

Thick-film PTC thermistors and LTCC structures: The dependence of the electrical and microstructural characteristics on the firing temperature

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Abstract

The electrical and microstructural characteristics of 1 k Ω /sq thick-film thermistors with high positive temperature coefficients of resistivity, i.e., PTC 5093 (Du Pont) fired either on “green” LTCC (low-temperature co-fired ceramics) substrates or buried within LTCC structures, were evaluated. The thermistors were fired at different temperatures to study the influence of firing temperature on the electrical characteristics. The noise indices of the surface resistors fired at temperatures between 850 °C and 950 °C were very low, around –30 dB. The TCRs of the evaluated PTC thermistors were over $3000 \times 10^{-6}/\text{K}$. The dependence of the resistivity on the temperature between –25 °C and 125 °C was linear, with the values of R^2 being better than 0.9999, regardless of the processing conditions. These results show that PTC thermistors co-fired on LTCC substrates can be used for temperature sensors in MCM-Cs as well as in MEMS structures. However, when the thermistors were buried in the LTCC substrates, the LTCC structures delaminated during firing and blisters formed, leading to high sheet resistivities and high noise indices. This delamination is attributed to the different sintering rates of the PTC and LTCC materials as well as to the expansion of the air bubbles captured in the viscous glass of the PTC material.

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1. Introduction

Thick-film resistors are made by screen-printing thick-film paste onto insulating, mainly alumina, substrates. After printing and drying, the thick-film pastes are fired in a belt furnace. Thick-film resistor pastes consist basically of a conducting phase, a lead borosilicate-based glass phase and an organic vehicle. This organic material is burned out between 300 °C and 400 °C during the high-temperature processing. The ratio between the conductive and the glass phases roughly determines the specific resistivity of the resistor. In most modern resistor compositions the conductive phase is either RuO₂ or ruthenates, mainly bismuth or lead ruthenates.^{1–5} During the firing cycle all the constituents of the resistor material react with each other. The

main change during firing is the transition from a mixture of glass grains and, usually, much finer grains of the conductive phase in the thick-film paste, into conductive chains throughout the sintered glass in the fired resistor. The resistors, however, are only a relatively short time (typically 10 min) at the highest temperature (typically 850 °C). Because of this, the reactions between the constituents of the resistor material do not reach equilibrium, so that the characteristics of the fired materials are, in a way, a compromise as a consequence of this frozen non-equilibrium.^{6–8}

The main requirements for “normal” thick-film resistors are long-term stability, relatively narrow tolerances of the sheet resistivities after firing, low noise indices and, in particular, low temperature coefficients of resistivity (TCR), which are, for most commercial resistor series, below $100 \times 10^{-6}/\text{K}$. However, for some temperature-sensing or temperature-compensating applications resistors with a large, positive and linear temperature dependence of resistivity are required. Thick-film thermistors

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with positive TCRs (PTC) have a positive and linear temperature dependence of resistivity, as described by the following linear equation:

$$R(T) = R_0(1 + aT) \quad (1)$$

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

PTC thick-film resistors are prepared by “loading” a high concentration of RuO_2 into a glass phase. RuO_2 has a relatively low specific resistivity, $40 \times 10^{-6} \Omega \text{ cm}$, and a positive, linear, metallic-like resistivity versus temperature dependence, with a TCR of $7000 \times 10^{-6}/\text{K}$ for single crystals and a few $1000 \times 10^{-6}/\text{K}$ for sintered microcrystalline samples.^{9,10} Due to the high concentration of RuO_2 , the sheet resistivities are relatively low, between $1 \Omega/\text{sq}$ and $10 \Omega/\text{sq}$. The majority of thick-film PTC thermistors are in this resistivity range.

The Du Pont 5093 PTC thermistors with a sheet resistivity of $1 \text{ k}\Omega/\text{sq}$ are currently the thermistors with the highest sheet resistivity values commercially available, to the best of the authors’ knowledge. The high resistivity is achieved with materials that are not based on ruthenium oxide, but on ruthenates with an addition of copper oxide.^{11,12} It is known that at high enough temperatures and/or long enough firing times the ruthenate conductive phase in most ruthenate-based thick-film resistors decomposes due to interactions with a glass phase into RuO_2 and, for example, PbO or Bi_2O_3 in the case of lead ruthenate or bismuth ruthenate, respectively.^{8,13}

Because of the added copper oxide, the RuO_2 , which is formed due to the decomposition of the ruthenate phase in the 5093 PTC thermistors during firing, crystallises in the form of needle-like grains, which produce the conducting network through the glass matrix. This is a result of a specific crystallographic relationship between the CuO and the RuO_2 ,¹⁴ and is shown schematically in Fig. 1a. The microstructure of the 5093 thermistor fired for 10 min at 850°C is shown in Fig. 1b.¹⁵ The needle-like RuO_2 grains are denoted “R”, and the SiZrO_4 particles are denoted “SZ”.

Ceramic multi-chip modules (MCM-Cs) are multilayer substrates with buried conductor lines, which means that they have a high density of interconnections. An additional advantage of the smaller size and higher density is the ability to integrate screen-printed resistors, or occasionally, capacitors and inductors. These screen-printed components can be placed either beneath the discrete components on the surface of the multilayer dielectric or buried within the multilayer structure. 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. To sinter to a dense and non-porous structure at these, rather low, temperatures, it has to contain some low-melting-point glass phase. LTCCs are either based on crystallisable glass or a mixture of glass and ceramics; for example, alumina, silica or cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$).^{16–20} The glass could presumably interact with, for example, thick-film resistors leading to changes in the electrical characteristics. Some of the

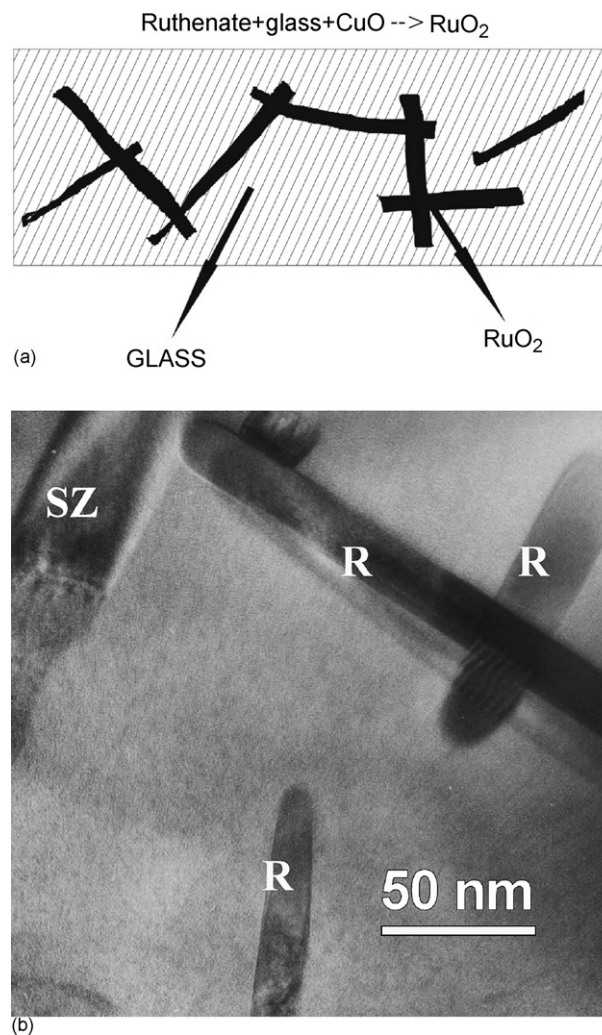


Fig. 1. (a) The ruthenate conductive phase in thick-film resistors decomposes due to interactions with a glass phase into RuO_2 . Due to added copper oxide the RuO_2 crystallises in the form of needle-like grains. Schematically. (b) TEM micrograph of 5093 thermistor, fired for 10 min at 850°C . Elongated RuO_2 particles are denoted “R” and SiZrO_4 particles are denoted “SZ”.¹⁵

results for the resistor/LTCC combinations and the influences on the electrical characteristics can be found in.^{21–24}

Thick-film resistors with high TCRs are of interest as temperature sensors in MCM-Cs as well as in MEMS (Micro Electro Mechanical Systems).^{25–28} The thick-film PTC thermistors were developed for firing on alumina substrates. Therefore, their compatibility and interactions with the rather glassy LTCC substrates, leading to changes in the electrical characteristics, need to be evaluated. The aim of this research was to study the characteristics of thick-film PTC 5093 thermistors fired either on or buried within Du Pont LTCC 951 substrates, and to obtain some understanding of the development of the thick-film thermistor’s microstructural characteristics and electrical characteristics, i.e., sheet resistivity, beta factor and noise, during the firing process. The thermistors were fired at temperatures from 850°C to 950°C , and also for a relatively long time (3 h) at 950°C to allow reactions to reach or at least to come close to equilibrium. The obtained results would be also usable for application were the

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