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An electrochemically synthesized sulfonated polyaniline layer for positive charge carrier injection improvement in conjugated polymer devices

Abstract We report the use of sulfonated polyaniline, SPAN, as a positive charge transporting layer in organic electronic devices, demonstrating that it can be used to significantly improve injection into conjugated polymers. The introduction of an intermediate SPAN layer improves device rectification, even when low-work-function anode materials such as tin oxide are used.

Keywords Charge transport · Conjugated polymers · Polyaniline · Sulfonated polyaniline

Introduction

In conjugated polymer-based devices, like organic light-emitting diodes, the current during operation is limited either by the electrode/organic semiconductor interface or by the organic semiconductor bulk characteristics. At low applied voltages the charge transport is limited by the potential barrier at the interface, whereas at higher applied voltages the transport commonly becomes limited by space-charge accumulation, due to the low charge carrier mobility values normally observed in these materials [1, 2, 3].

In several cases, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was successfully used as an intermediate layer, between the anode and the polymer active layer in light-emitting diodes and photodetectors, in order to effectively reduce the

energy barrier for positive charge injection/collection [4, 5, 6, 7, 8].

Such a layer is especially important when the electrode work-function is not high enough to nearly match the semiconducting polymer HOMO (highest occupied molecular orbital), so that a significant interfacial energy barrier $\varrho \gg kT$ (k is the Boltzmann constant and T the absolute temperature) for charge carrier injection may be present at the interface. Metal/PEDOT:PSS contacts are found to be ohmic and present low contact resistance (~ 7 Ω/mm^2) and permit, for example, the construction of polymer-based diodes with high rectification using two low-work-function metallic electrodes [9]. Polyaniline and its derivatives, as a single component or in the form of blends, has also been proposed as an alternative to PEDOT:PSS as a hole-transporting layer [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26].

Sulfonated polyaniline (SPAN), prepared either by chemical or electrochemical methods, presents lower contact resistance (~ 5 Ω/mm^2) to metals commonly used in electronics (Au, Cu and Al) [27] than PEDOT:PSS. This low contact resistance is important, since for SPAN bulk electrical resistivity of the order of 10^2 Ω m [27] the device resistance contribution determined by the SPAN film introduction is bulk dominated for SPAN film thicknesses larger than 50 nm. SPAN has the advantage that it is a single component material, potentially reducing the possibility of occurrence of problems originating from phase segregation of the hole-transporting layer components due to improper storage or handling. Compared to polyaniline, SPAN has additional advantages: it is mostly amorphous, it remains self-doped even in vacuum and it presents higher thermal stability [28]. Onoda and Yoshino [13] demonstrated that SPAN/poly(p-phenylenevinylene) (PPV) heterostructures produced using a PPV precursor and SPAN by a self-assembling technique are suitable for light-emitting diode applications.

In this contribution, we demonstrate that the introduction of an electrochemically deposited SPAN layer between a low-work-function anode, like tin oxide (TO),

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and an semiconducting polymer significantly improves the capability of the injection of positive charge carriers into the polymer. The effect is analogous to that observed when PEDOT:PSS is used in the same manner. The electrochemical preparation of SPAN films onto TO substrates advantageously allies synthesis and film deposition in a single step.

Experimental

SPAN electrodeposition was similar to that previously described [27], except that the electrolyte was composed of an aqueous solution of 0.10 mol/dm^3 metanilic acid $+ 0.20$ mol/dm^3 LiClO$_4$ $+ 0.01$ mol/dm^3 aniline $+ 0.20$ mol/dm^3 HClO$_4$ and that deposition was carried out using the potential pulse technique (square wave, frequency of 0.5 Hz, higher potential of 1.0 V, lower potential of 0 V). After synthesis, the SPAN films were reduced by polarizing to $+0.1$ V versus the normal hydrogen electrode for 180 s.

The morphology of SPAN film grown on TO/glass substrate was studied by scanning force microscopy (AutoProbeCP-Research Microscope). The scanning force microscopy images were acquired in non-contact mode, with silicon ultralever probes.

In order to investigate the influence of SPAN and PEDOT:PSS intermediate layers, we constructed devices for electrical measurements in a sandwich structure, using a patterned TO glass substrate. The hole transporting materials PEDOT:PSS and SPAN were deposited onto a TO layer, covering half of the TO film. This allows testing the current–voltage, $I(V)$, characteristics of the samples with two kinds of anodes, neat TO and TO with either PEDOT:PSS, which was deposited by spin-coating, or with SPAN, which was electrochemically deposited. The semiconducting polymer poly(3-hexylthiophene) was deposited onto TO, TO/SPAN or TO/PEDOT:PSS by spin-coating from chloroform solution. The aluminum anode was then evaporated to complete the devices.

The $I(V)$ characteristics of all devices were determined under dark conditions in a nitrogen atmosphere, using a Keithley 196 multimeter and a Keithley 230 voltage source. The applied voltage was scanned stepwise (steps of 0.05 V or 0.1 V) at a rate of 0.05 V s^{-1}, from 0 up to the maximum V value.

Results and discussion

The optical transmittance spectrum of electrochemically deposited SPAN is presented in Fig. 1 and does not differ from that of chemically synthesized SPAN [28]. The transmittance window matches the visible spectrum, making it suitable for a transparent electrode covering layer, for optoelectronic devices operating in the visible range of the spectrum.

The scanning force microscopy image of the SPAN grown on TO is presented in Fig. 2. It is possible to notice grains with $\sim$200 nm size for a 50 nm thick SPAN film, the same used later for devices. Similar morphology was found for SPAN films grown on indium-tin-oxide and Au substrates, essentially differing only by the lower dispersion of grain sizes presented by the former [29]. In multilayered devices an important issue is the intermixing of successively deposited layers. It is known that the PEDOT:PSS layer interacts, for example, with PPV, doping the electroluminescent polymer and producing a non-abrupt concentration profile interface and a quenching of the photoluminescence of the PPV [30].
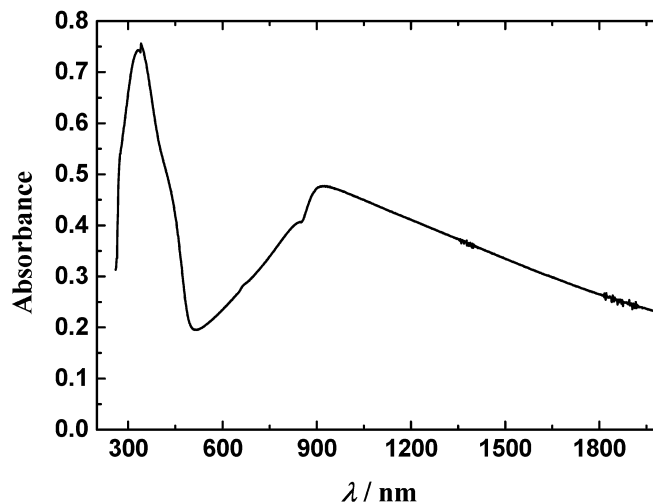

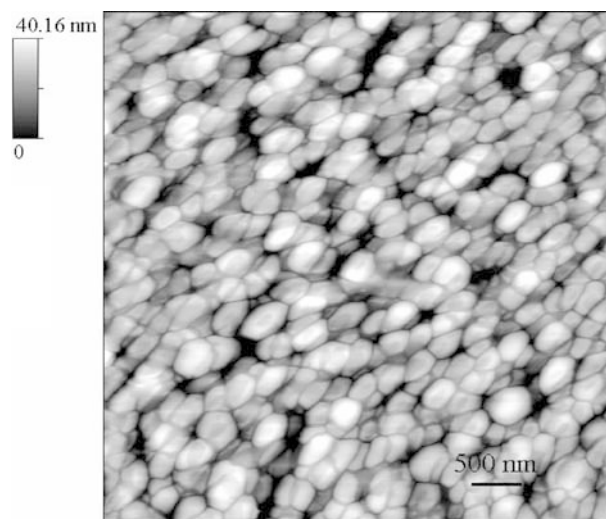**Fig. 1** SPAN absorption spectrum

Fig. 2 Surface image of SPAN deposited on TO

Other transparent conducting film substrates can also chemically interact with polymers deposited on them, in some cases suppressing the photoluminescence of the electroluminescent polymers. In the case of PPV, it was demonstrated that the photoluminescence quenching is lower on TO substrates than on indium-tin-oxide, due to the higher stability of TO [31]. SPAN is not soluble in organic solvents, allowing the deposition of polymers like poly(3-hexylthiophene) by spin-coating, without dissolution of the previously deposited SPAN layer, in some cases constituting an advantage.

The $J(V)$ characteristics of TO/poly(3-hexylthiophene)/Al and TO/PEDOT:PSS/poly(3-hexylthiophene)/Al are compared in Fig. 3 ($J =$ current density). When TO and Al are used as anode and cathode, respectively, the $J(V)$ characteristics are almost symmetric under forward and reverse bias. Upon insertion of a PEDOT intermediate layer the $J(V)$ characteristics change,
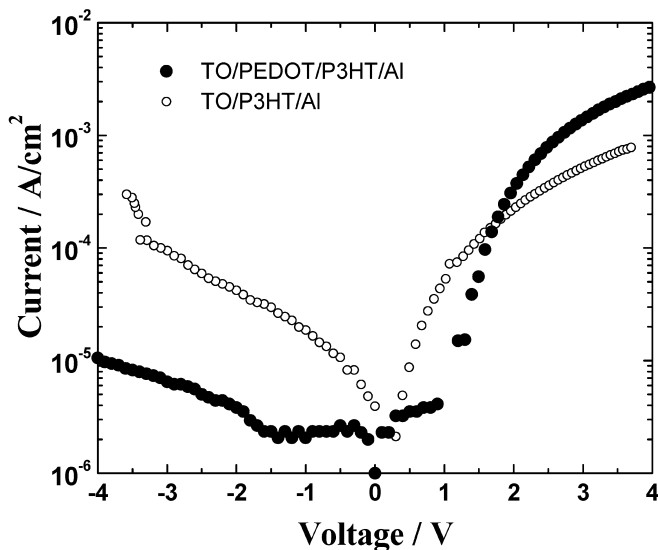
120

Fig. 3 $I(V)$ characteristics of TO/poly(3-hexylthiophene)/Al and TO/PEDOT:PSS/poly(3-hexylthiophene)/Al devices. Poly(3-hexylthiophene) layer thickness: 230 nm; PEDOT:PSS layer thickness: ~80 nm

Fig. 4 $I(V)$ characteristics of TO/poly(3-hexylthiophene)/Al and TO/SPAN/poly(3-hexylthiophene)/Al devices. Poly(3-hexylthiophene)layer thickness: 140 nm; SPAN layer thickness: ~50 nm

becoming asymmetric with a rectification value around 2×10^2 at 4 V. The difference in the work function values (in vacuum) of the electrodes ($\varphi_{Al}\approx4.3$ eV [32] and $\varphi_{PEDOT}\approx5.2$ eV [9]) introduces a built-in potential that can be seen in the $J(V)$ characteristics of TO/PEDOT/poly(3-hexylthiophene)/Al (solid circular curve in Fig. 3), where at low forward bias the intrinsic field is opposing the charge injection until around 1 V. Under higher voltages the injected current from the TO/PEDOT electrode is higher than the current injected from the neat TO anode. This trend is analogous to that observed when the electrical characteristics of Cu/MEH-PPV/Al and Cu/PEDOT:PSS/MEH-PPV/Al (MEH-PPV = poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]) devices are compared, concerning the rectification ratio and the positive bias behavior at low and high voltages [4]. It was demonstrated that the introduction of PEDOT:PSS as an intermediate layer effectively eliminates the potential barrier existing between the conducting electrode and PEDOT:PSS, so that the remaining effective barrier is only the one between PEDOT:PSS and the electroluminescent polymer [4, 33].

When SPAN is used as an intermediate layer, in spite of PEDOT:PSS, the same behavior is observed. The insertion of a SPAN layer modifies the $J(V)$ characteristics, leading to asymmetry in the $J(V)$ curve of TO/SPAN/poly(3-hexyl-thiophene)/Al devices, contrary to that observed with TO/poly(3-hexyl-thiophene)/Al devices. The asymmetry is a consequence of an increase in the current at forward bias and a reduction of the current at reverse bias. The rectification ratio of TO/SPAN/poly(3-hexylthiophene)/Al devices at 4 V (Fig. 4) is a little higher than that of TO/PEDOT/poly(3-hexylthiophene)/Al devices, $\sim1\times10^3$.
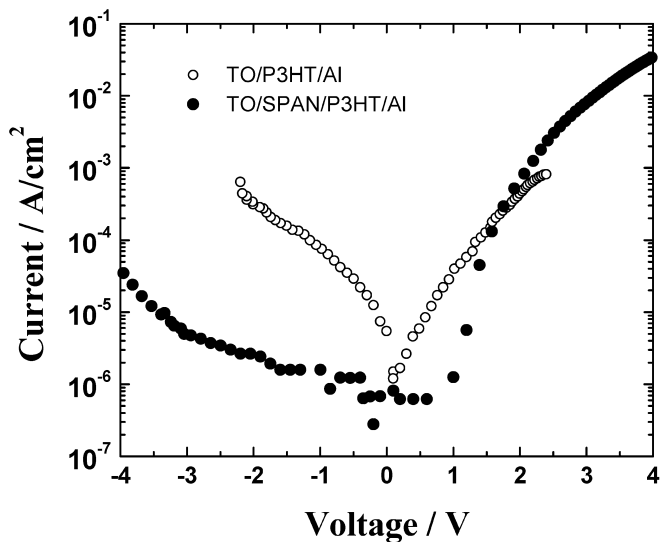
The ionization potential of poly(3-hexylthiophene), estimated using cyclic voltammetry, is approximately 5.1 eV [34, 35, 36]. Neglecting interface effects, the interface potential barrier for positive charge carrier injection from TO into poly(3-hexylthiophene) is then expected to be of the order of 0.8 eV, considering the TO work function ($\varphi_{TO}\approx4.3$ eV [31]). With the use of intermediate layers the potential barrier in the interface decreases, as indicated by the $J(V)$ characteristics. This is a decrease in the positive charge injection barrier after introduction of a PEDOT:PSS or SPAN layer is responsible for the increase in the current when TO is positively biased. Additionally, it also displaces the voltage value of the current onset to nearly 1 V, when compared to those devices without these layers, as a consequence of the built-in potential.

TO presents high stability and, together with SPAN, it allows the availability of a stable anode material combination, benefiting charge injection performance, similar to TO/PEDOT:PSS.

Conclusion

We have demonstrated that the introduction of an intermediate layer of electrochemically synthesized SPAN between the anode and the electroluminescent polymer in devices constructed with poly(3-hexylthiophene) improves the positive charge carrier injection from the anode into the poly(3-hexylthiophene). This behavior was demonstrated using TO, a low-work-function substrate. The recovery of TO substrates with SPAN permits improvement in its suitability for device applications where TO is used as a transparent anode.

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