Integrated thick-film hybrid microelectronics applied on different material substrates

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Abstract

In this work, we have modified a low-temperature thick-film system previously developed for aluminium and aluminium alloy substrates in order to adapt it to ferritic and austenitic stainless steel, and glass substrates, which, unlike the common alumina substrate material, cannot usually be exposed to the standard high-temperature 850 °C thick-film firing cycle. Such substrate materials are useful for several important applications: high-response piezoresistive thick-film sensors (steel), displays (glass), high power electronics (aluminium-based materials) and heaters (steel and aluminium). We have developed several thick-film systems (dielectrics, resistors and conductors) chemically compatible and suitable for a wide range of thermal coefficient of expansion (TCE) values. This paper reports preliminary results on the electrical properties of these systems: sheet resistance and its thermal coefficient (TCR), compared with those of commercial thick-film materials.

Key words: thick film dielectrics, low temperature, sensors, thick-film resistors, low-temperature firing.

Introduction

Thick-film technology applied to piezoresistive force or pressure sensing typically uses alumina as a substrate material, because it is the standard for thick-film technology [1]. However, alumina is not optimal for piezoresistive sensing applications, as its elastic modulus is high and its strength rather low [2]. Additionally, alumina is brittle and therefore ill suited to harsh environments and its heat dissipation capabilities are limited. Aluminium alloys [3] and stainless steels [4] offer advantages in applications such as high power electronics or high-range load cells, due to their excellent thermal dissipation, mechanical sturdiness, easy packaging and, in the case of the Al-Si system, adjustable TCE. Metallic materials also offer advantages such as robustness and ease of fabrication.

However, the high temperatures associated with commercial thick-film processing (850°C) are not compatible on the one hand with aluminium owing to its low melting point and on the other hand with high-strength steel, owing to degradation of mechanical properties of steel due to annealing or dimensional changes associated with martensitic transformation (which tend to destroy the thick-film layers). Additionally, standard thick-film materials are thermally matched to alumina, which has a rather low TCE of ca. 7 ppm/K, whereas steels and aluminium alloys range from 11 ppm/K to 24 ppm/K. Appropriate low-temperature thick-film systems (dielectrics, resistors and conductors) are therefore necessary.

In this work, we endeavour to investigate novel low-temperature thick-film dielectrics, conductors and resistors and present the resulting electrical properties of the resistors, compared with standard alumina-based systems. Relevant parameters such as adhesion, dissolution of filler powder in the glass matrix and temperature coefficient of resistance (TCR), are studied and discussed.

Experimental

The following substrate materials were used: 96% pure alumina (Kyocera, Japan, A-476, TCE = 7 ppm/K) as standard thick film substrate, EN AW 6060 aluminium alloy (AlMgSi0.5, TCE = 24 ppm/K), aluminium-silicon composites (Osprey CE9, Osprey CE11 and Osprey CE17, TCE=9 , 11 and 17 ppm/K), ferritic stainless steel 1.4016 (TCE = 11 ppm/K) and austenitic stainless steel 1.4435 (TCE = 17 ppm/K). The steels were chosen because they have representative chemical (surface oxide) and thermal expansion properties (ferritic: ca. 11 ppm/K; austenitic: ca. 17 ppm/K). The steels were pre-oxidised at 900°C during 1 hour in order to increase the adherence of the dielectrics. This oxidation was particularly necessary for the 1.4435 stainless steel.

Six thick film dielectric materials based on 2 lead borosilicate glasses (V6 and V8), loaded with different powder concentrations, were developed, evaluated, and compared with high temperature commercial dielectrics. The list is given in the **Erreur ! Source du renvoi introuvable.**. The filler powder (alumina, quartz or cristobalite) serves to dimensionally stabilise the dielectric, and to control its TCE.

Table 1:List of the studied dielectric compositions.

	Glass variant	%vol Alumina powder	%vol Cristobalite powder	%vol Quartz powder
V6A40	V6	40		
V8A40	V8	40		
V8C40	V8		40	
V8C50	V8		50	
V8Q40	V8			40
V8Q50	V8			50

The particle size is around 1 μm for alumina powder, between 10-20 μm for cristobalite powder (Figure 1) and between 20-30 μm for quartz powder. The particle size of cristobalite and quartz powder is too high and will be decreased in future studies.

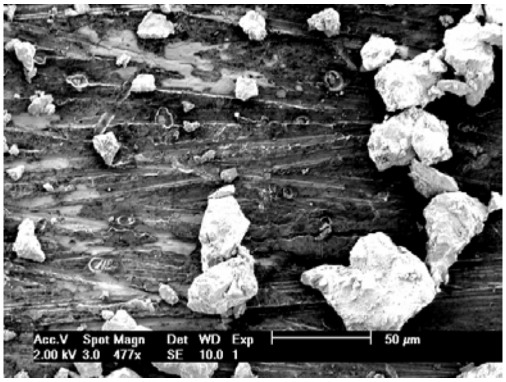

Figure 1: cristobalite powder

The composition (by mass) of the glasses is V6: 75% PbO + 10% B_2O_3 + 15% SiO_2, and V8: 85% PbO + 10% B_2O_3 + 5% SiO_2. In both cases, 2% Al_2O_3 was added to inhibit crystallisation [5]. The ideal firing temperature is around 600°C for V6-based materials and around 500°C for V8-based ones.

The above dielectrics have been compared with 3 commercial dielectric materials, which must be fired at 850°C: Electro Science Laboratories (ESL) 4916, Heraeus (Her) GPA, ESL 4924.

Commercial conductor materials adapted to the firing temperature were applied: ESL 9635B (Ag:Pd 3:1) for the high temperature range, ESL 9912 (Ag) for the intermediate temperature range 575-625°C, and ESL 590G (silver with glass frit) for 450-575°C. In this latter temperature range, a mix of ESL 9912 with V8 (used as a frit), was also used in an attempt to improve the chemical compatibility between conductor and resistor materials.

Samples for sheet resistance and TCR were 1.5 mm wide resistors of several lengths (Figure 2). 3 resistive compositions were used. DuPont (Du) 2041 was used at 850°C, ESL 3114 for the range 575 – 625°C and an experimental resistive composition, consisting of V8 glass loaded with RuO_2 nano-powder, was used for low firing temperature.

Table 2: List of experimental.

Substrate	Firing Range	Dielectric	conductor	Resistor
Alumina, 1.4016, 1.4435	850 – 920°C	Commer-cial	ESL 9635B	Du 2041
1.4016, 1.4435	575 – 625°C	V6-based	ESL 9912	ESL 3114
Al alloys	450 – 550°C	V8-based	ESL 9912 : V8 3:1	0.075-400-8

The firing temperatures for the dielectrics and conductors are listed in Table 3.

Table 3: Firing temperature of dielectrics and conductors.

Dielectrics	Conductor	Firing Temperature, °C
ESL 4916	ESL 9635B	850; 920
Her GPA	ESL 9635B	850; 920
ESL 4924	ESL 9635B	850; 920
V6A40	ESL 9912	575; 600; 625
V8A40	ESL 9912:V8 3:1	500; 525; 550
V8C40	ESL 590G	500; 525; 550
V8C50	ESL 590G	500; 525; 550
V8Q40	ESL 590G	500; 525; 550
V8Q50	ESL 590G	500; 525; 550

In all cases, the firing cycle started with a 15 min dwell at 370°C for organic burnout, followed by a 20 min dwell time at the indicated temperature. For each sample, three layers of dielectrics were screen-printed and fired according to the abovementioned cycle on each substrate in order to guarantee good insulation (40μm). The conductors were fired as indicated in Table 4.

Table 4: Firing temperature of resistors.

Resistor	Firing temperature
Du 2041	850°C
ESL 3114	625°C
0.075-400-8	500°C

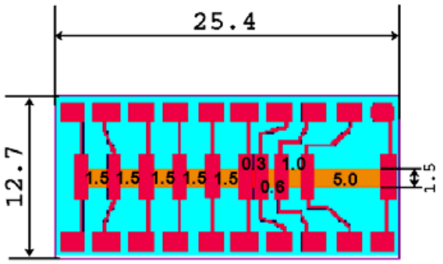

Figure 2: Layout of the test sample for measurement of electrical properties.

Sheet resistance and TCR were measured as a function of resistor length at 30°C and 100°C.

Results and discussions

- **X-ray diffraction (XRD):**

The dissolution temperature of cristobalite and quartz fillers in the V8 glass was evaluated by XRD (Figure 3). For both fillers (10% volume), dissolution of powders in the glass occurs from 525°C on.

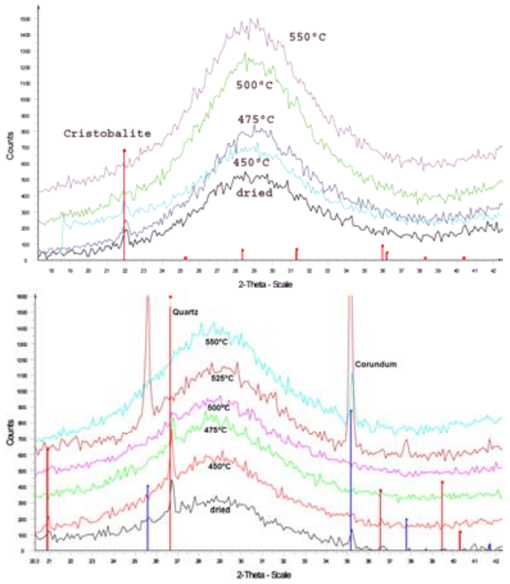

Figure 3: X-Ray diffraction of dielectrics based on V8 filled at 10% vol. with cristobalite and quartz.

- **Sheet resistance and TCR measurements:**

Aluminium samples (V8 dielectrics & resistor):

Figure 4 depicts the sheet resistance and the TCR of 0.075-400-8 resistors on V8 glass filled with cristobalite and quartz powders in function of the dielectric firing temperature and the powder concentration. On structurally sound dielectrics, sheet resistance is around 20 kOhm on 40% filled dielectrics, and around 40 kOhm on 50% filled dielectrics.

The dielectrics filled at 50% expectedly exhibit better dimensional stability than those filled at 40% (which flow too easily above 525 °C, encapsulating the conductor material), but require a higher firing temperature. The optimal firing range is 475-525°C for 40%, and 525-575°C for 50%. One must note that the optimal filler content depends on the ratio between the filler and glass particle sizes. We cannot see a large difference between the dielectrics filled with quartz and cristobalite, which is expected from their identical chemical composition.

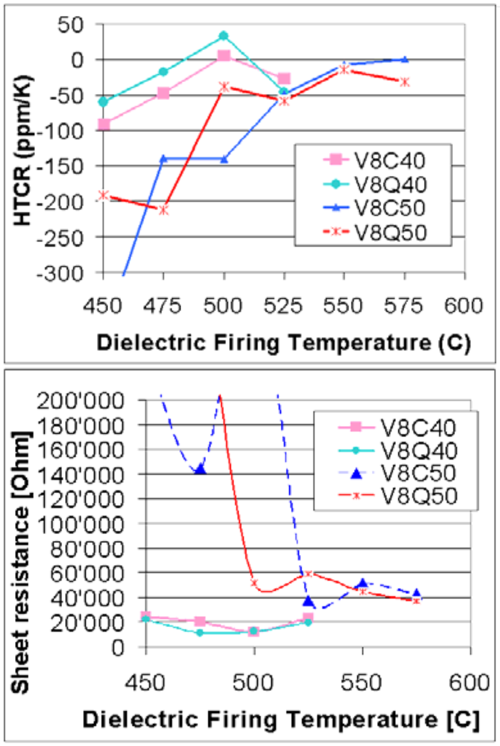

Figure 4: TCR and Sheet Resistance of 0.075-400-8 Resistor as a function of concentration and nature of the fillers on Al alloy substrates.

Al-Si composite samples (V8 dielectric & resistor):

Figure 5 represents the sheet resistance and the TCR of resistors on V8A40 dielectric, deposited on Al-Si composites, as a function of dielectric firing temperature and substrate material. The dielectric firing temperature was limited to 550°C, safely below the Al-Si eutectic at 577°C, and the resistor firing temperature was kept constant at 500°C. Unlike quartz or cristobalite, alumina powder does not strongly diffuse into the glass at these firing temperatures. V8A40 dielectric is thermally well matched to Osprey CE9 and Osprey CE11, as the TCE of V8A40 is slightly under the TCE of the substrate, ensuring a moderate compressive stress. For Osprey CE17, the TCE mismatch between the substrate and the dielectric becomes too high, affecting structural reliability: short and open circuits were observed. An optimal firing range of the dielectric is 500-550°C, but the conductor firing temperature should be limited to 500°C in order to avoid excessive interaction with the dielectric.

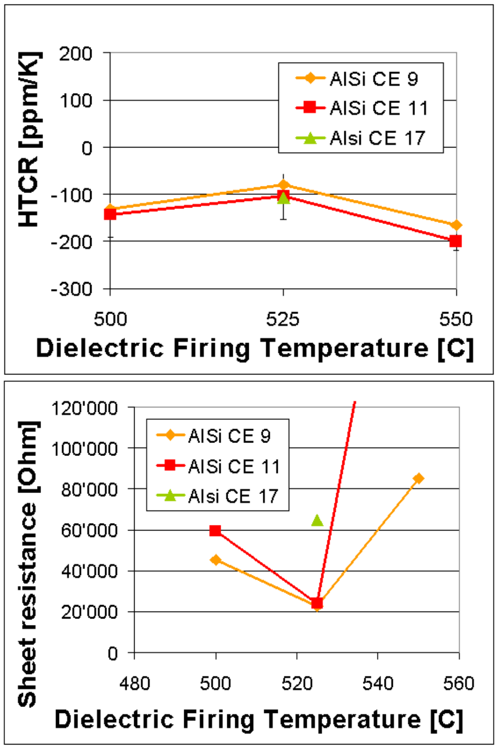

Figure 5: TCR and Sheet Resistance of 0.075-400-8 Resistor screen-printed on V8A40 on Al-Si composite substrates.

Stainless steel

- Low-temperature (V8 dielectrics & resistor)

For this study, half of 1.4016 stainless steel substrates have been oxidised 1 hour at 900°C in order to create an oxide layer on the substrate surface, thereby improving the adherence of the dielectric thick-film on the steel. This study has been carried out on both oxidised and non oxidised substrates, with the conductor and resistor fired at 500°C. Figure 6 shows the resulting sheet resistance and TCR values. For this temperature range, the steel pre-treatment has no significant effect on the resistor electrical properties.

Normal sheet resistance and TCR values are obtained for 40% filler for a dielectric firing temperature in the 500-575°C range (the dielectric is too porous below). On the other hand, abnormally low sheet resistance and correspondingly high TCR values are obtained on dielectric filled with 50% alumina. The cause must still be investigated, as no large chemical reactions are expected between dielectric and resistor, which here share the same matrix glass.

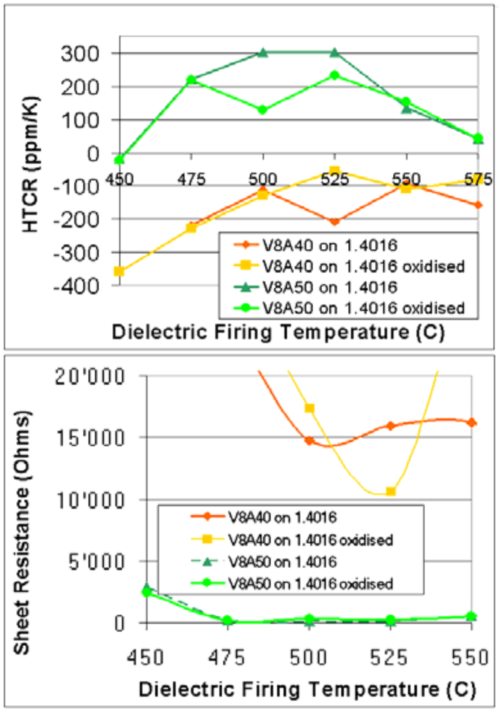

Figure 6: TCR and sheet resistance of 0.075-400-8 Resistor on dielectric as a function of powder concentration on oxidised and non oxidised 1.4016 substrates.

- Intermediate temperatures (V6 dielectrics & ESL 3114 resistor)

The conductor used for this study was ESL 9912, fired at the same temperature as the underlying dielectric. In this intermediate temperature range (575-625°C), the TCR of resistor, whatever the dielectric, depends on the type of steel. The TCR of resistors (Figure 8) on 1.4016 steel, oxidised or not, are stable and are shifted ca. +100 ppm/K relative to the alumina reference. This shift is even higher (+150 to +300 ppm/K) on 1.4435, these latter values being less reliable due to excessive thermal mismatch stresses.

- High temperatures (various commercial dielectrics & Du 2041 resistor)

For this study, the austenitic steel samples were pre-oxidised in order to improve the adherence of the dielectrics. Nevertheless, several problems were encountered with all samples fired at high firing temperature, precluding electrical measurement: excessive diffusion with the substrate, cracking or delamination due to the TCE mismatch with the commercial thick-film materials.

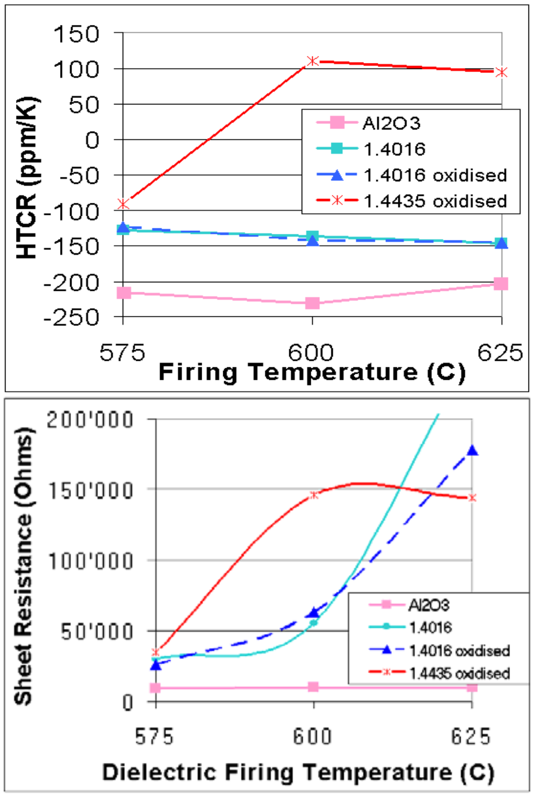

Figure 7: TCR and Sheet Resistance of ESL 3114 Resistor on V6A40 dielectric as function of dielectric firing temperature.

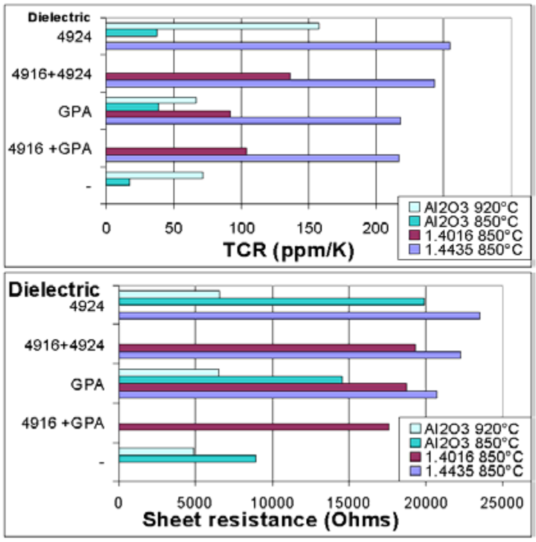

Figure 8: Sheet resistance of Du 2041 Resistor on commercial dielectrics in function of dielectric firing temperature.

At 920°C, all samples screen-printed with commercial dielectrics were destroyed because of excessive stresses. The electrical results obtained at 850°C are depicted on Figure 8. TCR values are shifted similarly to the previous study: +100 ppm/K on 1.4016 ferritic steel and +200 ppm/K on 1.4435 austenitic steel compared with values obtained on the reference alumina substrate material coated with the same dielectric in order to ensure similar surface chemistry.

Influence of substrate TCE on resistor TCR

The effect of the substrate TCE on TCR has been analysed previously [6, 7], assuming that piezoresistivity (which is commonly expressed in the form of gauge factors) is temperature independent.

$$TCR = \chi - \alpha + \left[\Gamma_L + 1 + (\Gamma_T - 1)\cdot\frac{1-3\nu}{1-\nu}\right]\cdot(\alpha_S - \alpha)$$

Γ_L and Γ_T are the longitudinal and transverse piezoresistive coefficients, χ the temperature coefficient of resistivity, α and α_S the resistor and substrate TCE values, and ν the Poisson's ratio of the resistor. The piezoresistive coefficients may be calculated from the longitudinal and transverse gauge factors K_L and K_T, obtained from bending tests of cantilever beams. In the case of flat bending beams (width >> thickness), the lateral strain is essentially zero, and we have:

$$\Gamma_L = K_L + K_T \frac{\nu}{1-2\nu} - 1 \text{ and } \Gamma_T = K_T \cdot \frac{1-\nu}{1-2\nu} + 1$$

Inserting these values into the previous equation, we get, for temperature independent gauge factors:

$$TCR = \chi - \alpha + (K_L + K_T)\cdot(\alpha_S - \alpha)$$

The value $TCR_0 = \chi - \alpha$ is the TCR of a free standing resistor material (or of a film lying on a thermally matched substrate). In case of temperature dependent gauge factors, the above equation must be modified. Taking the combined effect of strain and temperature on a resistor film, we get (R_0 = value at reference temperature T_0 and under no strain):

$$\frac{\Delta R}{R} = TCR_0 \cdot \Delta T + K_L \cdot \varepsilon_L + K_T \cdot \varepsilon_T$$

ε_L and ε_T are the resistor longitudinal and transverse strains. In the case of an unstressed substrate, these strains are only due to thermal mismatch. Therefore, we can write, assuming there is a "softening temperature" T_s at which strain is zero:

$$\varepsilon_L = \varepsilon_T = \Delta T_{th} \cdot (\alpha - \alpha_S) \text{ where } \Delta T_{th} = T_s - T$$

Combining the above expressions, taking the temperature derivative and grouping related terms, we now can get the actual TCR of the thermally strained resistor:

$$TCR = TCR_0 + (\alpha_S - \alpha)\cdot\left[K_L\cdot(1-\gamma_L\cdot\Delta T_{th}) + K_T\cdot(1-\gamma_T\cdot\Delta T_{th})\right]$$

The values γ_L and γ_T are respectively the temperature coefficients of K_L and K_T.

In practice, TFRs are almost never free-standing, and TCR_0 and α are not well defined. It is therefore more practical to get the TCR shift $\Delta TCR = TCR_2 - TCR_1$ between two different substrates (1 & 2):

$$\Delta TCR = (\alpha_2 - \alpha_1)\cdot\left[K_L\cdot(1-\gamma_L\cdot\Delta T_{th}) + K_T\cdot(1-\gamma_T\cdot\Delta T_{th})\right]$$

In the case of Du 2041 and ESL 3114, we have: $K_L + K_T \cong 20$ [8]. From our preliminary studies on Du 2041, γ_L and γ_T lie in the -0.03 to -0.01%/K range. T_s can be roughly estimated to be +300…600°C, giving an estimated $-\gamma\cdot\Delta T_{th}$ value range of +0.03 to +0.18. From this, we can estimate values of TCR shift, compared to alumina, of ca. +90 ppm/K on 1.4016 (ferritic, $\Delta\alpha \cong 4$ ppm/K) and +220 ppm/K on 1.4435 (austenitic, $\Delta\alpha \cong 10$ ppm/K). These values agree reasonably well with the experimental ones for both steels and both thick-film systems. Note that both contributions to the TCR shift (variation of strain * gauge factor, and thermal strain * variation of gauge factor) have the same sign, but the former is dominant.

Conclusion and outlook

The study has characterised a complete range of dielectric and resistor compositions. Our experimental low-firing thick-film compositions have demonstrated promising electric properties and chemical compatibility. They must nevertheless be improved and further characterised to obtain a stable low-temperature thick-film materials system suitable for deposition on heat-sensitive substrates such as steel, glass, titanium and aluminium alloys. Future work will concentrate on the following topics:

- Developing dielectric containing finer filler particles, whose TCE can be adjusted to achieve compatibility with various substrate materials.
- Improving adherence on stainless steel substrate by surface treatment or incorporation of adherence promoters.
- Improving reliability and reproducibility of resistor properties through additives.
- Measuring and optimising the gauge factor of the resistors for piezoresistive sensing applications.

Acknowledgements

This project was partially funded by the Swiss TOP Nano 21 programme. The authors also gratefully acknowledge Mr. Matthias Garcin for preparing the samples.

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