

THE INFLUENCE OF ZEOLITE-BASED FILTERS ON THE SELECTIVITY OF SEMICONDUCTOR GAS SENSORS

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1. Introduction

A gas sensor is usually defined by its sensitivity and selectivity. To achieve high sensitivity, a semiconducting material is often used as a sensing layer. This semiconductor is in the vast cases a metal oxide with some possible modification, like doping with a noble metal or mixing two metal oxides together [1]. One of the most studied and proofed material is tin dioxide. Even though there is still not completely clear theory about the working principle. There are many ways to prepare the metal oxide, but they are usually connected with financially demanding techniques like RF sputtering and photolithography. As an advantage, the resulting material is homogenous and in general good described. On the other hand, there are techniques which don't involve expensive equipment and under controlled environment can possess at least same results as above mentioned procedures. One those economically interesting method is sol-gel process. The principle remains in conversion of organometallic compounds to metal oxides using hydrolysis and calcinations [2].

Unfortunately the metal oxide sensitive layer itself doesn't possess selectivity to target gases. In the easiest case is enough to change operating temperature to increase selectivity. But this method works only if the material is stable in broad temperature range and even though the selectivity could be improved to a narrower group of gases. To considerably improve selectivity to few gases or sometimes to only one gas, the filters are used. The material of a filter could be organic (e.g. polymer) as well as inorganic compound. The inorganic compounds are in favor because of their so needed compatibility with metal oxides in a broad temperature region [3]. An example of such inorganic compound that can increase the selectivity towards one gas is a group of zeolites.

2. Experimental

Preparation of tin dioxide was based on sol-gel technique employing the tin(IV) chloride (99.995%, Aldrich) as a precursor. The liquid precursor was immersed in isopropanol (LC-MS CHROMASOLV® Fluka) in concentration range from 10 to 300 mg/ml. The created sol was stirred for about one hour and kept in dark place at laboratory temperature for at least two days. The deposition was done directly on the platform. As a platform for testing was used interdigitated structure (IDE). On the corundum substrate were photolithographically patterned platinum structures, including the pair of interdigitated electrodes, and a heating element and a thermometer – they were used for precise temperature control.

The deposition of sol took place using spin coating. Drop of isopropanol was placed on the IDE using a pipette. After evaporation of the isopropanol was placed a drop of sol on the IDE and the spin coating machine was started for a minute with a speed of 3800 rpm. After deposition a hydrolysis took place. The environmental humidity was in the range from 30 to 60 %. Next step was drying in the laboratory drying oven Binder E28 (Binder) for 15 min at

150 °C. Once finished the drying, the samples were directly transferred to Nabertherm L 40/11/P330 furnace for calcinations at temperature 450 °C for 5 hours. The thickness of the layer after deposition was measured by Tencor Alphastep 200 Profilometer.

The filter was based on commercially zeolites Beta and Y (both Zeolyst) with molar Si/Al ratio 12.5 and 6 respectively. The zeolites were calcined at 550 °C for 6 hours with a ramp of 1 °C/min. The zeolites were then applied on the sensitive layer by the mean of manual stencil printing. For this deposition was the zeolite blended with paraffin oil (meets analytical specification of Ph. Eur., BP, Sigma-Aldrich) in the mass ratio zeolite : paraffin oil 3 : 1. The stencil was made out of stainless steel. The paraffin oil was consequently removed from the filter layer in the furnace at temperature 350 °C for 2 hours.

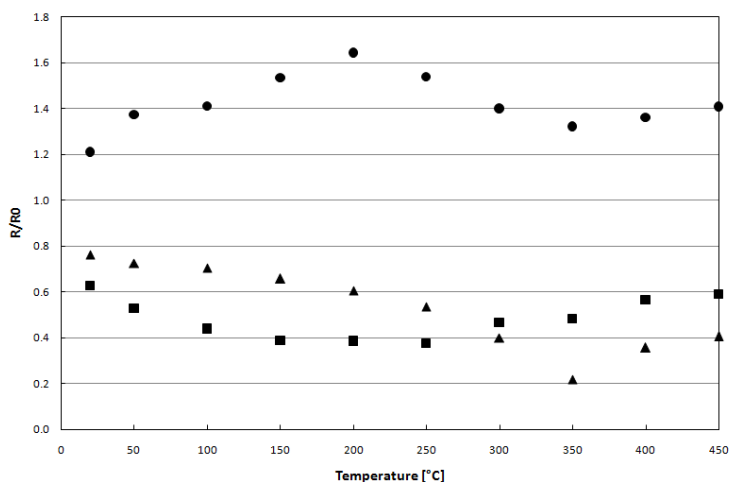
The measurement itself took place in the chamber made out of Makrolon®. The tested gases were ammonia, nitrogen dioxide and hydrogen sulphide. All of these gases were supplied by Linde a.s. in the concentration of 200 ppm (n/n). The rest of the mixture was synthetic air, which was as well used as a background and diluting gas for lower concentrations of tested gases. The measurement of sensor response was recorded using HIOKI HI-Tester 3235-50 LCR Bridge. The measuring frequency was set as 1 kHz; the applied voltage was 1 V. The temperature was driven by current source Tesla BK127 0-20V/0-1A and measured with a Multimeter Keithley 6517A. Operational temperature was studied between laboratory temperature and 450 °C.

3. Results and Discussion

The final thickness of the layer was in the range between 300 and 400 nm. The layer itself was completely transparent, with some minor cracks visible under optical microscope. These cracks were only on the surface and shallow. The compactness and adhesion of the layer were allowing easy deposition of filter layer. The composition and crystallinity of the tin dioxide were confirmed with and X-Ray dispersive diffraction with Bruker D8 instrument.

Response of the sensor at 350 °C reached 90 % of stable signal in less than 2 minutes. The selectivity and sensitivity of a sensor with only tin dioxide were first tested under different operating temperatures. Results are presented in the Fig. 1. It shows a typical property of semiconducting gas sensors – the resistance is as a response to reducing gases (e.g. nitrogen dioxide) increasing and vice versa for oxidizing gases (e.g. hydrogen sulphide). The temperature itself has discriminated three tested gases, but from the selectivity point of view was considered rather unsatisfying.

Fig. 1: *Response of the sensor to gases: (▲) ammonia 100 ppm; (■) hydrogen sulphide 10 ppm; and (●) nitrogen dioxide 10 ppm as a function of operation temperature.*



To improve selectivity to at least one gas at defined temperature were applied zeolites. The nature of zeolites is often

described as a mild acid. For this reason was the selectivity expected more on the acid gases, whilst basic gases (ammonia) should be blocked as the zeolites adsorbed them. This theory has been proven wrong, as pictured in Fig. 2. The decrease in sensitivity in Fig. 2 has the sensor shown only due to blocking of active surface area of tin dioxide. The same decrease was observed in the case of hydrogen sulphide and nitrogen dioxide as well. This effect has also prolonged the time to reach 90% response to 5 minutes. Nevertheless the sensor with zeolite Beta filter had shown its potential to increase sensitivity to nitrogen dioxide at temperature 150 °C from originally (without filter) 1:1 with ammonia to 3:1 in favour of nitrogen dioxide.

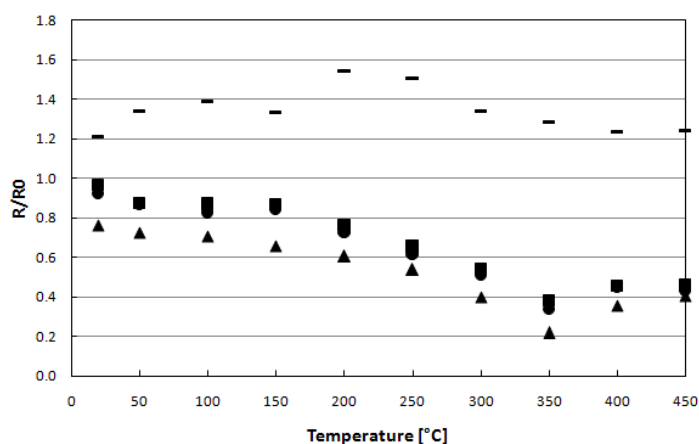


Fig. 2: The reaction on ammonia (100 ppm) of sensor with zeolite Beta filter (■); zeolite Y filter (●); and without any filter (▲) and reaction of the sensor with zeolite Beta filter (-) to nitrogen dioxide (10 ppm) as a function of temperature.

4. Conclusions

The simply procedure to prepare a sensitive and fast responding gas sensor using sol-gel technique was developed. The selectivity of the gas sensor was improved by applying zeolite as a filter layer. The increase of selectivity was achieved on the expense of response time and sensitivity. Fortunately were these drawbacks in lower order of magnitude than the improvement of selectivity.

Acknowledgement

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