Ferroelectrics, 1994, Vol. 151, pp. 85–90
Reprints available directly from the publisher
Photocopying permitted by license only

STRUCTURAL CHARACTERIZATION OF PROTON EXCHANGED $LiNbO_3$ BY MICRO-RAMAN SPECTROSCOPY AND POLARIZED VISIBLE LIGHT MICROSCOPY

DAVID D. TUSCHEL and GUSTAVO R. PAZ-PUJALT
Eastman Kodak Company, Rochester, New York, USA

(Received August 9, 1993)

Abstract $LiNbO_3$ wafers were proton exchanged (PE), annealed for various times, and the X-faces polished to provide a side view of the PE region. Micro-Raman images of the PE region were obtained by stepping a focused laser beam across the X-face starting below the PE region and moving parallel to the Z-axis towards the wafer surface. Micro-Raman images reveal that chemical bonding in the PE regions differ from that in $LiNbO_3$ and that chemical bonding in the unannealed PE region varies significantly with depth (along the Z-axis). Annealing reduced proton concentration by driving protons deeper into the wafer, thereby expanding the PE region. The duration of anneal does not significantly alter PE depth but does affect the chemical bonding and the PE/$LiNbO_3$ interface. Images of PE/$LiNbO_3$ were also obtained by polarized visible light microscopy. Contrast is observed between the PE region and $LiNbO_3$ when viewing transmitted Z-polarized white light. Exchange depths determined from polarized light microscopy are in good agreement with those obtained from micro-Raman images.

INTRODUCTION

Proton exchange (PE) of $LiNbO_3$ with subsequent annealing has become a widely used method of fabricating waveguides. PE causes the formation of a step-like extraordinary refractive index (n_e) profile in which Δn_e is ~0.12. However, the optical nonlinearity of the material is significantly attenuated and the device must be annealed to achieve partial recovery of the nonlinearity. An understanding of how PE subsequent annealing affect chemical bonding and crystal structure, which are related to refractive index and optical nonlinearity, would reveal optimal conditions for the more efficient design of PE waveguide devices. Characterization of the PE process and PE/$LiNbO_3$ structure has been done using X-ray diffraction, secondary ion mass spectrometry, infrared,[1] and Raman[2] spectroscopies. We recently reported the first micro-Raman depth profiles[3] of PE/$LiNbO_3$. In this paper present images of the PE region obtained by polarized light microscopy and micro-Raman spectroscopy, and demonstrate that they are nondestructive methods of measuring depths of and imaging chemical bonding in PE waveguides.

EXPERIMENTAL

Z-cut $LiNbO_3$ wafers were proton exchanged with pyrophosphoric acid at 260°C and annealed at 300°C for various times. The X-faces of the samples were polished to provide a side view of the PE region. Approximately 2 mm of material was removed thereby ensuring that the analysis probed H penetration along the Z-axis. Micro-Raman images of the PE region were obtained by stepping a 1.6 mW, 488.0 nm focused (0.6 μm diameter) laser beam at intervals as small as 0.2 μm, by means of an electronic translation stage across the X-face starting below the PE region and moving parallel to the Z-axis towards the wafer surface. The incident beam was Z-polarized and no analyzer was used. Spectra were obtained with an Instruments SA S3000 spectrometer outfitted with an Olympus MS Plan 100 (0.95 NA) microscope objective and using a photodiode array in the spectrograph mode. Polarized illumination light microscopy of PE/$LiNbO_3$ was carried out by placing a polarizer between the tungsten transmission lamp and the sample. No analyzer was used.

RESULTS AND DISCUSSION

Micro-Raman images of PE/$LiNbO_3$ from the portion of the spectrum related primarily to vibrational modes of NbO_6 octahedra are shown in Figure 1.

The spectra were acquired under identical conditions with Z-polarization, and all four images are on the same scale. The micro-Raman image of the unannealed sample reveals that the PE layer is 3.0-μm thick and that chemical bonding in it is heterogeneous. That the chemical bonding varies is revealed by the changing scattering strengths and band structures at different positions in the PE region. The bands at 153, 238, 254, 274, and 633 cm^{-1} , which are all strong in $LiNbO_3$, are significantly attenuated, and a strong band emerges at 690 cm^{-1} reaching its maximum intensity at 1.4 μm. The emergence of the 690 cm^{-1} band, in particular, reflects the change in NbO_6 chemical bond induced by PE. Two partially resolved bands at 640 and 670 cm^{-1} are predominant in the IR absorption spectrum[4] of $LiNbO_3$, whereas the powder macro-Raman spectra of $LiNbO_3$ and $HNbO_3$ obtained by us contain very weak and strong bands at 695 and 680 cm^{-1}, respectively.

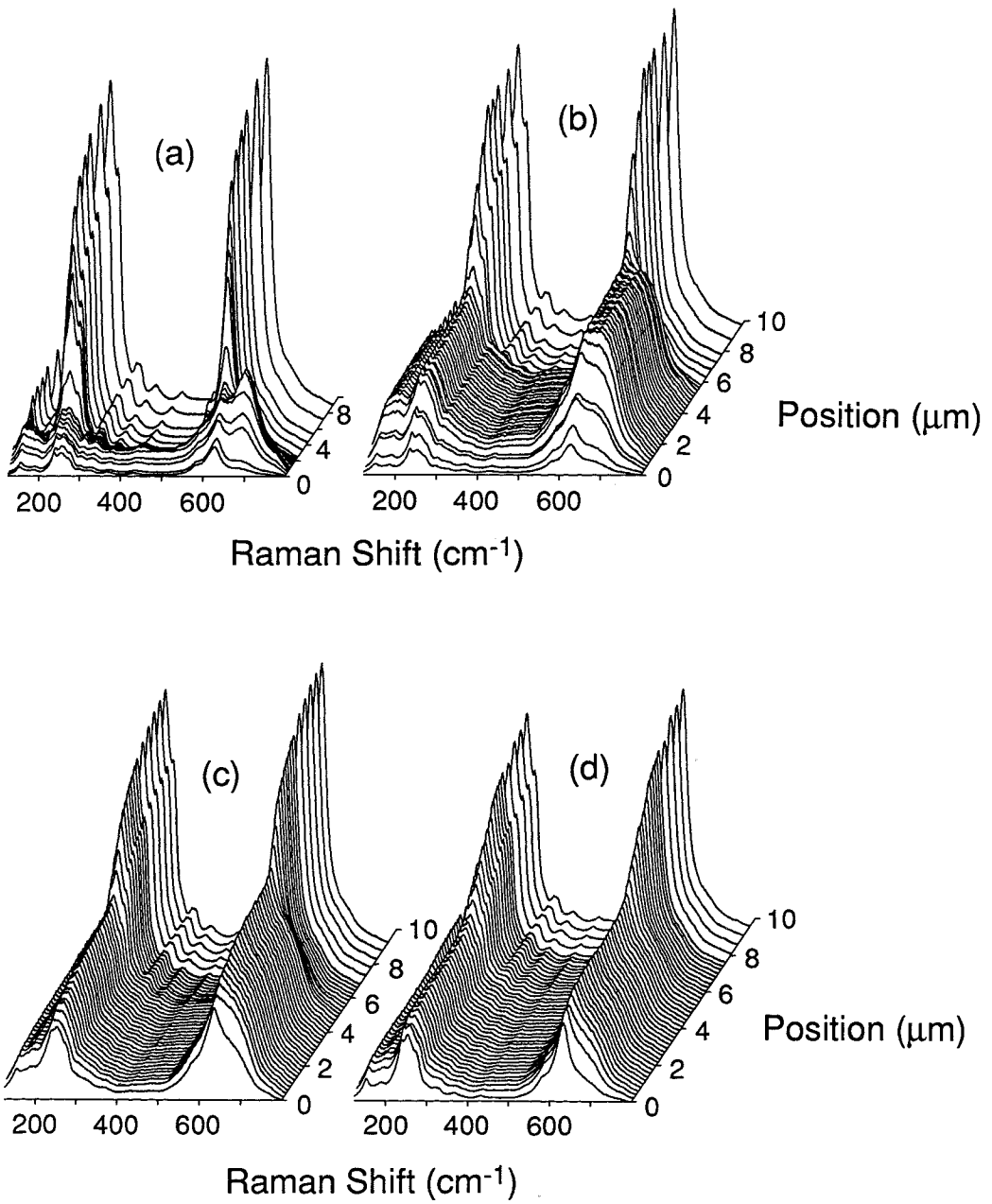

FIGURE 1 Micro-Raman images of PE/$LiNbO_3$; (A) Unannealed; Annealed for (B) 1 hr; (C) 4 hr; and (D) 10 hr.

Therefore, PE induces a change in the NbO_6 chemical bonding such that a vibrational mode, which is Raman inactive/IR active in $LiNbO_3$, becomes Raman active in PE/$LiNbO_3$. Also, PE causes the band resolution to diminish; note the near disappearance of the 153 cm^{-1} band and the emergence of a broad shoulder on the high energy side of it. This can be attributed to the loss of long-range translational symmetry resulting from partial replacement of Li. The Raman depth profile of the unannealed PE region is approximately symmetric about the 1.4 μm position. The significant attenuation of the NbO_6 bands indicates diminished nonlinear and electro-optic activity of the PE region because Raman scattering strengths are directly related to both of these properties.[5,6]

Annealing an exchanged sample for 1 hr: (a) reduces proton concentration by driving protons deeper into the wafer, thereby expanding the PE region to 4.9 μm, and by some losses to the air interface and (b) alters chemical bonding and makes it more uniform in the PE region beyond 1 μm. The shoulders on either side of the 254 cm^{-1} band increase, the NbO_6 band strengths partially recover, and the 690 cm^{-1} PE band shifts to 675 cm^{-1}. The changes are related to the bonding and the degree of distortion in the NbO_6 octahedra, and the partial recovery of the NbO_6 band strengths corresponds to the partial recovery of the optical nonlinearity with annealing. Heating an exchanged sample for 4 hr generates a 5.3 μm PE region that is even more uniform, and the micro-Raman image reveals that the PE/$LiNbO_3$ interface is not as sharp as in the 1 hr and unannealed samples. The shoulders of the 254 cm^{-1} band are weaker, the 633 cm^{-1} band is more resolved than for the 1 hr anneal, the 675 cm^{-1} PE band is now a moderate shoulder, and the NbO_6 band strengths show partial recovery. Heating an exchanged sample for 10 hr generates a more uniform 5.3 μm PE region with a PE/$LiNbO_3$ interface that is even more gradual than that for the 4 hr anneal. The shoulders of the 254 cm^{-1} band have weakened such that the 153 cm^{-1} band can now be resolved, the 633 cm^{-1} band is further resolved from a weak shoulder, and the NbO_6 band strengths show partial recovery. Finally, the micro-Raman image of sample annealed for 15 hr (not shown here) is almost identical to that for the 10 hr anneal, suggesting that the fullest spectral recovery possible was obtained by 10 hr of heat treatment. This study reveals that annealing beyond 1 hr does not significantly alter PE depth, but the duration of anneal does affect the chemical bonding, long-range translational symmetry of the PE region, and the PE/$LiNbO_3$ interface. Consequently, the determination of proton concentration alone is insufficient for a characterization of PE/$LiNbO_3$ waveguides.

The need to consider chemical bonding and long-range translational symmetry in a characterization of PE/$LiNbO_3$ is made clear by the Raman strength depth profiles of the OH stretch shown in Figure 2.

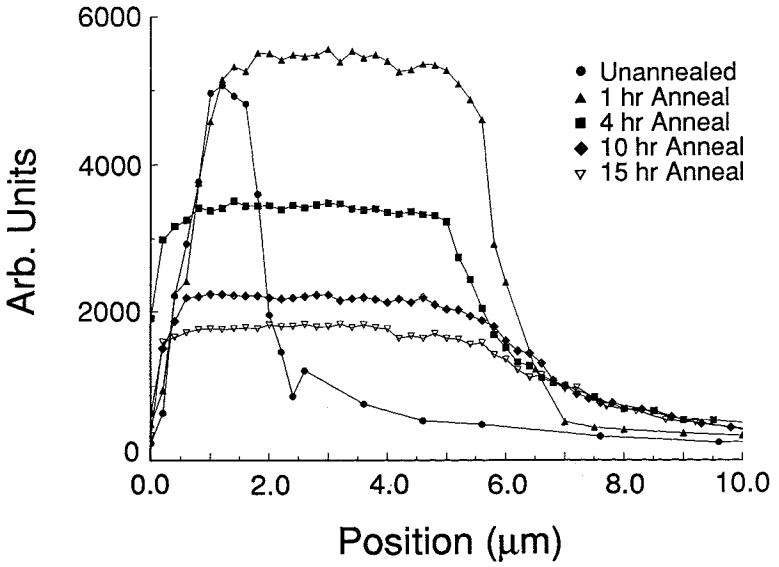

FIGURE 2 Raman strength (integrated intensity) depth profiles of PE/$LiNbO_3$ Z-polarized OH stretch.

Spectra from the OH stretching region were obtained at he same positions as the NbO_6 region spectra, and therefore, correspond to their low frequency counterparts in Figure 1. Spectra from the unannealed sample consist of strong, sharp, partially resolved bands at 3501 and 3508 cm^{-1} with a low frequency tail. Annealing weakens the Raman strength and causes a single, slightly broader band to appear at 3507 cm^{-1} (1 hr) and at 3510 cm^{-1} (4, 10, and 15 hr). These spectral changes can be attributed to changes in chemical bonding and H position relative to the NbO_6 octahedron, both of which affect the vibrational mode frequency and Raman scattering cross-section. Therefore, Raman and infrared strengths of the OH band can be used to determine proton concentrations only if the scattering cross-sections and absorptivities of the modes are accounted for. The depth profiles reveal that the primary effect of annealing is to broaden the PE region and cause it to be more homogeneous. The duration of the anneal determines the change in chemical bonding and the softening of the PE/$LiNbO_3$ interface. There is a direct correlation between the spectral changes in the OH stretching region and those in the NbO_6 spectral region.

Images of PE/$LiNbO_3$ were obtained by polarized transmitted visible light microscopy and are shown in Figure 3. Strong contrast is observed between the brown PE region and colorless $LiNbO_3$ when viewing the X-face with transmitted Z-polarized light. The PE region depths determined from polarized light microscopy are in good agreement with

those obtained from micro-Raman images. The degree of contrast is dependent upon anneal time, decreasing with longer anneal time. Y-polarized light yields a much weaker contrast than that for Z-polarized light, which also diminishes with increasing anneal time and is absent in the 15 hr sample. Also, the PE region appears violet when viewed with Y-polarized light. The optical effects observed by polarized light microscopy can be correlated to the changes in chemical bonding, manifest in the Raman spectra, which cause a piezochromic effect. A more detailed explanation of these effects based on local molecular orbitals and long-range translational symmetry will be presented in a future publication.

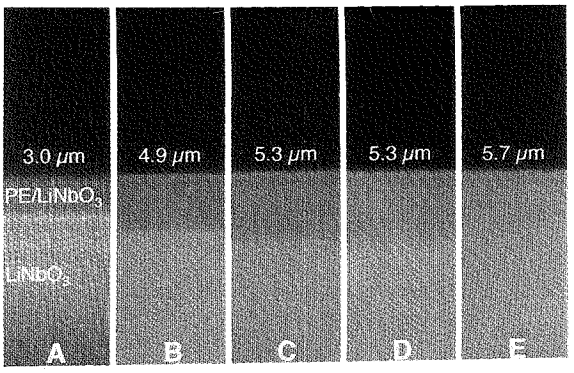

FIGURE 3 Transmitted Z-polarized light photomicrographs of $PE/LiNbO_3$ of the X-face: (A) Unannealed; Annealed for (B) 1 hr; (C) 4 hr; (D) 10 hr; and (E) 15 hr. The depth of the PE region is indicated in microns.

Polarized light microscopy and micro-Raman spectroscopy are nondestructive methods of measuring depths of and imaging chemical bonding and long-range translational symmetry in PE waveguides.

REFERENCES

1. C. A. Canali, G. Carnera, P. Della Mea, S. M. Mazzoldi, A. Shukri, A. C. G. Nutt, and R. M. De La Rue, J. Appl. Phys., 59, 2643 (1986).
2. I. Savatinova, S. Tonchev, and M. Kuneva, Appl. Phys. A, 56, 81 (1993).
3. G. R. Paz-Pujalt and D. D. Tuschel, Appl. Phys. Lett., in press.
4. M. I. Díaz-Güemes, I. González Carreño, and C. J. Serna, Spectrochim. Acta., 45A, 589 (1989).
5. W. D. Johnston, Jr., Phys. Rev. B, 1, 3494 (1970).
6. I. P. Kaminow and W. D. Johnston, Jr., Phys. Rev., 160, 519 (1967).