

# Work Function Characterization of Electroactive Materials Using an $E^{\text{MOSFET}}$

Dam Thi Van Anh, Wouter Olthuis, and Piet Bergveld

**Abstract**—Materials with redox properties have been widely used in sensing applications. Understanding the redox properties of these materials is an important issue. In order to investigate the redox properties, there are several methods, such as using the Kelvin probe and a conductivity sensor, or using other well-known electrochemical techniques. In this paper, we introduce another possibility to characterize redox materials by investigating their work function using an electrolyte metal-oxide semiconductor field effect transistor ( $E^{\text{MOSFET}}$ ) device, in which the studied redox material is applied as gate electrode. In the  $E^{\text{MOSFET}}$ , the conductivity of the channel is modulated by the work function of the studied material. The change in the work function of a redox material due to electrically and chemically induced processes will be shown by an example of the  $E^{\text{MOSFET}}$  having a potassium ferric ferrocyanide gate.

**Index Terms**—Electroactive material, electrolyte metal-oxide semiconductor field effect transistor ( $E^{\text{MOSFET}}$ ), work function.

## I. INTRODUCTION

**M**ATERIALS with redox properties have been widely used in sensing applications. Understanding the redox properties of these materials is an important issue. The electroactive properties of materials are often characterized by cyclic voltammetry, in which the oxidation ratio of the material is changed by applying a potential. In a cyclic voltammogram, the current  $I$ , which reflects the oxidation process of the material, depends nonlinearly on the applied potential. Redox couple peaks in the cyclic voltammogram which are typical for reduction and oxidation processes of redox materials can, however, be influenced and shifted due to insertion of other counter ions present in the solution.

The electroactive properties of the material can also be investigated by studying the change in its conductivity during the redox reaction. This measurement can simply be done by using a conductivity cell containing two interdigitated electrodes with a material film deposited on it. However, this method does not always give a precise result because the measured conductivity also depends on the conductivity of other ions or species which

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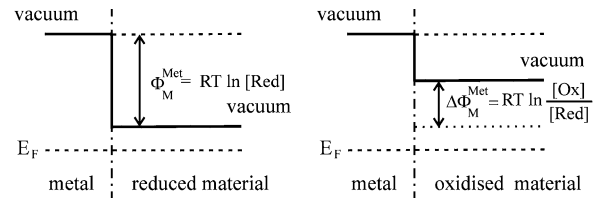


Fig. 1. Illustration of a change in the work function related to a redox process.

are present in the environment where the measurement is done. Moreover, the conductivity of the material may be changed, not only by electrochemical or chemical oxidation or reduction, but also by chemical exchange reactions, such as protonation in aqueous media or gas adsorption in a dry state [3]. Particularly, when the redox reaction of the material occurs in the gas phase (for example, in the case of gas sensors), a change in conductivity of the material due to chemical and physical absorbed effects is observed at only a very high temperature.

The redox properties of the electroactive materials can also be studied by measuring their work function using a Kelvin probe which consists of a vibrating capacitor. This method allows us to measure a change in the work function generated by the redox reaction of the material, between two surfaces. In this paper, we introduce a different possibility to characterize the redox materials by investigating their work function based on the field effect transistor principle.

## II. WORK FUNCTION AND ITS RELATION WITH THE REDOX PROPERTIES OF MATERIALS

In the solid phase, the work function  $\Phi$  of electrons of a material is defined as the difference between the Fermi energy  $E_F$  and the Volta energy, i.e.,  $-q\theta$ , which is the energy required to move an electron in vacuum from a distance of  $100 \text{ \AA}$  from the solid surface of the material to infinity

$$E_F = -\Phi - q\theta. \quad (1)$$

When an electroactive material is deposited on a metal electrode, the Fermi levels of the metal and the electroactive material are equal. It leads to a difference in the work function of electrons in the metal and the material,  $\Phi_M^{\text{Met}}$  (as shown in Fig. 1). The difference in the work function equals to the difference in the Volta energy of the metal and the studied material

$$-\Phi_{\text{Met}} - q\theta_{\text{Met}} = -\Phi_M - q\theta_M \quad (2)$$

or

$$\Phi_M^{\text{Met}} = \Phi_{\text{Met}} - \Phi_M = -q(\theta_{\text{Met}} - \theta_M). \quad (3)$$

When the metal electrode with electroactive material takes part in a redox process, the redox reaction between the material and other species occurs with the electron transfer as follows:



where Red and Ox are the characteristic redox couples for the electroactive material.

It should be noted that the redox process of the electroactive material can also be realized physically by applying an external current or potential as in the electrochemical methods. Depending on the redox reaction which occurs due to chemically and physically induced processes, a change in the work function of the material depends on a change in the oxidation ratio of the material, as shown in Fig. 1.

If the redox process occurs in a solution, the work function of the material can be written according to [4]

$$\Phi_M = \mu_e + z_i F \chi \quad (5)$$

where  $\chi$ ,  $z_i$ , and  $F$  are the surface potential, the valence of the ions involved in the redox process, and the Faraday constant, respectively, and  $\mu_e$  is the chemical potential of the electrons in the electroactive material, which depends on the oxidation ratio of the material as shown in Fig. 1

$$\mu_e = \mu_e^0 + RT \ln \frac{[\text{Ox}]}{[\text{Red}]} \quad (6)$$

where  $\mu_e^0$  and  $[\text{Ox}]/[\text{Red}]$  are the standard chemical potential and the oxidation ratio of the redox material, respectively. From this, the work function written in (5) can be represented as

$$\Phi_M = \text{const} + RT \ln \frac{[\text{Ox}]}{[\text{Red}]} + z_i F \chi. \quad (7)$$

Thus, according to (7), the redox reaction of the electroactive material can be studied by investigating a change in its work function depending on the redox reaction. In the conventional Kelvin probe technique, the work function of the material is measured by means of investigating a difference between the Volta potential of the metal and the material as shown in (3). In this paper, the work function will be studied based on the electrolyte metal-oxide semiconductor field effect transistor (<sup>E</sup>MOSFET) device.

### III. <sup>E</sup>MOSFET, STRUCTURE, AND WORKING PRINCIPLE

A MOSFET is a well-known device in integrated circuit technology, which is based on the creation of a conductive channel along the surface of a Si substrate and the modulation of this conductivity by a properly applied electrical field perpendicular to the Si surface. One of the most important parameters of a MOSFET is its threshold voltage  $V_T$  which reflects a difference in the work function of electrons in the gate electrode ( $\Phi_{\text{Met}}$ ) and Si ( $\Phi_{\text{Si}}$ ),  $\Phi_{\text{Si}}^{\text{Met}}$

$$V_T = \frac{\Phi_{\text{Si}}^{\text{Met}}}{q} + \text{const}. \quad (8)$$

This type of device can also be used for the characterization of the work function of redox materials being applied as gate electrode. For this purpose, the MOSFET has been modified to the

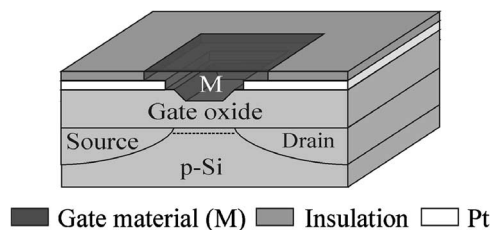


Fig. 2. Schematic cross section of the <sup>E</sup>MOSFET.

<sup>E</sup>MOSFET as sketched in Fig. 2, where the studied material is deposited on top of a gate oxide and contacted by a surrounding metal electrode made from a platinum. The conductivity of the channel is modulated by the work function of the studied material which is brought in direct contact with a solution. Then, the threshold voltage of this device can be calculated as

$$V_T = \frac{\Phi_M^{\text{Met}} + \Phi_{\text{Si}}^{\text{M}}}{q} + \text{const} \quad (9)$$

where  $\Phi_{\text{Si}}^{\text{M}}$  is the difference in the work function of electrons in the material and Si. In practical use, the Pt electrode is connected to the Si substrate and the  $\Phi_M^{\text{Met}}$  can be changed due to a possible electron exchange between two conducting materials: the studied material and Pt (as seen in Fig. 3). The second term in (9)  $\Phi_{\text{Si}}^{\text{M}}$ , which is typical for the sandwich of material/SiO<sub>2</sub>/Si, will remain constant because no direct electron exchange is possible. This term depends only on the fabrication parameters of the device. Moreover, the surface potential, which is developed at the material/solution interface by diffusion of small ions such as protons, does not change during the redox process, and, thus, it can be assumed that  $\chi$  [as shown in (7)] is constant during the redox reaction. By using this device, a change in the threshold voltage and thus the work function of the material due to a redox process can be characterized by measuring the change in the threshold voltage

$$\Delta V_T = \frac{\Delta \Phi_M^{\text{Met}}}{q} = \frac{RT}{F} \ln \frac{[\text{Ox}]}{[\text{Red}]}. \quad (10)$$

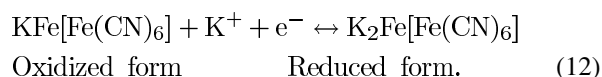
By choosing the situation, in which the material is nearly completely reduced as a set point for any measurement, the threshold voltage can be interpreted as

$$V_T = \frac{RT}{F} \ln \frac{[\text{Ox}]}{[\text{Red}]} \quad (11)$$

The threshold voltage, which is dependent on the change in  $\Phi_M^{\text{Met}}$  as seen in Fig. 3, gives only information about the bulk nature of the material. Any surface exchange process that gives a contribution to a surface potential does not influence the threshold voltage.

### IV. REDOX PROPERTIES OF POTASSIUM FERRIC FERROCYANIDE

The redox properties of potassium ferric ferrocyanide (PB) have been studied by investigating its reaction with hydrogen peroxide using the <sup>E</sup>MOSFET having a PB gate. The oxidation and reduction of PB are well known [5]



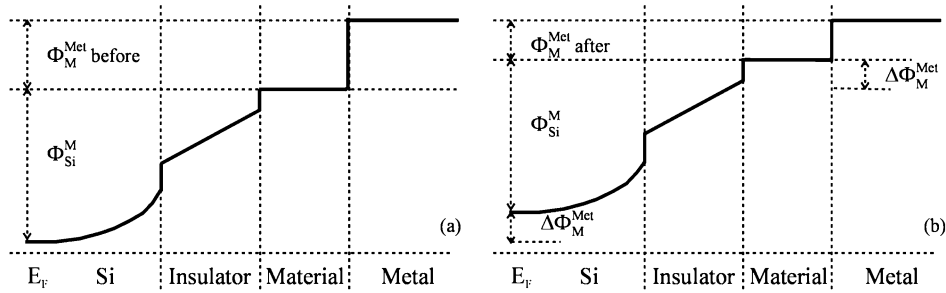


Fig. 3. Energy diagram of the  $E$ -MOSFET system (left) before and (right) after redox reaction.

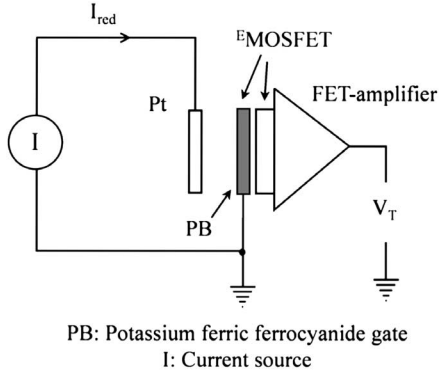
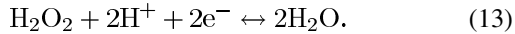


Fig. 4. Setup used to apply an external current between the gate and the solution.

At the same time, the hydrogen peroxide is reduced to water



According to (12) and (13), the threshold voltage of the  $E$ -MOSFET having the PB gate reflects the work function of PB which depends on its redox reaction

$$V_T = \frac{RT}{F} \ln \frac{[\text{KFe}[\text{Fe}(\text{CN})_6]]}{[\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]]} = \frac{RT}{2F} \ln[\text{H}_2\text{O}_2] \quad (14)$$

where  $[\text{KFe}[\text{Fe}(\text{CN})_6]]$  and  $[\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]]$  are the concentrations of the oxidized and reduced forms of PB, respectively. When the hydrogen peroxide concentration rises, the threshold voltage of the device increases with increasing oxidation ratio of PB.

Because at zero current, the exchange current between PB and hydrogen peroxide is small, it takes quite a long time to reach the equilibrium potential between the gate material and the solution. To accelerate this process, an additional external dc current is applied between the gate and the solution as shown in Fig. 4.

Then, (14) can be rewritten for the case when the current is applied

$$V_T = \text{const} + \frac{2.3RT}{2F} \log[\text{H}_2\text{O}_2] - \frac{2.3RT}{F\alpha} \log \frac{I}{I_{\text{PB}}} \quad (15)$$

where  $\alpha$  is the dimensionless transfer coefficient of the redox reaction of PB, and  $I_{\text{PB}}$  is the exchange current density between the PB gate and the solution which is dependent on the hydrogen peroxide concentration

$$I_{\text{PB}} = \text{const} \times [\text{H}_2\text{O}_2]^{1-\alpha}. \quad (16)$$

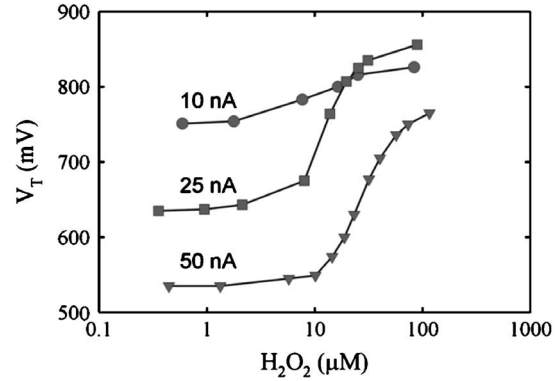


Fig. 5. Dependence of the threshold voltage on the hydrogen peroxide concentration at different values of the applied reducing current.

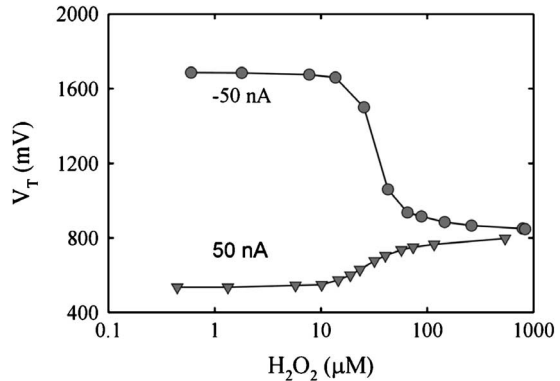


Fig. 6. Behavior of the threshold voltage dependent on the hydrogen peroxide concentration when the reducing or oxidizing currents of 50 nA are applied.

When the applied current flows from the solution to the gate (reduction current), the equilibrium is more quickly established, during which the PB gate is being reduced. Initially, without added hydrogen peroxide, the oxidation ratio and the work function of PB is determined by a competition between the reduction process (by means of applying the current) and the oxidation process due to oxidative agents present in the solution, such as dissolved oxygen. As seen in Fig. 5, a current of 10 nA is not high enough to reduce PB, and the PB gate is nearly oxidized completely by oxidative agents. Now, when the hydrogen peroxide is added, the work function of PB, i.e., the threshold voltage, changes only in a small range.

Increasing the value of the reducing current, the reduction of PB by the current predominates the chemical oxidation processes as shown in Fig. 5. It can be seen in this figure that at a same value of the hydrogen peroxide concentration, the

threshold voltage is decreasing with increasing value of the current. When the hydrogen peroxide concentration in the solution rises, the threshold voltage of the device increases and depends logarithmically on the concentration of the hydrogen peroxide, as described in (14). An observed super Nernstian dependence of the work function of PB on the hydrogen peroxide concentration, which is estimated about 400 mV/dec, can be explained by differentiating (15) with respect to  $\log([\text{H}_2\text{O}_2])$ . This sensitivity to the hydrogen peroxide is lower than the one that has been observed in the case of a redox polymer Os polyvinylpyridine containing an enzyme horseradish peroxidase [6]. From that, the transfer coefficient  $\alpha$ , which reflects the nature of the reaction between PB and hydrogen peroxide, is calculated to be 0.13

$$\frac{d(V_T)}{d\log([\text{H}_2\text{O}_2])} = \frac{2.3RT}{2F} + \frac{2.3RT}{F} \frac{1-\alpha}{\alpha}. \quad (17)$$

It can also be seen that, the higher the applied current, the higher the hydrogen peroxide concentration, at which the oxidation process of PB can occur. Moreover, the value of the applied current, at which the gate material is still in the reduced state, in the presence of a small amount of the hydrogen peroxide, gives the information about the catalytic property of this material to the hydrogen peroxide.

Because of the double properties of hydrogen peroxide which can be an oxidator or a reductor, depending on the potential of the gate material, the reduction of the PB by the hydrogen peroxide has been investigated by applying an external oxidizing current to the PB gate. A similar explanation can be achieved in the case that the oxidizing current is applied. As seen in Fig. 6, when an oxidizing current of 50 nA is applied to the PB gate, the PB is oxidized by the current. When the hydrogen peroxide is added in the solution, PB is reduced by the hydrogen peroxide; thus, the oxidation ratio of PB decreases, i.e., the threshold voltage of the device decreases with increasing the hydrogen peroxide concentration.

## V. CONCLUSION

The work function of a redox material is varied when the material takes part in a redox reaction with other species. The work function, which is linearly dependent on the logarithm of its oxidation ratio, can be measured by means of the  $\text{E}^{\text{MOSFET}}$  having the gate made from this material. It should be noted that, contrary to the conductivity method as mentioned in the introduction, with the  $\text{E}^{\text{MOSFET}}$  concept, the work function of the material could be measured at a low temperature range. The work function can also be changed in an electrical way when an external current is applied. The oxidation or reduction process of the material can be studied by applying the external reducing current or external oxidizing current, respectively. The influences of electrically and chemically induced processes on the work function of the material and a competition between them have been studied by using the  $\text{E}^{\text{MOSFET}}$ . Moreover, the transfer coefficient, which is characteristic for the redox reaction of the material, can be calculated.

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