

EVALUATION OF THE THERMOPHYSICAL CHARACTERISTICS OF A BUBBLING-TYPE REACTOR ON TRANSFORMATION OF SILICON TETRAFLUORIDE INTO MONOSILANE

N. V. Stepanenko,^a V. P. Vasilevich,^a and V. A. Nemtsev^b

UDC 532.529

The thermophysical aspects of silicon tetrafluoride transformation into monosilane are analyzed. An approximate mathematical model and calculation results are provided. The contribution of heat of the chemical reaction is evaluated.

The Republic of Belarus, having a developed branch of modern industry, microelectronics, urgently needs semiconductor silicon. At present, the most promising and most economical way of obtaining it is extraction of wastes of the industry producing phosphoric fertilizers from apatites. In our opinion, the greatest possibility of incorporation of such a nontraditional technology exists in the Republic of Belarus [1–3], the Russian Federation, and the Republic of Egypt, where the production of fertilizers from apatites and the microelectronic industry are being developed simultaneously.

Recently, some countries, e.g., Japan [4–7], Germany [8, 9], and the USA [10–12], have shown interest in the problem of obtaining monosilane (SiH₄) and semiconductor silicon from silicofluoric acid (SFA) and sodium silicofluoride (SSF).

In the technology of obtaining semiconductor silicon by successive chemical transformations of a secondary product of apatite processing — SFA (H₂SiF₆) and its salt SSF (Na₂SiF₆) — the process of monosilane production from silicon tetrafluoride (SiF₄) [1–3, 13–15] implemented in a bubbling-type reactor [16] is the most important and least studied one. As a component entering into the reaction with silicon tetrafluoride (STF), calcium hydride (CaH₂) [4–14] was used. Here CaH₂ is in a solution of the eutectic melt of lithium and calcium chlorides at a temperature of 635–670 K. A gaseous flow of STF is bubbled through the melt volume, and at the interface of the gas and liquid phases the following irreversible exothermal reaction proceeds:



where Q_{ch} is the thermal effect of the chemical reaction.

Use of the bubbling effect makes it possible to substantially intensify the physical and chemical processes owing to the direct contact of gas and liquid and to increase the interphase surface and organized circulatory motion of the phases, enhancing the interphase heat and mass transfer.

The aim of the present work is a thermophysical investigation of specific features in the behavior of the presented bubbling system intended for transformation of STF into monosilane and the influence of the chemical reaction on the thermal and physicochemical characteristics.

For definiteness of arguments, we have taken a model of the laboratory setup as a basis [16]. The thermal balance of this bubbling apparatus in general form is

$$Q_{\Sigma} = Q_{\text{h}} + Q_{\text{loss}} + Q_{\text{ch}}, \quad (2)$$

where Q_{Σ} is the sum of heat fluxes, Q_{h} is the heat flux from the outer heater to the reactor, Q_{ch} is the thermal effect of the chemical reaction, and Q_{loss} is the heat loss.

^aBelarusian State University of Informatics and Radioelectronics, Minsk; ^bInstitute of Energetics Problems, National Academy of Sciences of Belarus; email: irma@infonet.by. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 75, No. 6, pp. 58–60, November–December, 2002. Original article submitted June 20, 2002.

TABLE 1. Heat Balance of the Reactor

Q, W	SiF ₄ flow rate, liter/h		
	1.52*	10	15
Q_h	72	197	300
Q_{loss}	-80	-80	-80
Q_{ch}	8	53	80
Q_{Σ}	0	170	300

*Corresponds to a SiH₄ output of 500 g per 24 h.

Depending on the value of the gas flow rate in a bubbling (or dynamical) two-phase layer, different patterns of motion of the two-phase flow can be observed, namely, isolated bubbles, conglomerates of bubbles, and foam. For simplicity of analysis, we have chosen the first pattern.

Based on the previously developed mathematical models of dynamics of vapor-gas bubbles in the volume of a chemically reacting solution [17], we have suggested an approximate calculation scheme. In formulating a simplified mathematical model of the dynamics of a gas in a melt, the following assumptions have been made: the liquid is incompressible, the gas obeys the law of a perfect gas, the distribution of the thermophysical parameters in a bubble is uniform, the chemical reaction of SiF₄ transformation into SiH₄ is quasiequilibrium, and the solubility of the components is not taken into consideration. Since the shape of a bubble is nonspherical in the general case, we considered a spherical bubble with effective radius R and volume $V = 4/3\pi R^3$ [18].

Since calculation of the heat and mass transfer of a rising bubble with a surrounding liquid is complicated, in the calculations of Nusselt (Nu) and Sherwood (Sh) numbers instead of a system of differential equations for a liquid we used the following dimensionless relations [19]:

$$Nu = 2 + 0.16 Re^{0.55} Pr^{0.33}, \quad (3)$$

$$Sh = 2 + 0.46 Re^{0.55} Sc^{0.33}, \quad (4)$$

which satisfactorily approximate experimental data for the coefficients of heat transfer and mass transfer from the external surface of bubbles in flow for large Reynolds (Re) numbers $1 < Re < 105$ and in a wide range of Prandtl (Pr) and Schmidt (Sc) numbers.

To determine the speed (W) of rise of individual gas bubbles, use was made of the most generalizing dependences in a wide range of thermodynamic parameters and operating conditions at $\rho''/\rho' \ll 1$ [20]:

$$\begin{aligned} W &= 2R^2g/(9v') && \text{at } Re \leq 2; \\ W &= 0.33R^{1.28}g^{0.76}/(v'^{0.52}) && \text{at } 2 < Re \leq 4.02G^{-0.214}; \\ W &= 1.35(\sigma/(\rho'R))^{0.5} && \text{at } 4.02G^{-0.214} < Re < 2.35G^{-0.25}; \\ W &= 1.18(g\sigma/\rho')^{0.25} && \text{at } 2.35G^{-0.25} < Re < 3.3G^{-0.25}; \\ W &= (gR)^{0.5} && \text{at } Re > 3.3G^{-0.25}, \end{aligned} \quad (5)$$

where $G = gv'^4\rho'^3/\sigma$ and $v' = \mu'/\rho'$.

Using the developed approximate mathematical model, we carried out thermophysical calculations of a bubbling-type reactor. The range of change in the flow rate of the gaseous STF entering into the reactor was more than an order of magnitude. In the calculations made, the possible influence of the heat of chemical reactions of transformation (1) on the temperature of the liquid melt of the bubbling layer was noted, which has been confirmed experimentally. Moreover, the calculations have shown that at the expense of the physical and chemical transformations occurring in the bubbling layer the size of the gas bubbles increases (up to 300%).

The share of the contribution of heat of the chemical reaction was determined based on the following reasoning. A bubble bubbling in the eutectic melt consists of a mixture of gases of the STF and monosilane, whose quantitative ratio changes from the moment of bubble separation from the bubbling device to its escape from the melt: in the ideal case, the amount of STF changes from 100% to 0 while that of monosilane changes from 0 to 100%. In evaluative calculations, one can assume the heat capacity of a gas bubble to be averaged for the composition and range of inlet and outlet temperatures of gases. Thus, for the considered gas mixture in the temperature range 0–400°C the heat capacity was evaluated as $C_p \approx 12.6 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$. Here, the amount of heat required for heating the gas mixture from 0 to 400°C is 69.5 kJ/liter.

As is known from [15], the amount of heat of the chemical reaction released on transformation of 1 liter of STF into monosilane is 18 kJ/liter. The calculations show that without allowance for heat losses, the heat consumed for the initial heating of the reactor structure, for melting of eutectics with a prescribed rate, and for heating of the inert gas supplied to the reactor for the purposes of both the scavenging and mixing of the reacting gas mixture, the contribution of heat of the chemical reaction to the total heat balance can attain up to 26%. Naturally, each structure of the reactor will have its own components of the total consumed heat; they are determined in the design developments of the chosen type of reactor.

To illustrate the main components of heat balance (2), in the present work we have considered the first laboratory reactor used in a set-up of the Izmeritel Novopolotsk plant. Data of the calculations are provided in Table 1.

Analysis of operation of the reactor intended for monosilane production from STF has shown its quite satisfactory efficiency. At the same time, it should be noted that this reactor is still very far from having optimum parameters and design solutions.

Because of the imperfect system of heat supply and poor heat insulation, one observes, for instance, very great heat losses into the environment (at small flow rates of a supplied gas the relative heat losses attain 200–300%). The intensity of heat and mass transfer in the bubbling layer substantially depends on the diameters of the bubbles and the frequency of their separation, and these characteristics depend, in turn, on the diameters of the holes and the form of distributing collectors, the thermohydraulic parameters, and the physical properties of the system. The height of the bubbling layer is a value optimized with respect to many operation and design parameters.

In the calculations carried out, all properties were constant and, moreover, the thermophysical properties of the melt were determined as the additive values of the relative constituent components.

The main aim of the next state of the present investigation must be, in our opinion, the development of experimentally substantiated mathematical models and program complexes on the basis of the equations of conservation of the continuum mechanics and their study based on the mechanism of the physical and chemical processes of bubbling of chemical reaction gases through a melt as well as the determination of optimum operation parameters for intensification of heat and mass transfer and maximum obtaining of monosilane.

NOTATION

g , free-fall acceleration; ν and μ , coefficients of the kinematic and dynamic viscosity; ρ , mass density; σ , surface tension. Superscripts and subscripts: ' and ", liquid and gas, respectively; ch, chemical; h, heater; loss, losses.

REFERENCES

1. I. M. Lyashkevich, V. I. Khit'ko, N. F. Maksimenko, et al., *Tekhnika, Ékonomika, Organizatsiya*, No. 2, 42–43 (1996).
2. V. P. Vasilevich, A. V. Vasyukov, D. A. Kotov, N. V. Stepanenko, and V. N. Stepanenko, in: *Proc. Int. Sci.-Eng. Seminar "Modern Problems of Design and Manufacture of Radioelectronic Facilities"* [in Russian], Novopolotsk (2000), pp. 42–45.
3. V. N. Stepanenko, V. P. Vasilevich, O. G. Polyachenok, G. P. Dudchik, N. V. Varankova, and A. V. Vasyukov, in: *Proc. Int. Sci.-Eng. Conf. "Resource- and Energy-Saving Technologies in the Chemical Industry and Manufacture of Structural Materials"* [in Russian], Minsk (2000), pp. 46–48.
4. *Japan Patent Application* No. 57-11815 as of 24.06.80, MKI C 01 B 33/02.

5. *Japan Patent Application* No. 55-84649 as of 21.01.82, MKI C 01 B 33/02.
6. *Japan Patent Application* No. 63-74910, MKI C 01 B 33/10.
7. *Japan Patent Application* No. 61-28604 (1986), MKI C 01 B 33/10.
8. *FRG Patent Application* No. 3228177 as of 28.07.82 MKI C 01 B 33/02.
9. *FRG Patent Application* No. R3228177.3 as of 09.02.84, MKI C 01 B 33/2.
10. *US Patent* No. 4529576 as of 27.12.82, MKI C 01 B 33/2.
11. *US Patent* No. 4446120, MKI C 01 B 33/2.
12. MEMC Pasadena, Inc. *Internet for info*, contact MEMC at polysilicon@memc.com 11/16/200. Copyright@2000 MEMC Electronic Materials, Inc. All rights reserved.
13. E. P. Belov, E. N. Lebedev, and Yu. P. Grigorash, *Monosilane in Technology of Semiconductors* [in Russian], Moscow (1989).
14. *RF Patent* No. 2077483 as of 23.06.1997, MKI C 01 B 33/04.
15. O. G. Polyachenok, V. N. Stepanenko, V. P. Vasilevich, et al., *Vestsi Nats. Akad. Navuk Belarusi, Ser. Khim.*, No. 2, 101–105 (2001).
16. V. A. Nemtsev, N. V. Stepanenko, V. P. Vasilevich, and V. N. Stepanenko, in: *Proc. II Int. Sci.-Eng. Conf. "Problems of Design and Manufacture of Radioelectronic Facilities"* [in Russian], Vol. 1, Novopolotsk, 15–17 May 2002, Novopolotsk (2002), pp. 67–74.
17. V. A. Nemtsev and A. M. Cherkasin, *Mathematical Model of the Dynamics of a Vapor Bubble in the Bulk of a Chemically Reacting Solution* [in Russian], Preprint No. 38 of the Institute of Power Engineering Problems of the National Academy of Sciences of Belarus, Minsk (1998).
18. S. S. Kutateladze and V. E. Nakoryakov, *Heat and Mass Transfer and Waves in Gas-Liquid Systems* [in Russian], Novosibirsk (1984).
19. S. Soe, *Hydrodynamics of Multiphase Systems* [Russian translation], Moscow (1971).
20. F. N. Peebles and H. I. Garbel, *Chem. Eng. Progr.*, **49**, No. 1, 88–97 (1953).