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Microindentation of proton exchange layers on X cut of lithium niobate crystals

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HIGHLIGHTS

► Proton exchange increases ‘true’ hardness of lithium niobate and decreases crystal elasticity.
► Annealing improves elasticity and decreases the ‘true’ hardness of proton-exchange layer.
► Hardness and elasticity are not restored to the values for virgin lithium niobate after annealing.

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ABSTRACT

Microindentation of the proton exchange layers on X cut of lithium niobate single crystals was performed. The results were interpreted in the framework of the proportional specimen resistance model. It was found that proton exchange causes increase in the load-independent (“true”) hardness and decrease in the crystal elasticity. The elastic properties of proton exchange layers improve due to annealing while their load-independent hardness decreases. However, in all annealing conditions both hardness and elasticity cannot restore to the corresponding original values of the virgin lithium niobate.

1. Introduction

Lithium niobate (LN) is one of the most widely used materials to make optical waveguides in integrated optics. The advantage of LN is its excellent electro-optic and nonlinear optical properties as well as relatively high chemical and mechanical resistance.

A widely used method for obtaining waveguides in LN crystals is proton exchange (PE) [1] with frequently used source of protons being molten benzoic acid. PE in a $LiNbO_3$ crystal results in a thin (up to several μm in thickness) epitaxial layer of the $H_xLi_{1-x}NbO_3$ solid solution on the crystal surface and formation of waveguides consisting of one β phase layer or several sequential β phase layers of the $H_xLi_{1-x}NbO_3$ solid solution ($x = 0.4 \ldots 0.5$) [2]. The refractive index of the obtained PE layer is larger than that in the volume of the LN crystal, which makes possible light propagation in the layer due to the total internal reflection.

The properties of proton exchange layers are considerably different from those of the virgin LN. This manifests itself, for example, in the chemical resistance decrease as in contrast to LN, proton exchange layers are etched in the $HF + HNO_3$ solution [3]. PE should certainly change mechanical properties too. An efficient method to study mechanical properties and structure of the proton exchange layers is micro- and nanoindentation. In particular, the microindentation method was used to study differences in the mechanical properties on the opposite sides of an LN wafer [4]. The important property of any device material is its mechanical strength, represented by its hardness. Practically, microhardness is the resistance offered by a material to localized plastic deformation caused by indentation [5].

In the present work microindentation was used to study proton exchange layers obtained on X cut of LN single crystals in different conditions of PE and further annealing.

2. Experimental

Single crystal specimens of LN (X cut) with congruent composition, produced by Sipat, China, were used. The specimen surface

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roughness r_a was 0.3–0.4 nm. PE producing planar waveguides was performed in the molten benzoic acid (BA) at the temperatures of 175 °C, 190 °C and 210 °C during 2 h. The fabricated waveguides consisted of sequential β_1 and β_2 phase layers [3].

Some specimens were annealed under different conditions in an oven in air atmosphere with temperature stability ±1 °C. After annealing the specimens slowly cooled to room temperature in the oven.

To determine the refractive index (RI) profile of the extraordinary ray $n_e(x)$ the mode spectroscopy method was used. The prism coupling method was applied to measure the effective RI of waveguide modes at the wavelength $\lambda = 0.633$ μm. The $n_e(x)$ profile along the depth of the waveguide layer was reconstructed by the inverse Wentzel–Kramers–Brillouin method [6].

Microindentation was performed with the use of NanoTest-600 measuring unit by embedding the Berkovich indenter into the specimen surface with further analysis of load–depth curve using Oliver and Pharr method [7]. The conditions of the experiment were chosen according to the recommendations for brittle materials. The used loads varied from 7 to 500 mN and the indentation depth – from 0.2 to 2.2 μm, which corresponds to the depth of proton exchange layers formed in LN. For each specimen there were 10…12 indentation series consisting of 20…30 points each. The maximum load was held during 60 s to eliminate the effects of creep during unloading.

3. Results and discussion

The $\Delta n_e(0)$ values, depth of the planar waveguide and the number of supported modes considerably depend on PE and annealing conditions (Table 1). Un-annealed specimens are characterized by the stepped RI profile and $\Delta n_e(0) = 0.109…0.110$ for all PE regimes (Fig. 1). The increase in PE temperature to 210 °C leads to increase in the waveguide layer depth (Fig. 1a, Table 1). During slight annealing (300 °C, 1 h) the RI profile stays stepped, $\Delta n_e(0)$ decreases to some extent with the depth of the waveguide layer increased (Fig. 1). Annealing at temperature 300 °C is also accompanied by the formation of κ-phase [2]. The depth of waveguide layer increases markedly (Fig. 1b, Table 1) after annealing at the temperature of 370 °C for 240 min, the RI profile becomes flat, and $\Delta n_e(0)$ considerably decreases. The values of $\Delta n_e(0)$ show that the waveguide layer annealed at 370 °C consists of mainly α-phase [2].

The experiments prove considerable influence of the indentation depth h (or applied loading P) on the indentation layer mechanical characteristics (Figs. 2 and 3), which means that LN, as many other materials, exhibits indentation size effect (ISE) [8]. LN protonation at temperatures 190 °C and 210 °C during 120 min causes the apparent hardness to decrease to the indentation depth of 1.0–1.2 μm, at greater indentation depths the PE layers are harder (Fig. 2). The differences between H vs. h plots for the annealed specimens are not considerable (Fig. 3). The lowest values of the apparent hardness among the annealed specimens are observed for PE at 175 °C during 2 h and annealing at 300 °C during 1 h (Fig.3). The apparent hardness for the annealed specimens is greater than that for the un-annealed ones (Figs. 2 and 3).

Table 1
Characteristics of X-cut LN planar waveguides.

PE conditions (temperature, °C and time, min)	Annealing conditions (temperature, °C and time, min)	$\Delta n_e(0)$	Waveguide depth, μm	Number of modes
175, 120	–	–	–	1
175, 120	300, 60	0.0857	1.50	2
190, 120	–	0.1091	1.37	2
190, 120	300, 60	0.0872	2.22	3
190, 120	370, 240	0.0328	5.62	5
210, 120	–	0.1099	2.08	3
210, 120	300, 60	0.0901	2.94	4
210, 120	370, 240	0.0416	5.55	6

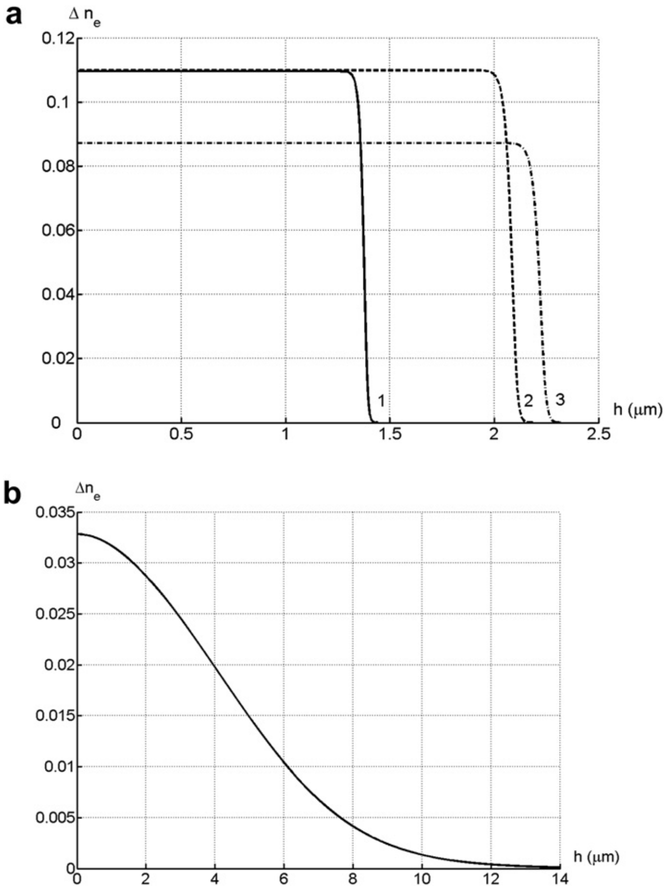

Fig. 1. Refractive index profiles. (a) 1 – PE: 190 °C, 2 h; 2 – PE: 210 °C, 2 h; 3 – PE: 190 °C, 2 h, annealing: 300 °C, 1 h; (b) PE: 190 °C, 2 h, annealing: 370 °C, 4 h.

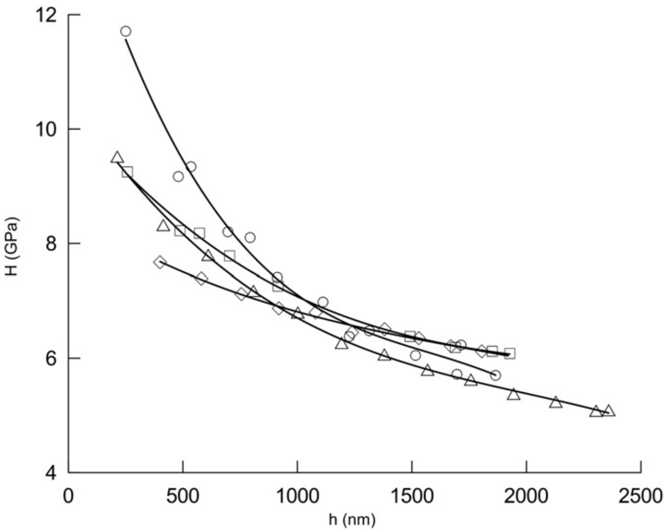

Fig. 2. Dependence of the hardness H on the indentation depth h: (○) virgin specimen; (△) PE 175 °C, 2 h; (□) PE 190 °C, 2 h; (◇) PE 210 °C, 2 h.