PECVD preparation of silicon and germanium with different isotopic composition via their tetrafluorides

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Abstract. Plasma-chemical reduction of silicon and germanium fluorides with different isotopic composition by hydrogen at low pressure was studied experimentally. Samples of silicon of natural isotopic composition and germanium polycrystalline "flakes" with isotopic numbers 72 and 74 were obtained and used to grow poly- and single crystals by the Czochralski method. The contamination by the most important impurities in each type of silicon and germanium was determined. A chemical mechanism for the reduction process was also proposed. It was shown that the direct method of reduction of isotopically-enriched fluorides is suitable for obtaining small amounts of high-purity isotopes of those elements to be used in unique physical experiments.

1. Introduction

Gaseous tetrafluorides of silicon and germanium are widely used in the PECVD technologies for preparation of thin-layer structures for multilayer cell elements, photodetectors, uncooled micro-bolometers [1-3]. Silicon tetrafluoride is of interest from the point of view of preparing bulk silicon samples with the purity grade required for photovoltaics taking into account its potentially high stocks as a byproduct of fluoride production [4]. In fact, there are no alternatives to the fluorides of silicon and germanium as initial substances for preparation of isotopic species of these IV-group elements, as there exist well-developed centrifugal technologies for enrichment of their isotopes [5]. The isotopes of silicon and germanium both in the form of thin layers and bulk crystals are used for the development of nano-electronic devices of new generation and in metrology [6,7] as well as for manufacturing the unique instruments in high-energy physics [8]. The PECVD technologies simplify considerably the process of conversion of fluorides into the target product, namely, films and polycrystalline powders (granulate) used for growth of crystals.

The goal of the present work is to systemize our recent results on preparation of bulk samples of silicon and germanium with different isotopic composition by PECVD, as well as to estimate the promising aspects of this approach for the solution of some practical problems.

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2. Experimental

The process of plasma-chemical hydrogen reduction of SiF_4 and GeF_4 was carried out in a set-up whose functional diagram is shown in figure 1.

The power of the RF generator (13.56 MHz) was 1 kW. The power applied to the area of plasma discharge was measured by a calibrated coupler in the range 300 – 700 W. The plasma density in this source can reach 5×10^{11} cm^{-3}.

The pressure during the experiment was in the range 0.1 – 0.3 Torr. The flow rate of the plasma gas $H_2 + SiF_4$ was set by mass flow controllers in the range 35 – 125 cm^3/min. The molar ratio H_2/SiF_4 was set in the range 2 – 6. The flow rate of the $GeF_4 + H_2$ plasma gas was varied in the range 70 – 120 cm^3/min, with the molar ratio H_2/GeF_4 being in the range 4 – 6.

Figure 1. The set-up for plasma reduction of silicon tetrafluoride in RF inductively-coupled discharge.

The plasma chemical reactor consisted of a quartz glass tube equipped with an inductor coupled to the RF generator via a matching device. The reactor comprised an additional tube-substrate upon which the elemental silicon and germanium were deposited in the form of polycrystals or "flakes" with an average size of several millimeters and thickness up to 100 µm. The duration of a single process with continuous deposition was four hours.

The emission spectra of $H_2 + SiF_4$-based plasma were studied by a Jobin Yvon HR 640 spectrometer in the range 190 – 750 nm (with a spectral resolution of 0.1 E).

The crystals of silicon and germanium were grown at the Leibnitz Institute of Crystal Growth (Berlin, Germany) by Dr. N. Abrosimov by the so-called "mini-Czochralski method" developed especially for growing crystals of isotopically pure silicon at extremely low loads of the crucible [9].

Secondary ion mass-spectrometry (SIMS), laser mass spectrometry (LMS), IR and Raman spectroscopy, and X-ray phase analysis were used to determine the elemental composition. The electro-physical parameters of silicon and germanium crystals were determined by standard techniques.

The experiments were conducted using silicon tetrafluoride of 99.99% purity with natural isotopic abundance (Astor Company, Sankt-Petersburg, Russia) and fluorides of germanium of 99,9% purity, namely, $^{74}GeF_4$ (enriched up to 86%) and $^{72}GeF_4$ (enriched up to 52%) (Electrochemical Plant JSC PA, Zelenogorsk, Russia).

3. Results and discussions

3.1. PECVD of silicon

The binding energy of Si-F is 5.6 eV (as a comparison, the binding energy of Si-H is 3.1 eV). This is why thermal decomposition or reduction to elemental silicon with the use of the known reducing agents is actually impossible [10]. A large number of papers have appeared (see e.g. [11–13]) devoted to the preparation of thin films of amorphous and micro-crystalline silicon from low-temperature non-equilibrium plasma based both on pure SiF_4 and on its mixture with silane and maintained by discharges of different types. However, it was only recently that this approach was used for the first time to prepare polycrystalline silicon powder [14]. A finely-dispersed powder of Si was prepared in a high-frequency induction discharge at 13.56 MHz, an input power of 4 kW and pressure of the gas
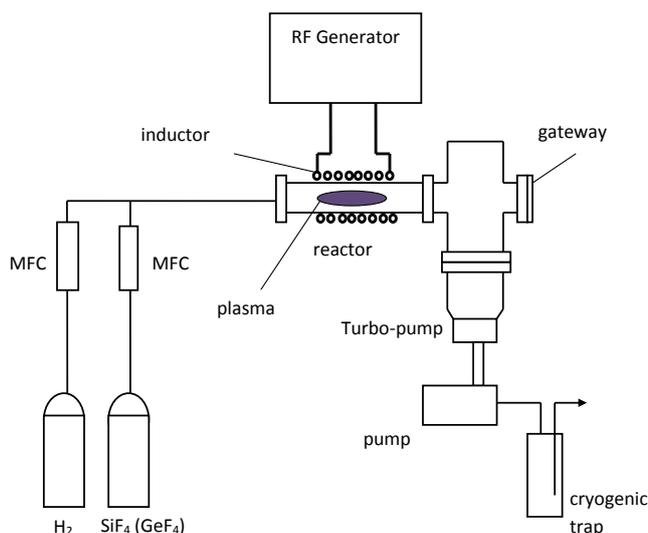
mixture SiF_4:H_2:Ar from 0.1 to 30 Torr; the process was organized in such a way as the silicon particles grew larger during the fluoride decomposition. The deposition rate was in the range from 0.5 to 5 g/hour. The authors of the cited patent [14] believe that, with the aim to increase the yield, the deposition process can be carried out at powers of up to 50 kW, pressure of $100 - 1000$ Torr and fluoride-hydrogen ratio of 1:1. However, data on the implementation of this technology, as well as quantitative data on the degree of purity of the prepared silicon are not given.

Our experiments were conducted at the lower pressure of $0.1 - 0.3$ Torr. The flow rate of the plasma gas $H_2 + SiF_4$ was set in the range $35 - 125$ cm^3/min. The molar ratio of H_2/SiF_4 was varied in the range $2 - 6$. The deposition rate of silicon under these conditions was 0.2 g/hour. We studied the dependence of the silicon yield on the specific energy input to the RF inductively-coupled discharge. The specific energy input (P) was defined as the ratio of the power (W) applied to the discharge from the source of RF oscillations to the plasma gas flow (Q):

$$P = W/Q. \tag{1}$$

The yield of silicon increased monotonically from 13 to 56 % as the energy input was raised from 7 to 25 MJ/mol. The further increase of the energy input of $25 - 37.3$ MJ/mol did not change the yield of silicon. Probably, the yield of silicon, equal to 56 % under these conditions, is of a quasi-equilibrium nature and the energy input value of 25 MJ/mol is the optimum one. The minimum energy input (the ratio of energy input to the degree of fluoride conversion) is 10.2 kWh per mol of silicon and corresponds to the "energy cost" of the product.

According to [15], the energy of free electrons in the plasma of a RF discharge is $7 - 10$ eV at a pressure of $0.1 - 0.3$ Torr. As it is indicated in [16], this energy is sufficient for the dissociation of the H_2 molecule and formation of atomic hydrogen. This is why we can assume with high probability that the reduction of SiF_4 occurs with the participation of $H^{\bullet}$. Other intermediate particles assisting the reduction of silicon tetrafluoride were identified from the emission spectra of plasma. The set of our and literature data [17-21] makes it possible to assume the following mechanism of solid-phase formation of silicon under the conditions of our experiment.

$$H_2 \rightarrow 2H, \tag{2}$$
$$SiF_4 + H^{\bullet} \rightarrow SiF_3^{\bullet} + HF, \tag{3}$$
$$SiF_3^{\bullet} + H_2 \rightarrow SiF^{\bullet} + 2HF, \tag{4}$$
$$SiF^{\bullet} \rightarrow SiF_{ads} + H^{\bullet} \rightarrow \textbf{Si}\downarrow + HF. \tag{5}$$

In addition, since the line corresponding to the $SiH^{\bullet}$ radical is present in the plasma emission spectrum, it is reasonable to assume that the following reactions take place:

$$SiF^{\bullet} + H_2 \rightarrow SiH^{\bullet} + HF, \tag{6}$$
$$SiH \rightarrow \textbf{Si}\downarrow + H. \tag{7}$$
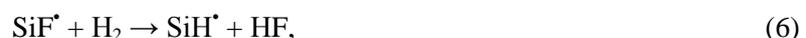
The silicon deposited on the inner surface of the reactor consists of "flakes" with a size of about $3 - 5$ mm and a polycrystalline structure, as evidenced by X-ray phase analysis. A bulk polycrystal of p-type with a mass of about 10 g, a concentration of carriers of 10^{17} cm^{-3} and a resistivity of $\rho = 0.3$ Ohm cm was grown from the prepared silicon by the Czochralski method.

Table 1 presents data on the content of impurities in the initial tetrafluoride, in the polycrystalline "flakes" immediately after deposition and in the bulk polycrystal.

The main conclusion from the data presented in table 1 is that the polycrystalline silicon "flakes" prepared were contaminated by oxygen, carbon, hydrogen, and, probably, by fluorine during the plasma-chemical deposition. The reason for the increased content of the latter two impurities is understandable. The sharp increase in the concentration of oxygen is connected with the process of oxidation of silicon powder with a developed surface during the contact with the environment. The

increase in the concentration of carbon is less clear and can be connected with the use of gaskets made of synthetic materials subjected to a relatively high temperature. The content of the cited gas-forming impurities in the crystal grown by the Czochralski method is decreased by more than an order of magnitude. It should be noted that the content of oxygen in the crystal, according to the data of IR spectroscopy and SIMS, is at the level of 10^{18} cm^{-3} (which is typical for the Czochralski method where oxygen enters the melt from the quartz crucible); that of carbon is at the level of 5×10^{17} cm^{-3} (which exceeds by an order of magnitude the content of this impurity in "Czochralski" silicon prepared by the known technologies). The content of electro-active impurities (P, As, B) does not increase during transition from gas to crystal.

Table 1. Comparison of the content of impurities (ppm wt) in the initial SiF$_4$, in polycrystalline silicon "flakes" after plasma chemical deposition and in the polycrystal prepared by Czochralski (Cz) method.

Impurity	SiF$_4$ (GC[a] and AAS[b] data according to certificates of manufacturer)	PECVD Si "flakes" (SIMS data)	Cz bulk silicon polycrystal	
			SIMS and IR data	LMS[c] data
H	0.1	3	<0.3	-
O	0,5	130 – 700	13	-
C	1.2	20 – 200	5	-
F	-	16 – 160	<16	<2
P	0.5	<2.5	<0.25	<0.6
As	0.5	<6	<0.6	0.3
B	0.5	<1	0.5-1	0.04

[a] GC - gas chromatography, [b] AAS - atomic absorption spectroscopy, [c] LMS - laser mass spectrometry.

Thus, the PECVD method makes it possible to prepare silicon polycrystals of satisfactory quality. However, to implement it even in an enlarged laboratory version it is necessary to solve a number of problems connected with increasing the process rate and the silicon yield, as well as with the extracting the prepared powder from the reactor without contact with the environment. If these problems are successfully solved, the technology proposed can be used, first of all, for production of silicon enriched with the silicon-28 isotope. The demand for this expensive material for metrology can amount to tens of kilograms per year [6].

3.2. PECVD of germanium

The binding energy of Ge-F is somewhat less than the binding energy of Si-F, namely, 4.8 eV. However, achieving a sufficiently high yield of germanium as a result of thermal decomposition or chemical reduction of the fluoride is quite problematic, as evidenced by thermodynamic calculations. Moreover, in contrast with silicon, during the plasma-chemical reduction of germanium tetrafluoride, apart from deposition of particles of polycrystalline germanium, formation of polyfluorogermanes of different compositions, easily hydrolyzed in air, was observed; this was proved by X-ray phase and mass spectrometric analyses. The yield of germanium is constant in the range of energy input from 27 to 50 MJ/mol and is 85 %. The minimum energy consumption is 8.6 kWh per mol of germanium. Meanwhile, the yield of polyfluorogermanes reaches 15 %. However, it was found that raising the energy to more than 70 MJ/mol results in increasing the yield of germanium up to 90 %, which is accompanied by a sharp drop in the efficiency of polyfluorogermanes formation. The deposition rate of germanium under our conditions was 5 g/h.

The reduction of germanium tetrafluoride by atomic hydrogen at a small energy input via the stages of fluorogermanes formation can be represented in the following way:

$$H_2 \rightarrow 2H^{\cdot}, \tag{8}$$
$$GeF_4 + H^{\cdot} \rightarrow GeHF_3 + F^{\cdot}, \tag{9}$$
$$GeHF_3 + H^{\cdot} \rightarrow GeH_2F_2 + F^{\cdot}, \tag{10}$$
$$GeH_2F_2 + H^{\cdot} \rightarrow GeH_3F + F^{\cdot}, \tag{11}$$
$$GeH_3F + H^{\cdot} \rightarrow GeH_4 + F^{\cdot}, \tag{12}$$
$$GeH_4 \rightarrow \mathbf{Ge}\downarrow + 2H_2, \tag{13}$$
$$F^{\cdot} + H^{\cdot} \rightarrow HF, \tag{14}$$
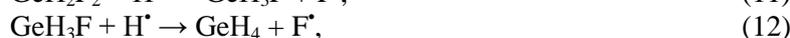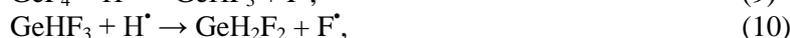
with subsequent polymerization of the fluorogermanes molecules. According to the literature data [22], in a certain temperature range in an electric discharge, formation of radicals of germanium fluorides $GeF^{\cdot}$ and $GeF_2^{\cdot}$ is possible followed by polymerization:

$$GeF_4 + 2H \rightarrow GeF_2^{\cdot} + 2HF, \tag{15}$$
$$nGeF_2^{\cdot} \rightarrow (GeF_2^{\cdot})n, \text{ where } n = 2\text{-}8 \tag{16}$$
or
$$nGeF_2^{\cdot} + mGeF^{\cdot} \rightarrow (GeF_2^{\cdot})_n(GeF^{\cdot})_m, \tag{17}$$
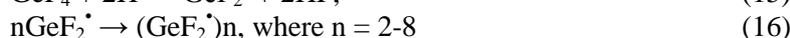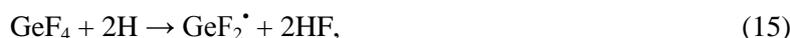
where n and m denote the mole number of the corresponding species.

This was proved by the initial increase in the yield of polyfluorogermanes with the increase of the energy input. However, as the energy input is raised further, the following processes can, probably, be the determinative ones in providing a high yield of germanium:

$$GeF_4 + H^{\cdot} \rightarrow GeF_3^{\cdot} + HF, \tag{18}$$
$$GeF_3^{\cdot} + H^{\cdot} \rightarrow GeF_2^{\cdot} + HF, \tag{19}$$
$$GeF_2^{\cdot} + H^{\cdot} \rightarrow GeF^{\cdot} + HF, \tag{20}$$
$$GeF^{\cdot} + H^{\cdot} \rightarrow \mathbf{Ge}\downarrow + HF. \tag{21}$$

As was already mentioned, we were provided with samples of GeF_4 with different degrees of enrichment by the isotopes ^{74}Ge and ^{72}Ge.

Table 2 presents the content of impurities in ^{74}Ge in the form of polycrystalline "flakes" immediately after deposition and in the single crystal prepared on its basis (with a mass of about 20 g). The charge carriers concentration in the single n-type crystal was $n = 9\times10^{14}$ cm^{-3}, with the resistivity being 1.9 Ohm cm. A slight dilution of the germanium-74 isotope was observed during growth (83 % against 85.9 %) connected with the use of a seed of natural germanium. As in the case of silicon,

Table 2. Comparison of the content of impurities (at/cm^3) in polycrystalline ^{74}Ge "flakes" after plasma chemical deposition and in the single crystal grown on its basis by the Czochralski method.

Impurity	Prepared by PECVD ^{74}Ge "flakes" (SIMS data)	^{74}Ge single crystal	
		SIMS and IR data	LMS data
H	$10^{17} - 10^{18}$	$10^{15} - 10^{16}$	-
O	$10^{19} - 10^{20}$	$10^{16} - 5\times10^{16}$ (1×10^{17} by IR-spectroscopy data)	-
C	$10^{18} - 10^{19}$	$10^{15} \times 10^{16}$	$<2\times5\cdot10^{19}$
F	$10^{18} - 10^{19}$	$10^{16} - 5\times10^{16}$	$<1.5\times10^{16}$
P	$<5\times10^{15} - 10^{16}$	$<5\times10^{15} - 10^{16}$	$<5\times10^{15}$
As	$<5\times10^{15} - 10^{16}$	$<5\times10^{15} - 10^{16}$	$<2.5\times10^{19}$
B	$<5\times10^{15} - 10^{16}$	$<5\times10^{15} - 10^{16}$	$<8\times10^{15}$

during the transition to the bulk crystal the content of the gas-forming impurities decreased and the content of the electro-active impurities was below the limit of detection by SIMS and LMS. While comparing the data of the tables 1 and 2, one can see that the germanium prepared by PECVD is characterized, as a whole, by a lower content of impurities as compared with silicon.

The mass of the prepared polycrystalline ^{72}Ge was about 50 g. Four single crystals were grown sequentially from this material. The mass of the last (the purest) crystal was 20.6 g. The concentration of charge carriers in its initial ("pure") part was $n = 3.5 \times 10^{12}$ cm^{-3} ($\rho > 40$ Ohm cm) (note the difference with the data for the ^{74}Ge crystal given above). The content of phosphorus and arsenic in the "pure" part was determined by IR spectroscopy at helium temperature. According to this data, the content of phosphorus was 8×10^{13} and 9×10^{12} cm^{-3}, the content of arsenic was 4×10^{14} and 7×10^{12} cm^{-3}, respectively. The content of oxygen in the samples investigated was determined by the same method at room temperature; it was less than 1.0×10^{15} cm^{-3}. In what concerns the characteristics quoted, the single crystal of ^{72}Ge corresponds to the best samples of semiconductor germanium. This is why the direct PECVD method proposed seems quite promising for the preparation of ^{76}Ge crystals with a degree of enrichment of about 8 0% which are planned to be used in the experiments on determining the neutrino mass within the framework of the GERDA project [8].

4. Conclusions
The experiments conducted indicate that the PECVD method based on a RF discharge with fluorides as the initial plasma-forming substances can be successfully used for the preparation of bulk samples of silicon and germanium. The substance deposited is in the form of "flakes", the bulk poly- or single crystals being subsequently grown from them. The main technological parameters are still inferior to those of germanium. The approach proposed is considered to be promising, first of all, for preparation of comparatively small (tens of kilograms) amounts of expensive isotopically pure crystals of silicon and germanium since their tetrafluorides enriched by centrifuging are commercially available.

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