Submitted to ESF - ORGANISOLAR Activity
"New Generation of Organic based Photovoltaic Devices"
February 17, 2010
Lecce, Italy

Characterization of Bulk Heterojunction Solar Cells by Spectroscopic Ellipsometry

Final Report

Sandro Lattante (PhD)[a]

Dipartimento di Ingegneria dell'Innovazione

Universitá del Salento

via per Monteroni 73100 Lecce - Italy

[a] e-mail: sandro.lattante@unisalento.it
Phone: +39 0832 297793

This is a final report on the research activity performed at LIOS, hosted by Prof. Niyazi Serdar Sariciftci, in the period January 11, 2010 - January 25, 2010.

The experimental work has consisted in the realization of a series of organic bulk heterojunction solar cells based on a P3HT:PCBM active layer fully in a inert atmosphere (glove box system) and of another series fully in air, with different realization parameters. All the realized samples have been electrically characterized (current-voltage characteristic in dark and under 1 sun). Selected devices have been encapsulated for future characterization.

The goals were:

- to train and supervisioning a young student during his Master Thesis activity;
- to find the best electrode configuration for subsequent spectroscopic ellipsometric characterization of the full device under operation;
- to test a simple and fast encapsulation process suitable for spectroscopic ellipsometric characterization of the device.

My stay in LIOS has been very fruitful, in particular I have had the opportunity to train one of my student in organic solar cell realization and characterization and to allow him to experience a work activity in a international environment like LIOS. I would like to thank ESF for the accepted grant.

The detailed report about the experimental results will be presented here; the discussion part will be mainly improved during writing future manuscript for possible publication.

Best Regards,

Sandro Lattante

February 17, 2010

I. INTRODUCTION

Organic photovoltaics is seen, by many authors, as the main research field towards dramatic cost reduction in converting solar energy into electricity: this is due to several reasons, among which the most attractive is the possibility of fast and cheap realization processes for large area cells starting from organic materials dissolved in common organic solvents - spin coating, screen printing, roll-to-roll, ink-jet printing - if compared to the standard inorganic counterparts production steps; moreover organic solar cell modules can be flexible allowing for an easy incorporation into textiles and/or portable energy generator. Dye-sensitized solar cell (DSSC or Graetzel cell) have a power conversion efficiency up to about 11% [1] and a bulk heterojunction solar cell with power conversion efficiency of 6% has been reported [2]. Besides the improvement in power conversion efficiency and in the knowledge of the physic principles behind the working processes of this kind of devices, there are still some aspects that have not been fully studied: one important parameter to be studied is the optical behaviour of the real device under real operation condition and the effect on these parameters of ageing of the device realized in standard atmosphere condition (not protected in a inert atmosphere environment). It is well known that oxygen and water exposure of the device results in a fast degradation, but this was studied basically monitoring the electrical properties (efficiency, fill factor, short circuit current, series resistance [3, 4]). It could be interesting to monitor what happens to the complex index of refraction of the layers (PEDOT:PSS and active layer) - oxygen and water exposure should modify also the optical properties of these layers - in order to have the right parameters to be used in modelling the field distribution inside the layers for optical optimization of the device.

In the following sections the preliminary results from this activity will be summarized.

II. EXPERIMENT

Several P3HT:PCBM bulk heterojunction solar cells have been realized following the structure glass/indium tin oxide/PEDOT:PSS/P3HT:PCBM/top electrode, both fully in a inert atmosphere (in the following these samples will be named GB samples) and room condition (A samples). The glove box system that allows for the realization of the GB samples consists of two interconnected glove boxes from MBraun: a spin coater is mounted in one glove box and a metal evaporator system from Leybold is mounted in the second one.

After etching of a thin layer of indium tin oxide (ITO), in order to pattern the bottom electrode surface, a thin layer of PEDOT:PSS from Bayer has been spin coated on top of the ITO. Subsequently a thin layer of P3HT:PCBM blend has been spin coated from 1:0.8 weight ratio chlorobenzene solution filtered by a 0.45 $\mu\mathrm{m}$ PTFE siringe filter. P3HT has been purchased from Rieke Metals and PCBM from Solenne bv. The P3HT:PCBM layer deposition has been performed in glove box for the GB samples: starting from this step the GB samples will never be exposed to standard atmosphere.

The top electrodes have been deposited by thermal evaporation under high vacuum. We have choosen for different samples the following electrodes: LiF/Al, Al, ultrathin Al (less than 10 nm), Ag, AlAg. The standard LiF/Al and Al devices have been realized as references samples, while the ultrathin Al, Ag (40 nm) and Al (7 nm)/Ag (33 nm) electrodes have been realized for samples that should be characterized by spectroscopic ellipsometry. The total number of realized samples is as follows:

- GB LiF/Al: 9 samples;
- A LiF/Al: 18 samples;
- GB Al: 5 samples;
- A Al: 5 samples;
- GB Al (10 nm): 2 samples;
- A Al/Ag: 2 samples;
- GB Ag: 4 samples;

Each sample consists of 3 independent cells with active areas comprised between 6 and 8 mm^2.

Current-Voltage characteristics have been measured by a computer controlled Keithley 236: measurements have been performed inside the glove box system for GB samples, and at room condition for A samples.

Selected samples have been encapsulated by thermal evaporation of 300 nm LiF layer onto the top electrodes followed by spin coating of a two components epoxy resin from CORE, resulting in a thin epoxy resin covering layer; the whole sample surface has been covered except for two thin stripes allowing the electrical connection of the devices to the external load. A similar process has been previously tested for Organic Light Emitting Diode [5] and here we are testing the quality of such thin encapsulation for solar cell devices.

III. RESULTS AND BRIEF DISCUSSION

In order to characterize the solar cells under operation by spectroscopic ellipsometry it is important that all the layers on top of the active layer (metal electrode plus encapsulant layers) are thin enough to allow for a sufficient transparency in the visible range: in fact, due to the nature of the spectroscopic ellipsometry measurement, the probe light should be incident from the top side of the cell, being the glass substrate on the bottom side too thick for allowing the optical characterization of the various layers constituting the device. The samples for spectroscopic ellipsometry belong all to the A series but have been ancapsulated immediately after the top electrode deposition in order to prevent oxygen and water exposure.

First of all the top metal electrode should be thin enough to let the probe light passing through and reaching the active layer: we have first tried to realize solar cells with a thin Al top electrode (10 nm), but this thickness is already higer than the penetration depth of visible radiation in aluminum and, on the other side, too thin to allow the cell working properly. These samples in fact were not operating and have been discarded. We have tried then with a 40 nm Ag top electrode: silver is quite transparent to the visible light up to 60 nm. Unfortunately, probably due to the diffusion of silver into the active material, also these cells were badly operating - some of them clearly shortcutted. Finally we have choosen the configuration of 7 nm of Al (transparent enough) followed by 33 nm of Ag: Al thin layer should avoid Ag diffusion into the active material. I-V characteristic of three of these cells are reported in Fig. 1. V_{oc} and then also the fill factor (FF) for these devices are very low if compared with the corresponding values for the GB series reference cells (LiF/Al - see Fig. 2). We speculate that this effect could be related to the junction between two different metals like Al and Ag in the top electrode, despite the very similar work functions. In order to check this possibility we are currently performing a numerical fit of the I-V characteristic to the following equation:

$$i = i_s(e^{\frac{\beta}{n}(V - V_{bi} - iR_s)} - 1) - i_{ph} + \frac{V - V_{bi} - iR_s}{R_p} \qquad (1)$$

being i_s and i_{ph} the diode saturation current and the photocurrent respectively, R_s and R_p the serial and parallel resistance respectively, n the ideality factor, V_{bi} the built in potential and finally

$\beta = q/kT$ the usual inverse thermal voltage. The numerical fit allow us to extract the various parameters, in particular the serial resistance R_s (that is usually studied by simpler and not so accurate graphical methods - see [4] for example) and the built in potential V_{bi}, allowing us to compare the resulting values between samples, taking as reference the extracted parameters from the LiF/Al top electrode samples (both GB series and A series). An example of this fit process is reported in Fig. 3 for a standard LiF/Al top electrode cell (FF = 51%). The preliminary results of this analysis (not reported) should be carefully checked on the whole series of samples and correlated with a possible explanation of the reported behaviour; this activity is still in progress.

All the working devices (both GB and A series) have been continously electrically characterized as a function of time (simple ageing characterization) at steps of about 24 h for 10 days: the above depicted fitting procedure is currently being applied to the whole data sets obtained. From these experiments it has been possible to select the devices to be tested also in the University of Salento under real ambient condition: this step is in progress in Lecce - Italy.

Secondly, the effect on the performance of the cells of the encapsulation process is being currently tested, both with on going I-V characterization in air and with the previously described fit procedure. From preliminary results we can argue that this encapsulation process did not negatively influence the performance of the devices. More time is necessary to furnish conclusive results.

IV. CONCLUSIONS AND PLANNED EXPERIMENTS/PUBLICATIONS

Several sets of bulk heterojunction solar cells have been realized and characterized with different parameterization. These cells have been tested and compared taking as references the standard ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al realized devices. The acquired data are currently being analised by means of numerical fitting process to the real diode equation including photocurrent, series and parallel resistance. Apart the laboratory activity, a young Master Thesis student has been practically and theoretically trained and supervised in the field of organic solar cell research activity.

The optical characterization of selected devices by spectroscopic ellipsometry is currently being developed and we are planning to publish the results of this activity in a peer rewieved paper in the next few months.

[1] Feifei Gao, Yuan Wang, Jing Zhang, Dong Shi, Mingkui Wang, Robin Humphry-Baker, Peng Wang, Shaik M. Zakeeruddin and Michael Graetzel, Chem. Commun., 2635 (2008)

[2] Sung Heum Park, Anshuman Roy1, Serge Beaupr, Shinuk Cho, Nelson Coates, Ji Sun Moon, Daniel Moses, Mario Leclerc, Kwanghee Lee, Alan J. Heeger, Nature Photonics **3**, 297 (2009)

[3] Andrea Seemann, H.-J. Egelhaaf, Christoph J. Brabec, Jens A. Hauch, Organic Electronics **10**, 1424 (2009)

[4] Kenji Kawano, Roberto Pacios, Dmitry Poplavskyy, Jenny Nelson, Donald D.C. Bradley, James R. Durrant, Sol. Energy Mater. Sol. Cells **90**, 3520 (2006)

[5] Jian-Ji Huang, Yan-Kuin Su, Ming-Hua Chang, Tsung-Eong Hsieh, Bohr-Ran Huang, Shun-Hsi Wang, Wen-Ray Chen, Yu-Sheng Tsai, Huai-En Hsieh, Mark O. Liu, Fuh-Shyang Juang, Jpn. J. Appl. Phys. **47**, 5676 (2008)

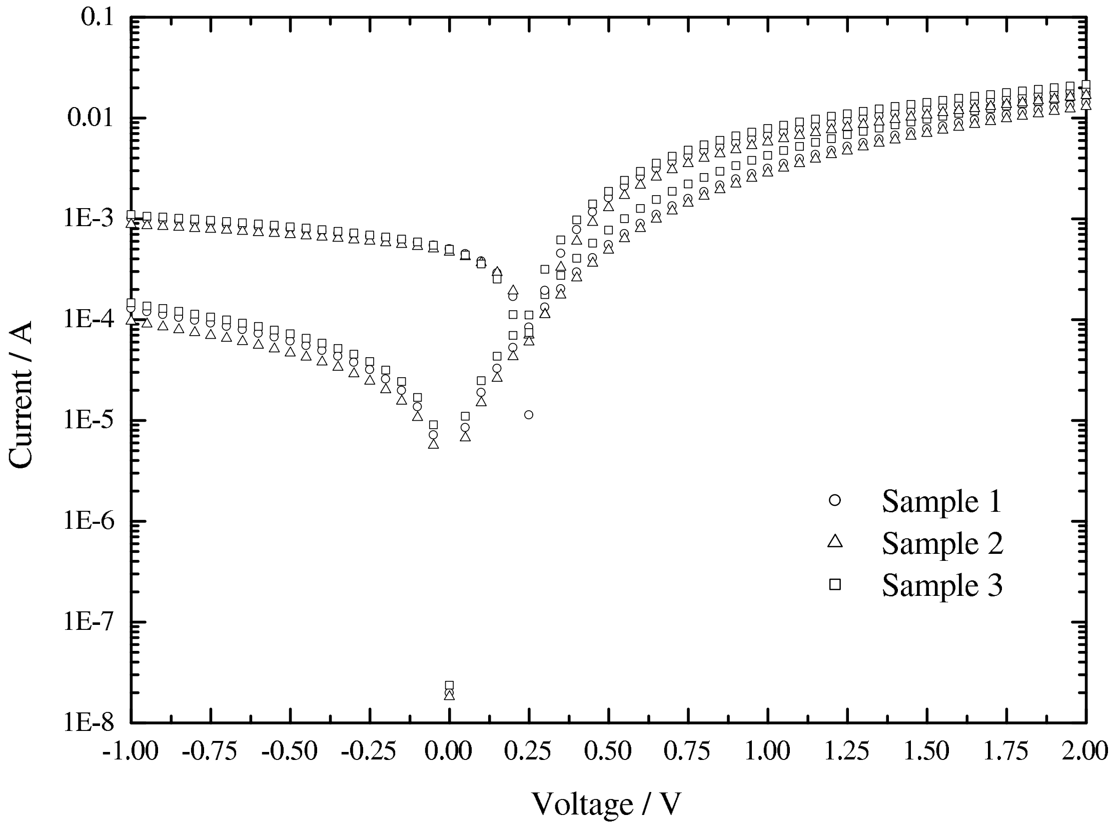

FIG. 1: Current-Voltage characteristic of three samples (A series) with Al(7 nm)/Ag(33 nm) top metal electrode.

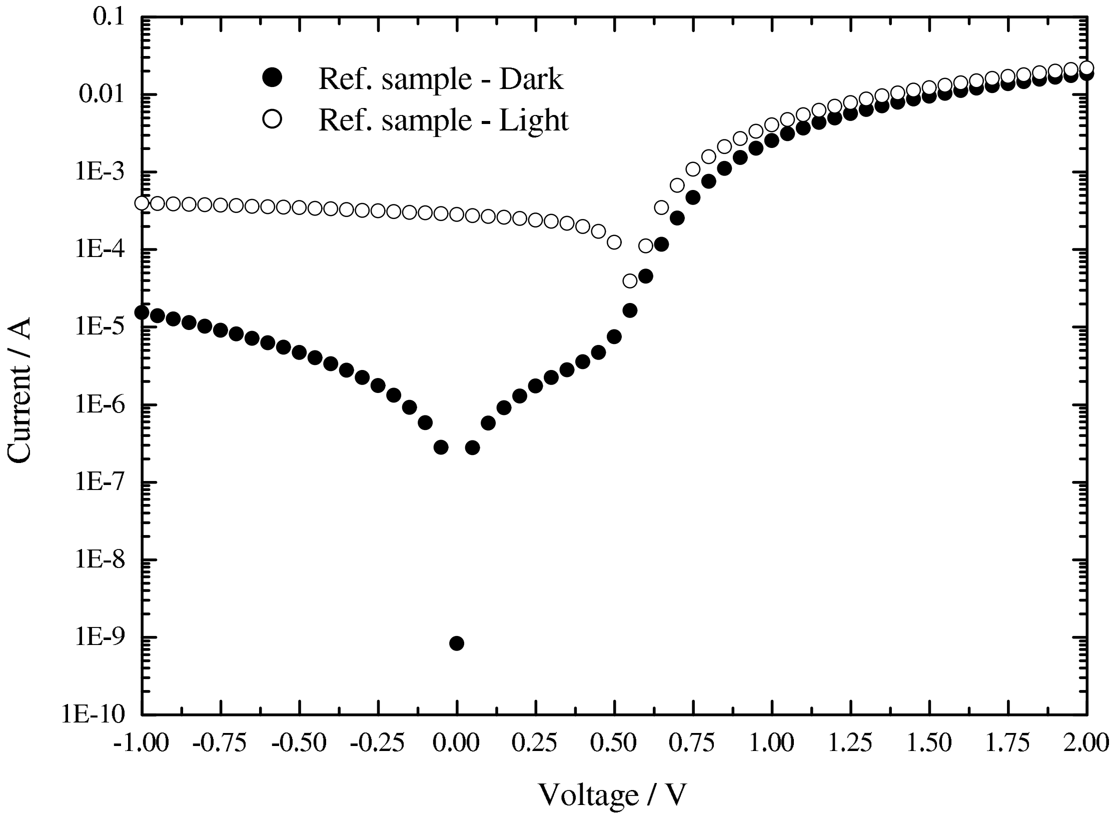

FIG. 2: Current-Voltage characteristic of the standard ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al reference sample (GB series)

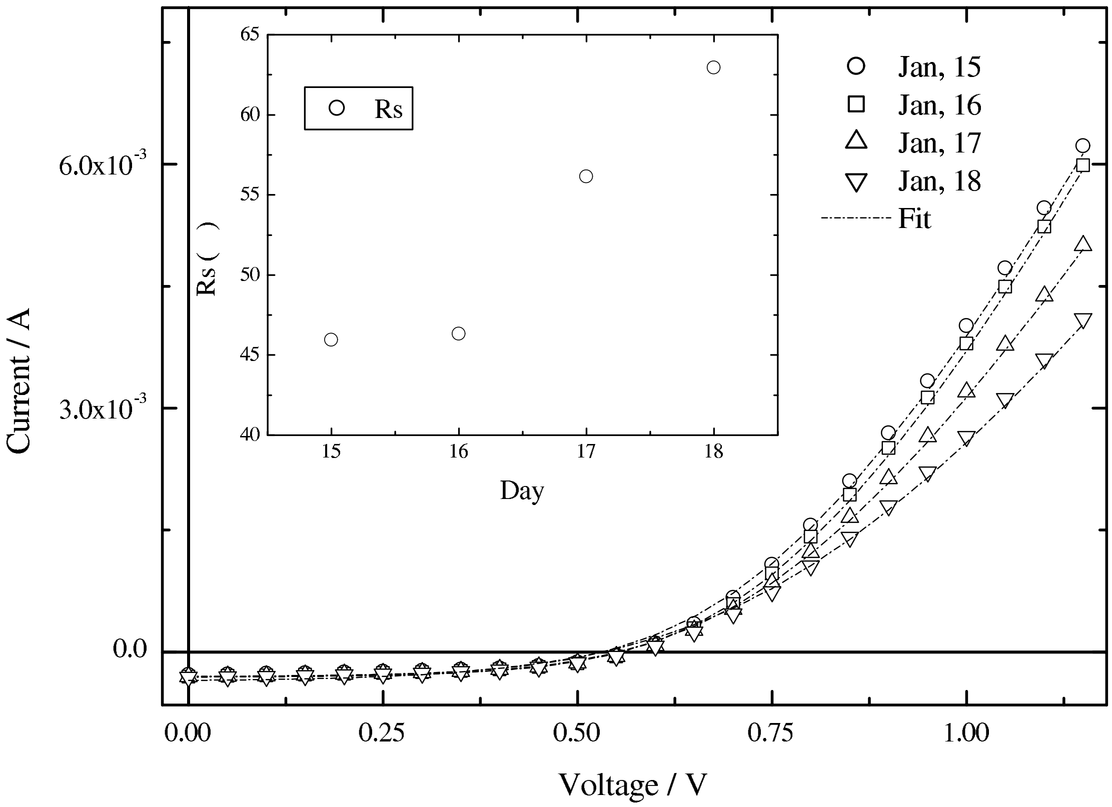

FIG. 3: Example of numerical fit to the I-V characteristic of the GB series reference sample measured for several days. Inset: Series resistance (Ω) as a function of time as extracted by the numerical fit.