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Heterojunction solar cells based on nanostructured black silicon

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Abstract. The influence of the black silicon (*b*-Si) morphology on the photovoltaic properties of heterojunction solar cell is investigated. We used cryogenic etching (-150 °C) in a SF_6/O_2 gas mixture to obtain *b*-Si structures and a total reflectance in the range of 1–3%. The height of the obtained *b*-Si structures varies from 200 to 760 nm, the shape from nanowires to cone-shaped. The heterojunction *a*-Si:H/*c*-Si was fabricated by PECVD at a temperature of 250 °C. The best heterojunction solar cell based on a 200 nm height cone-shaped *b*-Si demonstrates a promising passivation properties reaching open circuit voltage of 648 mV. With a short-circuit current density of 29.7 mA/cm² and fill factor of 67% a power conversion efficiency of 12.8% was achieved. The solar cells based on cone-shaped *b*-Si gain also in external quantum efficiency compared to nanowire *b*-Si.

Keywords: black silicon, amorphous silicon, heterojunction solar cell

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Гетероструктурные солнечные элементы на основе наноструктурированного черного кремния

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Аннотация. В данной статье исследовано влияние морфологии черного кремния (*b*-Si) на фотоэлектрические свойства гетероструктурного солнечного элемента. Для получения структур *b*-Si и общего коэффициента отражения в диапазоне 1–3% было использовано криогенное травление (-150 °C) в газовой смеси SF_6/O_2. Высота полученных структур *b*-Si варьируется от 200 до 760 нм, форма – от нитевидной до конусообразной. Гетеропереход *a*-Si:H/*c*-Si был изготовлен методом плазмохимического осаждения из газовой фазы при температуре 250 °C. Лучший гетероструктурный солнечный элемент на основе конусообразного *b*-Si высотой 200 нм демонстрирует многообещающие пассивирующие свойства, достигая напряжения холостого хода 648 мВ. При плотности тока короткого замыкания 29,7 мА/см² и коэффициенте заполнения 67% был достигнут КПД в 12,8%. Солнечные элементы на основе конусообразного *b*-Si также выигрывают по значениям внешней квантовой эффективности по сравнению с нитевидным *b*-Si.

Ключевые слова: черный кремний, аморфный кремний, гетероструктурный солнечный элемент

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Introduction

The energy of the future will largely consist of renewable energy sources. Photovoltaic conversion of solar energy is the most promising way to generate electricity. It is expected that the overall growth of global solar photovoltaic power could reach almost 260 GW by 2026 [1].

Silicon solar cells dominate the overall growing solar cell (SC) market due to their availability, durability and relatively low cost. The technology of solar cell production based on the amorphous/crystalline (*a*-Si:H/*c*-Si) heterojunction (HJT) is one of the most promising concepts for a highly efficient silicon solar cell [2]. To reduce optical losses and increase the efficiency of industrial heterojunction solar cells, pyramidal texturing is used, obtained by the alkaline anisotropic etching [3, 4]. However, this approach works effectively in a narrow range of wavelengths and angles of incidence. Relatively recently, a more efficient way to reduce reflection has been proposed by forming a nanostructured silicon surface, known as black silicon (*b*-Si). In turn, *b*-Si has excellent optical properties in both a wide wavelengths range (from 250 to 1200 nm) and incidence angles [5]. Due to this property, *b*-Si is an extremely promising solution for photovoltaic applications.

However, formation of *a*-Si:H/*c*-Si heterojunction based on *b*-Si have a problem of Si surface passivation being an important issue for HJT SC. The silicon surface is passivated with thin layers using the plasma-enhanced chemical vapor deposition (PECVD) method at low temperatures. The most popular is the use of an undoped layer of (*i*)*a*-Si:H, which makes it possible to obtain a record low surface recombination rate of 0.7 cm/s [6]. Thus, the passivation quality of the nanostructured silicon surface is a key point in the design of heterojunction *b*-Si solar cells.

In this article, the influence of the black silicon morphology on the photovoltaic properties of a solar cell based on *b*-Si is considered.

Experimental section

The *n*-type conductivity silicon wafers (100) with a resistivity of 2–3 Ω·cm were used as substrate material. The *b*-Si structures were obtained by cryogenic etching in SF_6/O_2 inductively coupled plasma without using a template. The addition of Ar (5 sccm) to the gas mixture of SF_6 (45 sccm) and O_2 (15 sccm) provide the cone-shape *b*-Si, while it does not affect the electrical properties [7]. Prior to *a*-Si:H deposition the substrates were cleaned using the Shiraki technology [8]. The native oxide was removed in 10% HF/H_2O solution at room temperature for 60 s. The intrinsic and *p*-doped layers were deposited on *b*-Si structures by PECVD from silane (SiH_4) and hydrogen (H_2) precursors at 250 °C. Trimethylboron (TMB) was added to deposit *p*-type *a*-Si:H layer. A 10 nm thick (*n*)*a*-Si:H layer was deposited on the back side of the substrates to obtain ohmic contact. Vacuum evaporated silver (Ag) layer was used for the bottom contact. Further, a layer of a transparent conductive electrode based on indium tin oxide (ITO) was sputtered on the front face to form the top electrode. On the front side, point contacts were formed using Ag paste, followed by drying at 180 °C for 10 min.

The current-voltage curves under AM1.5G simulator (Abet Technology SunLite) were measured using a Keithley 2400 sourcemeter. The external quantum efficiency (*EQE*) spectra were carried out using a Solar Laser M266 monochromator and a Stanford Research SR830 lock-in amplifier. The total reflection spectra were measured using an integrating sphere and an AvaSpec SensLine spectrometer.

Results and Discussion

Figure 1, *a*, *b* shows scanning electron microscope (SEM) images of the black silicon nanostructured directly after etching. The *b*-Si average height varies from 200 to 760 nm, the shape from nanowire to cone-shaped. Figure 1, *c* shows a SEM image of the 600 nm height cone-shape *b*-Si covered with *a*-Si:H layer that follows the contour of the *b*-Si. The somewhat conformal coverage of the *b*-Si nanostructure with ITO is visible (Fig. 1, *d*). The ITO is deposited on the *b*-Si nanostructure and also does reach it base.

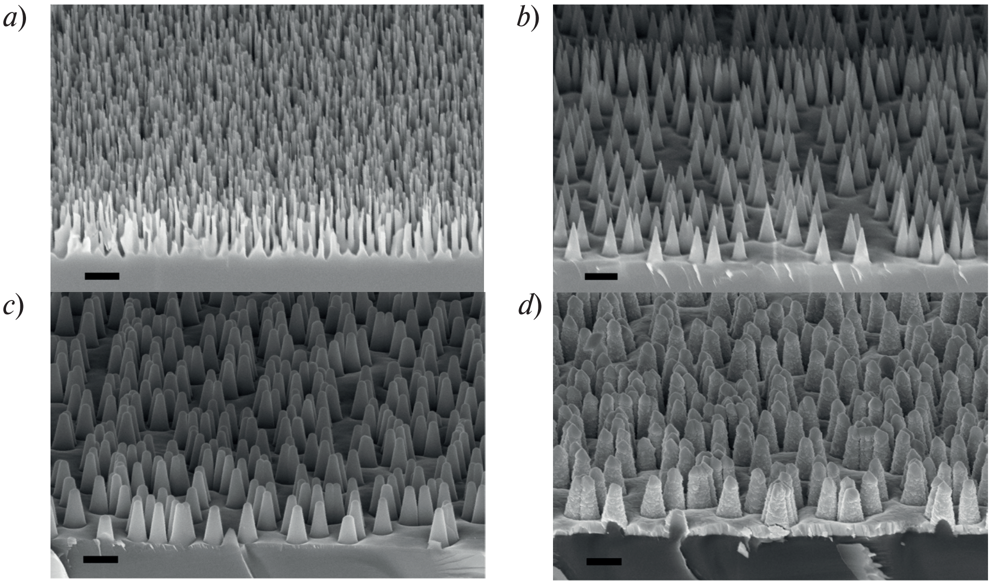

Fig. 1. SEM images of the *b*-Si different morphology: nanowire $h \sim 760$ nm (*a*); cone-shape $h \sim 600$ nm (*b*), covered with *a*-Si:H (*c*), *a*-Si:H and ITO (*d*). The scale bar is 500 nm

The *J*—*V* curves of the solar cells based on *b*-Si are shown in Fig. 2. Photovoltaic parameters such as open circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (*FF*) and power conversion efficiency (*PCE*) were calculated from illuminated current-voltage characteristics and are shown in Table. The active area of the solar cells was 16 mm² and the measurements were carried out using an aperture (area = 16 mm²).

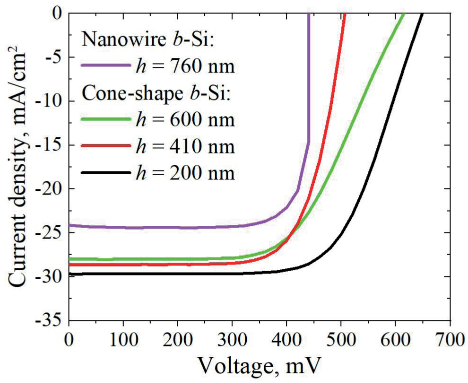

Fig. 2. *J*—*V* characteristics of the solar cells based on *b*-Si

Table

Photovoltaic characteristics of the solar cells based on black silicon

Solar cell	*h,* nm	V_{OC}, mV	J_{SC}, mA/cm^2	J_{SC},mA/cm^2 (by *EQE)*	*FF,* %	*PCE,* %
Nanowire *b*-Si	760	440	24.1	27.2	83	8.8
Cone-shape *b*-Si	600	620	28	28.7	60	10.3
	410	506	28.6	28.2	71.2	10.35
	200	648	29.7	29	67	12.8

Solar cells based on a cone-shaped *b*-Si exceed a SC based on nanowire *b*-Si by a value of V_{OC} up to 1.5 times (506–648 mV). At the same time, the V_{OC} and J_{SC} are higher for cone-shaped *b*-Si of lower height. It is worth noting that for SC based on nanowire *b*-Si *FF* is 83%. In the case SCs based on cone-shape *b*-Si, the reduction in *FF* can be explained by the impact of series resistance. The best heterojunction SC based on a cone-shaped *b*-Si with a height of 200 nm demonstrated an efficiency of 12.8%.

Figure 3 shows the total reflectance specter of the resulting *b*-Si with *a*-Si:H coating. It can be seen that *b*-Si sample has total reflectance below 3% up to 1000 nm. To study the spectral sensitivity of the solar cells based on *b*-Si, *EQE* spectra were measured and are also demonstrated in Fig. 3. The maximum *EQE* value is 91.1% and was achieved for SC based on a 200 nm height cone-shapes *b*-Si. A reduction of the *EQE* below ~850 nm wavelength are observed for others SCs with increasing height *b*-Si.

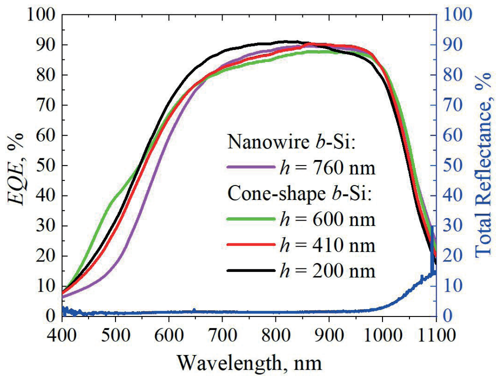

Fig. 3. *EQE* and total reflectance spectra of solar cells based on *b*-Si

The integrated current density and J_{SC} obtained by *EQE* and current-voltage measurements, respectively, were compared and shown in Table. The close of the J_{SC} values between these two measurements confirms the precision of the experimental data.

The J_{SC} decreasing to 24.1 mA/cm^2 for the SC based on nanowire *b*-Si is associated with a drop of *EQE* specter in the short-wavelength region. This can be explained by an increasing surface recombination as a result of insufficient passivation that confirm by low V_{OC}. In the case of SCs based on cone-shaped *b*-Si the spectral characteristics indicates lower recombination losses. According to the results obtained with a decreasing the height or density of cone-shaped *b*-Si structures surface passivation improves. However, decreasing density of *b*-Si structures leads to an increasing the total reflectance. Thus, decreasing the height of *b*-Si structures is main key to achieving better surface passivation.

Conclusion

Amorphous/crystalline silicon heterojunction solar cells based on black silicon with different morphology have been fabricated. All structures of *b*-Si achieve a total reflectance below 3% in a wide spectral range. The *EQE* results clearly disclose the advantage of lower height cone-shaped *b*-Si. The best heterojunction solar cell based on a 200 nm height cone-shaped *b*-Si demonstrated an efficiency of 12.8%. However, the achieved value of V_{OC} (648 mV) demonstrates that a good passivation of Si surface is obtained being a promising result for fabrication *a*-Si:H/*c*-Si heterojunction based on *b*-Si.

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