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The Effect of Degradation on the Active Layer in APFO3:PCBM Solar Cells

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Abstract

We have measured the effect of degradation on the I - V characteristics in APFO3:PCBM solar cells. The solar cell devices were subject to ambient air under simulated solar illumination. We found that the degradation resulted in a lowering of the fill factor and short circuit current while the open circuit voltage remained unchanged. In order to gain insight into what has caused the degraded I - V characteristics we have studied the active layer film using various techniques. We found clear spectral changes both in absorption and in photoinduced absorption spectroscopy correlated with increased carrier lifetimes and lowered mobility when comparing the degraded film with a pristine one. The results show a significant degradation of the active layer causing a lower fill-factor and short circuit current.

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1. Introduction

The need for cheap and environmentally friendly energy production has prompted extensive research in polymer solar cell materials. As the efficiencies increase and the limit for commercially viable materials approaches, it becomes increasingly more important to study the degradation mechanisms governing these

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new materials. The alternating polyfluorene co-polymer APFO3 [1] has gathered much attention over the past years. To the best of our knowledge, studies on the degradation mechanisms of this polymer are scarce. The thermo stability has been studied [2] but no reports were found on oxidative degradation. In this paper we have studied the effect of degradation on the electrical and optical properties of an APFO3:PCBM solar cell device aged under oxygen and simulated sunlight for three days. We have used absorption and photoinduced absorption spectroscopy to probe the degradation of the active layer and correlated the results with the I - V characteristics. The results are compared with those of a pristine device.

Nomenclature

APFO3	poly[2,7-(9-di-octyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]
PCBM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
ITO	indium tin oxide
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PA	photoinduced absorption
Photo-CELIV	photo charge extraction by a linearly increasing voltage

2. Experimental

Solar cell devices were fabricated as following. The ITO substrates (from Optrex Europe GmbH) were cleaned in ultrasonic bath with acetone for 10 minutes, with isopropanol for 10 minutes and with distilled water for 5 minutes. This was followed by a 10 minute ozone treatment followed by spin coating of PEDOT:PSS (AI 4083 from H. C. Starck) at 3000 rpm for 60 seconds. The active layer film was spin coated from a solution of APFO3:PCBM (1:4 ratio) at 370 rpm for 60 seconds (PCBM from Solenne). Finally a 0,4 nm layer of lithium fluoride (Sigma Aldrich) and 101 nm of aluminum (Testbourne) was thermally evaporated on top. One sample was aged under oxygen flow and simulated sunlight for three days, after which an attempt was made to recover the cell by vacuum annealing (unsuccessful). The sample was then sealed by a piece of glass glued over the devices with a UV-curing adhesive (DELO - Katiobond LP655). The reference sample was kept in the glove box and then sealed.

Photo induced absorption measurements were performed according to standard procedure [3]. The measurements were performed in room temperature with a laser intensity of 200 mW/cm² and the chopper frequency was set to 133 Hz. We obtained the lifetimes of the absorbing species from the phase using the method described in [4]. The measurements were carried out on the actual solar cell devices but next to the metal top electrode. We note that the metal electrode will somewhat protect the film from degradation, thus the obtained results from the PA may not be directly comparable to the I - V but qualitative conclusions can be drawn. Photo-CELIV measurements were carried out as reported elsewhere [5].

3. Results and Discussion

The I - V characteristics (measured at 300K) of a degraded and undegraded device are shown in Fig. 1. (a). The degraded device show a reduction in the short circuit current from 2,6 mA/cm² to 2 mA/cm² and a reduction in the fill factor from 41 % to 26 %. The open circuit voltage is fairly unaffected at around

1V. The power conversion efficiency correspondingly decreases from 1,1% to 0,5% (the low efficiency of the undegraded devices is due to non optimized thickness). The corresponding absorption spectrum is shown in Fig. 1. (b). A clear bleaching can be seen in the 500-650 nm range, that could partially explain the reduction of the short circuit current.

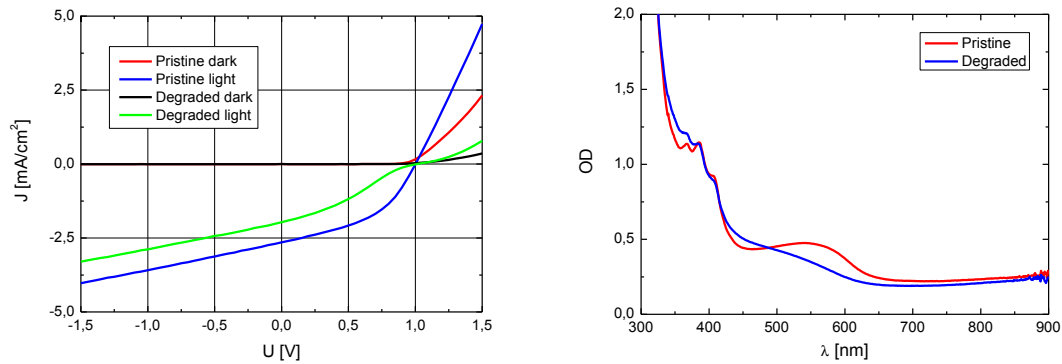


Fig. 1. (a) The I - V of a pristine and a degraded APFO3:PCBM solar cell; (b) the absorption spectrum of a pristine and a degraded APFO3:PCBM film

A lower fill factor can be attributed to several causes, mainly unbalanced charge transport [6] and contact related issues [7, 8]. When performing measurements on working solar cell devices it is difficult to separate effects of bulk related and contact/interface related factors. Therefore, photoinduced absorption was used as a tool to study the degradation of the active layer without impact of the contacts.

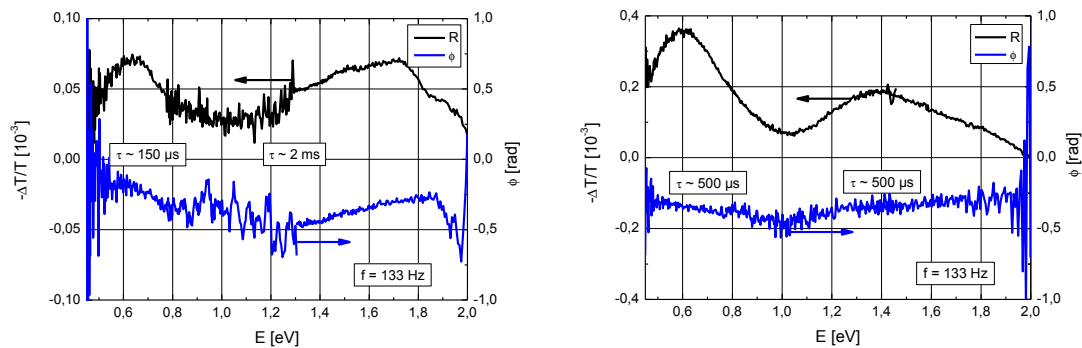


Fig. 2. The radius (R) and phase (ϕ) of a (a) pristine APFO3:PCBM film and (b) degraded APFO3:PCBM film.

The photoinduced absorption spectra for the pristine and degraded films are shown in Fig. 2. Clear spectral changes as a result of degradation can be seen. In the pristine film there seems to be one shorter living and one longer living species. The shorter living species (around 0,6 eV) has previously been attributed to charged photoexcitations or polarons [9]. The polaron concentrations can be estimated in the thin film limit as $n=PA/(d\sigma)$ where d is the thickness and $\sigma = 10^{16} \text{cm}^2$ is the absorption cross section. The

concentrations at 0,6 eV are roughly $5,4 \times 10^{16} \text{ cm}^{-3}$ for the pristine and $2,7 \times 10^{17} \text{ cm}^{-3}$ for the degraded case. The origin of the longer lived species is not clear but could possibly be related to Coulombically bound pairs. In the degraded film the phase is fairly constant indicating the presence of only one lifetime that is longer than the observed polaron lifetime in the pristine film. This implies that the recombination of charges is slower in the degraded film.

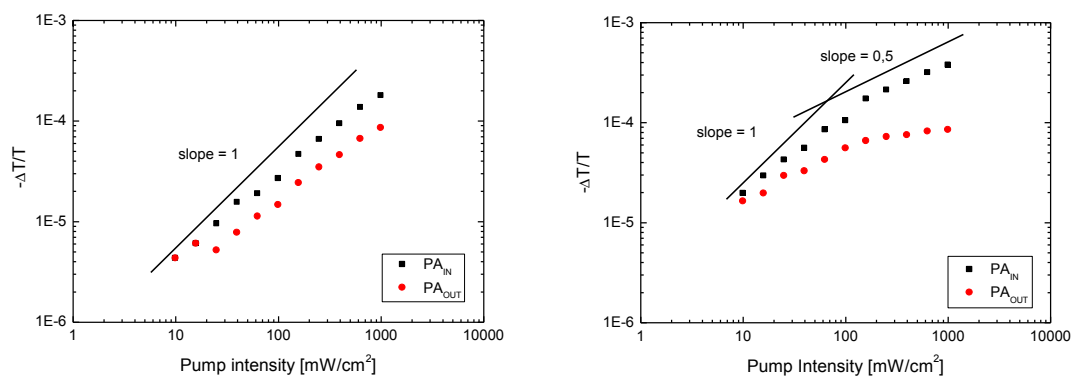


Fig. 3. (a) The intensity dependent PA (measured at 1,8 eV probe energy) of a (a) pristine APFO3:PCBM film; (b) degraded APFO3:PCBM film. The lines are only guides for the eye.

The intensity dependent PA is shown in Fig. 3 (a) and (b). At moderate excitation intensities the intensity dependence is seen to be roughly the same for both the pristine and degraded. In the pristine film the intensity dependence is roughly the same for all excitation intensities used, possibly with a slight deviation at higher intensities. In the degraded film the in-phase slope (in log-log scale) is close to 0,5 at higher intensities indicating bimolecular recombination.

Given that the polaron lifetime is longer and the polaron concentration is higher in the degraded film, the overall recombination has to be slower in the degraded film. Since the recombination is seen to be bimolecular in the degraded film and assuming Langevin type bimolecular recombination, the recombination rate $R = \beta_L n^2$, where β_L is the Langevin bimolecular recombination rate and n is charge carrier concentration, is directly correlated with the sum of the mobilities according to $\beta_L = e(\mu_n + \mu_p)\epsilon\epsilon_0$, where e is the electron charge, μ_n and μ_p is the electron and hole mobilities and $\epsilon\epsilon_0$ is the dielectric permittivity. Hence the mobilities are lower in the degraded film. This is supported by photo-CELIV studies that show a reduction of the average mobility by a factor of two (not shown). The lower average mobility could lead to imbalanced charge transport that would lead to a reduced fill factor. However, the effect of degraded contacts on the extraction rates cannot be ruled out. Lowered extraction rates most probably need to be taken into account in order to fully explain the observed I - V behavior.

4. Conclusion

The effect of oxidative degradation on the active layer in APFO3:PCBM solar cells has been studied. The results show bleaching of the absorption spectrum leading to lower short circuit current. Photoinduced absorption spectroscopy show longer polaron lifetimes and higher concentrations indicating slower recombination. The recombination is seen to be bimolecular in the degraded film, which means that the slower recombination can be correlated with a lower mobility in agreement with photo-CELIV data. The lowered mobility may cause a lower fill factor due to unbalanced charge transport. However, the effect of degraded contacts probably plays an important roll on the fill factor, this requires further studies.

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