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Formation of radial amorphous hydrogenated silicon *p-i-n* solar cells on silicon nanowire arrays toward flexible photovoltaics

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Abstract. The influence of silicon nanowire (SiNWs) geometry on the efficiency of radial *p-i-n* junction solar cell is studied using experimental measurements. Solar cells based on vertically aligned structures with the SiNWs less than 10 μm in height are practically on par with the planar element in terms of the open-circuit voltage, exceeding it in terms of short-circuit current density by up to 1.5 times (3.9–4.9 mA/cm^2). The increase in the short-circuit current density is associated with the broadening of the quantum efficiency (EQE) spectrum. There is a significant broadening of the EQE boundary to the short-wavelength region with a decrease in the diameter of the SiNWs (from 1.8 to 0.7 μm). A decrease in the open-circuit voltage and a decrease in the absolute value of EQE are observed for structures with SiNWs more than 10 μm in height.

Keywords: radial *p-i-n* junction, amorphous silicon, silicon nanowires, solar cell

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Материалы конференции

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Формирование солнечных элементов на основе вертикально-ориентированных структур с радиальным *p-i-n* переходом для гибкой фотовольтаики

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Аннотация. В работе исследуется влияние геометрии кремниевых нановолокон (КНН) на производительность солнечных элементов на основе радиальных *p-i-n* *a*-Si:H структур, осажденных на КНН. Солнечные элементы на основе вертикально-ориентированных структур с высотой КНН менее 10 мкм по значениям



напряжения холостого хода практически не уступают планарному элементу, а по значениям плотности тока короткого замыкания превосходят его до 1.5 раз (3.9–4.9 мА/см²). Увеличение значения тока короткого замыкания связано с расширением спектра квантовой эффективности, причем с уменьшением диаметра кремниевых нановолокон (с 1.8 до 0.7 мкм) наблюдается существенное расширение границы спектра квантовой эффективности в коротковолновую область. Для структур с высотой кремниевых нановолокон более 10 мкм отмечается снижение значения напряжения холостого хода и уменьшение абсолютного значения EQE.

Ключевые слова: радиальный *p-i-n* переход, аморфный кремний, кремниевые нановолокна, солнечный элемент

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Introduction

The terrestrial photovoltaic industry is still dominated by crystalline silicon (*c*-Si) solar cells due to their stability, relatively low cost and abundance of silicon [1, 2]. The record efficiency of silicon solar cells based on *a*-Si:H/*c*-Si heterojunction is currently 26.7% [3] and is approaching the 29.4% [4] Auger-recombination-constrained Shockley-Queisser limit. The use of multijunction solar cell was one of the ways to overcome theoretical limit and increase the total energy generated by the modules. A new design of a multijunction Si solar cell was proposed [5], where the bottom junction is based on *a*-Si:H/*c*-Si heterojunction, and the top junction is based on SiNWs coated with *p-i-n* structures of *a*-Si:H. The radial design of top *p-i-n* junction is a way to enhance absorption in undoped (*i*)*a*-Si:H layer without increasing its thickness and therefore can provide an increase in the short-circuit current density J_{sc} . Thus, it is possible to solve major problem of a classic planar *a*-Si:H/*c*-Si solar cell, which consists in current matching with the bottom junction. In addition, the use of SiNWs is a promising way to fabrication flexible solar cells. The SiNWs solar cell embedded in a polymer matrix have enhanced mechanical stability compared to conventional planar element.

The influence of SiNWs radius on the efficiency of *a*-Si:H/*c*-Si solar cells was experimentally studied [6]. It is reported that in order to reduce recombination losses, it is necessary to use SiNWs with a radius exceeding the space charge region in Si.

The computer simulation of multijunction solar cells based on *p-i-n* structures and SiNWs was carried out [7]. The dependence of the solar cell characteristics on the SiNWs geometry was calculated. It is shown that an increase in wire length leads to a decrease in the open-circuit voltage V_{oc} and saturation of J_{sc} . At the same time, the value of 10 μm is the critical length of the wire.

In this article, we study the influence of the SiNWs geometry on the efficiency of the top radial *p-i-n* junction using experimental measurements.

Experimental section

Double-sided polished *n*-type antimony doped Si (100) wafers (0.008 Ω·cm) were used for solar cell fabrication. A planar *p-i-n* structure was fabricated as a reference solar cell.

Vertically aligned structures were obtained using latex sphere lithography and dry etching in a SF_6/O_2 gas mixture at cryogenic temperatures ($-120\text{ }^\circ\text{C}$). Plasma etching processes were carried out using Oxford Plasmalab System 100 ICP380 setup. In general, the formation of SiNWs includes three subsequent dry etching steps. First, the reducing of the latex spheres diameter in O_2 plasma. Secondly, etching of SiO_2 layer in CHF_3 plasma via latex spheres. Thirdly, deep cryogenic etching of Si via the formed hard SiO_2 mask. We varied the etching time in O_2 plasma and the etching time in the cryogenic process to obtain SiNWs of different geometries. More details about the formation of SiNWs can be found in our previously published articles [8, 9]. The structure parameters of the obtained vertically aligned structures are shown in Table 1.

Table 1

Parameters of vertically aligned silicon structures

Etching time, sec		Structure parameter	
O_2 plasma	Cryoprocess	height, μm	diameter, μm
260	170	5.3	1.6
220		5.3	1.8
260	300	7	0.7
220		8.5	1.3
260	450	12	1.4

A $p-i-n$ $a\text{-Si:H}$ structure on SiNWs was deposited via plasma-enhanced chemical vapor deposition (PECVD) at a temperature of $250\text{ }^\circ\text{C}$ using the Oxford instruments Plasmalab 100 PECVD setup. Undoped (i) $a\text{-Si:H}$ layer was deposited from a gas mixture of silane (SiH_4) and hydrogen (H_2); n -type phosphorus doped $a\text{-Si:H}$ layer was deposited by adding phosphine (PH_3) to the gas mixture. P-type boron doped $a\text{-Si:H}$ layer was formed due to the addition of trimethylboron (TMB) to SiH_4 gas, respectively.

A 10 nm thick (n) $a\text{-Si:H}$ 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 side. On the front side, point contacts were formed using Ag paste, followed by drying at $170\text{ }^\circ\text{C}$ for 10 min. In the future, it is planned to optimize the front contact and form an Ag grid. Figure 1 shows a schematic of the radial $p-i-n$ solar cell design.

The $I-V$ curves under AM1.5G simulator (Abet Technology SunLite) were measured using a Keithley 2400 electrometer with software control in a LabVIEW environment. The EQE spectra were carried out using an SLS M266 monochromator, a halogen lamp and a reference solar cell based on $c\text{-Si}$. The total reflection spectra were measured using an integrating sphere and an AvaSpec SensLine spectrometer.

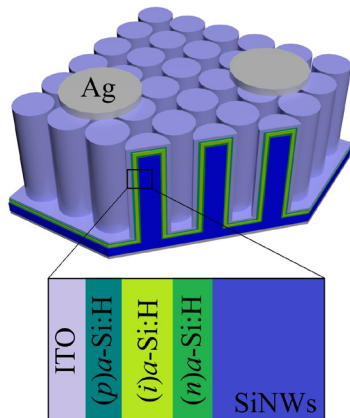


Fig. 1. Solar cell based on radial $p-i-n$ junction

Results and Discussion

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the morphology and structural properties of the obtained $p-i-n$ structures. The elemental composition was carried out directly in the TEM setup by the EDX studies.

Fig. 2, a shows a TEM image of a section on the SiNW covered with ITO. According to the TEM image, the ITO layer thickness is about 80 nm.

The elemental composition a section of the side SiNW surface is presented in Fig. 2, b . The spectral distribution of the EDX signal shows the components of the ITO layer on

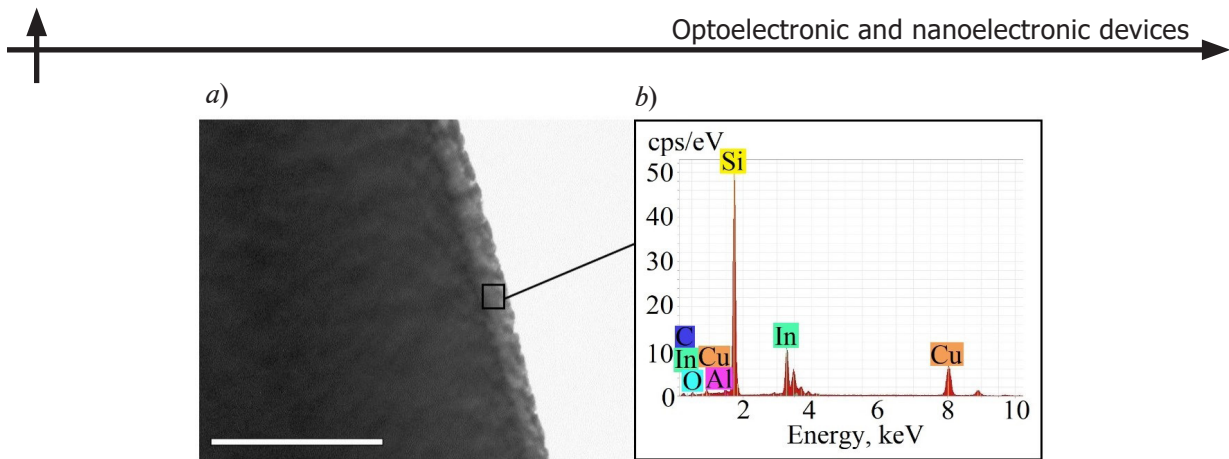


Fig. 2. TEM image of wire covered with ITO (a) and EDX spectrum from a section of the side SiNW surface (b); the scale bar is 500 nm

wire. The presence of copper and carbon in the EDX spectrum could be due to the experimental procedure of the analyses. Furthermore, the elemental mapping analysis was performed on the SiNW covered with ITO (Fig. 3).

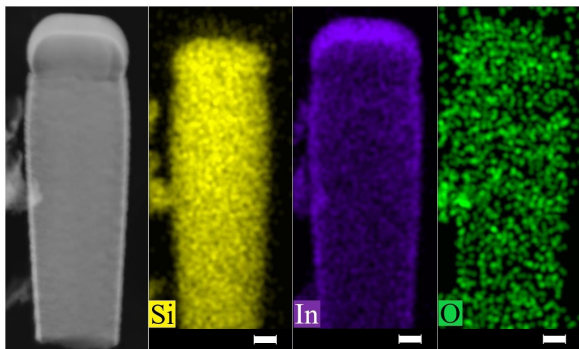


Fig. 3. HAADF STEM image and EDX-elemental mapping analysis on the wire surface; the scale bar is 0.2 μm

The elemental mapping analysis indicated the uniform distribution of Si, In and O on the wire. Thus, the ITO layer completely covers vertically aligned structures.

The $J-V$ curves and the photovoltaic parameters of the radial $p-i-n$ solar cell are shown in Fig. 4, a and in Table 2, respectively. Photovoltaic parameters such as V_{OC} , J_{SC} and fill factor (FF) were calculated from illuminated $I-V$ curves. To study the efficiency of the solar cells based on the $p-i-n$ structure, EQE curves were measured and are demonstrated in Fig. 4, b.

The characteristics of the solar cells based on radial $p-i-n$ structures with a SiNWs height of less than 10 μm demonstrate a definite advantage compared to the planar $p-i-n$ structure. In terms of V_{OC} radial $p-i-n$ structures are practically not inferior to the planar element, and in terms of J_{SC} they are exceeding it. The increase in J_{SC} is associated with the broadening of the EQE spectra, which are shown in Fig. 4, b. For solar cell based on the radial $p-i-n$ junction, a broadening of the boundary of the EQE spectrum is observed both in the long-wavelength region, but mainly in the short-wavelength region. Moreover, there is a definite dependence of the broadening of the EQE

The characteristics of the solar cells based on radial $p-i-n$ structures with a SiNWs height of less than 10 μm demonstrate a definite

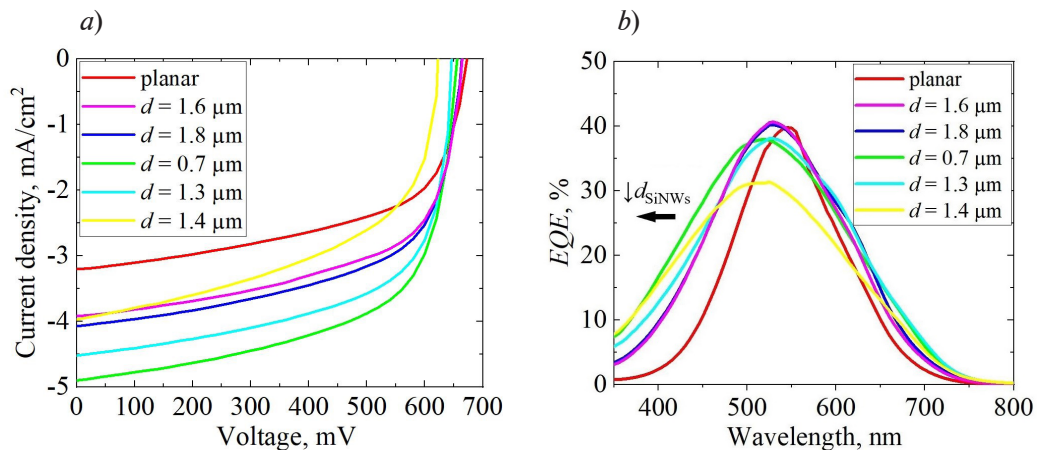


Fig. 4. $J-V$ characteristics (a) and EQE spectra (b) of solar cells based on $p-i-n$ structure

Table 2

Photovoltaic characteristics of the radial *p-i-n* solar cells

<i>p-i-n</i> structure		V_{OC} , mV	J_{SC} , mA/cm ²	FF, %
SiNWs				
height, μm	diameter, μm			
~5.3–7	1.6	660	3.9	60
	1.8	660	4.07	60
	0.7	660	4.9	61
~8.5–12	1.3	640	4.52	63
	1.4	620	3.97	52
planar		680	3.22	57

boundary to the short-wavelength region with a decrease in the SiNWs diameter. It is worth noting that for SiNWs with a height of more than 10 μm, there is a decrease in V_{OC} and a decrease in the absolute value of EQE. This is due to the fact that with such a long wire length at its base, light absorption will decrease. This leads to an uneven distribution of charge carriers. This effect was predicted during the computer simulation of the dependence of the solar cell characteristics on the geometry of SiNWs [7]. It has been shown that an increase in wire length leads to a decrease in V_{OC} and saturation of J_{SC} . At the same time, similarly, the critical wires length was about 10 μm, above which the efficiency of solar cells did not increase.

To analysis the causes for the detected dependence of the broadening of the short-wavelength boundary with a decrease in the SiNWs diameter, measurements of the optical properties of the studied structures were mainly carried out. Fig. 5 shows the total reflection spectra of the solar cells based on radial *p-i-n* structures. The dependence of EQE and total reflection on the wires diameter at a wavelength of 400 nm also is presented in right-upper corner. It can be seen that the total reflection in the short-wavelength region of the spectrum almost does not depend on the SiNWs diameter. Therefore, does not affect the position of the short-wavelength boundary. SEM images analysis for *p-i-n* structures deposited on SiNWs with different diameters showed that for them the thicknesses of the *a*-Si:H and ITO layers practically do not differ. It is possible that the expansion is related to optical phenomena, in particular the waveguide phenomenon on vertically aligned structures [10].

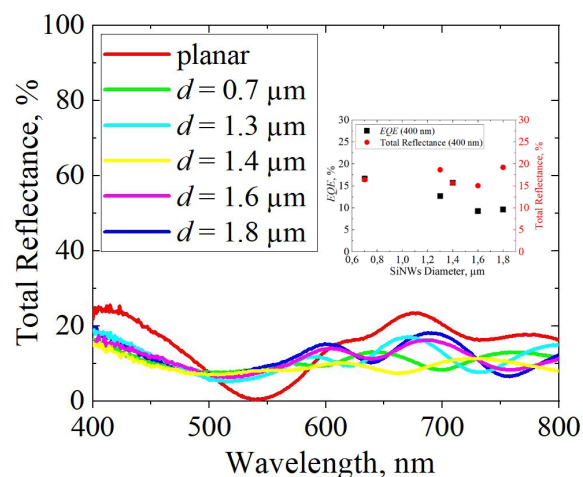


Fig. 5. Total reflection spectra of solar cells based on *p-i-n* structure

Conclusion

In this article, we investigated the influence of the SiNWs geometry on the efficiency of radial *p-i-n* junction solar cell. Solar cell based on vertically aligned structures with a wire height of less than 10 μm are practically not inferior to the planar element in terms of the V_{OC}



and in terms of J_{sc} exceed it up to 1.5 times (3.9-4.9 mA/cm²). The increase in J_{sc} is associated with the broadening of the EQE spectrum. There is a significant broadening of the EQE boundary to the short-wavelength region with a decrease in the wires diameter. This may be due to the waveguide phenomenon on SiNWs. For solar cells based on vertically aligned structures with a SiNWs height of more than 10 μm, a decrease in the V_{oc} and a decrease in the absolute value of EQE are observed, which is associated with low absorption at the base of the wires.

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