Synergistic Effect of Single-Walled Carbon Nanotubes and PEDOT:PSS in Thin Film Amorphous Silicon Hybrid Solar Cell

Alena K. Alekseeva, Pramod Mulbagal Rajanna,* Anton S. Anisimov, Oleg Sergeev, Sergei Bereznev, and Albert G. Nasibulin*

We propose a simple fabrication method of thin film hybrid solar cells by combining single-walled carbon nanotubes (SWCNTs) and poly(3,4-ethylene-dioxythiophene) polystyrene sulfonate (PEDOT:PSS) with hydrogenated amorphous silicon (a-Si:H). Electrically conductive polymer PEDOT:PSS introduced in a randomly oriented network of SWCNTs forms a coupled continuous heterojunction between PEDOT:PSS–SWCNT and a-Si:H. We fabricated and compared the performance of SWCNT/a-Si:H, PEDOT:PSS/a-Si:H and PEDOT:PSS–SWCNT/a-Si:H solar cells. The PEDOT:PSS–SWCNT/a-Si:H solar cells resulted to have an efficiency of 1.6% with state-of-the-art fill factor and open circuit voltage of 54% and 0.803 V, respectively.

1. Introduction

Under current development of solar cells, thin film technology with minimum material consumption allows fabrication of low cost devices. Amorphous silicon (a-Si) is promising material due to its unique mechanical, electrical and optical properties, which makes them compatible with roll-to-roll manufacturing and flexible device concept. Solar cells based on hydrogenated amorphous silicon (a-Si:H) usually have either p-i-n or n-i-p architecture. The presence of intrinsic layer is essential for extended electric field at the origin of photo-generation between the p- and n-layers. This assists in carrier travel and immediate separation of electrons and holes to avoid recombination due to extremely short travel distances caused by shorter lifetime of photo-generated carriers in a-Si:H. Typically in a-Si:H thin film, the p-doped layer is obtained by plasma enhanced chemical vapor deposition of gas mixture containing toxic diborane (B2H6) gas at relatively high temperature.

An alternative to replace p-a-Si:H layer is a SWCNT film. Exposed to air, SWCNTs absorb oxygen and becomes p-type semiconductor. The optoelectrical, chemical and mechanical properties of SWCNTs make them applicable in solar cells as a p-layer. SWCNT films on a contact with i-a-Si:H layer form heterojunction. It is important to have a continuous contact between SWCNTs and a-Si:H for an optimum charge transfer. If otherwise, it results in a very high resistance at the SWCNT/a-Si:H interface and extremely poor J–V characteristics. Several studies have reported hybrid solar cells based on amorphous silicon with SWCNTs exhibiting poor J–V characteristics, where fill factor (FF) and open circuit voltage (Voc) equals only to 20% and 0.35 V,[9] 19% and 0.5 V,[10] 28% and 0.3 V,[11] respectively.

In this paper, in order to obtain heterojunctions with continuous contact between SWCNT and a-Si:H we introduced an electrically conductive polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) in the SWCNT films. We compared the photovoltaic performance of SWCNT/a-Si:H, PEDOT:PSS/a-Si:H and PEDOT:PSS–SWCNT/a-Si:H solar cells. The combination of SWCNTs and PEDOT:PSS have better J–V performance with the state-of-the-art performance of FF = 54% and Voc = 0.803 V for such type of devices.

2. Experimental Section

In the current study three types of solar cells were fabricated at the same conditions: SWCNT/a-Si:H, PEDOT:PSS/a-Si:H and
PEDOT:PSS-SWCNT/a-Si:H. The fabrication process of the hybrid devices are as described. Al:ZnO, used as a back contact, was deposited on the glass substrates by sputtering. Plasma enhanced chemical vapor deposition (PECVD) with silane (SiH₄), hydrogen (H₂) and phosphine (PH₃) was used for deposition of n-doped (30 nm thickness) and intrinsic (250 nm thickness) layers of hydrogenated amorphous silicon on top of the Al:ZnO. In order to open the back contact, 6M of KOH aqueous solution was drop-cast on the top of the a-Si:H layers. The speed of chemical reaction of KOH with a-Si:H was increased by heating the substrates up to 160 °C on the hot plate. After 5 s, KOH was removed with distilled water. The obtained resistivity of the back contact was around 17 ohms-cm. Subsequently, natural oxide layer on a-Si:H was removed by HF vapor treatment for 10 s.

SWCNTs were synthesized by an aerosol chemical vapor deposition method described elsewhere. SWCNT films collected on a nitrocellulose filter at the outlet of the reactor are a mixture of metallic and semiconducting nanotubes, which exposed to air, demonstrates p-type conductivity. Thickness of the film was controlled by the collection time. SWCNT films with thickness of 60 nm were deposited on i-a-Si:H films using dry deposition method.

An electrically conductive PEDOT:PSS polymer, was chosen for application in SWCNT/i-a-Si:H heterojunction due to its high hole mobility and environmental stability. PEDOT:PSS was spin coated on top of the SWCNT/i-a-Si:H structures for 90 s at 3000 rpm with an acceleration speed of 800 rpm s⁻¹ from the mixture of aqueous suspension of 5 ml PEDOT:PSS (1.3 wt.% Sigma–Aldrich) with glycerine, N-methylpyrrolidone and isopropanol (IPA) in a ratio of 1:2:19 respectively.

Lastly, to evaporate residues from the solvent and to activate the acceptor states of the polymer the devices were annealed on the hot plate at a temperature of 160 °C for 10 min. Subsequent to annealing rectangular shaped front contacts were made at the edges out of silver paste on top of the structure. To harden the front contacts the devices were annealed at 160 °C for 5 min on the hot plate. The active area of the solar cells was around 0.5 cm². The schematic structure of the completed device is shown in Figure 1(a).

The current density–voltage (J–V) characteristics, which determine the performance of the fabricated solar cells, were obtained by a source-measure unit Keithley 2400 in a solar simulator Newport Corporation, Oriel Sol3A Class AAA (AM 1.5G illumination, intensity 100 mW cm⁻², temperature 25 °C). The external quantum efficiency (EQE) of the hybrid solar cells was measured using spectral response measurement system Bentham PVE300. The cross-section of PEDOT:PSS-SWCNT/a-Si solar cell was explored with Carl Zeiss NEON 40 EsB field emission SEM combining GEMINI lens design with an advanced Canion FIB column (equipped with Gallium liquid metal ion source). Prior to investigation, the sample was coated with thin metal contrast layer. The cross-section was formed with focused ion beam at 2 μA emission current, 30 kV acceleration voltage and 10 nA of milling current. Multi-step polishing was performed at milling currents from 200 to 20 pA. The SEM image was obtained at 20 kV acceleration voltage using in-lens secondary electron detectors. The work function was measured using Kelvin Probe Force Microscopy from Asylum Research – Cypher ES. Figure 1(b) show the cross-section SEM image.

3. Results and Discussion

The current density-voltage (J–V) characteristics of the three types of hybrid solar cells: PEDOT:PSS-SWCNT/a-Si:H, PEDOT: PSS/a-Si:H and SWCNT/a-Si:H were measured in the dark (Figure 2a) and under illumination (Figure 2b) with inset of a fabricated hybrid solar cell. We hereby clarify that only the best working cells are reported here for each of the three types of hybrid solar cells. The J–V characteristics measured in the dark clearly reveals the diode properties for all the three types of hybrid solar cells. Analyzing the dark J–V curve for all three types of solar cells, PEDOT:PSS-SWCNT/a-Si:H solar cell exhibits a higher reverse saturation current density (J₀) than the other two solar cells, while the shunt resistance (Rₛ) and diode ideality factor (n) are nearly the same. The calculated values for PEDOT:PSS-SWCNT/a-Si:H solar cell are respectively J₀ = 3.40 ± 0.01 x 10⁻⁴ mA cm⁻², Rₛ = 75.0 ± 0.5 MΩ cm⁻², Rₛ = 30.0 ± 0.5 kΩ cm⁻², and n = 1.05 ± 0.05.

The J–V curve shifts under illumination showing a typical photovoltaic behavior for all the three hybrid solar cells. However, solar cell with PEDOT:PSS-SWCNT and a-Si:H shows more desirable J–V characteristics than those with only PEDOT:PSS or SWCNT film. The PEDOT:PSS-SWCNT/a-Si:H solar cell exhibits a better performance: a short-circuit current-density of Jₘ = 3.56 ± 0.10 mA cm⁻², an open-circuit voltage of Vₜₐₓ = 0.803 ± 0.003 V, a fill factor of FF = 54 ± 3% and a

![Figure 1](image-url). (a) Fabricated PEDOT:PSS-SWCNT/a-Si:H solar cell; (b) cross-section SEM image of a PEDOT:PSS-SWCNT/a-Si:H solar cell.
efficiency of $\eta = 1.57 \pm 0.03\%$. Whereas, for the PEDOT:PSS/a-Si:H and SWCNT/a-Si:H solar cells $J_{sc}$ equal to 3.03 $\pm$ 0.10 and 2.80 $\pm$ 0.10 mA cm$^{-2}$, $V_{oc}$ equal to 0.710 $\pm$ 0.003 and 0.700 $\pm$ 0.003 V, FF equal to 40.4 $\pm$ 3.0% and 45.2 $\pm$ 3.0%, and $\eta$ equal to 1.03 $\pm$ 0.03% and 1.10 $\pm$ 0.03%, respectively (Table 1).

It is worth noting that fill factor and open circuit voltage of PEDOT:PSS-SWCNT/a-Si:H hybrid solar cell is found to be the state-of-the-art exceeding previously reported amorphous silicon hybrid solar cells using either SWCNTs or conductive polymer.[9–11,17–20] This can be explained by the introduction of PEDOT:PSS which fills the micropores of SWCNT film and forms continuous contact with i-a-Si:H. This leads to the formation of coupled heterojunctions between SWCNT/i-a-Si:H and PEDOT:PSS/i-a-Si:H rather than a usual single-heterojunction between SWCNT/i-a-Si:H as has been previously reported. Thus, in the PEDOT:PSS-SWCNT/i-a-Si:H solar cell, beyond the heterojunctions formed by PEDOT:PSS and SWCNT individually, their combined effect is more important. As shown in Figure 2 (d), the work function of SWCNT, PEDOT:PSS and PEDOT:PSS-SWCNT composite film are 4.6, 5.2, and 4.85 eV, respectively. The i-a-Si:H Fermi level position and mobility gap is taken from the literature.[21] The HOMO-LUMO gap of the PEDOT:PSS is estimated to be 1.5 eV.[22] The Fermi level offset between the PEDOT:PSS-SWCNT composite film produces a built-in voltage ($V_{bi}$) of about 0.7 V, which is larger than that of a SWCNT network and PEDOT:PSS individually. The estimated $V_{bi}$ is close to the measured $V_{oc}$ of PEDOT:PSS-SWCNT/i-a-Si:H and SWCNT/i-a-Si:H solar cells. Moreover, the high $V_{oc}$ in PEDOT:PSS/i-a-Si:H solar cell can be attributed to the high band gap of PEDOT:PSS, while the lower FF is possibly

Table 1. $J$–$V$ parameters of the fabricated solar cells: open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF), and power conversion efficiency ($\eta$).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS–SWCNT/a-Si:H</td>
<td>0.803</td>
<td>3.56</td>
<td>54.0</td>
<td>1.57</td>
</tr>
<tr>
<td>PEDOT:PSS/a-Si:H</td>
<td>0.710</td>
<td>3.03</td>
<td>40.4</td>
<td>1.03</td>
</tr>
<tr>
<td>SWCNT/a-Si:H</td>
<td>0.700</td>
<td>2.80</td>
<td>45.2</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Figure 2. (a) Dark and (b) photo $J$–$V$ characteristics of PEDOT:PSS–SWCNT/a-Si:H, PEDOT:PSS/a-Si:H and SWCNT/a-Si:H hybrid solar cells, with inset of a fabricated PEDOT:PSS-CNT/i-a-Si hybrid solar cell. (c) EQE spectrum; (d) schematic band diagram of the fabricated devices with the band offset at PEDOT:PSS/i-a-Si:H marked in red.
due to the high resistivity of PEDOT:PSS film and stronger recombination near the $V_{oc}$. A similar observation for C-Si has been reported by Hu et al. for PEDOT:PSS/Si nanowire hybrid solar cell.[23]

External quantum efficiency (EQE) measurements of all the three types of hybrid solar cells are shown in Figure 2(c). EQE spectrum for PEDOT:PSS-SWCNT/a-Si:H shows a higher EQE saturation value of 24% than the other two solar cells. Additionally, for SWCNT/a-Si:H solar cell shows a strong blue-shift which can be due to the strong absorbance of SWCNTs. However, all three EQE spectrums of the hybrid solar cells resembles to the standard a-Si:H solar cell in a wavelength of 300–800 nm. The current density from EQE and $J–V$ curve are in close match for all three solar cells. The sharp decrease in the EQE beyond 700 nm can be attributed to the a-Si:H mobility gap (1.7 eV).

Combining the $J–V$ parameters and EQE, the following analysis was made. The fabricated solar cell of PEDOT:PSS-SWCNT/a-Si:H exhibits the state-of-the-art fill factor and open circuit voltage; while the current density is lower due to an increased absorption of incident photons at the PEDOT:PSS-SWCNT layer (p-layer). Hence, the p-layer needs to be optimized in order to increase absorption and photo-generation of charge carriers in the i-a-Si:H. This potentially will lead to a higher photo-generated current density and efficiency.

4. Conclusion

We presented the fabrication method of a hybrid thin film amorphous silicon solar cell with p-layer from a combination of PEDOT:PSS and SWCNTs. The micropores in the SWCNTs were filled by PEDOT:PSS providing a continuous junction of the PEDOT:PSS–SWCNT mixture with a-Si:H. We exploited the synergistic effect of combination of PEDOT:PSS with SWCNTs on the properties of solar cells. We fabricated a PEDOT:PSS-SWCNT/a-Si:H hybrid solar cell with a state-of-the-art FF = 54% and $V_{oc} = 0.803 \text{ V}$, based on analysis of three types of solar cells fabricated under the same conditions. The efficiency of the as-designed PEDOT:PSS–SWCNT/a-Si:H solar cell is 1.6%, which has been enhanced by about 31% and 38% in comparison to the SWCNT/a-Si:H (1.1%) and PEDOT:PSS/a-Si:H (1%) solar cell fabricated using the same materials, respectively. Our current approach with the proposed materials makes the cells compatible to a roll-to-roll manufacturing process and allows utilizing them for flexible applications.

Acknowledgements

This work is supported by the Ministry of Education and Science of the Russian Federation through ERA-NET project (agreement 14.618.21.0003; identification number RFME-FI61815 × 0003). The authors also would like to acknowledge financial support from Estonian Research Council (project ETAG15028) and from German Federal Ministry of Education and Research (project BMBF, reference number 01DJ15030).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

amorphous materials, PEDOT:PSS, silicon, single-walled carbon nanotubes, solar cells, thin films

Received: October 1, 2017
Revised: November 16, 2017
Published online: