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Decomposition of SF_6 in the plasma medium of an electron beam

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Abstract. Sulfur hexafluoride (SF_6) is commonly used as an etching/etching-aid gas in fabricating the submicrometer features of modern integrated circuits because it has a higher fluorine content than CF_4 but does not undergo polymerization. However, the destruction of SF_6 has attracted much interest because of the important environmental issues and the toxicity of sulfur compounds. The results of experimental study of plasmachemical processes which are flowing past at injection of a high-current pulsed electron beam in a mixture of the gases SF_6, H_2, N_2, O_2 and Ar are introduced. Effective excitation of vibrational levels of the molecules occurs in the plasma of pulsed electron beam. The studies showed that in the conversion of sulfur hexafluoride plasma the electron beam pulse is realized effect. The parameters of electron beam are the following: electron energy is 400–500 keV, pulse duration at the half-height is 60 ns, frequency rate is up to 5 pulses per second, energy per pulse is up to 200 J. The electron beam is injected to the closed reactor through the anode foil. The isotope effect under the action of a pulsed electron beam on a gas mixture is considered.

Keywords: electron beam, nanosecond, sulfur hexafluoride, hydrogen, nitrogen, halides, reaction, isotopes, separation.

1. Introduction.

Sulfur fluoride is a stable chemical compound which possesses a very high electric strength [1]. This fact allows using it in the high-voltage energy setups and thermal nuclear reactors as isolating gas. Radio-frequency (RF) discharge plasma, which must be manipulated at low pressure, recently has become the most popular plasma technology used in the high-profit semiconductor industry, in both replicating patterns and depositing films. The discharge plasma can be manipulated at low substrate temperatures without changing its original properties and can replicate submicrometer patterns with anisotropic features. However, in the presence of an RF discharge, SF_6, acting as an etching/etching-aid gas, can be decomposed into lower fluorides of sulfur and can generate hazardous byproducts, such as S_2F_{10}, SO_2F_2, SOF_2, SOF_4, and SF_4. Particularly toxic is S_2F_{10}, which has an LC50 (concentration needed to kill 50 % of a defined experimental animal population of 0.1 mg/m^3). Because reducing or eliminating the toxicity of gaseous effluent from the RF discharge process is a serious concern [2–6].

In this work, plasmas in medium of an electron beam were used to decompose SF_6 [7–9]. The studies showed that in the conversion of sulfur hexafluoride plasma pulse the electron beam is realized effect. Mass spectrometric studies of the positive ion yield due to the electron impact ionization of sulfur hexafluoride molecules in the gas phase have been carried out. The exothermal reaction going is organized in the reactor volume. The oscillation-excited products of these reactions participate in the dissociation of initial halogenide molecules.

2. Experimental setup

The non-equilibrium plasma is formed due to the action of pulsed electron beam with the duration of not more than 10^{-9} s to the mixture of halogenides and gas-carrier. Nitrogen, hydrogen and oxygen are used as the gas-carrier. The processing of halogenides is performed by adding of diluent gas to the mixture of halogenide and gas-carrier up to the total pressure providing full absorption of nanosecond pulsed electron beam energy.

The analysis of plasmochemical processes which take place in gases at injection of pulsed high-current electron beam (HCEB) has shown, that the requirements which realized at stimulation

of gases, are favorable to organize of chain and catalytic processes. Thus, the energy of HCEB constitutes small part of a total energy expended on carrying out of reaction. The unique properties of plasma generated at affecting of pulsed electron beam (a high scale of no equilibrium, homogeneous stimulation of large bulks of gas at high pressures, high speed of stimulation), allow realizing new physical principles of initiation of chemical reactions. To them the dissociation of oscillating – activated molecules, chain plasmochemical processes, plasma-catalytic reactions etc. is referred.

During the study of the thermal dynamic modeling as well as the experimental research of sulfur hexafluoride reduction in the pulsed electron beam plasma have been performed. The modeling of chemical processes in the low-temperature plasma for equilibrium stage of the process was executed with the use of automotive system of thermal dynamic calculations "TERRA" [10]. The calculations have been performed for the temperature interval 300–4000 K and initial mixture pressure interval of 0.01–1.0 MPa. The final results of calculations were the values of equilibrium mole concentrations of chemical compounds the formation of which is possible under our conditions from the thermal dynamic point of view. Basing on this the diagrams of mole concentration dependences of the forming chemical compounds of the system under study on temperature and pressure are built.

Fig.1 shows the principal scheme of the experimental bench which was used for the performance of experiments [11].

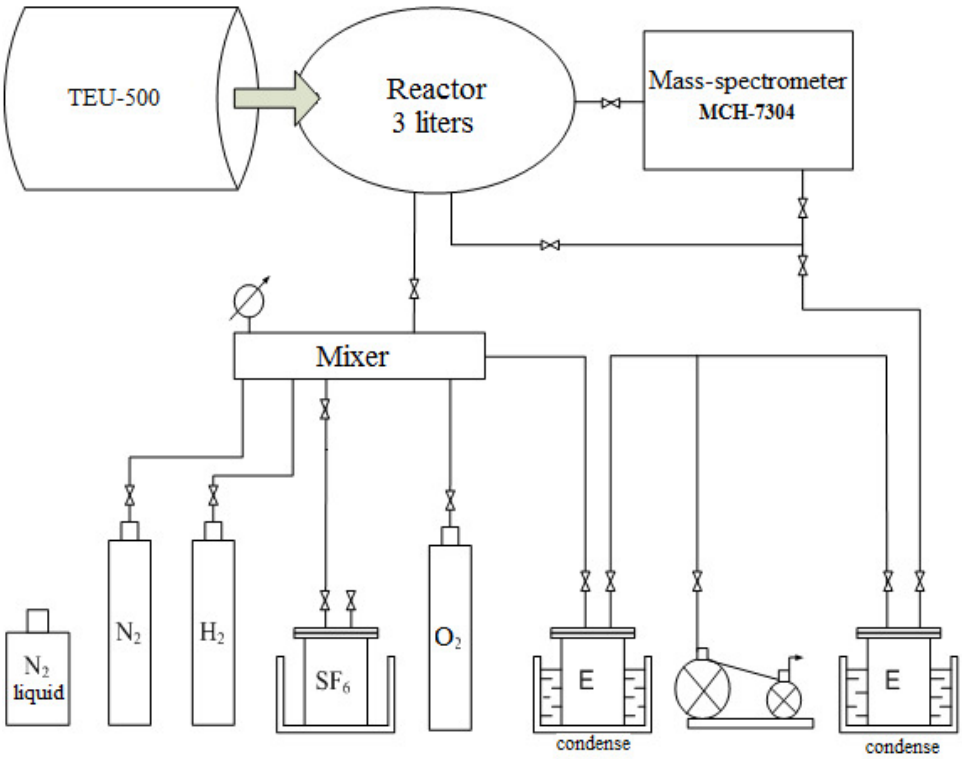

Fig.1. Schematic diagram of the installation.

The plasma chemical reactor is made in the form of tube with the inner diameter of 90 mm and 300 mm in length. The total volume is 3 liters. The injection of electron beam takes place to the reactor from the but-head through the aluminum foil 100 μm in thickness. The electron current density at the reactor input did not exceed 0.4 kA/cm^2. The interconnection modes with the injection to the reactor from 1 to 100 pulses have been studied. The energy input of electron beam into gas and energy consumptions for the plasma chemical synthesis was measured by the pressure

jump in the reactor. For the creation of pulsed electron beam the high-current pulsed electron accelerator TEU-500 was used [12]. The accelerator parameters are the following: kinetic energy of electrons is 450–500 keV, extracted current is up to 10 kA, pulse duration is 60 ns, frequency rate is up to 5 pulses per second, and energy per pulse is up to 200 J. For the determination of initial mixture content and conversion products the gas chromatograph TRACE DSQ was used. The peculiarity of this device is high sensitivity allowing to determine the substances from 1 μg per liter. The electron beam was injected to the closed reactor through the anode foil.

The investigations were performed for the planar configuration of the diode with planar cathode 43–60 mm in diameter. The FC planar collector 92 mm in diameter was used as an anode.

As an analytical device, we used a monopole mass spectrometer MCH-7304 with the digital indication of the mass number and the intensity of ion peaks. It can operate in the modes of manual, cyclic, and programmable sweeps of the mass spectrum and energies of ionizing electrons. The mass-spectrometer was used for the determination of initial mixture content of gases and reaction products. The output signal of mass-spectrometer was transferred to the computer through ADC LAN-7 with galvanic isolation. The content of gas mixture components was estimated by the corresponding peak area.

3. Results

Accomplished studies have shown that sulfur difluoride-oxide (SOF_2) is a major gas phase sulfur compound, synthesized in the conversion of sulfur hexafluoride (as a mixture with hydrogen and oxygen) in the plasma of a pulsed electron beam. (Fig.2).

The studies of the sulfur reduction from SF_6 under the action of pulsed electron beam to the gas-phase mixture SF_6+H_2+Ar have been done.

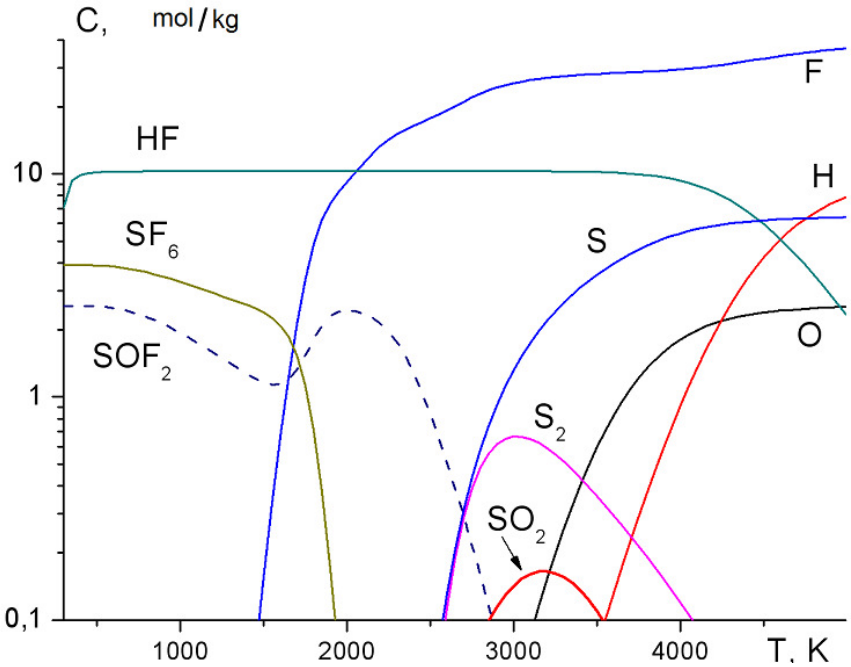

Fig.2. Thermodynamic modeling conversion of sulfur hexafluoride in a mixture of oxygen and hydrogen. The feed mixture (volume fraction) SF_6+H_2+O_2.

When sulfur hexafluoride decomposes the electron beam energy consumptions for the dissociation of one molecule of SF_6 did not exceed 2.1 eV. The performed studies of sulfur hexafluoride decomposition in the mixture with hydrogen and under the action of pulsed electron

beam showed that in our experimental conditions SF_6 radiolysis goes according to the chain mechanism. When calculating the energy input of electron beam for sulfur hexafluoride decomposition we did not consider the energy losses for argon molecule excitation and for reagent gas heating. That is why the real values of electron beam energy input for SF_6 dissociation is lower than 2 eV and correspondently lower than the standard enthalpy of SF_6 formation which equals 12.4 eV/molecule.

The electron beam energy input for sulfur hexafluoride dissociation in the mixture with nitrogen was also less than the standard enthalpy of SF_6 formation [13]. This indicates the realization of chain process initiated by pulsed electron beam. During the radiolysis of sulfur hexafluoride-nitrogen mixture by pulsed electron beam the nitrogen quantity reduction was not observed. That is why the source of energy for sulfur hexafluoride decomposition was not the exothermal reaction of nitrogen trifluoride synthesis but other exothermal processes. It is possible that a more significant input to SF_6 decomposition was brought by the ion-cluster mechanism of chain reaction. The presence of atoms of sulfur and buffer gas (nitrogen, sulfur hexafluoride and others) causes the cluster formation.

In this study, the effect of plasma on isotope separation has been demonstrated [14, 15]. Plasma was initiated due to the effect of pulsed electron beam with the duration of not more than 10^{-9} s on the mixture of hexafluorides sulfur and gas-carrier. As a gas-carrier, nitrogen, hydrogen and oxygen have been applied. The processing of halogenides sulfur is performed by adding of diluent gas and gas-carrier to the mixture of halogenides until the total pressure providing full absorption of nanosecond pulsed electron beam energy is reached. The studies showed that in the conversion of sulfur hexafluoride plasma pulse the electron beam is realized isotope effect. The content of S^{34} in the products exceeds the original 1.8 times, significantly higher than the measurement error.

The initial gas mixture: SF_6+H_2+Ar+O_2. Argon ($m/z = 40$) was introduced to normalize the recorded mass spectrum. Major peaks characteristic of the gas mixture in the reactor after exposure to the electron beam correspond to the $m/z = 2$, 67, 86 and 127. The peaks at $m/z = 18$ and 28 correspond to the background of the mass spectrometer (H_2O and N_2), the amplitude is not changed. Fig.3 presents the mass spectra of positive ions.

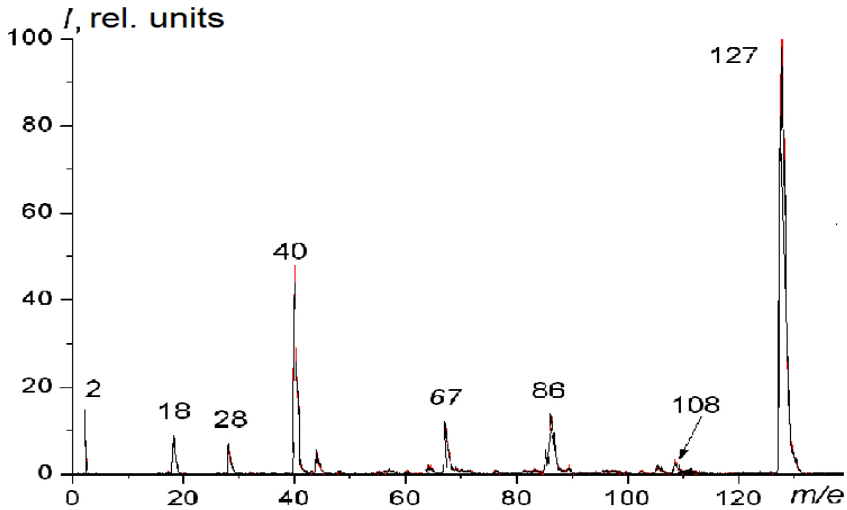

Fig.3. Mass spectra of positive ions of hexafluorides sulfur and difluoride sulfur oxide.

The thermal dynamic modeling showed that in case of plasma of SF_6 and H_2 all the elements such as S, HF, H_2F_2 and SF_4 are stable products of decomposition of sulfur hexafluoride in the

mixture with hydrogen. The calculations showed the possibility of condensed phase formation of sulfur monomer S, sulfur dimmer S_2 and of other clusters.

In our case, at the expense of dissociation of sulfur hexafluoride by electronic shock $SF_6+e \rightarrow S+6F$ and dissociative adhesion of low-energy electrons $SF_6+e \rightarrow (SF_6)^- \rightarrow S+6F$.

The atomic fluorine is formed, which initiates reactions in a mixture with molecular hydrogen. The major reaction is $H_2+F=HF+H+1.47$ eV.

The energy which is released in the exothermic reaction can be spent for initial decomposition of sulfur hexafluoride.

At injection HCEB in a mixture the temperature of gas increased not higher than 50°C. Other products of reaction, which one could enter to reacting with SF_6 in our requirements and to reduce to its loss, are not formed. The electron impact ionization of hexafluorides sulfur molecules results in the formation of a certain number of positive ions that increases with the ionizing electron energy.

4. Conclusion

The processing of halogenides is performed by adding of diluent gas to the mixture of halogenide and gas-carrier up to the total pressure providing full absorption of nanosecond pulsed electron beam energy. Mass spectrometric studies of the positive ion yield due to the electron impact ionization of sulfur hexafluoride molecules in the gas phase have been carried out. The exothermal reaction going is organized in the reactor volume. The oscillation-excited products of these reactions participate in the dissociation of initial halogenide molecules. The non-equilibrium plasma is formed due to the action of pulsed electron beam with the duration of not more than 10^{-9} s to the mixture of halogenides and gas-carrier. Nitrogen, hydrogen and oxygen are used as the gas-carrier. The studies showed that in the conversion of sulfur hexafluoride plasma pulse the electron beam is realized isotope effect. The content of S^{34} in the products exceeds the original 1.8 times, significantly higher than the measurement error.

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