REVIEW

Organic semiconductors in potentiometric gas sensors

Jiri Janata · Mira Josowicz

Abstract Solid-state potentiometric sensors based on the chemical modulation of the work function of organic semiconductors are discussed. The theory of the chemical work function modulation is briefly reviewed. There are several sensor configurations, in which this transduction principle can be employed. First is the Kelvin probe, second is the chemically sensitive field-effect transistor in which the conventional metal gate of the silicon-based transistor has been replaced by an organic semiconductor. Chemical modulation of work function enters also into the operation of the third type of sensor discussed in this review, on "organic field-effect transistor". It is shown that in reality such sensors are "field-modulated chemiresistors", rather than potentiometric sensors.

Introduction

In this review, we focus on solid-state potentiometric gas sensors, mainly on chemically sensitive field-effect transistors (CHEMFETs), which are based on modulation of the work function (WF) of materials. An electrically neutral gas forms a charge transfer complex with the organic semiconductor (OS), resulting in the shift of its Fermi level. The

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oldest representative of a work function CHEMFET is the insulated gate field-effect transistor (IGFET) with a palladium gate metal as the sensing material for hydrogen [1]. A much broader utility of the chemical modulation of the work function can be achieved when OS is used as the chemically sensing gate. Two fundamentally different types of sensors using the work function modulation principle will be examined in detail in this review. They are CHEMFETs and field-modulated chemiresistors.

Chemical modulation of the work function as sensing principle

One condition for using organic semiconductor materials in chemical sensing is the necessity to change their electronic properties upon interaction with a secondary dopant neutral molecule. That change takes place when a charge transfer complex is formed between the molecule and the matrix, by either donating or accepting a fractional charge. While the classification of donor and acceptor gases is useful, these terms are relative when organic semiconductors are concerned, depending on the work function of these matrices since they can be either electron donors or electron acceptors.

The gas exposure introduces changes, in analogy to the inorganic semiconductor, in the occupancy level at the valence band edge and the conduction band edge, and leads to the variation of the energy at the Fermi level, E_F. A new equilibrium state in the semiconductor is established by this secondary doping that is governed by the solubility properties of gas, G, in the semiconductor,

$$G = G^\delta \pm \delta e \qquad (1)$$

where δ is the fractional charge of electron transferred from the gas molecule to the polymer. The gas–semiconductor

equilibrium is governed by the charge transfer equilibrium of this system and obeys Henry's law:

$$K_G = \frac{[e]^{2\delta}}{\alpha P_G} \qquad (2)$$

where K_G is the equilibrium constant, P_G is the partial pressure of the gas, and α is the solubility of the gas G in the solid phase. Using Fermi–Dirac statistics, an expression linking the position of the Fermi energy level to the partial pressure of donor–acceptor has been derived [2]:

$$E_F = E^* + \frac{kT}{2\delta} \ln P_G \qquad (3)$$

Here, E^* is the Fermi energy at the unit partial pressure of the gas, k is the Boltzmann constant, and T is the absolute temperature.

Equation 3 has the familiar form of the Nernst equation for ion transfer across the interface between two condensed phases. Thus, E_F varies logarithmically with the concentration of the interacting gas (secondary dopant). The fundamental difference lies in the fact that the dependence of the Fermi energy level E_F on the partial pressure of the dopant gas contains in the multiplier a fractional value of the charge δ, while in the Nernst equation the multiplier has an integral value of the charge z of the partitioning ion. The standard energy E^* for both electron donor and electron acceptor molecules differs in the value of the dopant ionization equilibrium constants. In this model, it has been assumed that the value of the equilibrium constant in Eq. 2 remains constant as E_F changes. Unfortunately, that assumption is not entirely valid as the charge transfer changes the value of the equilibrium constant (Eq. 2). The transfer of fractional charge δ can be viewed as redox equilibrium between the dopant and the matrix. The electron acceptance number, δ, is relative and is governed by the difference between the Mulliken electronegativity coefficient χ and E_F, respectively.

$$\delta = \xi(E_F - \chi) \qquad (4)$$

The coefficient ξ is the unspecified coupling factor between the gas molecule and the electron affinity of the interacting matrix. It has been shown experimentally by the Kelvin probe and field-effect transistor (FET) measurements that for small (<100 meV) changes of E_F the value of δ is proportional to the difference between the Fermi energy level and the Mulliken electronegativity. It can be a positive or negative number [3, 4].

Measurement of the work function modulation

The difference between Nernstian and non-Nernstian potentiometry has been discussed in several articles [5, 6].
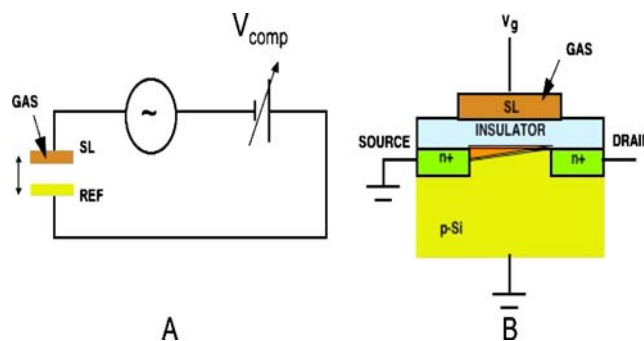

Fig. 1 Comparison of two types of potentiometric gas sensors based on work function modulation. **a** Vibrating capacitor (Kelvin probe) and **b** insulated gate field-effect transistor with selective layer (*SL*)

The underlying physics of the non-Nernstian sensing principle has its roots in the Kelvin probe measurement (Fig. 1a) [7]. It can be contrasted to the Poggendorff "null point" potentiometric method that underpins the Nernst-type potentiometric sensors, such as ion-selective electrodes (ISEs). The main difference is that only a fractional charge is partitioned between the molecules and the sensing matrix when a charge transfer complex is formed, whereas an integer value of charge, i.e., a complete charge separation, takes place between the solution and the selective membrane in conventional ISEs. The major practical implication is that ion-selective electrodes (Nernstian) require a stable reference potential for their operation. On the other hand, a separate reference electrode is not needed for work function CHEMFET (Fig. 1b) sensors relying on the formation of weak charge transfer complexes. That fact alone removes one of the outstanding problems of potentiometry and opens the door to miniaturization and large-scale integration of such sensors. How and where such operation is possible will be elaborated in this paper.

IGFETs are similar in their operation to the Kelvin probe [7]. Their threshold voltage V_T is directly related to the difference of the work function of silicon, ϕ_{Si}, and of the gate electronic conductor, ϕ_{OS}, in this case the organic semiconductor OS [8]:

$$V_T = \frac{\phi_{OS} - \phi_{Si}}{C_0} \qquad (5)$$

Their behavior is described by well-known equations for the IGFET operation in the linear region ($V_D < V_G - V_T$). The drain current I_D depends on gate voltage V_G and drain-to-source voltage V_D:

$$I_D = \frac{\mu_n C_0 W}{L} V_D \left(V_G - V_T - \frac{V_D}{2} \right) \qquad (6a)$$

In the saturation region ($V_D > V_G - V_T$):

$$I_D = \frac{\mu_n C_0 W}{2L} (V_G - V_T)^2 \qquad (6b)$$

where μ_n is the mobility of the minority carriers, C_0 is the capacitance of the gate, W is the width of the channel, and L is the length of the channel.

For sensing applications, the saturation regime is preferable because it yields the explicit relationship between the change of the Fermi energy level (i.e., work function) and the operating gate voltage, V_G. If the transistor is operated with constant current (i.e., in a feedback mode), Eq. 6b can be written as:

$$\sqrt{I_D} = \left(\frac{\mu_n C_0 W}{2L}\right)^{1/2} (V_G - V_T) \tag{7}$$

Thus, in the saturation region, the changes in the work function of the organic semiconductor can be directly related to the changes of the threshold voltage, V_T.

$$V_G = \left(\frac{2L I_D}{\mu_e C_0 W}\right)^{1/2} + V_T \tag{8}$$

The V_G response in a mixture of gases to the change of the partial pressure of the donor–acceptor gas can be formulated as

$$V_G = V_G^* + \frac{kT}{2\delta_G} \ln\left(P_G + \sum_i K_i P_i\right) \tag{9}$$

where V_G^* contains all constant terms related to the transistor and the selective layer, as well as the square root of the constant drain current. When the transistor is placed in the "zero gas", in which the partial pressure of the analyte gas G is zero ($P_G=0$), the output gate voltage V_G^0 is:

$$V_G^0 = V_G^* + \frac{kT}{2\delta_G} \ln \sum_i K_i P_i \tag{10}$$

It then represents the baseline value of the FET response. Equation 10 defines the selectivity coefficient, K_i, by analogy with the Eisenman–Nikolskij equation [9].

The step changes of the concentration of the analyte elicit corresponding step changes of V_G, which are obtained by subtracting Eq. 10 from Eq. 9:

$$V_G - V_G^0 = \Delta V_G = \frac{kT}{2\delta_G} \ln\left(\frac{P_G}{\sum_i K_i P_i} + 1\right) \tag{11}$$

Because the origin of the selectivity coefficient, K_i, depends on a priori unknown interaction of individual species with the matrix, it can be obtained only empirically. This is clearly the weak point of the charge transfer model, rendering it only semiquantitative. It places Eq. 11 in the same category of exactness as the Nikolskij–Eisenman equation, which is used for ion-selective electrodes [9].

The contribution of the interfering species to the overall response depends on the initial electron affinity (i.e., Fermi energy level) of the sensing layer and on the donacity of the zero gas. An example of potentiometric response of WF-CHEMFET is shown in Fig. 2. The sensing gate of the CHEMFET is composed of camphorsulfonic-acid-doped polyaniline dissolved in ionic liquid. The output gate voltage is changing reversibly as the concentration of ammonia in air changes. In this case, ammonia acts as the electron donor, thus lowering the work function of the p-type gate-selective layer (i.e., change in charge carrier concentration by the formation of a charge transfer complex). The value of the electron acceptance number, δ, determined from the slope of Eq. 11 was found to be 0.6 [10].

Organic semiconductors used in work function sensors

There are many organic semiconductors that have been used as functional materials in gas sensors. Here, we focus on the two largest groups, molecular organic semiconductors and conducting polymers. It is important to realize that the same material may behave differently in the different physical configurations of the sensors discussed in this review, i.e., in potentiometrically working CHEMFETs and in field-modulated chemiresistors (i.e. organic field-effect transistors, OFETs). An important factor is the processability of such materials that may be different in CHEMFETs and in chemiresistors, influencing differently their gas-sensing properties.
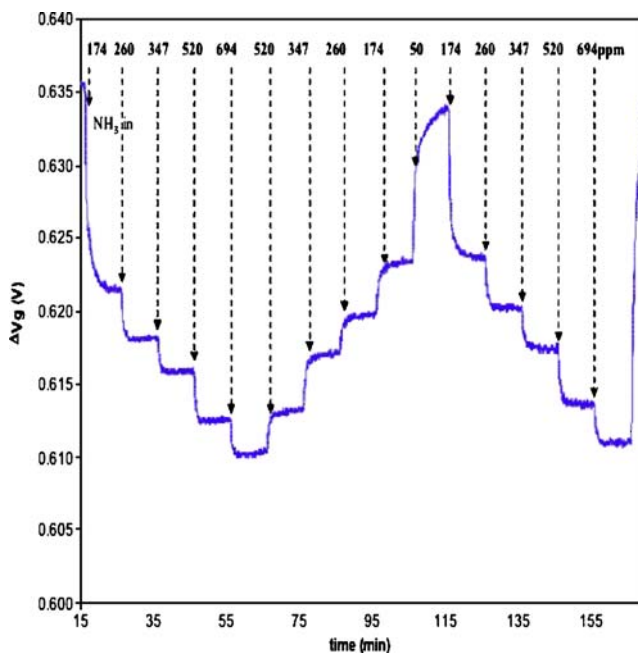

Fig. 2 CHEMFET response to stepwise exposure of ammonia gas in air with the polymer film gate processed from PANI·CSA containing 0.68 mol fraction of room temperature ionic liquid [10]

Porphyrins and phthalocyanines Porphyrins and phthalocyanines are pyrrole-based macrocycles. These p-type molecular organic semiconductors of structural rigid structure are useful for gas sensing at ambient and elevated temperatures up to ~200 °C. Almost all metals have been coordinated to the porphyrins [11] but not all of them were used as sensing layer. Their gas sensitivity depends on the oxidation state of the central metal atom and on the peripheral substituents that change the oxidation state of the metal [12]. A shorter aliphatic chain of porphyrin derivatives is advantageous in achieving higher sensitivity, good stability, and faster response [13]. There is also a possibility of weak interactions to the organic region of the phthalocyanine molecule for noncoordinating analytes, which may be governed by weak charge transfer interactions [14]. The interaction with oxidizing species such as ozone or NO_x leads to the formation of an oxidized metallophthalocyanine complex where the positive charge is delocalized over the phthalocyanine ring [15].

The advantage of using phthalocyanine films in FETs is that they can be used as thin films (~25 nm) [16]. That is important because with a thickness as high as 400 nm the crystallinity of the films increases and leads to a lower diffusion rate of absorbed molecules and a response time in the range of hours. The structure and the morphology of the molecular material have a drastic influence on the physicochemical properties of the films. The quality of the deposition is fundamental for an efficient and stable transduction of the sensing interactions. Each technique tends to produce films with peculiar features mainly due to the nature of the interaction with the transducer surface and to mutual interactions between the metalloporphyrin molecules. From the chemical sensor point of view, the location of binding sites is expected to influence the nature of the interaction of the gas molecules with the sensor. The less planar arrangement of porphyrins as compared to phthalocyanines reduces their stacking interaction and leads to conductivity that is lower than that of the phthalocyanine films. Because of that, their integration within the IGFET was tested using gate structure containing a thin, discontinuous layer of gold (60–70 Å) deposited over the silicon dioxide. It has been noted that the sensing properties depend on the porosity and thickness of the gold layer. Sensors with a continuous gold layer (>100 Å) did not give any response signal to methanol [17], in agreement with the WF modulation principle [9].

The sensitivity to NO_2 of copper phthalocyanine, CuPc, produced by thermal evaporation (150–200 Å) within the suspended gate (SG)-FET transducer in the presence of humidity was tested [18]. The response of the CuPc–SG-FET at 0% relative humidity to NO_2 in synthetic air shows a low detection limit (<50 ppb) and good sensitivity (20–70 mV per concentration decade). The presence of water

caused a significant baseline drift mainly due to the migration of the surface charge accidentally accumulated on the passivation layer covering the channel.

Work function studies of porphyrins using Kelvin probe technique utilizing solvent cast or Langmuir–Blodgett films showed that thin films of different porphyrins respond to saturated vapors of ethanol, triethylamine, and acetic acid [19].

Also, a new family of hybrid thin films based on hydroxygallium (HOGaPc) and cellulose (from a trimethyl-silyl derivative) prepared by spin coating allowed formation of films with different morphological configurations in a controlled way [20]. Kelvin probe measurements demonstrated a fast and sensitive change in the work function of this heterogenous material after cyclic exposures to ozone (O_3, 100 ppb) and nitrogen. Furthermore, it was observed that the presence of cellulose controls the arrangement of HOGaPc in the hybrid film that consequently also controls the relation between the structure and the properties of the film.

In summary, it can be said that the use of composites may open new possibilities for integration of metallo macrocycles as a polymer gate in CHEMFETs [21].

Conducting polymers Applications of conjugated polymers with alternating single and double carbon–carbon bonds in CHEMFETs have concentrated mostly on spin-coated or drop cast polymer films [22]. However, some of the conducting polymers are difficult to process due to their low solubility and high viscosity, which limit their use as gate materials. In order to overcome these difficulties, an electrochemical deposition process that combines the high processability of poly(phenylenesulfide-phenyleneamine) (PPSA) with the high conductivity of polyaniline has been developed [23]. In this process, a uniform 20-nm-thick layer of PPSA is spin-coated first, followed by the electrochemical growth of PANI up to several hundred nanometers thick over the PPSA film. The electrodeposition can be performed electrochemically by controlling the applied potential and the number of cycles.

Generally, the cast material on any sensor platform is described as a "hybrid film", implying that the polymer or the solvent is the major component of the system. However, as the casting solvent evaporates, the cast layer solidifies. That process is often the determining factor of the gas sensor performance since the porosity of the film is responsible for the rate of uptake–release of the gas analyte by the polymer matrix. Recently, we explored the preparation of a sensing layer "gel-like hybrid material" that is based on a mixture of polyaniline (PANI·CSA) and a room temperature ionic liquid [10]. The use of ionic liquids as a substitute for organic solvent is of great interest because of their low vapor pressure, nonvolatility, good solubility of

gases, and thermal stability. These gate-sensing materials show enhanced sensitivities, lower detection limit, and shorter response times than solid materials.

The availability of a variety of polymer precursors and different anionic dopants makes organic semiconductors very attractive sensing layers for sensors that can be operated at room temperature up to 90 °C. The sensitivity can be also changed using different substituents on the backbone [24]. The introduction of the side chains on the backbone of the polymer not only can increase the solubility of conducting polymers but also can adjust the space between molecules and introduce additional interactions with the analyte. It may enhance the response, shorten the response time, or promote sensitivity to other gases. For example, poly(N-methylpyrrole) yields a lower sensitivity to methanol than the unsubstituted poly(pyrrole) whereas poly(N-phenylpyrrole) does not show any sensitivity to methanol [25]. Utilizing anionic dopants with different chemical structures results in modification of the polymer properties, i.e., surface, morphology, solubility, and degree of water sorption [26].

Differences in performance were also observed when different solvents were used for the polymerization of the films. For example, a poly(phenylene) film when exposed to chloroform vapor behaves as an electron acceptor when it is electropolymerized in the presence of tosylate anion in acetonitrile, but as an electron donor when polymerized from dichloromethane [3]. Similar changes in work function sensitivities of polypyrrole (PPy) doped with various metallophthalocyanine tosylate anions (MePcTs, Me=Pb, Au, Fe, and Ni) were observed. PPy doped with NiPcTs, PbPcTs, Fe(II) PcTs, and AlPcTs yielded a negative change in the work function for NO_2, for tetrachloroethene (PER), and for dimethyl methylphosphonate (DMMP) whereas CuPcTs-, BF_4^--, and ClO_4^--doped PPy showed positive response for NO_2 and negative response for PER and DMMP [27].

Furthermore, the possibility of photochemical adjustment of the work function of a polyaniline gate conductor by irradiation dose control using triphenylsulfonium triflate salt as the photoacid generator has been demonstrated [28]. In that case, the doping level of PANI varies linearly, dependent on the irradiation dose. The presence of a plasticizer in the polymer matrix enhances the efficiency of the photoacid liberation and the rate of proton transport.

One of the most important methods to develop sensing materials for work function sensors can be accomplished by incorporating specific binding sites as a second component. That can be realized by a competitive doping carried out in solution which contains a predetermined mixture of anions. Cabala et al. [29] show that this type of doping is affecting not only the work function of the organic semiconductor but also the sensitivity to gases and vapors. The NO_x

sensitivity of PP/CuPcTS + ClO_4 (0.50) is *approximately* 70 mV (parts per million per decade)$^{-1}$, and PP/CuPcTS + ClO_4 (0.09) has a sensitivity of 87 mV (parts per million per decade)$^{-1}$. The sensitivity of these films has been found to be comparable with that of pure metal phthalocyanine films and higher than those of conducting polymer films.

The incorporation of the binding sites into conducting polymer such as nonconducting polymer, carbon fibers, metal clusters, and metal oxides is sometimes an easy way not only to avoid the complicated chemical syntheses but also to actually improve their sensing properties [21].

The feasibility of using organic–inorganic hybrid materials for gas sensing has been demonstrated by the use of poly(cyclophosphazene-benzoquinone) film doped with iodine for sensing of tributyl phosphate in the concentration range of 1.1 ppb up to 8.8 ppm [4]. The use of polypyrrole–MoO_3-layered nanohybrid material that consists of alternately stacked, negatively charged MoO_3 and positively charged PPy layers exhibits higher sensitivities to polar analytes such as formaldehyde and acetaldehyde, whereas it shows almost no response to toluene and benzene [30]. The direction of the charge transfer is determined by the relative magnitude of the electronegativity of the vapor and the work function of the polymer. The partial charge transfer affects the degree of the interlayer charge transfer from PPy to MoO_3.

The possibility to tune the work function magnitude of composite materials of polyaniline with metal clusters of different sizes and amounts according to the changes in the composition of the materials is feasible [31]. The amount of electronic charge transferred between gold particles and polyaniline depends not only on the electron affinity of the two materials but also on the size of the gold particles [32].

A method of selective doping of the polyaniline gate of a CHEMFET within an array of CHEMFETs with palladium clusters by an electroless relaxation process has been demonstrated [33]. The high selectivity of the doping process was proved by exposing those devices to hydrogen and ammonia mixtures [34]. The sensitivity of PANI to ammonia was in the range of ~30 mV per decade and showed negligible cross-sensitivity to hydrogen and humidity. The Pd-doped PANI film was sensitive to ammonia and hydrogen. Depending on the background humidity, the sensitivity of the hydrogen sensor was in the range of 150 mV per decade. No measurable responses of these layers to 1% nitrous oxide in air were detected.

Work function sensors

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 [9]. It is utilized in equilibrium potentiometric sensors, such as the macro-

scopic Kelvin probe and in its solid-state miniature counterpart, the CHEMFET. However, because WF is such a fundamental property of electronic materials, it enters also into operation of other types of chemical sensors, namely Schottky barrier junctions [35] and various forms of chemiresistors. In these sensors, the response is obtained while current is passing through the sensing material. The change of the bulk component of WF is always accompanied by the change of the concentration of the charge carriers. While the change in conductivity is irrelevant for CHEMFETs, it must be taken into account when the same material is used in a chemiresistor.

Unfortunately, the fundamental difference between "zero" and "finite" current operation has been ignored in "OFET sensors", in which the sensitive organic semiconductor is the active part (i.e., current passing part) of the device. OFETs exhibiting the chemically sensitive organic semiconductor as the current passing part are by all accounts chemiresistors and do not belong to the category of equilibrium, "zero current" potentiometric sensors. They are included in this review in order to highlight the fundamental difference between these two types of gas sensors. The distinguishing feature between a conventional chemiresistor and an OFET sensor is the presence of the gate electrode. Thus, CHEMFET and OFET are three-terminal devices but operate in a fundamentally different way [36]. The difference is shown in Fig. 3. The depicted transistor can be operated in two modes, which are distinguished by the current path. In the IGFET mode (Fig. 3a), the current passes through silicon substrate and the metal electrode(s) on top of the insulator serve only as

Fig. 3 Two types of gas sensors with OS selective layer: **a** traditional CHEMFET configuration and **b** OFET configuration

the gate contact(s) to the OS. There is no current passing through those gate electrodes. In that case, the electronically conducting gate replaces the conventional metal gate of the IGFET and the relationships between the drain-to-source current and the applied gate voltage (V_G) and the drain (V_D) voltage are described by the well-known transistor equations (Eqs. 6 and 6b). The sensing, analytical signal is obtained from the modulation of the threshold voltage, which depends on the difference of WF of the organic semiconductor and silicon (Eq. 11). The latter material serves as the stable reference point in such experiment. It is so because of the immunity of the Si–SiO_2–Si_3N_4 system to changes in the chemical environment. Thus, the work function of silicon and its stable Fermi level is the stable "reference potential" for operation of such potentiometric sensors. There is no ambiguity about the origin of the response, and the functional relationship between the partial pressure of the gas and the sensor output is clearly defined.

In the OFET configuration (Fig. 3b), the current is injected from the metal electrodes and passes through the organic semiconductor. In its path, it encounters at least three resistances: two at the contacts and one in the OS. The chemical modulation of work function affects all these resistances and contributes to the overall response of the device. The complications are compounded when a voltage is added to the opposite side of the insulator. In Fig. 3b, this electrode is called OFET "gate" electrode in analogy with the IGFET. Its purpose is again to create a perpendicular electric field that would modulate the current passing through the resistive structure on the other side of the insulator. In analogy to the chemical modulation, this electric field also affects all three resistances and does so in a highly nonlinear fashion. It is apparently this nonlinearity of the current–voltage relationship that gave rise to "OFET". Most such devices are made in planar configuration in which both the electrodes and the OS–dielectric interfaces are exposed to the same electric field. The "drain" and "source" electrodes are deposited either on the dielectric or on top of the OS, thus defining the "bottom geometry OFET" and the "top geometry OFET". It is a transistor only inasmuch "transistor" means "voltage-dependent resistor" [37]. A similar comparison of IGFET–OFET operation has been made by Bouvet [15], however, with significantly different conclusions than those presented here.

The first OFETs have appeared in early 1970s [38, 39]. The field of OFETs literally exploded in mid-1980s when the first claims of flexible, cheap, and printable "polymer electronics" have been made [40–42]. The subject has been first reviewed by Horowitz [43] and hundreds of OFET-related papers have been published since.

It has been recognized early on that the assumed analogy between IGFET and OFET may not fully apply and that the
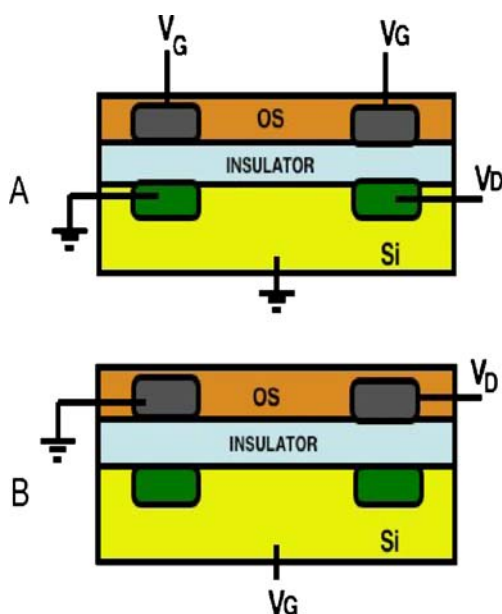
difference between the charge transport in the two types of devices and the effect of the perpendicular gate electric field are much more complex. Contact resistances of various origins have been implicated in the overall response [44, 45]. It has been shown by four-point probe measurements and by Kelvin probe microscopy that these contact resistances can be also modulated by the gate electric field [46–48]. It has been possible to dissect the individual field-modulated contributions and to show that the effect of gate voltage on the contact resistance of the drain electrode greatly exceeds the modulation of the interfacial conductivity of the organic semiconductor itself [48]. When that happens, the device functions as a field-modulated junction.

It is important to realize that even moderate applied drain voltages, e.g., $V_D > 3$ V, exceed the height of the Schottky barrier at the OS–metal junction. The overall voltage-dependent contact resistance is then due to the formation of the space charge created by depletion of the charge carriers at the vicinity of the drain electrode. This effect is analogous to formation of diffusion depletion layer at the electrode during an electrochemical experiment performed in the absence of supporting electrolyte. In that case, the depletion of the electroactive species (carriers) at the vicinity of the working electrode is tantamount to creating a virtual insulator and in formation of a corresponding space charge and a corresponding lateral electric field. The perpendicular field from the gate is then vectorially combined with the drain field. The resulting space charge and the resistance then depend on the microscopic details of the geometry of the metal contact, as well as on the intrinsic conductivity of the undoped OS. The variability of the geometry of the metal contact is one cause of great variability of the OFET results reported from different laboratories.

The properties of OFETs are affected by processes, which are substantially different from those governing the operation of inorganic semiconductor-based IGFETs, in which the formation and conductivity of the channel depends on the genuine semiconductor field-effect at the Si–SiO$_2$ interface. It can be stated unequivocally that the use of IGFET equations (Eq. 6) to describe the OFET operation is not appropriate [48]. It also means that OFETs cannot replace silicon IGFETs as analog electronic component; however, that fact does not negate their possible use as low-cost ON–OFF switches.

Organic field-effect transistors as field-modulated chemiresistors

It has been known that OFET operation is affected by the chemical ambient, namely by the presence of donor–acceptor gases, such as oxygen and NO$_2$, and by humidity.

This "problem" has been conveniently turned into an "advantage" by promoting OFET as a new type of "chemical sensor" for gases and vapors [49–55]. The subject of "OFET sensors" has been realistically reviewed [56]. In that review, the authors acknowledge some commonality of OFET with "chemiresistors" and recognize the fact that OFETs lack explicit, quantitative relationship between the concentration of the detected species and the device output. The results of OFET sensing are invariably given as "change of current" or "relative change of current". However, very little can be said about the origin of the current modulation.

The problem with the use of OFETs as chemical sensors have their origin in the physics of OFETs as outlined above. Similar to the effect of the gate electric field in OFET structures, chemical interactions affect all resistances in the current path [57]. That uncertainty can be again attributed to the different modes of operation of the two "field-effect structures" (Fig. 3). While the origin of response in CHEMFET can be unambiguously attributed to the modulation of work function of the organic semiconductor, it cannot be done so for the response of field-modulated chemiresistor. Introduction of the donor–acceptor gas can result in the net change of the carriers in the OS, leading to change of WF *and* the conductivity of the layer. The height of the Schottky barrier at the contact can be modulated as the result of modulation of the WF difference between the contact metal and OS [35]. If the guest molecule is electroactive, it can change the charge transfer resistance at the drain contact, by acting as redox species at that junction. Any and/or all of these mechanisms can operate simultaneously in relatively unknown proportions, making rational assignment of the origin of the sensor response difficult, if not impossible. Moreover, sustained passage of current through the OS can induce faradaic electrochemical changes at the vicinity of the electrodes. Such electrolytic damage is most likely the cause of the observed long-term instability reported for most field-modulated chemiresistors [58, 59]. The second, more likely reason for the instability is that the OS must be undoped in order to operate the OFET in accumulation mode. The p-conducting organic semiconductors are, in contrast to n-conducting OS, not stable in the ambient when completely undoped. Oxygen and water vapor act as dopants of the first choice. Doping, i.e., any interaction with gas–vapor molecules, suppresses the influence of the gate electric field modulation. In OS, the doping process can only be completely reversed by heating or by treatment in vacuum.

Drain-to-source and gate voltages in OFETs are typically in tens of volts. In many cases, such high voltages lead to electrical breakdown and appearance of leakage current through the gate dielectric. Such current then becomes an unknown component of the "drain current", further negat-

ing any use of conventional IGFET equations. Unfortunately, the gate leakage current measurements are rarely done, and even less frequently fully reported. However, they can be seen in some reported I_D–V_D curves. If there is a "nonzero" drain current, at $V_D = 0$, such current is a clear indication of the leakage, at nonzero applied V_G [60–62].

Addition of the gate electric field to the already complex operation of a chemiresistor does not make the situation simpler. Particularly troubling are the reports of various "field-enhanced" or "field-induced" chemical selectivities [49, 50, 63, 64]. If one or another gas molecule acts preferentially on one resistance in the current path, it may appear as "enhancement of selectivity". This again underscores the major difference in the applicability of field-modulated chemiresistors as chemical sensors. Field-modulated chemiresistors certainly do respond to changes of chemical environment, under well-controlled experimental conditions, but the meaning and value of such response is difficult to interpret. There is no explicit relationship between sensor output and the partial pressure of the analyte. Not surprisingly, these devices have been also promoted as "electronic noses" [63, 65]. The recently reported, rather sensational "field-enhanced chiral sensitivity" in such device belongs to that category. It cannot be rationalized by any known physics [66]

Conclusions

The differences between CHEMFET- and OFET-based sensors discussed in this paper go far beyond semantics. They are both three-terminal devices but are based on very different transduction principles. The response in the CHEMFET is due solely to the change of the work function of the sensing gate material. This change is then transduced to an electrical signal through traditional IGFET operational principles. It is a true equilibrium potentiometric sensor that does not require an external reference electrode. On the other hand, the transduction mechanism of the OFET is less clear-cut. Its functional characteristics are dominated by several poorly defined processes that depend mostly on the conditions at the metal–organic semiconductor interface of the contacts. The field modulation of the channel conductance at the OS–insulator interface apparently plays only a relatively minor role. The complexity and undefined nature of the overall transduction mechanism in OFETs are too high a price to pay for this questionable novelty. The role of the electric field in chemical selectivity of such sensors, if any, can be only indirect. In spite of their suggestive name, chemical sensors based on "organic field-effect transistors" are not equilibrium potentiometric sensors. They belong to the category of chemiresistors.

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