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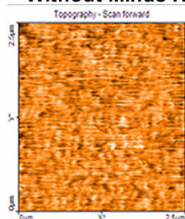
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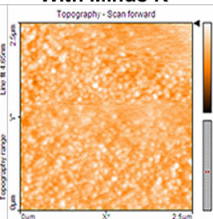
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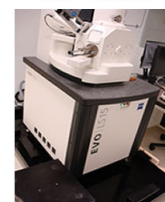
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Influence of the semiconductor oxidation potential on the operational stability of organic field-effect transistors

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During prolonged application of a gate bias, organic field-effect transistors show a gradual shift of the threshold voltage towards the applied gate bias voltage. The shift follows a stretched-exponential time dependence governed by a relaxation time. Here, we show that a thermodynamic analysis reproduces the observed exponential dependence of the relaxation time on the oxidation potential of the semiconductor. The good fit with the experimental data validates the underlying assumptions. It demonstrates that this operational instability is a straightforward thermodynamically driven process that can only be eliminated by eliminating water from the transistor. © 2011 American Institute of Physics. [doi:10.1063/1.3634066]

Progress in environmental stability, processability, and the increase of the field-effect mobility of organic semiconductors has triggered the use of organic field-effect transistors in the field of large-area electronics where numerous devices are integrated on low-cost substrates such as plastics. Examples are ultra low-cost contactless identification transponders (electronic barcodes) and pixel engines of flexible active matrix displays.¹⁻³ The bottleneck for commercialization is the operational reliability of the transistor. During prolonged operation, the threshold voltage—the gate bias at which the transistor switches on—shifts to the applied gate bias. The shift in threshold voltage leads to a monotonically decreasing source-drain current. Experimentally, it has been shown that the threshold-voltage shift follows a stretched-exponential time dependence⁴⁻⁶ as given by

$$\Delta V_{\text{th}}(t) = (V_G - V_{\text{th},0})(1 - \exp[-(t/\tau)^\beta]), \quad (1)$$

where V_G is the applied gate bias, $V_{\text{th},0}$ is the threshold voltage at time $t=0$, and β and τ are fit parameters. The exponent β is an indicator of the non-exponential behavior of the threshold-voltage shift. It is typically around 0.3 and shows a weak linear dependence on the temperature T .⁶ The parameter τ is referred to as the relaxation time of the threshold-voltage shift and is thermally activated as⁶

$$\tau = \tau_0 \exp\left(\frac{\epsilon_a}{k_B T}\right), \quad (2)$$

where k_B is the Boltzmann constant, τ_0 is a prefactor, and ϵ_a is the activation energy.

In Table I, values are compiled of τ_0 and ϵ_a measured for p -type field-effect transistors with SiO_2 gate dielectric using different semiconductors: poly(3-hexylthiophene) (P3HT), polytriarylamine (PTAA), polythienylene-vinylene (PTV), 3-butyl-quinquethiophene (3-BuT5), pentacene, and poly(9,9'-dioctyl-fluorene-co-bithiophene) (F8T2). These values were obtained by fitting the threshold-voltage shift as

a function of time to Eq. (1) and varying the temperature. This table shows that the activation energy ϵ_a depends surprisingly weakly on the organic semiconductor and that the differences in reliability are mainly due to differences in the prefactor τ_0 . There is no explanation yet for the value of this prefactor. The typical value of phonon-assisted attempt-to-escape times in disordered organic semiconductors is 10^{-14} s,⁷ orders of magnitude different from the values of τ_0 in Table I. This suggests that the large variation observed in the relaxation times for different organic semiconductors is not related to some phonon-assisted escape process.

In this letter, we will show that the relaxation time depends exponentially on the oxidation potential of the organic semiconductor, which is directly related to the energy of its highest occupied molecular orbital (HOMO). A quantitative theoretical interpretation is given based on a thermodynamic equilibrium between holes and protons in the semiconductor.

For the semiconductors in Table I, the HOMO energies were taken from literature or estimated from cyclic voltammetry measurements. In Fig. 1, the relaxation time τ at 25 °C is presented as a function of the HOMO energy. The relaxation time strongly increases with decreasing HOMO energy and appears to follow an exponential dependence. To explain this dependence, we use one of the accepted mechanisms for the occurrence of the instability. The threshold-

TABLE I. Prefactor τ_0 and activation energy ϵ_a of the relaxation time τ in Eq. (2) of the threshold-voltage shift of organic field-effect transistors with different semiconductors measured under vacuum conditions. The relaxation time at room temperature (25 °C) is also given.

Semiconductor	τ_0 [s]	ϵ_a [eV]	τ ($T=25$ °C) [s]	References
P3HT	3×10^{-3}	0.6 ± 0.1	4×10^7	Ref. 6
PTAA	8×10^{-4}	0.6 ± 0.1	1×10^7	Ref. 6
PTV	2×10^{-6}	0.62	6×10^4	Ref. 8
3-BuT5	3×10^{-7}	0.6 ± 0.1	3×10^3	Ref. 6
Pentacene	2×10^{-8}	0.67	4×10^3	Ref. 9
(Single crystal)				
F8T2	3×10^{-5}	0.52	1.5×10^4	Refs. 6 and 10

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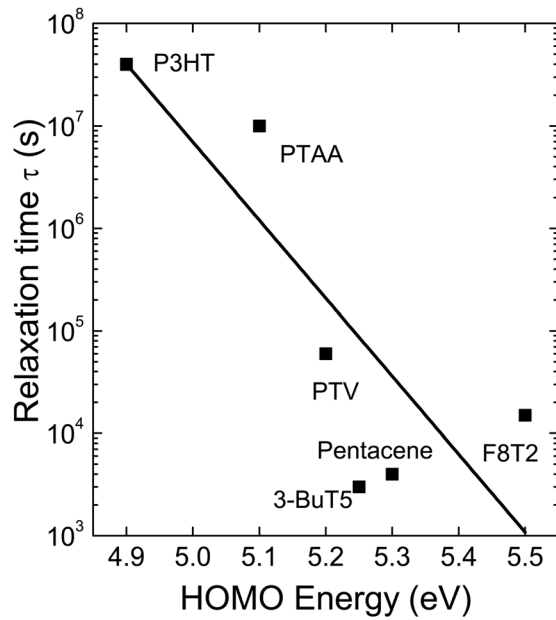
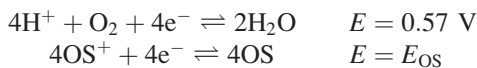


FIG. 1. Relaxation time τ at 25 °C from Table I as a function of the HOMO energy of the corresponding semiconductor (symbols). The fully drawn curve with slope $-1/2k_B T$ is a fit to the prediction equation (9), which follows from a thermodynamic analysis of the equilibrium between holes and protons in the semiconductor.

voltage shift could be quantitatively described by assuming the production of protons (H^+) from holes and water and the subsequent migration of these protons into the gate dielectric.¹¹ We note that even under vacuum conditions, water is expected to be present in the form of a monolayer adsorbed onto the SiO_2 surface.

Upon applying a negative gate bias, holes are accumulated in the organic semiconductor. Electrochemically, this is equivalent to an oxidation of the semiconductor. In turn, the oxidized semiconductor can oxidize water upon the production of protons. The corresponding half reactions are presented below together with the electrode potentials E ,



The electrode potentials are given versus the standard calomel electrode (SCE). The value for the oxidation potential of water is taken, assuming a pH of 7, and E_{OS} is the oxidation potential of the semiconductor. OS refers to a unit of the neutral organic semiconductor that can carry a charge and OS^+ to an oxidized unit carrying a hole.

The net result of the above reaction is that, in presence of water, holes can be reversibly converted into protons. The free energy change associated with the combined reaction equation (3) is given by

$$\Delta G = -nF(E_{OS} - 0.57V), \quad (4)$$

where $n=4$ is the number of electrons transferred in the reaction and F is the Faraday constant (the charge of a mole of electrons). The forward reaction in Eq. (3) proceeds when ΔG is negative, implying that $E_{OS} > 0.57$ V. The oxidation potential of the organic semiconductor is related to its

HOMO energy by $\epsilon_{HOMO} = e(E_{OS} + 4.4V)$, where e is the electronic charge.¹² Hence, the higher the HOMO energy, the larger the driving force to electrolytically produce protons, in agreement with the trend in Fig. 1. The trend of a decreasing relaxation time with increasing HOMO energy was recently also found by Lee *et al.*¹³ A quantitative analysis is presented below.

To describe the threshold-voltage shift, it was assumed that there is a thermodynamic equilibrium between holes in the accumulation layer and protons in the SiO_2 gate dielectric at the interface with the semiconductor, with the protons moving into the bulk of the SiO_2 predominantly by diffusion.¹¹ The time scale of the conversion of holes into protons was assumed to be much faster than that of the motion into the SiO_2 , so that the rate-limiting step for the shift is the motion of protons into the gate dielectric. The equilibrium between the surface density σ_{holes} of holes in the accumulation layer of the organic semiconductor and the volume density $\rho_{protons}$ of protons in the SiO_2 at the interface with the semiconductor can be expressed as

$$\rho_{protons} = \alpha \sigma_{holes}. \quad (5)$$

where the parameter α is a proportionality constant. The motion of protons in the SiO_2 is determined by their diffusion constant $D = D_0 \exp(-\epsilon_d/k_B T)$, where ϵ_d is the activation energy for diffusion of protons in SiO_2 . Within this framework, the relaxation time τ was derived as¹⁴

$$\tau \propto \frac{1}{\alpha^2 D} = \frac{1}{\alpha^2 D_0} \exp\left(\frac{\epsilon_d}{k_B T}\right). \quad (6)$$

It follows from Eq. (6) that the relaxation time depends on the semiconductor only through the parameter α . The activation energy for proton diffusion in SiO_2 is calculated to be $\epsilon_d = 0.5eV$,¹⁵ surprisingly close to the activation energies in Table I.

The difference in relaxation times for different semiconductors is due to different values of α . The parameter α represents a ratio between a proton and a hole concentration, which follows immediately from the equilibrium constant K of the combined reaction equation (3). We can write the equilibrium constant K for this reaction as

$$K = \frac{[OS]^4 [O_2] [H^+]^4}{[H_2O]^2 [OS^+]^4}, \quad (7)$$

where we have replaced the activity of the components by their concentrations. We note that O_2 can be present in the form of oxygen molecules solvated by water molecules.¹⁶ In equilibrium at temperature T , $\Delta G = -RT \log K$, where R is the gas constant. The concentration of neutral organic semiconductor units $[OS]$ is by definition unity. Together with Eq. (4) and the relation between ϵ_{HOMO} and E_{OS} , the following expression can then be derived for α :

$$\alpha = \frac{\rho_{protons}}{\sigma_{holes}} \propto \frac{[H^+]}{[OS^+]} \propto \frac{[H_2O]^{1/2}}{[O_2]^{1/4}} \exp\left[\frac{(\epsilon_{HOMO} - 4.97eV)}{4k_B T}\right]. \quad (8)$$

Substituting this expression in the expression equation (6) for the relaxation time, we obtain

$$\tau \propto \frac{[\text{O}_2]^{1/2}}{[\text{H}_2\text{O}]} \exp\left[-\frac{(\epsilon_{\text{HOMO}} - 4.97\text{eV})}{2k_{\text{B}}T}\right] \exp\left(\frac{\epsilon_{\text{d}}}{k_{\text{B}}T}\right). \quad (9)$$

We note that in the derivation above, we have assumed that $\rho_{\text{protons}}/\sigma_{\text{holes}}$ is proportional to $[\text{H}^+]/[\text{OS}^+]$. The replacement of σ_{holes} by $[\text{OS}^+]$ involves a replacement of a surface concentration by a volume concentration and should, therefore, be accompanied by a multiplication with a factor having the dimension of a length, which should be of the order of the thickness of the accumulation layer in the semiconductor (of the order of a nm). The replacement of ρ_{protons} by $[\text{H}^+]$ should be accompanied by a dimensionless factor accounting for the continuity of the chemical potential of the protons at the interface between the semiconductor and the gate dielectric. We have neglected the dependence of both factors on the semiconductor, assuming that such dependence is less important than the exponential dependence on ϵ_{HOMO} in Eq. (9).

We conclude from Eq. (9) that the activation energy ϵ_{a} in the relaxation time, Eq. (2), is not precisely equivalent to the activation energy ϵ_{d} for diffusion of protons in SiO_2 , but is corrected by a term $(\epsilon_{\text{HOMO}} - 4.97\text{eV})/2$, which is small for $\epsilon_{\text{HOMO}} \approx 5\text{eV}$. The uncertainties involved in the determination of ϵ_{a} , however, prohibit a quantitative analysis of this correction.

The fully drawn curve in Fig. 1 gives the dependence of the relaxation time on ϵ_{HOMO} according to Eq. (9). The slope is fixed to $-1/2k_{\text{B}}T$, while the proportionality constant is fitted to the data. The value of this constant cannot be verified due to the experimental uncertainties in the water content and partial oxygen pressure. However, even if the ambient conditions would be completely known, uncertainties would remain because of differences in water and oxygen uptake of the different organic semiconductors. Considering these uncertainties, we can say that the agreement between the measured and predicted dependence in Fig. 1 is very satisfactory.

The thermodynamic analysis above shows that with increasing HOMO energy, the driving force for electrolytic production of protons increases. In order to practically eliminate the operational instability, an organic semiconductor with a HOMO energy well below 5 eV should be used, for which ΔG in Eq. (4) becomes positive. Unfortunately, the

semiconductor then becomes environmentally unstable towards oxidation. Hence, stable organic transistors cannot be made by adjusting the HOMO energy, but only by eliminating water.

In summary, we have quantitatively explained the dependence on the semiconductor of the relaxation time in the operational instability of organic field-effect transistors. The orders of magnitude variation in relaxation times for transistors made from different organic semiconductors cannot be related to variations in an attempt-to-escape frequency. We have shown that the relaxation time scales exponentially with the HOMO energy of the semiconductor. A quantitative interpretation is presented based on the equilibrium of holes in the accumulation layer and electrolytically produced protons diffusing into the gate dielectric. A thermodynamic analysis has reproduced the exponential dependence of the relaxation time on the HOMO energy. The good fit with the experimental data validates the underlying assumptions. It demonstrates that the instability is a straightforward thermodynamically driven process that can only be eliminated by eliminating water from the transistor.

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