OES diagnostic of SF₆/Ar gas mixture of ICP discharges for LiNbO₃ etching

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Abstract. The results of a study of the influence of technological parameters of the process of plasma chemical etching in inductively coupled plasma on the emission spectra of fluorine and argon atoms are presented. The effects of inductively coupled plasma RF power, operating pressure and bias voltage were studied for 6 different sulfur hexafluoride argon (SF₆/Ar) gas mixtures: SF₆ (1.5 sccm)/Ar (9.2 sccm), SF₆ (7.8 sccm)/Ar (10.8 sccm), SF₆ (4.7 sccm)/Ar (6.0 sccm), SF₆ (7.0 sccm)/Ar (4.9 sccm), SF₆ (11.7 sccm)/Ar (5.4 sccm), SF₆ (9.4 sccm)/Ar (3.3 sccm). It is shown that a decrease in the operating pressure and an increase in the RF power of the inductively coupled plasma leads to an increase in the relative intensity of both argon and fluorine lines. Variations in the bias voltage have no significant effect on the emission intensity of the spectral lines of Ar and F.

1. Introduction

Monocrystalline lithium niobate is the basis for the creation of devices for the optical industry, including microwave photonics, which is currently the focus of research activities [1-4]. In recent years, a whole class of functional and digital integrated optical circuits (IOS) has been implemented on LiNbO₃ crystals, such as switching matrices, spectrum analyzers, microwave phase and amplitude modulators, holographic memory elements, biomedical devices, as well as sensors of physical quantities [5-11]. The use of lithium niobate as the main material of modern nonlinear optics, electro-optics and acoustoelectronics is due to the high values of electro-, acousto and nonlinear-optical coefficients [12-16]. In addition, devices made on the basis of lithium niobate have found wide application in the automotive and oil industries, as well as in aircraft engine building [17].

The key technological operation of creating such devices is the formation of structures of various configurations (holes, grooves, etc.) in/on lithium niobate substrates using plasma-chemical etching (PCE).

However, it is known that the main problem in the creation of deep structures in lithium niobate in a fluorine-containing plasma is the formation of a non-volatile compound LiF on the surface of the etching
windows [18]. In this regard, it is important not only to understand the influence of technological parameters on operating parameters, such as etching rate, etching anisotropy, selectivity, roughness, etc., but also the influence of technological parameters on the parameters of the plasma itself.

Plasma diagnostics includes many methods that allow you to determine the parameters of the plasma. Optical spectroscopy makes it possible to determine the electron density, the electron temperature and the electron energy distribution function, as well as to obtain information on the processes of radical formation in plasma [19-22].

In this work, we have studied the effect of inductively coupled plasma (ICP) RF power, operating pressure, and bias voltage on the emission intensity of fluorine and argon emission lines in a plasma-chemical etching system.

2. Experimental technique
The experiments were carried out on a specially designed installation for plasma-chemical etching with a source of inductively coupled plasma (figure 1) [23]. The reactor can be divided into two chambers, discharge and reaction. The reaction chamber is equipped with a viewing window made of KU-1 (FS UV) quartz, 35 mm in diameter, mounted on flange 3. The gases used were high-purity sulfur hexafluoride 99.998 (GOST TU 6-02-1249-83) and argon, mixtures of which the most promising for the implementation of the PCE process of lithium niobate.

![Figure 1. Simplified diagram of the reactor (left) and 3D model of the PCE facility (right):](image)

- 1 - discharge chamber; 2 - reaction chamber; 3 - flange for loading and unloading working samples; 4 - flange for joining with a vacuum pumping system; 5 - substrate holder with a heating element; 6 - cooled inductor; 7 - channel for supplying the working gas mixture; 8 - Faraday shield; 9 - electromagnetic shield of the inductor.

The spectra were recorded with an OceanOptics HR 4000 spectrometer in the wavelength range of 200 - 1100 nm with a resolution of ~ 0.02 nm with a spectrometer entrance slit of 5 μm. The spectrometer was coupled with the setup using a fiber-optic system for transmitting plasma discharge radiation to the entrance slit of the spectrometer (see figure 1). The spectra were processed using the SpectraGryph 1.2.14 software [24].
The following gas mixtures were selected to study the effect of ICP RF power, operating pressure and bias voltage on the emission intensity of the Ar and F emission lines:

SF<sub>6</sub> (1.5 sccm) / Ar (9.2 sccm) 85%, SF<sub>6</sub> (7.8 sccm) / Ar (10.8 sccm) 58%, SF<sub>6</sub> (4.7 sccm) / Ar (6.0 sccm) 56%, SF<sub>6</sub> (7.0 sccm) / Ar (4.9 sccm) 41%, SF<sub>6</sub> (11.7 sccm) / Ar (5.4 sccm) 32%, SF<sub>6</sub> (9.4 sccm) / Ar (3.3 sccm) 26%.

Plasma in the discharge chamber was generated by supplying RF power to the inductor from a GTVE-1000 generator operating at a frequency of 6.78 MHz and providing a smooth adjustment of the output power in the range from 0 to 1000 W. To create a negative self-bias voltage on the substrate holder, the reactor design provided for the possibility of supplying RF power to the table from a separate generator. The source of RF electromagnetic power was a Plasma-125I generator (13.56 MHz) equipped with a matching device.

3. Results and discussions

Figure 2 shows the emission spectra of pure Ar and SF<sub>6</sub> plasmas, the discharges of which were created under the conditions presented in Table 1. In both cases, the spectra contain a large number of lines, however, in argon plasma, the most intense emission lines are located in the region of 700-900 nm, while SF<sub>6</sub> plasma emits mainly in the range 600-800 nm. To analyze the effect of plasma generation parameters on its spectral characteristics, three lines (750.7, 811.5, and 842.2 nm) were selected in the argon plasma spectrum and four lines (685.7, 703.8, 720.3, and 775.5) in the SF<sub>6</sub> plasma spectrum.

Listed lines correspond to transitions:

\[3s^23p^5(^3P_{1/2})4p^2[1/2] \rightarrow 3s^23p^3(^3P_{1/2})4s^2[1/2] \ (750.7 \text{ nm})\]
\[3s^23p^3(^3P_{3/2})4p^2[5/2] \rightarrow 3s^23p^3(^3P_{3/2})4s^2[3/2] \ (811.5 \text{ nm})\]
\[3s^23p^3(^3P_{3/2})4s^2[3/2] \rightarrow 3s^23p^3(^3P_{3/2})4s^2[3/2] \ (842.2 \text{ nm})\]

excited argon atoms and

\[2s^22p^4(^1P)3p^2^4D_{5/2} \rightarrow 2s^22p^2(^3P)3s^2^4P_{3/2} (685.7 \text{ nm})\]
\[2s^22p^4(^1P)3p^2^4P_{3/2} \rightarrow 2s^22p^2(^3P)3s^2^2P_{1/2} (703.8 \text{ nm})\]
\[2s^22p^4(^1P)3p^2^4P_{3/2} \rightarrow 2s^22p^2(^3P)3s^2^2P_{1/2} (720.3 \text{ nm})\]
\[2s^22p^4(^1P)3p^2^4D_{5/2} \rightarrow 2s^22p^2(^3P)3s^2^4P_{3/2} (775.5 \text{ nm})\]

transitions of excited fluorine atoms formed during the dissociation of SF<sub>6</sub> in a discharge used to determine the characteristics of plasma [25–27].

![Figure 2. Optical emission spectra of argon and SF<sub>6</sub> plasmas.](image)

**Table 1.** Values of technological parameters of preliminary experiments to determine analytical lines

| W<sub>RF</sub>, W | U<sub>bias</sub>, V | P, Pa | Q<sub>Ar</sub>, sccm | Q<sub>SF6</sub>, sccm |
|----------------|----------------|------|-----------------|-----------------|
| 700            | -50            | 0.62 | 21.75           | 0               |
| 700            | -50            | 0.75 | 15.6            | 0               |
The first series of experiments was aimed at determining the effect of ICP RF power on the intensity of Ar and F radiation in SF$_6$/Ar plasma. In this series, the spectra of the discharge of six gas mixtures differing in the ratio of the components were studied. The experimental parameters are presented in Table 2. The bias voltage value in the entire series was fixed at -50 V, while the stage was located at a distance of 15 cm from the lower edge of the discharge chamber.

**Table 2.** Values of technological parameters of experiments aimed at determining the effect of RF power on the intensity of the Ar and F emission lines.

| W$_{RF}$, W | Q$_{SF_6}$, sccm | Q$_{Ar}$, sccm |
|------------|----------------|---------------|
| 700        | 650            | 550           |
| 700        | 650            | 550           |
| 700        | 650            | 550           |
| 700        | 650            | 550           |
| 700        | 650            | 550           |

The experimental results showed (see Figure 3) that, regardless of the ratio of the components of the gas mixture, the intensity of all analyzed Ar and F emission lines increases with increasing RF power. It can be assumed that the observed increase in the intensity of spectral lines is associated with an increase in the electron density in the discharge, which leads to an increase in the number of excited Ar and F atoms due to an increase in the probability of inelastic collisions of molecules and reagent atoms with high-energy electrons [28].

The second series of experiments was aimed at determining the effect of the operating pressure on the intensity of the Ar and F emission lines in the emission spectra of plasmas with various combinations of Ar and SF$_6$. The values of the RF power supplied to the ICP discharge, the bias voltage, and the distance from the substrate to the lower edge of the discharge chamber were fixed and were equal to 700 W, -50 V, 15 cm, respectively. The parameters of the second series of experiments are presented in Table 3. The results of measuring the intensity of the selected lines are shown in Figure 4.

![Figure 3. Dependence of the intensity of some emission lines Ar and F on the RF power of the ICP.](image)

It can be seen from the figure that, as in the case of the influence of the study of RF power, the dependence of the intensity of spectral lines on pressure is also characterized by a general trend,
however, in the latter case, with an increase in pressure, the intensity of the lines under consideration decreases with other fixed parameters of the experiment. Obviously, an increase in pressure in the chamber leads to a decrease in the mean free path of electrons and, as a consequence, to a decrease in their temperature and, hence, to a decrease in the number of excited fluorine and argon atoms. This explanation is consistent with the results published in [29, 30].

**Table 3.** Values of technological parameters of experiments aimed at determining the effect of pressure on the intensity of the Ar and F emission lines

| P, Pa | Q_{SF6}, sccm | Q_{Ar}, sccm |
|-------|---------------|--------------|
| 0.50  | 0.75          | 1.25         | -            | 1.5 | 9.2 |
| 0.75  | 1.00          | 1.25         | 1.50         | 1.75| 7.8 | 10.8|
| 0.5   | 0.75          | 1.00         | 1.25         | 1.5 | 4.7 | 6.0 |
| 0.75  | 1.00          | 1.25         | 1.50         | 1.75| 7.0 | 4.9 |
| 0.5   | 0.75          | 1.00         | 1.25         | 1.5 | 11.7| 5.4 |
| 0.5   | 0.75          | 1.00         | 1.25         | 1.5 | 11.7| 3.3 |

**Figure 4.** Dependence of the intensity of some Ar and F lines on the working pressure

The third series of experiments was aimed at determining the effect of the bias voltage on the intensity of the Ar and F emission lines in plasmas of the Ar/SF₆ mixture. The parameters of the experiments are shown in Table 4. The RF power was fixed at 700 W in all experiments. It was found
(see Figure 5) that the bias voltage does not make a significant contribution to the change in the intensity of the emission lines of argon and fluorine.

Table 4. Values of technological parameters of experiments aimed at determining the effect of the bias voltage on the intensity of the emission lines Ar and F

| U, V  | P, Pa | Q_{SF6}, sccm | Q_{Ar}, sccm |
|-------|-------|---------------|---------------|
| -50   | -100  | -150          | -200          | -250          | -300          |
| 0.5   | 1.5   | 9.2           |               |
| -50   | -100  | -150          | -200          | -250          | -300          |
| 0.65  | 7.8   | 10.8          |               |
| -50   | -100  | -150          | -200          | -250          | -300          |
| 0.5   | 4.7   | 6.0           |               |
| -50   | -100  | -150          | -200          | -250          | -300          |
| 0.65  | 7.0   | 4.9           |               |
| -50   | -100  | -150          | -200          | -250          | -300          |
| 0.5   | 9.4   | 3.3           |               |

Figure 5. Dependence of the intensity of the Ar and F emission lines on the bias voltage.

4. Conclusions

As a result of our studies, it was found that an increase in the RF power in an ICP discharge and a decrease in the operating pressure lead to an increase in the intensity of the Ar and F emission lines, while changes in the bias voltage do not significantly affect the intensities of the spectral lines considered. The observed increase in the intensity of the emission lines of argon and fluorine with an increase in the RF power is associated with an increase in the electron density in the plasma discharge, and in the case of a change in the pressure in the chamber, the intensity of the bands is determined by the electron temperature.

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