Microscopy and microRaman study of periodically poled domains in deeply thinned lithium niobate wafers

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The domain structure of poled deeply thinned lithium niobate is investigated as a function of sample thickness. Free-standing samples of thickness from 25 to 500 μm are prepared by a multiple-cycle polish and annealing procedure and then periodically poled. Using these samples and employing micro-Raman scattering and scanning electron, atomic force, and optical microscopy together, the domain broadening and poling voltage are found to vary in a regular and significant manner. The poled domains show a reduction in width spreading of 38% as the sample thickness is reduced from 500 to 25 μm . Micro-Raman probe measurements verify the quality and the uniformity of the poled domains and provide insight into their thickness-dependent poling contrast.

Keywords

Periodically Poled Lithium Niobate (PPLN); Domain Broadening; Poling in Thinned Lithium Niobate; Raman Spectroscopy

1. Introduction

Ferroelectric poling of periodic domains, such as used in the periodic poling of lithium niobate (PPLN) [1,2] and in other electro-optical devices, has become an essential technology for efficient control of guided-wave optical and infrared beams [3,4]. Thus, this technique allows quasi-phase-matching in nonlinear materials with non-phase-matched material refractive indices and, hence,

enhances the desired frequency conversion process. Two important issues in quasi-phase matching are the material quality and the dimensions of the patterned domain structure for progressively smaller poling dimensions. Understanding this issue is a particularly pressing problem for both nanodevice applications and more conventional integrated optical devices operating at short wavelengths in thin-film ferroelectric crystals, such as LiNbO_3 or LiTaO_3 [5]. For applications in discrete waveguide optical devices, frequency conversion that is designed to generate blue and near-UV radiation requires periods with resolution of $<1\ \mu\text{m}$ [1,6,7,8]. Other devices, such as switchable Bragg filters [9], backward second harmonic generation devices [10,11,12] and parametric oscillators [13], have similarly demanding requirements on poling resolution and quality. Thus understanding the materials properties of poling has basic device physics motivation.

Specifically fabrication and design of these domain-patterned devices requires consideration of domain broadening, a phenomenon in which the reversed ferroelectric domains broaden beyond (or expand wider than) their intended dimensions during the poling process. Because of this difficulty, several materials-based domain-fabrication techniques have been proposed, and in some cases been demonstrated, to achieve small periods and domain structures, such as proton exchange [14], overpoling [15], backswitching [16], and ultraviolet light illumination [17]. Many of these approaches impact the materials properties of domains. Thus proton exchange requires selective alterations to the crystal structure, and overpoling and backswitching tend to produce domains of non-uniform width. As a result of the importance of poled crystals, there have been many studies of these material structures using electron and optical microscopies, proximal probes, and X-ray scattering; see, for example, [18,19,20]. These and other studies (cited below) have shown the importance of materials factors such as poling voltage, strain, temperature, etc. in influencing the domain structure. However, it is interesting that there have been few if any reported systematic studies of the effects of sample thickness on the domain structure, despite the fact that it is generally believed to play an important role in domain structural properties [21,22].

In this report, periodic-domain poling is performed with the domain widths that are typical for many standard periodically poled lithium niobate devices, i.e., 10s of μm , which are values appropriate for 2nd order second harmonic generation. In our experiments, freestanding samples are carefully prepared using many cycles of polishing and annealing to have thicknesses ranging from 500 to 25 μm . Measurements are then made of the variation in critical external voltage necessary to pole the sample at each thickness. In addition, optical, electron, and proximal probe microscopy are then used to determine the variation in domain dimensions with thickness. A series of microRaman measurements at specific LiNbO_3 Raman modes are employed to verify the sample properties and to uncover the spatial uniformity of the poled and unpoled domains at each thickness. Raman measurements are also made of the thickness-dependent contrast between the two domain orientations.

2. Experimental

Our basic experimental approach was to examine the domain material and structure of periodically poled LiNbO_3 (LNO) for free-standing samples of different thickness, using various microscopies and microRaman spectroscopy. Each sample was prepared using polishing, annealing, photolithography, poling, etching, post-poling annealing, and imaging. Note that sample preparation was a *major issue* in this experiment since samples of less than $\sim 75\mu\text{m}$ s were fragile in handling and preparation of such deeply thinned samples is not discussed in the literature. Examples of the cross sections of these samples with thicknesses from 500 to 25 μm , obtained with SEM, are shown later in the **Results Section** below. In each case, the initial sample was a 500 μm -thick, Z-cut congruent LNO wafer, diced into 5×5 mm coupons. The Z+ side of each sample was polished to the desired thickness using chemical mechanical planarization (CMP). Polishing was carried out using diamond polishing pads with successively smaller particle size down to 0.5 micrometers so as to minimize surface scratches or abnormalities. The sample thickness was verified and measured by imaging the cross section with optical microscopy. Deviations in thickness were maintained at 6% or lower for all

samples and the sample thicknesses ranged from 500 to 25 μm . In order to relieve any internal strain in the crystal lattice that built up as a result of dicing and polishing, each sample was annealed at 600° C for 10 hours. To reduce lithium-ion out-diffusion, which would increase the required poling field [23], each sample was positioned between two larger LNO wafers during the annealing process. The efficacy of this process was confirmed by using Raman spectroscopy to compare the lithium concentration at the surface of an annealed and unannealed sample and it was found that the concentrations were equal within experimental error.

Poling was carried out using an electrolyte solution in contact with the Z⁺ and Z⁻ sides, with the poled pattern defined by a photoresist layer. Such electrolytic poling has been described extensively in prior publications [5,24,25]. The positive photoresist layer was spun onto the Z⁺ side of the mounted samples for 30 seconds at 4000 RPM and then baked at 60° C for two minutes. Lithographic patterning was done using laser writing (Heidelberg μPG 101 Laser Writer), so as to form a 1D periodic poling pattern into the photoresist over an area of $2 \times 3 \text{ mm}^2$ on the samples. The poling period was 37.2 μm and the exposed vertical stripe width was 9.3 μm , resulting in a 25% duty cycle. These particular pattern dimensions are typical for nonlinear-optical second-harmonic conversion from a wavelength of 1550 nm to 775 nm by second-order quasi-phase matching. These exposed vertical stripes defined the location of the poling electrodes for the saturated lithium chloride electrolyte solution contacted the sample surface in these regions. Following photolithography, the samples were post-baked at 100° C for 16 hours (an experimentally derived schedule which has been found, via Raman measurements, to relieve much of any handling-induced strain during fabrication and yet not disturb the poling period).

Fig. 1: Schematic of the poling setup. The external voltage is applied across the crystal via a lithium chloride solution in contact with the bare regions (i.e., regions where the resist is absent) of the surface. The materials used in the poling process are labeled in the figure; see Refs. [2,24,25] as examples of earlier discussions of this electrolytic approach to making structured electrodes.

Figure 1 shows a schematic sketch of the poling apparatus. Each sample was mounted on a glass substrate with a 3-mm-diameter through-sample via; the use of this via-mounted substrate reduced the mechanical pressure on each sample and, thus, prevented breakage during the poling process. After mounting each sample, the electrolyte reservoir was filled with the electrolyte, with care taken to avoid bubbles or partially filled structures. Using the apparatus sketched in **Fig. 1 (a)**, a voltage waveform (shown in **Fig. 2**) was applied via the electrolyte to the bare regions of sample surface; in each case the peak voltage was incrementally increased until the waveform was sufficient to pole the sample. It was possible to determine whether or not a particular waveform had poled the sample by monitoring the current through the poling circuit. A sharp spike in the current as the waveform reached the peak voltage indicated reversal of the ferroelectric domains; an expanded version of the waveform is shown in **Fig. 2 (b)**. The negative current pulse, seen when the applied voltage decreases suddenly from the poling level, is due to the displacement current rather than back-poling. This feature reflects the rapid change in the applied voltage and has been observed in the earlier work cited above.

After poling, the photoresist pattern was removed using acetone and piranha solution; the

sample was then etched with 49% hydrofluoric acid for ~10 minutes in order to allow visualization of the poled domains by either optical or scanning electron microscopy.

Fig. 2: Plot of a typical poling waveform, i.e., voltage vs. time. When the voltage crosses a critical threshold value, a current spike is seen, indicating the onset of poling current. The inset shows an expanded waveform for both current and voltage.

Material characterization, which was a crucial part of this experiment, was carried out using microRaman spectroscopy and electron (SEM), optical, atomic force microscopy (AFM) imaging. Cross sectional SEM microscopy, so as to observe the depth dependence of the poled region, was carried out by cutting the sample with a diamond saw and then carefully polishing of the sliced face, using the polishing procedure described above. The Raman instrumentation consisted of a focused beam, at a fixed excitation wavelength, so to enable an aerial image of the Raman response to be obtained. The instrument was equipped with an image-processing computer system, which enabled manipulation of the Raman image by spectral content, intensity, etc. as needed. Note that the use of Raman spectroscopy and imaging in LNO has been carried out by several groups, including those

examining the effects, such as strain, damage, and composition, from ion-implantation and other forms of materials processing [26,27,28,29]; thus it was an essential materials probe for our experiments.

3. Results and discussion

Microscopy Measurements

In order to examine the dimensional effects of ferroelectric poling, measurements were made of the external applied voltage, including the voltage needed to achieve poling, and the domain width as function of the sample thickness. The data showing the measurements of the voltage necessary for poling *vs.* thickness are shown in **Fig. 3**. Thus it is seen that the measured plot of poling voltage *vs.* thickness displays a linear behavior with a significant non-zero Y-intercept, indicating a nonzero offset of the poling voltage *vs.* thickness. Our experiments are not focused on obtaining the more basic quantity of the coercive field, which has been used to obtain for example, the magnitude of the internal field [30] or the effects of numerous field reversals on this internal field [24]. Nonetheless it is of interest to note that the coercive field for thicker samples (obtained by a simple spatial average along Z obtained by dividing critical voltage with the sample thickness) is approximately constant and close to a typical value of 22 kV/mm [15], a behavior suggested in earlier publications [5].

An important observation of our results is the nonzero Y-intercept appearing in the plot of poling voltage *versus* sample thickness. This intercept can be a result of several phenomena. The most obvious is existence of an internal field, which is undoubtedly present as a result of defects or defect clusters [30, 31], which dominate the poling energetics for samples without voltage or other conditioning [32,33]. In addition, our experiments have shown that the presence of surface defects affects poling voltage significantly, especially for low sample thickness. In particular, these results were suggested by repeated observations in our laboratory that if samples were not properly annealed and polished, the Y-intercept of the poling voltage would increase in magnitude. An example of data from one of these experiments is shown by the green triangles in **Fig. 3**. In addition, a related effect has

also been clearly shown, for example, in recent experiments in our group using poling of small-area patterns with prior surface polishing defects such as scratches [34]. In those experiments surface scratches were found to correlate with a higher voltage required for poling.

Fig. 3: The measured poling voltage vs. sample thickness. Notice that the y-axis intercept does not intersect the origin. Thickness error bars are standard deviations from a set of multiple thickness measurements at different locations for each sample. The voltage error bars are determined from the poling voltage step size. The three green triangles towards the lower left corner of the graph correspond to samples from earlier experiments conducted with a less refined polishing technique. The error margin for these three data points was ± 0.1 kV and less than ± 5 μm . Error bars were removed for visual clarity.

In order to investigate the effect of sample thickness on domain broadening, the widths of the inverted ferroelectric domains were measured via optical microscopy for each sample and the average widths were determined by repeating this measurement across the stripes. The pattern in the photoresist, was found to be $9.3 \mu\text{m}$ for all samples, thus the domain width after pattern transfer vs. poling would be expected to be constant in the absence of any domain broadening. In fact, the data, as shown in **Fig. 4**, shows that the domain width decreases with decreasing thickness as suggested, for example, in [21] and other early work. SEM cross-sectioning was also used to examine the domain broadening;

examples of these measurements are shown in **Fig. 5**. SEM measurements were also valuable in order to determine the same broadening behavior albeit from the perspective of an instrument with a different contrast mechanism. Further, the cross-section micrographs showed clearly that the domain broadening in a given sample was relatively uniform throughout the crystal depth, except for an induction area within $\leq 1\mu\text{m}$ of the surface, and a possible slight narrowing towards the Z- side. In particular, the average difference in domain width from the Z+ to Z- side was measured to be within 1-2% for each sample, that is, the width of the features were constant within the resolution of the optical image. In addition, there appeared to be no correlation between sample thickness and domain spreading throughout the depth of the crystal.

Fig. 4: Domain width vs. thickness. Both the error bars for the domain width and thickness are standard deviations obtained from a set of multiple measurements, as explained in the caption of **Fig. 3**. The inset shows the electric field plot obtained with a high-resolution finite element method Poisson computation for the field in the vicinity of the photoresist opening in the surface mask; the sample is $25\mu\text{m}$ thick, the opening is $9.3\mu\text{m}$ in width). More information is included in the Supplementary Materials Section.

Returning now to the decrease shown in **Fig. 4**, the overall domain width is well fit with a linear behavior, with a positive slope of the domain width/thickness ratio of $8\text{ nm}/\mu\text{m}$. While this trend does show a linear relationship between thickness and domain width, the data gives a R^2 correlation

coefficient of only 0.7, due to the scatter in the data. The error bars display the variance for each chip and show clearly the measured variability between chips. Note that several of the points are clear outliers since they are far off the measured plot. Clearly, there are additional stochastic factors that affect domain broadening – perhaps due to bubbles in the solution near the sample or the fact that near the onset of poling domain formation is highly nonlinear. Regarding the latter effect, the procedure, in which the voltage of the poling waveform is increased in discrete increments until poling, can lead to such a stochastic behavior since the value of the off-set to the exact poling voltage could not be determined for each measurement. Thus, for example, in some cases, the sample may be somewhat over-poled by an unknown amount. In fact, as demonstrated in [15], such over-poling results in domain broadening.

Fig. 5: a) SEM cross-section images of poled domains revealed by HF etching. For the 500- μm -thick sample, the domains are clearly wider than the domains in the 150 or 25- μm -thick sample domains. The etching between poled and non-poled domains appears different in this figure because the Y+ face is shown for the 25 and 150 μm samples while the Y- face is shown for the 500 μm sample. Panels b) and c) show zoomed out SEM images showing the full cross-section from Z+ to Z- sides with b) 150 μm and c) 500 μm thick samples, respectively. The uniformity of domain width through the depth of the crystal is seen.

The broadening of domains by electric-field poling in PPLN has been explored theoretically [35] by consideration of the local fringing electric fields and the compensation of charge. This theoretical model is based on a geometry that is very similar to the one used in our experiment. According to this model, in LiNbO_3 the domain broadening has been attributed to the very high transverse field near the top-surface edge of the photoresist/bare LNO interface. This field, which extends to a depth on the order of $1\text{ }\mu\text{m}$ in a $500\text{ }\mu\text{m}$ sample [35], causes charge to be injected under the photoresist/LNO interface, thus resulting in domain broadening. The calculation in Ref. [25] was based on the interface of a metal film directly on the oxide surface, thus we have used a model, which matches our materials interface more exactly, namely a polymer (dielectric A) and an electrolyte poling electrode (B). The lateral field is then calculated using a high-spatial-resolution finite element electric-field simulation (see **Supplemental Materials Section** for method and figure). Our calculation shows that as thickness increases the transverse fringing field magnitude increases; this result is thus consistent with observation that the width of the poled region expands as the thickness increases. This behavior is seen in the domain broadening increase seen in **Fig. 4**. Note also that domain broadening will obviously be modified by defect pinning or compositional effects (such as in proton exchange LNO) [18,36]. Alternately, in congruent LNO such as used here, a particularly important defect is a lithium deficiency [31].

MicroRaman Measurements

In the experiments above only the physical width of the poled sample and the poling waveform and voltage were measured. However in order to characterize the material properties of poled regions including orientation and spatial resolution, micro-Raman spectroscopy was used; see the **Supplemental Materials Section**. In addition, Raman measurements were used to study any internal structural changes in the lithium niobate domains induced by the poling, as well as the conditions of the samples following polishing. These measurements, which also included Raman-mode-specific imaging, were also used in examining thickness-dependent effects in poling. The effectiveness of Raman

characterization of PPLN has been shown in previous studies [37,38,39]. See also an excellent review of this topic in Ref. [40]. Thus to summarize, the Raman spectroscopy measurements used here were essential to determine the quality and uniformity of the poled regions and to also examine for several sample-thickness-related effects (see below).

Our choice as to which Raman crystal modes to use, was guided by the fact certain modes involve the motion of certain crystal-ion lithium species. These modes are particularly affected by poling as the lithium ions are displaced during the poling process. In addition, Raman spectroscopy was initially used in our experiments to determine the quality of the samples following polish thinning and in some cases other forms of processing, which strain the sample (see our comments elsewhere in this paper). In one of these cases, for example, it was observed that an application of coarse polishing led to the appearance of a normally forbidden mode, i.e., at 630 cm^{-1} . Only after careful finish polishing and annealing steps (see **Section 2: Experimental**) was this Raman mode eliminated and the samples used. Thus this result shows that one immediate application of the Raman probe in our work is as a simple probe of the state of the crystal and its near surface.

Figure 6 shows a series of linear 1D scans of the surface of the $150\text{ }\mu\text{m}$ sample. The figure is organized so as to display the signals recorded at wavelengths of specific transverse-optical (with the exception of the topmost spectral trace, which is longitudinal) Raman modes. Note that as described in an earlier study in [37], the domains can be readily detected or mapped by the dramatic changes in the Raman signal at the domain edges of the patterned stripes. In **Fig. 6**, the spatial scale is overlaid with a microscope image as seen in the inset and it is apparent that the dimensions of the Raman signals correspond to the edges of poled regions. In addition, as discussed in [37], a comparison of the Z- and Z+ surfaces showed clearly the reverse symmetry of the edge signals. Our data show, generally, that the optical TE modes exhibit this characteristic asymmetric behavior for the Z+ and Z- Raman signals, consistent with and attributed to the influence of surface internal fields transverse to the domain wall [37].

Fig. 6: A Raman scan using 5 different Raman wavelengths along the top surface of a poled 150 μm sample with the scan direction perpendicular to the long axis of the poling stripe. This microscope image of the poled sample surface shows the path of the scan (horizontal line) and poled (P) and non-poled (N-P) regions.

In addition to simple linear scanning, it was also possible to image the poled regions via scanning over a 2 dimensional grid. Thus **Fig. 7** shows such 2D scans of two modes, i.e., at 236 and 264 cm⁻¹, over the same area of the surface. The images for these two modes show the same two vertically oriented domains, where the sharp edges of the domains are the vertical high contrast lines. Although the two modes show similar features along the domain edges, there are slight differences between the two modes. The 236 cm⁻¹ mode, which is primarily a stretching mode between the Nb and O ions [41], has a weaker response in the poled region than does the 264 cm⁻¹ mode. Thus it was possible to discern changes in the overall signal levels between the non-edge regions of the poled and non-poled domains regions in both **Figs. 6** and **7**. For example, the 150 μm sample analyzed in **Fig. 6** had an average signal difference between the poled and non-poled regions of 2.3% for the 236 cm⁻¹

mode and 2.9% for the 264 cm^{-1} mode.

Fig. 7: Raman images of a poled 150- μm -thick sample at the Raman modes shown in the white boxes. Spatial dimensions are in μm . Note the relative uniformity of the poled region.

Finally, Raman imaging was also used in a more direct way to examine the overall *quality* of the poled regions. Thus, Raman spectromicroscopy was used to find that uniformity in poling did not vary significantly with sample thickness. For example, measuring the Raman intensity of the 264 cm^{-1} mode across poled samples 500, 150, and 100 μm thick, showed the variations to be 0.56%, 0.61%, and 0.70% in the poled region and 0.69%, 0.57%, and 0.84% in the non-poled region respectively. The other six modes measured here ($152, 236, 331, 432, 579$, and 874 cm^{-1}) had similar low values (all under 2%) of Raman intensity variation.

Note the presence of dark blue features on the side of the poled regions in **Fig. 7**. These features were examined carefully using optical and then AFM images subsequent to a Raman scan. It was found that these features correlated to side edge imperfections in lithographic patterning, most likely due to imperfect beam scan overlap. In addition, measurements were also made of the Raman signal contrast

between poled and unpoled regions as a function of sample thickness. Thus measurements were made of three representative sample thicknesses: 500, 150, and 100 μm , by averaging 50 locations on the poled and unpoled regions using an imaging (2-dimensional) scan. Our measurements showed that, for a probe of the 264 cm^{-1} mode, a 500- μm -thick sample had a poled/unpoled peak intensity difference of 1.9%, while a 150 μm sample had 2.9% difference, and a 100 μm sample had a 9.7% difference; similar values were seen for the probing the same three samples with the other six modes. In each case, the intensity difference between poled and unpoled regions increased with decreasing thickness. While this represents a relatively modest change in the poled to unpoled Raman intensity, it was persistent and real. One possible explanation for this effect is that there is a small amount of residual strain in the materials after poling and that this is most pronounced in the thinner samples, since it is known from several recent studies that in the presence of strain, the intensity of allowed Raman modes decreases [27]; note that this effect could be expected to mode dependent, although this dependence is at present unstudied. The small percentage change in the poled/unpoled ratio would make it difficult to detect this strain using a shift in the position of the Raman peak – a method also discussed in [33]. Finally to summarize this section, our Raman results show that the LNO properties of our poled samples are uniform, with possibly residual thickness-dependent strain.

4. Conclusion

The goal of this work was to examine thickness-dependent material effects in the poling of LiNbO_3 crystals. Our results show that the domain width increases as the sample thickness increases, a result consistent with the role of the increasing lateral field as the thickness increases. Our experiments also show that previously investigated Raman physics can be used as a reliable probing method to characterize the poled crystal. Our results show, for example, a high uniformity of the poled region of the crystal with well-defined edges even at smaller sample thicknesses as well as a thickness-dependent poling contrast. At present ion-slicing-based methods for poling much thinner samples are being

developed and the effects examined here can be examined in these samples, which have micrometer or even submicrometer thicknesses.

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