Four-terminal perovskite-silicon tandem solar cells for low light applications

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Abstract. Here novel high efficient semi-transparent perovskite solar cells (PSCs) based on ZrO$_2$ photoelectrodes were fabricated and were used as top elements in tandem systems with crystalline silicon (c-Si) solar cells in four-terminal configuration. The comparative analysis of photovoltaic parameters measured for PSCs, c-Si solar cells and PSC/c-Si tandem solar cells demonstrated that the use of ZrO$_2$ photoelectrodes allows to improve the PSC performance and to achieve efficiencies for PSC/c-Si tandem solar cell higher than for a standalone c-Si solar cell under varying illumination conditions.

1. Introduction

Nowadays the performance of conventional crystalline silicon (c-Si) solar cells under standard illumination conditions AM1.5G (1000 W/m$^2$) has nearly reached its theoretical maximum [1]. Furthermore, the power conversion efficiency (PCE) of c-Si solar cells drastically reduces as the light intensity decrease what limits their use in real weather conditions [2, 3]. To overcome these drawbacks an integration of c-Si solar cells as bottom elements into the tandem systems with top perovskite solar cells (PSCs) is provided [4]. Low cost and easily manufactured PSCs have attracted a considerable interest as the most demanded and cost-effective devices for tandem photovoltaics [5]. In contrast with c-Si solar cells PCE values of PSCs slightly decrease with light intensity drop and PSCs are able to perform under both low light and diffuse light conditions [3, 6].

In a typical PSC perovskite layer based on organic-inorganic hybrid compound with a common formula ABX$_3$, where A - CH$_3$NH$_3^+$, HC(NH$_2$)$_2^+$, B - Pb$^{2+}$, Sn$^{2+}$, X - I, Br, Cl, is deposited on the surface of nanostructured photoelectrode, usually TiO$_2$ [7, 8]. Using different types of photoelectrodes in PSCs allow to adjust the photoelectrical and optical characteristics of the top element and to optimize the configuration of perovskite-silicon (PSC/c-Si) tandem solar cells [9, 10].

In our previous works [11, 12] we demonstrated that very wide-bandgap nanostructured materials, like ZrO$_2$ with $E_g$ values of 5.26 and 5.53 eV for two direct band transitions, can be successfully used as photoelectrodes for PSCs. The incorporation of mesoscopic ZrO$_2$ layer into the PSCs with the standard architecture of glass/FTO/c-TiO$_2$/ZrO$_2$/CH$_3$NH$_2$PbI$_3$/Spiro-MeO-TAD/Au led to the improvement of photovoltaic (PV) performance of PSCs [12]. However, these PV devices cannot be used as top elements in tandem systems because of low optical transparency of Spiro-MeO-TAD layer and Au contacts in the visible range of solar spectrum. PTAA or P3HT as a hole transporting material and PEDOT:PSS-based counter electrode can be used for fabrication semi-transparent PSCs [13, 14].
In this study novel high efficient semi-transparent PSCs based on nanostructured ZrO$_2$ photoelectrodes were fabricated under ambient conditions and were used as top elements in four-terminal PSC/c-Si solar cells. The PV performance of PSCs, standalone c-Si and PSC/Si tandem solar cells was studied under varying illumination conditions. The comparative analysis of obtained results revealed a new approach to develop high efficient PV devices for real weather conditions.

2. Experimental

2.1. Fabrication of PSCs

ZrO$_2$ nanoparticles were obtained by hydrothermal treatment of co-precipitated zirconium hydroxide from solution of the corresponding metal salt [15]. TiO$_2$ nanoparticles (P25 Aerioxide Degussa) were purchased from Sigma-Aldrich (USA) and were used for fabrication state-of-the-art TiO$_2$ photoelectrode [16]. Thick pastes from MO$_2$ (where M – Ti, Zr) nanopowders were prepared in organic solvent following the method described in [17]. The pastes were dissolved in ethanol in mass ratio 1:5 and spin-coated onto FTO conductive glass (Solaronix, 2 × 2 cm) covered by compact layer (c-TiO$_2$) with subsequent annealing at 500°C for 30 min. Mesoscopic MO$_2$ photoelectrodes with thickness 180-220 nm and with the area $1.5 \times 1.5$ cm were obtained.

Perovskite (CH$_3$NH$_3$PbI$_3$) layer was formed on MO$_2$ photoelectrode surface using a conventional one-step deposition method [18]. PTAA with Li-TFSI and 4-tert-Butylpyridine additives in toluene was used as a hole transporting material. It was drop-casted onto the perovskite surface and then covered by counter electrode based on PEDOT:PSS according to the procedure described elsewhere [13]. PTAA, PEDOT:PSS, Li-TFSI and 4-tert-Butylpyridine were purchased from Sigma Aldrich. PSC fabrication process was provided under ambient conditions with a relative humidity ~ 40%.

2.2. Construction of four-terminal PSC/c-Si tandem solar cells

All fabricated PSC devices based on mesoscopic MO$_2$ photoelectrodes were used as top elements in four-terminal PSC/c-Si tandem solar cells. The c-Si solar cells with the size $1.7 \times 2.1$ cm were kindly provided by the research group of G. Untila from Skobeltsyn Institute of Nuclear Physics, Moscow State University, and were mechanically stacked with PSCs according the scheme on Figure 1.

Figure 1. The scheme of four-terminal PSC/c-Si tandem solar cell.
2.3. Characterization studies

The measurements of the PV parameters for PSCs fabricated, for c-Si solar cells and for PSC/c-Si tandem solar cells were provided under standard illumination conditions of 1000 W/m$^2$ (AM1.5G) using Solar Simulator Abet 10500 (Abet Technologies, USA). Neutral optical filters (Marumi, Japan) providing a uniform decrease of the light flux in the spectral range of 300-1100 nm were used to reduce gradually the illumination intensity from 1000 W/m$^2$ to 10 W/m$^2$. Illumination intensity values were monitored using reference cell (Abet Technologies, USA). PSCs and c-Si solar cells were covered by masks limiting active area to $1 \times 1$ cm.

The current–voltage ($J$–$V$) characteristics were measured by Semiconductor Characterization System 4200-SCS (Keithley, USA). The external quantum efficiency (EQE) spectra was recorded using QEX10 Solar Cell Quantum Efficiency Measurement System (PV Measurements, USA) in the range of 300-1100 nm.

3. Results and Discussion

3.1. PSCs with MO$_2$ photoelectrodes

Semi-transparent PSCs with the cell architecture of glass/FTO/c-TiO$_2$/MO$_2$/CH$_3$NH$_3$PbI$_3$/PTAA/PEDOT:PSS/FTO/glass were fabricated under ambient conditions. Comparative $J$–$V$ curves for all samples recorded under standard illumination (1000 W/m$^2$, AM1.5G) and EQE spectra are shown in Figure 2. The PV parameters of PSCs including short circuit current density ($J_{SC}$), open circuit voltage ($V_{OC}$), fill factor ($FF$) and power conversion efficiency (PCE) are listed in Table 1.

![Figure 2. $J$–$V$ curves (left) and EQE spectra (right) for the PSC devices based on mesoscopic MO$_2$ photoelectrodes (1 – TiO$_2$, 2 – ZrO$_2$).](image)

**Table 1.** The PV characteristics of PSC devices based on mesoscopic MO$_2$ photoelectrodes.

|       | $J_{SC}$, mA/cm$^2$ | $V_{OC}$, V | $FF$, a.u. | PCE, %  |
|-------|---------------------|------------|-----------|--------|
| TiO$_2$ | 17.58 ± 0.17        | 0.99 ± 0.01 | 0.69 ± 0.01 | 11.94 ± 0.15 |
| ZrO$_2$ | 16.30 ± 0.24        | 1.06 ± 0.02 | 0.74 ± 0.02 | 12.72 ± 0.29 |

PSC devices with mesoscopic TiO$_2$ photoelectrodes demonstrate the average PCE of 11.94%. The substitution of TiO$_2$ layer by a very wide-bandgap material leads to the improvement of the $V_{OC}$ value, which is attributed to the difference in the conduction band positions of TiO$_2$ and ZrO$_2$ [11, 12].
However, a drop in $J_{SC}$ values is found with incorporation of ZrO$_2$ materials (Figure 2), what can be explained by their insulating nature [12].

The highest average performance of 12.72% is demonstrated by PSC samples with ZrO$_2$ photoelectrode and it is 6.5% higher than for TiO$_2$-based device. The observed difference is due to the various charge transfer mechanisms. The charge transfer in TiO$_2$ layer is carried out through the conduction band whereas the charge transfer in ZrO$_2$ photoelectrode occurs via the hopping conduction mechanism through localized states within band gap [12]. As a result, the recombination losses at the ZrO$_2$/perovskite interface are lower than for TiO$_2$/perovskite.

PV characteristics for PSCs based on mesoscopic Mo$_2$ photoelectrodes were investigated under varying illumination conditions in the range 10-1000 W/m$^2$. The PCE values and PV parameters versus light intensity are presented in Figure 3. The data obtained demonstrate the outstanding low light performance for PSCs fabricated. Thus the efficiency of PV device with mesoscopic TiO$_2$ photoelectrode decreases slightly (no more than $\sim$20%) with the reduction of light intensity what correlates with literature data [6, 19]. At the same time, the PCE value for PSC based on mesoscopic ZrO$_2$ layer declined by only 10% with light intensity drop from 1000 W/m$^2$ to 10 W/m$^2$. Moreover small increase ($\sim$ 3%) was observed in the range 10-100 W/m$^2$ with a maximum at 60 W/m$^2$ (PCE = 13.06%). These results were obtained for the first time.

Figure 3. PCE values (left) and PV parameters (right) versus light intensity for the PSC devices based on mesoscopic Mo$_2$ photoelectrodes (1 – TiO$_2$, 2 – ZrO$_2$).

PV performance analysis shows that $J_{SC}$ and $V_{OC}$ values demonstrate a linear relationship to the light intensity for all the types of PSCs fabricated. At the same time $FF$ characteristics under varying illumination conditions are different (Figure 3). The $FF$ value of PSC with TiO$_2$ photoelectrode decreases slightly with the light intensity drop, while it increases for ZrO$_2$-based PSC. These data confirm that due to the very wide ZrO$_2$ bandgap and the hopping mechanism of electron transfer over localized states within this zone the recombination losses at the ZrO$_2$/perovskite interface is minimal. In addition, the light scattering effect within the photoelectrode, the most important factor for low light performance, is better in the mesoscopic ZrO$_2$ layer. It can be caused by more dense and uniform structure of ZrO$_2$ photoelectrode than for TiO$_2$ material.

3.2. PSC/c-Si tandem solar cells

All fabricated PSC devices based on mesoscopic Mo$_2$ photoelectrodes were used as top elements in four-terminal PSC/c-Si tandem solar cells. The $J$–$V$ curves measured under standard illumination (1000 W/m$^2$, AM1.5G) and the PV parameters for standalone c-Si sample and for bottom c-Si elements are shown on Figure 4 and in Table 2. The bottom c-Si cell performance is shown to be nearly independent on the type of photoelectrode in the top PSC that is probably due to the same thickness of Mo$_2$.
photoelectrodes. The overall conversion efficiency for four-terminal PSC/c-Si tandem solar cells is higher than for standalone c-Si sample and strongly depends on the top cell PCE. The best performance under standard illumination conditions (1000 W/m$^2$, AM1.5G) was achieved for tandem system with PSC based on mesoscopic ZrO$_2$. It was found to be 18.69%, which exceeded the PCE of a standalone c-Si solar cell by ~24% (Table 2).

![Figure 4](image.png)

**Figure 4.** The $J$-$V$ curves for c-Si solar cell and for bottom c-Si solar cells in tandem systems with top PSCs (T1 – PSC with TiO$_2$, T2 – PSC with ZrO$_2$).

|                         | $J_{SC}$, mA/cm$^2$ | $V_{OC}$, V  | $FF$, a.u. | PCE, %  |
|-------------------------|---------------------|--------------|------------|---------|
| Standalone c-Si         | 40.79 ± 0.23        | 0.55 ± 0.02  | 0.68 ± 0.02| 15.07 ± 0.11 |
| Bottom c-Si with T1     | 14.32 ± 0.14        | 0.53 ± 0.02  | 0.74 ± 0.01| 5.61 ± 0.15  |
| Bottom c-Si with T2     | 15.10 ± 0.18        | 0.54 ± 0.01  | 0.74 ± 0.01| 5.97 ± 0.22  |
| T1/c-Si                 | -                   | -            | -          | 17.55 ± 0.15 |
| T2/c-Si                 | -                   | -            | -          | 18.69 ± 0.24 |

**Table 2.** The PV characteristics for c-Si solar cell, for bottom c-Si solar cells in tandem systems and for PSC/c-Si tandem solar cells (T1 – PSC with TiO$_2$, T2 – PSC with ZrO$_2$).

The investigation of PV performance under varying illumination conditions in the range 10-1000 W/m$^2$ revealed that the efficiency of four-terminal PSC/c-Si tandem solar cells was significantly higher than for c-Si cell under low light conditions (Figure 5). The PCE value for tandem system with PSC based on mesoscopic ZrO$_2$ at 10 W/m$^2$ was found to be 12.27% that is ~6 times higher than the PCE value for a standalone c-Si solar cell (1.95%).

![Figure 5](image.png)

**Figure 5.** PCE values versus light intensity for standalone c-Si solar cell and for four-terminal PSC/c-Si tandem solar cells (T1 – PSC with TiO$_2$, T2 – PSC with ZrO$_2$).

The obtained data reveals that PSCs with novel photoelectrodes based on very wide-bandgap ZrO$_2$ material can be successfully used as top elements in tandem systems with the bottom c-Si cells and its...
allows to increase significantly the overall conversion efficiency of tandem solar cells not only under standard illumination conditions but also at low light intensities. In addition, mesoscopic ZrO$_2$ layer can be an efficient alternative to standard TiO$_2$ layer as photoelectrode for PSCs.

4. Conclusions
In this paper novel high efficient semi-transparent PSCs with the cell architecture of glass/FTO/c-TiO$_2$/ZrO$_2$/CH$_3$NH$_3$PbI$_3$/PTAA/PEDOT:PSS/FTO/glass were fabricated and were successfully used as top elements in four-terminal PSC/c-Si tandem solar cells. The efficiency of these tandem systems under standard illumination (1000 W/m$^2$, AM1.5G) was found to be 18.69%, what exceeded the PCE of state-of-the-art PSC/c-Si tandem solar cells by ~ 6.5% and the PCE of a standalone c-Si solar cell by ~ 24%. The PCE of developed tandem solar cells at 10 W/m$^2$ was found to be 12.27% that is ~ 6 times higher than the PCE of a standalone c-Si solar cell (1.95%). The obtained results demonstrate that the ZrO$_2$-based photoelectrodes are promising for the manufacturing high efficient PSCs and for improving the performance of PSC/c-Si tandem systems not only for standard illumination conditions but also for low light applications.

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