Effects of Firing Conditions on Thick-Film PTC Thermistor Characteristics in LTCC Technology

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Abstract

Thick film resistors are prepared as pastes, which are screen-printed and fired on dielectric substrates such as alumina and widely used in hybrid circuits. The final resistor properties are mostly influenced by the firing conditions and the interactions between the elements in the substrate and the resistor. In this study, conductor – resistor (PTC thermistor) pairs of selected compositions of different chemical origin are post fired on low temperature co-fired ceramic (LTCC) and alumina substrates, the latter being considered as the reference. The effects of firing temperatures on main thermistor characteristics such as temperature coefficient of resistance (TCR), standard deviation of TCR and non-linearity are presented and discussed.

Introduction

Low-temperature co-fired ceramic (LTCC) technology has become well-established due to its applications in wireless device, radar modules, packaging and all fields where high integration and reliability are important [1].

Recently, LTCC technology has also attracted much interest in the field of sensors and actuators due to ease of fabrication of complex 3–D structures, low cost, stability and ruggedness compared to silicon-based micro - electromechanical systems (MEMS). Devices such as flowmeters [2], pressure sensors [3], pumps and microreactors [4]. have been demonstrated. The ease of integration of fluidics and electrical functions into the same device while maintaining hermetic separation between the two is a strong advantage of LTCC technology.

Many devices such as flowmeters and microreactors require temperature-sensitive elements for their operation, which are screen-printed as thick films onto the LTCC device. However, these compositions have been developed for alumina substrates, and their compatibility with LTCC is questionable.

In this work, we examine the firing behaviour of two commercial thick-film positive temperature coefficient (PTC) thermistor compositions, on LTCC and alumina, as a function of LTCC and resistor firing temperature, and resistor termination material.

Experimental

The resistor test pattern shown in Figure 1 was used for electrical measurements. It comprises resistors of length 0.3, 1.0, 1.5 and 5.0 mm, with the 1.5 mm resistor repeated 5 times. Alumina (96%, Kyocera) or LTCC (Du Pont 951) was used as substrate material. The LTCC was pre-fired before deposition of resistors, at a peak temperature of T_s = 850, 875 or 900°C.

Conductor material for contacts and resistor terminations was Au (Du Pont 5744) or Ag:Pd:Pt (ESL 9562), where Ag:(Pd+Pt) = 25:1, referred to as "Ag" in this work. The conductor film was pre-fired at 850°C onto the alumina or LTCC substrate.

Figure 1. Thermistor test pattern layout.

One of the two PTC thermistor compositions, Du Pont 5092D (100 Ohm nominal sheet resistance) or Du Pont 5093D (1'000 Ohm), was then printed and fired at T_r = 850, 875 or 900°C, using a standard thick-film resistor firing profile, e.g. 10 min at peak and 45 min total firing time.

Samples were measured after firing at 30, 65 and 100°C, and a quadratic value-temperature curve was derived for each resistor. From this curve, the sheet resistance at 25°C (R_s) and the "hot" temperature coefficient of resistance (HTCR), between 25 and 100°C, were derived. For each preparation condition, 2 or 3 test patters were used in order to obtain a significant amount of identical resistors.

In order to better elucidate the structural evolution of the thermistors, dilatometry experiments were also carried out on pressed pellets of dried paste.

Electrical properties

Results as a function of resistor temperature, for a LTCC firing temperature T_s=875°C, are given in Figure 2 for the 1.5 mm long resistors.

Unexpectedly, the thermistors behave much better on the LTCC than on alumina. On LTCC, R_s and TCR values are more or less on par with the nominal ones [5] around 875°C firing temperature.

On alumina, on the other hand, process sensitivity is very high, as evidenced from the extended results shown in Figure 3, taken from another series of samples: there is a very narrow minimum of resistance vs. temperature for both compositions, around 825…830°C, where the nominal values are obtained.

For resistors fired at 850°C, the firing temperature of the substrate has little influence on the properties (Figure 4). This is expected since this LTCC material undergoes little structural transformations between 850 and 900°C [6].

For the 1.5 mm resistors, termination effects are in most cases small, as evidenced from the very close values of TCR between Au and Ag (Rs is not a sensitive indicator, because it is subject to fluctuations of printing thickness). The only exception is when the resistors are fired at 900°C (right side of Figure 2) – diffusion of Ag then becomes quite important.

The length effect is shown in Figures 5 to 7. Figure 5 shows a typical sample with Au terminations – there are very little termination effects, as expected for Au.

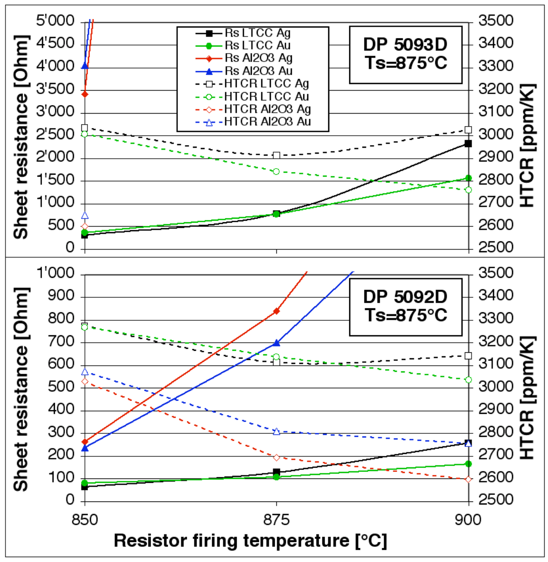

Figure 2. R_s and HTCR vs. resistor firing temperature.

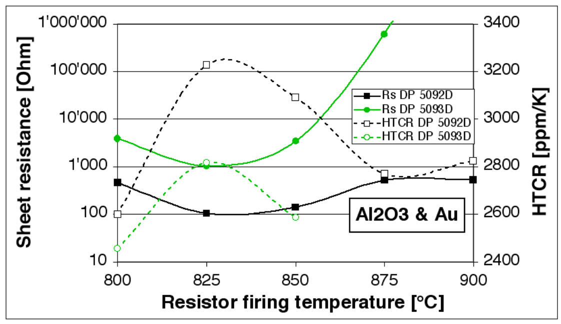

Figure 3. R_s and HTCR vs. resistor firing temperature, on alumina, extended temperature range. Note the logarithmic scale for Rs.

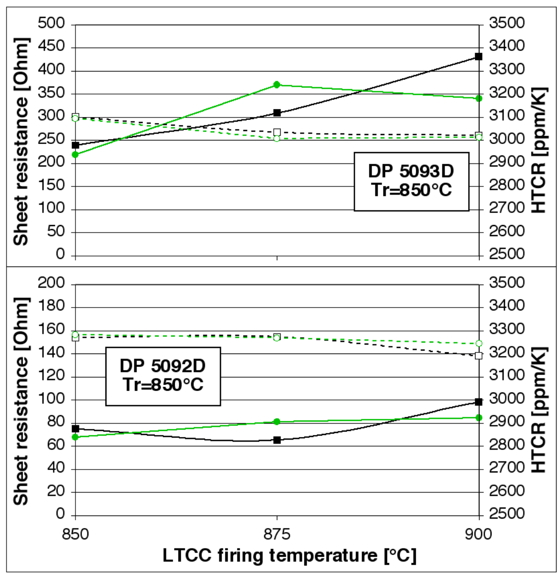

Figure 4. R_s and HTCR vs. LTCC firing temperature.

Ag terminations do not fare too badly, even for small lengths, at resistor firing temperatures up to 875°C. At 900°C, extensive diffusion sets in, and the properties are strongly affected, with an increase in R_s for shorter resistor lengths, which indicates the presence of a more insulating zone near the terminations. The LTCC firing temperature has little effect on this termination behavior, as evidenced from Figure 7.

Another important topic in thermistors used for temperature sensing is the reproducibility of the properties, especially of the TCR. Typical values are shown in Figure 8. Both thermistor compositions exhibit excellent reproducibility of TCR, which is only somewhat degraded at the highest firing temperature, presumably due to excessive diffusion of the Ag terminations.

The reproducibility of R_s is expectedly poorer, as variations of printing thickness affect it directly. At 900°C, it increases to high values (ca. 25%), presumably due to the same diffusion effects.

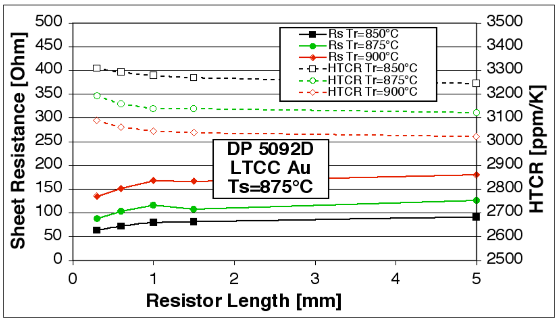

Figure 5. Typical length dependence of the properties, for Au terminations.

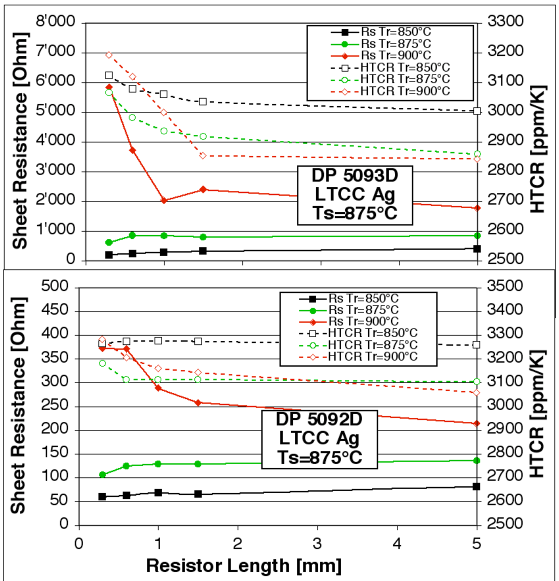

Figure 6. Length dependence of the properties for Ag terminations on LTCC, at various resistor firing temperatures.

The effect of Ag terminations on the statistical dispersion of properties becomes evident when comparing Figure 8 with Figure 9 (Au).

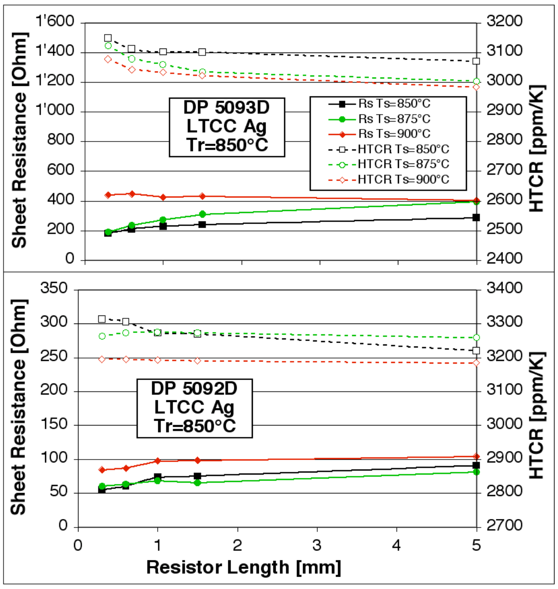

Figure 7. Length dependence of the properties for Ag terminations on LTCC, at various LTCC firing temperatures.

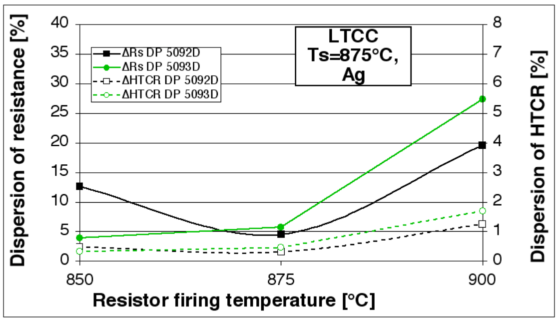

Figure 8. Dispersion of resistance and HTCR vs. resistor firing temperature, Ag terminations.

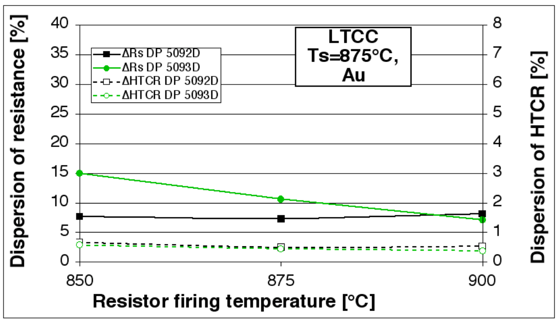

Figure 9. Dispersion of resistance and HTCR vs. resistor firing temperature, Au terminations.

Results - dilatometry

The dilatometric curves of the two thermistor compositions are shown in Figure 10. The materials shrink normally from ca. 550° to 800°C. However, above this temperature, a strong volume expansion is observed.

As these materials are glassy in nature, expansion due to abnormal grain growth is quite unlikely. The most likely cause is gas evolution, from a species which deoxidizes at this temperature, for example Pd. This will need to be confirmed by future experiments.

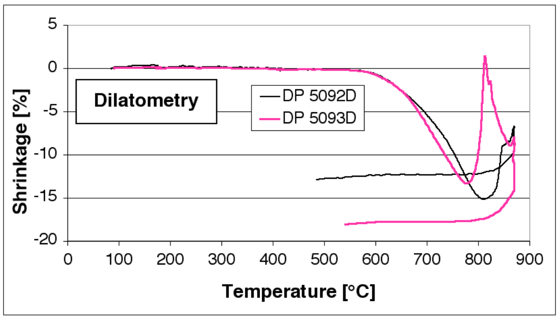

Figure 10. Dilatometric curves.

Conclusions

The Du Pont 5092D and 5093D compositions exhibit excellent compatibility with Du Pont 951 LTCC material when post-fired on it. Actually, the properties are much less sensitive to process conditions than on the "normal" alumina. Also, both Au- and Ag-base terminations may be used, with little effects on properties.

These compositions therefore are good candidates for use for thermal sensing or compensation in integrated LTCC devices. However, prior to that, their co-firing behavior and their dilatometric anomaly (sudden volume expansion) must be understood and mastered more fully.

References

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