Quantitative characterization of proton-exchanged layers in LiTa03 optoelectronic devices by line-focus-beam acoustic microscopy

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Quantitative Characterization of Proton-Exchanged Layers in $LiTaO_3$ Optoelectronic Devices by Line-Focus-Beam Acoustic Microscopy

J. Kushibiki, *Member, IEEE*, M. Miyashita, and N. Chubachi, *Member, IEEE*

***Abstract*— Application of line-focus-beam (LFB) acoustic microscopy is extended to quantitative characterization of proton-exchanged/annealed layers employed in $LiTaO_3$ optical waveguides. Several specimens of Z-cut $LiTaO_3$ substrates, processed under the fabrication conditions for second-harmonic generation (SHG) optoelectronic devices, were prepared for measurements of the leaky surface acoustic wave (LSAW) velocities. Remarkable decreases in LSAW velocity due to the processes of proton exchange and annealing were observed, providing very useful information on the proton concentration and depth in diffusion layer, and on the process temperature distribution. It is found that measurement sensitivity is highest in the Y-axis wave propagation direction and the resolution to the optical waveguide parameters of diffusion depth and refractive index is much greater than the conventional techniques. It is suggested that this ultrasonic method should be adopted as a new analytical technique for development and evaluation of device fabrication processes and systems destined for future mass production.**

LINE-FOCUS-BEAM (LFB) acoustic microscopy [1] has been proposed as a new technology for materials research as regards developments of waveguide-type optoelectronic devices, using $LiNbO_3$ and $LiTaO_3$ substrates, such as optical modulators for optical communications, optical information processing and optical sensing systems, and second-harmonic generation (SHG) devices for blue coherent light sources [2]. As the LFB system can be applied to thin-film or diffused/implanted layer structures as well as semi-infinite samples, there are many promising applications: 1) development and evaluation of optical- grade $LiNbO_3$ and $LiTaO_3$ crystals and wafers [2], 2) characterization of machining and polishing damage on the wafer surface, 3) characterization of Ti-diffused, proton-exchanged [3], [4], domain-inverted, and SiO_2-buffer layers, and 4) evaluation and establishment of device fabrication processes and systems.

In the present study, a proton-exchange fabrication process for optical waveguides [5] is investigated, and the LFB system is applied to analyze and evaluate $LiTaO_3$ optical waveguides and their fabrication processes employed for SHG devices [6]. The future possibility of using this ultrasonic system in the evaluation and establishment of device fabrication process conditions is explored.

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The authors are with the Department of Electrical Engineering, Tohoku University, Sendai 980-77, Japan.

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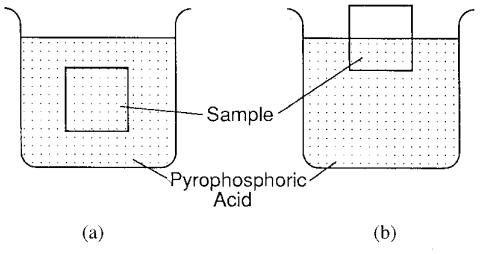

Fig. 1. Sample preparation.

Z-cut $LiTaO_3$ substrates (Yamaju Ceramics Co., Seto, Japan) were used for the experiments reported herein. The substrates, 15 mm × 15 mm × 0.5 mm, were processed under the conditions for fabrication of proton-exchanged and annealed waveguides for SHG optical devices [7]. In proton exchange, a substrate of $LiTaO_3$ is immersed in a heated pyrophosphoric acid solution at 260 °C for 14 min, to fabricate an optical waveguide at the surfaces with a greater extraordinary refractive index. As the optical propagation loss is relatively high, annealing at 420 °C for one min is also carried out in order to reduce propagation loss.

Two kinds of samples were prepared, as illustrated in Fig. 1. One kind is for experiments designed to understand changes in acoustic properties due to proton exchange and annealing. Two such proton-exchanged samples were prepared by completely immersing all the surfaces of the Z-cut $LiTaO_3$ substrates in pyrophosphoric acid solutions to the depth used in the normal device fabrication process, as shown in Fig. 1(a). One of these samples was annealed. The other kind is for simulation experiments to investigate the possibility of inhomogeneity evaluation in the fabrication processes, resulting from different proton concentration or distribution and temperature gradient. For this purpose, two proton-exchanged samples were prepared by immersing the substrates halfway in acid solutions, as shown in Fig. 1(b). One of these samples underwent annealing as well. In addition, a virgin Z-cut $LiTaO_3$ sample was also prepared, for comparison in experiments. Five samples, in all, were studied.

The details of the measurement method and system were described elsewhere [1]. The LFB system measures the phase velocity and attenuation of LSAW's, excited on the water-loaded sample surface, by measuring and analyzing the in-

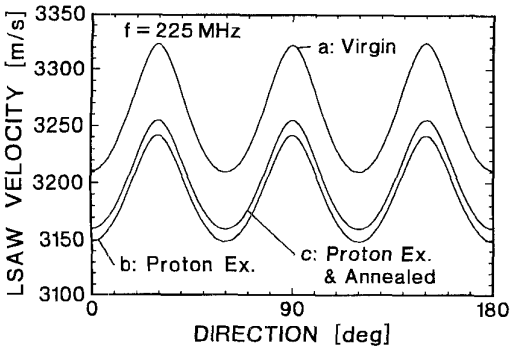

Fig. 2. Measured LSAW velocities for Z-cut $LiTaO_3$ samples.

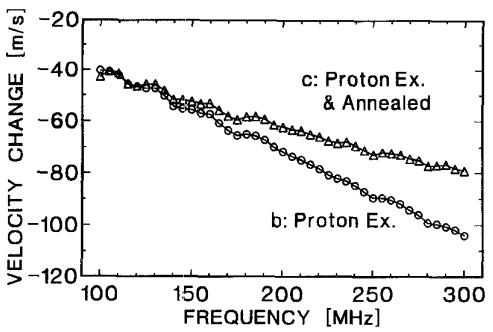

Fig. 3. Relative LSAW velocity dispersions for ZY-$LiTaO_3$ samples.

terference waveforms of the $V(z)$ curves obtained when the relative distance between the LFB ultrasonic device and the sample is varied. Here, evaluations are made using the LSAW velocity, and measurements are conducted on the $-Z$ faces of the crystal substrates because the SHG devices are formed on the $-Z$ faces [7].

In order to understand the variations in acoustic characteristics caused by proton exchange, the angular dependence of LSAW velocities was first measured near the center of the samples that had been subjected to proton exchange over their entire substrate surfaces. The ultrasonic frequency was set at 225 MHz, and the LSAW propagation direction was altered by 180° at intervals of 1°. Fig. 2 shows the measured results. The propagation directions of 0° and 180° correspond to the crystallographic X-axis, and 90° to the Y-axis direction. In this figure, (a) shows the measured results obtained with a virgin substrate, (b) those with a sample of proton-exchanged substrate, and (c) those which additionally received annealing. All samples of $LiTaO_3$ give symmetrical cycles for every 60°, reflecting the crystal symmetry. Proton exchange causes the LSAW velocity to decrease in all propagation directions. It is considered, from these results, that the diffusion layer with the acoustic property of a slower LSAW velocity is formed on the substrate surfaces. Changes in LSAW velocity due to the proton exchange were approximately 61.7–82.9 m/s for Z-cut $LiTaO_3$. When the sample is subjected to annealing, in addition to proton exchange, the LSAW velocity increases by approximately 11.1–13.4 m/s. Measurement sensitivity is highest in the Y-axis direction, and changes in LSAW velocity due to annealing are also largest in that direction. We, therefore, use the Y-axis direction wave propagation for the measurements reported below.

The sensitivity of the LFB system to the parameters of the optical waveguide, such as waveguide depth and refractive index, can be discussed comparing the data of velocity changes with the data reported for Z-cut $LiTaO_3$ optical waveguides. The depths are reported to be about 0.46 μm for the as-proton-exchanged waveguides [8] and to be approximately 1.9 μm [7] for the proton-exchanged/annealed waveguides. Further, the extraordinary refractive index for the proton-exchanged optical waveguides increases about 0.017 at 633 nm [6]. It can be found, from the system stability with the measurement accuracy of $\pm 0.005\%$ in velocity [2], that the LFB system has the capability to resolve easily the changes of diffusion depth of 1 nm for as-proton-exchanged substrates and of 5 nm for proton-exchanged/annealed substrates, and to resolve the change of the extraordinary refractive index of 4×10^{-5} for proton-exchanged optical waveguides at 225 MHz.

In general, dispersion must be observed in the LSAW propagation characteristics in layered media. Dispersion is dependent upon the product fH of ultrasonic frequency f and surface layer depth H [1]. To obtain dispersion characteristics of LSAW velocity in the proton-exchanged layers, frequency characteristics of LSAW velocity were measured at intervals of 5 MHz in the ultrasonic frequency range of 100–300 MHz for each sample of Z-cut Y-propagating (ZY) $LiTaO_3$. Fig. 3 shows the measured results of velocity changes relative to the results measured for the virgin sample. For both the proton-exchanged and proton-exchanged/annealed samples, it is clear that the LSAW velocity decreases as the frequency increases. The slopes of the straight line approximated by the least-squares method are -0.32 m/s/MHz for the proton-exchanged sample and -0.18 m/s/MHz for the proton-exchanged/annealed sample, respectively. It can be interpreted that, with annealing, protons diffused deeply into the substrate, and proton concentration and distribution were varied, resulting in the change of diffused depth (waveguide thickness), from 0.46 μm to 1.9 μm, so that the frequency dependence was changed. As the frequency increases, the elastic properties of the surface layer are better reflected for measurements, because the LSAW energy concentrates within approximately one wavelength beneath the sample surface. Therefore, measurements of the frequency characteristics of LSAW velocities provide us with very useful information on the proton concentration/distribution in the diffusion layer and on the diffusion depth associated with optical waveguide thickness.

Next, in order to demonstrate the possibility of evaluating device fabrication processes and conditions by the LFB system, samples were employed for which half of the substrate had been in the heated pyrophosphoric acid solution for proton exchange, and the LSAW velocities were measured at intervals of 0.5 mm at 225 MHz. Fig. 4 shows the velocity measurements on the sample surface along the path identified by the dotted line in the inset. The acid liquid surface at the time of proton exchange corresponds to the vicinity of position 0 mm in the figure. The LSAW velocities decrease continuously and monotonically in the direction of solution

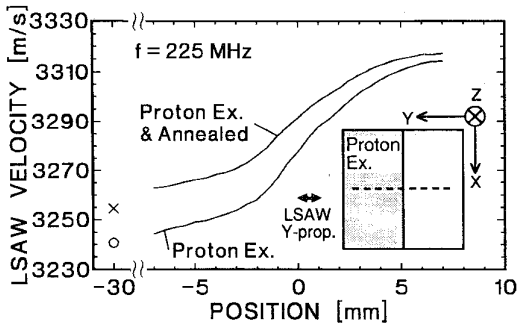

Fig. 4. LSAW velocity profiles for ZY-$LiTaO_3$ samples measured along the dotted line in the inset. The acid liquid surface is located around position 0 mm. o and × show the measured values for the as-proton-exchanged and proton-exchanged/annealed samples under the normal process conditions, respectively.

depth. Annealing results in an increase in LSAW velocity, with the increase being proportional to the solution depth position at which an area was proton-exchanged. The open circle in the figure shows the result measured for the sample processed only by proton exchange at the solution depth −30 mm from the liquid surface in the normal fabrication process, as shown in Fig. 1(a). The obtained value is 3241.5 m/s along the Y-axis direction. The LSAW velocity decreases even more in this case as the solution depth increases. The cross in Fig. 4 shows the result measured for the sample proton-exchanged/annealed in the normal process; 3254.9 m/s along the Y-axis direction. Even when the sample undergoes annealing, the LSAW velocity decreases as the solution depth increases. From Fig. 3, as LSAW propagation characteristics reflect the layered structure and show dispersion, it is considered that at a fixed frequency the LSAW velocity decreases in proportion to an increase in depth of the diffusion layer and to an increase in proton concentration in the diffusion layer. In Fig. 4, the depth and proton concentration in the diffusion layer are thought to be determined by different diffusion coefficients of protons in the substrate, related to such factors as the concentration distribution of protons and the temperature distribution on the surface of sample located in the solution. Within the range of the solution depths used for the measurements, it can be said that fabrication process conditions vary with position.

As seen in Fig. 4, in the area of the $LiTaO_3$ that was not in the acid solution, LSAW velocities also decrease depending upon the position on the sample surface, and annealing causes the LSAW velocity to increase. The changes in LSAW velocity, due to annealing in the area of $LiTaO_3$ substrate located outside of the pyrophosphoric acid solution, stands for the velocity recovery at the inhomogeneously proton-exchanged area actually produced by the acid vapor, from the other experimental result that no significant changes in the frequency dependence were observed for the virgin sample before and after annealing at 420 °C for one min.

This study has investigated a method for characterization and evaluation of proton-exchanged/annealed optical waveguides and of fabrication processes, utilizing Z-cut $LiTaO_3$ substrates, with the LFB acoustic microscopy system. It has been found, from measurements of the angular dependence of LSAW velocities, that the most suitable propagation direction for evaluation is along the Y-axis direction. It has been successfully demonstrated that the LFB system has the capability of high measurement accuracy in evaluating the optical waveguide parameters of diffusion depth and refractive index, that is superior to the conventional techniques of secondary-ion-mass spectrometry (SIMS) and the prism coupler method.

It will become one of the more important industrial tasks to establish the reliable and reproducible device fabrication processes at each stage of proton exchange and annealing, associated mainly with distributions of proton concentration and temperature, as well as to develop high-quality large-diameter substrates of $LiNbO_3$ and $LiTaO_3$ with optically homogeneous properties previously discussed [2]. Therefore, this ultrasonic method and system are expected to lead to a new analytical technology for development and evaluation of device fabrication processes and systems for the future mass-production, with the advantages of nondestructive and noncontacting measurements.

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