

# Screen-printed thick-films: From materials to functional devices

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## Abstract

The aim of the present paper is to demonstrate that the existence of a bulky sintered material, with the required properties for a potential application (called hereafter active material), does not necessarily mean a straightforward manufacturing of a corresponding functional planar thick-film device with the required properties. Many problems have to be solved at the level of each element of the micro-assembly, namely the substrate, the electrodes, the heating resistor, and of course the active material. Moreover, for a reliability approach, physico-chemical interactions in the whole micro-assembly have to be considered. Examples drawn from our own experience in the area, deal with super-thick copper pads, varistors, PZT-based pyroelectric sensors, semiconductor oxide gas sensors, zirconia oxygen sensors . . .

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## 1. Introduction

A few years before World War II, the screen-printing technology was already used in the U.S. to make metallic electrodes on mica sheets for condensers. In 1939, Dupont de Nemours manufactured silver screen-printing paste. The first mass-produced hybrid circuits date from 1943 and were used to build detonators.<sup>1</sup> Since then, and until the beginning of the nineties, the development of thick film hybrid circuits has regularly grown, thanks to the invention of the transistor and later to that of integrated circuits (IC). This permanent growth stopped at the beginning of the nineties for two reasons: (i) more and more electronic functions were integrated on IC, (ii) the development of SMT (surface mount technology) enabled to increase significantly the density of connected components, compared to hybrid thick film technology.

Until 10–15 years ago, most of the market of screen-printing pastes was devoted to electronic circuits. Commercial pastes were primarily developed for these applications, i.e. to make conductive, insulating or resistive thick films operated at temperatures lower than 150 °C.

This dominant application in the electronics area is less obvious today. For example, the manufacturing of heating res-

istors for car windshields or for kettles, and of platinum electrodes of zirconia oxygen gauges for car exhaust, now represents a significant percentage of the market of thick films. New pastes are also developed for emergent applications, as for making films or tapes of oxygen-conducting zirconia for fuel-cells, of PZT, of various gas sensors . . .

The activity of our team has grown in this context for the last 20 years. The basic idea was to valorise and functionalise inorganic materials, by tailoring them as miniaturized thick films, made with a cheap and reproducible technology. The potential applications were numerous. Pastes made of semiconductor oxides, of solid electrolytes, of materials with a catalytic activity have been manufactured to design gas sensors operating on various principles and allowing to sense new species. Zinc-oxide based pastes have been elaborated to make varistors, PZT-based pastes to make pyroelectric sensors . . . The aim of the present paper is to demonstrate that the existence of a material with the required properties for a potential application when elaborated as a sintered pellet or as a ceramic does not necessarily mean a straightforward manufacturing of a corresponding functional planar thick-film device with identical properties. The problematic will first be described. Then the various elements of the functional device, namely the substrate, the electrodes and the material of interest will be dealt with separately, before treating a case of more global interaction between the various ele-

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ments. Most examples are drawn from our own experiences in this area.

## 2. Problematic

The starting point is a material having the required properties for the application. This material will be called hereafter active material. The exit point is a functional planar device with the same properties. Fig. 1 shows schematically some thick-film functional devices: a microheater, a varistor, a semiconductor oxide gas sensor, a silicon carbide field effect transistor with a screen-printed platinum gate for engines lambda control,<sup>2</sup> and a YSZ exhaust NO<sub>x</sub> sensor integrating an oxygen pump, a potentiometric oxygen sensor and an amperometric oxygen sensor.<sup>3</sup> The screen-printing technology consists in depositing a paste with a given design on a substrate, drying and firing, and possibly repeating the operation one or several times with other pastes.

The first step in the conception of a functional device is often to make a paste with the powder of active inorganic material. The manufacturing of a paste with rheological properties compatible with screen-printing technology requires to mix the inorganic powder with an organic phase usually made of a large amount of solvent evaporating below 120 °C and of a small percentage of organic binder such as ethyl cellulose which will burn out at around 400 °C. An immediate conse-

quence of the presence of this organic phase is an increase of the porosity of the fired thick-film, compared to ceramics. This can be an advantage, as in the case of gas sensors in order to increase the exchange surface, and thus the interactions between the species to sense and the solid. This can also be a drawback, as for varistors with high current densities or as for solid electrolytes with high ionic conductivities.

Moreover, in order to ensure the coherence of the film during the firing process and its adhesion to the substrate, a few percents of inorganic binder made of a fusible phase such as a glassy frit or an oxide, are often added to the paste. Contrary to the organic binder, this inorganic binder is a permanent additive to the starting powder of active material. During the firing, chemical reactions will occur between the active material and the additive and also possibly between the material and the substrate, which itself contains inorganic additives as will be seen after. It is clear that the presence of these additives, even in amounts of only a few percents, may be sufficient to alter the properties of the active material. Conversely, there are some cases where the presence of these additives is favourable.

Commercial pastes are widely available to make metallic connections, electrodes, heating resistors or protective insulating layers. These pastes also contain a few percents amounts of inorganic additives, and possible chemical reactions of these additives with the thick film of active material cannot be excluded. Moreover, the presence of these

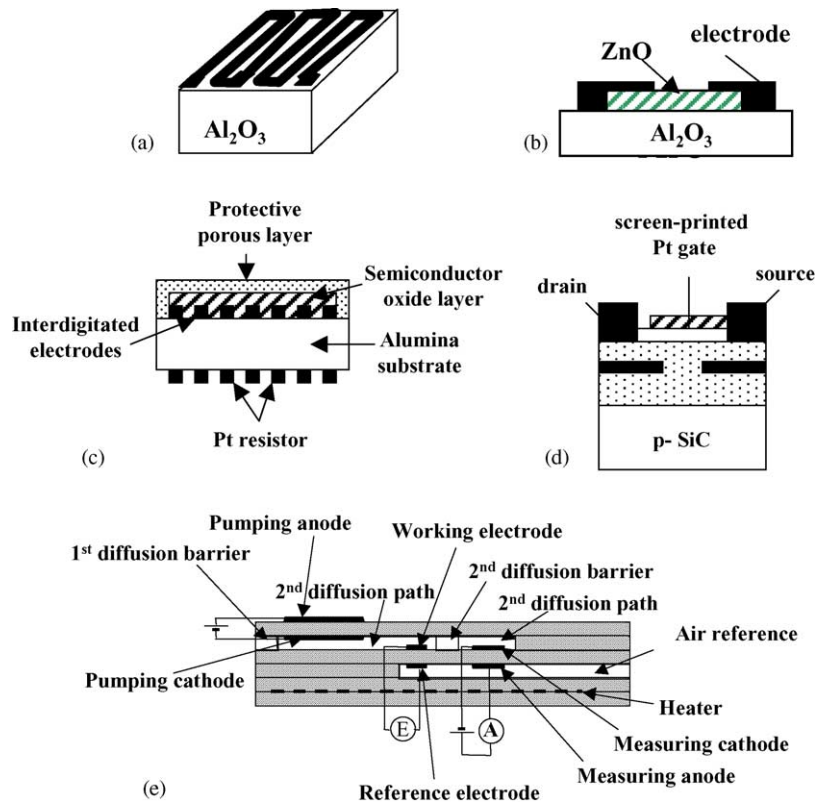


Fig. 1. Schematic drawings of planar: (a) heating resistor; (b) varistor; (c) semiconductor oxide gas sensor; (d) SiC field effect transistor car exhaust sensor (from<sup>2</sup>); and (e) zirconia NO<sub>x</sub> car exhaust sensor (from<sup>3</sup>).

additives may be critical in the manufacturing of porous electrodes sometimes used in gas sensors. Finally, it is important to note that most of these commercial pastes were originally developed for electronic applications, i.e. for operating temperatures lower than 150 °C. Even if the firing temperatures recommended by the manufacturers are in the range 600–1100 °C, it is difficult to predict how such films will withstand permanent temperatures of around 400 °C in semiconductor gas sensors or even higher in car exhaust sensors.

### 3. Basic elements of the functional thick-film device

It is clear from Fig. 1 that any screen-printed device usually requires a substrate, an active material and electrodes or metallic contacts.

#### 3.1. The substrate

The substrate certainly is the simplest part of the device to deal with. Its function is to support mechanically the thick layers and to ensure their adhesion on it. Substrates traditionally used for hybrid circuits are manufactured with the so-called doctor blade tape casting process. They are made of  $\alpha$ -alumina with 4% of silica and magnesium oxide. Alumina is chemically inert versus metals and versus most inorganic oxides up to 1000 °C. The 4%  $\text{SiO}_2/\text{MgO}$  promotes the adhesion of the thick film when reacting with the inorganic additives of the paste or with the active material itself.

When a better thermal conductivity of the substrate is required, aluminium nitride or silicon carbide-based substrates are preferred. However, the adhesion of inorganic oxide films usually require some surface pre-oxidation of such substrates. Moreover, silicon carbide may give intermetallic compounds with metallic pastes.

For planar oxygen zirconia sensors, as in Fig. 1e, the substrate itself, made of oxygen conducting YSZ, is active in the functional device. A compromise has generally to be found between the ionic conductivity and the mechanical properties of the substrate, the latter depending not only on the presence of additives, but also on the yttrium content.

#### 3.2. The electrodes

##### 3.2.1. Influence of the metal nature

**3.2.1.1. Semiconductor oxide gas sensors.** The operating of a screen-printed tin oxide gas sensor seems especially simple, since it only requires the measurement of the resistance variation of the  $\text{SnO}_2$  layer, when heated at several hundreds of degrees Celsius and exposed to a reducing gas. The nature of the metallic electrodes does not seem of primary importance, since any metal, whatever its nature, is supposed to yield the same value of the resistance, provided that the contact is ohmic. An initial study on this topic, carried out by Lalauze et al.<sup>4</sup> and numerous later studies including ours,<sup>5</sup> from which the following curves are extracted, demonstrate the

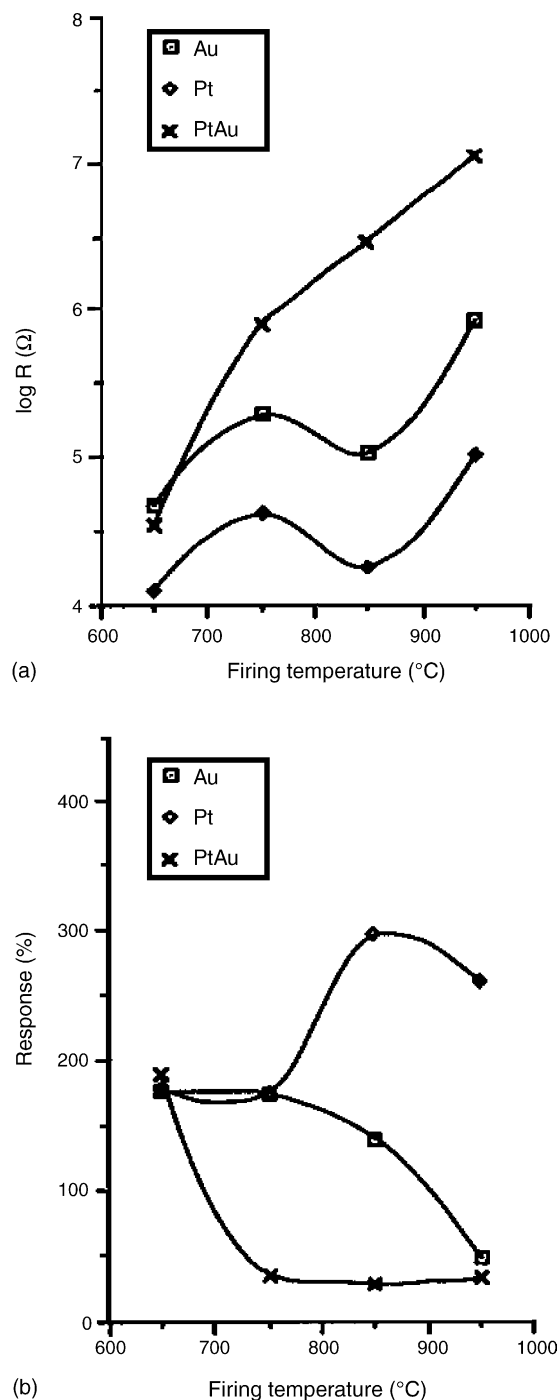


Fig. 2. (a) Resistance and (b) response to 1% methane at 400 °C of  $\text{SnO}_2$  thick layers as a function of the electrode metal and of the firing temperature of the tin oxide layer (from<sup>5</sup>).

contrary. Fig. 2 compares the resistance and the response to 1% methane (defined as the ratio  $(G - G_0)/G_0$  where  $G_0$  and  $G$  are the film conductances in absence and in presence of 1% methane in air) of a thick film tin oxide sensor at 400 °C with screen-printed electrodes differing in the metal nature. A similar comparison is carried out in Fig. 3 between two tin oxide thick films, both with gold electrodes, but screen-printed in

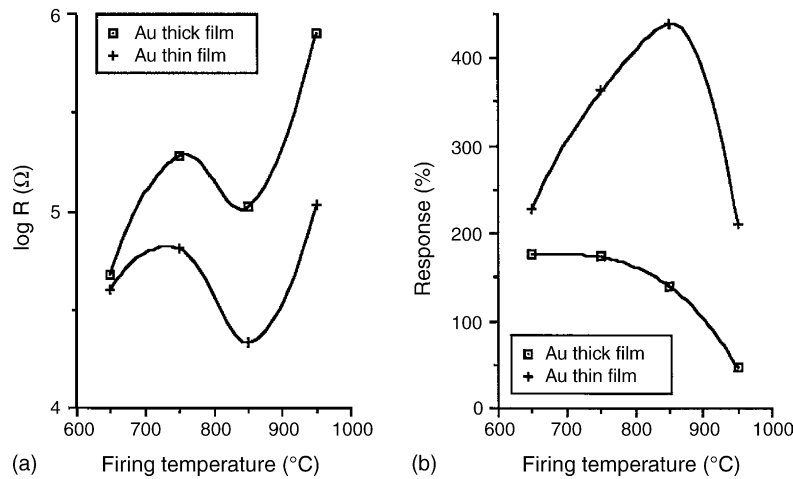


Fig. 3. (a) Resistance and (b) response to 1% methane at 400 °C of SnO<sub>2</sub> thick layers with screen-printed (thick film) and sputtered (thin film) gold as a function of the firing temperature of the tin oxide layer (from<sup>5</sup>).

one case (thick film) and sputtered in the other (thin film). Not only the nature of the electrode metal is important, but also the type of deposition. The proposed explanation was based on the existence of interface resistances between the electrodes and the tin oxide thick film, due to the inorganic binders contained in the metallic pastes. The laboratory made tin oxide paste did not include any inorganic additive in this case.

**3.2.1.2. Amperometric YSZ oxygen sensors.** In studying NO<sub>x</sub> amperometric sensors for car exhaust, we were confronted to the choice of a platinum paste in order to obtain a porous electrode ensuring a good triple contact between the oxygen ions of the YSZ substrate, the gaseous oxygen and the electrons provided by the metal. Platinum pastes developed for electronic applications led to very large current instabilities, probably because of an excess of inorganic binder, not compatible with the 700 °C operating temperature. As expected, a paste recommended by manufacturers for potentiometric zirconia sensors, yielded much better results. Nevertheless, a further reduction of instabilities and long-term drifts could be gained by adding a small percentage of YSZ powder to the platinum paste.<sup>6</sup>

**3.2.1.3. Varistors.** A recent study, carried out in our Laboratory shows the outstanding effect of the electrode on the non-linear coefficient  $\alpha$  of screen-printed ZnO-based varistors (Table 1).<sup>7</sup> A more detailed explanation is given in Section 4.

Table 1  
Non-linear coefficient  $\alpha$  for screen-printed ZnO-based varistors made with different electrode pastes (from<sup>7</sup>)

Electrode	$\alpha$
Ag ESL 9912 A	6 ± 2
Pt ESL 5545 LS	33 ± 1
Au ESL 8836	7 ± 1
AgPd ESL 9695	11 ± 2

### 3.2.2. Metallic interdiffusion at the electrode/wire junction

Another problem concerning the electrodes may arise from the sealing between the screen-printed electrodes and the connecting metallic wires. In the case of our semiconductor oxide gas sensors, the electrodes were usually made either of screen-printed gold or platinum. The sealing with the platinum wires was ensured by a drop of screen-printing paste of gold or platinum. The presence of metals of different nature is well known to give rise to interdiffusion processes, especially when the operating temperature of the device is high. This may lead to small holes which affect the original solidity of the sealing. The phenomenon, known as the Kirkendall effect, often occurs in microelectronics when soldering gold wires to aluminium tracks. In order to demonstrate the possible effect in our gas sensors, four series of samples were fabricated. Pads of either gold or platinum simulating the electrodes were screen-printed onto an alumina substrate and fired. A platinum wire was then sealed to these pads with a screen-printing paste of either gold or platinum. Each series of samples corresponded to one of the four possibilities:

- Au pad/Au sealing/Pt wire;
- Au pad/Pt sealing/Pt wire;
- Pt pad/Au sealing/Pt wire;
- Pt pad/Pt sealing/Pt wire.

All samples were fired 10mn at 850 °C. Ten samples of each series were tested after this first firing with a micro-machine measuring the tensile strength up to tearing. For all tested samples, the tearing forces were close to 2 N. Ten other samples of each series were further annealed for 48 h at 750 °C, in order to simulate the ageing process of the gas sensors, supposed to occur after several months at the operating temperature of 400 °C. After this second thermal treatment, the tearing forces remained in the same range for the Au pad/Au sealing and Pt pad/Pt sealing series, but were re-

duced to less than 1N for the mixed Au pad/Pt sealing and Pt pad/Au sealing series.<sup>8</sup>

### 3.2.3. Influence of the electrodes shape

The versatility of the screen-printing technology allows to give nearly any possible design to the electrodes. In some gas sensors, the shape of the electrodes has been shown to have influence on the properties of the sensing device.

In the previously mentioned study of amperometric exhaust sensors, simple oxygen pumping devices were made by screen-printing two identical platinum electrodes on the same side of a YSZ substrate.<sup>9</sup> One electrode served as cathode and the other as anode. The devices only differed by the length, the width and the spacing of the electrodes. For oxygen concentrations larger than 1% in nitrogen, the currents were proportional to the bias for all electrode designs. But for 0.1% oxygen in nitrogen, this was no longer true, and the extent of the non-proportionality was enhanced with narrow and close electrodes. This suggested that the behaviour of the oxygen pump shifted from the kinetics-limited region to the diffusion-limited one more easily in the latter case.

Another result concerns potentiometric carbon dioxide sensors based on LiSICON.<sup>10</sup> The lithium conductor active material is screen-printed on one side of an alumina substrate and a platinum heating resistor on the other (Fig. 4). Then a working electrode made of a mixture of lithium carbonate and of gold, and an open reference electrode made of gold are screen-printed on the LiSICON layer. As soon as the surface of the reference electrode becomes smaller than that of the working electrode, the response to carbon dioxide strongly drifts. If the asymmetry is deeply exaggerated, the response may even disappear.

## 3.3. The active material

### 3.3.1. Metals

**3.3.1.1. Copper.** Because of the larger porosity of screen-printed films than of bulky materials and also possibly because of the presence of additives, the conductivity of copper thick films is always lower than that of copper sheets. Moreover, the screen-printing technology normally limits the thickness of the films to about 20  $\mu\text{m}$ . Therefore, the possibility to replace the well established DBC technology (direct bonding of a copper sheet of 300  $\mu\text{m}$  on an alumina

substrate) by screen-printed thick films in power circuits appears very limited. Nevertheless, the screen-printing of 300  $\mu\text{m}$  dense thick films of copper would have the advantages to be more versatile than DBC in the design of prototypes. Moreover, the deposit of such super-thick copper films could be limited to the part of the substrate concerned with power circuits, the remaining part devoted to non-power circuits making only use of standard films. This approach was carried out in our group a few years ago<sup>11</sup> and super-thick copper films were obtained by using a fritless copper paste and by firing the deposit at 1066  $^{\circ}\text{C}$ , i.e. just above the copper–oxygen eutectic fusion temperature (1065  $^{\circ}\text{C}$ ). For a standard 20  $\mu\text{m}$  thick copper film, the firing temperature recommended by manufacturers is only 950  $^{\circ}\text{C}$ . Comparative thermal shock tests of inverters made with DBC and with this super-thick film technology demonstrated the validity and even the superiority of the latter.

**3.3.1.2. Platinum.** Screen-printed platinum is often used as heating resistor for various devices, as for example semiconductor oxide gas sensors which are normally operated around 400  $^{\circ}\text{C}$ . As stated before, platinum pastes were mostly developed for electronic circuitry operated below 150  $^{\circ}\text{C}$ . Using such a paste and firing the deposit at only 850  $^{\circ}\text{C}$ , which is in the range of temperatures recommended by manufacturers, leads to unavoidable drifts of the resistor when permanently heated at 400  $^{\circ}\text{C}$ . One solution to this problem is just to use higher firing temperatures (around 1100  $^{\circ}\text{C}$ ).<sup>8</sup> In some cases, this turns out to be insufficient. For example, while testing methane sensors with the Gaz de France Company, we noticed that the so-prepared platinum heaters still exhibited some long-term drift after several months of operation. But ageing the same sensors during a similar period even at higher temperatures in an external furnace, did not affect the resistance of the platinum resistor. The deposit of a layer of insulating glass above the platinum-heating resistor solved the problem. The phenomenon was therefore correlated to the electro-migration of some additive species to the platinum, under the influence of air oxygen.

### 3.3.2. Varistors, capacitors, pyroelectrics and solid electrolytes

It is easy to screen-print a zinc-oxide based powder with good varistor properties when sintered as ceramic. But keeping the high value of the non-linearity coefficient in the film is not straightforward. The approach developed in our group about 10 years ago<sup>12</sup> consisted in applying an isostatic pressure of several kbars to the so-called wet film, after the evaporation of solvents and before the firing. This additional step to the standard screen-printing procedure decreases significantly the porosity of the films and also enables to suppress inorganic additives, normally necessary for the adhesion on the substrate. Since the varistor properties are known to occur at the grain boundaries, the smaller porosity and the suppression of additives both contribute to improve significantly the film characteristics (Table 2).

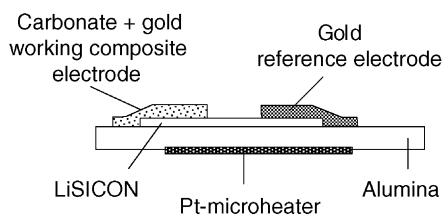


Fig. 4. Cross view of a potentiometric LiSICON-based sensor for carbon dioxide (from<sup>10</sup>).



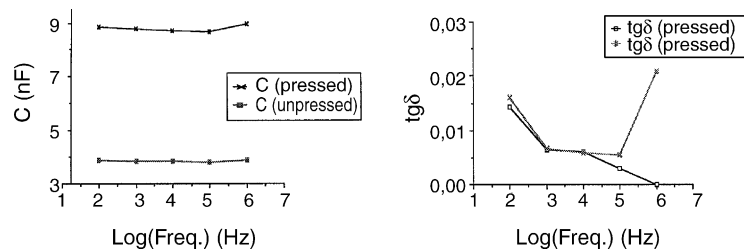


Fig. 5. Capacitance and loss angle of pressed and unpressed varistor thick layers versus frequency (from<sup>12</sup>).

The properties of screen-printed capacitors were also improved by this additional step of mechanical pressure.<sup>12</sup> Fig. 5 compares the capacitance and loss angle of pressed and unpressed samples versus frequency.

Similar results were obtained with PZT,<sup>13</sup> and the pressed films have pyroelectric coefficients similar to those of ceramics (Table 3).

Finally, in<sup>12</sup>, we suggested that this new step of mechanical pressure should also improve the ionic conductivity of YSZ films, but did not carry out the experiment ourselves. This was done a few years later by the team of Professor K.H. Härdtl at the Karlsruhe University of Technology (Germany) and their results confirmed our prediction.

### 3.3.3. Semiconductor oxide gas sensors

At the beginning of the eighties, we were looking for other semiconductor oxides than SnO<sub>2</sub>, with the aim to build more

Table 2

Comparison of electrical parameters for different low-voltage ZnO-based varistors (from<sup>12</sup>)

	Laboratory screen-printed varistors		Commercial samples	
	Unpressed	Pressed	Glaze varistor <sup>a</sup>	Ceramic <sup>b</sup>
$V_T$ (V)	2.4–10.1	16–18	6–21.5	8
$\alpha$	–	17–19	6.5–8.1	18
$R_L$ (M $\Omega$ )	2	0.1–0.5	2	2
$C$ (pF mm <sup>-2</sup> )	40	22–50	3	3
tg $\delta$	<0.07	0.15–0.20	<0.1	<0.1
$-10^4 K_V$ (K <sup>-1</sup> )	4.9–7.8	3.6–9	2.3	2.3

<sup>a</sup> Matsuchita.

<sup>b</sup> Gemov.

Table 3

Pyroelectric coefficient of PZFT thick films and ceramics (from<sup>13</sup>)

PZFT	Eutectic (%)	$p$ (300 K) (nC cm <sup>-2</sup> K <sup>-1</sup> )	$p$ (320 K) (nC cm <sup>-2</sup> K <sup>-1</sup> )
Unpressed thick film	2	5.5	6
	5	5	6
Pressed thick film (1 GPa)	2	17	20.5
	5	25	28
Ceramic	5	22	29

selective sensors. Iron oxide-based sensors fell in our scope of investigation, and some surprising results were obtained.

3.3.3.1. SrFeO<sub>2.8</sub>. In order to improve the adhesion of the film on the alumina substrate, the glassy binder CaO/B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (CaBAISi) was added to the supposedly active strontium ferrate.<sup>14</sup> Fig. 6 shows the response to methane of such layers (defined as the ratio  $(R_0 - R)/R_0$  where  $R_0$  and  $R$  are the film resistances in absence and in presence of 1% methane in air), as a function of the volume concentration of CaBAISi. It is worth noting that the strontium ferrate alone is completely insensitive to methane and that the inorganic binder has a highly positive effect in this case.

The X-ray and Mössbauer analyses of the film prepared with 44% CaBAISi, which is the binder content leading to the maximum response to methane, clearly show the quasi disappearance of the original SrFeO<sub>2.8</sub> phase to the detriment of SrFe<sub>12</sub>O<sub>19</sub>. In the Mössbauer spectrum shown in Fig. 7, only the additional lines with an isomer shift in the vicinity of 0 mm/s can be attributed to SrFeO<sub>2.8</sub>. All others are characteristic of SrFe<sub>12</sub>O<sub>19</sub>. This result means that most of the strontium has migrated to the glassy phase. Moreover, SrFe<sub>12</sub>O<sub>19</sub> is known to be a n-type semiconductor, whereas

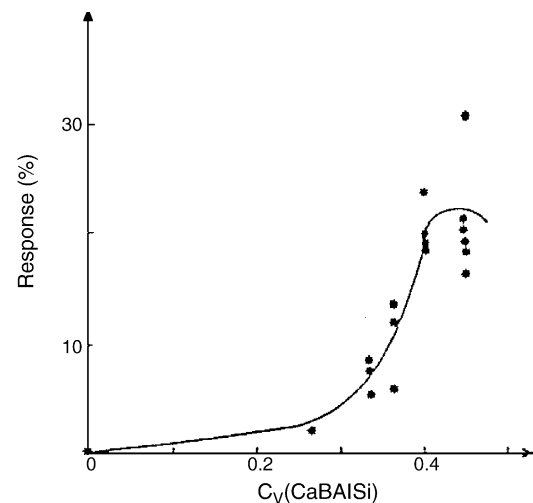


Fig. 6. Response to 1% methane at 470 °C of a screen-printed thick film of SrFeO<sub>2.8</sub>, as a function of the volumetric concentration of glassy binder CaO/B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (CaBAISi) (from<sup>14</sup>).

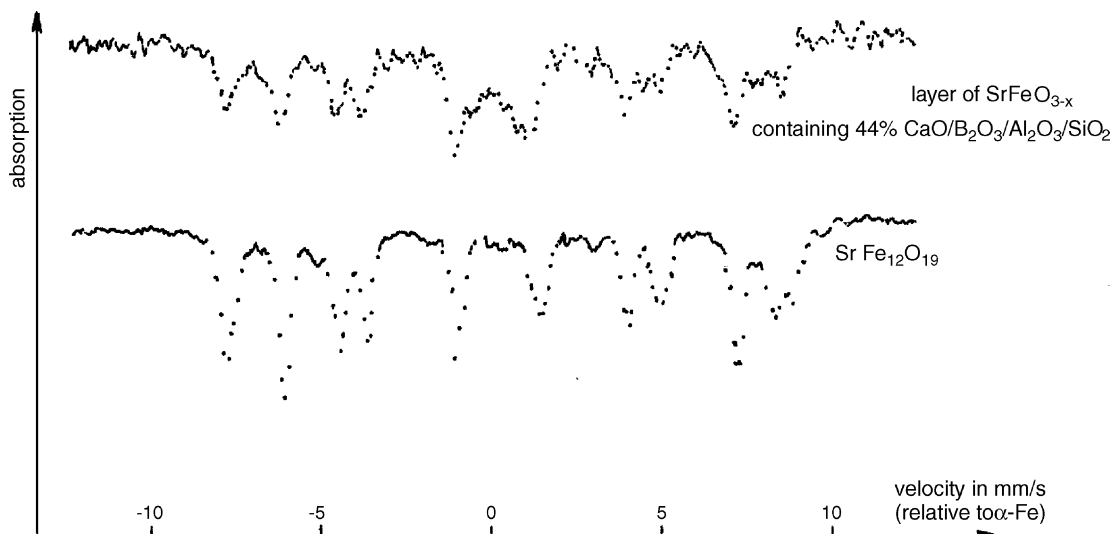


Fig. 7. Comparison between the room temperature Mössbauer spectrum of a screen-printed film of  $\text{SrFeO}_{2.8}$  containing 44 vol.% of glassy binder CaBAISi and that of  $\text{SrFe}_{12}\text{O}_{19}$  powder (from<sup>14</sup>).

the decrease of the film resistance when exposed to methane, supposes a p-type conductivity. These observations led us to the hypothesis that the electrical and sensing properties of the layers were governed by the shells of a grain-core/grain-shell structure, in which the core would consist mostly of  $\text{SrFe}_{12}\text{O}_{19}$  (Fig. 8).

**3.3.3.2.  $\text{Ca}_2\text{Fe}_2\text{O}_5$ .** In the search of making a sensor selective to a few ppm of phosphine, a thick layer made of calcium ferrate  $\text{Ca}_2\text{Fe}_2\text{O}_5$  without any additive, was pretreated with a high concentration of this gas (2000 ppm) in dry air for several hours at 360 °C.<sup>15</sup> Fig. 9 compares the response to phosphine of such layers before and after the pre-treatment. The pre-treatment not only dramatically enhances the response, but also reverses the type of semiconductivity from n to p. The reversal was confirmed by Seebeck measurements. Since no modification of the X-ray diffraction pattern of the layer occurs before and after the pretreatment, we again assumed a grain shell/grain core structure in which the very thin shell would control the electrical and sensing properties. It is interesting to note that the phosphine pre-treatment carried out on a pellet of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  did not lead to any modification neither

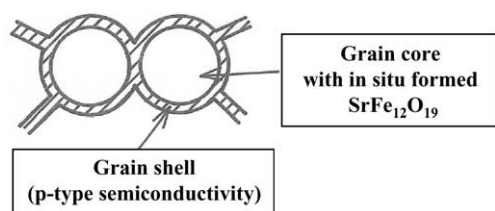


Fig. 8. Possible model based on a grain core/grain shell structure to explain the physico-chemical properties of a thick film of  $\text{SrFeO}_{2.8}$  containing 44 vol.% of glassy binder CaBAISi.

of the resistance nor of the response to 100 ppm phosphine (Table 4). This was explained by the too large amount of matter in the pellet to react with the gas, compared to the thick film.

**3.3.3.3.  $\text{Fe}_2\text{O}_3$ .** A similar phosphine pre-treatment was applied to thick films of iron oxide  $\text{Fe}_2\text{O}_3$  without any inorganic

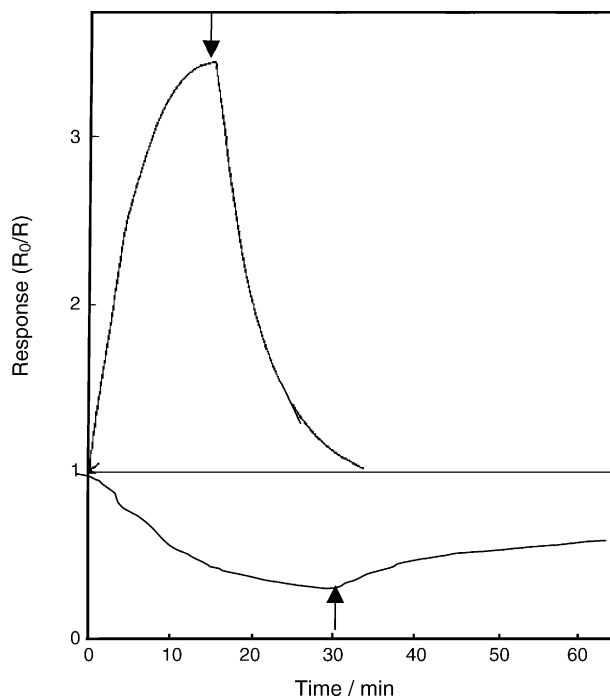


Fig. 9. Responses of a thick film of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  at 360 °C to 500 ppm phosphine in dry air before pretreatment (lower curve) and to 5 ppm after pretreatment (upper curve). The arrows indicate termination of  $\text{PH}_3$  exposure (from<sup>15</sup>).

Table 4  
Resistance and response to phosphine of  $\text{Ca}_2\text{Fe}_2\text{O}_5$

$\text{Ca}_2\text{Fe}_2\text{O}_5$	Resistance $R_0$ (k $\Omega$ )		Response to 100 ppm $\text{PH}_3$ in dry air ( $R_0/R$ )	
	Before pretreatment	After pretreatment	Before pretreatment	After pretreatment
Thick film	1230	9750	0.98	10
Sintered pellet	2.5	2.6	0.98	0.98

$R_0$  is the resistance in dry air and  $R$  the resistance in presence of 100 ppm  $\text{PH}_3$  (from<sup>15</sup>).

additive.<sup>16</sup> The response to phosphine was increased, but no change of the type of majority carriers was observed, the conductivity remaining of n-type. Again no change of the X-ray diffraction pattern due to the pre-treatment could be observed, but an infra-red study clearly shows the appearance of extra-bands (Fig. 10) which were attributed to P–O bonds.

The pre-treatment of these films ensures moreover an extraordinary selectivity to phosphine, as shown in Fig. 11. This result was explained on the basis of the grain core/grain shell model presented in Fig. 12. The very thin shell, not visible on the X-ray diffraction pattern would mostly consist of a

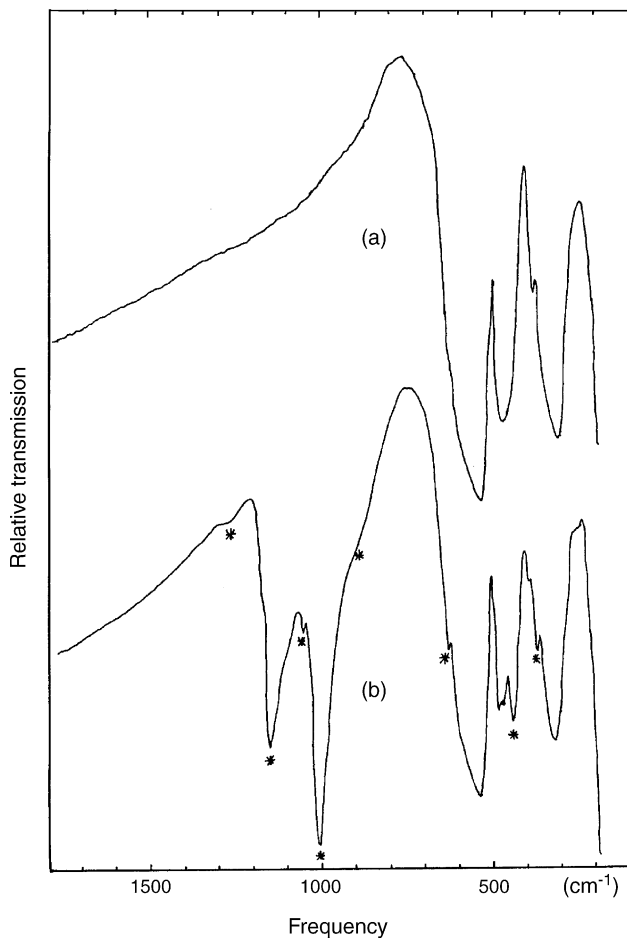


Fig. 10. Infrared spectra of  $\text{Fe}_2\text{O}_3$  thick films (a) before and (b) after phosphine pretreatment. Bands marked with (\*) are correlated to P–O bonds (from<sup>16</sup>).

phosphate lattice, as suggested by the IR results. Then, the adsorption of phosphine molecules at the surface of the grain shells would allow to rebuild the phosphate lattice partially destroyed by the exposition to air after the pre-treatment.<sup>17</sup>

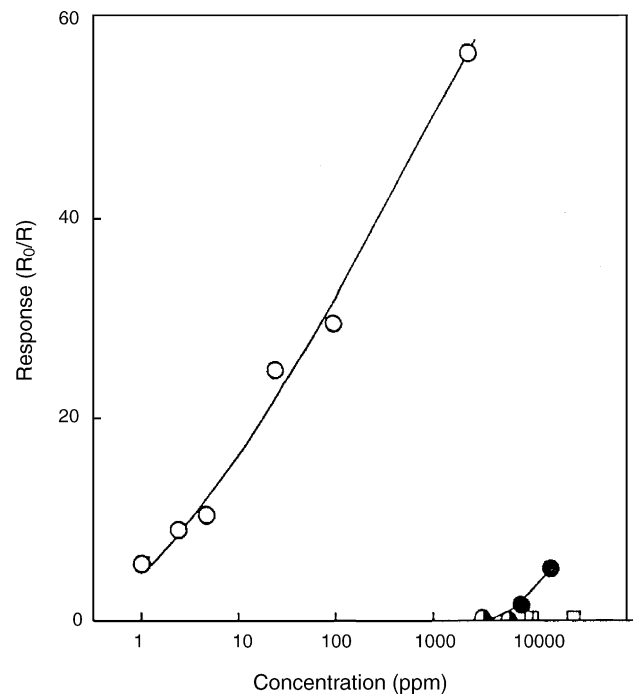


Fig. 11. Response of a  $\text{Fe}_2\text{O}_3$  thick film pretreated with 2000 ppm phosphine 3 h at  $360^\circ\text{C}$  to: (○)  $\text{PH}_3$ , (●)  $\text{H}_2$ , (◐) Co, (□)  $\text{CH}_4$  (from<sup>16</sup>).

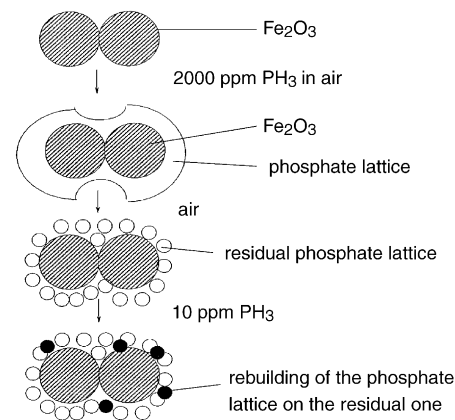


Fig. 12. Possible mechanism for explaining the effect of the pretreatment on the  $\text{PH}_3$  selectivity of a  $\text{Fe}_2\text{O}_3$  thick film (from<sup>17</sup>).



This would require less energy than adsorbing hydrogen or methane molecules.

#### 4. The whole functional thick-film device

In some cases, it is not possible to deal separately the problems of the substrate, the electrodes and the active material. A more detailed investigation of the results on ZnO-based varistors presented in Section 3.2.1.3 shows that the high value of  $\alpha$  does not originate from the metal nature but from the presence of Bi<sub>2</sub>O<sub>3</sub> in the platinum paste. The Bi<sub>2</sub>O<sub>3</sub> present in the platinum paste diffuses towards the previously deposited ZnO layer. This diffusion was shown to compensate the Bi<sub>2</sub>O<sub>3</sub> originally present as additive to the ZnO paste and absorbed by the substrate during the initial firing of the latter.<sup>7</sup>

Apart from physico-chemical interactions, there is another obvious case where the functional device has to be treated as a whole. It concerns reliability. At a stage of pre-industrialization, not only the basic elements have to be reliable, but the whole microassembly with its packaging and its connections. We had this approach when making series of prototypes of selective methane sensors in collaboration with the Gaz de France company about ten years ago.<sup>8,17</sup>

#### 5. Conclusion

The aim of the present paper was to show the difficulties which may arise when trying to manufacture a functional planar thick-film on the basis of an active material with potentially applicable properties. Many problems can be solved at the level of each element of the device, namely the substrate, the electrodes, the heating resistor, and of course the active material. In some cases, the properties of the thick film appear totally different from that of the sintered active material, and can be advantageously exploited. The functional device may require to be treated as a whole, as far as physico-chemical applications are concerned. This requirement becomes an imperative necessity when the reliability of the micro-assembly has to be taken into account, as in the case of manufacturing prototypes at a pre-industrialization stage.

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