Study of anomalous behaviour of LiTaO\(_3\) during the annealed proton exchange process of optical waveguide’s formation – comparison with LiNbO\(_3\)

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Abstract

This paper deals with a detailed study of changes that lithium tantalate (LT) and lithium niobate (LN) single crystals undergo during the annealed proton exchange (APE) process of optical waveguides’ formation. It is a well-known fact that several cases of anomalous behaviour are connected to the APE:LT samples, bringing thus an obstruction for the practical utilization of the APE:LT waveguides. As the LT crystal possesses even better optical properties than the LN crystal (e.g., it is less susceptible to optical damage), it is desirable to provide research focused on its behaviour during the APE process in order to acquire a control over the fabrication of the APE:LT devices. Neutron depth profiling (NDP), elastic recoil detection analysis (ERDA) and heavy ion ERDA (HI-ERDA) were performed to study changes in the surface of the LT and LN Z-cut wafers caused by the APE treatment and to determine the concentration depth profiles of the exchanged ions (lithium and hydrogen). Information on modifications of the crystals during the APE was obtained using X-ray diffraction (XRD) analysis. Optical/waveguiding properties of the samples were obtained by means of the standard mode spectroscopy at 633 nm. The experiments proved that the LT is significantly less affected by the APE process compared to the LN and that most characteristics of the APE:LT layers can be easily restored towards that of the virgin crystal by the annealing process.

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1. Introduction

Lithium tantalate (LiTaO\(_3\), LT) and lithium niobate (LiNbO\(_3\), LN) are a pair of very promising electro-optical crystals for a long list of utilization in photonics devices used for harnessing and distribution of optical radiation as, e.g., ultra-fast switches, multiplexors and demultiplexors and in the last decades also optical amplifiers and waveguide lasers \([1–3]\). Basic parts of most of such devices are optical waveguides. Generally, two main methods can be used for the fabrication of the optical waveguides in the optical crystals: (i) a high temperature in-diffusion of certain metal ions into the crystal wafer surface and (ii) a moderate temperature approach based usually on an ion-exchange process. In the case of LN and LT these are high temperature in-diffusion of titanium and annealed proton exchange (APE) \([4,5]\), respectively. While the photonics
structures based on the LN waveguides are nowadays widely used and almost commercially available, LT, despite its much better prognosis (due to its two orders of magnitude higher threshold of optical damage), has so far been much less utilized. The reason for that is: (i) a rather low Curie temperature (615 °C) of the LT (compared with the 1050 °C for the LN), that does not allow for using the high temperature fabrication approach and (ii) reported anomalous behaviour [4,6,7] of the APE:LT waveguides, compared to those made in the LN, that makes controlling of the fabrication process rather difficult.

To ensure that the fabrication process will result in the formation of the optical waveguides with fully reproducible properties, and in order to be able to tune the properties of the waveguides according to the desired application, one should fully understand the nature of the relations between the particular fabrication procedures and chemical composition and optical properties of the resultant optical layers.

As stated above, the APE process is the only feasible way of waveguide fabrication in the LT crystals. It is the aim of this paper to report on the effects caused by both fabrication steps of APE – proton exchange (PE) and annealing (A) of the as-exchanged samples – on modifications of the structure and composition of the surface layers in the LT single crystal wafers (put in comparison with those in the LN).

2. Experimental

In the experiments we used polished wafers of congruent LN and LT single crystals of crystallographic orientation (0001), so-called Z-cut, provided by AVTEX, Czech Republic. The wafers were thoroughly cleaned in 2-propanol before and after the fabrication process. The proton exchange (PE) occurred after immersing the samples into a molten proton source, which was environmental-friendly adipic acid buffered with a small addition (0.5 mol.%) of lithium carbonate. Duration of the PE reaction varied from 3 to 5 h and was performed at 213 °C. The as-exchanged samples were annealed (A), i.e., heated in air, immediately after PE in order to: (i) stabilise the layers’ properties, (ii) deepen the layers and (iii) achieve redistribution of the exchanged ions (protons and lithium ions). The annealing procedure was done at 350 °C for 0.5–10 h.

The optical/waveguiding properties of the fabricated layers, i.e., the number of guided modes and refractive index depth profiles of the formed waveguides, were determined by the standard mode spectroscopy at 632.8 nm (a prism coupling set-up). The $n(x)$ profiles were evaluated from the extraordinary (TE) modes’ spectra by means of the inverse WKB method [8].

The NDP (Neutron Depth Profiling) analysis brought information on the lithium distribution in the samples up to depths (typically in the LN and LT) of 7 μm. This method is based on the $^4\text{He}\left(n_{th},^4\text{He}\right)^1\text{H}$ nuclear reaction of thermal neutrons with $^6\text{Li}$ isotope [9]. The advantage of the NDP is mainly its non-destructiveness, profound range of inspection, and an excellent depth resolution of approximately 10–15 nm. The natural abundance of the “NDP active” $^6\text{Li}$ isotope is 7.5%, however, in the actual samples the $^6\text{Li}/^7\text{Li}$ ratio may significantly vary. Thus, to avoid uncertainty induced by this variation, for our considerations we rely on the relative changes in the lithium concentration rather than on their absolute values.

The ERDA (Elastic Recoil Detection Analysis) measurement provided concentration profiles of hydrogen incorporated into the samples surface up to the depth of 500 nm (again, typically for the LN and LT). The measurement was performed in a glancing geometry using a He$^+$ particle beam (2.68 MeV); recoiled protons were registered under the angle of 30° with a surface barrier detector covered with a 12 μm thick Mylar stopping foil. The obtained ERDA spectra were evaluated using the computer code SIMNRRA [10].

The HI-ERDA (Heavy Ion Elastic Recoil Detection Analysis) measurement was done to obtain simultaneous hydrogen–lithium concentration profiles. HI-ERDA was applied using 30 MeV Cl-ions from a 5 MV Tandem accelerator. Scattered ions and light recoils (except hydrogen) were detected by a Bragg Ionisation Chamber located under the scattering angle of 30°, hydrogen recoils were detected with a Si-detector covered by a 18 μm thick Al foil to stop all other recoils and scattered ions. The energy spectra of the separated elements were converted into concentration depth profiles by means of a computer code [11] using the stopping power data from Ziegler et al. [12].

The XRD analysis was performed on the D5005 diffractometer (Siemens/Bruker AXS) with a 1/4 circle Eulerian cradle using Cu–Kα radiation ($\lambda = 0.154$ nm). The samples were adjusted at high-angle LN and LT reflections with $\theta$ and $\chi$ axes; diffractograms were recorded by 1:2 coupled scans (step size = 0.05°).

3. Results

3.1. Chemical composition of the layers

Determination of the chemical composition of the fabricated layers revealed the extent of the difference in behaviour of the LT and LN crystals. It is a well-known fact [4,7] that to form APE:LT waveguides of similar properties as in the LN, substantially more fierce fabrication conditions have to be applied (higher temperature and/or longer times of PE) as the diffusion coefficients of the exchanged ions are much smaller in this case. The typical concentration profiles of lithium in the APE treated LT and LN wafers are shown in Fig. 1. One can see that the mobility of lithium ions (understand here as a “willingness” of the $\text{Li}^+$ ion to be exchanged) in the LT matrix is actually much smaller compared to the LN; the surface depletion of lithium after the APE process is lower – approx. 20% of the bulk value (compare with 40% in the LN) and involved much shallower depth of the exchanged layer – up to 1.5 μm (compare again with 4 μm in the LN).
The integral amount of depleted lithium (in the depth region from 0.2 to 4 μm) also significantly varies for both crystals — the amount of out-diffused lithium is almost one order of magnitude lower in the case of the APE:LT.

The NDP observation was confirmed by the ERDA analysis (see Fig. 2) — again, the amount and the depth of the hydrogen incorporation were found to be much smaller in the case of the LT substrates. The hydrogen concentration in the LN wafers treated by the 3- and 5-h PE process is almost the same (in the range of depth observed by ERDA), while this differs significantly in the LT samples. One of the anomalous features of the tantalate single crystal is presented in Fig. 2(a) — in contrast to the diffusion theory, the amount of the in-diffused protons decreases after longer time of the PE process. The same effect appeared during the HI-ERDA measurement (see Fig. 3).

An important fact revealed when the samples were subjected to HI-ERDA measurement — the “up-side-down” effect of the PE duration on the concentration of incorporated hydrogen in the LT (see Fig. 3(a)) resembles the effect of the long lasting annealing process in the LN (see Fig. 3(b)). During the post-exchange annealing (A), the H-doped layers are heated in air and consequently redistribution of protons takes place, i.e., the layers containing hydrogen are deepened and the surface hydrogen concentration decreases [5,13]. Typically (in LN, see Fig. 3(b)), the concentration of H⁺ is higher than that of Li⁺ ions after 0.5 h of A and then, after long lasting annealing (10 h), its concentration decreases towards the value lower than that of lithium.

Using the above mentioned analytical methods we found out that it is possible to (almost completely) reconstruct the chemical composition of the original LT matrix even after only 2 h of the annealing. From our previous experiments we know that the same effect is in the case of LN possible only after about 100 h of the annealing.

3.2. Modification of the crystal

The XRD measurement revealed changes in the internal strain induced by APE in the surface layers of the Z-cut LT wafers (see Table 1). As one can see, the strain that
occurred in the layers after the PE procedure decreases substantially with the post-exchange annealing duration; after the 2 h annealing it is even almost completely relaxed out. A similar effect was observed when studying chemical composition of the fabricated layers (see above) and also by the RBS (Rutherford Backscattering Spectroscopy)-channeling analysis, which confirmed the almost complete restoration of the original structure of the LT (for details see [14]).

It might be surprising that the internal strain in the exchanged layers decreased with prolonged time of proton exchange. However, the HI-ERDA analysis proved that using the 5 h PE process (compared to the 3 h PE) in the LT has a similar effect on the chemical composition of the surface layer as has the annealing in the LN. Therefore, bearing in mind that variations in the internal strain are associated with the changes in the chemical composition of the pertinent layer, the observed phenomenon seems to be logical.

Comparison of the XRD diffractograms confirms that the Z-cut APE:LT species differ from the Z-cut APE:LN ones (see Fig. 4). Despite the observed strain in the APE:LT, the APE:LN does not exhibit presence of the strain in the treated crystal; the spectra give evidence on the formation of the layers with more imperfect crystal structure instead.

3.3. Optical properties of the fabricated waveguides

It is known [4,7], that the behaviour of the LT crystal during the APE process is significantly different from that of the LN one (effect of the ion exchange is much weaker). For a comparison of waveguiding properties of the APE:LT and APE:LN, the fabrication conditions were chosen so that the formed APE:LT planar waveguides were supporting at least one optical mode. The resultant optical properties of the samples as determined by mode spectroscopy are given in Table 2. We expect that according to the

Fig. 3. Concentration profiles of H⁺/Li⁺ ions in APE:LT (a) and APE:LN (b) determined simultaneously by HI-ERDA (profiles of lithium were smoothed). Resemblance of the effect of prolonged PE (in LT) and prolonged A (in LN) is evident.

![Fig. 3](image_url)

Table 1

<table>
<thead>
<tr>
<th>Fabrication conditions (duration of PE/A) (h)</th>
<th>Internal strain [δd/d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/0.5</td>
<td>5.81 × 10⁻³</td>
</tr>
<tr>
<td>5/0.5</td>
<td>1.38 × 10⁻³</td>
</tr>
<tr>
<td>5/2</td>
<td>0.69 × 10⁻³</td>
</tr>
</tbody>
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Fig. 4. XRD spectra of the optical layers fabricated by APE in the Z-cut LT (a) and LN (b).
refractive index increments and shape of the refractive index depth profiles the fabricated APE:LN layers may be described as being similar to the β- or κ-phases reported in [15].

One can see that prolonging of the annealing time up to 2 h resulted in the formation of the two-mode optical waveguides despite the fact that all other analysis mentioned above (obtained chemical composition and crystal modification) proved “reconstruction” of the treated surface layers towards the virgin structure.

4. Discussion

The main difference between the LT and LN substrates – as shown in this study – is in the substantially lower permeability (i.e., higher chemical durability) of the LT for the exchanged ions (see Fig. 5). Consequently, the optical/waveguiding properties of the APE:LT samples are less pronounced compared to the APE:LN.

When carrying out the presented fabrication procedure (i.e., “soft proton exchange” from the point of view of the LT crystal modification), the 5 h PE appears to have a similar effect as the post-exchange annealing. The samples are no longer doped with protons, just the opposite – the redistribution of the H⁺ ions takes place so that the surface concentration of the already incorporated protons significantly decreases.

The experiments revealed that in the case of the APE:LT, fabricated by our procedure, the change of the chemical composition and crystal modification of the PE-treated samples can be directed towards those of the virgin crystal simply by a long-term annealing (2 h). At the same time, the waveguiding properties of the samples are preserved and, therefore, we can expect that the α crystallographic phase (which most of the possible phases resembles the virgin crystal [16]) was obtained in some of our samples.

5. Conclusion

We report about comparison between the APE:LT and APE:LN samples fabricated using non-toxic adipic acid. The obtained results proved that the already reported differences between both types of the waveguides can be attributed to lesser permeability of the LT crystal for the migrating ions (H⁺ and Li⁺). The APE procedure results in the case of the LT in shallower surface layers with less profound change in chemical composition and, similarly, a lower number of the guided modes. The very significant part of the fabrication process appeared to be the annealing of the as-exchanged waveguides that allowed for the restoration of the structure and the chemical composition of the exchanged layers towards that similar to the original crystal and this way to fabricate the optical waveguides in the desired α-phase.

So, relating to our experiments, it can be expected that if the suitable fabrication conditions were found, i.e., deeper APE:LT layers with more substantial change in their chemical composition (comparable to the presented APE:LN samples) were fabricated, the similar “intensity” of optical/waveguiding properties (e.g., higher increment of the refractive index) would be achieved also in the LT.

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References