

Bias-stress effect and recovery in organic field effect transistors: Proton migration mechanism

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ABSTRACT

Organic field-effect transistors exhibit operational instabilities when a gate bias is applied. For a constant gate bias the threshold voltage shifts towards the applied gate bias voltage, an effect known as the bias-stress effect. We have performed a detailed experimental and theoretical study of operational instabilities in *p*-type transistors with silicon-dioxide gate dielectric. We propose a mechanism in which holes in the semiconductor are converted into protons in the presence of water and a reversible migration of these protons into the gate dielectric to explain the instabilities in organic transistors. We show how redistribution of charge between holes in the semiconductor and protons in the gate dielectric can consistently explain the experimental observations. Furthermore, we explain in detail the recovery of a pres-stressed transistor on applying zero gate bias. We show that recovery dynamics depends strongly on the extent of stressing. Our mechanism is consistent with the known aspects of bias-stress effect like acceleration due to humidity, constant activation energy and reversibility.

Keywords: Bias-stress, recovery, protons, instabilities, organic transistor

1. INTRODUCTION

Organic field-effect transistors (OFETs) offer exciting possibilities for devices like low-cost contactless identification transponders, electronic barcodes, and pixel engines of flexible active matrix displays.^{1,2} However, a severe limitation of OFETs is their operational stability. During operation under a constant gate bias, the device current decreases monotonically with time leading to a gradual malfunctioning. This electrical instability is manifested as a shift of the threshold voltage with time.³⁻⁶ This effect is usually referred to as the "bias-stress effect" and its origin is not well understood.

The bias-stress effect has been extensively studied in *p*-type organic transistors with silicon-dioxide, SiO₂, as the gate dielectric.^{4,7-15} Even though choosing SiO₂ prevents effects of ionic movements, which are known to occur in organic gate dielectrics¹⁶ transistors with SiO₂ as gate dielectric suffer from the bias-stress effect. The effect is usually studied by applying a constant stressing gate bias and measuring the transfer curves for a small source-drain bias. The main observation in these measurements is that the whole transfer curve shifts in the direction of the constant stressing gate bias.

The threshold-voltage shift as a function of time is customarily fitted with a stretched-exponential function.^{13,17} Although, this fitting is successfully applied in describing the shift of threshold voltage, there is no agreement on the microscopic mechanism behind the effect. Several mechanisms have been suggested as an explanation, such as (i) trapping of mobile carriers in the bulk of the semiconductor,¹⁸ (ii) trapping in disordered areas of the semiconductor,⁹ (iii) trapping in regions in between crystalline grains of the semiconductor,¹⁹ (iv) trapping in states at the semiconductor/dielectric interface,¹⁰ and (v) pairing of mobile carriers to bipolarons in the semiconductor.^{7,20} Two other important observations are that the effect is influenced by humidity^{15,21,22} and that the effect is thermally activated, with an activation energy of about 0.6 eV, apparently independent of the organic semiconductor used.¹³

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Recently, we proposed a mechanism for the bias-stress effect that is based on production of protons from holes and water in the accumulation layer of the semiconductor and the subsequent migration of these protons into the gate dielectric.⁴ We showed that this mechanism can quantitatively explain the measured dependence of the threshold-voltage shift on time. Furthermore, we showed that this dependence can indeed be accurately fitted with a stretched-exponential function. Unlike other mechanisms, this mechanism predicts the occurrence of memory effects related to the biasing history of the transistor. Specific predictions about anomalous non-monotonic current transients derived from the model for the case of a dynamic biasing scheme were indeed experimentally verified.³

One of the aspects of the bias-stress effect is that it is reversible: on applying a zero gate bias after stressing, the threshold voltage shifts back towards its original value, an effect usually referred to as "recovery". We will show that our proposed mechanism can explain recovery as well and in particular, the effect of the extent of stressing on the recovery dynamics. We show that the recovery rate strongly depends on the extent of stressing: when the transistor has been stressed to the extent that the threshold-voltage has been shifted almost completely to the stressing gate bias, the time scale for recovery is much longer than when the transistor has only partially been stressed.

The paper is built up as follows. In Section 2, we present measurements of the bias-stress effect for a *p*-type OFET and discuss the main experimental features of the effect. In Section 3, we introduce the proton migration mechanism and discuss its experimental and theoretical basis. In Section 4, we discuss the modeling of the proton migration mechanism and its application to the bias-stress effect. In Section 5, we demonstrate how the proton migration mechanism can explain measurements on stress-recovery cycles with different extents of stressing. Finally, Section 6 contains a summary and the conclusions, as well as a discussion of the results.

2. EXPERIMENTS

We investigated the bias-stress effect for a *p*-type OFET fabricated using heavily doped *p*-type Si wafers as the common gate electrode with a 200 nm thermally oxidized SiO₂ layer as the gate dielectric. A schematic of bottom contact transistor is shown in Fig. 1. Using conventional photolithography, gold source and drain electrodes were defined in a bottom-contact device configuration with a channel width (W) and length (L) of 2500 μm and 10 μm , respectively. A 10 nm thick layer of titanium was used as an adhesion layer for the gold on SiO₂. The SiO₂ layer was treated with the primer hexamethyldisilazane (HMDS) prior to semiconductor deposition in order to passivate its surface. Polytriarylamine (PTAA) films were spun from a 1% toluene solution at 2000 rpm for 20 s, resulting in a film thickness of 80 nm. The electrical characterization was carried out using an HP 4155C semiconductor parameter analyzer under conditioned ambient atmosphere at a temperature of 30 °C. All measurements reported in the present paper have been performed on this transistor.

Fig. 2a shows the development in time of the transfer curves of the transistor, undergoing bias stress with a constant gate voltage $V_{G0} = -20$ V for a total time of 100 hours $\approx 4 \times 10^5$ s. To measure these transfer curves, a source-drain voltage of $V_{SD} = -3$ V was applied and the gate voltage was swept. A clear shift of the transfer curves in the direction of V_{G0} is observed. In the course of time, the threshold voltage V_{th} (defined here as the intercept of the extrapolated linear part of the transfer curve with the voltage axis) shifts all the way down to V_{G0} . The symbols in Fig. 3a show the threshold-voltage shift $\Delta V_{th}(t) = V_{th}^0 - V_{th}(t)$ as a function of time t . Here, V_{th}^0 is the threshold voltage shift at the start of the experiment, which is close to zero. In studies of the bias-stress effect it has become customary to describe the shift $\Delta V_{th}(t)$ with a stretched-exponential function,^{8,13,17} $\Delta V_{th}(t) = V_0 (1 - \exp[-(t/\tau)^\beta])$, where the prefactor V_0 is close to $|V_{G0}|$, τ and $0 < \beta < 1$ are fitting parameters. In Fig. 3a this function (dashed curve) yields a very good fit. The fit parameters are $V_0 = 19$ V, $\tau = 10^4$ s, and $\beta = 0.43$.

Many studies have shown that humidity has a profound influence on the bias-stress effect. Under vacuum conditions, with practically no water present on the SiO₂ interface, the bias-stress effect is greatly slowed down.^{8,13,21,22} Use of a hydrophobic organic gate dielectric practically eliminates the effect,²² while coverage of the SiO₂ with hydrophobic HMDS, octadecyltrichlorosilane (OTS) or a layer that is impenetrable to water does the same.^{11,12,15} These observations indicate that the threshold-voltage shift in organic transistors is related to residual water.

Bias-stress effect is thermally activated phenomenon.¹³ It was found that for transistors with SiO₂ as gate dielectric, the relaxation time τ decreases exponentially with increasing temperature, with an activation energy of about 0.6 eV irrespective of the organic semiconducting polymer. It was observed that other organic semiconducting polymers such as poly-3-hexylthiophene (P3HT), poly-thienylene-vinylene (PTV), and poly-dioctyl-fluorene-co-bithiophene (F8T2) showed under identical conditions thermally activated behavior with the same activation energy of 0.6 eV.¹³ The independence of the activation energy on the semiconductor indicates that the bias-stress effect in transistors with SiO₂ gate dielectric has a common origin.

Recovery of the original state of the transistor can be established by applying a zero bias to the gate electrode for an extended period of time.^{10,13} In this period, the transfer curve gradually shifts back to the transfer curve before stressing, as shown in Fig. 2b, where the transistor is recovering after 28 hours $\approx 10^5$ s of stressing. It has been found that the dynamics of V_{th} for recovery can also be fitted with a stretched-exponential function, but that the parameters are different than for stress.¹³ The symbols in Fig. 3b labeled by A represent the threshold-voltage shift as a function of time for the transfer curves in Fig. 2b. The shift can be fitted very well with the function $\Delta V_{th}(t) = V_1 \exp(-(t/\tau)^\beta)$, with the fit parameters $\tau = 7.7 \times 10^4$ s, $\beta = 0.58$, and $V_1 = 15.7$ V. The symbols in Fig. 3b labeled by B and C have been obtained by starting the recovery after 10^4 and 2×10^3 s of stressing, respectively. For these recovery curves we obtain stretched-exponential fits with $\tau = 6.5 \times 10^3$ s, $\beta = 0.3$, and $V_1 = 11.7$ V (B), and $\tau = 2 \times 10^3$ s, $\beta = 0.28$, and $V_1 = 8.4$ V (C). We will discuss these different recovery experiments in Section 5.

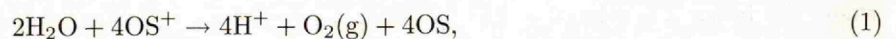
3. PROTON MIGRATION MECHANISM FOR THE BIAS-STRESS EFFECT

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 SiO₂ surface. The dynamics of this evolution is determined by the amount of water on the SiO₂, which can be regulated by treatment with the hydrophobic primer hexamethyldisilazane (HMDS).¹⁵ This time evolution shows that charges are moving around on the SiO₂ surface even in absence of a semiconductor. We propose that the involved charges are protons (H⁺), produced at the electrodes by electrolysis of water on the SiO₂.^{23,24} It was shown long ago that protons can be produced electrolytically from water on the SiO₂ surface by the replacement of water in the ambient by heavy water (D₂O) and the detection of deuterium gas (D₂) after performing surface-conductivity measurements.²⁵

Since organic semiconductors are permeable to water, water molecules can also reach the SiO₂ surface in the presence of an organic semiconductor. We therefore propose that in a *p*-type OFET under bias stress the electrolytic production of protons now takes place at the interface between the semiconductor and the SiO₂, where the whole accumulation layer in the semiconductor acts as a positive electrode. In this reaction, holes in the semiconductor are converted into protons. Calculations within the framework of density-functional theory (DFT) have shown that water at the Si-SiO₂ interface can undergo oxidation to produce protons in the presence of holes.²⁶ Although we do not know of equivalent studies for the interface between an organic semiconductor and SiO₂, it is natural to assume that the same reaction will take place. Regarding the above discussion, it is then also natural to assume that protons can be converted back into holes along with production of H₂.

The reversible motion of protons in SiO₂ has been demonstrated by memory effects occurring in Si/SiO₂/Si devices, where protons move through the SiO₂ from one Si layer to the other.^{27,28} DFT calculations on transport of protons in SiO₂ predict an activation energy of about 0.5 eV,²⁹ which is close to the 0.6 eV activation energy found in bias-stress experiments on different organic semiconductors.¹³ This strongly suggests that motion of protons in the SiO₂ determines the dynamics of the bias-stress effect.

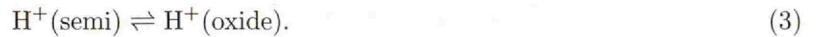
Based on these experimental and theoretical results we propose the following scenario. (i) In the presence of water, holes in the organic semiconductor, indicated below by OS⁺, can be converted into protons in the electrolytic reaction



where OS refers to electrically neutral sites in the organic semiconductor. (ii) Protons can be converted back into holes in the reaction



(iii) Protons in the accumulation layer of the semiconductor are in equilibrium with protons in the oxide at the interface with the semiconductor:



(iv) Protons in the oxide at the interface can diffuse into the bulk of the oxide.

It is reasonable to assume that the dynamics of the reactions Eqs. (1)-(3) is much faster than the diffusion of protons into the bulk of the oxide. This leads to the conclusion that the dynamics of the bias-stress effect is governed primarily by the motion of protons in the oxide and not by the specific details of the reactions. Under this assumption, there will be an equilibrium between the surface density $[\text{OS}^+]$ of holes in the semiconductor and the volume density $[\text{H}^+]$ of protons in the oxide at the interface with the semiconductor, leading to the linear relation

$$[\text{H}^+] = \alpha[\text{OS}^+], \quad (4)$$

where the parameter α is a proportionality constant, which is determined by the reaction constants. We treat α as a parameter in what follows.

4. MODEL FOR THE PROTON MIGRATION MECHANISM; APPLICATION TO THE BIAS-STRESS EFFECT

The proposed proton migration mechanism can be made quantitative in the following way. Under the assumption that the protons do not penetrate deep into the oxide, we can write down the following charge-balance equation while stressing the OFET with a constant gate bias V_{G0} :

$$\int_0^\infty p(x,t)dx + h_0(t) = c_0 \equiv \frac{CV_{G0}}{e}, \quad (5)$$

where $p(x,t)$ is the time-dependent volume density of protons in the oxide at a distance x from the interface with the semiconductor, $h_0(t)$ is the time-dependent surface density of holes in the accumulation layer of the semiconductor, C is the capacitance of the oxide per unit area, and e is the elementary charge. In principle, diffusion as well as drift of protons in the oxide occurs. In the present derivation we will neglect drift and only take diffusion of protons into account. Clearly, in the initial stage after the application of a gate bias there will be a large density gradient of protons in the oxide such that diffusion automatically dominates over drift. The advantage of neglecting proton drift is that a clear picture of the mechanism arises and that the modeling is considerably simplified. We can then write the equation of motion for protons in the oxide as

$$\frac{\partial}{\partial t} p(x,t) = D \frac{\partial^2}{\partial x^2} p(x,t), \quad (6)$$

with D the diffusion coefficient. This equation can be solved using the Green-function for the one-dimensional diffusion equation:

$$p(x,t) = \int_0^t \int_{-\infty}^\infty \frac{\exp\left[-\frac{(x-x')^2}{2D(t-t')}\right] s(x',t')}{\sqrt{4\pi D(t-t')}} dx' dt', \quad (7)$$

where $s(x,t)$ stands for the source term, which is equal to the proton flux into the oxide from the accumulation layer. This source term can be obtained by differentiating Eq. (5) with respect to time and using Eq. (6):

$$s(x,t) = -2D \frac{\partial p(x,t)}{\partial x} \Big|_{x=0} \delta(x) = -2 \frac{dh_0(t)}{dt} \delta(x), \quad (8)$$

where the factor 2 is related to the fact that we consider a diffusion problem in a half-space $x \geq 0$. Using the equilibrium condition $p(0,t) = \alpha h_0(t)$ and the above expression for the source term, we can calculate the proton density in the oxide at the interface as

$$p(0,t) = \int_0^t \frac{1}{\sqrt{4\pi D(t-t')}} \left(-\frac{2}{\alpha} \frac{dp(0,t')}{dt'} \right) dt'. \quad (9)$$

On applying partial integration and replacing $p(0, t)$ with $\alpha h_0(t)$, we obtain the following equation for the hole density in the accumulation layer:

$$h_0(t) = \frac{1}{2} \int_0^t \frac{t_0^{1/2}}{(t-t')^{3/2}} (h_0(t') - h_0(t)) dt' - \left(\frac{t_0}{t}\right)^{1/2} (h_0(t) - c_0), \quad (10)$$

where the characteristic time t_0 is given by

$$t_0 \equiv \frac{1}{\pi \alpha^2 D}. \quad (11)$$

We note that, unlike the relaxation time τ in the stretched-exponential fits to the threshold-voltage shifts discussed in Section 2, this characteristic time is related to physical parameters.

Eq. (10) can be solved for $h_0(t)$ by iterative numerical techniques. The threshold voltage is finally obtained as

$$V_{th}(t) = \frac{e}{C} (c_0 - h_0(t)). \quad (12)$$

The application of the model to the threshold-voltage dynamics during stressing discussed in Section I leads to the thick full line in Fig. 3a for the case that only proton diffusion in the oxide is taken into account. For this case the dynamics of the threshold-voltage shift is described by a universal curve with t_0 as the only parameter. Experimentally it has been established that the dynamics of the bias-stress effect is virtually independent of the value of the applied gate voltage.¹³ For the present case, we are able to obtain a good fit up to $t \approx 10^4$ s and extract $t_0 = 4.2 \times 10^3$ s.

The deviation from the experimental threshold voltage shift for longer times can be attributed to drift. As shown by the thin line in Fig. 3, an excellent fit to the experimentally determined time dependence of the threshold voltage is obtained when the drift-diffusion problem is solved with $D = 1.6 \times 10^{-19}$ cm²/s and $\alpha = 2.2$ nm⁻¹. For these values of D and α , we show the proton density profile in the gate oxide for different times in Fig. 4a. The penetration depth of the protons into the oxide is about 30 nm at the end of stressing in Fig. 2a ($t = 100$ hours $\approx 4 \times 10^5$ s). This is much smaller than the oxide thickness of 200 nm and hence consistent with our assumption that the protons do not penetrate deep into the oxide. The results displayed in Fig. 3a show that the diffusive flux of protons into the oxide dominates over the drift flux of protons till $t \approx 10^4$ s. We show in Fig. 4b the electric field profile in the oxide for different times. Since most of the proton charge stays close to the interface between the organic semiconductor and the oxide, the electric field varies strongly with distance near the interface, whereas there is practically no change in its value far from the interface.

5. RECOVERY

During recovery, under application of a zero gate bias the transfer curve of a transistor that has suffered from bias stress shifts back to the transfer curve before the bias stress. With time, threshold voltage shifts back to its original value. Although experiments have shown that the dynamics of the threshold-voltage shift for recovery is different from that for stress,¹³ there is no explanation for this finding. A systematic study of recovery and its dynamics is important for a better understanding of instabilities occurring in OFETs.

The different recovery experiments labeled by A, B and C in Fig. 2b discussed in Section 2 have been performed in order to investigate if the extent of stressing has an influence on the dynamics of the recovery. That indeed extent of stressing influences the dynamics of recovery is evident from the stretched exponential fits to the three cases as shown further on. The fits yield values for the relaxation time τ of 7.7×10^4 s (A, stressing for 10^5 s), 6.5×10^3 s (B, stressing for 10^4 s), and 2×10^3 s (C, stressing for 2×10^3 s), while the relaxation time for stress is $\tau = 10^4$ s; see Section 2. The conclusion is that the dynamics for recovery is different from that for stress and that the relaxation times decrease with decreasing stressing time. We checked that during each stressing period the curve in Fig. 3a is followed implying that the dynamics during stress remains unchanged.

The observation that the dynamics of recovery is influenced by the extent of stressing can be explained within the proton migration mechanism as follows. At the end of the stressing period, there is a density profile of protons extending into the oxide. During recovery, when the gate bias is zero, the density of holes in the accumulation layer vanishes. Because of the equilibrium condition Eq. (4) the density of protons at the interface between

oxide and semiconductor also vanishes. This leads to a diffusion of protons from the oxide back towards the semiconductor. Protons reaching the semiconductor get converted into holes and are carried away to the source and drain electrodes. This implies that the further away protons have diffused into the oxide during stressing, the longer it will take for these protons to diffuse back to the semiconductor. Since the depth of penetration of protons into the oxide depends on the extent of stressing, this rationalizes the observation that the time scale for recovery decreases with decreasing stressing period.

In order to describe the recovery dynamics quantitatively, we numerically solved the time-dependent proton-diffusion problem for all three stress-recovery cycles A-C. We note that, as in the previous section, we take into account only the diffusion contribution to the motion of the protons. Assuming that the device is being stressed for a total time t_{stress} before grounding the gate electrode we can write the gate voltage as a function of time in the following way:

$$V_G(t) = V_{G0}\theta(t) - V_{G0}\theta(t - t_{\text{stress}}). \quad (13)$$

In this expression, the first term can be interpreted as uninterrupted continuous stressing of the transistor with the gate voltage V_{G0} . The contribution of this term to the proton density at the interface can be calculated by taking into account a positive source term that is injecting protons in the oxide, in the same way as in Section 4. The second term ensures that at $t = t_{\text{stress}}$ the gate bias becomes zero such that for $t > t_{\text{stress}}$ the hole density in the channel goes to zero. The contribution of this term to the proton density at the interface can be calculated by taking into account a negative source term corresponding to extraction of protons out of the oxide. We can therefore write for the proton density at the interface:

$$\tilde{p}(0, t) = \int_0^t \frac{1}{\sqrt{4\pi D(t-t')}} [s(t') - s_{\text{rec}}(t')\theta(t - t_{\text{stress}})] dt', \quad (14)$$

where $s(t) = -(2/\alpha)dp(0, t)/dt$ and $p(0, t)$ is the density of protons at the interface for the case that the transistor is under continuous stress with the gate voltage V_{G0} . $s_{\text{rec}}(t)$ represents the source term that accounts for the second term in Eq. (13). For $t > t_{\text{stress}}$, $\tilde{p}(0, t) \equiv 0$ and therefore we can write:

$$\int_0^t \frac{1}{\sqrt{4\pi D(t-t')}} s(t') dt' = \int_{t_{\text{stress}}}^t \frac{1}{\sqrt{4\pi D(t-t')}} s_{\text{rec}}(t') dt'. \quad (15)$$

Writing $t = t_{\text{stress}} + \tilde{t}$ and using Eq. (9), we can write the above equation as

$$\int_{t_{\text{stress}}}^{t_{\text{stress}} + \tilde{t}} \frac{1}{\sqrt{4\pi D(t_{\text{stress}} + \tilde{t} - t')}} s_{\text{rec}}(t') dt' = p(0, t_{\text{stress}} + \tilde{t}). \quad (16)$$

Using Eq. (4), we can write $p(0, t) = \alpha h_0(t)$, where $h_0(t)$ is the corresponding hole density in the channel for the case that the transistor is under constant stress with the gate voltage V_{G0} . Writing $s_{\text{rec}}(t) = 2r(t)/\sqrt{t}$ in the equation above, we can derive the following equation for $r(t)$:

$$r(t) = \frac{2}{\pi} h_0(t_{\text{stress}} + t) - \frac{1}{\pi} h_0(t_{\text{stress}}) + \frac{2}{\pi} \int_0^t \sin^{-1} \left(\frac{2t'}{t} - 1 \right) \frac{dr(t')}{dt'} dt'. \quad (17)$$

This equation can be solved for $r(t)$ using iterative numerical techniques. The threshold voltage during recovery can then be calculated as

$$V_{\text{th}}(t) = \frac{e}{C} \left(c_0 - h_0(t_{\text{stress}} + t) - \int_0^t \frac{r(t')}{\sqrt{t-t'}} dt' \right). \quad (18)$$

The results for the recovery curves A-C are given by the thick lines in Fig. 3b, using exactly the same value t_0 as found in Section 4. The agreement with the measured data is surprisingly good. Apparently, the proton migration mechanism captures the dynamics of the threshold voltage for stress as well as recovery.

In Fig. 5 we show the proton density profiles in the oxide with proceeding recovery, calculated with the parameters $D = 1.6 \times 10^{-19} \text{ cm}^2\text{s}^{-1}$ and $\alpha = 2.2 \text{ nm}^{-1}$ similar to those in Section 4, for three different times after the start of recovery, indicated at the upper axis in Fig. 3b: 10^3 , 10^4 , and 10^5 s. The profiles labeled by

A, B, and C correspond to the same stressing periods as in Fig. 3b. We clearly see that with a shorter stressing period the protons are removed much quicker from the oxide during recovery than with a longer stressing period. To emphasize this point further, we indicate the total proton charge contained in the oxide by filled bars in the insets of Fig. 5. The hatched bars indicate the total proton charge normalized to the total amount of charge just before recovery, making clear that the *relative* recovery rate is faster in the case of a shorter stressing period. If the recovery dynamics would not depend on the stressing period, the normalized total proton charge would be the same for the situations A-C.

6. SUMMARY, CONCLUSIONS, AND DISCUSSION

We have developed a model for operational instabilities involving threshold voltage shifts in *p*-type organic field-effect transistors with silicon-dioxide as gate dielectric based on a proton migration mechanism. The model is based on the assumption that holes in the accumulation layer of the semiconductor react with water to produce protons establishing an equilibrium between holes and protons in the channel region. We further assume that these protons produced in the accumulation layer migrate into the oxide leading to a shielding of the gate electric field. The rate of removal of protons from the accumulation layer depends on the diffusion constant of protons in the oxide and is the rate limiting step in bias-stress effect.

The model can very accurately describe the bias-stress effect in these transistors, which is manifested as a shift of the threshold voltage towards a constant stressing gate voltage. The dependence of the threshold voltage on time follows a universal curve, with a characteristic time as the only parameter. This universal curve is very close to a stretched-exponential function, which explains the success of the description of the shift of the threshold voltage with time in terms of such a function. The model explains the role of water and the observation that the activation energy of the bias-stress effect is virtually independent of the organic semiconductor. The magnitude of the activation energy agrees with the reported value for transport of protons in the silicon-dioxide.

The recovery of a transistor that has been exposed to bias stress can also be described with the model. In recovery, protons that have migrated into the oxide during stressing diffuse back to the semiconductor, where they are converted back into holes that are carried away by the source and drain electrodes. This leads to a shift of the threshold voltage back to its original value. The model predicts that the extent of stressing has a large influence on the dynamics of the recovery. It takes much longer for a fully stressed device to recover than a partially stressed one. Therefore, the recovery curves for the threshold-voltage shift cannot be described by a single stretched-exponential function. Our model predictions obtained using the same characteristic time from the modeling of threshold voltage shift for stress is accurately followed by the measurements.

Despite the fact that the indications for the validity of the proton migration mechanism in these transistors are extremely strong, a definite proof for the mechanism is still missing. Direct demonstration of the electrolysis of water occurring in these transistors would provide definite proof. However, the predicted amounts of molecular oxygen and hydrogen produced in our experimental setup are extremely small. In fact, they are negligible in comparison to the natural abundances of these gases in ambient air. Exposure to heavy water and demonstration of the presence of deuterium gas after stress and recovery of a transistor would provide definite proof.

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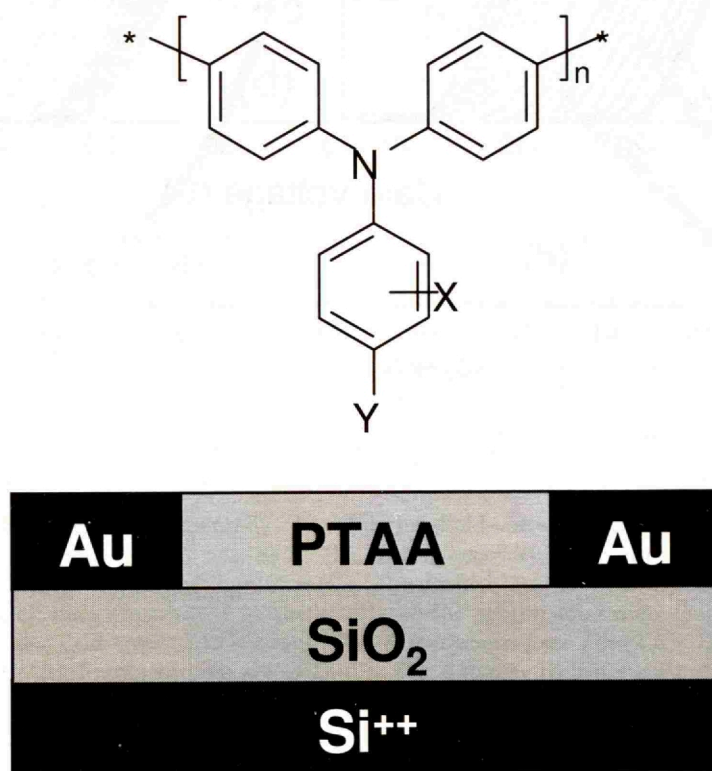


Figure 1. (Color online) Schematic of bottom contact transistor. Also shown is the chemical structure of the organic semiconductor PTAA.

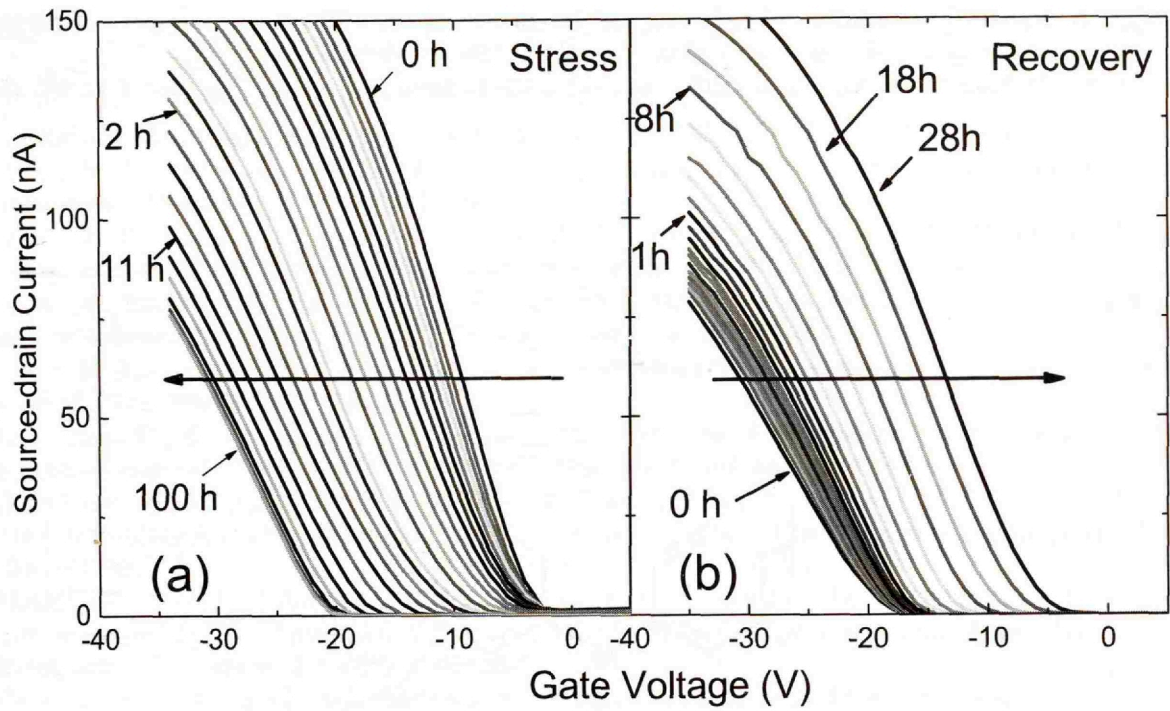


Figure 2. (Color online) (a) Transfer curves of the investigated *p*-type transistor in ambient atmosphere at a temperature of 30 °C for different stressing times, indicated in hours (h). The stressing gate bias voltage during stressing was $V_{G0} = -20$ V. (b) Transfer curves of the same transistor undergoing recovery with zero gate bias for different recovery times after 28 hours of stressing. The source-drain voltage while measuring the transfer curves was $V_{SD} = -3$ V. The horizontal arrows shows the shifts of the transfer curves with time.

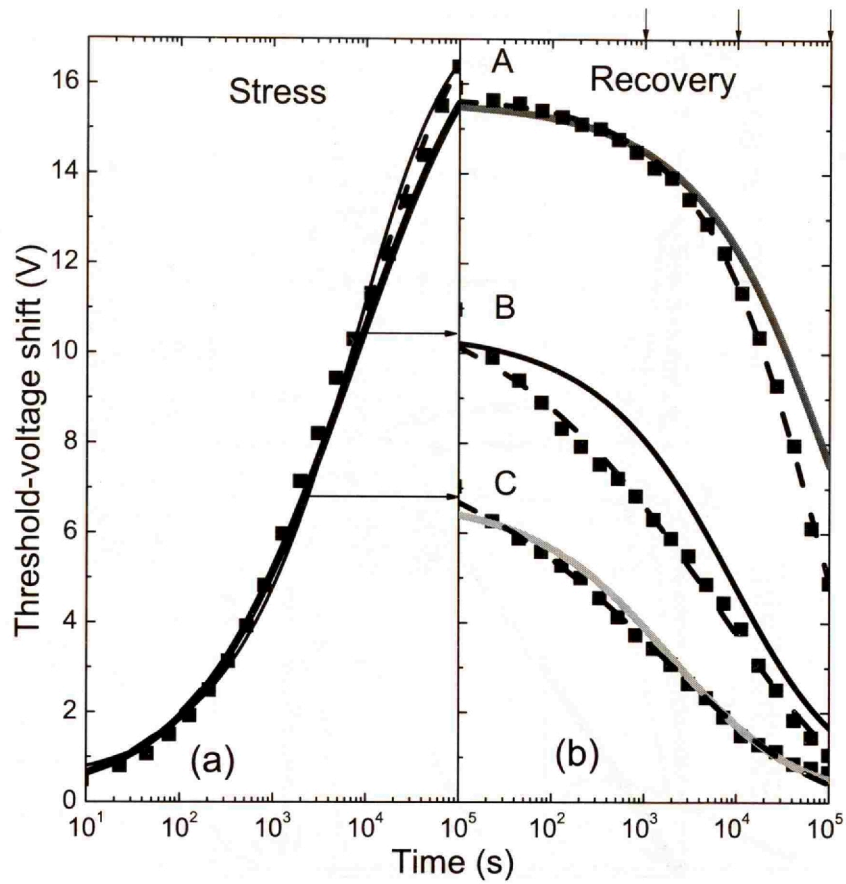


Figure 3. Color online) Symbols: experimentally obtained threshold-voltage shift $\Delta V_{th}(t)$ as a function of time t . (a) During stress with a gate voltage of $V_{G0} = -20$ V. (b) During recovery after three different stressing periods: 10^5 s (A), obtained from Fig. 2b), 10^4 s (B) and 2×10^3 s (C). The dashed lines in both (a) and (b) correspond to stretched-exponential fits. The thick lines correspond to the results of the proton migration mechanism. The thin line in (a) corresponds to a fit with also drift taken into account. The fit parameters are $D = 1.6 \times 10^{-19}$ cm²/s and $\alpha = 2.2$ nm⁻¹. The times at which the proton density profiles are plotted in Fig. 5 during recovery are indicated at the upper axis in (b).

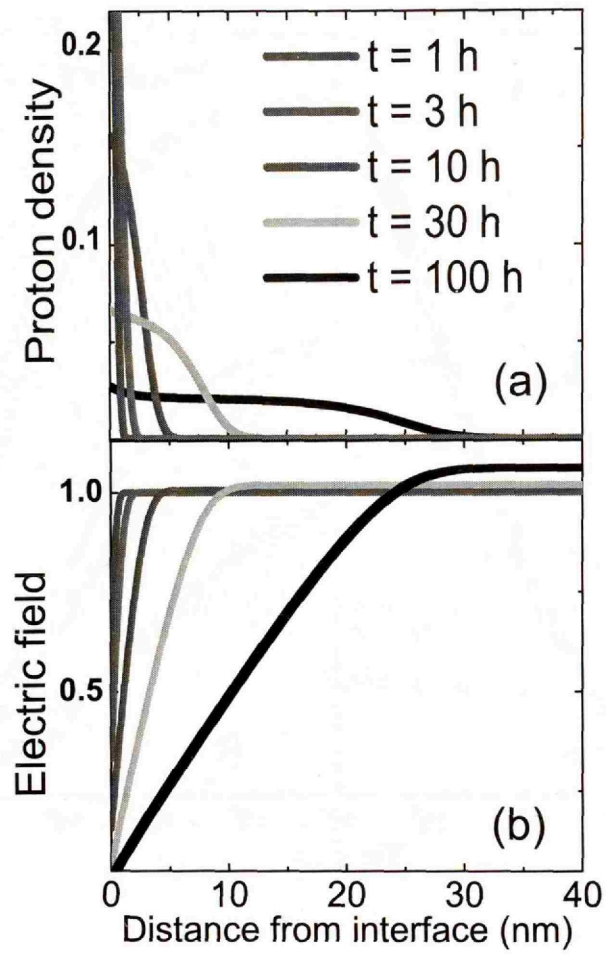


Figure 4. (Color online) (a) Proton density profile $p(x,t)/p(0,0)$ and (b) electric field profile $E(x,t)/E(0,0)$ in the oxide at different times after the start of stressing obtained by numerically solving the drift-diffusion problem related to the motion of proton in the gate dielectric.

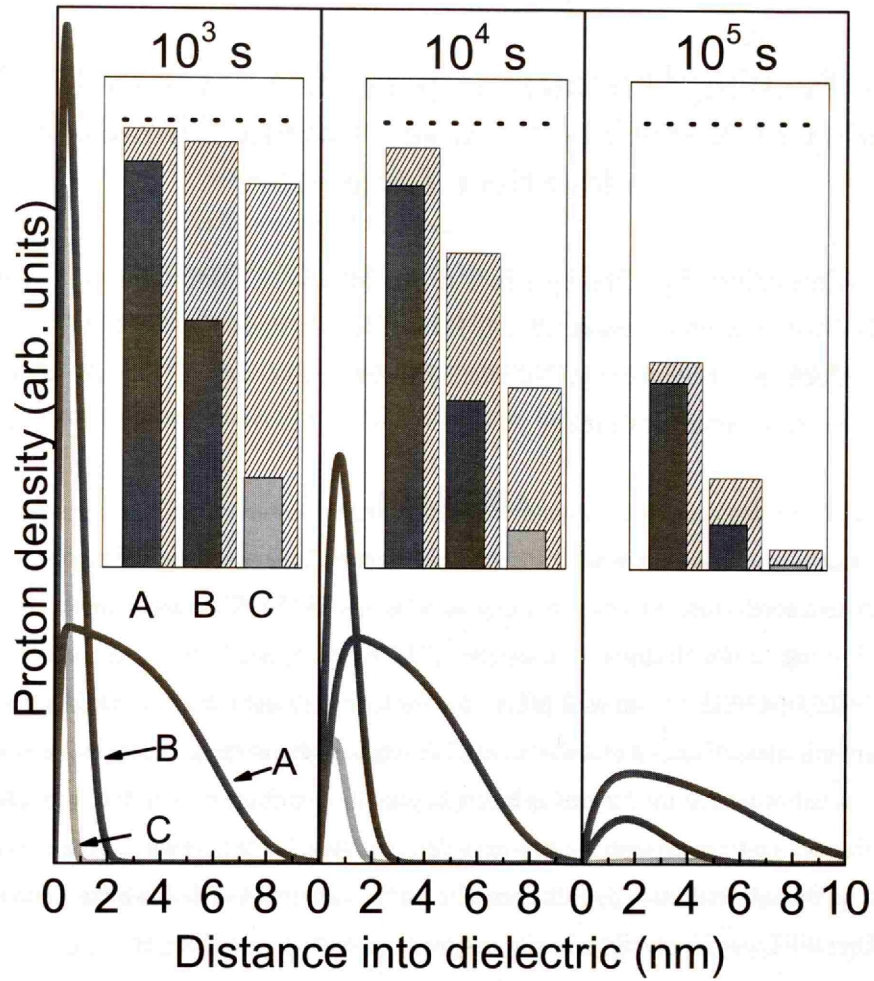


Figure 5. (Color online) Modeled proton density profiles in the oxide during recovery after a recovery time of 10^3 , 10^4 , and 10^5 s (left to right). A, B, and C refer to the same stressing periods as in Fig. 3b. Inset: bar diagrams representing the total charge (filled bars) in the oxide calculated from the model and the total charge normalized to that at the start of recovery (hatched bars). The dotted line represents the initial normalized charge at the start of recovery.