Werner Moritz

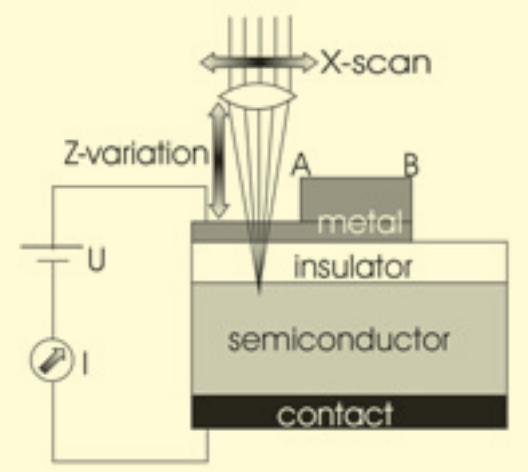
Chemical Semiconductor Sensors

Chemical sensors based of the field effect in the semiconductor were developed both for the detection of gases and ions in liquids. A lateraly resolved concentration measurement as well as an impedance analysis are likewise possible under use of the photoelectric effect in the semiconductor. The resolution of the method was improved by us down to the submicrometer range.

Do you know that you are the owner of at least one chemical sensor? Probably you are. In your car the three-way catalyst cleaning the exhaust gases is much improved in his behaviour by coupling it with the lambda sensor. In future not only exhaust gases will be controlled but also the gases inside the car. This will make travelling much more comfortable. Beside automotive market there are of course numerous other applications for chemical sensors. The number of substances which should be detected is rather high. But there is also a big number of principles of interaction with the sensor and of transducers which finally converts the chemical information to an electrical signal. An overview on this field is given in [1].

The physical principle we used for sensor developments in our group is the field effect in the semiconductor [2]. The most simple variant of such a sensor is shown in Fig. 1. Such a Metal/Insulator/Semiconductor (MIS) structure can be characterised as a gate area of a transistor, by high-frequency capacitance measurements or by the photo effect. The insulator is a multilayer system with a thickness of some 10 nm only. An advantage of MIS sensors is that, due to the insulator, no DC current can disturb the electrochemical equilibrium at the sensor interface. The metal in

Fig. 1
Schema of a MIS structure (for the determination of the optimum focus differences in transparencies at position A and the effective diffusion length differences in transparencies and electrical field in position B are used).



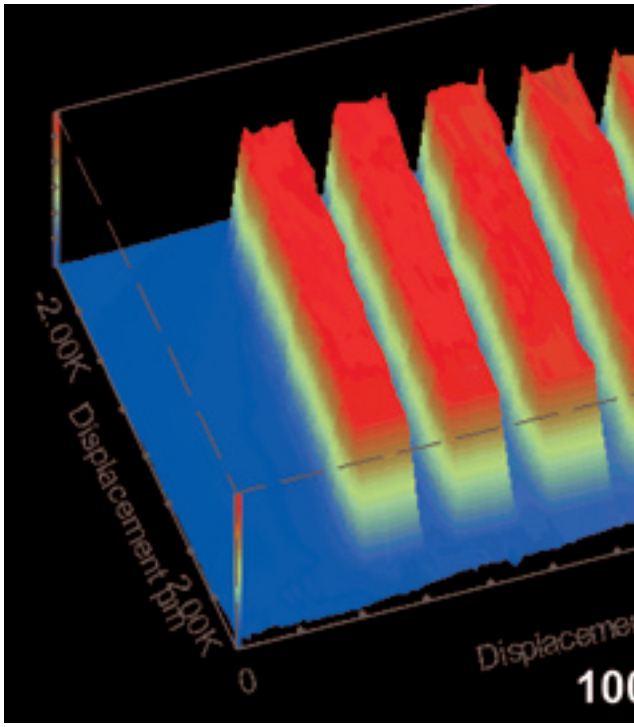


Fig. 4
Area scan of photocurrent measurements (polymer strip width 100 µm).

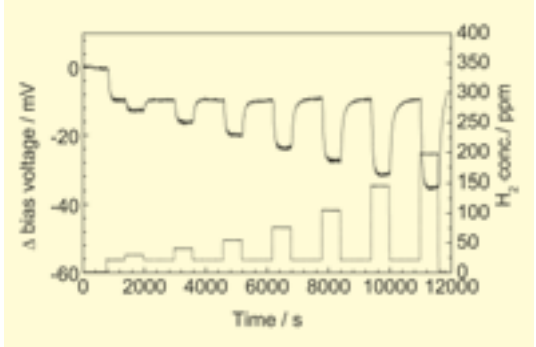
Fig. 1 can be replaced by a solution for the detection of ions in the analyte.

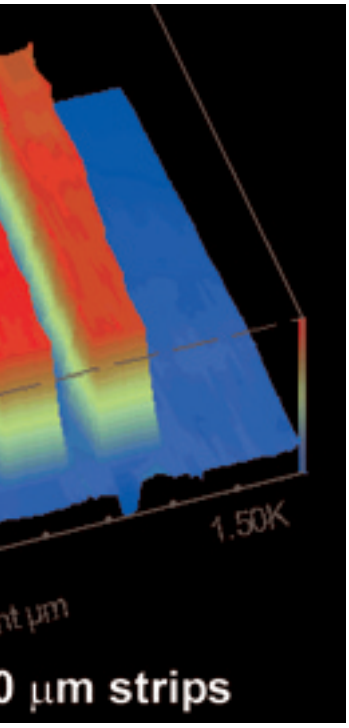
The super ionic conductor LaF_3

We developed several different sensors using the super ionic conductor LaF_3 as the upper part of the thin layer system. If the LaF_3 is in contact to a solution F^--ions are exchanged between the solid and the liquid phase leading to a potential difference at the interface according to the Nernst equation. We proved that for field effect semiconductor devices a thin polycrystalline film of only some nm provides a stable *fluoride ion sensor* without internal reference electrode. The kinetics of the ion exchange and the extremely slow dissolution of LaF_3 were investigated using isotope methods and impedance spectroscopy.

The combination of the fluoride ion sensor with a miniaturised flow through reactor containing CaF_2 can

Fig. 2
Response of the semiconductor sensor (solid line and left scale) to different concentrations of hydrogen (dotted line and right scale).





be used as a sensor for the determination of the *hardness of water*. If the microstructure of the CaF_2 is produced in a way leading to high mechanical stability and high surface area a fast response can be achieved. The application of CaF_2 as a thin layer on top of the LaF_3 covered by a polymer results in a miniaturised *reference electrode*.

Sensors for the detection of gases have been developed using the LaF_3/Pt interface. Our all solid state *oxygen sensor* working at room temperature overcomes disadvantages of other sensors which use liquids or need high temperature operation. To improve the lifetime of this sensor a thermal reactivation method was developed that allows to reach high surface temperature (700 K) within some 100 ns by resistive heating. A similar structure can be used for the determination of *fluorine* in gases at concentrations down to 0,01 ppm.

The high temperature semiconductor material SiC has to be used as epitaxial layer instead of Si to achieve sensors for the detection of *fluorocarbons* like CF_3CH_2F, CF_3CCl_3, $CHClF_2$, CF_3CH_2Cl and CCl_3F working at 400°C.

The response of our recently developed room temperature *hydrogen sensor* is shown in Fig. 2. Concentrations as low as 10 ppm can be detected without heating the sensor and therefore, at low power consumption as necessary for battery powered systems [3].

Scanning photocurrent microscopy

In the last few years, there has been growing interest in methods for laterally resolved investigations of thin layers, surfaces and interfaces. Numerous physical principles have been used to obtain different information about the local properties. A map of pH-values in an electrolyte near to an insulator surface can be obtained by the light-addressable potentiometric sensor (LAPS) technique suggested by Hafeman [4] in 1988, who carried out photocurrent measurements at electrolyte insulator semiconductor (EIS) structures, i.e. a structure as described above. The use of different surface layers results in sensitivities to, for example, potassium, calcium or magnesium. The LAPS principle has been applied for the detection of whole cells, spores and cell metabolism.

LAPS measurements are based on the photoeffect in MIS structures. Illuminating the structure with light that has an energy larger than the band gap results in the generation of electron hole pairs. The photocurrent as a function of external voltage is given in Fig. 3 (curve A). This voltage is influenced by the work function of the metal, charges in the insulator or a potential difference at the electrolyte/insulator (or metal/insulator) interface which can depend on the gas or ion concentration. This leads to a shift of the photocurrent curve on the voltage axis (shift of curve A to B in Fig. 3). This shift can be used as a measure of the gas or ion concentration.

Photocurrent measurements are advantageous in that charge carriers are only produced where light is injected (see Fig. 1). Due to the thin insulator (< 100 nm) only the electrical field from this area affects the photocur-

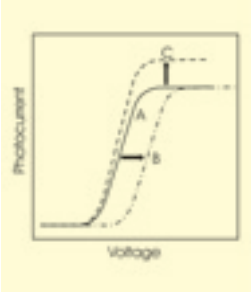
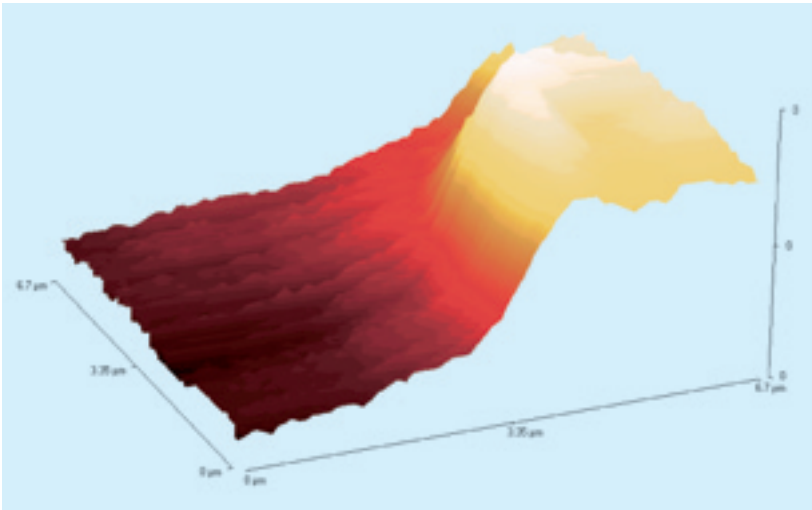


Fig. 3
Schema of photocurrent/voltage curves at Metal/Insulator/Semiconductor-structures (the insulator can be substituted by a multi-layer system); the shift of curve A to B representing the LAPS-principle is due to potential changes in the system; the shift of curve A to C representing the principle of SPIM is caused by changes in the impedance.

Fig. 5
Scan along an metal edge (as position B in Fig. 1) for a MIS structure using amorphous silicon.



Chemische Sensoren

Chemische Sensoren auf Basis des Feldeffekts im Halbleiter wurden sowohl für den Nachweis von Gasen als auch Ionen in Flüssigkeiten entwickelt. Eine ortsaufgelöste Konzentrationsmessung sowie eine Impedanzanalyse ist unter Nutzung des Fotoeffekts im Halbleiter ebenfalls möglich. Die Auflösung der Methode wurde von uns bis in den sub-Mikrometerbereich vorangebracht.

PD Dr. Werner Moritz
Born 1952. Study of chemistry at Humboldt-Universität zu Berlin (1973–77). 1977 Degree in chemistry. 1977 Emil-Fischer Price. 1981 Dr. rer. nat. on radiochemical investigations on corrosion of noble metals. 1981 Humboldt-Price. 1981–84 Scientific coworker in the industries. 1985 Senior research assistant at Humboldt-Universität zu Berlin. 1989 Habilitation. 1997 Senior academic assistant at Humboldt-Universität zu Berlin.

Contact
Humboldt-Universität
zu Berlin
Faculty of Mathematics
and Natural Sciences I
Department of Chemistry
Brook-Taylor-Str. 2
D–12489 Berlin
phone: +49-30-2093–5566
Fax: +49-30-2093–5559
E-Mail: werner.moritz@
chemie.hu-berlin.de
www.chemie.hu-berlin.de/
wmoritz/index.html

rent. This results in a lateral resolution of concentration measurements.

Photocurrent measurements at semiconductor/insulator-structures can be used not only for the detection of local differences of potential. We suggested to use differences in the photocurrent in the saturation region of the photocurrent curve (see Fig. 3) for scanning photo-induced impedance microscopy (*SPIM*) [5]. This technique is suitable for imaging the complex impedance of electrochemical and solid state systems with good spatial resolution. If a thin film has to be investigated, it has to be deposited on the semiconductor/insulator-structure. As the result, the photocurrent will be shifted as shown in Fig. 3. The difference in photocurrent is a function of the complex impedance of the layer added. Local differences in the impedance can be detected in the scanning mode. An additional variation of the modulation frequency of the light results in impedance spectra with lateral resolution. An example of impedance measurements at a microstructured polymer layer is given in Fig. 4.

The lateral resolution was found to be in the range of several 10 to some 100 µm when using silicon wafers as the semiconductor material. The main reasons for the limitation in resolution are the lateral diffusion of charge carriers in the semiconductor and electrical charges in the insulator.

This problem can be solved by choosing appropriate semiconductor substrates. We investigated thin Si-layers (SOI), GaAs and amorphous silicon with the aim to improve the lateral resolution of the method. All these field effect structures exhibited much better resolution than bulk Si. However, the quality of the insulator prepared on GaAs has not been sufficient for large area investigations. The best results were obtained using thin layers (0.3–1.5 µm) of amorphous silicon. As shown in Fig. 5 a resolution better than 1 µm was achieved. In Fig. 6 it is shown that structures as small as 400 nm can be visualised using photocurrent measurements and therefore, it can be really called microscopy.

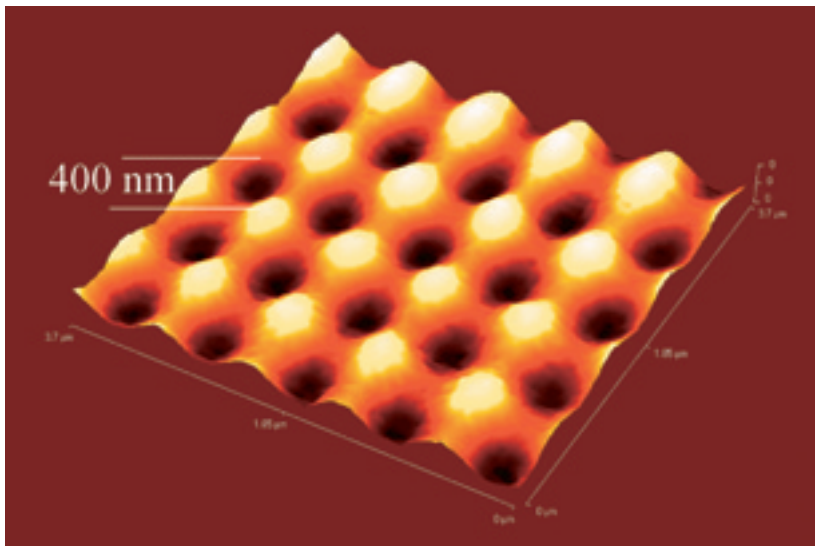


Fig. 6
Scan (3,7µm x 3,7 µm) of a sample with holes (400 nm in diameter) in the metal film.

Acknowledgements
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Members of the working group
Dr. A. Vasiliev; Dr. V. Filippov