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# **New transducer material concepts for biosensors and surface functionalization**

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## **ABSTRACT**

Wide bandgap materials like SiC, ZnO, AlN form a strong platform as transducers for biosensors realized as e.g. ISFET (ion selective field effect transistor) devices or resonators. We have taken two main steps towards a multifunctional biosensor transducer. First we have successfully functionalized ZnO and SiC surfaces with e.g. APTES. For example ZnO is interesting since it may be functionalized with biomolecules without any oxidation of the surface and several sensing principles are possible. Second, ISFET devices with a porous metal gate as a semi-reference electrode are being developed. Nitric oxide, NO, is a gas which participates in the metabolism. Resistivity changes in Ga doped ZnO was demonstrated as promising for NO sensing also in humid atmosphere, in order to simulate breath.

**Keywords:** Biosensors, wide band gap materials, ZnO, SiC, ISFET, functionalization, NO

## **1. INTRODUCTION**

Wide band gap, WBG, materials like SiC, GaN/ GaAlN, AlN, ZnO and Diamond perform the basis for multifunctional bio and chemical sensors. For example SiC devices based on 4H SiC have been operated up to 1000°C and proven to withstand harsh environment like exhaust gases and flue gases. An ammonia sensor for control of SCR, selective catalytic reduction, in diesel exhaust was demonstrated [1], while a SiC based sensor system for control of the combustion in wood fuelled household boilers (burners) is being commercialized [2]. For operation of SiC based gas sensors at temperatures above 400°C we have started a development of new contact materials [3].

The ISFET, Ion Selective Field Effect Transistor biosensor device was invented already in 1970 by Bergveld et al [4]. This silicon based device is for example used as a miniaturized pH device. Recently other semiconductors like the wide band gap, WBG, materials e.g. SiC, GaN/ GaAlN, AlN, ZnO and Diamond has been demonstrated as material for biosensing transducers. Transistors based on GaN/GaAlN were immobilized by penicillinase and enzyme substrate activity was measured [5]. Thin film bulk acoustic resonators based on AlN operated at a frequency of 1 GHz are developed as biosensors with potentially very high sensitivity due to the high operation frequency [6]. Interesting properties of these materials are chemical inertness, biocompatibility and also multisensing

properties. For example ZnO can be realized as a FET device, a resonator structure due to its piezoelectric properties and also a gas sensitive resistor [7]. The ZnO oxidic surface is especially interesting for direct biomolecule functionalization, while the Si surface normally has to be modified by a thermally grown oxide before functionalization. We have shown successful binding to ZnO and also SiC surfaces by e.g. APTES, which forms the basis for further attachment of many biomolecules [8-10].

NO / NO<sub>2</sub> (NO<sub>x</sub>) sensors are of great interest for numerous environmental purposes. For example the SCR process may also be controlled by a NO<sub>x</sub> sensor, however, the operation temperature should preferably be above 400°C. NO is also a gas active in the animal metabolism. The [nitrogen cycle](#), whereby chemical processes make atmospheric nitrogen available for use in plants and animals and then subsequently returned to the [atmosphere](#), is a critical process for life. Nitrogen is the essential multi-media stressor. Its ubiquity in the environment and necessity to life assures its ease of transport through biotic and abiotic cycles and interaction with aquatic, atmospheric, and terrestrial systems. Excess nitrogen in the environment is associated with many large-scale environmental concerns, including, [eutrophication](#) of surface waters, toxic algae blooms, hypoxia, [acid rain](#), nitrogen saturation in forests, and [global warming](#). Animal metabolism of NO results in production of [nitrite](#). The [metabolism](#) of nitrogen in proteins generally results in [excretion](#) of [urea](#), while animal metabolism of [nucleic acids](#) results in excretion of [urea](#) and [uric acid](#).

Due to the participation in the metabolism it is interesting to measure NO for example in people's breath. We have investigated Au and Pd nanoparticles as sensing layers in FET devices. Au nanoparticles show an increased response to NO and NO<sub>2</sub>. Pd showed an interesting fractal particle formation and also increased sensitivity to NO. The operation temperature is limited to about 300°C for Pd and even lower for Au, which is a limiting factor for some environmental purposes [11]. We have compared the resistivity change in ZnO due to oxygen of sensing layers based on ZnO nanoparticles or ZnO films [6]. Furthermore, we have investigated the resistivity change of Ga doped ZnO nanoparticles to NO<sub>2</sub> and compared that to undoped material. We found an increased stability and reproducibility in the response to NO<sub>2</sub> even at an operation temperature of 550°C [12].

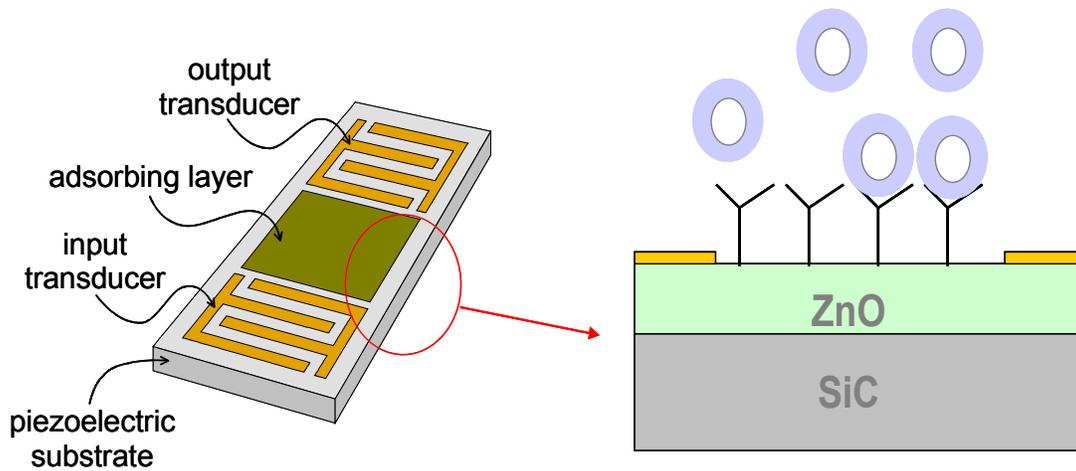


Fig. 1. Schematic drawing of a multifunctional sensor device which includes a transistor, a resonator and resistive measurements between the finger electrodes.

The goal of the work presented here is a multifunctional sensor device with integrated transistor, resonator and resistivity change measurements, which may be realized in a heterostructure device based on e.g. SiC / ZnO, see Fig. 1. We report on interesting NO sensing in humid atmosphere by resistivity changes in Ga/ZnO. We will also report on a development of an ISFET transducer with an integrated reference electrode for biomolecule detection in liquid phase. We show results from MOS capacitors for liquid measurements, which is a simplified version of a transistor device suitable for this demonstration.

## 2. EXPERIMENTAL

MOS components were processed using standard process technology. The gate SiO<sub>2</sub> was thermally grown. A thin film of 7 nm Al was evaporated on top of the SiO<sub>2</sub> and subsequently oxidized at 500°C to Al<sub>2</sub>O<sub>3</sub>. The contact on the rear side of the device was Al annealed in argon at 500°C. The thick contact of 5 nm Cr plus 250 nm Au was evaporated on top of the thick oxide for bonding as well as on the rear side to protect the Al contact during high temperature anneal of the gate area. A thin film of Cr plus Au was evaporated on the gate insulator. Subsequent oxidation at 300°C provides a porous metal film which does not peel off in liquid.

The Ga doped ZnO nanoparticles are electrosynthesized by the EDOC (electrochemical deposition under oxidizing conditions) process using a sacrificial anode. A Zn anode was used, the electrolyte was TBAB (tetrabutylammonium bromide, Fluka) and 2-propanol (Scharlau. Chemie S.A) and the capping agent was oleic acid (KEBO AB). For the Ga doping Ga(NO<sub>3</sub>)<sub>3</sub> x H<sub>2</sub>O was added to the electrolyte. The particles were drop deposited onto finger electrodes and dried, which also improves the adhesion of the particles. More details are found in Ref. [6].

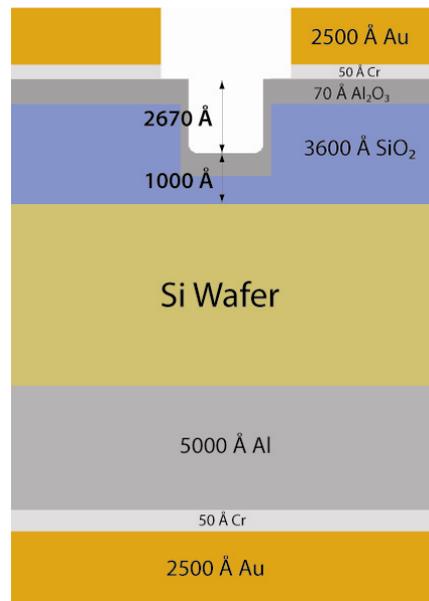
A computerized gas mixing system supplies the gases and the carrier gas was bubbled through water for measurements in humid atmosphere.

Standard resistivity (Keithley 2000 multimeter) and capacitive measurements (Boonton bridge) were performed.

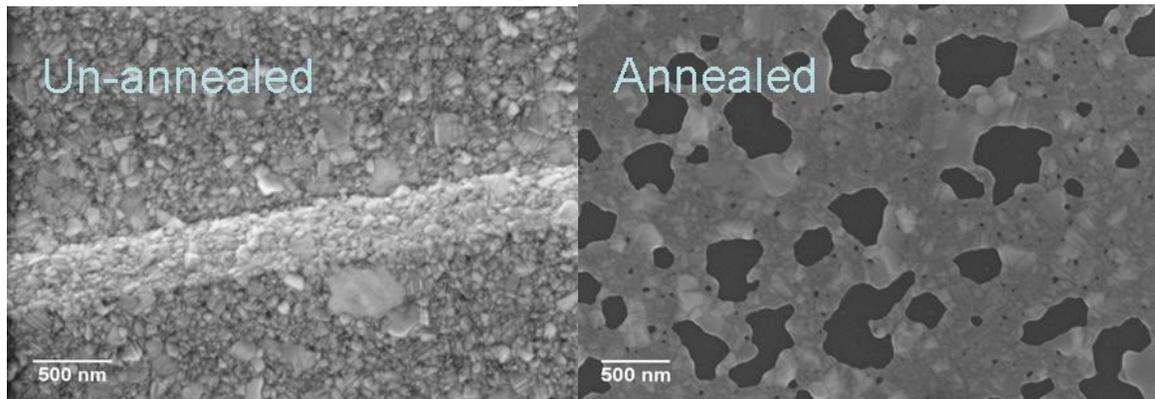
The Scanning electron microscopy, SEM, images were taken by a Zeiss Cross Beam 1540 EsB and a Leo 1550 VP Field emission SEM.

### 3. RESULTS

Field effect devices based on e.g. SiC and ZnO provide biosensing based on the voltage change between source and drain as a function of the gate voltage. Adsorbed biomolecules in the gate area, which provide a net charging effect or polarization are thus detected. A FET biosensor is normally based on an ISFET device, which is a transistor without a gate electrode, and requires an external reference electrode for operation. Here we have processed MOS capacitive devices as described in the experimental section. The gate area is provided with an Al<sub>2</sub>O<sub>3</sub> gate insulating layer on top of the SiO<sub>2</sub> to avoid in diffusion of e.g. protons from the solution in the liquid measurements. The device has a porous titanium gold layer as the reference electrode applied directly on top of the insulator, see Fig. 2. The titanium is an extremely thin layer in order to provide the porous gold film by appropriate annealing, see Fig. 3.



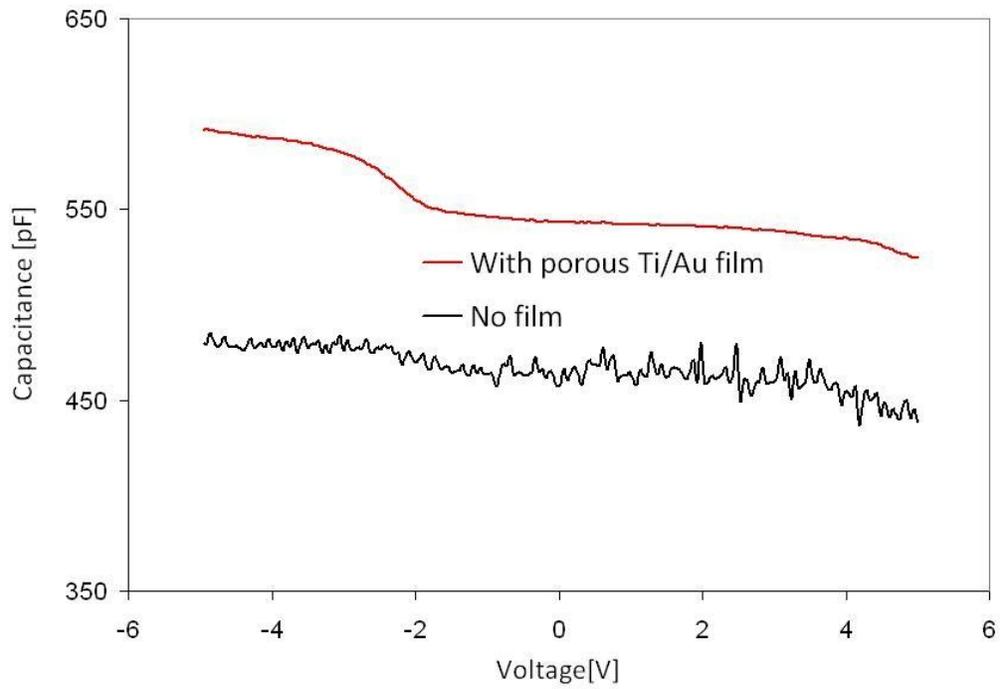
**Fig. 2:** Schematic diagram of the MOS capacitor device. A porous Ti/Au film (not shown) is added over the active area of the device.



**Fig. 3:** SEM image of sputtered Ti/Au film, not annealed, over the edge between the etched area and the top gold electrodes (to the left). Sputtered Ti Au film, annealed, showing porous structure with  $\text{Al}_2\text{O}_3$  surface revealed (to the right).

The capacitance versus voltage curve showed the normal shape with a maximum capacitance level and a transfer to a lower level for a certain applied voltage, see Fig. 4. The capacitor without the porous metal film shows a constant lower capacitance in a noisy signal. This reflects the fact that the capacitance here is measured over the area with thick insulator and thick metal contact, see Fig. 2. We will continue to investigate and characterize this interesting biosensor transducer structure.

It may be interesting to measure NO for example in the breath of human beings due to the presence of this gas in the metabolism. Breath is an environment with a high humidity. The measurements of  $\text{NO}_x$  sensitivity of Ga doped ZnO, as described in the introduction, was repeated in water vapor, see Fig. 5. The response to NO decreases somewhat in humid atmosphere but is still reasonably high and in fact the measurements are more stable. The surprising shape of the response, starting at a higher response level in the lower NO concentration, followed by a lower response for a higher NO concentration was found also in a non humid atmosphere. We will use DRIFT, diffuse reflectance Infrared transform, spectroscopy to try to find the reason for this interesting behavior [13].



**Fig. 4:** Capacitance measurements for a MOS capacitor device without and with a porous film pseudo-reference electrode.

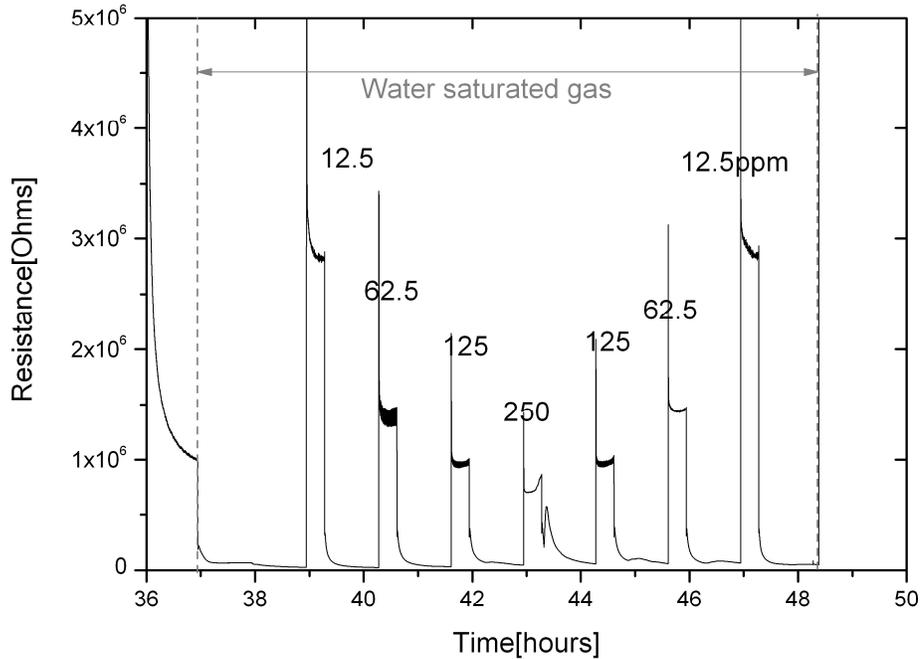


Fig.5. The resistivity change of Ga doped ZnO to NO between 12.5 ppm and 250 ppm. Operation temperature is 500°C. Note, the response level decreases for an increase of the gas concentration.

#### 4. CONCLUSIONS

We have taken several steps towards a multifunctional biosensor transducer based on wide band gap materials like SiC and ZnO. Successful functionalization by biomolecules was demonstrated for both materials. ZnO doped with Ga show resistivity changes for NO exposure, which seems to be stable also in humid atmosphere. NO measurements are important for many environmental purposes, and may be interesting for detection of NO in breath. A new type of ISFET device is under development with a porous gate metal as a semi-reference electrode.

## ACKNOWLEDGEMENTS

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