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Proton migration mechanism for the instability of organic field-effect transistors

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During prolonged application of a gate bias, organic field-effect transistors show an instability involving a gradual shift of the threshold voltage toward the applied gate bias voltage. We propose a model for this instability in *p*-type transistors with a silicon-dioxide gate dielectric, based on hole-assisted production of protons in the accumulation layer and their subsequent migration into the gate dielectric. This model explains the much debated role of water and several other hitherto unexplained aspects of the instability of these transistors. © *2009 American Institute of Physics*. [doi:10.1063/1.3275807]

Organic field-effect transistors (OFETs) are presently introduced in ultra-low cost contactless identification transponders (electronic barcodes) and in pixel drivers of flexible active matrix displays.[1,2] However, their operational instability is seriously impeding widespread commercial introduction.[3,4] The instability under application of a prolonged gate bias is due to a shift of the threshold voltage with time, leading to a decreasing source-drain current and finally to a disfunctioning of the transistors. This highly undesirable effect is referred to as the "bias-stress effect" and the identification of its origin is of paramount importance.

A very important and extensively studied class of organic transistors are *p*-type OFETs with a silicon-dioxide (SiO_2) gate dielectric. Using SiO_2 as gate dielectric is preferable to using organic gate dielectrics, for which the presence of ions and charge trapping is known to hamper operational stability.[5] Nevertheless, these transistors suffer from the bias-stress effect. Figure 1 shows the development in time of the transfer curves of a typical transistor undergoing stress under ambient conditions with a stressing gate voltage $V_G=-20$ V, briefly interrupted at specific times with a gate sweep to measure the transfer curve. As clearly observed, the main effect of the bias stress is a shift of the threshold voltage, V_{th} (defined here as the intercept of the extrapolated linear part of the transfer curve with the voltage axis), all the way down to V_G.

Figure 2 shows the threshold-voltage shift $\Delta V_{th}(t) = V_{th}(0) - V_{th}(t)$ as a function of time t (symbols). In studies of the bias-stress effect it has become customary to describe this shift with a stretched-exponential function,[6–8] $\Delta V_{th}(t) = V_0(1-\exp[-(t/\tau)^{\beta}])$, where the prefactor V_0 is close to the absolute value of the applied gate voltage, τ is a relaxation time, and $0<\beta<1$ is an exponent. As can be seen in Fig. 2 this function (dashed blue curve) yields a perfect fit. However, this is a purely empirical result. Other important but not understood observations are: (i) the effect is reversible: on grounding of the gate electrode of the transistor, V_{th} shifts back toward its original value; this backward shift or "recovery," occurring on a similar time scale, also shows a stretched-exponential behavior,[8] (ii) an increased humidity accelerates the effect,[9–11] and (iii) the effect is thermally activated, with a semiconductor-independent activation energy of about 0.6 eV.[8]

Several trapping mechanisms have been suggested as an explanation of the effect.[12–15] However, it is not clear how these mechanisms can explain all the above mentioned observations. In particular, the comparable relaxation times for stress and recovery are hard to explain. Moreover, the fact that the shift of V_{th} never saturates before reaching the applied stressing gate voltage would mean that it is never possible to fill all traps, i.e., the number of traps appears to be practically unlimited. Another proposed mechanism is based on the pairing of mobile holes into immobile bipolarons[16,17] but the predicted dynamics of the threshold-voltage shift deviates from the experimental findings for long times, as acknowledged by authors who have suggested this mechanism.[15]

Ion motion in the gate dielectric could in principle lead to reversible bias-stress effects. However, the fabrication

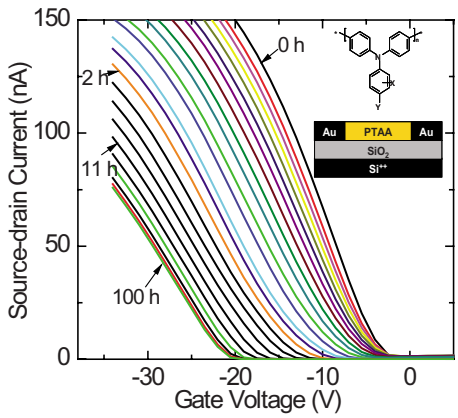

FIG. 1. (Color online) Transfer curves of a polytriarylamine (PTAA) transistor in ambient atmosphere at a temperature of 30 °C for different stressing times, indicated in hours (h): The gate bias during stressing is −20 V and the source-drain voltage during measurement of a transfer curve is 3 V. The inset shows a schematic cross section of the transistor and the chemical structure of PTAA, where X and Y are short alkyl side chains. The fabrication of the transistor was equivalent to that in Ref. 8, with pretreatment of the SiO_2 surface with HMDS. The transistor has a channel width and length of 2500 and 10 μm, respectively. The thickness of the organic semiconductor and the SiO_2 gate dielectric is 80 and 200 nm, respectively.

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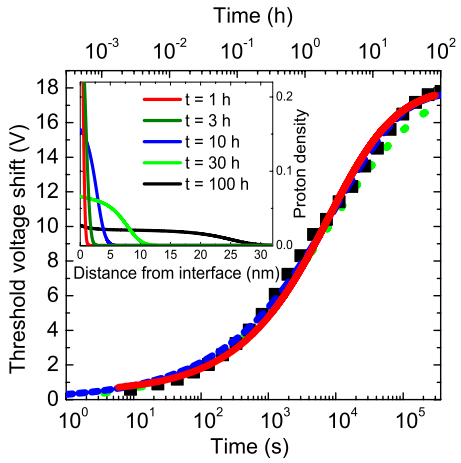

FIG. 2. (Color online) Symbols: experimental threshold voltage shift $\Delta V_{th}(t)$ vs time, obtained from Fig. 1. Dashed blue line: fit to a stretched-exponential function with $\beta=0.43$, $\tau=10^4$ s, and $V_0=19$ V. Solid red line: fit to the proton drift-diffusion model, with $D=1.6\times10^{-19}$ cm^2/s and $\alpha=2.2$ nm^{-1}. Dotted green line: the same, but with the drift contribution neglected. Inset: time evolution of proton density profile in the oxide, normalized to the density at the start of stressing at the interface with the semiconductor.

process ensures the absence of ions in the SiO_2 in the pristine device, so that any ions present in the SiO_2 should be produced during operation. In this letter, we propose a mechanism for the bias-stress effect based on the production of protons at the surface of the gate dielectric in the presence of holes and water. We further propose that these protons migrate into the gate dielectric. We will show that the resulting model can consistently and quantitatively explain the dynamics of the threshold voltage and all other known aspects of the bias-stress effect of these transistors. Moreover, we will show that the mechanism has a solid experimental and theoretical basis.

Recent measurements by scanning Kelvin-probe microscopy on a device of the same type as used here, but without a semiconducting layer, show a time evolution of the potential profile at the SiO_2 surface.[11] The dynamics of this evolution is determined by the amount of water on the SiO_2, which can be regulated by treatment with the hydrophobic primer hexamethyldisilazane (HMDS).[11] This time evolution shows that charges are moving around on the SiO_2 surface even in absence of a semiconductor. The nature of these charges was not established in Ref. 11. We now propose that the involved charges are protons (H^+), produced at the electrodes by electrolysis of water on the SiO_2. It was shown long ago that protons can be produced electrolytically from water on the SiO_2 surface by the replacement of water in the ambient by heavy water (D_2O) and the detection of deuterium gas (D_2) after performing surface-conductivity measurements.[18]

Since organic semiconductors are permeable to water (and also to gasses like oxygen and hydrogen), water molecules can also reach the SiO_2 surface in the presence of a semiconducting layer. We propose that the production of protons now takes place throughout the accumulation layer in the semiconductor by electrolysis of water in the presence of holes, effectively converting holes into protons. Calculations within the framework of density-functional theory (DFT) show that water at the Si–SiO_2 interface can indeed undergo oxidation to produce protons in the presence of holes.[19]

Reversible motion of protons in SiO_2 has been demonstrated by memory effects occurring in $Si/SiO_2/Si$ devices, where protons shuttle through the SiO_2 from one Si layer to the other.[20] DFT calculations on transport of protons in SiO_2 predict an activation energy of about 0.5 eV,[21] which is close to the 0.6 eV activation energy found in bias-stress experiments on different organic semiconductors.[8] This strongly supports our proposition that proton motion in the SiO_2 causes the bias-stress effect.

This experimental and theoretical evidence suggests the following scenario. (i) Holes (h^+) in the semiconductor can convert into protons in the presence of water by the electrolytic reaction $2H_2O+4h^+\rightarrow4H^++O_2(g)$. (ii) Protons can convert back into holes by the reaction $2H^+\rightarrow2h^++H_2(g)$. (iii) An equilibrium exists between protons in the accumulation layer of the semiconductor and protons in the oxide at the interface with the semiconductor: $H^+(\text{semi})\rightleftharpoons H^+(\text{oxide})$. (iv) Protons in the oxide at this interface can move into the bulk of the oxide. Since (iv) should be a very slow process, the reactions (i)–(iii) will establish an equilibrium between the surface concentration $[h^+]$ of holes in the semiconductor and the volume concentration $[H^+]$ of protons in the oxide at the interface with the semiconductor, which should be linearly related by

$$[H^+]=\alpha[h^+], \tag{1}$$

where the parameter α is determined by the reaction constants and the amount of water present in the semiconductor.

We evaluated this mechanism quantitatively, by numerically solving the drift-diffusion equation for the motion of protons in the oxide, using Einstein's equation for the relation between the mobility μ and the diffusion coefficient D, along with Poisson's equation for the electric field. From the resulting proton profiles (see Fig. 2, inset) it is straightforward to calculate the threshold voltage $V_{th}(t)$. As can be observed in Fig. 2 we obtain an excellent fit (solid red curve) to the experimental result. The only two fit parameters are $\alpha=2.2$ nm^{-1} and $D=1.6\times10^{-19}$ cm^2/s. With these values we find that at the end of stressing, at $t\approx4\times10^5$ s, the penetration depth of protons into the oxide is about 30 nm, i.e., considerably smaller than the oxide thickness of 200 nm. For comparison, we also show in Fig. 2 the predicted result for the case that the drift contribution to the proton current is neglected (dotted green curve). The good agreement up to $t\approx10^4$ s demonstrates that the proton migration mainly occurs by diffusion. We note that the resulting curve has in this case a completely universal shape, with $1/(\alpha^2D)$ as characteristic time scale. This explains the observation that many different types of organic transistors show very similar stressing behavior.

Our model also explains recovery. When the gate electrode of a transistor that has been stressed is grounded, the proton density in the oxide vanishes according to Eq. (1). The protons in the oxide will diffuse back toward the interface and convert back into holes, which migrate toward the drain and source electrodes. We checked that our model predicts recovery curves that can also be fitted well with a stretched-exponential function, with a similar relaxation time as in the stressing. Hence, our model can explain all observed aspects of the bias-stress effect in *p*-type OFETs with SiO_2 as gate dielectric, including the reversibility of the effect on a similar time scale, the activation energy, and the

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influence of water. We note that our model also accounts for the seemingly unlimited amount of traps: the diffusion of protons into the SiO_2 effectively provides a three-dimensional and therefore practically unlimited reservoir of traps. Finally, we suggest that the decrease of the slope with time of the linear part of the transfer curves in Fig. 1 is related to a reduced hole mobility in the accumulation layer due to the electrostatic interaction of these holes with an increasing amount of protons in the SiO_2.

A direct demonstration of the electrolysis of water occurring in these transistors would provide definite proof of our model. However, the predicted amounts of molecular oxygen and hydrogen produced in our experimental setup are far below the detection limits. Exposure to heavy water and demonstration of the presence of deuterium gas after stress and recovery of a transistor would provide definite proof.

In conclusion, we have proposed a mechanism for the bias-stress effect occurring in *p*-type transistors with a silicon-dioxide gate dielectric. The mechanism involves the exchange of holes in the semiconductor with protons in the gate dielectric in an electrolytic reaction involving water and the subsequent migration of these protons into the oxide. The resulting model can explain all observed aspects of the bias-stress effect in these transistors.

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