

Supplementary Information

Field effect transistor to enable registration of reaction energy pathways

Figures S1-S3

Supplementary Text

5 References (1 – 4)

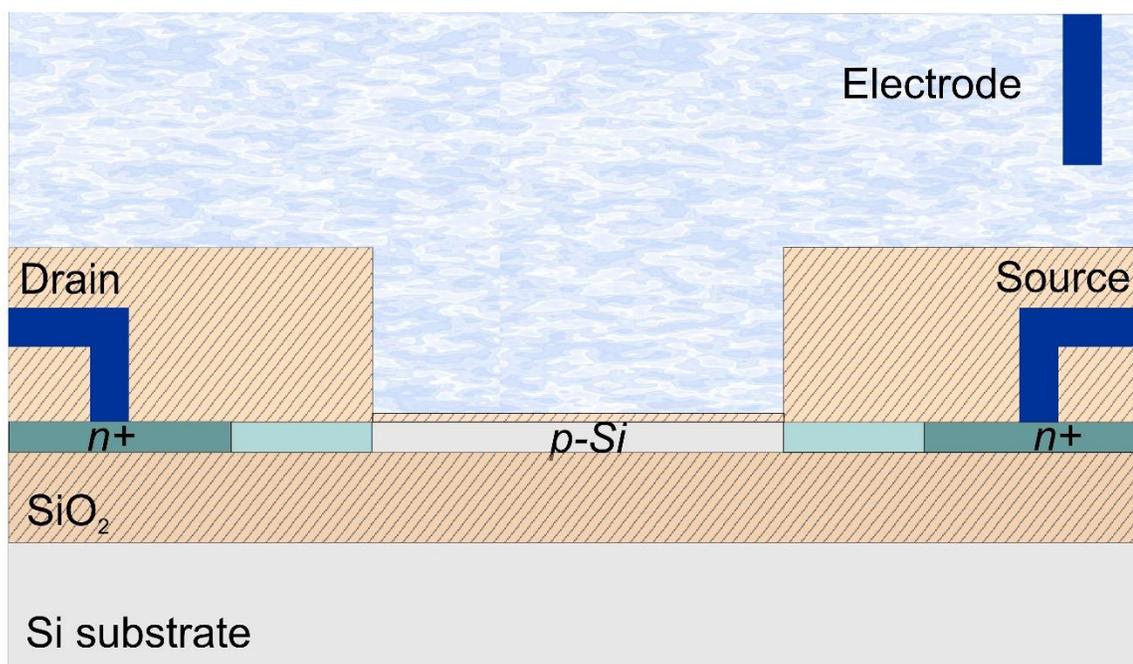


Figure. S1. FD SOI ISFET structure

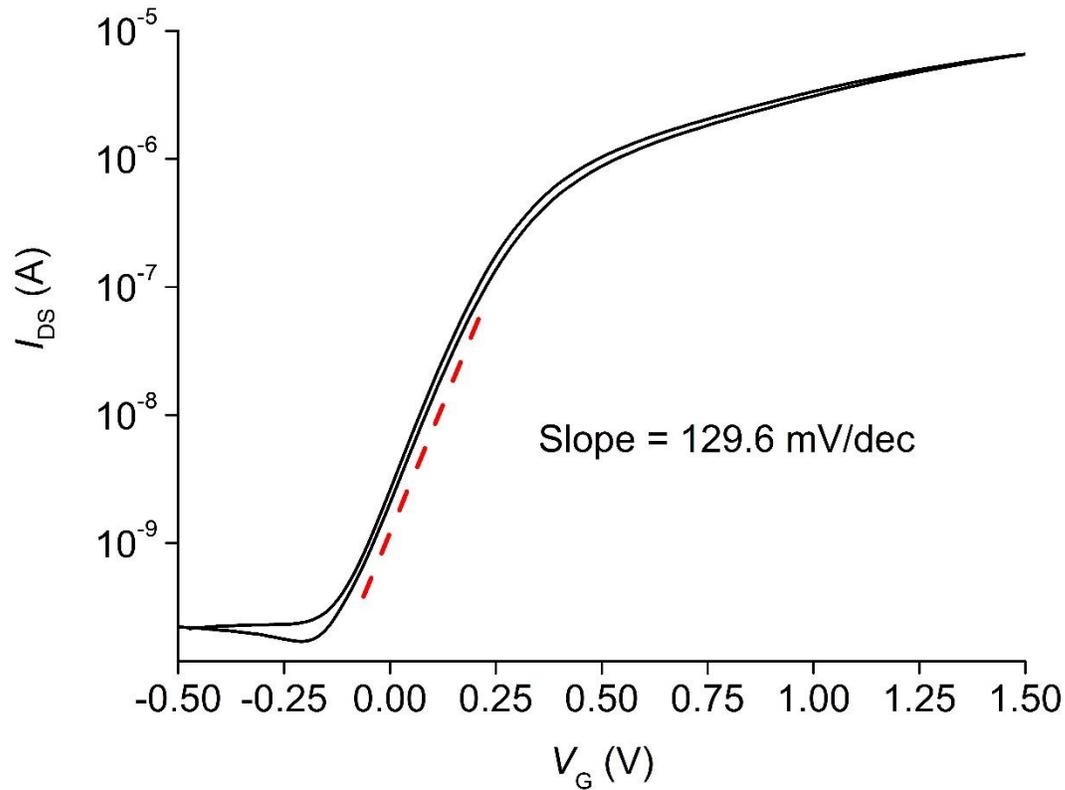


Figure. S2. Typical cyclic I_{DS} - V_G curve for the $100 \times 100 \mu\text{m}$ nMOS FET with a chemical SiO_2 insulating layer.

5 Supplementary Text (Principle of Work)

The work function of the material is determined by the chemical potential of the electrons. In the case of ISFETs, the gate is replaced by a solution, and therefore the threshold voltage depends on the chemical potential of the electrons in the electrolyte, μ_e . The electron energy diagram of an ISFET system with the redox electrode in steady state is shown in Fig. S3.

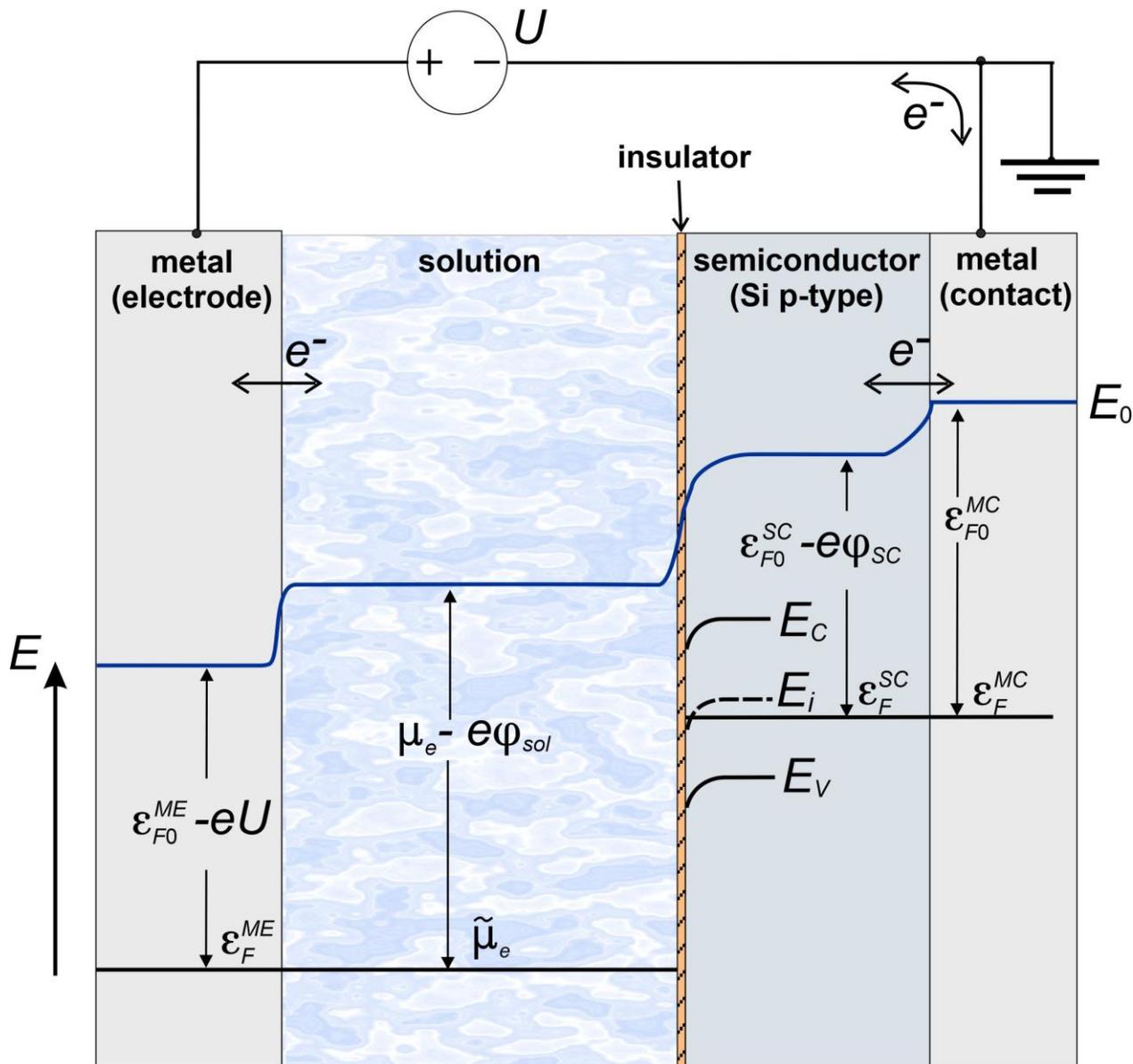


Figure S3. Electron energy diagram for ISFET structure (simplified) with redox electrode in steady state, characterized by the equality of electrochemical potentials in solution and in the electrode. (The potentials at the interfaces associated with dipole moments and particle adsorption are not shown.) E_0 is the vacuum level, E_C and E_V are the levels of the conduction and the valence band, respectively, and E_i is at the middle of the forbidden band; definitions of the remaining symbols are given in the text.

Consider its energy diagram under electrode–semiconductor bias at steady state (Fig. S3). In this system, a metal nonpolarizable redox electrode is placed in an electrolyte solution, is connected to a voltage source, and reversibly exchanges electrons with the electrolyte through redox reactions on the surface. The semiconductor is completely isolated from the electrolyte, ensuring the absence of faradic current through the semiconductor–electrolyte solution interface, and is connected through a metal contact to the common potential. In a stable state, the electrolyte is in thermodynamic equilibrium with the redox electrode, as is the semiconductor with the contact metal. The thermodynamic equilibrium is achieved owing to the exchange of electrons through the contact metal–semiconductor and electrolyte–redox electrode interfaces. The phases are charged, and the exchange charge accumulates at the interfaces of these phases and leads to a change in the potential inside the phase, leading in turn to a change in the electrochemical potential of each phase until equilibrium is reached. This equilibrium is characterized by the corresponding equality of electron electrochemical potentials:

$$\tilde{\mu}_e = \varepsilon_F^{ME} \quad (\text{S.1})$$

$$\varepsilon_F^{MC} = \varepsilon_F^{SC} \quad (\text{S.2})$$

where $\tilde{\mu}_e$ is the electrochemical potential of electrons in electrolyte, ε_F^{ME} is the electrochemical potential of electrons in the redox electrode (Fermi level), ε_F^{MC} is the Fermi level of the contact metal, and ε_F^{SC} is the Fermi level in the semiconductor. At the same time, the semiconductor is in a nonequilibrium state with the electrolyte, and under real conditions a leakage current always exists through the dielectric; this current, however, is negligible and does not violate conditions (S.1) and (S.2). Thus, the system as a whole is in a nonequilibrium steady state supported by a voltage source U .

The electrochemical potentials are related to the electric potentials for the phases under consideration as

$$\varepsilon_F^{ME} = \varepsilon_{F0}^{ME} - eU \quad (\text{S.3})$$

$$\tilde{\mu}_e = \mu_e - e\phi_{sol} - e(\chi_S^M + \chi_S^D) \quad (\text{S.4})$$

$$5 \quad \varepsilon_F^{SC} = \varepsilon_{F0}^{SC} - e\phi_{sc} - e(\phi_D + \phi_{SC}^D) \quad (\text{S.5})$$

$$\varepsilon_F^{MC} = \varepsilon_{F0}^{MC} \quad (\text{S.6})$$

where e is the elementary charge; μ_e is the chemical potential of the electrons in the electrolyte; ϕ_{sol} is the electric potential in the electrolyte volume (inner or Galvani potential); ϕ_{sc} is the electric potential in the semiconductor, ε_{F0}^{SC} and ε_{F0}^{MC} are the semiconductor and contact metal Fermi levels, respectively, at zero bias; χ_S^M and χ_S^D are the dipole layer surface potentials ¹ at the liquid–metal and liquid–dielectric interfaces, respectively; ϕ_{SC}^D is the potential associated with the dielectric–semiconductor interface (interface states); and ϕ_D is the potential associated with the fixed charge in the dielectric. From (S.1)–(S.6), one can obtain

$$\phi_{sol} = -\frac{\varepsilon_{F0}^{ME} - \mu_e}{e} + U - (\chi_S^M + \chi_S^D) \quad (\text{S.7})$$

$$15 \quad \phi_{sc} = -\frac{\varepsilon_{F0}^{MC} - \varepsilon_{F0}^{SC}}{e} - (\phi_D + \phi_{SC}^D) \quad (\text{S.8})$$

$$V_G = \phi_{sol} - \phi_{sc} \quad (\text{S.9})$$

where V_G is the interphase potential difference between electrolyte and semiconductor, which defines the semiconductor surface conductivity. χ_S^M and χ_S^D do not depend on V_G ², nor does ϕ_D , whereas ϕ_{SC}^D depends on V_G . Therefore, when U is changing, from (S.6)–(S.9) we have

$$20 \quad \frac{\partial V_G}{\partial U} = 1 - \frac{\partial(\chi_S^M + \chi_S^D)}{\partial U} + \frac{\partial(\phi_D + \phi_{SC}^D)}{\partial U} = 1 - \frac{\partial\phi_{SC}^D}{\partial\phi_{sol}} \frac{\partial\phi_{sol}}{\partial U} = 1 - \frac{\partial\phi_{SC}^D}{\partial\phi_{sol}} \quad (\text{S.10})$$

When μ_e is changing for any reason under $U = const$, and with this change the electrode with electrolyte are in a quasi-equilibrium state, from (S.7)–(S.9) it follows that

$$\frac{\partial V_G}{\partial \mu_e} = \frac{1}{e} \left(1 - \frac{\partial \phi_{SC}^D}{\partial \phi_{sol}} \right) \quad (\text{S.11})$$

Thus, the effect of a change in the chemical potential of the electrons on the surface conductivity of the semiconductor is equivalent to the effect of a change in U :

$$\left(\frac{\partial V_G}{\partial U} \right)_{\mu_e} = e \left(\frac{\partial V_G}{\partial \mu_e} \right)_U \quad (\text{S.12})$$

Therefore, it is possible to measure the change in μ_e in the structure if the response of the structure to the change in U is known in advance. The ISFET's response to a change in U at a constant drain-source voltage V_{DS} can be expressed as

$$\Delta I_{DS} = f(\Delta U)|_{V_{DS}, \mu_e} \quad (\text{S.13})$$

ΔI_{DS} can be measured, and the desired mode of the transistor can be determined by voltage U .

Then, the subsequent changes in μ_e in the solution at a fixed U can be determined:

$$\frac{\Delta \mu_e}{e} = f^{-1}(\Delta I_{DS})|_{V_{DS}, \mu_e} \quad (\text{S.14})$$

where $f^{-1}(\Delta I_{DS})|_{V_{DS}, \mu_e}$ is the inverse function of (S.13). Thus, the structure under consideration can be used as a sensor for detecting changes in the chemical potential of electrons in solution.

The chemical potential of electrons in solution, μ_e , is characterized by the equilibrium state of the redox reactions in solution (redox system) and corresponds to the oxidation–reduction potential on a vacuum scale³:

$$\mu_e = -neE_{redox}(vac. scale) \quad (\text{S.15})$$

where $E_{redox}(vac. scale)$ is the potential relative to the vacuum level, and n is the number of electrons involved in the redox reaction. Therefore, changes in the component composition of the redox system, caused by initialization of a homogeneous chemical reaction in solution, will be accompanied by a change in μ_e and consequently a change in the electrochemical potential $\tilde{\mu}_e$, because of the equation $\tilde{\mu}_e = \mu_e - e\phi_{sol}$. This will lead to a shift in the equilibrium of the electronic solution–electrode exchange.

Electron exchange occurs through a heterogeneous redox reaction at the electrode–solution interface, the rate of which can be much higher than the rate of the initiated homogeneous reaction in solution. In this case, the solution and the electrode can be considered to be in a state of quasi-equilibrium, characterized by the equality of the electrochemical potentials $\varepsilon_F^{ME} = \tilde{\mu}_e$. Since ε_F^{ME} is always constant, which ensures the connection to a voltage source U , $\tilde{\mu}_e$ will also remain constant: $\tilde{\mu}_e = \mu_e - e\phi_{sol} = const$ and $\Delta\mu_e = e\Delta\phi_{sol}$. Then, each state of a homogeneous reaction characterized by extent of reaction ξ_r will correspond to a quasi-equilibrium redox system with a quasi-equilibrium chemical potential $\mu_e(\xi_r)$ (or, according to (S.15), to $E_{redox}(\xi_r)$)

By initializing the reaction in solution, it is possible to measure the transient characteristics of $\mu_e(t)$ in the system, fixing its beginning and end ($\mu_e(t) = const$). Then, each extent of reaction ξ_r will correspond to the time t from the beginning of the reaction, and transient “redox” reaction profiles can be obtained.

Consider the case when a homogeneous reaction is a redox reaction whose components completely determine the redox system; i.e., all components of a heterogeneous reaction are involved in the homogeneous reaction. In general form, we can write



where O_i, R_i are donors and acceptors of i -redox pairs participating in the reduction half-reaction, and O_j, R_j are donors and acceptors of j -redox pairs participating in the oxidation half-reaction.

Then, the thermodynamic affinity A_r of the homogeneous reaction in the gate solution can be expressed in terms of the corresponding chemical potentials ⁴:

$$A_r = \sum_i (\mu_{i,O} - \mu_{i,R}) + \sum_j (\mu_{j,R} - \mu_{j,O}) \quad (\text{S.17})$$

Provided that the rate of the heterogeneous reaction of the solution–electrode electron exchange is much higher than the rate of the homogeneous reaction, each reaction state (S.16) characterized by the extent of reaction, ξ_r , corresponds to quasi-equilibrium heterogeneous reactions:



where n_i and n_j are the numbers of electrons participating in the half-reactions. From the conservation of charge in quasi-equilibrium, it follows that

$$\sum_i n_i = \sum_j n_j = N/2 \quad (\text{S.20})$$

The total affinity of the heterogeneous exchange will be equal to the sum of the affinities of all heterogeneous reactions (S.18), (S.19). Since the reaction components are under different potentials, the total affinity of heterogeneous reaction A_{RO} in this case must be written in terms of the electrochemical potentials of the reaction components:

$$A_{RO} = \sum_i (\tilde{\mu}_{i,O} - \tilde{\mu}_{i,R} + n_i \tilde{\mu}_e) + \sum_j (\tilde{\mu}_{j,R} - n_j \tilde{\mu}_e - \tilde{\mu}_{j,O}) \quad (\text{S.21})$$

The ions participating in the exchange reactions are in the liquid under the potential ϕ_{sol} ; therefore,

$$\tilde{\mu}_{i,O} - \tilde{\mu}_{i,R} = \mu_{i,O} - \mu_{i,R} + e\phi_{sol}(z_{i,O} - z_{i,R}) = \mu_{i,O} - \mu_{i,R} + e\phi_{sol}n_i \quad (\text{S.22})$$

where $z_{i,O}$ and $z_{i,R}$ are ion charges, and $z_{i,O} - z_{i,R} = n_i$. A similar relation can be written for the j -redox pairs. From (S.20) and (S.22), it follows that

$$A_{RO} = \sum_i(\mu_{i,O} - \mu_{i,R}) + \sum_j(\mu_{j,O} - \mu_{j,R}) + e\phi_{sol}N \quad (\text{S.23})$$

Quasi-equilibrium is characterized by zero affinity and the equality of the electrochemical potentials of the electrode and solution. Therefore, for all ξ_r , $A_{RO} = 0$ and $\tilde{\mu}_e = \varepsilon_F^{ME} = \text{const.}$ Under this condition, from the expressions (S.7), (S.17), and (S.23) it follows that

$$\Delta A_r = -N\Delta\mu_e \quad (\text{S.24})$$

where N is the total number of donor and acceptor electrons participating in the homogeneous reaction. Under constant temperature and pressure, A_r for a redox reaction is associated with the Gibbs energy of the reaction as

$$A_r = -\Delta_r G_m = \left(\frac{\partial G_r}{\partial \xi_r} \right)_{T,P} \quad (\text{S.25})$$

and (5) is a form of the well-known Gibbs energy conversion relation of an electrochemical reaction in the work of transferring an electric charge in a circuit $\Delta G_r = -nF\Delta E_{cell}$, indicating that the measured “redox” profiles will correspond to temporary changes in Gibbs energy during the reaction. By combining (S.14), (S.24), and (S.25), one can obtain

$$\frac{\Delta\mu_e}{e} = \frac{\Delta(\Delta_r G_m)}{Ne} = f^{-1}(\Delta I_{DS})|_{V_{DS}, \mu_e} \quad (\text{S.26})$$

Thus, the relative changes in the chemical potential of the electrons are equal to the relative changes in Gibbs free energy during the redox reaction. However, as N is difficult to define from experiment to experiment, measurement of $\mu_e(\xi_r)$ provides a more universal measurement scale.

References

1. Schmickler, W. & Santos, E. *Interfacial Electrochemistry*. (Springer Berlin Heidelberg, 2010). doi:10.1007/978-3-642-04937-8

2. *Electrochemistry at Metal and Semiconductor Electrodes*. (Elsevier, 1998).
5 doi:10.1016/B978-0-444-82806-4.X5000-4

3. Khan, S. U. M., Kainthla, R. C. & Bockris, J. O. M. The redox potential and the Fermi level in solution. *J. Phys. Chem.* **91**, 5974–5977 (1987).

4. Kondepudi, D. & Prigogine, I. *Modern Thermodynamics*. (Wiley, 2014).
10 doi:10.1002/9781118698723