Fabrication and characterizations of proton-exchanged $LiNbO_3$ waveguides fabricated by inductively coupled plasma technique

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This Letter reports the use of an inductively coupled plasma technique for fabrication of proton-exchanged (PE) $LiNbO_3$ (LN) waveguides. Planar and stripe waveguides have been formed in *Y*-cut LN which are difficult to obtain with the conventional molten acid method due to the occurrence of surface damage. Secondary ion mass spectrometry, scanning electron microscopy, and infrared absorption spectrum characterization results revealed that a uniform vertical PE profile with a single low order crystal phase has been directly obtained as a result of this unique process. X-ray photoelectron spectroscopy characterization of the treated surface revealed the existence of NbO as the cause for a sometimes darkened surface and confirms the ability to completely restore the surface to LN by oxygen plasma treatment. Atomic force microscopy measurement confirms that good surface quality has been maintained after regeneration of the surface to LN. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2191704]

Proton exchange (PE) is a conventional technique used to fabricate waveguides on a variety of lithium niobate (LN) substrates, including *X*-, *Y*-, and *Z*-cut types and substrates doped with MgO and ZnO. Benzoic, adipic, glutaric, octanoic, stearic, and pyrophosphoric acids and their mixtures are well-known proton donors.[1–4] Seven different crystallographic phases of $H_xLi_{1-x}NbO_3$, i.e., the α, κ_1, κ_2, β_1, β_2, β_3, and β_4 phases, have been identified in PE layers by secondary ion mass spectrometry (SIMS), Rutherford backscattering (RBS), x-ray rocking curve diffraction, infrared (IR) absorption spectroscopy, Raman spectroscopy, etc.[5] In order to obtain low order phase waveguides with high quality and low propagation loss, various methods have been intensively researched, including the annealing proton-exchanged (APE) process,[6] soft proton-exchanged (SPE) process,[7] and vapor-phase proton-exchanged (VPE) processes.[8] PE in water has also been used,[9] as well as double proton-exchanged process for *Y*-cut LN.[10] Among these, APE and SPE are more widely used, although APE requires properly matched initial PE conditions and SPE samples have to be immersed into melting acid diluted by Li compound at 300 °C for a long duration, in order to obtain an ideal exchange depth. In contrast, dry methods using hydrogen ion implantation[11] and hydrogen plasma techniques are so far rarely researched. Turcicova *et al.* used a capacitance (parallel plate) coupled plasma technique to operate a PE process in *X*-cut and *Z*-cut LN, giving H and Li concentrations similar to pure acid donors techniques, under comparatively high temperatures (about 570–640 °C) and high H_2 pressure (0.5 mbar). However, in subsequent thermal reoxidation in oxygen the original structure was not restored. Grainlike structures were formed on the treated surface, giving rather high propagate losses.[12]

Due to strong lattice deformations, PE waveguides are particularly difficult to obtain on *Y*-cut LN via the benzoic acid (BA) or similar molten acid processes.[13,14] Although it was possible to obtain reasonable PE layers at relatively low temperatures (up to ~160 °C) for short exchange times (up to ~60 min), damage started to occur in the LN surface when the temperature was increased or the exchange time was prolonged in order to obtain a deeper PE layer.

In this Letter, we report an inductively coupled plasma (ICP) based technique capable of fabricating PE waveguides on several types of LN surface, including *Y*-cut LN, without surface deformation or damage.

Our PE process was carried out in an Oxford Instruments Plasma Technologies (OIPT) ICP100 system using pure hydrogen as the process gas. A hydrogen pressure of 8 mTorr and flow rate of 50 SCCM was used. The ICP source rf power was set up to 1 kW in order to generate high density hydrogen plasmas, and a small rf electrode power (25 W) was applied to generate the necessary self-bias voltage attracting the H^+ ions onto the surface of the sample. The

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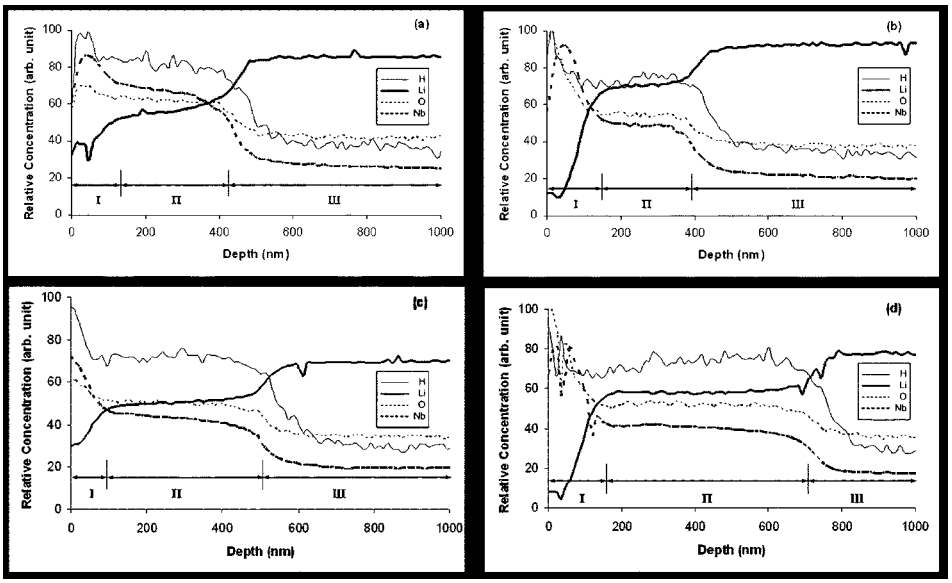

FIG. 1. SIMS profiles resulting from different PE processes, *Y*-cut LN treated by (a) H_2 plasma for 1 h, (b) H_2 plasma for 1 h and then O_2 plasma for 20 min, (c) H_2 plasma for 2 h, and (d) H_2 plasma for 2 h and then O_2 plasma for 20 min.

samples were placed on the lower electrode set at a temperature of 170 °C.

After the ICP PE process, the composition of the PE layers was investigated with a SIMS system attached to a focused ion beam (FIB) etching tool to obtained relative H and Li concentrations, as well as profiles of O and Nb. Depth profiles of these elements were obtained by etching the sample at a known etch rate with a high energy (25 keV) Ga^+ ion beam, thereby sputtering and ionizing species, and simultaneously measuring the intensity of the ion mass spectral lines corresponding to H^+, Li^+, Nb^+, and O^+. Figure 1 shows typical depth profiles obtained in this manner with three distinctive regions. In region I close to the sample surface, the Li concentration is quite low and demonstrates a rapid composition change from the surface to a depth of approximately 150 nm. Subsequently, the Li concentration stabilizes into a steplike region II extending from ~150 nm to more than 430 nm deep, where the concentrations of all species are approximately constant. Finally the profile makes the transition gradually into the substrate region III in Figs. 1(a) and 1(c). For prolonged exchanged times, region II extends deeper into substrate though maintains its characteristic steplike profile. However, region I and the transition towards region III are not obviously broadened in Figs. 1(b) and 1(d).

Similar ion species profiles for BA PE samples exchanged at 158 °C for 60 min are shown in Fig. 2. Compared with Fig. 1, the Li profile also has a nearly linear increase from the surface, but without any obviously steplike region II in Fig. 2. However, the H profile takes on such a steplike profile.

A vertical cross section of PE waveguides treated with H_2 plasma was made using FIB, by first etching a deep rectangular pit into the sample and then polishing the cross section to be examined using the ion beam. This allowed direct observation by secondary electron imaging. The sample shown in Fig. 3 has a window in a SiO_2 mask layer where PE has taken place. In this region, a brighter layer can be observed under the surface to approximately 150–200 nm depth, indicated by the white circle in Fig. 3. This brightness, which gradually reduces to that of the substrate, corresponds to region I in the SIMS H^+ profile shown in Fig. 1, and is believed to result from the higher secondary electron emission rate from the H-enriched thin layer. This layer does not exist under the SiO_2 mask.

In some cases, the treated LN surface became slightly darkened. X-ray photoelectron spectroscopy (XPS) analysis [Thermo VG Scientific Escascope; Al $K\alpha$ (1486.6 eV) x rays, 250 W (12.5 kV, 20 mA)] was used to investigate the LN surface changes after the ICP PE processing. Two characteristic peaks of Nb in the LN structure, $3d_{3/2}$ and $3d_{5/2}$, were, respectively, found at 210 and 207 eV binding energies

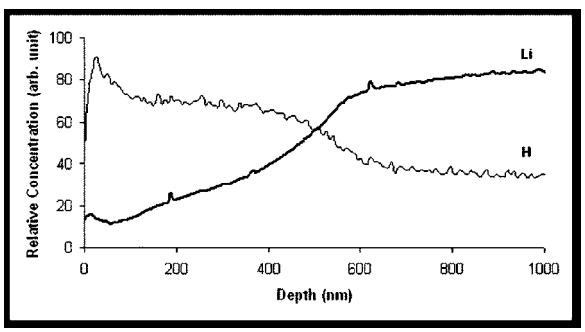

FIG. 2. SIMS profiles of PE *Y*-cut LN in BA at 158 °C for 1 h.

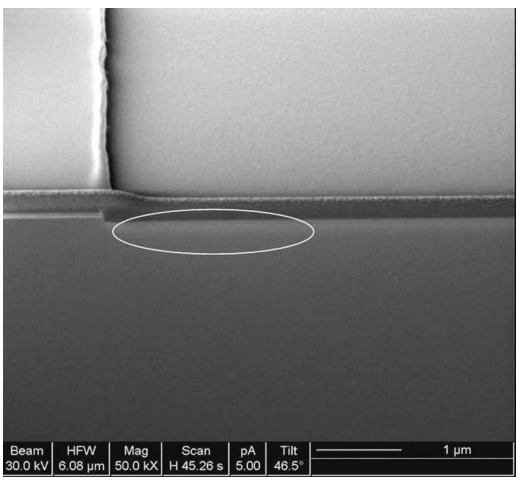

FIG. 3. FIB images of cross section. Channel of PE waveguide that was treated by H_2 plasma for 2 h was 8 μm wide with SiO_2 mask.

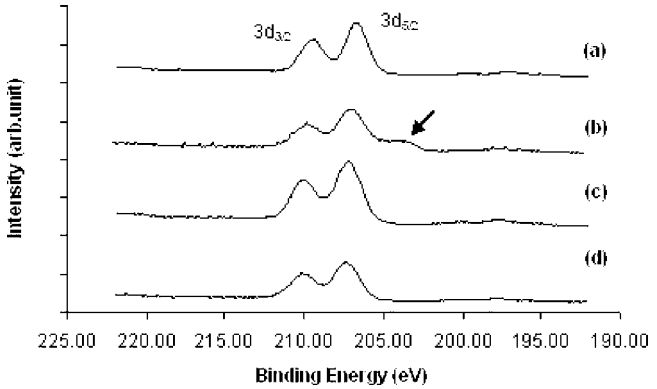

FIG. 4. XPS spectra of LN showing the spin-orbit splitting of the Nb 3*d* level: (a) virgin *Y*-cut LN, (b) treated by H_2 plasma for 1 h with the shift by arrow marked, (c) by H_2 plasma for 2 h and then by O_2 plasma for 10 min, and (d) by H_2 plasma for 2 h and then by O_2 plasma for 20 min.

from Nb spin-orbit splitting of the 3*d* level in Fig. 4(a). After being treated, using H_2 plasma, the Nb $3d_{3/2}$ and $3d_{5/2}$ peaks were shifted, respectively, to 207 and 204 eV in Fig. 4(b). This is an indication that F centers and F^+ centers were introduced in the near surface region, and NbO was formed. NbO is strongly absorbing in the visible region,[15] hence the surface darkens.

The darkened samples were subsequently treated in oxygen plasma at an oxygen pressure of 20 mTorr and a flow rate of 20 SCCM in the same ICP chamber. This treatment successfully recovered the surface to a high transparency. After O_2 plasma treatment, the oxygen concentration was remarkably increased in the surface and the near surface region I in Figs. 1(b) and 1(d). XPS analysis results in Figs. 4(c) and 4(d) showed that the NbO peak at 204 eV has disappeared after the O_2 plasma treatment, and only the peaks associated with Nb^{5+} at around 207 eV remain present. As both SIMS and XPS (not shown here) results suggest low Li concentration at the surface, it is likely that NbO has been mostly further oxidized to Nb_2O_5 at the near surface region, and the sample regained high transparency.

Atomic force microscopy (AFM) images in Figs. 5(a) and 5(b) show the topography of LN surfaces before and after ICP treatment. The surface roughness essentially remained the same as the virgin surface after H_2 plasma treatment. Also no obvious change in LN surface roughness was observed after different durations of O_2 plasma processing in Figs. 5(c) and 5(d).

IR absorption spectroscopy is usually used to identify crystallographic phases that exist in PE waveguides.[16,17] In plasma-treated samples, one sharp absorption band, due to the vibration of free OH groups was observed at $\sim 3480\ cm^{-1}$ which deepens and widens with prolonged exchanged time. However, another absorption band ($\sim 3250\ cm^{-1}$) of the hydrogen bonded OH^- group vibration spectrum, generally due to high order β_i phases, was not found. This demonstrates that H has been exchanged to definite depth and region II is in a single low order phase because of the uniform H and Li concentrations.

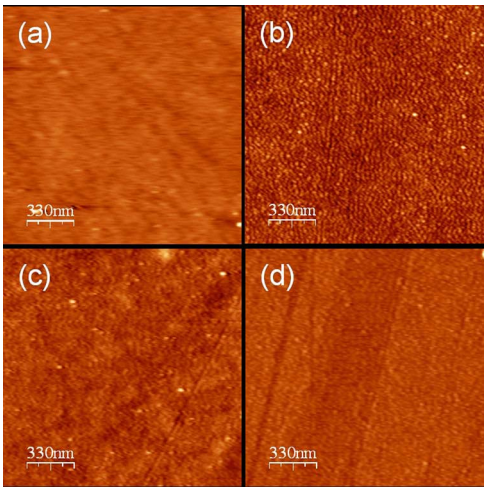

FIG. 5. (Color online) AFM images: (a) virgin *Y*-cut LN surface, (b) surface treated by H_2 plasma for 1 h, (c) by H_2 plasma for 2 h and then by O_2 plasma for 10 min, and (d) by H_2 plasma for 2 h and then by O_2 plasma for 20 min.

It has been demonstrated that the ICP techniques can be used to fabricate PE waveguides, especially on *Y*-cut LN, without deformation or surface damage. SIMS, SEM, and IR absorption spectrometry characterizations of the ICP PE samples revealed that a uniform vertical PE region with a single low order crystal phase was directly obtained. XPS characterization of the treated surface revealed the existence of NbO which darkened the surface, but the surface was completely restored to high transparency by oxygen plasma treatment. AFM confirmed that a good surface quality was maintained throughout.

[1] K. Ito and K. Kawamoto, Jpn. J. Appl. Phys., Part 1 **31**, 3882 (1992).
[2] J. M. Cabrera, J. Olivares, M. Carrascosa, J. Rams, R. Muller, and E. Dieguez, Adv. Phys. **45**, 349 (1996).
[3] P. Kolarova, J. Vacik, J. Spirkova-Hradilova, and J. Cervena, Nucl. Instrum. Methods Phys. Res. B **141**, 498 (1998).
[4] V. M. N. Passaro, M. N. Armenise, D. Nesheva, I. T. Savatinova, and E. Y. B. Pun, J. Lightwave Technol. **20**, 71 (2002).
[5] Yu. N. Korkishko and V. A. Fedorov, J. Appl. Phys. **82**, 1010 (1997).
[6] S. T. Vohra, A. R. Michelson, and S. E. Asher, J. Appl. Phys. **66**, 5161 (1989).
[7] Yu. N. Korkishko, V. A. Fedorov, E. A. Baranov, M. V. Proyaeva, T. V. Morozova, F. Caccavle, F. Segato, C. Sada, and S. M. Kostritskii, J. Opt. Soc. Am. A **18**, 1186 (2001).
[8] D. H. Tsou, M. H. Chou, P. Santhanaraghavan, Y. H. Chen, and Y. C. Huang, Mater. Chem. Phys. **78**, 474 (2002).
[9] J. Rams and J. M. Cabrera, Appl. Phys. A: Mater. Sci. Process. **81**, 205 (2005).
[10] M. Kuneva, S. Tonchev, M. Pashtrapanska, and I. Nedkov, Mater. Sci. Semicond. Process. **3**, 581 (2000).
[11] F. Lu, H. Hu, F. Chen, X. Wang, and K. Wang, Radiat. Eff. Defects Solids **159**, 309 (2004).
[12] H. Turcicova, J. Zemek, J. Toth, and I. Drbohlav, Surf. Interface Anal. **34**, 468 (2002).
[13] Y. Fei and H. K. Wong, J. Appl. Phys. **76**, 871 (1994).
[14] J. L. Jackel, C. E. Rice, and J. J. Veselka, Appl. Phys. Lett. **41**, 607 (1982).
[15] K. L. Sweeney and L. E. Halliburton, Appl. Phys. Lett. **43**, 336 (1983).
[16] A. Loni, G. Hay, R. M. De La Rue, and J. M. Winfield, J. Lightwave Technol. **7**, 911 (1989).
[17] M. M. Howerton, W. K. Burns, P. R. Skeath, and A. S. Greenblatt, IEEE J. Quantum Electron. **27**, 593 (1991).