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Preparation of Trichlorosilane by Plasma Hydrogenation of Silicon Tetrachloride

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Abstract—We have studied silicon tetrachloride hydrogenation in an rf (40.68 MHz) plasma and have determined the trichlorosilane yield as a function of the molar energy input, $H_2 : SiCl_4$ molar ratio, and pressure. The highest trichlorosilane yield achieved is 60%, and the minimum energy input is 0.3 kW h per mole of $SiHCl_3$.

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INTRODUCTION

Silicon tetrachloride is a major by-product in silicon production through hydrogen reduction of trichlorosilane and in silane production through trichlorosilane disproportionation [1]. In connection with this, there is considerable interest in the development of effective processes for silicon tetrachloride conversion to trichlorosilane with the aim of achieving waste-free high-purity silicon production.

$SiCl_4$ can be hydrogenated using highly reactive reductants [2–5] or high-temperature and catalytic hydrogen reduction processes [6, 7]. Grankov and Ivanov [8] described a commercial-scale process for the catalytic hydrogenation of silicon tetrachloride at elevated pressures of up to 4 MPa. The trichlorosilane yield of this process is up to 38%. Considerable promise is offered by plasma processes for silicon tetrachloride hydrogenation [9–11]. Using such processes, one can supply energy to a local region and activate more effective reaction mechanisms.

The effect of process parameters on the trichlorosilane yield of silicon tetrachloride hydrogenation in a hydrogen plasma has not yet been studied in sufficient detail. Sarma and Chanley [11] investigated the effect of the $H_2 : SiCl_4$ ratio on silicon tetrachloride conversion in an rf discharge, but they did not analyze the trichlorosilane yield as a function of pressure or energy input.

The purpose of this work was to assess the trichlorosilane yield of the plasma hydrogenation of $SiCl_4$ as a function of the main process parameters: molar energy input, pressure, and $H_2 : SiCl_4$ molar ratio.

EXPERIMENTAL

The apparatus used in our experiments is shown schematically in Fig. 1.

The power of the rf generator was 340 W, and it was operated at a frequency of 40.68 MHz. The power supplied to the discharge zone was 110–120 W, and the

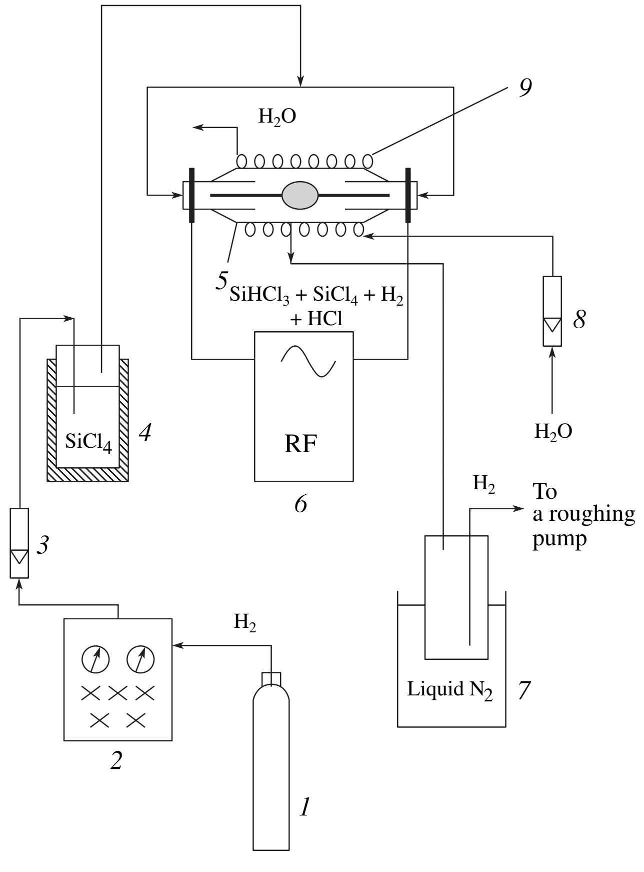

Fig. 1. Apparatus for plasma hydrogenation of silicon tetrachloride: (*1*) H_2 cylinder, (*2*) diffusion purification unit, (*3*, *8*) rotameters, (*4*) $SiCl_4$-filled bubbler, (*5*) reactor, (*6*) rf generator, (*7*) trap, (*9*) susceptor.

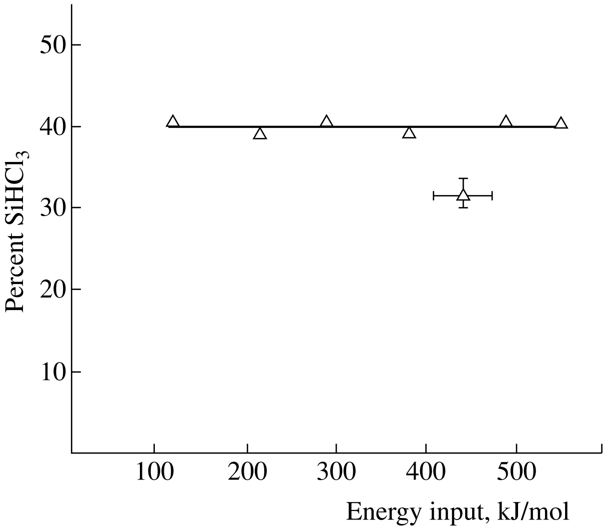

Fig. 2. Trichlorosilane yield as a function of the molar energy input for $SiCl_4$ conversion in a plasma discharge.

molar flow rate of the plasma gas, $H_2 + SiCl_4$, was varied from 0.7 to 3.42 mol/h. During the process, the pressure was varied from 0.7 to 101.08 kPa. The plasma reactor had the form of a quartz tube with electrodes along its axis. Lerage and Gerard [12] used tungsten and copper electrodes. The electrodes in our reactor were of silicon [13]. The use of silicon electrodes offers the possibility of reducing the contamination level in reaction products. After initiating a discharge by applying the rf voltage from the generator to the electrodes through a tuner, a mixture of silicon tetrachloride vapor and hydrogen was introduced into the discharge zone. The mixture was prepared by bubbling hydrogen through liquid silicon tetrachloride at a constant temperature. The flow rates of the reagents were monitored with rotameters and were controlled, together with the pressure, using inlet and outlet valves. The plasma power was determined calorimetrically as described by Krasheninnikov [14].

We measured the trichlorosilane concentration in reaction products at varied $SiCl_4$ hydrogenation conditions. The trichlorosilane content was determined by gas chromatography [15]. The detection limit was 1%.

The effect of the energy input on the trichlorosilane yield was studied at an $H_2 : SiCl_4$ molar ratio of 3.5.

The effect of the $H_2 : SiCl_4$ molar ratio (2.7–11.2) on the trichlorosilane yield was investigated at atmospheric pressure.

The pressure effect on the trichlorosilane yield was studied in the range 0.7–101.08 kPa at $H_2 : SiCl_4 = 3.5$, 6.2, and 8.9. The energy input was maintained constant at 300 kJ/mol.

RESULTS AND DISCUSSION

Figure 2 shows the plot of the trichlorosilane yield versus molar energy input. The molar energy input P was evaluated from the power W supplied to the discharge zone from the rf generator and the molar flow rate Q of the plasma gas. The power was maintained constant at 115 ± 10 W. The molar energy input was changed by varying the molar flow rate of the plasma gas and was determined as

$$P = W/Q.$$

The molar flow rate of silicon tetrachloride was varied from 0.15 to 0.7 mol/h, and the molar energy input, from 118 to 550 kJ/mol.

As seen in Fig. 2, the trichlorosilane yield is about 40%, independent of the energy input. The minimum energy input per mole of trichlorosilane is ~0.3 kW h/mol and is determined by the minimum power needed to maintain a stable discharge at the maximum flow rate of the plasma gas.

It was of interest to estimate the gas temperature in the discharge zone. To this end, we evaluated the power going to the heating of the gas in the discharge zone using a heat-balance equation taking into account the main contributions to heat exchange: the power removed from the plasma discharge zone through the electrodes (W_{el}), radiation heat loss (W_{rad}), and the power going to the heating of the gas (W_{gas}):

$$W = W_{el} + W_{rad} + W_{gas}. \tag{1}$$

The total discharge power was determined calorimetrically. The power removed through the electrodes and the radiation heat loss were calculated using a heat equation and the Stefan–Boltzmann law. From Eq. (1), the power going to the heating of the gas was determined to be 15 ± 3 W. The gas temperature T_{gas} in the plasma discharge zone was evaluated from the relation

$$W_{gas} = C_p Q(T_{gas} - T_{in}), \tag{2}$$

where Q is the flow rate of the reagents, C_p is the heat capacity of the gas, and T_{in} is the gas temperature at the reactor inlet. T_{gas} was found to be ~900 K.

In known plasma hydrogenation processes [16], the gas temperature T_{gas} exceeds 2000 K and is close to the electron temperature T_e. The reaction involves atomic hydrogen and proceeds according to the scheme [16]

$$H_2 \longrightarrow 2H^0,$$

$$SiCl_4 + 2H^0 \longrightarrow SiHCl_3 + HCl.$$

In the proposed process, T_{gas} is far lower, indicating that the mechanism of trichlorosilane formation differs from those in the processes described by Sivoshinskaya et al. [16].

It is of key importance, for commercial applications, to be able to perform silicon tetrachloride hydrogenation at atmospheric pressure. In connection with this, we determined conditions that were optimal in terms of the trichlorosilane yield of $SiCl_4$ hydrogenation at a pressure of 10^5 Pa.

The effect of the $H_2 : SiCl_4$ ratio on the $SiCl_4$ conversion to trichlorosilane and silicon (Fig. 3) was studied at a constant flow rate of silicon tetrachloride (0.7 mol/h) and constant discharge power (110 W). The highest trichlorosilane yield (44%) was achieved at $H_2 : SiCl_4 = 6.9$. At higher hydrogen concentrations, the trichlorosilane yield was lower. The silicon yield was found to rise steadily from 8 to 47% with increasing hydrogen concentration.

Note that our results on the trichlorosilane yield (Fig. 3) agree well with earlier data [11].

Since the reaction products contained neither SiH_2Cl_2 nor SiH_3Cl, the hydrogenation process can be represented by two reactions:

$$SiCl_4 + H_2 \longrightarrow SiHCl_3 + HCl, \tag{3}$$

$$SiHCl_3 + ç_2 \longrightarrow Si + 3HCl. \tag{4}$$

A similar result follows from thermodynamic analysis [17, 18].

Silicon tetrachloride hydrogenation with yields of up to 50% takes place at $T_{gas} < 1000$ K. This correlates with our estimate, $T_{gas} \sim 900$ K, and with the observed trichlorosilane yield, ~45%.

Figure 4 show pressure dependences of the $SiHCl_3$ yield. In the pressure range 0.7 to 10.1 kPa, no trichlorosilane was formed; the major reaction products were hydrogen chloride, silicon, and polychlorosilanes. Trichlorosilane formation in the reaction products was observed at pressures above 13.1 kPa. The highest trichlorosilane yield (60%) was achieved at 73.1 kPa.

The high trichlorosilane yield at pressures above 13.1 kPa suggests that trichlorosilane formation involves excited hydrogen molecules, H_2^*:

$$H_2 + e \longrightarrow H_2^- \longrightarrow H_2^* + e, \tag{5}$$

$$SiCl_4 + H_2^* \longrightarrow SiHCl_3 + HCl. \tag{6}$$

The vibration quantum of the H_2 molecule is 0.53 eV [19], while the heat effect of reaction (3) is 0.77 eV. Thus, the energy of the lowest vibrational level of the hydrogen molecule may notably reduce the activation energy of silicon tetrachloride hydrogenation [20].

The proposed mechanism is supported by the sharp maximum in $SiHCl_3$ yield at 73.1 kPa. As shown by Rusanov and Fridman [20], the use of the vibrational excitation energy of reagents is highly effective in surmounting the energy barrier of chemical reactions. Since the excitation cross section of the lowest vibrational level of the hydrogen molecule as a function of electron energy exhibits resonance [21], it is reasonable to assume that the maximum in trichlorosilane yield at a pressure of 73.1 kPa is due to the effective excitation of vibrations of hydrogen molecules in the discharge. High effectiveness of the vibrational excitation of molecules was also reported for some other plasma reactions [20].

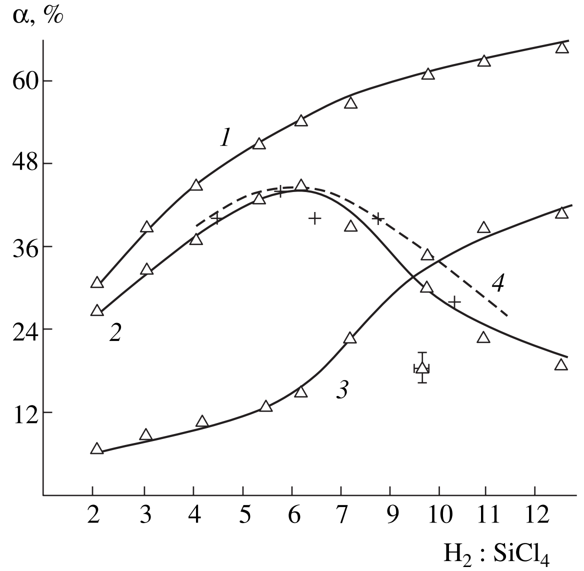

Fig. 3. (*1*) Overall $SiCl_4$ conversion, (*2*) trichlorosilane yield, and (*3*) silicon yield as functions of the $H_2 : SiCl_4$ molar ratio in the starting mixture; (*4*) data from Sarma and Chanley [11].

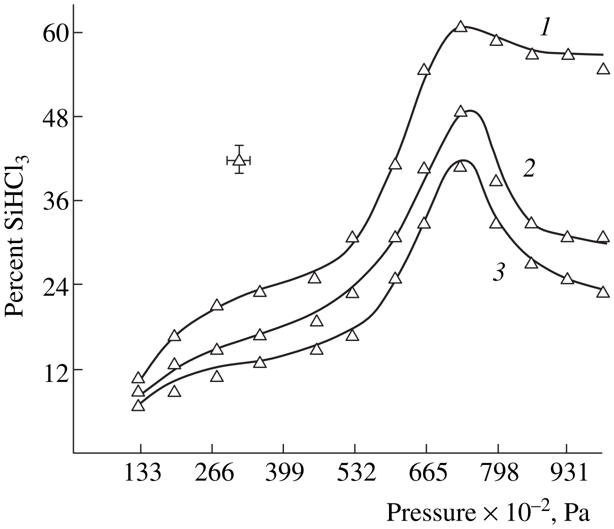

Fig. 4. Pressure dependences of the trichlorosilane yield at $H_2 : SiCl_4$ = (*1*) 6.2, (*2*) 3.5, and (*3*) 8.9.

It seems likely that raising the pressure to above 73.1 kPa reduces the fraction of vibrationally excited hydrogen because of the rise in the rate of vibrational–translational energy exchange. This may be responsible for the reduction in trichlorosilane yield at increased pressures. Moreover, in the pressure range in question the gas temperature may rise, leading to partial thermal decomposition of trichlorosilane.

CONCLUSIONS

The present results lead us to conclude that the pressure in the reaction zone plays a key role in determining the trichlorosilane yield of silicon tetrachloride plasma hydrogenation. The highest trichlorosilane yield (60%) is achieved at a pressure of 73.1 Pa. The maximum in the trichlorosilane yield as a function of pressure and $H_2 : SiCl_4$ ratio suggests that the formation of trichlorosilane involves vibrationally excited hydrogen molecules.

ACKNOWLEDGMENTS

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REFERENCES

1. Grankov, I.V., Zakharov-Cherenkov, V.K., Ivanov, L.S., and Sivoshinskaya, T.I., *Proizvodstvo poluprovodnikovogo kremniya za rubezhom* (Foreign Manufacturing of Semiconductor Silicon), Moscow: TsNIItsvetmet Ekonomiki i Informatsii, 1983.
2. Zhigach, A.F. and Stasinevich, D.S., *Khimiya gidridov* (Chemistry of Hydrides), Leningrad: Khimiya, 1969.
3. Taylor, P.A., Purification Techniques and Analytical Methods for Gaseous and Metallic Impurities in High-Purity Silane, *J. Cryst. Growth*, 1988, vol. 89, pp. 28–38.
4. Wilson, J.M., Radley, J.A., and Neale, E.D., UK Patent 745698, 1956.
5. Radley, J.A. and Elliot, G., UK Patent 838275, 1960.
6. Eugen, M.S. and Schwartz, R., US Patent 4217334. 1980.
7. Iya, S.K., Production of Ultra-High-Purity Polycrystalline Silicon, *J. Cryst. Growth*, 1986, vol. 75, pp. 88–90.
8. Grankov, I.V. and Ivanov, L.S., Intensification of Polycrystalline Silicon Production, *Tsvetn. Met.*, 1986, no. 6, pp. 60–64.
9. Sarma, K.R. and Rice, M.J., Jr., US Patent 4309259, 1985.
10. Karpov, A.P., Suris, A.L., and Shorin, S.N., Thermodynamic Analysis of Reduction of Chlorides, *II Simpozium po plazmokhimii* (II Symp. on Plasma Synthesis), Riga: Zinatne, 1975, vol. 2, pp. 178–181.
11. Sarma, K.R. and Chanley, C.S., US Patent 4542004, 1985.
12. Lerage, J.-L and Gerard, S., Fr. Patent 2530638, 1984.
13. Gusev, A.V., Devyatykh, G.G., Sukhkanov, A.Yu., et al., RF Patent 2142909, 1998.
14. Krasheninnikov, E.G., Rusanov, V.D., Sanyuk, S.V., and Fridman, A.A., Hydrogen Sulfide Dissociation in an RF Discharge, *Zh. Tekh. Fiz.*, 1986, vol. 56, no. 6.
15. Krylov, V.A., Salganskii, Yu.M., and Chernova, O.Yu., High-Sensitivity Gas-Chromatographic Determination of Carbon and Hydrogen-Containing Impurities in Silicon Tetrachloride, *Zh. Anal. Khim.*, 2001, vol. 56, no. 9, pp. 956–961.
16. Sivoshinskaya, T.I., Grankov, I.V., Shabalin, Yu.P., and Ivanov, L.S., *Pererabotka tetrakhlorida kremniya, obrazuyushchegosya v proizvodstve poluprovodnikovogo kremniya* (Recycling of Silicon Tetrachloride in Semiconductor Silicon Production), Moscow: TsNIItsvetmet Ekonomiki i Informatsii, 1989.
17. Wolf, E. and Teichmann, R., Zur Thermodynamik des Systems Si–Cl–H, *Z. Anorg. Allg. Chem.*, 1980, vol. 460, pp. 65–80.
18. Sirtl, E., Hunt, L.P., and Sawyer, D.H., High Temperature Reactions in the Silicon–Hydrogen–Chlorine System, *J. Electrochem. Soc.*, 1974, vol. 121, no. 7.
19. Huber, K.-P. and Herzberg, G., *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules*, New York: Van Nostrand, 1979.
20. Rusanov, V.D. and Fridman, A.A., *Fizika khimicheski aktivnoi plazmy* (Physics of Reactive Plasma), Moscow: Nauka, 1984.
21. Raizer, Yu.P., *Fizika gazovogo razryada* (Physics of Gas Discharge), Moscow: Nauka, 1987.