Depth profiling of the $d_{33}$ nonlinear coefficient in annealed proton exchanged LiNbO$_3$ waveguides

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We report depth profiling of the $d_{33}$ nonlinear coefficient in annealed proton exchanged LiNbO$_3$ waveguides using reflected second-harmonic generation from angle-lapped samples. At depths greater than the initial proton exchange depth the $d_{33}$ coefficient retains nearly its bulk LiNbO$_3$ value, but within the initial proton exchange region the value of $d_{33}$ varies with annealing time. These results reconcile previous conflicting measurements of the $d_{33}$ coefficient and explain the variation in the efficiency of guided wave frequency conversion devices with annealing.

Quasi-phase matched (QPM) frequency conversion in LiNbO$_3$ waveguides is an efficient method for the generation of short wavelength radiation from infrared laser diodes. While different techniques have been used to form the ferroelectric domain grating necessary for QPM, the annealed proton exchange (APE) process has been used exclusively to provide waveguide confinement. Contradictory measurements of the nonlinear optical properties of proton exchange (PE) and APE-LiNbO$_3$ waveguides have been previously reported. The $d_{33}$ coefficient of PE-LiNbO$_3$ has been measured to be between 0 (Refs. 4 and 5) and 0.63 (Ref. 3) of the bulk LiNbO$_3$ value. The effect of annealing is similarly controversial, with measurements of $d_{33}$ in APE-LiNbO$_3$ varying from 0% (Ref. 4) to 90% (Ref. 3) of the bulk value. Recently demonstrated guided-wave QPM second-harmonic generation (SHG) devices with normalized conversion efficiencies $> 600\%$/$\text{W cm}^2$ indicate that APE-LiNbO$_3$ waveguides must have a large nonlinear coefficient.

In this letter we report measurements of the depth dependence of the $d_{33}$ nonlinear coefficient in APE-LiNbO$_3$ waveguides using reflected SHG from angle-lapped samples. With a 532 nm fundamental wavelength, the 266 nm second-harmonic (SH) wavelength is above the APE-LiNbO$_3$ band edge so that only the SH generated within a 0.05 $\mu$m absorption depth of the surface is observed. The samples were angle lapped so that lateral position could be mapped onto depth into the sample, allowing depth profiling via lateral translation. This technique circumvented complications caused by the graded refractive index profile and the unknown spatial variation in the $d_{33}$ coefficient in the APE-LiNbO$_3$. The depth profiles presented here explain the variation in the $d_{33}$ values reported in the literature. Normalized conversion efficiencies calculated with our results are consistent with those observed from guided-wave QPM SHG devices.

APE waveguides were fabricated on $x$-cut LiNbO$_3$ by proton exchange in pure benzoic acid at 173 °C for 66 min to a depth of 0.42 $\mu$m, calculated using the results of Ref. 9, and annealed in air at 333 °C for varying times. The samples were then polished at a wedge angle $\approx 2$ mrad, with the actual relationship between lateral position and depth determined using surface profilometry. 532 nm radiation from an injection seeded Q-switched frequency-doubled Nd-YAG laser was focused onto the sample at normal incidence with a 30 $\mu$m FWHM spot and a peak intensity of $< 150$ MW/cm$^2$. The samples were scanned under the focused spot using a motorized translation stage and the reflected 266 nm SH was detected using a dichroic mirror, a solid blind photomultiplier, and a gated integrator. The fundamental and SH fields were polarized parallel to each other and the z axis of LiNbO$_3$ and thus were coupled by the $d_{33}$ nonlinear coefficient. To discriminate against polishing artifacts, each sample had an internal, unexchanged reference portion formed by masking half the sample with Al prior to proton exchange. The mask was removed by etching in NaOH prior to annealing. A portion of the sample remained unwedged, so that reflected SH could be obtained from the original surface. SHG and profilometry measurements were performed over the whole surface to eliminate errors associated with polishing skew. Figure 1 shows the sample orientation and geometry, with the dashed line indicating the beginning of the wedged portion of the sample and the origin for measurements of lateral position; negative values of lateral position represent data from the unwedged portion of the sample, i.e., the original surface.

Figure 2 shows the reflected SH power at 266 nm, normalized to the signal from bulk LiNbO$_3$ versus depth and lateral position for APE-LiNbO$_3$ waveguides annealed for 3, 5, 9, and 63 h. The error bars represent the variation in the depth measurement for 5 different scans. The figure inset shows the spatial step response of the detection system projected onto depth, measured by scanning the focused spot off the end of a bulk LiNbO$_3$ sample. This

![FIG. 1. Geometry of the wedged sample used for reflected SHG measurements.](image-url)
with an intensity of l/2 or l/4 that obtained from bulk APE-LiNbO, proton exchanged for 0.5 h and annealed for the original surface. Reference 2 reported no reflected SH unwedged samples, only probing a 0.05-thick region at lateral positions where polishing damage was observed. 350 °C, similar to our results when the probe is confined to regardless of annealing time at annealing temperatures of wedged portion of this sample.

The two previous measurements4a6 of the $d_{33}$ coefficient of APE-LiNbO, waveguides performed using reflected SHG with a 532 nm fundamental source were made on unwedged samples, only probing a 0.05-µm-thick region at the original surface. Reference 2 reported no reflected SH regardless of annealing time at annealing temperatures of 350 °C, similar to our results when the probe is confined to the unwedged part of the sample. Reference 4 reported that APE-LiNbO, proton exchanged for 0.5 h and annealed for 1.5 h at 310 °C or for 1 h at 350 °C exhibited reflected SH with an intensity of 1/2 or 1/4 that obtained from bulk LiNbO, For samples proton exchanged longer than 0.5 h, no reflected SH was observed, regardless of annealing time or temperature.

The absence of any reflected SH from the unannealed PE region could be explained by the formation of a PE-LiNbO, film with either inversion symmetry or a different $\chi^{(2)}$ tensor that did not result in any reflected SH. Similarly, the progression of the abrupt steplike recovery to the surface region with increasing annealing could be explained by the solid state epitaxial regrowth of the LiNbO, phase from the original interface between the PE film and the LiNbO, substrate. After the abrupt increase in the reflected SH from 0% to 80% of the bulk value there is a slower approach to the bulk value occurring over the next 0.5 µm in depth. In this region the measured $d_{33}$ value correlated with concentration, independent of annealing time, so we conclude that for low concentrations the $d_{33}$ coefficient is slightly reduced from its bulk value. While the details of the progression of the $d_{33}$ recovery to the original surface may be dependent on the orientation of the LiNbO, substrate and annealing temperature, it is unlikely that the $d_{33}$ coefficient of APE-LiNbO, waveguides fabricated on z- and x-cut substrates differ substantially at depths greater than the initial PE depth. Understanding the absence of reflected SH from the original surface of APE-LiNbO, may require microstructural and x-ray diffraction experiments to elucidate the crystal structure within the top 0.05 µm of the surface. This is of little practical importance since the modal amplitudes are very small at the surface. To design guided wave frequency conversion devices it is adequate to assume that at depths greater than the initial PE depth the $d_{33}$ coefficient nearly retains its bulk value throughout annealing, while variations occur within the original PE depth.

The measurements of the $d_{33}$ coefficient shown in Fig. 2 can be used to determine the normalized conversion efficiencies ($\eta$) for any guided wave nonlinear optical interaction. As an example, we compute $\eta$ for SHG of $\lambda_w=850$ nm radiation in z-cut, x-propagating APE-LiNbO, waveguides fabricated like those shown in Fig. 2. We assume first-order QPM over an interaction length $l$ with a uniform, depth-independent ferroelectric domain grating, which can be fabricated using an electric-field7 or electron-beam8 poling technique. With the output SH power given by $P_{2o}=\eta P_{o}^{2}$, $\eta$ is given by

$$\eta = \frac{8\pi^2 (d_{QPM})^2}{\chi_{eff}^{2}} \times \left| \int_{-\infty}^{+\infty} \int_{0}^{+\infty} d_{33}^{APE}(z) E_{2o}(y,z) E_{2o}(y,z) dy dz \right|^2,$$

where $d_{QPM} = 2d_{33}^{LiNbO3}/\pi$, $d_{33}^{APE}(z) = d_{33}^{APE}(z)/d_{33}^{LiNbO3}$, and the fields are normalized to carry unity power. The depth dependence of the refractive index profile was determined using a one-dimensional nonlinear diffusion model for the APE process10 and we assume a 4-µm-wide top-hat dependence for the lateral refractive index profile. We assume that the two-dimensional modes are separable, $E(y,z)=E_y(y)E_z(z)$, and compute the mode profiles at
FIG. 3. Fundamental ($\lambda_0=850$ nm) and SH ($\lambda_{2\omega}=425$ nm) modes (dotted lines), modal overlap (solid line), measured normalized nonlinear coefficient $d_{33}^{\text{APE}}$, the modal overlap with $d_{33}^{\text{APE}}$ (shaded region), and the H$^+$ concentration profile vs depth in APE-LiNbO$_3$ waveguides annealed for (a) 3 h and (b) 9 h. The abscissa is the same for (a) and (b).

$\lambda_0=850$ nm and $\lambda_{2\omega}=425$ nm using the effective index method. The depth overlap integral was evaluated using the depth dependence of the $d_{33}$ coefficient derived by taking the square root of the normalized reflected SH power given in Fig. 2. Shown in Fig. 3 versus depth are the optical modes, the measured normalized nonlinear coefficient $z_\eta(z)$, the modal overlap $E_3^0(z)E_{2\omega}(z)$; and as the shaded region, the modal overlap with the measured value of the nonlinear coefficient, $d_{33}^{\text{APE}}(z)E_0^0(z)E_{2\omega}(z)$, for waveguides annealed for 3 and 9 h; the data for a 5 h anneal are not shown for brevity. Also shown is the H$^+$ concentration profile, proportional to the index profile. At $\lambda_0$ the surface index changes are 0.0503, 0.0364, and 0.0230, for 3, 5, and 9 h anneals, respectively. The overlap using the measured value of $d_{33}^{\text{APE}}$ yields $\eta$ versus annealing of 410, 950, and 1090%/W cm$^2$. For comparison, the modal overlap assuming the $d_3$ coefficient to be independent of depth yields $\eta$ versus annealing of 2010, 1640, and 1280%/W cm$^2$. For unannealed waveguides $\eta=0$ since $d_{33}=0$ for unannealed PE-LiNbO$_3$. For anneal times longer than 9 h the modal overlap is removed from the region where $d_{33}=0$ and $\eta$ decreases because of reduced confinement. Figure 3 shows that the variation in $\eta$ with annealing is not due to a restoration in the $d_{33}$ coefficient of the APE-LiNbO$_3$ waveguide as much as a variation in the overlap integral due to a spatial redistribution of the modal fields away from the initial PE region.

There are two recent reports of guided-wave QPM SHG using depth-independent ferroelectric domain gratings, with $\eta$ of 600 (Ref. 7) and 700%/W cm$^2$ (Ref. 8) for devices with APE waveguides fabricated similarly to the ones modeled above. These values fall within the range modeled, indicating that the general form of the $d_{33}$ depth profile presented here allows reasonably accurate device modeling. However, waveguide loss, laser longitudinal mode structure, QPM grating and waveguide inhomogeneities, and the value of the $d_{33}$ coefficient of bulk LiNbO$_3$ (recently measured to be 23.7 pm/V$^{1/2}$ rather than the accepted value of 34.5 pm/V) render the modeling of the absolute $\eta$ of real devices difficult and questionable. Measurements of $\eta$ as a function of waveguide processing are ongoing to refine the models for the linear and nonlinear optical properties of APE-LiNbO$_3$.

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11. We assume $d_{33}=34.5$ pm/V for bulk LiNbO$_3$.