COMBINED PLASMA-SORPTION PROCESS FOR PRODUCING MONOSILANE FROM FLUORIDE RAW MATERIAL

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ABSTRACT

Monosilane (SiH_4) is obtained from sodium fluorosilicate - Na_2SiF_6. Technological route includes primary composition of Na_2SiF_6 to SiF_4 and NaF, plasma conversion of SiF_4 to fluorosilanes and sorption conversion of fluorosilanes to yield SiH_4, Na_2SiF_6 and HF.

INTRODUCTION

One of kinds of raw material for producing Si for microelectronic applications is sodium fluorosilicate (Na_2SiF_6) - a by-product of hydrometallurgical plants processing silicous ores containing fluorine. At heating Na_2SiF_6 decomposes to SiF_4 and NaF. There are several methods to reduce Si from SiF_4. One of them is hydrogen reduction of Si.

Nevertheless, thermodynamic analysis of interaction H_2 with SiF_4 shows that quantitative yield of silicon is practically non-attainable up to 6000 K. It means that downstream a plasma reactor there will be powerful recombination of SiF_n-molecules and quantity of elemental Si is miserable. There is strong similarity in behavior of (Si- F)-plasma

and (U-F)-plasma /1-2/.

Taking into account all this experience we reinforced plasma hydrogen reduction of Si from SiF_4 by sorption-chemical conversion of fluoro-silanes,obtained as a result of reduction aforesaid, on NaF. The effect of such conversion was reported in /3/.

SCHEME OF PLSMA-SORPTION PROCESS FOR OBTAINING MONOSILANE

Scheme of the process is shown in Fig.1. The raw material- Na_2SiF_6 decomposes to NaF and SIF_4:

$$Na_2SiF_6(s) \longrightarrow 2\ NaF(s) + SiF_4(g), \qquad (1)$$

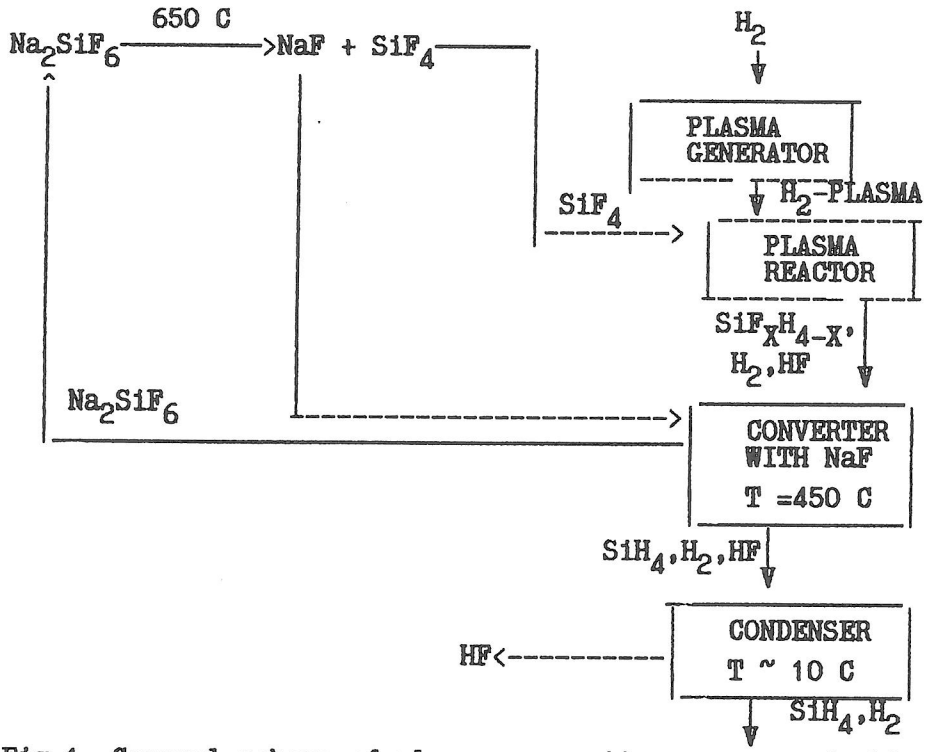


Fig.1. General scheme of plasma - sorption process of obtaining monosilane from sodium fluorosilicate.

Volatile SiF_4 is collected, compressed and then directed to H_2-plasma . Conversion of SiF_4 to fluorosilanes of general formula SiF_xH_{4-x} is described by equations:

$$SiF_4 + H_2 \longrightarrow SiHF_3 + HF, \quad (2)$$
$$SiHF_3 + H_2 \longrightarrow SiH_2F_2 + HF, \quad (3)$$
$$SiH_2F_2 + H_2 \longrightarrow SiH_3F + HF, \quad (4)$$
$$SiH_3F + H_2 \longrightarrow SiH_4 + HF. \quad (5)$$

Then fluorosilanes in mixture with hydrogen are directed into sorption-chemical converter where the SiF_xH_{4-x} converts to SiH_4 and Na_2SiF_6 in accordance with the equations (in the brackets there are theoretical yields of SiH_4):

$4\ SiHF_3 + 6\ NaF \rightarrow 3\ Na_2SiF_6 + SiH_4$; Yield of SiH_4 25 %; (6)
$2\ SiH_2F_2 + 2\ NaF \rightarrow Na_2SiF_6 + SiH_4$; Yield of SiH_4 50 %; (7)
$4\ SiH_3F + 2\ NaF \rightarrow Na_2SiF_6 + 3\ SiH_4$; Yield of SiH_4 75 %. (8)

This operation is refining because a lot of admixtures is absorbed on NaF.

Except these reactions there are a side process of sorption of HF on NaF and several parasitic reactions:

$$HF + NaF \longrightarrow NaF.HF, \quad (9)$$
$$SiHF_3 + NaF.HF \longrightarrow SiF_4 + H_2 + NaF; \quad (10)$$
$$SiF_2H_2 + 2NaF\ HF \longrightarrow SiF_4 + 2H_2 + 2NaF; \quad (11)$$
$$SiH_3F + 3\ NaF.HF \longrightarrow SiF_4 + 3H_2 + 3NaF. \quad (12)$$

Control of all these reactions is feasible by temperature operating modes. Sorption of HF on NaF takes place at the temperature of 250 C; at the temperatures of 450 C sorption of HF is thermodynamically prohibited and, therefore, there is no conditions for parasitic reactions 10-12.

There are two ways of separation of HF: sorption on NaF at 250 C or condensation at 10 C. We have tested both ways and selected condensation as more simple.

As a matter of principle, SiH_4 is intermediate product in producing Si and there is no a need to separate SiH_4 and H_2, and mixture of this substances is brought to the reactor for obtaining Si by decomposition of SiH_4.

EXPERIMENTAL

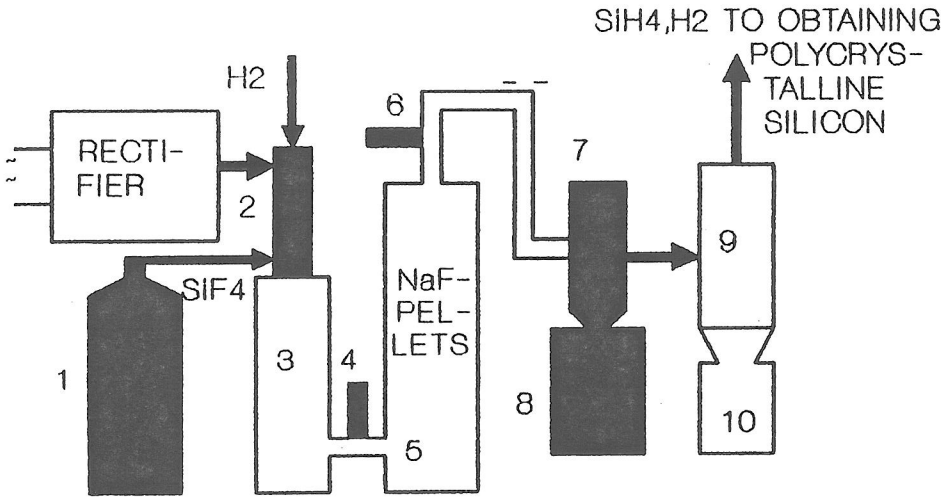
We researched the process aforesaid. But decomposition of Na_2SiF_6 to SiF_4 and NaF was conducted in another apparatus; SiF_4 was condensed into a cylinder with shut-off valve.

Scheme of experimental apparatus for plasma conversion of SiF_4 to SiH_4 is shown in Fig. 2. Plasma generator consists of thyristorized rectifier, arc hydrogen plasmatron and a system of control. Plasma reactor is supplied with water-cooled jacket. Sorption-chemical converter is filled in with NaF- pellets. There are two such column; one of them operates in operating mode of sorption- conversion, the other one - in operating mode of regeneration. The next elements of the apparatus are a metal-ceramic filter, a condenser supplied with collector of HF. The apparatus was equipped with vacuum probes for sampling of gas phase. The samples have been analyzed by mass-spectrometer.

Parameter of the experiments are as follows:
1. Power of rectifier ~ 50 kW. 2. Electrical power on plasmatron ~ 20 kW. 3. Silicon tetrafluoride feeding - 1-2.5 kg SiF_4/h (0.25-0.46 kg SiF_4 in a single run). 4. Mole ratio SIF_4/H_2 = 1/5.

RESULTS OF THE EXPERIMENTS

The results of the experiments on plasma-sorption conver-



1-CYLINDER WITH SiF4; 2-ARC PLASMATRON; 3-PLASMA REACTOR; 4-A SAMPLER FOR SiFxH4-x; 5-SORPTION CONVERTER; 6-A SAMPLER FOR SiH4; 7-FILTER; 8-CONTAINER; 9-CONDENSER OF HF; 10-COLLECTOR OF HF.

Fig. 2. Scheme of experimental apparatus for conversion of SiF_4 to monosilane.

sion of SiF_4 are as follows:

1. Gross-formula of fluorosilanes obtained in the experiments was $SIH_{1.8}F_{2.2}$.
2. Linear velocity of mixture of $SIH_{1.8}F_{2.2}$, HF, H_2 through the sorption-chemical converter at the volume velocity of the mixture of 0,026 nm^3/s was of 7,05 m/s.
3. Conversion degree of SiF_4 was of 100 %.
4. Attained conversion degree of fluorosilanes in the sorption-chemical converter was 40-65 % of theoretical one.

Raw material- SiF_4 obtained by thermal decomposition of Na_2SiF_6. Chemical composition: content of SiF_4 - 99.99 %;HF - 3.10^{-3} %;CO_2 - 10^{-3}%; H_2SiF_6 - 5.10^{-3}%; 5.10^{-3}%; CF_4 < 2.10^{-4}%, SO_2 < 10^{-3}%.

According to mass-spectrometric analysis, purity of the $SiH_{1,8}F_{2,2}$ obtained was as follows (%):D-7.10^{-5}, C- 10^{-5}, O-2.10^{-4}, Na-8.10^{-5}, F-9.10^{-6}, S-4.10^{-6}, Cl-4.10^{-5},K-2.10^{-5}, Ca-3.10^{-5},Sc- 2.10^{-5},Cr- 6.10^{-5},P-9.10^{-6},Fe-5.10^{-5},Ni-3.10^{-5}, Cu-9.10^{-5}, Zr-6.10^{-5}, As-4.10^{-5},Ag-5.10^{-6},Ba-2.10^{-6},Hf-5.10^{-6}, W- 9.10^{-6}. Contents of the other admixtures (Fe, I, Cs, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho,Er, Tm, Yb, Lu, Re, Os, Yr, Pt, Au, Hg, Te, Bi, Th) are less 10^{-6} %.

After sorption refining of monosilane its purity on some elements (O, Cl, K, Ca, Sc etc) increased (%): B-3.10^{-6}, C-10^{-5},O-2.10^{-5},P-5.10^{-5},S-6.10^{-6},Cl-10^{-5},K- 2.10^{-6},Ca-3.10^{-6}, Ge-7.10^{-5},As -4.10^{-5}, Sc-2.10^{-6},Zr-6.10^{-6},Sn-5.10^{-6}. Contents of the all other admixtures were less 10^{-6} %.

Most of elements determined is below the sensitivity level of mass-spectrometric analysis. Content of such admixtures as B, C, O, Na, S, Cl can be lowered some more using more pure raw material than SiF_4 of technical grade. There are several physical and chemical methods for more deep purification of SiF_4 before plasma-sorption conversion.

REFERENCES

1. I.N.Toumanov, K.V.Zirelnikov. Properties and application of (U-F)-plasma. Physics and Chemistry of Processing Materials,1991, N6,p.66-72.

2. I.N.Toumanov, K.V.Zirelnikov. Properties and application of (U-F)-plasma: Reactantless reduction of U from UF_6 in high frequency electrodeless discharge. Physics and Chemistry of Processing Materials,1992, N1,p.61-67.

3. US Patent N2933374/1955.