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Water-Related Instabilities in Pentacene Thin-Film Transistors

L. Mariucci,* S. Cipolloni, D. Simeone, M. Cuscunà, L. Maiolo,
A. Minotti, A. Pecora, A. Valletta and G. Fortunato

CNR-Consiglio Nazionale delle Ricerche-Institute for Microelectronics and Microsystems, Roma, Italy

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We have analyzed the hysteresis of the transfer characteristics of pentacene thin-film transistors (TFTs) measured under different environmental conditions (vacuum, oxygen, dry nitrogen, air and nitrogen with different relative humidities). The results showed that, whereas the characteristics in dry atmospheres are quite stable, the hysteresis increases with the percentage of moisture, indicating that adsorbed water is the main cause of the environmental instability in pentacene TFTs. In addition, transient current experiments have been carried out in air. Through these measurements, we have been able to evaluate a characteristic time of drain current reduction of several seconds. These results indicate that the environmental instability is not simply related to charge trapping in localized gap states and slower phenomena should also be considered.

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I. INTRODUCTION

In the last decade, organic thin film transistor (O-TFTs) have attracted considerable interest, thanks to their being a low-cost, low-temperature process that allows TFT fabrication on plastic substrate [1, 2]. Operational and environmental stability is a fundamental feature for O-TFTs applications, but unfortunately, it has been demonstrated that exposure to air is, in general, detrimental to their performance [3,4]. Indeed, on-current reductions, as well as hysteresis in the transfer characteristics of O-TFTs, measured in different ambient conditions, have been reported in the literature [5–10]. Although hysteresis has been observed in the transfer characteristics in vacuum conditions [6], larger hysteresis occurs when devices are measured in air [5, 8], indicating oxygen and/or water absorption in the organic film as the origin of the electrical instability [5]. It has been reported that hysteresis behavior depends on the fabrication process, [7, 10] as well as on gate dielectrics [8] and the hysteresis mechanisms have been ascribed either to charge injection into gate dielectric [7, 11] or to charge trapping in the semiconductor or at the dielectric/semiconductor interface [5,6,10].

In this research, in order to identify the main causes of hysteresis, we measured the transfer characteristics of pentacene TFTs in different environmental conditions and with different gases and relative humidities. In addition, the transient drain current has been measured in order to evaluate the characteristic time of the phenomenon.

*E-mail: luigi.mariucci@cnr.it; Fax: +39-64-993-4706

II. EXPERIMENTS AND DISCUSSION

Bottom-contact devices have been fabricated on heavily-doped silicon wafers (acting as gate electrode) with thermal silicon dioxide, 90-nm-thick, as gate dielectric. Source and drain gold contacts, 20-nm-thick, are defined using optical lithography and wet-etching (W = 200 μm, L = 100 − 20 μm). A thin film of polycrystalline pentacene (Sigma Aldrich, 99 % purity), 30-nm-thick, has been evaporated on a PMMA buffer layer used to improve the structural properties of pentacene (a more detailed description of the use of PMMA as buffer layer can be found in Ref. 12). Device electrical characteristics were measured in a MMR cryostat using a Keythley 236 source/measure unit and a Keythley 230 voltage source. Transient current measurements were carried out using an HP 54501 oscilloscope and a current amplifier. Measurements were performed under five different conditions: vacuum (10^{-2} mbar), dry nitrogen, dry oxygen, air with 50 % of relative humidity (RH) and nitrogen+moisture with RH = 90 %. Transfer characteristics were measured sweeping the gate voltage, V_{gs}, in both directions between 5 V and −30 V, in voltage steps of 0.5 V every 0.5 s.

In Figure 1 the transfer characteristics of bottom-contact pentacene TFTs measured in different environmental conditions are reported for both upward and downward voltage ramping. The devices exhibit, when

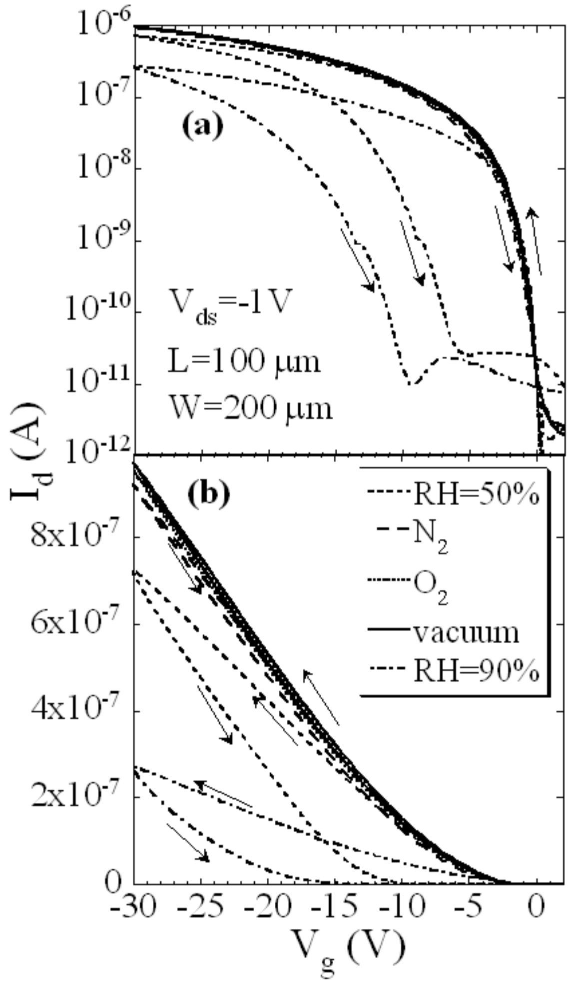

Fig. 1. (a) Semilogarithmic and (b) linear plots of transfer characteristics of pentacene TFTs measured under different environmental conditions.

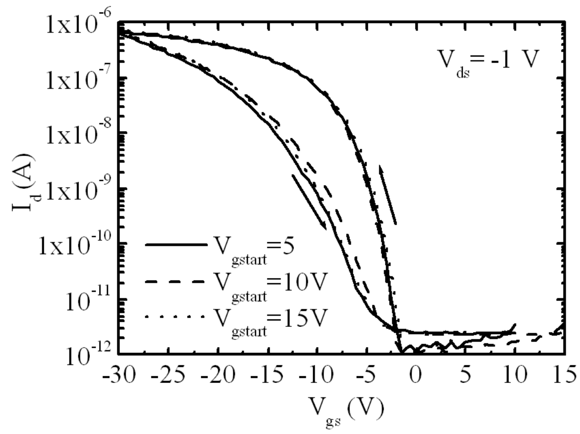

Fig. 2. Transfer characteristics of pentacene TFTs measured in air with different starting gate voltages.

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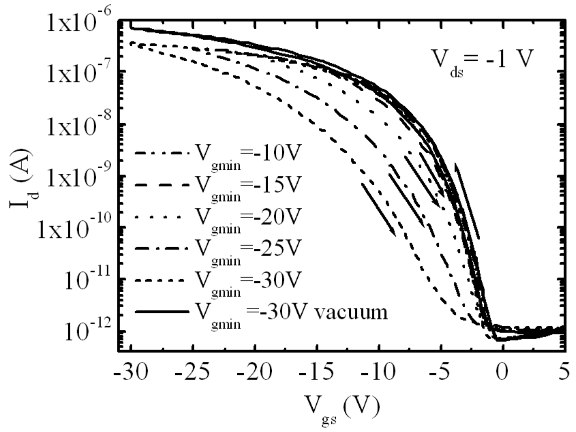

Fig. 3. Transfer characteristics of pentacene TFTs measured in air with different lower gate voltages.

measured in vacuum, a typical field effect mobility, μ_{FE}, of 0.5 cm^2/Vs, a subthreshold-slope of 0.4 V/dec, a threshold voltage $V_{th} \sim -8$ V and on/off an current ratio $I_{on/off} > 10^6$. As can be seen in Figure 1, devices show small hysteresis when measured under vacuum, dry oxygen and nitrogen atmospheres. On the contrary, when the measurements are performed in air or nitrogen with controlled relative humidity (RH equal to 50 % and 90 %, respectively), a large hysteresis is observed. It can be seen that when hysteresis occurs, the off-to-on sweep curves coincide with the vacuum and dry atmosphere curves in the subthreshold region down to about -3 V, whereas, at lower V_{gs}, a current decrease is observed. During the on-to-off sweep, the current remains lower than during the off-to-on sweep both in the on-region and the subthreshold region. In addition, in presence of moisture, the slope of the off-to-on curve in the on-region is lower than the slope in vacuum condition, resulting in an apparent decrease in field-effect mobility and the on-to-off curve is parallel to the vacuum curve, at least for RH = 50 %. It can be noted that the electrical characteristics, measured in atmosphere with moisture, are reproducible when repeated measurements are performed and that the hysteresis effect is fully reversible when the vacuum or dry atmosphere conditions are restored. In order to better characterized the hysteresis effect, we measured the transfer characteristics for different initial (Figure 2) and final (Figure 3) gate voltages and with different ramp rate (Figure 4). We found that, whereas the starting gate voltage has no effect on the characteristics, lower final gate voltage and slower ramp rate increase the hysteresis effect. These experimental results indicate that the hysteresis in the transfer characteristics is induced by slow trapping of positive charge, with the time constant being comparable to the measurement time. Moreover, our results clearly point out that this phenomenon is related to water absorption in the pentacene film while the characteristics are unaffected by the oxygen, sometimes indicated as the origin of defects and electrical instability in pentacene TFTs [5,13]. The water molecules seem to be quickly removed from the pentacene film, as con-

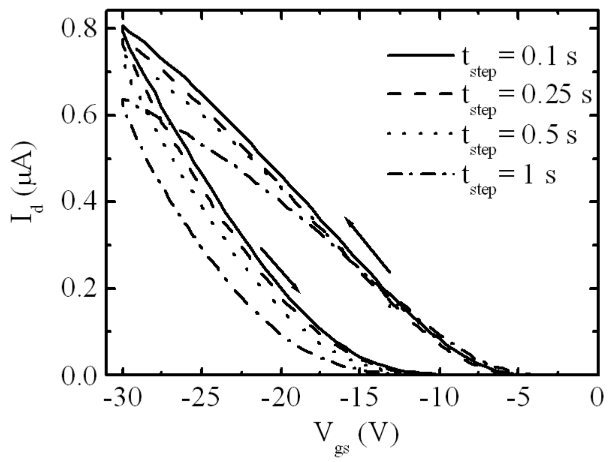

Fig. 4. Transfer characteristics of pentacene TFTs measured in air with different ramp rates.

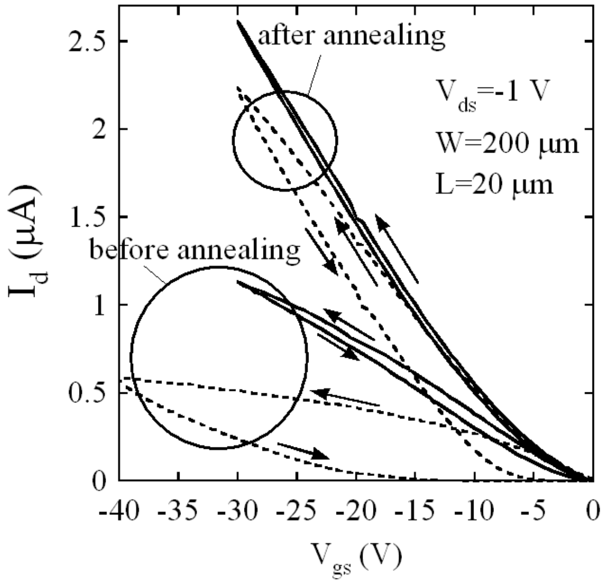

Fig. 5. Transfer characteristics of pentacene TFTs with a parylene passivation layer measured in vacuum (solid lines) and in air (dashed lines) before and after thermal annealing.

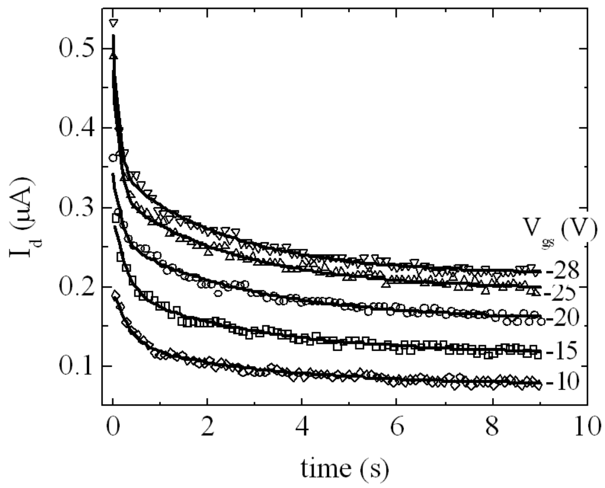

Fig. 6. Time dependence of the drain current (symbols) of a pentacene TFT measured in air after a gate voltage is applied at various gate voltages. I_d curves are fitted by using a two-exponential-decay function (solid lines).

firmed by repeated air/vacuum cycles, suggesting a weak interaction between water molecules and pentacene, as dipole-dipole interactions, rather then a strong chemical bond.

Considering the major role of moisture in the electrical instability of pentacene TFTs, a protective coating against the water is fundamental to prevent aging effects [14]. In this respect, we investigated the role of the parylene film that is usually used as a passivating layer, allowing pentacene patterning. Figure 5 shows the transfer characteristics of a pentacene TFT with a parylene passivation layer measured in vacuum and air conditions. As can be seen, large hysteresis is observed in the characteristics, showing that the parylene layer is not an efficient barrier against water diffusion. On the other hand, the parylene passivation layer allows the annealing of pentacene film, at temperatures up to 120 °C. After annealing, pentacene TFTs show improved characteristics with increased field-effect mobility and, as shown in Figure 5, a reduced hysteresis effect, probably as a consequence of improved structural properties of pentacene that reduce water diffusion.

As discussed above, hysteresis of the transfer characteristics is induced by slow charge trapping, with the time constant being comparable to the measurement time. In order to quantify the trapping time constant, we measured the transient drain current when the device was biased to different negative gate voltages starting from $V_{gs} = 0$ V (see Figure 6) in air condition (RH = 50 %). As can be seen, the drain current, after a fast decrease, tends to the equilibrium value quite slowly. The drain current variation can be fitted by using the sum of two exponential decays:

$$I_d = I_0 \exp(-t/\tau_0) + I_1 \exp(-t/\tau_1) + I_2,$$

where the fastest time constant, τ_0, is of the order of 0.1 − 0.2 s and τ_1 is between 2 and 3 s. The latter large time constant indicates that carrier trapping, responsible of hysteresis, is a rather slow phenomenon, implying trapping states with a very small cross-section. In Ref. 5 and Ref. 6, these trapping states are identified as acceptor states located in the lower part of the band gap (near the higher occupied molecular orbital, HOMO, of pentacene). Following this model, in the off-state, the traps are filled by electrons and negatively charged. During the off-to-on sweep, an excess of holes is induced, above the equilibrium population, to balance the trapped electrons. The induced free holes are then slowly captured by the charged acceptors and no negative charges are present during on-to-off sweep, resulting in the hysteresis effect.

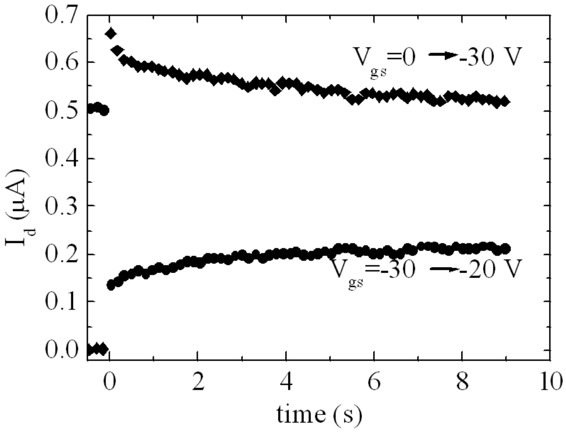

Fig. 7. Time dependence of the drain current of a pentacene TFT measured in air after a $V_{gs}= -30$ is applied (diamonds) and after changing V_{gs} from -30 V to -20 V (circles).

This model is in agreement with the experimental results reported in Ref. 5, showing an higher drain current during the off-to-on sweep when the measurements are performed in air. It should be pointed out that the slow trapping time indicates a very small value for the hole capture cross-section, σ_p, of acceptors states, estimated by Erlen *et al.* [6] to be of the order of 10^{-22} cm^{-2} by using a thermal velocity value of 10^3 cm/s. Even using such a low thermal velocity estimate, the estimated capture cross-section value seems to be very small compared to typical values usually obtained for charged traps in semiconductors ($10^{-14} - 10^{-16}$ cm^{-2}). We note that our experimental results show a different hysteresis effect, compared to the results in Ref. 5, with a decrease in the drain current when the devices are measured in atmosphere with high RH (Figure 1). This behavior is incompatible with the above proposed model whereas it can be explained by slow trapping of free holes in donor states during the off-to-on sweep with a progressive shift of the threshold voltage. The trapped charges are slowly released during the on-to-off sweep, resulting in the observed hysteresis. Indeed, as shown in Figure 7, the time constant of current variation during the on-to-off sweep is several seconds, as during the off-to-on sweep. In addition, our results indicate that the slow trap states are clearly related to the presence of water in pentacene film and are easily removed when water is removed. These evidences seem to exclude the trap states responsible of transfer characteristic hysteresis being metastable gap states, similar to a-Si:H localized states, that require high temperature to be annealed.

Street *et al.* [15] proposed that the slow formation of hole bipolarons is the primary stress mechanism in some polymer TFTs. The rate of bipolaron formation is very slow because of strong Coulomb repulsion of holes whereas the local structural distortion of the polymer induced by the trapped holes is immediately reverted

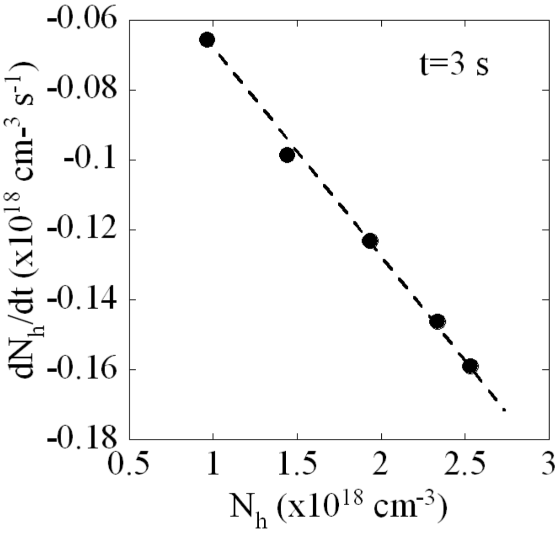

Fig. 8. The rate of decrease of the hole concentration, dN_h /dt, plotted versus the hole concentration, N_h, measured at constant time (t = 3 s) and various V_{gs}. DN_h/dt and N_h were calculated from the data shown in Figure 6.

when the carriers are removed. In order to verify if a similar mechanism can be applied to the hysteresis in pentacene TFT, we carried out the analysis performed in Ref. 15 on the transient current data, considering the variation (dN_h/dt) of the hole concentration as a function of V_{gs} at fixed measurement time (t = 3 s). The holes concentration can be obtained from the drain current, by using

$$I_d = (W/L)C_G\mu(V_{gs} - V_T)V_d = (W/L)\mu q N_h V_d d,$$

where C_G is the gate capacitance, μ is the field-effect mobility and d is the effective width of accumulation layer. Instead of the rather noisy experimental data shown in Figure 6, we calculated dN_h/dt and the N_h values by considering the double exponential fit and the result is in very good agreement with the experimental data. Figure 8 shows the rate of decrease of the hole concentration plotted versus the hole concentration, measured at t = 3 s for various gate voltages. The Figure shows a linear dependence of dN_h/dt with N_h, suggesting that the trapping mechanism involves only one hole, as in the case of polaron formation. However, it should be mention that also a quadratic dependence, as for the bipolaron model, cannot be ruled out. Therefore, we conclude that the hysteresis effect is induced by slow trapping of holes in defect states induced by the water diffused into pentacene film. These defects can be polarons, related to the interaction of free holes with the absorbed water molecules. This interaction produces lattice distortion and polarization of the pentacene-water complexes and should be sufficiently slow to account for the small capture cross-section of traps and the resulting slow trapping time.

III. CONCLUSIONS

We demonstrated that the variations in the transfer characteristics and the hysteresis are induced by water absorption in the pentacene layer when TFT is operated in an atmosphere with large relative humidity while the characteristics are unaffected by oxygen or a dry atmosphere. The water molecules are probably absorbed in the whole pentacene layer; however, because the hysteresis is reduced when the structural properties of the pentacene film are improved through thermal annealing, the water seems to diffuse into the material preferentially through more defected region of the film, such as the grain boundaries of polycrystalline film, as already reported in polymeric materials [16]. Experimental data indicate that when a negative bias is applied to the gate, the presence of water in the pentacene film promotes the slow trapping of holes in the TFT channel region, where the free carriers are accumulated, inducing the hysteresis effect. The measured time constant of charge trapping is of the order of several seconds implying trap states with small capture cross-section. These results can be explained by the formation of a polaron (or bipolaron) related to the interaction of free holes with absorbed water molecules. This interaction produces lattice distortion and polarization of the pentacene-water complexes and should be sufficiently slow to account for the small capture cross-section of traps and the resulting slow trapping time.

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