Investigation of near-surface layer dislocation density of lithium niobate single crystal wafers using chemical etching

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Abstract. Using chemical etching it was shown that the density of dislocation in lithium niobate (LN) single crystal wafers is higher near the surface in depth about 20 um than in the depth of crystal. It caused to change of diffusion coefficient during the waveguide formation with proton exchange (PE) method and can increase DC-drift of intensity optical modulators based on PE-waveguides.

1. Introduction

Lithium niobate (LN) crystal is a key material in the manufacture of basic elements of integrated optical circuits, in particular phase and intensity modulators. Distinctive features of LN single crystals are high electro-optical coefficients, high Curie temperature and the possibility of forming waveguide structures with low optical losses [1].

When considering the surface properties of LN single crystals of various cuts, additional opportunities are found for their fundamental research and applications [2]. It is known that the composition and structure of the near-surface layer of the LN crystal differ significantly from the rest of the material volume, which is clearly shown in [3]. These features of the structure of the near-surface layer have a deformation nature and arise during cutting and subsequent polishing of NL plates [3,4]. Many aspects of the formation and state of this layer were discussed repeatedly, but the real structure of this layer was not presented. In this case, the influence of inhomogeneities in the structure of the near-surface layer of the LN is the main factor associated with the instability of the optical characteristics of integrated-optical schemes [5] and the manufacture of proton-exchange waveguides [6]. Thus, the aim of this work is to reveal the real (dislocation) structure of the surface layer of LN single crystals.

2. Research methodology

In this work, we investigated LN single crystals of congruent composition in X- and Z-cuts. The identification of the real structure of the crystals under study was carried out by the method of selective etching of the working surface of single crystals, as well as the cross section (end) of the LN plates after fracture. The fracture was carried out according to the method described earlier in [3].
Etching of pre-purified samples was carried out in a potassium hydroxide (KOH) melt with the addition of 35 wt% NaOH, as described in [7]. The wet selective etching regime was identical for all samples.

The study of the etching pits on the working surface was carried out by the method of optical microscopy; the fracture structure, i.e. the cross-section of the plates - by scanning electron microscopy. Optical measurements were carried out using a Leica DMI8 microscope in reflected light in bright field mode.

Electron microscopic studies were carried out in the mode of secondary electrons at an accelerating voltage of 20 kV using a Hitachi S3400N microscope. Before the start of electron microscopic studies, a thin (~ 2 nm) metallic Au film was preliminarily deposited on all experimental samples using a compact SC7620 magnetron sputter.

3. Research methodology

It is known that during selective etching of single crystals, etching pits are formed on their surface, which have a certain geometric shape, depending on the crystal structure of the material and the crystallographic orientation of the etched plane [8]. Thus, in [9], it was shown that for Z-cut NL plates when etching the plane (0001), the pits have the form of regular triangles (symmetry axis of the 3-rd order), for planes perpendicular to the [10$ar{1}$0] direction, i.e. for the X-cut, the etch pits are rhombic. In the course of etching the working surfaces of the studied NL plates, numerous etching pits were found, corresponding to the dislocation structure of the NL surface layer. Etching patterns are shown in Figure 1 for X- and Z-slices left and right, respectively.

![Figure 1. Etching pits for NL X-cut (a) and Z-cut (b). Optical microscopy results.](image)

Figure 1 shows that on the surface of the plates of Z-cut shape of most of the etching pits has a symmetry of the third order, which is in good agreement with [9].

The displacement of the top of the pit indicates a deviation of the dislocation axis from the [0001] direction due to the presence of deformations. For an X-cut crystal, etching pits were obtained in the form of highly elongated and distorted rhombuses with long axes parallel to the crystallographic direction [01$ar{1}$1]. The strong distortion of the shape of the etching pits is also associated with the deformation of the crystal lattice in the near-surface layer of the crystal. The density of the etching pits is $8 \times 10^4$ cm$^{-2}$ for an X-cut crystal and $2 \times 10^4$ cm$^{-2}$ for a Z-cut.
The advantage of this technique for revealing the real structure of the near-surface layer of an LN single crystal is the simplicity and speed of the experiment, however, the fundamental disadvantage of this research method is that it does not allow one to get an idea of the distribution of dislocations in the bulk of the crystal. For this reason, the etching of fresh transverse chips of X- and Z-cut LN plates was carried out. The plates were split according to the method described in [3], thus, the breaks correspond to the spalls close to the planes $\{2\overline{1}1\}$ and $\{0\overline{1}0\}$. The indicated planes were etched.

In figure 2 shows the results of revealing the dislocation structure of the LN plates with X- and Z-cuts after fracture (cross section). Investigation of the cross-section of the LN plates after fracture makes it possible to show the real structure of the entire LN crystal as representatively as possible.

![Figure 2](image_url)

Figure 2. Etching pits of the LN after fracture (cross section): plane $\{2\overline{1}1\}$ (a) and $\{0\overline{1}0\}$ (b).

It can be seen that the near-surface layer has an increased density of not just point defects, but dislocations, in contrast to the rest of the material volume.

The depth of the defect layer is up to 50 µm for LN Z-cut (etching plane $\{2\overline{1}1\}$) and 10 µm for LN X-cut (etching plane $\{0\overline{1}0\}$). The formation of this defect layer occurs in the process of cutting and subsequent grinding of a single crystal boule. Similar features are typical for other single-crystal wafers, for example, for silicon carbide [10], which is also used to create integrated-optical devices.

4. Summary

Thus, by the method of selective etching, it was possible to reveal the real - dislocation structure of the damaged near-surface layer of LN crystals, which significantly differs in increased defectiveness from the rest of the volume of a single-crystal LN plate.

The results obtained are important, first of all, from a practical point of view. The presence of a defect layer can lead to both a deterioration in the characteristics of devices and a decrease in the stability of the operation of integrated optical devices based on single crystals of LN. In the near-surface layer, proton-exchange, titanium-diffuse, ion and laser waveguides are formed. The optical characteristics of waveguides are determined by the structure of a given subsurface layer. Undoubtedly, in the process of manufacturing and operating various integrated optical components based on LN, it is necessary to take into account the increased density of dislocations in its near-surface layer. In the future, it is planned to study the real structure of NL plates of various manufacturers and search for a method to reduce the defectiveness of the near-surface layer or to remove it.

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References

[1] Chen A and Murphy E 2012 *Broadband Optical Modulators: Science, Technology, and Applications* (CRC Press)

[2] Sanna S and Schmidt W G 2017 *J. Phys.: Condens. Matter* **29** 413001

[3] Sosunov A, Volyn' tev A, Tsiberkin K, Yuriev V and Ponomarev R 2017 *Ferroelectrics* **506** (1) 24–31

[4] Galinetto P, Marinone M, Grando D, Samoggia G, Caccavale F, Morbiato A and Musolino M 2007 *Opt. Lasers Eng.* **45** (3) 380–384

[5] Salvestrini J, Guilbert L, Fontana M, Abarkan M and Gille S 2011 *J. Light. Technol.* **29** (10) 1522–1534

[6] Kostritskii S, Korkishko Y, Fedorov V, Mitrokhin V, Sevostianov O, Chirkova I, Stepanenko O and De Micheli M 2014 *J. Eur. Opt. Soc. Rap. Public* **9** 14055

[7] Franko N, Ped’ko B and Sorokina I 2004 *Crystallogr. Rep.* **49** 94–99

[8] Sangwal K 1987 *Etching of Crystals: Theory, Experiment and Application* (North Holland)

[9] Nassau K, Levinstein H J and Loiacono G M 1966 *J. Phys. Chem. Solids.* **27** (6-7) 983–988

[10] Friedrichs P 2011 *Silicon carbide: Growth, defects, and novel applications*. (John Wiley & Sons)