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Electrical characterization of poly(3-methylthiophene) electrosynthesized onto a tin-oxide substrate

Abstract We have investigated poly(3-methylthiophene) (PMeT) thin films electrochemically synthesized directly onto a tin-oxide (TO) electrode. We find that the PMeT film thickness depends linearly on the charge density used during the electropolymerization. We have demonstrated that the current transport in PMeT films (solid phase) is space-charge limited or controlled by thermionic emission, depending on the electrode material. Using TO/PMeT/Ni devices we estimate the positive charge carrier mobility in PMeT to be around 4×10^{-4} cm^2 V^{-1} s^{-1}, and the potential barrier height for positive charge carrier injection at the Al/PMeT interface to be 0.17 eV.

Introduction

Conjugated polymers, e.g. poly(*p*-phenylenevinylene), polythiophene, poly-*p*-phenylene and its derivatives, have been the focus of intense research activity in recent years owing to their potential in optoelectronic device applications. Polythiophene and polythiophene derivatives were demonstrated to be suitable for photovoltaic device construction [1–4]. These polymers have received considerable interest because they have reliable mechanical adhesion to different standard electrodes and they exhibit good chemical and electrical stability in air and in water in both the reduced (undoped) state and the oxidized (doped) state. These polymers can be electrochemically synthesized on an electrode surface and subsequently undoped and doped reversibly. By simply altering the electrode potential, their electrical conductivity can span a range from semiconductor to conductor [5]. In 1984, Garnier and collaborators [6] reported the first description of photovoltaic cells with polythiophene and its derivatives. Electrochemically grown poly(3-methylthiophene) in the reduced (neutral) form behaves as a p-type semiconductor [6, 7].

Photovoltaic devices with conjugated polymers as the active layer for exciton generation and dissociation are constructed with one or more polymer (or even polymer blend) layers sandwiched between the electrodes. At least one of these electrodes must be transparent to permit the incident light to reach the active polymer layer.

As a transparent electrode material in organic devices, indium-tin-oxide (ITO) is the most popular, but tin-oxide (TO) has also been used in organic light-emitting devices [8], presenting some advantages due to a higher stability than ITO.

In this contribution we investigate poly(3-methylthiophene) (PMeT) electrochemically synthesized directly onto a TO electrode. We characterize the produced PMeT films using scanning electron microscopy (SEM), UV-visible spectroscopy and charge transport measurements.

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Experimental

TO films were prepared on glass substrates using the reactive chemical vapour deposition process [9]. Deposition conditions were adjusted in order to produce TO films with a thickness of 193 ± 20 nm, roughness (R_a [10]) of 2.5 ± 0.7 nm and electrical resistivity of 3.1×10^{-3} Ω cm. The TO films produced under these conditions present a work function of ~4.3 eV [8].

PMeT films were galvanostatically deposited onto TO in a single compartment cell with two electrodes. The synthesis electrolyte was a 0.02 mol L^{-1} Me$_4$NBF$_4$ (Aldrich) solution in acetonitrile containing the monomer 3-methylthiophene (Aldrich) in 0.1 mol L^{-1} concentration. The applied current density was 3.75 mA cm^{-2}. PMeT film thickness and roughness were determined using a

Dektak 3 surface profiler. The morphology of the PMeT film was analyzed with a Philips XL30 scanning electron microscope, operating at 20 kV. The absorption spectrum was measured in a 8452A HP-diode array UV-visible spectrophotometer.

For the charge transport measurements the PMeT film was reduced by polarizing it to −0.5 V/Ag for 60 s, in the single compartment cell with three electrodes. A Pt wire was used as the counter electrode and a silver wire as the reference electrode. The electrolyte was 0.1 mol L^{-1} Me_4NBF_4 in acetonitrile. The measurement was accomplished with an EG&G PAR potentiostat model 273A.

After PMeT film deposition onto TO and its reduction as described above, the second (top) electrode was deposited by resistive evaporation under vacuum, completing the device TO/PMeT/metal sandwich structure (metal: Al, Ni). Details of sample geometry are published elsewhere [11].

The current versus voltage $I(V)$ characteristics of the devices were determined by increasing the applied voltage stepwise (steps of 0.03 V) at a rate of 0.03 V s^{-1}.

Results

PMeT films with different thickness were synthesized electrochemically on TO by applying a current density of 3.75 mA cm^{-2} for different times in order to vary the charge density (from 50 to 350 mC cm^{-2}). The thicknesses of the PMeT films were measured and Fig. 1 shows the thickness variation of the film as a function of the charge density used for the electrosynthesis. Also, the morphology of PMeT films with different thickness were analysed using SEM. Figure 2 shows the micrograph of a PMeT film prepared with a charge density of 100 mC cm^{-2} (∼170 nm thickness).

The energy gap of PMeT was determined from the absorption spectra. The value, ca. 1.9 eV, was obtained from the absorption edge of PMeT in its reduced state (Fig. 3), agreeing with the value reported in the literature [12, 13].

The $I(V)$ characteristic of a TO/PMeT/Ni device is presented in Fig. 4. The straight continuous line indicates the region of the $I(V)$ curve where the current is space-charge limited, i.e., the current density can be well described by the Mott-Gurney equation [14–16]:
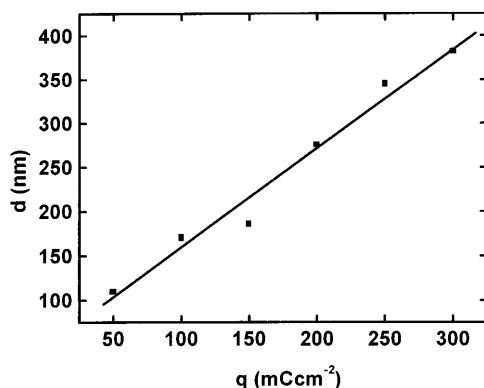
$$j = \frac{9}{8}\varepsilon\mu_{\text{eff}}\frac{V^2}{d^3} \qquad (1)$$

where ε is the PMeT dielectric constant (assumed to be 3 times the permittivity of vacuum, ε_0), μ_{eff} is the effective charge carrier mobility, d is the PMeT film thickness and
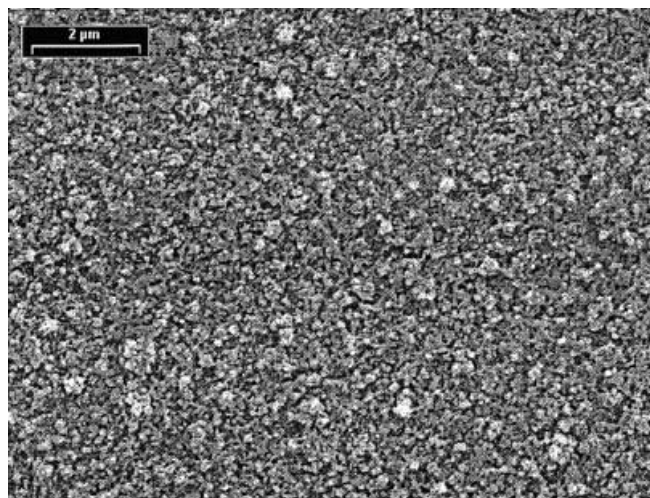

Fig. 2 Scanning electron micrograph (magnification 10000) of PMeT film prepared with a charge density of 100 mC cm^{-2} (170 nm thickness) on TO substrate
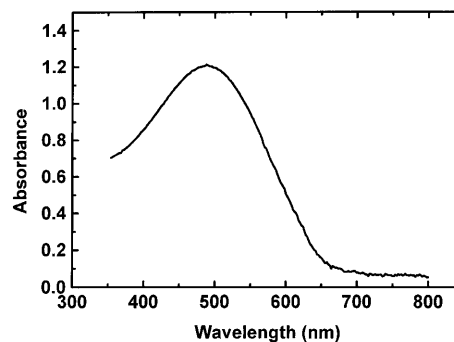

Fig. 3 Absorption spectra of PMeT film in the reduced state (170 nm thickness) on TO substrate
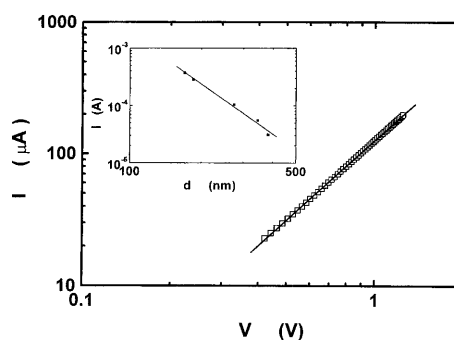

Fig. 1 Thickness variation of PMeT films as a function of the charge density used for electropolymerization onto the TO substrate

Fig. 4 $I(V)$ characteristics of a TO/PMeT/Ni device ($d = 382$ nm) for TO negatively biased. *Squares* indicate experimental results. The *straight continuous line* indicates the range that fits $I \propto V^2$ and is used to determine the mobility. *Inset*: $I(d, V = 1$ V$)$ dependence for TO/PMeT/Al samples with different thickness

V is the voltage (the derivation of Eq. 1 is presented in [14]). In the inset of Fig. 4 we present the $I(d)$ dependence, using the I value at $V = 1$ V, determined using samples of different thickness. The linear fit to these data gives $\partial \log I / \partial \log d = -2.9$, quite near the value expected from Eq. 1, which is -3. Fitting Eq. 1 to the $I(V)$ data of these TO/PMeT/Ni devices, the effective mobility of charge carriers in the PMeT was calculated to be $(4.2 \pm 0.4) \times 10^{-4}$ cm^2 V^{-1} s^{-1}. The roughness (R_a) of this PMeT film is equal to 140 nm, corresponding to 37% of the film thickness (382 nm).

For TO/PMeT/Al devices, the $I(V)$ characteristics plotted in log-log form do not present a linear behaviour, indicating that the transport is not space-charge limited. Considering that the transport in PMeT films obeys Eq. 1 when TO and Ni electrodes are used, the substitution of Ni by Al as the top electrode makes it reasonable to expect thermionic injection as being the charge transport limiting mechanism.

For injection-limited transport the Richardson-Schottky thermionic emission theory [17, 18] predicts:

$$j = qN_v\mu F \exp\left(-\frac{\phi}{\kappa T}\right)\exp\left(\frac{\beta F^{1/2}}{\kappa T}\right) \quad (2)$$

where F is the electric field strength, ϕ is the interface barrier height and

$$\beta = \left(\frac{q^3}{4\pi\varepsilon}\right)^{1/2} \quad (3)$$

where q is the elementary electronic charge. We plotted $\ln(j/F)$ as a function of $F^{1/2}$, obtaining a nearly linear region, as theoretically predicted (see Fig. 5). A linear dependence of $\ln(jd)$ on $d^{-1/2}$ is expected from Eq. 2 (considering that $F \approx V/d$). This plot can be seen in Fig. 6.

In Fig. 7 we present a plot of $\ln I$ against T^{-1}. From Eq. 2 it can be seen that

$$\frac{\partial \ln I}{\partial T^{-1}} = \frac{-\phi + \beta F^{\frac{1}{2}}}{\kappa} \quad (4)$$

From the experimental data presented in Fig. 7 we calculate $\partial \ln I / \partial T^{-1} = 1455.4$ K^{-1}, which corresponds to $\phi \approx 0.17$ eV (see Eq. 4).
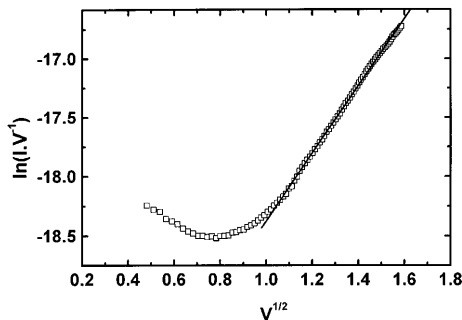

Fig. 5 $I(V)$ characteristics of a TO/PMeT/Al device ($d = 170$ nm). *Squares*: experimental data; *continuous line*: linear fit
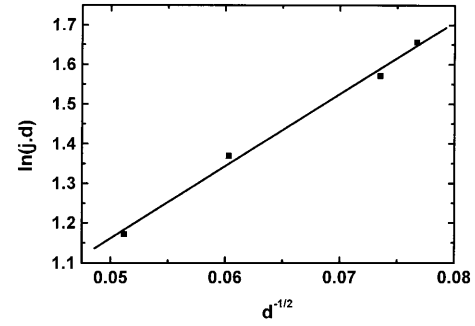

Fig. 6 $I(d)$ dependence of TO/PMeT/Al devices with different PMeT film thickness. Current values were taken for $V = 1$ V. *Squares*: experimental data; *continuous line*: linear fit
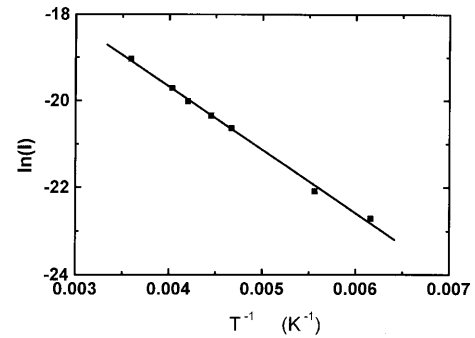

Fig. 7 $I(T)$ dependence of a TO/PMeT/Al device ($d = 275$ nm). Current values were taken for $V = 2.25$ V. *Squares*: experimental data; *continuous line*: linear fit

Discussion and conclusion

Electrochemical synthesis of the conjugated polymer is a very versatile method that allows easy control of the thickness of the polymer film. Figure 1 shows that the thickness of the PMeT film increases linearly with the amount of charge used for electropolymerization. From the micrograph of PMeT on TO (Fig. 2) it can be observed that the PMeT film presents a globular and porous morphology.

The experimental verification that $I \propto V^2$ (Fig. 4) in TO/PMeT/Ni and that $\partial \log I / \partial \log d \approx -3$ (inset of Fig. 4) demonstrates that the charge transport in the polymer films in these devices is space-charge limited, following the $I(V, d)$ dependence expected from Eq. 1.

The electrodes used in the TO/PMeT/Al devices present a work function value of ~4.3 eV [8]. Assuming the validity of Koopman's theorem [19], the expected values of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) level of the PMeT are approximately 4.5 eV and 2.6 eV, respectively. By this estimate the value of the energy gap, approximately 1.9 eV, obtained from absorption spectra (Fig. 3) was used. As a consequence, the energy barrier for positive charge carrier injection is expected to be significantly lower than that for negative charge carriers,
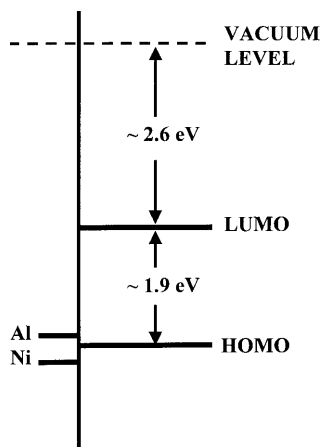
Fig. 8 Energy scheme of the metal/PMeT interface

making it reasonable to attribute the determined μ_{eff} value to positive charge carriers.

In Fig. 8 we propose the energy scheme of the metal/PMeT interface. Considering that the work functions of Al and TO are quite similar, an energy barrier for positive charge carrier injection from the Al and from the TO into the PMeT is expected. Further, the quasi-Fermi level is expected to be above the HOMO level. Under these conditions the interface may impose limits to the charge injection.

For a potential barrier of $\sim$0.2 eV expected for the Al/PMeT interface, the injection would be expected to be thermionic. As demonstrated in the section above, this case was experimentally observed in TO/PMeT/Al devices. The $I(V)$, $I(d)$ and $I(T)$ dependences agree with that expressed in Eq. 2.

The space-charge-limited transport observed in TO/PMeT/Ni is consistent with the scheme proposed in Fig. 8. In this case the quasi-Fermi level would be expected to be below the positive charge carrier mobility edge (which is expected to be quite near the HOMO) near the Ni electrode, filling eventual charge carrier traps. For filled traps, $\theta \approx 1$ and $\theta\mu \equiv \mu_{eff} \approx \mu$, which is the highest available mobility value for the charge carriers.

The value of $\mu \approx 4 \times 10^{-4}$ cm^2 V^{-1} s^{-1} is within the range of mobility values (10^{-3}–10^{-5} cm^2 V^{-1} s^{-1}) found for another polythiophene derivative, poly(3-hexylthiophene), P3HT [20–22]. The PMeT films present, however, a high roughness. Roughness values (R_a) for the samples used to determine the mobility were near 37% of sample thickness, so that the mobility values determined in the present work must be seen as only an estimate of the order of magnitude of the charge carrier mobility.

From the applications point of view, however, the roughness of the PMeT film can be an advantage. For photovoltaic devices, high film roughness implies an increased electrode contact area, which may benefit charge collection after exciton dissociation.

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