Electrical admittance studies of polymer photovoltaic cells

V. Dyakonov[a,*], D. Godovsky[a], J. Meyer[a], J. Parisi[a], C.J. Brabec[b],
N.S. Sariciftci[b], J.C. Hummelen[c]

[a]*Department of Energy and Semiconductor Research, University of Oldenburg, D-26111 Oldenburg, Germany*
[b]*Christian Doppler Laboratory for Plastic Solar Cells, University of Linz, 4040 Linz, Austria*
[c]*Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

Abstract

We investigate the electrical transport properties of ITO/conjugated polymer–fullerene/Al solar cells and the role of defect states with the help of admittance spectroscopy and $C(\omega)$–V measurements in the dark. A characteristic step in the admittance spectrum can be observed in the temperature range 40–320 K, originating from the electrically active defects. The activation energy determined from an Arrhenius plot was found to be 34 meV. The position of the step does not depend on the dc bias voltage which may indicate the pinning of the hole Fermi-level at the interface due to the high density of defect states. The diode capacitance as a function of the reverse bias depends strongly on the device preparation conditions and correlates with the device *I–V* characteristics. We found a completely bias independent capacitance under reverse bias for the cells with low-power efficiency and almost no rectification under illumination. On the other hand, the high-efficiency cells with good rectification under illumination demonstrate an increase of the capacitance with ac bias even at frequencies above 100 kHz. The former devices are found to be fully depleted, whereas in the latter, a formation of the space charge region can be assumed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interest in organic donor–acceptor polymer composites grows due to their use in active layers of photovoltaic devices. Photo-induced electron transfer in such composites is a recently discovered phenomenon on which the photovoltaic action of the electronic devices is based [1]. The formation of interpenetrating networks by conjugated polymers and fullerenes is an effective method to increase the charge-generating interface in photovoltaic devices and has been successfully utilized in efficient plastic solar cells. The charge transfer occurs within a sub-picosecond range and the separated state is metastable. The photo-generated charge carriers are then transported to the corresponding electrodes. The electron transport is believed to be the result of hopping between the percolating network of fullerene molecules and comprises one of the serious drawbacks for the fabrication of efficient devices. Therefore, the control over the morphology of the absorber layer is important. Another scarcely studied problem, which is also vital for photovoltaic properties of the metal/polymer–fullerene/metal structures, is the

formation of interfaces and the processes taking place at the contacts. During the recent years, the development of solar cells based on the composites of the derivatives of poly-phenylene-vinylenes and highly soluble derivatives of C_{60} delivered significant results. The energy conversion efficiencies (being restricted by the measurements for the monochromatic light at early stages) achieved reproducible values of 0.5–0.8% under AM1.5, as reported by several laboratories [2,3]. The recently achieved value of 3.2% (AM1.5) demonstrates the high potential of this approach [4]. In both "new" and "old" technologies, the same polymers–fullerenes are used as the absorber layer. Therefore, the electronic processes in the material are supposed to limit the device performance. Detailed electrophysical characterization of these devices is necessary for a deeper understanding of the material properties and the carrier recombination paths.

2. Materials and sample preparation

We have studied the admittance and capacitance–voltage ($C(\omega)$–V) behavior of the ITO/MDMO-PPV:PCBM/Al (poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV) conjugated polymer and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM)-soluble

* Corresponding author. Tel.: +49-441-7983538;
fax: +49-441-7983326.
E-mail address: dyakonov@uni-oldenburg.de (V. Dyakonov).

derivative of C_{60}) structures. The cells of 15 mm × 15 mm size were fabricated by spin-coating of the polymer–fullerene in *p*-xylene solution (1:3 weight ratio) on top of a patterned ITO contact on a glass substrate. We compare two different types of solar cells: low-energy conversion efficiency ($\eta_e < 0.5\%$) cells and high-energy conversion efficiency ($\eta_e = 2.5\%$) cells. Admittance measurements in the frequency range 0.1–10 MHz have been performed using a Solartron impedance analyzer 1260A equipped with a Solartron dielectric interface 1296A in combination with a variable temperature helium cryostat ($T = 40$–320 K). The measurements were carried out at an ac level of 50 mV in order to work close to the equilibrium which can be distorted due to high injection of charge carriers at forward bias. The same set-up allowed to carry out $C(\omega)$–V measurements whereby the ac voltage was superimposed with a dc bias between −2 and +2 V.

3. Admittance spectroscopy

The frequency-dependent contribution to the complex admittance, $Y = G + i\omega C$, can originate from the trap levels located in the bulk of the semiconductor material or at the interface. The presence of such states can be seen in the $C(\omega)$ dependence (ω: angular frequency), where the characteristic
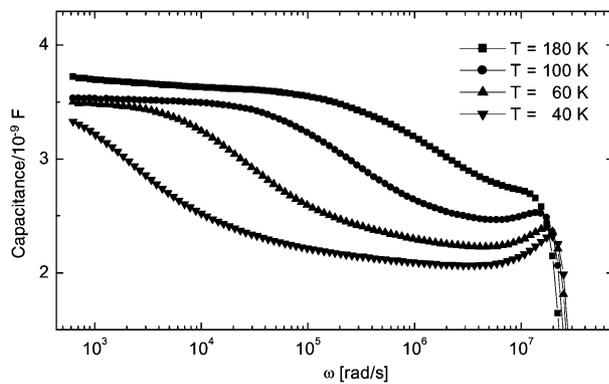
steps are expected. Fig. 1 shows the $C(\omega)$ response of an ITO/MDMO-PPV:PCBM/Al device at different temperatures. One step can be clearly seen. In the differentiated capacitance spectrum (Fig. 1, right), this step appears as a minimum, which enables to reveal the position of the step on the frequency axis more accurately. The position of the step does not depend on the bias applied, however, the step shifts to lower frequencies when cooling down the device from 300 to 40 K. The latter is indicative for a thermally activated process with an activation energy $E_A = 24$–34 meV corresponding to a shallow trap level (Fig. 2, left).

The $C(\omega, T)$ behavior in the high-efficiency cells is essentially the same. The same step is observed showing similar values of the thermal activation energy. As shown in Fig. 2 (right), the capacitance decreases with increasing frequency. Under applied bias from −2 to +2 V ($T = 40$ K), the position of the step does not shift along the frequency axis.

4. Capacitance–voltage measurements

We carried out $C(\omega)$–V measurements to reveal the presence of a space charge region, as a further contribution to the device capacitance. Fig. 3 demonstrates the $C(\omega)$–V behavior.
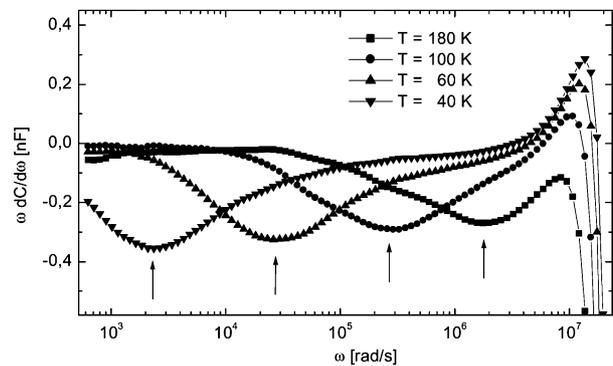

Fig. 1. Capacitance (left) and differential capacitance (right) of an ITO/MDMO-PPV:PCBM/Al cell measured at different temperatures.
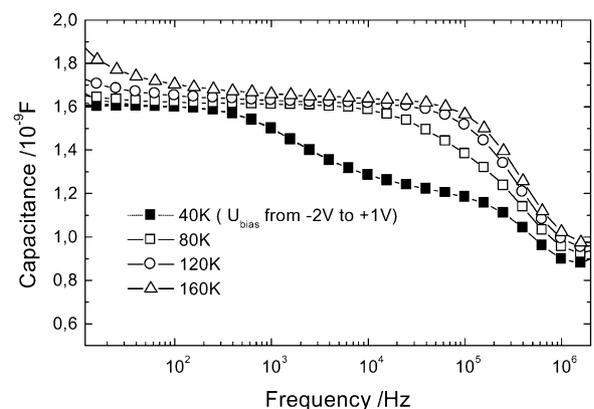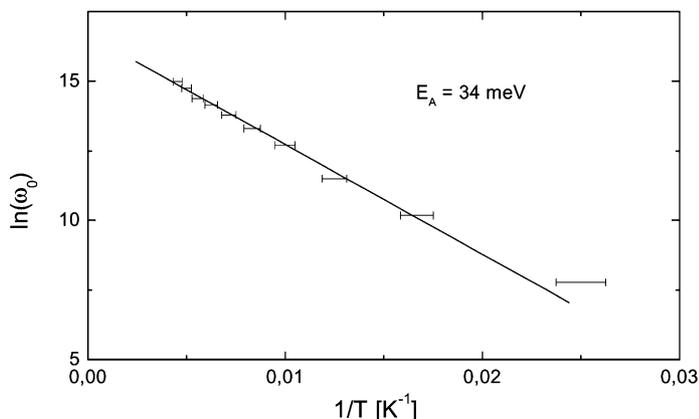

Fig. 2. Frequency minima derived from Fig. 1 ($\ln(\omega_0) \sim -(E_A/k)(1/T)$) (left). Capacitance vs. frequency at different temperatures and dc bias (right).
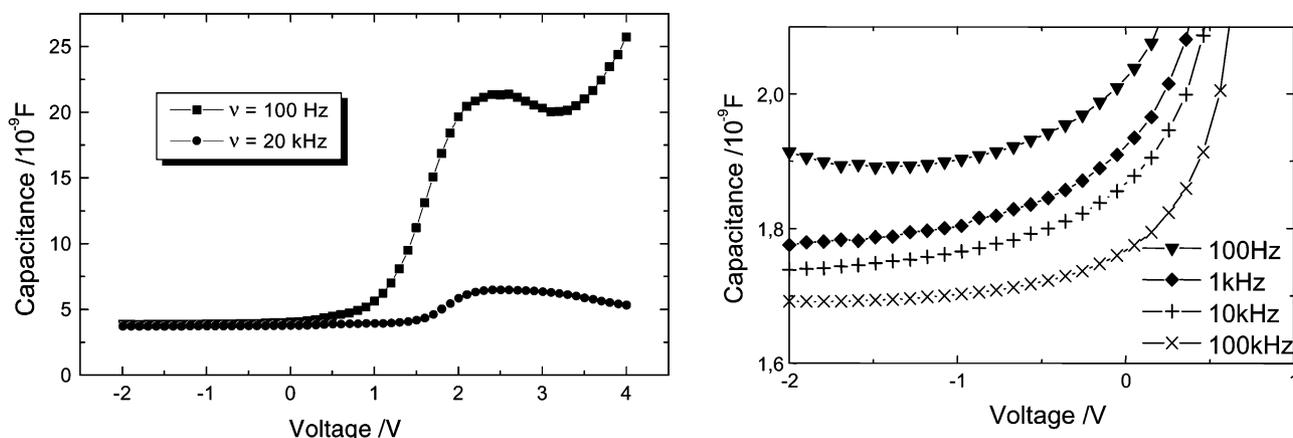
Fig. 3. $C(\omega)$–V dependence at $T = 293$ K in "low-efficiency" cell (left) and "high-efficiency" cell (right).

We found a bias independent capacitance under reverse bias in the "low-efficiency" cell. This indicates that the device is fully depleted. Surprisingly, the capacitance increases and shows a peak at forward bias. Although, we do not have a conclusive model to explain the appearance of the capacitance peak and even a further increase of the capacitance under charge injection conditions, the possible reason can be a charge accumulation layer at the metal/polymer and/or the metal/fullerene interfaces [5], or polymer–fullerene defects.

The $C(\omega)$–V dependencies of the "high-efficiency" cells differ drastically from the ones observed for "low-efficiency" devices, especially in the frequency range above 10 kHz (Fig. 3, right).

5. Discussion

The full set of the experimental data allows us to conclude that the electrically active defect states, which we observe in the $C(\omega)$ dependencies, are situated at the metal/polymer composite interface. The bias independent position of the step is an evidence for the Fermi-level pinning at the interface due to the high density of the defect states. We ruled out the bulk defects, since the process of bulk defect ionization in conjugated polymers consists of the hopping of a hole from the conjugated segment with an acceptor impurity (compensated state) to the neighboring conjugated segment. Such hopping should be bias dependent due to the effective lowering of the potential barriers in high electric fields (Pool–Frenkel mechanism).

Since the high-frequency capacitance at 40 K practically coincides with the calculated geometrical capacitance of the sample, we conclude that we do not observe the conformational polymer chains relaxation processes (dipole relaxation), which take place at much higher frequencies.

The analysis of temperature dependencies of the capacitance ($C \sim (\exp(-1/kT))^{1/2}$) along with the shape of the $C(\omega)$–V curves at 293 K (Fig. 3, right) draws us to the conclusion of a partial formation of the space charge layer at room temperature in the case of the "high-efficiency" cell (non-uniform distribution of free charge carriers throughout the device). The increase in the charge carrier concentration under illumination leads to an improvement of the space charge layer, resulting in a high rectification ratio and an increase in the filling factor (from 0.3 to 0.55) for "high-efficiency" cells. This is possible only by assuming that the charge carrier concentration in the "high-efficiency" cell is already in the range above 10^{14} cm^{-3}.

The behavior of the capacitance in the low-frequency range is well described in the frame of the Maxwell–Wagner representation, providing additional evidence for the high density of states at the metal/polymer interface.

6. Conclusions

We have examined the electrical transport properties of novel polymer–fullerene solar cells by means of admittance spectroscopy in the temperature range 40–320 K. We detect electrically active shallow acceptor levels with $E_A = 24$–34 meV situated, from our point of view, at the metal/polymer composite interface. The high density of interfacial states leads to the pinning of the Fermi-level. In contrast to the "low-efficiency" cell, the admittance spectra of the "high-efficiency" device provide evidence for the formation of the space charge layer at the metal/polymer composite contact, explaining the high rectification ratio and improved filling factor: two important parameters determining the increase in the cell efficiency.

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