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Gallium phosphide/black silicon heterojunction solar cells

E.A. Vyacheslavova [1] ✉, A.V. Uvarov [1], A.A. Maksimova [1, 2],
A.I. Baranov [1], A.S. Gudovskikh [1, 2]

[1] Alferov University, St Petersburg, Russia;
[2] St. Petersburg Electrotechnical University "LETI", St Petersburg, Russia
✉ cate.viacheslavova@yandex.ru

Abstract. A new type of heterojunction solar cell based on gallium phosphide/black silicon was considered. The nanostructured surface of black silicon (*b*-Si) was obtained by cryogenic etching in a SF_6/O_2 gas mixture. The average height of the *b*-Si structures varies from 1.4 to 2.1 μm. The heterojunction was fabricated by low temperature method such as plasma-enhanced atomic-layer deposition (PEALD). According to transmission electron microscopy, the thicknesses of the deposited GaP layer are fixed to be 30 nm. The layer consists of crystallites aligned along the crystal lattice direction, as well as their twins. This thin GaP layer allowed achieving a fill factor of 54.5% without transparent conductive oxide and with a test grid. The use of GaP layer as an emitter a broadening of the external quantum efficiency spectrum boundary in the short-wavelength region.

Keywords: black silicon, cryogenic etching, gallium phosphide, PEALD, heterojunction solar cell

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Гетероструктурные солнечные элементы на основе GaP/*b*-Si

Е.А. Вячеславова [1] ✉, А.В. Уваров [1], А.А. Максимова [1, 2],
А.И. Баранов [1], А.С. Гудовских [1, 2]

[1] Академический университет им. Ж.И. Алфёрова РАН, Санкт-Петербург, Россия;
[2] Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова (Ленина), Санкт-Петербург, Россия
✉ cate.viacheslavova@yandex.ru

Аннотация. Был рассмотрен новый тип гетероструктурного солнечного элемента на основе фосфида галлия/черного кремния. Наноструктурированная поверхность черного кремния (*b*-Si) была получена путем криогенного травления в газовой смеси SF_6/O_2. Средняя высота структур *b*-Si варьируется от 1.4 до 2.1 мкм. Гетеропереход был изготовлен с помощью низкотемпературного метода, такого как атомно-слоевое плазмохимическое осаждение (АСПХО). Согласно данным просвечивающей электронной микроскопии толщина нанесенного слоя фосфида галлия составляет 30 нм.

Слой состоит из кристаллитов, выровненных по направлению решетки, а также их двойников. Этот тонкий GaP слой позволил достичь фактора заполнения в 54.5% без прозрачного проводящего оксида и с использованием тестовой сетки. Использование слоя GaP в качестве эмиттера приводит к расширению границы спектра внешней квантовой эффективности в коротковолновой области.

Ключевые слова: черный кремний, криогенное травление, фосфид галлия, АСПХО, гетероструктурный солнечный элемент

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Introduction

The future global electricity generation will be largely powered by renewable energy sources. At the end of 2023, solar energy accounted for 73.1% of the renewable growth, with a capacity of 1.419 GW [1]. The overall growing solar cell market is dominated by silicon (Si) due to its availability, durability and cost-effectiveness. The technology of a solar cell production based on the amorphous/crystalline (*a*-Si:H/*c*-Si) silicon heterojunction is the main concept for a highly efficient Si solar cell. However, these heterojunction devices are limited by non-ideal optical and electronic properties. To reduce optical losses, an antireflection coating is used, as well as surface texturing (the formation of micron-sized pyramids). However, these approaches work effectively in a narrow range of wavelengths and angles of incidence. One of the effective methods of reducing optical reflectance in solar cells can be considered the use of a nanostructured black silicon (*b*-Si). Black silicon is a modification of silicon surface with extremely low reflectivity compared to the planar surface. The *b*-Si has excellent optical properties like low light reflection in both a wide wavelength range and incidence angles [2], and high absorption in the visible and infrared wavelength range [3]. It is worth noting, in the cases of a heterojunction based on *b*-Si, recombination at a nanostructured interface strongly affects efficiency. Gallium phosphide (GaP) can be a promising candidate for the passivating emitter layer of heterojunction cell. GaP has an indirect bandgap energy (2.27 eV) and a low lattice mismatch with Si, that provides to low parasitic absorption [4, 5]. Due to these properties, a conception based on GaP/*b*-Si heterojunction are an extremely promising solution for photovoltaic application.

Experimental section

Cryogenic etching (–150 °C) to obtain *b*-Si structures was carried out using p-type (1–20 Ω · cm) B-doped monocrystalline silicon (100). Before the etching process, the substrates were not cleaned of the native oxide (SiO_2). We used sulfur hexafluoride and oxygen (SF_6/O_2) mixture as process gases. At the beginning, accidental etching of the SiO_2 (ions and fluorine radicals F•) forms a rough surface. Isotropic etching of the Si surface by F• increases the roughness. Oxidation of the surface by O• radicals protects the roughness as Si etching occurs. A SiO_xF_y passivating layer is locally formed. Low temperatures and high oxygen content in the SF_6/O_2 (45/15 sccm) gas mixture lead to the formation of high-aspect structures.

After the etching, the samples were cleaned using the Shiraki technology [6]. To form thin GaP layers on the nanostructured *b*-Si surface, the PEALD method was used at a temperature of 380 °C [7]. This process consists of the exposure of precursors with the substrate surface in one assigned cycle. The cycle is repeated a set number of times. The trimethylgallium (TMG) metallic compound and phosphine (PH_3) gas were used as sources of Ga and P atoms. A pressure was 350 mTorr during deposition steps. The GaP layer was *n*-doped by silicon (SiH_4/H_2 gas mixture).

An aluminum (Al) layer was deposited on the backside of the samples to obtain ohmic contact. Further, the annealing of gallium phosphide was carried out for 1 minute in the rapid thermal annealing (RTA). The annealing temperature range was 600 to 700 °C. After that, a front contact in the form of a silver grid (1×1 cm) was formed. Figure 1 shows the design schematic of the GaP/*b*-Si heterojunction solar cell.

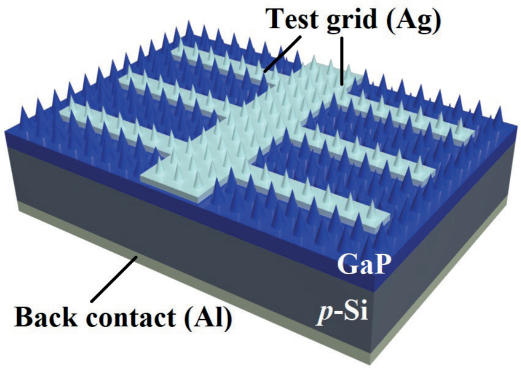

Fig. 1. Structure of the GaP/*b*-Si heterojunction solar cell

The current-voltage curves were measured using a solar simulator (Abet Technology SunLite) under AM1.5G and a Keithley 2400 electrometer with software control in a LabVIEW environment. The total reflection spectra were detected using an AvaSpec SensLine spectrometer with an integrating sphere. The external quantum efficiency (*EQE*) values were carried out with SLS M266 monochromator, a halogen lamp and a reference *c*-Si solar cell.

Results and Discussion

Surface morphology was characterized by a scanning electron microscopy (Supra 25 Zeiss). According to SEM, the etched silicon wafers consist of high density of *b*-Si structures (Fig. 2, *a*). The average height *b*-Si varies from 1.4 to 2.1 μm.

Transmission electron microscopy (TEM) were used to study the structural properties of the obtained GaP/*b*-Si structures. TEM images analysis showed that the GaP layer thickness was 30 nm. The layer consists of crystallites aligned along the crystal lattice direction, as well as their twins. The elemental composition was carried out directly in the TEM setup by the energy-dispersive X-ray (EDX) spectroscopy studies. The elemental mapping analysis indicated the uniform distribution of components (Ga and P) over the entire *b*-Si surface (Fig. 2, *b*). This indicates that there is no deficiency of either precursors in the structure during deposition.

The current density-voltage (*J*–*V*) curves of the heterojunction solar cells based on *b*-Si are shown in Figure 3, *a*. The measurements were obtained for an emitter coverage of ~80% using

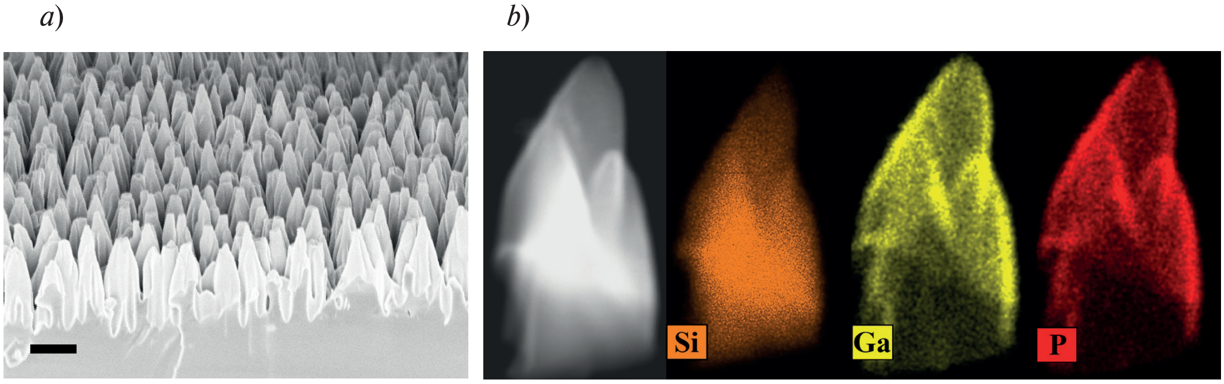

Fig. 2. SEM image (*a*), HAADF STEM image and EDX-elemental mapping analysis (*b*) of the *b*-Si coated with GaP. The bare scale is 1 μm

an aperture (area = 16 mm^2). The photovoltaic parameter values such as open circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (*FF*) and power conversion efficiency (*PCE*) summarized in Table.

It is worth noting, samples were annealed at various temperatures (T_{RTA} = 600...700 °C) to activate the phosphorus dopant. At 600–650 °C, there is no diffusion of phosphorus atoms into the silicon substrate. At 700 °C, the phosphorus atoms start to diffuse into the silicon surface layer, thereby improving the lateral conductivity. Thus, for a sample based on *b*-Si with a height of 1.4 μm, an improvement in the J_{SC} from 28.7 to 33.7 mA/cm^2 is observed during annealing at 700 °C.

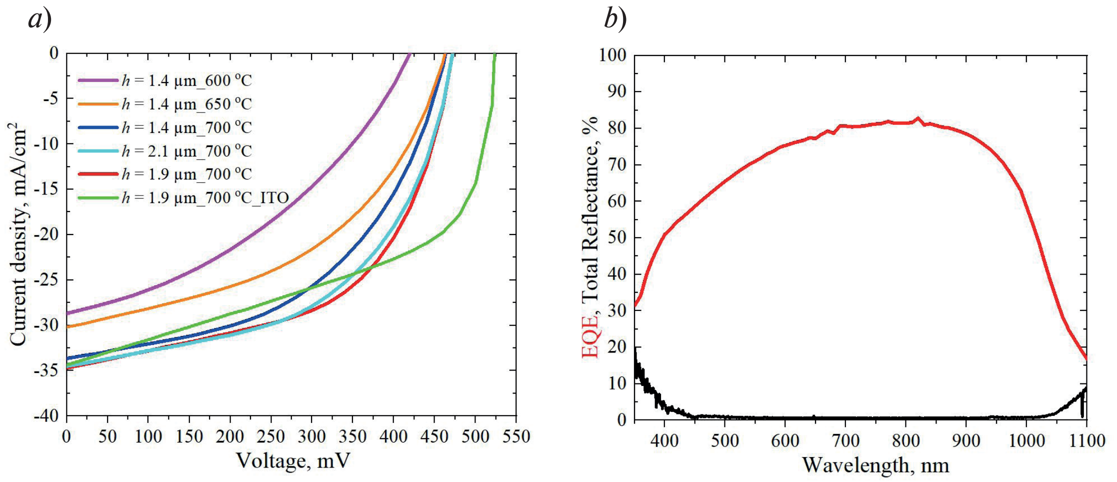

Fig. 3. *J*–*V* characteristics (*a*) and *EQE* spectrum (red line) (*b*) of the GaP/*b*-Si heterojunction solar cell

Table

Photovoltaic characteristics of the GaP/*b*-Si heterojunction solar cells

b-Si height, μm	T_{RTA} [°C]	ITO	V_{OC} [mV]	J_{SC} [mA/cm^2]	*FF* [%]	*PCE* [%]
~1.4	600	without	419	28.7	38.5	4.63
	650		463	30.2	46.5	6.5
	700		464	33.7	49.6	7.75
~2.1	700		472	34.5	52.6	8.56
~1.9	700		473	34.7	54.5	8.94
	700	with	530	34.3	50.5	9.19

The best GaP/Si heterojunction cell based on 1.9 μm height *b*-Si show a good performance achieving V_{OC} of 473 mV, J_{SC} of 34.7 mA/cm^2 and *FF* of 54.5% without transparent conductive oxide and with a silver (Ag) grid pitch of 2 mm. A power conversion efficiency of 9% was received. For the same solar cell with a layer of transparent conductive indium tin oxide (ITO), the V_{OC} was 530 mV. The magnetron sputtering process was used to formation of ITO thin film. However, there is a decrease in *FF* from 54.5% to 50.5% due to the shunt resistance.

Figure 3, *b* shows the total reflectance spectrum of black silicon coated with GaP. It can be seen that sample has total reflectance below 5% up to 1050 nm. The *EQE* spectrum was measured and is demonstrated in Figure 3, *b*. The maximum *EQE* value is 81.5% with shadowing with a silver grid. We can observe in the short-wavelength region a significant advantage of the GaP over *a*-Si:H on the *EQE* spectrum [8].

Conclusion

We have fabricated and investigated the GaP/*b*-Si heterojunction solar cells for the first time. The deposition of GaP layers on *b*-Si was carried out by the low temperature PEALD method. The elemental mapping analysis indicated the uniform distribution of components (Ga and P) over the entire black silicon surface. A GaP/*b*-Si solar cell efficiency of 9% was demonstrated. The *EQE* value is improving in the short-wavelength region through the lower light absorption of GaP layer.

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THE AUTHORS

VYACHESLAVOVA Ekaterina A.
cate.viacheslavova@yandex.ru
ORCID: 0000-0001-6869-1213

UVAROV Alexander V.
lumenlight@mail.ru
ORCID: 0000-0002-0061-6687

MAKSIMOVA Alina A.
deer.blackgreen@yandex.ru
ORCID: 0000-0002-3503-7458

BARANOV Artem I.
itiomchik@yandex.ru
ORCID: 0000-0002-4894-6503

GUDOVSKIKH Alexander S.
gudovskikh@spbau.ru
ORCID: 0000-0002-7632-3194

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