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Approaches to the development of environmentally friendly and resource-saving technology for solar-grade silicon production

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ABSTRACT

Currently, the main material for the production of solar cells is still silicon. More than 70% of the global production of solar cells are silicon based. For solar-grade silicon production the technologies based on the reduction of silicon from organosilicon compounds are mainly used. These technologies are energy-consuming, highly explosive and unsustainable.
The present paper studies the technology of purification of metallurgical-grade silicon by vacuum-thermal and plasma-chemical treatment of silicon melt under electromagnetic stirring using numerical simulation and compares this technology with the existing ones (silane technologies and Elkem Solar silicon (ESS) production process) in terms of energy consumption, environmental safety and the process scalability.
It is shown that the proposed technology is environmentally safe, scalable and has low power consumption. The final product of this technology is multicrystalline silicon, ready for silicon wafer production.

INTRODUCTION

The ecological safety of production is the most important factor of its development. Currently, the requirements for the production environmental safety are very high; therefore, the research and development of new technologies and equipment that provide a new, higher level of environmental safety are carrying out. The development of renewable energy, including photovoltaics, is also associated with ensuring the ecological safety.

The world market for photovoltaic systems as of 2016 was 76.6 - 77.3 GW [1]. The market was growing rapidly, so in the period of 2010-2016 a steady growth of up to 40% was observed.

Currently mono- and multicrystalline silicon is the basic material for solar cell production: 94% of the total solar cell production as of 2016 [1].

The basic solar-grade silicon production processes are as follows:

- metallurgical-grade silicon production by the carbothermic reduction from SiO_2 in arc furnaces;
- production of mono- and multicrystalline silicon for solar cells.

All the aforementioned productions have high energy consumption, use environmentally harmful and explosive substances [1]. Currently, investigations for the development of new environmentally friendly technologies for solar-grade silicon production are carried out [1-13, 17, 18].

The paper presents the results of a study on the development of silicon purification technology from various impurities using vacuum refining, plasma chemical purification under electromagnetic stirring of silicon melt and the comparison of this solar-grade silicon production technology with the existing technologies (trichlorosilane technology, silane technology with Siemens process, Union Carbide process (UCP), Elkem Solar silicon (ESS) production process). The comparison of the technologies was carried out according to the estimates of energy consumption, environmental impact, the technology scalability and the final product characteristics.

THE TECHLOLOGY FOR VACUUM-THERMAL AND PLASMA-CHEMICAL PURIFICATION OF METALLURGICAL-GRADE SILICON UNDER ELETROMAGNETIC STIRRING OF SILICON MELT

The basis of the new technology for metallurgical-grade silicon purification is vacuum-thermal and plasma-chemical purification of silicon melt with the subsequent directional crystallization.

The vacuum-thermal purification is based on evaporation of impurities with a high saturated vapour pressure at the silicon melting temperature [1].

The main purpose of plasma-chemical purification is to remove boron, which is difficult removed by other methods (vacuum refining, directional crystallization) [10, 11]. The method is based on transfer of boron to chemical compounds having a high saturated vapour pressure at the silicon melting point of B_xO_y oxides and $B_xH_zO_y$ compounds. Besides, during plasma-chemical purification effective removal of carbon takes place, which, being oxidized to CO monoxide, is removed from the melt surface. In the course of plasma-chemical purification, silicon melt is saturated with oxygen in the form of silicon monoxide SiO. To remove the oxygen impurity, subsequent vacuum refining electromagnetic stirring is required, during which the evaporation of SiO with a high saturated vapour pressure from the melt surface occurs.

Table 1 shows the efficiency comparison of vacuum-thermal, plasma-chemical purification, directional crystallization in relation to the basic impurities in metallurgical-grade silicon. The presented data were obtained by analyzing the publications [1-9] and the experimental studies carried out by the authors [11].

It is expedient to use the following sequence of silicon purification steps in a single technological cycle:

- vacuum refining: removal of phosphorus, sodium, zinc, magnesium, calcium, aluminium, oxygen, etc.;
- plasma chemical purification: removal of boron and carbon;

- additional vacuum refining: removal of oxygen introduced during plasma-chemical purification;
- directional crystallization: removal of metallic impurities, including a significant amount of metallic impurities – Fe and Ti, which have extremely low segregation coefficient values, which ensure their effective removal by directional crystallization under electromagnetic stirring.

For electromagnetic stirring of large volumes of silicon melt (500 kg and more) a system of multiple ring inductors generating traveling magnetic field can be used. The typical value of the traveling magnetic field frequency is within 10–200 Hz [15–17], which substantially simplifies the structural realization of electromagnetic stirring.

The final product of the proposed technology is a multicrystalline silicon ingot.

Table 1. Efficiency comparison of different purification methods in relation to basic impurities ((«--» - ineffective, «-» - slight removal, «+» - effective, «++» - very effective).

Impurity	Vacuum-thermal purification	Plasma-chemical purification	Directional crystallization
B	– –	++	–
P	++	–	–
C	-	++	+
O	++	Content is increased	– –
Al	+	–	+
Ca	+	–	+
Mg	++	–	+
Na	++	–	+
K	++	–	+
Fe	–	–	++
Ni	–	–	++
Cr	–	–	++
Mo	–	–	++
Ti	– –	–	++
V	–	–	++
Mn	+	–	++
Zn	++	–	++
Cu	+	–	++

Typical impurity concentrations in metallurgical-grade silicon are as follows: B – 2-10 ppmw, P – 5-100 ppmw, C – 10-1000 ppmw, Al – 500-2000 ppmw, alkali and alkaline earth metals (Na, K, Ca) – 100-300 ppmw, transition and post-transition metals (Fe, Ti, Cr, Ni, Cu, Zn, Mo) – 20-2000 ppmw. The target content of impurities should not exceed: for B – 0.3 ppmw, P – 0.8 ppmw, C – 43 ppmw, Al – 0.5 ppmw, metallic impurities not more than 4 ppmw.

Numerical simulation of vacuum-thermal and plasma-chemical purification of silicon under electromagnetic stirring of silicon melt

It is known that electromagnetic stirring results in intensification of purification and crystallization of melt [12-18]. In [13-16, 18] the numerical models and the results of numerical simulation of electromagnetic stirring of silicon melt are presented and the results of experimental studies are provided. The detailed consideration of impurity transport in silicon melt and their removal from the surface is not given. The present work provides numerical simulation of vacuum-thermal and plasma-chemical purification of silicon under electromagnetic stirring of silicon melt taking into account the impurity transport inside melt induced by electromagnetic stirring.

The technology research was conducted by numerical simulation using the COMSOL Multiphysics program. All the presented calculations were performed for a 5G crucible size (840x840x290 mm), a constant melt temperature of 1560 ºC, and axisymmetric electromagnetic stirring with an average melt velocity of 20 mm/s on the surface. The electromagnetic stirring parameters were selected on the basis of the studies conducted in [17]. The parameters used in the numerical simulation were as follows: the liquid silicon density was 2480 kg/m^3, the dynamic viscosity of liquid silicon was $5.24 \cdot 10^{-4}$ Pa·s [20], the electrical conductivity of liquid silicon was $1.38 \cdot 10^6$ S/m [20]. The dependencies presented in [21] were used in the model as the diffusion impurity coefficients. Figure 1 shows the geometry of the triangulation computational grid of silicon melt used in the calculations.

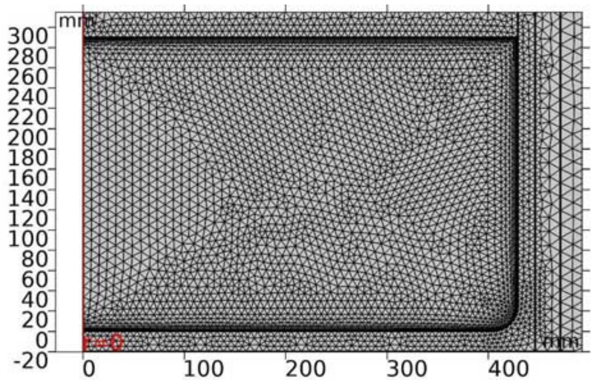

Figure 1. The geometry of a triangulation computational grid in silicon melt.

Numerical model of silicon purification by vacuum refining and plasma chemical purification under the conditions of electromagnetic stirring includes:

- Maxwell's equations in differential and integral forms:
- the equation for calculating the Lorentz force acting on silicon melt:

$$F_L = j \times B \tag{1}$$

where j is the current density, B is the magnetic induction value.

- the equation for calculating the induction current, arising in silicon melt as a result of the action of induced electromotive force:

$$j_i = \sigma(E + u \times B) \tag{2}$$

where σ is the liquid silicon conductivity, E is the electrical intensity and u is the flow rate of conducting medium (silicon melt) in the magnetic field.

- the Navier-Stokes equation and the continuity equation for calculating the liquid flow hydrodynamics:

$$\frac{\partial \vec{u}}{\partial t} = -\vec{u} \cdot (\nabla \vec{u}) + \frac{\eta}{\rho} \Delta \vec{u} - \frac{1}{\rho} \nabla p + \overrightarrow{F_m} \tag{3}$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \cdot \vec{u}) = 0 \tag{4}$$

where ρ is the density, $\bar{u}$ is the velocity field, η is the dynamic viscosity coefficient, p is the pressure, F_m is the vector field of volume forces.

- the continuity equation for calculating the impurity particle transport in silicon melt:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) + \vec{u} \cdot \nabla c_i = R_i \tag{5}$$

where D_i is the diffusion factor of impurity, c_i is the concentration of impurity, $\bar{u}$ is the vector field of the silicon melt mass flow, determining the mass-transport in silicon melt, induced by the Lorentz force, R_i is the rate of the impurity concentration change, and i – the impurity index.

- the equation of the boundary condition for calculating the metal impurity evaporation from the surface melt based on the Hertz-Knudsen approach [6]:

$$N_i = K_{c,i} \cdot c_i$$
$$K_{c,i} = \frac{\gamma_i M_{si} p_i^o}{\rho_{si} \sqrt{2\pi M_i RT}} \tag{6}$$

where $K_{c.I}$ is the evaporation coefficient of impurity, γ_i is the activity factor, M_{Si} is the silicon molar mass, p_i is the saturated vapor pressure of impurity, ρ_{Si} is the density of liquid silicon, M_i is the molar mass of impurity, R is the gas constant, T is the temperature.

- the equation of the boundary condition describing the complete impurity removal from the melt surface, used for calculation of purification from easily evaporable impurities during vacuum refining of P, Zn, Na and for calculation of boron and carbon removal at plasma chemical purification:

$$c_i = 0 \tag{7}$$

When calculating the plasma-chemical purification of silicon from boron impurities and the removal of oxygen impurities, the boundary condition (7) corresponding to the assumption of complete removal of impurities from the melt surface was used.

The calculation using the boundary condition (7) is an assumption of the model, the use of which is justified, since the initial level of the impurity concentration in silicon (10-1000 ppm) is substantially higher than the provided threshold of the maximum purity depth, the value of which is tenths of ppm for various types of impurities according to the summarized data. When providing certain thermodynamic conditions for effective removal of impurities (temperature, pressure, and the value of gas flow “washing” the melt surface), the impurity concentration on the surface can be considerably reduced compared to the target final concentration value, which ensures the removal of impurities from melt below the maximum allowable concentration.

Numerical simulation results and discussion

Figure 2 shows the dynamics of the average concentration decrease of various impurity types in the ingot volume.

The analysis of the dynamics of the average concentration decrease of various impurity types in the ingot volume shows that the impurities having high diffusion coefficients and evaporating intensively from the melt surface (phosphorus, zinc, and sodium) are the most effectively removed ones. Their concentration decreases by more than three orders of magnitude during 20 hours (Figure 2). The concentration of impurities with an average evaporation rate (aluminum and calcium) decreases by more than an order of magnitude. The concentration of such impurities as copper, iron, titanium is practically unchanged. The nonlinear nature of the impurity concentration decrease is primarily due to the decrease of the impurity flow to the melt surface that is connected with the decrease of the concentration gradient of impurities in melt and a corresponding decrease of the diffuse mass transfer.

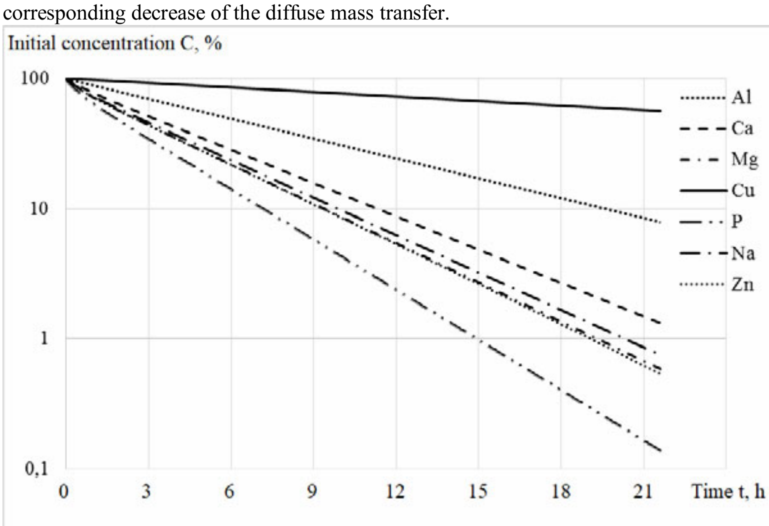

Figure 2. Time dependences of the average rated concentration decrease of different impurities (Al, Ca, Mg, Cu, P, Na, Zn) during vacuum refining at electromagnetic stirring (maximum surface velocity is 20 mm/s).

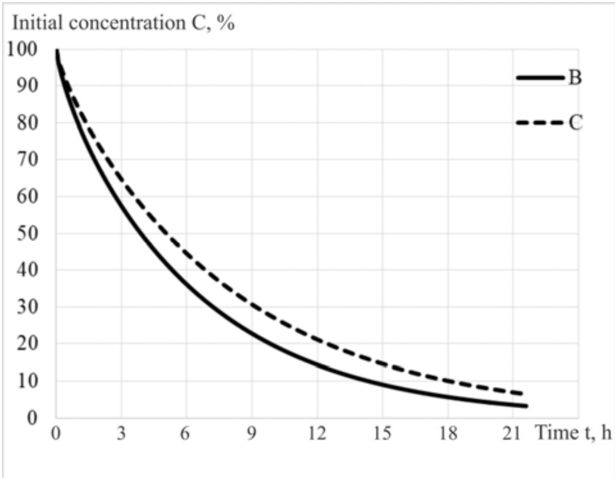

Figure 3. Time dependences of the average rated concentration decrease of B and C during plasma chemical purification at electromagnetic stirring (average surface velocity is 20 mm/s).

Calculation of plasma-chemical silicon purification under electromagnetic stirring shows that the concentration of boron and carbon decreases by more than an order of magnitude during 14-17 hours (Figure 3). The reduction of oxygen concentration by an order during additional vacuum refining is provided during approximately 8 hours (Figure 4).

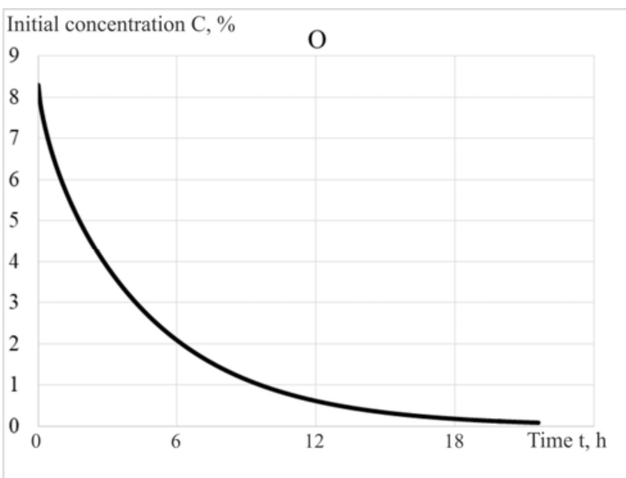

Figure 4. Time dependences of the average rated concentration decrease of oxygen during additional vacuum refining at electromagnetic stirring (average surface velocity is 20 mm/s).

The results of numerical simulation of vacuum refining and plasma chemical purification of metallurgical-grade silicon show that under the conditions of electromagnetic stirring with the average velocity on the melt surface of 20 mm/s during 20 hours, silicon is purified from main impurities by more than an order of magnitude that determines the silicon quality. These methods can be combined in a single technological cycle together with directional crystallization. The silicon purification technology, based on the combined use of these methods, is environmentally friendly and scalable. The final product of the proposed technology is a multicrystalline silicon ingot.

COMPARATIVE ANALISYS OF SOLAR-GRADE SILICON PRODUCTION TECHNOLOGIES

A comparative analysis of solar-grade silicon production technologies was carried out on the basis of the data on energy consumption, environmental safety of the processes, production scalability, and characteristics of the obtained product.

Proposed technology

The estimated energy consumption of the proposed technology was made according to the following data:

- the evaluation of the energy efficiency of the new technology included the overall costs of the directional crystallization (for an ingot weight of 500 kg) of 9.1 kWh/kg, the cost of electromagnetic stirring of less than 0.5 kWh/kg, the cost of vacuum refining and plasma chemical treatment of 10-15 kWh/kg. The energy consumption of infrastructure components (water and vacuum pumps, lighting, crucible and ingot loading and unloading devices) was 1 kWh/kg. Thus, the total energy consumption was 21-27 kWh/kg;
- the process time is no more than 70 hours.

Silane technologies

The silane silicon production technologies are based on the synthesis of silanes (trichlorosilane and monosilane) and the subsequent silicon reduction from these compounds by pyrolysis [1]. The source material is metallurgical-grade silicon obtained by the carbothermic reduction of silicon from quartz sand. For purification of metallurgical-grade silicon, it is converted into a volatile compound — trichlorosilane ($SiHCl_3$) by hydrochloration of metallurgical-grade silicon. For this, the following reactions are used:

$$Si(s) + 3HCl(g) \longrightarrow SiHCl_3(g) + H_2(g) \tag{8}$$

$$Si(s) + 4HCl(g) \longrightarrow SiCl_4(g) + 2H_2(g) \tag{9}$$

The reduction of silicon is carried out in Siemens reactors with the temperature of 1050 ºC - 1100 ºC:

$$SiHCl_3(g) + H_2(g) \longrightarrow Si(s) + 3HCl(g) \tag{10}$$

The characteristic property of this technology is the formation of a by-product ($SiCl_4$). At the same time for every mole of synthesized polysilicon 3-4 moles of silicon tetrochloride is necessary.

In Union Carbide process silicon is reduced from monosilane (SiH_4) [1]:

$$SiH_4(g) \longrightarrow Si(s) + 2H_2(g) \tag{11}$$

The reaction occurs at temperatures from 800 °C to 1000 °C.

In general, silane technologies have a number of serious disadvantages:

- large energy consumption at silicon production;
- the technologies are environmentally hazardous.

The technology uses harmful substances: chlorine (Cl), hydrogen chloride (HCl), silanes of different composition. E.g., according to the United Nations Classification the class of hazard of trichlorosilane is 4.3 (highly flammable substance when contacting with water).

The total energy consumption of silane processes is about 120-180 kWh/kg, but for modern manufacturing areas with a large production volume and several levels of processing of byproducts, the energy consumption of below 100 kWh/kg [1, 2] is achieved.

Elkem Solar Silicon production process

Elkem developed a chlorine-free solar-grade silicon production technology – Elkem Solar Silicon (ESS) production process. This process is based on metallurgical-grade silicon purification and consists of 5 independent processes combined together: metallurgical-grade silicon production, slag treatment, leaching, solidification, post treatment.

The first stage is the selection of raw material for the metallurgical-grade silicon production. During the second stage liquid silicon (MG-Si) is treated with calcium silicate slag to remove boron from melt in the slag composition. The third stage, leaching, solves the problem of removing basic metallic impurities and phosphorus. The fourth stage is the process of directional crystallization in the unit, specially designed for purification, and is also aimed at the removal of metallic impurities and phosphorus. At the fifth and final stages, the ingot obtained from stage 4 is divided into blocks after cutting (thin layers are removed from the top, bottom and on either side) [1]. The advantage of the ESS production process is low energy consumption per 1 kg of product: 30-40 kWh [19].

COMPARISON OF TECHNOLOGIES

Table 2 shows the comparative data of the analyzed technologies according to source materials, energy consumption, environmental safety, scalability of production, and the final product characteristics.

Table 2. Comparison of the main characteristics of the technologies.

Parameter	Silane technologies	Elkem Solar Silicon	New technology
Source material	MG-Si, HCl, H_2	SiO_2, C, acids, slag	MG-Si, UMG-Si
Achievable purity level, mass percentage	99,9999-99,9999999	99,999-99,9999	99,999-99,9999
Energy consumption, kWh/kg	100-140	30-40	<30
Environmental safety	Dangerous	Partially safe due to acids and slag availability	Safe
Scalability	Scale-free at the stage of silane production	Scalable	Scalable
Final product	Poly-Si	Poly-Si	mc-Si

CONCLUSION

The study of a new technology for solar-grade silicon production based on vacuum-thermal, plasma-chemical purification of metallurgical-grade silicon by the numerical simulation under electromagnetic stirring of silicon melt has been carried out. The possibility of implementing this technology on an industrial plant of directional crystallization with a 5G crucible is shown.

A comparative analysis of solar-grade silicon production technologies (trichlorosilane technology with the Siemens process, Union Carbide process, Elkem Solar Silicon production process and the proposed technology) in terms of energy consumption, environmental safety, production scalability has shown that the proposed technology has lower energy consumption and is environmentally safe and scalable.

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