

## Correlation between bias stress instability and phototransistor operation of pentacene thin-film transistors

Maarten Debucquoy,<sup>a),b)</sup> Stijn Verlaak, Soeren Steudel,<sup>b)</sup> Kris Myny, Jan Genoe, and Paul Heremans<sup>b)</sup>

*Polymer and Molecular Electronics, IMEC, Kapeldreef 75, 3001 Leuven, Belgium*

(Received 12 March 2007; accepted 8 August 2007; published online 5 September 2007)

The authors study the use of pentacene thin-film transistors as phototransistors. The shift in turn-on voltage ( $V_{on}$ ), responsible for the high photosensitivity of these devices, is shown to be strongly dependent on illumination time and applied gate voltage. The time dependence of this process is similar to the shift in  $V_{on}$  during bias stress experiments in the dark, and illumination can simply be accounted for as an acceleration factor for bias stress instability. By comparing the characteristics of devices with different gate dielectrics, trapping of electrons by OH groups at the gate dielectric interface is indicated as a main origin for these shifts. © 2007 American Institute of Physics. [DOI: 10.1063/1.2777177]

In recent years, several reports have mentioned a shift in threshold voltage ( $V_T$ ) and turn-on voltage ( $V_{on}$ ) upon the illumination of organic thin film transistors (OTFTs).<sup>1-3</sup> Typically, the transfer characteristics of *p*-type transistors measured under illumination are reported to shift toward more positive gate voltages with respect to the transfer characteristics in the dark. This shift can be as large as several tens of volts and thus results in a dramatic change in the current measured at constant voltage. This observation has been made both for small molecule and for polymer semiconductors. It is usually not accompanied by a change in mobility or subthreshold slope.

In this work, we analyze the time dependence of this light-induced shift in  $V_{on}$  of pentacene transistors. We show that the light-induced shift in  $V_{on}$  has a similar time dependence as dark bias stress, and that the mechanisms for these shifts are indeed related to each other. This observation is further corroborated by the experimental verification that transistors designed to show less light-induced voltage shift also suffer less from dark bias stress voltage instability.

In order to measure the time dependence of the light-induced shift in  $V_{on}$ , OTFTs were illuminated with a number of illumination periods ranging from 100 ms to 1000 s. During these periods, a constant illumination power  $P_{ill}$  and a constant gate-source voltage  $V_{GS,bias}$  are applied. In between the successive biased illumination periods transfer characteristics are recorded in the dark to determine the shift of  $V_{on}$  ( $\Delta V_{on} = V_{on} - V_{on,init}$ ). We prefer to track  $V_{on}$  rather than  $V_T$ , as  $V_{on}$  is mainly determined by trapped charges, while shifts in  $V_T$  in an OTFT can be due to changes of many more physical parameters such as the mobility and subthreshold slope. We define  $V_{on}$  as the gate-source voltage  $V_{GS}$  at which the drain current  $I_D$  reaches 0.1 nA. This current value is chosen to be low enough in the steep subthreshold region of our OTFTs to allow precise determination of  $V_{on}$  (typical subthreshold slope is  $S^{-1} = 0.39$  V/decade), yet sufficiently high to be easily measurable without noise. The  $V_{on}$  of the transfer curve preceding the first biased illumination period is called  $V_{on,init}$ .

Precautions were taken to minimize bias stress, and thus a possible shift in  $V_{on}$ , during recording of the transfer characteristics between the biased illumination periods. First, the transfer curves were measured with pulsed  $V_{GS}$  (pulse width=100 ms and pulse period=200 ms).<sup>4</sup> Second, the transfer curves were measured only from the previous  $V_{on}$  up to the new  $V_{on}$ , resulting in transfer curves of only a handful of points and at very small channel currents. With these measurement conditions, we can assure that the measured shift in  $V_{on}$  is the result of the applied biased illumination periods and not of stressing during the measurement of the transfer curve itself.

All devices were fabricated on a heavily doped silicon wafer, used as gate, with 100 nm of thermally grown  $\text{SiO}_2$ , used as a gate dielectric. Gold interdigitated source and drain electrodes were deposited on top of the  $\text{SiO}_2$  using a standard lift-off photolithography process. The source and drain electrodes were treated with a monolayer of 1-dodecanethiols, while the  $\text{SiO}_2$  was covered with a monolayer of octadecyltrichlorosilane (OTS) deposited from the gas phase.<sup>5</sup> Finally, 40 nm of pentacene was deposited in an ultrahigh vacuum chamber ( $10^{-8}$  Torr,  $0.25 \text{ \AA/s}$ , and  $T_{\text{substrate}} = 68 \text{ }^\circ\text{C}$ ). The characteristics of the OTFTs were measured with two computer-controlled Keithley 2602 units in a darkened nitrogen glovebox [ $\text{ppm}(\text{H}_2\text{O}) < 5$  and  $\text{ppm}(\text{O}_2) < 0.5$ ]. The devices were illuminated from the pentacene side with a light emitting diode (Fairchild MV8114,  $\lambda_{\text{peak}} = 660 \text{ nm}$ , spectral line half width=20 nm) at the absorption peak of pentacene. Illumination power was measured with a Newport UV-818 photodetector.

The inset of Fig. 1(a) shows typical transfer characteristics of our OTFTs prior to illumination. Figure 1(a) shows the shift of  $V_{on}$  ( $\Delta V_{on}$ ) vs  $t$  measured when the OTFT is biased in the on state during the biased illumination periods ( $V_{DS,bias} = -0.1 \text{ V}$  and  $V_{GS,bias} = -20 \text{ V} < V_{on,init}$ ), where  $t$  is the total illumination time accumulated over all illumination periods. We observe no influence of illumination on  $\Delta V_{on}$ . The observed power law evolution of  $\Delta V_{on}$  can be the short time range approximation of a stretched hyperbola or a stretched exponential function. Both functions are used since decades to describe  $\Delta V_{on}$  in bias stress experiments in the dark on hydrogenated amorphous silicon thin film

<sup>a)</sup>Electronic mail: maarten.debucquoy@imec.be

<sup>b)</sup>Also at Department of Electrical Engineering, Katholieke Universiteit Leuven, Leuven, Belgium.

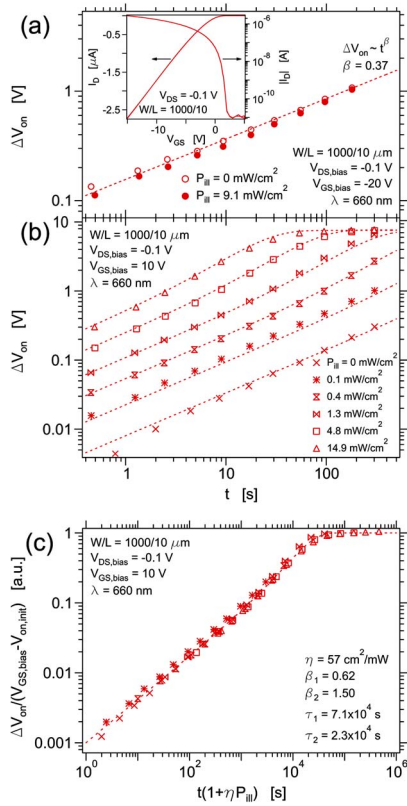


FIG. 1. (Color online) For a device with a gate dielectric covered with OTS: (a)  $\Delta V_{\text{on}}$  vs  $t$  with and without illumination when biased in the on state. The symbols represent the data and the dashed line the fit to a power law.  $V_{\text{GS,bias}} = -20$  V. The inset shows typical transfer characteristics. (b)  $\Delta V_{\text{on}}$  vs  $t$  for different illumination powers when biased in the off state ( $V_{\text{GS,bias}} = 10$  V). The symbols represent the data and the dashed lines, the fits to a double stretched exponential function. The fitting parameters are listed in Table I.  $\Delta V_{\text{on}} / (V_{\text{GS,bias}} - V_{\text{on,init}})$  vs  $t(1 + \eta P_{\text{ill}})$  from which the fitting parameters for the double stretched exponential function have been derived.

transistors<sup>6–8</sup> and, more recently, also in bias stress experiments in the dark on OTFTs biased in the on state.<sup>9–11</sup> We find the parameter  $\beta$  to be 0.37, corresponding to the values recently reported for bias stress experiments in the dark on pentacene OTFTs biased in the on state.<sup>11,12</sup>

Figure 1(b) shows  $\Delta V_{\text{on}}$  vs  $t$  when the OTFT is biased in the off state ( $V_{\text{DS,bias}} = -0.1$  V and  $V_{\text{GS,bias}} = 10$  V  $> V_{\text{on,init}}$ ) during the biased illumination periods. In this bias regime, illumination does have a pronounced influence on  $\Delta V_{\text{on}}$ . We find that all our measured data can be well described with a fitting function similar to a stretched exponential. The stretched exponential function,

$$\Delta V_{\text{on}}(t) = (V_{\text{GS,bias}} - V_{\text{on,init}}) \left\{ 1 - \exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right) \right\}, \quad (1)$$

can be derived assuming an exponential distribution of energy barriers which need to be overcome to trap a charge.<sup>6</sup> The trapping time is in this case given by  $\tau = \nu^{-1} \exp(E_A/k_B T)$  and  $\beta = T/T_0$ , with  $E_A$  the mean activation energy to overcome,  $k_B T_0$  the slope of the distribution in the activation energy, and  $\nu$  an attempt-to-escape frequency. The fitting function that we find to describe all our measured data is a double stretched exponential function, adapted to take into account the illumination power,

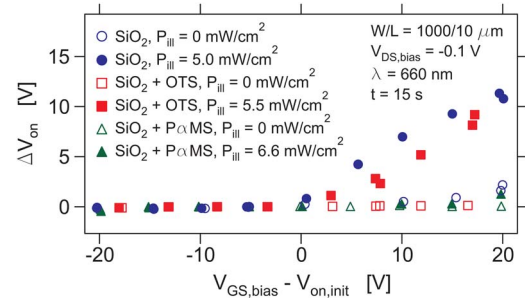


FIG. 2. (Color online)  $\Delta V_{\text{on}}$  vs  $V_{\text{GS,bias}} - V_{\text{on,init}}$  for three sets of devices with a different surface treatment of the gate dielectric, once in the dark and once under illumination. Illumination time was constant for all measured data points.

$$\Delta V_{\text{on}} = (V_{\text{GS,bias}} - V_{\text{on,init}}) \left[ 1 - \exp\left\{-\left(\frac{t(1 + \eta P_{\text{ill}})}{\tau_1}\right)^{\beta_1} - \left(\frac{t(1 + \eta P_{\text{ill}})}{\tau_2}\right)^{\beta_2}\right\}\right], \quad (2)$$

where  $\eta$  is an efficiency factor determining the acceleration of  $\Delta V_{\text{on}}$  by means of illumination and is chosen to achieve an optimal overlap in a  $\Delta V_{\text{on}} / (V_{\text{GS,bias}} - V_{\text{on,init}})$  vs  $t(1 + \eta P_{\text{ill}})$  plot, as shown in Fig. 1(c). The fitting curves with fitting parameters derived from Fig. 1(c) are added to Fig. 1(b):  $\eta = 57$  cm<sup>2</sup>/mW,  $\beta_1 = 0.62$ ,  $\beta_2 = 1.50$ ,  $\tau_1 = 7.1 \times 10^4$  s and  $\tau_2 = 2.3 \times 10^4$  s. The origin of this double stretched exponential fitting function is the underlying trap distribution, which is not studied in this work, but appears to necessitate taking into account two time constants. Remarkable in Eq. (2) and the excellent fits we obtain with it on our measurement data (Fig. 1(c)) is that illumination proves to simply provide an acceleration for bias stress. We attribute this effect to the fact that both are due to electron trapping. Indeed, electron trapping at the gate dielectric/organic semiconductor interface is the main suspect for the shift in  $V_{\text{on}}$  in organic phototransistors.<sup>13</sup> When illuminating the semiconductor, excitons are generated, a fraction of which are dissociated in electrons and holes. A positive gate bias under stress drives electrons to the semiconductor-gate insulator interface, where electron trapping occurs.

To further investigate this hypothesis, we have compared the bias stress behavior of OTFTs with different surface treatments, which have different densities of OH groups and, consequently, a different likeliness to allow electron trapping according to the work of Chua *et al.*<sup>14</sup> In one type of treatment, the monolayer of OTS was omitted and the pentacene was deposited on bare SiO<sub>2</sub>. In other series of experiments, a 4 nm thick layer of poly( $\alpha$ -methylstyrene) (P $\alpha$ MS) was spun on top of the SiO<sub>2</sub>. In this case, the source and drain electrodes were covered with a monolayer of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiols to confine the P $\alpha$ MS to the transistor channel.<sup>15</sup> Other processing steps were identical to the ones for an OTS treated device.

Figure 2 shows  $\Delta V_{\text{on}}$  for a fixed  $t$  and  $P_{\text{ill}}$  and for different  $V_{\text{GS,bias}}$ . Each point of Fig. 2 was measured on a different fresh OTFT. When biased in the on state ( $V_{\text{GS,bias}} < V_{\text{on,init}}$ ), neither illumination nor the treatment of the SiO<sub>2</sub> has a pronounced effect on  $\Delta V_{\text{on}}$ . On the other hand, when biased in the off state during illumination ( $V_{\text{GS,bias}} > V_{\text{on,init}}$ ), the accelerated shift in  $V_{\text{on}}$  with illumination and the linear depen-

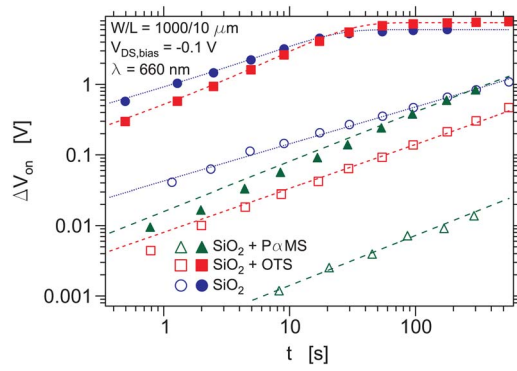


FIG. 3. (Color online)  $\Delta V_{\text{on}}$  vs  $t$  for three sets of devices with a different surface treatment of the gate dielectric, once in the dark (open symbols) and once under illumination (filled symbols) when biased in the off state. The symbols represent the data and the lines the fits to a double stretched exponential function. SiO<sub>2</sub>:  $V_{\text{GS,bias}}=15$  V and  $P_{\text{ill}}=0$  and  $8.4$  mW/cm<sup>2</sup>; SiO<sub>2</sub>+OTS:  $V_{\text{GS,bias}}=10$  V and  $P_{\text{ill}}=0$  and  $14.9$  mW/cm<sup>2</sup>; and SiO<sub>2</sub>+PαMS:  $V_{\text{GS,bias}}=10$  V and  $P_{\text{ill}}=0$  and  $14.6$  mW/cm<sup>2</sup>. The fitting parameters are listed in Table I.

dence of  $\Delta V_{\text{on}}$  on  $V_{\text{GS,bias}} - V_{\text{on,init}}$  can be verified for all three cases. It is observed that  $\Delta V_{\text{on}}$  for OTS-treated OTFTs is larger than for OTFTs with PαMS on top of the SiO<sub>2</sub>, but smaller than that for OTFTs on bare SiO<sub>2</sub>. This correlates well with the relative density of OH groups and reported electron trap densities at the surface of these dielectrics: OH groups at the surface of SiO<sub>2</sub> are known to induce electron traps while PαMS and, to a lesser degree, OTS are known to reduce this source of electron trapping.<sup>14</sup> We can therefore explain all our measurement results with a model that correlates the shift in  $V_{\text{on}}$  with electron trapping in the dielectric or at the dielectric interface. In this model, illumination accelerates the process by providing extra photogenerated electrons ready to be trapped.

The evolution of  $\Delta V_{\text{on}}$  with  $t$  for the three different surface treatments is compared in Fig. 3 together with the appropriate double stretched exponential fitting functions. Table I summarizes the fitting parameters for the three types of dielectric surfaces together with typical values for the transistor parameters  $V_{\text{on,init}}$  and hole mobility  $\mu_h$ . To derive values for  $\tau_2$  and  $\beta_2$  for a PαMS treated sample, illumination times up to  $10^4$  s would be necessary. Variations on all parameters were small for OTFTs on the same sample, and sample to sample variations were not larger than 15%, which is much smaller than the differences between the three dielectric surfaces. As expected, the  $\tau$  values increase with a decrease of the initial concentration of the OH groups at the

TABLE I. Fitting parameters for the double stretched exponential function and typical values for the transistor parameters of devices with different surface treatments of the gate dielectric. The hole mobility was calculated from the linear regime.

	$V_{\text{on,init}}$ (V)	$\mu_h$ (cm <sup>2</sup> /V s)	$\eta$ (cm <sup>2</sup> /mW)	$\beta_1$ (a.u.)	$\beta_2$ (a.u.)	$\tau_1$ (s)	$\tau_2$ (s)
SiO <sub>2</sub>	7.5	0.2	48	0.53	1.52	$1.3 \times 10^4$	$8.4 \times 10^3$
SiO <sub>2</sub> +OTS	2.0	0.6	57	0.62	1.50	$7.1 \times 10^4$	$2.3 \times 10^4$
SiO <sub>2</sub> +PαMS	0.0	0.1	20	0.71		$2.7 \times 10^6$	

interface. The  $\tau$  value for the bare SiO<sub>2</sub> sample approaches the timescale on which Chua *et al.* report the SiO–H band in the attenuated total reflection–Fourier transform infrared spectrum to decrease in a similar device.<sup>14</sup>  $V_{\text{on}}$  can only shift to more positive voltages when electrons get trapped over the complete channel length, a process requiring electrons that are either supplied by injection from the contact or by photogeneration. With this in mind, we can attribute a physical meaning to the parameter  $\eta$ , namely, as being the ratio of the photogenerated to the injected electrons,

$$\eta \propto \frac{\eta_{\text{abs}} q}{I_{\text{dark}} h\nu}, \quad (3)$$

with  $\eta_{\text{abs}}$  the absorption in the channel region of the OTFT,<sup>1</sup>  $q$  the elementary electron charge,  $I_{\text{dark}}$  the dark electron current, and  $h\nu$  the photon energy. This explains the lower  $\eta$  value for the PαMS treated sample as the dark electron current is remarkably higher in this sample. Finally, the  $\beta$  values on the three surfaces are found to be very similar to each other.

We conclude that the reported organic phototransistor behavior of pentacene OTFTs, where  $V_{\text{on}}$  (and  $V_T$ ) is observed to shift as a result of illumination, is caused by trapping of electrons at OH groups which are located at the gate dielectric/organic semiconductor interface. The illumination accelerates this process by providing an excess of photogenerated electrons which are attracted toward the interface by the positive gate bias. Dielectric surfaces that are less amenable to electron trapping result in less bias stress instability and, as a corollary, to a smaller phototransistor effect.

One of the authors (M.D.) thanks the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen) for financial support. This work was performed in collaboration between IMEC and TNO in the frame of the Holst Center.

- <sup>1</sup>Y.-Y. Noh, D.-Y. Kim, and K. Yase, *J. Appl. Phys.* **98**, 074505 (2005).
- <sup>2</sup>M. C. Hamilton, S. Martin, and J. Kanicki, *IEEE Trans. Electron Devices* **51**, 877 (2004).
- <sup>3</sup>S. Dutta and K. S. Narayan, *Adv. Mater. (Weinheim, Ger.)* **16**, 2151 (2004).
- <sup>4</sup>A. Salleo and R. A. Street, *J. Appl. Phys.* **94**, 471 (2003).
- <sup>5</sup>D. Janssen, R. De Palma, S. Verlaak, P. Heremans, and W. Dehaen, *Thin Solid Films* **515**, 1433 (2006).
- <sup>6</sup>W. B. Jackson, J. M. Marshall, and M. D. Moyer, *Phys. Rev. B* **39**, 1164 (1989).
- <sup>7</sup>F. R. Libsch and J. Kanicki, *Appl. Phys. Lett.* **62**, 1286 (1993).
- <sup>8</sup>S. C. Deane, R. B. Wehrspohn, and M. J. Powell, *Phys. Rev. B* **58**, 12625 (1998).
- <sup>9</sup>A. Salleo, F. Endicott, and R. A. Street, *Appl. Phys. Lett.* **86**, 263505 (2005).
- <sup>10</sup>H. L. Gomes, P. Stallinga, F. Dinelli, M. Murgia, F. Biscarini, D. M. de Leeuw, T. Muck, J. Geurts, W. Molenkamp, and V. Wagner, *Appl. Phys. Lett.* **84**, 3184 (2004).
- <sup>11</sup>G. Gu, M. G. Kane, and S.-C. Mau, *J. Appl. Phys.* **101**, 014504 (2007).
- <sup>12</sup>D. Kawakami, Y. Yasutake, H. Nishizawa, and Y. Majima, *Jpn. J. Appl. Phys., Part 2* **45**, L1127 (2006).
- <sup>13</sup>Y. Hu, G. Dong, C. Liu, L. Wang, and Y. Qiu, *Appl. Phys. Lett.* **89**, 072108 (2006).
- <sup>14</sup>L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, and R. H. Friend, *Nature (London)* **434**, 194 (2005).
- <sup>15</sup>K. Myny, S. De Vusser, S. Studel, D. Janssen, R. Muller, S. De Jonge, S. Verlaak, J. Genoe, and P. Heremans, *Appl. Phys. Lett.* **88**, 222103 (2006).