

Study of the effect of spin-coating parameters and PEDOT:PSS suspension composition on the characteristics of *b*-Si/PEDOT:PSS solar cells

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This study investigates the effects of spin-coating parameters, annealing conditions, and PEDOT:PSS suspension composition on the performance of solar cells based on nanostructured „black silicon“. The optimal rotational speed, annealing temperature, and duration were found to be 3000 rpm, 130 °C, and 10 minutes, respectively. The formation of a native silicon oxide layer over 30 minutes was found to enhance device characteristics. Furthermore, the addition of 6 vol.% isopropyl alcohol and 7.5 vol.% dimethyl sulfoxide as co-solvents to the PEDOT:PSS suspension significantly improved solar cell performance.

Keywords: Hybrid solar cells, black silicon, PEDOT:PSS.

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Polythiophenes (specifically, PEDOT:PSS) are now used often both as transparent anodes and as emitters for *n*-Si. At present, the maximum demonstrated efficiency of such a planar structure is ~ 14.5 % [1]. However, simulation results reveal that the theoretical efficiency of PEDOT:PSS/*n*-Si solar cells may exceed 20 % [2].

Certain high-boiling aprotic organic solvents, such as dimethyl sulfoxide (DMSO), screen the Coulomb attraction of PEDOT and PSS chains and alter the configuration of PEDOT:PSS grains. This leads to an increase in electrical conductivity [3], since a reduction in PSS concentration in the layer, which is also caused by the introduction of DMSO into a PEDOT:PSS suspension, enhances the intermolecular mobility of charges [3]. It was demonstrated in [3] that the conductivity of PEDOT:PSS is affected by the ratio of quinoid and benzenoid forms of PEDOT. When DMSO is introduced into the suspension, the percentage of the quinoid form, which is characterized by a higher intramolecular charge mobility and may be regarded as additional doping, increases, leading to a reduction in equilibrium concentration of injected minority carriers.

Silicon with a nanostructured surface, which is called „black silicon“ in literature, may be used to suppress reflection losses. Black silicon (*b*-Si) produced by cryogenic etching exhibits both broad-band antireflection (400–1150 nm) and enhanced absorption of low-energy photons near silicon's bandgap [4]. However, uniform application of PEDOT:PSS onto the nanostructured surface with a high aspect ratio is required in this case.

The addition of low-boiling solvents and non-ionic surfactants reduces the surface tension of the suspension, which

results in a more uniform application of polymer coating. It is likely that, in contrast to non-ionic surfactants, low-boiling solvents, such as isopropyl alcohol (IPA), have the capacity to reduce the surface tension of the suspension without any negative effect on the electrical properties of the layer and the solar cell as a whole.

In the present study, we investigated the influence of spin-coating speed, annealing duration and temperature, volume fraction of co-solvents (DMSO, IPA) in the PEDOT:PSS suspension, and the air exposure time required for a native SiO_x oxide layer to form on a silicon wafer after HF treatment. The design of a solar cell based on a hybrid heterojunction and the scanning electron microscopy (SEM) images of the PEDOT:PSS/*b*-Si structure before and after Ag grid deposition are presented in Figures 1, *a, b*. The back ohmic contact to the *n*-Si substrate was formed by depositing a thin layer of (*n*)*a*-Si:H with subsequent thermal evaporation of silver. The front contact to the PEDOT:PSS layer was also formed by thermal evaporation of silver through a mask.

The current–voltage curves were recorded using an Abet Technologies solar simulator (AM1.5G, 100 mW/cm²) and a Keithley 2400 source meter through a 4 by 4 mm aperture. All solar cell samples (except for the series with added DMSO and IPA) used black silicon with a nanoneedle height of 6.6 μm and PEDOT:PSS (Sigma-Aldrich, highly conductive, 3.0–4.0 % aqueous suspension).

A series of samples was prepared by spin-coating with varying rotation speed, annealing temperature, and annealing time to determine the optimal application parameters. The best sample in the series (see the table) was the one

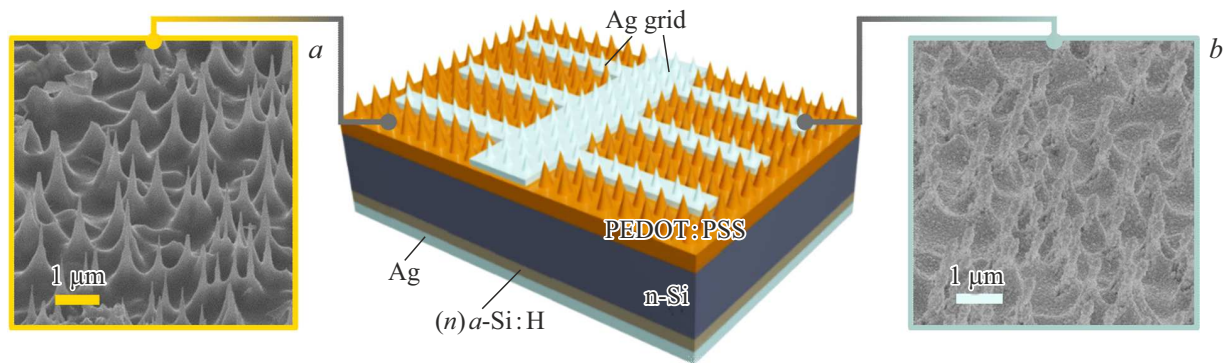


Figure 1. Design of a solar cell based on PEDOT:PSS/b-Si and SEM image of the surface structure before (a) and after (b) the deposition of Ag.

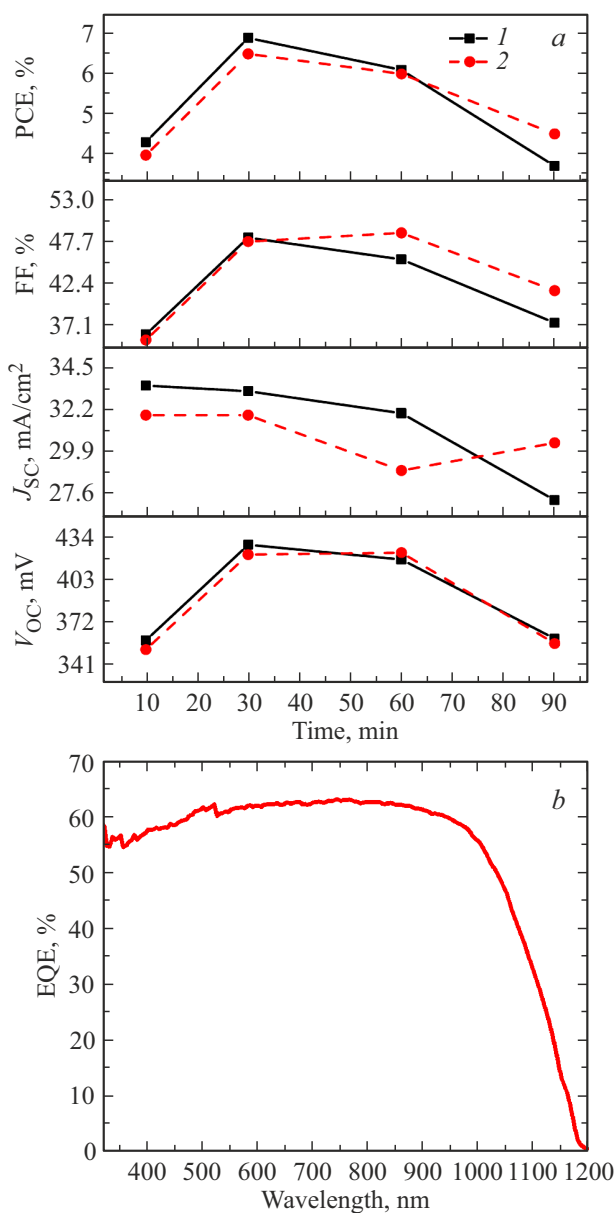


Figure 2. Dependences of the characteristics of PEDOT:PSS/b-Si on the holding time after treatment in HF (a) with additional annealing (2) and without it (1); EQE spectrum (b).

obtained at a rotation speed of 3000 rpm and an annealing temperature of 130 °C (10 min).

A temperature of 110 °C is likely to be insufficient for complete evaporation of solvents from the PEDOT:PSS layer, and a rotation speed of 1000 rpm is insufficient to obtain a uniform layer, since the sample had visually significant edge effects. A speed of 5000 rpm is, conversely, proves excessive.

The series of samples obtained with different PEDOT:PSS layer annealing times makes it clear that the optimal time is 10 min. Apparently, annealing for 5 min is insufficient for complete evaporation of solvents from the layer, while a 15 min period is too long. It was reported in [5,6] that the conductivity of the PEDOT:PSS layer decreases beyond a certain time and temperature of annealing. This may explain the degradation of characteristics of the solar cell in the present case.

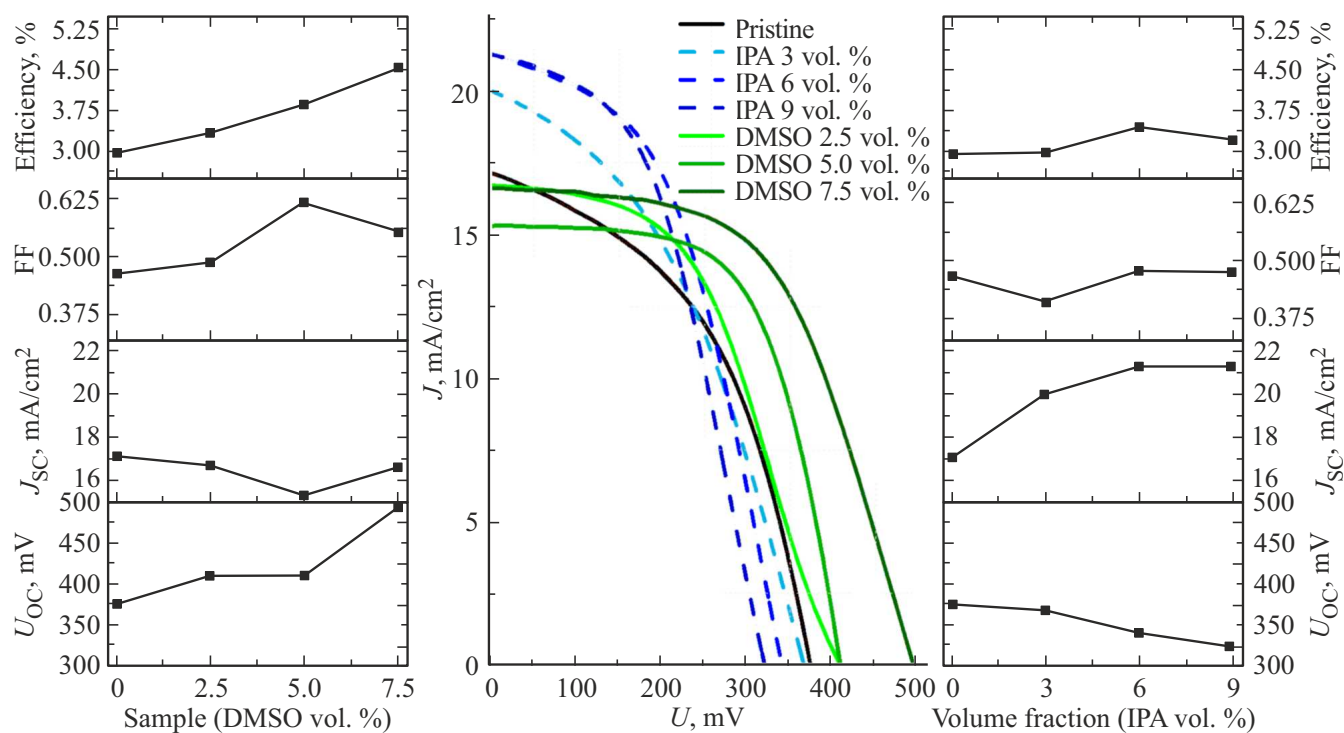
Introducing a delay between PEDOT:PSS deposition and spin-coating enhances solar cell performance. Specifically, the sample where PEDOT:PSS was spun 5 min after application outperforms the sample where PEDOT:PSS was spun immediately after application: it has a 1.26 times better V_{oc} value (320–406 mV) and a 1.64 times better J_{sc} value (17.2–28.2 mA/cm²).

The series of PEDOT:PSS/b-Si samples with varying times of air exposure the silicon wafer in atmosphere after removal of the native oxide in HF was obtained at 3000 rpm and annealed at 130 °C. It follows from Figure 2 that the optimal holding time is 30 min: a layer of native oxide with a thickness of < 1.5–2 nm forms again on silicon within this time interval, ensuring better wettability without any significant increase in series resistance of the cell. A thicker oxide layer reduces the cell performance due to a higher series resistance [7].

Additional annealing at 100 °C was also carried out after the application of the front contact. It was reported in [8] that one of the mechanisms of degradation of conductivity of the PEDOT:PSS layer is its hygroscopicity. However, contrary to expectations, additional annealing before the measurement of solar cell characteristics often had a negative effect on them. This implies that the annealing

Set of samples prepared with different rotation speed and annealing temperature and duration values

Sample No.	Spin-coating, rpm	Annealing		V_{oc} , mV	J_{sc} , mA/cm ²	FF, %	PCE, %
		T , °C	t , min				
1	1000	110	10	260	30.85	33	2.66
2	3000	110		360	35.6	36	4.63
3	3000	130		380	33.6	37.5	4.8
4	5000	130		360	34.5	36.6	4.55
5	3000	130	5	220	30.04	28.8	1.9
6			10	380	33.6	37.5	4.8
7			15	360	28.27	34.6	3.52

**Figure 3.** CVCs (b) and characteristics of solar cells with different volume fractions of DMSO (a) or IPA (c).

process itself induced the performance degradation, likely through a thermally-driven mechanism. Figure 2, *b* shows the *EQE* spectrum of the solar cell, which was held for 60 min after removal of the natural oxide layer before the application of PEDOT:PSS, after additional annealing. The maximum *EQE* value is 63.3 %, and the current density is 26.2 mA/cm².

The series of solar cell samples with added DMSO and IPA (Figure 3) was prepared with the use of black silicon with a nanoneedle height of 8.3 μm and PEDOT:PSS (Orgacon, high-conductivity grade, 1.1% aqueous dispersion, surfactant-free). These samples were held for 30 min after removal of the natural oxide layer and annealed for

10 min at 120°C. Spin-coating was carried out at a speed of 300 rpm (20 s) with a subsequent increase in speed to 3000 rpm (40 s).

It follows from Figure 3 that the addition of isopropyl alcohol to the PEDOT:PSS suspension leads to a significant increase in short-circuit current density. This may be attributed to an enhancement of coating uniformity due to better wetting of the substrate, which results in a reduction in sheet resistance (ρ , Ω/sq). The reduction in open-circuit voltage values is caused by the mandatory application of an aperture, since the short-circuit current is more sensitive to the irradiation area. Charges formed in the inactive region continue to recombine, which reduces somewhat the open-

circuit voltage. This effect is characterized by a two-diode model with one of the diodes left unexposed to radiation.

The most pronounced increase in open-circuit voltage (24.37%) was observed in the series with DMSO. The short-circuit current exhibits nonsystematic variation within 10.76%, which can be attributed to the poor wettability of the substrate by the PEDOT:PSS suspension.

Thus, the optimal spin-coating (3000 rpm, 1 min) and annealing temperature (130 °C) and time (10 min) regimes were determined. The efficiency at the indicated parameters was 4.8%. It was demonstrated that a thin layer of natural oxide improves substrate wettability and solar cell performance. The sample prepared with a 30-minute interval between the oxide layer removal and the application of PEDOT:PSS had the highest efficiency (6.9%). Improved wetting by the PEDOT:PSS suspension containing isopropyl alcohol and changes in the properties of the layer obtained from compositions containing dimethyl sulfoxide were confirmed. These changes, which provide greater intramolecular charge mobility, are reflected in the characteristics of solar cells. The highest efficiency of 3.5 and 4.5% was demonstrated by structures with 6 vol.% isopropyl alcohol and 7.5 vol.% dimethyl sulfoxide, respectively (the initial efficiency was 3%).

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Conflict of interest

The authors declare that they have no conflict of interest.

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