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Journal of the European Ceramic Society 25 (2005) 2137–2140
www.elsevier.com/locate/jeurceramsoc

Optimization of SnO_2 screen-printing inks for gas sensor applications

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Available online 5 April 2005

Abstract

Conventional screen-printing inks are constituted of the active material, tin oxide in this study, organic and mineral binders. This last constituent is beneficial to the mechanical strength and adhesion of thick films, especially onto micro-hotplates, but is detrimental to the electrical properties required for sensor applications. An innovative solution consists in its replacement by a precursor which is transformed into SnO_2 during the thermal annealing of the layers. Inks containing a tin powder, an organic binder and either a gel or an alkoxide as precursor, with various compositions were studied. The organic binder is necessary to adjust the rheological properties of the ink, but it creates porosity and decreases the conductance. The addition of a gel allows to improve electrical properties but complicates ink preparation, and the adhesion remains insufficient. The use of an alkoxide (tin(II) 2-ethylexanoate) at a low content (15 wt.%) combined with the organic binger (24 wt.%) and tin oxide powder promotes both adhesion and conductance. Moreover, the low decomposition temperature of the alkoxide (300 °C) allows to decrease the annealing temperature of the layers which reinforces the compatibility of screen-printing with micro-hotplate technology.

Keywords: Sensors; Screen-printing; Electrical conductivity; Precursors-organic; Porosity

1. Introduction

Screen-printing technology is a low cost technology which allows to deposit thick films (a few to hundreds micrometers) and is widely used in the field of gas sensors since many years.[1,2] This technique is often used to elaborate the metallic tracks acting as electrical abductors (gold) or heating resistance (platinum) on ceramic substrates, or more scarcely the sensing elements based either on semi-conducting oxides[3,4] or solid electrolyte.[5] However, for sensing materials, a major problem to solve is the screen-printing ink composition in order to fit with electrical properties requirements. Conventional inks incorporate a mineral binder phase (glass) which gives the mechanical strength of the layers and their adhesion onto the substrates, but it presents a negative effect for electrical conduction.[6,7] In case of ceramic substrates with a high surface rugosity or including binders at their surface, it is possible to avoid or at least reduce the inorganic binder content in the ink. For smooth surfaces such as Si-based wafers which are more and more used as micro-machined substrates,[3,4] the adhesion of the sensing thick film becomes critical. Thus, in a previous paper,[7] we proposed a solution consisting in the replacement of the mineral binder of conventional ink by a gel precursor of the active material, tin oxide. The new ink, named gel ink, improved both electrical conductivity and adhesion of the resulting devices. However, the gel synthesis complicates the process and the resulting inks are not very stable. So, investigations presented in this paper concern the replacement of the gel by the organic precursor itself which is a tin alkoxide. The performances of sensors issued from the gel ink and from the alkoxide ink are presented.

2. Experimental

Three types of inks with various compositions were prepared using commercial constituents which are a tin oxide powder, organic vehicles and an alkoxide (tin(II) 2-ethylexanoate):

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doi:10.1016/j.jeurceramsoc.2005.03.020

- conventional inks without mineral binder only contain SnO_2 powder and the organic vehicle;
- gel ink is constituted by SnO_2 powder, a gel prepared from the alkoxide and the organic binder. The process of gel preparation is described elsewhere;[7]
- alkoxide ink is similar to gel ink but the gel is replaced by the alkoxide.

These inks were deposited using a semi-automatic Aurel C890 screen-printing machine, with 180 mesh mask. After deposition, the films were dried at 100 °C during 10 min and then annealed under ambient air at 650 °C during 2 h.

In order to perform physico-chemical characterizations and electrical measurements, layers were deposited onto α-alumina substrates. Large deposits (25 mm × 25 mm) were used for material characterizations using conventional techniques like X-ray diffraction, thermogravimetric analysis, specific area measurements, porosimetry and scanning electron microscopy (SEM). For sensor fabrication, sensing elements of 4 mm × 2 mm were deposited on 3.81 cm × 0.51 cm alumina substrate equipped with a platinum heater on the opposite face. The sensors were tested under air and carbon monoxide (300 ppm in dry air) at 500 °C, using a DC electrical circuit. The second type of substrates used in this study is Si-based micro-hotplates, onto which deposits of 300 μm × 500 μm were performed. These devices were dedicated to test the compatibility of screen-printing with micro-hotplate technology, and to evaluate the adhesion of the layers thanks to a cutting test:[7] observations of wafers after cutting enable to determine if the thick layers can withstand this treatment, and thus present a satisfying adhesion.

3. Results and discussion

Before studying the influence of the gel or of the alkoxide in the ink, it is necessary to understand the effect of the organic binder on the resulting layers. Its first role is to adjust the rheological properties of the ink which must have a thixotropic behavior. Moreover, in our previous paper,[7] we have shown that an increase of the organic binder content decreases the ink viscosity but also the electrical conductance of the obtained layers. Results obtained under air with four inks containing 20, 25, 35 and 40 wt.% of organic binder are reported in Fig. 1. For each ink composition, various thickness layers were obtained, resulting from 1 to 4 successive deposits during screen-printing process. The influence of the thickness for a given composition has been investigated in a previous study.[8] Concerning the influence of the organic binder, two phenomena can be observed when its content increases:

- at a fixed number of deposit, the resulting thickness decreases;
- at a given thickness, conductance is decreased as mentioned previously.

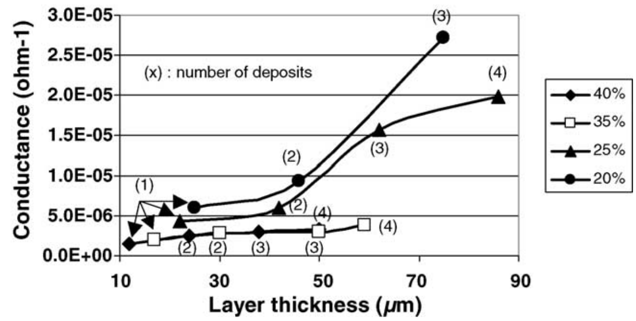

Fig. 1. Influence of organic binder (wt.%) in a conventional ink without mineral binder on the sensors thickness (function of deposits number) and their conductance under air at 500 °C.

The two results are a consequence of the binder elimination during annealing of the layers. The higher the organic fraction is, the less tin oxide content there is, resulting in thinner layers. Moreover, the organic vehicle creates porosity during its removal and the values of conductance can be correlated to the porous volume of the layers. Fig. 2 shows that inks containing high fraction of organic binder are more porous and less conductive, the comparison being made at a constant thickness of nearly 25 μm for the four compositions. Hence, the role of the organic binder is significant as it modifies the final thick film properties.

The objective of the gel ink is to avoid the presence of mineral binder in the final layer and to improve the mechanical adhesion. The gel is a SnO_2 precursor and will be consequently transformed into SnO_2 during the annealing, inside the layer and may create chemical bonds with both the initial powder and the substrate surface. Moreover, as its transformation occurs at relatively low temperature (300 °C),[7] such a solution is interesting to lower the annealing temperature compared to conventional inks, and thus to improve the compatibility with micro-machined substrates which usually can not withstand temperatures higher than 600–650 °C.

In order to simplify the process and avoid the gel synthesis, we decided to introduce directly the tin(II) 2-ethylexanoate alkoxide in the ink. The thermal decomposition of the alkoxide was studied in the same conditions as the gel,[7] and SnO_2

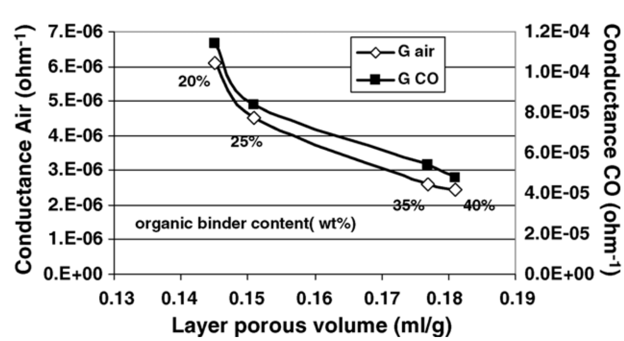

Fig. 2. Correlation between conductance under air and CO (300 ppm) at 500 °C and the porous volume of thick films (around 25 μm), depending on the organic binder content (wt.%).

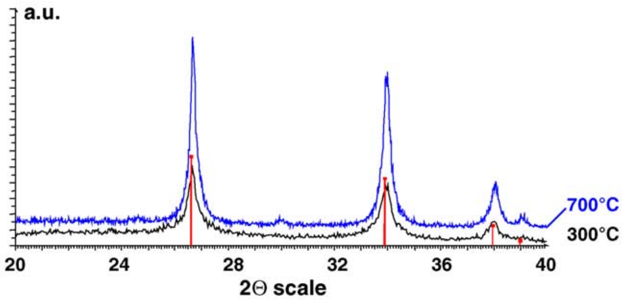

Fig. 3. X-ray diffraction patterns of SnO_2 powders resulting from alkoxide thermal treatment at 300 and 700 °C.

Table 1
Characteristics of powders issued from the gel and alkoxide thermal treatments at 300 and 700 °C

Powder	Annealing temperature (°C)	Crystallite size (nm)	Specific area (m^2/g)
Ex-gel	300	4	142
	700	30	14
Ex-alkoxide	300	17	73
	700	55	12

powders resulting from these two precursors at different temperatures were analyzed. Fig. 3 shows X-ray diffraction patterns of powders issued from the alkoxide at 300 and 700 °C during 12 h. Crystallites sizes determined from the width of diffraction peak and specific areas of powders issued from the gel and the alkoxide are reported in Table 1. These results indicate that the crystallization and the grain growth of ex-alkoxide powder is more rapid than that of the gel. To compare electrical performances, two inks with the same composition were prepared: SnO_2 powders 66 wt.%, gel or alkoxide 27 wt.% and organic binder 7 wt.%. SEM observations (Fig. 4) of the surface of deposits onto micro-hotplates reveal that the ex-alkoxide layer is more homogeneous and has less cracks. Despite these morphological differences, electrical performances are quite similar for both ex-gel and ex-alkoxide sensors (Fig. 5). Conductances under air and CO are strongly increased compared to the conventional ink only containing SnO_2 powder and the mineral binder. However, a strong difference between this two layers is their adhesion.

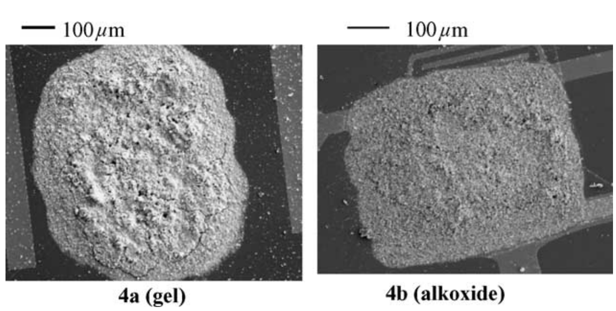

Fig. 4. SEM observations of the surface of 300 μm × 500 μm thick films prepared from gel ink (a) and alkoxide ink (b), after deposition and annealing.

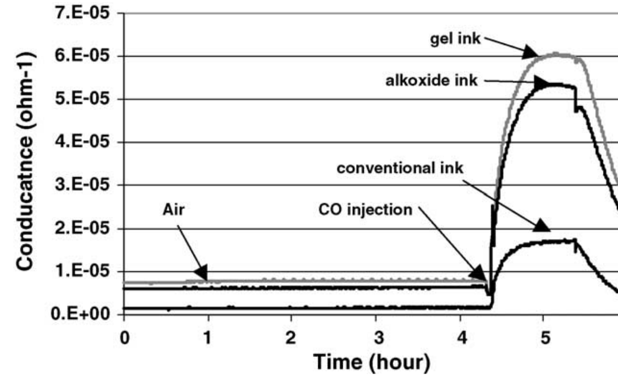

Fig. 5. Comparison of conductances at 500 °C of sensors prepared from conventional, gel and alkoxide inks.

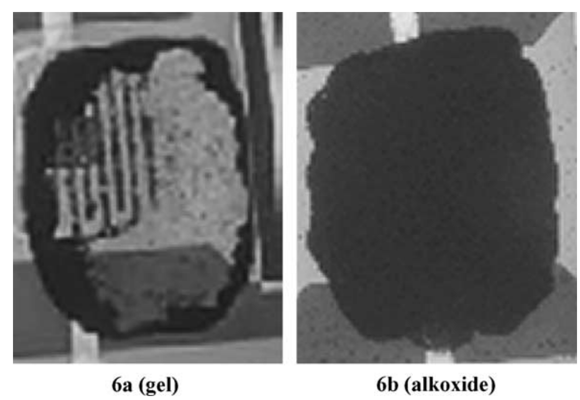

Fig. 6. SEM observations of the surface of 300 μm × 500 μm thick films prepared from gel ink (a) and alkoxide ink (b), after the cutting test.

After the cutting test, films issued from the alkoxide ink are less damaged compared to ex-gel layers which have been partly withdrawn from the substrate (Fig. 6). This difference of behavior may be linked to the texture of the films (Fig. 4), and to the higher reactivity of the alkoxide (crystallization, grain growth) which may enhance bonding with initial SnO_2 grains (commercial powder) and the substrate.

Previous results prove that the alkoxide ink is more efficient than the gel one. However, as the final sensor properties depends on the ink composition, we studied six alkoxide inks with different contents of SnO_2 powder and organic binder (Table 2). SEM observations of the resulting layers indicate that inks A and B which do not contain organic binder lead to completely cracked films. The conductance of the cor-

Table 2
Composition (wt.%) of alkoxide inks

Inks	SnO_2	Alkoxide	Organic binder
A	63	37	0
B	50	50	0
C	67	26	7
D	64	26	10
E	66	17	17
F	61	15	24

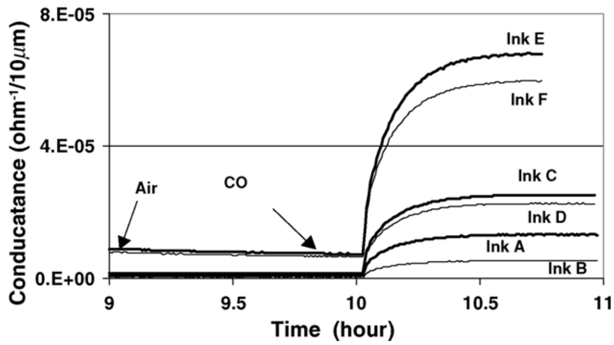

Fig. 7. Influence of alkoxide ink composition (Table 2) on air and CO (300 ppm) conductances (normalized to 10 μm) at 500 °C.

responding sensors (normalized to a constant thickness of 10 μm) is quite low (Fig. 7). This behavior is explained by the high viscosity of these two inks which do not have the required rheology for screen-printing: the organic binder is thus an indispensable constituent. The behavior of inks C and D on one hand, and E and F on the other hand is similar. Their morphology is the same as the one shown in Fig. 4b. The only slight difference concerns ink F which is more fluid due to its high organic binder content. The surface of ink F film is more homogeneous and the resulting layers are thinner, around 10 μm compared to 20 μm for inks E and D films and 30 μm for ink C films. Concerning conductances, Fig. 7 shows that, for the same thickness, sensors issued from inks E, F are more conductive than the ones resulting from inks C, D. As for the influence of the organic binder content (Fig. 2), the effect is correlated to the porosity of the layers: layers C and D are more porous (pore vol. 0.16 ml/g) and less conductive than E and F layers (pore vol. 0.12 ml/g). Concerning adhesion properties estimated from the cutting test, no clear difference can be pointed out for inks C to F which present good properties. On the contrary, as it could be expected, the adhesion of layers A and B is quite poor.

Hence, the optimization of alkoxide ink composition can be mainly performed in regards of the electrical conductivity, and thus of the porosity of the layers. The presence of organic binder is necessary. Then, the addition of the alkoxide (for example, 15 wt.% for ink F) improves both electrical performances and adhesion: the desired effect of the alkoxide consisting in a better sintering of the layer due to chemical bonds, and a consequent lower porosity is reached. However, if the alkoxide content increases too much (for example, 26 wt.% for ink C), the porosity increases compared to previous case, which is explained by the strong weight loss during its thermal transformation. Hence, the composition of ink F represents a good compromise. The stability of sensors developed with ink F have been tested in a laboratory bench for an isothermal running at 500 °C during more than 900 h: any significant deviations of the conductance under air and CO were observed during this test.

4. Conclusion

The results presented in this paper show that the morphological and electrical properties of SnO_2 thick films are strongly dependant on the ink composition used for their elaboration. The substitution of mineral binders used in conventional inks by a tin oxide precursor is an innovative solution which improves the performances of the resulting sensors. The introduction of the initial alkoxide instead of its gel simplifies the ink preparation and is beneficial to the adhesion properties onto micro-machined substrates. Another advantage is that it is possible to reduce the annealing temperature (650 °C) compared to conventional inks (850 °C), which reinforces the compatibility of screen-printing with microhotplate technology.

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