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Phthalocyanine - Based Field-Effect Transistors as Gas Sensors

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Abstract

In this review, a description of molecular field-effect transistors is given, in comparison with gate-modified inorganic counterparts. The different processes involved in gas sensing are summarized. The advantages of transistors on resistors are demonstrated. Sensitivity of molecular field-effect transistors to strong oxidizing species like ozone is detailed and compared to their sensitivity to humidity and volatile organic compounds. Application to ozone monitoring in urban atmosphere is also presented.

Introduction

Gas sensing by measurement of the electrical property changes in molecular materials following their adsorption on a solid surface has been widely investigated. Most studies have dealt with molecular resistors since the studies of Bott and Jones [1] but only few studies concerned transistors. A very interesting work is that of Laurs and Heiland who studied the effect of oxygen, iodine, bromine and also lithium on the conductivity of various phthalocyanines.[2] Without using the term “transistor” they prepared p and n-type field-effect transistors (FETs) and studied their sensitivity to oxidizing gases. They showed that the influence of oxidizing gases like oxygen on the surface conductivity reversed its sign when the field-effect changed from p to n type as a result of lithium vapor exposure. These studies carried out in ultra-high vacuum chamber deal with gas sensing but not with sensors. Indeed,

different qualities are required to actually obtain sensors. Among them, sensitivity, selectivity and stability are probably the main, but reversibility, reproducibility, response and paralysis times and their insensitivity to factors of influence (temperature, pressure ...) are also important intrinsic qualities to get a sensor. Depending on their particular applications and on the demand other qualities must be fulfilled. A sensor must be miniature, robust, with a sufficient lifespan, should consume low energy, allow an uninterrupted monitoring, of simple implementation, and deliver easily exploitable signals, all for the lowest possible cost.

Demands of gas sensors come from the organisms in charge of the air quality control. Indeed, these sensors would allow multiplying the density of measurements and then to get a more accurate cartography of atmospheric pollution than with the analyzers, which are expensive compared to miniaturized sensors. Another emerging application is the indoor pollution control.[3]

In that review we will distinguish the FETs in which the molecular material is used as semiconductor, called hereafter molecular FETs from those made from silicon and where the gate, modified by a molecular material, is exposed to gases. For that second type of device, usually called chem-FET, we will use the term gate-modified FET.

I. Description of field-effect transistors

I.1. MOSFET

The most widely used FET is the Insulated Gate FET (IGFET) based on two opposite n/p junctions. Silicon IGFETs are rather known as MOSFETs (Metal Oxide Semiconductor FETs) because their insulating layer is a silicon oxide film thermally grown upon a silicon substrate.

Let us consider a MOSFET with an n-channel in the enrichment regime (Fig. 1). In the absence of any polarization, the capacity MOS remains in depletion mode and the transistor is normally blocked (Fig. 1a). The application of a positive gate-to-source voltage V_{GS} higher than the threshold voltage V_T of the capacity creates an inversion layer of the n-type, called

channel, between the source and the drain. If a positive drain-to-source voltage V_{DS} is applied a current I_{DS} circulates in the channel. Because of that polarization, the inversion layer is more pronounced near the source than near the drain. For a high polarization of the drain the electron density in the inversion layer decreases and the current starts to saturate. For a certain value of that polarization, the capacity MOS is not any more in inversion mode near the drain, it is the pinching mode (Fig. 1b). Beyond this polarization, the current is ensured by the free carriers in the conducting channel up to the point of pinching and then propelled towards the drain by the electric field that exists in the space charge region. This transistor works with a n-channel but the equivalent exists with a p-channel with reversed polarizations.

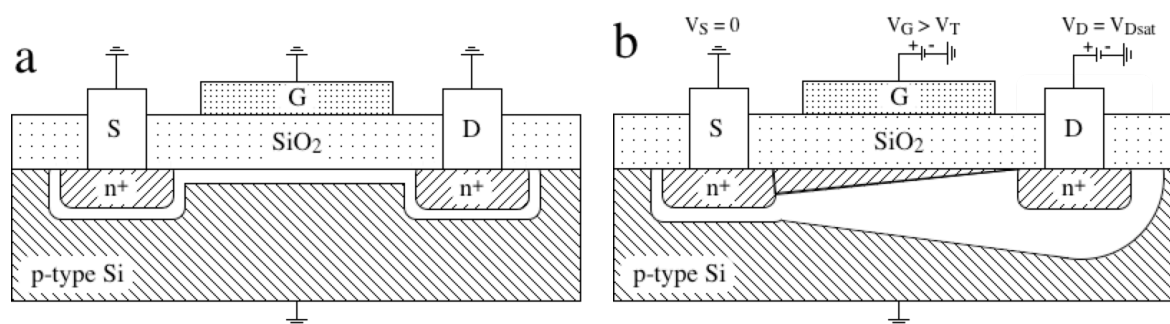


Figure 1. Schematic illustration of a MOSFET with a n-channel in the enrichment regime, in its blocking mode (a) and in the pinching off mode (b).

1.2. Molecular FET

The first phthalocyanine - based transistors [4-6] were described in the mid to late 1980s, simultaneously with polymers[7-9] and α -sexithiophene,[10] then with pentacene[11] and fullerenes.[12, 13] Very recently, n-channel transistors were obtained with withdrawing moiety-substituted molecules such as fluorine phthalocyanines,[14] α , α' - diperfluorohexyl-substituted sexithiophene[15, 16] and with perylenetetracarboxylic dianhydride or related molecules.[17-19] We will see that p and n-type FETs can be useful to detect different type of chemical species.

An electron-active molecular material thin film is deposited between two gold electrodes (source and drain) on a dielectric material (SiO_2 , Si_3N_4 or a polymer, thickness

typically 1000-3000 Å) covering a metallic electrode (Fig. 2). If a negative gate voltage is applied the positive charge carriers existing in the semiconductor are attracted towards the dielectric material, while the negative charge carriers are repulsed that create a channel where the density of majority charge carriers is higher than in the bulk. Although the mechanisms are totally different the basic equations of classical silicon MOSFETs[20] can be adapted to molecular transistors.[21] The variation of the source-to-drain current I_{DS} as a function of the source-to-drain voltage V_{DS} and of the grid voltage V_{GS} is well established (eq. 1).[21]

$$I_{DS} = \frac{Z\mu C_i}{L} V_{DS} \left(V_{GS} - V_T - \frac{V_{DS}}{2} \right) \quad (1)$$

where Z is the channel length, L the inter-electrode distance, C_i the capacitance of the insulator per unit surface and V_T the threshold voltage (eq. 2). V_T has another origin than in the classical MOSFETs where it corresponds to the voltage required to get the strong inversion. In molecular FETs V_T has been associated to the presence of traps of structural origin, or to ions or other impurities at the semiconductor - dielectric material interface.[22, 23]

$$V_T = -\frac{ehn_0}{C_i} \quad (2)$$

where h is the thickness of the molecular layer and n_0 the density of charge carriers without grid voltage.

At $V_{DS} = V_{GS} - V_T$, the $I_{DS} = f(V_{DS})$ curve reaches a maximum and a pinch off of the channel occurs. For $V_{DS} > V_{GS} - V_T$ the channel is no longer continuous and the corresponding current is called saturation current (eq. 3).

$$(I_{DS})_{sat} = \frac{Z\mu C_i}{2L} (V_{GS} - V_T)^2 \quad (3)$$

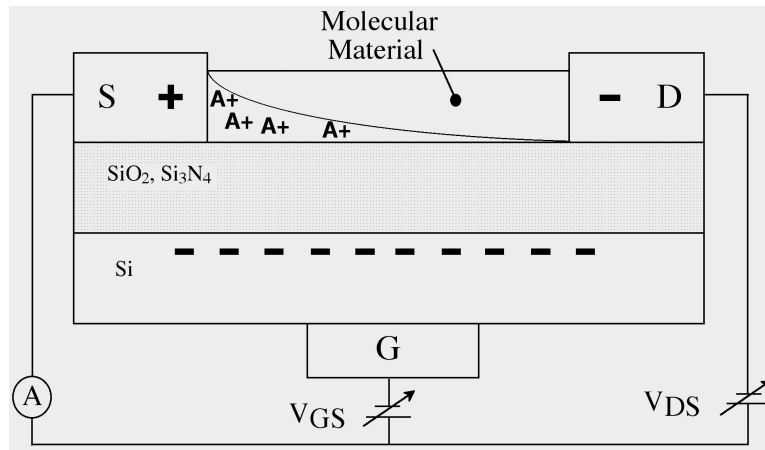


Figure 2. Schematic illustration of a molecular FET with a p-type molecular material in its pinching off mode ($V_D < V_G < 0$).

The curve $\sqrt{(I_{DS})_{sat}} = f(V_{GS})$ allows to deduce the mobility μ , which is called the field-effect mobility. V_T is deduced from the intersection of this curve with the x-axis ($V_{GS} = V_T$). Contrary to what happens for classical MOSFETs, in molecular FETs the bulk current, I_b , cannot be neglected and has to be taken into account in parallel with the channel current I_{DS} in order to get the total current I_t . In the absence of gate voltage and in the ohmic domain, I_b is proportional to V_{DS} . So, at saturation (i.e. $V_{DS} = V_{GS} - V_T$), the I_{on}/I_{off} ratio can be calculated (eq. 4).

$$I_{on}/I_{off} = \frac{(I_{DS})_{sat}}{I_b} = \frac{C_i}{2hne} (V_{GS} - V_T) \quad (4)$$

According to this model, the I_{on}/I_{off} ratio can be improved by decreasing the free charge carrier density and the thickness of the active part of the FET, and by increasing the capacitance of the insulating material. As a consequence, the field-effect is easier to highlight in an insulator as nickel phthalocyanine NiPc than with a semiconducting material as lutetium bisphthalocyanine LuPc₂. [21] It has been shown that, contrarily to the macroscopic conductivity, the field-effect observed in a FET is very sensitive to the surface states, particularly at the insulator-molecular material interface.

II. FET as gas sensor

II.1. Origin of the sensitivity

II.1.a. Adsorption processes

The adsorption of molecules on a surface is a key step in any gas sensing process. In many cases the surface is already covered by another type of molecule, usually dioxygen or water that has to be removed to allow the adsorption of molecules to be detected. In physisorption (or physical adsorption) the attraction forces between atoms of the sensing layer and those of the gaseous phase are electrostatic forces of van der Waals type, thus of weak energy (from 2 to 10 kJ mol⁻¹). In chemisorption (or chemical adsorption) a chemical bond involving substantial rearrangement of electronic density is formed between the adsorbate and substrate. The involved energies are significant, from 40 to 800 kJ mol⁻¹. Chemisorption is often a dissociative process, which may be irreversible, whereas physisorption is a non-dissociative and reversible process. Chemisorption is often a thermally activated process with kinetics of adsorption very variable whereas physisorption is a non-activated and usually fast process.[24] The Langmuir isotherm established ninety years ago gives the fraction θ of occupied sites ($0 < \theta < 1$) as a function of the partial pressure P of the adsorbing gas.[25, 26]

The adsorption of gases onto molecular material films has been largely studied.[27, 28] Experimental data related to the adsorption of gases onto molecular layers show that θ varies as a power of the gas concentration. To formalize those results the authors use the Freundlich isotherm, which is close to the Langmuir isotherm, but where all the sites are not considered as energetically equivalent because of the existence of grain boundaries and defects. In fact, the assumptions associated to the development of the Langmuir adsorption represent an ideal form seldom found in thin polycrystalline layers. The Freundlich isotherm is rather an empirical model. However, with a relatively small range of partial pressures, far from saturation of the surface, the curve associated to the Langmuir isotherm between θ and P may

be described by a power law. After adsorption, diffusion phenomenon is the second important parameter that influences gas sensor responses.

It is well known that structure, morphology and surface chemical composition of molecular films, which depend on preparation conditions, have implications on adsorption and diffusion processes.

II.1.b. Redox processes

Phthalocyanines and related molecules, as porphyrins and naphthalocyanines, can be oxidized and reduced by redox active species. The electrical properties of molecular materials depend on the density of charged species. Consequently, a molecular material in contact with a strong oxidizing gas will become more conductive.

Let us see the relationship between the redox potentials of molecular materials and their electrical properties. The conduction process is due to an electron transfer from molecule to molecule. It has been demonstrated that in a molecular material constituted of molecular units A, the creation of charge carriers corresponds to the oxidation of one molecular unit and the reduction of another one.[29, 30] The elementary steps consist in an electron transfer (E.T.) from one molecule to another follow-up by a separation of the newly created charges (C.C.) (eq. 5). In the intrinsic case the density n (or p) of charge carriers is related to the oxidation and reduction potentials, E^{ox} and E^{red} respectively, of A in the solid state (eq. 6).



$$n = p = [A^+] = [A^-] = [A]_0 \exp\left(\frac{E_0^{\text{red}} - E_0^{\text{ox}}}{2kT}\right) \quad (6)$$

where $[A]_0$ is the density of molecular units in the solid state, approximately 10^{21} cm^{-3} .

Conductivity σ is the product of the density of charge carriers by their mobility μ and the charge of an electron. Mobility μ is lower in molecular materials than in silicon, usually in the range 10^{-4} - $10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with a maximum of $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. For metallophthalocyanines as

NiPc, whose $E^{\text{ox}} - E^{\text{red}}$ value is about 1.9 V,[31] the calculated intrinsic density of charge carriers is $n = p = 10^5 \text{ cm}^{-3}$. They belong to insulating materials. On the contrary, LuPc₂, which is a radical species, can be easily oxidized and reduced. Due to its very low $E^{\text{ox}} - E^{\text{red}}$ value (0.48 V), LuPc₂ exhibits a very high density of charge carriers, $5 \cdot 10^{16} \text{ cm}^{-3}$ (ca. 10 ppm), i.e. more than in silicon. It appears that LuPc₂ was the first intrinsic molecular semiconductor.[30, 32]

An oxidizing species I_A (resp. reducing species I_D) will generate extrinsic positive (resp. negative) charges (eqs. 7, 8). Then, the extrinsic density of charges is proportional to the exponential of ($E_A^{\text{ox}} - E_{I_A}^{\text{red}}$) (resp. ($E_{I_D}^{\text{ox}} - E_A^{\text{red}}$)).



In most of the molecular materials, a very small amount of impurities is sufficient to increase the conductivity of the material, which is intrinsically an insulator. Even for semiconductors such as LuPc₂, with a very high intrinsic density of charge carriers (10 ppm), the conductivity can be multiplied by a factor 1000 with a concentration of doping agent of 1 %, if an efficient charge transfer is considered. It means that doping of molecular materials is always easy. In the case of insulators the sensitivity is so high that it becomes extremely difficult to measure the intrinsic conductivity. However, doping effects are of the utmost importance since they are at the origin of the conductimetric sensors.[30]

Oxidation of CuPc at room temperature causes the increase of the conductivity by several orders of magnitude up to a plateau. LuPc₂ showed higher sensitivities to NO₂ than the non-radical phthalocyanines.[33] For radical phthalocyanines, in the first stage the conductivity readily increases as in CuPc, then it goes through a maximum and decreases. Indeed, because of the low oxidation potential of the radical lutetium compounds, a very high concentration of phthalocyanine molecules can be oxidized. The holes displacement by

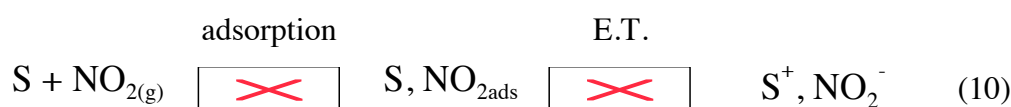
hopping from one oxidized molecule to another neutral one becomes more and more difficult since there are less and less available neutral molecules left for holes to hop into. In addition, hoping between two oxidized molecules involves a doubly oxidized species, which is very unlikely because it requires too much energy, $E = 1.23$ eV in the case of LuPc₂, associated with a new equilibrium (eq. 9).



When the concentration of extrinsic charge carriers increases their mobility decreases and also their conductivity. The existence of a maximum of conductivity occurs for LuPc₂ only with relatively strong oxidizing species. Oxygen gas that presents a small electron affinity value does not induce such effect on the conductivity of all phthalocyanine layers even at high concentrations.

Even though the adsorbed species are not redox active in nature, other physical parameters, such as the dielectric constant of the material and the ionic conductivity for examples can be affected. In the original hydrogen sensor of Lundström[34] with a non-modified Pd-gate MOSFET, or in the case of gate-modified FETs[35] and Schottky diodes,[36] the variation of the work function of the sensing electrode is at the origin of the current modification of the device.

The information delivered by the sensor will be pertinent if the variation of the signal is a reliable picture of the variation of the gas concentration. Consequently, the reaction between the gaseous species to be detected and molecules of the sensing layer should be reversible. Let us consider the case of nitrogen dioxide, NO₂. After the adsorption step, oxidation occurs through an electron transfer from NO₂ to the sensing layer S (eq. 10).



Due to its high instability, the case of ozone (O_3) is more complex and other intermediate species have to be considered. The reaction steps in ozone decomposition were elucidated with carefully designed experiments that used isotopic substitution.[37] They can be applied to understand the behavior of ozone on phthalocyanine materials and particularly the reversibility of the oxidation process. The key step is the dissociative adsorption of O_3 leading to highly reactive atomic oxygen, which reacts with a second ozone molecule to form an adsorbed peroxide species and gaseous oxygen (eqs 11-13).



Reversibility of the phthalocyanine oxidation can occur with desorption of one dioxygen molecule whereas the starting oxidizing species (O_3) is decomposed.

II.2. Gate-modified FET

MOSFETs have been modified by deposition of Langmuir-Blodgett (LB) films of substituted cobalt porphyrins[38, 39] and octahexyl metal-free phthalocyanine[40] on p-type MOSFETs (Fig. 1). It is worth to mention that two different procedures were applied to acquire data, which can make uneasy a comparison between the devices.

In the first case, no gate voltage is applied and exposure to NO_2 induces a modification of the gate potential by a partial oxidation of molecular material. The variation of I_{DS} as a function of V_{DS} at various concentrations can be compared to the characteristics $I_{DS} = f(V_{DS})$ of a non-modified MOSFET at various gate voltages (Fig. 3). At $V_{DS} = +5$ V, 10 and 20 ppm NO_2 concentrations induce a current I_{DS} equal to 0.3 μA and 0.65 μA , respectively. These values are equivalent to those obtained with gate voltages of 0.80 and 0.90 V.[38] Response time is approximately 10 min, with a recovery time of 1 h for a 5 ppm concentration with a 39

layer LB-MOSFET. However thinner films and higher concentrations provide faster responses. Working at 85 °C, NO₂ can be detected at the ppm level, with no sensitivity to H₂, NH₃, CO and H₂S at 500 ppm levels. When the enhancement n-channel MOSFET is replaced by a MOSFET designed as a depletion p-channel, sensitivity can be improved to 0.1 ppm.[41] Surprisingly, at this concentration NO₂ acts as a negative gate voltage.

In the second case,[40] a determined gate voltage is applied and a delay is observed in the response of the drain current. At first, I_{DS} increases slowly, then rapidly up to a saturation value. Thus, the curve I_{DS} = f(t) has the same shape than the I_{DS} = f(V_{DS}) curve showed in the previous case. The response of the device, defined in that case as the variation of I_{DS} as a function of time, ΔI_{DS}/Δt, increases with the NO₂ concentration in the range 2-14 ppm. This approach has been used recently with samarium bis(octa octyloxy-phthalocyanine),[42] but with no apparent advantage due to the radical nature of the molecule.

In any case, sensitivity to NO₂ is higher with gate-modified transistors than with non-modified metallic gates.[43]

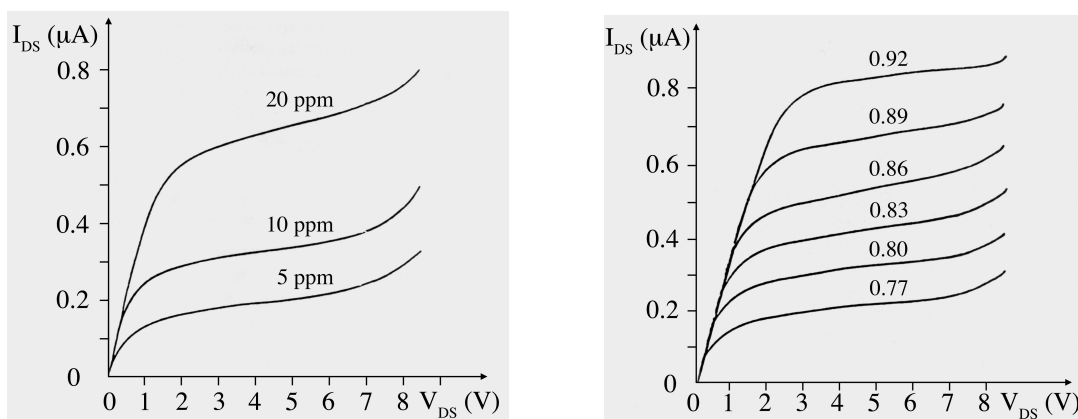


Figure 3. Characteristics of a FET where the gate is a LB film (39 layers of CoPorBr) when exposed to NO₂ (V_{DS} = 3 V) (left); characteristics of the equivalent MOSFET (right). Modified from [38].

II.3. Molecular FET

Early in the preparation of molecular FETs, effects of atmosphere appeared. For example, it was shown that with LuPc₂ majority charge carriers could change from n-type

under vacuum to p-type in air.[21] In the case of non-radical metallo-phthalocyanines (MPc), a p-type behavior was evidenced under vacuum with a negligible current at zero gate-source voltage (I_{off}). In air, due to dioxygen or related oxidizing species, extrinsic generation of charge carriers occurs, which increases significantly the conductivity at $V_{\text{GS}} = 0$. Simultaneously the saturation current increases, but less than I_{off} , leading to a lower amplification factor. In the same time, the threshold voltage increases and the FET mobility decreases.[22] It is important to note that, in air, I_{DS} can be increased by a positive gate-source voltage and decreased by a negative V_{GS} value, the FET working in enhancement mode and in depletion mode, respectively (Fig. 4).

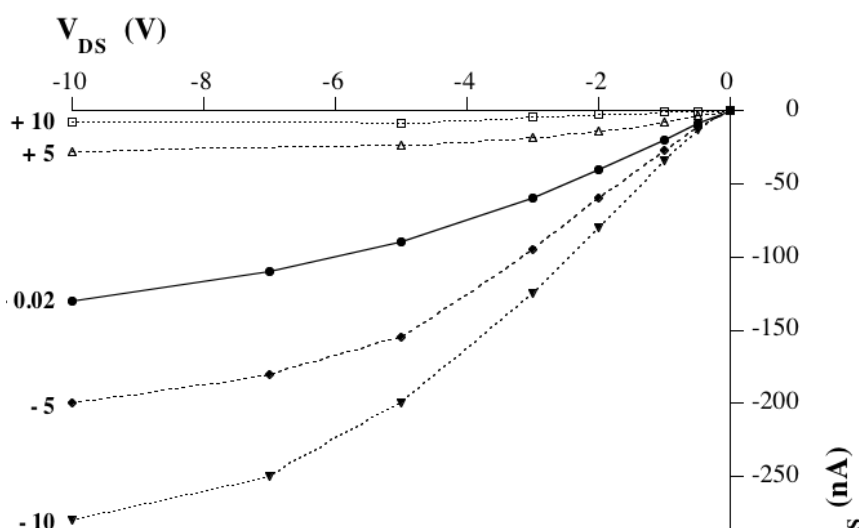


Figure 4. Variation of I_{DS} as a function of V_{DS} for a NiPc - based FET in an air-containing metallic box, which excludes the presence of ozone in contact with the device. V_{GS} values are indicated in volts.

In FETs several parameters can be affected by gaseous species and molecular FETs can be considered potentially as multi-parameter gas sensors.[44] After these general considerations let us detail humidity sensors, volatile organic compounds (VOCs) sensors and oxidizing gas sensors. Up to now, phthalocyanines have been used for humidity and VOCs sensing only in resistors and not in transistors, even though they could be used favorably in

such devices. It is the reason why the next two sections deal with sensors based on other molecular materials.

II.3.a. Humidity

When a pentacene FET is exposed to humidity its saturation current decreases as well as its FET mobility.[45] Above 30% in relative humidity (RH), a change of 0.7% in the saturation current per 1% change in RH is obtained for a 500 Å - thick film, whereas sensitivity decreases to 0.3% when the thickness of the pentacene layer is increased to 1000 Å. Below 30% in RH, the thicker films seem more sensitive but with memory effects. That is a general behavior for gas sensors due to slow diffusion of molecular species in and out of the sensitive layers. I_{Dsat} and mobility decreasing were also observed with 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA) that leads to n-type FETs.[46] It means that H₂O does not act on the generation of charge carriers, but rather as traps of the pre-existing free carriers. With NTCDA an additional phenomenon occurs, which is its possible hydrolysis. Even though no difference between anhydrous NTCDA and NTCDA exposed to humidity was observed by infrared studies in the same conditions than the FETs exposure, however even 1% hydrolysis corresponds to a high concentration of protons in the molecular layer. Ionic conductivity can occur, which could explain the slight increasing of I_{off} . Moreover, the dynamic range for the variation of I_{Dsat} is only of one order of magnitude for NTCDA FETs.

II.3.b. VOCs

Sensitivity to VOCs has also been studied with various molecular FETs using oligothiophenes, phthalocyanines and fluorinated 1,4,5,8-naphthalene-tetracarboxylic-diimide (NTCDI).[47, 48] I_D decreases when devices are exposed to saturated vapor of the analyte. For example, the current I_D of an α,ω -dihexyl- α -sexithiophene - based FET decreases by 7% due to a 5 s exposure time to 1-hexanol. As for water on pentacene, the FET mobility decreases. The degree of sticking measured with a quartz-coated microbalance does not necessarily correlate linearly with the vapor pressure value, but the current change is in close

correlation with the mass uptake of odorant that adhered to the sensitive layer.[47] For example, the response of a poly-dipentoxo-tertiophene FET to 1-hexanol is 10 times higher than to ethyl alcohol.[49] Thanks to an electrical bias cycle recovery is ensured after about 1 min, which is a short time compared to sensor standards but represents 12 times the exposure period. The recovery time without reverse bias is approximately 1 h. It was shown that the sensing response of oligothiophene FETs towards alcohols enhanced as the number of grain boundaries increased. A map illustrating the effect of 16 analytes on 11 sensor materials was published, suggesting possible applicability in the field of olfactory sensor arrays.[48]

II.3.c. Oxidizing species

A sensor that exhibits sensitivity to ozone concentration below 10 ppb has been prepared with a NiPc - based FET.[50, 51] A dynamic procedure working out of the equilibrium state allows to get rid of drift phenomena. A process where 2 min exposure alternates with 8 min static rest period leads after a conditioning period to a stable and reproducible signal. The drift of I_{off} is about 0.15 nA per cycle, i.e. only 2% of the current. The derivative dI_{DS}/dt gives a response of the sensor independent of the exact exposure time (Fig. 5).

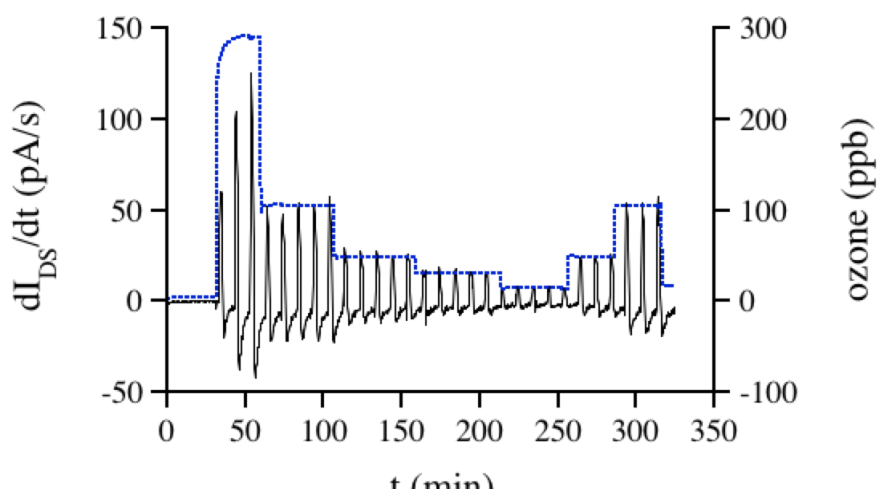


Figure 5. Response dI_{DS}/dt of a NiPc - based FET exposed to various ozone concentrations (---) in air.

The maximum value of the derivative is linearly correlated to the ozone concentration in air ($55 \text{ pA ppb}^{-1} \text{ min}^{-1}$) between 0 and 150 ppb, that is to say in the range encountered in urban atmosphere. This ozone sensor has been used in real situation (Fig. 6a). The use of a dynamic rest instead of a static rest reduces the duration of the recovery period, but is not necessary to achieve a good reproducibility, contrarily to what happens with more stable gases, as NO_2 . Another advantage of this device is to work at room temperature. A miniaturization of that ozone sensor has been achieved.[51]

Due to its high instability, ozone is not supposed to diffuse inside the molecular film. However, a negative gate voltage can attract the positive charges created at the air-thin film interface by oxidization of the molecules, and surface sites remain available for new oxidizing processes.[51] Although ozone cannot diffuse into the film as it is the case for NO_2 , oxidation in the bulk can occur. It has been demonstrated that only the superficial layer of the molecular film is degraded by ozone, allowing a long sensor life span.[50] Moreover, it has been shown that application of a positive gate voltage accelerates the recovery of the initial state, as seen for VOCs, suggesting that positive charges involved in the redox processes can migrate away from the dielectric-semiconductor interface.[52]

Sensitivity to NO_2 was found to be approximately 5 times smaller than to O_3 .[53] However, it is not sufficient to get good results in polluting gas control in atmosphere. Indeed, during a day, the ratio $[\text{NO}_2]/[\text{O}_3]$ varies between 10^2 and 10^{-2} (Fig. 6b). Thus that sensor is able to give reliable maximum values of the ozone concentration, but when the ratio $[\text{NO}_2]/[\text{O}_3]$ is higher than 10 the response of the sensor is more related to the NO_2 concentration (Fig. 6a). It is the reason why new methodologies have been developed,[54] including the use of selective filters[55, 56] but not yet applied to molecular FET - based sensors.

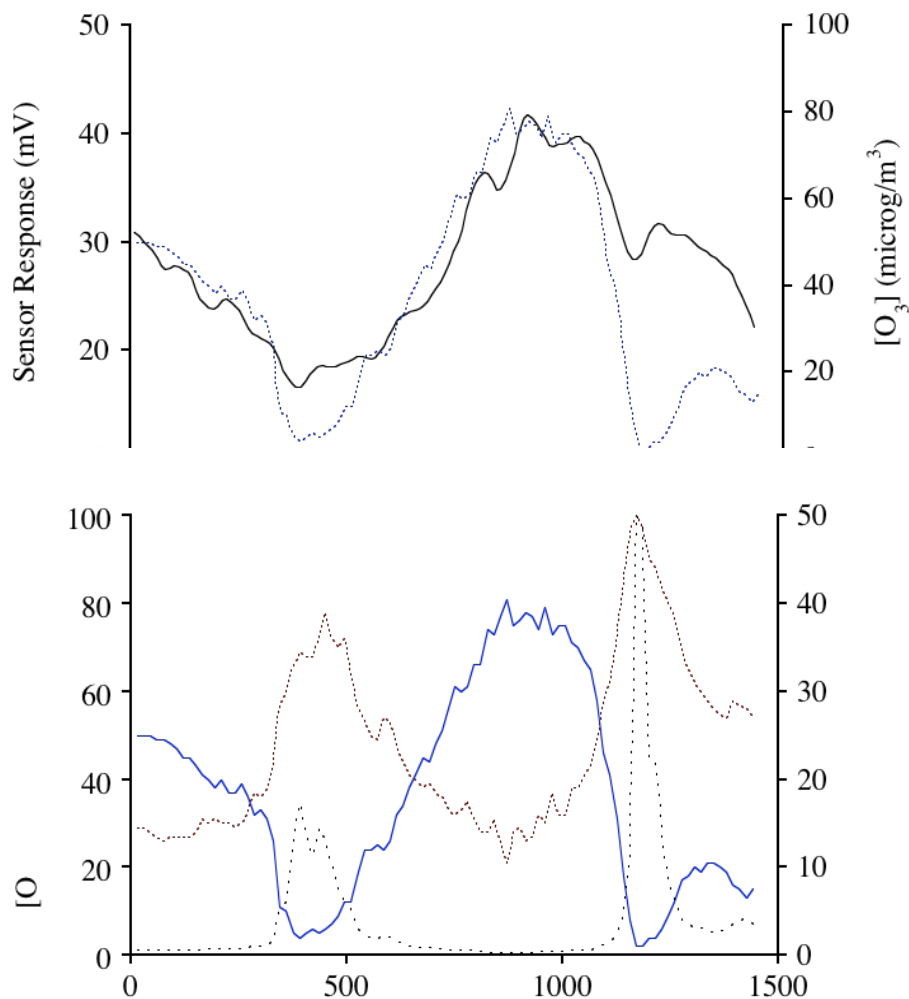


Figure 6. top) Response $(dI_{DS}/dt)_{\max}$ of a NiPc - based FET to ozone during a day in a Paris suburb, compared to the ozone concentration (---) and bottom) variation of ozone and nitrogen dioxide (.....) concentrations during the same day, and the $[NO_2]/[O_3]$ ratio (---).

Measurements of relative humidity were realized to quantify its effect on the sensor. Some results were published on synergy between water vapor and NO_2 at room temperature.[57] In our conditions, namely temperature, pollution rate and range of measured humidity (between 20% and 40%), very weak influence of relative humidity variations on the

sensor signal was observed. Considering other gases like O₂ or CO their action can be neglected compared to that of O₃ and NO₂. If fluorinated phthalocyanines are used the corresponding molecular FETs, of n-type, are sensitive to reducing species like ammonia,[58] as it is the case for resistors.[59]

Conclusion

Phthalocyanines and related molecules have been used in molecular FET structures as sensing materials for various gases. Dynamic procedures using short exposure periods led to the best results, as for molecular resistors. Several advantages of transistors over resistors exist, namely i) the possibility to use very thin films (200-500 Å) since the gate potential increases the current, ii) the possible measurement of several parameters, more or less independent of each other and iii) the improvement of the reversibility of the adsorption processes when a reverse bias is applied. Such advantages do not exist with gate - modified FETs for which the adsorbed species act on the device current through a modification of the work function of the gate. Whereas water and volatile organic compounds act as traps and lead to a current decreasing, oxidizing species such as ozone and nitrogen dioxide act as true dopants. Sensitivity to humidity is weak compared to that of capacitive humidity sensors already commercialized.[60] Discrimination between different VOCs has been proved using a series of sensors. Nevertheless experimental processes have to be carried out in the absence of strong oxidizing species to allow the use of electronic nose based on molecular FETs. The high sensitivity of molecular FETs to ozone allowed to develop an ozone sensor working for atmospheric pollution control. The use of selective filters or devoted thermal methodologies developed for phthalocyanine - based resistors could be applied to molecular FETs to suppress the interference between NO₂ and O₃.

In any case, not only the choice of the molecular material and the type of transducer, but also the methodology must be adapted to each particular application.

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List of Acronyms

FET: Field-Effect Transistor,

MOSFET: Metal Oxide Semiconductor FET,

IGFET: Insulated Gate FET,

Gate-modified FET: a FET whose the gate modified by a molecular material is exposed to a gas,

Molecular FET: a FET in which the active material is a molecular semiconductor.