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Influence of processing and conduction materials on properties of co-fired resistors in LTCC structures

H. Birol *, T. Maeder, P. Ryser

Swiss Federal Institute of Technology, Lausanne, Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut de Production et Robotique (IPR), LPM, CH-1015 Lausanne, Switzerland

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Abstract

The motivation of this study is the need for fundamental understanding of the effects of processing conditions on the electrical properties of low-temperature co-fired ceramic (LTCC) tapes, those screen printed with commercial thick-film pastes of electronic components for increased reliability. The method of the study is realized by analyzing the physical and chemical effects of mono/multilayer firing and firing temperatures on the temperature coefficient of resistance (TCR) and sheet resistance (SR) values of the positive temperature coefficient (PTC) resistors screen-printed on LTCC tapes. The results are discussed with respect to the information obtained by the scanning electron microscopy (SEM), electro dispersive X-ray analysis (EDXS), X-ray and dilatometry analysis. It is shown that the content of pastes combined with varying processing conditions result in deviation from expected TCR and SR values due to the chemical and/or mechanical reactions.

Keywords: LTCC; Electrical properties; Sintering; Microstructure-final; Electron microscopy

1. Introduction

Integration of low-temperature co-fired ceramic (LTCC) tapes with commercial thick-film pastes of electronic components such as conductors, resistors, etc. has opened new gates to advanced packaging possibilities for versatile applications.[1–5] In spite of a distinction in their functions, these materials have common features in their contents such as functional elements, glass and organics, each with a specific task to accomplish during processing.[6–11] Functional elements are those, which determine physical and electrical properties, whereas glass aids low temperature sintering, densification, dimensional stability, adherence to substrate and determine final resistor properties. Organics, on the other hand, provides a medium for efficient blending of these elements for appropriate rheology and handling. Although these material systems are commercially developed and traded in large amounts with producer specifications, their handling requires extreme attention as the processing conditions directly influence the final properties. This occurs as a result of the variety and extent of physical and chemical interactions occurring between the materials during firing.

Thus, the driving force of this study is to understand the effects of the paste composition and the influence of mono/multi layer lamination of selected tape–conductor–TFR systems fired at different temperatures on temperature coefficient of resistance (TCR) and sheet resistance (SR) values. We aim to analyze and demonstrate the results using characterization techniques such as scanning electron microscopy (SEM), electro dispersive X-ray analysis (EDXS), X-ray and dilatometry.

2. Experimental procedure

In order to study the effect of processing conditions on properties of TFR's using LTCC technology, we selected an LTCC tape[12,13] (Dupont 951-AX)–conductor (Ag:Pd-based Dupont 9473–referred to as Ag from here on- and Au-based Dupont 5744)–positive temperature coefficient (PTC) resistor (ESL 2612 with TCR of 2400 ppm/K and sheet resistance of 100 Ω/□ at 25 °C) system. The selected conductor-resistor combinations were then screen-printed in two different ways: (1) on a single LTCC layer (referred to co-fired), or (2) on a single LTCC layer that is laminated with a second blank tape of same dimension (referred to as buried), according to product specification sheets. This was followed by firing of each screen-printed series at three different peak temperatures: 850, 875 or 900 °C. Firing was

* Corresponding author. Tel.: +41 21 693 77 58; fax: +41 21 693 38 91.
E-mail address: hansu.birol@epfl.ch (H. Birol).

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The layout	Number of resistors	width / length (width =1.5 for all)
	5	1
	1	5
	1	2.5
	1	1.5
	1	0.3

Fig. 1. The layout for test patterns.

carried out in air atmosphere using a heating rate of 5 °C/min, with a 120 min organics removal dwell stage at 440 °C and a 25 min dwell at the peak temperature.

For electrical characterization, resistances were measured at 30, 65, 100 °C between consecutive pads (Fig. 1) by Keithley 2000 mm and Keithley 7000 scanner using four-wire method while a Pt-1000 PTC resistor recorded the temperatures. TCR and standard deviation values measured at 30 and 100 °C were calculated according to the following relation:

$$\mathrm{TCR} = \frac{10^6(R_{100} - R_{30})}{R_{30}(T_{100} - T_{30})} \quad (1)$$

$$\mathrm{S.D.} = \sqrt{\frac{n\sum y^2 - (\sum y)}{n(n-1)}} \quad (2)$$

where R is the resistance at a temperature T, S.D. is the standard deviation, n is the number of values y (sheet resistance or TCR).

TCR and SR values versus processing parameters shown in this paper were selected among resistor dimensions of 1.5:1.5, width to length ratio for a better statistical presentation, as each screen-printed test pattern contains five such nominally identical resistors (Fig. 1).

SEM analysis was carried out on cut and diamond-polished cross-sections of the samples. Images were taken at BSE (backscattered electron) mode for observation of phases and EDXS analysis was made on various selected areas for elemental characterization. The oxygen amount is calculated by stoichiometry after the atomic percentages of the elements are normalized to 100. For X-ray and dilatometric analysis, the organic content of the tape and thick-film pastes was first dissolved in acetone using an ultrasonic bath. The solvent was then evaporated at 250 °C.

3. Results

3.1. TCR and SR

TCR and SR versus processing parameters are presented in Fig. 2a and b. The dashes on the graphs indicate the values specified by the producer and the error bars at the end of the columns stand for the S.D. The results demonstrated that the TCR values fell in a close range to the specified ones for co-fired samples, Ag being slightly closer than Au. However, for Ag, the standard deviation was more than that of Au. The situation for the buried resistors, on the other hand, was much more different. TCR values out of the acceptable range in addition to the increased S.D. and irreproducibility were the characteristics of these samples. In some cases, open circuits were even observed. Similar results

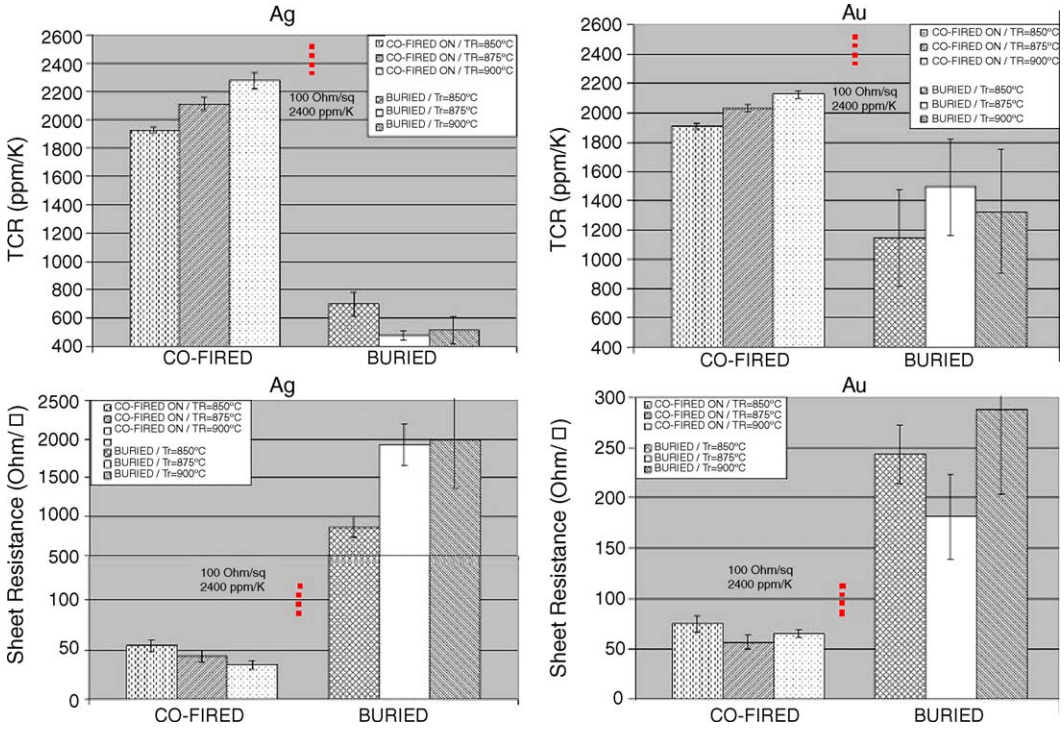


Fig. 2. (a) TCR and SR at different processing conditions for Ag (left column) and Au conductors. For SR, only values of co-fired resistors are presented. (b) TCR and SR at different processing conditions for Ag and Au conductors. Note the dissimilar graphics for SR of Ag and Au.

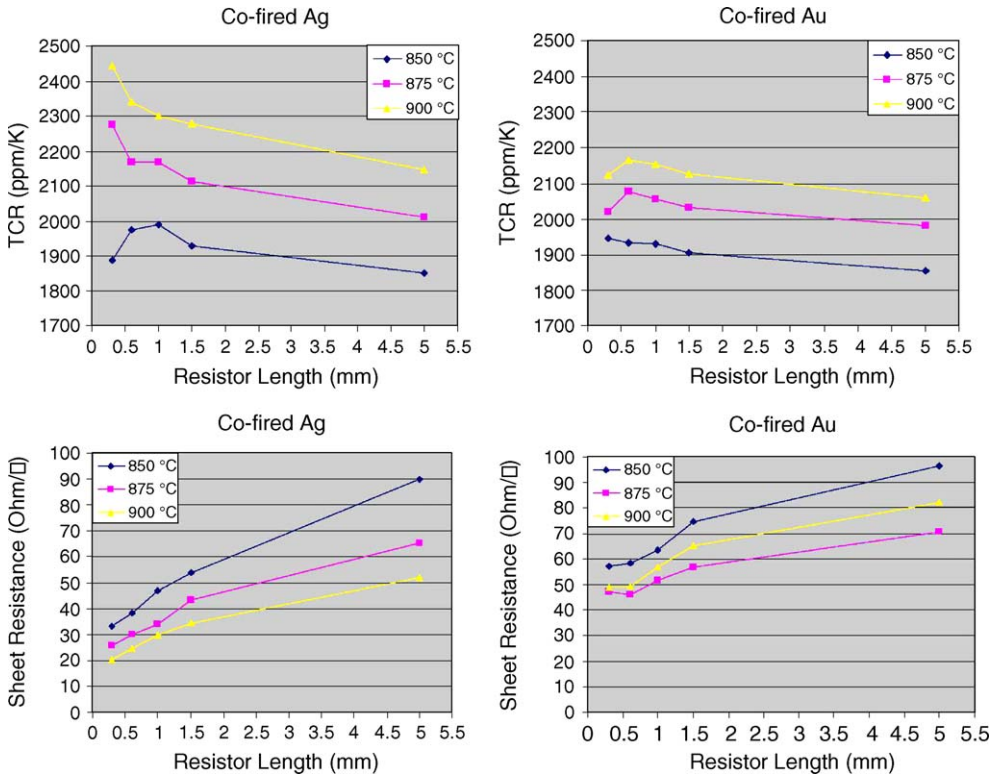


Fig. 3. Termination effects on TCR and SR with respect to resistor length for Ag (left column) and Au conductors, fired at different temperatures.

to TCR were obtained for SR values. Although SR values close to standards were obtained for co-fired resistors, a wide dispersion was observed for buried ones (Fig. 2). Between the two conductors, Au showed a better SR value than Ag at all temperatures.

3.2. Length effects

Following the TCR and SR measurements, we focused on the resistor length effect, which is a strong indicator of conductor-resistor incompatibility and diffusion. We analysed the TCR versus resistor length relation for co-fired samples (Fig. 3). Although TCR is expected to be independent of resistor length, a decrease in TCR value with increasing resistor length was observed. The decrease was significant for Ag, but very small for Au. We made the same analysis for SR with respect to the resistor length and obtained a relation as shown in Fig. 3. Termination effects cause an increase in SR upon increasing resistor length, which agrees with the observed decrease of TCR. As for TCR, the length effect is larger on Ag than on Au.

4. Discussions

The results described above showed two results: firstly, strong physical and/or chemical reactions for buried resistors compared to co-fired ones, and, secondly, significant termination effects with Ag and limited ones with Au. These results allowed us to better focus our further investigation methods.

We started our investigations with SEM. Fig. 4 shows the buried resistors for both conductor systems fired at 875 °C. Resistors fired with Ag show a reaction zone filled with

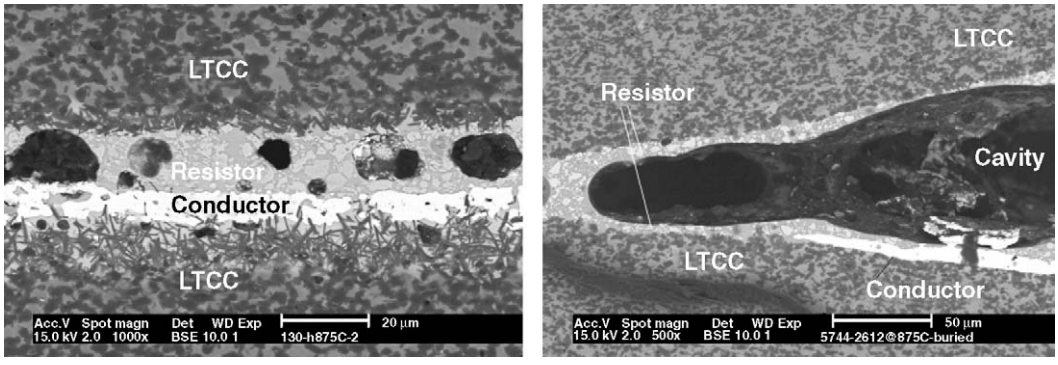
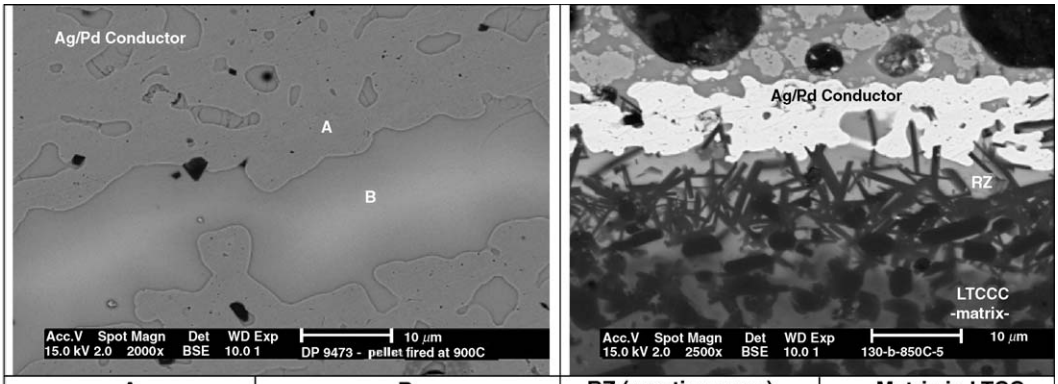


Fig. 4. Buried resistors with Ag (left) and Au. The reaction zone under the Ag conductor is seen as light grey matrix with needle-like particles dispersed both on it and the other side of the resistor. Black holes on the resistor are polishing defects (left) Au has a termination with destroyed conductor and resistor pads (right).



A		B		RZ (reaction zone)		Matrix in LTCC	
Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %
Ag	76	O	57	O	59	O	55
Pd	24	Zn	10	Na	4	Al	10
		Al	4	Al	10	Si	26
		Si	8	Si	15	Pb	2
		Bi	18	Pb	4	Ca	3
		Others	3	Bi	6	Na	2
				Others	2	Others	2

Fig. 5. EDXS analysis of Ag pellet (left) and RZ-reaction zone (light grey) and LTCC matrix (dark grey). RZ contains glass species from both LTCC matrix and the conductor. Image on the right is an LTCC structure fired at 850 °C.

needle-like particles, which is aligned only through the conductor line. The thickness of this zone was observed to strongly increase with increasing firing temperature. In order to better understand the materials interactions, we also carried out in parallel X-ray and EDXS analysis on pellets of the individual thick-film compositions. In Ag, two phases are observed in the pellet (Fig. 5): Ag-Pd alloy (also confirmed by X-ray analysis), and glass phase mainly composed of Bi-Zn-Si oxides (probably also B which we cannot detect by EDXS). We continued elemental analysis on the Ag-LTCC reaction zone. The data from multiple points were obtained with high reproducibility and can be seen in Fig. 5. These results showed the existence of elements from the glass phase of the LTCC tape (Pb-Si) and the conductor (Bi-Zn-Si) in the reaction zone, indicating strong chemical interaction between these glasses. Traces of Ag, both in the reaction zone and the needle-like structures, and discontinuous Ag lines were other remarkable observations for resistors fired with Ag.

Buried resistors with Au on the other hand, exhibit severely destroyed contacts. The conductor lines were displaced due to swelling as a result of organics burnout, tearing the resistor pads as well. Although this looks like a delamination problem at first look, our studies strive to understand the exact nature of this effect, bearing in mind high temperature deformation due to chemical reactions (e.g. reduction of certain elements, etc.). To understand this problem, we compared the shrinkage behaviour of the individual elements by pelletized powders. Fig. 6 shows the dilatometry analysis of the conductors and the tape used. It was clearly seen that both conductors behaved similarly up to 600 °C, whereas Au rapidly expanded starting from 700 °C up to the end of firing cycle, deforming the tape. Besides, X-ray and EDXS analysis showed a pure Au phase in the content of the paste with a trace amount of oxide that we could not exactly identify yet. This clearly excludes widespread chemical interactions between LTCC and Au, in contrast to Ag, and leads to continuous conductor lines in co-fired samples (Fig. 6).

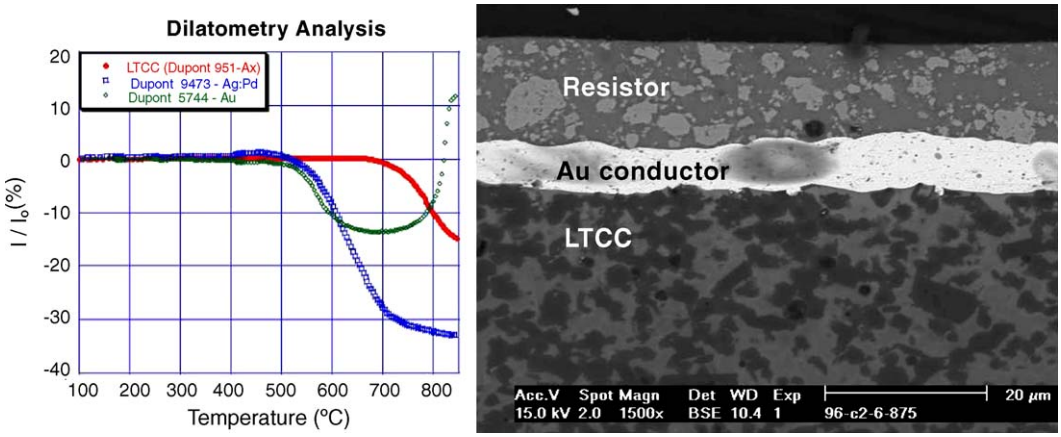


Fig. 6. Dilatometry analysis of the tape and the conductors used (left). Au expands starting from 700 °C, which is around the onset temperature for the tape shrinkage. Au conductor on a co-fired resistor–tape system (right).

5. Conclusion

It was seen that the buried resistors prepared using Ag and Au conductors yielded unreliable TCR and SR values due to different causes. In case of resistors with Ag, the main reason was related to the formation of a reaction zone at the terminations due to chemical interaction of the glasses in the structure of the LTCC tape and the conductor. Secondly, the glass phase of the conductor spreading over the tape area resulted in discontinuous conductor line. Apart from these two effects, trace amounts of Ag were found indicating a diffusion problem. These factors all added up to increased standard deviation and higher susceptibility to termination effects.

In contrast to Ag, resistors with Au were mainly altered by the expansion behaviour of the Au paste during firing. Its expansion at a temperature range where the tape was not sintered in addition to the accumulation of organics burnout products in the buried zone led to the destruction of terminations. On the other hand, the Au lines were very dense and continuous in co-fired resistors, as the conductor had no glass phase reacting with the environment, which resulted in limited termination effects.

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