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INVESTIGATION OF CONVERSION PROCESS OF $SICL_4$ + CCL_4 MIXTURE BY RF (40.68 MHZ) ARC DISCHARGE

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Abstract. A contracted RF (40.68 MHz) arc discharge of atmospheric pressure, stabilized between two rod electrodes, was used to obtain trichlorosilane by the reaction of hydrogen reduction of silicon tetrachloride ($SiCl_4$). In model mixtures of macro-composition in the ratio $H_2/SiCl_4/CCl_4$=10/1/1, it was shown that C and SiC are the main solid-phase product which are deposited on the surface of electrodes in the form of dendrides. The temperature of the ends of the electrodes determined using emission thermometry is 1600 K. The thermodynamic analysis of H_2+$SiCl_4$+CCl_4 system confirms that the formation of C and SiC occurs in the temperature range of 1600 K. The deposition of solid-phase products occurs on the electrodes in the zone of high electric field strength.

Keywords: RF arc discharge, conversion process of $SiCl_4$+CCl_4, thermodynamic analysis.

1. Introduction

The study of the process of hydrogen reduction of $SiCl_4$ to $SiHCl_3$ is an urgent task since these compounds are the main by-product and the starting material, respectively, in the processes of obtaining silicon and silane [1]. In [2] a method of plasma-chemical synthesis of trichlorosilane under conditions of RF (40.68 MHz) arc discharge, providing a high (up to 60%) yield of trichlorosilane with low energy consumption, was proposed. It is known that, along with the main synthesis reaction, the reactions involving micro-impurities occur in the volume of gas discharge which leads to the change in their chemical form and concentration [3–6]. The content of impurities in silicon tetrachloride, that are formed in the process of obtaining polycrystalline silicon and silane, is at the purity level of the original trichlorosilane. A significant place among impurities is occupied by the impurities of chlorohydrocarbons and, in particular,CCl_4. In [7] it was shown that the content of chlorine hydrocarbon impurities in the products of hydrogen reduction of $SiCl_4$ in this type of discharge decreases from 10^{-4} to 10^{-7} mass %. Lowering the concentration of these micro-impurities at the stage of trichlorosilane synthesis will allow to obtain semiconductor silicon of higher purity in the future. It is necessary, nevertheless, to establish the chemical form of these impurities.

2. Description of RF plasmatron

RF plasmatron consists of silica tube with two coaxially arranged silicon electrodes. The distance between the electrodes is 10 mm. To initiate a discharge, it is necessary for the E/P value be at least 26 V/(cmTorr) [8]. The measurement of the electric field was carried out using the indicator Ya6P-110. The maximum value of the electric field E was 6×10^3 V/cm. When the pressure in the reactor is 760 Torr, the field strength is not sufficient for ionization of the inter-electrode space. The initiation of the discharge was carried out under reduced pressure of 100 Torr. In this case, the ratio $E/P = 60$ V/(cmTorr) which is quite enough for gas breakdown. The type of discharge is shown in Fig. 1a. The discharge glow occupies the inter-electrode area, envelops the electrodes and spreads in the volume of the reactor. When pressure increases up to atmospheric the contraction of the discharge occurs. The discharge at atmospheric pressure using hydrogen is shown in Fig. 1b. The discharge is an AC electric arc with a frequency of 40.68 MHz burning between the electrodes. When $SiCl_4$ entered the plasma, the discharge was transformed into a stable spherical formation of bright blue color shown in Fig. 1c. In this case there is a strong heating of the end parts of the electrodes in contact with the plasma. The electric current in the gas under these conditions is determined by the characteristics of the external circuit. The characteristic value of the total current determined by the method described in [9] was $I \approx 2$ A.

Estimation of the current can also be made using the current density of thermionic emission, and the temperature of the electrodes. For the used material of the electrodes (silicon) and the known area of the heated surface, the current density is determined by the formula:

$$j = A \times T^2 exp(-\frac{e\varphi}{kT}), \quad (1)$$

where A for silicon is in the range 50–120, $e\varphi$ - 3.6 eV [8].

In order to determine the temperature of the ends of the electrodes in the range of 350–950 nm, the

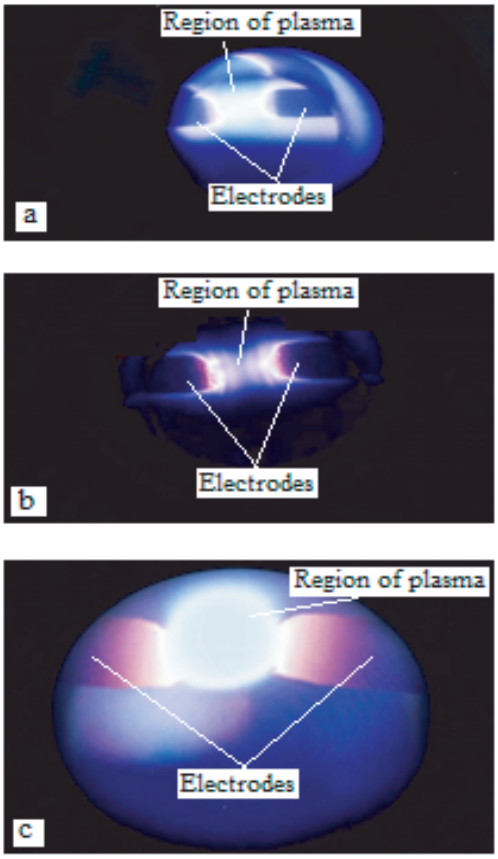

Figure 1. View of gas discharge; a - P=100 Torr H_2, b - 760 Torr H_2, c - 760 Torr H_2+$SiCl_4$.

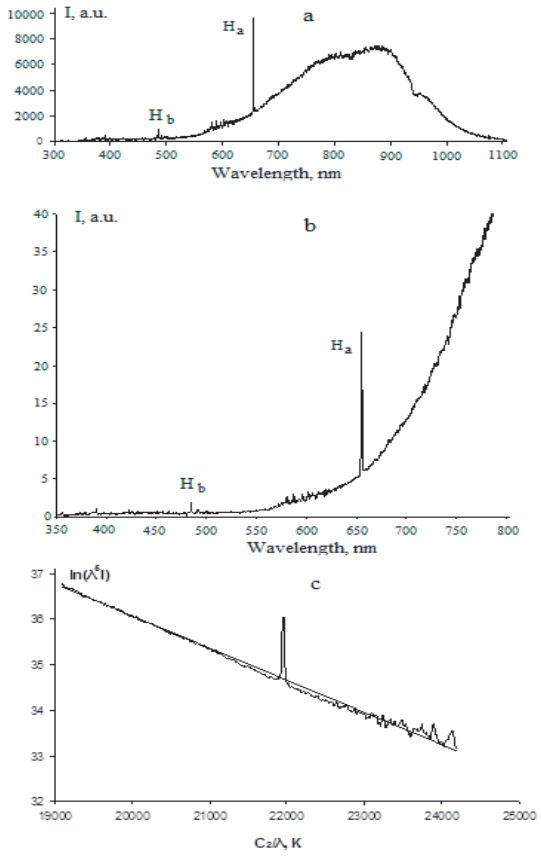

Figure 2. Emission spectrum of the discharge in hydrogen before (a) and after (b) adjustments and in Wynn coordinates (c)

emission spectrum of hydrogen, as well as chemically active plasma was investigated using the emission spectrometer HR4000CJ-UV-NIR. To determine body temperature with unknown values of emissivity, the emission spectrum was analyzed in the approximation of a gray radiator, the spectrum of which with accuracy to emissivity ε corresponds to the Planck spectrum [10]:

$$I(\lambda, T) = \varepsilon(\lambda, T)\frac{2hc^2}{\lambda^5}\frac{1}{exp(\frac{hc}{\lambda k_b T} - 1)}, \qquad (2)$$

In the course of the analysis, the spectral range of measurements was chosen for which the dependence of the emissivity on the wavelength is weak compared to the curvature of the continuous spectrum. In the selected wavelength range, the spectrum constructed in Wynn coordinates $\ln(\lambda^5 I)$ - C_2/λ is linear (the unit is neglected in the sum), and the proportionality coefficient is $1/T$:

$$\ln(\lambda^5 I) - \ln(\frac{\varepsilon C_1}{hc}) = -\frac{C_2}{\lambda}\frac{1}{T}, \qquad (3)$$

where $C_1 = 2hc^2 = 37418\,\mathrm{W}\cdot\mu\mathrm{m}^4/\mathrm{cm}^2$, $C_2 = hc/k_b = 1.4388\cdot10^4\,\mu\mathrm{m}\cdot\mathrm{K}$.

Fig. 2 shows the emission spectrum of the discharge in hydrogen before (a) and after (b) the correction which amends the spectral sensitivity of the measuring circuit. The same spectrum after adjustment, in Wynn coordinates is shown in Fig. 2c. The temperature of the ends of the electrodes determined in this way is 1600 K. It can be assumed that gas in the near-electrode region has the same temperature. Knowing the area of the heated surface of the electrode, estimated by the formula (1), the current is $I \approx 2.5$ A which by order of magnitude coincides with the value I determined by the method [9].

3. Experimental

In order to determine the main products into which chlorine hydrocarbon impurities and in particular CCl_4 can transfer, the hydrogen reduction process was studied on the model mixture of macro-composition in the $H_2/SiCl_4/HCl_4$ ratio from 10/0.1/1 to 10/1/1. The total flow of plasma gases was 700 cm^3/min. Power input to the plasma discharge zone was calculated as difference in power of respectively reflected and incident waves measured by directional coupler with directive gain of 30 dB and an oscilloscope, and was equal to 500 ± 30 W. The total degree of chloride conversion and the presence of gas-phase reaction products were determined by gas chromatography with an accuracy of 1 mol %. X-ray analysis of the obtained solid-phase products was carried out on XRD-7000 diffractometer. Morphological studies were conducted using scanning electron microscopy methods.

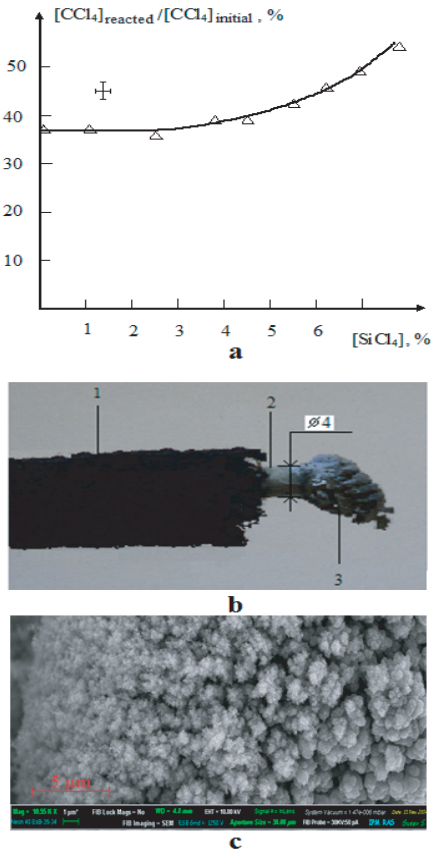

Figure 3. a - Dependence of conversion degree of CCl_4 on the content of $SiCl_4$ in the initial mixture;b - View of electrode: 1 - nozzle, 2 - silicon electrode, 3 - deposited SiC and c - morphology of deposited SiC.

The dependence of the degree of conversion of CCl_4 on the content of silicon tetrachloride in the initial mixture is shown in Fig. 3a. It can be seen from the graph that when the content of $SiCl_4$ in the mixture is from 0 to 3%, the degree of conversion of CCl_4 is 38%. With an increase in the concentration of $SiCl_4$ from 3 to 8%, the degree of conversion begins to increase and is 57% when the concentration of $SiCl_4$ in the mixture is 8%.

Gas chromatographic analysis showed that in the absence of $SiCl_4$ in the initial mixture, the reaction products contain CCl_4, HCl and a small amount (less than 5% mole.) of chloroform. During the experiment, there is also an intensive release of solid deposits on the surface of the electrodes in the form of dendrites (see Fig. 3b,c). It was shown that the main solid-phase product are C and SiC.

4. Thermodynamic analysis

In order to analyze the equilibrium composition of the main transformation products at a pressure of 1 atm., thermodynamic modeling was carried out for $H_2/SiCl_4/CCl_4$ mixture. The software package Chemical Thermodynamics Calculator, which implements the Gibbs method with fixed T and P, was used. Formulas (7) obtained in the conditional minimization of Gibbs energy (4) express the component concentrations through Lagrange non-identified multipliers. Solving the balance equations (5) and (6) in terms of phases f_0 and elements j_0 relative to $\{\lambda_j\}$ after substituting (7) into (5) and (6) determines the equilibrium composition of the heterophase system.

$$G(T,P,\{n_j\})/RT = \sum_i n_i(g_i + \ln n_i) - \sum_f \overline{n_f} \ln \overline{n_f} \tag{4}$$

$$\sum_i n_i a_{if} - \overline{n_f} = 0, f = 1C \dots f_0 \tag{5}$$

$$\sum_i n_i a_{ij} - b_j = 0, j = 1C \dots f_0 \tag{6}$$

$$n_i = \overline{n_f} \exp(\sum_j a_{ij}\lambda_j) \tag{7}$$

$$g_i = \triangle_f H^o(298)/RT - \Phi^o_{298}/R + \begin{cases} \ln \tilde{P}, & \text{vapor} \\ 0, & \text{condensate} \end{cases} \tag{8}$$

The values g_i contain the initial thermodynamic information for each i-th component. The matrix $A_{ij} = \{a_{ij}, a_{if}\}$, in addition to the stoichiometric coefficients of the participation of the j-th element in the chemical formula of the i-th substance, includes the coefficients of belonging of the i-th component to phase f $a_{if} = \{1, 0\}$. According to the initial chemical composition of the reagents, the elemental composition b_j of the system in the balance equations (6) is calculated.

5. Discussion of results

Fig. 4a shows the temperature dependence of the equilibrium composition of the main conversion products at a pressure of 1 atm. for $SiCl_4$+CCl_4+10H_2 system. It can be seen that in the region of $T = 1600$ K there are condensed phases C and SiC. Thus, the results of experimental studies show the possibility of formation of C and SiC in the realized experimental conditions. Thermodynamic analysis confirms that the formation of these products is observed at $T = 1600$ K, i.e. at a temperature determined using emission thermometry which is characteristic of the ends of the electrodes and the near-electrode region.

Deposition of carbide occurs at the electrodes in the zone of high electric field strength due to which the molecules acquire an induced dipole moment. In the process of burning of the discharge, the electrode acquires a negative charge relative to the plasma volume. At the same time, due to electrostatic interaction, positively charged carbon or silicon atoms, which are part of the dipole, are attracted to the electrode surface. During adsorbtion on the surface of the electrode, the atoms of carbon and silicon form phases of C and SiC. The proposed mechanism of deposition is shown in Fig. 4b.

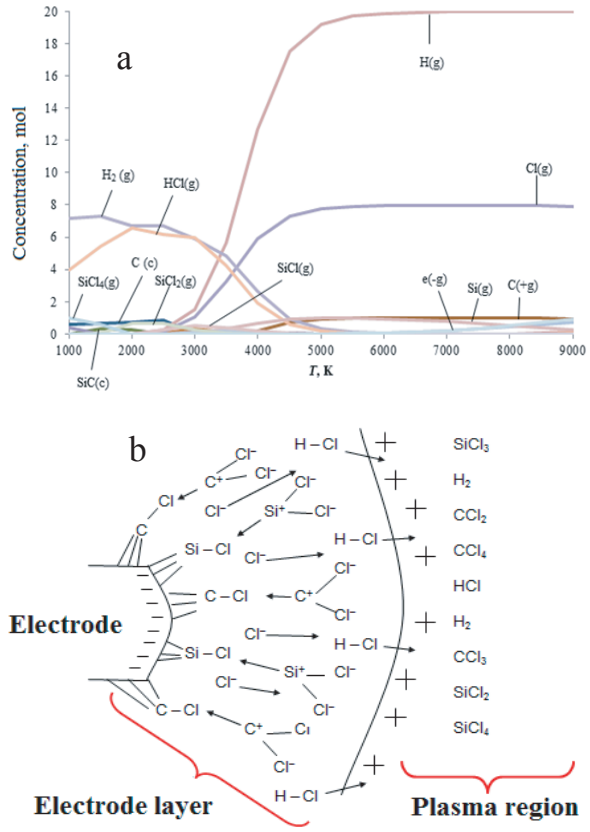

Figure 4. a - Temperature dependence of composition of the main conversion products at 1 atm. pressure for $SiCl_4+CCl_4+10H_2$ system, b - Mechanism of deposition of SiC.

6. Conclusions

As a result of the research, the conditions for breakdown in RF (40.68 MHz) contracted arc discharge of atmospheric pressure on hydrogen stabilized between two rod electrodes were determined. The method of emission thermometry was used to determine the temperature of the heated ends of the electrodes in contact with the plasma and the electrode areas, that was 1600 K. Heating the electrodes to the given temperature contributes to the deposition of the phases C and SiC on them which is confirmed by thermodynamic analysis. It can be assumed that in the process of plasma-chemical hydrogen reduction of $SiCl_4$ the impurities of chlorohydrocarbons behave in a similar way which leads to the effect of additional purification.

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