintered LTCC substrates, with and without barrier layers, and on alumina substrates. The PZC films were fired for 8 h at 800 °C.

coercive field is roughly twice as high for the LTCC/barrier structure (over 50 μC/cm^2) than for the alumina substrates (25 μC/cm^2).

The microstructures of the cross-sections of the samples with and without the alumina barrier are shown in Figs. 2 and 3, respectively. The LTCC substrate is on the bottom. The LTCC material is a mixture of a darker alumina-rich phase and a lighter silica-rich phase. In Fig. 3 there is an approximately 25-μm thick alumina layer between the LTCC and the bottom gold electrode. Due to the presence of the lead germanate liquid phase during firing at 850 °C the alumina layer is densely sintered.

For the case of the PZT thick-film fired on the LTCC/gold structure (Fig. 2) the approximately 20-μm-thick layer at the LTCC/gold interface is richer in PbO (around 30 wt.%) than the LTCC material itself (around 10 wt.%). The EDS microanalysis of the PZT layer showed, besides Pb, Zr and Ti, a relatively high concentration of Si (around 6 wt.% of SiO_2). Ge from the PGO was not detected due to its low concentration and low atomic weight. The results, therefore, indicate

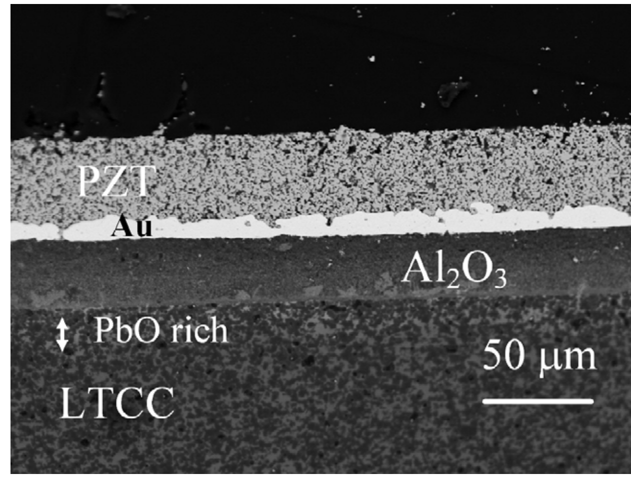

Fig. 3. Microstructure of the cross-section of the LTCC/Al_2O_3 barrier/gold/PZT structure, fired at 800 °C. Back-scattered electrons image.

the diffusion of PbO into the LTCC and, more significantly, the diffusion of SiO_2 into the PZT during the firing of the thick-film structure. Presumably, the silica reacts with PZT forming low-permitivity lead-based silicates and lowers the dielectric constant of the PZT layers.[11]

For the case of the samples with the alumina barrier interposed between the LTCC substrate and the gold conductor the concentrations of PbO in the PbO-rich layer near the LTCC/gold interface, and of SiO_2 in the PZT layer were 16 wt.% and 2 wt.%, respectively. Both values are markedly lower than those for the samples without a barrier layer. The obtained results indicate that the densely sintered alumina-based barrier between the glassy LTCC substrates and the PZT thick films, while not entirely preventing, significantly minimises the interactions between the LTCC and the PZT materials, and therefore improves the PZT characteristics.

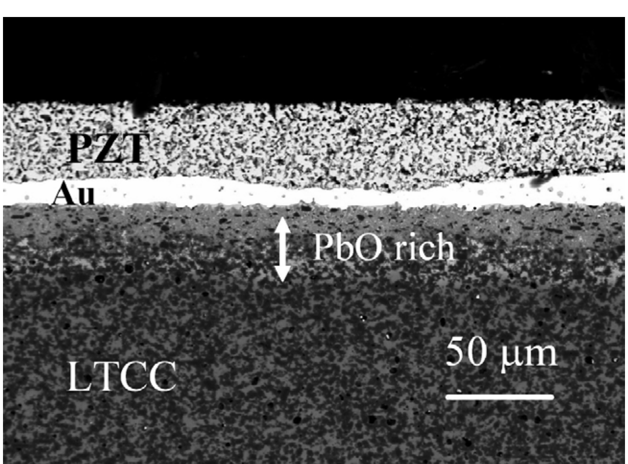

Fig. 2. Microstructure of the cross-section of the LTCC/gold/PZT structure, fired at 800 °C. Back-scattered electrons image.

4. Conclusions

The electrical and microstructural characteristics of $PbZr_{0.53}Ti_{0.47}O_3$ thick films with the addition of 6 mol% PbO and lead germanate ($Pb_5Ge_3O_{11}$) on LTCC substrates with the alumina barrier layer were measured and compared with the characteristics of similar structures printed either on alumina or prefired LTCC substrates. In order to lower the sintering temperature of the alumina barrier layer to 850 °C lead germanate was also added. The electrical characteristics of the PZT layers that were fired at 800 °C on the LTCC substrates with an alumina barrier were better than those of the samples without a barrier layer. The remanent polarisation and the dielectric constant are similar to the values obtained for the alumina substrates, whereas the coercive field is two times higher. The alumina-based barrier between the LTCC substrates and the PZT thick films decreases the interactions, mainly the diffusion of silica from the LTCC to the PZT and the lead oxide from the PZT into the LTCC substrate, and therefore improves the PZT characteristics.

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