

Plasma chemical production of stable isotopes of germanium from its fluorides^{*}

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Abstract. The reduction process of $^{72}\text{GeF}_4$ in hydrogen plasma of RF-discharge (13.56 MHz) was experimentally investigated. It was found that ^{72}Ge , polyfluorogermanes and gaseous HF were the main products of conversion. The behavior of the main electroactive impurities and of metal impurities in the process of hydrogen reduction of $^{72}\text{GeF}_4$ was considered. Based on the data of emission spectroscopy of chemically active plasma, assumptions were made about the main plasma-chemical reactions responsible for the process of hydrogen reduction of $^{72}\text{GeF}_4$. A single crystal of *n*-type with concentration of charge carriers of $<1 \times 10^{13} \text{ cm}^{-3}$, $\rho = 47 \Omega \text{ cm}$ was produced using a Czochralski method after the process of zone recrystallization of ^{72}Ge .

1 Introduction

Germanium tetrafluoride is the most suitable starting substance with respect to its physical and chemical characteristics for production of five isotopic varieties of germanium by the centrifugal method [1]. Isotopes of germanium find their application in fundamental investigations, e.g., for registration of the process of neutrinoless double β -decay of the nuclei of germanium isotope enriched with ^{76}Ge isotope [2]. For this purpose a high-purity single crystal of ^{76}Ge is required with enrichment of 88% in amounts from several tens to several hundreds of kilograms. The application of germanium isotopes is of interest for investigation of processes depending on nucleus spin. The detector, fabricated from monocrySTALLINE germanium-73 with semi-integral value of nuclear spin 9/2, is used in experiments on searching for “dark matter” [3]. On the other hand, germanium, depleted with ^{73}Ge isotope, is a promising material for investigation of the processes depending on electron spins and nuclei in solid bodies [4,5]. High cost of enriched germanium demands the minimization of reversible and irreversible losses of substance at the preparation step. That is why the development of highly-efficient single-stage methods for extraction of isotopically modified germanium from its tetrafluoride is an important task. The plasma chemical methods for reduction of germanium tetrafluoride are

quite promising. Previously [6] we have shown the possibility to prepare polycrystalline powder of Ge in $\text{GeF}_4 + \text{H}_2$ plasma maintained by RF (13.56 MHz) inductively-coupled discharge.

The goal of the present work is to investigate and analyze the process of plasma chemical reduction of germanium tetrafluoride in hydrogen plasma, examine the content of prepared products and prepare high-purity isotopically enriched single crystal ^{72}Ge of semiconductor quality.

2 Experimental

In this work germanium tetrafluoride with a purity of 99.99%, enriched with ^{72}Ge isotope up to 51.65%, was used. The process of plasma chemical reduction of germanium tetrafluoride in RF inductive and capacitive discharges was carried out on the setup with the principal scheme shown in Figure 1.

The power of the RF oscillations was 1 kW with a frequency of 13.56 MHz. The power, input to the zone of plasma discharge, was determined as the difference in power of the corresponding reflected and incident waves measured with a directional coupler with directivity coefficient 30 dB and was changing in the range $(500\text{--}950) \pm 30 \text{ W}$. The consumption of plasma-forming gas $\text{H}_2 + \text{GeF}_4$ was set by flow rate regulators in the range $(75\text{--}200) \pm 5 \text{ cm}^3/\text{min}$. During this experiment the pressure was changed in the range of 0.1–10 torr. The mole ratio H_2/GeF_4 was changed in the range of 2–25. The plasma

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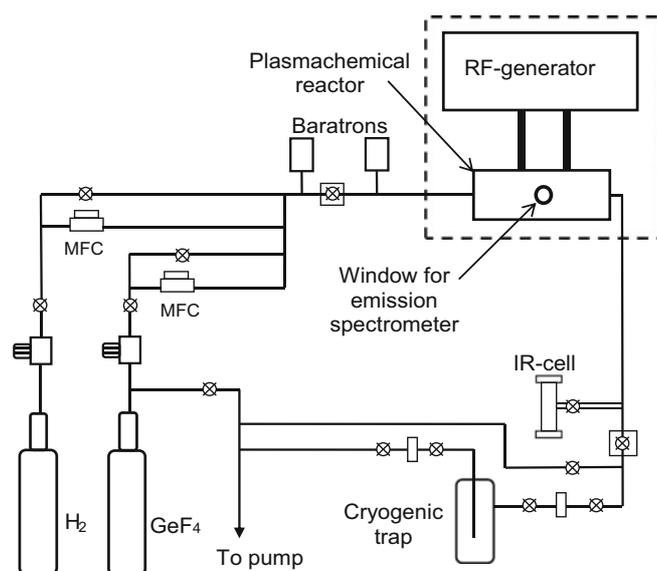


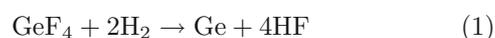
Fig. 1. Setup for plasma chemical reduction of GeF_4 in hydrogen plasma.

chemical reactor was composed of a quartz glass tube with an installed inductor or ring electrodes connected with RF generator via the matching device. Additional tube-substrate was placed in the reactor upon which the reaction products deposited. The quartz trap device was mounted at the outlet of the tube-substrate to provide complete catching of the condensed phase for trapping the polymerization products, while for trapping the gaseous products the cryogenic trap was used. The conversion process of germanium tetrafluoride into germanium as well as other possible by-products of reaction was experimentally investigated. The total degree of conversion of GeF_4 was determined by the method of IR spectroscopy with an accuracy of 0.1% mole (Bruker Vertex 80v spectrometer). The yield of germanium and polyfluorogermanes was determined by a gravimetric method with accuracy of 1×10^{-3} g. The chemical composition of polyfluorogermanes was determined by mass spectrometry by a Polaris Q instrument with an ion mass analyzer. The emission spectrum of the chemically active plasma was investigated in the range of 350–950 nm by emission spectrometer HR4000CJ-UV-NIR. The concentration of the main electroactive impurities and of metal impurities in the initial germanium tetrafluoride as well as in germanium and polyfluorogermanes was determined by mass spectrometry on sector high-resolution mass spectrometer with ionization in inductively coupled plasma ELEMENT-2. The ingot of polycrystalline germanium was formed in argon at atmospheric pressure. The process of zone recrystallization was carried out in an environment of high-purity hydrogen in a quartz glass container with coating from amorphous silicon dioxide. The zone was heated with an electromagnetic field at a frequency of 440 kHz. The rate of zone movement was 10 cm/h; the number of passes was 10. The Czochralski method was used for preparation of a single crystal of germanium.

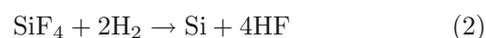
3 Results and discussion

In the process of experiment the deposition of elementary germanium on the inner tube-substrate and the appearance of a deposit of brown color were observed. It was pointed out in reference [7] that this residue of undetermined composition is formed during decomposition of germanium difluoride at temperatures higher than 130 °C and probably represents the polymer $(\text{GeF}_2)_n$. With the increase in temperature this product transforms into elemental germanium. In a mass spectrum of the deposit (Fig. 2a) the following fragment ions of different mass are observed: GeF^+ ($M = 91.5$), GeF_2^+ ($M = 109.2$), Ge_2F_4 ($M = 219.2$), Ge_2F_5^+ ($M = 239.0$), Ge_3F_6^+ ($M = 329.0$), Ge_3F_8^+ ($M = 366.9$) which proves the possibility of formation of the compounds of $(\text{GeF}_2)_n$ type.

As was previously explained, the conversion degree of germanium tetrafluoride was determined by the method of IR spectroscopy (Fig. 2b). Apart from the characteristic vibration bands of Ge-F bonds at 800, 1533 and 1592 cm^{-1} , in the IR-spectrum of the initial GeF_4 the band of impurity absorption at 1030 cm^{-1} , corresponding to Si-F vibrations of SiF_4 molecules, was observed which is a characteristic impurity in GeF_4 [8,9]. The content of SiF_4 was about 3% mol. In the IR-spectrum of the gas mixture, escaping from the reactor of gas mixture, the intensive absorption of HF molecules was observed in the range of 4000 cm^{-1} as well as the band in the range of 3000 cm^{-1} referring to molecules of HCl. Hydrogen fluoride is one of the reduction products of GeF_4 :



and, perhaps, of the impurity molecules SiF_4 :



The appearance of a weak band of HCl molecules is, perhaps, due to hydrogen reduction of the impurity of germanium tetrafluoride to GeF_4 . Unfortunately, its identification by the method of IR-spectroscopy is impossible due to overlapping of absorption bands Ge-F and Ge-Cl.

Characteristic vibration bands of GeF_4 molecules in exhaust gases were not observed under the given conditions for spectra registration which proves the complete conversion into solid-state reaction products with corresponding value of energy input. It should be noted that the intensive absorption bond of Si-F is still observed. It is, possibly, connected either with low efficiency of the concurrent reaction (4) or (which is more probable) with etching of the walls of the quartz reactor by hydrogen fluoride. At the maximum value of energy contribution 15.4 MJ/mol under RF inductively-coupled plasma the degree of conversion of GeF_4 into Ge is 86%. At the same value of energy contribution under RF capacitive discharge the degree of conversion of GeF_4 into Ge is not more than 35%.

In the process of plasma chemical reduction of germanium tetrafluoride with the value of energy contribution of 15.4 MJ/mol the behavior of the main electro-active

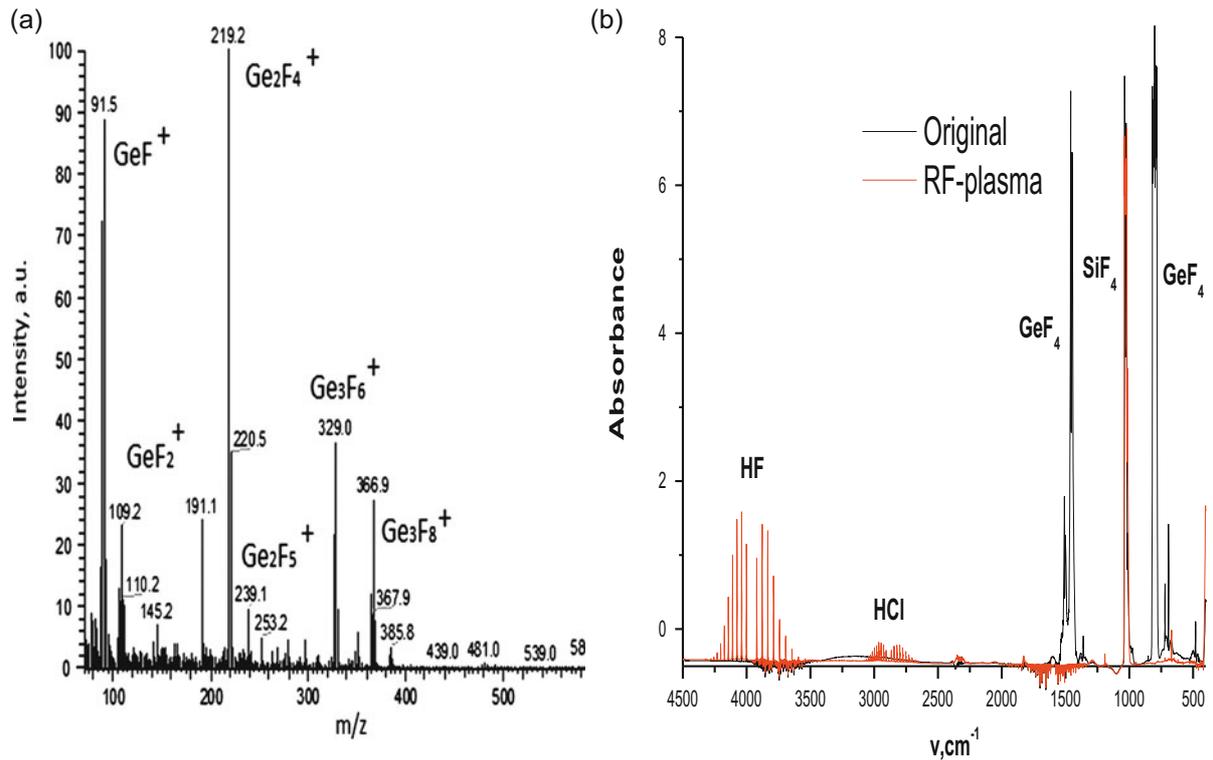


Fig. 2. Mass-spectrum of polyfluorogermanes (a); IR-spectrum of initial GeF₄ and gas mixture after reactor (b).

impurities B, P, Al, As, Sb and of metal impurities was studied. Table 1 shows the content of these impurities in the initial GeF₄, Ge as well as in polyfluorogermanes. It follows from the table that during reduction the effect of redistribution of impurities is observed contained in the initial germanium tetrafluoride between the synthesized Ge and polyfluorogermanes. It can be assumed that these impurities in germanium tetrafluoride exist as well in the form of fluorides of XF_n type (where X is the atom of impurity, n = 3–6) and have different interaction cross-sections with free plasma electrons. This fact determined the redistribution of their concentrations in the reaction products.

With the aim to get a more detailed representation of the mechanism of hydrogen reduction of germanium tetrafluoride under the optimum conditions for preparation of germanium investigations of the composition of chemically active plasma by emission spectroscopy method were carried out.

Figure 3 shows the emission spectra of RF plasma of H₂ + GeF₄ mixture under the conditions of inductively-coupled (H₂/GeF₄ = 4, p = 0.25 torr) and capacitive (H₂/GeF₄ = 4, p = 3.5 torr) discharges. The lines at 486.13 and 656.2 nm wavelengths are observed in the spectrum of inductively coupled discharge corresponding to the emission of atomic hydrogen H_β and H_α as well as the lines of the alpha-Fulcher series in the 575–625 nm range and the lines in 390–450 nm range connected, according to [7], with GeF radicals. The lines corresponding to the GeF₂ radicals, present in the 320–390 nm range [10], as

well as to free fluorine at 703.75 nm [11], were not registered in the spectrum.

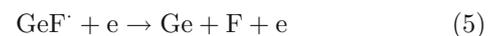
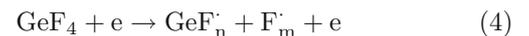
The lines characteristic of radicals GeF and GeF₂, are not registered in the spectrum of capacitive discharge but the line at 385 nm wavelength is registered connected with GeH radicals as well as the line at 703 nm wavelength connected with atomic fluorine.

Taking into consideration the peculiarities observed in emission spectra as well as the formation of Ge, (GeF₂)_n and HF, the following reaction stages can be proposed to describe the mechanism of reduction of GeF₄ with hydrogen.

The formation of atomic hydrogen takes place in both types of discharge:



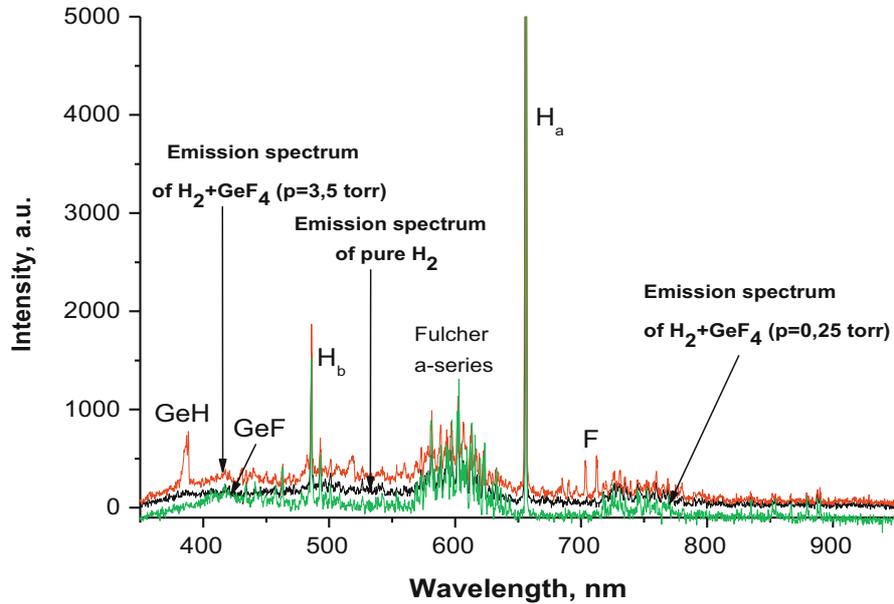
The formation of germanium-containing radicals as well as of Ge and (GeF₂)_n in inductively-coupled plasma is possible by reactions (4)–(7):



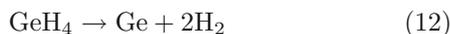
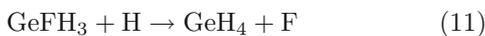
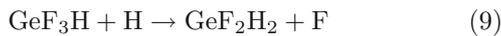
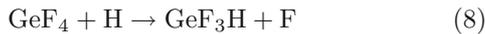
Under capacitive discharge the most probable is the process of interaction of atomic hydrogen with GeF₄

Table 1. Content of impurities in the GeF₄, Ge and polyfluorogermanes.

| Impurities (ppm wt.) | Initial GeF ₄ (expressed as met. Ge) | Ge | Poly-GeF |
|-------------------------|--|-------------|--------------|
| B | 1.2 ± 10% | <0.3 ± 20% | <0.3 ± 20% |
| As | 1.6 ± 10% | 0.9 ± 10% | 0.4 ± 10% |
| Sb | <0.002 ± 20% | 0.003 ± 20% | <0.002 ± 20% |
| Al | 10.3 ± 10% | 4.2 ± 10% | 5.2 ± 10% |
| P | <3 ± 20% | <3 ± 20% | <3 ± 20% |
| Ti | 2.47 ± 10% | 1.1 ± 10% | <0.9 ± 20% |
| Cr | <0.1 ± 20% | 0.2 ± 10% | <0.1 ± 20% |
| Cu | 0.6 ± 10% | 0.4 ± 10% | <0.1 ± 20% |
| Zn | 0.8 ± 10% | 1 ± 10% | <0.3 ± 20% |
| Mn | <0.04 ± 20% | 0.07 ± 10% | <0.04 ± 20% |
| Mo | 0.018 ± 10% | 0.017 ± 10% | <0.005 ± 20% |
| Mg | <1.3 ± 20% | <1.3 ± 20% | <1.3 ± 20% |
| W | <0.06 ± 20% | <0.06 ± 20% | <0.06 ± 20% |
| Se | <0.4 ± 20% | <0.4 ± 20% | <0.4 ± 20% |


Fig. 3. Emission spectrum of pure H₂ and H₂ + GeF₄ mixtures.

molecules with successive substitution for the atoms of fluorine by hydrogen with subsequent formation of fluorogermanes and germane with further thermal decomposition according to reactions (8)–(12):



The formation of the ingot of polycrystalline germanium was carried out by the Czochralski method in argon under atmospheric pressure. The average rate of drawing was 1.5 cm/min. The prepared crystal of ⁷²Ge with a mass of 35 g was of *n*-type conductivity with a specific resistance $\rho = 0.8 \Omega \text{ cm}$. Further it was subjected to zone recrystallization in the environment of high-purity hydrogen in a quartz glass container coated with amorphous silicon dioxide. The zone was heated with an electromagnetic field at frequency of 440 kHz. The zone pass rate was 10 cm/h. After 10 passes of the zone the single crystal was prepared with specific resistance $\rho = 50$ and $4 \Omega \text{ cm}$ at the front and end of the ingot, respectively. Then by the Czochralski method the *n*-type single crystal of ⁷²Ge was grown with a mass of 12 g (Fig. 4). The concentration of charge carriers in the initial (pure) part was $< 1 \times 10^{13} \text{ cm}^{-3}$, $\rho = 47 \Omega \text{ cm}$.

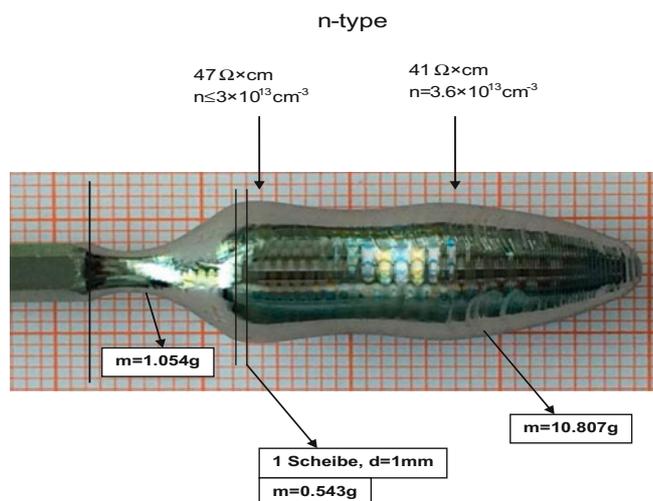


Fig. 4. Single crystal ^{72}Ge .

4 Conclusion

As a result of the conducted investigations we can conclude that it is possible to prepare germanium by direct plasma chemical reduction with hydrogen in RF discharge. The main condensed products are germanium and polyfluorogermanes and the main gaseous product is hydrogen fluoride. Under the conditions of inductively-coupled discharge at a pressure of 0.25 torr the radical mechanism of germanium formation with participation of GeF^{\cdot} is the main one while under the conditions of capacitive discharge at a pressure of 3 torr the germanium is prepared by reaction between atomic hydrogen and germanium

tetrafluoride via formation of intermediate compounds, i.e., fluorogermanes, fluorine and germane (GeH_4). With the use of further technological steps we show it is possible to produce single crystalline isotopically enriched germanium of semiconductor grade.

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