POTENTIOMETRY IN GAS PHASE

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Dedicated to the memory of Professor Jaroslav Heyrovský on the ocassion of the 50th anniversary of the Nobel Prize for polarography.

In order to yield analytically useful information every potentiometric measurement requires stable and reproducible reference potential. That requirement has to be satisfied for potentiometry performed in liquid or gas phase alike, although two fundamentally different mechanisms lead to formation of the measurable cell voltage. It is shown that the Fermi level of silicon used in insulated gate field-effect transistors (IGFET) provides an exceptionally stable and robust reference potential. A semi-quantitative dependence of IGFET output on partial pressure of the analyte gas is presented.

Keywords: Reference potential; Work function; Charge-transfer potentiometry; Kelvin probe; Field-effect transistor; Schottky junction; Gas-phase electrochemistry.

At first sight the notion of gas phase potentiometry appears to be self-contradictory. Formation of interfacial potential difference requires partitioning of charges between the conducting phases that share at least one common charge carrier. Here the molecule of interest is electrically neutral gas, whose partitioning cannot lead to formation of interfacial potential difference. Clearly, the processes involved in gas phase potentiometry must be different from those leading to the formation of the equilibrium interfacial potential as described by the Nernst equation. It is indeed so. Although the final outcome of gas potentiometry is again a functional relationship between partial pressure of gas and a cell voltage, the mechanisms of its formation and its measurement are fundamentally different. The underlying step in gas-phase potentiometry is the formation of charge transfer complex between electronically conducting phase (metal or semiconductor) and a molecule that can exchange partial charge with such material.

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Let us assume that the gaseous molecule G forms a charge transfer complex with the semiconductor matrix S and exchanges a fractional charge δ

$$G + S = G^{\delta^{\pm}} * S^{\delta^{\mp}} . \qquad (1)$$

In other words, G acts as a dopant that changes the density of mobile charges in the solid phase. Sharing of electron between the donor/acceptor molecule and the solid phase changes its Fermi level, and thus the bulk component of its work function, WF. The change of WF due to such doping can be used as the transduction principle in gas sensors, which relate the potentiometric signal to the partial pressure of the donor/acceptor gas[1]. Examples of atmospheric measurement of change of WF are discussed in this paper. The experimental methods that require vacuum, such as photoelectron spectroscopy, are not included in this discussion, because they are not amenable to implementation for chemical sensing.

Kelvin Probe

The first and the oldest measurement of a work function change that can be realized under atmospheric pressure is the Kelvin probe[2–5]. In that experiment the electronic material to be doped forms one plate of a capacitor and the other plate is the inert "reference" material, typically a noble metal (Fig. 1A). The value of the capacitance is periodically changed by mechanically vibrating one plate, hence the name "vibrating capacitor". If the work functions of the two plates are different, the difference of the outer (Volta) potentials creates a fluctuating electric field in the gap of the vibrating capacitor and periodically varying current is generated in the external circuit. By placing a DC voltage source in series with the capacitor it is possible to null out the electric field and consequently null out the AC current. The required change of the compensating voltage ΔE is then equal to the difference of the work functions of the sample plate (ϕ_S) and of the reference plate (ϕ_R)

$$e\Delta E = \Delta\varphi = \phi_S - \phi_R . \qquad (2)$$

Work function of material is defined as energy needed to remove one electron from the Fermi level and place it just outside the electrostatic field of the material. Therefore, it is expressed as energy per electron with units eV. It is the sum of the chemical potential of electron μ^e and of the energy of the electric field of the dipoles χ present at its surface. Therefore,

$$\Delta E = (\mu_S^e - \mu_R^e) + e(\chi_S - \chi_R). \quad (3)$$

The vibrating capacitor technique is sometimes incorrectly called "contact potential measurement" or "surface potential measurement". That terminology apparently originates from the fact that there are two contributions to the nulling voltage, ΔE. The first is the contact potential V_C. It forms at the interface between the sample and the reference materials of the capacitor as the result of the difference of the chemical potentials of electron in the two materials (Eq. (3)). As any single potential, it is not experimentally accessible. On the other hand the label "surface potential measurement" has its origin in the fact that the electric field originating from the immobile surface charges on an insulating substrate can be detected by the vibrating capacitor (e.g. by an electrostatic atomic force microscope). However, since there is no defined Fermi level in an insulator, such measurement does not yield the value of work function of the insulator. It is important to realize that a dipole moment exists at any surface of a conductor, even in the absence of the adsorbate, because such surface represents a physical discontinuity. Because of the presence of ubiquitous and largely unknown surface dipole component the reproducible and stable reference

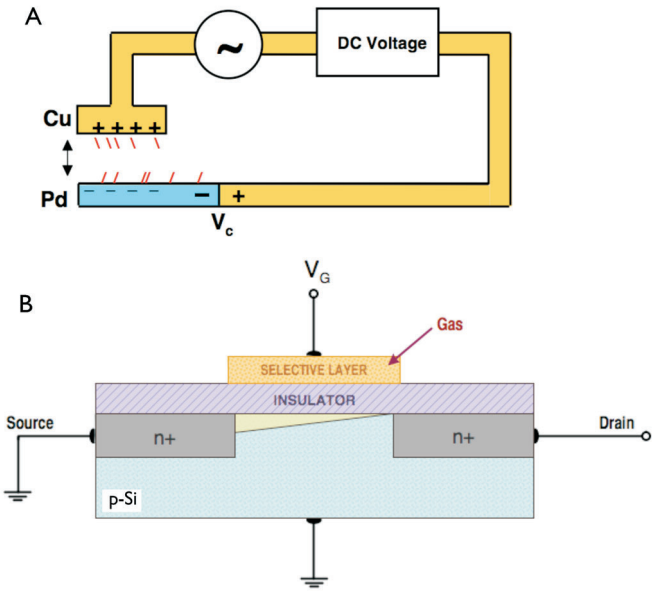

FIG. 1
Schematic of A Kelvin probe and B insulated gate field-effect transistor (IGFET)

potential at the interface involving gas or vacuum cannot be experimentally realized. That is the major impediment for the use of Kelvin probe as a chemical sensor[5].

Field-Effect Transistor

An insulated gate field-effect transistor (IGFET) with interactive gate conductor as the sensing material is a miniature equivalent of the Kelvin probe (Fig. 1B). It is a 3-terminal device in which the magnitude of the drain current I_D passing through the channel formed between the drain and source terminals, depends on the on the applied drain voltage V_D and on the density of mobile charge in the channel. That charge is modulated by the electric field in the gate dielectric. It is possible to select the applied gate voltage V_G in such a way that there is no electric field in the gate dielectric and no charge at the two plates of the gate capacitor. Under such conditions no bending of the energy levels occurs at the Si/SiO_2 interface and the applied gate voltage is called flat-band voltage $(V_G)_{FB}$. This would correspond to the zero field condition in the Kelvin probe. By comparison, there is no change of the gate geometry in the IGFET. Thus, under these conditions the flat-band gate voltage V_{FB} is related to the difference of work functions of silicon ϕ_{Si} and work function of the gate conductor (ϕ_{OS}). The earliest example of this type of potentiometric sensor was the $Pd/SiO_2/Si$ field-effect transistor, which selectively and reversibly responds to hydrogen and hydrogen-liberating species[9]. A much broader applicability of charge transfer modulation has been achieved by replacing the Pd gate conductor with organic semiconductors (OS) that can "dissolve", i.e. form a charge transfer complex, a wide variety of gases and vapors[4]. Thus, a new class of potentiometric gas sensors known as "work-function chemically sensitive IGFETs" has been born.

$$(V_G)_{FB} = (\phi_{OS} - \phi_{Si}) + \frac{Q_{SS} + Q_{ox} + Q_B}{C_0}. \qquad (4)$$

The charges Q_{ss}, Q_{ox} and Q_B correspond to surface states and trapped charges in the gate dielectric and the charges in the channel, respectively. The latter includes both mobile charges and fixed ionized dopant atoms. They depend on fabrication and are specific to the particular device[6]. The nominal capacitance of the gate is C_0.

It is important to note that even at the flat-band conditions the drain current may have a non-zero value, due to mobile channel charges.

There are two limiting regimes of operation of a FET: linear and saturation regime. When operated in the saturation regime i.e. $V_D > (V_G - V_T)$, the drain current equation relates V_G to I_D

$$I_D = \frac{\mu_n C_0 W}{2L}(V_G - V_T)^2 . \quad (5)$$

The channel width W, the channel length L and the mobility of minority carrier μ_n (electron for *n*-channel devices) are again device specific. The threshold voltage V_T is the applied gate voltage at which the drain current is "turned on". It is an important operational parameter for the transistor. Equation (*5*) can be rearranged for the "constant current operation"

$$V_G = \left(\frac{2LI_D}{\mu_e C_0 W}\right)^{1/2} + V_T . \quad (6)$$

The threshold voltage is again dependent on the difference of work functions of the organic semiconductor and doped silicon and is therefore modulated by interaction of the OS with the donor/acceptor gas according to Eq. (*1*). At constant drain current the density of mobile charges in the channel are also constant and the only variable term in Eq. (*4*) is the work function of OS.

Applying the Fermi–Dirac doping equation[7] for crystalline semiconductors to gas–organic semiconductor interaction allows us to estimate the effect of charge transfer doping on the work function of OS [1].

$$\phi_{OS} = \phi_{D(A)} + \frac{kT}{2\delta} \ln P_G \quad (7)$$

where P_G is the partial pressure of the donor/acceptor gas and $\phi_{D(A)}$ is the intrinsic value of the work function of the OS (donor or acceptor). Combining Eqs (*4*), (*6*) and (*7*) and lumping all constant, device related terms into one "const." yields[8]

$$V_G = \text{const.} + \frac{kT}{2\delta} \ln\left(P_G + \sum_i K_i P_i\right) \quad (8)$$

in which term $\sum_i K_i P_i$ represents the doping effect of components of the background gas other than the donor/acceptor gas of interest G. Constant

K_i has the meaning of selectivity coefficient in the same sense as the selectivity coefficient in the Eisenman–Nikolskii equation for ion selective electrodes[8].

In the absence of the active gas, i.e. in the "zero gas" (background) the baseline value of the gate voltage is V_G^0

$$V_G^0 = \text{const.} + \frac{kT}{2\delta} \ln \sum_i K_i P_i \ . \qquad (9)$$

It is assumed that the "const." term in Eqs (*8*) and (*9*) and the selected value of the constant drain current I_D remain constant throughout the measurement. Subtraction of the two equations yields the functional relationship between the change of the gate voltage ΔV_G and the change of the donor/acceptor gas as it is stepped from zero to the finite partial pressure P_G. It is equal to the change of the work function of organic semiconductor

$$V_G - V_G^0 = \Delta V_G = \frac{kT}{2\delta} \ln \left(\frac{P_G}{\sum_i K_i P_i} + 1 \right). \qquad (10)$$

The experimental observable, ΔV_G, has the same meaning and function as the compensating voltage ΔE has in the Kelvin probe experiment. In either experiment no current passes through the sensing layer, which means that they are performed at equilibrium conditions and both Kelvin probe and work function IGFET belong to "zero current potentiometric sensors".

The experimental validity of the Eq. (*10*) hinges on the assumption of constant work function of silicon (Eq. (*4*)). Such assumption is valid for broad range of operating temperatures and pressures, due to excellent passivation characteristics of the silicon dioxide (and silicon nitride) which are used to protect the silicon. Since all the "device specific parameters" are also constant, the only experimentally vulnerable place is the interface of the OS and the dielectric. It is so because the electric field emanating from adsorbed dipoles contributes to the overall work function value of the OS. It is important to note that adsorption of any species at the outer surface of the active layer does not have any effect. In other words it is only the interfaces that form the gate capacitor that are critical[8].

The semblance of Eq. (*7*) to the Nernst equation, or Eq. (*8*) to the Nikolskij–Eisenman equation for ion selective electrodes, is more than fortuitous. The conceptual similarity can be seen if the Fermi–Dirac equation, describing the dependence of the Fermi energy in a doped semiconductor (i.e. its chemical

potential) on the dopant concentrations converted to its logarithmic form and rearranged.

$$N_D^+ = N\left[1 - \frac{1}{1 + \frac{1}{g_D}\exp\frac{\phi_D - \phi_F}{kT}}\right] \qquad (11)$$

In that case N represents the sum of the primary neutral electron dopant atoms N_D and dissociated atoms N_D^+

$$\phi_F = \phi_D + kT \ln \frac{N_D}{g_D N_D^+} . \qquad (12)$$

The value of the degeneracy factor g_D is generally not known for organic semiconductors. The main difference between the Nernst equation and the Eq. (*8*) or Eq. (*10*) is that the integer value of charge (i.e., whole charge) has been replaced by a fractional charge δ. Equation (*8*) or (*10*) can be used to estimate the value of the fractional charge involved in the secondary doping process from the plot of ΔV_G vs log P_G (Fig. 2).

An example of the response of WF-IGFET with polyaniline (PANI), which is a p-type semiconductor, to ammonia[10] (electron donor) is shown in Fig. 2. The response is stable and reversible. The fractional charge δ exchanged in the reaction

$$\text{PANI} + \text{NH}_3 = (\text{PANI})^{\delta-} * (\text{NH}_3)^{\delta+} \qquad (13)$$

has been evaluated from both the ascending and descending portions of the response curve for sensing layers containing different ratio of PANI and ionic liquid (Table I).

Schottky Diodes

There is another class of sensors, in which the analytical information is dependent on the contact potential difference at the interface of an OS and the contact metal. When an OS forms a contact with a metal, Schottky barrier may be formed, if $\phi_{OS} > \phi_M$ for p-type and $\phi_{OS} < \phi_M$ for *n*-type OS. Such contact can give rise to a non-linear, chemically modulated resistance, by modulation of the ϕ_{OS}. The information is obtained by passing current through the junction. Electrodes made of noble metals, of different contact area are used in construction of Schottky diodes (Fig. 3). Although Schottky

barriers are formed at both electrodes it is the smaller of the two electrodes where the measurable Schottky effect is localized, due to the high current density at that contact. The current passing through the Schottky diode is a function of the applied voltage (Fig. 4) and concentration of the analyte. Such effect has been used for chemical sensing[11,12]. In order to avoid the non-linearity, the measurement is usually performed by applying constant current through the junction and evaluating the shift of the bias voltage in the junction-controlled region (usually < 0.5 V). If the contact is oxide-free the junction current density for $V >> 3kT/e$ is given by

TABLE I
Evaluation of fractional charge from WF-IGFET response to ammonia[a]

Sensing layer Mole fraction of IL/PANI	Step up δ	Step down δ
0.0/1.0	0.55	0.77
0.51/0.49	0.60	0.50
0.68/0.32	0.61	0.59
0.76/0.24	0.49	0.42

[a] Evaluated from response[10] shown in Fig. 2.

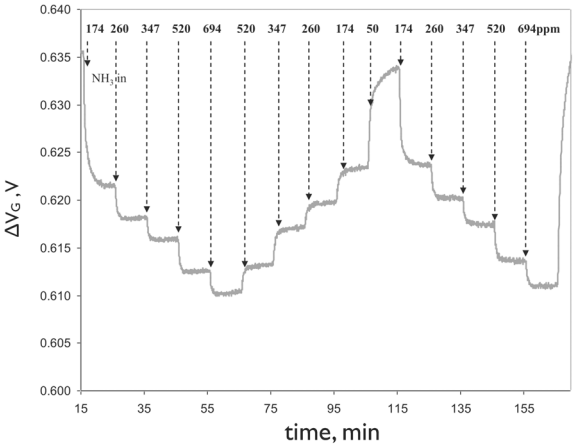

FIG. 2
Response of WF-IGFET with chemically sensitive gate to step changes of partial pressure of ammonia in air[10]. The sensing layer is organic gel containing 0.68 mol fraction of 1-butyl 3-methylimidazolium bis(trifluoromethane)sulfonimide and 0.32 mole fraction of PANI doped with camphorsulfonic acid in 1:2 ratio of CSA:aniline

$$J = A_R T^2 \exp\left[\frac{-(\phi_B - eV)}{nkT}\right] \quad (14)$$

where n is the ideality factor, k is the Boltzmann constant, V is the bias voltage, T is the temperature, e is the elementary charge, A_R is the Richardson constant for thermionic emission of electrons, and $\phi_B = WF_{OS} - WF_M$ is the effective barrier height. The saturation current density J_0 (extrapolated to $V = 0$) is

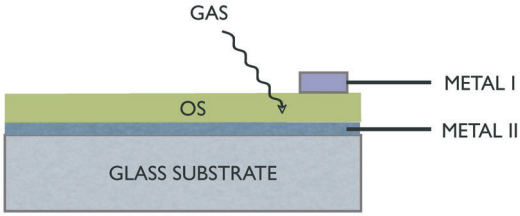

FIG. 3
Schematic of Schottky barrier junction diode. In ref.[11], the metal I is Au dot (1 mm diameter) and metal II is Pt sputtered on glass. The sensing OS is polypyrrole-Cu phthalocyanine-tetrasulfonate

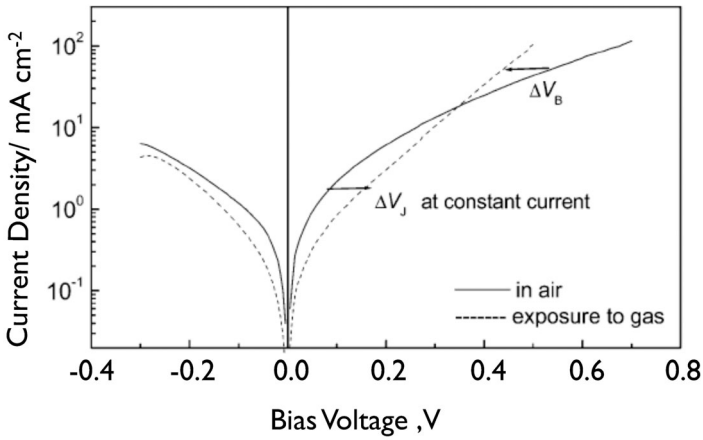

FIG. 4
Logarithmic current density–voltage bias curve of Schottky barrier junction diode, showing the junction-controlled (V_J) and bulk-controlled (V_B) operating regimes (reprinted with permission from ref.[12])

$$J_0 = A_R T^2 \exp\left[\frac{-\phi_B}{kT}\right]. \qquad (15)$$

Because of the simplicity of their construction, the Schottky barrier junctions offer an attractive possibility of measurement of chemical modulation of WF_{OS}. However, there are complications inherent to the non-zero current operation of these devices. Passing current through interfaces between dissimilar conductors leads to a charge injection of electrons or holes (majority carriers) at the interface. It is governed by the kinetic factors affecting the charge transfer, e.g. thermionic emission and tunneling, as well as by the relevant carrier transport mechanisms. The OS used in Schottky diodes are highly doped and conducting, which ensures that the bulk resistance is minimal and the mass transport of the carriers across the depletion layer is Fickian. This is in stark contrast with the undoped, low conductivity OS used in organic field-effect transistors (OFET), in which the depletion layer formed at the drain contact is dominated by the electric field-dependent migration. In either case the formation of a mass transport limited depletion layer represents a depletion resistance, which contributes to the voltage drop in the overall signal. The effect of the depletion resistance contribution depends not only on the current density at the junction, but also on the geometry of the contact. It is an inevitable consequence of passage of current and it represents a fundamental difference between utility of the "zero" and the "finite" current sensors. In non-zero current sensors the final response depends not only on the rate of charge transfer at the Schottky barrier junction, but also on the rate of mass transport of the charge carriers through the depletion layer. Another complicating factor can be the bulk resistance of the OS, which may contribute to the overall resistance value of the device. In order to ensure that the current depends only on the Schottky barrier (Eqs (*14*)–(*15*)) the diode is operated at low bias voltage where the current is junction controlled (Fig. 4) and can be described by the Mott–Schottky equation (Eq. (*14*)). Only in that case the modulation of WF_{OS} can be obtained and the WF_M of the contact metal can be used as the necessary reference.

Other contacts, called heterojunction contacts, are formed between two dissimilar semiconductors, e.g., OS and an inorganic semiconductor such as silicon. The same chemical modulation of the junction barrier could apply there, however, a typical problem then arises from the presence of oxide layers which form on surfaces of low WF materials. The protection of the junction from the atmospheric effects is possible, but not when the junc-

tion is used for chemical sensing. In either type of the junction the OS can be doped with different anions, which affects their response time and sensitivity[11,13].

CONCLUSIONS

Both the Kelvin probe and the WF-IGFET have one important requirement in common[8]: *The interactive (selective) layer must form one plate of the capacitor*. That capacitor can be the gas-filled gap of the vibrating capacitor or the gate insulator of the IGFET. The other plate of the capacitor is silicon, which is shielded from chemical effects of the ambient atmosphere by the exceptionally high encapsulation properties of silicon dioxide and silicon nitride passivation layers. Therefore the $Si_3N_4/SiO_2/Si$ system fulfills all requirements of a well-behaved, reference plate for the measurement of the Volta potentials and work function. In spite of its high quality such reference potential cannot be used to establish the absolute scale of work functions of various materials which could be deposited on the gate insulator. The reason for this limitation is the fact that each transistor has its own, inherent specific set of parameters that are due to the fabrication process. They have been discussed in the context of Eqs (*5*) and (*6*). Once a device is fabricated these specific parameters are constant. Therefore, for measurements of relative changes of work function, namely during the secondary doping process, silicon in the FET configuration offers exceptionally high quality reference potential. The most important practical outcome is that no additional macroscopic reference electrode is needed.

Both Kelvin probe and WF-IGFET are equilibrium, "zero-current" potentiometric sensors. It means that no current passes through the organic semiconductor and their response depends only on the modulation of its work function. On the other hand, Schottky barrier junctions are non-equilibrium, finite-current potentiometric sensors. They yield useful empirical responses, in which the work function modulation is implicit. However, it can be contaminated by other factors, such as conductivity of the materials, parasitic conductivities, and the device geometry. It is interesting to note that the so called "non-equilibrium ion sensors"[14], which again operate under non-zero current conditions, suffer from the similar limitations. Although they yield a "response" curves, no equilibrium thermodynamic parameters can be extracted from such data.

Constructive discussions of Schottky diodes with K. Potje-Kamloth are greatly appreciated.

REFERENCES

1. Janata J.: *Anal. Chem.* **1991**, *63*, 2546.
2. Lord Kelvin: *Philos. Mag.* **1898**, *46*, 82.
3. Janata J., Josowicz M.: *Anal. Chem.* **1997**, *69*, 293A.
4. Janata J., Josowicz M.: *Acc. Chem. Res.* **1998**, *31*, 241.
5. Phillips G.: *J. Sci. Instrum.* **1951**, *28*, 342.
6. Sze S. M.: *Physics of Semiconductor Devices*. Wiley, New York 1982.
7. Janata J., Josowicz M.: *J. Solid State Electrochem.* **2009**, *13*, 41.
8. Janata J.: *Principles of Chemical Sensors*. Springer, New York 2009.
9. Lundstrom I., Shivaraman S., Svensson C., Lundkvist L.: *Appl. Phys. Lett.* **1975**, *26*, 55.
10. Saheb A., Josowicz M., Janata J.: *Anal. Chem.* **2008**, *80*, 4214.
11. Nguyen V. C., Potje-Kamloth K.: *Thin Solid Films* **1999**, *338*, 142.
12. Potje-Kamloth K.: *Chem. Rev.* **2008**, 367.
13. Cabala R., Meister V., Potje-Kamloth K.: *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 131.
14. Bakker E., Pretsch E.: *Anal. Chem.* **2002**, *74*, 420A.