THEORETICAL ANALYSIS AND MODELING OF THE OBTAINING OF POLYCRYSTALLINE SILICON IN A FLUIDIZED-BED REACTOR

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A theoretical analysis has been performed and basic problems of the technology of obtaining polycrystalline silicon by pyrolytic decomposition of monosilane in a fluidized-bed reactor have been considered. A one-dimensional, two-phase model of this process and basic results of mathematical modeling have been presented.

The problem of development of new low-cost technologies of obtaining polycrystalline silicon for photoelectric transducers is closely related to the prospects for development of solar power engineering. The main factor determining these prospects is the level of scientific and technological advances in the field of silicon technology.

It has historically evolved that silicon raw material for production of solar cells is mainly the waste of the semiconductor industry. Clearly, the possibilities of obtaining such an expensive waste are limited and do not meet the demand for photoelectric transducers.

In the known effort to obtain inexpensive polycrystalline silicon for photoelectric transducers, one either failed to attain the required output, or the purity of the silicon was insufficient for the high efficiency of solar cells, or the price of the silicon obtained was unacceptable for production of photoelectric transducers.

The traditional technology of production of polycrystalline silicon [1] suggests that one initially obtain metallurgical silicon by direct carbon reduction of high-purity silica in arc furnaces at 1800°C. To obtain higher-purity silicon it is chlorinated to $SiCl_3$ or $SiHCl_3$, which are subjected to deep purification by rectification, sorption, or special heat treatment and then are hydrogen-reduced at $1100–1200^{\circ}$C. One deposits the silicon reduced on silicon bars of length up to 150 cm and diameter 5–10 mm, increasing it to 150 mm (Siemens process) (Fig. 1). The production is rather energy-consuming: the total expenditure of energy in obtaining a marketable product attains 250 kW·h/kg.

Although more than 80% of the worldwide production of semiconductor silicon is based on this method, it has a number of substantial drawbacks: the energy consumption and discontinuity of the process, the low yield of silicon (the maximum extraction of silicon possible in theory is about 60%; in actual practice it amounts to 15–30%), the release of hydrogen chloride as a by-product, causing corrosion of the equipment, and the need for hydrogen dilution of the reaction mixture to prevent homogeneous nucleation. Furthermore, one is not necessarily able to achieve a high degree of cleaning of the impurity hydrides.

The use of monosilane as a working gas in a modified Siemens process enables one to reduce the temperature of the process to $800–850^{\circ}$C, to increase the silicon yield to 94–98%, and to ensure additional cleaning of the impurity hydrides. At the same time, serious drawbacks persist; among them are the long duration of the process and thus the high energy consumption and hydrogen dilution of the monosilane fed to the reactor.

Thus, the current processes of obtaining polycrystalline silicon are characterized as energy-consuming, low-efficiency periodic processes, which are determining factors in the high cost of silicon produced by these methods: 50 to 60 U.S. dollars per kg, depending on the demand/supply ratio.

In this connection, of particular interest is the technology of obtaining granular polycrystalline silicon by pyrolytic decomposition of monosilane in a fluidized-bed reactor (Fig. 2). Microgranular particles of the starting silicon (nuclei) of size 100–200 μm are introduced into the reactor; thereafter a mixture of monosilane with hydrogen or inert gas (argon, nitrogen) is fed. A uniform distribution of the gas flow over the cross section is ensured by a gas-distrib-
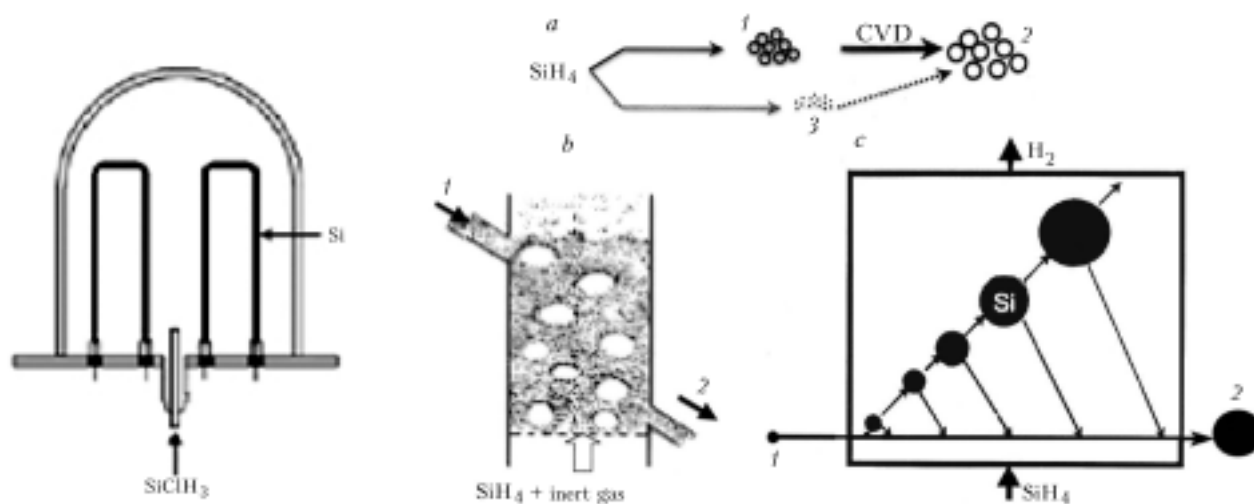
Fig. 1. Reactor for obtaining silicon rods by the technology of the Siemens Company.

Fig. 2. Pyrolysis of monosilane in a fluidized-bed reactor: a) scheme for obtaining polycrystalline silicon [1] microgranular silicon nucleus particles, 2) polycrystalline granulated silicon; 3) fines]; b) diagrammatic representation of the fluidized-bed reactor [1] feeding of microgranular silicon nucleus particles, 2) discharge of polycrystalline granular silicon]; c) growth of silicon particles during the process of pyrolytic decomposition of monosilane in the fluidized-bed reactor [1) starting silicon nucleus particle, 2) polycrystalline granular silicon particle obtained].

uting grid with a free area of 1.2–2.0%. At a temperature of 600°C or higher, the monosilane is decomposed to form silicon, which is deposited on the surface of fluidized silicon particles. Once a certain size is attained, the silicon particles descend to the lower part of the reactor and are discharged from it.

The fluidized bed ensures intense heat exchange between the fluidized particles and the gas flow and between the bed and the heat-exchange surface, with the result that the area of contact of the reagents sharply increases and the temperature and concentration characteristics in the reactor's working zone are equalized.

The above advantages determine the high output of the reactor with a simultaneous considerable reduction in the energy consumption. From the viewpoint of the industrial implementation of the fluidized-bed technology, the comparative simplicity of the equipment and the possibility of organizing a continuous automated technological process are of considerable importance. All this gives grounds to assume that the method discussed is promising for production of inexpensive polycrystalline silicon for solar power engineering.

At the same time, a fluidized-bed reactor has certain drawbacks (eliminated only with the corresponding designs), for example, the removal of nucleus granules and abrasive wear of the equipment are possible. The chemical reaction of pyrolysis of monosilane is characterized not only by the heterogeneous gas-phase deposition of silicon on nucleus granules. A substantial influence on the yield of polycrystalline silicon is exerted by the formation of aerosol particles and the agglomeration of neighboring silicon particles and by the deposition of silicon on the reactor walls.

The role of the gaseous components fed to the reactor is dual: keeping microgranular silicon particles in a fluidized state and pyrolytic decomposition in the reaction zone to isolate a solid phase, i.e., silicon. The hydrodynamics of the fluidized-bed reactor changes with increase in the size of the starting nucleus granules, which can necessitate automatic control of the velocity of the gas-flow fed.

Despite the prospects of the method in question and the presence of a certain theoretical and experimental base in this field, the largest worldwide producers of silicon have not yet achieved serious success in industrial implementation of the method. Therefore, the development of methods of theoretical description of the process of obtaining granular polycrystalline silicon in a fluidized-bed reactor is necessary for both a deeper understanding of it, optimiza-

tion of the operating parameters, and elimination of undesirable effects and passage from laboratory experiments to a pilot-scale commercial production. Of certain practical interest is the possibility of implementing a fundamentally new technology of production of polycrystalline silicon; the technology has been proposed in Belarus and is based on the use, as a raw material, of the secondary fluoride-containing product of processing of an apatite concentrate into phosphoric fertilizers [2]. The technological scheme is assumed to obtain sodium fluorosilicate from the fluorosilicic acid. In the first step, a gaseous tetrafluorosilicate is released as a result of the thermal decomposition of sodium fluorosilicate. In the second step, we have chemical conversion of the latter to monosilane; in the third step, we have pyrolytic decomposition of monosilane to form silicon and hydrogen.

Based on an analysis of the literature data [3–9] on the kinetic regularities of pyrolytic decomposition of monosilane and the theoretical models describing the process in a fluidized-bed reactor, we have singled out the main stages constituting the mechanism of this process.

Unlike the chemical decomposition of silicon from monosilane on large billets, where the productivity of the process is limited by the small surface area of a billet and by the diffusion transport of monosilane to it, fluidized particles have a developed surface in the fluidized bed and, when the temperature of the bed is fairly high and its height is sufficient, the productivity of the process is determined by the flow rate of the gas phase. Granular silicon is formed very intensely in the fluidized-bed reactor; its amount is doubled over a period of 3–4 h.

The fluidized bed, possessing a high specific surface, significantly reduces the role of the gas-phase decomposition of monosilane and of the subsequent formation of aerosol particles. It turned out that, when the selected temperature of the fluidized bed and flow rate of the gas mixture are optimum, the fraction of the silicon (fed to the reactor) that is accounted for by the formation of such particles is no higher than 10% with initial concentrations of monosilane of up to 80 vol.%.

The optimum fluidized-bed temperature at which the high rate of deposition of silicon combines with the fairly low fraction of the aerosols formed is 600–650°C. Higher temperatures of the fluidized bed do not increase the productivity of the process. The optimum velocities of the gas mixture lie within $(3–8)U_{\mathrm{mf}}$.

The problem of agglomeration of silicon particles and clogging of the gas-distributing device has been revealed. To eliminate these undesirable effects it was proposed that the temperature of the gas-distributing device be maintained at a level no higher than 350–400°C by water cooling of the reactor's lower part.

The capacity of the fluidized-bed reactor for operating with a 100% concentration of monosilane without formation of a considerable amount of aerosols has been established experimentally, which makes it possible to raise productivity.

To model the operation of a fluidized-bed reactor we used a tested and economical method of calculation of processes occurring in pyrolytic decomposition of monosilane; it is based on a one-dimensional phenomenological two-phase model. This is a model of a fluidized bed with emulsion and bubble phases, whose difference from the standard two-phase models lies in allowing for the nonisothermality of the bubble phase and the change in the flow rate of the gas mixture over the reactor's height. The model includes equations that reflect changes in the average volume of bubbles, the fraction of the volume occupied by them, and their velocity and temperature, and also the mass flows of the chemical components in both phases. The emulsion phase is considered to be stationary, and the rate of filtration of the gas through it is always equal to the minimum-fluidization rate U_{mf}. The temperature of the emulsion phase and the void volume fraction in it are taken to be constant. The change in the average volume of the bubbles with their rise is represented as a result of the superposition of several processes: (1) growth in the average size of the bubbles in an isothermal fluidized bed with a constant flow rate of the gas as a result of their coalescence; (2) expansion of a bubble due to the heating of the bubble phase; (3) change in the bubble volume as a result of the mass exchange with the emulsion phase.

We have considered a scheme of step-by-step buildup of the diameter of silicon particles in a fluidized-bed reactor of diameter 150 mm (production prototype). The initial height of the fluidized bed was 600 mm in each step, and the step was completed once a bed height of 1200 mm had been attained. After the completion of each step, the silicon particles grown were distributed in two reactors of the same type and the next step was realized. It was assumed that the void volume fraction of the emulsion phase and the volume fraction of the bubble phase change only slightly; therefore, the height of the fluidized bed is in proportion to the cubed size of the silicon particles. Thus, if we consider the process consisting of six successive steps, the final diameter of the silicon particles must be equal to

TABLE 1. Initial and Final Size of Silicon Granules for Different Steps of the Process of Deposition

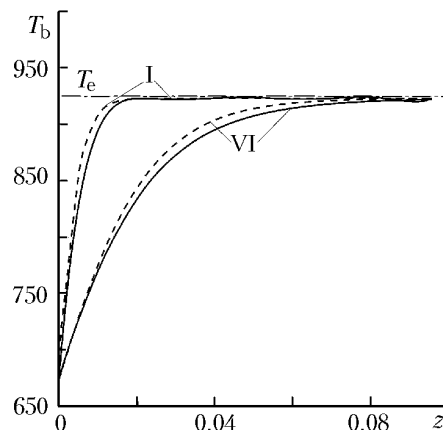| Step No.	I	II	III	IV	V	VI
Initial diameter, $d_{p,i}$, mm	0.125	0.157	0.198	0.250	0.315	0.397
Final diameter, $d_{p,fin}$, mm	0.157	0.198	0.250	0.315	0.397	0.500

Fig. 3. Temperature profiles in the bubble phase in the Ist and VIth steps of the process: dashed curves, beginning of the step, solid curves, end of the step. T_e = 923 K and G_{SiH_4} = 46.5 N liters/min.

four initial diameters. It is precisely such a six-step process of deposition of silicon that has been demonstrated in the present work with the order of the initial and final particle diameters indicated in Table 1.

The system of ordinary differential and algebraic equations was solved using a computer code based on the Runge–Kutta method. As a result of the solution we found the changes in the following distributions over the reactor's height with time: the temperature of the bubble phase, the concentrations of the chemical components in the bubble and emulsion phases, and the type of bubbles and their volume fraction. Also, we computed the changes in the average silicon-particle size and the fluidized-bed height with time. Furthermore, we determined the running and integral degrees of conversion of monosilane to granular silicon.

The modeling was carried out in the range of reactor temperatures 600–675°C. The temperature of the gas at entry into the fluidized bed was assumed to be 400°C. The composition of the starting monosilane–hydrogen mixture was taken to be the same in all the calculations: SiH_4 — 80% and H_2 — 20%. We considered versions with two flow rates of the gas mixture: 46.5 and 66.4 N (normal) liters/min, which corresponds to 3.5 and 5.0 kg/h respectively in terms of pure silicon.

Evaluations of the characteristics of interphase heat exchange and numerical calculation of the process show that equalization of the temperatures between the bubble and emulsion phases occurs at a small distance from the site of entry of the gas mixture into the reactor (Fig. 3). Thus, in the Ist step of the process, the phase temperatures coincide, in practice, even at a distance of 2–3 cm from the reactor's base, whereas in the final (VIth) step, the temperatures are equalized at a distance of 6–8 cm. Thus, the fluidized bed is a well-thermostatted system, which makes it possible to finely control the temperature of the process.

The distributions of the relative concentrations of monosilane and hydrogen over the bed's height in both phases of the step are presented in Fig. 4. As follows from the evaluations of the kinetic parameters, the rate of the reaction of decomposition of monosilane in the bubble phase turns out to be much slower than the rate of its pyrolysis on the particles of the emulsion phase. Thus, the bubble phase is a reservoir of monosilane, whereas the emulsion phase is a zone of its decomposition and production of the target product.

At a lower reactor temperature (T_e = 873 K) (see Fig. 4), monosilane has no time to be expended in the reactor completely; therefore, the degree of its conversion turns out to be lower than unity. It significantly decreases with increase in the particle size and becomes equal to approximately 0.7 for the final step of the process. At the same time, monosilane is consumed completely, in practice, in the reactor having a high temperature (T_e = 923 K).
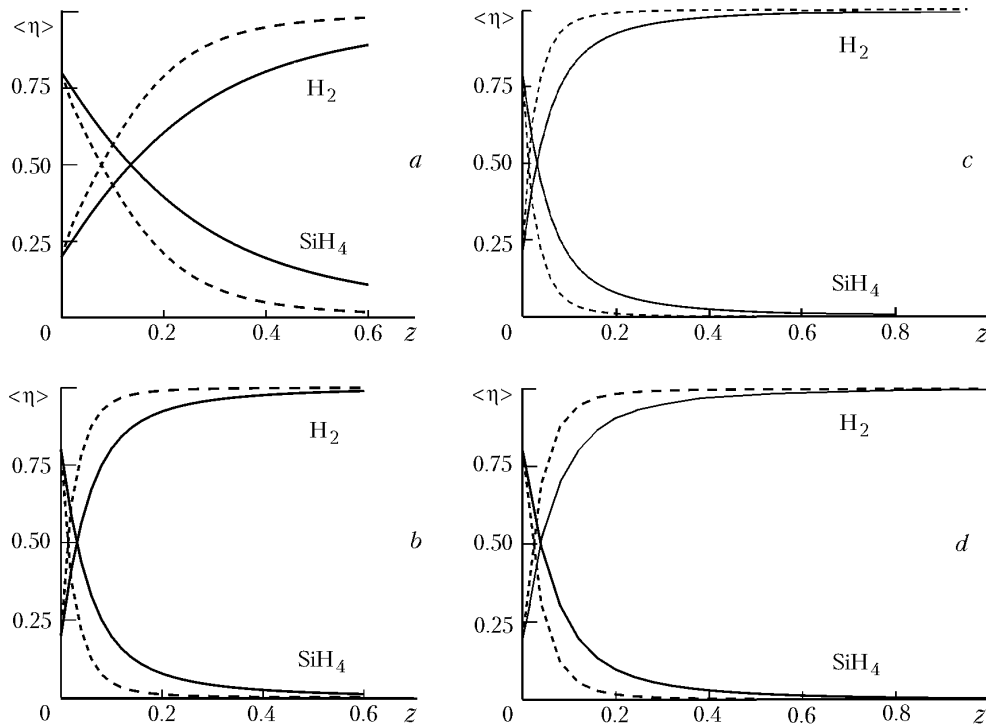
Fig. 4. Concentration distribution of monosilane and hydrogen over the bed's height at reactor temperatures of 873 K (a and c) and 923 K (b and d), solid curves, bubble phase, dashed curves, emulsion phase; a and b, beginning of the IIIrd step, c and d, end of the IIIrd step.
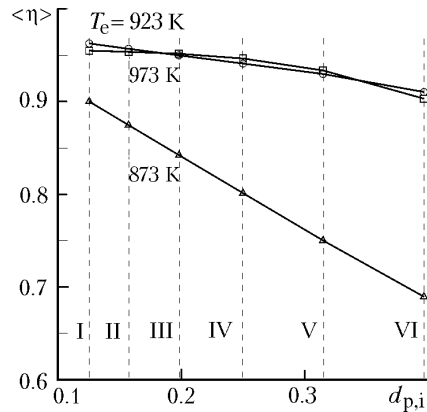

Fig. 5. Average degree of conversion vs. initial diameter of silicon particles; Latin figures correspond to Nos. of steps of the process.

The change in the average degree of conversion of monosilane at different instants of the process is illustrated in Fig. 5, in which the values of the average degree of conversion of monosilane at different instants of the six-step process of obtaining silicon granules are shown.

The characteristics of the process of deposition of silicon from an SiH_4–H_2 mixture with a silicon flow rate of 3.5 kg/h in the reactor with a fluidized bed of initial height $H = 0.60$ m at two temperatures are given in Table 2. It is seen that the durations of the steps increase at a low temperature of the reactor, when the degree of conversion of monosilane is low. Also, it is noteworthy that for the final (VIth) step the velocity of the gas mixture entering the reactor turns out to be only 2.8–3.0 times higher than the minimum fluidization rate. Thus, further increase in the particle size turns out to be impossible, in practice, for the selected parameters of the process. At the same time, the limit

TABLE 2. Calculated Characteristics of the Process of Deposition of Silicon at 873 K and 923 K (for $X_{SiH_4} = 0.8$ and $G_{SiH_4} = 46.5$)

$d_{p,i}$	$\langle\eta\rangle$	U_{mf}	U/U_{mf}	U_{max}/U_{mf}	t	$d_{p,fin}$
			T_e = 873 K			
0.125	0.901	0.63	27.8	193	4.47	0.157
0.157	0.876	1.00	17.6	154	4.58	0.198
0.198	0.844	1.58	11.1	122	4.78	0.250
0.250	0.804	2.53	7.0	97	5.0	0.315
0.315	0.755	4.00	4.4	77	5.33	0.397
0.397	0.698	6.35	2.8	61	5.78	0.500
			T_e = 923 K			
0.125	0.965	0.61	30.6	200	4.17	0.157
0.157	0.961	0.96	19.4	161	4.19	0.198
0.198	0.957	1.52	12.2	128	4.19	0.250
0.250	0.953	2.43	7.7	101	4.22	0.315
0.315	0.949	3.85	4.8	80	4.25	0.397
0.397	0.946	6.10	3.0	64	4.25	0.500

of the maximum permissible velocity of the gas mixture due to the removal of particles from the reactor is attained in none of the steps of the process.

Experiments on the laboratory setup with a fluidized-bed reactor have shown a satisfactory correlation with the predictions of the theoretical model [10].

NOTATION

d, diameter, mm; G, flow rate, liters/min; H, height of the fluidized bed, m; T, temperature, K; t, time, h; U, rate, m/sec; X, concentration; z, vertical coordinate, m; $\langle\eta\rangle$, degree of conversion. Subscripts: b, bubble phase; e, emulsion phase; max, maximum value; mf, minimum fluidization; p, particle; i, at the beginning of a step; fin, at the end of a step.

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