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Sulfonated polyaniline/poly(3-methylthiophene)-based photovoltaic devices.

Abstract A sulfonated polyaniline (SPAN) film as an intermediate layer between the electrode, tin oxide (TO) and the active layer improves the efficiency of photovoltaic devices based on poly(3-methylthiophene), PMT. In TO/SPAN/PMT/Al devices, the incident-photon-to-collected-electron efficiency reaches 12.1% and power conversion efficiency 0.8% under monochromatic irradiation (λ = 580 nm; 0.8 W/m^2). Under AM 1.5 conditions 1000 W/m^2, a power conversion efficiency of 0.04% is reached.

Keywords Organic photovoltaics · Sulfonated polyaniline

Introduction

Organic photovoltaic devices had their efficiency improved by different strategies in the last years. In homolayer devices it is important to use electrodes with different work functions[1, 2] to produce a built-in potential, which improves the charge transport and consequently, device efficiency. Devices presenting multilayer structures [3–4, 5, 6, 7, 8, 9, 10] or blends[11, 12] as active layers have reached better efficiencies than organic photovoltaic devices with homolayer structures. The use of electrodes modified by organic layers has

been an interesting way to increase the efficiency of the organic devices. Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) blend (PEDOT:PSS) layers, for example, have improved the efficiency of organic optoelectronic device by lowering the potential barrier for positive charge carriers between the electrode and the active layer and consequently, increasing the built-in electric field inside the active layer[13, 14]. Polypyrrole [15] and sulfonated polyaniline (SPAN) [16, 17]films were used to produce effects similar to those of PEDOT:PSS. Sulfonated polyaniline is attractive because it is a self-doped polymer[18], being potentially less susceptible to the variation of electrical properties occasioned by dopant drift due to high electric field or to phase segregation phenomena observed in multicomponent materials.

In a previous article [19] we demonstrated that organic photovoltaic devices whose active layer is made of poly(3-methylthiophene) (PMT) presented higher efficiency when a SPAN layer is introduced between the transparent electrode and PMT, due to field redistribution inside the device, produced by the introduction of the SPAN film . In the present work, we use TO/SPAN/PMT/Al (TO: tin-oxide) structures to investigate the influence of SPAN and PMT film thickness (respectively d_{SPAN} and d_{PMT}) on device performance. For photovoltaic device applications, PMT is interesting because electrochemically synthesized PMT presents a large exciton diffusion length [2] and also because the maximum of the absorption spectrum of PMT [2] almost matches the maximum of the solar irradiance spectrum.

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Experimental

Devices were prepared using TO-covered glass substrates. Films of TO were produced by chemical vapor deposition[20], having a thickness of 470 nm and electrical resistivity of 6×10^{-5} Ω .m (determined by four-point probe technique). The work function of these TO films is of the order of 4.3 eV[21].

Films of SPAN were electrochemically deposited on to the TO [16]. Electrodeposition of SPAN was similar to that described in [16], except that the electrolyte was composed of an aqueous solution of 0.10 mol L^{-1} metanilic acid + 0.20 mol L^{-1} $LiClO_4$ + 0.05 mol L^{-1} aniline + 0.30 mol L^{-1} $HClO_4$ and that deposition on to TO was carried out using the potentiostatic condition, with different deposition times. After deposition, films were polarized at 0.0 V *versus* Ag/AgCl for 180 s to reduce the SPAN film.

By applying a current density of 3.7 mA cm^{-2}, PMT was galvanostatically deposited onto TO/SPAN. The electrolyte was a 0.02 mol L^{-1} solution of $(CH_3)NBF_4$ in acetonitrile containing the monomer, 3-methylthiophene, in 0.1 mol L^{-1} concentration. After synthesis the films were polarized at −0.2 V versus Ag/AgCl for 50 s to reduce the PMT.

The thickness and roughness of TO, SPAN and PMT films were determined using a Dektak3 surface profiler.

Devices were made in sandwich structures, TO/SPAN/PMT/Al, with Al electrode being deposited by thermal evaporation under vacuum. The light source for the action spectra measurements was a tungsten lamp from a modified Beckman Acta MIV spectrophotometer. The excitation source irradiance was measured in the sample position using a calibrated HUV–11000BQ photodiode from EG&G (the wavelength range was scanned at 4 nm/s). The current–voltage I(V) characteristics of the devices were determined by increasing the applied voltage stepwise (in steps of 0.01 V) at a rate of 0.01 V s^{-1} . The photocurrents were measured using a Keithley 6517A electrometer. A 150 W xenon lamp Thermo Oriel solar-simulator was used for device characterization under AM 1.5 irradiance conditions.

Results and discussion

Films of SPAN produced on to TO following the procedure described above showed a thickness dependence on deposition time t (SI units) that can be fitted by

$$d_{SPAN} = 10^{-9}(12.41 + 0.12t).$$

In Fig. 1, we present the I(V) curve for a TO/SPAN/Al device. The I(V) dependence is linear, indicating ohmic behavior. This linear dependence was observed in all samples, independent of SPAN film thickness in the device. This observation is in agreement with previous results [16] of ohmic contact, independent of film thickness and of the work function value of the metal electrode observed for several metals, and with measurements[17] in organic diodes made of neat TO and TO/SPAN anodes. The SPAN resistivity, calculated using our data, equals 10^3 Ω m.

In Fig. 2, we present the incident-photon-to-collected electron efficiency (IPCE) data, obtained using monochromatic irradiation through the TO electrode, for
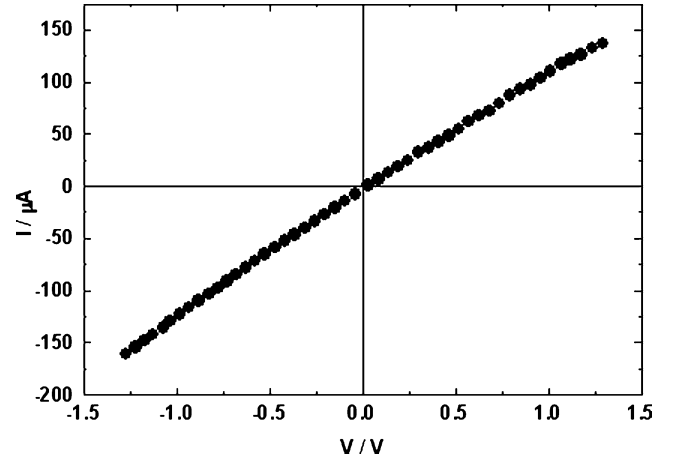

Fig. 1 I(V) for a TO/SPAN/Al device, with d_{SPAN} = 122 nm and $V \equiv V_{TO} - V_{Al}$

three devices with different d_{SPAN} and constant PMT thickness, d_{PMT}. The IPCE was calculated using [19]

$$IPCE = \frac{1.24 \times 10^{-6} J_{sc}}{\lambda I_\lambda}, \tag{1}$$

where J_{sc} is the short-circuit current density, λ = 580 nm is the wavelength, and I_λ = 0.8 W/m² the irradiance at wavelength λ. The specific value of λ = 580 nm was chosen because it corresponds to a high solar irradiance spectral region and because it corresponds to a local IPCE maximum in our devices.

We measured the I(V) characteristics of the devices under the same irradiance conditions (λ = 580 nm; I_λ = 0.8 W/m²) and calculated the fill factor FF:

$$FF = \frac{V_p.I_p}{V_{oc}.I_{sc}}, \tag{2}$$

where V_p and I_p represent the maximum-power-rectangle V and I values, respectively; and V_{oc} represents the open circuit potential. Knowing FF, we calculated the power conversion efficiency η:

$$\eta = \frac{V_{oc}.J_{sc}.FF}{I_\lambda}. \tag{3}$$

In Fig. 3, we summarize the results of IPCE and η for devices of different d_{SPAN} and d_{PMT}. In Fig. 4, the values of V_{oc} and J_{sc} for the same set of devices can be shown. In Fig. 3, we observe that the highest incident-photon-to-collected-electron efficiency of such devices, expressed by the IPCE is observed for devices with d_{PMT} = 189 nm, $d_{SPAN} \approx 120$ nm. This higher IPCE determines the maximum value of η, which is also observed when d_{PMT} = 189 nm and $d_{SPAN} \approx 120$ nm.

Cui and Park [22], have pointed out that the polyaniline (PANI) film features, for PANI that is potentiostatically deposited on to Pt substrates, are different at the various stages of the deposition, with the first PANI layers presenting shorter chain length than the

Fig. 2 IPCE for TO/SPAN/ PMT/Al devices with constant d_{PMT} (189 nm) and different d_{SPAN}, with illumination through TO (λ = 580 nm and I_λ = 0.8 W/m^2). Circles: d_{SPAN} = 79 nm; squares: d_{SPAN} = 122 nm; triangles: d_{SPAN} = 153 nm. Inset: $J(V)$ for a TO/SPAN/PMT/Al device (d_{SPAN} = 122 nm; d_{PMT} = 189 nm), in the dark (*solid circles*) and under monochromatic illumination (*open circles*), λ = 580 nm, I_λ = 0.8 W/m^2, through TO electrode, with $V \equiv V_{TO} - V_{Al}$

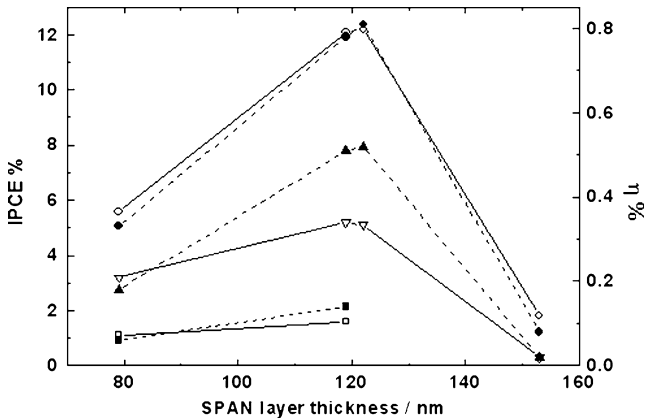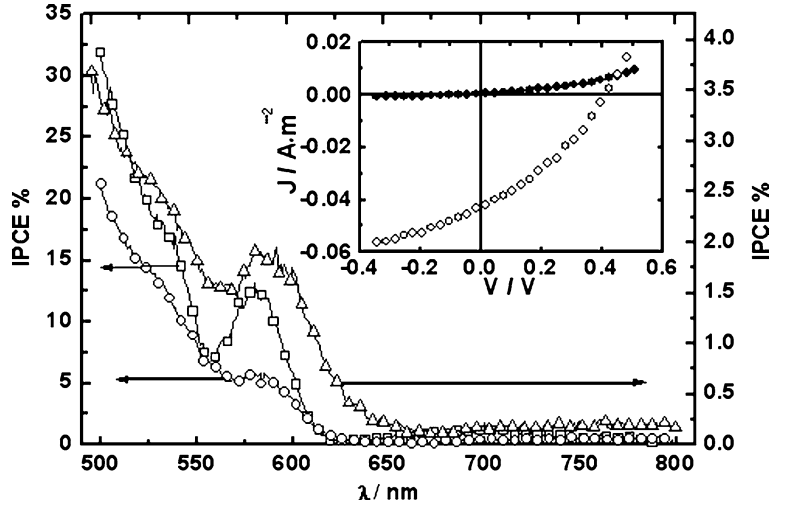**Fig. 3** IPCE (*open symbols*) and η (*solid symbols*) for TO/SPAN/ PMT/Al devices with different d_{SPAN} and d_{PMT} (squares: d_{PMT} = 160 nm; circles: d_{PMT} = 189 nm; triangles: d_{PMT} = 235 nm). Monochromatic illumination through TO, with λ = 580 nm and I_λ = 0.8 W/m^2
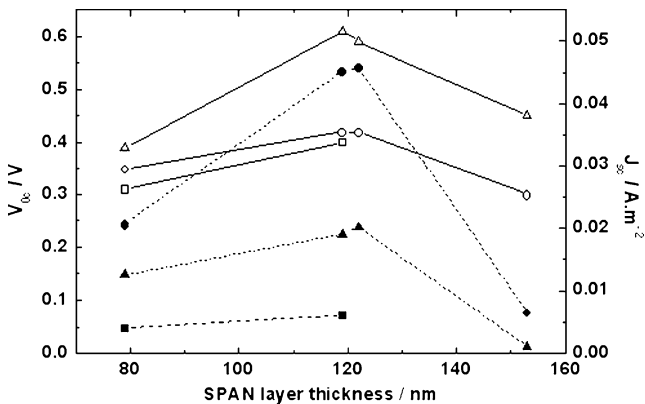
last ones. The initial increase of device efficiency with increasing of d_{SPAN} suggests that this behavior also happens with the SPAN films of the present work. Moreover, W. Lee et al. [23] have emphasized that the presence of SO$^-_3$ groups strengthens the interchain interactions, so that thicker SPAN films would have longer and more organized chains, improving charge carrier mobility. When the film gets thicker, however, its resistance increases and for this reason the device efficiency is expected to decrease for large d_{SPAN}. Higher series resistances limit the performance of the device because they result in an increasing potential drop inside the device as the current density increases, reducing the $V_p I_p$ product and, as a consequence, *FF* and η.

The maximum voltage supplied by these devices, V_{oc} is also dependent on d_{SPAN}. Like polypyrrole[15] and PEDOT:PSS[13, 14], SPAN was used to reduce the potential barrier for positive charge carrier injection from the anode into the electroluminescent layer in organic light-emitting devices [16, 17] increasing the built-in electric field inside the active layer. In the specific case of
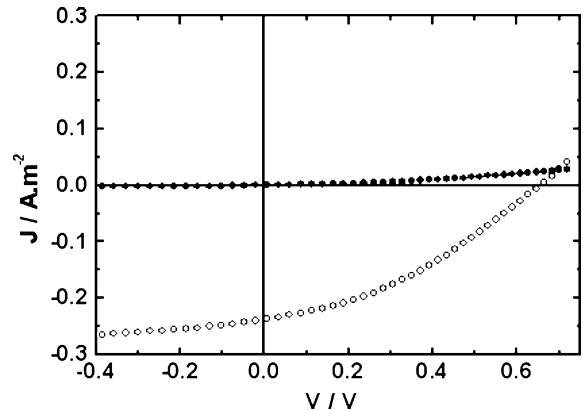

Fig. 4 V_{OC} (*open symbols*) and J_{sc} (*solid symbols*) for TO/SPAN/ PMT/Al devices with different d_{SPAN} and d_{PMT} (squares: d_{PMT} = 160 nm; circles: d_{PMT} = 189 nm; triangles: d_{PMT} = 235 nm). Monochromatic illumination through TO, with λ = 580 nm and I_λ = 0.8 W/m^2

Fig. 5 $J(V)$ for a TO/SPAN/PMT/Al, with d_{SPAN} = 122 nm and d_{PMT} = 189 nm, with $V \equiv V_{TO} - V_{Al}$ in dark (*solid circles*) and under AM 1.5 condition (*open circles*). Illumination through TO electrode

photovoltaic devices, this built-in electric field is responsible for the carrier drift to the electrodes and determines V_{oc}, which should be so high as possible. In this context, thin SPAN layers appear to be inefficient in promoting the necessary charge displacement to move the relevant energy levels redistributing the electric field inside the device and producing the built-in electric field in the PMT layer. But when d_{SPAN} is too large, V_{oc} tends to decrease, probably due to the accumulation of charge carriers in the SPAN layer. The presence of the SPAN layer is necessary to produce the built-in electric field inside the PMT layer, since the electrodes, TO and Al, present almost the same work function ($\sim$4.3 eV), as cited before.

The influence of the PMT layer on device performance is distinct from that of SPAN. In the case of increasing d_{PMT} a reduction of the average electric field throughout the PMT layer may occur, which, in the limit of thickness being much larger than the depletion layer, strongly drops the charge transport capability of the device. But the PMT layer is responsible for photon absorption, so that if d_{PMT} is too small, absorption and, consequently, also the photocurrent, are reduced. Apart from these contributions, the optical field distribution in the device and with respect to exciton dissociation interfaces must be considered because the layer thickness is significantly larger than the exciton diffusion length in electrochemically synthesized PMT[2].

In Fig 5, we present the $J(V)$ characteristics at high irradiance (1000 W/m^2) of the device that presented the best efficiency under monochromatic irradiation (d_{SPAN} = 122 nm, d_{PMT} = 189 nm). The $J(V)$ curve was recorded under AM 1.5 spectral distribution. Under this condition, the power conversion efficiency was $\sim$ 0.04%.

Another point that deserves some comments is the IPCE of these devices in the short wavelength region, around 500 nm. As can be seen in Fig. 2, the IPCE is rather high, having values higher than 30%, characterizing these devices as efficient photodetectors in this spectral range.

Conclusion

We have investigated TO/SPAN/PMT/Al devices and found the thickness that maximizes device efficiency. Sulfonated polyaniline was introduced in order to produce a built-in potential, since the electrodes, TO and Al, present almost the same work functions. We found that the efficiency of these devices depends on both, SPAN and PMT thickness, with a maximum at

d_{SPAN} = 122 nm and d_{PMT} = 189 nm. Lower d_{SPAN} implies in reduced V_{oc} and higher d_{SPAN} increases the series resistance of the device reducing, in both cases, the device power conversion efficiency.

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