# EXPERMAT' 87

Bordeaux 24-27 novembre/November 1987

## Abstracts / Résumés

*Abstracts received until October 20, 1987*

*Résumés reçus au 20 octobre 1987*

"Gassensitive Layers based on Modified Silicates"

K.H.Haas, F.Hutter, H.Schmidt
Fraunhofer-Institut für Silicatforschung, Neunerplatz 2
8700 Würzburg, Federal Republic of Germany

## Introduction

Selectively adsorbing layers play an important role in the development of sensing devices based on microelectronic structures. The sensitive material should be able to be adapted to various problems (e.g. different gases, sensitivities or selectivities) without varying basic compositions or procedures. For this purpose we use organically modified silicates as starting point for the preparation of adsorbing layers. The schematic structure principle of these materials is shown below.

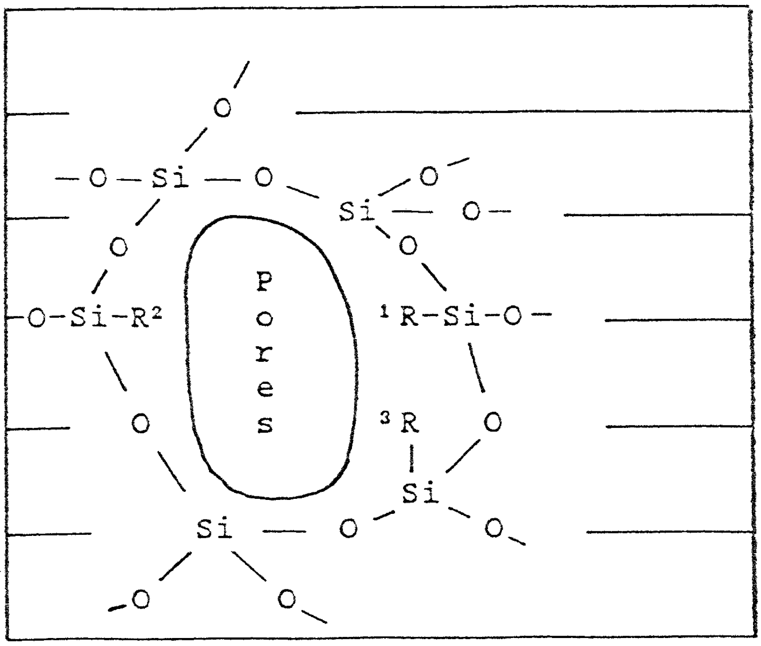


Figure 1: Schematic structure units of organically modified silicates; $^1R$, $^2R$, $^3R$: organic groups

Modified silicates are non-crystalline solids built up by a network of siloxane bonds (Si-O-Si) with functional organic groups connected to this network by silicon-carbon bonds. The adsorption properties of these materials are determined by choosing appropriate functional groups and porosity. It is shown that the adsorption of gas molecules changes the electrical properties of interdigitated planar capacitor structures coated with modified silicates. Measurements with $SO_2$, $CO_2$, $NO_2$ and $NH_3$ are reported.

The adaptability of organically modified silicates for the requirements of gas sensitive materials

Gas sensitive materials should interact fast and reversibly with very few molecules of one type selectively, thereby changing at least one physical property of the sensitive material to be measured by an appropriate method. If an electrical property (e.g. dielectric constant, conductivity) is changed, the possibility to trigger a microelectronic device is opened. Organically modified silicates were prepared by the sol-gel process /1/. Substituted and unsubstituted silicon alkoxides were used as starting materials. The reaction in solution leads to colloidal particles by polycondensation - the sol. Further condensation solidifies the sol to a gel, which can be dried and densified at elevated temperatures (up to 150°C) to a non-crystalline solid. By choosing an appropriate functional organic group R the properties of the modified silicates can be influenced, leading finally to centers for specific adsorption, reaction or even catalytic reaction of gas molecules. Also porosity and specific surface area of the material can be influenced by the reaction conditions (time, temperature, solvent, catalyst). The preparation of modified silicate layers is possible during the sol phase by a conventional spin-on coating technique, since the viscosity can be controlled by the chemical reaction.

Experimental results and discussion

To answer the question whether modified silicates change their electrical properties by interacting with specific gases, we used a planar capacitor structure on an alumina substrate with interdigitated aluminum electrodes which was supplied by the Fraunhofer-Institut für Festkörpertechnologie in München. This structure was covered with a layer of a modified silicate and the capacitance and conductance of the whole device were measured in different gas atmospheres. By using different modifications of the silicate layers we obtained different sensitivities of our sensor structure. Some results are shown below.

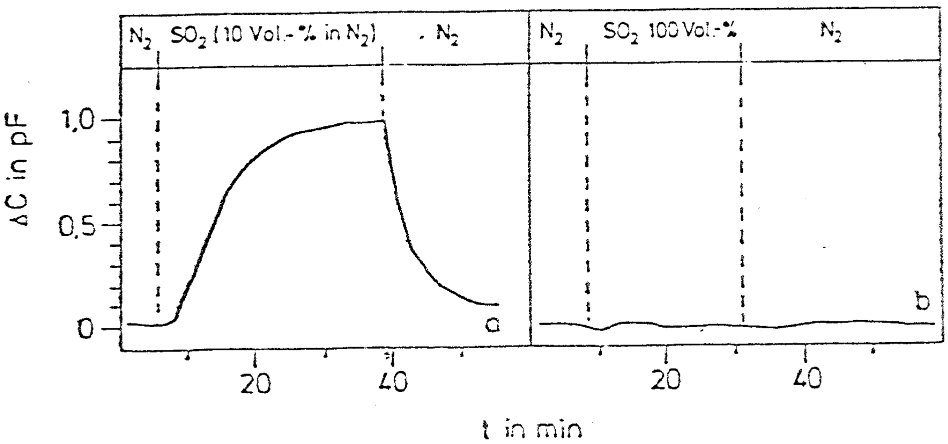


Figure 2: Change of capacitance with time of interdigitated planar capacitors coated with different layers of organically modified silicates in $SO_2$-containing atmospheres compared to an atmosphere of dry nitrogen ; the functional groups are as follows:
a) $R = -(CH_2)_3-N(C_2H_5)_2$   b) $R = -(CH_2)_3-NH_2$

As can be seen from fig. 2b layers of modified silicates containing primary amino groups ($-NH_2$) are little or not affected by $SO_2$. In contrast, if the layers contain tertiary amino groups ($-N(C_2H_5)_2$) ≡ NND, the capacitance is significantly affected by $SO_2$ (fig. 2a). This can be explained by the formation of adducts between $SO_2$ and tertiary amines /2/, leading to an increase of the dielectric constant of the modified silicate layer.
Another example for tailoring sensitivities of modified silicate layers is shown in figure 3.

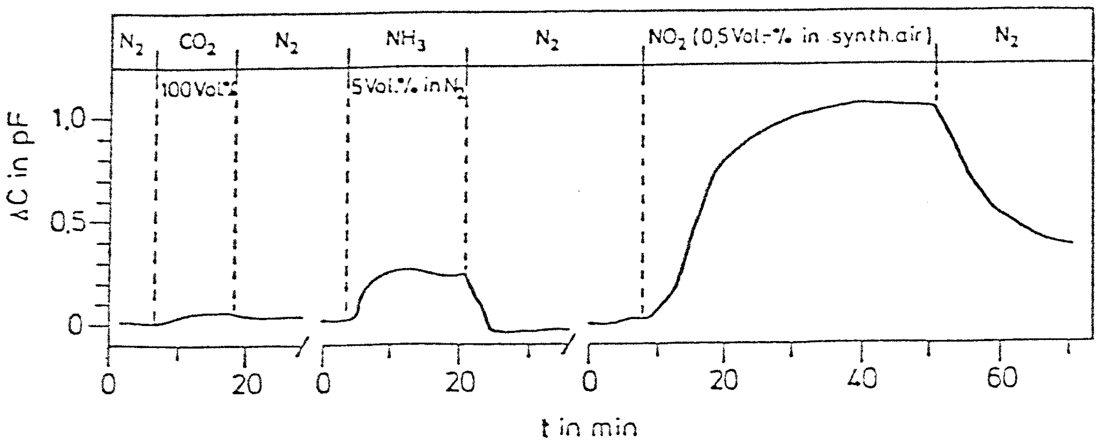


Figure 3: Change of capacitance with time of an interdigitated planar capacitor coated with a layer of organically modified silicate ($R = -(CH_2)_3-CN$) containing copper(II) ions in different gas atmospheres compared to an atmosphere of dry nitrogen

This layer exhibits extremely different sensitivities for the gases $CO_2$, $NH_3$ and $NO_2$. The sensitive material consists of a cyanopropylsiloxane layer containing copper(II) ions. The mechanism of chemical interaction of the gases mentioned above with reactive centers in the metal-containing siloxane layer is not yet fully understood. We suggest that copper ions are important as coordinative centers for this sensitive layer, because cyanopropylsiloxane layers without copper(II) ions show almost no sensitivity at all.
Problems arising from atmospheric water (polar gases always interfere with polar functional groups in the respective layers) were partly solved by using two component polymeric systems, with silicate modifications by alkyl groups which decrease the uptake of water by the modified silicate layers to a bearable degree. Figure 4 shows the change in capacitance of layers of copolymers between NND and propyl groups in atmospheres of 20 % relative humidity (compared to an atmosphere of dry nitrogen).

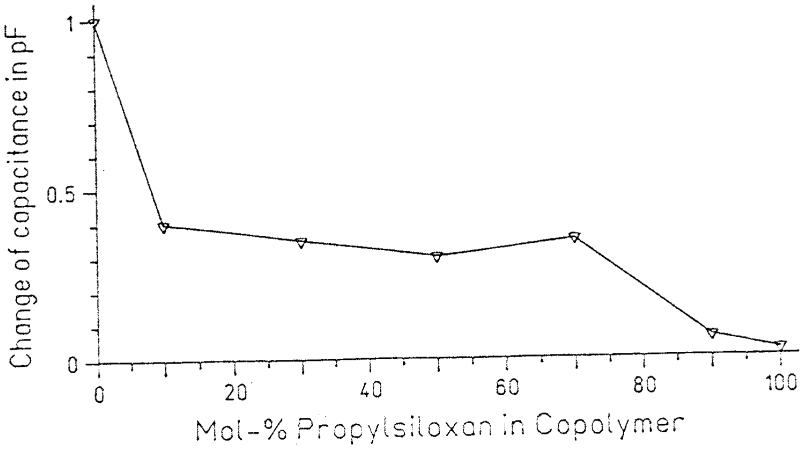


Figure 4: Increase in capacitance of layers of copolymers NND/propylsiloxane in atmospheres of 20% rel. humidity as a function of propylsiloxane content, after reaching the equilibrium capacitance values.

As expected the sensitivity decreases with increasing content of the hydrophobic propylsiloxane component. The respective sensitivity of these layers against $SO_2$ is shown in figure 5.

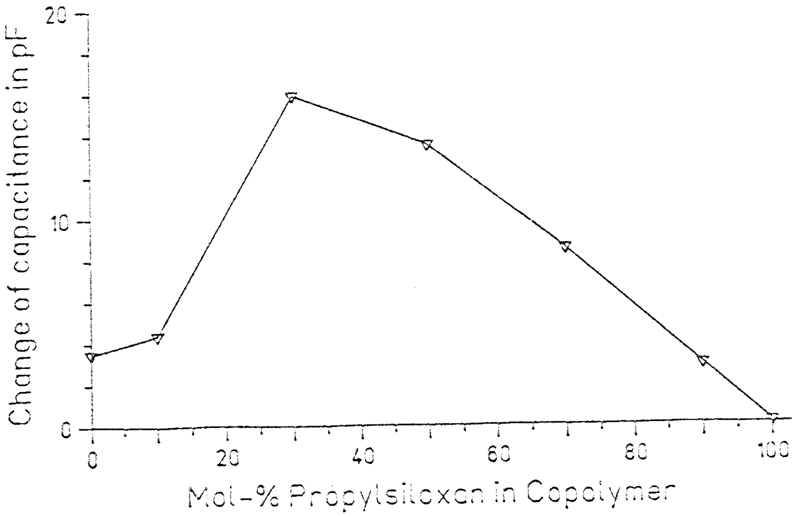


Figure 5: Increase in capacitance of layers of copolymers NND/propylsiloxane in $SO_2$-containing atmospheres (10 vol.-% in $N_2$) as a function of propylsiloxane content, after reaching the equilibrium capacitance values.

Unexpectedly the sensitivity of these copolymers does not continously decrease with increasing content of propylsiloxane. The reason for the experimentally detected increase probably is a better availability of reactive centers for

$SO_2$-adsorption. This can be due to an appropriate texture of the material in the presence of a certain amount of propylsiloxane. For a better understanding of this behaviour further investigations are necessary.
The adsorption of various gases by the modified silicates in bulk has been proved independently by gravimetric adsorption measurements which show different adsorption characteristics depending on the functional groups R used in the preparation of the layers.
Measurements with other microelectronic devices (MOS-FETs) coated with modified silicate layers were done in the Fraunhofer-Institut für Festkörpertechnologie in München /3/.
These measurements have shown, that microelectronic devices can be triggered by the adsorption of gases using organically modified silicates as gate insulating materials.

Conclusions

Modified silicates can be adapted to different sensing problems by modification of the sensitive material and these materials are basically useful for sensor development. Further investigations have to be done with respect to material and system improvement.

Literature

/1/ Schmidt, H. and Seiferling, B.
Mat. Res. Soc. Symp. Proc. 73 (1986) 739

/2/ Grundnes, J. and Christian, S.
J. Amer. Chem. Soc. 90 (1968) 2239

/3/ Drost, S. ; Endres, H.-E. and Obermeier, E. in :
Proceedings of 2nd International Meeting on Chemical Sensors, Bordeaux, Juli 7-10,
Editors: J.-L. Aucouturier et al. (1986) 439