## ISSN 2518-1726 (Online), ISSN 1991-346X (Print)

## ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Әль-фараби атындағы Қазақ ұлттық университетінің

# ХАБАРЛАРЫ

## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН Казахский национальный университет имени Аль-фараби

## NEWS

OF THE NATIONAL ACADEMY OFSCIENCES OF THE REPUBLIC OF KAZAKHSTAN Al-farabi kazakh national university

SERIES PHYSICO-MATHEMATICAL

## 3 (325)

## **MAY - JUNE 2019**

PUBLISHED SINCE JANUARY 1963

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

Бас редакторы ф.-м.ғ.д., проф., ҚР ҰҒА академигі **Ғ.М. Мұтанов** 

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## «ҚР ҰҒА Хабарлары. Физика-математикалық сериясы».

### ISSN 2518-1726 (Online), ISSN 1991-346X (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РҚБ (Алматы қ.) Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 01.06.2006 ж. берілген №5543-Ж мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет. Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18, <u>http://physics-mathematics.kz/index.php/en/archive</u>

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Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

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## «Известия НАН РК. Серия физико-математическая».

### ISSN 2518-1726 (Online), ISSN 1991-346X (Print)

Собственник: РОО «Национальная академия наук Республики Казахстан» (г. Алматы) Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан №5543-Ж, выданное 01.06.2006 г.

Периодичность: 6 раз в год. Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел.: 272-13-19, 272-13-18, http://physics-mathematics.kz/index.php/en/archive

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Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75.

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News of the National Academy of Sciences of the Republic of Kazakhstan. Physical-mathematical series.

### ISSN 2518-1726 (Online), ISSN 1991-346X (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty) The certificate of registration of a periodic printed publication in the Committee of information and archives of the Ministry of culture and information of the Republic of Kazakhstan N 5543-W, issued 01.06.2006

Periodicity: 6 times a year Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18, http://physics-mathematics.kz/index.php/en/archive

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Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

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N E W S OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN PHYSICO-MATHEMATICAL SERIES

ISSN 1991-346X Volume 3, Number 325 (2019), 120 – 129 https://doi.org/10.32014/2019.2518-1726.31

ISSN 2224-5278 UDC539.216: 538.9

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## HIGH-TECH PRODUCTION OF PHOTO-ENERGY IN KAZAKHSTAN BASED ON THE SARYKOL QUARTZ DEPOSIT

**Abstract.** The technology of silicon purification to solar grade silicon for metallurgical silicon obtained from the Sarykol quartz deposit by carbothermic reduction is presented. This technology is based on metallurgical methods of purification, namely gas-slag refining and directional crystallization. Silicon ingots are grown from the solar grade silicon using "monolike" technology. Photovoltaic converters are manufactured and investigated. Solar cells from "monolike" silicon have a higher efficiency of 17-18.4%, in comparison with solar cells made from multicrystalline silicon. Converters with high efficiency were tested for the light-induced degradation effect.

Key words: solar grade silicon, silicon purification, monolike technology, solar cell.

**Introduction.** Kazakhstan is implementing the KazPV Project - "Creating of the production of photovoltaic modules based on Kazakhstan silicon", that includes the production of metallurgical grade silicon (MG-Si) and solar grade silicon (SoG-Si), the production of solar cells and photovoltaic modules. The cluster for the production of photovoltaic modules includes three domestic enterprises: MC KazSilicon LLP, Kazakhstan Solar Silicon LLP and Astana Solar LLP.

MG-Si was obtained at the enterprise KazSilicon by the carbothermal method by reduction of highpurity Sarykol quartz by carbon. The MG-silicon purification technology has been developed. SoG-Si was obtained using the developed technology, from which silicon ingots were grown using the "monolike" technology (ML-Si). Solar cells with an efficiency of 17-18.4 % were manufactured based on ML-Si. The solar cell panels were used in the first Kazakhstan Power Plant AstanaSolar with capacity of 250 kW. This technology is the basis for the creation of the industrial production of materials, solar cells, photovoltaic modules and photovoltaic stations.

## Methods

**MG-Si production and purification up to SoG-Si.** The raw materials used for the experiments were studied before melting for the production of metallurgical silicon. Analysis of the quartz of the Sarykol deposit showed that the phosphorus content is the lowest in the world (compared to Australian quartz, considered one of the best in the world, the phosphorus content is 2-6 times lower), the boron content is similar to the Australian deposit and ranges from 1 ppm to 3-4 ppmw. It was found that a distinctive feature of the Sarykol deposit, compared with other global deposits of quartz, is that the impurities of boron, phosphorus and other chemical elements are outside the crystal lattice of the main component of mineral raw materials. This allows, based on the principles of condensed matter physics and materials science, to develop a highly efficient technology for silicon purification to "solar quality" and ensure its use in industrial environments with less financial and resource costs compared to the technologies used in practice. The silicon coming from the furnace needs additional cleaning. One of the options for the purification of metallurgical silicon may be gas-slag refining, i.e. purging of liquid silicon with a special

composition of gases in combination with the addition of fluxes. The article by A. Istratov and others[1] reports on purging the silicon melt with such gases as Cl<sub>2</sub>, SiCl<sub>4</sub>, CO<sub>2</sub>, water vapor, or their combinations. These gases react with dissolved impurities in silicon and form volatile compounds that evaporate from the melt. For example, the chlorides of many metals are volatile compounds. According to the authors, this method is effective in Al, Ca, C, Mg, Fe, B, P, and Ti removing.

Mixtures of SiO<sub>2</sub>, CaO, CaCO<sub>3</sub>, Na<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, BaO, B<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub>, and other oxides and fluorides are used as fluxes. During the purification process, at high temperatures, the fluxes react and create a complex glass phase - slag phase, that can react with impurities in the MG-Si melt and create a combination of oxides. These oxides can be solid, liquid or gaseous and can be caught in the slag phase or released in the gas phase from the MG-Si melt. Elements such as Al, Ca and Mg are oxidized and the degree of purification is determined by the Eq. (1), (2), (3):

$$4Al + 3SiO_2 = 3Si + 2Al_2O_3 \tag{1}$$

$$2Ca + SiO_2 = Si + 2CaO$$
(2)

$$2Mg + SiO_2 = Si + 2MgO$$
(3)

Theoretically, this allows you to remove Al, Ca and Mg to very low levels, but in practice this is hampered by large heat losses occurring during this operation. In order to avoid crystallization of the melt, oxygen is purged, as a result of which an exothermic oxidation of silicon to a dioxide occurs.

After completion of the oxidative refining in the ladle, the slag, that contains some of the impurities, is removed mechanically or settles to the bottom, and the liquid silicon is poured into a special mold. The separation of slag from silicon is due to the difference in density and viscosity of the slag and silicon itself, so that separation is possible. Consequently, a high CaO content will lead to a low viscosity of the slag, which will sink to the bottom of the ladle, while the CaF<sub>2</sub> viscosity will increase, which will cause it's floating up in the molten silicon. Thus, the condition of the difference of properties in density and viscosity for slag-forming additives is necessary to achieve a good separation [2].

When using silicon in photovoltaic applications, special attention is paid to such impurities as boron and phosphorus, since these elements are the main alloying elements in p-type and n-type silicon. These impurities are contained in concentrations of  $1^{st}-2^{nd}$  orders of magnitude higher than the required level in metallurgical silicon.

The slag purification of metallurgical silicon, carried out at MK KazSilicon LLP, is based on a flux containing SiO<sub>2</sub>. Carrying out slag purification experiments consisted of adding several components of the corresponding fluxes to the MG-Si melt to remove impurities from the MG-Si melt by selecting of the composition of the slag mixture.

**Boron removal process.** The boron removal process occurs due to the oxidation of boron elements in the MG-Si melt according to three chemical reactions (4), (5), (6):

1 - Boron oxidation:

$$[B] + (3/4) O_2 \to (1/2) B_2 O_3 \tag{4}$$

2 - Boron oxide absorption, that appeared as a result of the first reaction:

$$(1/2)B_2O_3 + (3/2)O^{2-} \to BO_3^{3-}$$
 (5)

3 -Final expected boron removal result:

$$[B] + (3/2)O^{2-} + (3/4)O_2 \to BO_3^{3-}$$
(6)

**Phosphorus removal reaction process.** As for phosphorus, it is possible to purify the MG-Si melt due to the transfer of phosphorus into the slag according to the following two reactions (7) and (8):

$$[P] + (3/4)O^{2-} \rightarrow P^{3-} + (3/4)O_2(7)$$

or

$$[P] + (3/2)O^{2-} + (5/4)O_2 \to PO_4^{3-}$$
(8)

The oxygen ions required for the oxidation reaction will be supplied into the slag phase due to the decomposition of simple oxides, the slag components that are used for purification. For example, for the  $SiO_2$ -CaO slag, oxygen will be supplied according to the following reactions (9), (10):

1 - CaO Flux Disintegration:  $CaO \rightarrow Ca^{2+} + O^{2-}$ (9) 2 - SiO<sub>2</sub> flux Disintegration:

 $SiO_2 \rightarrow [Si] + O_2$ 

As for the other slags mentioned above, such as BaO, Na<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>, etc., the same decay reactions will occur during the purification process. For example, for Na<sub>2</sub>O, the following reaction(11) occurs:

 $Na_2O \rightarrow 2Na + + O_2$ -

(11)

(10)

When conducting experiments at MC KazSilicon LLP, the flux mixture was added directly during the process of pouring liquid silicon from the furnace into the metallurgical ladle. The average weight of the pouring was about 1 ton.

After the end of the pouring, the ladle was distilled off into a sump to continue refining, the time of which was about 60 minutes. Due to the fact that during this time there was the possibility of crystallization of the molten silicon, the ladle was driven under a special heater designed for this purpose.

The slag resulting from the refining forms creates slag crust on the surface of the liquid metal, which is removed mechanically after the draining of refined liquid silicon into the mold.

For experiments on the removal of boron and phosphorus impurities, several mixtures of flux components were used, representing 2, 3 or 4 component systems, such as, for example, SiO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>, CaO-CaF<sub>2</sub>-BaCO<sub>3</sub>, etc.

Based on the fact that the tests were carried out directly on an industrial scale and given the economic factor, the mass content of the mixture of flux components to the mass of liquid silicon was taken approximately equal to 10%. During the pouring of metallurgical silicon into the ladle from the furnace and refining, the oxygen-air mixture was supplied. The range of consumption of oxygen and air was 1.43 -  $2.18 \text{ m}^3$ /s and  $5.18 - 9.83 \text{ m}^3$ /s, respectively.

To determine the effectiveness of slag purification, several tests were carried out, where the time for refining was the same as for cleaning with only one gas-air mixture. Table 1 shows the average value for the removal of Al and Ca in percent, for several issues both with and without fluxes.

Name of impurities	Aluminum removal,%	Calcium removal,%
Without fluxes	77,73	91,82
With flux (SiO <sub>2</sub> -Na <sub>2</sub> CO <sub>3</sub> )	94,75	94,63

Table 1 - Effect of fluxes on the removal of Al and Ca impurities

In the project implementation, an optimized slag purification technology using various fluxes, as well as purification by the crystallization method, was developed [3]. After conducting pilot tests, the SoG-Si obtained by the carbothermic method from the quartz of the Sarykol field after all stages of purification, as well as solar cells created from the material obtained, was investigated.

Table 2 presents the results of analyzes of quartz used to obtain silicon and silicon itself.

ruoie 2 concentrations of impairines and runious suges of pulliteration	Table 2 - Concentrations	of impurities	after various	stages	of purification
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Metarial type	Impurities concentration, ppm wt				
Material type	Boron	Phosphorus	Metals		
Quartzite	1,3	0,32	125		
MG-Si	15,4	68	400		
Purified MG-Si (UMG-Si)	<5	8	2500		
SoG-Si	0,2	0,57	<3		
The analyzes were carried out in certified laboratories Schmid Pilot Production (SPP, Germany) and the National Renewable					

The analyzes were carried out in certified laboratories Schmid Pilot Production (SPP, Germany) and the National Renewable Energy Laboratory, NREL, USA.

Growing and investigation of ML-Si ingots. In order to increase the efficiency of solar cells and reduce production costs, a process of silicon ingots production, using the so-called monolike technology has been developed. The aim of this work was to study the effect of a higher concentration of impurities in SoG-Si on the formation of crystalline defects (mainly dislocations) in single-crystal structures. Single-

crystal structure visualization, mapping of the lifetime of minority carriers and photoluminescence were used for studying the properties of a monolike ingot obtained on an industrial scale from Kazakhstan's SoG-Si.

ML-Si ingots of p-type conductivity were manufactured using ECM technology in a PV 600 furnace [4] and weighed about 450 kg. The process of growing ML-Si ingots consists of four stages and takes 78 hours. Silicon is heated to a melting point of 1423°C. Crystallization occurs from the bottom to the top part of the ingot using thermal dissipation, which is carried out under conditions of a homogenized furnace temperature to limit thermal deformations.

Silicon ingots were cut into bricks after the crystallization process. Then ingots were cut into wafers of size 156x156 mm and 180 microns thick. The lifetime of minority charge carriers (electrons) was measured immediately after cutting without additional processing. The measurements were carried out using Microwave Photoconductive Decay ( $\mu$ -PCD) technology by Semilab WT2000 equipment. This technique does not allow to measure the real lifetime, however, mapping by the obtained values allows to qualitatively evaluate the uniformity of the distribution of the lifetime of the ingot and to identify areas with defects that limit the lifetime. Resistivity was also measured on bricks, using Semilab WT2000 equipment. The uncalibrated photoluminescence (PL) image was obtained on a BT LIS-R2 equipment with laser illumination (915 nm), equivalent to 1 solar constant; the illumination time was 1 s. In addition, the ingots were investigated using infrared Fourier transform spectrometry (IFTS).

The concentration of dopants in the initial SoG-Si needs to be adjusted to achieve the required boron and phosphorus values. As shown in [5]and[6], doping of silicon with gallium allows compensation of phosphorus, despite phosphorus high concentration. Schmidt et al. [7] showed that doping of silicon with gallium does not reduce the carrier lifetime and does not increase the concentration of structural defects in crystalline silicon.

Comparison of the calculated and measured resistivity along ingot height, represented in Fig. 1, shows that doping with gallium can lead to a resistance of the order of 1.5  $\Omega$  cm, while the stability of the resistance is maintained until the crystallization fraction reaches 95% without changing the conductivity type of silicon. The carrier mobility ( $\mu$ ) was calculated using the obtained concentrations of boron, phosphorus and gallium, as well as the Arora model [8]. The resistivity ( $\rho$ ) was calculated from the obtained values of mobility and concentrations of dopants, using Eq. (12):

$$\rho = 1/\mu qp$$

(12)

where  $\mu$  is the mobility of charge carriers, q is the electron charge, p is the effective concentration of charge carriers equal to the difference between the concentrations of acceptor and donor impurities (NB + NGa-NP).

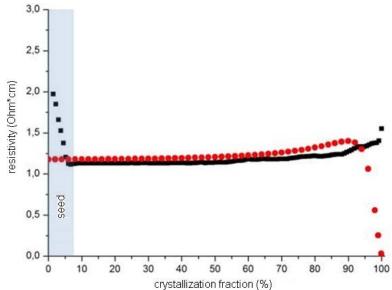
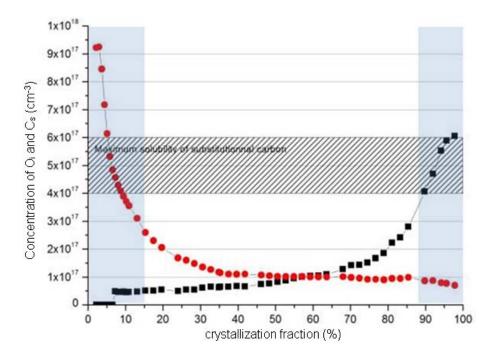


Figure1 - Comparison of the resistivity change dependency along the ingot height, calculated (points) and measured (squares)

Grown ingots contain impurities that lead to the formation of defects that impair the electrical and physical properties of silicon. Namely, oxygen and carbon are the main impurities in standard mc-Si and ML-Si, and are often found in the form of sediment due to the processes occurring during the growth of crystals. Various types of SiO<sub>2</sub> and SiC precipitates and oxygen-containing defects can be observed depending on the temperature conditions and the initial concentration of oxygen and carbon. They can be deposited on the boundaries of the grains and dislocations and, thus, change their electrical characteristics. Therefore, they can affect the recombination in the volume of silicon and the properties of the p – n junction if they penetrate into the space charge region. In addition, it is also known that oxygen forms complexes with boron (B-O), which can significantly reduce the lifetime.



Figuer 2 - The concentration of O<sub>i</sub> (points) and C<sub>s</sub> (squares) obtained by IFTS measurements along the ingot height. The shaded rectangles highlight the cut off areas on the top and bottom of the ingot, the shaded area shows the maximum solubility of Cs in silicon

Fig. 2 shows the changes in the concentration of interstitial oxygen  $[O_i]$  and carbon substitution atoms  $[C_s]$  with an increase of the crystallization fraction obtained by IFTS measurements along ingot monolike height. There is a high concentration of oxygen at the bottom of the ingot due to contact with a quartz crucible. The high concentration of carbon in the top of the ingot is due to its low segregation coefficient. From the analysis of grown monolike ingots, it can be seen that the useful part of the ingot contains a rather low concentration of  $O_i$  and  $C_s$  (<3•10<sup>17</sup> cm<sup>-3</sup>). At such concentrations, the formation of SiC inclusions is unlikely, and the probability of formation of B – O complexes is significantly reduced.

Damage to the seed with raw materials multiplies and spreads dislocations towards the top of the ingot. A sufficiently high source of stress (3 MPa at the melting point [9]) can occur at high temperatures, and plastic deformation of the seed, which leads to the creation of dislocations. The source of stress can be silicon raw materials loaded on the seed or silicides (SiC,  $Si_3N_4$ ,  $SiO_2$ ) formed on the surface of the seed. With the concentration of stresses caused by microscopic points of contact, the dislocation creation threshold is easily exceeded. These mechanisms mainly depend on the flatness and surface state at the seed/crucible and seed/seed boundaries.

Fig. 3 presents the results of photoluminescent analysis performed on the wafers along the height of the marginal and central bricks. The results show that the multiplication of dislocations is higher with a higher curvature of the crystallization front. Thus, temperature conditions and equipment influence on the multiplication of dislocations. The results of the analysis show a clear advantage of monolike ingots compared to standard multicrystalline ingots.

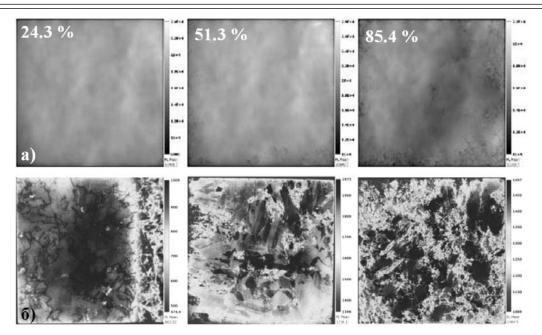


Figure 3 - The uncalibrated image of the photo luminescent analysis of the wafers along the height of the central ML-Si brick (upper row of cells) in comparison with a standard multicrystalline ingot (lower row of cells). The images indicate percent crystallization fraction

## Results

**Manufacturing and investigation of solar cells.** For the study of the possibility of using monolike silicon for the production of high-efficiency solar cells, wafers were chosen along the height of the central ingot. Solar cells were manufactured using the standard Al-BSF architecture [2], according to which the solar cell has a uniform n-type phosphoric emitter on the top part, and is electrically-passivated with SiNx:H layer function also as an anti-reflective coating. The back side of the solar cell is passivated by the p + area, called BSF (back surface field), as a result of screen printing and burning of the back contact from aluminum paste. The charge carriers are assembled on a solid aluminum rear contact and on an H-shaped silver front contact made in the form of a grid.

IV parameters were measured on ready-made solar cells under standard testing conditions (STC). The measured parameters of the solar cells, such as the open-circuit voltage ( $V_{oc}$ ), short-circuit current ( $J_{sc}$ ), fill factor (FF) and efficiency ( $\eta$ ), were obtained from the measured IV characteristics. In addition, the current-voltage characteristics were measured on solar cells after the degradation test under illumination. The solar cells with the highest efficiency were used to study the effect of degradation of solar cells under lighting (LID). LID measurements were carried out on a device fixing a change in Voc, at a constant temperature (65°C) and illumination (43 mV $\approx$ 1.1 Sun), every second. Full results are presented in [10].

## The influence of gettering effect on the lifetime of charge carriers.

Fig. 4 shows the measurement results of  $\tau_{eff}$  for silicon wafers before and after gettering. Samples after phosphorus diffusion showed a significant increase in  $\tau_{eff}$ , regardless of the type of material used. It is known that metallic impurities are one of the main factors reducing  $\tau_{eff}$  in silicon. Metal impurities can create precipitates in crystallographic defects or can be dissolved in the bulk of silicon, which in turn forms deep energy levels in the forbidden zone, such as interstitial iron atoms (Fe<sub>i</sub>), which increases the recombination activity and lowers  $\tau_{eff}$ . Impurities with a fairly high diffusion coefficient in the process of diffusion of phosphorus diffuse into the n-type layer and form electrically inactive clusters - the gettering process due to the difference in dissolution coefficients at high temperatures. However, it can be seen that the measured  $\tau_{eff}$  is higher for ML-Si, due to the higher initial (before gettering)  $\tau_{eff}$  ( $\tau_0$ ) value (Fig. 4). The higher  $\tau_0$  for ML-Si is explained by the better crystal structure of this sample and the smaller amount of metallic impurities in the bulk of the wafer.

The measured values of  $\tau_{eff}$  and  $\tau_0$  decrease with an increase in the crystallization fraction, which is explained by an increase in the density of crystallographic defects and an increase in the concentration of impurities due to the effect of segregation during growth. This is confirmed by lower values of  $\tau_{eff}$  and  $\tau_0$  for wafers from the marginal brick of the ingot, due to the higher concentration of defects. It should be noted that the increase in  $\tau_{eff}$  after the gettering process is lower for the last crystallized fraction (Figure 4). The absence of an increase in  $\tau_{eff}$  after the gettering process shows that in this case  $\tau_{eff}$  is more limited by crystallographic defects than by the concentration of impurities.

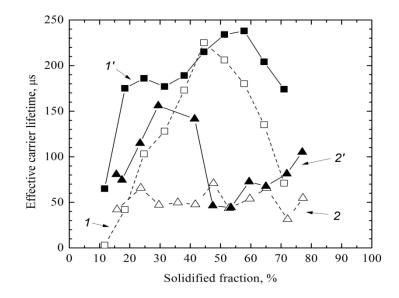


Figure 4 - Comparison of the effective lifetime (with an excessive concentration of charge carriers,  $\Delta n = 1 \cdot 10^{15} \text{ cm}^{-3}$ ) on the ML-Si wafers of the central brick and mc-Si, depending on the height of the ingot: 1 - ML-Si wafers before gettering, 1'- ML-Si wafers after gettering, 2 - mc-Si wafers before gettering, 2' - mc-Si wafers after gettering

Based on the data obtained, we can conclude that the use of moonlike technology for growing silicon ingots is more promising; silicon grown using this technology has better electrical characteristics. Therefore, solar cells made of ML-Si should have a higher efficiency.

Fig. 5 shows the distribution of  $J_{sc}$  and  $V_{oc}$  of solar cells from central ingots of ML-Si and mc-Si, depending on the crystallization fraction. The values of  $J_{sc}$  and  $V_{oc}$  directly depend on the  $\tau_{eff}$  and the diffusion length of the electrons and correlate well with the measured values of  $\tau_{eff}$ . It can also be seen that the values of  $J_{sc}$  and  $V_{oc}$  are higher for solar cells made of ML-Si, that was expected due to a higher  $\tau_{eff}$ .

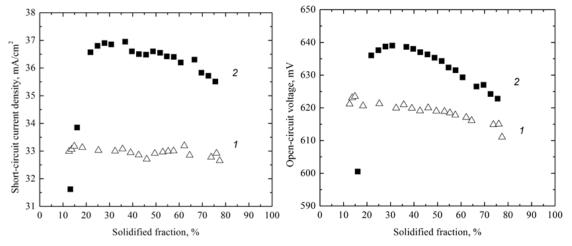


Figure 5 - Comparison of changes in Voc (left) and Jsc (right) along the height of ingots for solar cells made of ML-Si and mc-Si: 1 - mc-Si, 2 - ML-Si

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Fig. 6 shows the distribution of the efficiency of Al-BSF solar cells based on silicon wafers along the height of the bricks. As expected, after measuring  $\tau_{eff}$ , solar cells made from ML-Si have higher efficiency values due to better performance. The maximum value of the efficiency for solar cells made of ML-Si was 18.4%. In[11], a significant decrease in the efficiency along the height of the ML-Si ingot was reported, which was explained by an increase in the density of dislocations. In contrast to our case, very precise control of the crystallization process is not capable of limiting the crystallographic defects formation in the bulk of the crystal. As a result, solar cells produced from a material of this level are less limited in efficiency due to recombination losses, and this explains the presence of a wide area with a very slight decrease in efficiency. These results show that controlled multiplication of dislocations has a significant impact on the production process of solar cells by not only increasing the efficiency limits, but also narrowing the distribution area.

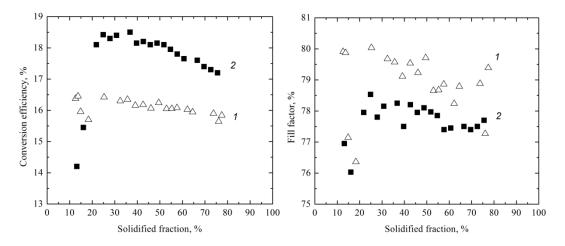


Figure 6 - Comparison of changes in efficiency (left) and fill factor (right) along the height of ingots for solar cells made of ML-Si and mc-Si: 1 - mc-Si, 2 - ML-Si

On the other hand, solar cells made of ML-Si have a fill factor lower than mc-Si solar cells (Fig. 6). These results can be explained by the incomplete refinement of the process and technological regimes for creating solar cells. Since the fill factor depends on the quality of the process of metallization and diffusion of phosphorus (the creation of the n-layer). However, even with smaller values of the fill factor, solar cells made of ML-Si have a higher efficiency. What shows a further opportunity for increasing the efficiency of solar cells by adjustment of technological processes and modes.

At the end of the investigation, solar cells with high efficiency were tested for light degradation to obtain more complete results. These tests are important because of the formation of boron-oxygen complexes (B-O) as a result of exposure to light. These complexes, in turn, are electrically active recombination centers and can significantly reduce the efficiency of solar cells[12].

It was found that the average value of the relative degradation of efficiency is about 1%. The obtained results show an insignificant effect of LID on the efficiency of solar cells produced from ML-Si, that well correlates with theoretical data on the formation of B-O complexes with oxygen concentrations above  $3 \cdot 10^{17}$  cm<sup>-3</sup>. According to measurements the concentration of interstitial oxygen [O<sub>i</sub>] in the ML-Si does not exceed  $3 \cdot 10^{17}$  cm<sup>-3</sup> for the regions of the ingot used in the creation of solar cells. Unlike silicon grown by Czochralski technology, in which [Oi] reaches about  $8 \cdot 10^{17}$  cm<sup>-3</sup>, silicon grown by monolike technology is less susceptible to the formation of B-O complexes and consequently the degradation of the efficiency of solar cells when exposed to sunlight.

On the other hand, on the researched solar cells, the LID effect increases with an increase in the crystallization fraction and therefore with decreasing [Oi] and it can be concluded that in this case the LID effect is more associated with other processes and mechanisms than the formation of B-O complexes. A recent paper [13-15]reported that metal impurities such as copper form electrically active precipitates in the bulk of silicon when exposed to light and can cause degradation of the electrical characteristics of solar cells. In addition, [16]reported on the influence of the architecture of solar cells on the effect of

degradation during illumination; it was shown that solar cells with a passivated surface are more sensitive to degradation.

### Discussion

Potential production of photovoltaic cells from Kazakhstan p-type silicon purified by metallurgical using the advantages of monolike technology investigated.

It is shown that the content of oxygen and carbon impurities is very low, which prevents the formation of  $SiO_2$  and SiC precipitates. In addition, it has been shown that monolike-grown ingots are practically free of microcrystalline regions, and that a limitation of the dislocation density can be achieved in industrial technology. The optimization of the technology was based on precise control of the curvature of the crystallization front in the process of directional solidification, since the curvature of the front is a key factor in the quality of crystallization.

It is shown that silicon ingots grown using the monolike technology have a higher carrier lifetime compared to standard mc-Si. In addition, it is shown that in the process of creating solar cells, the lifetime of charge carriers increases due to the effect of gettering, without additional purification processes. The advantages of the developed technology were observed at the level of solar cells, by increasing the efficiency and reducing the distribution of efficiency along the ingot height. It is shown that solar cells made of ML-Si have a rather low degradation of efficiency when exposed to light.

The maximum efficiency for solar cells made of ML-Si was 18.4%. In addition, according to the results of recent work, an increase in the efficiency of solar cells up to 20% and higher is expected due to the adjustment of the production process of solar cells to ML-Si wafers.

In conclusion, ML-Si grown from silicon of solar grade in the near future may be a breakthrough in PV industry, due to the high potential for the production of solar cells with high efficiency and significant reduction in production costs.

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## САРЫКӨЛ КВАРЦ КЕН ОРНЫ НЕГІЗІНДЕ ҚАЗАҚСТАНДА ФОТОЭНЕРГЕТИКА ҚҰРУДЫҢ ЖОҒАРЫ ТЕХНОЛОГИЯЛЫ ӨНДІРІСІ

Аннотация. Сарыкөл кен орнынан карботермиялық қалпына келтіру арқылы алынған кварцтан металлургиялық кремнийді күн сапалы кремнийге дейін тазалау технологиясы ұсынылады. Берілген технология тазалаудың металлургиялық әдістеріне – газды қожбен тазарту және бағытталған кристалдануға негізделген. Алынған күндік кремнийден "monolike" технологиясымен құймалар дайындалды. Мульти-кристалданған кремнийден алынған түрлендіргіштермен салыстырғанда өте тиімді – 17-18,4% болатын фотоэлектрлік түрлендіргіштер дайындалып, зерттелді. Өте тиімді түрлендіргіштер жарықтық деградацияның тестінен өткізілді.

Түйін сөздер: күн сапалы кремний, кремнийді тазарту, "monolike" технологиясы, күндік элемент.

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## ВЫСОКОТЕХНОЛОГИЧНОЕ ПРОИЗВОДСТВО ПО СОЗДАНИЮ ФОТОЭНЕРГЕТИКИ В КАЗАХСТАНЕ НА ОСНОВЕ КВАРЦЕВОГО МЕСТОРОЖДЕНИЯ САРЫКОЛЬ

Аннотация. Представлена технология очистки металлургического кремния до кремния солнечного качества, полученного из кварца Сарыкольского месторождения карботермическим восстановлением.

Данная технология основана на металлургических методах очистки – газошлаковым рафинированием и направленной кристаллизацией. Из полученного солнечного кремния выращены слитки по технологии "monolike". Изготовлены и исследованы фотоэлектрические преобразователи, которые имеют более высокую эффективность – 17-18,4%, по сравнению с преобразователями из мультикристаллического кремния. Преобразователи с высокой эффективностью были подвергнуты тестам на световую деградацию.

Ключевые слова: кремний солнечного качества, очистка кремния, технология "monolike", солнечный элемент.

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#### REFERENCES

[1] A.A. Istratov, T. Buonassisi, M.D. Pickett, M. Heuer, E.R. Weber. Materials Science and Engineering B, 134, PP.282–286, (2006).doi:10.1016/j.mseb.2006.06.023

[2] Handbook of Photovoltaic Science and Engineering, Second Edition, edited by Antonio Luque and Steven Hegedus. John Wiley & Sons Ltd, Second edition (2010).

[3] B.N. Mukashev, A.A. Betekbaev, D.A. Kalygulov, A.A.Pavlov, D.M. Skakov, Physics and Engineering of Semiconductors, Volume 10, 1421, (2015) (in Russ.).

[4] Betekbaev A.A., Mukashev B. N., OunadjelaK. Pavlov A.A., Pellegrin I. and Shcolnik V.S., 24th Workshop on Crystalline Silicon Solar Cells & Modules: Materials and Processes. Breckenridge, Colorado, USA, pp. 101-107, (2014).

[5] Kirscht, F., Heuer, M., Käs, M., Rakotoniaina, J.-P., Jester, T., Metallurgically Refined Silicon for Photovoltaics. Proceedings CSSC-6, Aix-les-Bains, France, (2012).

[6] A.A. Betekbaev, B.N. Mukashev, L. Pelissier, P. Lay, G. Fortin, L. Bounaas, D.M. Skakov, A.A.Pavlov. Journal of Higher Educational Institutions. Materials of Electronic Technology. 103-109, (2015).DOI: <u>10.17073/1609-3577-2015-2-103-109</u>.ISSN: 1609-3577, (In Russ.).

[7] Schmidt J., Bothe K. Phys. Rev. B, vol. 69, pp. 24107-24115, (2004).

[8] N.D. Arora, J.R. Hauser, D.J. Roulston. 29th IEEE PVSC. 292 (1982).

[9] Gallien B. PhD Thesis, Université de Grenoble, (2014).

[10] A.A. Betekbaev, B.N. Mukashev, L. Pelissier, P. Lay, G. Fortin, L. Bounaas, D.M. Skakov, D.A. Kalygulov, T.S. Turmagambetov, V.V. Lee, ΦΤΠ,8, 1106, (2016) (in Russ.)

[11] Trempa M. и др. Journal of Crystal Growth, Vol 351, pp. 131-140, 2012.

[12] K. Bothe, and J. Schmidt. J. Appl. Phys. 99, 013701, (2006).

[13] T. Turmagambetov, S. Dubois, J.-P. Garandet, B. Martel, N. Enjalbert, J. Veirman, and E. Pihan. Phys. Status Solidi C. 11, 1697, (2014).

[14] T. Turmagambetov, S. Dubois, J. P. Garandet, H. Lignier and N. Enjalbert. Solar Energy Materials & Solar Cells, 157, p. 558–564, (2016).

[15] E. A. Dmitriyeva, D. M. Mukhamedshina, K. A. Mit', I. A. Lebedev, I. I. Girina, A. I. Fedosimova, E. A. Grushevskaja. Doping of fluorine of tin dioxide films synthesized by sol-gel method. News of National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technology sciences.Volume 1, Number 433 (2019), PP.73–79, http://dx.doi.org/10.32014/2019.2518-170X.9 ISSN 2224-5278.

[16] M. Cascant, N. Enjalbert, R. Monna, S. Dubois. 29th EU PVSEC, Munich, Germany, 2570, (2014).

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ISSN 2518-1726 (Online), ISSN 1991-346X (Print)

Редакторы М. С. Ахметова, Т.А. Апендиев, Д.С. Аленов Верстка на компьютере А.М. Кульгинбаевой

Подписано в печать 10.06.2019. Формат 60х881/8. Бумага офсетная. Печать – ризограф. 8,3 п.л. Тираж 300. Заказ 3.

Национальная академия наук РК 050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19