



The multimodal detection as a tool for molecular material-based gas sensing

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ABSTRACT

The adsorption of a target gas on a material induces a change in several physical characteristics, such as the dielectric constant, the work function or the conductivity. The use of different transducers sensitive to the variation of these parameters appears to be a relevant methodology worthy of investigation. In the field of sensors, molecular materials present interesting and potentially valuable features as sensing elements for real gas sensor applications. In this article, we review the different types of conductimetric transducers and also show how a molecular material-based microwave transducer can be used for gas sensing. Among conductimetric transducers, resistors have been historically the most commonly exploited way for the detection and quantification of gas pollutants. Herein, we focus on new transducers, either based on the well-known OFETs, or on transducers combining two molecular materials, namely the p–n junctions and the brand new molecular semiconductor–doped insulator (MSDI) heterojunctions. The sensitivity of the devices is demonstrated through the detection of ammonia and ozone in the range of ppm and ppb, respectively.

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1. Introduction

Pollution, indoors or outdoors, inside buildings or due to motor vehicles, or related to specific industrial wastes, constitutes a topic of increasing interest. Among pollutants, ozone (O₃) and nitrogen dioxide (NO₂) must be measured in the ppb range in big cities, while olfactive pollutants (amines and sulfur derivatives) have to be detected in the ppm range [1]. Though no relation should be made between the presence of an odor and toxicity, since in many cases perception occurs on levels quite below the exposure limit, the perceived olfactory pollution can be quite real to the locals, and subjected to wind orientation and variations. The case of ammonia (NH₃), an olfactive pollutant, must be considered in a particular way because it is involved in many industrial applications [2]. Indeed, liquid ammonia is used as cryogenic fluid, in particular in the cold rooms and more generally in food conservation, as a replacement of fluoro-carbons. Any leak can prove to be detrimental for the workers carrying out their tasks inside or in the vicinity of these installations. NH₃ is also encountered on industrial breeding sites as a product of the natural transformation of animal excrements. The control of its concentration will make it possible to optimize ventilation of the buildings and ensure the good health of both animals and people. In addition, in the industry of manures,

NH₃ concentration must be controlled and kept below the alarm threshold of 50 ppm in the air.

The sensors available on the market are mainly of two types [1]. The first are conductimetric sensors, generally using non stoichiometric metal oxides like SnO_{2-x}, which present a long life span, can operate from ppm to percent ranges and are available at low costs. But their main drawbacks are the requirement of a high working temperature, usually in 300–500 °C range, and the lack of selectivity. The other kind of commercially available ammonia sensors, of the electrochemical type, is sensitive in the ppm range. Those are generally selective but are also much more expensive because their manufacture does not allow their production in series by the microelectronics technologies and because they require a costly electrolyte [3]. Moreover, their lifetime is shorter than this of inorganic sensors [4], partly due to the consumption of the electroactive reactant contained in the electrolyte. Consequently, their replacement cost is high. Additionally, they are rather temperature sensitive.

Among all the physical parameters modified by the adsorption of gases, the most involved in molecular material-based gas sensors is the work function [5]. Modulation of the work function of electronic materials by interaction with gases and vapors is without a doubt a viable and well-defined sensing principle [6]. It is used in equilibrium potentiometric sensors, such as the macroscopic Kelvin probe and in its solid-state miniature counterpart, the field-effect transistor, used as chemical sensors (ChemFET). However, because the workfunction is such a fundamental property of electronic materials it is also directly involved in other kind of chemical

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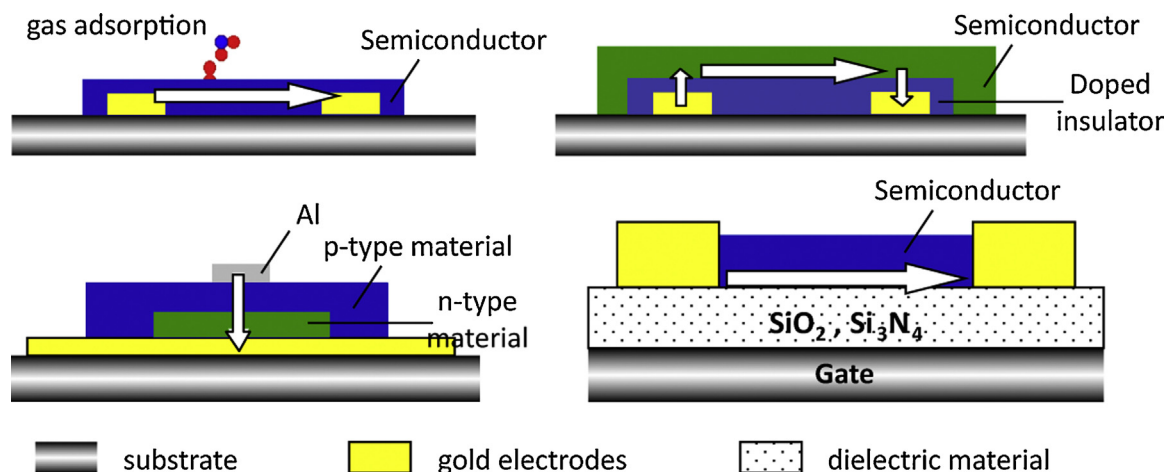


Fig. 1. Schemes of conductimetric sensors; top left: resistor [1], bottom left: p–n junction [22], top right: MSDI [23] and bottom right: FET [18]; the white arrows indicate the main conduction pathways.

sensors, namely junctions [7] and various forms of chemiresistors [8]. In these sensors, the response is obtained while current is passing through the sensing material. Elsewhere, the microwave electromagnetic propagation depends not only on the dielectric constant of a material and its conduction but also on the geometry of the device. This is at the origin of the development of microwave transducers for chemical sensing using sensing materials in the form of pressed pellets [9,10]. A microwave-based measurement system was also introduced recently by Moos et al. based on the perturbation measurement of a cavity [11–13]. It allows to detect the status of automotive catalysts by the determination of the oxygen loading state of three-way catalysts [11], the ammonia loading of zeolite-based ammonia selective catalytic reduction catalysts [12] or the status of lean NO_x traps as well [13].

We chose to illustrate this paper on conductimetric and microwave transducers by examples of phthalocyanine-based chemical sensors. Of course, what we developed on transduction modes could be achieved with other molecular materials, in particular with other phthalocyanines. For a general review on phthalocyanines as sensitive materials for chemical sensors, see the work by Zhou et al. [14], in which electronic conductance and mass-sensitive sensors are particularly discussed.

2. Conductimetric transductions

With molecular materials, as with inorganic materials, most of the conductimetric gas sensors are resistors (Fig. 1). In these devices, the current variation is due to a variation of the conductivity of the material following upon the gas adsorption. If a charge transfer can occur between the adsorbed gas and the sensing material, as it is the case with redox active species, a variation of the density of free charge carriers occurs. Thus, an oxidizing gas induces an increase of the density of majority charge carriers in p-type materials, whereas an electro-donating species will induce a decrease of this density. The reverse phenomena are observed with n-type materials. When non-redox active species are involved, the adsorption process can lead to a variation of the dielectric constant, which induces also a modification of the transport properties. Generally, the effect of redox active species is stronger than this of non-redox active species.

A field-effect transistor (FET, Fig. 1) instead of a resistor allows the use of very thin sensing layers, the source-to-drain current being modulated by applying a gate voltage [15–18]. The advantage of using very thin films is that it diminishes the diffusion phenomena. However, the main difference between resistors and

FETs is that they can provide more information from changes in multiple properties on exposure to a target gas, e.g. the bulk conductivity, as for resistors, but also field-induced conductivity, the threshold voltage and the FET mobility [19]. Furthermore, the application of an opposite transverse field during the recovery periods allows to accelerate the reversibility of the detection process.

Whereas organic FETs [20,21] and diodes [22] have been prepared after their inorganic counterparts, we designed and characterized a new molecular material-based device (Fig. 1). Molecular semiconductor–doped insulator (MSDI) heterojunctions were built combining a molecular semiconductor (MS) and a doped-insulator (DI) [23]. MS must be more conductive than the sub-layer to take advantage of the heterojunction. Up until now, the intrinsic molecular semiconductor [24], namely the lutetium bisphthalocyanine (LuPc_2) and lanthanide triple-decker complexes have been used as MS [25]. DI can be p-type materials, as non-substituted phthalocyanines (Pc), e.g. the copper phthalocyanine (CuPc, called F0 in Fig. 2) or sexithiophenes, or n-type materials, as fluorinated Pc ($\text{Cu}(\text{F}_{16}\text{Pc})$, called F16 in Fig. 2) or perylene derivatives [26]. MSDIs have been used as new transducers for gas chemosensing, toward ozone in air, at 90 ppb [23] and ammonia in argon, at 35 ppm (Fig. 2) [27]. For the gas sensing experiments, the samples were constantly polarized to 1 V. p-Type materials lead to MSDIs that exhibit a positive response to ozone and a negative response to ammonia, whereas MSDIs prepared from n-type materials exhibit a positive response to ammonia and negative response to ozone. The remarkable point is that the only material in contact with the analytes is, in all cases, the very same semiconductor.

The variation of the work function is always accompanied by a change in the density of the charge carriers, so, this must be taken into account in the present sensors. Thus, gas sensor tests were performed to check the potentialities of hybrid films made from cellulose and hydroxygallium phthalocyanine (HOGaPc) [28]. In particular, the synergetic behavior between the film-forming materials allows a fast and sensible change in surface potential, measured using the Kelvin–Zisman vibrating capacitor probe, after cyclic exposures to ozone (O_3 , 100 ppb) and nitrogen (Fig. 3). The variation of the surface potential for a film of pure HOGaPc (not shown here) was only one fourth of that observed for the hybrid film, moreover with a lack of reversibility. It was shown that the hybrid film acts not only as an active layer in detecting the oxidant atmosphere with higher sensitivity and stability, but exhibits also a fast recovering of the initial properties, compared to the behavior of a pure phthalocyanine. Clearly, the polymer attenuates the inherent crystallization tendency of the phthalocyanine.

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