Experimental verification of the of contamination reduction of silicon during electron beam melting due to the use of a gas-dynamic window

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Metallurgical process of producing initial rods for FZ silicon single crystal application was described before. Purity of pulled ingots was satisfied, but some impurities level was over required level. Concentrations of these impurities such Fe; Cr; Cu; Al; O₂ been decreased by gas dynamic window and electric trap in laboratory scale equipment. Present article described results of experiments on industry scale equipment with application gas dynamic window for purifying indicated impurities in initial rods and results received in FZ silicon single crystals, grown from that rods, for concentrations of Aluminum and Oxygen.

1. Introduction

Monocrystalline silicon used for the manufacture of power semiconductor devices and detectors is produced by crucible-free zone melting (FZ). The reason for this is the purity of the single crystals, which cannot be achieved in any other process. The development of the method in terms of increasing the diameter of single crystals lags behind the method of growing from a crucible, primarily due to the absence of corresponding initial rods. Today their maximum diameter does not exceed 180 mm. In our opinion, a promising process is the production of initial rods for FZ not using the conventional Siemens process, which is already used in industry today, but by growing the rods from silicon melt. We develop the most promising process of growing the silicon rods from a melt located in its own skull using electron beam heating (Skull Melting with Electron Beam Heating - SMEBH). A number of attempts have been made to apply silicon skull melting earlier. However, this did not succeed, since the authors, for example, [1,2], faced the difficulty in increasing the diameter of the growing crystal over 40 mm. In the process of growing from a crucible using the electron beam heating, we obtained a rod suitable for the FZ process, namely 300 mm in diameter and 80 kg in weight [3]. The concentration of most of the controlled impurities in the resulting rod is comparable to the purity of the reference sample made from silicon obtained by the FZ process. However, in the silicon residues after the process, a whole spectrum of metallic impurities was observed, indicating the introduction of contaminants into the melt during the growth (see Table 2, line 1, process 28) and the increased oxygen content. In the case of electron beam melting of metals, this amount of contamination can be neglected, but for semiconductors this level of impurity concentration is too high.

In [3], assumptions were made about the sources of the impurity background formation of the process and it was proposed to control concentration of impurities not in the grown crystal, where, due to the small distribution coefficients of metallic impurities, their content is not significant, but in the silicon residue from the process, enriched with introduced impurities. In our opinion, the most interesting is the control of the aluminum content. The distribution coefficients of these metal impurities, except for aluminum, when drawn from the melt are in order of 10⁻⁵ and they are practically absent in the rod and even more in the single crystal. In addition, to determine the concentration of aluminum in single crystals, there is a method for controlling its content by Low-Temperature FTIR spectroscopy, with sensitivity up to ppta units.
2. Experimental
The aim of the work is experimental verification of aluminum and oxygen content in silicon during its processing when growing rods in a SMEBH in the installation described in [3], and in silicon single crystals obtained from these rods using the FZ process. To carry out the SMEBH process, a cold crucible is used with a heat insulator placed inside, in which silicon is placed [3]. In this process, silicon is heated by two cold-cathode electron-beam heaters (EBH), using a mixture of gases consisting of hydrogen and less than 1% oxygen. Under the influence of the applied voltage, in the gas-discharge chamber of an electron-beam heater with a cold cathode, plasma ions bombard the cathode and initiate the creation of electrons directed to the treated surface [4]. Work [5] describes the use of devices for reducing contamination of the melt in laboratory equipment and shows that the most difficult impurity to remove is aluminum.

The silicon rod was grown in the SMEBH process. The EBH of installations were equipped with gas dynamic windows (GDW) (Fig. 1). The results of using the GDW are described in [5]. In this case, the crucible contained a skull, as illustrated in Fig. 1. Silicon doped with boron to a concentration of ~ 0.3-0.5 ppma was used as a raw material. The aluminum content in the initial silicon, the residues of molten silicon after the process, and in the rod was determined by ICP MS, and the oxygen content by FTIR spectroscopy at room temperature.

![Figure 1](image1.png)

**Figure 1.** Connection diagrams of the gas dynamic window and the process of growing a rod
a- silicon skull. b- silicon melt. c- silicon rod

A single crystal with a diameter of 65 mm was grown from a part of the obtained rod by the FZ method in an argon atmosphere. The single crystal was cut as shown in Fig. 2. In samples (1, 3, 5, 7), the content of aluminum and oxygen was controlled at a temperature of 7K by FTIR spectroscopy method.

![Fig 2](image2.png)

**Fig 2.** Scheme of sampling from the FZ single crystal of silicon.
The measurement results are shown in Table 1. The same table contains data on process # 28 described in [3] and measurements of the aluminum concentration in a single crystal grown from a similar rod [6].

### Table 1. Experimental and comparative data on the processes of obtaining rods in SMEBH and control FZ of single crystals produced from these rods

| Impurities          | concentration of impurities | k of impurities in SMEBH | concentration of impurities in grown single crystal | k of impurities in FZ process |
|---------------------|-----------------------------|--------------------------|--------------------------------------------------|-------------------------------|
|                     | raw materials | residues of melt | archived rod | Sample 1 | Sample 3 | Sample 5 | Sample 7 | |
| Aluminium, ppba     | 40            | 4400            | 240           | 0.0545  | 14.0     | 20.4     | 21.2     | 0.0883 |
| Oxygen, ppba        | 160           | 250             | 400           | 1.6     | 60.0     | 60.0     | 60.0     | 0.15   |
| Aluminium, ppba [3,6]| 24000         | 996             | [3]           | 0.0415  | 34 [6]   | 94[6]    | 96 [6]   | 0.0964 |

3. Discussion of the results

Table 1 shows the concentration of aluminum and oxygen in the entire process of manufacturing a FZ crystal of a silicon single crystal using the technology with growing an initial rod in SMEBH. From the presented data it can be seen that that in the process of melting and growing, the loaded silicon is doped with aluminum and oxygen. The concentration of aluminum in the rod decreases. In the FZ process, after deep crystallization purification at the beginning of the process (sample 1), the melt was saturated with aluminum due to displacement, after which a stable concentration of impurities along the length of the single crystal was established. The oxygen content in the rod after SMEBH is higher than in the residual of melt. The oxygen concentration in the FZ process dropped by a factor of ~ 7 with respect to the original rod.

Obviously, the high-energy particles formed in the EBH plasma and the electrons directed to the melt bombard all surfaces of the gas-discharge chamber and the beam guide. In these collisions, metal atoms are knocked out of the surfaces, of which structural elements are composed, both in the form of neutral atoms and anions. This mixture, getting into the process chamber, creates a partial pressure of metal and oxygen vapors above the melt, which leads to alloying of the melt with the mentioned impurities. Verification of sources of pollution with the use of laboratory equipment and their assessment are given in [5]. From the introduction of contaminants from the gas generating the plasma, GDW was used. In addition, a "trap" was used [5] in the form of an electrode to reduce contamination from materials located inside the process chamber. The authors of [5] found that the “trap” does not affect the concentration of aluminum in the melt, and GDW removes the hydrogen-oxygen gas mixture saturated with oxygen and vapors of iron, chromium, aluminum and copper. For a more complete assessment of the results we obtained, Table 2 provides a comparative information on the effect of GDW on contamination of the melt residues (row 1 process 28 without GDW and row 2: processes 80_81 with the use of GDW). The purifying factor shown in row 3 of the table: it is the ratio of the data in row 1 to the data in row 2. The values of the concentrations of the studied impurities in the rod grown in process 28, measured by the ICP MS method, are given in row 4. By the ratio of these lines 1 and 4 we can calculate the effective distribution coefficient of impurities during growth in the SMEBH, and in the 5th row is showed the equilibrium distribution coefficients of these impurities during silicon crystallization are given for reference.

### Table 2. Comparative data obtained in [3] and [5].

| Process data           | Al  | Cu  | Fe  | Cr  | O2  |
|------------------------|-----|-----|-----|-----|-----|
| #28, without GDW, ppba | 20  | 57  | 190 | 7   | 6420|
| #80_81_85, with GDW, ppba | 7.83 | 7.15 | 34.4 | 2.5 | 250 |
| Purifying factor       | 3   | 8   | 6   | 3   | 26  |
It can be seen from the presented data that the effective distribution coefficients of all impurities (except copper) are in satisfactory agreement with the values of their equilibrium distribution coefficients. The use of GDW increases the cleaning efficiency for aluminum 3 times according to Table 2, and more than 5 times according to Table 1. In our opinion, taking into account the concentration of controlled impurities, the data show satisfactory agreement. The value of the effective distribution coefficient of aluminum in the SMEBH is \( (4.15-5.45) \times 10^{-2} \), and in the FZ process \( (8.83-9.64) \times 10^{-2} \).

The indicated values are estimated, since the process of silicon doping with aluminum occurs during the entire growing process.

**Conclusions**

1. Experimentally, using an installation for growing large-diameter rods from a skull with electron-beam heating, silicon rods were obtained, from which single crystals were grown by the FZ method. During the entire technological process, the concentrations of aluminum and oxygen impurities were determined.

2. The concentration of aluminum in silicon rods obtained using a Gas-Dynamic Window, decreased 3 times according to [5], and five times according to the results of our process compared to the process 28 described in [1]. In single crystals grown from the corresponding rods, the aluminum concentration also differs by a factor of 5. Thus, the experimental results obtained in the laboratory setup [5] are in satisfactory agreement with the data of our industrial process.

3. The oxygen content in the remnants of the melt in our process remained at the same level as in the experimental processes [5].

4. It was found that the Gas-Dynamic Window provides practically the same results when carrying out the processes of electron beam melting of silicon in laboratory and industrial installations.

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**References**

[1] An. Kravtsov. “Developing of silicon growth techniques from melt with surface heating”, IOP Conf. Series Materials Science and Engineering 355 (2018) 012037

[2] Charles W Hanks, Charles D A Hunt “Method for growing crystals”, Patent US 3494804 A Continuation-impart of application Ser. No. 659,175,Aug. 8, 1967. This application July 15, 1968, Ser.No. 744,874, Int. Cl. B013 17/06; US. Cl. 148—1.6 11

[3] T.F. Ciszek “Growth of 40 mm diameter single crystals by a pedestal technique using electron beam heating”, ”Journal of crystal growth” No. 12 (1972), page 281-287.

A. Krauze, J.Virbulis, An. Kravtsov. “Modeling electron beam parameters and plasma interface position in an anode plasma electron gun with hydrogen atmosphere”, IOP Conf. Series Materials Science and Engineering 355 (2018) 012008

[4] Kravtsov, J. Virbulis, A. Krauze “Reduction of impurity sources in Si crystal growth system with electron gun beam heating” FM&NT 2020, will be printed in IOP Conf. Series Materials Science and Engineering.

[5] Kravtsov. “Contamination of Silicon during Electron Beam Melting”, in 32 European Photovoltaic Solar Energy Conference and Exhibition, Munich, Germany, 2016.

[6] E. Falkevich; E. Pulner; I. Chervony; L. Shvartsman; V. Yarkin; I. Sally “Technology of semiconductor silicon” Moscow Metallurgy, 1992, 408 pages.