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Influence of the densification parameters on screen-printed component properties

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Abstract

Standard screen-printing is a very versatile technology for the elaboration of thick films and hybrid circuits. However, in order to obtain components with particular properties such as gas sensors, varistors, PZT-based pyroelectric sensors, super-thick copper pads, etc., a better control of the layer compacity is necessary. This has been made possible, thanks to the preparation of specific inks and thanks to the development of new fabrication processes. Most examples will be drawn from our own experience.

Keywords: Densification; Sensors; Varistors; Films; Ferroelectric properties

1. Introduction

Standard screen-printing technology has been principally developed for hybrid circuits manufacturing. The advantages are well known: versatility in the conception, miniaturisation, mass production at low cost, etc. This technology may also be used to elaborate other thick-film components (chemical and physical sensors, heating resistors, varistors, capacitors, etc.). Moreover, the development of inks specific to the required application is relatively simple, at least at the laboratory level. However, a good control of the ink composition, screen-printing parameters, drying and firing process, is often necessary to obtain a layer compacity adapted to the desired properties. For example, porous layers will be preferentially used to develop catalytic and semiconductor oxide gas sensors. Conversely, conductors, varistors, dielectrics, etc. need compact layers. Thus, because of the poor densification generally obtained with the standard process, the original solution proposed herein is to add a new step to the standard screen-printing process, by applying uniaxial or isostatic pressure onto the oven-dried layers at room temperature. Besides pressure application, other possibilities to increase the compacity of films containing a small amount of inorganic binder are to add a temporary eutectic phase and/or to fire at a peak temperature close to the melting point of the active material.

In this paper, we present the basis of the standard screen-printing process and of the modifications introduced to enhance the densification of the films. We then focus on the correlations between the compacity and the component properties. Examples, mostly drawn from our own experience, deal with gas sensors, varistors, PZT-based pyroelectric sensors, super-thick copper pads, etc.

2. Processing and densification of thick films

2.1. Ink preparation

While conductive, resistive and dielectric pastes are commercially available, fabrication of our own inks may be necessary for specific applications. The latter contain two main constituents: about 60–80 vol.% of inorganic materials, which give the required electrical and mechanical properties to the film, and about 20–40 vol.% of a temporary organic vehicle, which controls the rheological properties of the ink.[1] The organic part contains ethylcellulose, terpineol, dibutyl phthalate and butyl carbytol. The inorganic fraction consists of a powder of active material(s) such as semiconductor ox-

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ide, varistor, PZT, metal, etc. which normally will determine the characteristics of the component.

A controlled concentration of inorganic binder (glass frit, fusible phase, etc.) is usually added to ensure the cohesion and/or the compacity of the layer and its adherence to the substrate. However, a particular attention to the influence of the inorganic binder on the required electrical properties of the layers must be paid. When the electrical properties are mostly dependent on those of the active material, a significant amount of glass frit will obviously modify the electrical performance of the layers. The effect may be beneficial: in resistors, for example, both resistance and TCR can be adjusted, by selecting an optimal concentration of glass frit. Conversely, in varistors, the addition of glass frit destroys the non-linear effect.

2.2. *Screen-printing*

Thick layers of some tens to hundreds of micrometers are obtained by a transfer of the ink through a screen onto the substrate. The final thickness of the layer depends strongly on the screen, the thickness of the emulsion, the settings of the screen-printing machine (squeegee pressure and speed, screen–substrate distance, etc.) and the ink viscosity.

2.3. *Drying*

The samples are dried for 20 min at 120 °C in an oven to eliminate the solvents. It is important to emphasise that the lack of compacity of the films mostly originates from the removal of this volatile part.

2.4. *Pressure application (optional)*

Because of the poor densification generally obtained with the standard process, it is not easy to manufacture screen-printed capacitors or varistors whose performances are comparable to those of ceramic components.

The original solution proposed herein is to add a new step to the standard screen-printing process, by applying uniaxial or isostatic pressure up to 5×10^8 Pa onto the oven-dried layers at room temperature. In both cases, 30% reduction of the thickness of the oven-dried layer is obtained. A densification close to that of ceramics may thus be expected.[2]

2.5. *Firing*

Unpressed or pressed samples are fired in a conventional belt furnace at peak temperature from 850 to 1100 °C. In the whole furnace, the atmosphere is either dry air or nitrogen containing 5–10 ppm oxygen. For higher temperature (up to 1450 °C), a laboratory prototype furnace has been specially designed to control the temperature profile. A particular attention has to be given to the strong chemical interactions between the layers themselves and/or between the films and the substrate, which can occur during firing.

Densification of the layers is of course dependent on the firing temperature cycle. Besides pressure application, addition of small amount of inorganic binder and/or a temporary eutectic phase and firing at a peak temperature close to the melting point of the active material are expected to increase the compacity of thick films.

3. Gas sensors

Screen-printed chemical sensors have been developed for the last 20 years, using different detection principles: semiconductor, catalytic, solid electrolyte, etc.

3.1. *Semiconductor oxide gas sensors*

The design of a semiconductor gas sensor is shown in Fig. 1a. Interdigitated gold electrodes and a platinum resistor are screen-printed on each side of an alumina substrate. The sensitive layer is then deposited above the electrodes and fired at 850 °C. Sometimes it is desirable to deposit a porous membrane on the sensitive layer for protection or filtering purposes.[1] Finally, the sensor is connected on a socket with Pt wires (Fig. 1b).

A glass binder is often needed for the reasons discussed previously. The addition of only 2 wt.% of CaBAlSi glass frit ($CaCO_3$, B_2O_3, Al_2O_3, SiO_2) to 10 wt.% Pd-doped SnO_2 leads to a reduction by a factor of about 20 of the response towards 1% CH_4.[1] The collapse may have two reasons: the inhibition of the sensing properties of tin oxide and/or that of the catalytic activity of palladium. Response to CO is also reduced by addition of CaBAlSi to SnO_2.[3]

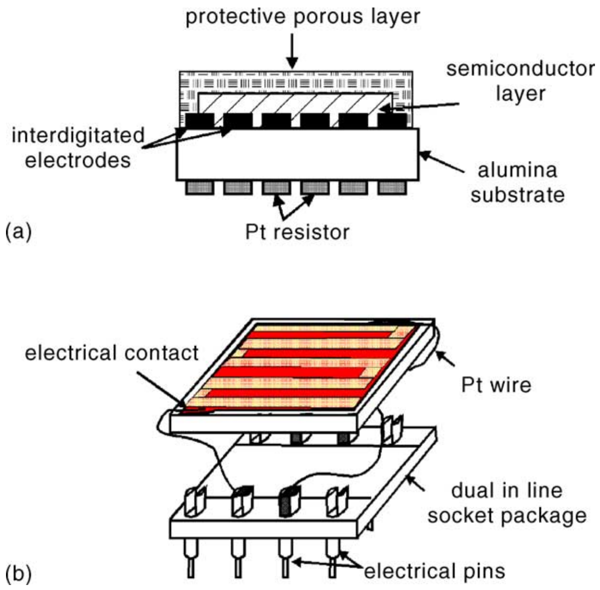

Fig. 1. Typical design of a screen-printed semiconductor gas sensor: (a) cross-section; (b) sensor mounted on a socket.

Conversely, a highly favourable influence of the glass binder was observed with $SrFeO_{3-x}$ semiconductor layers towards CH_4.[4] The addition of 40 vol.% CaBAlSi leads to a response to 1% methane of about 25%, whereas no detection is observed without binder.

3.2. Catalytic gas sensors

Catalytic gas sensors consist of an alumina substrate with a heating platinum resistor, coated on both sides with a catalytic deposit made of alumina powder either Pd- or Pt-doped.[5] The heating resistor also enables measurement of the temperature increase, i.e. the sensor response, correlated to the combustion of a reducing gas. The inhibition of the catalytic activity of Pd by CaBAlSi towards methane combustion is again clearly demonstrated in Table 1. A similar evolution is observed with ethanol.[1]

3.3. Solid electrolyte gas sensors

Conversely to semiconductor oxide and catalytic gas sensors, the densification of glass-free solid electrolyte layers may have a strong benefit effect on the sensing properties. Screen-printed yttrium-doped zirconia films have been shown to exhibit rather poor oxygen sensing properties compared to ceramics, in both designs of potentiometric and amperometric sensors.[6] This has been attributed to the porosity of the YSZ screen-printed layer, which likely induces diffusion of gaseous oxygen in the electrolyte as well as a lower ionic conductivity. Obviously, application of a mechanical pressure onto an oven-dried zirconia screen-printed layer was suggested by us as a potential solution to solve these problems.[2] This has been demonstrated a few years later by Prof. K.H. Haerdlt.[7]

4. Low voltage varistors

The $I(V)$ characteristic of varistors can be expressed by the empirical relation $I = kV^{\alpha}$, where k is a constant and α the non-linear coefficient. Up to now, the strong non-linear varistor effect is believed to take place at the grain boundaries. The presence of the glass phase in the so-called ZnO "glaze varistors" is prejudicial to electrical properties as clearly demonstrated in Fig. 2.[8,9] It is thus believed that the glass binder may envelop or react with the grain-boundary phases. Consequently, pressure application on glass-free varistors layers should enhance their electrical characteristics.

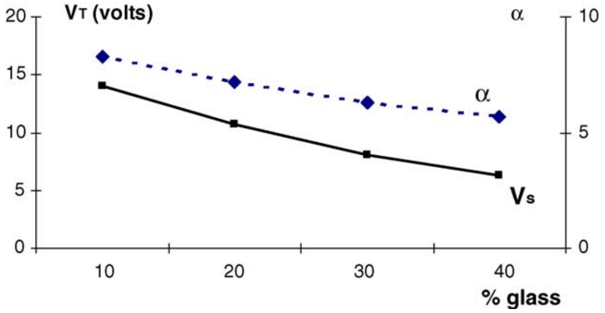

Fig. 2. Influence of the glass concentration on the threshold voltage (V_T) and the non-linear coefficient (α) of glaze varistors.

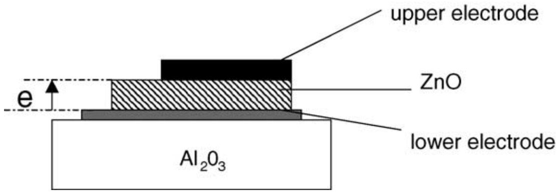

Fig. 3. Cross-section of sandwich varistors.

Planar varistors have been designed with a sandwich configuration (Fig. 3).[2] The common platinum electrode is first screen-printed on the alumina substrate and fired at 950 °C. Then, a ZnO-based ink (95% ZnO + other oxides) is screen-printed, oven-dried, eventually pressed and fired for 15 min at 1150 °C. Finally, upper silver electrodes deposited above the varistor layer are fired at 850 °C. Unpressed varistors were mostly short-circuited. The non-linear coefficients of pressed varistors, higher than that of the so-called "glaze varistors", approach those of commercial ceramic varistors (Table 2).

Table 1
Influence of glass (CaBAlSi) on the sensitivities of catalytic Pd-doped Al_2O_3 layers towards CH_4 and C_2H_5OH at 400 °C

Catalytic layer	Al_2O_3:Pd	(Al_2O_3:Pd) + 7 wt.% glass
Temperature increase (1% CH_4) (°C)	10.7	0
Temperature increase (1% C_2H_5OH) (°C)	27	15

Table 2
Characteristics V_T and α for different low voltage varistors

	Laboratory screen-printed varistors		Commercial samples	
	Unpressed	Pressed	Glaze varistor[a]	Ceramic[b]
Threshold voltage (V_T (V))	2.4–10.1	16–18	6–21.5	8
Non-linear coefficient (α)	–	17–19	6.5–8.1	18

[a] Matsuchita.
[b] GEMOV.[2]

Table 3
Influence of the sample preparation on the pyroelectric coefficient[11]

	p(300 K) (nC cm^{-2} K^{-1})	p(320 K) (nC cm^{-2} K^{-1})
Unpressed	5.5	6
Pressed (uniaxial, 4 × 10^8 Pa)	17.3	20.6
Pressed (isostatic, 4 × 10^8 Pa)	15.2	19.3
Ceramic	14.2	16.9

Table 4
Influence of the firing temperature on the adhesion and the resistivity of the super-thick copper layers and DBC[12]

	Thick film (Dupont QP153)		Thick film (laboratory ink)	DBC
Thickness (μm)	319	319	275	300
Firing temperature (°C)	900	1065	1065	1065–1080
Temperature cycle	1 h	20 min	20 min	–
Peel strength (±0.1 N mm^{-1})	1.3	1.5	4.1	3.6
Resistivity (±0.2 μΩ cm)	2.5	2.3	2.2	1.8

Moreover, current surge tests performed with high-energy pulse have also shown the outstanding behaviour of these pressed screen-printed varistors.[10]

5. Application to pyroelectric components

Up to now, pyroelectric coefficients of screen-printed layers have been shown to be lower than those of corresponding ceramics.[11] This difference is thought to be due to the lack of layer compacity. Application of a mechanical pressure onto screen-printed pyroelectric layers should again increase the compacity and thus improve the pyroelectric properties.

The pyroelectric ink is based on lead zirconate (PZNFT) mixed with 2% of an eutectic phase (PbO, PbF_2). The pressed or unpressed pyroelectric layer, deposited on a previously fired gold electrode, is sintered at 900 °C. Finally, a gold electrode is screen-printed and fired on top of the PZNFT layer. Then, the samples are polarised for 10 min under 50 kV cm^{-1} at 90 °C.

The pyroelectric coefficient $p(T)$, deduced from the relation $i = S \times dP_s/dt = S \times dP_s/dT \times dT/dt$, where S is the surface of the sample, is measured during the temperature cycle between 0 and 60 °C at a constant rate of 5 °C min^{-1}. The values of p at 300 and 320 K are reported in Table 3. The beneficial effect of the mechanical pressure is clearly demonstrated. The pyroelectric coefficient of the pressed thick film samples is close to those of the corresponding bulk ceramics. However, no noticeable difference is observed between uniaxial and hydrostatic pressure.

6. Copper super-thick films for power application

For high power devices, the standard thickness of screen-printed copper films (about 10 μm) does not allow high current densities. Metallized alumina substrates with 300 μm copper foil called DBC (direct bonding copper), are normally used for this application. However, commercially available DBC necessitate custom fabrication by chemical etching of the foil. This process may turn out to be long and expensive for prototypes and/or small series production. Therefore, we proposed the fabrication of unusual screen-printed super-thick films as an alternative solution to DBC.[12]

The deposition of high copper thicknesses (>250 μm) on alumina requires particular screen-printing conditions. Using Dupont QP153 ink, we improved the densification and adhesion properties of the copper layers on alumina thanks to a firing temperature increase close to the Cu–CuO eutectic temperature (1065 °C instead of 900 °C) combined with a multi-print (two to three superimposed layers). Electrical resistivity and peel strength measurements reported in Table 4, illustrate the beneficial effect of this special process. Moreover, in order to improve the resistivity and the adherence of the super-thick copper layers, we successfully developed our own copper ink without any inorganic binder.[12] The properties of these multi-print super-thick copper layers clearly appear comparable to those of the DBC (Table 4). Super-thick and dense copper layers fired at 1065 °C were shown to be an alternative solution to DBC for the fabrication of power hybrid prototypes.

7. Conclusion

The aim of this paper was to emphasise the influence of the densification parameters of screen-printed layers on their final properties. Though most results presented above are drawn from our own experience, many other authors have also pointed out this influence.

Interesting results can still be obtained with the standard screen-printing process. For example, well-controlled porous thick films have been developed to achieve unusual potentiometric ZrO_2-based CO selective sensor against H_2, H_2O, SO_x and NO_x[13] or amperometric zirconia O_2 sensor.[14] In the same way, pyroelectric sensors based on PZT porous layers exhibit higher figures of merit in voltage and current compare to PZT ceramics.[15] Another type of porous thick films application such as lanthanum–strontium cobaltite cathode for zirconia-based solid oxide fuel cells is also very promising.[16]

Nevertheless, improvements of the densification process of thick films may be required when firing occurs at temperatures lower than the sintering ones of bulk materials. In this context, some efforts have been done recently on powder preparation and ink composition.[17–21]

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