Optimization of SnO_2 screen-printing inks for gas sensor applications.

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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 (E), Screen-printing, Electrical Conductivity (C), Precursors-organic (A), Porosity (B)

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) :

- 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 minutes and then annealed under ambient air at 650°C during 2 hours.

In order to perform physico-chemical characterizations and electrical measurements, layers were deposited onto α-alumina substrates. Large deposits (25*25 mm^2) 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*2 mm^2 were deposited on 3.81*0.51 cm^2 alumina substrate equipped with a platinum heater on the opposite face. The sensors were tested under air and carbon monoxide (300ppm 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*500 μm^2 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 on 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 figure 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.

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. Figure 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't 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 powders resulting form these two precursors at different temperatures were analyzed. Figure 3 shows X ray diffraction patterns of powders issued from the alkoxide at 300 and 700°C during 12 hours. 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). Conductance's 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. 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 6 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 don't contain organic binder lead to completely cracked films. The conductance of the corresponding sensors (normalized to a constant thickness of 10μm) is quite low (Fig. 7). This behavior is explained by the high