



Agenzia Nazionale per le Nuove Tecnologie,
l'Energia e lo Sviluppo Economico Sostenibile



Ministero dello Sviluppo Economico

RICERCA DI SISTEMA ELETTRICO

Studio di strati compositi di nanotubi di carbonio per il miglioramento di celle solari

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Report RdS/2011/152

STUDIO DI STRATI COMPOSITI DI NANOTUBI DI CARBONIO PER IL MIGLIORAMENTO DI CELLE SOLARI

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Settembre 2011

Report Ricerca di Sistema Elettrico
Accordo di Programma Ministero dello Sviluppo Economico – ENEA
Area: Produzione di energia elettrica e protezione dell'ambiente
Progetto: Ricerca su celle fotovoltaiche innovative

Responsabile Progetto: Paola Delli Veneri, ENEA

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1. Introduction

Bulk Heterojunction Polymer Solar cells with an active layer containing the P3HT polymer as p-type and PCBM – a modified fullerene – as n-type material are the state-of-the-art devices for organic photovoltaics. The schematics of a typical device structure is shown in Fig. 1: On a glass or a plastic substrate the front contact is realized by the deposition of a transparent conducting oxide (for example Indium tin oxide (ITO)), covered by a spin-deposited hole conducting PEDOT:PSS layer. The active layer – consisting of an intermix of n-type and p-type organic semiconductor, as mentioned before, is then deposited by spin-coating on top of the front-contact and successively the back contact is realized by the evaporation of aluminium. The morphology of the active layer is very critical, because after separation of the charge carriers at the heterointerface between the two active layer constituents, the holes have to reach the front contact and electrons the aluminium back contact. That means that both P3HT and PCBM have to form continuous chains that are connected to the respective contacts.

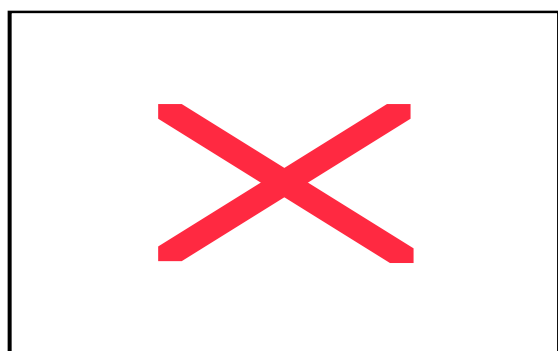


Fig.1 Basic structure of a Hetero-Bulk polymer solar cell.

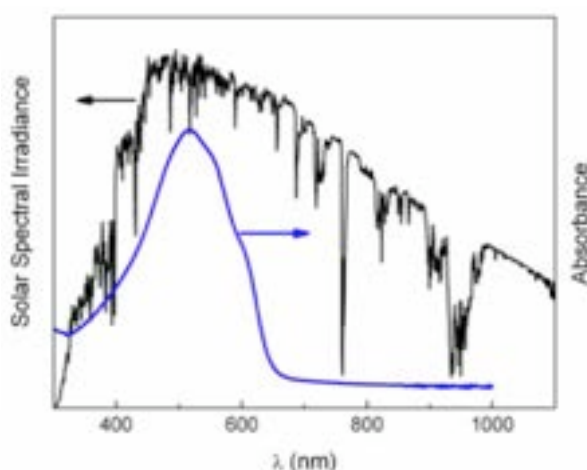


Fig.2 AM1.5 solar spectrum and absorption spectrum of a P3HT/PCBM polymer solar cell.

In Fig. 2 the typical absorption spectrum of a P3HT/PCBM polymer solar cell has been plotted together with the AM1.5 solar spectrum. While a good overlap in the blue and green spectral regions is observed, the absorption of this type of polymer solar cells is neglectable for wavelength above 650nm. One way to increase the conversion efficiency of the polymer solar cell is therefore to modify the active layer absorption by the addition of materials, that are absorbing the light in the red and infrared spectral region.

Possible candidate are inorganic quantum dots (QDs). A particular interesting feature of quantum dots is the enability of the absorption spectra by changing the dot diameter. This kind

of “bandgap engineering” (see Fig.3) enables to obtain a suitable absorption wavelength with a large variety of materials. In the present study we choose InP/ZnS quantum dots with an emission peak wavelength of about 660 nm.



Fig.3 InP/ZnS quantum dots with different diameters – the right most QD’s are the ones used in this work.

A drawback of quantum dots as active material for use in solar cells, however, is the electric transport. In order to profit from the additional absorption, the charge carriers have to be again macroscopically separated. In order to have a sufficient conduction, a rather high concentration of QDs is needed. An alternative way in order to obtain conduction is the addition of another type of conducting material. An interesting candidate are carbon nanotubes (CNTs). Thin films containing CNTs have already been demonstrated to be able to substitute in some applications of organic solar cells or organic light emitting diodes the transparent conducting oxide as front contact. Here we investigate the possibility to use them as well in the active layer together with the InP/ZnS quantum dots. Because the final complete active layer composition together with P3HT and PCBM is rather complex, as a first step we investigate here the combination of quantum dots with carbon nanotubes in a isolating polymer matrix, namely PMMA. This gives the possibility to get insight into the interplay between InP/ZnS QDs and CNTs alone. In particular the dependence of the optical and electrical properties of the thin films as a function of some specific parameter can be investigated. In the particular case we varied the CNT concentration in the film, maintaining all the other parameters constant.

2. Development of a InP/ZnS Quantum Dot + MWCNT System in PMMA matrix

2.1 Nanocomposite sample fabrication

Two different types of substrates – glass and crystalline silicon – have been used. On each type of substrates 7 different sample types have been prepared, as summarized in Table 1 and schematically shown in Fig.4. Besides the pure PMMA samples three samples with different concentrations (1%, 4% and 7%) of Multi-walled carbon nanotubes (MWCNTs) and three samples with InP/ZnS quantum dots with a fixed concentration of 5% and again the above mentioned three different CNT concentrations have been prepared.

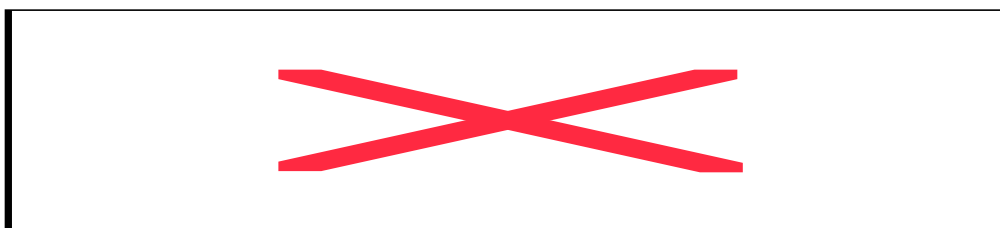


Table 1 Overview over the 14 different deposited samples types.

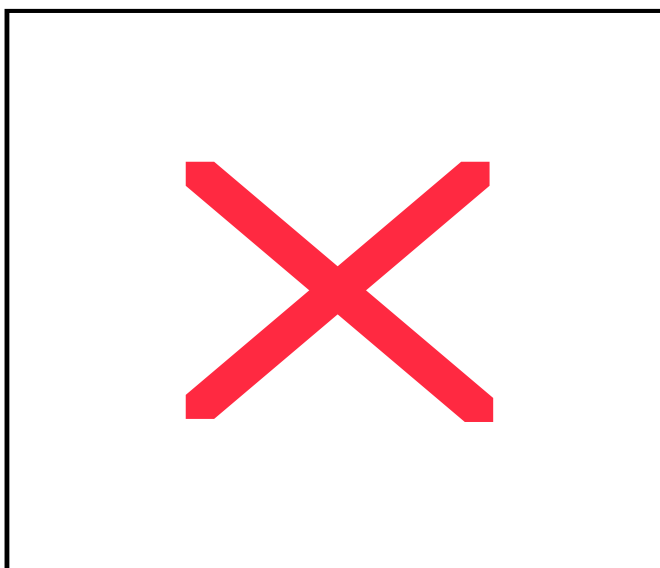


Fig.4 Schematics of the different produced samples.

The Polymethyl-methacrylate (PMMA) powder was solved into Dimethylformamide (DMF) to create the PMMA solution that has later been spin coated on the different substrates or served as the basis for the more complex subsequent solutions with CNTs and QDs respectively. The solution was then stirred for 30 min, resulting in a transparent and colourless solution

The preparation of the solution of PMMA with carbon nanotubes was done in the following way: 5mg of non functionalized MWCNTs were solved in 2ml of DMF inside a tube. The tube was sonicated for 30min at room temperature. For the 1% solution few CNT clusters were visible and for the 4% and 7% solutions more clusters were visible in the otherwise homogeneously black solution. In the next step the MWCNT solution was mixed with the PMMA solution in order to obtain the three different concentrations of MWCNTs. The three different solutions were then sonicated for 60min at a temperature of 40°C.

Another set of tubes was processed the same way without sonication directly after the CNT addition. These were used for the preparation of the solution containing either CNTs as well as quantum dots. InP/ZnS quantum dots were added to this solutions with the three different

MWCNT concentrations in a quantity resulting in 5wt% QD concentration. Also in this case subsequently the combined solutions with CNTs and QDs have been sonicated for 60 minutes at 40°C. The preparation of the later solution is schematically shown in Fig.5.

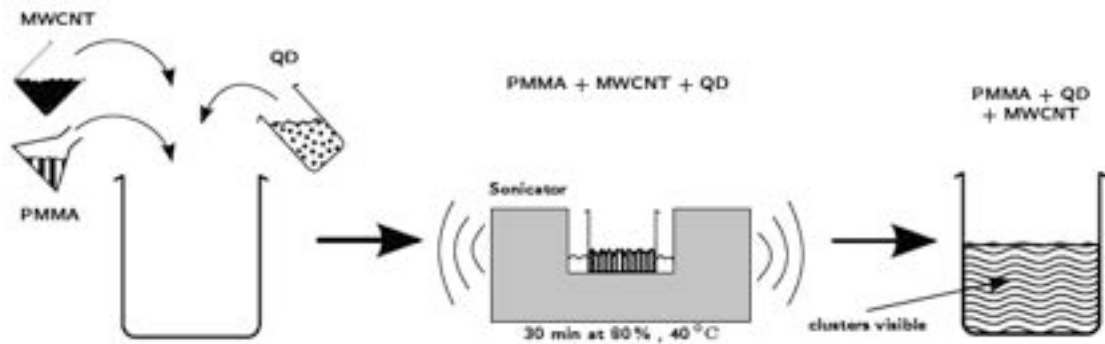


Fig.5 Processing of the PMMA solution, containing the carbon nanotubes and the quantum dots.

Before the spin-coating deposition the substrates cut into 2,5 cm x 2.5 cm squares, then sonicated in acetone for 30min at 40°C and subsequently dried with nitrogen, as shown in Fig.6.

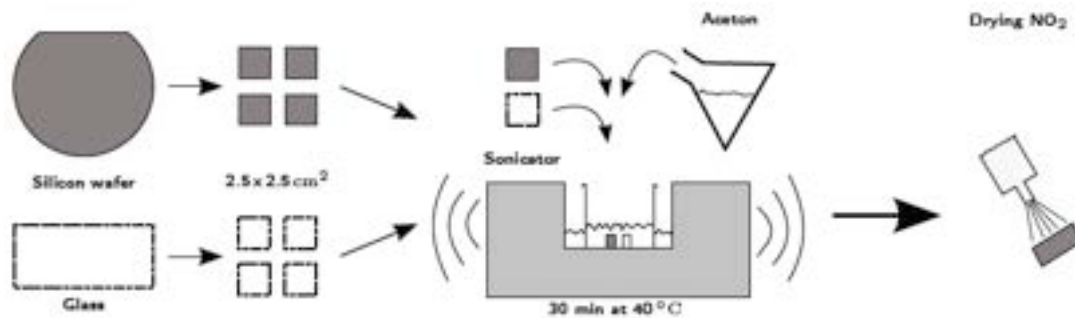


Fig.6 Preparation of the substrates.

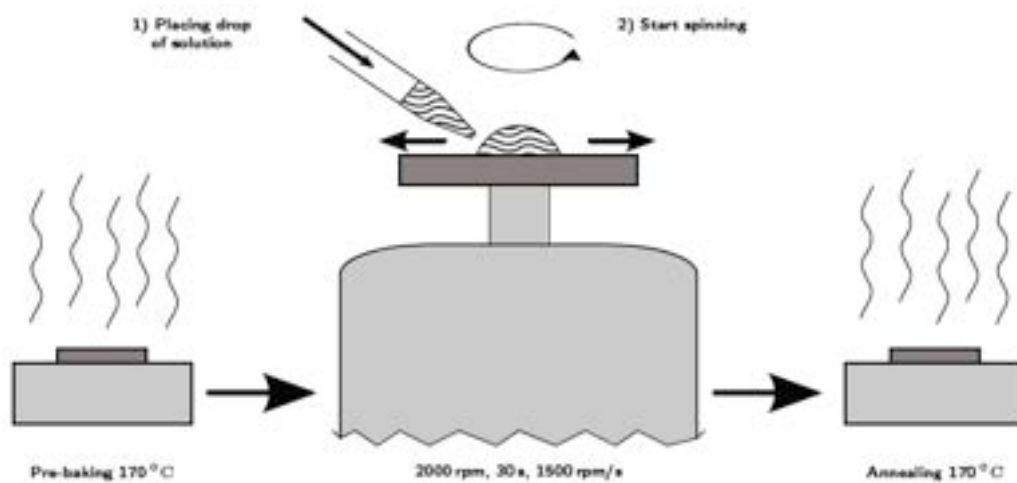
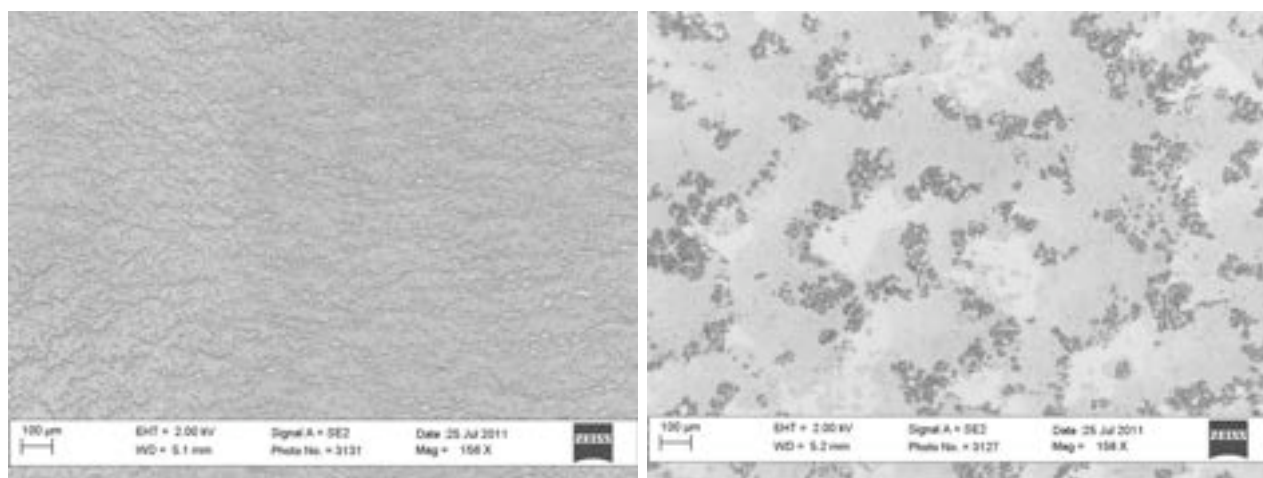


Fig.7 Spin-coating deposition process.

Subsequently the solutions were deposited on to the substrates by spin-coating with the following parameters: single step with a speed of 2000rpm for 30s with an acceleration of 1500rpm/s. Before the spin-coating 0.3ml of solution was homogeneously distributed on the substrates. Before applying this specific parameters the spin-coating process has been optimized by varying the parameters using a purely PMMA in DMF solution in order to obtain a homogeneous film with a thickness between 200nm and 300nm, as determined using a profilometer. The samples were before and after spin-coating annealed for 2min at 170°C on a hot plate. The spin-coating process is schematically shown in Fig.7.

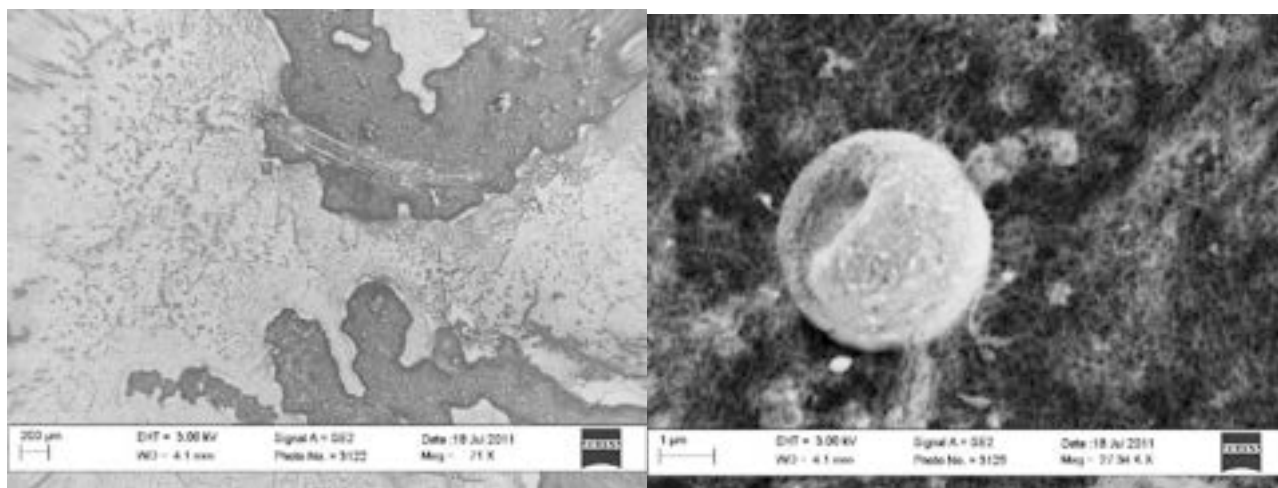
2.2 Sample morphology



a)

b)

Fig.8 SEM images of the samples with QDs and a) 1% CNTs and b) 4% CNTs.



a)

b)

Fig. 9 SEM image of the sample with QDs and 7% CNTs at two different magnifications.

In Fig. 8. And Fig.9 typical SEM images of the deposited films are shown. It can be seen that the CNT distribution shows, in particular for the films with a high concentration of carbon

nanotubes a rather inhomogeneous distribution is found. In the nanocomposite films with QDs and 7% CNTs we observed a very particular feature, namely spheres with a diameter of about $3\mu\text{m}$ consisting of an agglomeration of carbon nanotubes. Probably either the quantum dots or polymer spheres seem to act as a sort of seed for the formation of the spheres consisting of CNTs.

2.3 Optical characterization of the solutions and of the nanocomposite films

During film processing the different solutions, used for the spin-coating preparation of the samples, have been optically characterized, measuring the photoluminescence spectra. The results are shown in the following figures.

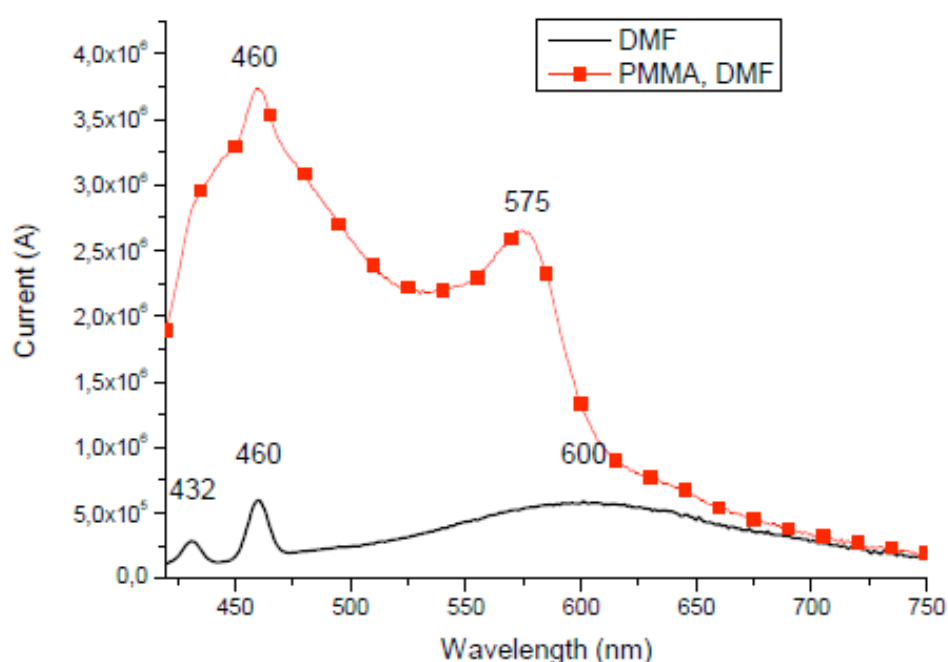


Fig.10 PL spectrum of the DMF solvent, with and without addition of PMMA.

In Fig. 10 we observe three typical peaks related to the DMF solvent at 432nm, 460nm and a broader peak at 600nm. Adding the PMMA we observe an additional peak around 575nm and the two DMF peaks at 432nm and 600nm are only visible as small shoulders in the PL spectrum.

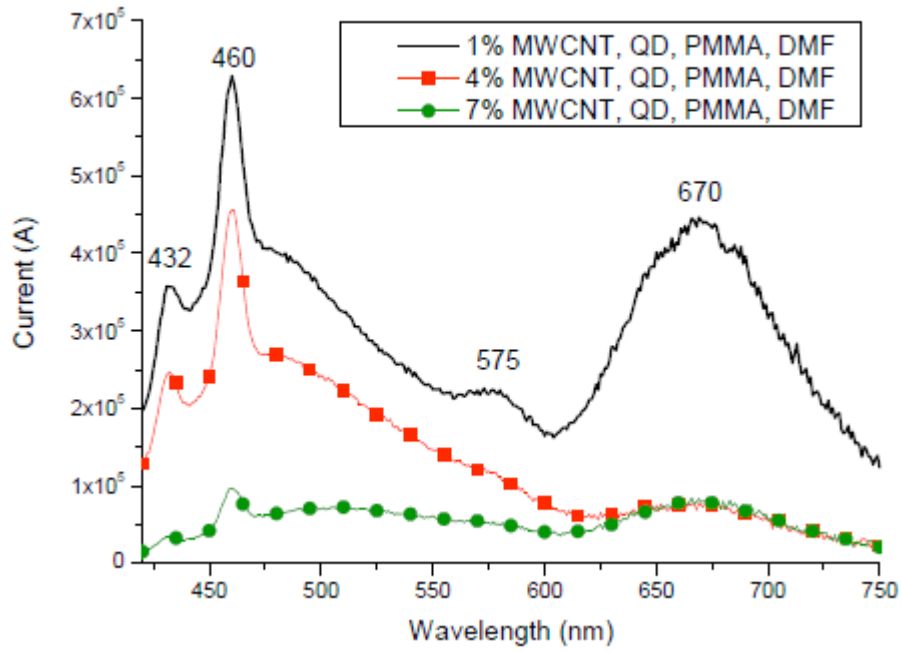


Fig.11 PL spectrum of the solutions containing QDs and different CNT concentrations.

In Fig.11 we plotted the PL peaks for the solutions containing additionally as well the InP/ZnS quantum dots as different concentrations of carbon nanotubes. One can observe, that with increasing CNT content the PMMA peak at 575nm is decreasing, while for all three concentrations of CNTs a relatively broad peak centered at 670nm is visible. This peak can be clearly identified as the emission peak of the InP/ZnS quantum dots.

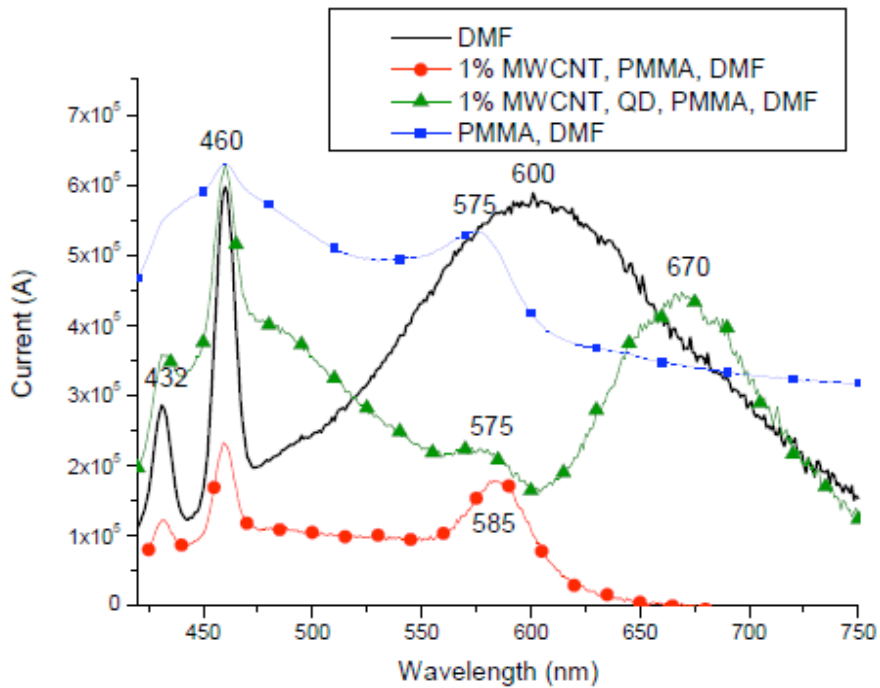


Fig.12 Comparison of the PL spectra of all solutions used in the fabrication of the samples with 1% CNT content.

In Fig.12 for comparison the PL spectra of all the solutions, used in the fabrication of the films with 1% carbon nanotubes, are plotted together. One can clearly see that the 670nm peak is present only in the quantum dot containing solution and not related to the carbon nanotubes.

The next photoluminescence spectra (Fig.13 and Fig.14) are measured on the nanocomposite films. The y-axis, given in current, refers to the photocurrent of the detector used for the PL measurements.

The results shown in Fig.13 are measured on the deposited films containing quantum dots and 1% MWCNTs. We see basically the broad red emission peak at 670nm with a FWHM value of 67nm, related to the quantum dot emission. This confirms the successful incorporation of the quantum dots into the deposited films. This emission peak could, however, only be observed on the sample with a low content of carbon nanotubes (see Fig.14). A possible explanation for this suppression of the QD photoluminescence with increasing CNT content is that the nanotubes are optically shielding the quantum dots, for example by the formation of the spheres, observed in Fig.9. Another explanation would be the quenching of the PL by efficient charge carrier separation. It is for example well known, that the photoluminescence of P3HT is quenched by the addition of the fullerenes.

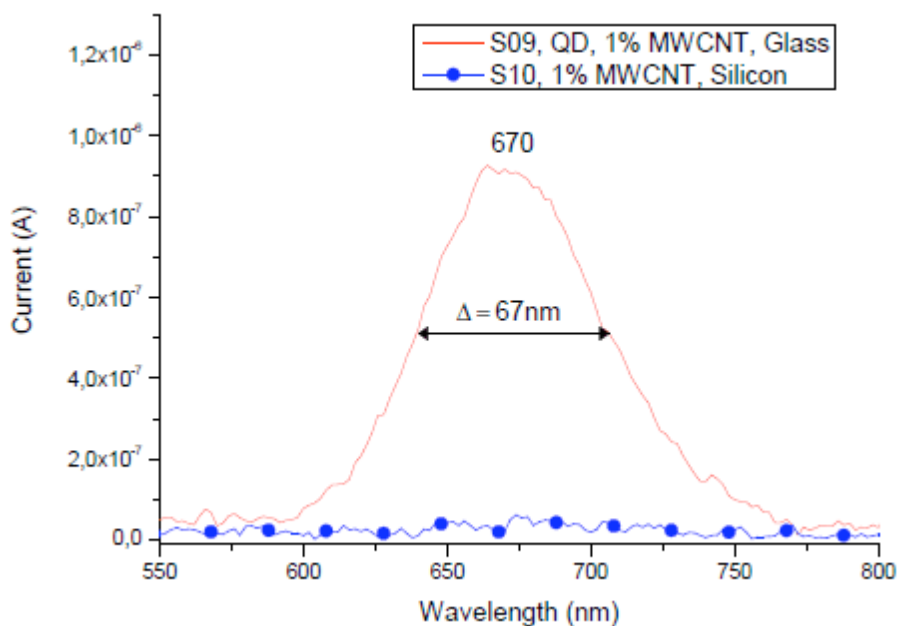


Fig.13 Comparison of the PL spectra of the nanocomposite film with 1%MWCNTs and 5%QDs, deposited on different substrates.

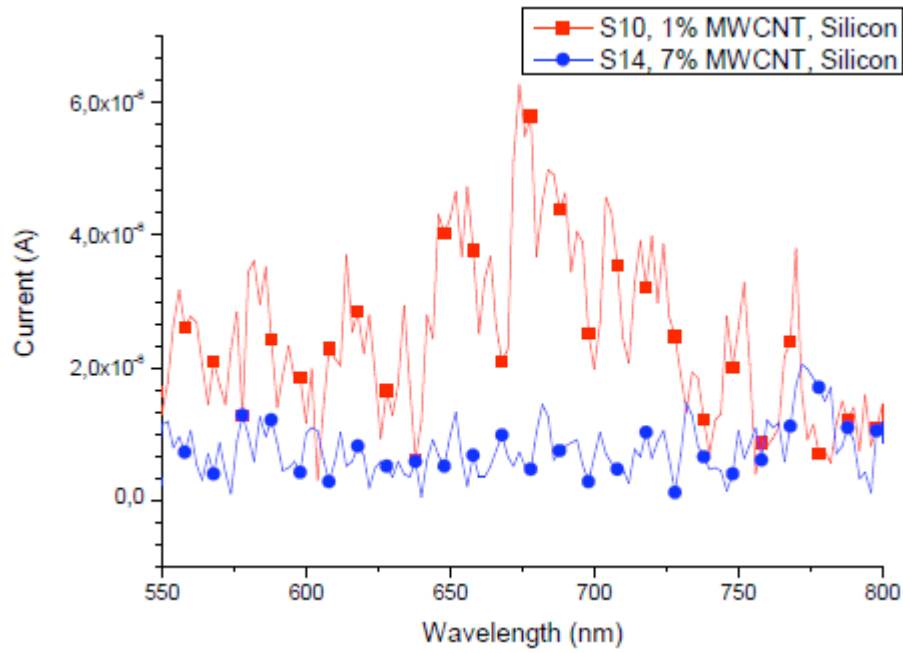


Fig.14 Comparison of the PL spectra of the nanocomposite film with and without 5% QDs, and different concentrations of MWCNTs.

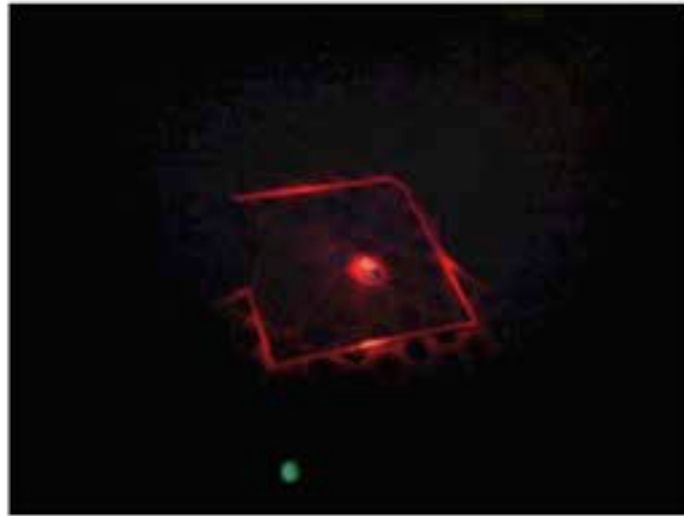


Fig.15 Optical image of the photoluminescence of a nanocomposite film with 1% MWCNTs and 5% QDs, deposited on a glass substrate.

In Fig. 15 we see an image of the photoluminescence of the nanocomposite film with 1% MWCNTs and 5% InP/ZnS QDs deposited on a glass substrate. A strong photoluminescence located only in one spot on the sample is shown, indicating the non-homogeneous nature of the film. The glass substrate acts also as a waveguide. Therefore the red light at the edges of the substrate is observed. It should be noted, that in the case of a fluorescence collector this effect is utilized for light concentration for solar cell applications.

Measuring the optical transmittance as a function of wavelength (see Fig.16) in the case of the samples with 1% MWCNT concentration an enhancement of the transmittance is observed as

compared to the pure glass substrate. This can be explained by the nanocomposite film acting as an antireflective coating for the glass substrate. Increasing the carbon nanotube concentration to 4%, we observe an about 8% decrease of the optical transmittance in the whole investigated spectral range from 400nm up to 800nm. Increasing the CNT concentration further to 7%, the transmission loss, compared to the uncoated substrate, is higher than 25%. By adding the QDs to the film, the picture changes. Here we observe a decrease of the transmission only for the sample with the highest CNT concentration of 7%. This decrease is clearly less pronounced as compared to the case of the sample with the same CNT concentration but without quantum dots. This fact is a strong indication that the QD incorporation is altering the CNT distribution. If we assume that a certain fraction of the nanotubes form the spheres, that we observed in the SEM image, this fraction is missing in the rest of the film. This could explain that the 7% CNT film in the presence of the QDs shows a transmission comparable to a 4-5% film without QDs. Slightly more than 2% of the quantum dots could be found in the form of spherical agglomerations.

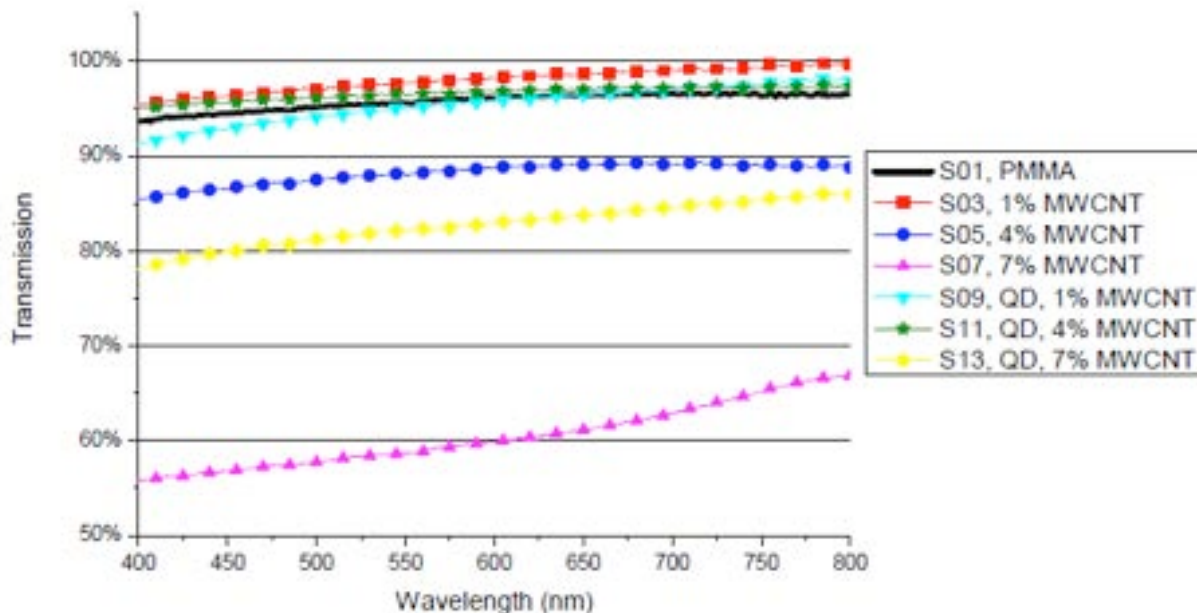
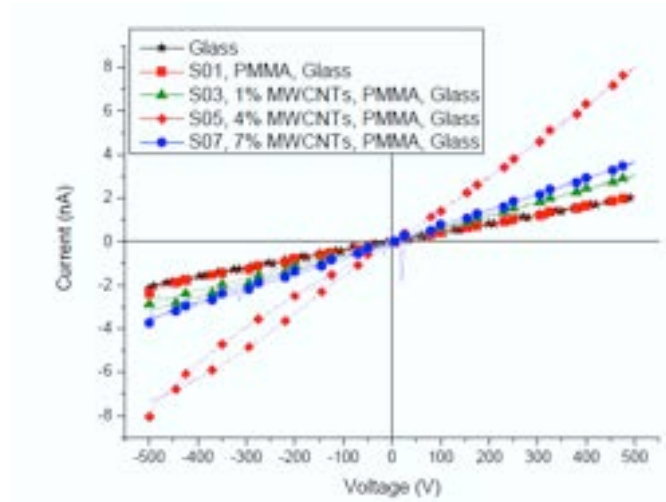
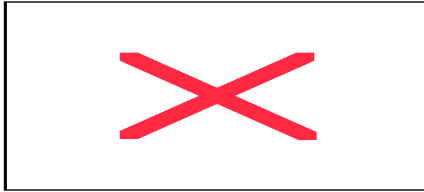


Fig.16 Optical transmission spectra of PMMA films on glass, with and without MWCNTs and QDs.

2.4 Electrical characterization of the nanocomposite films

Besides the optical properties, the electrical conduction of the nanocomposite films is crucial for their future use in polymer photovoltaic cells. In order to measure the electrical properties, we used two configurations: In the first case (Fig.17a) we applied two silver paste stripes (about 10mm long and with a gap of 1mm) on top of the film deposited on glass substrate. The measured current-voltage characteristics for this films are shown in Fig.17b. The addition of the pure PMMA film is not changing the conductivity, confirming the good isolation properties of this film. It should be mentioned that the non-zero conductivity for these two

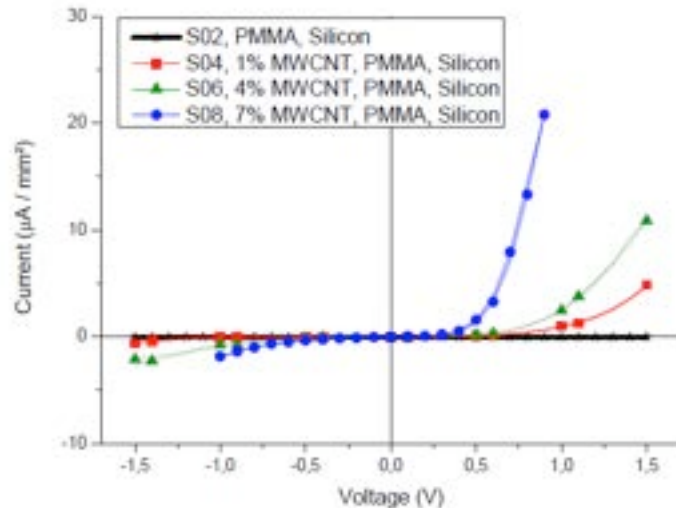
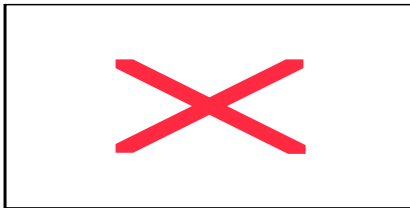
samples are due to the conductivity of the glass substrate. For all three nanocomposite films, however, we observe a clear increase of the conductivity, but not in a monotonic way with the CNT content. The smallest conductivity increase is found for the 1% CNT sample, the highest one for the 4% CNT sample and an intermediate value for the 7% CNT sample. This non-monotonic behavior can be eventually explained by the increasing inhomogeneity of the sample with increasing CNT content, as observed in the SEM images. Therefore the effective formation of a percolation network is not reached for the 7% sample. All measured characteristics in sandwich configuration were symmetric and only in the case of the 4% CNT containing film we observed a small hysteresis in the current-voltage characteristics for negative applied voltages.



a)

b)

Fig 17 Current-voltage characteristics measured for the films with and without different concentrations of CNTs in coplanar configuration.



a)

b)

Fig 18 Current-voltage characteristics measured for the films with and without different concentrations of CNTs in sandwich configuration.

In order to test the vertical electrical transport, we performed an electrical characterization in sandwich configuration, where the films have been deposited on crystalline silicon (see

Fig.18a). The resulting current-voltage characteristics are shown in Fig.18b. Again very low conduction is found for the pure PMMA film. Increasing the CNT concentration of the film, we see the formation of a diode like behavior of the samples, with a asymmetric current-voltage characteristics. The forward bias direction is found for positive voltages applied to the top contact as referred to the bottom back contact on the crystalline silicon. With increasing CNT concentration the onset voltage for conduction decreases monotonically down to a value of about 0.5V in the case of the sample with a 7% CNT concentration. The system can be modelled as a type of Schottky diode, where the silicon substrate plays the role of the semiconductor, while the MWCNTs act as metallic contact. The resulting I-V characteristics is therefore enabling to give an estimation of the effective vertical conduction in the nanocomposite layer. For a more detailed analysis in the future, temperature dependent current-voltage characteristics should be done as well as capacitance spectroscopy. As a first example of the latter technique we present in Fig.19 the frequency dependent capacitance, measured in coplanar geometry on the sample with the purely PMMA layer.

Taken the literature value of the dielectric constant of PMMA as given and knowing the contact area, this enables us to determine electrically the thin film thickness. In the present case we calculated a thickness of about 200nm. This is in good agreement with the film thickness, determined by using the profilometer.

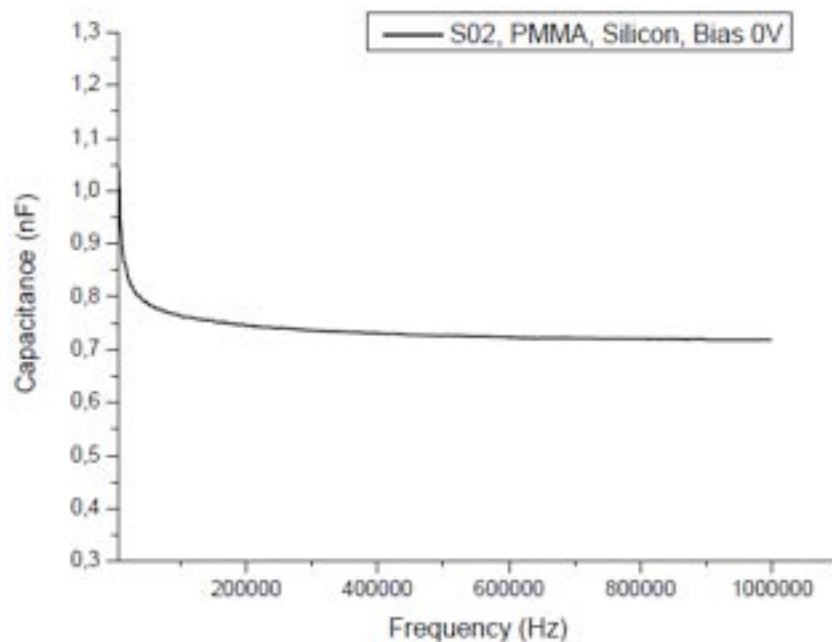


Fig.19 Frequency dependance of the capacitance of a pure PMMA film deposited on a crystalline silicon substrate.

3. In-situ I-V-characterization in the glove-box

The project is the "Development of a compact system of measures for the electro-optical characterization of polymeric solar cells in the glove-box." The work includes the development of an electro-optical setup for the characterization IV dark and IV under illumination, including

the implementation of software for instrument control and for the extrapolation of the parameters of the solar cells.

The introduction of a compact measuring system inside the glove-box, environment of controlled atmosphere with low oxygen and moisture, allows to characterize the solar cells before degradation.

The measurement setup is shown in Fig.20 and consists of a Personal Computer with

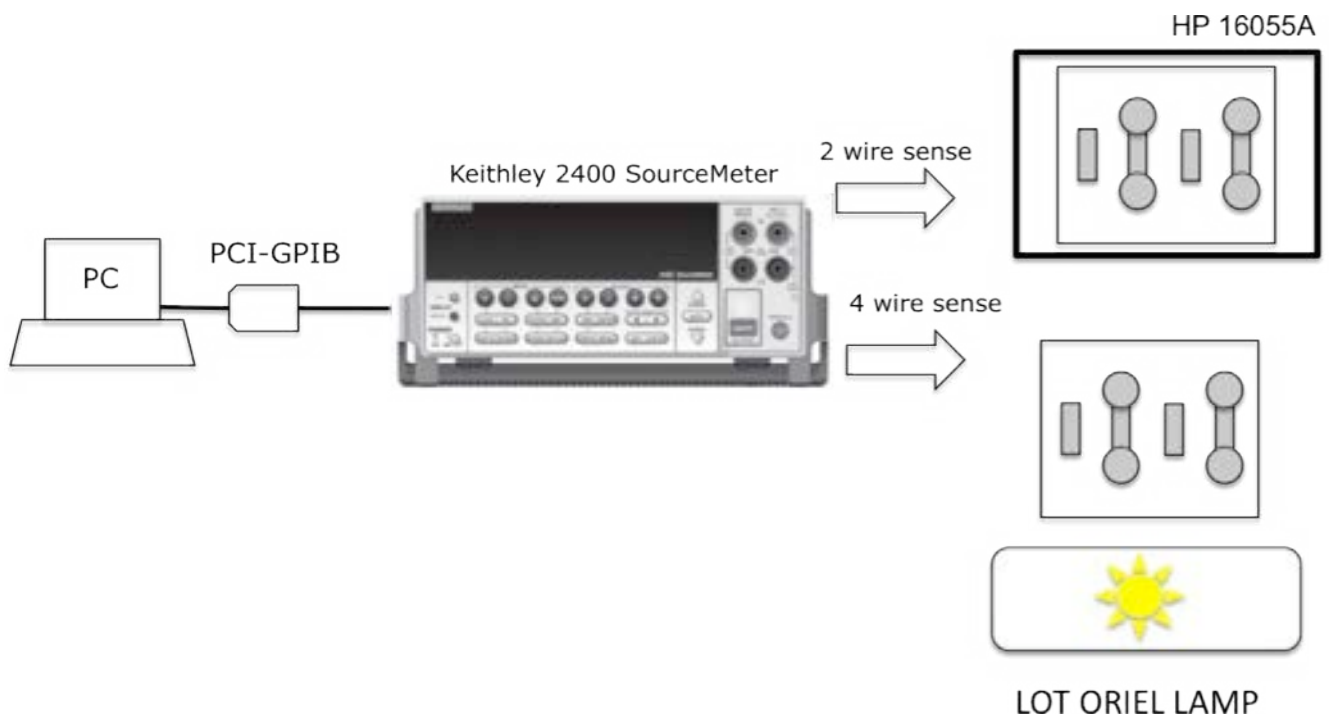


Fig.20 Measurement setup for characterizing electro-optical to be inserted in the glove-box.

PCI-GPIB interface, by a Keithley 2400 SourceMeter, by a xenon lamp Lot Oriel LSN251, by a test equipment HP 16055A, by a four probes and a fiber optics. The software part was implemented using Labview 7.1.

The characterization procedure is divided in two parts:

- Analysis IV using the 2-wire mode sense;
- Analysis IV under illumination via 4-wire sense mode with extrapolation of the parameters.

In both cases the SourceMeter, remotely controlled via Labview, supplies a voltage and measuring a current. It is also possible to make a dark analysis using the 4 wire sense mode, Fig.21.



Fig.21 Screenshot of software index.

3.1 I-V dark analysis (2-wire sense)

The measurement setup is shown in Fig. 23, where the front contact of a solar cell is connected to the positive test lead (+) and the back-contact to the tip negative (-).

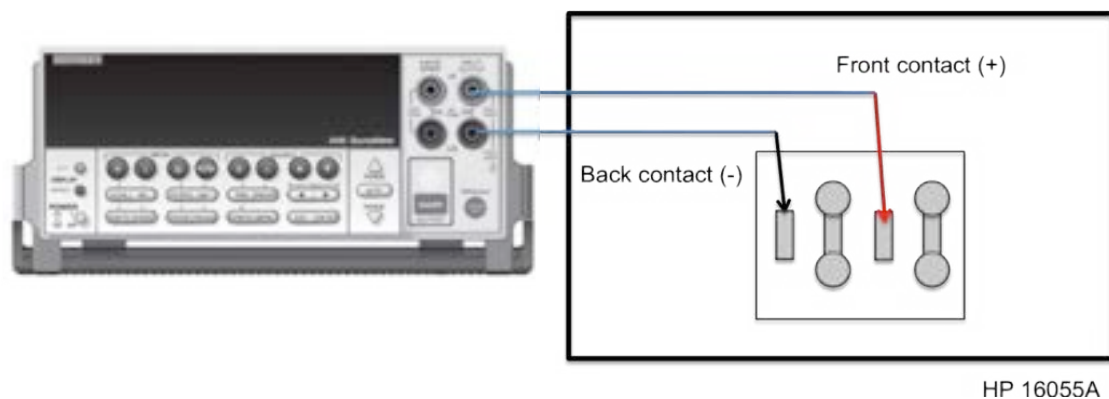


Fig.23 Measurement setup for the I-V dark.

The HP 16055A test equipment provides an electrostatic shield and prevents light to excite the device for a stable measurement of the current order of pA. The maximum applicable voltage is ± 200 V DC

Using 2-wire sense mode, it requires a voltage that varies from a minimum to a maximum value at a given step and measure the current. In this procedure require that the voltage test leads are the same as the current measure. With the use of Reverse Mode is possible to analyze the Dark IV characteristic to study a possible hysteresis in the device.

The code snippet sent to 2400 SourceMeter via GPIB is follows:

```
*RST
:SYST:AZER:STAT ON
:SYST:BEEP:STAT 0
```

In this way the instrument is reset and is ready for the next measurement.

```
:SOUR:FUNC VOLT
:SOUR:VOLT:MODE FIX
:SOUR:VOLT:RANG 10
:SOUR:VOLT:LEV 2.000000
```

The instrument is set as a source of tension to be applied to the device, defining the working range, the level of tension and the ways in which the voltage must be applied.

```
:SENS:CURRE:PROT 1050E-3
:SENS:FUNC "CURRE"
:SENS:CURRE:RANG:AUTO ON
:FORM:ELEM CURRE
```

The instrument is set to measure the current, setting the compliance equal to 1.05 A, it also enables the instrument to interpret the characters in the input buffer as current values .

```
:OUTP ON
:READ?
```

The code sets the imposed voltage and measuring the current.

At the end of the measuring procedure the applied voltage is disabled by the command

```
:OUTP OFF
```

to ensure an adequate safety level to the operator.

The software "J-V Dark 2 wire" creates a default folder in C: \ I_V_Measures \ Dark_2_ wire and saves all the data in text files.

The Fig.24 shows the control panel software that consists of a screen for the characterization of the solar cell and another for displaying the saved files.

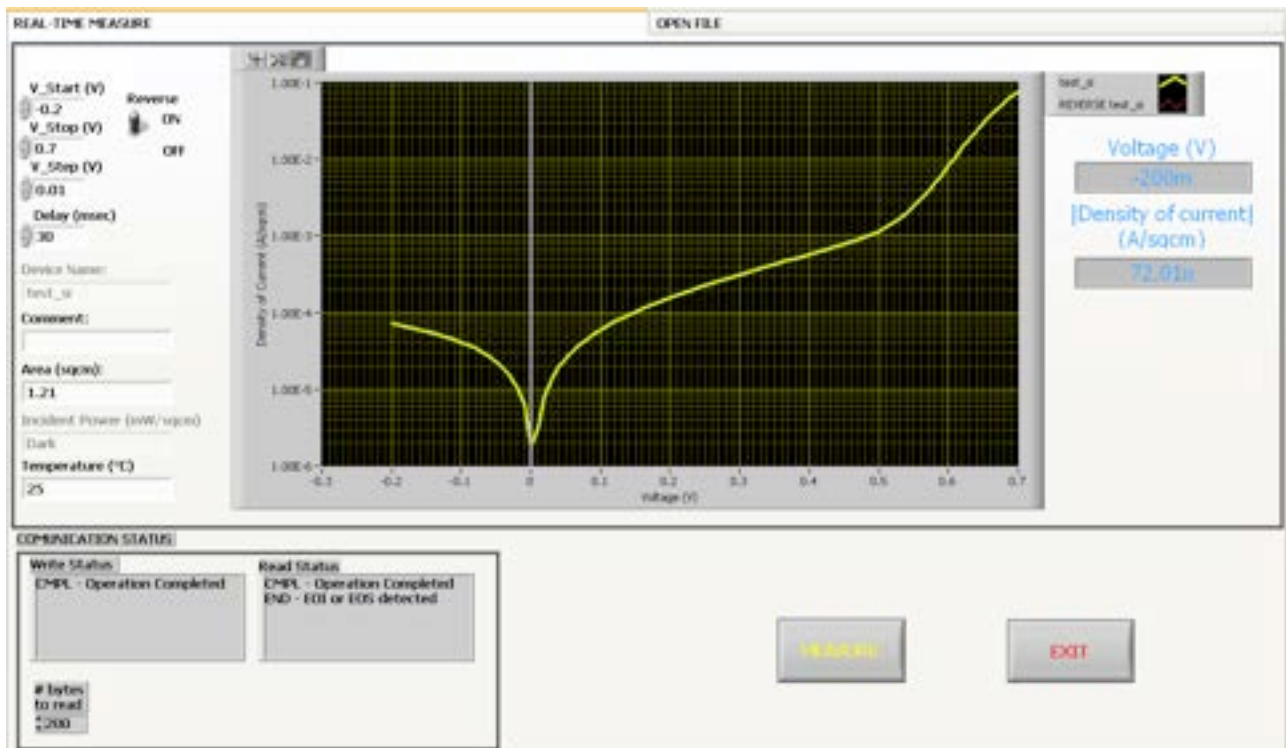


Fig.24 Screenshot dark 2 wire, real time measure tab.

3.2 I-V analysis under illumination (4-wire sense)

The characterization is performed using four probes, Fig.25, the external probes set the voltage while the internal probes measuring the voltage and current across the device.

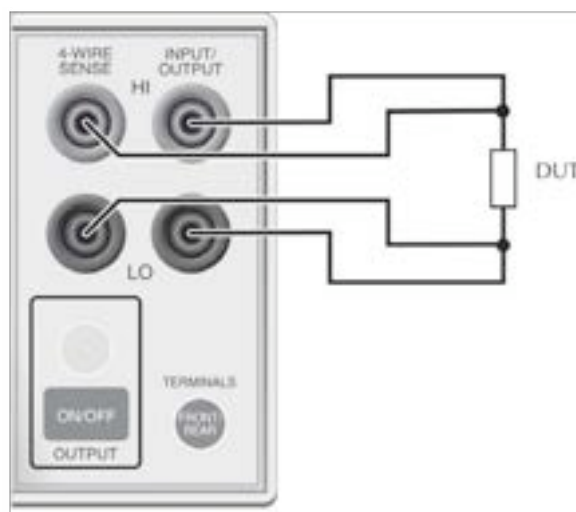


Fig.25 4-wire connections.

The measurement setup used is shown in Fig.26, in this mode, the voltage is measured across the solar cell, and if the voltage amplitude detected is less than value programmed, the SourceMeter increases the voltage to obtain the required value.

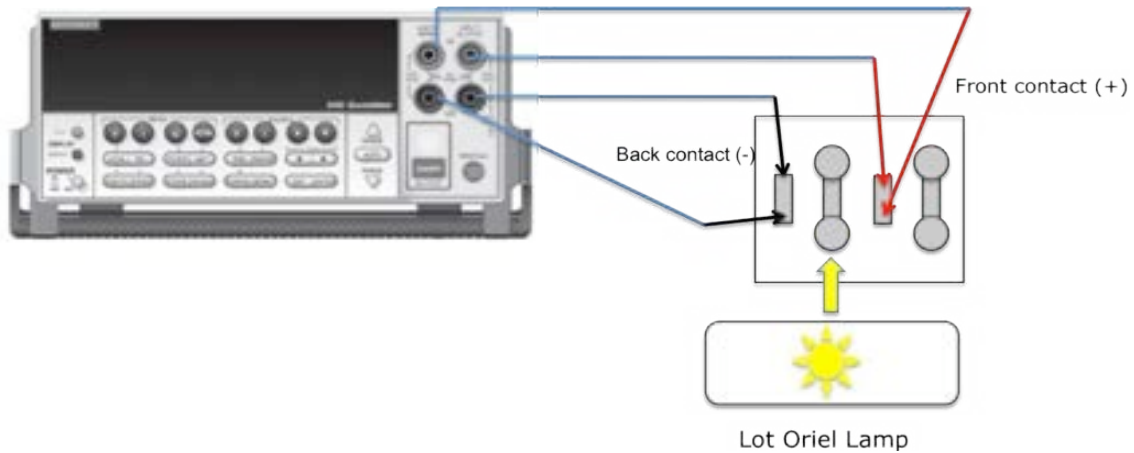


Fig.26 Setup for measuring I-V under illumination.

The software performs a check between the solar cell contacts and the probes. As soon as the measured voltage differs from the programmed value of 10 mV, a warning message is shown that advise the operator to control the probes and the solar cell contacts.

The code snippet sent to 2400 SourceMeter via GPIB is follows:

```
*RST
:SYST:AZER:STAT ON
:SYST:BEEP:STAT 0
:SOUR:FUNC VOLT
:SOUR:VOLT:MODE FIX
:SOUR:VOLT:RANG 10
:SOUR:VOLT:LEV 0.500000
:SENS:CURR:PROT 1050E-3
:SENS:FUNC "CURR"
:SENS:CURR:RANG:AUTO ON
:FORM:ELEM CURR
```

With this comamnd is enabled 4-wire sense mode, otherwise the SourceMeter works in default 2-wire sense mode.

```
:SYST:RSEN ON
:OUTP ON
:READ?
```

The code sets the imposed voltage and measuring the current.

Afterwards the instrument is enabled to impose voltage and voltage measuring sending the following code:

```
:SENS:FUNC "VOLT"  
:SENS:CURR:RANG:AUTO ON  
:FORM:ELEM VOLT  
:SYST:RSEN ON  
:OUTP ON  
:READ?
```

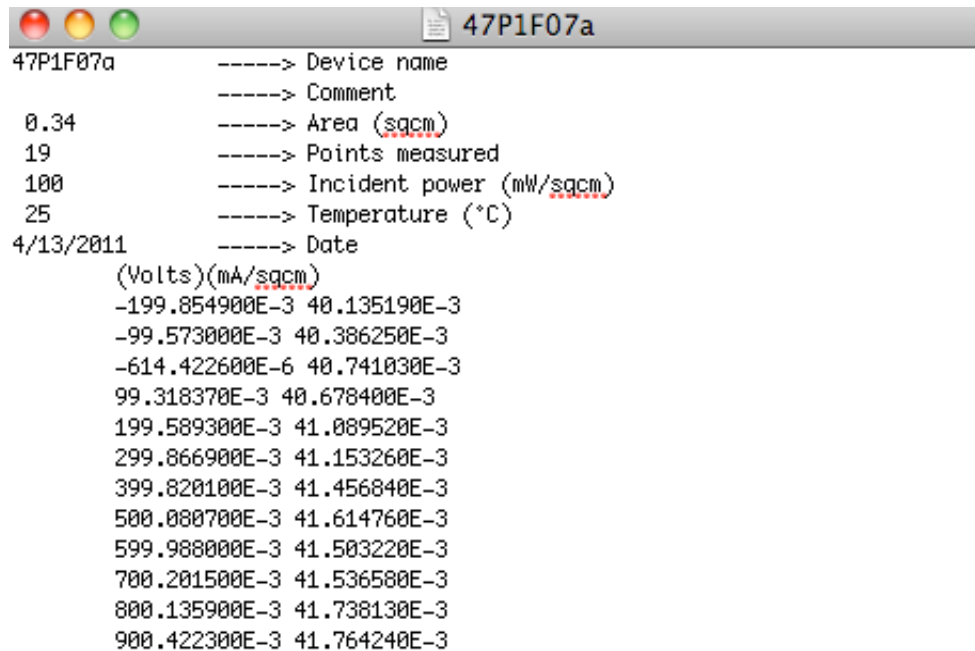
At the end of the measuring procedure the applied voltage is disabled by the command

```
:OUTP OFF
```

to ensure an adequate safety level to the operator.

The software "J-V Light 4 wire" creates a default folder in C: \ I_V_Measures \ Light_4_ wire and saves all the data in text files.

The file format is shown in Fig.27, where the data are stored in addition to other informations useful for the compatibility with the software Turbo IV, already used for the extrapolation of the solar cell parameters.



47P1F07a

47P1F07a	-----> Device name
	-----> Comment
0.34	-----> Area (sqcm)
19	-----> Points measured
100	-----> Incident power (mW/sqcm)
25	-----> Temperature (°C)
4/13/2011	-----> Date

(Volts)(mA/sqcm)

-199.854900E-3	40.135190E-3
-99.573000E-3	40.386250E-3
-614.422600E-6	40.741030E-3
99.318370E-3	40.678400E-3
199.589300E-3	41.089520E-3
299.866900E-3	41.153260E-3
399.820100E-3	41.456840E-3
500.080700E-3	41.614760E-3
599.988000E-3	41.503220E-3
700.201500E-3	41.536580E-3
800.135900E-3	41.738130E-3
900.422300E-3	41.764240E-3

Fig.27 File format.

To ensure a correct extrapolation of the solar cell parameters, the light source consists of a lamp Lot Oriel 300 W LSN251, an optical fiber and a lens, should be characterized in terms of the spectral matching compared of the sun spectra AM 1.5, and spatial uniformity across the illuminated¹ area equal to 100 mW/cm².

By placing the solar cell at a distance of 4 cm from the light source, and making a direct measurement of the incident power, the value of 100 mW/cm² at the solar cell surface is obtained.

Through the calculation of the mismatch factor M it is obtained the class of the light source and a measure of how its spectrum is different from AM 1.5 spectra. Every small change has an impact on an error of the short circuit current I_{sc} .

The Fig.28 shows the control panel software that consists of a screen for the characterization of solar cell, a screen for the report of the measures and another for displaying the saved files.

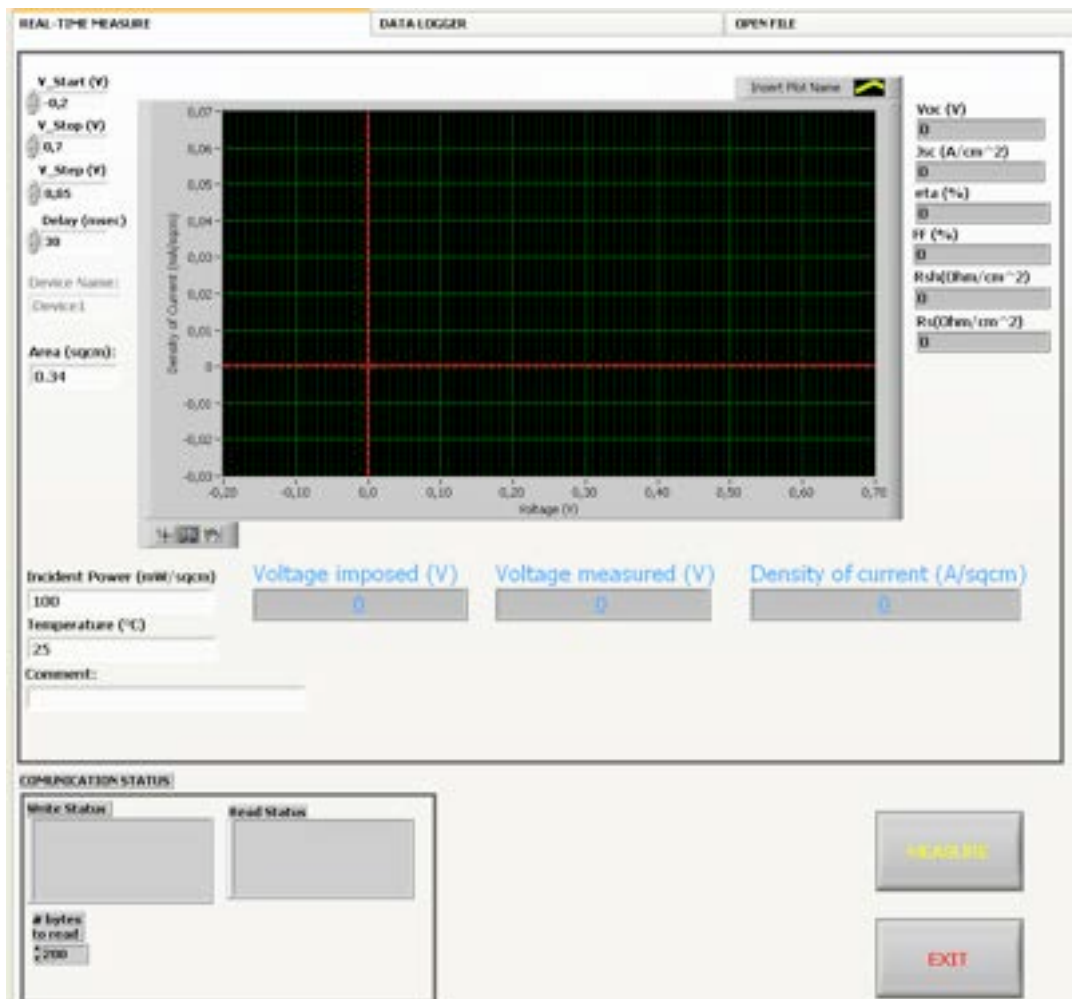


Fig.28 Screenshot light 4 wire under illumination, real time measure tab.

¹ It should also consider the temporal stability over time of the light source which causes variations of the spectrum and spatial uniformity.

4 Conclusions

Within the frame work of this project a new nanocomposite film, based on the combination of InP/ZnS quantum dots for enhanced optical absorption in the red part of the solar spectrum and of multi-walled carbon nanotubes for the increase of the thin film electrical conductivity has been developed using the spin-coating deposition technique. As a matrix for the test of this new combination of nanoparticles electrically non-conducting PMMA has been used. The measurement of the morphology of the films by SEM imaging and of the optical properties by photoluminescence and transmittance revealed a rather complex interplay between nanotubes and quantum dots. In particular, there we found a strong tendency of the nanotubes in the case of a high concentration of CNTs to agglomerate in spherical configuration. Electrical conductivity measurements in coplanar and sandwich configuration enabled to verify the degree of increase of the sample conductivity by the nanotube addition. In particular the measurements in sandwich configuration revealed the formation of a Schottky diode type behavior in a structure where the PMMA/CNT film has been deposited directly on a crystalline silicon substrate. The homogeneity of the films is still poor, which has been for example revealed by photoluminescence imaging.

The authors want to thank Carmela Borriello, Tiziana di Luccio, Pasquale Morvillo ed Anna De Girolamo Del Mauro