Title: *"Electronic noses based on organic field-effect transistors"*

Acronym: ***GASFET*** *(Gas Analysis Sensors Field-Effect Transistor)*

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Abstract: The proposed GASFET is a gas sensor using a polymeric field-effect transistor. The aim of this project is to understand and fabricate a polymeric FET that is able to sense selectively a variety of gases. A quantitative model needs to be developed to describe the electronic properties of an organic FET during/after interaction with a gas. Ultimately, the design of smarter electric noses will lead to a better description of smell (sensitivity) and a broader application range (selectivity).

Duration: The project will start in September 2008. The duration of the project will be 4 years (until 2012) for the PhD student.

Estimated Costs

Infrastructure:

- A set-up has to be built in which organic FETs can be characterized in a (quantitative) controllable atmosphere. This characterization chamber with gas inlets is already designed and developed, but needs to be built. This set-up (probe station, scroll- and turbo pump) will be home-built in the 4th quarter 2008 and will be operational in January 2009. Estimated costs: 60 kEuro.

Introduction and Application:

Over 35 years of effort is invested to create and design electronic noses in the field of gas sensing for the detection of individual components or mixtures of gases/vapors. Gas sensors are increasingly needed for industrial health and safety, environmental monitoring and processing control.[1] Since the 1970s, many types of sensor have been developed based on the different physical and chemical mechanisms. Absorption/desorption of heat in calorimetric sensors, the change of electrical conductance in metal oxide semiconductor field-effect transistors (MOS-FETs), the frequency shift due to the mass change in micro-gravimetric quartz sensors or the change of electrical resistance in conductivity sensors are prime examples of the sensors based on the physical properties.[2]

The main limitation in using sensors based on chemical mechanisms is the loss of selectivity and sensitivity upon miniaturization. There are three major classes of chemical sensors currently being investigated and developed: Chemiresistors, ChemFETs and optical sensors[3] among which optical sensors have been disregarded here due to the main disadvantage of consisting of bulky and (mostly) expensive optical detection equipment like photo-detectors, lasers, beam splitters, mirrors, lenses, etc., which limits the number of applications and portability.

Chemiresistors are the simplest sensors available, consisting of two contact points and a chemiresistive material. A typical material used in Chemiresistors is tin oxide, for detection of e.g. carbon monoxide. The resistance of a chemiresistive material is proportional to the analyte concentration (number of interactions) in the ambient environment. These sensors combine advantages of compact size, simple fabrication, low cost and simple read-out electronics. In spite of these advantages commercial arrays of chemiresistive sensors (called electronics noses) are still in the prize range of thousands of dollars. Although these metal oxide sensors have been used for several decades, stability, selectivity and sensitivity of these chemiresistors is a concerning issue, posing limitations on their application. Most important of all is the low signal-to-noise ratio upon miniaturization, since the integrity of the transuded signal that carries the chemical information depends on the sensing area.[4] On the other hand the inorganic semiconductor materials used in fabrication of these sensors, such as oxides and catalytic metals, are sensitive to the alcohols, but generally are poor for detecting sulfur- or nitrogen-based odors[1] limiting the sensitivity power of the sensor.

In contrast to the above-mentioned classes, chemical sensors based on a field-effect transistor structure (ChemFETs) are capable of much higher signal-to-noise ratios; a small shift of the threshold voltage can change the electric current in the channel by orders of magnitude at zero gate voltage. The complex structure of the ChemFETs, due to the use of a reference electrode, is the main disadvantage, which increases the costs of a sensor array even more. Although the transduced signal does not depend on the sensing

area, they are inherently much larger than Chemiresistors and require more complex measurement overhead. In order to improve the signal-to-noise ratio, often the third component like amplifier and current converting systems, are incorporated in the sensor. Organic thin films transistors (OTFT) in a bottom gate configuration can be used as chemical sensors. Such a device can work as multiparametric sensors, because on and off current variations can be used to identify chemical species.[5] The vapor sensors based on the OFET are similar to nearly all other sensor technologies that have been developed, where the sensor is a discrete electronic component which is connected to other electronic systems whose function is to amplify/process data from the sensor.[6]

The main goal in the research field for the gas sensors recently is to create a technology that can detect a wide range of odors, vapors and gases at useful concentration levels with sufficient reproducibility, selectivity, and stability to use as electronic noses. Such sensors can be useful in a number of applications including food processing, agriculture, environmental, and medical diagnostics and industries.[7] The development of the gas sensors for low costs and low power devices will open new market opportunities like warning systems for the professional and consumer market and also impact the safety of people at work and at home. For example: functional packaging of food products plays an essential role in maintaining and monitoring the product quality over longer periods of time. Sensors incorporated in the packaging materials can prevent the unnecessary destruction of food products (in Europe about 1/3 of all food products are not consumed but are discarded as waste). Indicators based on novel sensors can inform the consumer about the quality of the product or (for example) the ripeness of contained fruits. Packaging that include sensors and possibilities to communicate with devices in their vicinity can signal problems with storage conditions that could result in quality deterioration or can warn for potential safety problems. Active packaging could release substances at a specific point in time to optimize the quality (e.g. ripeness) when the product is consumed.

The advantages of using electrically conductive polymers, which currently find their use in commercial applications, are the low cost of manufacturing large-area processing on flexible substrates, availability of a wide range of material, and interesting properties such as a room temperature response that is fast, repeatable, and reversible.[8] Another important property of polymer-based sensors is the chemical flexibility of the active layers that can be used to attain a selective device by using side-chain functional groups to confer broad selectivity to a chemical sensor and finally easy processing compare to oxides, involving methods like spin-coating or Langmuir-Blodgett.

Improvement in understanding of the electrical properties of a large variety of polymers and knowing that electronic properties of certain conducting polymers can be modified by the presence of gases is now leading to a new generation of chemical sensors.[9] However, in the few results published so far the fundamental knowledge on the electrical processes in organic semiconductors in the presence of gases and vapors is missing. The process for detecting different vapors is based on functionalized conjugated materials; chemical information/interaction can change the electrical signal through this material, which is the main principle for construction of sensors.

All the basic knowledge on the FET operation without interaction with gases is present in our group, which forms a firm base for the implementation of this project. Besides the new probe station with gas inlets, the applicant's lab is fully equipped for this type of research. All relevant techniques and knowledge has been developed in the past few years, including semiconducting polymer synthesis, device fabrication, photolithography, extensive electrical characterization, and device modeling.[10]

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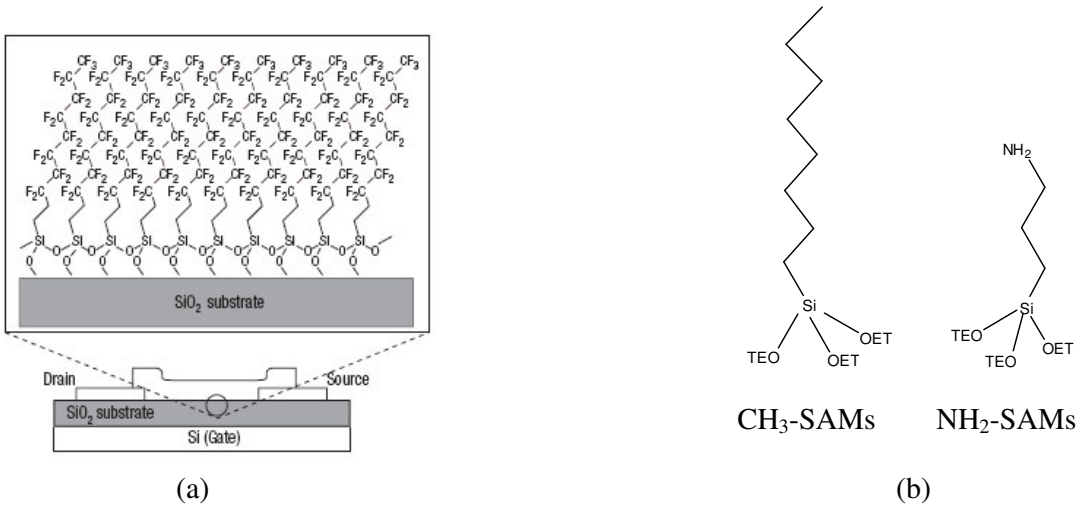

Figure 6. The OFET structure and related SAM molecules. a) Illustration of organic OFET with a SAM made from $(CF_3)(CH_2)_9Si(OC_2H_5)_3$ molecules on a SiO_2 gate insulator. b) The $(CH_3)(CH_2)_7$ $Si(OC_2H_5)_3$ and $(NH_2)(CH_2)_3Si(OC_2H_5)_3$ molecules that can be used for the functionalization of the SiO_2 with CH_3- and NH_2 groups.[24]

The amine end group on the organosilane molecule changes the effective charge carrier concentration at the insulator/semiconductor interface due to its high electron density and positive charge-trapping properties. Obviously, the change in the charge carrier density affects the *I–V* characteristics and the 'turn–on' (or threshold) voltage of the FET when kept under the same biasing conditions. The large shift in threshold voltage cannot be explained by the very small dipole moment along the axis of the molecules, and thus do not induce large changes in surface potential. However, the lone pair (2 unshared electrons in a vacant orbital on one atom (N)) on the amino group can trap positive carriers at the interface.[24] For example: The I_D-V_G characteristics of a p-type pentacene FET with four different SAMs treatments at a constant source-drain voltage of V_D= -80 V, the value of the I_D strongly depends on the molecule used at the interface. The I_D value at V_g=0 V is enhanced by six orders of magnitude in devices with F-SAMs compared with that of NH_2-SAMs, indicating that the surface carrier is significantly modulated by changing the SAMs molecules. The V_{th} (threshold voltage) shifts to positive values as the NH_2 SAMs is replaced by the perfluorinated SAMs. This shift is associated with an increased mobility. Clearly, this enables the electrical detection of different interface functional groups in the FET due to the presence of that specific end group. Modification of this SAM by a reactive or functional group results in selective sensing similar to using SAMs on the source and drain electrodes (Figure 4). The addition of a weak acid will result in an interaction between the amino surface groups. Consequently, the lone pair on the N-atom will be shared due to this interaction and the charge trapping of positive charge carrier will diminish.

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