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# Thermal ageing of bulk heterojunction polymer solar cells investigated by electric noise analysis

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## ABSTRACT

Temperature is one of the most specific external parameters that can accelerate the degradation rate in polymer:fullerene solar cells. To detect modifications of the active layer materials, electric noise spectroscopy is a sensitive experimental technique. A detailed characterization of the dc electric transport and voltage–noise properties shows how thermal ageing is detrimental for the investigated bulk heterojunction photovoltaic system. In particular, an increase of the energy barrier height at the interface between the metal contact and the blend, and a simultaneous decrease of the charge carrier zero-field mobility, evaluated through the analysis of the flicker noise component, are observed as a consequence of a thermal treatment. These effects can be related to morphological changes of the solar cell active layer and interface, and are revealed by monitoring the noise level.

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## 1. Introduction

In the last few decades, conjugated polymers have emerged as a new class of semiconductors which combine unique optoelectronic properties and the key technological advantages of plastics [1], for example solution processing at low temperature. They have, therefore, attracted increasing interest for the development of flexible, large area and low cost electronic applications, from light emitting diodes to thin film transistors and solar cells [2–4]. Solar cells based on organic materials have already been reported in the late 70s, although with very poor conversion efficiencies. These early organic photovoltaic (OPV) devices were based on a single organic layer sandwiched between two electrodes, thus forming a Schottky diode. For a review of such devices, the reader is for example referred to the work of Chamberlain in 1983 [5]. In 1986 Tang reported the first organic solar cell based on the donor–acceptor concept in a bilayer structure [6]. In the 90s, the introduction of the bulk heterojunction (BHJ) concept allowed enhancing the device efficiency to about 3% [7], marking a breakthrough in the field of OPV. In the BHJ, the active layer consists of an intermixing of the donor and acceptor materials so that a fine interpenetrating network builds up with extended donor–acceptor interfaces distributed in the bulk.

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The reference system in BHJ cells is represented by a composite between the conjugated polymer poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), a soluble derivative of the fullerene C<sub>60</sub>. Solar cells based on P3HT:PCBM have demonstrated efficiencies of about 5% [8]. Recently, the power conversion efficiency of tandem OPV devices reached certified values above 9% [9], thanks to the development of new low-bandgap polymers that allow for better light harvesting [10].

One major weak point of OPV devices is the poor stability of the organic photoactive materials under operating conditions [11]. Most of the conjugated polymers rapidly degrade when exposed to ambient air and light, thus limiting the lifetime of the whole device. Indeed, it has been widely reported that degradation pathways, due to unstable morphologies, photo-oxidation, indium diffusion, and thermal stress occur at every layer and interface of OPV devices [12,13]. In particular, temperature has been identified as one of the most important external parameters that can accelerate the degradation rate [11,14]. Regarding P3HT, it is well-known that thermal annealing after active layer deposition can favor the formation of an ordered polymer phase [15,16]. This ordering of the polymeric chains due to thermal treatment, however, makes P3HT more prone to oxidation. The temperature increase may induce phase separation between P3HT and PCBM, leading to an undesirable vertical structure which can drastically influence the solar cell performance [15,16].

Degradation studies performed using Fourier transform infrared spectroscopy (FTIR), ultraviolet photoelectron spectroscopy (UPS), angle-resolved X-ray photoelectron spectroscopy (AR-XPS)

have been reported in the literature [17,18]. However, these techniques, specific for the structural characterization of the organic films and interfaces, need to be accompanied by complementary measurements that can provide additional information regarding the electronic transport in the material. In this respect, the study of the low-frequency electric noise spectrum has already proven to be a powerful and non-destructive spectroscopic analysis useful to investigate electric transport processes in several systems, such as manganites [19], carbon nanotubes composites [20], novel superconductors [21], and graphene devices [22]. In this work, the dynamic behavior of the charge carriers has been successfully monitored by studying the fluctuation mechanisms. The detailed characterization of these processes, which are sensitive to all temperature-induced transformations occurring in the devices under test, represents an innovative tool to reveal technological information that might lead to the fabrication of more efficient organic solar cells.

## 2. Experimental

P3HT and PCBM were dissolved in a mixture of ortho-dichlorobenzene and tetralin as already reported in [23]. To fabricate the photovoltaic cells, indium tin oxide (ITO) coated glass slabs were patterned, etched in an HCl bath, and ultrasonicated several times in isopropyl alcohol. An oxygen plasma treatment was also performed in order to remove organic residues from the surface. Poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS) was then spun on top of the ITO and dried at 180 °C for 10 min in air. To complete the devices, the samples were transferred to a nitrogen filled glovebox where spin coating and thermal annealing (150 °C for 10 min) of the active layer, as well as cathode evaporation (Ca/Al) took place. The active area of the devices was about 0.5 cm<sup>2</sup>.

All the experimental investigations were carried out by using a thermoelectric cooler (i.e., Peltier device), with a temperature range of operation between 270 and 360 K. The temperature was stabilized with a computer-controlled PID loop to better than 0.1 K. The current–voltage measurements were made in current-pulsed mode by using an active dc current source (model Keithley 220), and by recording the voltage response with a digital nanovoltmeter. The noise measurements were made by biasing the samples with the Keithley or alternatively with a battery-operated dc current supply; the output voltage signal was amplified with a PAR5113 preamplifier and analyzed by a dynamic signal analyzer HP35670A. The spectral density of the voltage fluctuations was calculated by averaging a large number ( $\geq 100$ ) of measured traces. The used standard four-probe technique, alone, does not eliminate completely the external noise contributions due to contact resistance fluctuations. In order to avoid the presence of spurious noise components in the real spectral trace of the samples, a specific experimental technique, based on a sequence of four-probe and two-probe noise measurements, was used to determine the contact noise contributions. The details of the experimental setup are reported in [24].

## 3. Results and discussion

### 3.1. Electric transport properties

Recombination kinetics plays a major role for the current–voltage ( $I$ – $V$ ) characteristics of BHJ solar cells. It is well-known that charge carrier recombination and applied dc bias current ( $I_{DC}$ ) are closely related by  $R_{rec} = (dV_F/dI_{DC})$ . Here,  $R_{rec}$  is the recombination resistance of electrons and holes [25], and  $V_F = V_{DC} - I_{DC}R_S$  is the

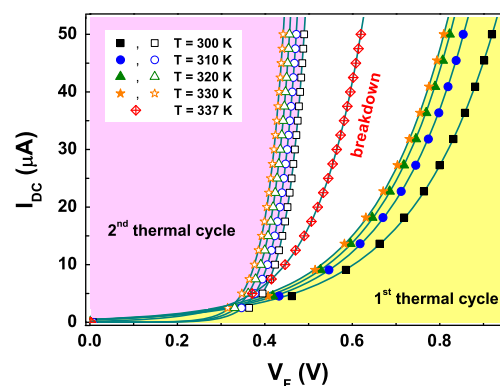
forward voltage without the contribution of the device series resistance  $R_S$  [26]. Several studies of P3HT:PCBM photovoltaic devices have shown that these cells can be seen as Schottky diodes from the point of view of current transport [27–29]. Therefore,  $I$ – $V$  curves can be modeled using the classical Schottky–Richardson emission law [30]:

$$I_{DC} = AA_R T^2 \exp\left(-\frac{\Delta}{k_B T} + \frac{eV_F}{nk_B T}\right), \quad (1)$$

where  $A$  is the area of the cell active layer ( $\approx 0.5$  cm<sup>2</sup> for the case here reported),  $A_R$  the effective Richardson constant,  $T$  the absolute temperature,  $\Delta$  the barrier energy at the metal–blend interface,  $n$  the ideality factor,  $e$  the electron charge, and  $k_B$  the Boltzmann constant.

The  $I$ – $V$  characteristics of a typical P3HT:PCBM solar cell investigated in this work, in dark conditions and at temperatures from 300 to 340 K, are shown in Fig. 1. A monotonic decrease of  $R_{rec}$  is found with increasing temperature (full symbols), whereas a modification occurring in the device active layer is clearly evident at 337 K. Indeed, the measurements performed after this 1st thermal cycle, and at the same temperatures (open symbols), show a strong reduction of  $R_{rec}$ . Whether the event seen at 337 K represents an effective “breakdown” of the photovoltaic device is still an open question.

The best fitting curves to the  $I$ – $V$  experimental data (Fig. 1 solid lines) are obtained by using Eq. (1). The corresponding fitting parameters are reported in Table 1, where the first column refers to the time elapsed between subsequent measurements. For this time scale, moisture and thermo-oxidation do not play a decisive role without light exposure [31,32]. A strong reduction of  $R_S$  and  $n$  is found when the temperature of 337 K is approached. All these



**Fig. 1.** Current–voltage characteristics of a typical device during the 1st (full symbols - yellow region) and the 2nd (open symbols - pink region) thermal cycles, respectively. A “breakdown”, characterized by an active layer modification, occurs at 337 K. The best fitting curves with Eq. (1) are also shown as solid lines. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

**Table 1**

Best fitting values of the parameters in Eq. (1), monitored in time and temperature. The Richardson constant  $A_R$  is fixed to 120 A cm<sup>-2</sup> K<sup>-2</sup>.

Time (min)	$T$ (K)	$R_S$ ( $\Omega$ )	$n$	$\Delta$ (meV)
0	300	3340 $\pm$ 67	7.62 $\pm$ 0.04	776 $\pm$ 5
10	310	3027 $\pm$ 60	6.74 $\pm$ 0.04	807 $\pm$ 5
20	320	3134 $\pm$ 63	6.27 $\pm$ 0.04	837 $\pm$ 5
30	330	2871 $\pm$ 57	6.12 $\pm$ 0.03	859 $\pm$ 5
40	337	2670 $\pm$ 53	3.709 $\pm$ 0.003	911 $\pm$ 8
50	300	453 $\pm$ 9	1.604 $\pm$ 0.001	962 $\pm$ 6
60	310	376 $\pm$ 7	1.534 $\pm$ 0.001	987 $\pm$ 6
70	320	308 $\pm$ 6	1.482 $\pm$ 0.001	1011 $\pm$ 7
80	330	263 $\pm$ 5	1.435 $\pm$ 0.002	1035 $\pm$ 7

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