APPLICATION OF RF (40.68 MHZ) ARC DISCHARGE FOR PLASMA CHEMICAL CONVERSION OF VOLATILE CHLORIDES OF SILICON AND GERMANIUM

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Abstract. The processes of hydrogen reduction of silicon and germanium chlorides are studied under RF conditions (40.68 MHz) of contracted atmospheric pressure arc discharge stabilized between two rod electrodes. The main gas-phase and solid products of plasma-chemical transformations are determined. Using the hydrogen reduction of $SiCl_4$ as an example, the numerical simulation of gas-dynamic and heat exchange processes for this type of discharge was performed. The studies were carried out for the optimal conditions for obtaining trichlorosilane using modern computational technologies of fluid dynamics which made it possible to detail the velocity and temperature fields, the gas flow rates in the plasma region, and also determine the main temperature zones affecting the hydrogen reduction process.

Keywords: RF arc discharge, reduction of volatile chlorides, simulation of gas-dynamic.

1. Introduction

Silicon and germanium remain the most popular material for microelectronics, photovoltaics and optics. The technologies of their industrial production, based on the synthesis and purification of their chlorides, require constant improvement in connection with the increased requirements for the environmental safety of production. Thus, for silicon tetrachloride, there is a need to process it into chlorosilanes - the initial products of the synthesis of silicon. The production of germanium from its tetrachloride is characterized by multistage which leads to an additional flow of impurities into the target product. In this regard, the study of the applicability of plasma-chemical technologies for the direct synthesis of silicon and germanium from $SiCl_4$ and $GeCl_4$ is an actual task. In the development of plasma methods, much attention is paid to the diagnosis of reactive plasma, which allows determining the gas temperature, classifying intermediate particles and establishing the mechanism of chemical reactions [1]. In some cases, when the plasma zone is small or unavailable for physical diagnostic methods, information about the temperature and the basic mechanisms of chemical reactions can be obtained by examining the gas-dynamic and heat exchange features of the process [2, 3]. One of the ways to study gas-dynamic and heat exchange processes is their numerical simulation [4–6]. The purpose of this work was to study the influence of the main technological parameters of the process of hydrogen reduction of $SiCl_4$ and $GeCl_4$, such as pressure and the ratio of reagents on the degree of conversion, as well as an estimate of the gas temperature in the gas discharge zone using computational fluid dynamics.

2. Experimental

Experiments on the investigation of the reduction processes of silicon and germanium tetrachlorides in hydrogen plasma were carried out on installation which schematic diagram was described in detail in [7, 8]. The power of high-frequency oscillator was 340 W, the frequency was 40.68 MHz. The flow of plasma-forming gas $H_2+SiCl_4(GeCl_4)$ was varied in the range of 100–700 cm^3/min. The pressure during the experiment was kept constant at 760 Torr. The molar ratio $H_2/SiCl_4(GeCl_4)$ was changed in the range of 2–15. The plasma-chemical reactor was a tube of silica glass, along the axis of which the electrodes were placed. A high-frequency voltage was applied to the electrodes from the generator through a matching device and the discharge was ignited between the electrodes. A vapor-gas mixture of silicon tetrachloride and hydrogen was supplied to the discharge volume. The power supplied to the plasma discharge zone was determined by the calorimetric method according to the method [9]. The dependence of the yield of chlorosilanes and chlorogermans as well as silicon and germanium on the conditions of plasma-chemical reduction was experimentally investigated. The yield of silicon and germanium was determined by the gravimetric method with an accuracy of $1 \cdot 10^{-4}$ g. The content of chlorosilanes and chlorogermanes was determined by gas chromatography with the detection limit of 0.1% and IR spectroscopy with a resolution of 0.1 cm^{-1}.
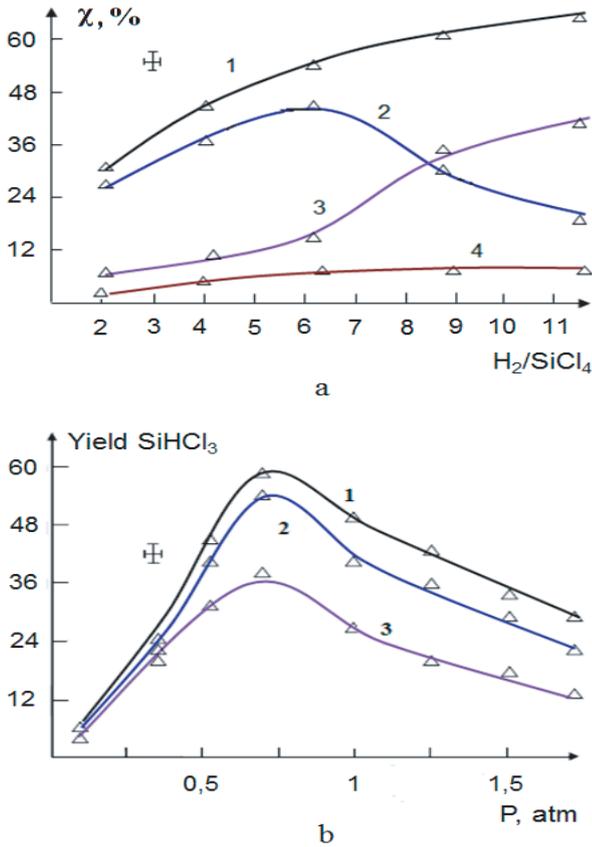
Figure 1. a is the dependence of the total degree of conversion of $SiCl_4$ (1), the percentage of yield of $SiHCl_3$ (2), Si (3) and SiH_2Cl_2 (4) on $H_2/SiCl_4$ ratio; b is the dependence of the yield of $SiHCl_3$ on the pressure in reactor, $H_2/SiCl_4 = 6$ - (1), 4 - (2), 9 - (3).

3. Mathematical Model

The mathematical model was built in homogeneous formulation of the problem and included five different media: H_2, $SiCl_4$, air - liquids and solids - silicon and silica. The thermophysical and transport characteristics of these media are taken from [10, 11]. The reactor was a silica tube with a diameter 60 mm where nozzles-electrodes were coaxially arranged to meet each other. The diameter and length of the nozzle 10 mm and 50 mm, the length of the end portion of the nozzle is 15 mm. The diameter and length of the electrode 6 mm and 70 mm, the distance to which the electrode leaves the nozzle is 10 mm. The distance between the electrodes is 7 mm, the diameter of the outlet of the reactor is 10 mm. The problem of heat transfer in the hydrodynamic flow of a mixture of ideal gases is considered in the mathematical formulation. The mode of flow of gases is turbulent. The mixture interacting in the flow is considered taking into account heat transfer by means of convection and heat conduction and is described by the following system of partial differential equations:

$$\frac{\partial \rho_i}{\partial t} + \mathrm{div}(\rho_i \vec{V}_i) = 0, \qquad (1)$$

$$\frac{\partial(\rho_i \vec{V}_i)}{\partial t} + \nabla(\rho_i \vec{V}_i \otimes \vec{V}_i) = -\nabla p + \nabla \tau_i, \qquad (2)$$

$$\frac{\partial(\rho_i c_{pi} T)}{\partial t} + \mathrm{div}(\rho_i c_{pi} T \vec{V}_i) =$$
$$= \mathrm{div}(\lambda_{ie} \nabla T) + \mathrm{div}(\vec{V}_i \tau_i) + \frac{\partial p}{\partial t} + S_E, \qquad (3)$$

where index $i = 1$ refers to H_2, $i = 2$ - to $SiCl_4$, $i = 3$ - to air, $i = 4$ - to silica, p is the absolute pressure, T is the absolute temperature, ρ_i is the density of corresponding environment, ρ_1, ρ_2 are calculated from the equation of ideal gas, ρ_3, ρ_4 are constants, $\vec{V}_i$ is the velocity vector of corresponding environment, S_E is the power induced by discharge, τ_i is the stress tensor connected with the rates of deformation generalized by Newton′s hypothesis $\tau_i = \mu_{ie}(\mathrm{div}(\vec{V}_i) + \mathrm{div}(\vec{V}_i))^{\mathrm{T}} - \frac{2}{3}\delta \mathrm{div}(\vec{V}_i))$, μ_{ie}, λ_{ie} are effective viscosity and thermal conductivity of environment, correspondingly, $\mu_{ie} = \mu_i + \mu_{it}$, $\lambda_{ie} = \lambda_i + \lambda_{it}$, μ_i, λ_i are the laminar viscosity and thermal conductivity, μ_{it}, λ_{it} are turbulent (vortex) viscosity and thermal conductivity which are interconnected through the turbulent Prandtl number and determined by the chosen model of turbulence [12]. The plasma region was a ball with a radius of $R/2 \approx 7\,\mathrm{mm}$ in contact with the electrodes. The temperature of the electrode in the places of their contact with the plasma is set at $\approx 1760\,\mathrm{K}$. To simulate the plasma, an energy source is created in the reactor. The region of energy release is a cylinder at the base of which a circle with a radius of $P = 1.375\,\mathrm{mm}$ and a height $H = 2.5\,\mathrm{mm}$. The density of energy release is given by the formula

$$q = 10^9(1 - 8 \cdot 10^5(h + H)^2)\pi P^2), \qquad (4)$$

where h is the cylinder height.

The density of energy release is set thus so that the total value in the field of energy release corresponds to 15 W. For silica walls of the reactor, only the energy equation is solved which reduces to the heat conduction equation for solid walls. Note that the gases in the problem are considered to be the compressible liquids. The system of equations (1)-(3) is closed by the transport SST model of Menter turbulence [13]. This model is a combination of the $k-\omega$ model (a more accurate description of flows near the walls) and the $k-\varepsilon$ model (simulation of currents far from solid boundaries).

4. Discussion of the results

The dependence of the degree of conversion of $SiCl_4$ to chlorosilanes and silicon on the ratio of reagents in the initial mixture is shown in Figure 1a. The maximum yield of $SiHCl_3$ (44%) is observed when the ratio $[H_2]:[SiCl_4]=6.9$. With further increase in the concentration of hydrogen, the yield of trichlorosilane decreases. The yield of Si with increasing hydrogen concentration monotonously increases from 8 to 47%, and SiH_2Cl_2 from 3 to 8%. It should be noted that the results on the yield of trichlorosilane (Fig. 1a)
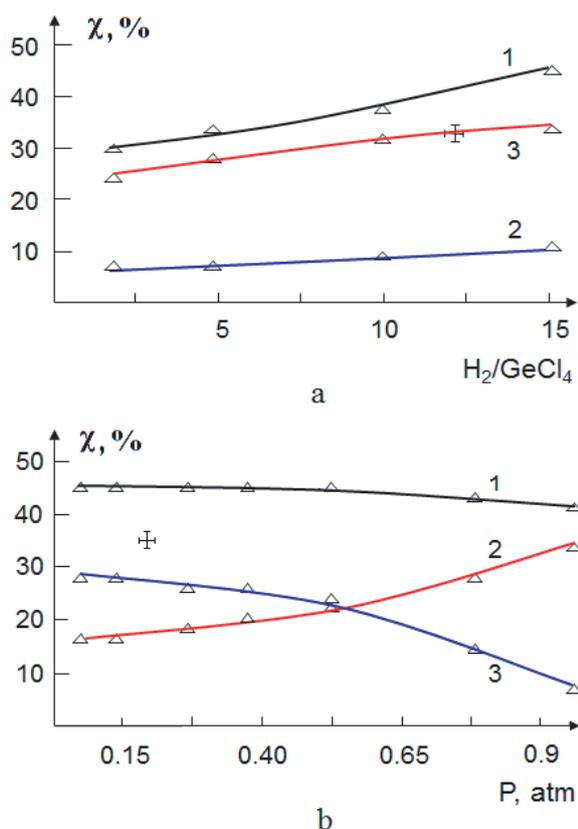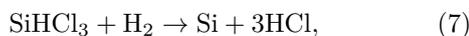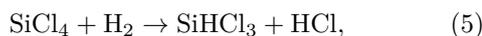
Figure 2. a is the dependence of the total degree of conversion of GeCl$_4$ (1) and percentage yield of Ge (2) and GeHCl$_3$ (3) on H$_2$/GeCl$_4$ ratio; b is the dependence of the total degree of conversion of GeCl$_4$ (1) and the percentage yield of GeHCl$_3$ (2) and Ge (3) on the pressure in reactor.

Figure 3. View of electrodes after hydrogenation processes reduction of a - GeCl$_4$, b - SiCl$_4$

are in good agreement with the data of [14]. The main, in the realized experimental conditions, are the reactions:

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl, \qquad (5)$$

$$2SiHCl_3 \rightarrow SiCl_4 + SiH_2Cl_2, \qquad (6)$$

$$SiHCl_3 + H_2 \rightarrow Si + 3HCl, \qquad (7)$$

With an increase in pressure above 1 atm., a greater discharge contraction is observed and, at constant power, the discharge ignition stops at a pressure of 1.75 atm. Depending on the pressure (Fig. 1b), an extreme view of the dependence of the yield of trichlorosilane is observed with the maximum at pressure of 0.75 atm. With an increase in pressure above 1 atm., a greater discharge contraction is observed and, at constant power, the discharge stops at a pressure of 1.75 atm. For the process of hydrogen reduction GeCl$_4$, depending on the increase in the ratio of reagents (Fig. 2a) in the initial mixture, the degree of conversion also increases. The main products GeHCl$_3$ and Ge are formed by the reactions:
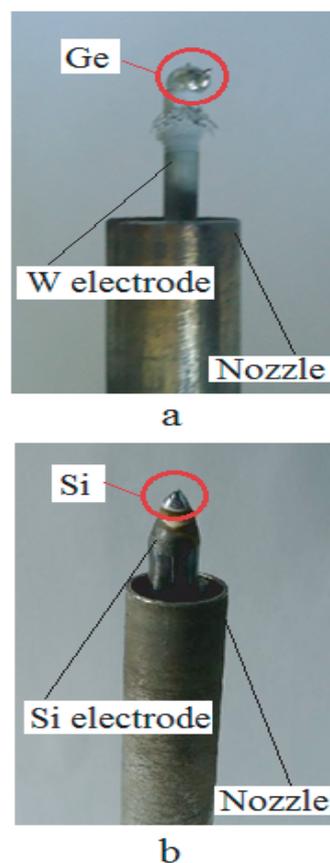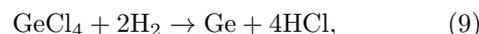
$$GeCl_4 + H_2 \rightarrow GeHCl_3 + HCl, \qquad (8)$$

$$GeCl_4 + 2H_2 \rightarrow Ge + 4HCl, \qquad (9)$$

The dependence of GeCl$_4$ conversion on pressure (Fig. 2b) is not expressed by the maxima. A decrease in GeCl$_4$ conversion and Ge yield is observed while the yield of GeHCl$_3$ increases. The deposition of Si and Ge on the electrodes is shown in Fig. 3. It is seen that in both cases the formation of ingot-like, compacted are formed at the ends of the electrodes. Fig. 4 a shows a view of the gas discharge at atmospheric pressure. In the physical experiment, the plasma formation zone is a ball with a radius of ~ 7 mm, slightly offset to the upper surface of the reaction chamber due to the fact that the output of the reacted gas mixture is located on top. This zone, according to the simulation (Fig. 4b), is in the temperature range 900–1700 K. The temperature value of 1700 K corresponds to the area of contact of the electrode with the plasma. It is in this area, as well as in the area surrounding it, during the experiment the deposition of silicon and germanium is observed. Simultaneously with the deposition, the material melts, resulting in a compacted, ingot-like sample (Fig. 3). 900–1700 K high-temperature zone is also a source of atomic hydrogen which contributes to the reduction of SiCl$_4$ and GeCl$_4$. Fig. 4c, d show an isothermal surface with $T = 900$ K corresponding to the plasma region and the streamline of the gas mixture through this surface, respectively. According to the conducted numerical experiments, 95% of the
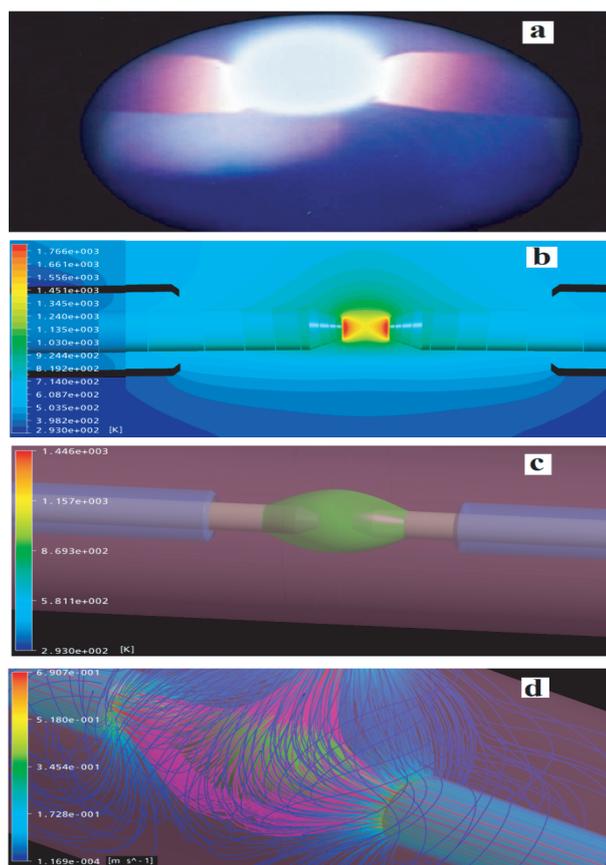
Figure 4. a is the view of gas discharge; b is the distribution of temperature field in plasma zone as well as along the electrode; c is the nozzle-electrode system with isothermal surface 900 K; d are the lines of gas mixture flows in nozzle-electrode-isotherm system 900 K.

gas mixture passes through this surface. Therefore, it can be argued that in the reaction chamber of this configuration there is a full interaction of the gas mixture with the plasma, in which the reaction of reduction of silicon tetrachloride to trichlorosilane takes place. The obtained data on the coefficient of the gas mixture entering the plasma region allow us to state that the yield of trichlorosilane equal to 45% is close to thermodynamically equilibrium at $T = 900$ K.

5. Conclusions

Under the conditions of RF (40.68 MHz) of a contracted arc discharge of atmospheric pressure, hydrogen reduction processes of silicon and germanium chlorides are investigated. The main products of the hydrogen reduction process are Si, Ge, $SiHCl_3$, SiH_2Cl_2 and $GeHCl_3$. Based on the results obtained using numerical simulation, it can be concluded that the temperature of the reaction area of a chemically active plasma is 900–1700 K, and the amount of the gas mixture passing through this region is close to 100%. In this case, the formation of condensed phase is observed at the ends of the electrodes at a temperature

close to 1700 K, and the formation of chlorosilanes and chlorogermanes at a temperature of about 900 K.

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