THE QUALITATIVE ANALYSIS OF THE COMPOSITION OF THE RF DISCHARGE PLASMA BY MEANS OF MASS-SPECTROMETRY

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In this paper presents the research results of mass-spectroscopy of the RF discharge plasma in the controlled magnetic fields. The discharge was conducted in the gases containing halogens and mixtures with the oxygen. The evolution of the main plasma components from the oxygen content was investigated.

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INTRODUCTION

Plasma in gases, which contain halogens in pure form or in admixtures with other gases, is widely used for plasma-chemical processing of different semiconductor materials. The mixtures of the gases, which containing halogens most often used with the addition of oxygen (O_2). However, not all processes occurring in plasma-chemical reactor (PCR) sufficiently explored. Therefore, these researches are attracting the attention of national and foreign researchers.

The chemical processes occurring in PCR are multivariate and extremely complex. Probe techniques do not allow fully understand the component composition and to determine the main parameters of chemically active of the plasma of high - frequency discharges.

The mass spectrometry is one of the most effective methods of the control of plasma-chemical processes that occur in the PCR. This method of analysis of the plasma environment allows determining the qualitative composition of plasma and choosing the most effective operating conditions of the discharge processes for optimum etching of technological layers.

Such research is allowing to predict the formation of harmful gases that can endanger human health and life, is gives the opportunity to prevent their release into the atmosphere.

Therefore, research in this area will enable more clearly understand the kinetics of physical and chemical processes that occur in the PCR. This in turn will improve the results of the process of plasma-chemical etching (PCE) of materials.

1. MAIN PART

1.1. EXPERIMENTAL COMPLEX

Mass-spectra of chemically active gases are formed in the reactor chamber obtained using the mass spectrometer MX-7304 [1]. The oil vapor of diffusion pump is a strong hindrance for the analysis of plasma components. Since, they have wide range masses of in the range of 30…150 amu. The best way was to ensure no oil pumping, which schematically shown in Fig. 1. The high vacuum ensured by means of magnetic discharge pump PMDC 100. It is connected to the mass spectrometer flexible sleeve made of stainless steel. Pre vacuum created in PMDC-100 via diffusion pump. After this, the volume of the mass spectrometer is overlapping from the vacuum post PCR with using a mechanical valve. The mass spectrometer MX-7304 was connected to the camera PCR through the flange with a metal seal and fluoropolymer hoses.

It was created to avoid the influence of RF and magnetic field of the mass- analyzing sensor of the mass spectrometer.

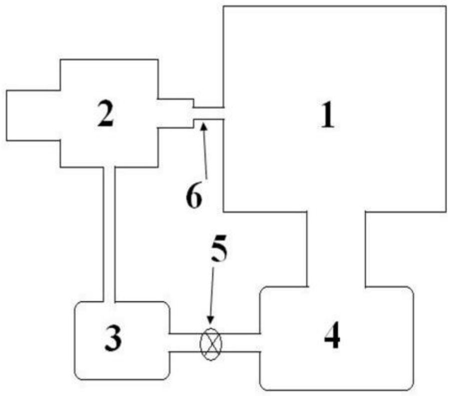

Fig. 1 Scheme of the experimental complex:
1 – PCR; 2 – mass-spectrometer (MX-7304);
3 – magnetic discharge diode cooled pump
(PMDC-100); 4 – diffusion pump;
5 – valve; 6 – the connecting hose

The researches of chemically active plasma were performed on the plasma-chemical reactor with the closed electron drift [1]. RF discharge is formed between two electrodes one of which (active) in the form of three sided prism. The processed samples placed on the surface of this electrode, and to him was applied RF voltage. The outer, grounded electrode has a cylindrical shape and the length of 420 mm. The chemically active plasma formed in crossed RF electric and controlled magnetic fields depending on the gases which inlet in the plasma-chemical reactor.

The gas composition for the treatment of process layers can vary depending on the task. It all depends on the desired selectivity etching process of one-layer relative to another, anisotropy etching, and the required profile.

In this work, we used the following gases: Sulfur hexafluoride (SF_6), Freon-14 (CF_4), Freon-218 (C_3F_8) in the mixture of oxygen (O_2). These gases were chosen for research because they are most commonly used in the electronics industry for carrying out plasma-chemical etching of materials.

1.2. RESULTS AND DISCUSSION

Mass spectra of plasma gas mixtures (a) SF_6/O_2, (б) CF_4/O_2 та (в) C_3F_8/O_2 shown in Fig. 2. Analysis of the mass spectrograms shown that common to all is the presence of residual gases: H_2^+ (2 amu), N^+ (14 amu), O^+ (16 amu), H_2O^+ (18 amu), N_2^+ (28 amu), CO^+ (28 amu), O_2^+ (32 amu), Ar^+ (40 amu), CO_2^+ (44 amu). The discovered peak of argon selected as the value of the calibration weight.

The ion HF^+ observed at all mass spectrogram. It is formed due to the high reactivity of atomic fluorine with atomic hydrogen and products of dissociation of sulfur hexafluoride with water vapor. Desorption of their can occur with the inner surface of the chamber walls of the PCR.

The peaks SF^+ (51 amu), SF_2^+ (70 amu), SF_3^+ (89 amu), SF_4^+ (108 amu) and SF_5^+ (127 amu) are observed in the mass spectrogram (see Fig. 2,a). They are the main decay products of sulfur hexafluoride. Maybe peak CF observed, but it is poorly divided with molecules of nitrogen and carbon monoxide.

It should be noted a large number of oxy-fluoride: SOF_2, SO_2F_2, SOF_4 etc. Sulfuryl fluoride (SO_2F_2, 102 amu) and thionyl fluoride (SOF_2, 86 amu) are the dangerous substances. They can cause pulmonary edema in concentrations that exceed maximum permissible norm [2]. Since, they are insoluble in water; this class of substances is dangerous when working with sulfur hexafluoride.

On the mass spectrogram in the gas mixture CF_4/O_2 (see Fig. 2,b) detected atomic carbon ion (12 amu) and the radical ions CF_2^+ and CF_3^+. They are responsible for the polymerization of carbon - fluoride on the surface of the processed samples at plasma-chemical etching.

The molecule C_2 (24 amu) is not observed. Oxygen reacts with these radicals, freeing up additional fluorine atoms and the resulting reactions [3] molecules are formed CO (28 amu), CO_2 (44 amu), COF (47 amu).

At the same time, there is an extremely toxic substance phosgene fluoride (COF_2, 66 amu). Its toxic effect is ability to easily hydrolysable in contact with mucous membranes of the respiratory tract and lungs. As the result, stands out hydrogen fluoride, this causes severe chemical burns inside the lungs. The hydrolysis of fluoride phosgene, which happens either in the air or directly on mucosa of its effects on the body, is equally dangerous [4].

Analysis of the mass spectrum of the plasma C_3F_8/O_2 (see Fig. 2, c) showed a large number of small oligomers formed in the process of dissociation C_3F_8. The molecules C_3F_7, C_3F_6, C_2F_5, C_3F_4, and C_2F_4 have very small intensity. The intensity of peaks decreases with the addition of oxygen. This is due to the interaction of fluorine-carbon radicals with atomic and molecular oxygen. The discharge mode was selected in which manages to get rid of fluoropolymer films on the surface of the processed sample using this methodology.

The radical CF^+_3 have a very high intensity, which is 5 times more compared with the intensity of the CF^+_2. Atomic carbon observed but the molecule C_2 in the plasma of CF_4/O_2 was not detected. The minor peaks CFO and COF_2 are observed in this gas mixture.

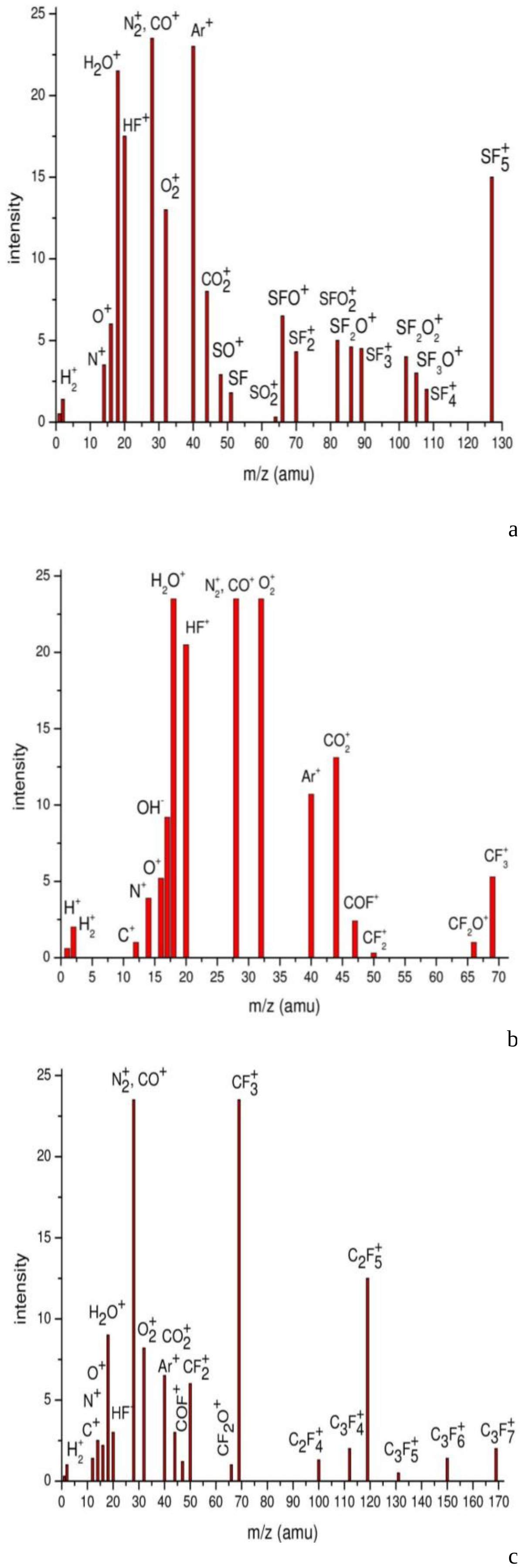

Fig. 2. Mass-spectrograms: SF_6/O_2 (a); CF_4/O_2 (b) and C_3F_8/O_2 plasma (c). Process parameters U_{bias} = 100 B, P = $5.0 \cdot 10^{-5}$ Torr, I_d = 7 A, P = 1000 W

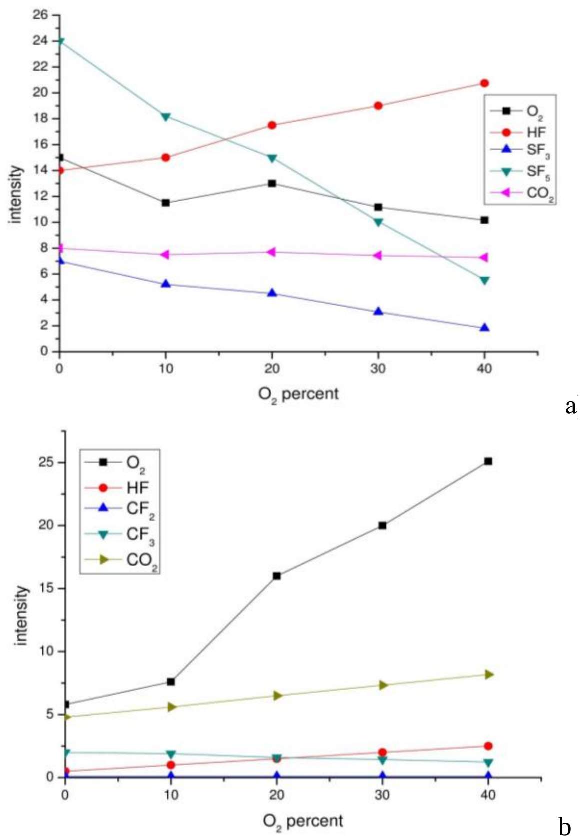

Fig. 3. The evolution of the intensity of the main components of the O_2 content plasma in the chamber rector: in SF_6 (a); in CF_4 (b)

The evolution of the main plasma components are observed on the mass spectrogram depending on changes in the content of oxygen (O_2) in the reactor chamber during the discharges in mixtures of oxygen with sulfur hexafluoride shown in Fig. 3.

There is an almost linear decrease in the intensity of the radical ions SF_5^+, SF_3^+, with the increase of the amount of oxygen in the discharge (see Fig. 3.a). This may be due to the occurrence of a number of possible chemical reactions, which shown in the article [5]. The decrease in the intensity of the peaks of the lower fluorides, said the increase in the number of oxidation reactions, leading to decrease in their concentration in the reactor volume.

There is a growth of intensity HF^+ with increasing content of O_2 in the reactor chamber. This indicates the increase in the concentration of atomic fluorine.

The intensity of the CF_3^+ (see Fig. 3,b) decreases with the addition of O_2 in CF_4. This increases the intensity of CO_2 due to the high reactivity of carbon with oxygen.

CONCLUSIONS

Depending on the oxygen, content in the PCR chamber was observed decrease in the intensity of the primary product of the working gas reactions. This indicates an increase in the number of oxidation reactions.

The research of freons showed the presence of carbonyl radicals and their decrease depending on the oxygen content.

The toxic substances were found which could threaten human health. The gas composition and regimes of discharges were selected under which harmful substances are practically not observed.

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АНАЛИЗ СОСТАВА ПЛАЗМЫ ВЧ-РЯЗРЯДА МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ

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Представлены результаты масс-спектрометрических исследований плазмы ВЧ-разряда в управляемых магнитных полях. Разряд проводился в чистых галогенсодержащих газах и в смеси с кислородом. Исследована эволюция основных компонентов плазмы от содержания кислорода.

АНАЛІЗ СКЛАДУ ПЛАЗМИ ВЧ-РОЗРЯДУ МЕТОДОМ МАС-СПЕКТРОМЕТРІЇ

В.В. Гладковський, Б.П. Полозов, О.А. Федорович

Представлено результати мас-спектрометричних досліджень плазми ВЧ-розряду в керованих магнітних полях. Розряд проводився в чистих галогеновмісних газах і в суміші з киснем. Досліджено еволюцію основних компонентів плазми від вмісту кисню.