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Domain dynamics in stoichiometric lithium tantalate revealed by wet etching and on-line second harmonic generation

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The effect of chemical etching on the stability of domains in periodically poled stoichiometric lithium tantalate is studied by on-line second harmonic generation and microscopy. It is found that wet etching directly after poling leads to domain-wall movement, resulting in back-switching or domain merging. Head-to-head domains tend to backswitch, while tail-to-tail domains merge. For samples where the domain structure stabilized for longer time, no domain motion is observed when etched. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Periodically poled LiTaO3 (LT) is a potentially attractive ferroelectric material for quasi-phase matched (QPM) UV-light generation since it has a shorter cut-off wavelength than other well-established ferroelectric nonlinear optical oxides such as LiNbO3 and KTP. However, the standard congruent material suffers from photorefractive damage, which, in practice, has limited its use in the UV region. It is expected that near-stoichiometric LT (NSLT) would be a superior material choice in this context, as the defect concentration, which directly relates to the damage, is strongly reduced. However, NSLT growth is complicated and challenging since it requires a highly precise control over the temperature and the melt composition. On the other hand, the stoichiometry of congruently grown LT crystals can be dramatically improved by post-growth diffusion of Li2O into the crystal at high temperatures to compensate the Li2O deficiency, forming the so-called vapor-transport-equilibrated (VTE) stoichiometric LT (SLT). The coercive field is drastically reduced for SLT, which facilitates the fabrication of quasi-phase matching (QPM) devices. However, it is known that the lower defect density, and consequently less pinning sites, in conjunction with the reduced coercive field of this material, may cause unstable domain structures. In fact, it has been observed that even moderate heat treatment can lead to domain backswitching in NSLT.

The standard technique to study domain structures for periodically poled ferroelectrics is by using domain-selective etchants, mostly based on hydrofluoric acid (HF). For LT, HF attacks the Z+ face, while the Z− face is essentially untouched. It is known that charged domain walls (DWs), due to their large surface energy, can become unstable when exposed to chemical etching. For instance, Shur et al. demonstrated that chemical etching of Mg-doped NSLT results in reconfiguration of the domain structure. Since the domain-stability mechanisms for VTE SLT are not well known, their investigation could lead to improvement in fabrication of short-period devices and would also shed some light onto the domain-wall dynamics of this material.

Previously, it has been demonstrated that on-line second harmonic generation (SHG) can be an excellent non-invasive tool to study the macroscopic behavior of the QPM structure during the polarization reversal process. In this work, we study the impact of chemical etching on the domain stability of VTE SLT after poling. Our findings are obtained by monitoring the SHG signal on-line during the etching process, followed by post-etching characterization of the domain structure with optical microscopy and a profilometer. We show that chemical etching right after poling can induce DW motion, without any applied external field. Furthermore, we demonstrate that when the original domain configuration is head-to-head (HH) or tail-to-tail (TT), the DW movement results in backswitching or merging of neighboring domains, respectively.

II. EXPERIMENTS

For our experiments, we used commercial, 1 mm thick, VTE SLT crystals (Raicol Crystals Inc., Israel). The wafers were cut into pieces of 11 × 4 mm2, and the end-faces were polished to an optical finish for laser excitation. The samples were then photo-lithographically patterned with a period of 12.13 μm on the Z+ face, and the pattern was covered with a 50 nm-thick titanium film. The resulting metal/insulator duty-cycle was 43%/57%. Afterwards, the samples were connected to the external poling circuit using liquid electrodes (LiCl-based water solution; molar ratio, 1.9:5:5) and poled by applying a single, 5 ms long, triangular pulse with an electric-field magnitude that varied between 280 and 350 V/mm. The samples were investigated using on-line second harmonic generation during and after the poling.

In order to investigate the stability of the periodically poled domain structure, the temporal evolution of the second harmonic signal was monitored, while the crystals were etched with concentrated HF (~40%), which is the most common concentration for revealing domain structures after poling. As the SHG amplitude corresponds to the number of antiparallel domains in the beam path, the reduction of the signal during etching then reflects the presence of fewer...
reversed domains. The experimental setup is depicted in Fig. 1. We used a tunable continuous wave Ti:Sapphire laser emitting at 860 nm as a pump. The fundamental beam was launched along the crystal’s x-axis, focused to a beam waist of 50 μm by a lens with a focal length of 50 mm, and polarized parallel to the crystal z-axis. The beam propagated ~150 μm below the patterned face of the sample.

The generated SHG light (λ = 430 nm, corresponding to 3rd order QPM) was separated from the pump by a color glass filter (BG40) and monitored with a photodetector (S120VC, Thorlabs, Inc.). We have to note that similar to Ref. 14, our on-line technique monitors the accumulated domain response rather than the switching dynamics of the individual domains. It is expected that, since the wet etching does not involve large external fields or external charge injection, the transformations of the domain grating will be slow (millisecond range or slower). The on-line SHG setup hence warrants a fine temporal resolution for these experiments. We have studied samples that were etched shortly after poling (~15 min) and those that have rested approximately 48 h before they were etched. We identify them by “lapse time” and call it “short” and “long” lapse times, respectively. Note that for each sample, we have recorded the SHG signal right after poling in order to use it as a reference for later investigations.

Figure 2 shows the SH time-evolution for two representative VTE SLT samples poled under similar conditions after HF droplets were placed on their patterned face. Note that the metal-photoresist pattern was still on the crystal when the HF was dropped. The pattern dissolved in HF within about 5–10 s and had no impact on the result. For all samples studied, no decay of the SH signal was observed prior to etching. The sample with long lapse time (blue curve) shows no reduction in the SHG signal during etching, suggesting that the domains had stabilized during the lapse time. However, for the short lapse-time sample (red curve) and other samples etched under the same conditions, a significant decay in the SH power was seen, implying that the domains were still unstable shortly after poling. The decay was typically 40%–80% over a time span of one to two hours, and then it stopped, as can be seen in Fig. 2.

Note that the SHG signal fluctuations resulted from a small power instability in the Ti:Sapphire laser which is amplified through the SHG process and does not correspond to any domain dynamic phenomena.

Since no SHG decay was observed, compared to the reference value, in long lapse-time samples, we conclude that 48 h is enough to stabilize the domain structure and chemical etching does not have any impact on the sample performance while etching shortly after poling results in significant reconfiguration of the domain structure. Although charged domain-walls are energetically unfavorable, they commonly appear during polarization-switching under periodic electrodes, especially for short-period poling. These charged walls are initially unstable, but with time, they are compensated through bulk screening, reaching a more stable state. However, the bulk screening process in LT is slow. Thus, when the crystal is exposed to chemical etching during the stabilization phase, screening charges on the surface will be removed, and the chemical etching may assist the depolarization field causing domain-wall movement.16 The domain wall will then aim to obtain a lower-energy domain configuration with uncharged DWs.

Note that for the same lapse-time, on-line chemical etching and conventional chemical etching (i.e., immersing the sample in the HF solution) resulted in similar SHG decay, which confirms that the irradiation of the sample with the laser beam has no effect on the domain-wall movement during the chemical etching. Thus, the online SHG proved to be an effective non-contact tool to monitor the dynamics of the macroscopic stability of the periodically poled structures.

After the SHG/etching experiments, the samples were further examined under an optical microscope and with a profilometer (KLA Tencor P-15) to investigate the post-etching domain structure. Considering that the etch rate for our samples is ~0.15 nm/s for the Z− domain-face, while the Z+ face remains relatively untouched, we could estimate the time for which each individual domain was stable by measuring the topographic height of the etched relief relative to the Z+ face. Three clearly distinct cases could be observed depending on the type of charged walls/domain configuration created during poling: “Straight” (i.e., uncharged DW) remained the same, domains that had a HH configuration...
prior to etching predominantly stabilized by backswitching, while TT domains merged with neighboring domains to form larger domains. A sketch of the domain configurations is depicted in Fig. 3.

A representative example of HH domains and their rearrangement after etching is shown in Fig. 4. Fig. 4(a) shows the former $Z^+$ face and Fig. 4(b) the same area on the former $Z^-$ face. The corresponding etch profile of Fig. 4(a) is depicted in Fig. 4(c). The arrow in Fig. 4(a) shows domains with lower contrast. The contrast difference in Fig. 4(a) corresponds to the etch depth difference (shallow and deep domains) of the etch profile in Fig. 4(c). These domains with low contrast had switched back during etching and were therefore etched for a shorter time (only until the back-switching occurred). The black arrow in Fig. 4(b) indicates the same position as the arrow in Fig. 4(a). Evidently, these domains had never reached the opposite side during poling, ending in the bulk of the crystal, which corresponds to the HH domain configuration as depicted in Fig. 3(a). Clearly, the uncharged DWs at the left of this region had remained stable during etching.

Figure 5 shows a representative example of TT domains that merged during etching. Figure 5(a) shows the domain structure on the former $Z^+$ face, and Fig. 5(b) shows the same region on the opposite face. The topographic profile of the former $Z^+$ face is shown in Fig. 5(c). Note the lower contrast DWs marked by the black arrow in Fig. 5(a). These DWs look similar to their neighboring walls marked by orange arrows. However, the region marked by the black arrow has outer DWs with different contrast, which can also be seen in the corresponding etch profile in Fig. 5(c). Moreover, the region marked by the black arrow has a
different polarity compared with its neighboring areas as can be recognized from the corresponding area on the former Z$^-$ face in Fig. 5(b). The regions marked with orange arrows represent the HH domain configuration, similar to what is shown in Fig. 4, while the region marked with the black arrow illustrates former DWs that moved and merged together during the chemical etching. This can be understood by the fact that these domains, marked by the black arrow, present on the Z$^+$ face prior to etching, had merged in the bulk of the crystal, resulting in a TT configuration.

It is important to note that for domains with inclined walls (i.e., the leftmost domain walls depicted in red in Figs. 3(a) and 3(b)) that reached the opposite polar face during poling, DW movement follows the same behavior: they either backswitch, or merge, in order to obtain uncharged DWs, depending on their original DW configuration. The fact that a domain has reached the opposite polar face itself does not warrant a more stable domain configuration during the chemical etching process. On the other hand, if the DWs are uncharged, i.e., the domain width is maintained through the crystal’s thickness, the etching process has no major impact on the domain structure.

It is worth mentioning that contraction along the domain length (i.e., along the y direction) is also observed for all domain configurations. Figure 6 shows the domain contraction along the y-direction on the former Z$^+$ face (Fig. 6(a)) and the corresponding area on the former Z$^-$ face (Fig. 6(b)). It is clear from the image that domain contraction on the Z$^+$ face is limited to the size of the domain on the Z$^-$ face. Domain contractions up to hundred micrometers were observed in the y-direction. The domain motion stopped when the DWs became uncharged, i.e., when the domains had the same length in the y-direction on both polar faces. Unfortunately, this was not monitored with the on-line SHG technique since this is only observed at the edge of the domain-grating and the pump beam was placed at the center of the grating.

### III. CONCLUSIONS

In summary, we have investigated the impact of chemical etching on the domain stability of VTE SLT after periodic poling. It was found that domains were stable two days after poling, while domain backswitching, domain merging, and domain wall movements were seen in samples etched shortly after poling. Our results demonstrate that on-line SHG is an efficient method to monitor the domain dynamics during the etching process. Etching helped to reveal both head-to-head and tail-to-tail domain configurations, and it was possible to show that the former led to backswitching, while the latter resulted in domain merging.

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FIG. 6. (a) The former Z$^+$ face of a crystal poled with 12.13 $\mu$m period domains and the (b) corresponding Z$^-$ face. The domain contraction can be clearly seen in (a).