Separation of Silicon Isotopes by Silicon Tetrafluoride–Silane Technology[1]

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Abstract—Silane enriched in silicon isotopes was obtained in high yield by reacting SiF_4 with a solution of $NaAlH_4$ in diethylene glycol dimethyl ether in a purpose-designed apparatus. Chemical analyses are presented for isotopically enriched silicon obtained by the thermal decomposition of silane.

It is advantageous to obtain single-crystal monoisotopic silicon by the following sequence of processes: synthesis of SiF_4 with the natural isotopic composition, centrifugal separation of the silicon isotopes in SiF_4, conversion of SiF_4 into silane, preparation of polycrystalline silicon, and growth of silicon single crystals.

Reaction between SiF_4 and H_2 is thermodynamically implausible; at the same time, SiF_4-to-SiH_4 conversion can be achieved using a metal hydride.

Aluminum hydride compounds attract researchers' interest for the following reasons:

as distinct from alkali and alkaline-earth hydrides, which are ionic compounds, aluminum hydride compounds are soluble in some organic solvents, enabling rapid silane reduction with a high reaction yield;

aluminum hydride compounds and their conversion products in the reaction with silicon tetrafluoride have much lower vapor pressures than silane and, therefore, can easily be separated from silane.

A survey of aluminum hydride compounds is presented in [1].

In this work, we employed sodium aluminum hydride, $NaAlH_4$, as a reducer and diethylene glycol dimethyl ether (diglyme) as a solvent since $NaAlH_4$ contains as many as four hydrogen atoms per formula unit and is well soluble in diglyme (up to 3 mol/l). Furthermore, diglyme has a high boiling point ($\simeq 160°C$), facilitating the removal of the solvent vapor from SiH_4. SiF_4-to-SiH_4 conversion,

$$SiF_4 + NaAlH_4 = SiH_4 + NaAlF_4,$$
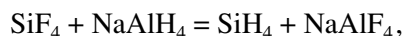
was carried out by bubbling SiF_4 through an $NaAlH_4$ solution in diglyme at atmospheric pressure. The silane yield between 0 and 60°C was above 99%.

Our SiF_4 conversion plant is schematized in Fig. 1.[2]

Given that diglyme may contain moisture, peroxides, organic hydroxy compounds (e.g., incompletely methylated diethylene glycol), aldehydes, ketones, and other compounds reactive with $NaAlH_4$, it was purified before solution preparation.

Since $NaAlH_4$ is highly reactive, its solution in diglyme was prepared in a dry argon atmosphere.

The solution was fed into a stirred reactor together with SiF_4 carried by helium. The resulting silane was directed to another reactor, where it was purified from SiF_4 and phosphorus and arsenic hydrides [2]. Next, the gas mixture was passed through a cryogenic trap to remove the diglyme vapor. The cooling agent used was a solid–liquid heptane mixture with an equilibrium temperature of –94°C.

The gas phase was analyzed during the process on an LKhM-80 gas chromatograph.

In chromatographic analysis, we used two 2-m columns, one packed with Polisorb-1 and the other with a molecular sieve, and a thermal-conductivity detector. The interval between two analyses was determined by the analysis time, which was no longer than 3 min. Using gas chromatography, we were able to follow the purging of the apparatus and delivery lines before admitting the reactants, the progress of conversion, SiF_4 breakthrough, and adsorption purification of silane.

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[1] Presented in part at the All-Russia Conference *High-Purity Monoisotopic Silicon: Preparation, Analysis, and Properties,* Nizhni Novgorod, Russia, 2001.

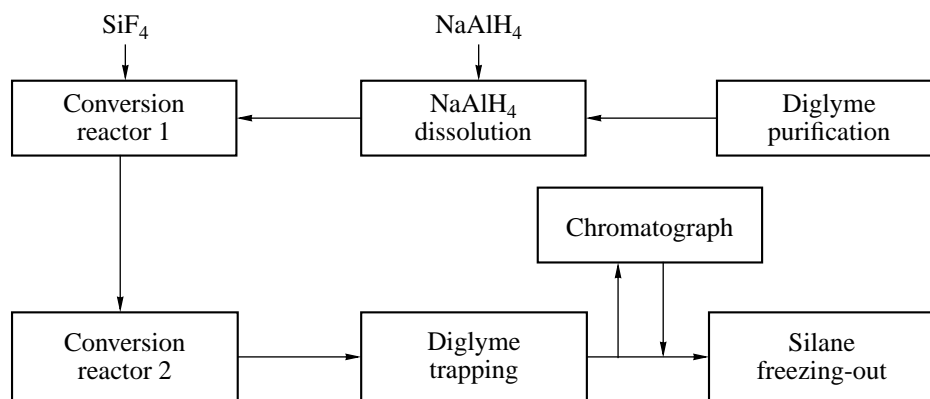[2] The plant was designed and has been operated for several years at the Khlopin Radium Institute.

Fig. 1. Flow diagram of SiF_4-to-SiH_4 conversion with the use of $NaAlH_4$.

An analysis of the silane obtained by a similar process was reported in [3] (vol %): SiH_4, 95.5; $C_2H_5SiH_3$, 2.45; C_2H_6, 0.95; H_2, 0.1.

Table 1. Methane concentration in silane as a function of conversion temperature

t, °C	13	25	50
mol % CH_4	0.8	2.9	10.6

Table 2. Impurity concentrations in silicon (cm^{-3})

| Element	Unmodified silicon	^{28}Si (99.9%)	^{30}Si (99.1%)
B	$<2 \times 10^{15}$	$<1 \times 10^{15}$	$<1 \times 10^{15}$
As	2.3×10^{19}	$<1 \times 10^{17}$	$<1 \times 10^{17}$
C	2.9×10^{20}	3×10^{18}	2×10^{17}
F	1×10^{19}	2×10^{17}	4×10^{17}
Al	$<2 \times 10^{17}$	4×10^{15}	$<1 \times 10^{15}$
Cl	4.3×10^{18}	1×10^{16}	1×10^{16}
Ti	1.6×10^{18}	$<1 \times 10^{16}$	$<1 \times 10^{16}$
Cr	$<1 \times 10^{17}$	$<1 \times 10^{16}$	$<1 \times 10^{16}$
Mn	$<2 \times 10^{15}$	$<1 \times 10^{15}$	$<1 \times 10^{15}$
Fe	2.5×10^{18}	$<1 \times 10^{16}$	$<1 \times 10^{16}$
Ni	6.6×10^{17}	$<1 \times 10^{17}$	$<1 \times 10^{17}$
Mo	$<1 \times 10^{16}$	1×10^{16}	$<1 \times 10^{16}$
K	2×10^{16}	3×10^{15}	1×10^{15}
Na	7×10^{15}	$<1 \times 10^{15}$	$<1 \times 10^{15}$
Mg	9×10^{15}	2×10^{15}	$<1 \times 10^{15}$
Ca	3×10^{16}	$<1 \times 10^{15}$	2×10^{15}
Ta	1.4×10^{17}	6×10^{16}	$<1 \times 10^{16}$

The compounds other than silane result from the reaction between SiF_4 and $NaAl(C_2H_5)_2H_2$ impurity in $NaAlH_4$ [2]. We did not detect C_2H_6 or $C_2H_5SiH_3$ but detected methane in the product. Since the methane concentration in the gas phase depended on the reaction temperature (Table 1), methane formation seems to be inherent in the process in question. The mechanism of methane formation is still unclear.

Methane and silane were separated chromatographically (Fig. 2). This process is not connected with SiF_4 conversion and will not be considered here.

For lack of instruments for elemental analysis of the gas phase containing SiF_4 and SiH_4, we analyzed polysilicon deposited on a hot molybdenum wire through silane pyrolysis. Monoisotopic polysilicon was obtained in the same way.

Polysilicon was analyzed by secondary ion mass spectrometry on a CAMECA IMS-4f instrument, using a Cs^+ or O_2^+ primary-ion beam.[3] We recorded the signals of negatively and positively charged secondary ions and/or diatomic clusters of all expected impurity elements. The mass spectra were interpreted using the relative sensitivity factors given in [4].

Silane was produced from isotopically unmodified SiF_4 obtained by the thermal decomposition of Na_2SiF_6 at 750°C,[4]

$$Na_2SiF_6 \longrightarrow SiF_4 + 2NaF,$$
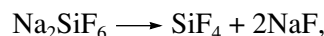
and from SiF_4 isotopically enriched by the method devised at the NPO Radium Institute.[5]

Table 2 presents the chemical analyses of isotopically unmodified and enriched silicon samples.

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[3] Mass spectrometric analysis was carried out at the Ioffe Physicotechnical Institute, Russian Academy of Sciences, St. Petersburg.
[4] SiF_4 was prepared at the Khlopin Radium Institute.
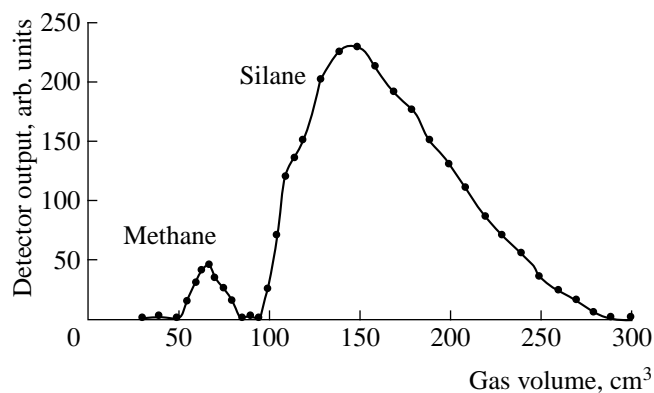[5] Isotopic enrichment was carried out at the Tsentrotekh-EKhZ Science and Technology Center.

Fig. 2. Chromatogram of a methane–silane mixture.

In preparing those samples, we did not remove methane from the unmodified silane. $^{28}SiH_4$ and $^{30}SiH_4$ were purified of methane by adsorption. Apparently, our adsorbent removed many other impurities.

The production rate of our plant is 0.5 mol/h. Using this plant, we produced hundreds of grams of $^{28}SiH_4$ and tens of grams of $^{29}SiH_4$ and $^{30}SiH_4$.

CONCLUSION

The operation of the plant described here has demonstrated that the reduction of SiF_4 with $NaAlH_4$ ensures a high yield of silane pure enough to produce high-quality polysilicon. Therefore, this process can be integrated into single-crystal monoisotopic silicon technology.

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