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HELIOTECHNICAL MATERIALS SCIENCE

Electrophysical and Optical Properties of Silicon Produced by Multiple Remelting of Metallurgical Silicon by Concentrated Solar Beams (Review)

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Abstract—The review describes a new method for refining silicon—multiple melting of industrial silicon in open air in a solar furnace. The results of three-, five- and eightfold refining are given. In all cases, a sample of melted silicon with simple ohmic contacts during heating at $T > 30°C$ becomes a current and voltage generator, which is explained by the processes of self-organization of deep-lying impurities, leading to their periodic distribution along the sample. From such silicon, *p–n* transfer is obtained, which opens possibilities for practical application.

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1. INTRODUCTION. STANDARD TECHNOLOGY FOR REFINING SILICON

Silicon is the basis of the modern semiconductor electronics. Usually it is produced by the so-called chlorosilane processing method. Thirty-five years since this method was developed, it has hardly changed and has all the disadvantages of 1950s chemical technology: high energy capacity, low silicon yield (6–10%), and a high level of technological danger due to the fact that trichlorosilane is environmentally hazardous. The standard scheme of silicon production by this method is shown in Fig. 1. A quartzite and coke mix in an electric-arc furnace at temperatures higher than 1750°C transform into metallurgical silicon. Then this metallurgical silicon is dissolved in hydrochloric acid, which leads to generation of trichlorosilane (and hydrogen escapes). Then the produced trichlorosilane is refined using the multiple sublimation method and finally settles on a silicon filament heated up to 1350–1390°C. Only after this is monocrystal silicon grown from the obtained raw polycrystalline silicon using Czochralski method. In parts 4 and 5, this method is environmentally hazardous, because during sedimentation trichlorosilane escapes as a toxic agent.

2. NEW METHOD FOR PRODUCING SILICON IN A SOLAR FURNACE

The Physical-Technical Institute of the Academy of Sciences of Uzbekistan has demonstrated the fundamental possibility of remelting waste silicon monocrystals using the Solar Furnace [1]. The authors of [2, 3] proposed production of polycrystalline silicon by an environmentally safe method using the Solar Furnace. In this method especially, hazardous points 4 and 5 are replaced by multiple remelting of metallurgical silicon in open air using a solar furnace. Figure 2 shows the diagram for producing of silicon according to this method.

In the case of silicon production by the multiple remelting method, the original structure of the production unit was used (Fig. 4).

3. RESULTS OF EIGHTFOLD REMELTING OF METALLURGICAL SILICON

A.S. Saidov published results of eightfold remelting of KR3 grade metallurgical silicon using the solar furnace are published [4]. X-ray structural analysis showed that such silicon includes Si, 99.9 wt %, and impurities: Fe, 0.31 wt %; Al, 0.02 wt %; Ca, 0.17 wt %; P, 0.01 wt %; C, 0.01 wt %; Mn, 0.02 wt %; Ti, 0.02 wt %; B, 0.001 wt %; Cu, 0.03 wt %; and Cr, 0.009 wt %; i.e., the weight content of impurities decreased to 1% and KR3 grade silicon was refined up to 99.9 wt %. Measurements of the temperature dependences of the current and voltage appearing in the studied structures with purely ohmic contacts in darkness (without the action of light or external electric field) showed that starting from 25°C, the current (up to 3×10^{-2} μA at $T = 165°C$) and voltage (3.5×10^{-1} mV at $T = 200°C$) are generated therein, the values of which increase as far as the temperature increases, while in standard n-silicon structures, the current and voltage do not change within this temperature interval, which corresponds to classical concepts.

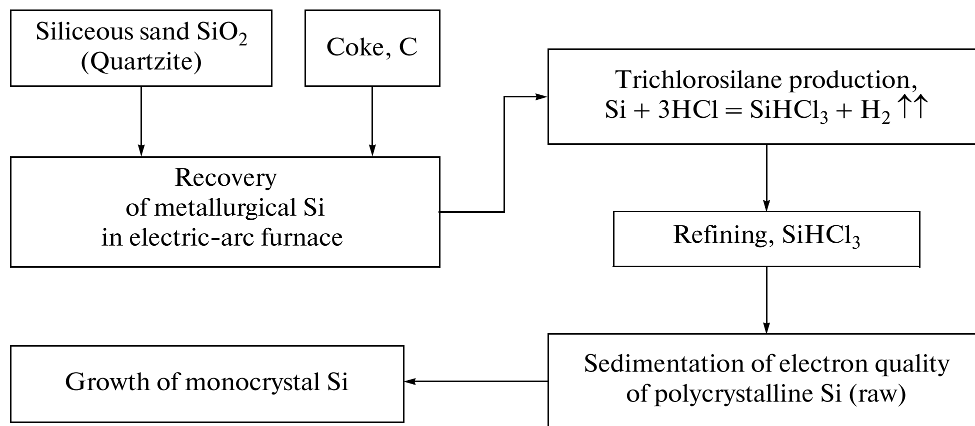


Fig. 1. Simplified processing scheme of silicon production for solar energy industry.

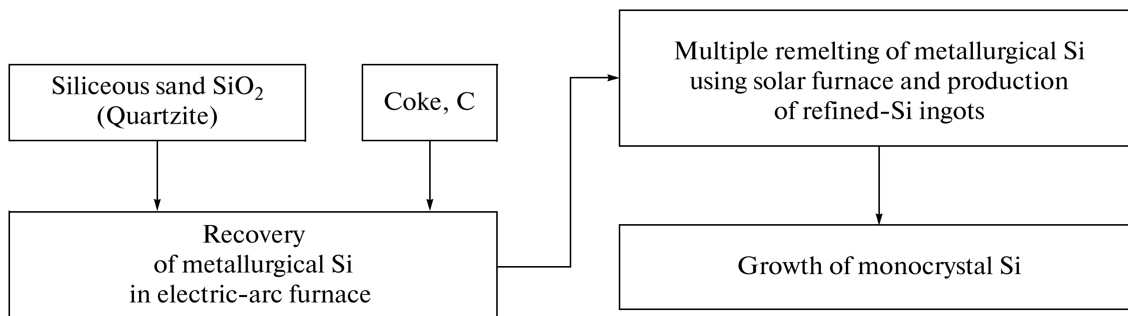


Fig. 2. Simplified processing scheme of silicon production using solar furnace.

Thus, this structure with purely ohmic contacts under the action of temperature becomes a kind of current and voltage generator. This phenomenon was observed for the first time. It mainly recalls the behavior of typical electrets, in which, under the action of particular external factors, only the voltage is generated. However, some significant differences can also be specified: (1) the obtained material is a low-ohmic semiconductor with the specific resistance ~0.1 Ohm cm, but not a dielectric like a common electret; (2) the state of electrets leading to current generation occurs only under the action of temperature, and the obtained material differs from usual thermal electrets in this characteristic, since the action of temperature and field is necessary for them; (3) in the obtained material, only the space charge appears, while in the electrets, there are not only space, but also surface charges; (4) the appearing current $\sim 10^{-7}–10^{-8}$ A; i.e., it is a few orders higher than in common electrets.

To explain the observed effect, it was assumed that that during melting of industrial silicon using the solar furnace in open air, numerous impurities in the material become weakly polarized, i.e., representing large domains (or molecules) with positive and negative edges. Before heating they are located chaotically, which leads to the absence of internal electric field in the material. Apparently under the action of the temperature, these domains (molecules) become ordered and the internal electric field and, therefore, the internal electrical barriers appear. As a result the free carriers created due to the thermal action are divided at these internal barriers, and this is the reason for appearance of the current and voltage, which increase with temperature.

4. RESULTS OF FIVEFOLD REMELTING OF METALLURGICAL SILICON

Silicon obtained by fivefold remelting of metallurgical silicon in open air using the solar furnace is studied. The initial material was common KR3 grade silicon (specifications: Si, 96 wt %; Al, 1.5 wt %; Fe, 1.5 wt %; Ca, 1 wt %; etc.). After fivefold remelting in open air using the solar furnace, the material was subjected to X-ray structural analysis; the results showed its following weight composition: Si, 98.77 wt %; Fe, 0.41 wt %; Al, 0.0163 wt %; Se, 0.015 wt %; Ca, 0.2185 wt %; Pb, 0.0007 wt %; P, 0.11 wt %; Mn,

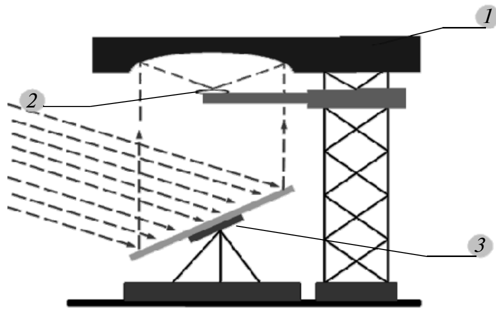


Fig. 3. General scheme of plant with concentrator and heliostat. *1*, concentrator; *2*, production unit; *3*, heliostat.

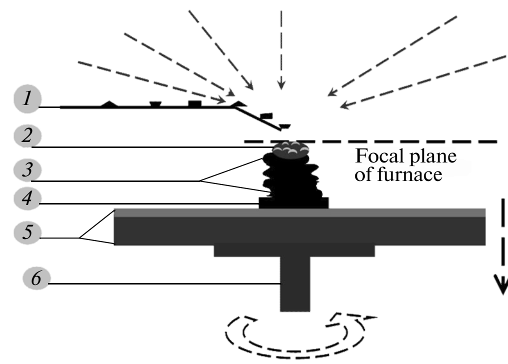


Fig. 4. Scheme of production unit. *1*, industrial silicon supply; *2*, melted industrial silicon; *3*, produced silicon ingots; *4*, base of monocrystal silicon; *5*, table of production block; *6*, turning mechanism.

0.047 wt %; Cu, 0.0185 wt %; Ag, 0.00041 wt %. As well, its atomic composition was as follows: Si, 99.1 at %, Fe, 0.21 at %, S, 0.79 at %, Al, 0.01 at %, Se, 0.0053 at %, Ca, 0.15 at %, P, 0.10 at %, Mn, 0.02 at %, Cu, 0.008 at %, Pb, 0.0001 at %, Ag, 0.00011 at %. Thus silicon was obtained with the purity 99.1 at %. The samples had a large-grain structure with the grain sizes ~1×2 mm^2 (80–85%) of different orientation and do not have shunt metal inclusions. They had *n*-type of conductance without preliminary doping.

The plates ~500 μm and 40 mm diameter are cut of the polycrystalline silicon ingots with the purity 99.1 at % obtained by such method which later were smoothed from one side and polished from the other side, in details [4].

The polycrystalline silicon ingot obtained in such a way is shown in Fig. 5a, and the plate cut of it, in Fig. 5b.

A thin layer of the ohmic contact was applied to the smoothed side by the vacuum deposition method described in [5], and to the polished side, the metal ohmic contact in the form of mesh produced of titanium and nickel alloy. Thus, a semiconducting structure was created with two common ohmic contacts, similar [4] to the structure of eightfold remelted silicon.

Then the temperature dependences of the current and voltages were studied for this structure; the results are shown in Figs. 6a and 6b.

It is clear from these figures that beginning at a temperature ~30°C, current and voltages are generated; i.e., they become a kind of current and/or voltage generator. Thus, after fivefold remelting, certain specific properties of the material appear that were observed in the eightfold remelted industrial silicon [4].

5. COMPARATIVE ANALYSIS OF THE RESULTS OF FIVE- AND EIGHTFOLD REMELTING OF METALLURGICAL SILICON

Silicon multiple remelting using the solar furnace under insignificant action of temperature becomes a current and/or voltage generator. Table 1 compares the observed currents and voltages (the data for eightfold remelted silicon are taken from [4]).

It is seen from Table 1 that the initial metallurgical silicon generates neither current nor voltage, and five-

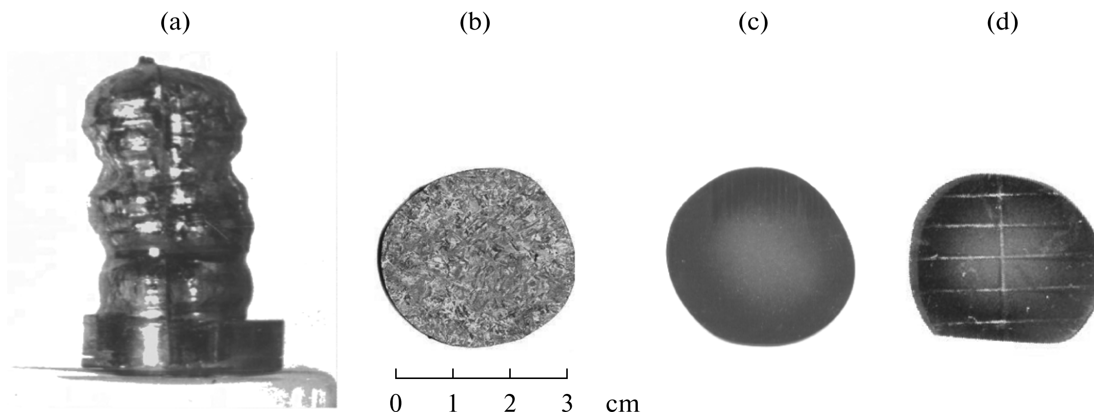


Fig. 5. View of silicon ingot obtained by fivefold remelting of KR3 grade silicon (a), section of plate cut from it (b), polished side of plate (c), plate with ohmic contacts (d).

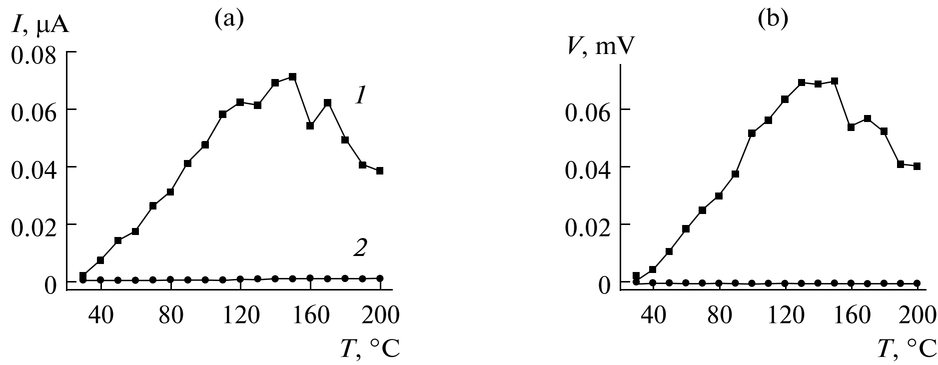


Fig. 6. Temperature dependences of current (a) and voltage (b) appearing in n-Si structure with ohmic contacts made of fivefold solar-remelted industrial silicon (curve *1*) and standard n-polysilicon (curve *2*) obtained only under temperature action.

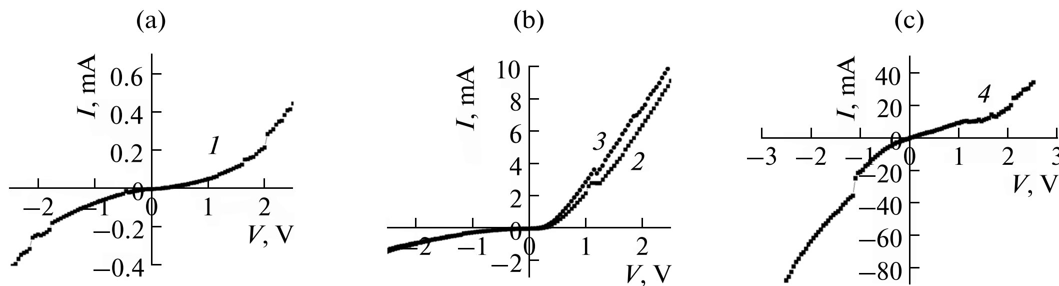


Fig. 7. Volt–ampere characteristics of n-Si-structure with ohmic contacts made of fivefold solar-remelted industrial silicon at different temperatures: curves *1*, 30°C (a); *2*, 50°C; *3*, 100°C (b); *4*, 150°C (c).

fold remelted silicon provides the maximum current and voltage values.

6. VOLT–AMPERE CHARACTERISTICS OF STRUCTURES WITH OHMIC CONTACTS OF FIVEFOLD REMELTED SILICON FROM INDUSTRIAL SILICON

The authors also studied the volt–ampere characteristics of these structures with common ohmic contacts. The results are given in Fig. 7. It is clear that at a temperature of 30°C, nonohmic contacts appear just as it was mentioned in [4] for structures produced from eightfold melted silicon.

7. STUDY OF THE IMPURITY COMPOSITION OF THE OBTAINED SILICON

The impurity composition of the studied materials was analyzed to understand the physical processes responsible for the observed effect.

Table 1. Comparative values of currents and voltages generated upon temperature action in silicon obtained by five- and eightfold remelting of metallurgical silicon using solar furnace

Temperature, °C	Industrial silicon	Fivefold remelted silicon	Eightfold remelted silicon
	current (I, μA)	current (I, μA)	current (I, μA)
30	–	0.002	0.005
150	–	0.071	0.028
200	–	0.038	0.033
Temperature, °C	voltage (V, mV)	voltage (V, mV)	voltage (V, mV)
30	–	0.006	0.053
130	–	0.686	0.25
200	–	0.402	0.329

The spatial distribution of the impurities along the sample in the wt % and at % was studied on ab Elan DRC-II mass spectrograph. Table 2 lists some impurities to compare the changes introduced by different amounts of remelting. It should be noted that the maximum concentration values were selected.

Figures 7 and 8 shows results of studying the weight and atomic composition for fivefold remelted metallurgical silicon [6].

It is clear that most of these deep-lying impurities have a very high concentration. Because the concentration of all impurities changes periodically along the length of the sample, Table 3 gives the maximum and minimum concentrations.

As the studies carried on on the Elan DRC-II have shown, the distribution of all these impurities along the length of the sample was not only heterogeneous, but periodic to a particular degree. Figure 9 shows the results of the concentration distribution for the basic deep-lying impurities determined from these measurements.

Thus, it follows from Figs. 8–10 that all of the studied impurities are distributed periodically in space. This is apparently the result of the self-regulation process occurring during melting. The the extent of the change in concentration from the minimum to maximum along the length of the sample is approximately 4 mm for all impurities, i.e., exceeding the grain diameter, and there are no grounds to assume that the nature of the observed phenomena is related the processes at the grain boundaries. The appearance of a spatially periodic distribution of impurities definitely proves the appearance of internal potential n–n+ isotype barriers, which in turn means appearance of internal electrical fields.

Table 2. Comparative weight composition (%) of silicon of different types

Impurities	Technical specifications of KR3 grade metallurgical silicon	Fivefold remelted silicon	Eightfold remelted silicon
Si	96	98.77	99.4
Fe	1.5	0.41	0.31
Ca	1	0.21	0.17
Al	1.5	0.016	0.02

Table 3. Content of the main impurities in silicon obtained by fivefold remelting of metallurgical silicon in the open air in the solar furnace

Elements	Concentration maximum, cm^2	Concentration minimum, cm^2
Si	4.95×10^{22}	4.88×10^{22}
Fe	5.05×10^{20}	9.50×10^{19}
S	3.96×10^{20}	1.06×10^{20}
Ca	2.80×10^{20}	7.69×10^{19}
P	8.85×10^{19}	1.55×1019
Mn	7.09×10^{19}	1.23×10^{19}
Se	6.05×10^{19}	3.00×10^{17}
Al	2.49×10^{19}	7.15×10^{18}

8. THEORETICAL ASSUMPTIONS OF THE OBSERVED EFFECT OF CURRENT AND VOLTAGE GENERATION IN SILICON MULTIPLE REMELTED USING THE SOLAR FURNACE

The studies show that distribution of all impurities bears has not only a uniform, but to a particular degree periodic character. Let us try to understand which physical processes can lead to such an unusual distribution of impurities.

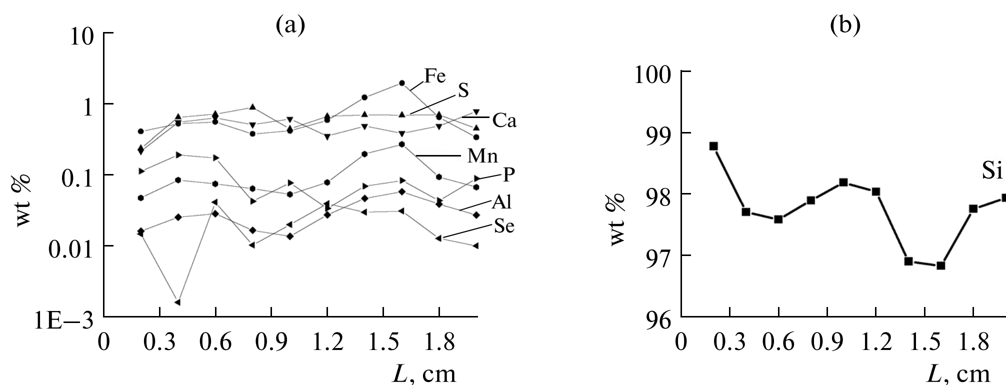


Fig. 8. Spatial distribution of impurities (a) and silicon (b) along sample in weight percent for silicon obtained by fivefold remelting of metallurgical silicon using solar furnace.

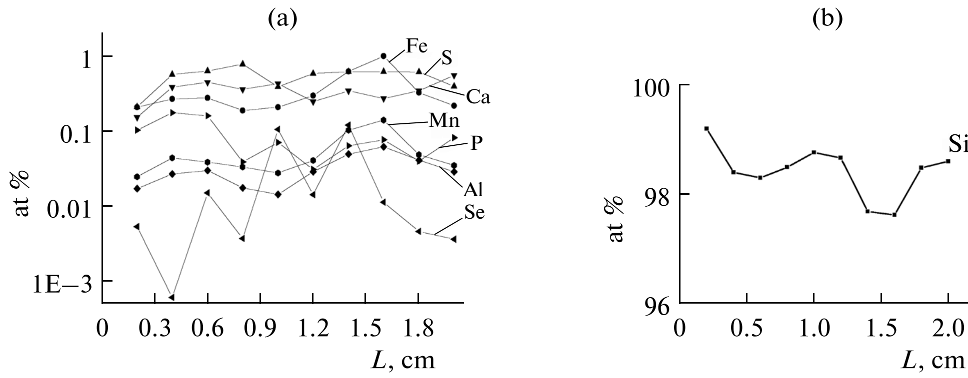


Fig. 9. Spatial distribution of impurities (a) and silicon (b) along sample in atomic percent for silicon obtained by fivefold remelting of metallurgical silicon using solar furnace.

As is known, the number of vacancies in a material always depends heavily on temperature (see, e.g., [7, p. 249]):

$$V_{\text{vac}} = N_a \exp(-\Delta E_{\text{vac}}/kT), \quad (1)$$

where V_{vac} is the total concentration of vacancies at this temperature; N_a is the initial concentration of atoms ($\approx 10^{22}$ cm^{-3}); ΔE_{vac} is the activation energy of vacancies, usually 1–3 eV depending on the material; k is the Boltzmann constant; and T is temperature.

In contrast, in the course of melting, large portions of energy are released corresponding to the specific melting heat not only of silicon but also all the impurities contained in it—iron, aluminum, calcium, carbon, manganese, etc. Correspondingly, this energy can be spent for destruction of the material lattice, i.e., to change not only the long-range, but also short-range order—in other words, for the creation of different defects, particularly, vacancies. In this case, it is of no importance whether these are Schottky single vacancies or pairs of Frenkel defects of the type "positively charged interstitial ion–negatively charged vacancy." It is important that their number can be significantly large. It is known that forbidden area, so that the vacancies themselves can be an additional recombination channel [8] (this recombination channel is shown in Fig. 11a by the dotted line). At the same time, heating of the material is followed by the release of a large number of free carriers. Thus, in the course of melting, we are dealing with the subsystems of free charge carriers (electrons and holes) and different types of impurities and vacancies. Because it is impossible to consider all available impurities without resorting to computer simulation, let us limit ourselves to only certain impurities and show that even in a sufficiently simple system with three mutually interacting subsystems—free carriers, vacancies, and impurities—the development of self-organization processes of the type first predicted in [9, 10] and later studied with different models in [11, 12] is possible. Let us consider that according to modern representations, impurities creating several levels in the forbidden area, such as silver, manganese, etc., often occupy different places in the silicon lattice having a stable position at a site and state in the interstice, which represents an

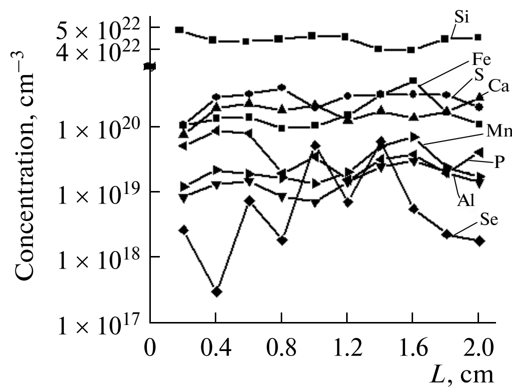


Fig. 10. Spatial distribution of concentrations of silicon and impurities along sample for silicon obtained by fivefold remelting of metallurgical silicon using solar furnace.

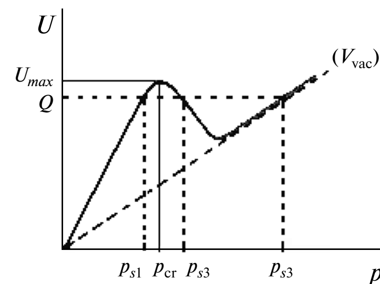
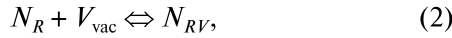


Fig. 11. Dependence of recombination velocity of nonequilibrium charge carriers U at level of excitation. Dotted line, share of recombination velocity introduced directly by recombination through vacancies; p_{s1}, p_{s2}, p_{s3}—special points of Eq. (3) under stationary conditions; p_{cr}, critical value of concentrations at which maximum recombination velocity is achieved.

association of this impurity with the vacancy and can be described by a reversible quasi-chemical reaction:



$$N_R + V_{\text{vac}} \Leftrightarrow N_{RV}, \qquad (2)$$

where N_R is concentration of deep-lying impurities playing the role of recombination centers, and N_{RV} is the concentration of "impurity + vacancy" type complexes.

Thus it is necessary to mathematically describe the three subsystems interacting between each other—free carrier, subsystem, and vacancy subsystems.

Because only quasi-neutral processes are considered and in the system the number of free electrons and holes are linearly related $n \approx p$, it is possible to approximately describe the state of the subsystem of free charge carriers by the ambipolar equation, just as it is usually done [13, 24, 54] when describing injection and photoexcitation processes:

$$\frac{\partial p}{\partial t} = D_{\text{eff}}\frac{\partial^2 p}{\partial x^2} - U + Q, \qquad (3)$$

where p is the concentration of free holes, $D_{\text{eff}} = \frac{2D_nD_p}{D_n + D_p}$ is effective diffusion coefficient taking into account the possibility of joint ambipolar diffusion of holes and electrons in the studied material, $D_n = \frac{kT}{q}\mu_n$, $D_p = \frac{kT}{q}\mu_p$, are the coefficients of diffusion of electrons and holes, respectively, q is the electron charge, k is the Boltzmann constant, μ_n and μ_p are the mobilities of electrons and holes, U is the recombination velocity of free charge carriers, and Q is a term describing generation of free charge carriers within the unit time due to thermal energy acting on the material in the course of its remelting.

Now it is necessary to add this equation to the equations describing the subsystems of vacancies V_{vac} and deep recombination centers N_R:

$$\frac{\partial V_{\text{vac}}}{\partial t} = -\frac{V_{\text{vac}} - V_0}{\tau_V} + \gamma e^{-\frac{\Delta E_{\text{vac}}}{kT}} p, \qquad (4)$$

$$\frac{\partial N_{RV}}{\partial t} = -\frac{N_{RV} - N_{RV0}}{\tau_{RV}} + \beta N_R V_{\text{vac}}, \qquad (5)$$

where V_{vac} and N_{RV} are the concentrations of vacancies and defect-impurity complexes of the vacancy + impurity type, respectively, V_0 and N_{RV0} are the initial concentrations of vacancies and defect-purity complexes, τ_V is life time of vacancies, τ_{RV} is life time of defect-impurity complexes, γ is the effective coefficient describing the creation of vacancies during excitation of the material, β is effective coefficient describing the creation of defect-impurity complexes of the impurity + vacancy type, and t is time.

Equation (3) is quite common, describing the ambipolar transfer of free charge carriers under conditions of external action, in this certain case, thermal energy. Equations (4) and (5) describe the state of vacancies and defect-impurity complexes of the "vacancy + impurity" type appearing under the action of thermal energy. At that the second member in the equation (4) describes generation of vacancies not only under the action of temperature but also as a result of an increase in the excitation level of free charge carriers. This is possible if it is assumed that the portion of energy released during the act of recombination of free charge carriers is sufficient to form a vacancy. In this case it is not important whether it will be single Schottky vacancies or Frenkel pairs of the type "interstitial + vacancy" ion. It is significant that they can appear; i.e., recombination-stimulated formation of vacancies is possible. The first term in Eq. (4) describes recombination of vacancies; it is assumed that the recombination velocity of vacancies is linearly related to their concentration, and their life time τ_V is constant. Equation (5) describes the generation and recombination of defect-impurity complexes of the "vacancy + deep impurity center" type. It is assumed that the number of such defect-impurity complexes also linearly increases with an increasing concentration of vacancies and their life time τ_{RV} is constant.

According to Shockley–Read statistics, the recombination rate is

$$U = N_R R, \qquad (6)$$

where N_R is total number of recombination centers and

$$R = \frac{c_n c_p (pn - n_i^2)}{c_n(n + n_1) + c_p(p + p_1)}, \qquad (7)$$

where c_n and c_p are the coefficients of trapping of electrons and holes, respectively, to a recombination center; n_i is the specific concentration, and n_1 and p_1 are the so-called Shockley–Read statistic factors depending on the activation energy of the deep-lying impurity level.

For a sufficiently high level of excitation under conditions of quasi-neutrality when $n \approx p > n_1, p_1$, (7) can be written as $R \approx c_{\text{eff}}p$, where $c_{\text{eff}} = \frac{c_n c_p}{c_n + c_p}$ can be called the effective trapping coefficient. However, in the considered case, a significant number of deep-lying impurities playing the role of recombination centers during excitation of the material can be combined into complexes with vacancies, forming associates of the "deep-lying impurities + vacancy" type. Such impurities associated into complexes have much less possibilities of trapping electrons and holes, and their recombination ability decreases considerably. For simplicity let us consider that they cannot participate in the recombination process at all, and then the num-

ber of efficiently operating recombination centers N_{eff} will be:

$$N_{\text{eff}} = N_R - N_{RV}, \quad (8)$$

and the recombination velocity passing through these centers will be defined as follows:

$$U = (N_R - N_{RV})c_{\text{eff}}p. \quad (9)$$

Under stationary conditions when $\frac{\partial p}{\partial t} = 0$, $\frac{\partial V_{\text{vac}}}{\partial t} = 0$, $\frac{\partial N_{RV}}{\partial t} = 0$, from (4) and (5) (under the assumption that the initial concentrations of vacancies V_0 and defect-impurity complexes N_{RV0} are low) we find the concentrations of vacancies and defect-impurity complexes steady-state at these excitation levels:

$$V_{\text{vac}} = \tau_V \gamma e^{-\frac{\Delta E_{\text{vac}}}{kT}} p, \quad (10)$$

$$N_{RV} = \tau_{RV} \beta \gamma \tau_V e^{-\frac{\Delta E_{\text{vac}}}{kT}} N_R p. \quad (11)$$

Then substituting (11) into (9), the final expression is obtained for the recombination velocity:

$$U = N_R c_{\text{eff}} p - N_R c_{\text{eff}} \beta \gamma \tau_V \tau_{RV} e^{-\frac{\Delta E_{\text{vac}}}{kT}} p^2. \quad (12)$$

Thus a new expression is obtained for the recombination velocity of the free charge carriers, which differs from the common one by the presence of a second term describing reconstruction of the recombination centers in the process of the temperature action on the material. Consideration of expression (12) shows that there is a maximum value of the recombination velocity achieved for the critical concentration value (Fig. 11):

$$p_{\text{cr}} = \frac{e^{\frac{\Delta E_{\text{vac}}}{kT}}}{2\beta\gamma\tau_V\tau_{RV}}, \quad (13)$$

i.e., it depends only on the properties of the material and temperature.

Under stationary conditions ($\frac{\partial p}{\partial t} = 0$) taking into account expression (12) for the recombination velocity, it is possible to obtain an equation from (3) describing the distribution of the concentration of nonequilibrium charge carriers in the material:

$$\frac{\partial^2 p}{\partial x^2} + Q - N_R c_{\text{eff}} p + N_R c_{\text{eff}} \beta \gamma \tau_V \tau_{RV} e^{-\frac{\Delta E_{\text{vac}}}{kT}} p^2 = 0. \quad (14)$$

The exact solution to this equation under conditions when there is no excitation at the sample edges [0, w] (as is usually done when solving the self-organization problem) was found in [6] through the elliptic integral of the first kind.

However, for small deviations of the nonequilibrium concentration of holes from its value at a particular point p_{s2} (Fig. 11), the magnitude of the elliptic integral is small ($k < 1$) and this solution can be simplified and written approximately as follows:

$$p \approx p_{s2} + (p(0) - p_{s2})\cos\left[\frac{x}{L_{\text{eff}}}\left(1 - \frac{k^2}{4}\right)\right], \quad (15)$$

where the characteristic length of the appearing distribution of the concentration L_{eff} is defined by the expression $L_{\text{eff}} = \sqrt{\frac{D_{\text{eff}}}{\left|\frac{dU}{dp}\right|_{p = p_{s2}}}}$, i.e., it directly depends on the change in the recombination velocity on the decreasing section of the dependence $U(p)$, and p_{s2} is the concentration of free charge carriers in at particular point lying on the decreasing section of the dependence $U(p)$; $p(0)$ is the concentration at the sample edge.

Thus, the appearance of the decreasing section on the recombination velocity dependence specified by inhibition (suppression) of recombination due to the appearance of defect-impurity complexes leads to the occurrence of a periodic spatial distribution of the concentration of free charge carriers (instead of the common exponential distribution of a particular kind). At the same time, in the considered case, the defect-impurity complexes are directly related to the free charge carriers (see (11)), so that they also form a spatially heterogeneous, periodic structure:

$$N_{RV} = \tau_{RV}\beta\gamma\tau_V e^{-\frac{\Delta E_{\text{vac}}}{kT}} N_R \times \left\{p_{s2} + (p(0) - p_{s2})\cos\left[\frac{x}{L_{\text{eff}}}\left(1 - \frac{k^2}{4}\right)\right]\right\}. \quad (16)$$

Since the considered defect-impurity complexes represent associates of the "impurity + vacancy" type, it turns out that the impurities are distributed along the space periodically as a result of self-organization (self-regulation) processes occurring in the course of melting. This is proved by the experimentally obtained distribution of impurities shown in Fig. 10. A periodic distribution of impurities in the film can be clearly seen in it.

The appearance of a spatially periodic distribution of impurities proves the appearance of internal potential isotype barriers, i.e., barriers of the $n - n^+$ type, which in turn means the occurrence of internal electrical fields. Therefore, it can be expected that with the appearance of free charge carriers, the current in this material will be divided at these potential barriers, as a result of which the current and voltage can appear, which are cooperative (synergetic, specified by the self-organization processes of impurities in the course of melting) in their nature. Indeed, as is shown in

Fig. 6, in a material into which only simple ohmic contacts are placed, under the action of very small temperatures, currents and voltages appear, which change together with temperature; i.e., both the current and voltage are generated in a sample with ohmic contacts made of polycrystalline silicon obtained by fivefold remelting using the solar furnace within the temperature range 20–200°C.

One can try to estimate the value of the occurring voltage. As is clear from Fig. 10, as a result of the appearance of a periodic distribution of deep-lying impurities, the total semiconductor contains a large number of isotype transfers. The diffusion potential of each of them can be described as follows:

$$V^0_{n^+-n} = \frac{kT}{q}\ln\frac{n_n^+}{n_n}. \quad (17)$$

Let us estimate this value for the largest transfers in the considered material, and exactly for the isotype transferred created by iron. As is clear from Fig. 10, $n_n^+ = 4 \times 10^{20}$ cm^{-3}, $n_n \approx 2 \times 10^{20}$ cm^{-3}; i.e., the difference in concentration is only 2. Then, at ambient temperature, from (17) we obtain $V^0_{n^+-n} = 0.018$ V; therefore, the voltage appearing while dividing the nonequilibrium charge carriers in such a transfer will be two or even three times less. Thus, appearance of a synergetic voltage of 0.006 V can be expected, which agrees well with the experimental data in Fig. 6b.

9. PHOTOSENSITIVITY OF THE SPECTRUM

We also studied the photosensitivity of the spectrum of this R_{ohm}–n–Si–R_{ohm} structure. Figure 12 shows the results of measuring its volt photosensitivity on a IK-21 spectrometer at ambient temperature.

It should be especially noted that this material has hardly any current sensitivity—currents generated in the structure were no more than 10^{-15} A and could not be measured with the used equipment. As is clear from Fig. 12, the studied structure has a significant spectrum volt sensitivity. Its maximum value is 5.5 μV within the interval 0.27–0.7 eV, and the total observed spectrum proves the sensitivity of the initial material in the infrared (IR) region of the spectrum. The studies showed that the initial material—KR3 grade metallurgical silicon—does not possess such sensitivity, nor do common monocrystal silicon and common polycrystalline silicon.

Thus, the studied fivefold remelted silicon possesses sensitivity in the IR region of the spectrum; as is clear from Fig. 12, there is a volt sensitivity plateau in the range 0.4–0.7 eV. The reason for this sufficiently uncommon photosensitivity is evidently the presence in the studied material of a high concentration of deep-lying impurities that, as stated in [6], underwent self-organization in the course of multiple remelting.

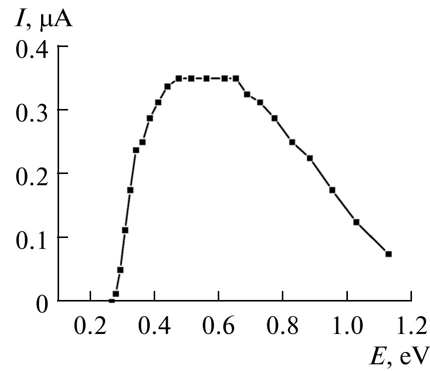


Fig. 12. Spectral volt photosensitivity R_{Ohm}–nSi–R_{Ohm} made of n-type silicon produced by fivefold remelting of KR3 grade metallurgical silicon in open air using solar furnace at ambient temperature.

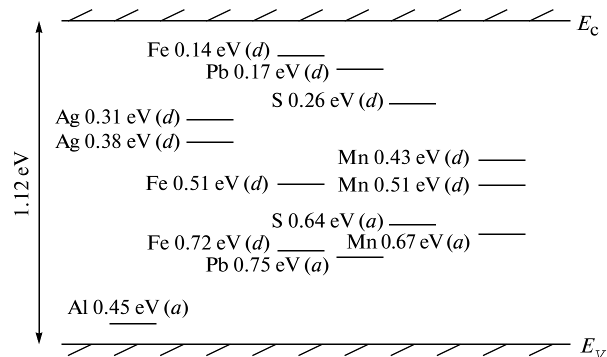


Fig. 13. Location of impurity levels of elements with highest concentration in forbidden zone of silicon produced by fivefold remelting of metallurgical silicon using solar furnace.

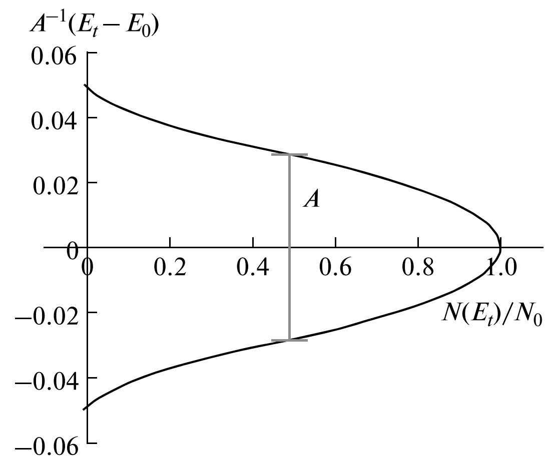


Fig. 14. Function $N(E_t)$ (1) of distribution of local energy states in forbidden zone.

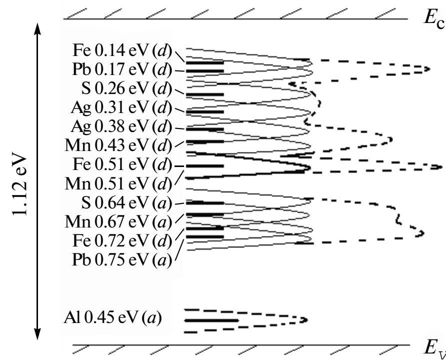


Fig. 15. Quality picture of diffusion of impurity levels with high concentration in forbidden zone of studied silicon produced by fivefold remelting of metallurgical silicon using solar furnace.

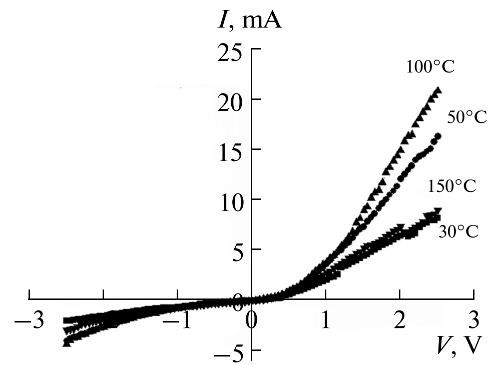


Fig. 16. Volt–ampere characteristics of n–p structure created based on fivefold remelted silicon by boron diffusion obtained at different temperatures.

These are sulfur, iron, aluminum, selenium, lead, argentums, etc. (Table 3). The location of deep-lying impurities in the forbidden zone of silicon is shown in Fig. 13. (Data from [14, p. 26]).

It should be noted that all these impurities have very high concentrations from 5×10^{20} cm^{-3} with Fe and to 10^{17} cm^{-3} with Ag (Table 3). Due to the high concentration, all these impurities will have not the same discrete level in the forbidden zone, but a diffuse band $\sim 10^{-1}$ eV corresponding to it. A. Rose theoretically substantiated this in his early works [15, pp. 49–50], which was then experimentally proved by many authors, particularly in the works of A.A. Lebedev et al. [16–19]. Much of this experimental data is also presented in monograph [20, p. 148].

It is known that the "diffused" impurity spectrum $N(E_t)$ appearing during diffusion of small impurity levels is well described by a Gaussian curve (Fig. 14):

$$N(E_t) = N_0 \exp[-A^2\{E_t - E_0)^2], \qquad (18)$$

where N_0 is the density of local states corresponding to energy $E_t = E_0$, i.e., the energy of the discrete level that has undergone diffusion; E_t are the levels correspond-

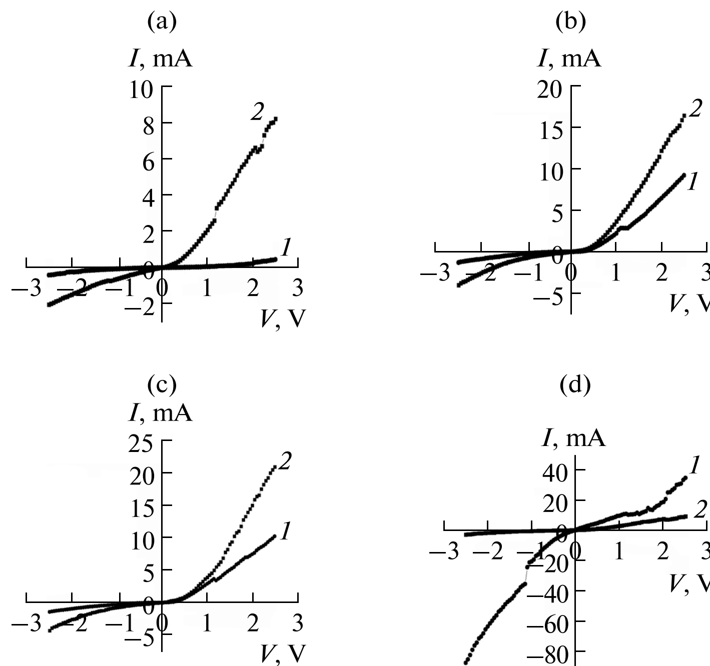


Fig. 17. Volt–ampere characteristics of R_{Ohm}–n–R_{Ohm} structure made of fivefold remelted metallurgical silicon (curves *1*) and corresponding volt—ampere characteristics of n–p structures (curves *2*) at same temperatures: (a) 30°C, (b) 50°C, (c) 100°C, and (d) 150°C.

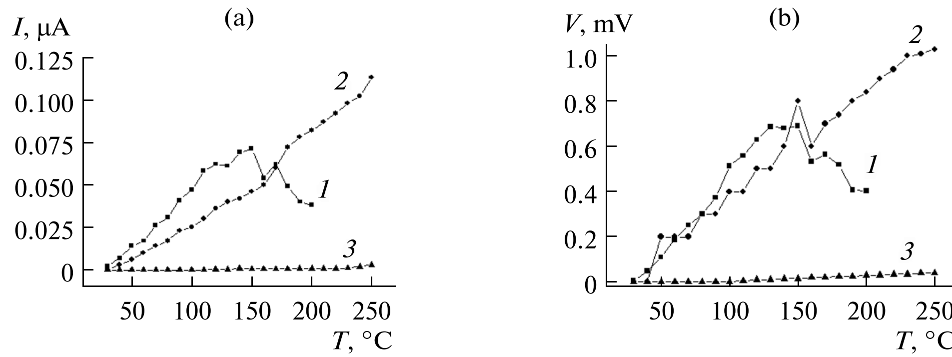


Fig. 18. Temperature dependences of current (a) and voltage (b) appearing in *n–p* Si structure created by boron diffusion based on fivefold remelted metallurgical silicon (curves *2*) and these dependences for the structure with simple ohmic contacts produced of fivefold remelted metallurgical silicon (curves *1*), and standard photoelement of *n*-polysilicon (curves *3*) obtained exclusively under temperature action.

ing to the diffused spectrum; A^{-1} is halfwidth of diffusion.

As for the deep-lying impurities, there is no uniform analytic description of their diffusion. However, expression (18) is assumed to be a sufficiently satisfactory approximation for them as well [20].

If these representations are used, it is possible, using the data of Table 3, to construct the quality pattern obtained as a result of diffusion of the deep-lying impurity levels of the studied material (Fig. 15). It follows from Fig. 15 that within the energy interval 0.26–0.77 eV, a single diffusion band is formed, which explains appearance of the IR sensitivity shown in Fig. 12.

10. STRUCTURE WITH *p–n* TRANSFER MADE OF SILICON PRODUCED BY FIVEFOLD REMELTING OF METALLURGICAL SILICON

Since it turned out that Si produced by fivefold remelting in open air using the solar furnace detects the IR-sensitivity of the spectrum, it is of interest to prepare the *n–p* transfer from it using boron diffusion. The contacts to the obtained structure were done by the same method [5]. Figure 16 shows the volt–ampere characteristics of the obtained *n–p* structure at different temperatures .

For comparison Fig. 17 shows the volt–ampere characteristics of the $R_{Ohm} - n - R_{Ohm}$ structure made of fivefold remelted metallurgical silicon and the corresponding volt–ampere characteristics of *n–p* structure at the same temperatures (curves *1* are taken from Figs. 7a–7d).

It is seen that at ambient temperature, the structure with ohmic contacts has almost no rectifying properties, while the structure with *n–p* transfer at the same temperature has a quite good rectification, which is improved with increasing temperature up to 100°C. At the same time, it is clear from Fig. 17d that at 150°C, the current in the structure with *n–p* transfer decreases sharply, while in the structure with simple ohmic contacts, it increases.

The influence of temperature on the obtained *n–p* structure was also studied. It turned out that this structure, as well as the structure with simple ohmic contacts, becomes a current and voltage generator for insignificant temperature changes. The results of the studies are given in Figs. 18a and 18b.

Comparative analysis of curves *1* and *2* in Figs. 18a and 18b shows that within the temperature interval 30–160°C, the $V(T)$ dependences in both structures is approximately equal, but then the voltage in the simple structure begins to decrease, while in the structure with *n–p* transfer, it increases and achieves a value of 1.03 mV at $T = 250$°C. As for the changes in current with temperature growth, as is clear from curves *1* and *2* in Fig. 17a up to 140°C in the structures with simple ohmic contacts, the current is two times larger, and only beginning from 140°C does the current decrease, and in structures with *n–p* transfer, it increases up to 0.11 μA at $T = 250$°C (despite the common photoelements ensuring a current of 10^{-4} μA and voltage of $\sim 10^{-4}$ mV).

CONCLUSIONS

Thus, as a result of fivefold remelting of KR3 grade metallurgical silicon in open air using the solar furnace, it was refined up to 99.9 at %. This proves that a chloride-free, environmentally safe method of remelting using the solar furnace is promising.

The obtained silicon of sufficiently high purity has some rather uncommon characteristics—upon insignificant changes in temperature, the semiconducting structure with simple ohmic contacts made from it turns into a current and/or voltage generator ($I \sim 0.075$ μA and $V \sim 0.7$ mV).

The studied silicon has a spectrum volt sensitivity in the infrared region of the spectrum.

The *n–p* structures produced from such fivefold remelted metallurgical silicon also have the ability to generate current ($I \sim 0.11$ μA) and voltage ($V \sim 1.1$ mV) upon temperature changes within the range 30–250°C (despite common photoelements ensuring a current of 10^{-4} μA and voltage of ~10^{-4} mV). The rectifying properties of these *n–p* structures worsens with increasing temperature, as well as in the common photoelements, while in structures with simple ohmic contacts, this ability only improves with temperature growth. In *n–p* structures made of remelted metallurgical silicon, worsening of the rectifying properties begins at significantly higher temperatures (higher than 100°C) than in common silicon photoelements and diodes (~60–70°C).

Apparently, the effects of current and voltage generation, as well as the ppearance of photosensitivity in the infrared region of the spectrum, are synergetic in nature, i.e., appearing as a result of self-organization (self-regulation) processes of deep-lying impurities in this material upon its multiple remelting.

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