INFLUENCE OF DEFECT STATES ON THE ELECTRICAL PARAMETERS OF P3HT:PCBM SOLAR CELL

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1. Introduction

The understanding of origin of defects in photovoltaic active materials and their influence on organic solar cells (OSC) is an important condition for development of organic photovoltaics. The defects create electronic states in band gap which cause charge capture or recombination and thus affect degradation of OSC parameters. This situation is depicted in Fig. 1. Defects in organic materials can have structural and/or chemical nature [1].

Structural defects contribute to static and dynamic disorder, which give rise to tail states [2]. These states are diffused in the region near band gap edges. Their presence is typical for amorphous structures and is responsible for decrease of charge mobility due to process of charge capture and emission (Fig.1.).

The chemical defects are result of incorporation of impurities into semiconductor substance. These defects create well localized states in the band gap, which have detrimental effect for OSC since they cause recombination of charge. Oxygen can be incorporated in OSC in various ways. In the P3HT:PCBM-based OSC, it reacts with alkyl chains or thiophene rings of P3HT [3,4], PCBM molecules [5] as well as with other OSC components. The chemical degradation caused by reaction of organic semiconductor with atmospheric oxygen can be prevented by encapsulation of OSC.

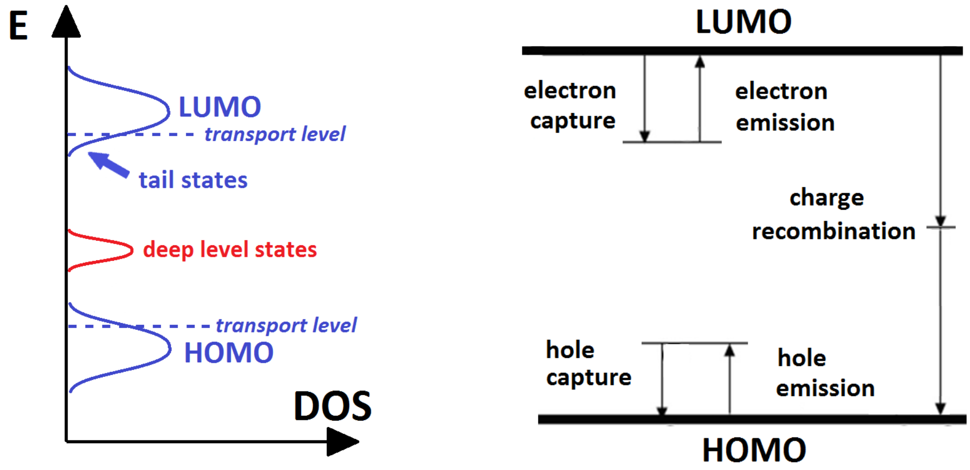

Fig.1: *Energy distribution of electronic states in semiconductors (left) and processes related to defect states where arrows denote electron motion (right).*

2. Analysis of Defects

Several methods have been applied for analysis of defect-related electronic states in organic photovoltaics. These methods are based on measuring electronic or optical properties which result from charge trapping and release. The electronic techniques include thermally stimulated currents [6], impedance spectroscopy [7], and DLTS techniques [8]. The optical techniques are based on photoluminiscence and electroluminiscence effects.

Deep level transient spectroscopy (DLTS) is highly sensitive method which offers information mainly about energy and concentration distributions of deep levels. Charge DLTS (Q-DLTS) is a modification of this technique convenient for investigation of traps in organic semiconductors. This method is based on filling of traps by voltage pulse and measuring of emitted charge in defined time instants (time window) at applied bias voltage. The Q-DLTS signal is dependent on the temperature and time window. Energy position of trap can be determined from DLTS spectra using relation:

$$\varepsilon_T \sim T^2 . \exp\left(-\frac{E_T}{kT}\right) \qquad (1)$$

where E_T is activation energy of the thermal emission of charge from the trap, T is temperature and ε_T is emission rate which is inversely proportional to time window in the peak of DLTS spectrum.

3. Preparation of Samples

Prepared OSC consists of glass substrate covered with ITO layer, active layer of the organic blend (130±10 nm), and calcium/silver stack layer (15±3 nm/150 nm). Active layers were spin-coated and annealed in nitrogen atmosphere in glove box. The annealing process comprised solvent and thermal annealing. Solvent annealing refers to slowed drying of the freshly deposited film in enclosed Petri dish (21 cm^3) at room temperature for 20 min. The samples were then annealed thermally at 110°C for 5 min. After deposition of the cathode, the samples were immediately transported to glove box with inert atmosphere and every second sample was encapsulated with cover glass fixed by epoxy glue. Each sample had eight electrodes with active area of 1.5 mm^2 formed by 1 mm wide strip of ITO electrode and perpendicularly oriented 1.5 mm wide strip of Ca/Ag electrode.

4. Characterization of Samples

OSC samples were characterized by measuring current-voltage characteristics (J-V curves) under standard illumination (AM1.5G, 1000 W/m^2), isothermal and temperature dependent Q-DLTS spectra (bias voltage -0.05 V, voltage pulse -0.5 V). The measured electrical parameters of OSC were correlated with isothemal Q-DLTS peak localized at the rate window of 16 μs for the temperature of 298 K. The activation energy of about 0.15 eV above HOMO of P3HT for this peak was determined from set of Q-DLTS temperature scans (Arrhenius plot using Eq.1). Measurements were carried out on series of five encapsulated (EC) and non-encapsulated (NEC) samples fabricated in different dates and data collected in the period of 34 days. Representative data from all of these series are presented.

5. Results and Discussion

The degradation of light J-V curves of EC and NEC samples is shown in Fig. 2. In both cases degradation of short circuit current density (J_{sc}) and series resistance (R_S) were most pronounced. These parameters of NEC degraded about 2 times more than those of EC during 34 days: J_{sc} to 2.3 $mAcm^{-2}$ and R_S to 41 $\Omega.cm^2$ for NEC samples with respect to 5.8 $mAcm^{-2}$ and 20 $\Omega.cm^2$ for EC samples. This difference is most probably a result of defect creation evoked by oxygen and/or humidity. Open-circuit voltage (V_{OC}) reduction is an accompanied effect of weaker quasi-Fermi level splitting due to higher charge recombination at the defects.

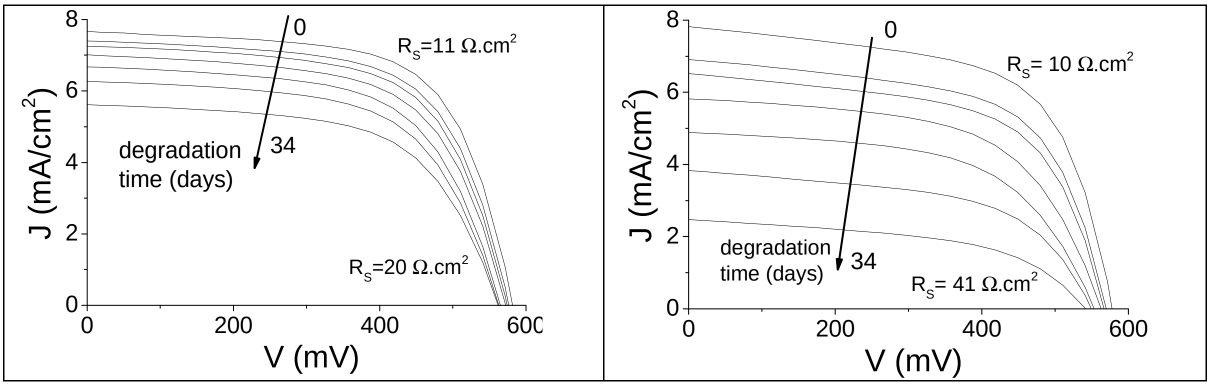

Fig. 2: *Degradation of light J-V curves of encapsulated (left) and non-encapsulated (right) OSC. Degradation time in the arrow direction: 0 days, 1 day, 2 days, 5 days, 12 days, 19 days, and 34 days.*

Isothermal Q-DLTS spectra measured at room temperature are seen in Fig. 3. The change of the spectra of EC samples was negligible, while spectra of NEC samples significantly changed during monitored period. The formation of deep states located at 0.15eV above HOMO of P3HT was efficiently prevented by encapsulation, which can be interpreted by elimination of specific source of degradation such as oxygen and/or humidity.

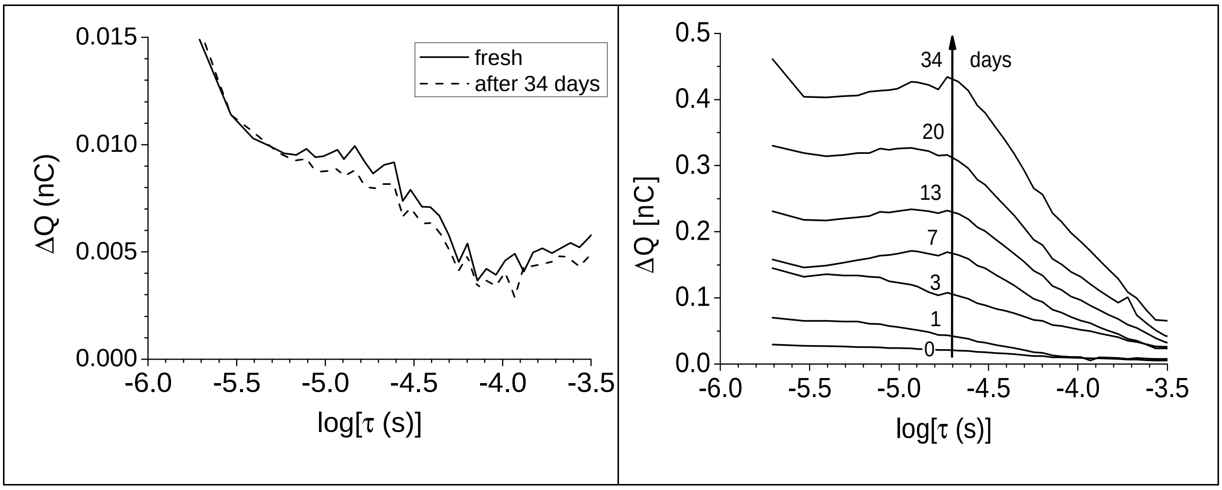

Fig. 3: *Isothermal Q-DLTS spectra of encapsulated (left) and non-encapsulated (right) OSC measured at different degradation time periods.*

The correlation of electrical parameters of OSC (J_{SC}, V_{OC}, and fill factor, FF) with Q-DLTS peak is shown in Fig. 4. The OSC parameters of NEC samples are well-correlated with the amplitude of Q-DLTS peak, which directly corresponds to defect concentration. In addition, two phases of degradation process can be recognized in this case. The slope of J_{SC} correlation changes from -0.13 to -1.24 in logarithmic scale. Up to the Q-DLTS peak amplitude of 0.15 nC, this dependence is similar to the relation $J_{SC} \propto N_T^{-0.14}$ determined also by A. Guerrero et al. [4] from capacitance-voltage measurements, where N_T represents concentration of traps. The increase of the slope for larger amplitudes (higher defect concentration) suggests the change of recombination mechanism of photoexcited charge carriers. On the other hand, there is no such correlation for EC samples. In spite of preventing ambient atmosphere the degradation of these samples takes place as well. It means that this degradation is caused by other kind of defects where oxygen and/or humidity is not involved, e.g., morphological defects induced by light illumination.

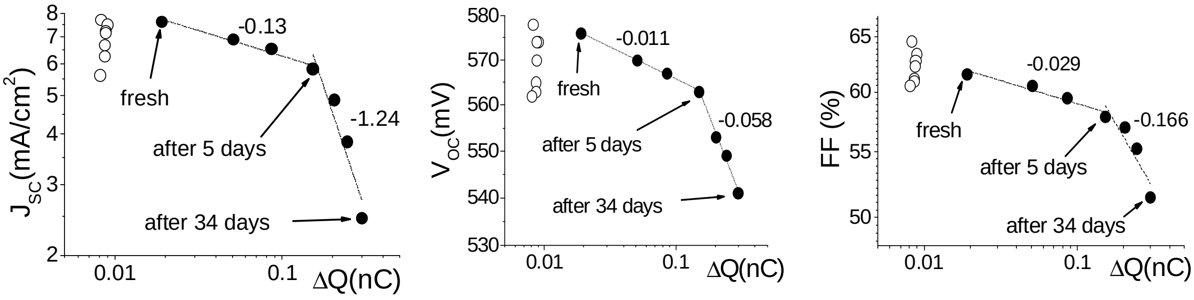

Fig. 4: *Correlation between isothermal Q-DLTS peak (at τ=16 μs for T=298 K) and electrical parameters of OSC (J_{SC}, V_{OC}, FF) in logarithmic scale. Non-encapsulated OSC denoted by full marks and encapsulated by empty marks.*

6. Conclusion

The experimental results showed and suggest a strong impact of ambient air (oxygen and/or humidity) on degradation of electrical parameters of OSC and confirmed the importance of OSC encapsulation. The degradation affected predominantly photocurrent and series resistance of OSC both in encapsulated and non-encapsulated cells. The encapsulation by cover glass fixed with epoxy glue suppressed the degradation process about 2 times. The OSC encapsulation prevented the formation of deep states located at 0.15 eV above HOMO of P3HT and thus eliminated specific source of chemical degradation caused by ambient air.

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