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

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ABSTRACT

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.

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 μm [1,6–8]. Other devices, such as switchable Bragg filters [9], backward second harmonic generation devices [10–12] 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 require 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, [18–20]. 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

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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 freestanding 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 ~75 μm 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 μm 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 h. To reduce lithium-ion outdiffusion, 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 s at 4000 RPM and then baked at 60 °C for 2 min. 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 × 3 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 h (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 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, we applied a voltage waveform (shown in Fig. 2) 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 the inset of Fig. 2. 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 min in order to allow visualization of the poled domains by either optical or scanning electron microscopy.

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 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 [26–29]; thus it was an essential materials probe for our experiments.

3. Results and discussion

3.1. 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 [23]. 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 [10], a