Structural changes in Vapour-Assembled N-octylphosphonic Acid Monolayer with Post-Deposition Annealing: Correlation with Bias-Induced Transistor Instability

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ABSTRACT

We report on the link between the structure of n-octylphosphonic acid (C_8PA) monolayer implemented in low-voltage organic thin-film transistors (OTFTs) based on aluminium oxide/C_8PA/pentacene and the kinetics of the transistor bias-induced degradation. Structural changes in the vapour-deposited C_8PA monolayer, studied by Fourier Transform Infrared (FTIR) spectroscopy, are induced by annealing. Changes in the threshold voltage, subthreshold slope, field-effect mobility, and the transistor on-current are measured as functions of the bias stress time and fitted with stretched exponential functions. The presence of C_8PA molecules physisorbed to the monolayer and/or the increased disorder between the aliphatic tails results in substantial degradation of the subthreshold slope and faster reduction in normalized mobility, while slowing the degradation of the threshold voltage. The removal of all physisorbed molecules and improved order between aliphatic tails achieved via optimized post-deposition annealing leads to an improved, microscopically-less-varied interface between C_8PA and pentacene. Consequently, the degradation of the subthreshold

slope becomes negligible, the reduction in normalized mobility becomes smaller and the degradation of the threshold voltage dominates. The equilibrium value of the normalized on-current after prolonged bias stress is ~ 0.16 regardless of the disorder in C_8PA monolayer, indicating that even though the structure of the monolayer affects the kinetics of the transistor degradation process, the same bias stress condition ultimately leads to the same relative drop in the on-current.

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1. Introduction

Alkyl phosphonic acids (C_nPA) are becoming a material of choice for passivation of high-k inorganic oxides (aluminium oxide (AlO_x), hafnium oxide (HfO_2), etc.) in organic thin-film transistors with ultra-thin gate dielectrics [1–5]. A monolayer of phosphonic acid inserted between the inorganic oxide and the organic semiconductor provides three main benefits: (i) the density of the charge carrier traps associated with the surface –OH groups of the oxide is reduced because these groups act as binding sites for the chemisorbed alkyl phosphonic acid molecules; (ii) the thickness of the phosphonic acid monolayer diminishes the polarization effect of the high-k oxide even for alkyl phosphonic acids with as few as eight carbon atoms [6]; and (iii) the low surface energy of the organic monolayer may reduce the density of defects in the subsequently deposited conjugated polymer.

To date such monolayers have been assembled from solutions [1–6]. Although there is a general agreement that alkyl phosphonic acids with shorter aliphatic tails form more disordered monolayers, the corresponding transistor performance varies widely. While studying the effect of the aliphatic chain length (C_6PA–$C_{18}PA$) on thin-film transistors, Acton at al [6] obtained the highest mobility and low threshold voltage for HfO_2/C_nPA/pentacene transistors using C_8PA. This coincided with the largest pentacene grain size and a large disorder between aliphatic tails of C_8PA monolayer. Fukuda et al [4] observed the highest as-fabricated field-effect mobility, threshold voltage and on/off current ratio for AlO_x/C_nPA/pentacene transistors implementing $C_{14}PA$ monolayer for which the largest pentacene grain size was observed. However, when transistors with $C_{14}PA$ and $C_{18}PA$ monolayers were subjected to similar bias stress, a slightly smaller decrease in the drain current with bias stress time was observed for transistors with $C_{18}PA$, in which the pentacene grain size was smaller and the order between the aliphatic tails should have been better. Finally, Hill at al [2] performed similar experiment and achieved the best transistor

performance for C_8PA monolayer. In addition, they obtained similar mobilities and threshold voltages for transistors with C_6PA and $C_{14}PA$ monolayers, even though the grain size of pentacene grown on these two monolayers was vastly different. These results point to the fact, that both the pentacene morphology and the structure of the alkyl phosphonic monolayer affect the performance of the as-fabricated transistors and their long-term bias stability. This is in agreement with the recent results from poly(3-hexylthiophene) OTFTs that show that the gate dielectric plays a more critical role in the transistor bias-induced degradation process and, in fact, the degradation in the transistor on-current can be separated into charge trapping in the semiconductor-side and the gate-dielectric-side of the semiconductor/dielectric interface [7].

We have recently developed a solution-free growth of n-octylphosphonic acid (C_8PA) monolayer using vacuum thermal evaporation [8,9]. In this process, a thickness equal to a few monolayers of n-octylphosphonic acid is deposited on aluminium oxide and the physisorbed molecules are subsequently removed by thermal heating. The process leads to a chemisorbed monolayer of C_8PA [9]. When such a monolayer is implemented in low-voltage organic thin-film transistors (OTFTs) based on pentacene, the performance of the as-fabricated transistors substantially changes with the duration of the desorption/post-deposition annealing of C_8PA monolayer [8], pointing to the importance of the monolayer microstructure in the charge carrier transport within the transistor. Shorter post-deposition annealing can also result in C_8PA thickness larger than a monolayer (cca 1.5 monolayers) [8] that is mimicking the results obtained during the solution self-assembly [10]. Consequently, such dry process can be used as a tool for correlating the structural changes in the C_8PA monolayer with the short- and long-term transistor performance, while eliminating the effect of possible solvent traces. Understanding this link comprises an important step toward stable OTFTs.

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2. Experimental details

Transistors, metal-insulator-metal structures (MIM) and samples for Fourier Transform Infrared (FTIR) measurement were fabricated on Eagle 2000 glass. For FTIR, a blanket layer of aluminium was thermally evaporated and UV/ozone oxidation was used to form thin AlO_x [11] with low surface roughness of ~0.48 nm [8]. C_8PA was thermally evaporated on top of AlO_x and subsequently heated to 160°C for 25, 90 and 210 minutes. FTIR of C_8PA/AlO_x was measured with Nicolet 380 spectrometer.

The transistor and metal-insulator-metal (MIM) structures encompass the same AlO_x/C_8PA bi-layers. The top electrode of the MIM structures is formed by Au. 50-nm-thick pentacene and 50-nm-thick Au source/drain contacts complete the transistors. The fabrication details are described in detail elsewhere [8]. The electrical characterization of the MIM structures and transistors was performed with Agilent B1500A semiconductor device analyser under dark ambient environmental conditions. The capacitance of MIM structures was measured between 1 kHz and 1 MHz. The transfer characteristics of the OTFTs were measured in a sweep mode. The OTFT parameters were extracted from the transfer characteristics using the standard MOSFET equations.

During the bias-stress measurement performed under dark ambient conditions the voltage of −3 V was applied on the gate terminal for a total time of 5000 s, while the source and drain electrodes were grounded. This configuration imposes larger changes in the threshold voltage when compared to biasing gate and drain electrodes simultaneously [12,13]. The bias stress was interrupted at certain time intervals to measure the transistor transfer characteristics. These were used to extract the threshold voltage, subthreshold slope, field-effect mobility, and the on-current (defined as drain current at V_{GS} and $V_{DS} = −3$ V) as functions of the bias stress time. The bias-stressed transistors had channel length of 50 μm and channel width of 1000 μm.

3. Results

3.1. Transistor performance as a function of C_8PA desorption/annealing

Figure 1 shows the cross-section of pentacene OTFTs. The initial transistor parameters for four C_8PA post-deposition desorption/annealing times of 25, 60, 90 and 210 minutes are given in [8]. The removal of the physisorbed molecules is not fully completed in 25 minutes, resulting in a mean thickness of ~ 1.5 monolayers. The reduction in the mean thickness of C_8PA monolayer between 60 and 90 minutes is < 9%. When the annealing time is increased from 90 to 210 minutes the change in the C_8PA thickness is negligible; however, the mean field-effect mobility is increased by 50%, the threshold voltage by 10%, the on/off current ratio by a factor of 2.5, while the subthreshold slope is reduced by 17% and the off-current by a factor of 2, all as a result of the microscopic changes within the C_8PA monolayer (see section 3.3).

Classical transmission line method [14] was employed to extract the source/drain contact resistance R_c from a series of transistors with varying channel length L. When the field-effect mobilities are corrected for the extracted value of $R_c = 6.14$ MΩ, the values are more than doubled, leading to mobility of 0.091 cm^2/Vs for transistors with C_8PA annealed for 210 minutes. Taking into account our room temperature deposition of pentacene that leads to grain size of ~ 150 nm, such value is similar to mobilities obtained by others [4,6] for comparable pentacene grains.

Finally, our non-optimized pentacene growth that results in small pentacene grains is not very sensitive to the changing microstructure of the underlying organic monolayer [8]. Therefore, as will be shown in following sections, the effect of the C_8PA monolayer on the long-term transistor stability is not obscured by the varying properties of the organic semiconductor, even though the initial field-effect mobility is lower.

3.2. Bias-induced OTFT degradation

The increasing C_8PA annealing time results in both higher gate dielectric capacitance and higher initial threshold voltage. Consequently, the induced capacitive charge ($Q = C|V_{GS} - V_t|$) in the beginning of the transistor bias stress experiment is the same within ±5% for all C_8PA annealing times. Figure 2 shows the degradation of the OTFT parameters as a function of bias stress time. Figures 2 (a) and (b) depict the changes in the threshold voltage and subthreshold slope, respectively. Figures 2(c) and (d) show the normalized filed-effect mobility and the normalized on-current. AlO_x/C_8PA OTFTs with C_8PA annealed for 210 minutes exhibit very small increase in the subthreshold slope, smallest reduction in the normalized field-effect mobility and the largest threshold voltage shift after the bias stress. Shorter C_8PA annealing times lead to a larger change in the normalized mobility and the inverse subthreshold slope, and a smaller threshold voltage shift after the bias stress. However, the change in the normalized on-current after the 5000-second bias stress is comparable for all samples, as can be seen in Figure 2(d).

The stretched exponential functions are used to fit the threshold voltage, subthreshold slope, field-effect mobility, and the drain current presented in Figure 2. The form of these stretched exponential equations depends on whether a change in the parameter or the normalized parameter is fitted:

$$\Delta V_t = |V_t(t) - V_t(0)| = |V_t(\infty) - V_t(0)| \cdot \left[1 - e^{-(t/\tau_{Vt})^{\beta_{Vt}}} \right] \tag{1}$$

$$\Delta S(t) = S(t) - S(0) = \left(S(\infty) - S(0) \right) \left[1 - e^{-(t/\tau_S)^{\beta_S}} \right] \tag{2}$$

$$\frac{\mu(t)}{\mu(0)} = \frac{\mu(\infty)}{\mu(0)} + \left[1 - \frac{\mu(\infty)}{\mu(0)} \right] \cdot e^{-(t/\tau_\mu)^{\beta_\mu}} \tag{3}$$

$$\frac{I_d(t)}{I_d(0)} = \frac{I_d(\infty)}{I_d(0)} + \left[1 - \frac{I_d(\infty)}{I_d(0)}\right].e^{-(t/\tau_{Id})^{\beta_{Id}}} \qquad (4)$$

Here $\Delta V_t(t)$ is the threshold voltage shift, $V_t(t)$ is the threshold voltage after t seconds of bias

stress, $V_t(0)$ is the initial threshold voltage before the application of the electrical bias, $V_t(\infty)$

is the equilibrium threshold voltage after prolonged electrical bias, τ_{Vt} is a time constant and

β_{Vt} is the stretching parameter ($0 < \beta_{Vt} \leq 1$). Similarly, $\Delta S(t)$ is the change in the

subthreshold slope after t seconds, $S(t)$ is the subthreshold slope after t seconds of bias stress,

$S(\infty)$ is the equilibrium subthreshold slope after very long time, $S(0)$ is the initial subthreshold

slope before the application of the electrical bias, τ_S is a time constant, and β_S is the

stretching parameter. $\frac{\mu(t)}{\mu(0)}$ is the field-effect mobility after t seconds of bias stress normalized

with respect to the initial mobility, $\frac{\mu(\infty)}{\mu(0)}$ is the normalized equilibrium mobility after

prolonged electrical bias, τ_μ is a time constant, and β_μ is the stretching parameter. Finally,

$\frac{I_d(t)}{I_d(0)}$ is the normalized drain current after t seconds of bias stress, $\frac{I_d(\infty)}{I_d(0)}$ is the normalized

equilibrium drain current after prolonged electrical bias, τ_{Id} is a time constant, and β_{Id} is the

stretching parameter. Table I lists the time constants and the stretching parameters obtained

from the stretched exponential fits to the data shown in Figure 2.

Table I. Time constants and stretching parameters obtained from Figure 2 using Eqs. (1)-(4).

C_8PA annealing time (min)	τ_{Vt} (s)	β_{Vt}	τ_S (s)	β_S	τ_μ (s)	β_μ	τ_{Id} (s)	β_{Id}
25	3.3×10^6	0.15	4.0×10^4	0.35	4.5×10^2	0.61	3.0×10^2	0.29
60	8.8×10^3	0.23	7.0×10^4	0.36	5.7×10^2	0.61	3.7×10^2	0.30
90	1.6×10^3	0.26	5.3×10^6	0.42	5.7×10^2	0.61	1.8×10^2	0.33
210	7.5×10^2	0.28	3.7×10^{10}	0.72	7.0×10^2	0.65	1.4×10^2	0.34

The time constants and stretching parameters presented in Table I suggest that the threshold voltage shift, subthreshold slope and normalized field-effect mobility do not follow the same kinetics. The time constant of the threshold voltage shift decreases with the rising C_8PA annealing time, while the stretching parameter increases. The stretched exponential fit presented for OTFTs with C_8PA annealed for 25 minutes should be taken with reservation, since its correlation factor R^2 is only 0.91. The time constant and the stretching parameter of the subthreshold slope change depend strongly on the annealing time of the C_8PA monolayer. As the annealing time rises from 25 to 210 minutes, the time constant increases from 4.0×10^4 to 3.7×10^{10} and the stretching parameter rises from 0.35 to 0.72.

The drop in the field-effect mobility exhibits low time constant and relatively high stretching parameter regardless of the C_8PA annealing time. In fact, the C_8PA annealing time does not have large effect on these parameters. The equilibrium value of $\frac{\mu(\infty)}{\mu(0)}$ is 0.53, 0.62, 0.65, and 0.67 for C_8PA annealing times of 25, 60, 90, and 210 minutes, respectively. Finally, increasing C_8PA annealing time leads to a slight decrease in the time constant of the normalized drain current and a small increase in the stretching parameter. The equilibrium value of $\frac{I_d(\infty)}{I_d(0)}$ is ~ 0.16 for all C_8PA annealing times, indicating that even though the structure of the monolayer (see section 3.3) affects the kinetics of the transistor degradation process, the same bias stress ultimately leads to the same normalized equilibrium drain current.

3.3. Changes in C_8PA structure with annealing

Figure 3 shows the relevant sections of the FTIR spectra of C_8PA/AlO_x bi-layers with C_8PA annealed to 160°C for 25, 90, and 210 minutes, as well as the reference non-annealed AlO_x layer without C_8PA monolayer. Figure 3(a) depicts a broad absorption band at ~1110

cm^{-1} associated with Al–O–P stretch mode resulting from the phosphonate head group bonded to the surface of aluminium oxide [15]. The band is centred near 1110 cm^{-1} and it is shifted to slightly higher wave numbers for C$_8$PA annealed for 25 minutes when compared to that annealed for 90/210 minutes. The integral intensity of the peak is reduced between 25 and 90 minutes and then slightly increased after the 210-minute annealing. In addition, the right shoulder of the peak (near 1150 cm^{-1}) is reduced with the increasing annealing time. The reference AlO$_x$ sample exhibits a peak located near 1100 cm^{-1}, associated with the Al–OH groups [16], that overlaps with the band of the phosphonate salts. The absorbance of this band is decreased when the AlO$_x$ is annealed for 3 hours [9]. Consequently, the reduction in the integral intensity of the 1110 cm^{-1} band between 25- and 90-minute anneals may be associated with the reduction in the Al–OH mode, while the increase in the integral intensity of this band between 90- and 210-minute anneals is associated with C$_8$PA monolayer.

Figure 3(b) shows the vibrations of the P=O bond of C$_8$PA at ~1204, 1226, and 1244 cm^{-1} [17] and a vibration at 1263 cm^{-1} assigned to the methyl group. In addition, the reference AlO$_x$ sample exhibits a vibration at 1255 cm^{-1} that is not observed after the 3-hour anneal. The amplitude of the P=O vibrations is reduced between the 25- and 90-minute anneal and then marginally increased after the 210-minute annealing. Vibrations in the region of 2500-2800 cm^{-1} and 2200-2400 cm^{-1} associated with the P–OH groups of C$_8$PA [17] are not observed irrespective of the annealing time.

Absorbance peaks in the region of 2800–3000 cm^{-1} shown in Figure 3(c) correspond to the symmetric/asymmetric stretching modes of CH$_2$/CH$_3$ groups; with the symmetric CH$_3$ stretching mode being very weak. The centre of the symmetric and asymmetric CH$_2$ stretching mode is located at ~ 2853 cm^{-1} and 2925 cm^{-1}, respectively. These values are similar to those reported for C$_8$PA monolayers assembled from solutions [6]. Since the C$_8$PA molecules are attached to the AlO$_x$ surface and thus immobilized, changes in these peak

positions with annealing are unlikely. On the other hand, changes in the molecular alignment are possible because C_8PA source material readily evaporates at a temperature of 160°C. Increase in the annealing time from 25 to 90 minutes increases the full width at half maximum (FWHM) of CH_2 stretching modes by 1-2 cm^{-1}. Further increase in the annealing time from 90 to 210 minutes reduces its FWHM to or below the value achieved for C_8PA annealed for 25 minutes. In addition, the increase in the annealing time from 25 to 90 minutes leads to a decrease in the amplitude and integral intensity of all four peaks, accompanying the removal of the remaining physisorbed C_8PA molecules. On the other hand, the increase in the annealing time from 90 to 210 minutes leads to a substantial increase in the amplitude of all four peaks. This is related to a change in the alignment of C_8PA molecules since the annealing cannot add molecules to the monolayer. On average, the intensity rises by 39% and the integral intensity by 45%. The slight change in the mean C_8PA thickness (capacitance data) also suggests an increased average tilt of the molecules away from the surface normal by ~ 2°.

4. Discussion

4.1. As-fabricated OTFTs

In pentacene OTFTs the acceptor-like states with a characteristic energy $E(0/-)$ above the HOMO act as dopants while the donor-like states with the characteristic energy $E(+/0)$ above the HOMO are hole traps. The acceptor-like states are in a neutral charge state when the Fermi level is moved close to the HOMO, i.e. the transistor is in accumulation. They become negatively charged when the Fermi level is moved away from the HOMO, i.e. the transistor is in depletion. Negatively-charged acceptor-like states manifest themselves as a shift in the transistor onset voltage toward positive values and an increase in the transistor off-current. (Onset voltage V_{onset} is the gate voltage for which an onset of the drain current I_d

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is observed.) Similarly, the donor-like states are in a neutral charge state when the Fermi level is moved away from the HOMO, i.e. the transistor is in depletion. They become positively charged by capturing mobile holes when the Fermi level is moved closer to the HOMO, i.e. the transistor is in accumulation. Although these trapped holes are part of the electrostatic charge induced by the gate electrode, they do not contribute to the drain current. Consequently, more negative gate voltage is needed to induce the same concentration of mobile holes, resulting in a shift of the threshold voltage toward more negative values. As the transistor goes from the depletion into accumulation and the Fermi level is moved toward the HOMO, the acceptor-like states go from negative to neutral charge state, while the donor-like states transform from neutral to positive charge state. The as-fabricated OTFTs exhibit different onset and threshold voltages and subthreshold slopes as a function of the C_8PA annealing time. The threshold voltage shifted from ~ -1.2 V to ~ -1.4 V when annealing time of the C_8PA layer was raised from 25 to 210 minutes [8], indicating that short C_8PA anneal results in acceptor-like states or their dominance. A similar behaviour of the threshold voltage was described by Scheinert et al. [18] and Völkel et al. [19] for pentacene OTFTs using amorphous silicon and density of states model, respectively. Scheinert et al. [18] suggested that both donor and acceptor states are present close to the HOMO of pentacene and concluded that the presence of acceptor states leads to larger transistor off-current. This is in agreement with our experimental finding that the off-current is reduced from 4.57×10^{-12} A to 0.66×10^{-12} A when the C_8PA annealing time is increased from 25 to 210 minutes, and thus confirms the presence of acceptor-like states for short anneal.

Another possibility includes an existence of negatively charged immobile species in the presence of hydroxyl groups, as demonstrated in the case of silanols (Si–OH) when silicon dioxide is used as a gate dielectric [20]; and electrochemical reactions that involve adsorbed water when the device is exposed to ambient air [21]. The existence of the P–OH

groups of the physisorbed phosphonic acid molecules would provide such species. Since the capacitance confirms that the C_8PA thickness for the shortest anneal is slightly more than a monolayer, the largest density of P–OH groups is expected for the 25-minute anneal. (A slightly lower water contact angle of C_8PA annealed for 25-minutes also points to the possible presence of hydroxyl groups [8].) This would lead to the highest density of P–O$^-$ groups and the lowest transistor threshold voltage, as is indeed observed. The removal of the physisorbed C_8PA molecules with the increasing annealing time leads to the reduced number of P–OH groups and the more negative threshold voltage.

4.2. OTFT bias stress

Eqs. (1)-(3) assume different degradation kinetics for the threshold voltage, subthreshold slope and the field-effect mobility. Previous experimental results suggest that this may be the case. For example, the exposure of pentacene OTFTs to ambient atmosphere, mainly lowers the field-effect mobility [12], [22] as a result of the oxidation of the central benzene ring of pentacene. This aging phenomenon does not affect the subthreshold slope but it leads to the reduction in the on-current and rise in the off-current [22]. In OTFTs based on semi-crystalline polythiophene the observed irreversible degradation in the subthreshold slope is unrelated to the threshold voltage shift [23].

In optimized field-effect transistors, the bias-induced degradation proceeds through the shift in the threshold voltage, while the changes in the mobility and subthreshold slope are negligible. However, if very large gate-source/drain voltage is applied, degradation in all transistor parameters is observed and this behaviour is not unique to OTFTs [24,25]. The stretched exponential function dictates that while the initial degradation is faster-than-exponential, the degradation stops eventually, as one would expect in the case when the threshold voltage of the transistor approaches the gate bias voltage. The smaller the value of

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β, the faster is the initial degradation. Assuming that the degradation of various transistor parameters requires a channel formation near the semiconductor/dielectric interface, the degradation of the threshold voltage, subthreshold slope and the field-effect mobility would cease when the gate voltage is not high enough to cause the accumulation of holes.

As can be seen from Table I, the stretching parameters of the threshold voltage shift, change in the subthreshold slope, normalized mobility, and the normalized on-current are increasing with the rising annealing time of C_8PA monolayer. This implies that the time response becomes less stretched and the distribution of the trapping energies ΔE_T responsible for the degradation of any transistor parameter becomes narrower ($\Delta E_T = k_B T/\beta$ [7]). In another words, the microscopic environments at or near the semiconductor/dielectric interface become less varied.

The time constant of the threshold voltage shift decreases with the increasing C_8PA annealing time, indicating that the equilibrium is reached faster. Zschieschang et al. [12] observed a rise in the stretching parameter β_{Vt} from 0.29 to 0.42 as V_{DS} increased from 0 to 2 volts. Zhang et al. [26] and Gu et al. [27] obtained β_{Vt} ~0.4 for higher V_{DS}. Our transistors exhibit an increase in β_{Vt} with increasing C_8PA annealing time, reaching a value of 0.28 after the 210-minute anneal, which is similar to the value reported for zero V_{DS} in [12]. According to Shang et al. [28], similar bias-induced threshold voltage shift is observed when pentacene and various gate dielectrics are used. Since in our transistors the V_t shift depends on the C_8PA annealing time, one would infer that the charge trapping responsible for this shift is not related to the semiconductor.

Contrary to the threshold voltage, the time constant of the subthreshold slope increases with the annealing time, meaning that is takes longer to reach the equilibrium. The increase in the inverse subthreshold slope of the transfer characteristic with bias stress is typically associated with the generation of additional defect states at the

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semiconductor/dielectric interface. As the annealing progresses, the generation of such states is suppressed and their energy distribution becomes narrower.

The time constant and the stretching parameter of the normalized mobility are not particularly sensitive to C_8PA annealing time, suggesting that the primary factor controlling the mobility degradation is not the structure of the organic monolayer, even though a small change in the water contact angle of C_8PA with annealing is observed, leading to minor change in the morphology of the subsequently deposited pentacene [8]. In agreement with the previous observations we believe that the oxidation of pentacene is the main factor and the minor variations in the pentacene morphology may account for some differences in the reduction of the normalized mobility with the bias stress time [12,29].

Finally, the degradation of the drain current is a combined effect of changes in the threshold voltage, mobility, and the subthreshold slope. The time constant of the normalized drain current is slightly decreasing with the increasing C_8PA annealing time, meaning that the equilibrium is reached a bit faster. Nevertheless, the final equilibrium value does not depend on the structure of the organic monolayer, even though the degradation of the threshold voltage, subthreshold slope and possibly mobility exhibit correlation with the microstructure. Lastly, one should be reminded that the effect of pentacene on the transistor stability cannot be decoupled from that of C_8PA. However, as mentioned in section 3.1, the microstructure of C_8PA has only minimal effect on the pentacene growth due to its non-optimized growth condition.

The FTIR data confirm that the increase in the annealing time from 25 to 90 minutes leads to the removal of the remaining physisorbed C_8PA molecules, while slightly increasing the disorder between the aliphatic tails and shifting the vibrations of the phosphonate salts to lower wavenumbers. These microscopic changes manifest themselves as reduced degradation of the subthreshold slope and normalized mobility and an increased degradation of the

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threshold voltage. Extension of the annealing time from 90 to 210 minutes primarily improves the molecular alignment within the organic monolayer and, consequently, the degradation of the subthreshold slope is much suppressed, while the degradation of the threshold voltage dominates. While the microscopic origin of the degradation of various transistor parameters is not conclusive, the molecular disorder within the C_8PA monolayer and the presence of physisorbed molecules manifest themselves as increased degradation of the subthreshold slope and field-effect mobility. Optimized post-deposition annealing improves the interface between C_8PA and pentacene and the bias-induced degradation of the OTFTs resembles that of OTFTs with solution-assembled alkyl phosphonic acids [12].

Comparing the properties of the as-fabricated transistors to their degradation behaviour, one would conclude that the presence of acceptor-like states/hydroxyl groups resulted in severe degradation of the subthreshold slope and increased degradation of the field-effect mobility. On the other hand, the reduction/absence of acceptor-like states/hydroxyl groups led to reduced degradation of the subthreshold slope and field-effect mobility.

5. Conclusion

The bias-induced instability of low-voltage transistors based on pentacene and thin AlO_x functionalized with vapour-deposited n-octylphosphonic acid (C_8PA) monolayer is studied as a function of the C_8PA microstructure, where the C_8PA structural changes are induced by post-deposition annealing. The capacitance and FTIR data confirm that the increase in the annealing time from 25 to 90 minutes at 160°C leads to the removal of the remaining physisorbed C_8PA molecules, while slightly increasing the disorder between the aliphatic tails and shifting the vibrations of the phosphonate salts to lower wavenumbers. These microscopic changes lead to reduced degradation of the subthreshold slope and

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normalized mobility and an increased degradation of the threshold voltage. Extension of the annealing time from 90 to 210 minutes primarily improves the molecular alignment between the aliphatic tails and, consequently, the degradation of the subthreshold slope is much suppressed, while the degradation of the threshold voltage dominates.

Stretched exponential functions are fitted to the changes in the threshold voltage, subthreshold slope, and normalized field-effect mobility as functions of the bias stress time. The different time constants and stretching parameters suggest that these transistor parameters do not follow the same kinetics. Nevertheless, their stretching parameters are increasing with the rising annealing time of C_8PA monolayer. This implies that the time responses become less stretched and the distribution of the trapping energies responsible for the degradation of any transistor parameter becomes narrower. Consequently, the microscopic environments at or near the semiconductor/dielectric interface become less varied. The equilibrium value of the normalized on-current after prolonged bias stress is ~ 0.16 for all C_8PA annealing times, indicating that even though the structure of the monolayer affects the kinetics of the transistor degradation process, the same bias stress ultimately leads to the same relative drop in the on-current.

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Figure captions:

Figure 1. OTFT cross-section.

Figure 2. Threshold voltage shift (a), change in the inverse subthreshold slope (b), normalized field-effect mobility (c), and normalized drain current at V_{gs} and $V_{ds} = -3$ V (d) as functions of bias stress time. The data is fitted with stretched exponential functions defined by Eqs. (1)-(4).

Figure 3. Sections of FTIR spectra of C_8PA/AlO_x bi-layer with C_8PA annealed for various times. AlO_x reference layer is shown as well.

Au

pentacene

Al

glass

n-octylphosphonic
acid

aluminium
oxide