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An investigation of thick PZT films for sensor applications: A case study with different electrode materials

**Darko Belavič · Marko Hrovat · Marina Santo Zarnik ·
Janez Holc · Marija Kosec**

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Abstract Lead zirconate titanate (PZT) is a piezoelectric material that can sense or respond to mechanical deformations and can be used in ceramic micro-electro-mechanical systems (C-MEMS). A thick-film paste was prepared from a pre-reacted PZT powder ($PbZr_{0.53}Ti_{0.47}O_3$) and thick-film technology (screen-printing and firing) was used to deposit the PZT layers on LTCC tapes and on alumina substrates. The microstructural, electrical and piezoelectric characteristics of the thick PZT films on relatively inert alumina substrates and on LTCC tapes were studied. Preliminary experiments indicated that due to the interaction between the printed PZT layers and the LTCC substrates during firing the electrical characteristics deteriorate significantly. To minimise the influence of substrate-film interactions different electrode materials and the use of additional intermediate layers as a barrier were evaluated. The dielectric permittivities, dielectric losses, and piezoelectric coefficients (d_{33}) were measured. The dielectric permittivities of the thick films fired on LTCC substrates were lower (210 with gold electrodes and 430 with silver electrodes) than those measured on alumina substrates (500). The piezoelectric coefficients d_{33} were measured with a Berlincourt piezometer. The d_{33} values measured on the LTCC substrates were relatively low (60–80 p*C*/*N*) compared with the values obtained for the alumina substrates (around 140 p*C*/*N*). The lower dielectric constants and piezoelectric coefficients d_{33} of the films on LTCC substrates are attributed to the formation of phases with a lower permittivity. This was a result of the diffusion of SiO_2 from the LTCC into the active PZT layer. The diffusion of silica was confirmed by the SEM and EDS analyses.

Keywords Thick-film PZT · Piezoelectric characteristics · Alumina substrate · LTCC substrate

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, primarily on alumina substrates, is a relatively simple and convenient method for producing piezoelectric layers with a thickness of up to 100 μm. The characteristics of thick-film ferroelectrics are similar to those of bulk materials [1]. The compositions of piezoelectric thick-films are almost exclusively based on $Pb(Zr_{1-x}Ti_x)O_3$ solid solutions, often referred to as PZT. The PZT material for sensors and actuators was a ferroelectric thick-film paste based on PZT 53/47 powder ($PbZr_{0.53}Ti_{0.47}O_3$). The material was made at the Jožef Stefan Institute.

The substrates for thick PZT films are mainly alumina or silicon [2, 3]. However, LTCCs (low-temperature co-fired ceramics) have some advantages over alumina substrates: mainly a lower Young's modulus (alumina 215–414 GPa,

D. Belavič (✉) · M. S. Zarnik
HIPOT—R&D d.o.o.,
Trubarjeva 7,
Sentjernej, 8310, Slovenia
e-mail: darko.belavic@ijs.si

M. Hrovat · J. Holc · M. Kosec
Jozef Stefan Institute,
Jamova 39,
Ljubljana, 1000, Slovenia

LTCC 90–110 GPa), which is important for sensor and actuator applications. Some of the characteristics of fired LTCC laminates in comparison with alumina are presented in Table 1.

LTCC materials are sintered at the low temperatures typically used for thick-film processing, i.e., around 850 °C. LTCC technology is a three-dimensional ceramic technology utilizing the third dimension (z) for the interconnects layers, the electronic components, and the different 3D structures, such as cavities, channels, diaphragms, cantilevers, bridges, or other structures. These possibilities are widely used for the production of high-density ceramic interconnections and increasingly also for MEMS (micro-electro-mechanical systems) [4–5].

The LTCC tape consists of alumina and glass particles suspended in an organic binder. The materials are either based on crystallisable glass or a mixture of glass and ceramics, for example, alumina, silica or cordierite ($Mg_2Al_4Si_5O_{18}$) [6]. The composition of the inorganic phase in most LTCC tapes is similar to, or the same as, materials in thick-film multilayer dielectric pastes. To sinter to a dense and non-porous structure at these, rather low, temperatures, it has to contain some low-melting-point glass phase. This glass could presumably interact with other thick-film materials (in our case thick-film PZT), leading to changes in the electrical characteristics [6–7].

Due to the chemical composition of an LTCC material and the shrinkage of an LTCC tape during sintering, special thick-film materials were developed. On the other hand, some special thick-film materials, such as PZT thick-film material, have not yet been developed for applications on LTCC tape. As a result, these materials can only be used on a pre-fired LTCC laminate. But before their application, the compatibility and the characteristics of these materials must be carefully investigated and evaluated.

Table 1 Some characteristics of fired LTCC and 94.0–99.5% Al_2O_3 ceramics.

Characteristic	LTCC	Al_2O_3
TEC ($\times 10^{-6}$/K)	5–7	7.6–8.3
Density (g/cm^2)	2.5–3.2	3.7–3.9
Flexural strength (MPa)	170–320	300
Young's modulus (GPa)	90–110	215–415
Thermal cond. (W/mK)	2.0–4.5	20–26
Dielectric constant	7.5–8.0	9.2–9.8
Loss tg. ($\times 10^{-3}$)	1.5–2.0	0.5
Resistivity (ohm cm)	10^{12}–10^{14}	10^{12}–10^{14}
Breakdown (kV/100 μm)	>4	3–4

Our preliminary investigations [8–10] and data from the literature [11–12] indicated that due to the interaction between the printed thick-film PZT layers and the LTCC substrates during firing the electrical and piezoelectic characteristics deteriorate significantly.

2 Experimental

PZT 53/47 powder ($PbZr_{0.53}Ti_{0.47}O_3$) with an excess of 6 mol% PbO was made from high-purity oxides (PbO, ZrO_2, and TiO_2). To this was added 2 wt% of lead germinate (the composition $Pb_5Ge_3O_{11}$) as a sintering aid. After the synthesis, both compositions were ball milled and dried. A thick-film paste was prepared from this material (PZT with 2% PGO) and an organic vehicle (ethyl cellulose, alpha-terpineol and butil carbitol acetate) by mixing on a three-roller mill.

For the microstructural investigation, and electrical and piezoelectrical characterisation a special test pattern was designed. This test pattern consists of 16 thick-film elements (capacitors) with lateral dimensions 4.7×4.7 mm and a thickness of about 50 μm. The top view of test sample is shown in Fig. 1 and the cross-section of thick-film structures is shown in Fig. 2. The test samples were made on alumina (which was used as a reference) and on pre-fired LTCC substrates. The dimensions of the substrates are 30.0×30.0×0.4 mm. The pre-fired LTCC substrates were prepared by laminating two layers of the LTCC tape

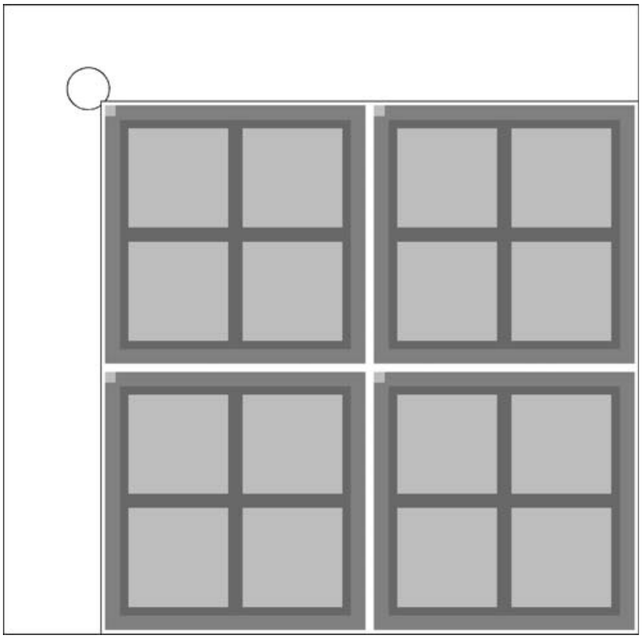

Fig. 1 The test sample of 16 thick-film elements—capacitors on the substrate

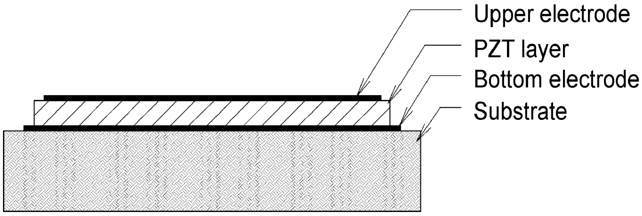

Fig. 2 The cross-section of thick-film PZT-on-substrate structure (schematic—not to scale)

(Du Pont, 951) at 70 °C and at a pressure of 200 bar. This laminate was then sintered in a one-step process with a special burnout-and-firing temperature profile with a peak temperature of 875 °C.

The thick-film structures were prepared by first printing and firing the gold or the silver conductor layer as bottom electrodes of the capacitors for 10 min at 850 °C. Over these electrodes the active PZT film was printed twice and fired, and then again printed twice and fired for 18 min at 850 °C. On the top of this structure the gold or the silver conductor layer, as the upper electrodes of the capacitors, was printed and fired for 10 min at 850 °C. In some test samples a barrier layer, based on PZT, as a first layer on the LTCC substrate was used. This layer acts as an intermediate layer between the LTCC substrate and the active PZT structure. The function of this layer is to prevent or to minimize the chemical interactions between the printed thick-film PZT layers and the LTCC substrates during the firings.

The approximate thicknesses of the test structures after the thermal treatments were as follows: gold electrode, 3 μm; silver electrode, 20 μm; active PZT layer, 50 μm; and intermediate PZT layer, 15 μm.

Six different types (combinations of substrate, electrode and barrier) of test samples were fabricated for the structural and electrical investigations. All the types were made with the same thick-film PZT material and with the same technological process. The list of test samples is shown in Table 2.

Table 2 List of test samples.

Test samples	Substrate	Electrode	Barrier
Type 1	Al_2O_3	Au	No
Type 2	Al_2O_3	Ag	No
Type 3	LTCC	Au	No
Type 4	LTCC	Au	Yes
Type 5	LTCC	Ag	No
Type 6	LTCC	Ag	Yes

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 microstructural and compositional analyses. The EDS spectra were quantified using the ZAF (*Z*—atomic number correction, A—absorption correction, and F—fluorescence correction) method and a library package of virtual standards. The library contains pre-recorded standard-element profiles under the same experimental conditions.

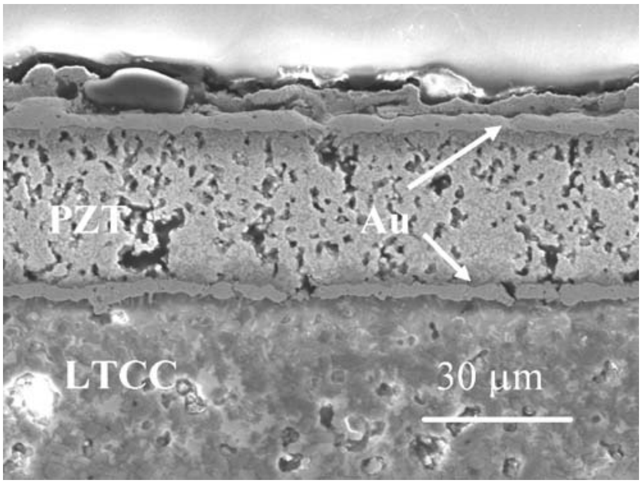

Fig. 3 Microstructure of the cross-section of the test sample type 3

The electrical characteristics of all the capacitor test samples were measured. The dielectric permittivity and the dielectric losses were measured with an HP-4284 Precision LCR Meter at a frequency of 1 kHz. After this measurement the samples were heated to 160 °C and polarised with an electrical field of 100 kV/cm for 20 min and then cooled to room temperature.

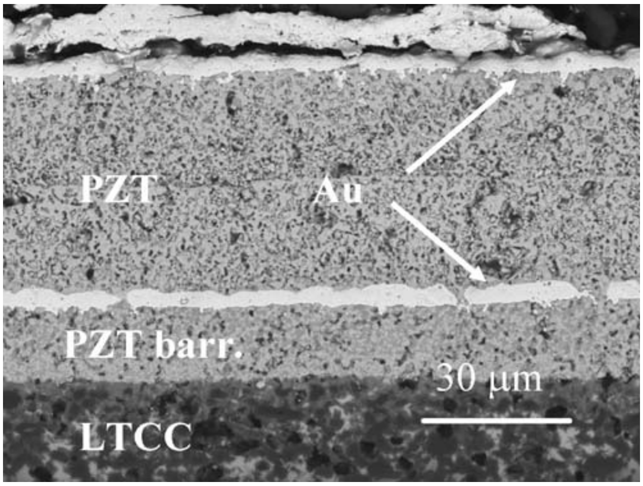

Fig. 4 Microstructure of the cross-section of the test sample type 4

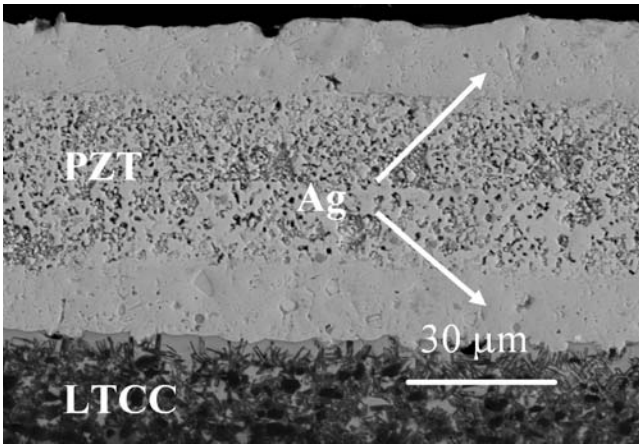

Fig. 5 Microstructure of the cross-section of the test sample type 5

The values of the piezoelectric coefficient d_{33} were estimated by using the conventional Berlincourt method at 100 Hz with a "Piezometer system PM 10". The standard samples for this method are bulk pellets with defined dimensions. As our thick-film samples fired on rigid substrates are non-standard, the obtained values are only used for the benchmarking of different technologies.

3 Results and discussion

The microstructures of the cross-sections of the samples with and without the PZT barrier on LTCC substrates are shown in Fig. 3 (gold electrodes, without barrier), Fig. 4 (gold electrodes, barrier), Fig. 5 (silver electrodes, without barrier) and Fig. 6 (silver electrodes, barrier). 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. The thickness of the PZT barrier layer is around 15 μm. During firing the PbO diffused from the PZT films, either from the active layers or from the barrier layers, into the LTCC. The lighter layers on the top of the LTCC substrates are rich in PbO. The estimated depth of the PbO diffusion layer is between 20 and 30 μm.

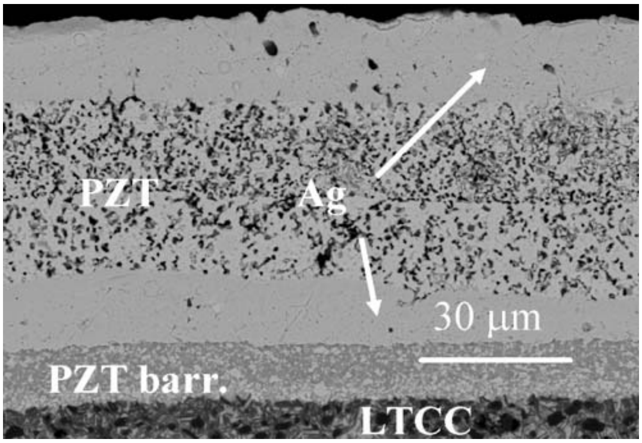

Fig. 6 Microstructure of the cross-section of the test sample type 6

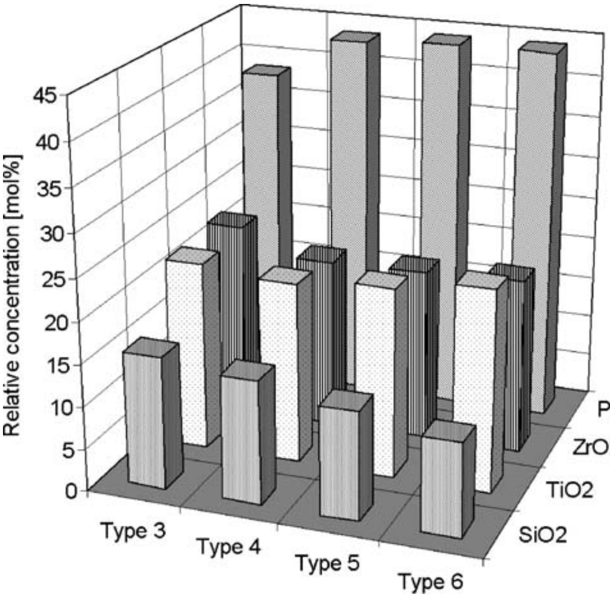

Fig. 7 Relative concentration of the oxides in the PZT layer of different types of samples

The EDS microanalysis of the PZT layers showed, besides Pb, Zr and Ti, a relatively high concentration of Si, indicating the diffusion of the silica-rich glassy phase from the LTCC into the PZT. The concentrations of the oxides in the PZT layers with silver and gold electrodes, and with or without the barrier, are shown in Fig. 7. The concentrations of SiO_2 are higher for structures with gold electrodes (around 15%) than for silver electrodes (around 12%). The difference is attributed to the thicker silver electrodes, which act as a barrier to the diffusion. The intermediate PZT layer, as an added barrier, also slightly decreased the SiO_2 concentration.

Table 3 Electrical characteristics (dielectric constant ε', dielectric loss tan δ, and piezoelectric constant d_{33}) of the PZT layers on the alumina and LTCC substrates.

Test samples	(pC/N) d_{33}	(@1 kHz) ε	tan δ
Type 1	138	490	0.020
Type 2	96	515	0.028
Type 3	78	200	0.016
Type 4	81	225	0.011
Type 5	61	410	0.017
Type 6	58	445	0.011

The dielectric permittivities (ε), dielectric losses (tan δ), and piezoelectric coefficients (d_{33}) were measured for the capacitors on all types of substrates and are presented in Table 3. Two main influences on the measured properties can be observed, i.e., the substrate and the electrodes, while the additional intermediate PZT layer does not have a significant influence on the properties.

The influence of the additional intermediate PZT layer on the piezoelectric coefficients (d_{33}) is within the measurement uncertainty. In contrast, the structures on the LTCC substrate with the additional intermediate PZT layer have between 10% and 15% higher values of the dielectric permittivity.

4 Conclusions

The compatibility of thick-film piezoelectric (lead zirconate titanate—PZT) material with LTCC substrates (Du Pont 971) was studied. Thick-film PZT material was evaluated as a possible actuator or sensor for C-MEMS. For the investigation of the properties the thick-film PZT ($Pb(Zr_{0.53}Ti_{0.47})O_3$) paste was screen-printed and fired on LTCC substrates and alumina as a reference. The values of the dielectric permittivity (ε) and the piezoelectric constant (d_{33}) of the PZT layers on the LTCC substrates were about half those of the values on the alumina. The additional PZT intermediate layer between the LTCC substrate and the active PZT layer increases the values of the dielectric constant by about 10–15%. For thicker bottom and upper silver electrodes the values of the dielectric permittivity (ε) are higher and the values of the piezoelectric constant (d_{33}) are lower.

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