Some applications of carbon nanotubes in photovoltaics

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Abstract — Experimental results on single-walled carbon nanotubes (SWCNTs) and nanocomposite materials ITO/SWCNTs/Al, Au/SWCNTs/*n*-Si/Al, Al/SWCNTs/P3OT/ITO and Au/SWCNTs/P3OT/*n*-Si/Al, where P3OT is conducting polymer with conjugated bonds poly-3-oxythiophene have been reported. Composite films were obtained by spin-casting from a solution on indium-tin oxide (ITO) and glass substrates and studied using absorption spectroscopy and electrical characterization methods. The carbon nanotubes are photosensitive and all solar cells structures show photovoltaic behavior, with different open circuit voltages. It is proposed that the main reason of photosensitivity is the photoinduced electron transfer at the nanotube/polymer interface. The results show that the composite on SWCNTs base represents a new class of organic semiconducting material that is promising for organic photovoltaic cells.

Keywords: laser ablation, SWCNTs, 3rd generation solar cells

I INTRODUCTION

Recently, there are intensive efforts in the elaborating solar cell organic structures with high performance and cost-effective manufacturing methods [1]. Different competitive technologies include solar cells based on organic molecules (with efficiencies of 7%) [2], colloidal quantum dots (efficiencies reaching 6%) [3], and dye-sensitized solar cells (efficiencies up to 12%) [4]. An alternative approach is to combine inexpensive materials with well-established semiconductors (e.g. silicon) to create new architectures that have the potential of simplifying fabrication processes and lowering cost. To this end, researchers have explored various candidates, particularly transparent conductive films of carbon nanotubes (CNTs), graphene and semiconducting polymers that can be conveniently deposited on commercial Si wafers to make efficient solar cells [5-7].

Recently, researchers have particularly studied CNT-silicon solar cells that were fabricated by transferring a semi-transparent CNT film onto a n-type single-crystalline Si wafer to form Schottky junctions and heterojunctions [5,6,8]. By applying a series of doping and gating methods such as $SOCl_2$ treatment [8], ionic liquid electrolyte infiltration and electronic gating [6] as well as nitric acid doping, the power conversion efficiencies of these CNT-Si cells have been continuously pushed from initially about 1.3% to 13.8% during the past several years, indicating a very promising architecture with reduced manufacturing cost and also the potential of achieving high performance.

Here, we report Technology and some applications of single wall carbon nanotubes in photovoltaics. The main original idea is to introduce the perfect and monodisperse SWCNTs as active part of heterostructures of solar cells. The spin-coating was applied in technology of obtaining controllable layer thickness. For SWCNTs integration on 3rd generation of solar cells, blends of SWCNTs with organic conjugated polymer and monocrystalline semiconductor has been performed.

II METHOD OF EXPERIMENT AND RESULTS

Experimental results on single-walled carbon nanotubes and nanocomposite materials on their base with conjugated bonds polymer poly-3-oxythiophene and n-Si have been done. These are a new group of materials heterostructures: Au/SWCNTs/P3OT/*n*-Si/Al, Au/SWCNTs/*n*-Si/Al, ITO/SWCNTs/Al and Al/SWCNTs/P3OT/ITO for application in photovoltaic.

The technology for obtaining SWCNTs was developed in the Centre for Surface Science and Nanotechnology, from Polytechnic University of Bucharest, with application of excimer laser ablation in vacuum environment. Laser-assisted SWCNTs formation has been performed in a novel custom designed laser ablation chamber for UV laser vaporization experiments. SWCNTs were produced by ablating a Co/Ni-doped graphite target by means of a Compex Pro 205 (Coherent) pulsed KrF excimer laser (wavelength 248 nm; pulse length 25 ns; repetition rate of 30 Hz and laser intensity 3:5 x 108 W/cm^2).

The laser beam was focused on a 20 mm^2 spot perpendicularly to the target surface. In order to ensure a uniform target surface ablation, the target was rotated during ablation. The graphite target was fabricated by a novel preparation route, by adding Co/Ni (with 0.6 at% Co and 0.6 at% Ni) catalyst powders to a carbon adhesive, Graphite Cement GC-8010B (supplied by Metal Forming).

Unpurified and purified SWCNTs were added to distilled water and then introduced in an ultrasonic bath to disperse the nanoparticles for 15 min. Using a thin dropper a droplet was collected from the solution and studied by transmission electron microscopy (TEM) equipment. The high quality of produced SWCNTs was proved by careful morphological analysis. The TEM

imagines (Fig.1) show that the obtained carbon single walled nanotubes have a diameter ranging from 1.2 to 1.4 nm, which is confirmed also by micro Raman spectroscopy measurements. More details of the synthesis process and electron microscopy investigations are given in [9,10].

Preparation of the composite solutions was performed using a series of mixing and sonication steps. The necessary amount of regioregular P30T was dissolved in chloroform using ultrasonication to achieve the concentration 15 mg/ml in solution. Composite dispersion was performed by combining the appropriate mass of purified SWCNTs to the P3OT solution at desired doping levels. The final solution was deposited on a 2.5 x 2.5 cm^2 ITO glass substrate or n-Si by drop cast and spin-coating technique (1500 rpm) at room temperature. To complete the solar cell fabrication, Al and Au contacts was applied to the heterostructure composites layers by thermal evaporation under vacuum with standard shadow mask configurations (Fig. 2).

Optical absorption was determined using a combination of UV-visible transmission spectra measured with a SPECORD UV/VIS spectrophotometer.

The I-V characteristics were monitored using a E5-11 source measurement unit connected to PC.

The as-produced SWCNTs contain two types of impurities: transition metal catalyst particles (typically Co and Ni) and carbon species, which include amorphous carbon, fullerenes, multishell carbon nanocapsules, and nanocrystalline graphite. A representative TEM image of the ablated products after purification step is shown in Fig. 1). It can be seen that all most of the catalyst particles have been removed. Moreover, a notable quantity of carbonaceous species is observed on recorded pictures. In order to remove this carbonaceous species, further thermal oxidation treatments should be performing on the as chemical purified samples [10.

The nanocomposites and solar cell heterostructures were obtained by deposition of SWCNTs and P3OT solutions mixed in a solvent, compatible for both components. SWCNTs have been dispersed in the solvent and mixed together with the solution containing P3OT. In this way gel solutions with different ratio of SWCNTs:P3OT:n-Si were obtained for experimental investigations. Deposition of thin layers of mixed solution was carried out on n-Si or ITO and SnO_2 coated glass substrates by spin-coating or casting methods followed by drying them up. The thickness of prepared thin films varies depending on the condition of deposition from 0.2 to 2.0 μm with random orientation of carbon nanotubes. On the outer surface of Al layer an electrical contact was deposited. For measures of organic photovoltaic cells transparent glass substrates with ITO or SnO_2 coating have been used. Both ITO and SnO_2 layers are transparent for light, and serve as electrodes for solar cell element.

The samples of the investigated solar cells structures as illustrated in Fig.2 have been investigated and optical absorption spectra of SWCNTs and the composites SWCNTs/P3OT have been also registered (Fig.3,4). The optical band gap (E_g) of the nanocomposite was estimated to be around 2.4 eV, which correlates with the values reported in the literature for the P3OT optical band-gap. The optical band gap (2.4 eV) is in very good agreement with those values reported in the literature [8]. At room temperature E_g for P3OT corresponds to the difference between the energy position of highest occupied molecular orbital (HOMO), which is estimated at ≈ 5.4 eV, and LUMO, respectively ≈ 3 eV [7,8] proving the quality of prepared structures.

All structures exhibits good photosensitivity in the visible spectrum. The current-voltage characteristics of the structures have measured both in the dark and under light illumination through the ITO or SnO_2 layers. Experimental results on optical, electrical and photoelectric data are interpreted in the framework of the theoretical model which considers the process of exciton formation in SWCNTs as a result of photon absorption, with subsequent diffusion to the boundaries of the contact between SWCNTs/P3OT, its further dissociation into an electron and a hole, and final transition of the hole to P3OT. At the final stage of the process the charge carriers move separately to the external electrodes, generating the contact potential difference.

Experimental results obtained from optical, electrical, and photoelectrical measurements indicate on promising perspective for integration of SWCNTs structure in fabrication of 3D generation solar cells. In this context we suppose that application of conductive polymer nanocomposites with low specific density resistance could be a good solution.

The logarithmic current density (J) versus the voltage (V) of the P30T/SWCNTS hetrostructures as photovoltaic cell in dark and under light is plotted in Fig. 5. The as recorded current density J_{SC} = 0.09 mA/cm^2 under light is in good agreement with values reported by work [9]. However, even if the current density fits the reported values, its magnitude is slightly higher for higher values of applied voltages. This behavior could be related with the leakage currents of high magnitude in the measured structures. It is reported by the literature that the leakage current is caused by the current through local defects in the organic hetero-junction or due to the shunts at the edges of solar cells [8]. In our case, the magnitude of the leakage currents is more related with local defects induced into the organic heterojunction by the presence of the residual metallic catalysts used during the laser ablation synthesis, also observed on TEM images. Further purification experiments are in progress in order to establish the optimal parameters for a complete digestion of metals by chemical attack. Thus, a drop of the leakage current is expected. Next experiments on SWCNTs nanocomposites and structures on their base for solar cells application are in progress in order to identify other conducting polymers for formation of SWCNT-based nanocomposites and optimal parameters for solar cell elements.

III CONCLUSIONS

Experimental results obtained from optical, electrical, and photoelectrical measurements indicate on promising perspective for integration of SWCNTs structure in fabrication of 3D generation solar cells. In this context we suppose that application of conductive polymer in nanocomposites with low specific density resistance could be a good solution. Further experiments on SWCNTs nanocomposites and structures on their base

are in progress in order to identify other conducting polymers for formation of SWCNT-based nanocomposites and optimization of the parameters for solar cell elements.

SWCNTs were successful synthesized in a novel custom design ablation chamber. The high quality of produced SWCNTs was proved by careful morphological analysis. The TEM recorded imagines shown that the obtained SWCNTs has a diameter ranging from 1.2 to 1.4 nm, values confirmed also by micro Raman spectroscopy analysis. The produced mixtures of Co/Ni catalysts were used for preparing the ablated targets following a new preparation technique. The influence of an acid digestion of metallic catalysts on the ablation products was pointed out by means of TEM analysis. Results about the optical and electrical measurements make evident the promising integration of SWCNTs on the fabrication of the 3D generation of solar cells.

We show that SWCNTs work as an active photosensing material to n-type Si junctions. Thus, P3OT, SWCNTs and Si contribute to photocarrier generation. A high interfacial area between entrapped SWCNTs and n-Si should result in efficient photocarriers separation and collection at external electrodes. In addition, n-Si carrier mobility (up to approximately 1 $cm^2/(V\ s)$ is higher than amorphous Si, and therefore, n-Si is more suitable for PV applications than other amorphous Si or colloidal semiconducting materials. The proper design of the SWCNTs structure enables localization of solar light, which minimizes reflection and scattering losses.

Our innovative solar cells of third generation are based on SWCNTs band gap structures using their exceptional optical and electrical properties.

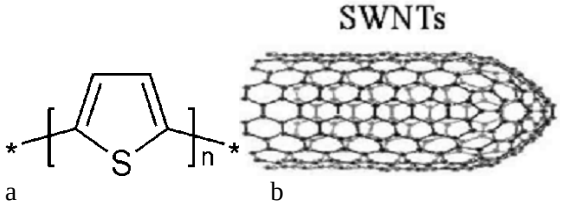


Fig. 1. The chemical structure of P3OT (a) and images of a SWCNTs (b).

The cost-effective processing, light-weight, flexibility, and robustness are important to consumer and industrial needs for clean energy technology approach. We believe that the proposed innovative solar cells could find their niche in the market of electronic and communication equipment, airborne applications, offshore platforms, and emergency power systems.

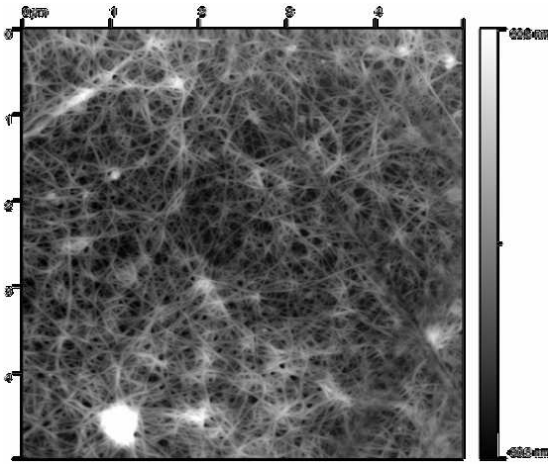


Fig. 2. TEM image showing the distribute on of SWCNTs

The major advantages of our solar cells over other organic/composite/hybrid of third-generation PVs are high carrier mobility of SWCNTs (> 200000 $cm^2/(V\ s)$), and their absorption in spectral range and large interfacial area (specific surface area to volume 200 – 100 m^2/cm^3) between entrapped SWCNT and n-Si enabling efficient photocarriers generation and capability for the proper design crystals to minimize optical losses in thin film, feature of cost-effective fabrication method (solution deposition).

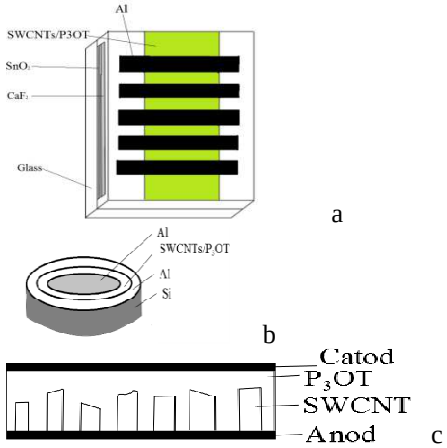


Fig. 2. Scheme of various heterostructures investigated in this work.

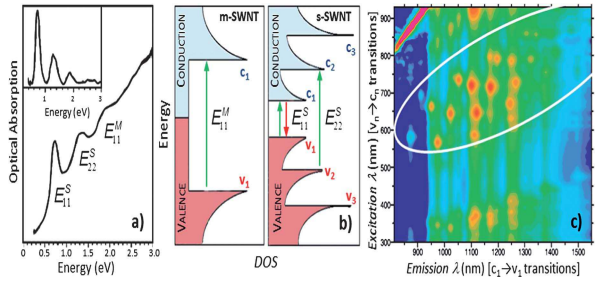


Fig. 3. Characteristics of single wall carbon nanotubes: optical absorption (a) energy structure (b) and their distribution in heterostructures (c).

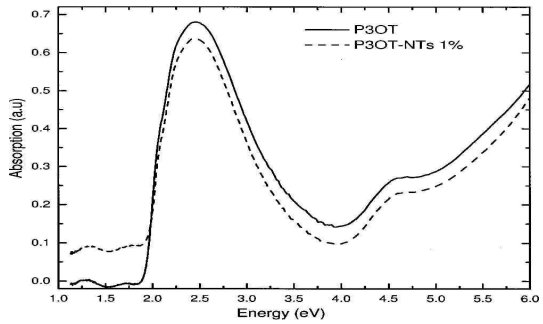


FIG. 2. Absorption spectra of a 60 nm thick layer of P3OT and of a P3OT-SWCNTs composite **(**1 wt % Nts) on a quartz substrate. The optical band gap of the composite is at 2.4 eV

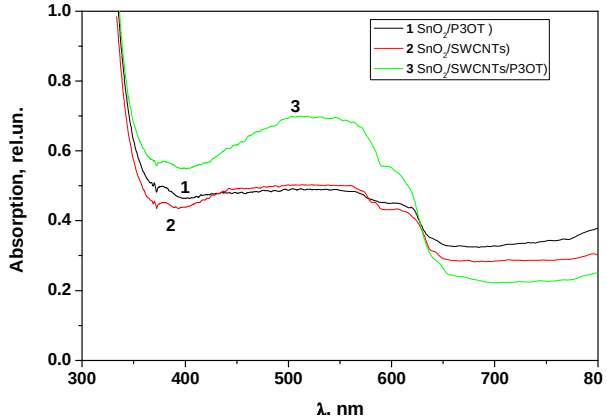
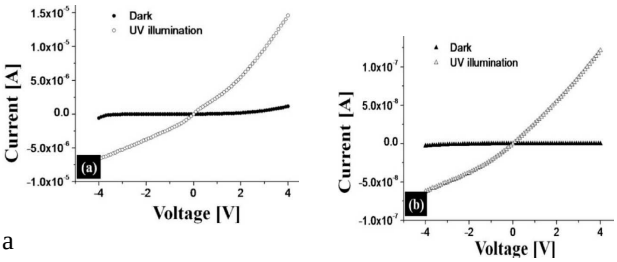


Fig.4. Distribuția spectrală a fotoexcitarii in rezultatul absorbției de lumina a structurilor de tip „sandwich” SnO_2/SWCNTs/P30T.



a b

Fig. 5. I-V characteristic of the heterostructures (a) Al/SWCNTs/P3OT/n-Si/Al and (b) Al/SWCNTs/P3OT/Al.

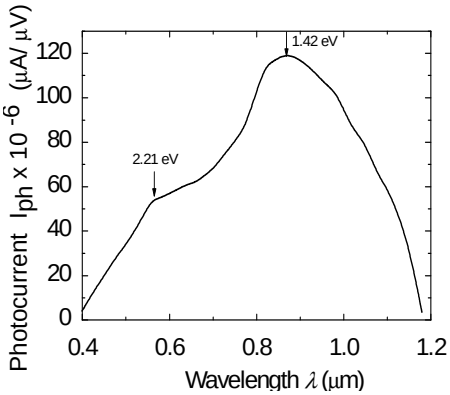


Fig. 6. Spectral distribution of photocurrent in heterostructure Al/SWCNTs/P3OT/Al, measured at V = +1.0 V to upper illuminated electrode.

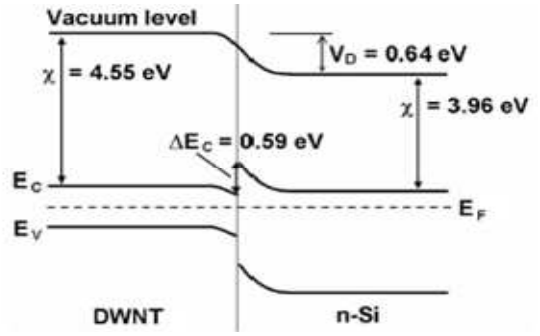


Fig. 7. The energetic band diagram of HS SWCNTs/n-Si/

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