

PEDOT:PSS/planar-Si Hybrid Solar Cells with 12.70% Efficiency

Yuanfan Zhao¹, Dan Xie¹, Jianlong Xu¹, Tingting Feng¹, Xiaowen Zhang¹,
Tianling Ren¹, Miao Zhu², and Hongwei Zhu²

¹Tsinghua National Laboratory for Information Science and Technology (TNList)

Institute of Microelectronics, Tsinghua University, Beijing 100084, China

²State Key Laboratory of New Ceramics and Fine Processing

Key Laboratory of Materials Processing Technology of MOE

School of Materials Science and Engineering, Tsinghua University, China

Abstract— In the paper, we demonstrate efficient hybrid solar cells based on the Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) and planar Silicon with a hydrogen-terminated Si (H-Si) surface. PEDOT:PSS/planar Si hybrid solar cells show high power conversion efficiency (PCE) of 8.27 ~ 12.70%. The cell with the PCE of 12.70% presents short circuit current density (J_{SC}), open circuit voltage (V_{OC}) and fill factor (FF) of 20.92 mA/cm², 0.63 V and 70.26%, respectively. The better contact of PEDOT:PSS film with the Si substrate is contributed to the formation of effective PEDOT:PSS/Si heterojunction, resulting in the enhanced photovoltaic performances.

1. INTRODUCTION

Although conventional crystalline silicon solar cells have achieved much higher power conversion efficiency (PCE) [1], they suffer from expensive fabrication costs due to their high temperature steps, material scarcity as well as complicated equipments [2]. Therefore, some alternative solar cells based on new device structures and materials have been designed and reported. Among them, the conductive polymer Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonic acid) (PEDOT:PSS) has attracted great interests owing to its high transparency, excellent conductivity and mechanical flexibility which is a promising candidate for further solar cell materials [3].

In the PEDOT:PSS/planar Si hybrid solar cells, the PEDOT:PSS works as a hole collecting layer and form a heterojunction with Si to induce a built-in electric field where the photo-generated carriers are separated to generate photocurrent [4]. Generally, in the process of solar cells preparation, a diluted HF solution treatment is needed to remove the native oxide layer on Si substrates to obtain clean silicon surface. After the HF solution treatment, H-Si bonds terminated surfaces are formed [5]. According to the reports [6, 7], however, almost all the PEDOT:PSS/planar Si cells with a H-Si interface achieve lower PCE probably due to difficulty of PEDOT:PSS film formation on the Si surface. In order to overcome it, the diluted HF treated Si substrates are exposed in air for some hours to form an ultrathin SiO₂ layer, which brings in a favorable contact between PEDOT:PSS and planar Si resulting in good interface for photo-excited carrier separation [8, 9]. However, the oxide layer between PEDOT:PSS film and Si substrate will degrade its performance due to the higher series resistance (R_S) [7].

Recently, Liu et al. have reported that some surfactants such as Triton X-100, etc. are added into the PEDOT:PSS solution [10, 11] to enhance its wettability and make PEDOT:PSS well contact with the hydrophobic H-Si surface [12] leading to better diode characteristics. Other ways such as modifying PEDOT:PSS solutions with other polymers could improve the built-in potential as well as suppress photo-generated carrier recombination [10, 12] or increase the hole mobility of the PEDOT:PSS films [11]. However, any polymer additives added into PEDOT:PSS solutions will change its perfect inherent electrical properties, thus it is necessary to further investigate the PEDOT:PSS/planar Si solar cells to improve the solar cell properties including alternative cell structure or the process optimization.

In our work, we designed a new solar cell structure with pristine PEDOT:PSS solutions being deposited on the planar crystalline Si that achieves high PCE of 8.27 ~ 12.70%. In our PEDOT:PSS/planar Si hybrid solar cells, junction region between PEDOT:PSS and planar Si is defined, which is surrounded by the SiO₂ insulating region. The hydrophilic insulating region can make sure better contact between PEDOT:PSS and planar Si in junction region, which is contributed to the formation of the PEDOT:PSS/Si heterojunction. The preparation processes are discussed and the results are investigated.

2. EXPERIMENT

The PEDOT:PSS/planar Si hybrid solar cells were fabricated using single crystal n-type Si (100) wafers with a resistivity of $2 \sim 3 \Omega \cdot \text{cm}$ and the thickness of about $550 \mu\text{m}$ (Figure 1(a)).

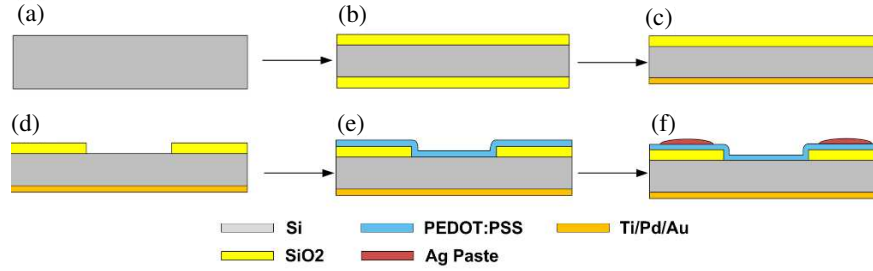


Figure 1: Illustration of the PEDOT:PSS/Si hybrid solar cell preparing processes. (a) The start silicon wafer. (b) A 300 nm-thick SiO_2 layer was thermally grown on the silicon surface and then the backside was etched by HF solution. (c) Ti/Pd/Au layers of 5/10/30 nm was deposited backside as bottom electrodes. (d) The $3 \times 3 \text{ mm}^2$ junction area was patterned by lithography and the SiO_2 layer was then etched until Si surface by RIE. (e) The PEDOT:PSS solutions was spin-coated on Si substrate. (f) Silver paste was applied onto the PEDOT:PSS film as top electrodes.

A 300 nm-thick SiO_2 layer was thermally grown on the silicon surface as the insulating layer (Figure 1(b)). Ti/Pd/Au layers of 5/10/30 nm were deposited backside by electron beam evaporation as bottom electrodes (Figure 1(c)). The $3 \times 3 \text{ mm}^2$ junction area was patterned by lithography and the SiO_2 layer was then etched until Si surface by reactive ion etching (RIE) (Figure 1(d)). After that, the wafer were cut into small pieces as the cell substrates. The substrates were dipped in diluted HF solution for 10 s to remove the native oxide layer of junction region immediately after being ultrasonically cleaned in acetone, ethanol and deionized (DI) water. The PEDOT:PSS (Clevios, PH1000, 20 wt.%) solutions mixed with Dimethyl Sulfoxide (DMSO, 5 wt.%) were then spin-coated onto the Si substrates (Figure 1(e)), followed by a thermal annealing process at 140° for 10 min. Finally, silver paste was applied onto the PEDOT:PSS film as top electrode. Figure 1(f) shows the structural schematic of the finished PEDOT:PSS/Si hybrid solar cell.

3. RESULTS

The top-view SEM image of PEDOT:PSS film is shown in Figure 2(a). It can be seen that the spin-coated PEDOT:PSS film is uniform and almost no defect exists in it. Figure 2(b) presents the cross-sectional SEM image of the PEDOT:PSS/planar Si solar cell. It exhibits a clear and good interface between PEDOT:PSS film and Si substrate and demonstrates the thickness of PEDOT:PSS film is about 56 nm.

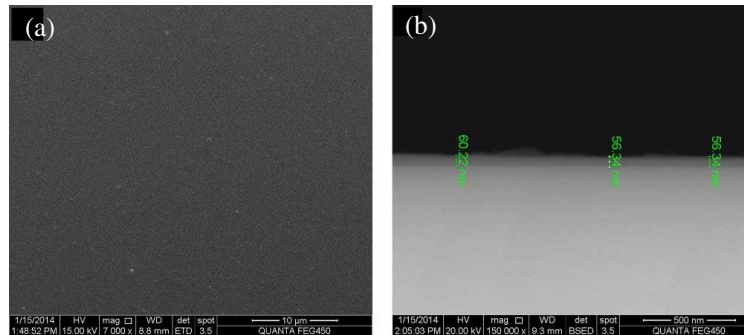


Figure 2: (a) Top-view SEM image of the PEDOT:PSS film. (b) Cross-sectional SEM image of the solar cell.

In our experiments, 16 solar cells were fabricated and a PCE distribution of $8.27 \sim 12.70\%$ with an average PCE of 9.94% was achieved. The highest PCE of 12.70% exhibited J_{SC} , V_{OC} and FF of 20.92 mA/cm^2 , 0.63 V and 70.26% , respectively. Figure 3(a) shows the Current density-Voltage (J - V) characteristics of five representing solar cells under illumination of AM1.5G, 73 mW/cm^2

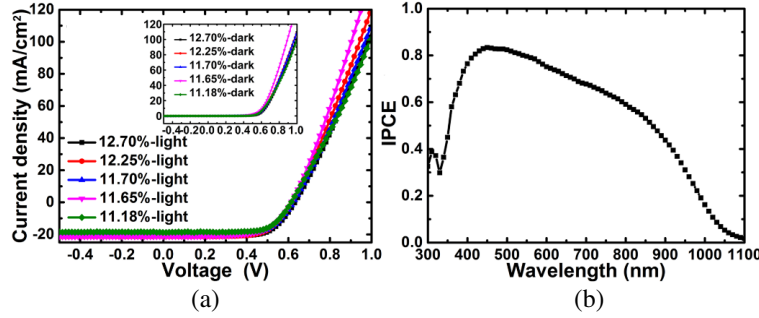


Figure 3: (a) The current density-voltage (J - V) characteristics of five representing solar cells under illumination of AM 1.5G, 73 mW/cm² simulated sunlight. The inset shows the corresponding J - V curves of such five solar cells in dark. (b) The IPCE spectrum of the one typical solar cells.

simulated sunlight calibrated by a standard cell unit, and Table 1 shows their photovoltaic parameters of J_{SC} , V_{OC} , FF , PCE, R_S and shunt resistance (R_{SH}). Standard diode characteristics can be found in both dark and light J - V curves. The cells also has a lower R_S , a large R_{SH} and a higher V_{OC} , FF which together account for the high PCE. Figure 3(b) presents the monochromatic incident photon-to-electron conversion efficiency (IPCE) characteristics of one typical sample. It indicates that the cells could absorb the photons whose wavelength is less than 1100 nm and the visible light (350 ~ 770 nm) can be absorbed strongly with an average IPCE of 73.46% consistent with the high J_{SC} .

Table 1: Summary of the photoelectric parameters of the typical solar cells.

No.	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	R_S ($\Omega \cdot \text{cm}^2$)	R_{SH} ($\Omega \cdot \text{cm}^2$)	PCE (%)
1	630.68	20.92	70.26	3.86	2.36E5	12.70
2	615.62	21.30	68.17	3.68	2.53E5	12.25
3	623.14	20.23	67.78	3.65	1.26E3	11.70
4	608.09	21.29	65.67	2.80	4.76E3	11.65
5	608.08	18.40	72.92	4.40	2.87E4	11.18

4. DISCUSSION

During our experiments, it is found that the PEDOT:PSS aqueous solutions can't form good films on the hydrophobic H-Si surface, which is the main reason for the poor performances of the PEDOT:PSS/planar Si structure solar cells with H-Si surface. However, our designed cell structure with effective junction region and SiO₂ insulating region could solve this problem. The SiO₂ insulating region surrounding the junction area is hydrophilic [13] which lowers the PEDOT:PSS solutions surface tension and makes it spread onto the junction region with a very small contact angle, resulting in uniform and high quality PEDOT:PSS film on the silicon surface. In this way, PEDOT:PSS forms a direct contact with H-Si surface which can be proved in Figure 2(b), resulting in effective PEDOT:PSS/Si heterojunction and better photovoltaic performances.

5. CONCLUSION

In summary, the PEDOT:PSS/planar Si hybrid solar cells with high PCE value of 8.27 ~ 12.70% have been fabricated and investigated. The solar cell with a PCE value of 12.70% exhibited J_{SC} , V_{OC} and FF of 20.92 mA/cm², 0.63 V and 70%, respectively. The device design of junction region and SiO₂ insulating region can make sure the better contact between PEDOT:PSS film and planar Si, which is contributed to the formation of the PEDOT:PSS/Si heterojunction. Therefore, R_S is lower and R_{SH} is much higher, as well as the enhanced photovoltaic performances are obtained.

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