

# Spectral sensitivity dependence on the details of preparation for P3HT:PCBM bulk heterojunction solar cells

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**Abstract.** The performance of bulk heterojunction P3HT:PCBM polymer solar cells is studied using current-voltage and spectral sensitivity measurements. Front transparent contacts of either ITO or a sputtered multilayer  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  transparent conductive electrode are applied. Thin PEDOT:PSS and P3HT:PCBM polymer layers are deposited on these substrates by spin coating. The degradation of the solar cells is studied by subjecting them to UV irradiation. The obtained spectral sensitivity curves are analyzed in comparison with the optical absorption spectra of the transparent electrodes and active layers employed. It is observed that there is a pronounced dependence of the spectral sensitivity curves on the thermal treatment and UV irradiation applied to the solar cells. The performance of the multilayer  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  transparent conductive electrodes is also studied in comparison with that of the ITO ones.

## 1. Introduction

The design and study of solar cells employing polymer materials is a field of intense activity in recent years. This is due to the results up to now, which promise easy to produce, low cost, non-toxic photovoltaic devices. One of the properties very important for long serving structures like solar cells is their stability. This challenge is especially significant for polymer solar cells. There are many ways in which they can degrade connected with the different layers comprising them [1]. In this contribution we present data on the degradation of encapsulated P3HT:PCBM bulk heterojunction solar cells under concentrated UV radiation from a solar simulator. This type of treatment is studied less often. The concentration is needed in order to speed up the degradation as the exposure of the studied cells to real conditions of solar irradiation for more than 30 hours failed to produce a noticeable deterioration of their performance. Besides, the filtered UV radiation does not increase noticeably the temperature of the cells and thus excludes heating effects. The aim of this contribution is to study the effects of degradation using the solar cell spectral sensitivity spectra.

As explained in [2] the multilayer transparent conductive films  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  are studied because they avoid the use of expensive indium, can be thinner and more transparent for the same conductivity and can be deposited at lower temperature. According to the authors of [3] a thin amorphous  $\text{TiO}_x$  layer can play the role of electron collection and hole blocking layer and contribute to the air stability of the solar cells. In this report  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  films are experimented as front contacts in P3HT:PCBM bulk heterojunction polymer solar cells and as a potential intermediate layers in tandem polymer solar cells. Immediately on top of the transparent conductive film PEDOT:PSS hole conducting layer is deposited. If the combination works the electrons and holes will recombine at the interface between the two films.



## 2. Experimental

The samples studied in this work are deposited as described previously [2, 4]. The solar cells consist of the following layers: front transparent contact, PEDOT:PSS, bulk heterojunction P3HT:PCBM, back contact of Ag deposited by sputtering without annealing in the vacuum chamber.

The front transparent contact is either ITO used as purchased or  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  multilayer contact deposited in our laboratory. The method used for forming the contacts is RF magnetron sputtering. The equipment allows the deposition of layers using three targets at the same time. The multilayer contacts are formed on glass through a shadow mask by depositing of  $\text{TiO}_2$ , Ag,  $\text{TiO}_2$  consecutively. The  $\text{TiO}_2$  layers are 25 nm thick as measured by ellipsometer. The Ag layer has granular structure which is discussed in more detail below. The pattern of the front transparent contacts on the glass is similar to the one of the purchased ITO covered glass which is used as standard substrate and front contact. However, the active area of the cells in the case of our shadow mask is  $3.75 \text{ mm}^2$  instead of  $4.5 \text{ mm}^2$ .

The active area of the samples is encapsulated and electrical connection legs are mounted as described in [3]. Post-production annealing of some of the samples is performed by heating the already encapsulated cells on a hot plate at  $150^\circ\text{C}$  for 10 min.

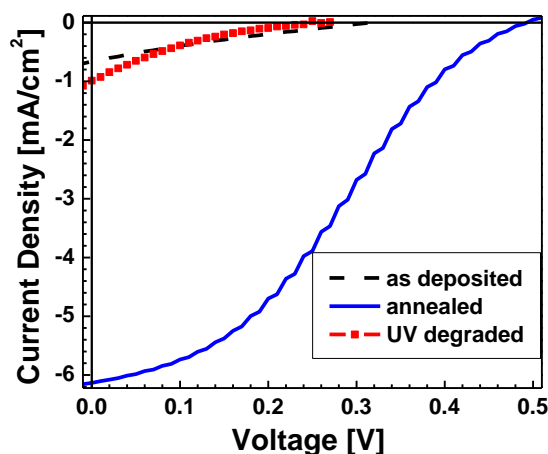
Current-voltage (J-V) measurements upon illumination by a halogen lamp are carried out by a computer controlled home-made potentiostat. The spectral response measurements are performed on a computer controlled set-up including a halogen lamp, a DK-240 monochromator, a focusing lens and a chopper as light source, and a home-made current amplifier and Brookdeal 401 lock-in amplifier for the photocurrent measurement. The illumination spectrum is corrected using a calibrated Si diode from Hamamatsu. The optical transmission of individual layers is measured by a Shimadzu UV-3600 double beam spectrometer.

UV degradation of the cells is performed with a solar simulator modified with a UV-pass-filter and a lens to concentrate the illumination intensity on the sample 70 times. Samples are irradiated for intervals from 2 to 18 hours and their I-V curves are measured periodically.

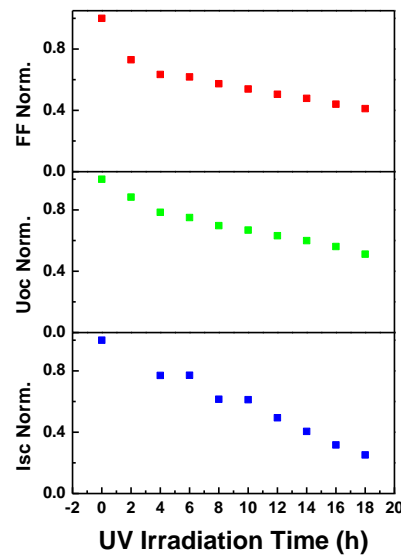
## 3. Results and discussion

### 3.1. Effect of degradation and annealing

Figure 1 shows typical current-voltage characteristics of the solar cells with ITO front contact as deposited, after post-deposition annealing and after 18 hours of UV degradation of an annealed sample. It is obvious that post-deposition annealing improves significantly the parameters of the polymer solar cells as already reported in [4]. Figure 2 demonstrates the evolution of the main parameters of the solar cells during the UV irradiation. It is the short circuit current ( $I_{sc}$ ) that gets the greatest reduction of its values followed by an almost 50% decrease of the open circuit voltage ( $U_{oc}$ ).



**Figure 1.** J-V characteristics of polymer solar cells with ITO front contact - as deposited, after annealing and after 18 hours UV degradation of the annealed cell.

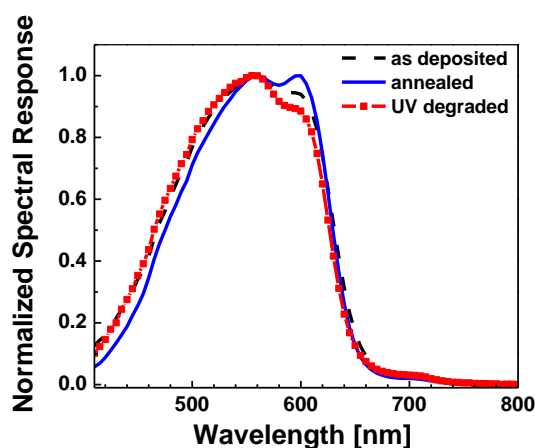


**Figure 2.** Evolution of J-V parameters with the time of UV irradiation.

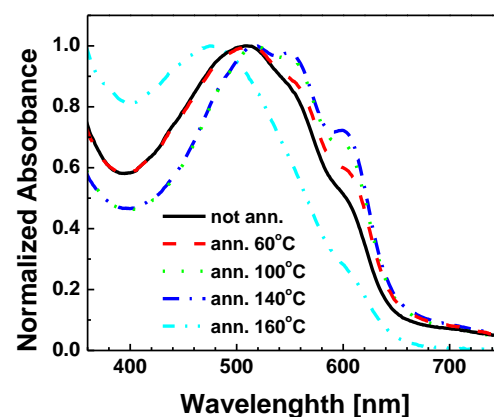
Consequently, the fill factor (FF) falls by more than 50% as well. Concentrated UV irradiation affects the cells strongly and as seen in figure 1, the solar cell parameters return to values similar to the ones before post-production annealing.

In an attempt to learn more about the details of the degradation process the spectral response curves of as deposited, annealed and UV degraded (18 h) solar cells are measured. Typical spectra are shown in figure 3. Figure 4 shows the absorption spectra of the bulk heterojunction P3HT:PCBM layer as deposited without any treatment and annealed for 30 min at four different temperatures as indicated in the figure. More details about the interpretation of the dependence of the absorption spectra on the annealing temperature are given in [5].

The optical absorption of the bulk heterojunction P3HT:PCBM layer in the visible part of the spectrum is due to the polymer P3HT [6]. It demonstrates three main absorption peaks: 517 nm attributed to  $\pi$ - $\pi$  absorption and the 552 and 602 nm ones - due to vibronic absorption in P3HT in the



**Figure 3.** Normalized spectral sensitivity curves of polymer solar cells with ITO front contact - as deposited, after annealing and after 18 hours UV degradation of an annealed cell.



**Figure 4.** Normalized absorption of P3HT:PCBM layers annealed at different temperatures in Ar as indicated in the figure.

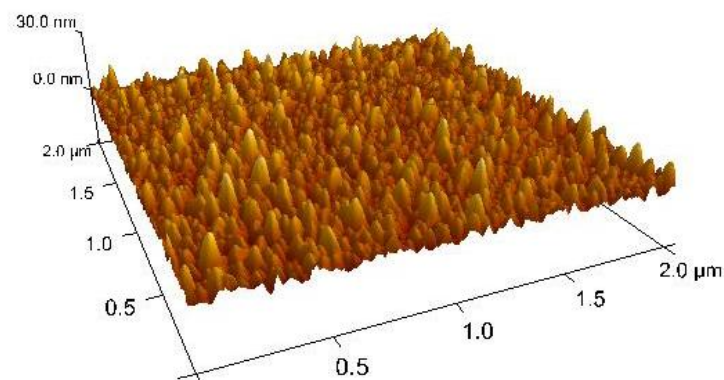
solid state. The 602 nm band is connected to interchain interaction and has a higher intensity for higher degree of interchain order. These features are clearly visible in the absorption spectra in figure 4 and are best expressed in the films annealed at 140°C.

The spectral response curves in figure 3 exhibit clearly visible the bands at 552 and 602 nm. The absorption peak at 517 nm (cf. figure 4), however, cannot be distinguished as a peak in the spectral response. Perhaps, as in inorganic solar cells the separation and extraction of carriers is hindered for higher energy photons. The difference between the spectral response of the three kinds of samples studied is in the relative intensity of the 602 nm vibronic band. Post-deposition annealing sharpens that band and presumably increases the interchain order of the polymer. This can be correlated with the improvement of the solar cell parameters which has been observed by a number of authors [7, 8]. Of course this improvement may have other reasons connected with the contacts as well [9]. The fact that this band weakens after the UV degradation process could be an indication that the fall in the values of the main solar cell parameters can be connected in part to chemical processes occurring in the active layer under the influence of the high energy UV radiation and deteriorating the interchain order.

### 3.2. $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ front transparent contacts

The experiment of applying the multilayer  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  transparent film as front contact aims to find out whether a functioning solar cell could be formed using it and to compare that cell with the one with ITO front contact. A positive result would allow the preparation of a tandem organic solar cell in which the combination of the  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  multilayer with PEDOT:PSS hole transporting layer could be used as an intermediate layer between the two subcells. If the structure works the electrons and holes will recombine at the interface between these two layers.

As mentioned in the Experimental section the multilayer  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  transparent film consists of two 25 nm  $\text{TiO}_2$  dielectric layers and a granular Ag layer sandwiched between them. The size, shape and density of the metal granules were investigated with AFM on specially prepared samples. Silver was deposited on a polished silicon wafer under the same conditions that were used in the multilayer. In figure 5 an AFM image of this layer is presented.



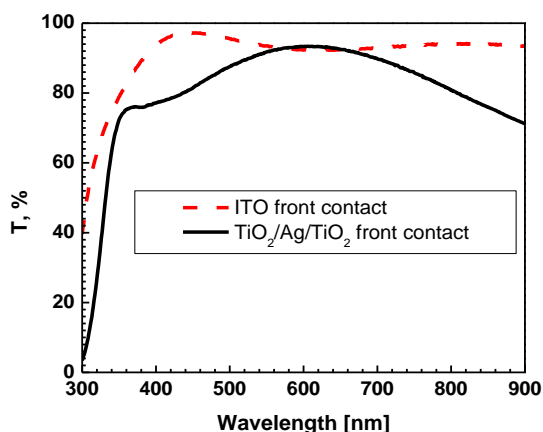
**Figure 5.** 3-D AFM image of metallic granules.

Analysis of the AFM data have show that the metal Ag layer has granular structure with grain height of 10-20 nm and width of about 80 nm.

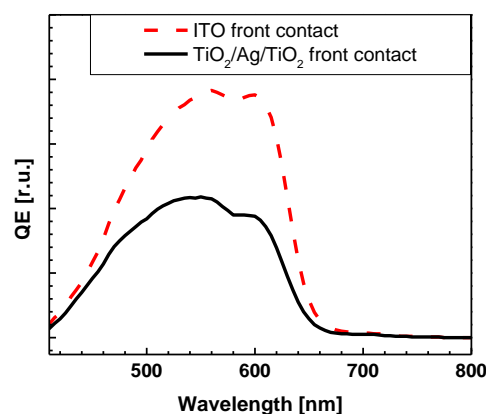
Figure 6 compares the transparency of the ITO front contact and the multilayer sputtered  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  contact experimented in this work. It can be seen that the multilayer contact has comparable transparency to the ITO one. The reason for the fall in transparency in the 400-500 nm range has not been clarified but it is outside the absorption range of the active layer of the solar cell and would not affect its performance significantly. The conductivities of the two transparent contacts

are very similar as well, 20 and 17  $\Omega/\square$ , respectively. The  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  layer demonstrates metal-like electron conductivity and its optical transmission falls above 700 nm due to the reflection connected with free carriers.

Figure 7 shows the quantum efficiency curve measured on two typical solar cells differing only in the type of front contact. The curves are given in relative units but their values can be compared. It can be seen that the shape of the quantum efficiency curves are very similar but the values of QE are smaller for the multilayer  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  transparent front contact. Possible reasons are the high contact resistance or the unfavourable for the hole transport mutual valence band (HOMO) energy positions of PEDOT:PSS and  $\text{TiO}_2$  [10]. However, experiments indicate that the  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  multilayers behave more like degenerate semiconductor or metal than as a wide bandgap semiconductor.



**Figure 6.** Optical transmission of the two different front transparent contacts used.



**Figure 7.** Relative quantum efficiency of the solar cells with different transparent front contacts, as shown in the figure.

Still our results show that there is a functioning solar cell with the new  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  front transparent contact. Its quantum efficiency is lower than that of the ITO containing one and further experiments are needed to optimize this solar cell architecture.

#### 4. Conclusion

The effect of concentrated UV radiation on bulk heterojunction P3HT:PCBM polymers solar cells has been studied. This kind of irradiation is interesting because it speeds up the solar cell degradation and separates the effect of light from that of heat. The latter often recovers some of the degradation. Concentrated UV irradiation strongly affects both the short circuit current and the open circuit voltage. The study using the spectral sensitivity curves of the solar cells shows that the degradation possibly results from the loss of polymer interchain order in the active layer of the cells.

The sputtered  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$  front transparent contact exhibits good transparency and lateral conductivity. Functional solar cells are realized using that contact instead of ITO. The shape of the quantum efficiency curves of the polymer solar cells is not affected by its use in the place of the ITO front electrode. However the current density is reduced. This is most probably due to high contact resistance or an energy barrier at the interface.

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## References

- [1] Grossirod N, Kroon J M, Andriessen R and Blom P W M 2012 *Org. Electron.* **13** 432
- [2] Sendova-Vassileva M, Dikov Ch, Popkirov G, Lazarova E, Gancheva V, Grancharov G, Tsocheva D, Mokreva P and Vitanov P 2013 *J. Phys.: Conf. Series* **514** 012018
- [3] Kuwabara T, Nakayama T, Uozumi K, Yamaguchi T and Takahashi K 2008 *Sol. Energ. Mat. Sol. C.* **92** 1476
- [4] Sendova-Vassileva M, Popkirov G, Vitanov P, Dikov Ch, Gancheva V, Tsocheva D and Mokreva P 2012 *J. Phys.: Conf. Series* **398** 012049
- [5] Sendova-Vassileva M, Bakardjieva V, Ivanova T, Lazarova E, Gancheva V, Tsocheva D, Mokreva P, Terlemezyan L and Vitanov P 2013 *CR Acad Bulg Sci* **10** 1393
- [6] Li P, Chen L J, Niu G X, Zhang T, Xiang J, Cai L, Hu Y, Zhang Y J, Wan K M and Song Q L 2014 *Sol. Energ. Mat. Sol. C.* **125** 96
- [7] Dennler G, Scharber M C and Brabec C J 2009 *Adv. Mater.* **21** 1323
- [8] Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K and Yang Y 2005 *Nat. Mater.* **4** 864
- [9] Ahlswede E, Hanisch J. and Powalla M 2007 *Appl. Phys. Lett.* **90** 063513
- [10] Kim J Y, Lee K, Coates N E, Moses D, Nguyen T-Q, Dante M and Heeger A J 2007 *Science* **317** 222