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## Photovoltaic devices based on electrodeposited poly(3-methylthiophene) with tin oxide as the transparent electrode

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**Abstract** We report on the use of electrodeposited poly(3-methylthiophene) (PMeT) in photovoltaic devices. Photocurrent measurements in devices with PMeT as the active conjugated polymer layer were carried out showing that the combination of Ni and tin oxide (TO) as electrode materials presents advantages relative to Al and TO. The choice of these electrode materials permits the carriers with the lowest mobility, the negative charge carriers, to be collected near the exciton generation/dissociation region, i.e. near the transparent TO electrode, avoiding the tendency for space charge accumulation and consequently the reduction of device efficiency.

**Key words** Poly(3-methylthiophene) · Tin oxide · Photovoltaic devices

### Introduction

Organic photovoltaic devices are commonly constructed in a sandwich structure, with the conjugated material sandwiched between two electrodes, one of them transparent. For this type of application the most used transparent electrode material is ITO (indium-tin oxide). ITO is, in most of the cases, a high work function material, with the work function value depending on details of the sample treatment [1, 2, 3]. The second electrode normally is a metal, in several cases aluminum. The difference in the work function values originates an electric field, which permits exciton dissociation inside

the organic material even in the absence of an external applied voltage.

In conjugated polymers and molecules it is commonly observed that the mobility of positive charge carriers ( $\mu_+$ ) is some orders of magnitude larger than the mobility of negative charge carriers ( $\mu_-$ ) [4, 5, 6, 7]. As a consequence, if the work function of the transparent electrode is higher than that of the opposite electrode, a problem of organic device configuration emerges. Most of the light is absorbed and gives rise to excitons near the transparent electrode. The difference in the work functions of the electrodes produces an internal electric field directed from the metal to the ITO. If excitons are dissociated the positive charge carriers are collected in the ITO and the negative charge carriers are collected in the metal. This means that the low mobility (negative) charge carriers have a larger path to the collection electrode than the high mobility (positive) charge carriers. Under this set of conditions there is a tendency of space charge accumulation with a consequent compensation of the electric field due to the electrodes, reducing the device efficiency.

Owing to the difference in carrier mobilities ( $\mu_+ > \mu_-$ ), it would be better to collect the negative charge carriers in the transparent electrode, near to the generation region, collecting the positive charges in the opposite (metal) electrode. This situation can be achieved using TO (tin oxide) as a transparent electrode and a high work function ( $\phi$ ) metal as the opposite electrode. TO films produced by reactive chemical vapor deposition (CVD) present  $\phi_{\text{TO}} \approx 4.3$  eV [8], whereas metals such Au, Ni, or Pd present  $\phi > 5$  eV [9].

In this communication we report on photovoltaic devices constructed in a sandwich structure using TO and Ni as electrodes (fulfilling the requirements expressed in the above paragraph) and electrodeposited poly(3-methylthiophene) (PMeT) as a conjugated polymer. Polythiophenes have received considerable interest because of their reliability in mechanical adhesion to different standard electrodes and the exhibition of good chemical and electrical stability. Additionally, TO is

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known to present a better stability than ITO [8, 10] and the TO and PMeT production processes are relatively non-expensive, an interesting advantage especially in cases of device fabrication.

## Experimental

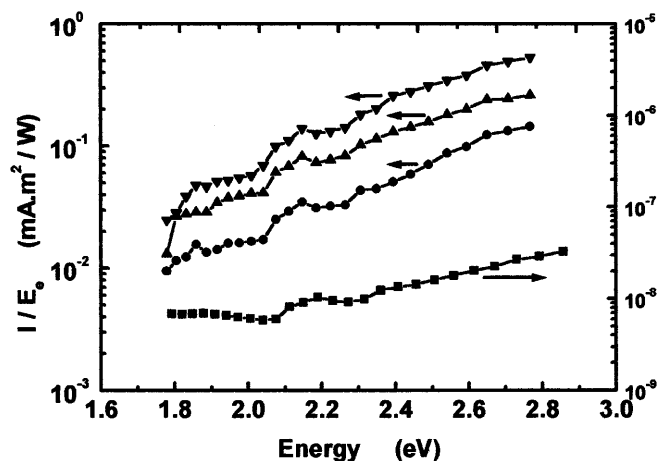
TO films were prepared on glass substrates using reactive CVD [11]. The deposition conditions were adjusted in order to produce TO films with a thickness of  $193 \pm 20$  nm, roughness ( $R_a$  [12]) of  $2.5 \pm 0.7$  nm and electrical resistivity of  $3.1 \times 10^{-3} \Omega \text{ cm}$ . The TO films produced under these conditions present a work function of  $\sim 4.3$  eV [8].

PMeT films were galvanostatically deposited onto TO, following a procedure described previously [13]. The positive charge carrier mobility in PMeT films produced by this method was estimated as being  $4 \times 10^{-4} \text{ cm}^2/\text{V s}$  [13]. After PMeT film deposition onto TO and its reduction [13], the second (top) electrode was deposited by resistive evaporation under vacuum, completing the TO/PMeT/metal sandwich structure (metal: Al, Ni) of the device. Details of the sample geometry are published elsewhere [14]. The PMeT layer thickness ( $d$ ) was determined using a surface profiler.

A modified Beckman Acta MIV spectrophotometer was utilized as the primary light source for the photocurrent measurements. The width of the input and output slits were selected in order to give an output with a spectral width of about 10 nm. In order to allow for the comparison between different devices, the spectrophotometer output was characterized as a function of photon energy. The excitation source irradiance was measured in the sample position using a calibrated HUV-1100BQ photodiode from EG&G. The device photocurrents were measured using a Keithley 6517A electrometer.

## Results

Figure 1 shows the results of photocurrent measurements of a TO/PMeT/Ni device as a function of photon energy from 1.7 eV up to 2.8 eV (region of the absorption peak of PMeT [13]). The PMeT layer was 170 nm thick and the device had an active area of about  $2 \text{ mm}^2$ .



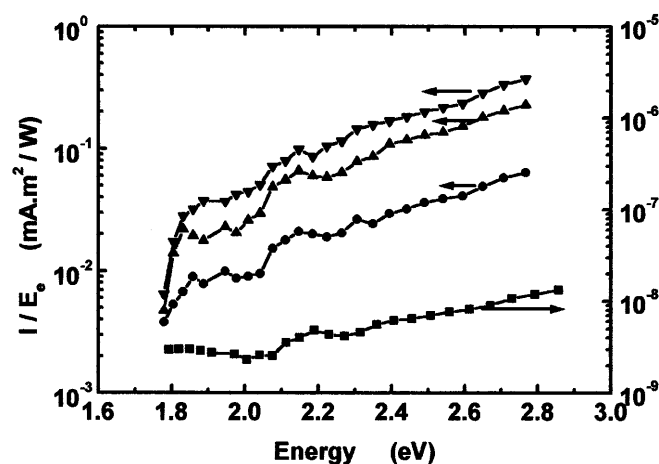
**Fig. 1** Photocurrent/irradiance ratio for a TO/PMeT/Ni device after background current subtraction. PMeT layer thickness: 170 nm; device area:  $2 \text{ mm}^2$ ; squares: without applied voltage; circles: 1.5 V; up triangles: 2 V; down triangles: 3 V; TO positively biased

In Fig. 2 we present, for comparison, the photocurrent/irradiance as a function of photon energy of a device with similar characteristics, except that the Ni electrode was substituted by Al, keeping the same irradiance conditions. Before plotting Figs. 1 and 2 the background current under darkness conditions (see Table 1) was subtracted. In both cases the TO acted as the positive (electron collecting) electrode.

The open-circuit voltage measured in the PMeT devices is presented in Table 2 and compared with a PPV-based device [PPV = poly(*p*-phenylenevinylene)] made with a Pd electrode ( $\phi_{\text{Ni}} \approx \phi_{\text{Pd}}$ ) [9].

## Discussion

As one can observe, the device shows an increase in efficiency with the increase of the applied voltage



**Fig. 2** Photocurrent/irradiance ratio for a TO/PMeT/Al device after background current subtraction. PMeT layer thickness: 170 nm; device area:  $2 \text{ mm}^2$ ; squares: without applied voltage; circles: 1.5 V; up triangles: 2 V; down triangles: 3 V; TO positively biased

**Table 1** Background current of the devices at different applied voltages

Applied voltage (V)	Background current density ( $\text{mA}/\text{mm}^2$ )	
	TO/PMeT/Ni	TO/PMeT/Al
0	$1 \times 10^{-6}$	$5 \times 10^{-7}$
1.5	$1 \times 10^{-3}$	$5 \times 10^{-4}$
2.0	$3 \times 10^{-3}$	$5 \times 10^{-4}$
3.0	$1 \times 10^{-2}$	$4 \times 10^{-3}$

**Table 2** Open-circuit voltage ( $V_{\text{oc}}$ ) of single polymer layer photo-voltaic devices

Device	$d$ (nm)	$V_{\text{oc}}$ (V)	Ref.
TO/PMeT/Ni	170	0.056	This work
TO/PMeT/Al	170	0.050	This work
TO/PPV/Pd	160	0.052	[15]

between the electrodes. This result is expected since higher electric fields enhance exciton dissociation and charge transport.

Comparing Figs. 1 and 2, it can be observed that without any applied voltage the photocurrent is higher in the Ni electrode device. This increased efficiency of the Ni electrode device is due to the built-in electric field originated inside the polymer layer as a consequence of the higher difference in the work function values,  $\Delta\phi$ , of Ni ( $\sim 5.1$  eV [9]) and TO (4.3 eV [8]) than Al and TO. The exact electric field distribution inside the polymer layer cannot be given because information on trap concentration, distribution and donor/acceptor character is not available. However, assuming the absence of depletion layers and that the barriers at the interface are formed obeying Schottky's rule, the built-in electric field can be estimated as:

$$\Delta\phi/qd \approx 0.8/(1.7 \times 10^{-7}) = 4.7 \times 10^6 \text{ V/m} \quad (1)$$

where  $q = 1.6 \times 10^{-19}$  C. Under applied voltage conditions the Ni electrode device is also more efficient, as can be seen when Figs. 1 and 2 are compared. This efficiency increase can be explained by considering that if TO is positively biased, then the built-in potential observed in the Ni electrode device contributes to an electric field enhancement (see the energy diagram, Fig. 3).

If the photocurrent/irradiance ratio at 500 nm wavelength (approximate maximum PMeT absorption [13] and solar spectral irradiance [16]) is plotted against applied voltage for both the Ni and the Al electrode devices, it can be seen that the efficiency of the Ni electrode device increases linearly with applied voltage between 1.5 and 3.0 V. The photocurrent/irradiance ratio of the Al electrode device at 3 V applied voltage is lower than the Ni electrode. However, if it is displaced by 0.73 V it intercepts the Ni electrode curve (see Fig. 4). Considering that  $\phi_{\text{Al}} \approx 4.3$  eV (it depends on crystalline

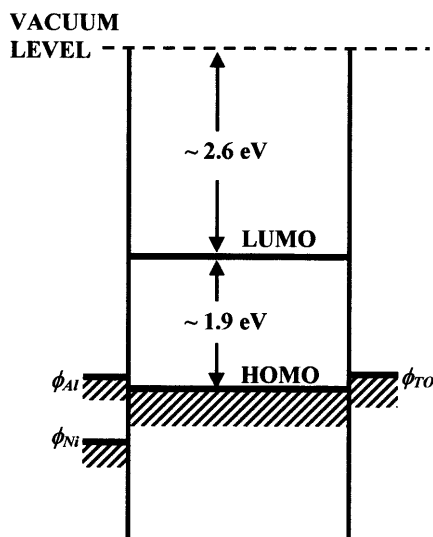


Fig. 3 Energy diagram of the TO/PMeT/metal device

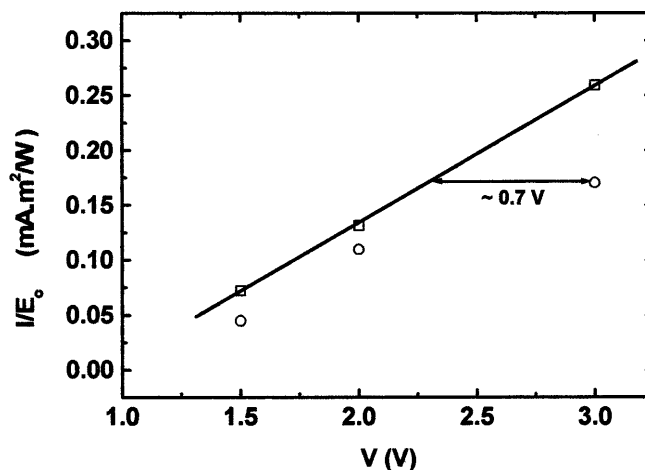


Fig. 4 Photocurrent/irradiance ratio for TO/PMeT/Al (circles) and TO/PMeT/Ni (squares) as a function of applied voltage. The continuous line fits the TO/PMeT/Ni points

orientation [9]),  $\phi_{\text{Ni}} - \phi_{\text{Al}} \approx 0.8$  eV, so the device efficiency difference may be attributed to the choice of metal electrode and the consequent built-in electric field. The same is not true for lower applied voltages, but such deviations can be expected for the Al electrode device since depletion layers are formed only for applied voltages different from zero.

The open-circuit voltage value measured in Ni/PMeT devices is also larger than that of Al/PMeT devices, indicating that even when interface polarization, depletion layer formation, metal electrode oxidation, surface states and other common effects occur, the advantage of the Ni/PMeT/TO device remains observable.

## Conclusions

In conclusion, we realized photocurrent measurements on photovoltaic devices using TO and Ni as electrodes and electrodeposited PMeT as the active layer. Using TO as the transparent electrode and the high work function metal Ni as the second electrode, it was possible to observe an increase in the efficiency when an external voltage was applied, keeping the TO as the positive electrode.

TO/PMeT/Ni devices present several advantages when compared to other organic devices. TO and PMeT are environmentally stable when compared with ITO and PPV, for example. Ni is also more stable than other common organic device electrode materials, e.g. Al, Mg or Ca. Furthermore, owing to the difference of work function values between TO and Ni, this electrode materials combination permits the less movable negative charge carriers to be collected near the exciton generation/dissociation region.

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