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REFINING METALLURGICAL SILICON

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ABSTRACT

The review presents modern technologies used to refine metallurgical silicon to a purity of 5–6 N for photovoltaic cells. Refining of silicon is performed using an intermediate metal Al to capture silicon impurities after its fusion with Si. The removal of C, Ca, Fe, Ti, P from the Al-Si melt with Si is shown. After a two-time directional crystallization of the melt, Si of a purity acceptable for use in photovoltaic technologies was produced. Positive results were obtained during plasma remelting with the simultaneous application of gases in the core: Ar–H_2, H_2–H_2O, O_2, or H_2 in an Ar-based plasma. The electromagnetic stirring of the bath provides accelerated mass transfer in the liquid compared to the reaction rate on the surface with control of the surface shape. Removal of metal impurities Na, Ca, Ba, and Al up to 90–100 % was achieved using 30 % H_2 in Ar plasma. Carbon removal was observed using oxygen in the plasma at temperatures above 1530 °C. It was found that H_2 is more effective in plasma than O_2. A constant voltage in the liquid bath increases the refining efficiency by 10 times. The best results in removing boron from molten silicon were obtained by blowing the melt with humidified argon or water vapor. The resulting silicon product had favorable electronic properties. It is noted that during electron beam remelting, it is possible to purify silicon from elements with high vapor pressure and perform oxidative refining from boron impurities using a mixture of oxygen and inert gas with application of a cold hearth and zone recrystallization. In the process of EBCZM, after increasing the vacuum depth, the amount of oxygen and phosphorus in silicon can be reduced by a factor of 10.

KEYWORDS: metallurgical silicon, purification, vacuum and oxidative refining, plasma remelting, electron beam melting, silicon, solar grades, impurity elements

INTRODUCTION

Having a number of advantages, in particular, natural abundance, silicon is the most suitable material for solar photovoltaic power generation [1]. Requirements to silicon of solar grades (SoG–Si) for photoelectric converters (PEC) are much higher than those for metallurgical silicon from carbothermic reduction of silica (MG–Si), and additional refining is required to produce it. In view of the difference in the requirements for purity of silicon for the electronic and photoelectric industry and high equipment cost, the interest in investigation of different methods of development of the technologies for direct production of SoG–Si silicon remains relevant. The work presents the known technologies of refining MG–Si metallurgical silicon.

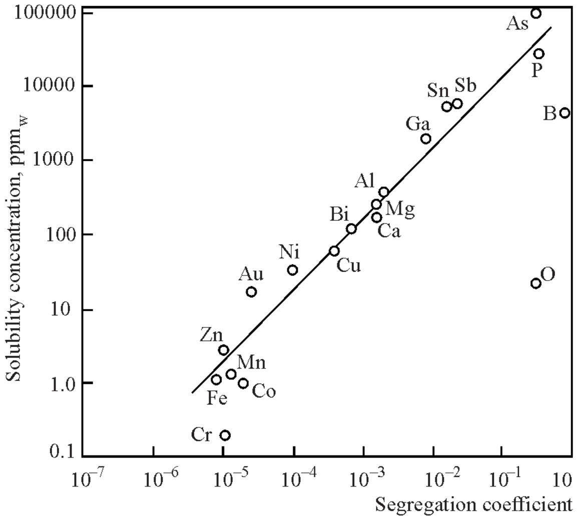

Figure 1. Solubility of some elements in silicon in the solid state, depending on the segregation coefficient [2]

INVESTIGATION PROCEDURE, EQUIPMENT AND MATERIALS

The technologies of metallurgical silicon refining to purity suitable for manufacture of photoelectric converters were selected as the object of studies.

Silicon refining with a solvent is one of the metallurgical approaches to produce SoG–Si from MG–Si using an intermediate metal, acting as an impurity trap during solidification after its fusion with Si. During cooling the pure silicon crystals precipitate from the melt, and the impurities together with the intermediate metal are forced to the solidification front, and remain in the liquid phase. The product (Si) is extracted by liquid filtering methods, leaching or electrochemical dissolution of the solidified alloy and electromagnetically induced separation. The intermediate metal should have a high affinity to boron and phosphorus, which have a low coefficient of segregation in silicon, readily dissolve in liquid silicon and have a low solubility in solid silicon (Figure 1) [2].

Al can be the intermediate metal. The process of C, Ca, Fe, Ti, P removal from Al–Si melt was studied in [3, 4]. Results showed only partial removal of these elements from Si. In works [5–8] aluminium was used as a cleaning agent to produce silicon of solar grades. As a result, Fe, Ti content in silicon was markedly reduced, and after two-times directional crystallization Si of a purity acceptable for application in photoelectric technologies was produced. The authors of work [9] reported a lowering of Fe, Zr, V, Ca, Ba, P, Cu, Ti, Cr and Mn concentration due to refining with aluminium. Boron content remained unchanged, and P content decreased from 45 to 15 ppm. Effective removal of Fe, Ti, Cu, Mn and Ni impurities, compared to P and B, is shown in works [10, 11]. In keeping with the obtained results, the coefficients of segregation between solid Si and Si–Al melt decrease at lower temperatures (at 1000 °C [10]), which is more favourable for Si refining, than the coefficient of segregation between the solid and liquid silicon at its melting temperature of 1414 °C [11]).

PLASMA MELTING AND REACTIVE GAS

Alongside the traditional refining stage, experiments with simultaneous application of gases of different composition bled into the active zone were conducted during plasma melting to increase the effectiveness of boron removal during solvent refining. The authors of work [12] performed experiments in Ar–H_2 atmosphere, based on the results of work [13], where the method of a melting zone was studied in the mixture of H_2–H_2O. Increase of specific resistance of silicon produced by this method was noted, in connection with boron evaporation. A more advanced method consists in silicon melting by a plasma torch when feeding reactive gas. Furtheron this procedure was studied, as a rule, using O_2 or H_2 in Ar-based plasma to remove boron. Some important experimental results are given in the Table 1 [14–17].

Boron is the most difficult to remove impurity in silicon, its limit concentration for silicon of SoG–Si class is ≤0.3–0.4 ppm_w. Under oxidizing conditions boron can form a range of oxides, the lightest of which are BO [18] or HBO [19] (in H_2–H_2O atmosphere). A serious limitation of plasma melting process is the fact that just the upper surface of the silicon bath is exposed to the influence of the plume so that impurity removal depends on their diffusion to the surface. Bath stirring with the new technique of electromagnetic stirring was used in work [20]. This method ensures accelerated mass transfer in the liquid, compared to the rate of the reaction on the surface, enables monitoring the surface shape, controlling the induction effect. Using the same procedure, the authors of [21] determined that phosphorus can evaporate in the form of P_2 at silicon melting temperature, but effective removal of boron will require the presence of H_2 (or H_2O) and O_2 to form HBO. This, however, caused problems associated with silicon loss, as well as passivation of silicon surface due to formation of a layer of solid SiO_2.

In work [22] it was found that H_2 is more effective in plasma than in O_2, for removal of metal impurities. Effectiveness of Na, Ca, Ba and Al removal was 90–100 % with application of 30 % H_2 in Ar plasma. Carbon removal was observed with application of oxygen in the plasma at temperatures above 1530 °C. Authors of [23] modified the process, applying constant voltage to the liquid bath, which increased the refining effectiveness 10 times at 105 V positive bias. During plasma melting and hydrogenation of the silicon bath [24] hydrogen presence in the plasma led to removal of residual oxygen in the silicon deposit and promoted defect passivation. Produced silicon product had favourable electronic properties.

The best results on boron removal from molten silicon were achieved during melt blowing by humidified argon or water vapor [25, 26]. Combination of the process of growing silicon ingots and its refining is a promising direction in creation of new technologies of silicon ingot production. In work [27] a 100 mm long ingot with a dense and homogeneous structure was produced (its drawing rate was 1.5 mm/min), using continuous melting of silicon in a sectional mould (to compensate for ingot expansion during crystallization) with application of high-frequency heating. At the final melting stage, due to application of a uniformly heated graphite body in the unit upper part, an upward directed crystallization of the ingot was ensured under the condition of its blowing with a gaseous reagent (Ar–1.2 % H_2O in the amount of 0.04 g/min), total gas mixture flow rate being 4 l/min. Boron content in silicon at blowing for 15 min decreased by 4 ppm_w (from 28 to 24 ppm_w).

Table 1. Experiments with plasma melting

Parameters	Scale	Significant results
Ar–0.079 up to 0.1 vol.% O_2 [14]	250 g	Increase in O_2 addition improves B removal
Ar–1.24 vol.% H_2O, 25 min [15]	5 g	[B] was decreased from 35.7 to 0.4 ppm_w
Ar–0.66 vol.% O_2, 30 min	10–40 g	[B] was decreased from 12 to 3 ppm_w
Ar–H_2O, from 15 to 60 min [16]	–	[B] removal speed increases with increase in H_2O addition
Ar, Ar + He, Ar + H_2 w/H_2O to 14.2 vol.% [17]	0.6 to 300 kg	[B] constantly decreases to <0.1 ppm_w; higher temperatures accelerate boron oxidation

The problem of manufacturing photoelectric converters (PEC) to meet the requirements of 99.9999 % SoG–Si (0.3 ppm_w B and 1.5 ppm_w P) may be solved by development of laboratory equipment with induction crucibleless suspension melting [28–30]. PWI developed and manufactured a stand for studying the processes of silicon refining from boron during induction suspension melting at temperatures of 2150–2250 °C, with the time of keeping silicon in the liquid state of 1–5 min and blowing with argon-based mixture (O_2–10 % H_2). Melting was conducted in a sectional crucible in an argon atmosphere. Intensive stirring of a silicon drop in an electromagnetic field during blowing with argon-hydrogen mixture in the presence of oxygen in metallurgical silicon promoted formation of volatile compounds of B–O–H system. In keeping with the derived data, at holding of a liquid silicon drop for 5 min boron content decreased from 0.00141 (14.1 ppm_w) to 0.00118 wt.% (11.8 ppm_w), i.e. by 16.4 %.

ELECTRON BEAM REMELTING, EVAPORATION METHODS

At present, solar panel PECs are manufactured from SG–Si silicon, including mono-crystalline-Si [31], multi-crystalline-Si, and thin film-Si PEC are also becoming widely accepted [32]. Electron beam remelting (EBR) is one of the most effective methods of silicon refining. Research works [33–35] performed in PWI electron beam units on refining scrap (mono-crystalline Si scrap), and commercial silicon (TU 48-0106.01–04) are known, and structural features of high-purity silicon produced by vacuum (VR) and oxidative refining (OR) of metallurgical silicon have been studied. The works present the technological features of EBR–VR or OR application. Attempts have been made to improve the vacuum melting technology using the electron beam, in order to remove phosphorus. Behaviour of metal and non-metal impurities during removal, depending on melting time, beam power or gas blowing (Ar or O_2) was studied. As a result, the amount of P decreased from 40 to 3 ppm_w, and B content did not change [36, 37]. In works [38, 39] crushed leached MG-Si of 99.92 % purity and whole metallurgical silicon of initial purity of 99.88 % were melted by the electron beam to make 25 mm thick discs 99 mm in diameter. Silicon of 5N purity was produced, but its purity was limited by regions in the disc upper and edge part. Refining from metal impurities was higher than 99 %, from phosphorus — 98 % (0.4 ppm_w), however, boron removal was not effective. The authors of work [40] studied phosphorus removal using electron beam method in the periodic and continuous configuration. In experiments with periodic action phosphorus removal rate is proportional to the temperature at the interface, and it depends on beam power, but with power increase the silicon evaporation rate be comes higher. In the continuous experiments phosphorus level of ≤0.1 ppm_w has been achieved at up to 50 kg/h silicon feed rate and up to 250 kW beam power, and it led to considerable silicon loss.

In work [41] the ecological cleanliness of EBR process is noted and the possibility of vacuum refining of silicon through evaporation of impurities with high vapour pressure and zone recrystallization is reported in [42]. The possibility of silicon cleaning in one technological cycle of vacuum and oxidative refining with a mixture of oxygen with inert gas is emphasized (in particular, to remove boron impurity in the form of BO, B_2O, B_2O_3 boron oxides). The author proposed a scheme of EB process of refining lumpy crystalline silicon using a cold hearth for evaporation of elements with a high vapour pressure and oxidative refining from boron impurities, and a mould for zone cleaning from Al, Cu, Fe, Ti impurities. A technology of cleaning using quartz glass has been developed.

ELECTRON BEAM CRUCIBLELESS ZONE MELTING

Work [43] presents data on the influence of sterility of vacuum melting chamber on the content of background and volatile impurities in silicon single-crystals, produced by the method of electron beam crucibleless zone melting. The problem of silicon cleaning from oxygen is relevant when it is used as radiation resistant material. Oxygen presence in silicon lowers the electronic instrument response speed and is the cause for unreproducible instrument parameters [44, 45]. During electron beam crucibleless zone melting silicon cleaning from alloying and background impurities is caused by zone recrystallization and impurity desorption from the sample surface [46]. Content of impurities in silicon is influenced by residual atmosphere in the melting vacuum chamber. This must promote impurity desorption from silicon sample surface during melting. Investigations using the infrared (IR) spectroscopy method showed that after chamber purging with helium and with increase in vacuum depth the oxygen content decreases by more than an order, while phosphorus content decreases by an order.

The authors of this paper considered the peculiarities of vacuum and oxidative refining during electron beam melting of metallurgical silicon of different purity. Ingots of initial metallurgical silicon were produced by electron beam melting in a cold copper crucible, in order to conduct the research (Figure 3). To produce silicon ingots, EBR of lumpy MG-Si was conducted by gradually increasing the power of the electron beam (EB), and refining proper was per-

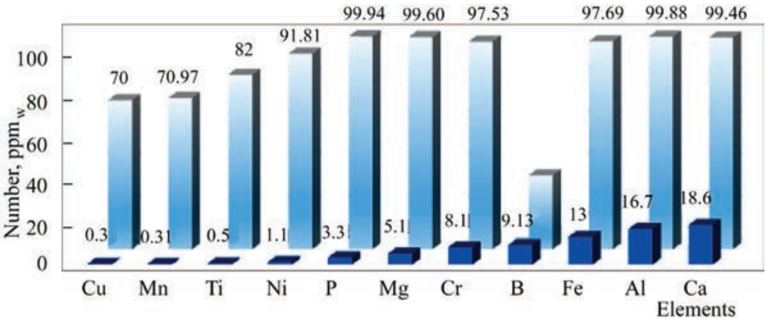

Figure 2. Impurity element content in the initial state in metallurgical silicon of Kr0 grade (GOST 2169–69) and degree of their cleaning after EBR and oxidative refining

formed at a constant beam power with melt soaking for a controlled (17 min) period of time. For subsequent crystallization, EB power was gradually reduced, ensuring a temperature gradient from the ingot edge to its center, promoting the process of zone cleaning during melting, as well as compensation of Si volumetric expansion during ingot crystallization to prevent its cracking. Technological time of conducting the experiment was 20 min. Produced ingots had the shape of a convex disc 95 mm in diameter and 30 mm thick (Figure 3). After completion of the stages of vacuum and oxidative refining, the power of heating the silicon bath was gradually reduced up to the moment of complete crystallization of the produced ingot material [47].

At the same temperature and pressure of conducting the technological process more probable is melt refining from impurity elements, having higher partial pressure (vapour pressure), allowing for its coefficient of distribution/activity in the melt [9–14]. Refining kinetics essentially depends on the technological parameters, as the real processes occur under considerably non-equilibrium thermodynamic conditions.

During heating of initial silicon by the electron beam the vapour phase over solid silicon and its melt is made up of Si gas (g), Si_2 (g), Si_3 (g). Up to the temperature of 1227 °C predominantly Si (g) is present in the vapour phase, at 1727 °C it is 94.8 % Si(g), 4.94 % Si_2 (g) and 0.26 % Si_3 (g). Silicon vapour pressure in the melting point (1417 °C) is equal to $5.66\cdot10^{-7}$ atm. Silicon begins to noticeably evaporate at temperatures above 1527 °C.

In silicon-oxygen system there are two silicon oxides: SiO with melting temperature of 1702 °C, boiling temperature of 1880 °C, and silicon dioxide SiO_2 with T_m = 1723 °C. SiO forms during SiO_2 reduction by silicon at high temperatures.

During metallurgical silicon recrystallization by the electron beam under vacuum, vacuum refining proceeds in the formed ingot, which is based on the difference in vapour pressure of different elements. Components, for which vapour pressure is higher than that of silicon vapours, will be removed. Figure 4, *a* shows vapour pressure in the melting point of metal impurity elements.

In boron-oxygen system, B_2O_3 boron oxide is the most stable in the solid state. This modification melts in the temperature range of 325–450 °C. At boron oxide heating with elementary boron above 1000 °C, there are heat-resistant linear molecules O=B=B=O in the vapours. Degree and speed of silicon cleaning from boron strongly depend on temperature. Boron starts to noticeably evaporate at temperatures above 2027 °C, in the melting point of 2075 °C the vapour pressure is equal to $1.37\cdot10^{-5}$ atm, and evaporation rate becomes equal to $4.122\cdot10^{-5}$ g/(cm^2·s) [15]. For effective cleaning the melt temperature should have been increased up to 2500 °C and higher.

The difference in the rate of silicon and boron evaporation from the silicon melt can be judged from literature data, for instance, for 2127 °C temperature, it is equal to (102.8 and 0.7)$\cdot10^{-4}$ g/(cm^2·s). Accordingly, it leads to selective evaporation of silicon in the form of oxides, and, as a result, to increase in boron content in the melt.

To study the possibility of MG–Si refining from impurities with low partial pressure (B, P, Bi, etc.), EBR was followed by oxidative refining (OR), which consists in melt treatment with gases/vapour, which contain the oxidizer (water vapour, oxygen) with high chemical affinity to impurities with formation of highly volatile compounds/oxides.

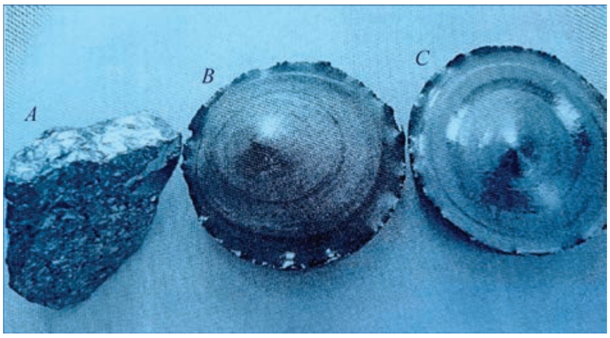

Figure 3. Initial metallurgical silicon (*A*) and ingots after vacuum (*B*) and oxidative (*C*) refining

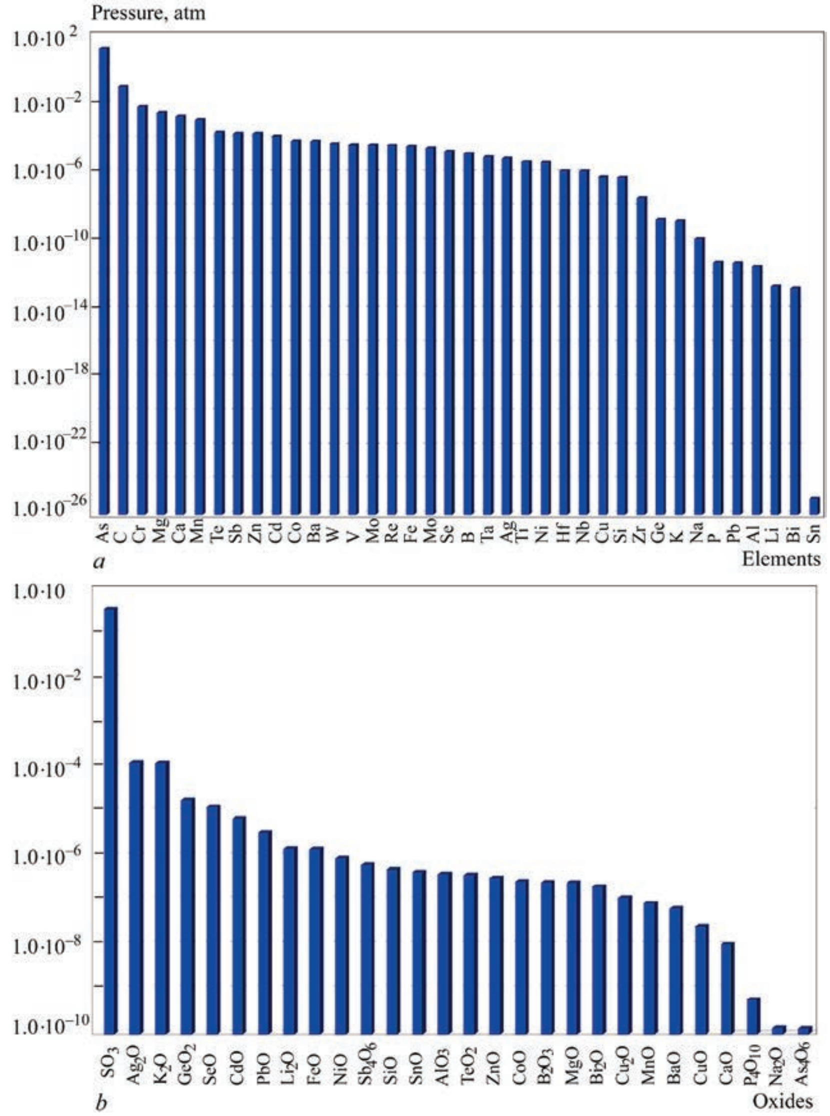

Figure 4. Partial pressure of saturated vapour in the melting point of impurity elements of metals (*a*) and oxides (*b*)

Figure 4, *b* gives the vapour pressure in the melting point of oxide impurity elements.

Volatility of monoatomic phosphorus is low, and diatomic phosphorus is the lightest (P_2). Phosphorus removal can be performed with humidified air with formation of PH_2, PH_3, PN at temperatures of 1400–1500 °C. At higher temperatures thermal decomposition of these light components occurs, and, as a result, at the temperature of ~1700 °C silicon cleaning from phosphorus through PH_2, PH_3, PN becomes practically impossible.

During performance of experimental oxidative refining (OR) of MG–Si, oxygen with flow rate of 70–80 ml/min was used during EBR for treatment of metallurgical silicon melt. An additional factor for refining from impurities in EBR is their fragmentation and partial removal, as a result of local overheating of inclusions in the zone of EBR high-energy impact [16]. Inclusions, which differ significantly by their thermal-physical parameters (heat conductivity, heat capacity) compared to the main component of the melt (Si), are quickly overheated, partially sublimated, destroyed and removed from the melt. The above-described process in the from of microexplosions with partial removal of the material particles from the melt surface is often observed visually during performance of the technological process of EBR of metals and alloys in general and of MG–Si, in particular.

The effectiveness of metallurgical silicon refining was determined by the following formula

$$C_{\mathrm{ef}} = (C_{\mathrm{in}} - C_{\mathrm{vr.or}}).100/\mathrm{C}_{\mathrm{in}},$$

where C_{ef} is the refining effectiveness; C_{in} is the concentration of initial silicon impurities; $C_{\mathrm{vr.or}}$ is the impurity concentration after electron beam vacuum and oxidative refining.

Figure 5, *a*, *b* shows the results of the effectiveness of evaporation of impurities from metallurgical silicon (*a*) and higher purity silicon (*b*).

Obtained results confirmed the effectiveness of MG–Si cleaning from metal impurities of Sb, Cr, Mo, K, Ti during vacuum refining and possibility of clean-

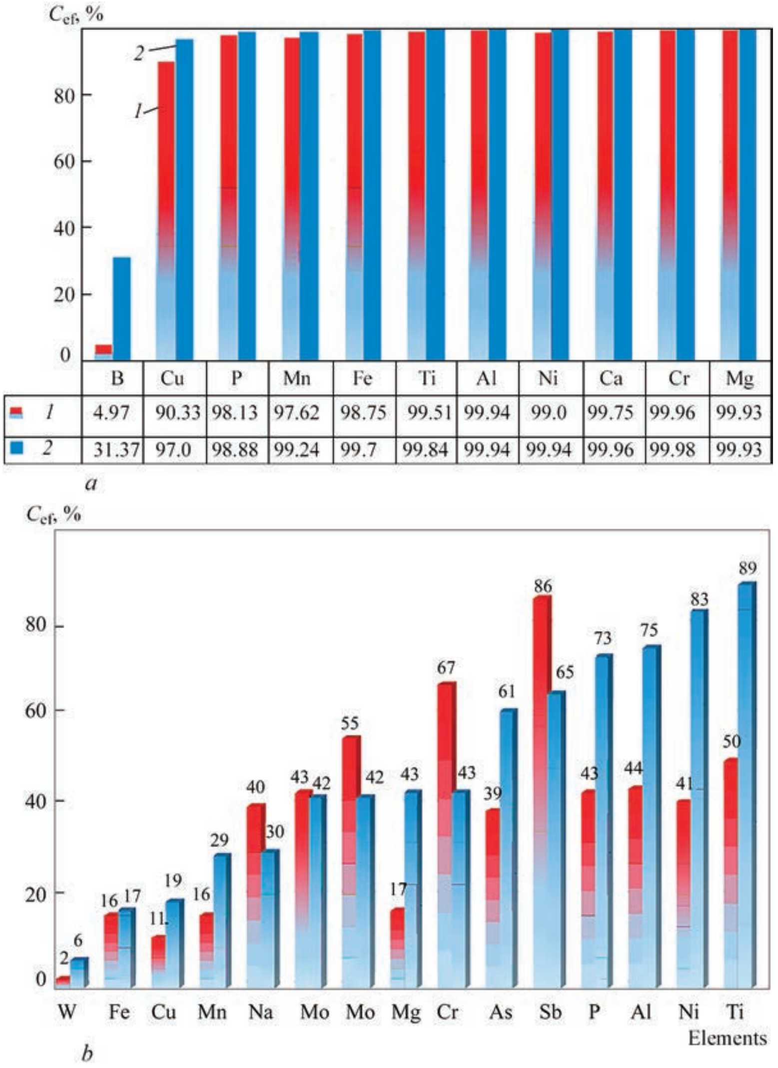

Figure 5. Effectiveness of refining samples of metallurgical silicon (*a*) and higher-purity silicon (*b*) after vacuum and oxidative refining: *1* – vacuum refining; *2* – oxidative refining

ing from Ti, Ni, Al, As, P and partially boron during oxidative refining. More effective refining of silicon from impurity elements and boron during EBR can be expected under the condition of a developed surface of the melt and greater duration of the ingot surface staying in the molten state.

CONCLUSIONS

1. Modern technologies are presented, which are used for refining metallurgical silicon.

2. Intermediary metal (Al) acts as an impurity trap during silicon refining after its fusion with Si. Low temperatures (beyond 1000 °C) are more favourable for Si refining. Partial removal of C, Ca, Fe, Ti, P and an abrupt lowering of Fe, Ti content in Al–Si melt with Si is shown. Double directional crystallization of the melt allowed producing Si of the purity acceptable for application in photoelectric technologies.

3. For boron removal positive results were obtained during plasma remelting with simultaneous use of gases bled into the active zone: Ar–H_2, H_2–H_2O, O_2 or H_2 in Ar-based plasma.

4. The technique of electromagnetic stirring of the bath ensures accelerated mass transfer in the liquid, compared with the speed of reaction on the surface, and surface shape is controlled.

5. It is found that H_2 is more effective in the plasma than O_2 for removal of metal impurities: effectiveness of Na, Ca, Ba and Al removal was equal to 90–100 % at application of 30 % H_2 in Ar plasma, and carbon removal was observed during oxygen application in the plasma at temperatures above 1530 °C.

6. Constant voltage on the liquid bath increases the refining effectiveness 10 times. Obtained silicon product had favourable electronic properties.

7. The best results on boron removal from molten silicon were obtained during melt blowing with humidified argon or water vapour.

8. The possibility of silicon cleaning from elements with a high vapour pressure and oxidative refining from boron impurities in one technological cycle of vacuum and oxidative refining with a mixture

of oxygen with inert gas, using a cold hearth and zone recrystallization is noted.

9. During electron beam crucibleless zone melting silicon cleaning from alloying additives and background impurities is caused by zone recrystallization and impurity desorption from the sample surface. After increasing the vacuum depth, oxygen content decreases by more than an order, with phosphorus content decreasing by an order.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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