

Chemical Modulation of Work Function as a Transduction Mechanism for Chemical Sensors

JIŘÍ JANATA* AND MIRA JOSOWICZ

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received May 19, 1997

Work function (WF) plays a key role in many physical and chemical phenomena, such as the semiconductor field-effect,¹ photo- and thermionic electron emission,^{1,2} catalysis,³ etc. This fundamental property of electronically conducting materials is defined⁴ as “the minimum work required to extract an electron from the Fermi level E_F of a conducting phase through the surface and place it in vacuum just outside the reach of the electrostatic forces of that phase”, into a so-called vacuum level. Since even a clean surface is a physical discontinuity, a surface dipole η with its associated electric field always appears at the surface of a condensed phase. Thus the work of extracting the electron can be conceptually divided between the work required to free the electron from the bulk and the work associated with its passage through the surface. The discussion of chemical modulation of WF in this Account is therefore divided into two parts: bulk modulation and surface modulation. We also guide the reader through the concept of utilization of the charge-transfer complex formation in solid-state chemical sensors for the detection of electrically neutral species. Finally, we will show how this effect can be measured and utilized in solid-state chemical sensors for electrically neutral species.

Professor Jiří Janata is Georgia Research Alliance Eminent Scholar in the School of Chemistry and Biochemistry, Georgia Institute of Science and Technology. Between 1991 and 1997, he was an Associate Director of Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, in Richland, WA. Prior to that appointment he was Professor of Materials Science and Professor of Bioengineering at the University of Utah for 17 years. He was born on July 12, 1939, in Czechoslovakia where he received his Ph.D. degree in analytical chemistry from the Charles University (Prague) in 1965. His current interests include interfacial chemistry, chemical sensors, and electroanalytical chemistry with particular emphasis on development of chemical sensors for environmental applications.

Mira Josowicz was born on December 28, 1948, in Katowice, Poland. After receiving her Ph.D. degree in chemistry from the Technical University, Munich, she was a research scientist at the University of Bundeswehr, Neubiberg, Germany. Following her habilitation, in 1991 she moved to the U.S. and became a Senior Staff Scientist at the Pacific Northwest National Laboratory in Richland, WA. She is now Senior Research Scientist in the Department of Chemistry at the Georgia Institute of Technology. Her interests include applied electrochemistry, organic semiconductors, and chemical sensors.

Chemical Modulation of Bulk Component of Work Function

When two dissimilar electronic conductors are placed in contact, electrons flow from the material that is less noble (e.g., copper) to the more noble material (e.g., palladium) until an electrostatic equilibrium is reached and the contact potential V_c is formed at their junction. The contact potential is the most ubiquitous of all interfacial potentials, because of the multitude of possible combinations of electronic conductors, yet its absolute value cannot be measured.

When ions are partitioned between a solution of electrolyte and an ion-selective membrane, an interfacial potential is established that can be viewed as an analogue of a contact potential, the contact being made by the transferring ions. This type of charge transfer is described by the well-known Nernst equation, $\pi = \pi^0 + (RT/zF) \ln a_i$, where the interfacial potential is defined “per mole”. It is important to realize that in both cases an integral value of charge z (i.e., one electron or one ion) is transferred which alters the electrostatic equilibrium at the interface and leads to an integral value of slope of the dependence of the interfacial potential on the logarithm of the activity of the charged species in the two phases. In the case of a multivalent ion with charge z , this slope has a value of RT/zF . Thus, for example, at 25 °C the slope of the response of an ion-selective electrode is 59 mV/decade of change of concentration of the univalent ion, 29 mV/decade of concentration change of the divalent ion, etc.

The situation is substantially different in the case of chemical modulation of the work function.⁵ For example, when electrically neutral molecular hydrogen dissociates at the surface and dissolves in palladium, it changes the electron affinity of the metal, thus its work function and consequently the contact potential between palladium and copper. The origin of the contact potential is again the distribution of electrons between Pd and Cu, but the *cause of the change* of this distribution is the interaction between palladium and hydrogen. In order to scope the analytical usefulness of this type of interaction, we shall examine the more general reaction between neutral gas molecules and a semiconductor. Since the Fermi level is defined with respect to one electron, the slope of the work function response is expressed in terms of kT .

If a donor molecule, e.g., gas G, enters the semiconductor matrix, it transfers (or accepts) a fraction of its electronic charge to (or from) the semiconductor according to

$$G = G^\delta + \delta e \quad (1)$$

This charge-transfer equilibrium can be written as

* To whom correspondence should be addressed. Phone: (404) 894-4828. Fax: (404) 894-7452. E-mail: jiri.janata@chemistry.gatech.edu.

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

where K_G is the equilibrium constant, P_G is the partial pressure of the gas, and α is the solubility of G in the solid phase. Thus the product αP_G is the concentration of dissolved gas G in the solid phase.

The ease with which a molecule forms an ion, either by accepting or donating one electron, is given by the average of its molecular electron affinity, E_a , and its ionization potential, I_p , the so-called Mulliken electro-negativity coefficient χ ⁶:

$$\chi = 0.5(E_a - I_p) \quad (3)$$

On the other hand, the ability of a semiconductor to donate or accept electrons is uniquely related to the energy of the electron in its Fermi level, E_F . The transfer of fractional charge δe can be viewed as a redox equilibrium between the dopant and the matrix in which the role of the electron donor, and of the electron acceptor, is relative and governed by the difference between χ and E_F , respectively.

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

The coefficient ξ is a proportionality constant that will be discussed later.

The Fermi energy (level) is derived from the Fermi–Dirac statistics which describes the distribution of indistinguishable, *non-interacting* particles in n available energy levels. It can be used for electrons or holes, the chief formal difference being in the presence of the degeneracy factor g which in silicon is 2 for a donor and 4 for an electron acceptor. The values of g for an organic semiconductor are not known a priori. Otherwise, the arguments concerning the interactions of the donors and acceptors are the same. The non-Fermi–Dirac distribution of indistinguishable *interacting* particles has been also developed.⁸ Both forms of the statistics of the particle distribution lead to the same final result in this analysis.

The occupancy of the levels by the donor molecules D is

$$N_{D^+} = N \left[1 - \frac{1}{1 + \frac{1}{g_D} \exp \frac{E_D - E_F}{kT}} \right] \quad (5)$$

where $N = N_D + N_{D^+}$, the Fermi level, E_F , is the average value of energy of electrons in the phase, and E_D is the dopant energy level. The basic premise of calculation of the Fermi level is the condition of charge neutrality in the bulk of the phase.¹ In other words, there is no internal electrical field in the bulk of the semiconductor. As long as the charge remains inside the phase, the Fermi level, E_F , equals the chemical potential of the electron. The experimental observation of the charge-transfer complex formation under these conditions can be made, e.g., spectroscopically.^{7,8}

Rearrangement of eq 5 yields

$$E_F = E_D + kT \ln(N_D / g_D N_{D^+}) \quad (6)$$

Thus, E_F varies logarithmically with the concentration of the primary dopant. The energy band structure of organic semiconductors is more complicated than that of silicon. Nevertheless, the coupling of the secondary dopant, such as a gas molecule, is expected to occur through one of the energy levels defined by the primary dopants. For the time being, it is not necessary to specify what this state may be. In the case of some organic semiconductors, it could be the polaron or the bipolaron state which has been shown to form charge-transfer complexes with various organic vapors.⁸

We shall now use N as the total primary dopant concentration (e.g., the donor) and link it to the charge transfer from the gas molecules through the electron-exchange equilibrium. The ionization equilibrium involving this level is

$$N_D = N_{D^+} + e \quad (7)$$

$$K_D = N_{D^+} ([e] / N_D) \quad (8)$$

Combining eq 2 and 7 then yields

$$N_D / N_{D^+} = (K_G \alpha P_G)^{1/2\delta} \quad (9)$$

and substitution into eq 6 yields for a n-type semiconductor

$$E_F = E_D + \frac{kT}{2\delta} \ln \frac{K_G \alpha}{(g_D K_D)^{2\delta}} + \frac{kT}{2\delta} \ln P_G \quad (10)$$

or

$$E_F = E_{D^*} + (kT/2\delta) \ln P_G \quad (11)$$

where the standard dopant energy level at unity partial pressure of gas G is

$$E_{D^*} = E_D + \frac{kT}{2\delta} \ln \frac{K_G \alpha}{(g_D K_D)^{2\delta}} \quad (12)$$

Equation 11 is the relationship between the position of the Fermi level in an n-type semiconductor, and the partial pressure of the donor molecules in the gas phase. A similar relationship can be derived⁵ for the p-type semiconductor for which the ionization of a discrete acceptor state N_A is given as: $N_A + e = N_{A^-}$.

The resemblance of eq 11 to the Nernst equation is more than coincidental; the fundamental difference lies in the fact that the change of the experimentally observable parameter E_F with the partial pressure of dopant gas has a fractional value given by the δ , while in the Nernst equation the slope has an integral value given by the charge z on the partitioning ion. Thus eq 11 can be viewed as a more general form of the Nernst equation that includes the charge-transfer modulation of the Fermi level of electronic conductors.

Formation of charge-transfer complexes is a common occurrence in organic chemistry, and there are also analytical reactions that utilize this type of interaction. The

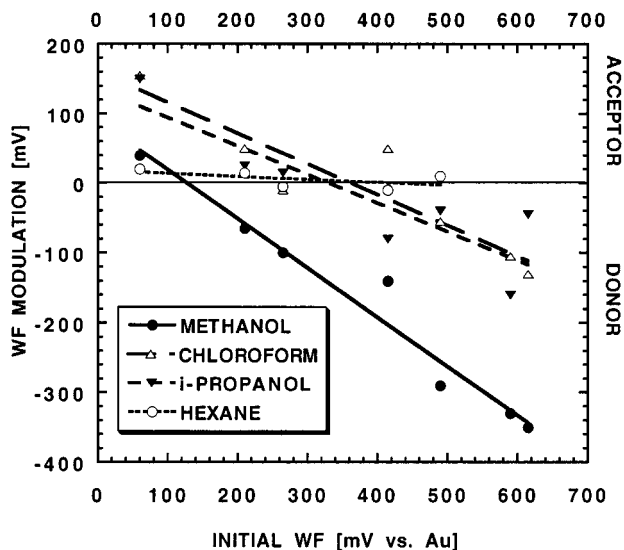


FIGURE 1. Dependence of WF modulation (response) of series of conducting polymers having different values of initial WF. Designations "acceptor" and "donor" refer to the vapor. Reprinted with permission from ref 9. Copyright 1996 VCH.

materials particularly suitable for this type of transduction are organic semiconductors because they can be penetrated by a wide variety of gases. They are also the materials on which the validity of eq 11 has been experimentally verified. The direct confirmation of the relationship between the electron affinity of the polymer matrix (expressed as the initial value of the WF) and its response to the secondary doping was made.⁸ In those experiments various formulations of conducting polymers were prepared, and the value of their initial work function in nitrogen has been determined with the Kelvin probe. The polymers were based on polypyrrole and *p*-polyphenylene doped with different levels of different anions. This provided a series of materials with the WF ranging between +60 to +615 mV (versus Au reference plate). The polymers were then exposed to stream of the following vapors (in nitrogen): CH₃OH (4.6 mM), *i*-C₃H₇OH (0.8 mM), *n*-C₆H₁₄ (1.6 mM), and CHCl₃ (1.2 mM). The concentrations were determined by gas chromatography. Following the exposure to a given vapor, WF reached an equilibrium value in less than 60 s. In those experiments the observed modulation of WF was the difference between the vapor and the nitrogen value for each polymer. The results in Figure 1 show that a given gas can behave with respect to the matrix either as a donor or as an acceptor of electrons depending on the initial value of the WF of the polymer. Since the gas type and the doping concentration remained constant throughout those experiments, the only variable parameter was the initial value of the WF of the polymer. Thus the slope of the lines in Figure 1 is the coefficient ξ in eq 4. The points at which these lines intercept the "zero" WF modulation lines correspond to the condition when no charge transfer takes place, i.e., $\delta e = 0$ and $E_F = \chi$ for a given gas molecule/polymer combination.

It is possible to obtain the value of fractional charge δ from eq 11. This was done for modulation of WF of poly-

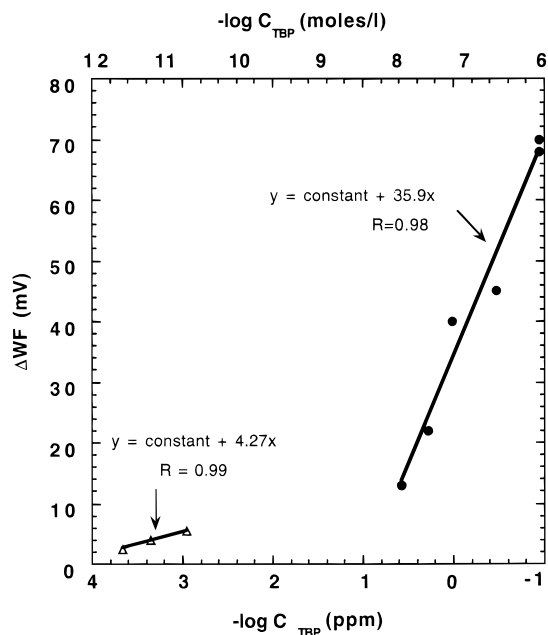
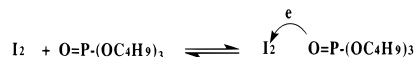


FIGURE 2. Dependence of ΔWF on $\log C_{TBP}$. The charge-transfer coefficient determined from the slope in the ppm region is $\delta = 0.82$. The molar concentration of the gas in the polymer is included for comparison.

(phosphazene)/benzoquinone layers containing iodine by tributyl phosphate (TBP) vapor¹⁰ and for polypyrrole by methanol.^{11,12} The corresponding reaction¹¹ caused by charge transfer between iodine and TBP is given by the equilibrium reaction



The δ value for this reaction was determined from the slope of the ΔWF vs $\log C_{TBP}$ plot as 0.82 (Figure 2). It should be noted that at the low concentrations (parts per billion range), the observed change of WF is apparently dominated by the surface contribution. For this determination we also need to know the solubilities α of the vapors in the polymer. They can be determined gravimetrically as was done for similar measurements for methanol.^{11,12} Since the charge-transfer complex is a dipole, it is possible that the solubilities of these vapors in the polymer are some function of the E_F .

In this derivation we assumed that the charge-transfer complex is formed between the p- or n-primary dopant and the gas acts as a secondary dopant. In fact, the interaction of the secondary dopant with any energy state in the matrix is possible that would lead to the same result as long as the exchanged electron density becomes part of the electron population governed by the Fermi-Dirac statistics. The most important outcome of this derivation is that a fractional value of the slope in eq 11 is possible and can be determined. It simply depends on the ability of the entering molecule to exchange a charge density with the matrix. The analytical utility of this relationship has been shown for several inorganic gases.^{8,10,13-16}

Chemical Modulation of the Surface Component of Work Function

The subject of modulation of surface properties, including the work function, by adsorption of gases has been treated comprehensively both from the catalysis¹⁷ and chemical sensing¹⁸ point of view. It has been shown that the interaction occurs through partial charge transfer between the surface energy states at the semiconductor and the chemisorbed gas. This type of charge transfer modulates both the work function (surface component) of the semiconductor and the surface conductivity. The latter is the underlying principle behind the operation of the chemiresistors utilizing tin and zinc oxides.¹⁹

The relationship between the partial pressure of the adsorbing gas and the change of the work function depends on the type of the adsorption isotherm, on the conductivity of the solid, as well as on the amount of the transferred charge. It is safe to say that the dynamic range for this type of interaction is limited by the maximum number of the surface adsorption sites and that the response follows some form of a power law given by the adsorption isotherm. In the section dealing with the mode of measurement of WF modulation, we shall see that this type of interaction may or may not contribute to the overall response of the sensor depending on how the layer is incorporated into the sensor structure.

Measurement of Work Function Modulation

Kelvin Probe. The classical method of measurement of work function difference (ΔWF) is the vibrating capacitor^{20,21} (Figure 3B). Its operation is based on the fact that there is an electric field in the capacitor formed from two materials of different work function. For thermodynamical reasons it is not possible to measure the absolute value of work function of one plate of a capacitor without making some "extrathermodynamical" assumptions. In the case of a copper/palladium junction, the copper plate becomes positively and the palladium plate negatively charged resulting in the voltage V_C . A galvanometer and a variable voltage source, E_{cell} , placed in series complete the circuit. As the distance between the two plates is periodically changed, the galvanometer registers a time-varying current of the frequency of the mechanical vibration. Next, a compensating voltage E_{cell} from the variable voltage source is applied until the galvanometer registers zero alternating current. Under those conditions, the charge, the voltage, and the electric field across the capacitor are all zero. In other words, the electrons have been "pushed back to where they came from", and at that point the E_{cell} equals the WF difference of the two plates.

It is important to point out the major difference between Kelvin probe potentiometry and Nernstian potentiometry. In the case of Nernstian potentiometry, we have a complete separation of charge that changes the electrostatic (Galvani) potentials of the two phases. Therefore, we can use a voltmeter for the measurement of the cell voltage. In that case there are two contributions to

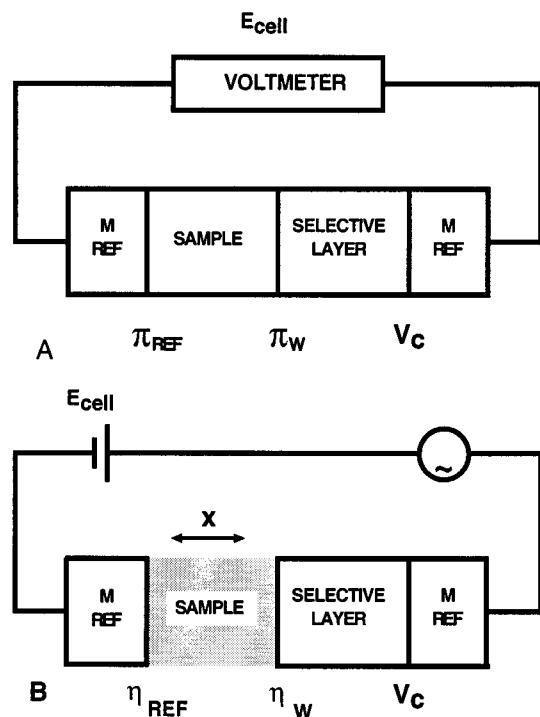


FIGURE 3. Measurement of the cell voltage E_{cell} in (A) Nernstian and (B) non-Nernstian potentiometry. V_C is the contact potential, η_{REF} and η_W are the surface components of WF of the reference and selective layer (working) plate, and x is the variable distance between the plates. π_{REF} and π_W are the interfacial potentials between the sample solution and the reference electrode and the working electrode, respectively.

the E_{cell} (Figure 3A): the potential of the working electrode and the potential of the reference electrode system. The surface dipoles, even if present, do not affect the measurement.

In the case of the WF modulation by absorption of electrically neutral species, the Galvani potential of the phase changes only as a result of the secondary process—transfer of electrons to the *two* neighboring electronic conductors. Such an effect cannot be measured by a voltmeter because the resulting change of the two interfacial potentials is the same and they cancel out. The only alternative is to interface one side of the modulated phase to an insulator. In that case the contributions to the E_{cell} are the contact potential V_C and the two surface potentials η from the working plate and the reference plate of the vibrating capacitor, respectively (Figure 3B)

$$E_{cell} = V_C - \eta_W - \eta_{REF} \quad (13)$$

The obvious practical problem is the stability of the two surface contributions and also the necessity to separate the bulk contribution from the surface contribution of the selective layer. In order to minimize the adsorption effects on the reference plate, it is possible to deposit a few hundred angstroms of an inert material, e.g., silicon nitride, onto the surface of the metal reference plate. It slightly decreases the signal-to-noise ratio of the measurement, but it minimizes possible adsorption in many cases.

Semiconductor Field-Effect. There is an entire class of solid-state semiconductor devices that operate on the basis of the so-called “semiconductor field-effect”¹ and that are miniature “cousins” of the Kelvin probe. The most common is the insulated gate field-effect transistor (IGFET). The essential element in the operation of the IGFET is the metal-insulator-semiconductor (MIS) capacitor. Let us form this capacitor from palladium (to be modulated by hydrogen), silicon dioxide (insulator), and p-type silicon (semiconductor) and examine the energy levels in this structure (Figure 4).²² In a “thought-experiment” (Figure 4A), the junction is disassembled by division through the insulator, and the two halves are first treated as electrically isolated objects. Throughout this text we have been using “WF” as the acronym for “work function”. In the ensuing equation we use the common symbol ϕ for work function of a material. There are three electron work functions to be considered: that of palladium, ϕ_{Pd} , that of an arbitrary metal which does not interact with hydrogen, ϕ_M , and that of silicon, ϕ_{Si} . The insulator is considered to be “ideal” which means that it does not contain mobile charges and, therefore, does not have a defined Fermi level. Because the two halves are not connected, their energy levels are in an arbitrary undefined position with respect to each other. On the other hand, metal M and palladium (also M and silicon) form ohmic junctions, the Fermi levels in those materials must be equal, and contact potentials appear at those interfaces.

In Figure 4A we show graphically both the surface and the bulk terms ($\phi_B + E_g/2$) for the work function of silicon. Let us specify that there is no electric field and therefore no space charge at the insulator/silicon interface. In other words, the potential difference between the surface and the bulk of the semiconductor is zero ($\phi_{SB} = 0$) and the energy bands are flat. This arbitrary, but convenient, state is called the flatband condition. We will maintain the flatband condition throughout the ensuing manipulations, with the help of an externally applied flatband voltage V_{FB} , if necessary. The Fermi level inside the palladium layer is flat by virtue of the high conductivity (no electric field can exist inside a metal at equilibrium). It is further assumed that no trapped charges or oriented dipoles exist inside the insulator or at its interfaces.

Now we rejoin the two halves (Figure 4B). The connecting lead is made again from the same metal M so that no additional contact potentials develop (they would not affect the final result anyway). We now use the Fermi level in silicon as the starting point and pass the test charge through this structure in a counterclockwise direction until it is returned to the starting point, adding the work at each step—positive when we move up and negative when we move down. In essence, we are performing a thermodynamic cycle on this structure. The position of the vacuum level above silicon is defined by ϕ_{Si} . Because of the stipulated flatband condition, the vacuum level over the insulator is flat; i.e., no electric field is present in the insulator. That defines the position of the Fermi level inside the palladium layer which is ϕ_{Pd} below the vacuum

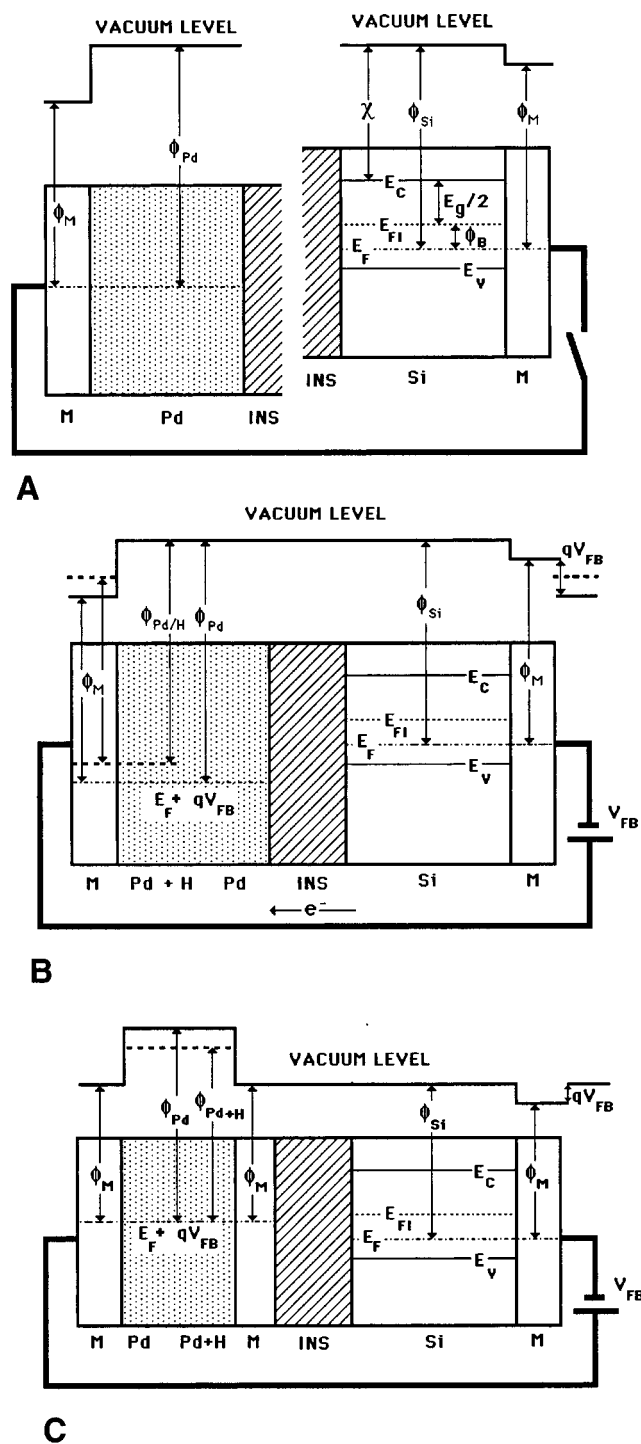


FIGURE 4. A thought-experiment with palladium—insulator—silicon junction under the flatband condition. (A) The junction is divided through the insulator and the two halves are electrically isolated. (B) The two halves are rejoined and the vacuum levels are matched (see the text). (C) A layer of metal M has been interposed between the palladium layer and the insulator.

level. Because there is an ohmic contact (exchange of electrons) between M and Pd, the Fermi level inside M is the same as that in the Pd layer and defines the position of the vacuum level for M (ϕ_M above the Fermi level). The metal M on the left-hand side of Figure 4B is the same as on the right and so is the vacuum level. Because the

Fermi levels in M and in Si are equal, there is a contact potential at that interface. The sum of the energy contributions in this cycle is then

$$\phi_{\text{Si}} - \phi_{\text{Pd}} + \phi_{\text{M}} + qV_{\text{FB}} + (\phi_{\text{Si}} - \phi_{\text{M}}) - \phi_{\text{Si}} = 0 \quad (14)$$

or

$$qV_{\text{FB}} = \phi_{\text{Pd}} - \phi_{\text{Si}} = \Delta\text{WF} \quad (15)$$

Now we see that the vacuum levels above the same metal M are *not equal*. The resulting difference is the flatband voltage V_{FB} which must be externally applied in order to maintain the flatband condition. Thus, the flatband voltage (multiplied by the test charge) equals the difference in the electron work function of Pd and Si. In the non-ideal junctions, there are other charges and dipoles in this structure which must be added to the overall V_{FB} .

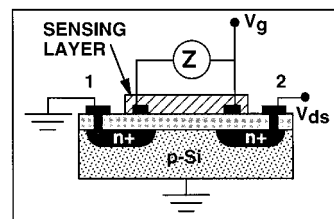
If hydrogen is introduced into palladium at high concentration, the work function of Pd decreases as is indicated by the dashed line in Figure 4B. Because hydrogen does not interact with metal M (by definition), the magnitude of its work function is not affected, but its vacuum level is displaced upward by the contact potential. In order to satisfy the flatband condition, the V_{FB} must be reduced accordingly, relative to its previous value. Such a change of the V_{FB} can be measured. Let us pause and take an inventory of the situation up to this point: (1) we have a plausible mechanism of modulation of both components of WF of a selective layer (palladium); (2) we have at least two methods of measurement of this effect—the Kelvin probe and devices based on semiconductor field-effect. However, the placement of the selective layer within the structure used for either measurement determines whether the effect is observable or not. In order to explain this caveat, we shall add another layer of the same metal M between Pd and the insulator in structure shown in Figure 4C. This would correspond to a “real life” situation when we would try to connect a selective layer by a wire to the MIS structure or a Kelvin probe. It is not necessary to perform the same Carnot cycle as we have done in Figure 4B. Instead, we add the individual energy contributions in the cycle which begins and ends at the silicon Fermi level (anticlockwise):

$$\phi_{\text{Si}} - \phi_{\text{M}} + \phi_{\text{Pd}} - (\phi_{\text{Pd}} + \phi_{\text{M}}) + qV_{\text{FB}} + (\phi_{\text{Si}} - \phi_{\text{M}}) - \phi_{\text{Si}} = 0 \quad (16)$$

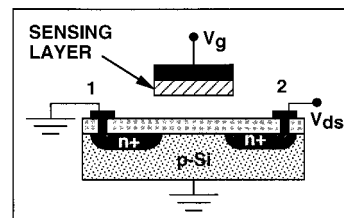
or

$$qV_{\text{FB}} = \phi_{\text{M}} - \phi_{\text{Si}} \quad (17)$$

We see that the work function of palladium, ϕ_{Pd} , has disappeared from the flatband voltage, the same way as ϕ_{M} has disappeared from eq 15. This means that despite the modulation of the work function of Pd (or any other selective layer) in this structure, there is no effect on the flatband voltage. The contact potential between Pd and M has changed, but because there are *two ohmic junctions* between Pd and M, the change of those potentials cancels out. This situation can be generalized by the statement



IGFET



SGFET

FIGURE 5. Schematic diagram of (A) IGFET and (B) SGFET. The selective layer is a conducting polymer. In the IGFET there are two additional contacts through which the impedance (Z) of the layer can be measured.

that: *In order to observe the flatband voltage change due to chemical modulation of the electron work function of the layer, one interface of this layer must be capacitive.* The corollary of this statement is that *measurable response to the modulation of work function originates only in the layer adjacent to the insulator.* Such a condition is satisfied in the structure shown in Figure 4B but not in Figure 4C.

This condition is also satisfied in the Kelvin probe measurement where the selective layer is interfaced to the gap which is an insulator. However, now we see a subtle yet an important difference between the Kelvin probe and a MIS-type measurement; in the Kelvin probe it is the *surface* of the selective layer which contributes the surface term η_{REF} to the E_{cell} . In the MIS structure it is the *interface* between the solid insulator (silicon dioxide) and the selective layer that contributes to the overall signal.

Insulated Gate Field Effect Transistors. There have been several field-effect devices of this type described.²² They are variations on the same basic principle of the insulated gate field-effect transistor (IGFET). Here we present two basic forms utilizing the MIS structure discussed above. The detailed explanation of the operation of these devices can be found in standard texts.¹ The structure of a regular IGFET is shown in Figure 5A. We chose to make the gate electrode of this transistor from Pd in order to utilize the elements of the previous discussion. The MIS structure (Pd/SiO₂/Si) in this case is the gate itself. The conductivity of the channel region between the drain and source electrodes is modulated by the electric field in the gate capacitor. Thus, the current in the channel becomes a measure of the charge on the silicon “plate” of the gate capacitor. At this point we should see the relationship between this device and the Kelvin probe. In the latter, we would have to vibrate the plates in order to null out the electric field; in the IGFET we measure the drain-to-source current I_D in order to

obtain the information about the charge on the gate capacitor. For $V_D > V_G - V_T$, the drain current is given by

$$I_D = \frac{W\mu_m C_0}{2L}(V_G - V_T)^2 \quad (18)$$

where W , L , and C_0 are constants given by the geometry of the transistor, μ_m is the electron mobility in silicon, and V_G is the applied gate voltage. The threshold voltage V_T is defined as

$$V_T = V_{FB} + 2\phi_{FI} - [(Q_{SS} + Q_B)/C_0] \quad (19)$$

The intrinsic Fermi level of silicon, ϕ_{FI} , is not affected by the environment because the bulk of silicon is well protected by the oxide and silicon nitride layers. The term $(Q_{SS} + Q_B)/C_0$ in eq 19 represents residual charges in the transistor which also do not change. Thus, the only variable term in eq 19 is the V_{FB} which responds to the work function changes of Pd according to eq 15. This device was first introduced by Lundstrom and has been intensively studied ever since.²³ We have recently used the same structure but with a polyaniline active gate deposited directly at the solid gate insulator.^{24,25}

The second type of IGFET bears resemblance to the Kelvin probe. It is called the suspended gate field-effect transistor (SGFET)²⁶ because the gate conductor is suspended approximately 1 μm above the gate insulator, thus forming a gap (Figure 5B). It is possible to deposit an electrochemically selective layer under this suspended metal bridge and then modulate this layer chemically. Suspended gate field-effect transistors, selectively sensitive to alcohol vapors,²⁷ hydrogen cyanide,¹⁴ tributyl phosphate,⁹ hydrogen, and ammonia, have been described.²⁸

Conclusions

We have shown that a rather unusual combination of two old principles, the Kelvin probe and an (expanded) form of the Nernst equation, can lead to a new class of chemical sensors based on modulation of work function of the chemically selective layer. The principles on which the Kelvin probe operates are mirrored in solid-state field-effect transistors. The obvious advantage of these devices is that they can be fabricated in silicon and assembled as large sensing arrays. There is a growing library of materials suitable for selective detection of electrically neutral species based on charge-transfer complex formation. Furthermore, we have shown that the selectivity of these materials can be electrochemically tuned. In order to illustrate this possibility, we have synthesized electrochemically polymers according to the information presented in Figure 1. Polymers have been prepared with the initial value of WF ranging from 60 to 615 mV (vs Au). Exposure of these polymers to five organic vapors showed a remarkably different pattern of selectivity (Figure 6). Moreover, for each vapor a material could be synthesized such that it had "zero" response to the vapor and could be used as the "reference" layer.

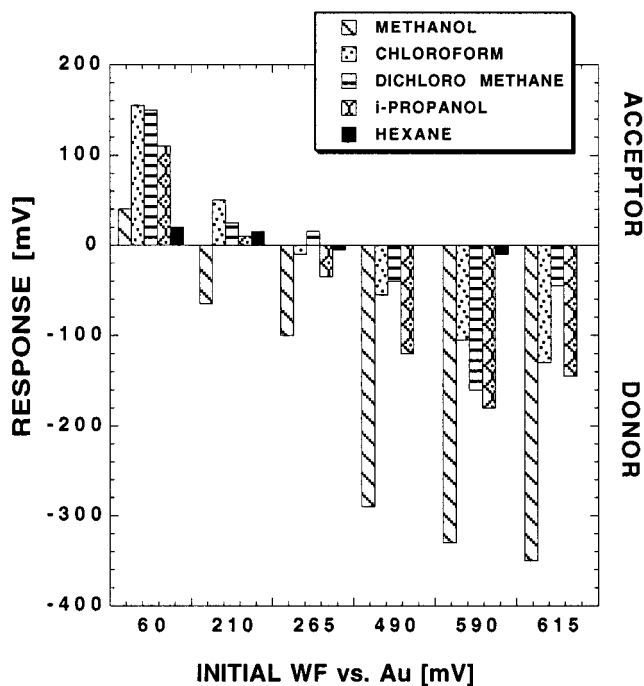


FIGURE 6. Patterns of response (WF modulation) of six conducting polymers, prepared with different values of the initial WF, to five organic vapors.

One of the most attractive features of sensors fabricated in silicon is the possibility of formation of large multi-sensing arrays. Combination of this fact with the flexibility, versatility, and tuneability of electrochemically synthesized materials allows us to make a safe prediction that a new class of rationally designed and microfabricated multisensing arrays can be developed in the near future.

This work was supported in the early stages by the Office of Naval Research and in the last four years by the DOE's Office of Nonproliferation and National Security.

References

- (1) Sze, S. M. *Physics of Semiconductor Devices*; John Wiley: New York, 1969.
- (2) Allen, F. G.; Gobelli, G. W. *Phys. Rev.* **1962**, *127*, 150–158.
- (3) Vayenas, C. G.; Jaksic, M. M.; Bebelis, S. I.; Neophytides, S. G. In *Modern Aspects of Electrochemistry*; Bockris, J.O. M., Conway, B. E., Eds., Plenum Press: New York, 1996; Vol. 29, pp 57–202.
- (4) Trasatti, S.; Parsons, R. *Pure Appl. Chem.* **1986**, *58*, 37–55.
- (5) Janata, J. *Anal. Chem.* **1991**, *63*, 2546–2550.
- (6) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782–793.
- (7) Reiss, H. *J. Phys. Chem.* **1985**, *89*, 3783–3791.
- (8) Blackwood, D.; Josowicz, M. *J. Phys. Chem.* **1991**, *95*, 493–502.
- (9) Li, Jing; Janata, J.; Josowicz, M. *Electroanalysis* **1996**, *8*, 778–783.
- (10) Khoklov, M. L.; Legin, E. K.; Klimov, V. D.; Nabiev, Sh. *Radiokhimiya* **1990**, *32*, 32–36.
- (11) Topart, P.; Josowicz, M. *J. Phys. Chem.* **1992**, *96*, 7824–7830.
- (12) Topart, P.; Josowicz, M. *J. Phys. Chem.* **1992**, *96*, 8662–8666.

- (13) Langmaier, J.; Janata, J. *Anal. Chem.* **1992**, *64*, 523–527.
- (14) Li, Jing; Petelenz, D.; Janata, J. *Electroanalysis* **1993**, *5*, 791–794.
- (15) Josowicz, M.; Janata, J. *Anal. Chem.* **1986**, *58*, 514–517.
- (16) Papez, V.; Josowicz, M. *J. Electroanal. Chem.* **1994**, *365*, 139–150.
- (17) Morrison, S. R. *The Chemical Physics of Surfaces*; Plenum Press: New York, 1977.
- (18) Göpel, W. *Progr. Surf. Sci.* **1985**, *20*, 9–103.
- (19) Heiland, G.; Kohl, D. In *Chemical Sensor Technology*; Seiyama, T., Ed.; Elsevier: New York, 1988; Vol. 1.
- (20) Lord Kelvin *Philos. Mag.* (5th series) **1898**, *46*, 82–120.
- (21) Ritty, B.; Wachtel, F.; Manquenouille, R.; Ott, F.; Donnet, J. B. *J. Phys. E: Sci. Instrum.* **1982**, *15*, 310–317.
- (22) Josowicz, M.; Janata, J. *Chemical Sensor Technology*, Seiyama, T., Ed.; Elsevier: New York, 1988; Vol. 1, pp 153–177.
- (23) Lundstrom, I.; Shivaraman, M. S.; Svensson, C.; Lundquist, L. *Appl. Phys. Lett.* **1975**, *26*, 55–57.
- (24) Liess, M.; Chinn, D.; Petelenz, D.; Janata, J. *Thin Solid Films* **1996**, *286*, 252–255.
- (25) Domansky, K.; Li, Jing; Janata, J. *J. Electrochem. Soc.* **1997**, *144*, L75–L78.
- (26) Blackburn, G.; Levy, M.; Janata, J. *Appl. Phys. Lett.* **1983**, *43*, 700–702.
- (27) Josowicz, M.; Janata, J. *Anal. Chem.* **1987**, *59*, 253–258.
- (28) Domansky, K.; Baldwin, D.; Grate, J.; Hall, T. B.; Li, Jing; Josowicz, M.; Janata, J. *Anal. Chem.* **1998**, *70*, 473–481.

AR9700668