

Reversible oxygen doping of conjugated polymer and its dedoping studied by Mott–Schottky analysis

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ABSTRACT

One of the important factors influencing on organic solar cells efficiency is doping of the polymer by atmospheric oxygen. It is known already that the doping may be partially reversed by annealing of the device, but the phenomenon is not well-studied yet. In this paper we studied processes of doping and dedoping of conjugated polymers, using well-known poly(3 hexylthiophene) (P3HT) and derivative of novel low-bandgap polymer poly(3,4-ethylenedioxy-selenophene) (PEDOS-C₁₂), by impedance spectroscopy.

Possibility of dedoping under annealing was examined for both of the polymers. Influence of annealing atmosphere and sample preparation conditions on dedoping process were studied along with dynamics of self-doping and dedoping processes and influence of light on self-doping dynamics. Dedoping dynamics in inert atmosphere turn out to be biexponential.

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1. Introduction

One of the main application areas for conjugated polymers is organic electronics, in particular, organic photovoltaics. Organic solar cells have some attractive advantages in comparison with traditional silicon solar cells like flexibility, semitransparency, ease of manufacturing, etc. But organic solar cells are not widely used today because of their relatively low efficiency (below 10% [1]) and low stability (the efficiency of P3HT-based solar cell decreases dramatically in a few days [2–4]).

One of the crucial factors influencing on organic solar cells efficiency is doping of the polymer. It is well-known that some polymers (widely used P3HT for example) are inclined to self-doping by atmospheric oxygen in contact with air [5–8]. Doping of the active layer of organic solar cell may lead to decreased short-circuit current [9] and fill factor because of reduced charge generation region [10,11]. Thus, organic solar cell degradation with time may be also connected with gradual oxygen doping of the polymer [12].

Minimization of manufacturing cost of organic solar cells is desirable in industrial manufacturing. So most of the steps including solution stirring, film casting and device posttreatment better be performed under ambient conditions. Hence, studying and describing the processes of polymer interaction with atmospheric oxygen and finding ways to prevent or reverse polymer's oxygen doping are really important.

Recently a number of papers devoted to processes and mechanisms of interaction between P3HT and oxygen were published [12–15]. In [14,15] two possible mechanisms (reversible and irreversible) of polymer-oxygen interaction were suggested. Schematic representation of these mechanisms is shown on Fig. 1. One of the channels (irreversible channel, red color on Fig. 1) is a chemical oxidation of the polymer and it only occurs under illumination. The other channel (reversible, green color on Fig. 1) is related to formation of weak charge-transfer complex (CTC) between polymer and oxygen proposed by Abdou et al. [16], and it occurs both in dark and under illumination. Since bonding energy of the CTC is relatively weak it can dissociate under influence of high temperatures, and in [12–15] possibility of dedoping of P3HT thin film under annealing in vacuum or in inert atmosphere was proved experimentally. But this problem isn't fully studied yet. First of all, possibility of dedoping was shown qualitatively, but there are no quantitative evaluations of dedoping level yet. It remains unclear if the dedoping effect under annealing is common phenomenon or it only takes place for P3HT. Further, it was shown that polymer's solution can be doped with oxygen [16], but it is unclear if this process is reversible too. Furthermore the doping and dedoping processes dynamics and environment influence on dedoping process are still unexamined. So generalization of doping and dedoping processes with quantitative evaluations should be performed.

Direct measurements of doping concentration in a polymer film may be convenient to study doping and dedoping processes. One of the possibilities to measure doping concentration is based on Schottky barrier formation when a p-doped semiconductor contacts with metal with lower workfunction. Inverse square of the

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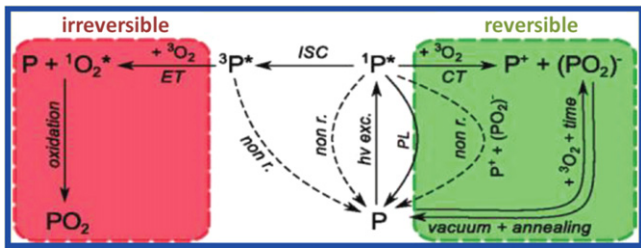


Fig. 1. Schematic representation of reversible and irreversible interactions between polymer and oxygen [14].

barrier's capacitance is a linear function of bias voltage (it also called Mott–Schottky behavior) [17,18]:

$$\frac{1}{C^2} = \frac{2(V_s - V)}{S^2 q N_a \epsilon \epsilon_0} \quad (1)$$

Here C is the barrier capacitance, V_s is Schottky barrier height, V is bias voltage, S is contacts area, q is elementary charge, N_a is doping concentration, ϵ is relative permittivity of the active layer and ϵ_0 is vacuum permittivity. Schottky barrier's height (also called as flat-band voltage) is determined by difference between Fermi levels of the polymer and the electrode.

The width of the depletion layer can be calculated as [17]:

$$W = \sqrt{\frac{2\epsilon\epsilon_0(V_s - V)}{qN_a}} \quad (2)$$

Thus, one of the simple ways to estimate doping concentration of polymer's film is a device construction, where Schottky barrier capacitance can be measured [9].

2. Sample preparation and experimental

To study self-doping and dedoping processes of conjugated polymers samples based on widely used polymer P3HT (Fig. 2a) and novel promising low band-gap polymer PEDOS-C₁₂ [19] (Fig. 2b) were made.

Dichlorobenzene solution of polymers was prepared at concentrations of 30 g/l for P3HT and 10 g/l for PEDOS-C₁₂. Solutions were stirred on a magnetic stirrer for at least 12 h at 75 °C. Diodes were fabricated on ITO-covered substrates. Thin layer of PEDOT:PSS was spin-casted at 3000 rpm for 2 min on the substrate from aqueous solution first. Then substrates was annealed at 150 °C for 15 min in air to remove any remaining water of the PEDOT:PSS film. The polymer film was then spin-casted from solution at 1000 rpm for 2 min. The whole sample preparation process was performed in air and self-doping of the polymer solution was occurring. One control sample based on P3HT was prepared in an argon glovebox.

After polymer film casting the second electrode was thermally evaporated through a mask. The evaporation was done at 7×10^{-6} mbar pressure. Aluminum was chosen as an electrode for P3HT-based samples as it is well-known that Schottky barrier forms on the P3HT-Al interface [13,20]. For PEDOS-C₁₂-based sample the second electrode was made of CaAl since its Fermi level is lower than the polymer's HOMO (Fig. 2b). Schematic picture of the sample is shown on Fig. 3. Thicknesses of the films were estimated using conventional AFM profiling as 220 ± 20 nm for P3HT-based diodes and 30 ± 20 nm for PEDOS-C₁₂-based one.

The samples were measured using Elns Z-1000P impedance analyzer. To estimate realistic concentration of acceptor impurities a proper frequency of AC voltage should be chosen. This frequency may be chosen from capacitance–frequency analysis. Fig. 4 shows frequency dependent capacitance for a P3HT-based diode. As clear from the figure, capacitance doesn't saturate on presented frequency scale. However, it increases rapidly up to 10 kHz and grows

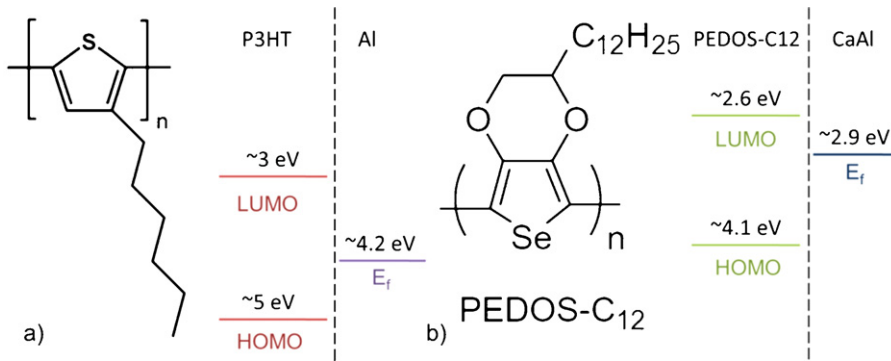


Fig. 2. Structural formulas and energy level diagrams for P3HT (a) and PEDOS-C₁₂ (b).

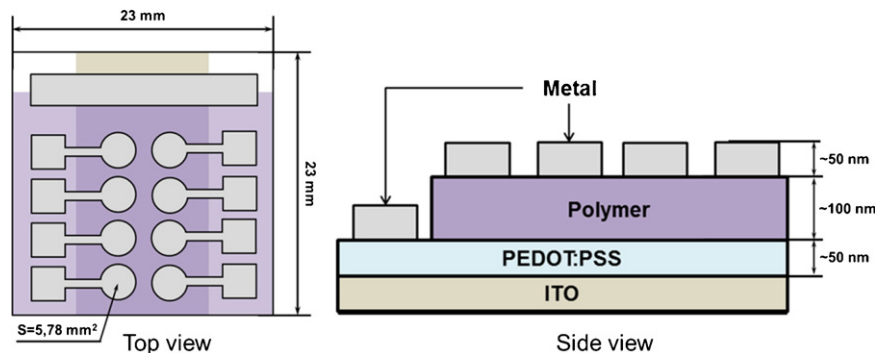


Fig. 3. Schematic image of the sample.

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