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Ceramic MEMS Platforms for Metal Oxide Gas Sensors: Compatibility of Sensing Layers with Thick Film Materials

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Summary:
The problem of the compatibility of the glass ceramic materials used in thick film technology and, in particular, in ceramic MEMS technology, with sensing layers (SnO_2, TiO_2, In_2O_3, ZnO) was studied in detail. It was demonstrated that long term operation at high working temperature (up to 450ºC) and, especially, technological annealing of the sensing element at temperature up to 750ºC leads to the dissolution of the glass components in the sensing layer. The application of such elements as Bi and Pb in the glass leads to the dramatic poisoning of the sensing layers.

Keywords: gas sensors, thick films, screen printing, glass ceramics, sensing layers, compatibility of materials.

Introduction

The thick film technology is widely used for the fabrication of both experimental and commercial gas sensors. Glass binder is an element of all parts of the sensor made by screen printing: microheaters, substrates, insulation layers, etc. Glass is also a component of the LTCC (low temperature co-fired ceramics) used in gas sensor technology. Therefore, a possible poisoning of the sensing material of gas sensor with glass components is a very important issue for long-term stability of gas sensors.

Our very early results showed that, solid state interaction of RuO_2 with PbO in commercial thick film inks used as a material for the heaters leads to the formation of lead ruthenates and to the drift of the microheater resistance. Another example of the importance of this problem is the strong difference in the stability of thermo-catalytic sensors made using uncoated and glass coated Pt wire: slow reaction between Al_2O_3/Pt/Pd catalyst and SiO_2 of Pt wire shell leads to the formation of alumosilicates and, respectively, to much stronger drift of the sensor signal compared to uncoated Pt wire at working temperature of 450ºC.

In numerous publications about thick film and LTCC platforms for semiconductor gas sensors, the influence of the composition of platform materials to the properties of gas sensor is not considered as a rule, although this role is really important. At least, we did not meet such publications touching specially this issue.

In our research of the ceramic MEMS devices [1], we met a problem of dramatic drop of the SnO_2-sensor response in the case of the application of inadequate glass for the fabrication of the elements of the cantilever: cantilever body, Pt leads to the sensing material, insulation, etc. This was a reason to start this research.

Experiment

In the experiment we used two types of substrates. The first one was described in [1], photo of the substrate is presented in Fig. 1.

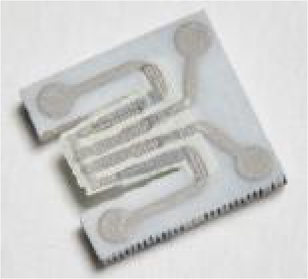

Fig. 1. Photo of the screen-printed cantilever type ceramic MEMS with Pt microheater, Pt contacts, glass-ceramic insulation between microheater and contacts. The chip is to be packaged in TO-5 holder.

Another substrate was used for the investigation of the dissolution of glass components in sensing layers. We used alumina ceramic substrates (30x16 mm^2) screen printing coated with glass under investigation. The glass layer was fired at 850ºC for 15 min. The glasses studied in this work are listed in Table 1. After this, the sensing layers consisting of ZnO, SnO_2, In_2O_3, or TiO_2 nanoparticles (~ 10 nm) made by sol-gel technology were deposited using screen printing as ink in mixture with terpineol on whole surface of the glass layer.

Tab. 1: Composition of glasses used in the experiments as a coating of alumina substrate.

Glass type	Glass composition, wt. %
PD-Sn	BaO — 30-45%, SiO_2 — 20-30%, B_2O_3 — 20-30%, CaO — 8-12%, SnO_2 — 5-12%, MnO_2 — 0,1-3%, CuO — 0,1-3%
PD-HS	SiO_2 — 42%, B_2O_3 — 4,5%, CaO — 3,5%, MgO — 1,5%, BaO — 31%, Al_2O_3 — 16%
PPL	Bi_2O_3 — 66%, PbO — 18,5%, SiO_2 — 7,5%, B_2O_3 and ZnO — 8%

To simulate the typical process of the sensing layer firing, the layer of oxide on the glass surface was heated from room temperature to final temperature of 720 ºC for 15 min, then was kept at 720ºC for 15 min, and finally the plate was cooled during 15 min. Earlier [2], we found this procedure to be optimal for the fabrication of SnO_2 based gas sensing layers. The thickness of metal oxide layer after firing was equal to 12 μm. Then, the sensing material was removed from the glass coated alumina with plastic squeeze, which doesn't damage glass sublayer. The sensing material powder was collected for further study at the Laboratory of chemical analysis of the NRC Kurchatov Institute (ICP-AES) and at the Kurnakov Institute of general and inorganic chemistry (ICP-MS). For comparison, we studied in the same way the sensing layers deposited onto uncoated alumina substrates. To study the influence of the glass composition onto sensing properties we used sensor microheaters with different glasses; the sensing layers were ZnO and SnO_2.

Results and discussion

The powder obtained from the substrate coated with PPL glass (Table 1) was strongly contaminated by Bi and Pb diffusing from the glass to the sensing layer. Only 15 min at 720ºC of the contact between two layer was sufficient to change completely the composition of the sensing layer. On the other hand, the composition of the oxide layers deposited onto the surface of the glasses without Bi and Pb were not changed significantly. An example of the results obtained using ICP-AES is presented in Tab. 2.

Similar results were obtained as well with other sensing materials investigated in this work. All of them are strongly contaminated by Pb and Bi after annealing at 720 ºC for 15 min.

Tab. 1: Contaminants (in wt. %) of SnO_2 after deposition and firing on the surface of glasses mentioned in Table 1.

	PPL	PD-Sn	PD-HS
Ca	0.056	0.042	0.061
Mg	0.060	0.047	0.060
Ba	0.034	0.0066	0.0065
Fe	0.039	0.040	0.085
Ni	0.0071	0.0076	0.0069
Cr	0.0014	<0.0020	<0.0020
Cu	0.0028	0.0028	0.0027
Sb	<0.005	<0.005	<0.005
Pb	3.8	0.0089	0.012
Bi	14.8	<0.0050	0.015

The results obtained with the application of ICP-AES and ICP-MS strongly correlate with the gas sensitivity of the sensors fabricated using the substrate shown in Fig. 1. Typical value of the bare SnO_2 sensing layer response is of factor of 10 at the H_2 concentration equal to 200 ppm. The sensing layer deposited onto substrate with Pt leads made with PPL glass has a response of about factor of 2 under the same conditions. Both SnO_2 and ZnO based sensors on substrates with Bi and Pb containing glasses in contrast to substrates with PD-HS and PD-Sn glasses demonstrate dramatic decrease in gas response to NO_2. This sensitivity drop can be related with a change in acidic and basic properties and with the re-crystallization of the material due to the incorporation of Bi and Pb.

Conclusion

Important role of the thick film substrates and microhotplates in the sensing properties of semiconductor layers was demonstrated. The application of Bi and Pb containing glasses in all elements of microhotplates should be excluded. The sensing layers and glass components used in gas sensors should be tested for their compatibility regarding a possible dissolution of glass components in the sensing layer material and its influence onto both chemical stability and recrystallization of the last one.

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