FLUCTUATION ANALYSIS OF WORK FUNCTION OF ORGANIC SEMICONDUCTORS

Ryan M. WEST[1], Colby R. WATTS[2], Mira JOSOWICZ[3] and Jiří JANATA[4,*]

*Georgia Institute of Technology, School of Chemistry and Biochemistry,
901 Atlantic Drive, NW, Atlanta, GA 30332-0400, U.S.A.; e-mail: [1] gtg897u@gmail.com,
[2] colby.r.watts@gmail.com, [3] mira.josowicz@chemistry.gatech.edu,
[4] jiri.janata@chemistry.gatech.edu*

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With this paper we honor birthdays of our colleagues who are present and former members of the "Polarografický Ústav": Michael Heyrovský (80), Robert Kalvoda (85), Lubomír Pospíšil (70), Karel Štulík (70), Jiří Volke (85) and Petr Zuman (85).

We demonstrate, for the first time, work function fluctuations of a polyaniline film when used as the gate conductor of an insulated-gate field-effect transistor. The work function fluctuations induce drain current fluctuations, which are in excess of the channel noise of the transistor and the Nyquist noise of the polyaniline film. Using the fluctuation-dissipation theorem, it is determined that the fluctuations have a Lorentzian-like spectrum and are thermally activated with an activated energy of ca. 300 meV. The activation energy, as well as the corner frequency and magnitude of the fluctuations, depend on the applied electric field at the polyaniline–insulator interface. These results, along with coherence measurements, suggest that the fluctuations originate near the interface in the space-charge region of polyaniline. This technique provides kinetic and thermodynamic information about the gate conductor, at equilibrium, which cannot be extracted using other techniques that measure work function. Furthermore, by this technique it is possible to distinguish the fluctuations of the work function from the Nyquist noise. This approach should be generally applicable to any semiconducting material used as the gate conductor of a field-effect transistor.
Keywords: Statistical mechanics; Kinetics; Materials science; Work function; Organic semiconductors; Semiconductor field-effect; Fluctuation-dissipation theorem; Field-effect transistor.

Work function (WF) is a fundamental thermodynamic property of any electronic material. It describes the partial molar free energy of an electron at equilibrium, i.e. its electrochemical potential referenced to the vacuum reference level. It is the work required to remove an electron from the bulk of

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the material, through the electrostatic barrier at the material surface and place it outside the electrostatic field, in the vacuum reference level. As a result, WF is highly sensitive to the material bulk structure, oxidation state, and the structure of the interface/surface. Organic semiconductors (OS) have been used extensively as active components of organic electronics, including various optoelectronic and electronic solid state devices[1,2] as well as solid-state chemical sensors[3,4]. Unlike silicon, OS are subject to modulation of their WF by secondary doping, i.e. by interaction with donor/acceptor gases[5]. Work function can be exploited in a new class of solid state chemical sensors[6], but it may cause problems in other types of organic electronic devices in which rigorous encapsulation (i.e. passivation) is required and is of paramount importance. In general, structure-function relationships of OS are far more complex than those of inorganic semiconductors and remain an area of active research. Work function measurements are useful for studying these relationships.

Ability to measure WF and its changes under equilibrium, atmospheric conditions is essential, whether the secondary doping occurs as a beneficial or an adverse effect. There are two principal approaches to performing such measurements: Kelvin probe (vibrating capacitor)[7] and an insulated gate field-effect transistor (IGFET)[8]. In the former the material of interest forms one plate of a capacitor, whose capacitance is changed by periodically varying the distance between the plates, hence the "vibrating capacitor". The resulting oscillating signal is nulled-out by applying a compensating voltage that is proportional to the difference of the work functions of the two plates forming the capacitor. Such method is by definition *deterministic*. The IGFET is unique in that true equilibrium (in the material of interest) is not only maintained but required, i.e. no mechanical or electrical perturbations of the material are induced. Furthermore, the IGFET is capable of measuring WF changes in real-time and such measurements are only limited by the response time of the device itself. For the devices used in this study the upper frequency limit is in the MHz range.

Here we introduce a new and unique method for measurement of equilibrium and dynamic properties of organic semiconductors under atmospheric conditions. Our approach is based on fluctuation analysis of drain current noise in an IGFET in which the gate conductor is the material under study. A similar approach was used for fluctuation analysis of ion selective field-effect transistors[9]. For more details, there are a number of books and reviews available on both device physics[10,11] and fluctuation analysis[12–14]. The key point to be made (and to be taken advantage of) is that all thermodynamic quantities fluctuate around their equilibrium values. Hidden within this “noise” is information about the fluctuating quantity and the underlying kinetic process(es), such as the time constant. In this paper, the drain current, $I_D(t)$, of an IGFET with polyaniline gate electrode is the experimental observable. At steady-state, i.e. constant current and drain voltage, $I_D(t)$ can be written as the sum of a DC component (mean current), I_{DC}, and fluctuations around this mean value, $i(t)$, commonly referred to as “noise”

$$I_D(t) = I_{DC} + i(t). \tag{1}$$

The information is obtained from $i(t)$ and I_{DC} is ignored. In the saturation regime, the drain current of an *n*-channel, enhancement mode IGFET is determined by the applied gate voltage, V_G, and threshold voltage of the device, V_T, according to

$$I_D = \frac{\mu_n C_O W}{2L}(V_G - V_T)^2 \tag{2}$$

where μ_n is the electron mobility in the channel, C_O is the capacitance of the gate insulator, W is the width of the channel, and L is the channel length. In Eq. (*2*) the trapped charges in the dielectric and the surface states are ignored for simplicity. For an ideal IGFET the V_T is defined by the difference in work function, $\Delta\phi$, between the gate conductor (i.e. OS) and the p–Si substrate according to

$$V_T = \frac{\phi_{Si} - \phi_{OS}(t)}{e} \tag{3}$$

where e is the charge on an electron (1.602×10^{-19} C). The time dependence of $\Delta\phi_{OS}$ is due to equilibrium fluctuations. The transconductance, g_m, of the transistor is given by

$$g_m = \left(\frac{\partial I_D}{\partial V_G}\right)_{V_D} = \frac{\mu_n C_O W}{2L}(V_G - V_T)\,. \tag{4}$$

It is clear that fluctuations in both V_T and V_G contribute to $i(t)$. The first term on the right in Eqs (*2*) and (*4*) is assumed to be constant and therefore will not contribute to the noise. In addition to these “transduced” fluctuations, intrinsic resistance noise of the channel, which is typically $1/f$, also contributes to $i(t)$.

The drain current noise can be written in the frequency domain as the sum of three spectral densities

$$S_{I_D}(f) = g_m^2 S_{V_G}(f) + g_m^2 S_{V_T}(f) + \frac{A}{f} \quad (5)$$

where A is a constant of the device and $S_x(f)$ denotes the noise spectral density of the fluctuating quantity x. The spectral density $S_x(f)$ is a measure of the variance per frequency and is obtained by taking the absolute value squared of the Fourier transform of the fluctuating signal and dividing it by the frequency interval. According to the Wiener–Khinchine theorem, $S_x(f)$ is the Fourier transform of the time-autocorrelation function of the noise[13]. The first term on the right-hand side of Eq. (5) is the drain current noise induced by gate voltage fluctuations. Fluctuations in gate voltage can be caused by either a noisy voltage source and/or by the intrinsic voltage fluctuations in the gate conductor known as Johnson noise (or thermal noise). Johnson noise is due to random motion of charge carriers within the conductor and is linked to the real part of the impedance Z_{re} by the Nyquist equation[12,13]

$$S_V(f) = 4k_b T Z_{re}(f) \quad (6)$$

where k_b is the Boltzmann constant and T is the temperature in K. All conducting materials, at equilibrium, generate voltage noise given by Eq. (6), irrespective of the material or the mode of conduction. The second term on the right-hand side of Eq. (5) is the noise caused by the fluctuations of WF of the OS. In this study, it is the entity of interest. In order to demonstrate this new approach we have used a common organic semiconductor polyaniline (PANI). We will show that the middle term in Eq. (5) dominates $i(t)$ for IGFETs with PANI gate conductor.

Extraction of information from $S_I(f)$ is facilitated using the fluctuation-dissipation theorem[13] which allows extraction of kinetic information from experimental observation of a system in true thermal equilibrium. For an arbitrary fluctuating quantity with underlying exponential kinetics the power spectral density is given by a simple Lorentzian

$$S(f) = \frac{2\sigma^2}{f_\tau \pi} \frac{1}{1 + (f/f_\tau)^2} \quad (7)$$

where σ^2 is the variance of the fluctuating signal, f is the frequency, and f_τ is the corner frequency which is related to the time constant of the dominating kinetic process by

$$f_\tau = \frac{1}{2\pi\tau} . \tag{8}$$

The variance can be computed from equilibrium statistical mechanics, and thus contains information about the equilibrium state of the system. On the other hand, f_τ depends on the rate constants. Thus, from the measurement of noise spectral density of an (exponential) kinetic process, at equilibrium, both kinetic (f_τ) and equilibrium (σ^2) information can be obtained. By using the relationships given by Eqs (*3*), (*4*) and (*8*) for an IGFET we can study WF fluctuations in organic semiconductors used as the conducting gate material.

EXPERIMENTAL

Figure 1a shows the circuit used for measuring drain current fluctuations of IGFET. The gate voltage was applied by a 12 V lead-acid battery through a variable 10 kΩ resistor and a low-pass filter (f_{LP} = 1.59 Hz). The drain voltage is provided by a 6 V lead-acid battery. The drain current was measured across a low-noise, high precision (0.01%) 10 kΩ resistor (Mills MR102T 0829) and AC-coupled into a low-noise pre-amplifier (SR560) and amplified 1000×. The amplifier was AC powered after it was determined that this did not introduced significant noise. The output was then fed into a 24-bit data acquisition card (National Instruments USB-4431) at a sampling rate of 100,000 kS/s. Spectral densities were computed from 100 ms of data (10,000 samples) to give a frequency range of 10–100,000 Hz. 5000 of these spectra were averaged for each spectrum presented in this paper. Electromagnetic shielding was provided by a 1/4″ thick stainless steel, grounded faraday cage.

The preparation and characterization of the films and transistors are given elsewhere[15]. The IGFETs are *n*-channel, enhancement mode devices. Current–voltage characteristics (I_D–V_D and I_D–V_G) and leakage tests were performed on each IGFET before and after measurements. All devices behaved according to standard IGFET equations and no leakage current was detected. Typical threshold voltages for the IGFETs were 0.25–0.5 V. Figures 1b and 1c show top view and cross-section, respectively, of the chip containing four IGFETs. The bottom two IGEFTs have platinum metal gate electrodes (Pt-IGFET) while the, otherwise identical, IGFETs at the top have open gate insulators with Pt metal contacts on either side of the channels over which a continuous, doped polyaniline film was cast (PANI-IGFET). The gate channel dimensions are: W = 400 μm, L = 20 μm (drawing is to scale). Thickness of the PANI film is approx. 350 nm. The composite gate insulator consists of 80 nm of SiO_2 and 80 nm of Si_3N_4 (high temperature). The capacitance of the gate is 5 pF. The platinum contacts were used to measure the film resistance. The resistances were on the order of 1 MΩ. The chips were mounted on 28-pin headers with silver epoxy and wire-bonded for electrical contact. The IGFET devices were operated in the saturation regime. Note that no current passes through the thin (350 nm) PANI layer during measurement; true equilibrium

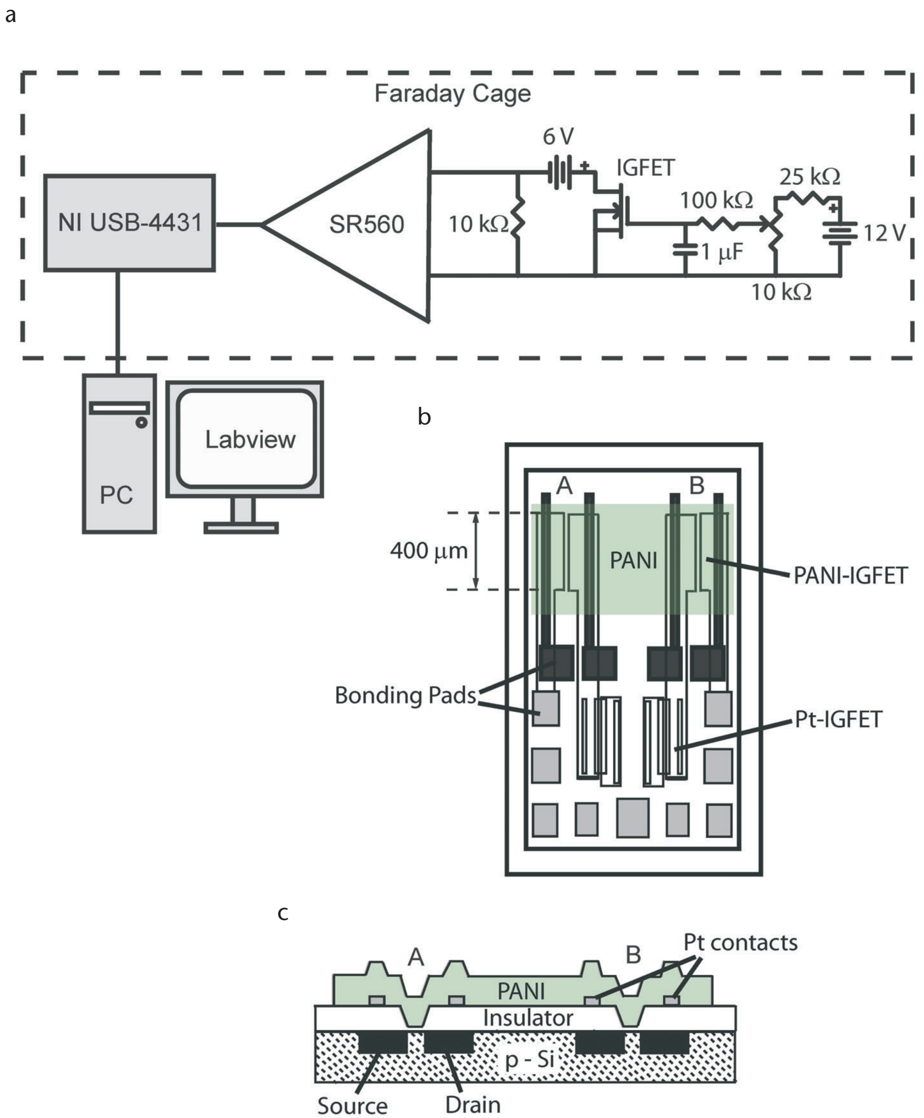

FIG. 1
Instrumentation used for fluctuation analysis of IGFET: The circuit used for IGFET operation and drain current measurement along with faraday cage, pre-amplifier and data acquisition card (a). Transistor chip housing four geometrically identical insulated gate field-effect transistors; two with platinum metal gate (Pt-IGFET) and two with open gate insulator over which a doped polyaniline film is cast (PANI-IGFET) (b). Cross-section of the PANI-IGFET (c)

is a necessary condition if kinetic information is to be extracted[16]. The temperature was controlled via water circulating through a thin, glass flow-cell mounted on the top of the chip header. The flow-cell and header were in direct thermal contact. The top of the chip (and PANI film) were separated (by air) from the flow cell by less than 0.5 mm. Thermal equilibrium was verified by monitoring drain current at constant gate voltage until no drift was noticeable.

RESULTS

Typical drain current noise spectral density of a PANI-IGFET is shown in Fig. 2 (green). The inset in Fig. 2a shows one 100 ms segment of drain current noise from which the spectral density was calculated. The same data is shown in Figs 2a and 2b except that in the latter the spectral density has been multiplied by the frequency. In this representation the corner frequency is easily identified as a peak. The arrows in both Figs 2a and 2b point to the corner frequency at ~3000 Hz. The spectral shape is characteristic of a kinetic process with smeared exponential relaxation. As such it could not be fit by a single Lorentzian (light blue curve in Fig. 2b). However, it retains its characteristic Lorentzian shape. Because spectral densities are additive (Eq. (*5*)) it is possible to separate the individual contributions and to isolate the "excess noise" from which the information of interest is extracted. It has been determined that the drain current noise of the PANI-IGFET is in excess to all other noise sources present in the measurement set-up. The intrinsic channel noise (the flicker noise) was measured using the geometrically identical Pt-IGFET on the same chip (see Fig. 1b), under identical operating conditions. As shown in Fig. 2 (red curve), the Pt-IGFET drain current noise is at least one order-of-magnitude lower than the drain current noise observed at the PANI-IGFET. Also, the spectral shape is different. For comparison, thermal noise of the 10 kΩ measurement resistor (at zero current), along with line noise (the "spikes") and amplifier noise, is shown in Fig. 2 (dark blue curve) on the same scale.

There is no current passing through the PANI film. However, because it is a resistor it contributes to gate voltage fluctuations as the Nyquist noise due to the random motion of charge carriers in the film (Eq. (*6*)). In order to determine the extent of the Nyquist contribution of the PANI film, the equivalent drain current spectral density, $S_{I,Ny}$, was calculated, using the Nyquist equation, according to

$$S_{I,Ny} = 4k_B T Z_{re} g_m^2 \qquad (9)$$

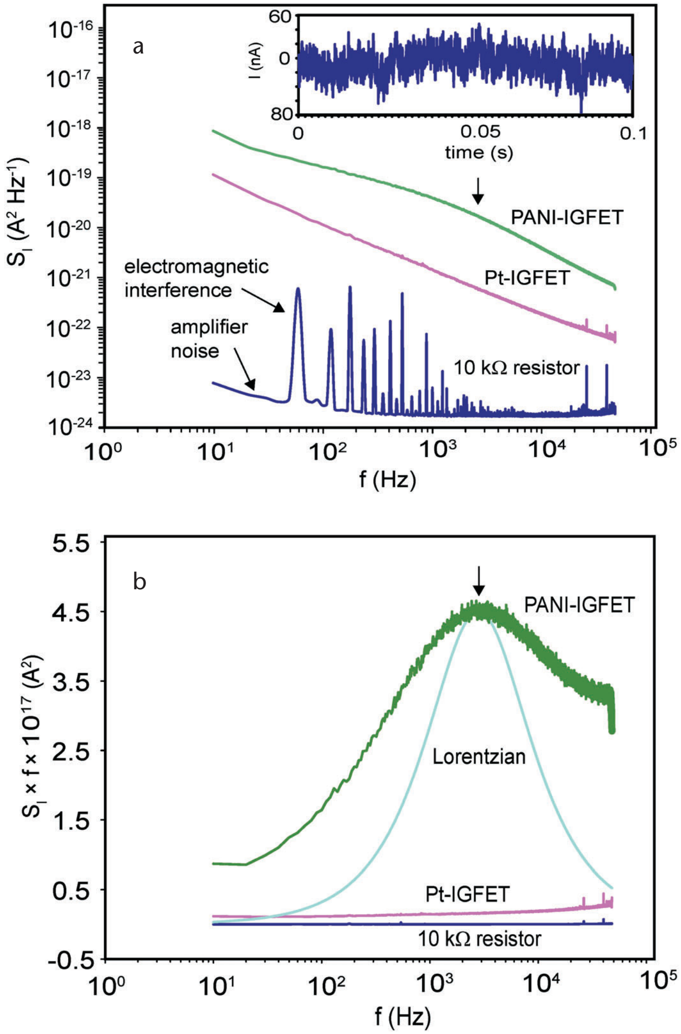

FIG. 2

Spectral density of drain-current fluctuations for PANI-IGFET (green) and Pt-IGFET (red). Both a and b show the same data in different representations. The arrow around 3000 Hz points to the average corner frequency. The inset in a is one segment of the raw time record collected over 100 ms interval. 5000 of such segments were collected for Fourier analysis. For comparison, equivalent Nyquist noise from the 10 kΩ resistor is presented on the same scale (dark blue). The spikes are due to line noise and the slight upward slope at low frequencies is caused by amplifier noise. The light blue curve in b is a theoretical Lorenztian calculated from Eq. (*7*) where Z_{re} is the real part of the impedance, and g_m is the PANI-IGFET transconductance as given in Eq. (*4*). In order to display the two spectral densities on the same scale the Nyquist noise ($S_{I,Ny}$) was converted using the appropriate transconductance (Eq. (*9*)). The impedance Z_{re} was measured from the Pt gate contacts to source (i.e. to the ground) with a DC bias of 1.5 V and AC amplitude of 10 mV. The result is shown in Fig. 3. The real component Z_{re} of impedance was also measured independently between the two Pt gate contacts at the top of the gate. The noise contribution calculated from this measurement was nearly identical to the one calculated from the gate-to-source measurement and again negligible compared to the work function contribution $S_{I,W}$. Therefore, it is concluded that observed fluctuations in threshold voltage responsible for the PANI-IGFET drain current noise can be attributed solely to thermally induced, spontaneous, and stochastic fluctuations of work function of the polyaniline gate conductor (Eq. (*3*)). Therefore, the possibility of separating the Nyquist and the WF fluctuations is probably the most valuable methodological aspect of this work.

In order to elucidate the effect of electric field on work function fluctuations, the spectral densities were obtained at V_G = 1.0, 1.25, 1.5, and 2.0 V

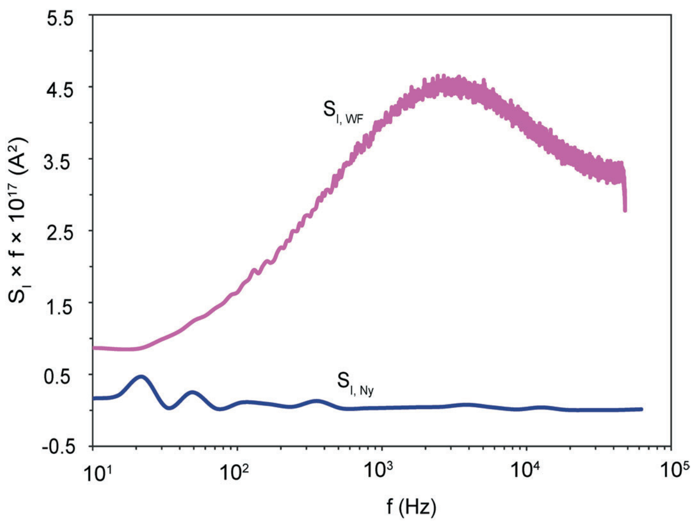

FIG. 3
Two contributions to the drain current spectral density S_I of a PANI-IGFET. $S_{I,WF}$ fluctuation (red) and equivalent Nyquist noise $S_{I,Ny}$ (blue) originating from the resistance Z_{re} of PANI (Eq. (*6*)). Both contributions were measured at V_G = 1.5 V

(Fig. 4). Using Eqs (*3*) and (*4*), the drain current fluctuations are expressed as fluctuations of work function so that the magnitudes can be compared. First we show that the time constant decreases with increasing gate voltage. This may be a result of the increasing electric field or the increase in charge carrier density. The magnitudes of the peaks shown in Fig. 4 are proportional to the variance, σ^2, of the work function fluctuations

$$f_\tau S_{WF}(f_\tau) = f_\tau \frac{2\sigma^2}{f_\tau \pi} \frac{1}{1+(f/f_\tau)^2} = \frac{\sigma^2}{\pi} \qquad (10)$$

where f_τ is the corner frequency. Surprisingly, the variance also decreases with increasing gate voltage. In general, the variance of any thermodynamic fluctuation is proportional to the size of the system for extensive quantities, while the opposite is true for intensive quantities[17]. Since work function is an intensive quantity, the decrease in magnitude may indicate that the system size is increasing. Obviously, the thickness of the PANI film did not change. It is possible, however, that the measured noise originates only in a subsection of the film. In order to examine this possibility, drain current fluctuations were measured, simultaneously, on two PANI-IGFETs,

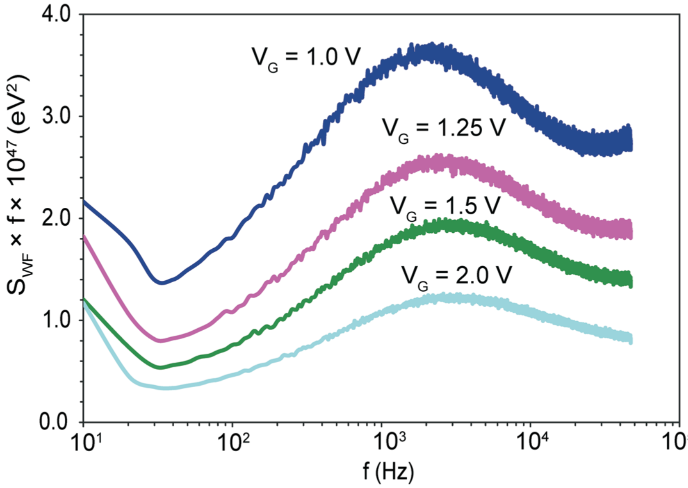

FIG. 4
Power spectral density of work function fluctuations S_{WF} measured at four applied gate voltages V_G at 298 K. The corresponding transconductances were: g_m = 107.68 uS @ V_G = 1 V, g_m = 180.964 uS @ V_G = 1.25 V, g_m = 176.465 uS @ V_G = 1.5 V, and g_m = 353.333 uS @ V_G = 2.0 V

A and B, sharing a common PANI gate conductor (see Fig. 1). The coherence between those two IGFETs was calculated from the cross- and auto-spectral densities. The coherence is a normalized measure of the common signal between the two IGFETs [18]. These measurements have shown that the fluctuations are not spatially correlated within the bulk of the film. The most likely explanation of such a lack of correlation is that the inherent resistance of the PANI film acts as a low-pass filter that does not allow correlation of the signal. Therefore, the observed noise must originate at the region that couples with the channel through the electric field, i.e. the space charge at the interface between the dielectric and the PANI layer. As the gate voltage increases, the number of particles in this region also increases, thus, decreasing the variance of fluctuations. The fluctuations of the bulk component of the WF are possible, indeed very likely, but at present lie outside the observation window of the resistive PANI film. The dependence of the variance on the applied gate voltage, i.e. on the electric field at the interface further corroborates this space charge model.

To further probe the origin of work function fluctuations in the PANI gate conductor, the kinetics were studied as a function of temperature at constant gate voltage of 1.5 V (Fig. 5). The inset clearly shows that both the

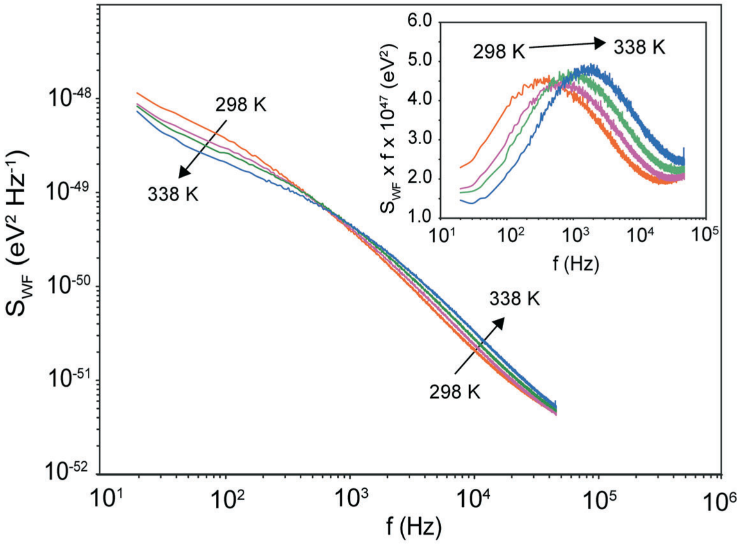

FIG. 5
Temperature dependence of WF measured in the range 298–338 K. The “isosbestic point” at ~700 Hz is more clearly visible in the power spectral density representation while the shift of the corner frequency is more visible in the inset. All measurements were done at V_G = 1.5 V

magnitude and the corner frequency are increasing with increasing temperature. Increase of the magnitude is attributed to the thermodynamically driven dependence of noise variance on the thermal energy. The evolution of the corner frequency is due to the temperature-dependence of the time constant of a kinetic process. Note that the spectral density appears to be temperature independent at ca. 600 Hz. This apparent isosbestic point is also seen when the temperature dependence is probed at other gate voltages. We propose that this isosbestic point, which changes its location with gate voltage, is attributed to the continuously distributed, field-dependent time constant of the Lorentzian noise (see Fig. 2b)[19]. As the temperature increases, the distribution is shifted to higher frequencies. Such isosbestic point would not be present in the temperature-dependence of a pure Lorentzian noise.

The dependence of the corner frequency on temperature was investigated at gate voltages of 0.75, 1.0, 1.5, and 2.0 V (Fig. 7). As shown in Fig. 6, the corner frequency follows the Arrhenius temperature dependence (R^2 > 0.99), confirming that the work function fluctuations are caused by a thermally activated process. The activation energies at each gate voltage were calculated from the slope of the Arrhenius plot (see inset). The activation energy decreases with increasing gate voltage from 350 meV at 0.75 V to

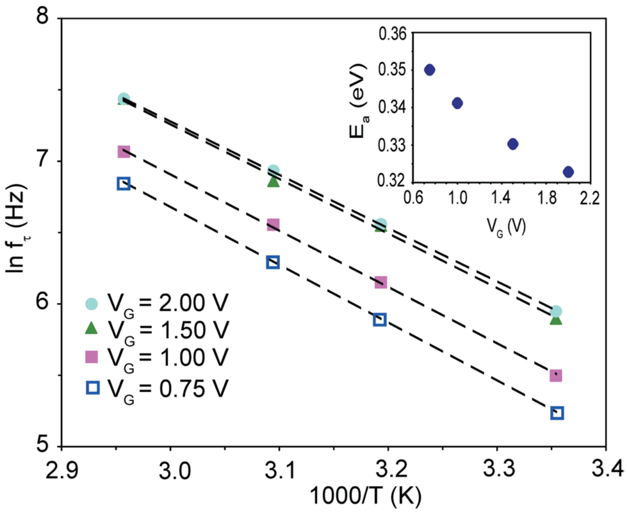

FIG. 6
Arrhenius plot of logarithm of corner frequency shift f_τ (in Hz) for various gate voltages. Inset: plot of activation energy E_a (in eV) as the function of applied gate voltage

320 meV at 2.0 V. This implies that either the increasing electric field or the increasing charge carrier density lowers the activation energy. The temperature dependence of the variance was also investigated at the same four gate voltages. The increase in noise variance with temperature is nearly linear. Interestingly, the variance is more susceptible to temperature changes as the gate voltage decreases. This can be understood in terms of the size-dependence argument as already mentioned above; as gate voltage is increased, the size of the region coupling to the transistor channel also increases, and the variance decreases. Thus, the slope of the variance with respect to temperature decreases with increasing gate voltage.

CONCLUSIONS

It has been shown that the "excess noise" (Figs 2 and 3) observed in the drain current of a PANI-IGFET can be attributed to the equilibrium thermal fluctuations of the work function of the organic semiconductor. Using the fluctuation-dissipation theorem the kinetic properties can be evaluated from the power spectral density of the fluctuations of drain current in the IGFET. In the temperature range 298 to 338 K a clearly distinguishable, yet broad, characteristic frequency is observed around 3 kHz. The origin of these fluctuations is unclear at this point but it can be associated with fluctuations of the charge carrier density, with the thermal motion of the poly-

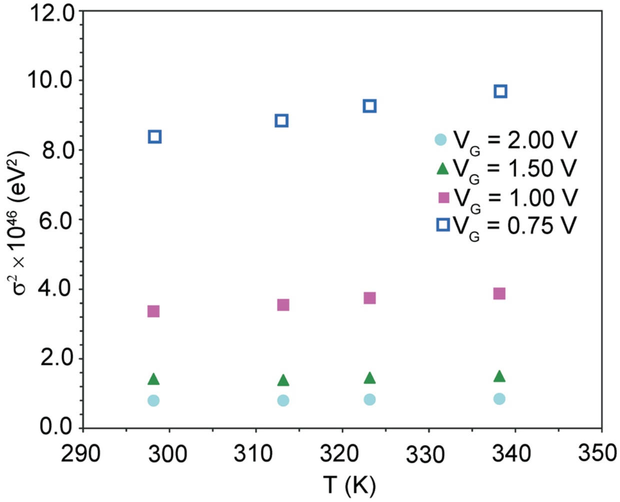

FIG. 7
Temperature dependence of WF variance, σ_{WF}, for different applied gate voltages

mer chains, with the kinetics of mobile charge trapping/de-trapping, or stochastic fluctuations of the dipoles at the OS–insulator interface. It is an activated process, with activation energy in the range 0.32–0.35 eV. It is interesting to note that this activation energy depends on the electric field at the insulator/PANI interface. It is decreasing with increasing electric field and so is the magnitude of the fluctuations. A similar trend of activation energy with gate voltage has been observed from drain current measurements of organic field effect transistors (OFET)[20]. The activation energy was due to trapping at single grain boundaries of sexithiophene. We can deduce from the field dependence of the magnitude, as well as the absence of coherence between channels A and B, that the fluctuations have a finite correlation length. A useful analogy is that of local concentration fluctuations in an electrolyte solution. Macroscopically, the solution has a mean conductivity and ionic strength, but in any small volume element these properties fluctuate. Furthermore, the fluctuations in two different volume elements, while statistically the same, are not correlated: they are not fluctuating "in sync". Likewise, the work function of the OS, while having an average macroscopic value, can fluctuate locally within the film. Because of the direct coupling to the channel through the electric field, the WF fluctuations within a correlation length of the OS–insulator interface are the only ones detectable with this approach.

On the basis of the experimental evidence presented in this paper we propose a model of silicon–insulator–OS junction, as it exists in the gate of a field-effect transistor with OS gate conductor. It should be noted that unlike in the so-called "organic field-effect transistors" (OFET) no current passes through the OS. Therefore, the material is in true thermal equilibrium and the silicon part of the device represents the "observation tool". The physical representation of this model is shown in Figs 8a and 8b. In the saturation regime, a space charge, of equal but opposite charge, is formed on each side of the insulator as shown in Fig. 8a. Charge neutrality condition is satisfied in the bulk. Because the WF fluctuations have a finite correlation length, the drain current is only affected by fluctuations near the OS–insulator interface. Fluctuations in the OS space charge, q_{sp}^{+}, are coupled to fluctuations of the charge in the channel, q_n^{-} through the electric field in the insulator. The energy diagram, under flat-band conditions, is shown in Fig. 8b. The flat-band condition implies no band-bending in the OS (no space charge) and a flat vacuum level across the insulator. This condition is used here only as an aid to illustrate how fluctuations in work function, σ_{WF}, result in measurable fluctuations in flat-band voltage, σ_V, i.e. threshold voltage fluctuations. Although we believe that the work function

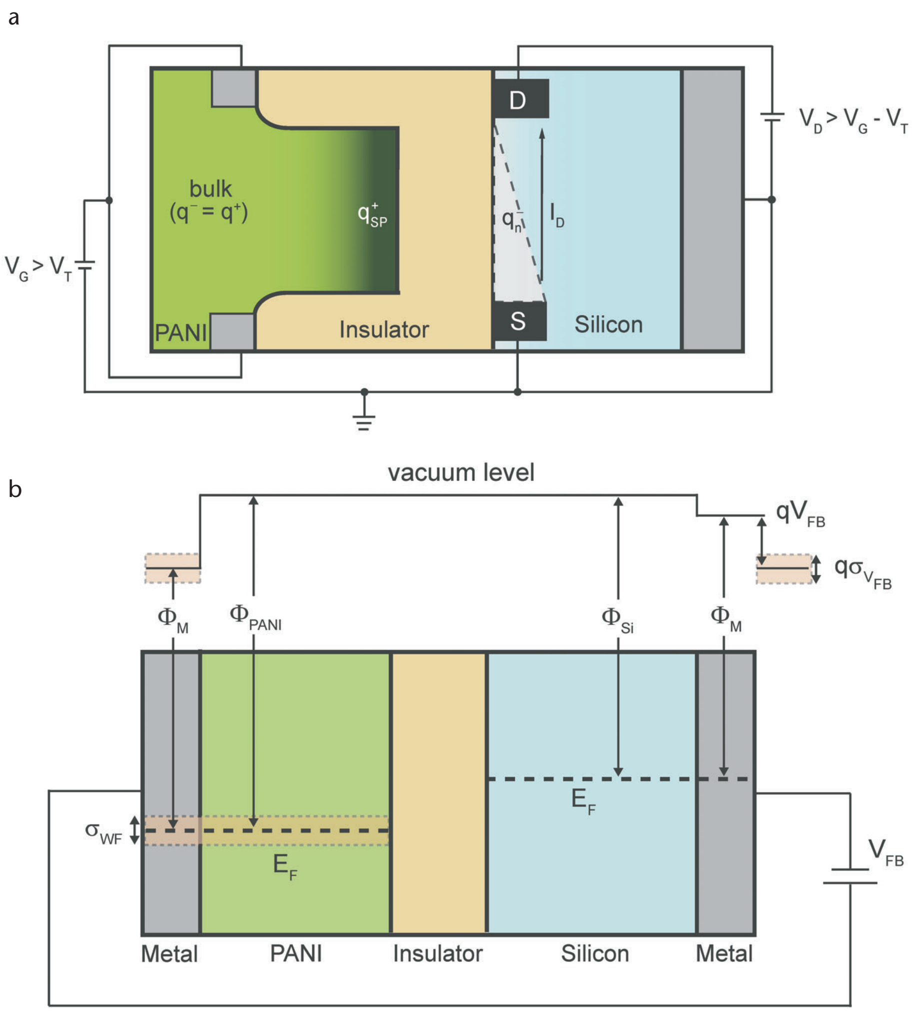

FIG. 8
a Proposed model of gate capacitor for interpretation of work function fluctuations in PANI-IGFET. The device is operating in the saturation regime, $V_G > V_T$ and $V_D > V_G - V_T$. The space charge in the OS, q_{SP}^+ is coupled to the channel in the silicon, q_n^-, through the electric field. Fluctuations of q_n^- result in fluctuations of drain current I_D. b Energy band diagram of the silicon–insulator–OS junction under flat-band conditions (adapted from Janata[8]). Here, the flat-band voltage, V_{FB}, is applied so that no electric field is present in the insulator, i.e. the vacuum level is flat across the silicon–insulator–OS interface. Fluctuations of OS work function are depicted by the small band around the OS Fermi level

fluctuations occur independently of space charge formation, we cannot rule out that the presence of the space charge at the insulator is necessary for the measurement of the fluctuations, much like the passage of current is necessary for the measurement of resistance. To our knowledge the equilibrium fluctuation analysis of IGFET with OS gate is the only feasible experimental approach for obtaining kinetic information about WF fluctuation and its spatial origin. It is interesting to note that, the calculation of the impedance of the PANI from the observed noise would yield an unrealistically high value of approxomately 10 GΩ. It would contradict the value of impedance directly obtained from ac measurement between the two Pt contacts. It further underscores the unique advantage of this technique to yield information about dynamics of fluctuations in the space charge region. Thus it provides a direct information about the equilibrium surface field-effect in organic semiconductors.

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