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Thick-film temperature sensors on alumina and LTCC substrates

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Abstract

The electrical and microstructural characteristics of 1 kΩ/sq. thick-film thermistors with high positive or negative temperature coefficients of resistivity, i.e., PTC 5093 (Du Pont) and NTC 4993 (EMCA Remex), fired on alumina or co-fired on "green" low-temperature co-fired ceramic (LTCC) substrates, are compared. The active phase in both materials (the ruthenium oxide and the semiconducting spinel in the PTC and NTC thermistors, respectively) is not present in the dried films but is formed during firing. The differences in the measured electrical parameters (sheet resistivities, temperature dependence of resistivities and noise) of the thermistors, fired on alumina or on LTCC were attributed to the interactions between the thermistor layers and the glassy LTCC substrates. The inter-diffusion of oxides, mainly PbO and SiO_2, was confirmed by microanalysis.

Keywords: Films; PTC; NTC; LTCC; Interactions; Electrical parameters; RuO_2

1. Introduction

The main requirements for thick-film resistors are long-term stability and relatively narrow tolerances of the sheet resistivities after firing. An important characteristic is a low temperature coefficient of resistivity (TCR), which for most modern resistors is around or under $50 \times 10^{-6}\,K^{-1}$. However, for some temperature-sensing applications resistors with a large temperature dependence of resistivity (thermistors) are required. Thick-film thermistors with positive TCRs (PTC) have a positive and linear temperature dependence of resistivity while thermistors with negative TCRs have a large and strongly non-linear dependence.

PTC thick-film resistors have a metallic-like dependence of resistivity versus temperature One way to prepare PTC thermistors is to "load" a high concentration of RuO_2 into the glass phase. RuO_2 has a relatively low specific resistivity, $40 \times 10^{-6}\,\Omega\,cm$, and a positive, linear, metallic-like dependence of resistivity versus temperature, with a TCR of $7000 \times 10^{-6}\,K^{-1}$ for single crystals and a few $1000 \times 10^{-6}\,K^{-1}$ for sintered microcrystalline samples.[1,2]

The dependence of the resistance versus temperature for PTC resistors is described by the following linear equation:

$$R(T) = R_0(1 + aT) \tag{1}$$

where R_0 (Ω) is the resistance at room temperature; T, absolute temperature (K) and a, TCR (1/K).

Materials with large negative TCRs (NTC) are based on solid solutions of transition-metal oxides. Mostly, due to their long-term stability, the compounds are solid solutions of Mn_3O_4, Co_3O_4 and NiO oxides with the spinel structure (general formula AB_2O_4). The dependence of the resistance

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versus temperature is normally written as:

$$\beta = \ln\left(\frac{R_1/R_2}{(1/T_1) - (1/T_2)}\right) \qquad (2)$$

where R_1 and R_2 are the resistances at T_1 and T_2; T, absolute temperature and β, thermistor constant (also called the beta factor or the coefficient of temperature sensitivity).

The values of the resistivities and the beta factors of NTC thick-film materials depend on the ratio of the oxides (Mn_3O_4, Co_3O_4 and NiO). The resistivities range from a few hundred Ω cm to a few tens of kΩ cm, and the beta factors from 2500 K to 4000 K.[3–5] The compositions with a minimum resistivities, maximum beta factors and the lowest temperature coefficients of expansion ($8.2 \times 10^{-6}\,K^{-1}$) are manganese rich. A partial substitution of the iron oxide on the B sites or the copper oxide on the A sites increases or decreases the resitivities.[6–9]

As mentioned before, the resistivities of different spinel compositions are between a few hundred Ω cm and a few tens of kΩ cm, and can be increased up to 1 MΩ cm with the partial substitution of manganese ions with iron ions or decreased to a few tens of Ω cm with the partial substitution with copper ions. However, due to the dimensions of the thick-film resistors (the fired thickness of thick-film layers is usually between 10 μm and 20 μm) the values of the sheet resistivities (Ω/sq.) are between 2 and 3 orders of magnitude higher than the resistivities (Ω cm) of the materials themselves. Therefore, materials for thick-film NTC resistors usually include some phase with a low specific resistance, generally RuO_2. The addition of ruthenium oxide decreases the specific resistance, reduces the noise and improves the stability of the resistors.[6,10] However, due to the RuO_2 high positive TCR (see above) it also decreases the beta factors.

Ceramic multi-chip modules (MCM-Cs) are multilayer substrates with buried conductor lines, which means they have a high density of interconnections. Low-temperature co-fired ceramic (LTCC) materials, which are sintered at the low 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. LTCCs are either based on crystallisable glass or a mixture of glass and ceramics.[11,12]

Thick-film resistors with high TCRs are of interest as temperature sensors in MCM-Cs as well as in MEMS (Micro Electronical Mechanical Systems).[13,14] However, as the thick-film PTC and NTC thermistors are developed for firing on alumina substrates, their compatibility and interactions with the rather glassy LTCC substrates, leading to changes in the electrical characteristics, needs to be evaluated.

The aim of this paper is to compare the characteristics of 1 kΩ/sq. thick-film PTC (5093, Du Pont) and NTC (4993, EMCA Remex) thermistors fired on 96% alumina and on Du Pont LTCC 951 substrates. The nominal TCR of PTC 5093 and the beta factor of NTC 4993 are $2750 \pm 250 \times 10^{-6}\,K^{-1}$ and 1200 K, respectively.

2. Experimental

The PTC 5093 and NTC 4993 thermistors were screen printed and fired for 10 min at 850 °C on 96% alumina and on green LTCC (951, Du Pont) substrates. The LTCC substrates were made by laminating three layers of LTCC tape at 70 °C and at a pressure of 200 bar. The thick-film thermistors were terminated with Pd/Ag electrodes that were prefired at 850 °C on alumina substrates, and co-fired together with printed thermistors and LTCC substrates. The dimensions of the resistors for microstructural analysis and X-ray diffraction (XRD) analysis, which were printed and fired without conductor terminations, were 12.5 mm × 12.5 mm.

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 energy-dispersive X-ray analyser (EDS) was used for the overall microstructural and compositional analysis. Boron oxide, which is also present in the glass phase, cannot be detected in the EDS spectra because of the low relative boron weight fraction in the glass and the strong absorption of the boron Kα line during EDS analysis in the glass matrix. Dried thermistors (150 °C) and thermistors fired at 850 °C were analysed by XRD analysis with a Philips PW 1710 X-ray diffractometer using Cu Kα radiation. X-ray spectra were measured from $2\Theta = 20°$ to $70°$ in steps of 0.02°.

Cold (from −25 °C to 25 °C) and hot (from 25 °C to 125 °C) TCRs were calculated from resistivity measurements at −25 °C, 25 °C and 125 °C. The current noise was measured in dB on 100-mW loaded resistors using the Quan Tech method (Quan Tech Model 315-C).

3. Results and discussions

X-ray spectra of the Du Pont LTCC 951 tapes, unfired and fired at 850 °C, are shown in Fig. 1.[15] The unfired material is a mixture of alumina and glass. After firing, peaks of anorthite ($(Na,Ca)(Al,Si)_4O_8$) phase appear. The peaks of alumina and anorthite are denoted by "A" and asterisk, respectively.

3.1. PTC 5093 thermistors

The conductive phase in un-fired PTC 5093 thermistors is based on $(Bi,Gd)_2Ru_2O_7$ ruthenate with a Bi/Gd ratio of (roughly) 1/2.[16] The microstructures of the surfaces of the PTC 5093 thermistors dried at 150 °C and fired at 850 °C are shown in Figs. 2 and 3, respectively. The larger grey particles in the dried paste are glass phase, based on lead-boro-silicates with the addition of Al_2O_3, ZrO_2 and BaO. The molar ratio of SiO_2/PbO is around 3/1. The micrometer- or sub-micrometer-sized white particles are ruthenate phase, rich in ruthenium, gadolinium and bismuth, i.e., $(Bi,Gd)_2Ru_2O_7$. After firing the surface is glassy and densely sintered. The small black

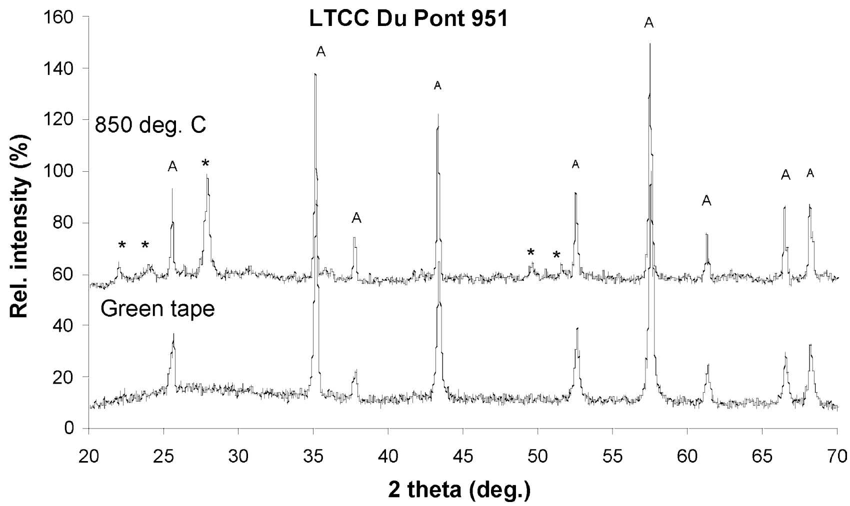

Fig. 1. X-ray spectra of green and fired (850 °C) Du Pont LTCC 951 tapes.[16] The peaks of alumina and anorthite are denoted "A" and asterisk, respectively.

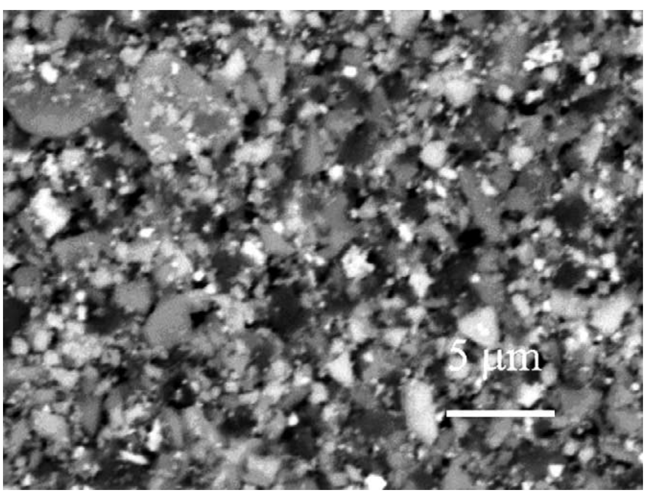

Fig. 2. The microstructure of the surface of the PTC 5093 thermistor dried at 150 °C.

"dots" are too small for an accurate EDS microanalysis, but they appear to be rich in Si and contain a relatively high concentration of Cu. The larger dark particles are rich in Si and Zr, and are presumably $SiZrO_4$.

Cross-sections of the PTC 5093 thermistors fired on alumina and LTCC substrates are shown in Figs. 4 and 5, respectively. The microstructure of PTC 5093 on alumina shows three distinct layers: the layer with small, sub-micrometer-sized round inclusions on the top (left side of Fig. 4); the middle layer with whitish areas, rich in Ru, in the glass phase; and a darker glassy layer, rich in alumina, near the alumina substrate. The glass infiltrates into the substrate to depths of around 5 μm, promoting the growth of Al_2O_3 grains, presumably due to a dissolution–precipitation mechanism. The EDS microanalysis of the light-coloured spots shows a high concentration of Ru and Cu with only traces of Bi and Gd. The results indicate the decomposition of ruthenate into Bi_2O_3 and Gd_2O_3, which are dissolved in the glass and RuO_2. The

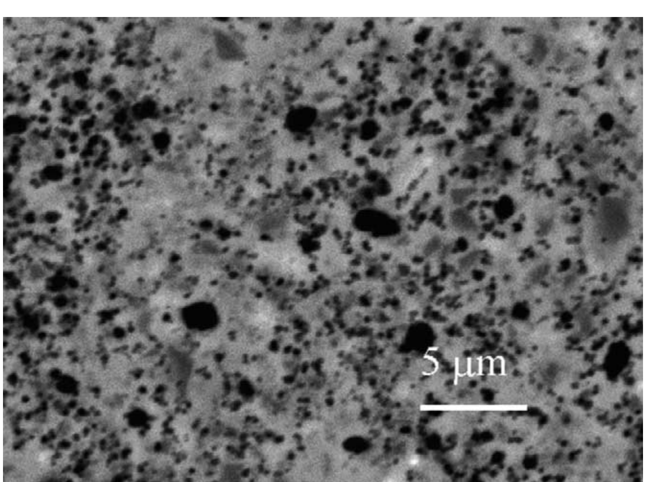

Fig. 3. The microstructure of the surface of the PTC 5093 thermistor fired at 850 °C.

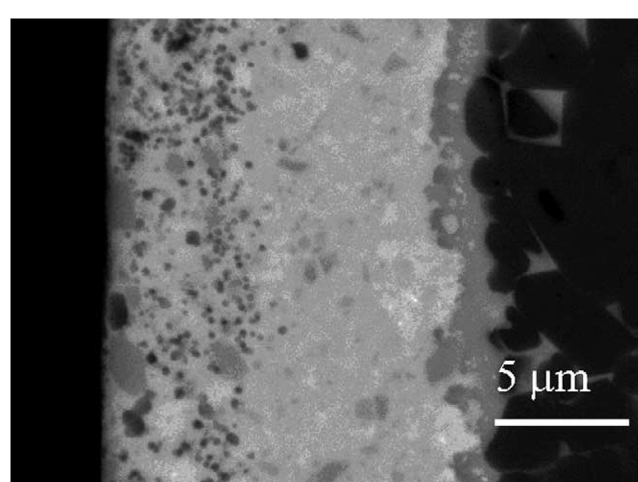

Fig. 4. Cross-section of PTC 5093 thermistor fired at 850 °C on alumina. The alumina substrate is on the right.

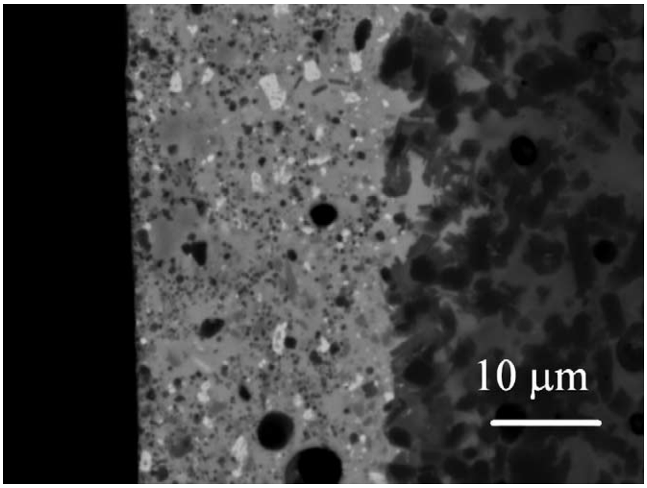

Fig. 5. Cross-section of PTC 5093 thermistor fired at 850 °C on LTCC. The LTCC substrate is on the right.

microstructure of the PTC 5093 on LTCC (Fig. 7) is more homogenous. Again, some interaction at the interface between the PTC film and the substrate can be observed.

The EDS microanalyses over the whole cross-sections of the PTC films (area 15 μm × 15 μm) on the alumina and LTCC substrates are presented in Table 1. The compositions are given for elements in at.%. The higher concentration of Al and the lower concentration of Pb in the films, fired on LTCC substrates indicate the diffusion of Al_2O_3 from the LTCC into the PTC and of the PbO from PTC into the LTCC.

The X-ray diffraction spectra of the PTC 5093 thermistors dried at 150 °C and fired at 850 °C on alumina and co-fired on LTCC substrates are shown in Fig. 6. The spectrum of ruthenium oxide, denoted "RuO_2", is also included. The peaks of ruthenate phase in the dried films are denoted "RU". The dried PTC 5093 composition is based on ruthenate, with an addition of Cu_2O. After firing for 10 min at 850 °C the peaks of ruthenate and Cu_2O disappear and the peaks of RuO_2 appear.

Table 1
The EDS analyses of the concentration of elements in at.% of over the 15 μm × 15 μm area of the cross-sections of the PTC films, fired at 850 °C on alumina and LTCC substrates

Element (at.%)	Al_2O_3 substrate	LTCC substrate
Al	2	4
Si	19	20
Cu	3	3
Zr	2	2
Ru	2	2
Ba	<1	<1
Gd	<1	<1
Pb	6	3
Bi	1	<1
O	63	63

The peaks at 2Θ ~20° and ~53° in the XRD spectra can be attributed to the two of four strongest reflections, i.e., (1 0 1) and (3 1 2), of the $ZrSiO_4$ compound (JCPDS file PDF-83-1383), which was detected with EDS analyses in the microstructures of the thermistor material. Note that the peaks at 2Θ ~27° (2 0 0) and at 2Θ ~35° (1 1 2) are overlapping with peaks of RuO_2. The decomposition of ruthenate and the formation of the RuO_2 is presumably due to the interaction between the glass phase and the ruthenate in the PTC 5093 thermistor. Adachi and Kuno,[17,18] who studied high-temperature interactions between $PbO–B_2O_3–SiO_2$ glasses and $Pb_2Ru_2O_{6.5}$ or RuO_2, reported the disappearance of $Pb_2Ru_2O_{6.5}$ and the formation of RuO_2 at higher firing temperatures. The decomposition of the ruthenate phase depends on the concentration of PbO in the glass, i.e., the lower the concentration of the PbO in the glass the lower the temperature of the decomposition will be. A similar mechanism can presumably be applied here. The (Bi,Gd)-ruthenate decomposes to Bi_2O_3 and Gd_2O_3, which are dissolved in the glass, and to the RuO_2.

Usually, rather high temperatures and long firing times (e.g., 950 °C and a few hours) are required for "normal", low-TRC ruthenate-based resistors, the characteristics of which

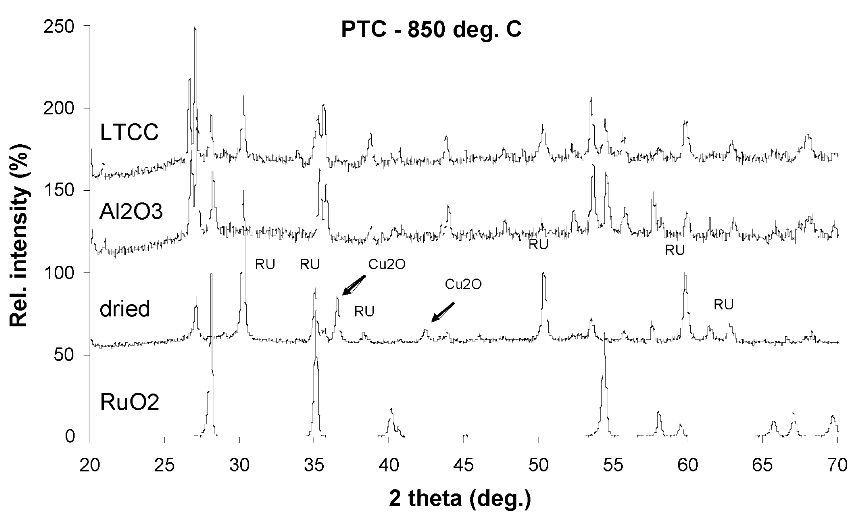

Fig. 6. The X-ray diffraction spectra of the PTC 5093 thermistors dried at 150 °C and fired at 850 °C on alumina and on LTCC substrates. The spectrum of ruthenate, denoted "RuO_2", is also included. The peaks of ruthenate phase in the dried films are denoted "RU".

Table 2
Sheet resistivities, cold (−25 °C to 25 °C) and hot (25 °C to 125 °C) TCRs, beta factors and noise indices of the PTC 5093 thermistors on alumina and on LTCC substrates

Substrate	R sheet (Ω/sq.)	Cold TCR ($\times 10^{-6}\,K^{-1}$)	Hot TCR ($\times 10^{-6}\,K^{-1}$)	Noise (dB)	Noise (μV/V)
A_2O_3	850	2570	2580	−11	0.28
LTCC	180	3070	3075	−32	0.02

have to be reasonably independent of the processing parameters for the phase transformation of the conductive phase from the ruthenate to the RuO_2 to take place.[19,20] The results of the EDS analysis of the glass phase in the PTC 5093 resistor and in the “normal”, i.e., low-TCR thick-film 1 kΩ/sq. resistor, showed that the molar SiO_2/PbO ratio in the PTC 5093 thermistor is significantly higher (more than 3) than in the “normal”, low TRC resistor (around 2). A relatively low concentration of lead oxide in the PTC 5093 thermistors means that the reaction between the ruthenate and the glass occurs at lower firing temperatures, i.e., below 850 °C.

The sheet resistivities, the cold (−25 °C to 25 °C) and hot (25 °C to 125 °C) TCRs, and the noise indices of the PTC 5093 thick-film thermistors fired for 10 min at 850 °C on alumina and on LTCC substrates are shown in Table 2. The sheet resistivities versus temperature are shown in Fig. 7. The noise is given in (dB) and in (μV/V). These are related with the simple equation:

$$\text{noise (dB)} = 20 \log \text{noise} \left(\frac{\mu V}{V}\right) \tag{3}$$

The PTC 5093 thermistors co-fired on LTCC (as compared to resistors fired on alumina substrates) have lower sheet resistivities (180 Ω/sq. versus 850 Ω/sq.), around 20% higher TCRs ($3070 \times 10^{-6}\,K^{-1}$ versus $2570 \times 10^{-6}\,K^{-1}$), and significantly lower noise indices (−11 dB versus −32 dB).These results could be attributed to the interaction between the PTC films and the LTCC substrates during firing, as described above.

3.2. NTC 4993 thermistors

The microstructures of the surfaces of the NTC 4993 thermistors dried at 150 °C and fired at 850 °C, are shown in Figs. 8 and 9, respectively. The dried paste is a mixture of lighter grains (glass phase) and darker grains. The light grains are composed mainly of SiO_2 and PbO with around 5 mol.% of alumina. The EDS analysis of the darker phase shows the presence of Mn, Co, Ni, Cu and Ru oxides. The elemental ratio between Mn-, Co- and Ni-oxides is roughly 6/2/1, which puts this composition close to those of the materials with the

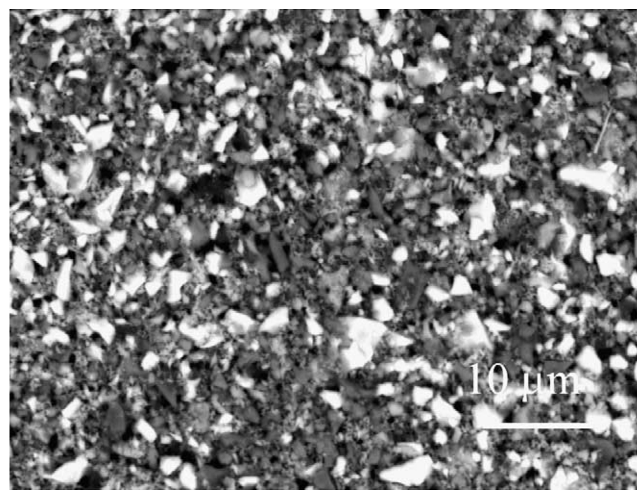

Fig. 8. The microstructure of the surface of the NTC 4993 thermistor dried at 150 °C.

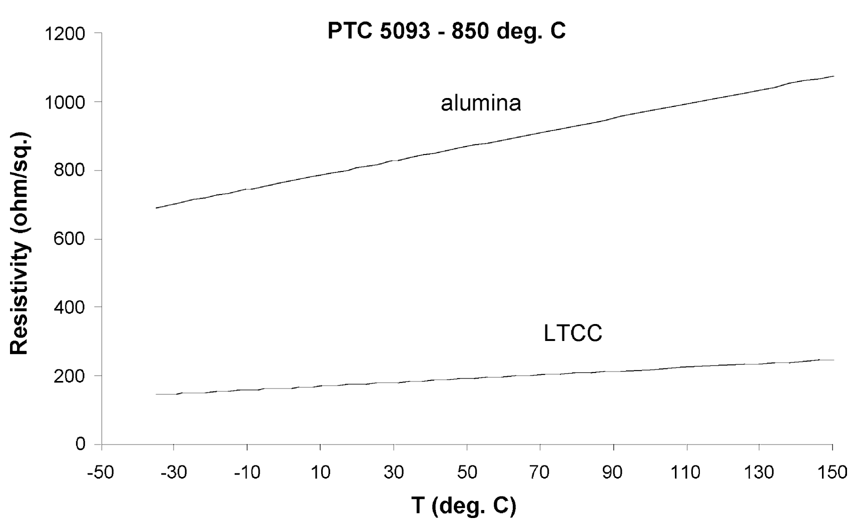

Fig. 7. The sheet resistivities vs. temperature for PTC 5093 thermistors fired at 850 °C on alumina and on LTCC substrates.

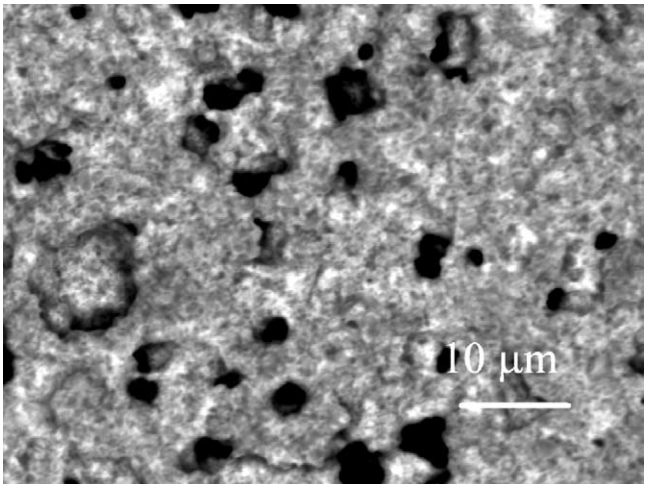

Fig. 9. The microstructure of the surface of the NTC 4993 thermistor fired at 850 °C.

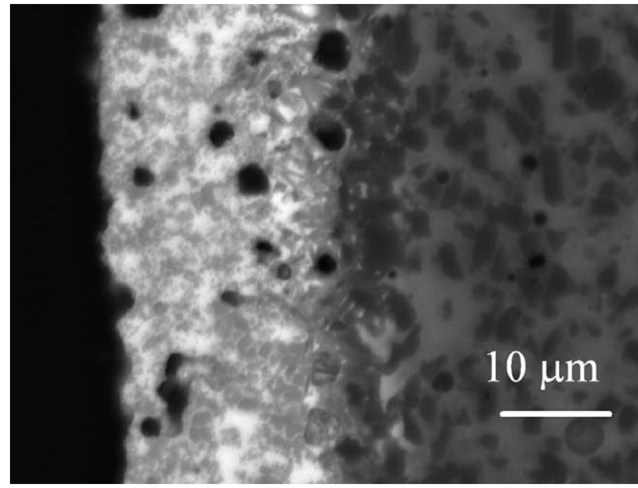

Fig. 11. Cross-section of 4993 NTC thermistor fired at 850 °C on LTCC. The LTCC substrate is on the right.

lowest specific resistances.[5] The microstructure of the surface of the thick-film thermistors fired at 850 °C is glassy and porous with pore dimensions up to 10 μm. The lighter phase is a glass phase.

Cross-sections of the NTC 4993 thermistors fired at 850 °C on alumina and LTCC substrates are shown in Figs. 10 and 11, respectively. In both cases the films are porous. An interaction layer on the interface between the NTC film and the substrate is observed for both substrates. The thin, light-coloured phase on the alumina side is lead-oxide rich and indicates the diffusion of PbO into the alumina ceramics. The darker interface within the LTCC substrate near the interface is rich in alumina, which presumably diffused from the LTCC into the NTC film.

The EDS microanalyses over the whole cross-sections of the NTC films (area 20 μm × 20 μm) on the alumina and LTCC substrates are presented in Table 3. The compositions are given for elements in at.%. A higher concentration of SiO_2 in the NTC films fired on LTCC substrates than in the films-fired on alumina substrates indicates a significant diffusion of silica from the LTCC into the thick-film NTC thermistors during firing.

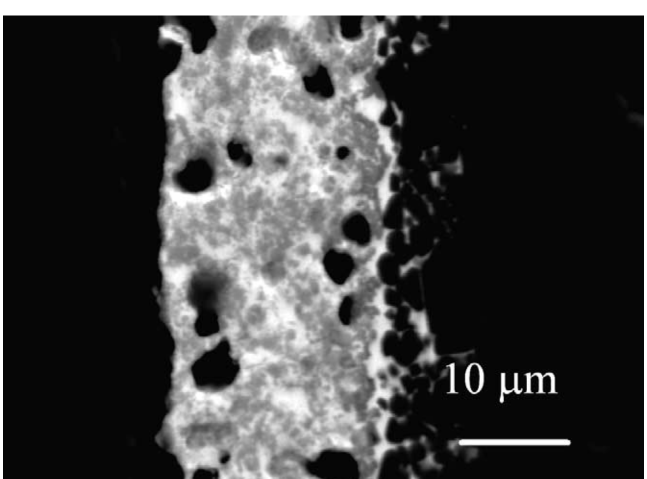

Fig. 10. Cross-section of 4993 NTC thermistor fired at 850 °C on alumina. The alumina substrate is on the right.

The X-ray diffraction spectra of the NTC 4993 thermistors, dried at 150 °C and fired at 850 °C on alumina and co-fired on LTCC substrates are shown in Fig. 12. The spectrum of ruthenium oxide, denoted "RuO_2", is also included in the graph. It is interesting to note that peaks of spinel phase (denoted "SP") appear after firing, but are not present in the dried thick-film. This means that the active phase is formed during the firing and is not included as a prereacted compound. In fired layers the X-ray analyses show mainly spinel and RuO_2, which is added to the thick-film NTC materials, as mentioned in Section 1, to decrease the specific resistance and to improve the stability and the current noise. The presence of a few (non-marked) X-ray peaks, most notably the one at $2\Theta = 38°$, could be tentatively attributed to un-reacted oxides.

The sheet resistivities, cold (−25 °C to 25 °C) and hot (25 °C to 125 °C) TCRs, the beta factors and the noise indices

Table 3
The EDS analyses of the concentration of elements in at.% of over the 20 μm × 20 μm area of the cross-sections of the NTC films, fired at 850 °C on alumina and LTCC substrates

Element (at.%)	Al_2O_3 substrate	LTCC substrate
Al	7	7
Si	5	9
K	<1	<1
Ca	<1	<1
Mn	11	11
Co	4	4
Ni	2	2
Cu	6	5
Ru	2	2
Pb	4	4
O	58	56

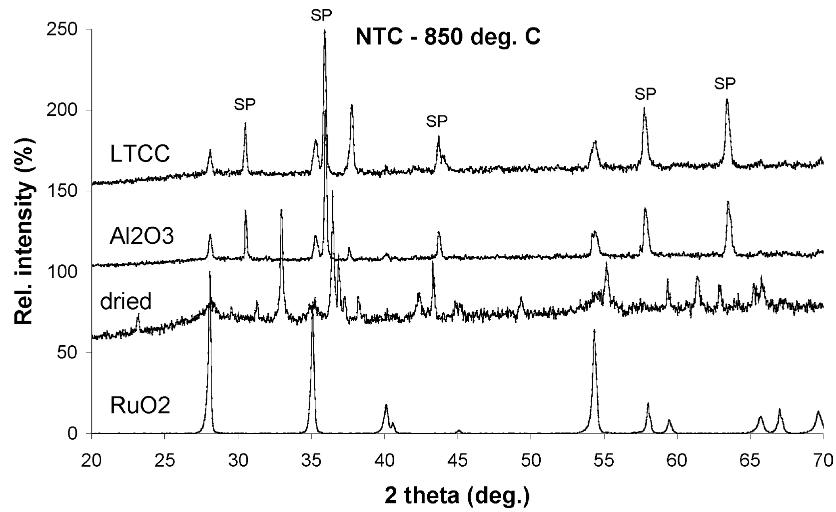

Fig. 12. The X-ray diffraction spectra of the NTC 4993 thermistors dried at 150 °C and fired at 850 °C on alumina and on LTCC substrates. The spectrum of ruthenate, denoted "RuO_2", is also included. The peaks of spinel phase are denoted "SP".

Table 4
Sheet resistivities, cold (−25 °C to 25 °C) and hot (25 °C to 125 °C) TCRs, beta factors and noise indices of the NTC 4993 thermistors on alumina and on LTCC substrates

Substrate	*R* sheet (Ω/sq.)	Cold TCR ($\times 10^{-6}$ K^{-1})	Hot TCR ($\times 10^{-6}$ K^{-1})	β (K)	Noise (dB)	Noise (μV/V)
Al_2O_3	550	−22700	−6510	1240	−12.2	0.25
LTCC	2250	−41500	−7550	1660	7.4	2.34

of the NTC 4993 thick-film thermistors, fired for 10 min at 850 °C on alumina and on LTCC substrates, are shown in Table 4. The logarithm of resistivity versus temperature is shown in Fig. 13. The noise is given in (dB) and in (μV/V) (see Eq. (3)).

The sheet resistivities of the NTC 4993 thick-film resistors are, at room temperature, around 500 Ω/sq. on alumina, while on the LTCC substrates they are four times higher. Similarly, the cold and hot TCRs and the beta factors of the thermistors fired on LTCC are higher than the values for the samples fired on alumina. These results can be attributed to the diffusion of the glassy phase from the LTCC substrates into the NTC films during firing. The additional glass presumably "breaks up" some of the conductive paths through the resistor film,

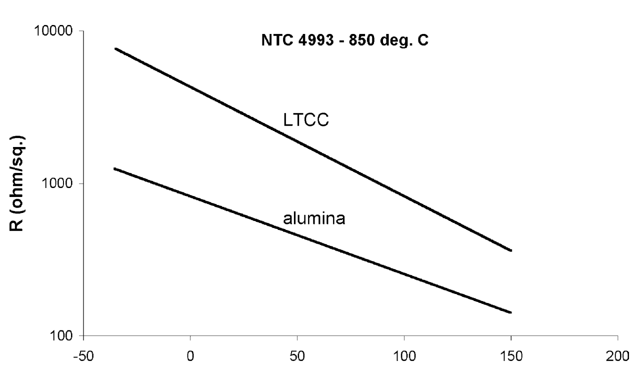

Fig. 13. Logarithm of resistivity vs. temperature for NTC 4994 thermistors, fired at 850 °C on alumina and on LTCC substrates.

thereby increasing the sheet resistivities as well as the noise indices. Just for a comparison, the noise indices of the "ordinary" thick-film resistors with low TCRs and with the same nominal sheet resistivities, i.e., 1 kΩ/sq., are around −18 dB (0.1–0.2 μV/V).[19]

4. Conclusions

The electrical and microstrutural characteristics of 1 kΩ/sq. PTC 5093 (Du Pont) and NTC 4993 EMCA Remex thick-film thermistors, fired either on alumina or co-fired on "green" LTCC substrates, were compared. The dried PTC 5093 composition is based on ruthenate. After firing for 10 min at 850 °C the peaks of ruthenate and the peaks of RuO_2 appear. The decomposition of the ruthenate and the formation of the RuO_2 is presumably due to the interaction between the glass phase and the ruthenate. The PTC thermistors fired on LTCC (as compared to the resistors on alumina substrates) have around four times lower sheet resistivities, higher TCRs and significantly lower noise indices. These results can be attributed to the interaction between the PTC films and the LTCC substrates during firing. The EDS microanalysis indicated the diffusion of Al_2O_3 from the LTCC into the PTC and of PbO from the PTC into the LTCC.

In the fired layers of the NTC 4993 thermistors the X-ray analyses showed mainly the spinel phase and the RuO_2. The active phase is formed during the firing and is not included as a prereacted compound. The NTC resistors fired on LTCC (as compared to resistors on alumina substrates) have higher sheet resistivities, higher beta factors, and also significantly higher noise indices. SEM and EDX analyses indicated the interaction between the NTC and LTCC materials, mainly the diffusion of the glass phase from the LTCC substrate into the NTC resistor.

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