Organic Electronics 15 (2014) 1056–1061

Contents lists available at ScienceDirect

Organic Electronics

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

Flexible organic field-effect transistors based on electrospun conjugated polymer nanofibers with high bending stability

Alessandro Manuelli [a], Luana Persano [a,b], Dario Pisignano [a,b,c,*]

[a] Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia, via Barsanti, I-73010 Arnesano, LE, Italy
[b] National Nanotechnology Laboratory of Istituto Nanoscienze-CNR, Università del Salento, via Arnesano, I-73100 Lecce, Italy
[c] Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, via Arnesano, I-73100 Lecce, Italy

ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 13 February 2014
Accepted 20 February 2014
Available online 5 March 2014

Keywords:
Polymer nanofibers
Electrospinning
Plastic electronics
Flexible electronics
Poly(alkylthiophene)s

ABSTRACT

We report on flexible, single electrospun nanofiber field-effect transistors made by a blend of poly(3-decylthiophene) and poly(3-hexylthiophene), assessing for the first time the performances of this class of devices in terms of stability upon repeated tensile bending. Charge-carrier mobilities in the nanofiber-based device are estimated of the order of 10^{-3} $cm^2/(V\,s)$. Repeated cycles of bending and relaxing are performed, and the evolution of the device current–voltage characteristics is monitored up to 1000 cycles. We find that during bending the mobility is higher than that measured in planar conditions, and that after about 100 bending cycles it rapidly stabilizes. The here observed bending stability suggests a high compatibility of electrospun nanofibers with devices fabricated by roll-to-roll processes, and with bendable or wearable electronics.

1. Introduction

The availability of solution-based methods for nanopatterning, together with low cost and flexibility, are universally desired features which make organic electronics of very wide interest in both the scientific community and industry [1–8]. In the last decade, the development of methods fully exploiting bendable, rugged and extremely cheap organic and plastic materials has provided electronics with functionalities not achievable with conventional, wafer-based devices, leading, for instance, to paperlike electronic displays [9], novel pressure-sensing architectures and electronic skins [8,10–13], flexible vertical light-emitting diodes [14] and batteries [15,16], and bendable memories [17] and circuits [18], all of which could be further integrated with solution-processable electronic materials such as semiconducting polymers. In particular, the well-assessed electronic properties of π-conjugated polymers, and their capability to be processed by large-scale and cost-effective printing and spinning techniques, have been applied to diverse applications such as radio frequency identification tags, integrated logic circuits, displays and sensors [1,5,6,18]. Among other conjugated compounds, poly(alkylthiophene)s (PATs), with their peculiar self-assembling properties and environmental stability, are likely the most used family of polymers in organic thin-film field-effect transistors (OFETs) [18–24]. Allowing these materials to be patterned or nanostructures composed of them to be produced, nanofabrication technologies have the potential both to increase the component density in single chips, through channel size reduction and realization of addressable matrices, and to provide devices with enhanced functionalities.

Electrospinning [25,26], which is based on an electric field-induced, uniaxial elongation of a polymer solution with sufficient molecular entanglement, is particularly

* Corresponding author at: Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, via Arnesano, I-73100 Lecce, Italy. Tel.: +39 0832298104.
E-mail addresses: manuelli_a@yahoo.it (A. Manuelli), luana.persano@nano.cnr.it (L. Persano), dario.pisignano@unisalento.it (D. Pisignano).

http://dx.doi.org/10.1016/j.orgel.2014.02.016
1566-1199/

relevant in this respect, allowing active fibers with potentially kilometric length to be realized. Nanofibers made of semiconducting polymers can exhibit remarkable performances [20,27–32] and generally improved supramolecular order compared to thin films. Unfortunately, electrospinning of conjugated polymers is often made difficult by the poor viscoelastic behavior of those solutions, which motivates using blends incorporating electrically inert compounds such as poly(ethylene oxide) [18,30,32] or poly(ε-caprolactone) [30,32]. In addition, the process can easily determine the incorporation of oxygen and moisture if performed in air, which can lead to electronic defects [28]. Furthermore, despite of many claims supporting the ease of integration of electrospinning technologies with flexible electronics, the stability of nanofiber-based device conduction during and after bending is still not assessed. In this work, we propose active nanofibers, due to their geometry and conformability, as building blocks for reducing bending-induced damage in organic electronics, thus allowing devices with very high bending stability to be realized.

The stability of bendable transistors and inverters has been investigated by pentacene films used in combination with C_{60} (found to be stable over few bending cycles) [33], with hexadecafluorocopperphtalocyanine in devices sandwiched between the substrate and an encapsulation layer to induced compressive and tensile strains to cancel each other [34], and with gold nano-particles in memories (over several hundreds of cycles) [35]. Transistors with a printed triarylamine copolymer and a perfluoropolymer dielectric layer show a saturation current increased by 60% after 1000 bending cycles [36].

Here, nanofiber-based OFETs are, for the first time, measured under bending conditions with repeated tensile stressing. During initial bending the charge-carrier mobility (μ) is higher than that measured in planar conditions, and after 100 bending cycles it stabilizes, up to 1000 performed cycles.

2. Results and discussion

Our flexible OFETs are based on a blend [24] of regioregular poly(3-decylthiophene) (P3DT) and regioregular poly(3-hexylthiophene) (P3HT) electrospun fibers as active elements, and fully plastic dielectric and gate electrode, both processed from solution with no further process step such as UV curing used in previous reports on nanofiber-based transistors. Notwithstanding its relatively lower conduction properties, P3DT is used for blending due to its better processability, which makes possible electrospinning pure PAT-based nanofibers. The fabrication steps are shown in Fig. 1. P3DT/P3HT blends (89%/11% w/w referred to solid content) are dissolved in chloroform at 54 °C with polymer/solvent concentration of 0.3–6% w/w. Electrospinning is performed in a glove box system with $[O_2] < 0.1$ ppm at 21 °C by injecting 0.4 mL of highly-concentrated solution in a syringe tipped with a 27-gauge stainless steel needle. The used flow rate is 7.5×10^{-3} μL/min, and the total bias is 11 kV, applied over a spinneret-collector distance of 20 cm. Poly(ethylene terephthalate) (PET) substrates with gold interdigitated electrodes are positioned on the collector for fiber deposition. Afterwards, a 1.3-μm thick film of poly(methyl methacrylate) (PMMA) is deposited by a doctor blade system and a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) gate electrode is finally realized by drop-casting.

Having a very smooth organic-dielectric interface is critical for device operation and stability. To this aim a single solvent is conveniently used in electrospinning, avoiding eventual fiber porosity which may arise from phase-separation phenomena favored by using immiscible components and solvent mixtures [37]. The atomic force microscopy (AFM) micrographs of doctored P3DT/P3HT films and electrospun fibers (Fig. 2a and b) evidence homogeneous and smooth surfaces, with an overall peak-to-peak roughness of 1 nm or lower (inset of Fig. 2b), as needed for thin-film OFETs with state-of-art bending stability [34]. Each spun fiber reveals a neat rounded structure which is well retained upon deposition across gaps between metal electrodes (Fig. 2c). The resulting flexible chip consists of 28 transistors in top-gate configuration, arranged in 4 rows (Fig. 3a), and the device response is measured before, during, and after bending (Fig. 3b–d, details in the Materials and methods Section). The substrate is bent along an axis passing exactly through the measured transistors. Bending radii, R_b, are of about 5 mm, corresponding to a tensile strain, $\varepsilon \cong D/2R_b$, where D is the substrate thickness, of about 1.7%, applied parallel to the current flowing between source and drain electrodes (i.e. parallel to the nanofiber longitudinal axis). Fig. 3b and c presents the current–voltage characteristics of nanofiber transistors, for gate voltages (V_{GS}) decreasing from 0 to −50 V, before and during bending, respectively. The drain current (I_{DS}) dependence on the drain voltage (V_{DS}) highlights the typical p-type behavior of PAT-based OFET, working in accumulation mode. The device regularly operates in its bent state. I_{DS} variations from before to during bending are within 3% (Fig. 3d), and by the slope of $|I_{DS}|^{1/2}$ one cannot appreciate significant variations of the threshold voltage (V_{TH}). V_{TH} has positive values, indicating accumulated holes which are intrinsically present in the conduction channel, which can be related to residual impurities from the fabrication process as frequently observed in nanofiber-based transistors [28]. In the supposed saturation regime one has $I_{DS} = \frac{W}{2L} C\mu (V_{GS} - V_{TH})^2$, where C is gate dielectric capacitance per unit area, W is the width of the semiconducting element (here roughly given by the diameters of fibers bridging source and drain), and L is the channel length, respectively, and the calculated charge carriers mobility is about 5.0×10^{-3} cm^2/(V s) and 3.8×10^{-3} cm^2/(V s) before and during bending, respectively. These values are more than one order of magnitude higher than those measured in films with the same active blend, for which $\mu = 6–7 \times 10^{-5}$ cm^2/(V s). One should bear in mind that, while the focus of the present study is not on achieving high OFET mobility, at least two strategies can be followed in order to improve conduction performances up to μ values of 1 cm^2/(V s) of more with our device geometry, namely either directly doping nanofibers (for instance by $NOPF_6$ solutions) [38], or using ion-gel, polyelectrolyte gate dielectrics [32,39]. Both these methods allow an