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PLASMA INVESTIGATIONS

Experimental Study of the Plasmochemical Method for the Direct Production of Silicon from Quartz

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Abstract—The results of experimental studies of the nonequilibrium plasmochemical method for production of polycrystalline silicon from quartz are presented. It was shown that polycrystalline silicon in the form of spherelike particles with an average size of 100–200 μm and purity of 99.8–99.9% can be obtained with a yield of up to 60% using the electric arc installation developed.

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INTRODUCTION

One of the drawbacks of existing technologies [1] used to obtain polycrystalline silicon of solar (or higher) purity is that the materials used for fabrication are derived from industrial silicon, which in turn is a product of raw quartz processing. This leads to the multistage nature of these technologies, resulting in the relatively high cost of silicon produced. In this regard, there is a need to develop new technologies and methods for the direct processing of raw quartz materials to highly pure polycrystalline silicon.

A promising direction for its implementation is plasmochemical methods [2], scientific and practical interest in which arose quite a long time ago. The possibility of obtaining silicon from quartz by the plasmochemical method with hydrogen was first mentioned in [3]. In [4, 5], the results of theoretical and experimental study of obtaining silicon monoxide using electric arc hydrogen-containing plasma were shown. Currently, experimental studies of plasma methods for reduction of silicon by hydrocarbons from silicon monoxide [6] and by hydrogen from amorphous silicon [7] are being carried out.

This paper presents and discusses results of experimental studies of the plasmochemical method [8] for obtaining polycrystalline silicon from quartz (SiO_2), based on the nonequilibrium gas-phase process of binding of oxygen by hydrogen atoms, which is obtained from dissociation of SiO_2 with the formation of Si and O atoms in the flow of inert gas plasma.

PLASMOCHEMICAL METHOD

The proposed plasmochemical method is as follows. Inert plasma-forming gas (Ar), hydrogen, and fine quartz concentrate in a stream of carrier gas (Ar) are fed into the discharge chamber of a stationary plasma torch. Evaporation of the initially solid particles of quartz and dissociation of SiO_2 molecules into atoms (with formation of a pair of silicon and oxygen atoms) and molecular hydrogen acting as a reducing element occurs in the first phase, the homogenization phase, in a high temperature (6–13 kK) plasma flow of inert gas and hydrogen.

Then in the second phase, the plasmochemical reactions phase, a complex of chemical reactions of binding of free oxygen to hydrogen (with formation of water) with a sharp decrease (due to nonequilibrium conditions) of gas-phase oxidation of silicon to SiO and SiO_2 take place upon rapid cooling from ~6 to 2 kK of the obtained gas-phase atomic mixture. The phase is carried out in a water-cooled channel, the plasmochemical reactor (PCR), that is directly connected to the nozzle of the plasma torch. The conditions of nonequilibrium of the reaction of silicon oxidation are provided by the choice of sizes and operating parameters of the PCR, at which the "flight" time of the gas mixture through the PCR will be substantially less than the relaxation time of oxidation of silicon to SiO.

In the last phase, volume condensation of the obtained Si vapors with formation of polycrystalline silicon occurs. The silicon volume condensation phase takes place in the reactor-condenser directly connected to the plasma-chemical reactor, with the passage of which the flow temperature falls to normal values. A collector of formed polycrystalline silicon particles and other solid processing products is installed at the bottom of the reactor-condenser.

EXPERIMENTAL SETUP

Figure 1 shows the experimental setup, the basic units of which are electric microplasmotron *1*, cylindrical water-cooled plasmochemical reactor *2*, and thermoinsulated reactor-condenser *3*. The stainless

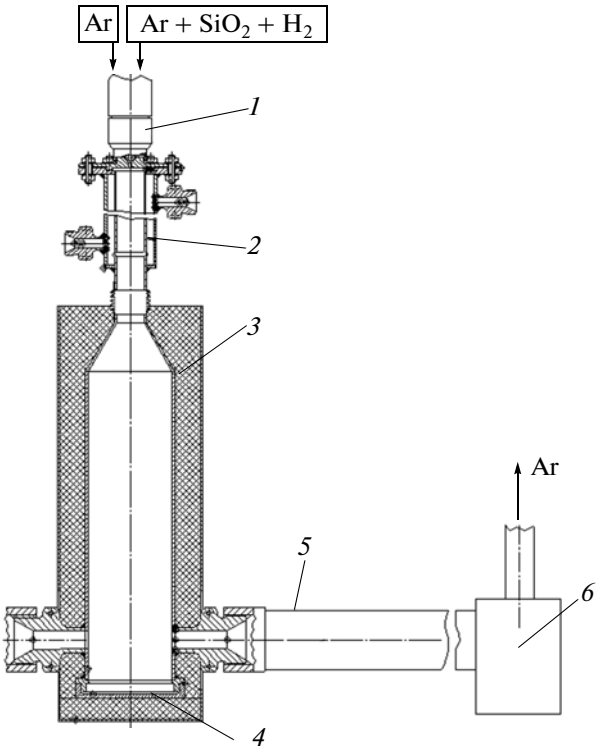

Fig. 1. Experimental setup: (*1*) electric arc microplasmotron; (*2*) water-cooled plasmochemical reactor; (*3*) thermoinsulated reactor-condenser; (*4*) bottom-collector of processing products; (*5*) hose; (*6*) bubble separator.

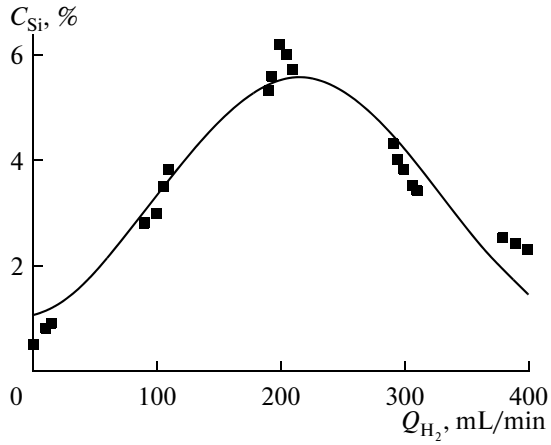

Fig. 2. Influence of hydrogen consumption on silicon yield.

steel bottom cover *4* is attached to the flange of the reactor-condenser with a threaded connection and is designed to collect the condensed processing products. Gaseous and condensed fine reaction products are removed through two symmetrically arranged nozzles on the side of the reactor-condenser, and then through hoses *5* enter bubbling water separator *6*, in which fine separation of solids from the stream should occur.

A stationary water-cooled argon arc plasma torch with an inner diameter of the exit nozzle of 2.7 mm and a maximum consumption of electric power up to 3.0 kW was used in this experimental as a plasma torch. This plasma generator allows one to organize steady burning of the discharge on a mixture of argon and hydrogen, to intensify the processes of heating and evaporation of the particles, and to arrange the supply of quartz concentrate and hydrogen directly into electric arc. The supply of quartz concentrate was carried out with a special dispenser by the flow of carrier gas, argon. The total consumption of primary and carrier gas could be varied from 2.0 to 5.0 L/min, and the hydrogen flow rate, from 0 to 400 mL/min. The efficiency of discharge was in the range of 0.4–0.6.

RESULTS

The quartz concentrate obtained by traditional methods by crushing of granular quartz of Zelenodolsk deposit was subjected to plasmochemical processing. The experiments were performed for quartz concentrates of various initial dispersions. The main series of experiments was carried out for the polydisperse fraction with particles of size less than 100 microns. However, according to the results obtained by laser diffractiometry, not less than 80% (by weight) of quartz particles had sizes in the range of 4–70 μm, about 10% of the mass was particles with size less than 20 μm.

Data on the quantity of impurities in experimentally used quartz concentrates determined by ICP-spectrometry indicate that the processed concentrates are heavily contaminated with Al (340 ppm), K (155 ppm), Fe (80 ppm), Ti (85 ppm), and other elements, with a total impurity concentration of about 750 ppm.

Portions (10 g) of concentrates were subjected to plasmochemical processing at fixed values of the volume consumption of the main (1.8 L/min) and carrying (1.0 L/min) gas and at a given electrical power of the plasma torch P_{el} from the range of values of 2–3 kW. Hydrogen consumption varied from 50 to 400 mL/min.

Processing products collected in the condenser of solid products of the reactor-condenser and dry residue of the bubbling water separator for each mode of operation of the installation were analyzed for detection polycrystalline silicon in them, determination of its purity, and the form of its presence. Investigations were carried out using X-ray diffraction analysis (DRON-3M X-ray diffractometer, analyzing radiation Cu–Kα), scanning electron microscopy (Zeiss Ultra plus based on the Ultra 55 with INCA Energy energy dispersive analysis system), and optical microscopy (OLIMPUS BX51microscope).

As a result of X-ray diffraction analysis (XRD), it was revealed that the main substances collected from the bottom of the reactor-condenser are different phases of silicon dioxide, the amount of which depends on the operational parameters of processing, and polycrystalline silicon. No appreciable amounts of

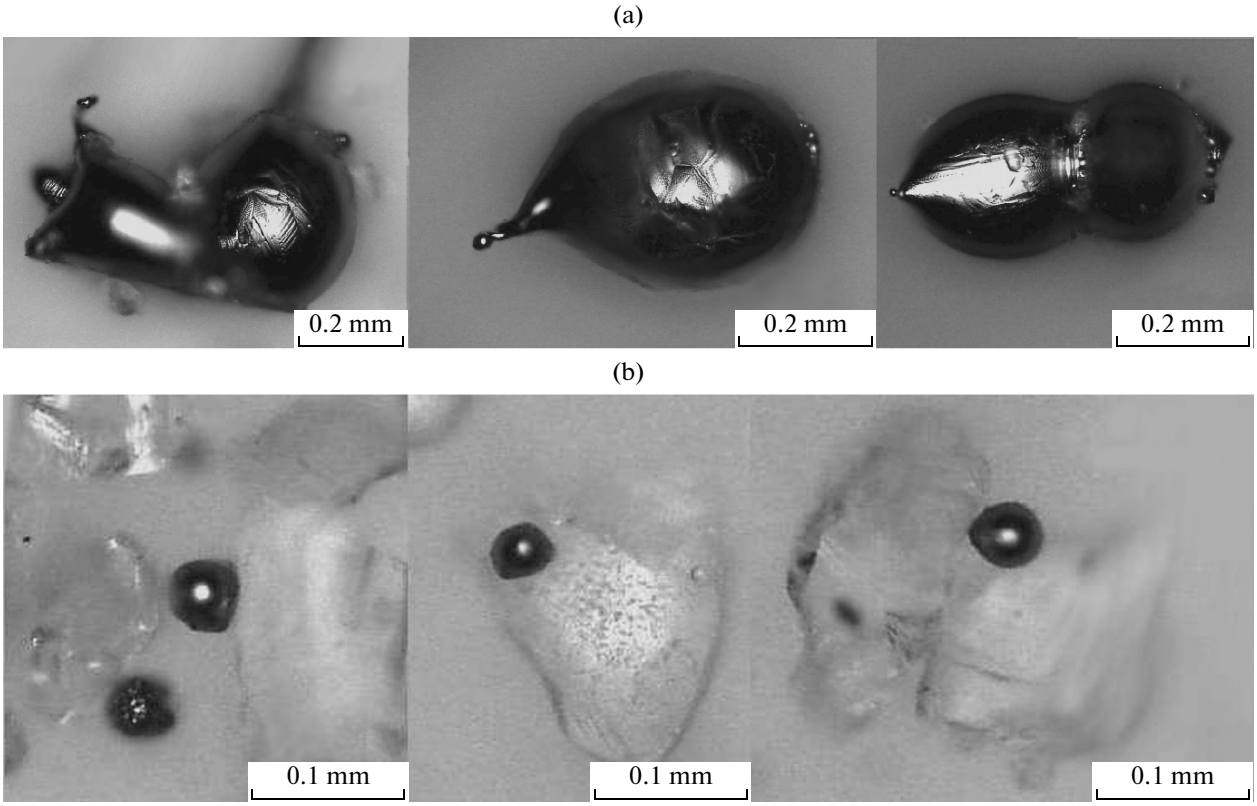

Fig. 3. Optical photographs of (a) free silicon particles and (b) silicon particles condensed on the surface of nonevaporated quartz.

crystalline phases of other substances were registered within the accuracy range of XRD.

It was found that the particle size and phase composition of the solid residue from the bubble separator approximately coincide with the particle size and phase composition of the material collected from the bottom of the reactor-condenser. However, the mass of solid residue was at least an order of magnitude smaller than that of products from the bottom of the reactor-condenser. The gas stream coming out of the bubble separator contains nanoparticles of silicon oxides, forming agglomerates with an average size of 10–20 μm.

Fused quartz powder collected from the bottom of the reactor-condenser located in the products may be in the crystalline or amorphous phase. Its quantity is dependent mainly on the flow of hydrogen in the investigated range of energy-power parameters of the plasma torch and the increase in the amorphous phase of quartz from 10 to 40% with a decrease in the crystalline phase from 90 to 55% with increase in flow rate from 50 to 400 mL/min. Thus, in accordance with the results of optical microscopy, the particles of molten amorphous quartz are usually of oval or elongated shape with a maximum linear dimension of 100 μm. The particles of crystalline quartz mostly have a size of 30–50 μm; particles of size less than 20 μm are virtually absent. This picture of quartz products indicates that the particles of size less than 20 μm were evaporated, medium-sized particles melted, and larger particles were split into smaller ones under the influence of thermobaric stress.

It was revealed that the increase in the plasma torch power leads to an increase of the silicon mass produced, so that appreciable amounts (up to 6%) of polycrystalline silicon are recorded at the maximum plasma torch electrical power of 3 kW.

The quantity of accumulated silicon depends on hydrogen consumption. Figure 2 shows the dependence of the "yield" of polycrystalline silicon C_{Si} (ratio of produced silicon mass to the entire mass of products) from the hydrogen consumption Q_{H_2} (electric power of plasma torch, 3 kW; total plasma gas flow rate, 2.8 L/min). As can be seen, the dependence is nonmonotonic. When the hydrogen flow rate is about 200–250 mL/min, the amount of accumulated silicon is maximal and its maximum yield is 5–6%. The presence of an extremum is, probably, due to the fact that low (<100 mL/min) consumption of hydrogen is not enough to bind free oxygen and for formation of water, and at high flow rates (>300 mL/min) losses of silicon are associated with the formation of SiH increase.

Based on the results obtained by optical microscopy, it is revealed that the accumulated polycrystalline silicon is mostly shiny spherelike particles with

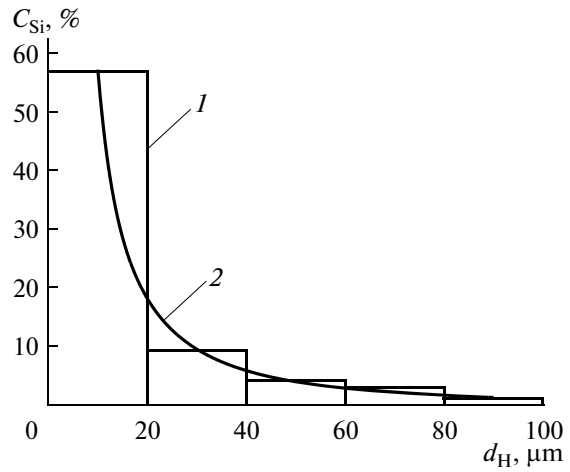

Fig. 4. Dependence of the initial diameter of quartz particles on (*1*) silicon yield and (*2*) the corresponding approximating curve.

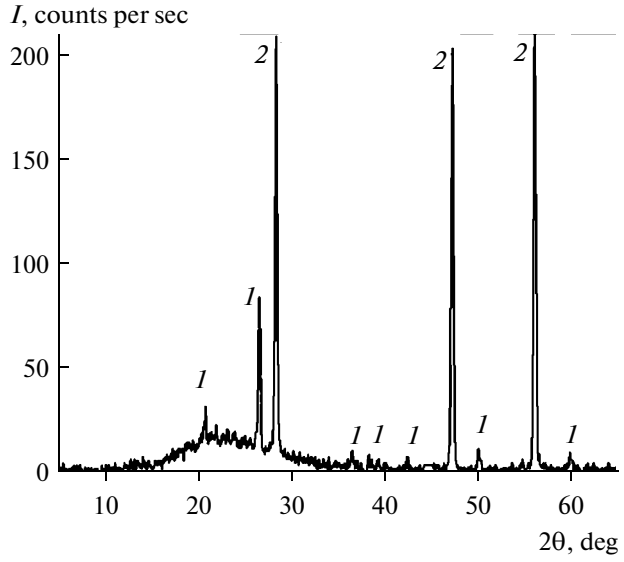

Fig. 5. X-ray diffractogram of product obtained from quartz with an initial dispersion of ≤20 μm, and recorded crystalline phases: (*1*) quartz; (*2*) polycrystalline silicon.

sizes of 1–400 μm. The most common particle size is about 100–200 m (Fig. 3a). At the same time, a small amount of silicon (with dimensions of 1–10 μm) is condensed on the surface of unevaporated quartz particles (Fig. 3b). The shape of silicon particles clearly indicates the crystallization of silicon from the melt, and particles were in flight at the moment of crystallization.

Selected particles of silicon were subjected to grinding and to investigation of thin sections by electron microscopy with the energy dispersive analysis system in order to determine the chemical composition and purity of silicon. From the results of tests, it follows that usually silicon particles are in the form of a solid monolith with a fairly uniform distribution of silicon over the cross section. The purity of silicon obtained in this installation may be as high as 99.8–99.9%, which corresponds to silicon of improved metallurgical quality. The main polluting elements are Mn (0.03–0.04%), Fe (0.01–0.03%), Al (0.02–0.03%), and Cu (0.01–0.02%). Here we draw attention to the fact that the number of major metallic impurities in silicon exceeds the amount of these substances in the original quartz, which shows the influence of erosion products of plasma torch electrode assembly on the purity of the product. In addition, the effect of electrode erosion is manifested in the fact that quite large (up to 100 μm) copper particles and particles that are an alloy of copper and silicon (with a silicon content of less than 10% by weight) were detected in the processed products.

The emergence of internal cavities (probably filled with gas–liquid inclusions) that cover the surface of the particle was recorded in individual particles of silicon. Obviously, a release of dissolved gases and water vapor during crystallization of the melt took place during their formation.

The presence of a significant amount of SiO_2 in various phase states in the products of plasmochemical processing of polydisperse quartz concentrate with a particle of size less than 100 μm, as well as a slight yield of polycrystalline silicon, indicates, first of all, the low efficiency of evaporation of quartz particles. This is due, firstly, to the relatively low residence time of particles in high-temperature region of the plasma jet of the employed microplasmotron, and, secondly, to the size of the initial particles of the quartz concentrate. Series of experiments on plasmochemical processing of polydisperse quartz concentrates were specially prepared from the original of five groups of quartz concentrates with sizes of 0–20 μm, 20–40 μm, 40–60 μm, 60–80 μm, and 80–100 μm in order to determine the effect of the initial size of the processed quartz particles on the efficiency of silicon production. Figure 4 shows the diagram dependence of silicon "yield" C_{Si} on the size of processed particles d_H. It is experimentally proved that C_{Si} silicon increases approximately by $C_{Si} \sim d_H^{-1.6}$ (curve *2* in Fig. 4) with decreasing d_H "yield," reaching the maximum values (~60%) when using the fraction with particle sizes less than 20 μm. A typical X-ray pattern of products of plasma chemical processing of this fraction is shown in Fig. 5. It clearly shows three strong lines of crystalline silicon. The phases of crystalline (30%) and amorphous (10%) quartz are also present in the products. No other phases have been recorded. Note that the resulting polycrystalline silicon is characterized by high crystallinity of the structure, as evidenced by the width (1–3°) of diffraction peaks of silicon on the X-ray patterns (Fig. 5). The established fact of a significant increase in the efficiency of plasma chemical pro-

cessing of quartz into silicon with a decrease in the size of quartz particles confirms the important role of the evaporation of quartz particles.

CONCLUSIONS

The possibility of a nonequilibrium plasmochemical method for producing polycrystalline silicon in the form of spherelike particles with an average size of 100–200 μm, purity of 99.8–99.9%, with a yield of silicon up to 60% was experimentally proved.

In conclusion, we should note that the proposed use of the plasmochemical method of the direct production of silicon from SiO_2 using hydrogen is more efficient than the method [6] of reduction of silicon from SiO using hydrocarbon as a reducing element, in which the yield of silicon (indirect data) does not exceed 15%.

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SPELL: 1. polycrystalline, 2. plasmochemical, 3. nonequilibrium, 4. thermoinsulated