

INVESTIGATION INTO FINE TECHNOLOGY FOR ION-PLASMA ETCHING OF QUARTZ, LITHIUM TANTALATE, LITHIUM NIOBATE AND LANGASITE

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Abstract

The work is aimed at finding optimal conditions for manufacturing fine piezoelectric membranes and high-frequency resonators. The mechanism of argon plasma etching of piezoelectric crystals has been studied. For this purpose, the SIMS method has been used with a special ion source (FAB) and an electronic control and output processing system.

Introduction

Ion-plasma etching is the most promising method to form a production process for manufacturing sensors of piezoelectric quartz - SiO₂ and promising piezoelectric crystals: lithium tantalate - LiTaO₃, lithium niobate - LiNbO₃, lanthanum gallosilicate (langasite) - La₃Ga₅SiO₁₄. However, the features of ion-plasma etching of quartz and, especially, multicomponent piezoelectric crystals are not studied in practice. The necessary investigations have been carried out in this paper and recommendations are given regarding technology for ion-plasma etching of quartz and piezoelectric crystals of more complex composition.

Experimental technique. To study the piezoelectrical monocrystal sputtering process, a secondary ion mass spectrometer (SIMS) with a source of accelerated atomic particles of inert gas (argon) has been used. The experiment included both time dependence recording of emitted different atomic and molecular specimen components, which is typical to the SIMS method, and a specifically developed technique for studying sputtering selectivity.

The possibility of applying the experimental technique and conditions is proved theoretically as follows. The current of secondary ions emitted during specimen sputtering is determined by expression:

$$I_k^+(E) = \beta_k^+(C_k) \cdot Y_k(E) \cdot C_K \cdot I_0(E), \quad \text{where}$$

$\beta_k^+(C_k)$ is the degree of ionisation of the sputtered particles of the k-th component, $Y_k(E)$ is the sputtering coefficient of the k-th component, C_K is the concentration, $I_0(E)$ is the current of primary

ions, E is the energy of primary ions. By measuring the dependences on $I_0(E)$ for all the components and their compounds under the same conditions of the source of primary particles and on the invariable concentration of the elements on the surface, we can obtain the necessary information about change in the dependence of relative sputtering coefficients of the specimen components on the energy of primary particles:

$$\begin{aligned} I_k(E)/I_n(E) &= \beta_k^+(C) \cdot C_k \cdot Y_k(E) \cdot I_0(E) / \\ &/ \beta_n^+(C) \cdot C_n \cdot Y_n(E) \cdot I_0(E) = \\ &= \alpha_{kn} \cdot Y_k(E)/Y_n(E) \end{aligned}$$

To realise these conditions, it is necessary that the surface composition of the specimen exposed to radiation have no time to change during the measurements of selective dependences $I_k(E)/I_n(E)$. It was established theoretically and experimentally that in this case the optimal current density of bombarding argon particles should be an average of no more than 5 $\mu\text{A}/\text{cm}^2$, and the maximal time of radiation should not exceed 0.5 s. Less than one monolayer is etched then during the measurement time. The required conditions were realised on the MI1201E mass spectrometer equipped with a more versatile and powerful source of inert gas ions.

During the experiment, residual gas pressure in the reaction chamber did not exceed 10^{-7} - 10^{-4} Pa. For the most part, $I_k(E)$ was measured at 64 points, and the range of bombarding particle energy could be varied within 0.25...5.75 keV, if necessary. The time reading of a single curve was 32 s. The heaviest element forming part of the specimen was selected as the n-th (reference) element. That was tantalum for lithium tantalate, niobium for lithium niobate, lanthanum for langasite, silicon for quartz. The instrument control mode, measurement process and measurement processing were executed using the computer. A large number of evidence was obtained as a result of investigations, and only part of it is presented below.

Study results of selective etching of lithium tantalate LiTaO_3 and lithium niobate LiNbO_3 plates. The emission dependences of different atomic and molecular ions emitting from the surface of lithium tantalate x-cut plates during the etching process are characterised by their nonmonotone form (Fig. 1).

The change of emission is the strongest over the range of 0...2 keV, followed by the minimum in the region of 2 keV, which changes into a smooth rise with a sloping maximum at high energies. When the specimen surface is bombarded with low-energy (of the order of 0.5 keV) argon ions, the intensity of $I_{\text{O, Li}}(E)/I_{\text{Ta}}(E)$ falls, indicating that the concentration of lithium and oxygen atoms decreases on the surface of lithium tantalate. Energy augmentation of accelerated argon ions, however, leads again to an increase in concentration of these components. The dependences for the currents of lithium and oxygen emission coincide practically over the whole range of primary particle energies. That assumes that the complexes of Li-O which arise as a result of breaking the bonds of Ta-O during the radiation are formed on the specimen surface with radiation-enhanced diffusion thereof.

The largest number of weakly bound components on the surface of lithium tantalate is observed upon etching the upper layer of 0.45-0.5 μm (determined experimentally) destroyed by mechanical lapping and which consists rather of Ta oxides than the appropriate stoichiometrically bound components of lithium tantalate, if we judge from the nature of emission of the crystal components.

Upon radiation etching of the disturbed layer on the surface of lithium tantalate, the energy dependences of emission for all the elements were measured during the etching process at the energy of accelerated argon ions of 2 keV and then 3.5 keV. In the latter case, the emission of lithium increased again, and the increased etching energy caused the inverse processes to develop - restoration of initial component concentration on the specimen surface (Fig. 2).

After an equilibrium is established, the relative emission of all the components from the specimen surface roughly corresponds to their value at the beginning of bombardment. Thus, stoichiometric etching is practically the result of bombarding lithium tantalate with argon at the energy of 3.5 keV. When further increasing the radiation energy, as follows from Fig. 1-2, oxygen depletion of the surface is observed.

Important distinctions in the regularities of selective processes were not discovered in etching lithium niobate of SAW-cut as compared to lithium tantalate. A slightly more complicated character of these processes is likely to be related to a different

crystallographic orientation of the plate surface with respect to the beam of accelerated particles. As a whole, the conclusions drawn for etching of lithium tantalate are true for lithium niobate as well.

Study results of selective etching of lanthanum gallosilicate plates. The energy dependences of atomic ions forming part of langasite with reference to lanthanum are shown in Fig. 3.

These dependences are obtained for the y-cut of the langasite surface with the destroyed layer having been etched (0.5-1 μm). The fact that the intense maximum of oxygen emission exists in the region of 2 keV can be attributed to an active loss of oxygen from the specimen. The energy dependences of emission for silicon and gallium resemble the corresponding dependences for lithium in lithium tantalate, but with the energy of less than 1 keV, which can be accounted for by the increased mobility of these elements and a large number of them existing in a weakly bound state on the specimen surface. This leads to their selective removal at the energies of less than 2 keV, simultaneously with oxygen removal.

The analysis of change in energy dependences of the elements on the langasite surface during the etching process in one of the experiments was carried out on the specimens after preliminary long-duration bombardment of the plate surfaces for 3.5 hours at the energy of 1 keV (Fig. 4) and then once again 2.5 hours later at the energy of 2 keV.

Comparing them with Fig. 3 shows the distinction between the etching processes. A distinctive feature is the ascending branches occurring at the energies of more than 3 keV with the peak intensities changing significantly (especially that of oxygen). Moreover, as the etching goes on, this tendency enhances with the relative emission of these components decreasing as a whole. This dependence undergoes significant changes for La-O as well. As a whole, at all energies during the etching, change in the stoichiometric composition of the langasite surface is prone to enrichment in lanthanum with changes of that kind leading to a film of lanthanum oxide being formed on the surface and the surface becoming simultaneously amorphous as the final result.

Studies of the processes leading to membrane surface amorphism. To study this phenomenon, change in energy dependences of components emitted while the surface of different dielectrics becoming amorphous has been investigated. Fused quartz and crystalline quartz were chosen as 'reference' objects.

Fused quartz. Oxygen emission increases monotonically with the energy of argon atomic particles growing as well, and no distinguishing features as peaks on the emission curves are observed. The curves for Si-O go across the slanting maximum in the region of 1-2 keV and have a typical 'tail' at high energies. These dependences are used as the basis for the features of amorphism developed on the surface of the materials under investigation.

Crystalline quartz. Originally, the energy dependences of quartz component emission features the presence of a crystalline structure with a typical degree of surface amorphism after mechanical treatment. That can be seen from the characteristic maxima present on all the energy dependences in the region of 2 keV. Further exposure to radiation leads to the corresponding maxima decreasing, and then after etching for approximately 2 hours (dose of 10^{18} cm²) complete amorphism of the quartz surface can be observed. That is indicated by the fact that the energy dependences of the quartz exposed to radiation are in agreement with the identical dependences for quartz glass.

Tantalate and lithium niobate. The analysis of emission energy dependences for the components of these materials shows that under all bombardment conditions the surface is enriched with tantalum or niobium or oxides thereof, and the development of amorphism processes are only observed in a slight degree. That is in qualitative agreement with a well-known criterion for amorphisation of chemical compositions exposed to radiation, in accordance with its amorphisation

occurs when compositions with covalent bonds prevailing (for example Si-O) are bombed with ions, and crystallinity retains or radiation-enhanced crystallisation takes place in compositions with ion bonds prevailing therein. The presence of lithium proper as a component in the tantalate and niobate composition increases significantly the fraction of chemical bond ionicity, facilitating the retention of their crystalline structure over a wide range of radiation exposure.

Langasite. For langasite, as previously mentioned, gallium, silicon and oxygen depletion of the surface and its enrichment in gallium and its oxides can be observed at all energies of argon atoms. The formation of an amorphous and polycrystalline film of LaO - LaO₂ composition and a significant fraction of the amorphous phase together with a crystalline (perhaps polycrystalline) structure on the surface is observed during the ion etching process. For membrane manufacturing, it is preferable to use the bombarding atom energy of 3.5 keV.

Conclusion

Evidence for the mechanism of physical monocrystalline dielectric sputtering process and technological conditions for etching dielectrics of complex chemical compound using inert gas flow of accelerated atomic particles is obtained based on the experimental investigations presented. The investigation results can be used to develop a manufacturing process for monocrystalline membranes without using chemically active agents in the plasma.

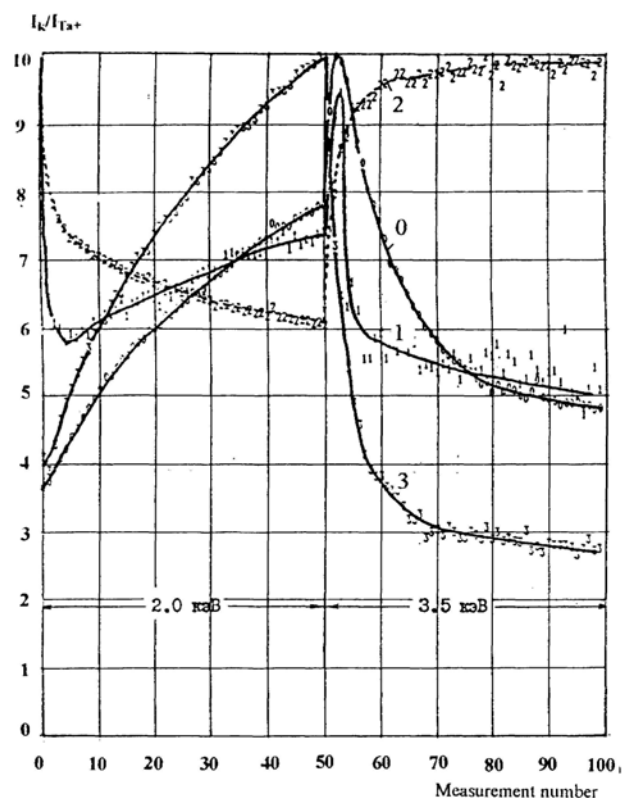


Fig. 2. Dependence of I_k/I_{Ta+} in lithium tantalate on the measurement number (0...50 - 40 $\mu A/cm^2$, 50...100 - 5 $\mu A/cm^2$): 0 - I_{Li+}/I_{Ta+} ; 1 - I_{O+}/I_{Ta+} ; 2 - I_{TaO+}/I_{Ta+} ; 3 - I_{TaOLi+}/I_{Ta+} .

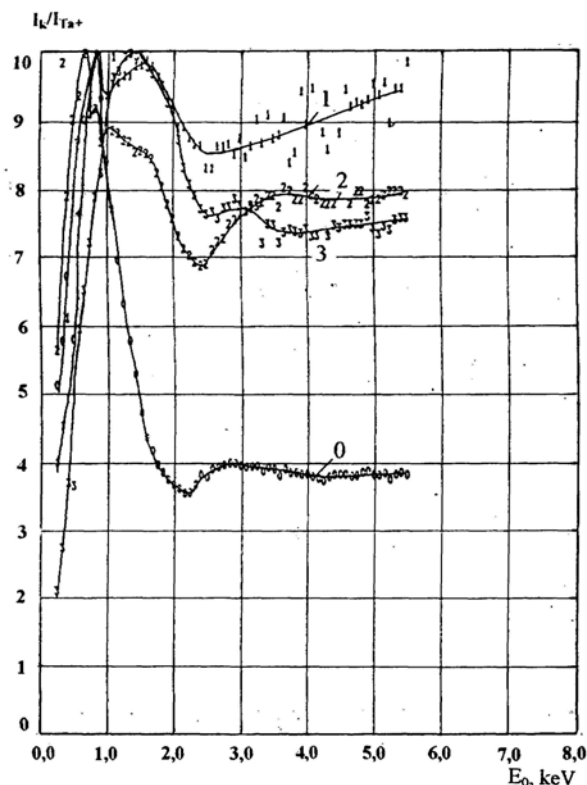


Fig. 1. Dependence of I_k/I_{Ta+} in lithium tantalate on the argon ions energy: 0 - I_{Li+}/I_{Ta+} ; 1 - I_{O+}/I_{Ta+} ; 2 - I_{TaO+}/I_{Ta+} ; 3 - I_{TaOLi+}/I_{Ta+} .

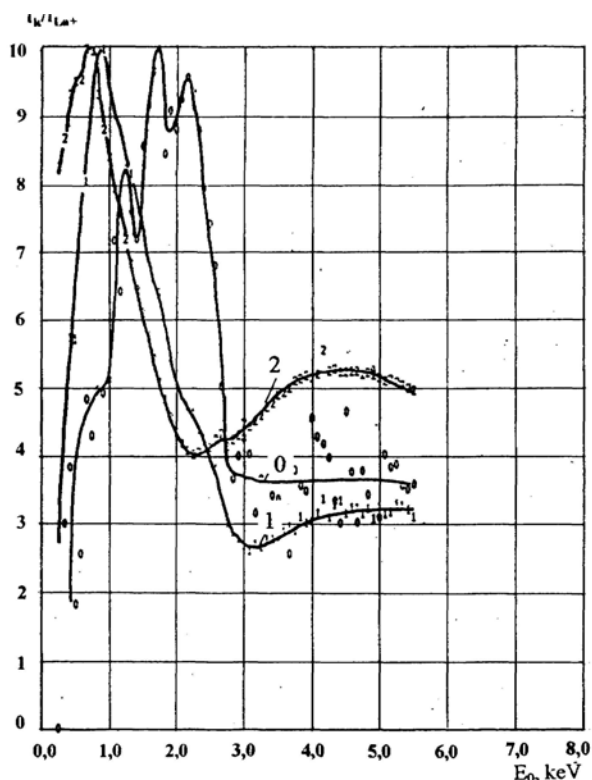


Fig. 3. Dependence of I_k/I_{La+} in langasite on the argon ion energy: 0 - I_{O+}/I_{La+} ; 1 - I_{Si+}/I_{La+} ; 2 - I_{Ga+}/I_{La+} .

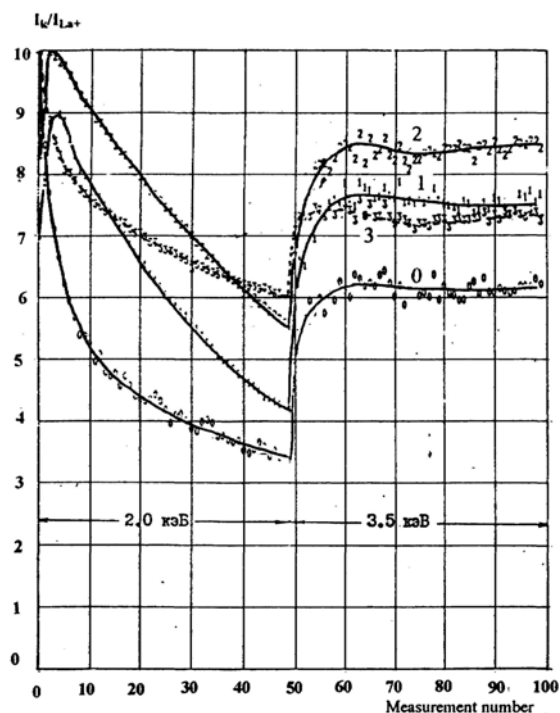


Fig. 4. Dependence of I_k/I_{La+} in langasite on the measurement number (0...50 - 40 $\mu A/cm^2$, 50...100 - 5 $\mu A/cm^2$): 0 - I_{O+}/I_{La+} ; 1 - I_{Si+}/I_{La+} ; 2 - I_{Ga+}/I_{La+} ; 3 - I_{LaO+}/I_{La+} .