Metallurgical silicon refining using electron-beam plasma

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Abstract. The possibilities of plasma-chemical refining of metallurgical silicon have been demonstrated. It is shown that by electron-beam refining it is possible to reduce the concentration of phosphorus and boron, as well as the main metallic impurities by evaporation of both these impurities and their volatile compounds.

1. Introduction
Despite the development of new technologies for creating solar cells [1, 2], silicon still occupies a dominant position, more than 95% of solar modules are manufactured on its basis [3]. In 2020, more than 135 GW of new solar photovoltaic electricity generation capacity was installed, and the cumulative photovoltaic installations exceeded 750 GW [3]. The main technology for the production of silicon for solar cell manufacturing is the Siemens process, which involves the use of chemically aggressive and environmentally unsafe silicon chlorides, which are then converted into pure silicon using a large amount of energy. The request for such silicon is estimated at 30 thousand tons per year [3]. Metallurgical approach is an alternative way to obtain solar-grade silicon, which ensures environmental friendliness and energy efficiency. Unlike the traditional method, metallurgical approach does not require energy- and material-intensive conversion of silicon into intermediate volatile compounds, and purification occurs in the melt by removing impurities due to their evaporation, oxidative refining, including the use of plasma, transfer of impurities into slag or directed crystallization processes.

For purification of metallurgical silicon from highly volatile impurities, electron beams with energies from units to hundreds of kilowatts are widely used; at that, the process pressure also varies in a very wide range [4, 5].

Boron is one of the most difficult to recover impurities and cannot be removed by vacuum evaporation or directional crystallization because it has a low vapour pressure and a high segregation coefficient. At the same time, its content in silicon greatly affects its electrical properties, since it is an alloying element that has a decisive influence on the efficiency of a solar cell. Plasma technologies [6-8], transfer of boron from the melt to the slag [9-11], and use of gas mixtures H₂-H₂O [12-14] are more effective ways to remove boron. The use of mixtures of hydrogen and water vapours presupposes the formation of volatile boron compounds in the form of BₓOᵧ, BₓHᵧOₓ, and BₓHₓ (BHₓ).

The main difficulty of this approach is organization of effective contact of the melt volume of silicon with the flow of oxygen- and hydrogen-containing gas. The plasma cleaning method is based on the use of a plasma-forming hydrogen-containing gas. The plasma cleaning method is based on the use of a plasma-forming gas containing oxidizing particles that interact with the silicon melt [15, 16]. The gases used in plasma refining are similar to those for oxidative gas cleaning, but the use of plasma makes this process more efficient due to the greater reactivity of the oxidizing particles.
addition, the use of plasma provides additional heating in the reaction zone, which also increases the efficiency of removing unwanted impurities.

For the refining of metallurgical silicon produced at “KazSilicon” Metallurgical Combine” LLP, electron-beam equipment with a beam power of 1.8 kW at a pressure in the refining chamber of up to $10^{-2}$ torr was used.

2. Experiment

For the process of refining metallurgical silicon, an electron-beam plasma-chemical method has been developed. At the first stage of cleaning, the sample is melted using an electron beam in a cooled graphite crucible. In this case, the removal of highly volatile metal impurities and phosphorus from the melt took place. To remove impurities with a low saturated vapor pressure, oxidative refining was used at the second stage. At both stages, there was separation of impurities over the sample volume, depending on their segregation properties.

Experiments on refining metallurgical silicon were carried out at Kutateladze Institute of Thermophysics. The block diagram of the experimental setup is shown in Figure 1.

![Figure 1](image_url)

Figure 1. Scheme of experimental setup: 1 - electron gun; 2 – nozzles block, 3 - electron beam, 4 - crucible, 5 - supersonic gas jet, 6 - focusing lens, 7 - water-cooled collector, 8 - metallurgical silicon, 9 - differential pumping section, 10 - vacuum chamber.

The experimental conditions are shown in Table 1. In all modes, metallurgical silicon was preheated by an electron beam in a carrier gas flow at a pressure of $2 \times 10^{-3}$ torr for 15 minutes, except for mode 4 in which non-oxidative refining was carried out. Further, in modes 1-3, oxidative electron-beam refining was carried out at a pressure of $5 \times 10^{-3}$ torr. After the experiments, the samples were cooled for half an hour.
### Table 1. Conditions for silicon refining.

| Mode number - cycle number | Flow rate Ar, l/min | Flow rate N<sub>2</sub>, l/min | Flow rate H<sub>2</sub>, l/min | Flow rate O<sub>2</sub>, l/min | Flow rate H<sub>2</sub>O, g/min | Number of cycles in one experiment, pcs | Cycle time, h | Total experiment time, h |
|---------------------------|---------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------------------------|---------------|--------------------------|
| I - 1                     | 1.5                 | 0                             | 0                             | 0                             | 0                             | 4                                 | 0.25          | 2                        |
| I - 2                     | 1.5                 | 0                             | 0.5                           | 0                             | 1                             | 4                                 | 0.25          | 0.5                     |
| II - 1                    | 0                   | 2.5                           | 0                             | 0                             | 1.67                          | 1                                 | 0.25          | 2                        |
| II - 2                    | 0                   | 2.5                           | 0                             | 0                             | 4                             | 4                                 | 0.25          | 2                        |
| III - 1                   | 0                   | 2.5                           | 0                             | 0                             | 1.67                          | 1                                 | 0.25          | 2                        |
| III - 2                   | 0                   | 2.5                           | 0                             | 0                             | 1.67                          | 4                                 | 0.25          | 2                        |
| IV - 1                    | 0                   | 0                             | 0                             | 0                             | 1.67                          | 1                                 | 0.50          | 0.5                     |

The content of impurities in the sample was determined by the atomic emission spectral method on a ThermoScientific iCAP-6000 spectrometer and in a direct current arc on a PGS-2 spectrometer.

Refining efficiency was determined by the formula:

\[
C_{ef} = \frac{(C_{ini} - C_{ebr}) \times 100}{C_{ini}}
\]

where \( C_{ef} \) is the efficiency of refining; \( C_{ini} \) is the concentration of impurities in the source material; \( C_{ebr} \) is the concentration of impurities in the material after electron-beam refining.

#### 3. Results

Table 2 shows the content of impurities for all purification modes, including the analysis of the initial metallurgical silicon.

### Table 2. Data of component analysis in modes 1-4.

| Element | Initial Si, ppm | After mode I, ppm | After mode II, ppm | After mode III, ppm | After mode IV (region 1), ppm | After mode IV (region 2), ppm |
|---------|----------------|-------------------|-------------------|--------------------|-------------------------------|-------------------------------|
| B       | 12.0           | 14.0              | 10.0              | 10.0               |                              |                               |
| P       | 92.0           | 12.0              | 7.0               | 5.0                |                              |                               |
| Al      | 6.0            | 10.0              | 14.0              | 2.2                | 4.6                          | 10                            |
| Ba      |                | 0.2               |                   |                    | 31                            | 4.2                           |
| Ca      | 41.0           | 5.0               | 25.0              | 36.0               |                              |                               |
| Cr      |                | 6.5               |                   |                    | 120                           |                               |
| Cu      | 11.0           | 6.0               | 3.5               | 1.2                | 5.0                          | 10                            |
| Fe      | 1400.0         | 710.0             | 580               | 390                | 380                          | 11000                         |
| Mn      | 220.0          | 3.0               | 28                | 4.7                | 32                           | 20                            |
| Nb      |                | 14                |                   |                    | 14                            | 98                            |
| Ni      | 60.0           | 64.0              | 26                | 18                 | 14                           | 480                           |
| Ti      |                | 140               |                   |                    | 140                           | 14000                         |
| V       | 210.0          | 180.0             | 80                | 62                 | 33                           | 1200                          |
| Zr      | 4.0            | 4.0               | 2.0               | 1.0                | 0.6                          | 45.0                          |

Figure 2 shows the sample areas that correspond to «region 1» and «region 2» for the sample obtained in mode 4.
Elemental analysis data showed that highly volatile impurities such as aluminum, copper, and manganese are removed quite effectively, as well as the main nonmetallic alloying impurity, phosphorus. With an increase in the refining time, further purification of silicon is observed for all studied elements, although the refining rate is significantly reduced. An increase in the concentration of aluminum in modes 1 and 2 is apparently associated with its segregation properties. It can be seen from the table that the use of water vapor has led to a more efficient purification of metallurgical silicon.

Figure 3 shows the efficiency of phosphorus and boron refining. Analyzing the presented results, it can be seen that the phosphorus removal efficiency significantly exceeds that for boron and is about 95%. Less effective removal of boron is associated with the dependence of formation of its volatile compounds on the melt temperature, whose concentration decreases significantly with an increase above 1600°C [5]. Also, the low efficiency of boron removal can be explained by the geometry of the gaseous reagent supply to the silicon melt, in which volatile impurity compounds removed by evaporation are blown back to the surface of the melt.

Figure 4 shows that purification from impurities forming volatile oxides occurs quite efficiently, and with an increase in the exposure time, the process does not reach saturation, and it can be assumed that a further increase in the refining time will enables obtaining purer silicon.

![Figure 2. Photo of a silicon sample.](image)

![Figure 3. Boron and phosphorus refining efficiency.](image)

![Figure 4. Efficiency of refining metal impurities.](image)
The weak effect of exposure time on the efficiency of removing impurities, presented in Figures 5 and 6, can be explained as follows. At the initial moment of the experiment, the sample consists of small pieces of silicon ranging in size from 2 to 5 mm, which have a significant surface area for efficient evaporation of impurities. In the process of refining, silicon melts, and the surface of interaction of the plasma with the material is significantly reduced, being limited by the crucible area. And, as a consequence, the process begins to be determined by the rate of diffusion of impurities to the surface. So, with an increase in the refining time by the factor of 4, the concentration of all impurities decreases relative to the initial level, however, the refining rate, expressed in units of ppm per minute, decreases by more than an order of magnitude. For example, for copper it is 10 times, and for manganese it is 24 times (Fig. 6). Thus, for efficient refining, it is necessary to maximize the convection of impurities to the surface of the melt, which in our case is complicated by the use of a high, narrow crucible.

![Image](image1.png)

**Figure 5.** The dependence of the concentration of boron and phosphorus on the time of refining.

![Image](image2.png)

**Figure 6.** The dependence of the concentration of metallic impurities on the time of refining.

Distribution of impurities concentrations between regions of sample is shown in Figure 7. Significant redistribution of impurities over the sample volume is observed. As it can be seen from the Figure 7, some of impurities demonstrate high separation between the regions of the sample due to their segregation properties. To obtain pure silicon, it is sufficient to use a part of the sample depleted in impurities.

![Image](image3.png)

**Figure 7.** Distribution of impurity concentrations between regions of sample.
4. Summary
The article presents the possibilities of plasma-chemical refining of metallurgical silicon. It is shown that the use of water vapor as a reagent in oxidative refining leads to more efficient refining of metallurgical silicon than when using a mixture of hydrogen and oxygen. The slowdown in the efficiency of refining with time is primarily associated with a decrease in the surface of evaporation of impurities in the crucible when the silicon sample is melted. The use of an electron beam allows the achievement of significant redistribution of particular impurities over the sample volume, which ensures purification of initial silicon due to the segregation effect.

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