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A promising way to improve the efficiency of silicon solar elements — introduction of whiskers with $p-n$ junction

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A new approach to increasing the efficiency of silicon solar cells (SCs) is presented, which consists in the creation of surface light-trapping structures with a high antireflection ability in the form of systems of pointed whiskers (NCs) with coaxial $p-n$ junctions. The coaxial geometry of the $p-n$ junction is justified in terms of the efficiency of collection and separation of minority charge carriers (NCCs) due to the built-in electric field across the junction. Received solar cells with improved photoelectric characteristics and an efficiency factor (COP) of 20.43%.

Keywords: solar cell, light absorption, $p-n$ junction, silicon.

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It is vitally important for modern civilization, which has a strictly limited number of energy sources available to it, to solve the urgent problem of enhancing the efficiency of conversion of solar energy [1]. More than 90% of solar cells (SCs) are currently fabricated from single-crystal Si and have a low efficiency (15−16%) [2]. There are two major paths toward the development of solar photovoltaic energetics: enhancement of the efficiency of silicon photovoltaic converters (PVCs) and reduction of their production costs.

The second path requires reducing the cost per unit installed peak capacity of photovoltaic systems by a factor of at least 2 [2,3]. High prices on SCs are largely attributable to the costliness of the crystal substrate material. Therefore, cost improvement may be achieved by reducing the thickness of photocells and through the use of cheap low-quality materials. However, this solution is ineffective, since it entails a drastic reduction in the SC efficiency.

The high level of bulk recombination of light-generated minority carriers (MCs), which raises the optical resistance of a semiconductor and reduces the efficiency, is the major physical obstacle on the first path (enhancement of the SC efficiency). Given MC lifetime $\tau_n = 2\,\mu$s in p-Si and electron mobility $\mu_n = 0.14\,\mathrm{m}^2/(\mathrm{V}\cdot\mathrm{s})$ at $T = 300\,\mathrm{K}$, we find using the Einstein relation [2] that diffusion transport length L_n of free electrons to their recombination is $\sim 85\,\mu$m. The value of L_n for lower-quality Si is even lower. Optical absorption thickness $1/\alpha$ for p-Si is $\sim 125\,\mu$m. Here, α is the absorption constant averaged over the spectrum. Thus, thicker Si photoplates are needed to ensure complete absorption of the energy of light. MCs should then diffuse over long distances without recombination, and this necessitates the use of structurally perfect and costly single crystals. In addition to high MC recombination levels, all photovoltaic materials (Si included) feature large refraction indices n_{21} at the air−semiconductor interface, which makes them highly reflective.

The aim of the present study is to propose such engineering solutions that minimize the current drawbacks of silicon solar energy converters.

The proposed SC design features a Si wafer with a surface ensemble of vertically oriented pointed (conical) Si whiskers ($1.5-5.0\,\mu$m in height and less than $1\,\mu$m in diameter) with a coaxial $p-n$ junction through free regions of the substrate surface. Pointed Si whiskers are introduced into the SC structure in order to minimize optical, recombination, and electric (Ohmic) losses by producing the effect of a medium with a vertical refraction index gradient (black Si effect), orthogonalizing the direction of radiation absorption and MC collection, and increasing the effective thickness of the photovoltaic layer, respectively [4–6]. The capacity of systems of pointed whiskers to redirect light to a solid layer of Si as a material with a continually varying refraction index [7] may de utilized in light absorption. If an array of pointed whiskers with different ratios of length l to diameter d is used in such conditions when wavelength $\lambda \geqslant d$, light penetrates through the structured surface as through a film with a continually varying effective permittivity [8]. Specifically, the average refraction index at the interface between a whisker point and air is close to unity. The factor of filling of any given horizontal plane with silicon increases as one approaches the substrate, and effective index n_{21} also increases to above-unity levels. The refraction index at the substrate reaches the n_{21} value for pure Si. The reflectance of such structures decreases from $\sim 30\%$ for plane Si wafers to 1% or lower [9]. Incident light may pass through a large number of submicropoints, which form a unified hierarchical structure with permittivity anisotropy that ensures high antireflection efficiency. Light transmitted through a system of pointed whiskers remains a packet of locally plane waves in the substrate, thus enhancing the wide-band absorption efficiency and preventing parasitic light transmission through the photovoltaic layer. This is the first key benefit of SCs with pointed whiskers.

An SC structure with a coaxial (radial) $p-n$ junction may also be significantly more efficient than a structure of the common plane-parallel geometry with a plane $p-n$ junction. In order to achieve this enhancement, one needs to keep curvature radius r of a coaxial $p-n$ junction at a level well below the diffusion length of MCs in a semiconductor. A photovoltaic structure featuring an array of Si rods on a substrate may raise the effective photovoltaic cell thickness. The light absorption band in each rod goes in the vertical direction, while charge carriers are released in the perpendicular direction through side walls [10]. Pointed whiskers with a coaxial $p-n$ junction provide an opportunity to enhance the effective optical material thickness while creating short paths for transport of excited carriers in the direction orthogonal to light absorption [9]. Length l of grown whiskers may exceed optical absorption thickness $1/\alpha$; i.e., $l > 1/\alpha$ ($1/\alpha \geqslant 125\,\mu$m for Si) [11]. This enhancement of the effective optical material thickness is the second key benefit of SCs with whiskers. The orthogonalization of directions of light absorption and carrier collection is the principal idea behind the concept of PVCs with a coaxial $p-n$ junction. The distinct geometry of whiskers with a coaxial $p-n$ junction allows one to increase the effective width of the depletion region, which occupies up to 50% of the MC collection region by volume.

The PVC efficiency is characterized by the ratio of output electric power P_{out} to net incident optical power P_{in} [1]. Efficiency measurements are commonly performed under standard AM1.5G irradiation with an intensity of 1000 W/m^2. The current density in a plane diode SC (and a cell with a coaxial $p-n$ junction) is defined by the difference between densities of short-circuit current J_{sc} and diode current

$$J = J_{sc} - J_0\left(\exp\left[\frac{eU}{ckT}\right] - 1\right), \tag{1}$$

where $c = 1-2$ is the SC „ideality" factor, J_0 is the saturation current density that is equal to the maximum backward current through the diode and is independent of voltage U at $eU > kT$, e is the electron charge, and k is the Boltzmann constant. Open-circuit voltage U_{oc} (at open terminals) for the modified SC design may be written as [12]

$$U_{oc} = \frac{kT}{e}\ln\left(\left[\frac{J_{sc}}{J_0\chi}\right] + 1\right). \tag{2}$$

where χ is the ratio of the average whisker lateral surface area to the base area.

Let us consider an „optically thick" Si photocell with a thickness of $125\,\mu$m, a p-type collector, and an n-type emitter of a negligible thickness. It is assumed that this cell is free of surface recombination and has fine photovoltaic characteristics ($J_{sc} = 42.2$ mA/cm^2, $U_{oc} = 0.706$ V) and $\eta = 24.7\%$ [13]. The saturation current density for a Si photocell with these parameters at $T = 300$ K, $L_n = 125\,\mu$m, $\tau_n = 4.3\,\mu$s, a hole mobility of $0.05\,\mathrm{m^2/(V\cdot s)}$, and a minority carrier density of $1.96\cdot10^3$ cm^{-3} is $J_0 \approx 5.8\cdot10^{-14}$ A/cm^2. Let us calculate parameters U_{oc}, J_{sc}, and η of SCs with plane and coaxial $p-n$ junctions formed in cylindrical and pointed whiskers with a radius of 125, 100, 10, and $1\,\mu$m. Several assumptions are made to simplify calculations. Whisker radii are set equal to MC diffusion length L_n in p-Si. The n-region thickness is assumed to be negligible. Dependences of fill factor FF on the MC diffusion length and the density of whiskers on the substrate are not taken into account. The independence of FF of the diffusion length should have no influence on the calculated SC parameters if the density of MC traps in the depletion (space charge) region is maintained at a relatively low level ($\sim 10^{14}$ cm^{-3}). The calculation results are given in the table.

The values of J_{sc} for a plane $p-n$ junction were calculated as $J_{sc} = 42.2(L_n/L)$, where 42.2 mA/cm^2 is the short-circuit current of the best SC [13] and $L = 125\,\mu$m is the cell thickness. In the case of a cylindrical $p-n$ junction and normal light incidence, the irradiated area is also equal to the SC substrate area. Therefore, we assume that the light flux is constant and $J_{sc} = \mathrm{const}$ under the condition that all MCs reach a $p-n$ junction within the diffusion length. The effective surface, which increases by S_{lat}/S_{ax} (S_{lat} and S_{ax} are the lateral surface area and the base area of whiskers) with decreasing r, was taken into account in calculations of J_{sc} for SCs with pointed whiskers.

Although the analysis was simplified, the obtained results still demonstrate that a coaxial $p-n$ junction is preferable. It can be seen from the table that the efficiency difference between SCs with coaxial and planar $p-n$ junctions becomes more pronounced as L_n decreases (under the condition that $r \leqslant L_n$). Thus, in contrast to the planar geometry, the coaxial $p-n$ junction geometry holds promise for materials with small diffusion length $L_n \ll 1/\alpha$. This is the third key benefit of SCs with whiskers. Optimally pointed whiskers for SCs with coaxial $p-n$ junctions should have base radius r that is significantly shorter than L_n of electrons in the p-type whisker core (or holes if the central rod is n-type): $r \ll L_n$ ($r < 1\,\mu$m for Si).

The SC constructed here has the structure of a diode formed due to diffusion of n-type impurities (phosphorus) into a p-type KDB Si(111) wafer (boron with a density of $3\cdot10^{16}$ cm^{-3}, the MC lifetime is $\sim 5\,\mu$s) with a thickness of $300 \pm 20\,\mu$m, a resistivity of $0.5\,\Omega\cdot$cm, and a surface structured with pointed whiskers that have different base diameters falling within the range from 100 to 1000 nm (the average diameter is 650–750 nm) and a length of 1.5–5.0 μm. The n-type shell in the PVC structure is thin ($\sim$ 100–150 nm) and doped heavily with phosphorus to a density of $\sim 1\cdot10^{19}$ cm^{-3}. The p-type whisker core has an average diameter of 500–650 nm at the base and a dopant impurity density of $\sim 5\cdot10^{16}$ cm^{-3} that ensures MC

Comparison of parameters of SCs with plane, coaxial cylindrical, coaxial conical $p-n$ junctions

Electron–hole junction type	Solar cell parameters	Whisker radius (or diffusion length of MCs in p-Si L_n) $r = L_n$, μm			
		125	100	10	1
Plane $p-n$ junction	J_{sc}, mA/cm^2	42.2 [13]	33.8	3.38	0.338
	U_{oc}, V	0.706 [13]	0.700	0.641	0.581
	FF, %	82.8 [13]	82.8	82.8	82.8
	η, %	24.70 [13]	19.60	1.80	0.20
Coaxial cylindrical $p-n$ junction	χ	2.00	2.50	25.00	250.00
	J_{sc}, mA/cm^2	42.2	42.2	42.2	42.2
	U_{oc}, V	0.567	0.561	0.502	0.442
	FF,%	82.8	82.8	82.8	82.8
	η, %	19.80	19.60	17.50	15.40
Coaxial conical $p-n$ junction	χ	2.04	2.55	25.50	255.00
	J_{sc}, mA/cm^2	42.2	42.2	46.9	57.2
	U_{oc}, V	0.566	0.560	0.514	0.450
	FF,%	82.8	82.8	82.8	82.8
	η, %	19.80	19.80	19.96	21.34

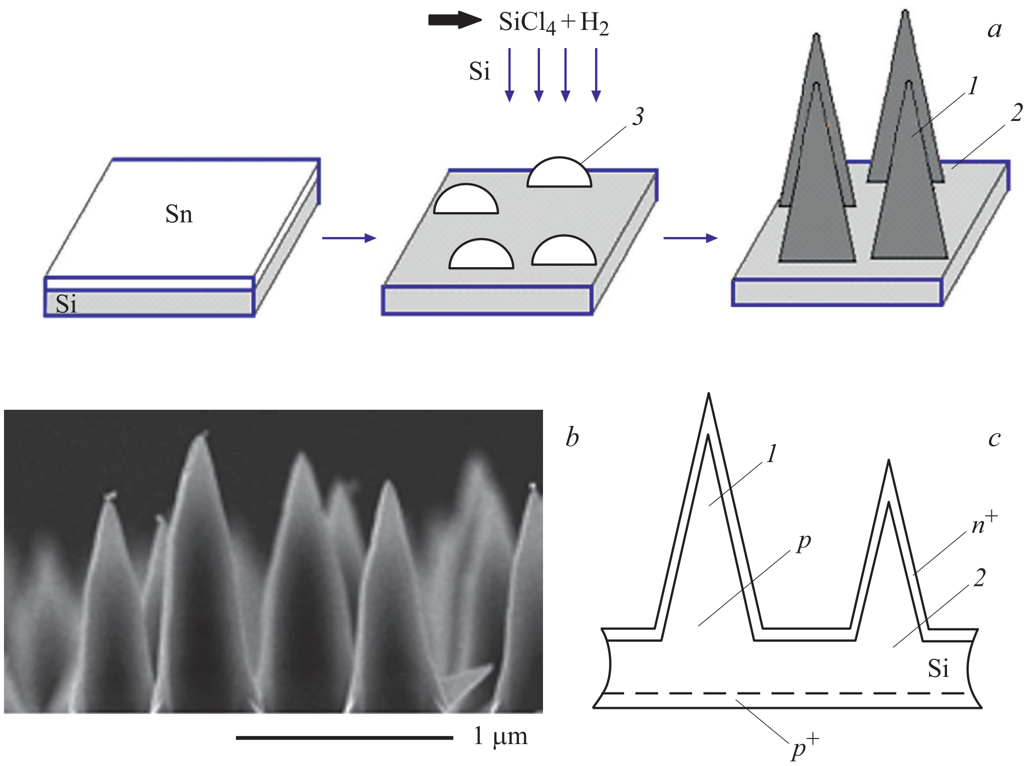

Figure 1. Diagram of the process of fabrication of Si whiskers (a), their external appearance (b), and structural diagram of an SC (c). *1* — Whisker, *2* — substrate, *3* — Sn catalyst. The lower part of the Si wafer is doped with a p^+ acceptor impurity and, combined with the inner core part of conical rods, forms the collector SC region. The outer shell of Si cones is doped with an n^+ donor impurity and, combined with the upper part of the substrate, forms the emitter SC component.

diffusion to the $p-n$ junction. A p^+ layer was formed on the back of the wafer. The procedure outlined in [9] was used to fabricate pointed whiskers with different submicron sizes. Fine Sn particles served as a metal catalyst (Fig. 1, a). Tin is an isovalent impurity in Si and does not produce deep energy levels [14]. In addition, Sn and Si form a constitution diagram with a pronounced eutectic, which facilitates the chemical evaporation of Sn in the process of whisker growth, thus establishing the conditions for growth of pointed structures [15] (Fig. 1, b).

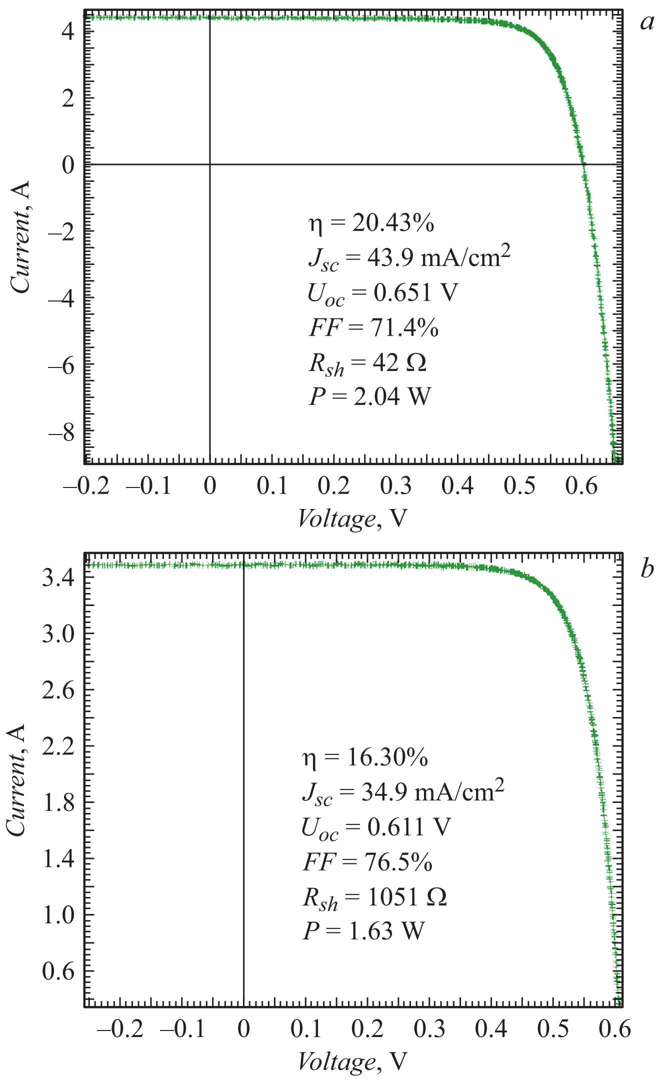

Figure 2. Comparison of current–voltage curves. *a* — Test SC structure with pointed whiskers, *b* — reference sample (textured Si wafer with a coating fabricated following the classical process [16]). The measurement conditions were as follows: sample area — 100 cm^2, temperature — 297.8 K, illumination intensity — 1000 W/cm^2.

A liquid boron source containing BBr_3 was used for Si doping in the process of whisker growth to create *p*-type regions (Fig. 1, *c*). Post-growth diffusion doping with phosphorus was carried out using PCl_3 to form *n*-type regions. An antireflection TiO_x film was deposited into the wafer. Pastes containing Ag and Al were deposited by screen printing with subsequent firing through the TiO_x layer to produce Ohmic contacts.

The current–voltage curves obtained under illumination demonstrate that the efficiency of fabricated SCs is 20.43% (Fig. 2, *a*). It should be noted that open-circuit voltage U_{oc} for the SC with whiskers (0.651 V) is just 0.04 V higher than the corresponding voltage for the reference plane PVC ($U_{oc} = 0.611$ V), while fill factor FF is 5.1% lower (Fig. 2, *b*). The increase in short-circuit current $J_{sc} = 43.9$ mA/cm^2, which is higher than the one for the reference plane SC sample (34.9 mA/cm^2) and the calculated value for a plane $p{-}n$ junction (33.80 mA/cm^2; see the table), is evidently related to an optimistic enhancement of the optical PVC absorption coefficient induced by pointed whiskers. The photocurrent increased by 26%. Both the effect of light trapping by pointed whiskers [5] and efficient orthogonal MC collection contribute to the increase in J_{sc}. It can be seen from Fig. 2, *a* that $U_{oc} = 0.651$ V; i.e., it is lower than the open-circuit voltage of an ideal plane SC (0.706 V), but higher than the calculated value (0.450 V) (see the table). This may be attributed to the fact that experimental samples are essentially a combination of plane and coaxial $p{-}n$ junctions. The shape of the measured current–voltage curve suggests that a 5% enhancement of FF of the experimental sample (relative to the reference one) is attributable to the likely presence of a current leakage channel, which forms parallel to the $p{-}n$ junction due to an insufficiently high parallel resistance ($R_{sh} = 42\,\Omega$) and shunting of the $p{-}n$ junction, and that the assumed lack of dependence of FF on L_n has no effect on calculated parameters.

Having taken the influence of physical and technological factors into account, we managed to raise the efficiency of SCs with pointed whiskers by 4.13% relative to the efficiency of plane-parallel SCs; the electric PVC power enhancement is 25%. The SC design with coaxial $p{-}n$ junctions opens up fresh opportunities for reducing the PVC thickness and utilizing cheaper lower-quality Si.

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Conflict of interest

The authors declare that they have no conflict of interest.

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