Plasma-enhanced CVD preparation of isotopes of group IV and VI elements

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Abstract. The plasma-chemical reduction was studied experimentally of molybdenum, sulfur and germanium fluorides with different isotopic composition by hydrogen in plasmas sustained by inductively coupled (IC) and capacitively-coupled (CC) RF discharges. The emission spectra of plasmas recorded under different experimental conditions are discussed. Reaction mechanisms are proposed. In the case of $^{98}$MoF$_6$ reduction in CCP, the combined radical-atomic mechanism including intermediate MoF$_3$ resulting in bulk and powder $^{98}$Mo formation was established. In the emission spectrum of the $^{32}$SF$_6$ + H$_2$ system in ICP at 0.2 Torr, only lines assigned to SiF$_2$, SiF and F$_2$ originating from the decomposition of $^{32}$SF$_6$ and a fast reaction of its products with the reactor’s quartz walls were observed. Due to this etching process, the yield of $^{32}$S was moderate. Increasing the pressure in the reactor above 1 Torr resulted in an increase of the $^{32}$S yield. The mechanism of $^{72}$GeF$_4$ reduction depends on the pressure and plasma type. At 0.25 Torr in ICP, a $^{72}$Ge deposit was formed via the $^{72}$GeF radical; however, at 3.5 Torr in CCP, the mechanism changed to a molecular one. Results of the study of the structure and the isotopic and chemical purity of isotope samples obtained are briefly presented.

1. Introduction

The RF glow discharges used for plasma-enhanced chemical vapor deposition (PECVD) consist of partially ionized gases containing ions, electrons and a variety of neutral species in both ground and excited states. Plasmas are ignited and sustained by applying an RF voltage at frequencies between 50 kHZ and 13.56 MHz to a low pressure (~10 mTorr – 10 Torr) gas. These conditions produce a highly reactive environment. E.g., the electron (and positive ion) densities are between $10^8$ and $10^{12}$ cm$^{-1}$, and the average electron energies are several electron volts, while the ion (and neutral) energies are at least two orders of magnitude lower. Because of such differences in the particles’ energies, the term nonequilibrium plasmas is used to describe these discharges. The electrons gain energy via acceleration by an alternating electric field, which results in elastic collisions between the high-energy electrons and the neutral gas molecules. These impact reactions can be assigned to three general categories: excitation, dissociation, and ionization. The excitation and dissociation processes generally require energies of a few electron volts or less. As a result, the discharge produces a large concentration of free radicals, both by direct dissociation and by electronic excitation into an
antibonding states that may ultimately lead to dissociation. By comparison, the ionization of most molecules or atoms requires electron energies above ~ 7 eV, so relatively few ions are formed. The ratio of the electron concentration to the neutral species (radicals, molecules) concentration is less than 10^3. This property leads to the fact that neutral species, rather than ions, are the primary contributors to solid phase deposition. That is, neutrals are not more chemically reactive, but are present in much higher concentrations compared to the ions.

Depending on the experimental conditions, the solid deposits have different chemical and phase structures. This is why the PECVD method is widely used for laboratory and industrial production of different chemical substances and elements.

The advantage of this approach is clearly demonstrated in the case of precursors with high-energy chemical bonds. Inorganic fluorides of different elements belong to this group of substances. Besides, fluorine is monoisotopic, so that the volatile fluorides are used in centrifugal processes of isotopic separation (enrichment). The classical illustration of this approach is the isotopic enrichment of uranium hexafluoride.

This report summarizes the main results of recent investigations carried out at the Institute of Chemistry of High-Purity Substances and the Institute of Applied Physics of Russian Academy of Sciences in Nizhny Novgorod in creating the physical-chemical background of plasma-chemical production of chemically and isotopically pure IV and VI group elements (molybdenum, sulfur and germanium) from their enriched fluorides.

Some of the molybdenum isotopes are valuable tools for studies of mineral metabolism in humans [1]. In recent years, a significant interest appeared in uranium-molybdenum (UMo) fuel to be used in Material Test Reactors [2]. This interest was due to the fact that UMo fuel is mechanically stable, even at high uranium concentrations and high U-burnup. For this goal, Mo in a bulk form is required, depleted of ^{95}Mo and with a high thermal neutron cross-section. Of the greatest interest is to use the ^{95}Mo, ^{96}Mo, ^{99}Mo, and ^{100}Mo stable isotopes for production of ^{97}Ru, ^{96}Tc, ^{95m}Tc, and ^{99m}Tc radioisotopes which, in their turn, are widely used in medicine for diagnostic and treatment of cancer and cardiovascular disease. The most popular are the radio-pharmaceutical drugs based on ^{99m}Tc which originate from ^{99}Mo with a half-life of 66.02 hours. The radiative capture method for ^{99}Mo production from ^{98}Mo nano-powder targets is very promising among all other reactor and non-reactor alternatives.

Production of high-purity isotopically enriched sulfur ^{32}S is an important task for determining the isotopic effect influence on the elementary sulfur properties, as well as on the properties of sulfur-based vitreous and semiconductor compounds, such as germanium sulfides or arsenic sulfides glasses and films in terms of their optical and physical characteristics [3].

The isotopes of germanium, both in the form of thin layers and bulk crystals, are used for the development of nano-electronic devices of a new generation, as well as for manufacturing unique instruments in high-energy physics [4].

2. Experimental

The starting fluorides, namely ^{98}MoF_6 (98.5% enriched), ^{32}SF_6 (99.6% enriched), and ^{72}GeF_4 (52% enriched) were produced by SC “PA Electrochemical Plant”, Zelenogorsk, Russian Federation.

The process of their plasma chemical hydrogen reduction was carried out in the set-up shown in figure 1. The power of the RF generator (13.56 MHz) was 1 kW. The power applied to the plasma discharge area was measured by a calibrated coupler in the range 300 – 700 W.

The process of plasma-chemical reduction was studied in capacitively-coupled plasma (CCP) for ^{98}MoF_6, ^{32}SF_6 and ^{72}GeF_4, and inductively-coupled plasma (ICP) for ^{32}SF_6 and ^{72}GeF_4. The difference in these types of plasmas is that the plasma-sustaining capacitively-coupled discharge at a pressure P ~ 1 – 10 Torr is characterized by a low current strength (10^{-6} – 10^{-1} A) and a high voltage value (10^2 – 10^3 V). The plasma-sustaining inductively-coupled discharge at a pressure P ~ 0.1 – 1 Torr is characterized by a high current strength (10^2 – 10^3 A) and a low voltage value (1 – 10 V). The different parameters of these discharges result in different mechanisms of electron production and in
different plasma-chemical reactions mechanisms. Thus, one can also expect differences in the deposited materials structure.

The flow rate of the plasma-forming gas $\text{H}_2 + \text{MF}_n$ (M = $^{98}$Mo, $^{32}$S, $^{72}$Ge; $n = 4, 6$) was adjusted by mass-flow controllers and was equal to $0 – 310 \pm 5 \text{ cm}^3/\text{min}$. The dilution ratio for $\text{H}_2/\text{MF}_n$ varied from 2 to 25. The plasma chemical reactor was made of quartz with an inductor coil or ring electrodes powered by the RF-generator through a matching device. In the case of CCP, a quartz trap was placed below the quartz reactor to collect the Mo powder. In the case of ICP, an additional quartz tube, the substrate, was placed inside the reactor where the reaction products were deposited. There was a cryogenic trap at the output of substrate tube designed to completely entrap the condensed phase. The total degree of conversion of fluorides to molybdenum, sulfur and germanium was determined by IR spectroscopy (a Bruker Vertex 80v spectrometer) with an accuracy of 0.1%. The condensed phase yield was measured gravimetrically with an accuracy of $1 \times 10^{-3}$ g. The emission spectrum of the chemically active plasma was examined in the range 350 – 950 nm by an HR4000CJ-UV-NIR emission spectrometer. The characterization of $^{98}$Mo, $^{32}$S and $^{32}$Ge in a solid form (layers, powder, bulk) was carried out by XRD, SEM, and EDX. For isotope and impurities, the controlling methods of SIMS, laser-mass-spectrometry, ICP mass-spectrometry and atomic-emission spectrometry were used.

3. Results and discussions

3.1. PECVD of molybdenum
In CCP, the molybdenum was mainly deposited on the inside surface of the quartz tube in the form of a thick layer, but a small part (less than 3%) was deposited as powder in the special trap. The absence of $^{90}$MoF$_6$ vibrational modes in the FTIR spectrum of the exhaust gases is indicative of the practically total conversion of $^{98}$MoF$_6$ to solid reaction products. To obtain more detailed information about the hydrogen reduction mechanism under the given experimental conditions, spectra of chemically-active plasma of the $\text{H}_2 + ^{98}\text{MoF}_6$ mixture were acquired by emission spectroscopy.

The spectrum of CCP of $\text{H}_2 + ^{98}\text{MoF}_6$ with ratio $\text{H}_2/^{98}\text{MoF}_6 = 4$ and pressure $p = 3 \text{ Torr}$ contains the lines at 486.13 and 656.2 nm originating from emission of atomic hydrogen $H_\beta$ and $H_\alpha$, respectively, while the line at 703 nm was assigned to atomic fluorine (figure 2). We suggest several basic reactions responsible for hydrogen reduction of $^{98}$MoF$_6$ in CCP:

$$H_2 \rightarrow 2H,$$  
$$^{98}\text{MoF}_6 + e \rightarrow ^{98}\text{MoF}_3 + F,$$  
$$F + H \rightarrow HF.$$  
$$^{98}\text{MoF}_6 + e \rightarrow ^{98}\text{MoF}_4 + 2F,$$  
$$^{98}\text{MoF}_3 + e \rightarrow ^{98}\text{Mo} + 3F,$$  
$$^{98}\text{MoF}_4 + e \rightarrow ^{98}\text{MoF}_2 + F.$$  

3
The formation of traces of $^{98}\text{MoF}_4$, $^{98}\text{MoF}_3$ and the predominant formation of $^{98}\text{Mo}$ according to reactions (2), (3) and (4) was confirmed by XRD, and the hydrogen fluoride byproduct according to reaction (5), by the FTIR spectra of the exhaust gases.

The space-centered $^{98}\text{Mo}$ thick layer deposited from CCP contains, according to the EDX data, fluorine (1.3% at) and oxygen (12.0 % at) due to adsorption from the atmosphere during storage. The powder collected in a small amount in the quartz trap, located at the reactor output, also contains the $^{98}\text{Mo}$ powder phase with an average particles size of 25 – 28 nm (XRD data).

The isotopic content did not change as going from the starting gas to solid samples. This means that no isotopic dilution takes place that could be caused due to molybdenum content in the apparatus. The chemical purity of $^{98}\text{Mo}$ samples depends on a) supply of impurities from construction materials, and b) adsorption from atmosphere during storage. The conversion degree of $^{98}\text{MoF}_6$ to $^{98}\text{Mo}$ is more than 85%. Concerning the thick layer (bulk) $^{98}\text{Mo}$, the deposition rate is equal to approximately 1 g/h. The content of main impurities in $^{98}\text{Mo}$ is less than 0.1 ppm wt.

3.2. \textit{PECVD of sulfur}

Figure 3 shows the emission spectra of ICP at $p = 0.2$ Torr and of CCP at $p = 1$ Torr. We observed intensive bands at 486.13 and 656.2 nm referring to atomic hydrogen $\text{H}_\beta$ and $\text{H}_\alpha$, as well as weaker bands at 390, 440, 490, 517, 538, 552, 636 and 925 nm. The bands at 390, 440 nm can be assigned to $\text{SiF}_2$ and $\text{SiF}$ radicals [5,6], and the bands at 490, 517, 538, 552 and 636 nm, to the active particle $\text{F}_2^*$ [7,8]. It is a well known fact that $^{32}\text{SF}_6$ is an extremely active etchant with respect to Si and $\text{SiO}_2$ [9,10]. This is why one can get indirect information about the mechanisms of its plasma reduction by the appearance of bands referring to $\text{SiF}_2$, $\text{SiF}_2$ and $\text{SiF}$ radicals and their intensity, as well as by registration of the $\text{SiF}_2$ band with various intensity in the IR spectrum of the exhaust gases. One can conclude that the band of $\text{SiF}$ is quite intensive in the spectrum recorded at $p = 0.2$ Torr. As the pressure increases up to 0.7 and 1 Torr and as going to CCP, the $\text{SiF}$ band intensity decreases sharply and the $\text{SiF}_2$ band disappears. The $\text{F}_2^*$ band disappears simultaneously, but at the same time the $\text{H}_\beta$ appears, while it was absent in the spectrum at 0.2 Torr. It was impossible to assign the band at 925 nm. It should only be noted that its intensity decreases while the reactor pressure is increased. Based on these experimental data, as well as on the mechanism of
intermediate reactions proposed in [9-11], the $^{32}$SF$_6$ reduction process in quartz reactor, including the interaction of the corresponding active particles with the surface at 0.2 Torr, could be described by the following reactions:

$$
\text{H}_2 \rightarrow 2\text{H},
$$

(6)

$$
^{32}\text{SF}_4 + \text{e} \rightarrow ^{32}\text{SF}_3 + \text{F} + \text{e},
$$

(7)

$$
\text{SiOF} + ^{32}\text{SF}_3 \rightarrow ^{32}\text{SOF}_2 + \text{SiF}_2.
$$

(8)

$$
\text{SiF}_2 + \text{F}_2 \rightarrow \text{SiF}_4.
$$

(9)

$$
\text{F} + \text{H} \rightarrow \text{HF}.
$$

(10)

While the pressure increases, the rate of reactions (6-14) essentially decreases, although the SiF band is still observed. Herewith, one observes a reduction of $^{32}$SF$_6$ with formation of elemental sulfur, as studied in[12]:

$$
\text{H}_2 \rightarrow 2\text{H},
$$

(15)

$$
^{32}\text{SF}_6 + 6\text{H} \rightarrow ^{32}\text{S} + 6\text{HF}.
$$

(16)

The conversion degree of $^{32}$SF$_6$ to $^{32}$S under the given conditions is equal to 70%. The deposition rate of $^{32}$S is equal to 0.25 g/h. The content of main impurities in $^{32}$S prepared by this method is less than 0.1 ppm wt.

The high-purity $^{32}$S obtained was used for the synthesis of glass of the $^{72}$Ge-$^{32}$S system; its IR transmission spectrum was studied in comparison with the same glass prepared from Ge and S of natural isotope composition.

### 3.3. PECVD of germanium

The plasma-chemical hydrogen reduction of $^{72}$GeF$_4$ was studied in ICP and CCP. The analysis of exhaust gases, of the chemically active plasma and of the condensed phase by emission- and FTIR-spectroscopy, as well as by mass spectrometry (MS), made it possible to propose a mechanism accounting for the formation of the intermediate species and the final products observed.

Figure 4 shows the emission spectra of RF plasma of the $\text{H}_2 + ^{72}\text{GeF}_4$ mixture in both types of plasma. The lines at 486.13 and 656.2 nm wavelengths are observed in the spectrum of ICP and correspond to the emission of atomic hydrogen $\text{H}_\beta$ and $\text{H}_\alpha$.

The lines of $\alpha$-Fulcher series in 575 – 625 nm range, the lines connected with the $^{72}\text{GeF}$ radical [13] in the 390 – 450 nm region, and with the $^{72}\text{GeF}_2$ radical in the 320 – 390 nm region [14], are present as well. The line at 703.75 nm, which could be assigned to free fluorine [15], was not registered in the spectrum.

As for the spectrum of CCP, the line at 385 nm, assigned to the $^{72}\text{GeH}$ radical [16], as well as the line at 703 nm connected with atomic fluorine [15], are observed, but the lines that could be assigned to the above-mentioned radicals $^{72}\text{GeF}$ and $^{72}\text{GeF}_2$ are absent.

Taking into consideration the peculiarities observed in the emission spectra of both types of plasma, as well as the formation of a $^{72}$Ge deposit, and ($^{72}$GeF)$_n$ and HF molecules confirmed by MS and FTIR, the following reaction steps can be proposed to describe the mechanism of reduction of
The formation of atomic hydrogen takes place in both types of discharge (17). The formation of germanium-containing radicals, as well as of condensed $^{72}$Ge and ($^{72}$GeF$_2$)$_n$ in ICP, can be explained by reactions (18–21).

\[
\text{H}_2 \rightarrow 2\text{H},
\]

\[
^{72}\text{GeF} + e \rightarrow ^{72}\text{Ge} + F + e,
\]

\[
^{72}\text{GeF}_2 \rightarrow (^{72}\text{GeF}_2)_n,
\]

\[
^{72}\text{GeF}_3\text{H} + \text{H} \rightarrow ^{72}\text{GeFH}_3 + F,
\]

\[
^{72}\text{GeFH}_3 + \text{H} \rightarrow ^{72}\text{GeH}_4 + F,
\]

\[
^{72}\text{GeF}_4 + e \rightarrow ^{72}\text{GeF}_n + F + e,
\]

\[
^{72}\text{GeF} + \text{H} \rightarrow ^{72}\text{Ge} + \text{HF},
\]

\[
^{72}\text{GeF}_4 + \text{H} \rightarrow ^{72}\text{GeF}_3\text{H} + F,
\]

\[
^{72}\text{GeF}_2\text{H}_2 + \text{F} \rightarrow ^{72}\text{GeF}_2\text{H}_2 + F,
\]

\[
^{72}\text{GeF}_2\text{H}_2 + \text{H} \rightarrow ^{72}\text{GeFH}_3 + F,
\]

\[
^{72}\text{GeH}_4 \rightarrow ^{72}\text{Ge} + 2\text{H}_2.
\]

In CCP, the most probable process is the interaction of atomic hydrogen with the $^{72}$GeF$_4$ molecule with subsequent substitution of fluorine atoms for hydrogen and formation of fluorogermane and germane molecules in a gas phase with further thermal decomposition of GeH$_4$, according to 22-26.

One can conclude that, as going from CCP at 3.5 Torr to ICP at 0.25 Torr, a change in the reaction mechanism of germanium formation takes place. In the first case, the radical mechanism with participation of $^{72}$GeF is a basic one and formation of metal $^{72}$Ge and condensed polymeric ($^{72}$GeF$_2$)$_n$ product is observed. In the second case, the interaction of atomic hydrogen with germanium tetrafluoride with fluorogermanes, fluorine and germane as intermediate products is responsible for germanium formation. The conversion degree of $^{72}$GeF$_4$ to $^{72}$Ge is 95%. The maximum deposition rate of $^{72}$Ge is about 4 g/h. The approach described made it possible to prepare a sample of enriched polycrystalline $^{72}$Ge with the following content of the main impurities: B<0.02; P<0.2; Sb~0.003; Al<0.03; As<0.01 ppm wt. The single crystal grown from it has the concentration of electroactive impurities <10$^{13}$ cm$^{-3}$.

4. Conclusions

We presented some results regarding an experimental study of isotopic hydrogen reduction of isotopic enriched molybdenum, sulfur and germanium fluorides in RF inductively and capacitively coupled plasma. It was shown that formation of a solid deposit in a bulk or powder form, as well as of intermediate products, depends on the pressure in the reactor and the reaction mechanism. Optical emission spectra of the systems studied are helpful for describing this mechanism. In the case of $^{98}$MoF$_6$ reduction in CCP, a combined radical-atomic mechanism was proposed including intermediate MoF$_3$ formation resulting in bulk and powder $^{98}$Mo deposition. In the case of the $^{32}$SF$_6$ + H$_2$ system in ICP, a strong etching ability towards the reactor quartz walls was observed. It can be minimized along with a rise of the $^{32}$S yield by increasing the reactor pressure. The deposition of polycrystalline $^{72}$Ge was effective both in ICP at low and in CCP at an order of magnitude higher pressure due to the different reaction mechanisms. The main characteristics of prepared materials are briefly discussed.

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