Comparison of Crystal Lattice Changes Caused by APE Treatment of Er:LiNbO$_3$ and by Localised Er Doping into LiNbO$_3$ Obtained by RBS-Channeling and XRD Analysis

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Abstract

Lithium niobate containing erbium (Er: LiNbO$_3$), which is often used as non-linear optical material, was studied by Rutherford Backscattering Spectroscopy (RBS) - channelling analysis and X-Ray Diffraction (XRD). The Er^{3+} doping was done by both bulk doping and by localised doping. The studied samples were virgin Er: LiNbO$_3$ wafers, and Annealed Proton Exchange (APE) treated wafers in order to increase the refractive index in the surface layer and to create the planar optical waveguides. Moreover, erbium ions were introduced into the surface of pure LiNbO$_3$ wafers by Er-moderate temperature localised doping. The APE: Er: LiNbO$_3$ samples showed modifications of the crystal lattice compared to the virgin Er: LiNbO$_3$; the Er localised doping samples even exhibited the tendency to form an amorphous surface layer in which the Er ions were incorporated.

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Introduction

Several techniques for the incorporation of Er^{3+} ions into lithium niobate have been investigated over the last few years. The most common technique is bulk doping of the substrates, which is done during the crystal growth, however, for many reasons, localised doping with laser-active particles, which occurs in the well defined area in the substrates surfaces, is a much more suitable alternative. Diffusion from a thin film of metallic erbium deposited onto a substrate wafer is a well-developed technique nowadays [1]. In this paper, the possibility of medium-temperature (below 600 °C) localised doping of Er^{3+} ions into lithium niobate has been studied as well, using in-diffusion of erbium from a melt containing erbium salt. The Er position in virgin Er:LiNbO$_3$ crystal lattice was studied and compared with the Er position in APE treated samples [2], [3]. The above-mentioned treatments are used to fabricate low-loss optical waveguides that are basic parts of many optoelectronic (photonics) devices. Rare earth (RE) dopants are used to develop new materials for applications such as lasers, optical amplifiers or waveguide lasers. The positions of the RE dopants often rely on the ability to introduce the appropriate additives into a selected lattice site, either during the crystal growth, or afterwards by diffusion. Crystal changes in the case of the APE-treated samples occurred as was concluded from RBS-channeling and XRD measurement. We present here the evaluation of the relative defect density of the APE treated

samples and the samples treated by Er-localised diffusion as deduced from the RBS-channeling technique.

Experimental

The congruent Er:LiNbO$_3$ single crystal containing 5000 ppm of Er was grown by the standard Czochralski method (AVTEX Turnov). The crystal was cut into 0.7 mm thick wafers corresponding to the x- (<11-20>), y- (<01-110>) and z - (<0001>) cuts, in which the planar waveguides were fabricated by the APE process at 213 °C for 3 hours using adipic acid as the proton source. The wave-guides were single mode at λ=1.5 μm and the depth of the incorporated protons reached to about 10 μm into the wafer, as did also the depletion of lithium. Localised in-diffusion of the erbium ions from an external source was provided by immersion of the substrate wafers into reaction melts containing 10 weight % of Er(NO$_3$)$_3$ and kept there at 350°C for times varying from 138 to 168 hours. The post-diffusion annealing processes were done under ambient or oxygen atmosphere in a standard laboratory oven. The RBS-channeling experiments were performed at the Forschungzentrum Rossendorf, Dresden, Germany using a beam of 1.8 MeV He$^+$ ions from a Van de Graaff accelerator and the standard measuring procedure [4]. Elastic Recoil Detection Analysis (ERDA) measurement was used for hydrogen depth profiling of the APE treated samples. The glancing geometry ERDA measurement with He$^+$ ion beam was performed to obtain the hydrogen content in the surface layer. In ERDA measurement we used 2.68 MeV He$^+$ ion beam and the recoiled protons were registered under the angle of 30^0 by a surface barrier detector covered with 12 μm thick Mylar stopping foil**.** XRD measurements were performed on D5005 (Siemens/Bruker AXS) with 1/4 circle Eulerian cradle and Cu-Kα radiation (λ= 0.154 nm). The samples were adjusted at high-angle Er:LiNbO$_3$ reflections with θ and χ axes; diffractograms were measured by 1:2 coupled scans (size step = 0.05°).

Results

We present here a comparison of the RBS-channelling study provided with APE:Er:LiNbO$_3$ and LiNbO$_3$ treated by moderate-temperature localised Er-doping. As already found, the APE caused an expansion of the treated surface area that results in increased dimensions of the elemental unit cell in the appropriate (x and y) direction perpendicular to the surface of the pertinent cut [5]. From the RBS-channelling spectra we can see that the minimum yield for APE treated samples increases in comparison to the virgin samples (see Figure 1). The relative density of the dislocation centres for APE:Er:LiNbO$_3$ samples can be determined as: N_D/N= (y cut – 39 %, z cut – 20,8 %, x cut – 17,8 %). N_D/N is deduced from the equation $N_D/N = (\kappa_D - \kappa_V)/ 1-\kappa_V$, κ_V is minimum yield in the aligned virgin spectra and κ_D is the minimum yield in aligned spectra of treated samples. The APE treatment modified a layer 10 microns thick, so in the RBS-channelling spectra only a signal from the modified layer appears. The minimum yield κ_{min} of the virgin crystal is the lowest for the z-cut (2.9 %) and the highest for x-cut (4.76 %). The APE treatment caused the highest κ_{min} for the APE y- cuts and the lowest for the x- cuts, when compared with virgin ones, Figure 1a and Figure 2a. From the XRD measurement it can be deduced that the lattice constant in x and y direction is increased, as it was also shown in other papers [6], [7]. XRD measurement in Figure 1b and Figure 2b shows broadened peaks and shifted peak maxima connected with crystal quality changes and deviation of the APE crystal lattice from the original one in the y-cut and x-cut . The crystal lattice changes should be strongly connected to the hydrogen incorporation into the Er:LiNbO$_3$ structure. The highest hydrogen content determined from ERDA spectra was observed in the APE:Er:LiNbO$_3$ y cut (19 % of hydrogen in the surface layer 194 nm thick and 16 % below the surface layer). The lowest hydrogen content we detected on the surface of z cut, (11 % in the 97 nm thick layer and 8 %

below the surface layer). APE treated x cut exhibits medium hydrogen content of 13 % in the 105 nm thick layer and 10 % below the surface layer). The y-cut seems to be the one most influenced, in which the higher content of hydrogen was observed. The APE procedure influences the crystal in another way compared to the localised diffusion of the erbium ions. We can evaluate also the κ_{min} value for samples treated by localised in-diffusion of the erbium ions. Ratio N_D/N for the samples treated by Er localised doping is following (z cut – 7,5 %, y cut - 16 %, x cut – 35 %). Minimum yields for samples treated by localised doping are lower compared to the APE samples for the z and y cuts, but the localised doping procedure affected mostly the x cut. We conclude from the RBS-channelling spectra that localised Er^{3+} diffusion does not stress the crystal lattice so much; it just creates the amorphous layer in which Er is localised (see Figure 3). The Er depth profile is independent on the half width of the surface peak, so the depth of incorporated Er is not affected by the level of crystal damage.

Conclusion

The studied samples were virgin Er: $LiNbO_3$ wafers and APE-treated wafers in order to increase refractive index in the surface layer and to create the planar optical waveguides. Erbium ions were introduced into the surface of pure $LiNbO_3$ wafers by Er moderate temperature localised doping. The APE: Er: $LiNbO_3$ samples showed an increase of the crystal lattice along the x and y axis compared to the virgin Er: $LiNbO_3$ and APE treatment modified mostly y-cut which should be connected to the higher hydrogen content incorporated. Localised doping samples even exhibited the tendency to form an amorphous surface layer in which the Er ions were incorporated and the highest modification is observed in the case of the x-cut.

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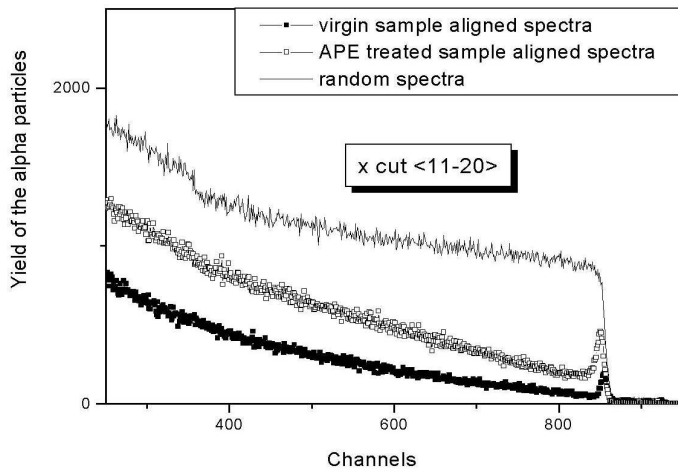
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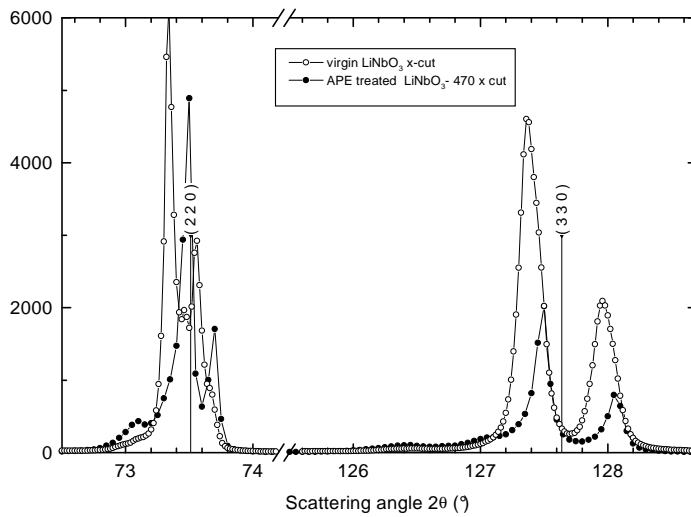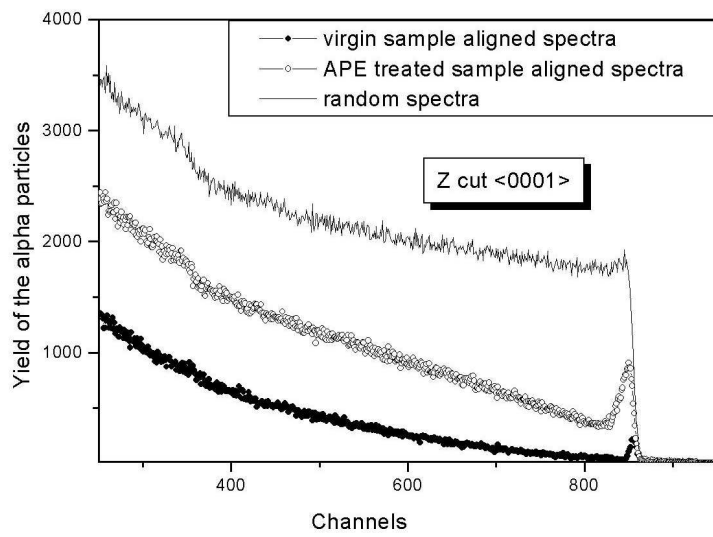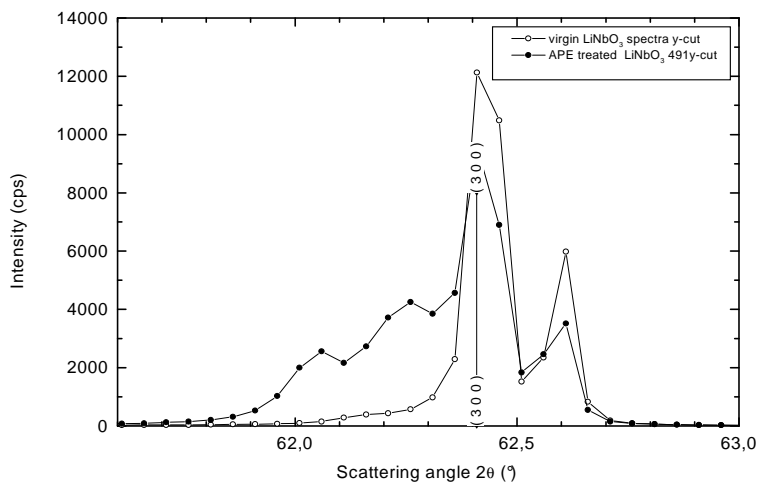

b)

Figure 1

Comparison of virgin Er:LiNbO$_3$ sample and APE:Er:LiNbO$_3$ treated sample (z cut). **a)** RBS-channelling aligned spectra **b)** XRD spectra

a)

b)

Figure 2 Comparison of virgin Er:LiNbO$_3$ sample and APE:Er: LiNbO$_3$ treated sample (y cut). **a)** RBS-channelling aligned spectra **b)** XRD spectra.
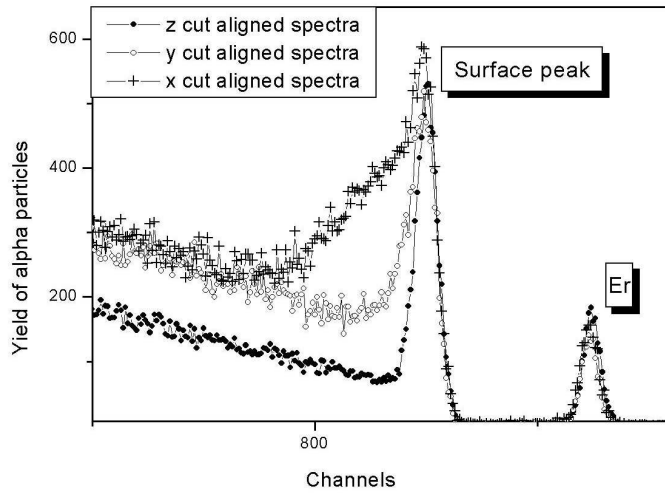
Figure 3 RBS-channelling aligned spectra of x, y, z cut LiNbO$_3$ samples modified by Er localised doping