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A new method of metallurgical silicon purification

I.E.Maronchuk, O.V.Solovyev, I.A.Khlopyonova

Kherson National Technical University,
24 Beryslavsky Road, 73008 Kherson, Ukraine

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Studied have been individual purification stages of metallurgical silicon by recrystallization from the Ga-Si system melt followed by isolation and washing of crystals using chemical methods. The technological sequence for silicon purification has been developed. The method makes it possible to purify silicon containing at least 98.0% Si by weight. The subsequent purification by crystallization from the melt provides the product purity level up to 99.999 mass.%

Исследованы отдельные стадии очистки металлургического кремния перекристаллизацией из расплава системы Ga-Si с последующим выделением и промывкой кристаллов химическими методами. Разработана технологическая схема очистки кремния. Способ позволяет очищать кремний с содержанием более 98,0 масс. % Si. При последующей кристаллизационной очистке выращиванием слитка из расплава можно повысить уровень чистоты продукта до 99,999 масс. %.

At present, silicon of "solar" grade is used in the production of photoelectric converters (PEC). The material manufacturing process comprises the following stages: silicon dioxide reduction using the well-known techniques [1], its purification by chlorination and rectification, reduction of silicon chlorides with hydrogen, and single crystal growing using Czochralski technique. The existing purification techniques are, however, expensive and dangerous for environment. In this connection, the purification methods free of those drawbacks are needed. The silicon purification in solutions-melts of low-melting metals [2] is among such methods. In this work, a relatively inexpensive, high-productive and environmentally safe method for metallurgical silicon purification is presented. The product obtained is suitable for production of the "solar" grade silicon crystals. The parameters of minor charge carriers (MCC) in that material will not differ significantly from those of the KSD-5 "solar" silicon single crystals produced today in Ukraine. The MCC in the new material show a long lifetime and a relative high mobility that is sufficient to provide solar converters with efficiency of about 15%. The developed method of silicon purification is based on distinctions in physicochemical properties between the main component and impurities [3], namely, in solubility, volatility, and segregation factor at the phase interface.

To purify metallurgical silicon from a solution-melt, a technologic plant has been developed that makes it possible to purify silicon at temperatures up to 1000 °C at the heating rate controllable within the 1 to 10 deg/min range in vacuum and in a purified nitrogen flow and at the cooling rate from 5 to 30 deg/min. An autonomous cooling system of the plant makes it possible to operate it in rather prolonged high-temperature processes, thus providing the operation convenience and reliability.

The KR-1 grade silicon (98.0 mass.% Si) was used as the initial material. The main impurities are shown in Table. The metal-solvent was selected taking into account its

required properties: low melting point, a good dissolving ability for silicon, chemical inertness thereto, and a low segregation factor, thus providing a high efficiency of crystallization purification. Gallium, indium, aluminum, tin, lead, and some other metals met these requirements. The optimum metal is gallium that makes it possible to lower considerably the purification temperature as compared to other metals-solvents. The silicon solubility in gallium is as high as 10%. In this work, the high-purity gallium of GL-00 grade was used. The use of atomic nitrogen in the purification process provided formation of various nitrides of metals and non-metals that were removed as slags, by the reactor purging or by chemical washing at subsequent stages. The particle size of the initial metallurgical silicon was not critical in the method. The amounts of initial components were calculated basing on the fact that, according to the phase diagram, gallium dissolves at 1000 °C about 10% of silicon. Thus, taking into account the atomic masses of the components, about 10 g of silicon is completely dissolved in 250 g of gallium.

The purification flow chart is presented in Fig. 1. The process comprises the following stages: dissolution of silicon in gallium and transfer of impurities into the melt; the melt cooling and separation of silicon crystals therefrom using vacuum filtration [4] through a filter with 30 μm mesh size; acid washing of silicon to remove gallium.

The purification was carried out as follows. The initial gallium and silicon were introduced into a crucible that was placed onto the bottom of a quartz reactor. Then the reactor was evacuated and heated according to the temperature and time schedule presented in Fig. 2. The system was held under 10^{-5} Torr pressure for 30 min to remove the volatile impurities. Then atomic nitrogen was introduced into the reactor, thus providing formation of nitrides at elevated temperatures, and the temperature was changed periodically within 100° to 920 °C limits to dissolve the small crystals and to drive the impurities back by the

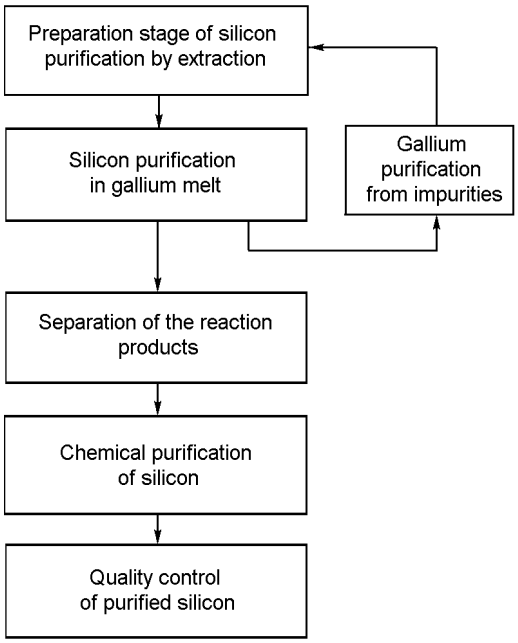

Fig. 1. Flow chart of silicon purification in gallium melt.

Table. Concentrations of impurities in metallurgical silicon, the segregation coefficients and solubility thereof, the impurity concentrations after purification in gallium melt

Impurity	Concentration in metallurgical Si $\times 10^{-6}$%	Solubility, cm^{-3} at 1000 °C	Segregation coefficient	Concentration in purified Si $\times 10^{-6}$%
Al	1600	$2 \cdot 10^{19}$	$2 \cdot 10^{-3}$	150
B	45	$6 \cdot 10^{19}$	$8 \cdot 10^{-1}$	1
P	300	$1.5 \cdot 10^{21}$	$3.5 \cdot 10^{-1}$	0.3
Cr	140	10^{15}	$1.1 \cdot 10^{-5}$	
Fe	2100	$1.5 \cdot 10^{15}$	$8 \cdot 10^{-6}$	<10
Mn	70	$3.5 \cdot 10^{16}$	10^{-5}	<5
Ni	50	$5 \cdot 10^{17}$	$(8–30) \cdot 10^{-6}$	<10
Ti	165	$1 \cdot 10^{16}$	$3.6 \cdot 10^{-6}$	<10
V	100	10^{17}	$8 \cdot 10^{-6}$	<5
Ga	–	$2 \cdot 10^{19}$	$8 \cdot 10^{-3}$	300

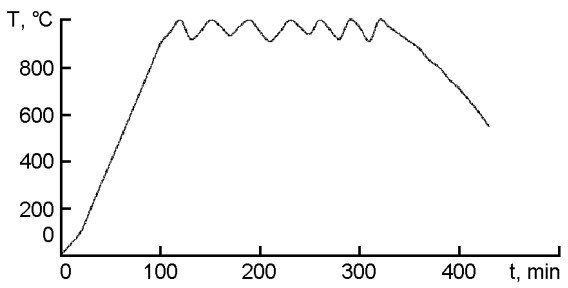

Fig. 2. Temperature and time schedule of the metallurgical silicon purification process.

crystallization front, thus favoring enlargement of more pure crystals. The melt was stirred during the whole stage to provide the homogeneous distribution of Si particles in the Ga melt bulk, thus preventing the floating of undissolved silicon. Moreover, the stirring intensified the silicon crystallization. The purification extent by recrystallization depends on the equilibrium distribution coefficient (D_e) of an impurity between the crystals and the solution. The D_e values for main impurities in silicon taken from [5] are presented in Table. The effective distribution coefficient (D) depends, in turn, on the crystallization conditions, particularly on temperature, and differs from the equilibrium one. Thus, at the process temperature 1000 °C, $D<<1$ for all the main impurities, that is, the crystallization results in depletion of the crystals of the impurities, because those are driven back by the crystallization front. The purity of the purified material is influenced by the solubility limits of the main impurities in silicon. The solubility limits values at 1000 °C taken from [5] are presented in Table. Nevertheless, a high vapor pressure of phosphorus at that temperature and rather low segregation coefficients of Fe, Al, Ca, Ga, etc. did not influence significantly the purity of silicon obtained. The boron impurity having the distribution coefficient close to unity was removed as follows. Starting from 900 °C, boron forms boron nitride BN with atomic nitrogen having a structure like to graphite or diamond. Thus, the formed BN floated as a slag and was removed later by purging and chemical treatment.

During the melt cooling, the crystallization rate of silicon increased at first, attained a maximum, and then decreased; as a result, silicon precipitated as single-crystalline particles with mean size depending on the cooling duration, Fig. 3. The silicon crystals were separated from gallium melt

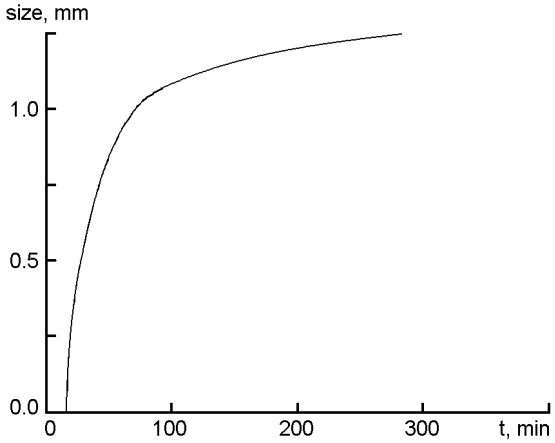

Fig. 3. Dependence of the mean crystal size on the melt cooling duration.

by vacuum filtration through a filter with 30 μm mesh size followed by acid treatment of silicon to remove the residual eutectic melt. As the solvent, hydrochloric acid was selected forming water-soluble chlorides. An additional purification effect was attained using nitrohydrochloric acid (aqua regia, $HCl:HNO_3$ = 3:1).

The impurity concentrations in silicon were measured using IR spectrometry. The concentrations are presented in Table.

The developed purification method of metallurgical silicon provides purification of silicon at a purity at least 98.0 mass.%. The plant designed provides rather prolonged processes at high temperatures. The use of atomic nitrogen in the purification process provided formation of various nitrides of metals and non-metals that were removed as slags, by the reactor purging or by chemical washing at subsequent stages. The formation of silicon nitride Si_3N_4 is unlike, because a higher temperature of 1100 to 1300 °C is necessary that is not used in this process. It is inexpedient to increase the process temperature (and thus the Si solubility), because increased Ga vapor pressure results in its loss and the reactor contamination due to precipitation on the walls. The temperature decrease deteriorates the process productivity due to lowering of silicon solubility in gallium. Therefore, the selected temperature of 1000 °C is the optimum and provides the highest efficiency. The melt-solution stirring enhances the growth rate of more pure crystals.

It follows from the study results that a high cooling rate results in an increased yield of fine fraction, but the purification efficiency is enhanced. At a low cooling

rate, the larger silicon grains contain impurities in increased concentrations. Thus, the purification is to be carried out under conditions providing the formation of small pure crystals. Thus, the proposed purification process with temperature variations makes it possible to obtain a fraction of larger crystals with lowered impurity content due to dissolution of smaller crystals and the impurity driving back by the crystallization front, thus resulting in growth of larger and more pure crystals.

The gallium content in the purified silicon corresponded to its solubility limit at the specified purification temperature. The subsequent growing of single crystalline ingots by Czochralski technique the silicon was purified from gallium. The grown ingots having the specific resistance of 0.25 to 0.2 Ω·cm are suitable for PEC manufacturing.

To conclude, the individual stages of metallurgical silicon purification by recrystallization form malted Si-Ga system followed by separation and chemical washing of the crystals have been studied. The technological sequence for silicon purification has been developed. The use of gallium as the solvent for silicon has made it possible to lower considerably the purification temperature due to Si solubility in Ga attaining 10%. Various purification regimes have been checked, in particular, the temperature variation influence has been studied. The purification efficiency has been established to depend on the crystallization conditions and the grain size of the purified silicon. The method makes it possible to purify silicon containing at least 90.0% Si by weight. The subsequent purification by crystallization from the melt provides the product purity level up to 99.999 mass %.

References

1. E.S.Falkevich, Technology of Semiconductor Silicon, Nauka, Moscow (1992) [in Russian].
2. Proc. Book of 2nd All-Union Conf. on Scientific Principles and Technology of Complex Utilization of Ores and Concentrates, Inst. of Metallurgy, Moscow (1986), p.292 [in Russian].
3. V.N.Lozovsky, N.F.Politova, O.V.Lastushkina, B.P.Masenko, *Neorg. Mater.*, **27**, 663 (1991).
4. B.A.Sakharov, Metallurgy and Technology of Semiconductor Materials, Nauka, Moscow (1972) [in Russian].
5. V.M.Glazov, V.S.Zemskov, Physico-chemical Principles of Semiconductor Doping, Nauka, Moscow (1967) [in Russian].

Новий метод очищення металургійного силіцію

І.Е.Марончук, О.В.Соловйов, І.А.Хлопенова

Досліджено окремі стадії очищення металургійного силіцію перекристалізацією з розплаву системи Ga-Si з наступним виділенням і промиванням кристалів хімічними методами. Розроблено технологічну схему очищення силіцію. Спосіб дозволяє очищувати силіцій з вмістом більш, ніж 98,0 мас. % Si. При наступному кристалізаційному очищенні вирощуванням злитка з розплаву можна підвищити рівень чистоти продукту до 99,999 мас. %.