Thin Solid Films 608 (2016) 97–101

Contents lists available at ScienceDirect

Thin Solid Films

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

Poly(3-hexylthiophene): TIPS-pentacene blends aiming transistor applications

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ARTICLE INFO

Article history:
Received 24 December 2015
Received in revised form 28 March 2016
Accepted 12 April 2016
Available online 13 April 2016

Keywords:
TIPS-pentacene
P3HT
Semiconductor blends
Vertical segregation
Surface treatment
Mobility
OFET

ABSTRACT

Poly(3-hexylthiophene):6,13-bis(triisopropylsilylethynyl)-pentacene (P3HT:TP) blends with a ratio of 1:1 (wt/wt) were deposited via spin coating on anodized oxide (Al_2O_3). A phase separation of the compounds was observed, resulting in the formation of crystalline aggregates of TP molecules that segregate vertically on the surface. The form of segregation depends on the oxide surface treatment used. Spectroscopy analysis shows a higher molecular order of P3HT in the blend than for neat film and that TP molecules are also distributed in the polymeric matrix. Regarding the OFET characteristics, charge carrier mobilities of 1.2×10^{-3} cm^2 V^{-1} s^{-1} and 2.0×10^{-3} cm^2 V^{-1} s^{-1} were obtained from devices for untreated and (hexamethyldisilazane) HMDS-treated Al_2O_3 gate dielectric, respectively. These results confirm that P3HT:TP blends have good potential as an active layer in organic field effect transistors (OFETs).

1. Introduction

There are basically two types of organic semiconductors, conjugated polymers and conjugated small molecules. Among the polymeric semiconductors, the poly(3-hexylthiophene) (P3HT), a derivative of thiophene stands out, and among the small conjugated molecules the TIPS-pentacene (TP), a pentacene derivative. The thin film morphology for these semiconductors is influenced by several parameters, such as, deposition method, solvent, evaporation rate and, in particular, the thermal treatment [1,2].

In P3HT, the film structure is formed by interconnected crystalline lamellae embedded in an amorphous matrix. Studies show that the orientation of the lamellar domain is influenced by molecular weight [3,4]. In P3HT with low molecular weight, the charge carrier is only highly effective on the lamellar domains, and throughout the film is reduced by the lack of interconnection between the domains. The lamellar domains in high molecular weight films are smaller, allowing best interconnections and, consequently, better mobility [5].

In the case of TP, the mobility depends strongly on the crystal orientation, crystalline domain size, presence of cracks and crystallite thickness, reaching values of 1.8 cm^2 V^{-1} s^{-1} [6,7]. These parameters are determined by solvent choice, solution concentration, temperature of thermal treatment, methods of deposition and substrate materials. In general, high boiling point solvents allow slow crystal growth, forming large lamellar domains making it possible to obtain higher mobility. In these cases, heat treatment with high temperature is required for complete solvent evaporation, but temperatures higher than 60 °C can crack the film, damaging it [8]. However, TP films prepared by solution show high mobility but its processing is very difficult.

Thin films of TP prepared by spin coating exhibit high crystalline order, which extend over a large area, but for reasons mentioned above, it is not easy to obtain a large number of devices with uniform characteristics. The mobility may vary from 5.0×10^{-4} to 2.8×10^{-1} cm^2 V^{-1} s^{-1} depending on the rotation speed [9]. In other deposition techniques, such as inkjet printing or drop casting, the mobility varies from 2.5×10^{-4} to 0.24 cm^2 V^{-1} s^{-1} [10]. Then the challenge of making good devices is not easy for any technique. That is to say, the mobility may vary up to three orders of magnitude due to loss of control of crystalline growth.

One possible means of improving the morphology of the TP is to develop polymer blends, in which we can control the grain size, crystallinity of the film and other parameters. One factor that should be considered in blend developing using two semicrystalline materials is the phase segregation in the polymeric matrix. Phase segregation is dependent on the polarity difference between the two components of the mixture, so the crystallization process and crystal orientation can be also influenced by the degree of phase separation between the two constituents. These behaviors can be explained by the theory of Flory–Huggins [11]. Thus, the film formation may be dominated by two interaction factors: solvent–solute and solute–solute [12]. In the first case,

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http://dx.doi.org/10.1016/j.tsf.2016.04.018

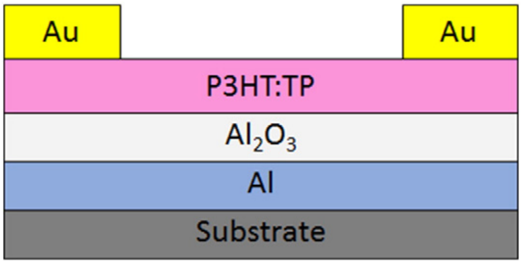

Fig. 1. Bottom-contact top-gate architecture of transistor.

the solvent evaporation in the top surface leads to a higher concentration of the solute, and as result there is a bigger proportion of the more soluble component in this interface and, consequently, a vertical segregation. For the second case, the solidification of the two components affects the film structure, since in the crystallization process, the first part solidified is expelled to the surface.

In this work, we report the study of a blend with P3HT in order to control crystallographic growth of TP and its evaluation for using in organic field effect transistors (OFETs). The aim is to match the properties of each semiconductor in a single device using anodized aluminum oxide (Al_2O_3) as insulator gate.

2. Experimental details

Transistors were manufactured using a bottom-gate top-contact architecture, as shown in Fig. 1. A 200 nm layer of Al was deposited on a glass substrate via thermal evaporation in high vacuum ($<10^{-6}$ Torr). Then a layer of Al_2O_3 with thickness of 60 nm was grown by anodization leaving a residual Al layer to be used as the gate electrode. The surface of the Al_2O_3 was treated by immersing it in a solution of hexamethyldisilazane (HMDS) for 30 min and then rinsed with acetone and dried with nitrogen flow.

P3HT and TP, obtained from Sigma-Aldrich, were dissolved in toluene with a ratio of 1:1 wt/wt. The solution was filtered using Millex® HV PVDF 0.45 μm filters and deposited by spin coating onto Al_2O_3 with a constant rotation of 2000 rpm for 60 s in an inert atmosphere (*glovebox*). The P3HT:TP films were thermally treated at 100 °C for 2 h to remove the solvent, thereby obtaining the semiconductor blend. The transistor was completed by evaporation of source and drain electrodes of Au in a high vacuum ($<10^{-6}$ Torr) using a shadow mask. The length and width channels are 90 μm and 3 mm, respectively. P3HT:TP films were characterized morphologically using scanning electron microscopy (SEM) with a Carls Zeiss equipment, EVO LS15 model (Laboratory LabMMEV at FCT/UNESP), and atomic force microscopy (AFM) with a Nanosurf microscope, model easy Scan 2, tip of silicon nitride and tapping mode. Structural analysis was performed by Raman spectroscopy using a Renishaw micro-Raman spectrograph, model in-Via, coupled to a Leica optical microscope, which 100× objective lens allows collecting spectra with ca. 1 μm spatial resolution, CCD detector, laser at 633 nm and 1800 grooves/mm grating with additional edge filter leading to a spectral resolution of ca. 4 cm^{-1}, and a computer-controlled three-axis-encoded (XYZ) motorized stage. The transistors Al/Al_2O_3/P3HT:TP were electrically characterized by output and transfer curves using a semiconductor characterization system (Keithley 4200 SCS).

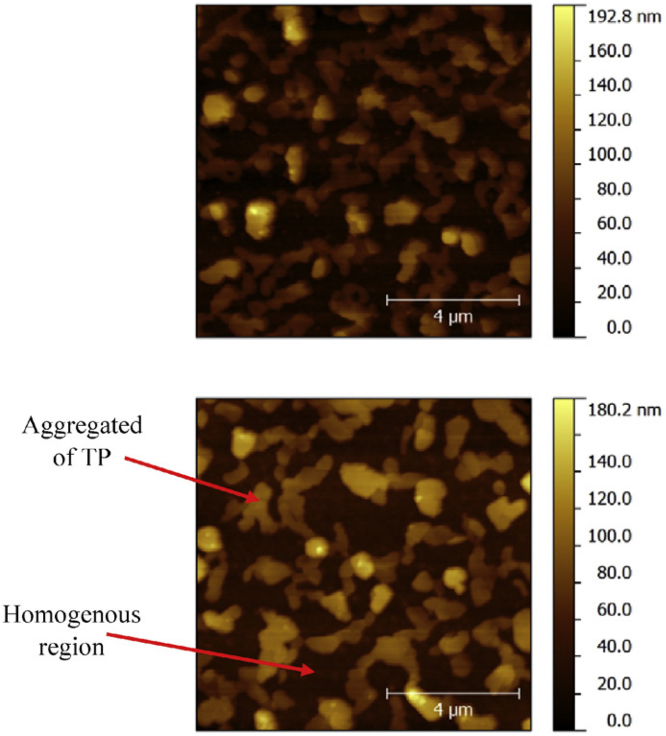

Fig. 3. : AFM topographic images of P3HT:TP films on Al_2O_3. (a) Untreated and (b) HMDS-treated. The arrows point to aggregates of the TP and homogeneous regions, as indicated. Surface rms roughness of Fig. 3a and 3b are 26.4 and 27.5 nm, respectively. The scanned area is 10 μm × 10 μm.

3. Results and discussion

Fig. 2a and b shows the surface image of P3HT:TP blends deposited onto Al_2O_3, untreated and HMDS-treated, respectively. We can observe a difference in the morphology of surface film deposited on untreated Al_2O_3 compared with the treated Al_2O_3. A better homogeneity of the blend can be obtained with HMDS-treated oxide and consequently, an improvement of its structural organization. Phase segregation of TP is observed in polymeric matrix of P3HT due to its high crystalline orientation, forming aggregates through π–π interactions in the surface. However, continuous domain is not formed in the TP phase, i.e., the aggregates are not percolated.

AFM images (10 × 10 μm) of P3HT:TP blend on Al_2O_3 untreated and HMDS-treated are shown in Fig. 3a and b, respectively. Films of blend on

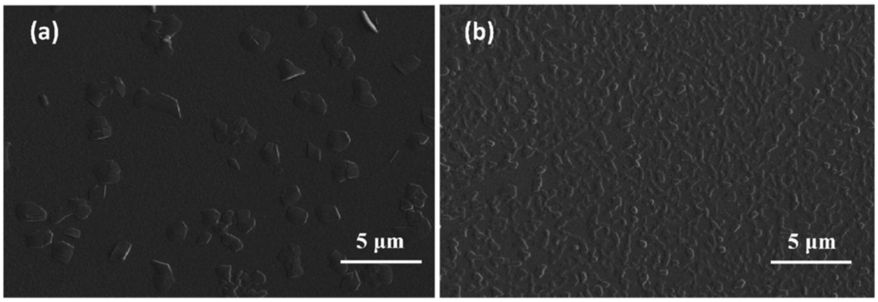

Fig. 2. SEM images of P3HT:TP films on Al_2O_3. (a) Untreated and (b) HMDS-treated. Scale bar: 5 μm. Magnification: 10,000×.