

FEATURES OF PLASMA CHEMICAL ETCHING OF LITHIUM TANTALATE SUBSTRATE (LiTaO₃)

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The results of researches of plasma chemical treatment of lithium monocrySTALLINE tantalate (LiTaO₃) from gas type, bias voltage (energy of chemically active ions) and from current of additional bias generator are given. A closed-loop electron drift plasma chemical reactor and gas mixtures containing Ar, Ar + ClC₄, and Ar + SF₆ were used for the experiments. It was found that the etching rate of LiTaO₃ for the discharge in the gas mixture Ar + CCl₄ is 14 times higher than all other mixtures that were used. It is shown that the proposed idea and approaches of Li-TaO₃ processing can be effectively applied for the production of optical systems with a minimum core thickness of about 2...3 μm.

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INTRODUCTION

Lithium tantalate crystal (LiTaO₃) is a multifunctional material of opto- and acoustoelectronics, which is widely used in nonlinear optical systems and pyroelectric devices, in the manufacture of which it is necessary to introduce minimal surface damage [1]. It should be noted that monocrySTALLINE LiTaO₃ is particularly resistant to wet chemical etching of any kind. However, good results in the etching of such materials have been achieved in dry plasma chemical etching, but there are still some difficulties. First, it is necessary to remove the surface charge from the processed material, because Li-TaO₃ is a dielectric. This problem can be solved by connecting a RF offset generator to the active electrode with a frequency of 100 to 500 kHz. However, it is necessary to minimize the impact of one generator on another. Secondly, there is a significant amount of chemical bond that needs to be broken in the crystal lattice. For example, the binding energy in LiTaO₃: LiO – 3.4 eV, TaO – 8 eV, TaO₂ – 1.9 eV. As can be seen from these data, the energy of chemical bonding in crystal molecules is comparable to the ionization energies of individual atoms (Li – 5.39 eV, Ta – 7.88 eV, O – 13.61 eV). The amount of chemical bond energy in the molecules formed during plasma chemical etching is much lower. Therefore, still such conditions must carry out for LiTaO₃ treatment. The first condition is to increase the energy of the interacting ions and bring the process to physical sputtering. The second condition is to choose the composition of the working gases, which when interacting with the substrate material will give volatile compounds with a bond energy greater than in the crystal lattice.

1. EXPERIMENTAL RESULTS AND DISCUSSION

A plasma chemical reactor with a closed electron drift was used to etch LiTaO₃ substrates in Fig. 1 [2]. Argon, xenon, carbon tetrachloride and SF₆ were tested as working gases. The RF discharge was ignited in a gas mixture of Ar + CCl₄ in a ratio of 1: 1 at a RF discharge current of 10 A and a pressure of 5·10⁻² Torr.

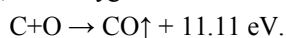


Fig. 1. Image of the plasma chemical reactor

A 440 kHz RF generator was used to remove the surface charge. The bias voltage was adjusted using controlled magnetic fields and an additional generator in the range from 100 to 1000 eV. To avoid etching of the entire sample, except for the core, we used a specially made protective mask made of steel 12X18H10T. The control of the qualitative composition of the plasma was carried out using the modernized spectral complex KSOU-23 [3], in addition, a mass spectrometric analysis of the composition of the plasma was performed. Analysis of emission spectra showed (Fig. 2) that metal impurities formed by spraying the surface of the active electrode and protective mask, which include iron, chromium, nickel, titanium, etc., in plasma at energies of chemically active ions greater than 200 eV are present [4]. The obtained spectra have a rather complex structure, which makes it impossible to fully process them with the identification of all the elements that are present there. However, this makes it possible to link the obtained etching rate of the material to a specific

spectrum of emission. Knowing the general appearance of the spectrum, it is possible to control the rate of etching or sputtering of the material.

The study of the chemical composition of the reacting gases and chemical kinetics was carried out using a time-of-flight mass spectrometer MX-7304A. The analysis of the obtained mass spectrograms revealed ions of atomic chlorine CCl_4^+ , CCl_2^+ , CCl^+ . The obtained results made it possible to understand the chemical processes that occur in the gas phase during the etching of LiTaO_3 . However, it is not possible to record chemical compounds such as TaCl_2 , TaCl_3 or others, because the mass values of these compounds are outside the measuring range of the device (from 1 to 200). The choice of carbon tetrachloride as the working gas is based on the idea of using an exothermic reaction of carbon, which can be formed by dissociation of the molecule CCl_4 , with oxygen:



The research results showed that with a chemical etching-sputtering it is possible to obtain much higher processing rates of the material. Conventional physical sputtering of substrates made it possible to obtain rates of not more than $0.05 \mu\text{m}/\text{min}$, which is unsuitable for etching several tens or hundreds of micrometers.

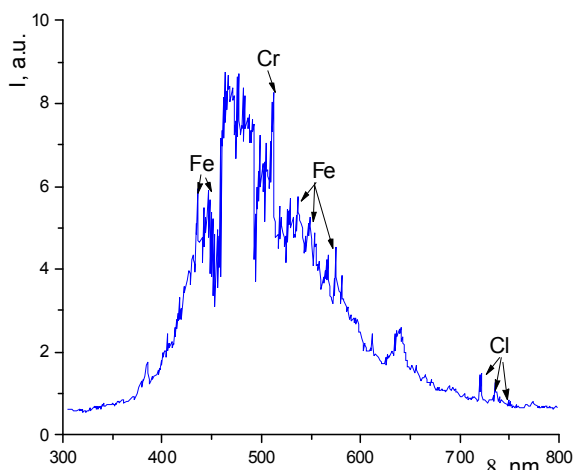


Fig. 2. The emission spectrum of chemically active plasma during the etching of LiTaO_3

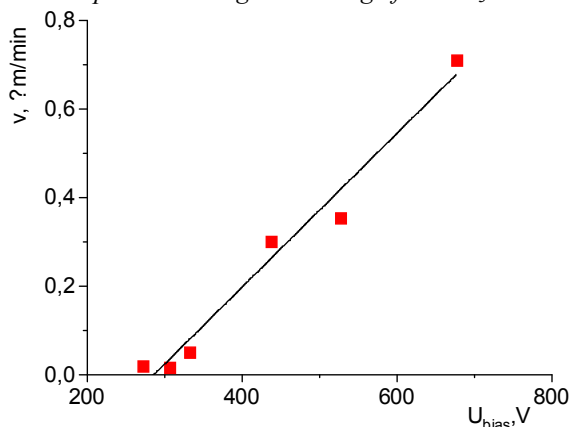


Fig. 3. The dependence of the rate of plasma chemical etching of LiTaO_3 on the bias voltage

In Fig. 3, the dependence of the rate of plasma chemical etching-sputtering of LiTaO_3 substrates de-

pending on the self-bias voltage (ion energy) is presented. As can be seen from the graph, the etching rate is a linear function of the ion energy and it increases from 0.05 to $0.7 \mu\text{m}/\text{min}$.

However, it should be noted that LiTaO_3 substrates do not withstand thermal stress and undergo degradation and destruction at such treatment rates.

It was also recorded that the etching process is strongly influenced by the RF offset generator. There is a sharp decrease in the etching rate to $0.05 \mu\text{m}/\text{min}$ with a decrease in the discharge current from 3 to 1 A with constant other discharge parameters.

The effect of "eating" areas of material adjacent to the edges of the metal mask covering the sample was detected by etching LiTaO_3 . The depth of etching of the material at the edges is 2 times greater than the depth of etching in the central part of the processed sample. This effect may be due to the following two factors.

The first factor is an increase in the constant field strength at the sharp edges of the mask. As shown, the etching rate increases with increasing ion energy, which leads to much deeper etching in places adjacent to the edges of the mask. The second factor is the charging of the dielectric surface in the central part to a certain potential, which limits the flow of ions to the substrate.

The latter factor can be easily counteracted by connecting an additional shift generator with a frequency of 440 kHz. As mentioned above, the connection of this generator allows you to remove static charge from the surface of the dielectric and thus improves the uniformity of etching of the material.

As the results of the research, plasma chemical etching of LiTaO_3 substrates with a total thickness of $200 \mu\text{m}$ was performed. The test samples had to be etched to $2 \dots 3 \mu\text{m}$. The destruction of the tested samples was observed during one-sided etching caused by defects that are on the untreated side of the sample. The sequential etching technology on both sides of the sample was used to eliminate the influence of defects on the reverse side.

After plasma chemical etching, the test samples were purified in plasma of chemically neutral gas (argon). The cleaning time was $3 \dots 5$ min. In this case, if the etching rate of the samples in the reactive plasma was $0.7 \mu\text{m}/\text{min}$, then in the argon plasma did not exceed $0.05 \mu\text{m}/\text{min}$.

It is known that the aggressiveness of chlorinated gases leads to the wear of the vacuum units of the experimental installation. Therefore, a series of experiments were performed using fluorine-containing gases, such as sulfur hexafluoride (SF_6). The RF discharge was ignited in a gas mixture of $\text{Ar} + \text{SF}_6$ in a ratio of 1:1. The processing time was up to 30 min at an RF discharge current of 10 A, a pressure of $5 \cdot 10^{-2}$ Torr. After treatment LiTaO_3 in $\text{Ar} + \text{SF}_6$, a layer of sulfur was recorded on the floor. The etching of the material was virtually absent. The deposited layer of sulfur serves as a stop layer, which practically shields the test sample from chemically active ions.

CONCLUSIONS

The process of lithium tantalate treatment by plasma chemical etching in various gas mixtures using a plasma

chemical reactor with a closed electron drift (coaxial magnetic field) has been developed. It is shown that an etching rate of up to 0.7 $\mu\text{m}/\text{min}$ can be obtained. However, special attention should be paid to the manufacture of protective equipment, as well as to ensure the removal of static charge, which is formed by charging the surface of the processed dielectric. The original technology of etching of LiTaO_3 to the thickness of the core of about 2...3 microns is offered. This plasma treatment technology can be used in the development of optical systems with different core thickness based on LiTaO_3 .

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ОСОБЕННОСТИ ПЛАЗМОХИМИЧЕСКОГО ТРАВЛЕНИЯ ПОДЛОЖЕК ТАНТАЛАТА ЛИТИЯ (LiTaO_3)

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Приведены результаты исследований плазмохимической обработки монокристаллического танталата лития (LiTaO_3) в зависимости от рода газа, напряжения смещения (энергии химически активных ионов), а также от тока дополнительного генератора смещения. Для экспериментов использован плазмохимический реактор с замкнутым дрейфом электронов и газовые смеси, содержащие Ar , $\text{Ar} + \text{CCl}_4$ и $\text{Ar} + \text{SF}_6$. Обнаружено, что скорость травления LiTaO_3 для разряда в газовой смеси $\text{Ar} + \text{CCl}_4$ в 14 раз выше всех используемых смесей. Показано, что предложенная идея и подходы обработки LiTaO_3 могут быть эффективно использованы для производства оптических систем с минимальной толщиной активной зоны около 2...3 мкм.

ОСОБЛИВОСТІ ПЛАЗМОХІМІЧНОГО ТРАВЛЕННЯ ПІДКЛАДОК ТАНТАЛАТУ ЛІТІЮ (LiTaO_3)

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Приведено результати досліджень плазмохімічної обробки монокристалічного танталату літію (LiTaO_3) в залежності від роду газу, напруги зміщення (енергії хімічно активних іонів), а також від струму додаткового генератора зміщення. Для експериментів використано плазмохімічний реактор із замкнутим дрейфом електронів та газові суміші, що містять Ar , $\text{Ar} + \text{CCl}_4$ та $\text{Ar} + \text{SF}_6$. Виявлено, що швидкість травлення LiTaO_3 для розряду в газовій суміші $\text{Ar} + \text{CCl}_4$ у 14 разів вища від усіх інших використовуваних сумішей. Показано, що запропонована ідея та підходи обробки LiTaO_3 можуть бути ефективно застосовані для виробництва оптичних систем з мінімальною товщиною активної зони близько 2...3 мкм.