Hybrid solar cells based on PEDOT:PSS/Si heterojunction obtained by spin coating on silicon fiber array

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This article presents the results of formation of hybrid solar cells based on PEDOT:PSS/Si heterostructure on the surface of substrates with an array of vertically oriented silicon fibers. The effect of the concentration of the surfactant Triton X-100 on the uniformity of the coating of the array of vertically oriented silicon fibers and the photoelectric parameters of the solar cells was studied. Based on the results of scanning electron microscopy measurements of the obtained structures, a qualitative improvement in the coating of the silicon fiber array with a PEDOT:PSS layer by adding surfactant was shown. Excessive concentration of surfactant leads to deterioration of the photoconversion properties of solar cells based on the PEDOT:PSS/Si heterostructure.

Keywords: PEDOT:PSS, Si, solar cells, heterostructures.

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1. Introduction

Currently solar cells (SC) based on silicon cover over 90% of market of ground photovoltaics, this is due to material accessibility, which resources in Earth's crust are practically unlimited, due to high level of technology development of silicon wafers production and sufficient resistance to sun radiation of silicon. The maximum efficiency of conversion 26.81% was achieved in 2022 for SC based on heterostructure amorphous/crystalline silicon, which approached the theoretical maximum $\sim 29\%$ [1]. In the last few years, there was a sharp increase in the number of studies on the search for completely new materials that can potentially replace amorphous silicon in the creation of heterostructure-based SC on crystalline silicon substrates. One of the development ways the creation of hybrid SC may be using organic conductive material poly(3,4-ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS). Films of this polymer material, besides high electric conductivity, have high transparency in visible range, high mechanical flexibility and possibility of simple production from the aqueous solution. Currently the record of efficiency of silicon photovoltaic converters using PEDOT:PSS layers is 16.2%, which is far from the value 21.30% expected as per calculations [2,3]. Combination of materials PEDOT:PSS and Si is of greatest interest when forming flexible SCs using thin ($< 50\,\mu$m) silicon substrates. Surface modification in form of silicon fibers ensures, on one hand, mechanical strength increasing of crystalline silicon substrates, and from other hand — decreasing of optical reflection of light from face surface of SC. Previously we showed the principle possibility of SC formation based on PEDOT:PSS/Si using G-coating method, which has size limitation of studied structures [4]. Use of surfactants ensures space filling between silicon fibers with aqueous solution of PEDOT:PSS without use of G-coating method and transition to more simple and scalable method of spincoating. This paper relates to formation and study of hybrid solar cells based on heterojunction PEDOT:PSS/Si, produced by spincoating method on surface of substrates with array of silicon fibers.

2. Samples and experimental details

As initial substrate the crystalline silicon was used with double-side polishing $380\,\mu$m thick of *n*-type of conductivity with resistivity $0.2\,\text{Ohm}\cdot\text{cm}$. Method of cryogenic plasma-enhanced chemical etching using microsphere lithography the array of cylindrical silicon fibers with close-packed arrangement (Figure 1, *a*) was obtained [5]. Fibers height was $6\,\mu$m, and diameter was $1.2-1.4\,\mu$m (Figure 1, *b*). Diameter selection of silicon fibers is determined by the need to keep the conductivity channel in center of fibers upon radial deposition of emitter, considering value of region of spatial charge equal to ~ 200 nm. Distance between fibers is necessary for further incapsulation and possibility of such structures thinning to obtain flexible solar cells based on the crystalline silicon.

After formation of the fibers array the silicon substrates were subjected to chemical treatment by Shiraki method to delete organic and inorganic contaminants [6].

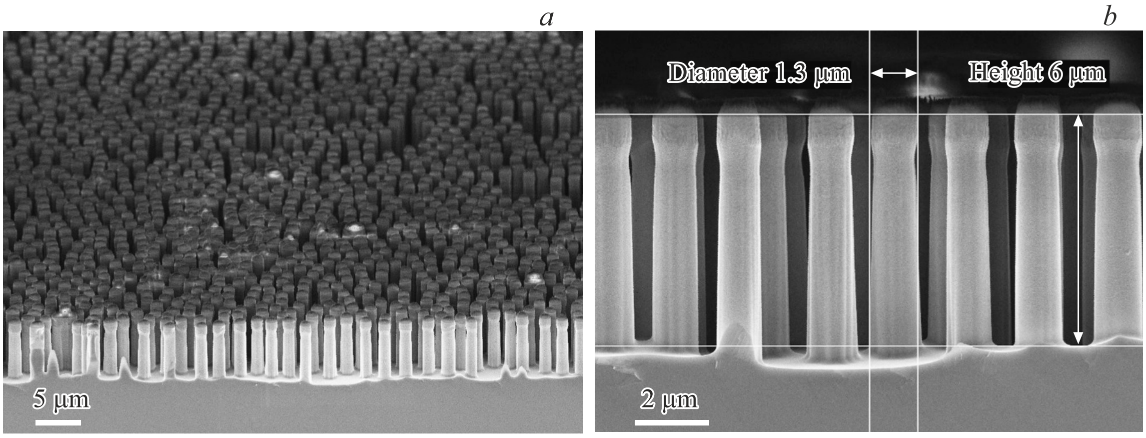

Figure 1. SEM-images of surface of vertically oriented Si structures (*a*) and individual fibers (*b*) on substrate of crystalline silicon obtained by method of microsphere lithography and cryogenic plasma-enhanced chemical etching.

Rare ohmic passivation contact comprising combination of layers *a*-Si:H(*i*)/*a*-Si:H(*n*) with thicknesses 5 and 10 nm, respectively, was formed by method of plasma-enhanced chemical vapor deposition at temperature of 250°C and power density of capacitively-coupled plasma 11 mW/cm^2. To gather carriers on the rare contact a layer of silver 500 nm thick was deposited using thermal evaporation in vacuum. Just prior to PEDOT:PSS deposition the substrates were treated in 10% solution of HF/H_2O to remove natural oxide layer from silicon surface. Next, an aqueous solution of PEDOT:PSS 3.4 vol% (Sigma-Aldrich) was deposited on the substrate by spincoating at a rotation speed of 2000 rpm, followed by drying at 120°C for 5 min. Front ohmic contacts to layer PEDOT:PSS were formed using low-temperature silver paste, sintered at 100°C for 10 min. The surfactant Triton X-100 as part of aqueous solution of PEDOT:PSS varied from 0 to 0.1 vol% to improve uniformity of surface coating of silicon fibers. Uniform coating of layers PEDOT:PSS on surface of vertically oriented silicon fibers (see Figure 2) was studied using the scanning-electron microscope Zeiss SUPRA 25. The photovoltaic properties of the produced structures were studied by method of current-voltage characteristics (I-V) in dark and under illumination with spectrum AM1.5g with intensity 1000 W/m^2, also spectra of quantum efficiency (EQE) were measured in wavelength range 350–1200 nm. Due to different work regions of samples the short circuit density in I-V was recalculated by integration of EQE spectra.

3. Results and discussion

The silicon substrate with array of silicon fibers has low reflective index (10–15%) in visible and close infrared range of wavelengths, this opens perspectives for its use for the solar cells. However, the high aspect ratio of such structures significantly complicates the formation on their surface of thin uniform layers of the emitter and transparent conductive coatings. Unlike other methods of PEDOT:PSS deposition, precipitation from the aqueous solution allows for uniform coating of such structures, and the only limitation is the presence of a capillary effect in the space between the columns. One of the methods reducing this effect influence is surfactant addition to the aqueous solution for surface wetting improvement. In this paper for evaluation of the surfactant effect on photovoltaic parameters of SCs the following volume concentrations in aqueous solution of PEDOT:PSS were used: 0.001, 0.01 and 0.1 vol%. The obtained aqueous solutions were used during SC formation on silicon substrates with array of silicon fibers. The structures with the surfactant concentration of 0 and 0.1 vol% were studied by the method of scanning electron microscopy (Figure 2, *a* and *b*).

The photovoltaic parameters of SC based on heterojunction PEDOT:PSS/*n*-Si, obtained on surface of array of silicon fibers

Concentration Triton X-100, vol.%	V_{oc}, mV	I_{sc}, mA/cm^2	I_0 (at −1 V), mA/cm^2	PCE, %
0	522	26.3	0.23	4.23
0.001	495	25.8	0.14	4.99
0.01	492	26.6	0.15	4.05
0.1	496	27.4	1.73	4.13

In the obtained image (Figure 2, *a*) we see that without surfactant use PEDOT:PSS film nonuniformly coated the surface of array of silicon fibers due to the presence of the capillary effect. Such stripes are formed over the entire surface of substrate due to insufficient wetting of silicon surface. When adding 0.1 vol% of surfactant (Figure 2, *b*) the significant wetting improvement is observed, and the substrate is uniformly coated with PEDOT:PSS layer without cavities formation. Also note that when adding 0.1 vol% of surfactant the surface of PEDOT:PSS layer becomes more

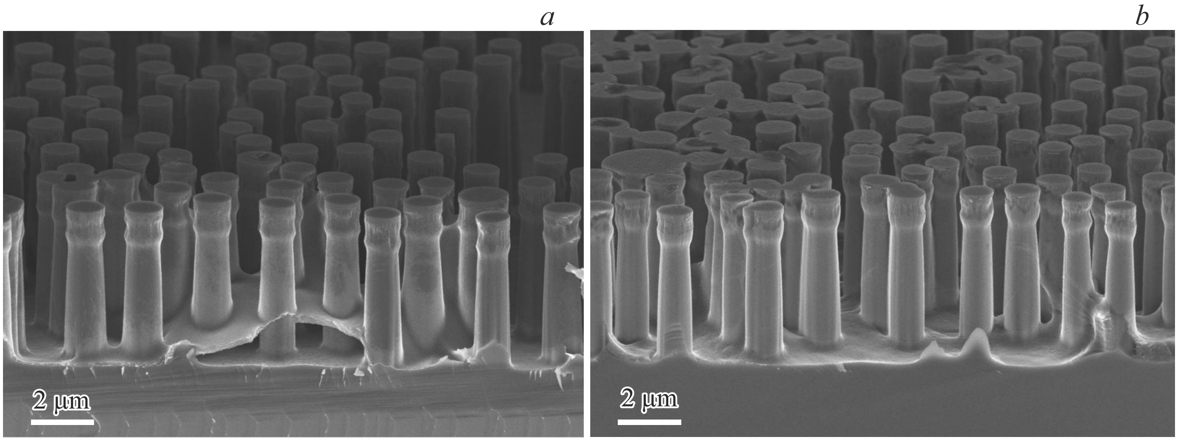

Figure 2. SEM-image of vertically oriented Si structures coated with layer PEDOT:PSS without addition of Triton X-100 (*a*) and with addition of 0.1 vol% of Triton X-100 (*b*).

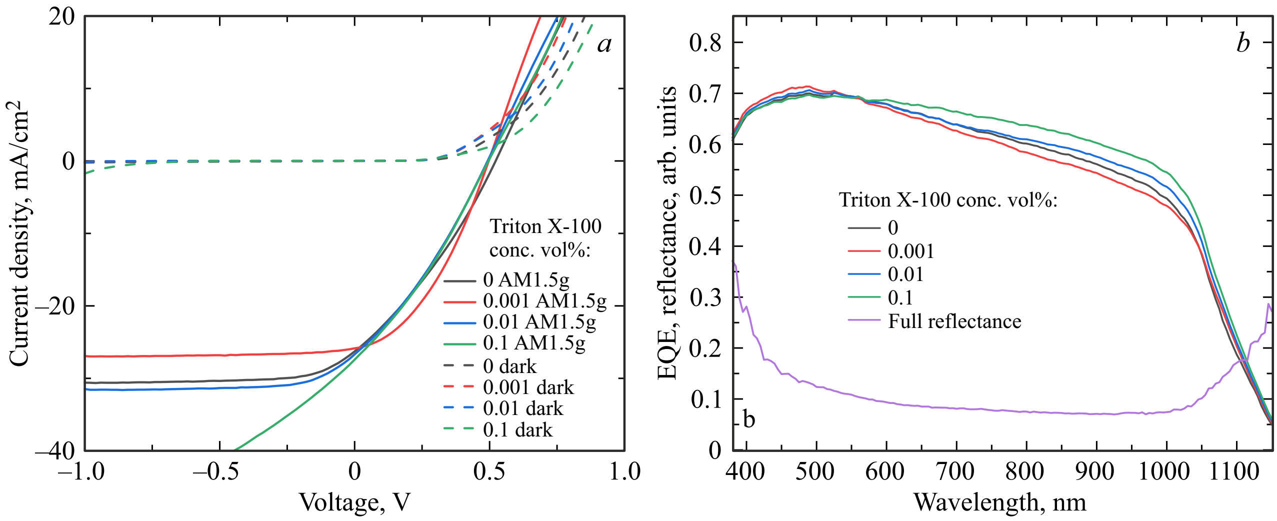

Figure 3. Current-voltage curves (*a*) and spectra of EQE and full reflection (*b*) of photoconverter structures based on heterojunction PEDOT:PSS/*n*-Si, obtained on surface of array of silicon fibers.

rough, which can say about significant change in layer composition.

To determine the influence of surfactant concentration on the electrophysical properties, I-Vs of the obtained structures PEDOT:PSS/*n*-Si were studied (Figure 3, *a*). The best open circuit voltage (V_{oc}) 522 mV was shown by structures obtained without the surfactant use. When adding Triton X-100 even in concentration of 0.001 vol% V_{oc} drop from 522 to 495 nV occurs. Further surfactant concentration increasing does not affect significantly on value of V_{oc}. Note that at surfactant concentration 0.1 vol% reverse current of SC (I_0) significantly increases, which confirms the shunt resistance decreasing. This can be result of roughness increasing, shown in SEM-image (Figure 2, *b*). The best conversion coefficient (PCE) 4.99% was shown by structure with surfactant content 0.001 vol%. Short circuit current (I_{sc}) also depends on surfactant content in PEDOT:PSS layer. This can be associated with both quality of interface between PEDOT:PSS layer and Si, and with change in thickness of PEDOT:PSS layer. Qualitatively difference between these two effects can be determined by spectra of external quantum efficiency (EQE) (Figure 3, *b*). Main effect on the short circuit is made by long-wavelength region of spectrum from 600 to 1100 nm. This is associated, first of all, with light absorption in PEDOT:PSS layer, and by different thickness of this layer [7,8]. In short-wave region of spectrum the best result was shown by layer with surfactant content 0.001 vol%, which says about better quality of interface between PEDOT:PSS layer and Si in this structure.

4. Conclusion

It is shown that produced SC PEDOT:PSS/Si have I-V typical for photoconverting structures based on silicon. Concentration of surfactant Triton X-100 significantly affects the wetting of silicon substrate and uniformity of coating of array of silicon microcolumns with high aspect ratio. Qualitative improvement of coating of array of silicon microcolumns with PEDOT:PSS layer by addition 0.1 vol% of surfactant is shown. Note that for the studied structures decrease in quantum efficiency in long-wavelength region of spectrum is typical, which can be associated with partial absorption of radiation in PEDOT:PSS layer. On other hand, in short-wave region of spectrum the best result is shown by layer containing surfactant 0.001 vol%, which says about low recombination on silicon surface and high quality of interface. The paper results can be used during formation of high effective SCs based on substrates of crystalline silicon using polymer material PEDOT:PSS as emitter.

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Conflict of interest

The authors declare that they have no conflict of interest.

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