Dissociation and synthesis of target components during laser ablation of LiNbO$_3$

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Abstract. This paper shows the results of thermodynamic analysis of interfacial interaction in the lithium-niobium-oxygen system. The temperature dependences of the change in the Gibbs free energy calculated, taking into account the non-linear temperature dependences of the thermophysical properties of materials. Additionally, estimated the possibility of dissociation reactions of lithium and niobium oxides, as well as the reactions of lithium and niobium with oxygen. The results obtained can be used in the design and manufacture of integrated acousto-optic and piezoelectric devices, as well as for sensitive elements of sensors using various effects of surface acoustic waves.

1. Introduction

Over the past few years, the range of wireless wearable sensors and portable electronic devices has significantly expanded, in most cases, electrochemical batteries are used to power them [1-3]. Even though the performance of electronic devices is increasing every year [4-7]. However, significant progress in the creation of promising batteries has not yet been achieved. A promising approach in the field of energy harvesting is the development of piezoelectric transducers, which converts the mechanical energy of the environment into electrical energy [8]. These transducers can be used as the power sources for wearable electronics devices [9].

Due to the unique combination of LiNbO$_3$ piezoelectric, optical and ferroelectric properties, it can be considered that the backbone of promising piezoelectric energy converters, which are distinguished by high efficiency and environmental safety and fabricated by microelectronic technology. Nevertheless, at the current stage of technological development, it is challenging to build devices based on ferroelectric films due to the problems associated with insufficient development of the production technology. Most ferroelectric and piezoelectric materials (BaTiO$_3$, PbTiO$_3$, LiNbO$_3$) are multicomponent oxides, which significantly complicates the process of creation and their integration with the technology of micro- and nanoelectronics.

Pulsed laser deposition (PLD) is one of the most promising methods for the fabrication of multicomponent oxides films, due to a large number of technological parameters, which makes it possible to control the composition of the films formed, as well as their morphological and electrical properties. In the literature, the stoichiometry transfers during PLD process studied insufficiently. It is considered that incongruence ablation does not have a significant impact on the deposition. Nevertheless, laser ablation is a high-energy process and, therefore, when a laser pulse is applied to a
multi-component target, the molecules of the target can dissociate, and as a result, the properties of grown films might be different from initial target properties (structure, composition) [10].

Therefore, the goal of this work is studying thermodynamics regularities of target material dissociation and synthesis processes during laser ablation of LiNbO₃ target.

2. Theoretical analysis
In order to study the phase formation processes during laser ablation of lithium niobate target, the possibility of chemical dissociation and synthesis of LiNbO₃ in the passage space at temperatures from 550 °C to 8500 °C is estimated. The Gibbs free energy change (ΔG) dependences on temperature were calculated using the chemical analysis software package FactSage 6.2 (GTT-Technologies, Germany), which has a regularly updated electronic database in the field of chemical thermodynamics.

In the study of thermodynamic regularities, we took into account the possibility of interaction between the target components between themselves and the background atmosphere in the growth chamber. To simplify the perception of the results, stoichiometric coefficients in the equations of chemical reactions were taken into account but were omitted.

3. Results and discussion
In order to analyze possible dissociation reactions of LiNbO₃ during laser ablation, decomposition reactions of lithium niobate in a vacuum (10⁻⁵ Torr) and oxygen atmosphere (10⁻² Torr) were identified.

Figure 1 shows the temperature dependences of change in the Gibbs free energy for LiNbO₃ dissociation reactions of target components during laser ablation of LiNbO₃ target.
Figure 1 (a, b) Temperature dependences of $\Delta G$ for dissociation reactions of LiNbO$_3$ in (a) vacuum and (b) oxygen atmosphere

The analysis of the presented dependences showed that the most probable dissociation reaction of lithium niobate in vacuum and oxygen atmosphere at an oxygen pressure of $10^{-2}$ Torr is leading to the reaction $\text{LiNbO}_3 = \text{Li}_2\text{O} + \text{Nb}_2\text{O}_5$, which begins at temperatures above 1230 °C and 1540 °C, respectively. If the temperature increases to 1760 °C (for vacuum) and 2189 °C (for oxygen atmosphere, pressure of $10^{-2}$ Torr), LiNbO$_3$ can dissociate on Li$_2$O and Nb$_2$O$_5$. With a further increase in temperature up to 5140 °C, LiNbO$_3$ dissociated into individual elements. At a temperature of 5190 °C in a vacuum, lithium niobate can decompose on Li$_2$O$_2$ and NbO. When the oxygen pressure is $10^{-2}$ Torr, the $\Delta G$ value of the other reactions is positive over the entire considered temperature range. Their flow in the forward direction in the temperature range from 550 °C to 8500 °C is impossible.

Obtained during the decomposition of LiNbO$_3$ oxides of niobium and lithium can also dissociate into individual elements. Figure 2 shows the temperature dependences of $\Delta G$ for dissociation reactions of lithium oxides in vacuum and oxygen atmosphere.
During the analysis of the obtained dependences, it was established that the Li$_2$O$_2$ decomposition into Li$_2$O and oxygen proceeds in the forward direction in the entire considered temperature range both in a vacuum and in an oxygen atmosphere at a pressure of $10^{-2}$ Torr. In the temperature range above 1500 °C, the competing reactions are the dissociation reactions of Li$_2$O$_2$ and Li$_2$O into individual elements. It should be noted that the presence of oxygen stabilizes lithium oxides, which prevents their thermal dissociation.

Figure 3 shows the temperature dependences of $\Delta G$ for dissociation reactions of niobium oxides in vacuum and oxygen atmosphere.
When analyzing the dependences of the reactions of decomposition of niobium oxides, it is possible to identify temperature ranges in which the occurrence of a particular reaction will be more likely. For a vacuum in the temperature range from 8500 °C to 3100 °C, the most suitable reaction will be the decomposition of Nb₂O₅ into individual elements. In the temperature range from 3000 °C to 1800 °C, competing for Nb₂O₅ decomposition reactions are possible.

In the process of the laser plume propagation from the target to the substrate, the temperature in it decreases, creating favorable conditions for the reactions of the interaction of components from the atmosphere of the growth chamber.

4. Conclusion
As a result of the thermodynamic analysis, the temperature ranges of formation of lithium and niobium compounds with oxygen were determined. Noticeably, the creation of oxides Li₂O and Nb₂O₅ is most feasible compared to the formation of other oxide phases. It was theoretically calculated that the dissociation of LiNbO₃ is a multistage process, which correlated to the results presented in [11]. In the first stage of the ablation process, lithium niobate dissociates into oxides with lower oxygen content. At temperatures above 1777 °C, the oxides decompose and complete dissociation of the target material into Li, Nb, and O₂. When the plasma plume expands, the processes of interaction of Li and Nb with O₂ occur with the formation of oxides, caused by a decrease in temperature. Obtained results can be used in the design and manufacture of piezoelectric energy harvesters based on LiNbO₃ films. The region of high temperatures corresponds to the base of the laser plume arising from the ablation of the target, the region of low temperatures is the tip of the plume.

The results obtained can be used in the design and manufacture of integrated acoustic-optic and piezoelectric devices, as well as sensitive elements of sensors using various effects of surface acoustic waves.

Acknowledgments
This work was financially supported by the Russian Foundation for Basic Research (project № 18-29-11019 mk). The work was done on the equipment of the Research and Education Centre «Nanotechnology» and Collective Use Centre «Nanotechnology», Southern Federal University.
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