Applied Surface Science 257 (2011) 9386–9389

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Effect of molecular structure on bias stress effect in organic thin-film transistors

A.K. Diallo [a,c,*], F. Fages [a], F. Serein-Spirau [b], J.-P. Lère-porte [b], C. Videlot-Ackermann [a,*]

[a] Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), CNRS UPR 3118, Campus Luminy, Aix Marseille Université, Case 913, 13288 Marseille Cedex 09, France
[b] Equipe Architectures Moléculaires et Matériaux Nanostructurés, UMR CNRS 5253, Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34293 Montpellier Cedex 05, France
[c] Laboratoire de Chimie et Physique des Matériaux (LCPM), Université de Ziguinchor, Senegal

ARTICLE INFO

*Article history:*
Received 17 May 2011
Received in revised form 7 June 2011
Accepted 7 June 2011
Available online 14 June 2011

*Keywords:*
Oligomers
Thin films
Transistors
Bias stress effect

ABSTRACT

Two thiophene-phenylene semiconductors, bis(2-phenylethynyl) end-substituted oligothiophenes (diPhAc-*n*Ts, $n = 2, 3$), were studied as active layers in organic thin film transistors (OTFTs). Structural and electrical properties of such high vacuum evaporated thin films were compared to pentacene. All three oligomers behave as p-type semiconducting layers into OTFTs. In the same preparation and measurement conditions, diPhAc-3T possesses two of incontrovertible attributes of OTFTs for low cost applications, a high air-stable mobility at low substrate temperature ($T_{sub}$), i.e. typically 25 °C together with a reduced bias stress effect compared to the well-known pentacene semiconductor. This study brings to light on the role of the molecular structure involved in the active layer in thin-film devices and describes effects as thin film morphology as important parameters when optimizing the structure of OTFTs.


## 1. Introduction

Organic semiconductors remain attractive for the realization of electronic devices with low cost integrated circuits, flexible matrix displays, and sensors. Their fabrication processes are less expensive compared to inorganic material technology and can offer the opportunity to produce devices at low temperature and on large-area plastic substrates. Several organic semiconductors used as active materials demonstrated field effect activity in transistor application. Pentacene, a linear acene consisting of five fused benzene rings which acts as a p-type semiconductor and now commercially available, is certainly the organic semiconductor the most studied in the field-effect transistors research activity. Historically, it was among the first semiconductors used in devices such as organic thin film transistors (OTFTs) in the early 1990s. With the accumulated data and knowledge on it, pentacene has become a reference, especially with high purity degree achieved in the material coupled together with the fine control of morphology in thin films leading to one of the highest hole mobilities (exceeding $1\,cm^2/V\,s$) for polycrystalline films [1]. High-performance pentacene devices have also been fabricated using polymer dielectrics with carrier mobilities as large as $3\,cm^2/V\,s$ [2]. However acenes have the main disadvantage to photo-oxidize easily in both the solution and the solid state. Pentacene is not spared with a lack of air stability of devices over time [3–10]. Atmospheric moisture alone was shown to cause pentacene transistor degradation and the use of pentacene thin films as humidity sensors was even proposed. Additionally, it was found that the field-effect mobility of the device decreased by 30% and the on/off current ratio decreased to one fifth after the OTFTs had been stored in atmosphere for 500 h [10]. Small molecules such as oligothiophenes are promising organic semiconductors due to their good performances in term of mobility comparable to either amorphous silicon or pentacene [11]. Unfortunately, oligothiophenes based thin film transistors face a real stability challenge when they operated in ambient atmosphere (which is essentially due to the oxygen and water molecules) or after bias stress application [12]. The lack of stability evidenced by both environmental aging and drift of transistor characteristics under bias stress application reduce the reliability of the device and make it commercially unviable.

Oxygen and moisture [14,15] are very harmful to the organic device performance and generate deep trap states in the band gap of organic semiconductors leading to electrical parameter drifts. The creation of trap states in organic active layer in relation with these impurities was reported to affect the electrical characteristics of device, particularly the onset voltage, substhreshold current, threshold voltage and charge carrier mobility as observed by several authors [15–17,10,18–20]. Recently, it was reported that a prolonged polarization of gate electrode named bias stress tends to shift the threshold voltage, degrade the substhreshold slope and increase the off current [13]. To minimize the bias stress effect, some research groups have achieved enhanced stability through

* Corresponding author. Tel.: +33 0 614248193; fax: +33 0 491418916. 5. (C. V.-A.).
*E-mail addresses:* diallo@cinam.univ-mrs.fr (A.K. Diallo), videlot@cinam.univ-mrs.fr (C. Videlot-Ackermann).

0169-4332/$ – see front matter 
doi:10.1016/j.apsusc.2011.06.014

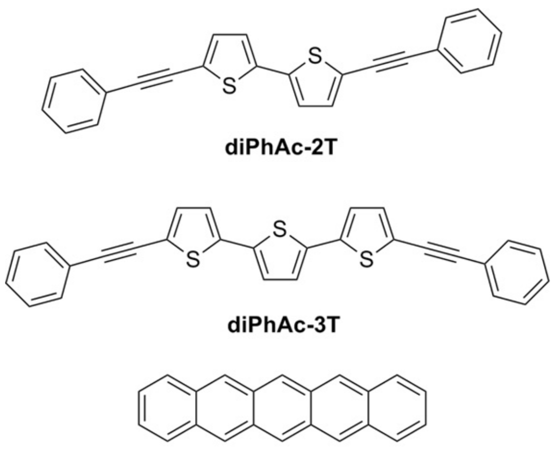


**Fig. 1.** Chemical structures of diPhAc-2T, diPhAc-3T and pentacene.

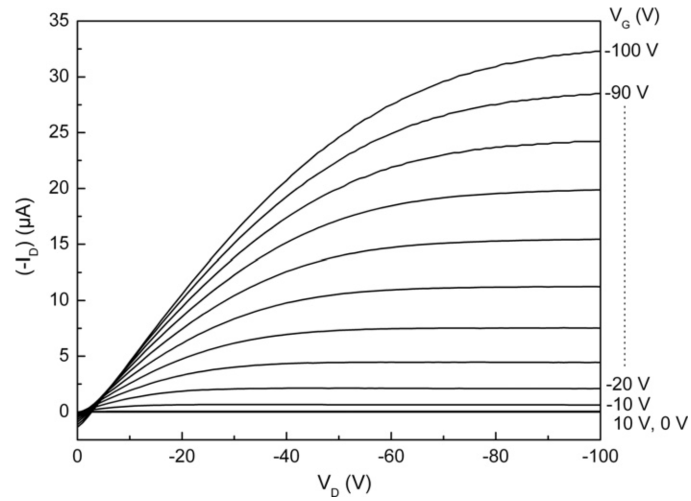


**Fig. 2.** Output characteristic of a diPhAc-3T based-OTFT on bare $Si/SiO_2$ substrates at $T_{sub}$ = 25 °C.

processing steps [21], low duty cycle gate polarization [22] and material engineering [23].

In this context, it is necessary to develop a new class of molecules which exhibit air-stability with good electrical performance under bias stress. P-channel phenyl-oligothiophene derivatives containing acetylenic spacers (diPhAc-2T and diPhAc-3T on Fig. 1) were synthesized in good yields and characterized in terms of electronic structure and film-forming properties [24]. We could observe that the introduction of structural modification in the aromatic backbone affects the carrier mobility of materials. In particular, introducing acetylenic spacers raises the carrier mobility at low substrate temperature. Additionally, OTFT devices based on the longer oligomer, diPhAc-3T, are found to be significantly air-stable, thus underscoring the potential of acetylenic containing π-conjugated oligomers. In the present work, we point out in particular the bias stress stability in OTFT devices based on both diPhAc-2T and diPhAc-3T organic semiconductors. By a comparison with pentacene, the impact of molecular structure on bias stress effect, associated to the thin film morphology, is discussed.

## 2. Experimental part

The syntheses of diPhAc-2T and diPhAc-3T have been described previously [24]. Pentacene was commercially available by Sigma Aldrich. Fig. 1 shows the chemical structure of diPhAc-2T, diPhAc-3T and pentacene semiconductors. The Bottom-Gate Top-Contact configuration was used for the OTFT devices. Based on diPhAc-2T and diPhAc-3T semiconductor. Highly n-doped silicon wafers, covered with thermally grown silicon oxide $SiO_2$ (3000 Å), used as gate and dielectric, respectively, were purchased from Vegatec (France) as device substrates. The capacitance per unit area of bare silicon dioxide dielectric ($Si/SiO_2$) layer was 12 nF/cm$^2$. The semiconductor layer was vacuum deposited onto the insulating layers using an Edwards Auto 306 apparatus, at a rate of 4–7 nm/min under a pressure of $1–2 \times 10^{-6}$ mbar to a nominal thickness of 50 nm as determined with an in situ quartz crystal monitor. Substrate temperature ($T_{sub}$) during deposition was controlled to be 25 °C. The gold (Au) source and drain electrodes (channel length $L$ = 50 μm, channel width $W$ = 1 mm) were evaporated on top of the organic thin film through a shadow mask. Current–voltage characteristics were obtained with a Hewlett–Packard 4140B pico-amperemeter-DC voltage source. All the electrical measurements were performed at room temperature under ambient atmosphere without any particularly precaution. The source-drain current ($I_D$) in the saturation regime is governed by the equation:

$$(I_D)_{sat} = (W/2L)C_i\mu(V_G - V_T)^2$$

where $C_i$ is the capacitance per unit area of the gate insulator layer, $V_G$ is the gate voltage, $V_T$ is the threshold voltage, and $\mu$ is the field-effect mobility.

Thin film morphology has been investigated using a high resolution scanning electron microscope (JEOL JSM 6320F).

## 3. Results and discussion

Bottom-Gate Top-Contact (BGTC) thin-film transistors were fabricated in the manner described in the experimental part. Drain and source Au electrodes were deposited on top of the semiconducting layer after the latter was evaporated onto bare $Si/SiO_2$ substrates at $T_{sub}$ = 25 °C. All measurements were performed in air at room temperature. For all three oligomers, diPhAc-2T, diPhAc-3T and pentacene, transistor activity is observed by application of negative drain and gate voltages to operate in the accumulation mode demonstrating that all three behave as p-type semiconductors in air. Fig. 2 shows typical output characteristics of OTFTs in the saturation regime using diPhAc-3T as active layers deposited

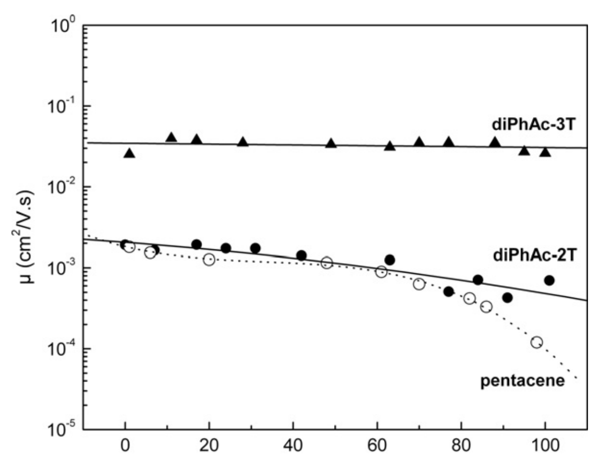


**Fig. 3.** Plots of hole mobility ($\mu$) *vs.* storage days for diPhAc-2T, diPhAc-3T and pentacene based-OTFTs on bare $Si/SiO_2$ substrates at $T_{sub}$ = 25 °C.