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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Formation of Impurity Si_2OH_6 in Silane Synthesized from Silicon Tetrafluoride

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Abstract—The possibility of the reduction of hexafluorodisiloxane by calcium hydride in the synthesis of silane from silicon tetrafluoride has been studied. This reaction is shown to be not decisive for oxygen contamination of silane. The most likely reason for the appearance of impurity Si_2OH_6 in "fluoride" silane is the $Ca(OH)_2$-catalyzed reaction of silane with trace water. The concentration of impurity Si_2OH_6 in silane at the stage of synthesis may be efficiently decreased by the preliminary purging of calcium hydride with a hydrogen (grade A) flow.

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Oxygen is a limited admixture in silicon used for the production of semiconductor devices, along with boron, phosphorus, and carbon. Its concentration must not exceed 10^{15} at/cm^3. Oxygen is also one of the limited impurities in the synthesis of a high-purity structurally perfect monoisotopic ^{28}Si single crystal used as the basis in the manufacturing of the standard mass. Interstitial oxygen is known to reduce the density of a silicon crystal [1].

Impurity oxygen in polycrystalline silicon and films manufactured from silane may appear from various sources. It is known [2] that silane reacts with oxygen to form suspended submicron-sized silicon dioxide particles [3, 4] according to the reaction

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O. \quad (1)$$

Thermodynamic and quantum-chemical calculations [5] indicate the possibility of a reaction between silane and water at least in two stages as follows:

$$SiH_4 + H_2O \longrightarrow SiH_3OH + H_2, \quad (2)$$

$$SiH_3OH + SiH_4 \longrightarrow SiH_3{-}O{-}SiH_3 + H_2. \quad (3)$$

However, the kinetic restrictions of reactions (2) and (3), which are poorly studied in gas phase [6], should be taken into account in practice. The hydrolysis of monosilane is actively catalyzed by alkalies and well-developed surfaces (for example, of storage cylinders) [7]. Reactions (1)–(3) may be considered as universal sources of impurity oxygen in silane independently of the method of its synthesis.

In this work we consider silane synthesized from silicon tetrafluoride by its reduction with calcium hydride [8] by the reaction

$$SiF_4 + 2CaH_2 = SiH_4 + 2CaF_2. \quad (4)$$

A specific feature of "fluoride" silane is the presence of impurity fluorosilanes SiH_xF_{4-x} resulting from the incomplete reduction of SiF_4 according to reaction (4) at a level of 10^{-3} mol %. By analogy with chlorosilanes, these admixtures can be hydrolized by trace water to give disiloxane, for example, by the reaction

$$2SiH_3F + H_2O \longrightarrow Si_2OH_6 + 2HF. \quad (5)$$

On the other hand, hexafluorodisiloxane Si_2F_6O, whose concentration may reach several percents, is the major molecular admixture in silicon tetrafluoride [9]. It may be supposed that the reduction of hexafluorodisiloxane proceeds simultaneously with reactions (4) and (5) as follows:

$$Si_2OF_6 + 3CaH_2 \longrightarrow Si_2OH_6 + 3CaF_2, \quad (6)$$

thus making a certain contribution to the oxygen contamination of "fluoride" silane.

The objective of our work is to verify this supposition.

EXPERIMENTAL

The reaction of silicon tetrafluoride with calcium hydride was studied at room temperature. Frionally distilled silicon tetrafluoride of natural isotopic composition was used. According to IR Fourier spectroscopy, it contained $(2.0 \pm 0.6) \times 10^{-1}$ mol % of impurity Si_2F_6O. Calcium hydride was synthesized by the hydrogenation of distilled metal calcium swarf with hydrogen purified on a palladium filter. Mechanically dispersed calcium hydride inside a box purged by dry nitrogen was placed into a 200-cm^3 stainless steel reactor. Then, gaseous silicon tetrafluoride was admitted to the reactor, the reactor was attached directly to the

Table

Sample no.	c, mol %			
	concentration in SiF_4 (IR)	concentration in SiH_4 (CMS)		
		Si_2OH_6	Si_2OH_5F	$Si_3O_2H_7F$
1	0.20 ± 0.06	1.1 ± 0.4	–	–
2	0.01 ± 0.005	1.2 ± 0.3	$(8 \pm 3) \times 10^{-2}$	$(1.5 \pm 0.5) \times 10^{-2}$
3	0.10 ± 0.05	$(1.5 \pm 0.6) \times 10^{-2}$	$(3 \pm 1) \times 10^{-4}$	$(4 \pm 2) \times 10^{-5}$
4	1.50 ± 0.75	$(1.3 \pm 0.4) \times 10^{-1}$	$(3 \pm 1) \times 10^{-4}$	$(6 \pm 2) \times 10^{-5}$
5	0.30 ± 0.15	$(9.7 \pm 1.0) \times 10^{-4}$	–	–
6	8.0 ± 4.0	0.9 ± 0.3	$(5 \pm 2) \times 10^{-2}$	$(8 \pm 3) \times 10^{-3}$

inflow system of an MI-1309 mass spectrometer equipped with an electron impact ion source, and vapor phase samples were taken directly into the ionization chamber. The concentration of impurity hexafluorodisiloxane was measured in arbitrary units as the percent ratio of the intensities of base ($Si^{28}F_4^+$, $m/e = 104$) and impurity ($Si_2^{28}O^{16}F_6^+$, $m/e = 186$) molecular ions. The ion source had an ionizing voltage of 50 V, collector current of 1.5 mA, and accelerating voltage of 1.5 kV. Silicon tetrafluoride samples from the reactor were periodically analyzed during one month.

The silicon tetrafluoride samples used to synthesize silane had different impurity hexafluorodisiloxane concentrations: 99.99% monoisotopic $^{28}SiF_4$ (sample 1, NTTs Tsentrotekh, St. Petersburg), 99.99% SiF_4 of natural isotopic composition (sample 2, ZAO Astor, St. Petersburg), 99.99% monoisotopic $^{28}SiF_4$ (sample 3), 99.9% monoisotopic $^{29}SiF_4$ (sample 4), 99.9% monoisotopic $^{30}SiF_4$ (sample 5, OAO PO EKhZ, Zelenogorsk).

The heavy dump fraction (sample 6) obtained after recovering ^{28}Si isotopes from a natural mixture by centrifugation was also used for the synthesis of silane. According to the data of mass-spectrometry, this fraction had the following isotopic composition, %: Si^{28}, 58.8; Si^{29}, 24.7; Si^{30}, 16.5. The impurity hexafluorodisiloxane concentrations determined for these samples by IR Fourier-transform spectroscopy are given in the table.

Silane synthesis from initial samples 1, 2 and 6 was carried out according to the method described in [10, 11] by passing a flow of silicon tetrafluoride mixed with hydrogen (grade A) through a calcium hydride bed. Before synthesis of silane from samples 3, 4 and 5, calcium hydride and the entire laboratory unit were purged by a hydrogen (grade A) flow for 16, 8, and 24 h, respectively.

The impurity composition of synthesized silane was studied by IR Fourier-transform spectroscopy [12] and chromatography/mass spectrometry (CMS) [13, 14].

RESULTS AND DISCUSSION

As determined by mass-spectrometric analysis, the concentration of impurity hexafluorodisiloxane remains constant when fractionally distilled silicon tetrafluoride is in contact with calcium hydride at room temperature for one month. Hence, it has been established that hexafluorodisiloxane does not react with calcium hydride at room temperature and is stable in gas phase in a mixture with SiF_4, in agreement with [15].

Both the IR spectroscopy data [16] and CMS studies performed in this work show that hexafluorodisiloxane, along with disilane, is the major molecular admixture in silane synthesized by the reduction of SiF_4 (table). It should be noted that impurity Si_2H_5FO and $Si_3H_7FO_2$ were also revealed by CMS in the synthesized silane samples, but their concentrations were one order of magnitude lower than that of Si_2H_6O . In principle, the presence of these admixtures in silane may result from both reaction (6) and hydrolysis of fluorosilanes.

The table shows that the hexafluorodisiloxane concentrations in samples 1, 2, and 6 differ by three orders of magnitude. However, the same table shows that the Si_2H_6O concentration in silane synthesized from these samples according to the method [10] is at a level of 1.0%. Therefore, it might be thought that, even if hexafluorodisiloxane enters reaction (6) in the considered system at 250–300°C, this reaction is not decisive for the oxygen contamination of "fluoride" silane.

Reactions (2) and (3) are the most probable source of impurity Si_2OH_6 in "fluoride" silane. The process may be catalyzed by $Ca(OH)_2$ formed by the reaction of residual water with calcium hydride [17, 18]. The possibility of reaction (5) or analogous reactions with other fluorosilanes likewise cannot be ruled out completely. The thermodynamics and kinetics of the first two stages of hydrolysis of fluorosilanes are close to those for SiF_4 owing to the presence of the Si–F bond in their molecules. The hydrolysis of an SiF_4 molecule is thermodynamically forbidden [5], but at the same time, the activation barrier to the formation of Si_2F_6O

is much lower than for reaction (3) [19]. On the whole, this matter requires deeper studies.

From the analysis of samples 3–5, it can be seen that the preliminary purging of calcium hydride and the entire laboratory unit with a hydrogen (grade A) flow efficiently decreases the content of residual water, and the more prolonged is the purging, the lower the concentration of impurity Si_2OH_6.

In summary, the possibility of the reduction of hexafluorodisiloxane with calcium hydride in the synthesis of silane from SiF_4 has been studied. This reaction is shown to be not determinative for the oxygen contamination of silane. The reaction of SiF_4 with trace water, probably catalyzed by $Ca(OH)_2$, is most likely to cause the appearance of impurity Si_2OH_6 in "fluoride" silane. However, the hydrolysis of impurity fluorosilanes cannot be ruled out completely. It has been established that the preliminary purging of calcium hydride and the entire laboratory unit with a hydrogen (grade A) flow efficiently decreases the concentration of impurity Si_2OH_6 in silane at the stage of synthesis and excludes the need for deep purification from this low-volatile admixture by cryofiltration.

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