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ORMOSILES - A NEW CLASS OF MATERIALS FOR SENSITIVE LAYERS IN THE DEVELOPMENT OF GAS SENSORS

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Abstract
Organically modified silicates (ORMOSILes) can give a new starting point for the preparation of reactive layers. These non-crystalline solids are built up by a network of siloxane bonds (Si-O-Si) with functional organic groups connected by silicon-carbon bonds. The properties of ORMOSILes can be tailored by choosing appropriate functional groups and reaction conditions, which will determine structure and microstructure (e.g. porosity). It is shown that the adsorption of gases on the surface of ORMOSIL layers change the electrical properties of interdigitated planar capacitor structures. Measurements with SO_2, NH_3, NO_2 are reported.

1. Requirements for gas sensitive materials

A crucial point in the development of gas sensors is the preparation of a gas sensitive material. In the ideal case it should interact selectively with only one type of gas molecules. The reaction should be fast and reversible thereby causing a detectable change of at least one material property. To trigger a microelectronic device requires the change of an electrical property (dielectric constant, conductivity). Furthermore, it should be possible to prepare layers of these materials for the device coating by methods conventionally used in microelectronics.

2. The development of sensitive ORMOSILes

The advantage of ORMOSILes for the development of such materials can be explained by their variable structure. General preparation methods are described in (1,2). ORMOSILes (fig.1) consist of a three-dimensional, non-crystalline network built up by siloxane bonds (Si-O-Si). Functional organic groups (R) are connected with this network via silicon-carbon bonds. The network itself can be modified substituting a silicon by a

heteroatom (e.g. Ti, Zr, B, Al) or by crosslinking organic groups (e.g. vinyl groups) to a intertwined network. Thus ORMOSILes may vary in their properties between inorganic materials and organic polymers.
The preferred method for building up the Si-O-Si network of ORMOSILes is the sol-gel process, that means the controlled hydrolysis and condensation of appropriate alkoxides. The properties of the resulting product can be tailored by choosing the appropriate type of silane (or silanes), functional organic groups, other condensable components (e.g. $Ti(OR')_4$), reaction and curing conditions (time, temperature, solvent, catalyst). By this way it should be possible to develop chemically interactive ORMOSILes to react with a gas molecule in one or the other of the following different ways: adsorption, chemical reaction or catalytic reaction of one or more type gas species on the surface.
For the development of a gas sensitive system, the field effect transistor (FET) should be a suitable monitoring device, since there should be a good chance, that a change in the electrical properties of the ORMOSIL by interaction with a gas will be transduced into microelectronic signals. In order to test this possibility in a material research program fast and simply, a planar capacitor with interdigitated aluminum electrodes was designed and produced by the Fraunhofer-Institut für Festkörpertechnologie as a test structure which could be coated easily by an ORMOSIL layer. The capacitance of the whole device was then measured in dependence of the gas atmosphere. Starting point for the development of a material sensitive to specific gas molecules is their well-known chemistry. Especially the interaction center to the gas has to be fixed in the polymer matrix of an ORMOSIL. First measurements reported in the following section used the adsorption processes of gases as interaction principle to get sensitive materials.

3. Results and discussion

Layers of ORMOSILes (0.2 to 1 µm thick) can be prepared on the provided test structures by spin thinning. This is an advantage of the sol-gel process, because it is possible to use homogeneous liquid solutions, and cure them subsequently to ORMOSIL-polymers. In the following measurements of several ORMOSIL-coated interdigitated structures are presented.
An ORMOSIL built up by cocondensation of 3-aminopropyltriethoxysilane ($H_2N-CH_2-CH_2-CH_2-Si(OC_2H_5)_3$) and tetraethoxysilane

($Si(OC_2H_5)_4$) showed a strong adsorption of CO_2. A CO_2 uptake of about 10 wt.-% (at 40 °C and 1000 hPa CO_2 pressure) could be measured, however, on test structures coated with this material no signal was observed in CO_2 so far. The example demonstrates, good adsorption does not necessarily lead to a change of the electrical properties. Therefore electrical measurements have to be performed to find suitable materials and effects for further developments.
To detect SO_2 gas, an ORMOSIL was prepared containing tertiary amino groups (by condensation of $(C_2H_5)_2N-(CH_2)_3-Si(OC_2H_5)_3$), because it is known that SO_2 can form adducts with tertiary amines (3). The measurements with this ORMOSIL are shown in fig.2a. The capacitance is significantly influenced by SO_2, in contrast to an ORMOSIL with primary amino groups (fig.2b).
To transduce some of the known adsorption properties of copper(II)-chloride (4) into a polymer matrix, an ORMOSIL was prepared by condensation of 3-cyanopropyltriethoxysilane ($NC-CH_2-CH_2-CH_2-Si(OC_2H_5)_3$) containing $CuCl_2$. Fig.3 shows the different sensitivities of this layer. In spite of decreasing concentration of the gases (CO_2, NH_3, NO_2) the relative change in capacitance was increased. Further experiments with this material are descibed in (5).

5. Conclusions

It could be shown that different ORMOSIL layers can change their electrical properties in dependence of the gas atmosphere. In spite of many remaining difficulties ORMOSILes may be a promising way to sensitive materials for gas sensors. Measurements with other microelectronic devices (e.g. MOS-FET) coated with ORMOSIL were performed in the Fraunhofer-Institut für Festkörpertechnologie in Munich (5).

6. References

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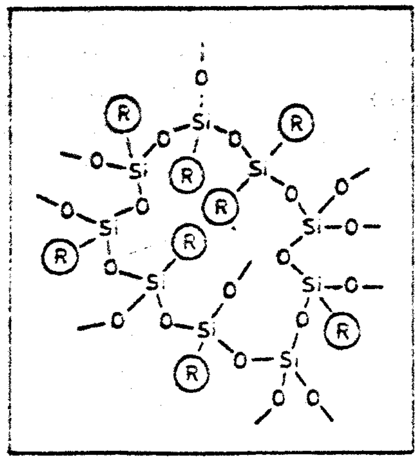

fig.1 Schematic structure of an ORMOSIL
R: organic group

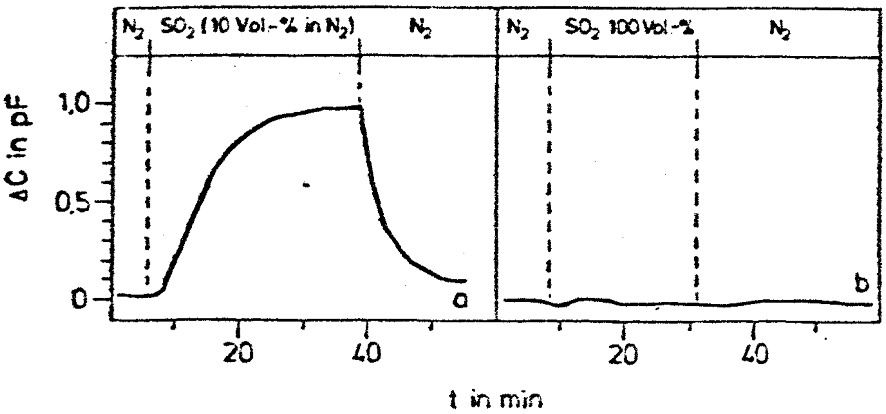

fig.2 Change of the capacitance (ΔC) of an interdigitated planar capacitors coated with different ORMOSIL-layers in SO_2 containing atmospheres
a: $R = -(CH_2)_3-N(C_2H_5)_2$ b: $R = -(CH_2)_3-NH_2$

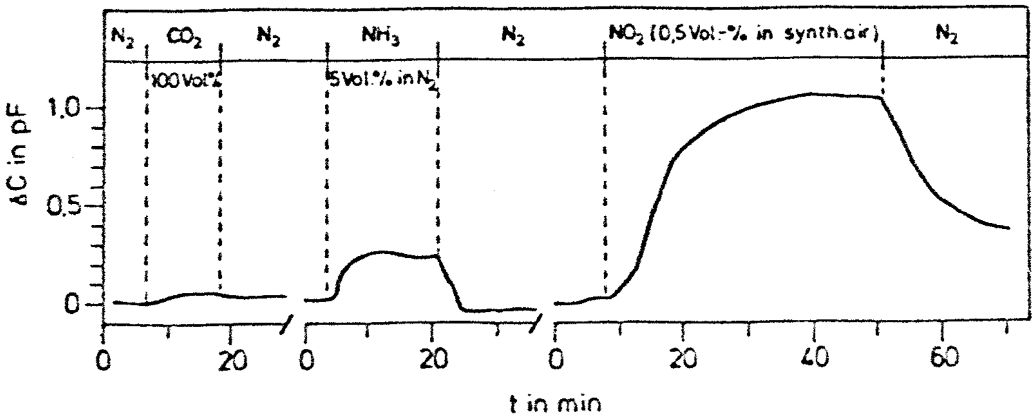

fig.3 Change of the capacitance (ΔC) of an interdigitated planar capacitor coated with an ORMOSIL (143cI, $R = -(CH_2)_3-CN$ containing copper(II)-ions) in different gas atmospheres