Ferroelectrics, 2001, Vol. 257, pp. 191-202
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Recent Achievements in Domain Engineering in Lithium Niobate and Lithium Tantalate

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We present a survey of our recent study of the field-induced domain kinetics in single-crystalline congruent lithium niobate (LN) and lithium tantalate (LT). The proposed backswitched poling by field application to the lithographically defined metal strip electrodes allows to produce periodical micro-scale structures for nonlinear optical application and to demonstrate the first achievements in domain nano-technology.

Keywords: ferroelectrics, nonlinear optics, domain kinetics, domain manipulation, nanotechnology, switching, backswitched poling

INTRODUCTION

Fabrication of ferroelectric domain patterns with periods about several microns is one of the most important problems of the micro-domain engineering in ferroelectrics. The solving of this problem will allow to improve the characteristics of electro-optical and nonlinear optical devices.[1] The engineerable (periodically poled) nonlinear optical materials are widely used for the development of tunable coherent light sources based on quasi-phase matching.[2-6] Lithium niobate $LiNbO_3$ (LN) and lithium tantalate $LiTaO_3$ (LT) are the best materials for such applications due to large electro-optical and nonlinear optical coefficients.

Two different branches of domain engineering have been developed recently: predetermined and self-organized domain patterning. In the first one the domain patterns are determined in details by spatial distribution of external action (mostly electric field). The second one is the formation of quasi-regular patterns as a result of self-maintained domain evolution.

In this paper we demonstrate the recent achievements in application of both approaches in LN and LT. The spontaneous backswitching after poling field removing was used for production of high-fidelity domain patterning in thick wafers and quasi-periodic nano-scale domain patterns. We demonstrate the frequency multiplication of the domain patterns as compare with electrode ones[6-8] and self-maintained formation of oriented nano-scale domain arrays.[9]

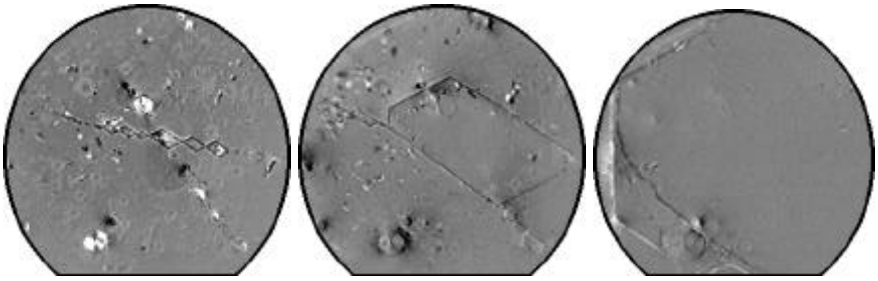
IN SITU OBSERVATION OF DOMAIN KINETICS

We investigated in details main stages of the domain evolution in LN and LT using i*n situ* optical observation of the instantaneous domain patterns during poling. The 0.2 mm-thick wafers were cut perpendicular to the polar axes. For switching in uniform electric field the polar surfaces were covered by the circular transparent electrodes (1-mm-diameter) of liquid electrolyte (LiCl water solution) using special fixture. The set of instantaneous domain patterns visualized by polarizing microscope was TV recorded with subsequent image processing. This technique allowed to obtain the direct information about the domain shape evolution. We extracted the field dependence of the sideways wall motion velocity, which is of principal importance for poling procedure optimization.[4]

Instantaneous domain patterns in lithium niobate

The domain kinetics in LN shows up as formation and growth of several regular shaped domains (Fig. 1). Nevertheless one can see the irregularities in wall propagation due to interaction with individual domains, but the preferential walls orientation is brightly demonstrated from the beginning to the end of switching process.

The typical evolution of the domain structure in LN is the nucleation along the electrode edges and propagation of the domain



(a) (b) (c)

FIGURE 1 Evolution of domain structure during repoling in uniform external field in LN. Diameter of poling area 1 mm, E = 15.3 kV/mm.

walls to the center of the electroded area. The surface defects drastically change this scenario. The small scratch in the center of electroded area is a source of artificial nucleation sites (Fig. 1). The domains arise in the center of the electroded area and grow to its boundary. All domain walls are strictly oriented along **Y** directions. Any instantaneous local deviation from the allowed crystallographic orientations disappears rapidly by the propagation of domain steps along the wall.

The average sideways wall motion velocity extracted from the set of instantaneous patterns[10] demonstrates the conventional field dependence in wide velocity range

$$V(E) = V_\infty \exp[- E_{ac}/(E - E_{th})], \quad (1)$$

where $\mathbf{E_{ac}}$ - activation field, $\mathbf{E_{th}}$ - threshold field, V_∞ - constant.
For poling $\mathbf{E_{th}}$ = 17.8 kV/mm and for repoling $\mathbf{E_{th}}$ = 14.0 kV/mm.

Peculiarities of domain growth in lithium tantalate

In LT, contrary to LN, the density of arising individual domains is about 1000 mm^{-2} and the nucleation along the edges of electrodes is negligible (Fig. 2a). The triangular shape of growing domains is more irregular due to permanent merging of the moving walls with individuals. The tendency for a reconstruction of the regular domain shape after merging was also obtained (Fig. 2b).

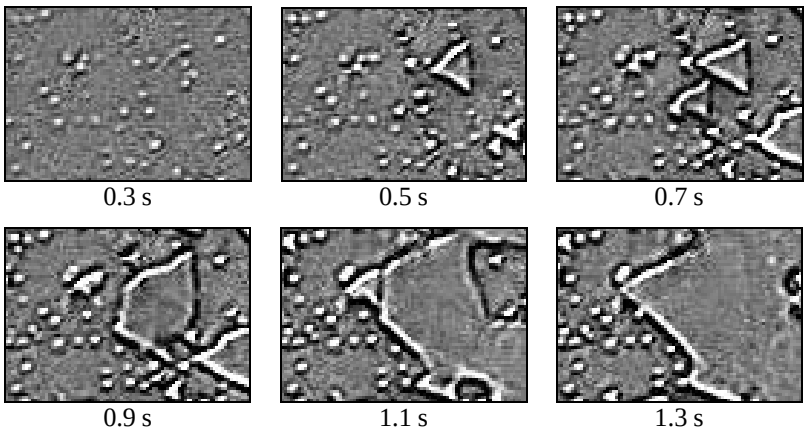
The coexistence of "fast-growing" and "slow-growing" domains (Fig. 3) is in accord with recent publications of V.Gopalan.[11,12] The small slow-growing domains appear only at the very beginning of the

(a) (b) (c)

FIGURE 2 Evolution of domain structure during poling in uniform external field in LT. Diameter of poling area 1 mm, E = 19.2 kV/mm.

switching process (Fig. 3a) and then enlarge extremely slow ($\mathbf{v_s}$ ~ 1 μm/s). The fast-growing domains are formed by merging of neighboring slow domains and demonstrate jump-like anisotropic growth (Fig. 3b-f). Sideways wall motion of fast-growing domain represents the sequence of step generation acts through wall merging with slow-growing domains. The arisen steps rapidly propagate along the wall.

The motion velocity of fast walls essentially depends on their orientation. In addition to normal "flat" fast walls oriented in $\mathbf{Y}^+$ direction with $\mathbf{v_f}$ ~ 20 – 60 μm/s we obtained the "zig-zag" super fast walls oriented in $\mathbf{Y}^-$ direction with $\mathbf{v_{sf}}$ ~ 130 μm/s (Fig. 4).



0.3 s 0.5 s 0.7 s

0.9 s 1.1 s 1.3 s

FIGURE 3 Domain growth by wall merging with slow isolated domains during poling in uniform external field in LT. E = 19.2 kV/mm.

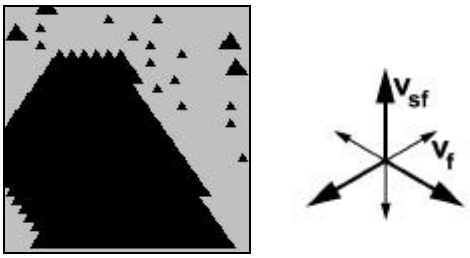


FIGURE 4 "Fast" and "super-fast" domain wall motion by merging with "slow" isolated domains. Result of computer simulation.

Thus the following mechanism of wall propagation in LT was proposed. The position of slow domains is defined by residual domains and spatial distribution of bias field. Slow domain growth is obtained up to wall merging of neighboring slow domains. Fast wall motion represents the sequence of the two-stage acts: 1) step generation by wall merging with slow domains, 2) rapid growth of arisen steps (Fig. 5).

Domain evolution scenario changes as a result of cycling (Fig. 6). First poling (E = 22.5 kV/mm) is characterized by relatively low nucleation density and ideal triangular domain shape (Fig. 6a). The higher nucleation density and irregular domain shape were observed during subsequent switching in the same field (Fig. 6b). Whereas the evolution of maze domain structure (Fig. 6c) was obtained for subsequent switching in low field (E = 15 kV/mm).

The obtained behavior can be attributed to the evolution of spatial distribution of bias field during cycling.[13] Only first poling goes in uniform bias field and each poling cycle changes the bias field distribution according to domain kinetics.

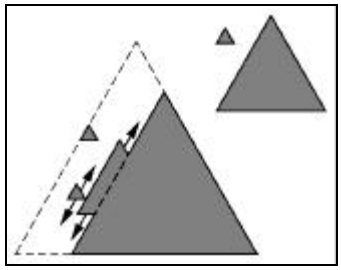
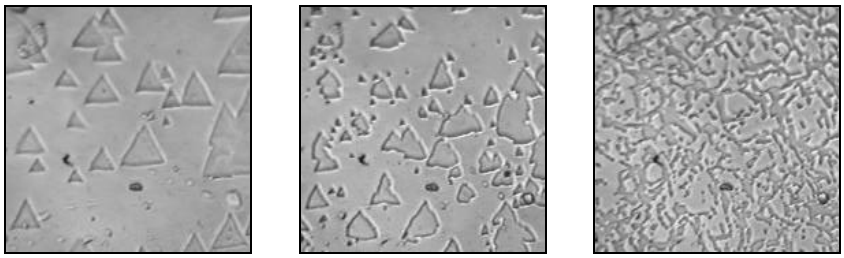


FIGURE 5 Scheme of domain growth during poling in uniform external field in LT.



(a) (b) (c)

FIGURE 6 Domain patterns during cyclic switching in uniform electric field in LT: (a) first poling in E = 22.5 kV/mm, (b) subsequent poling in E = 22.5 kV/mm, (c) repoling in low field E = 15 kV/mm.

PERIODIC DOMAIN PATTERNING

Periodic domain structures were prepared in optical-grade single-domain 0.5-mm-thick LN and 0.3-mm-thick LT wafers of congruent compositions cut perpendicular to polar axis. The wafers were lithographically patterned with periodic strip metal (NiCr) electrodes deposited on $\mathbf{Z}^+$ surface only. Electrodes in LN were oriented strictly along one of **Y** axis. Patterned surface was covered by an insulating layer (0.5-μm thick photoresist or spin-on-glass) (Fig. 7a).

A high electric pulse greater than coercive field (E_c = 21.5 kV/mm) was applied to the structure through the fixture containing a liquid electrolyte (LiCl).[3,4] The waveform for backswitched poling consists of three levels: I - "high field", II - "low field" and III - "stabilization field" (Fig. 7b). The switching from single domain state takes place at "high field" and the backswitching (flip-back)[5-8] occurs at "low field". The duration of the "high field" stage $\mathbf{Dt_{sp}}$ and the field-diminishing amplitude **DE** are the crucial parameters for

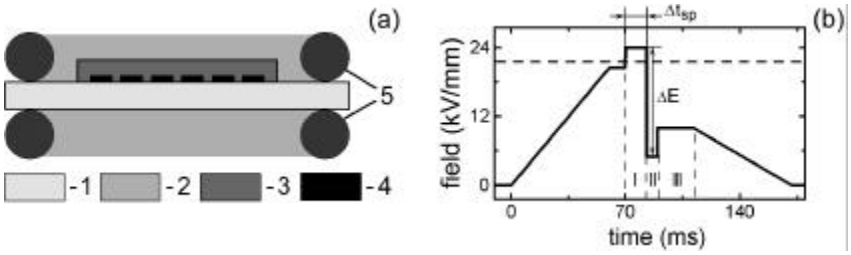


FIGURE 7 (a) Scheme of experimental setup: 1 - wafer, 2 - liquid electrolyte, 3 - insulating layer, 4 - periodic electrodes, 5 - O-rings. (b) Backswitched poling voltage waveform: I - high-field stage, II - low-field stage, III - stabilization stage.

backswitching kinetics. The domain patterns at **Z** surfaces and polished **Y** cross-sections were revealed by etching for 5-10 min by hydrofluoric acid without heating.[4] The obtained surface relief was studied by optical and scanning force (SFM) microscopes.

FREQUENCY MULTIPLICATION OF DOMAIN PATTERNS

We studied in details the domain evolution during backswitching in LN. First, we demonstrated that trivial backward motion of the existing domain walls in laminar domain structure allows to improve the periodicity thus producing the high-fidelity predetermined domain patterns by backswitched poling.[5-8] Second, we found that backswitching leads to spatial frequency multiplication of domain pattern as compare with the electrode one.[5,6,10] This effect is due to the fact that in proper conditions the nucleation occurs along the electrode edges or in the vicinity of the existing domain walls (Fig. 8a) while the wall motion is negligible.

Let us consider the stages of backswitched domain evolution for wide (about 3-μm-width) electrodes (Fig. 8). The patterns were observed in different partially backswitched samples. The initial nucleation along electrode edges (Fig. 8a) and subsequent merging lead to formation of a couple of strictly oriented sub-micron-width domain stripes under each electrode (Fig. 8b). This process can be considered as "frequency tripling". The width of the stripes can be controlled by duration of backswitching stage. The typical depth of the backswitched domains is about 20 - 50 μm.

For longer backswitching stage new couple of nanodomain arrays appears in nonelectroded area along the electrode edges (Fig. 8c). The "frequency pentaplication" effect was observed on this way. It was shown that the distance between secondary and initial stripes (structure period) is determined and can be controlled by the thickness of the artificial insulating layer.[10,14]

The last backswitching stage (Fig. 8d) presents the violating of the structure period by stripe merging in wide backswitched domains, which in turn grow and merge with non-switched ones.

The stripes merging can lead to useful "frequency doubling" for narrow electrodes and long enough backswitching time.[5,6,10]

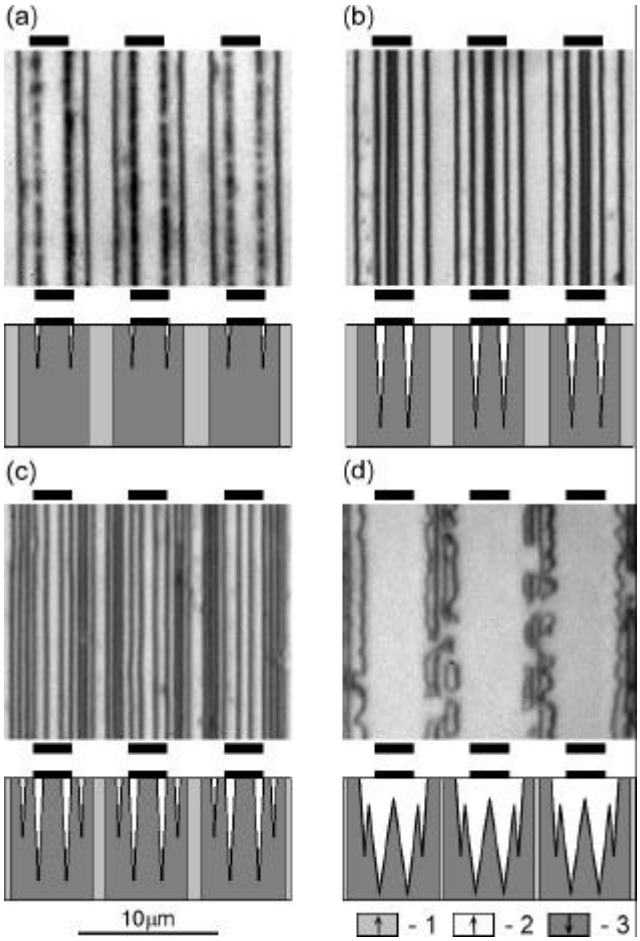


FIGURE 8 Stages of the domain evolution during the domain frequency multiplication process in LN. $\mathbf{Z}^+$ view. Black rectangles show the positions of the electrodes. Domain patterns were revealed by etching and visualized by optical microscope.

NANODOMAIN ENGINEERING IN LITHIUM NIOBATE

Recently we discovered in LN the effect of self-maintained spontaneous decay of stripe domain through arising and growth of oriented nanoscale domain arrays.[9,10,14,15] Domain patterns visualized by SFM demonstrate the highly organized quasi-periodical structure of domain arrays (Fig. 9, 10). Each quasi-regular array is comprised of the nanoscale domains with diameters 30-100 nm and average linear density exceeding 10^4 mm^{-1}.

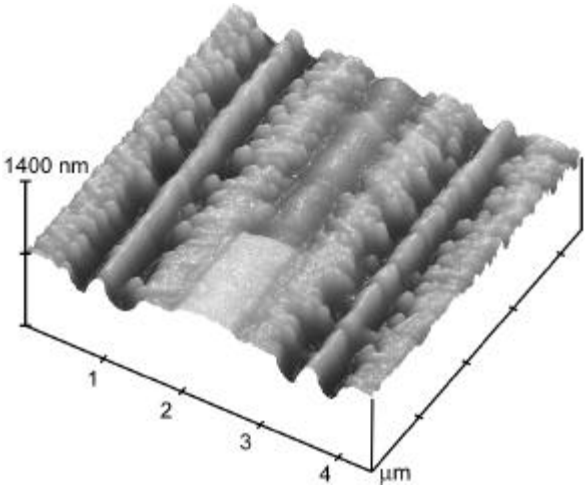


FIGURE 9 SFM image of nanodomain arrays in LN oriented along $\mathbf{Y}^-$ directions (at 60 degrees to the electrode edges) with the fragment of electrode. $\mathbf{Z}^+$ view. Domain patterns were revealed by etching.

Array orientation can be selected between two possible crystallographic directions by parameters of voltage waveform: duration of "high field" stage $\mathbf{Dt_{sp}}$ and the value of jump from "high" to "low" field (field-diminishing amplitude) **DE** (Fig. 7b). For short $\mathbf{Dt_{sp}}$ ~ 5 ms and low **DE** ~ 2 kV/mm the domain arrays are oriented in three **Y** directions (Fig. 9) at 60 degrees to the electrode edges.

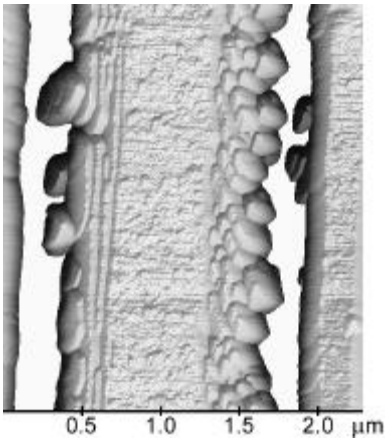


FIGURE 10 SFM image of nanodomain arrays oriented along **X** directions at 30 and 90 degrees to the electrode edges in LN. $\mathbf{Z}^+$ view. Domain patterns were revealed by etching.

For long $\mathbf{Dt_{sp}}$ ~ 5 ms and $\mathbf{DE}$ > 10 kV/mm the domain arrays are strictly oriented in six **X** directions (Fig. 10). The individual nanoscale domains are triangular shaped. The nucleation along the electrode edges and consequent formation of strip domains are observed also.

APPLICATION OF THE BACKSWITCHED POLING FOR 2.6 mm PATTERNING

We have applied the backswitching method for 2.6-μm periodical poling of the LN 0.5-mm-thick substrates. It is seen that the domain patterns on $\mathbf{Z^-}$ prepared in fragments of 3-inch-diameter substrate are practically ideal (Fig. 11a). It must be pointed out that to our knowledge all to date attempts to produce the periodic domain structures with such period in 0.5-mm-thick LN by conventional poling method have not met with success.

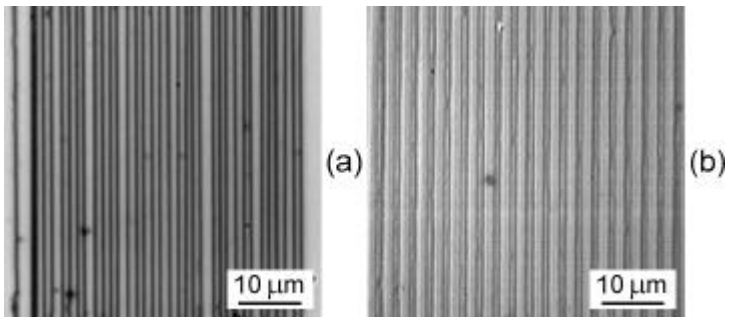


FIGURE 11 Domain patterns for 2.6 μm period (a) $\mathbf{Z^-}$ view in LN and (b) $\mathbf{Z^+}$ view in LT revealed by etching and visualized by optical microscopy.

The continuous-wave (CW) single-pass second harmonic generation (SHG) of blue light in 4-μm-period 0.5-mm-thick 50-mm-length backswitched-poled LN devices was obtained[7,16-18] Using the CW Ti:sapphire pump laser 6.1%/W efficient first-order generation of 61 mW at $\mathbf{l}$ = 460 nm was achieved, indicating an effective nonlinearity about one half of the nominal value. It was shown that the sample phase matches over the full 50 mm length.[17]

Moreover laser-diode-pumped SHG was performed with InGaAs single-stripe diode master oscillator.[18] The oscillator was single frequency and tunable from 874 to 936 nm, with maximum output of 20 mW at 930 nm. The pump power after the amplifier and

two pairs of optical isolators was > 2 W. With 1.5 W of laser-diode power, 60 mW of SHG at 465 nm was produced, given a normalized conversion efficiency of 2.8%/W. An improved efficiency of 3.4%/W was obtained by expansion and spatial filtering of the diode beam before it was focused into the periodically poled LN.[18]

We applied the optimized method for 2.6-μm periodical poling of the LT 0.3-mm-thick substrates. It is seen that the domain patterns prepared in fragments of 2-inch-diameter substrate on $\mathbf{Z}^+$ are practically ideal (Fig. 11b). The detail optical testing of the obtained domain structures will be done later.

The new important information about the domain kinetics in LN and LT during backswitched poling was obtained as a result of aforementioned investigations. The real-time observation of the domain kinetics during poling is a powerful instrument for optimization of the poling technique. The proposed technology based on the controlled backswitching demonstrates the new possibilities in the domain engineering. The backswitched poling enables higher fidelity and shorter period patterning. The achievements in domain frequency multiplication and nanodomain engineering show the way to overcome the micron-period barrier in domain patterning.

ACKNOWLEDGMENTS

The research was made possible in part by Program "Basic Research in Russian Universities" (Grant No.5563), by Grant No.97-0-7.1-236 of the Ministry of Education of the Russian Federation, by Grant No.98-02-17562 of the Russian Foundation of Basic Research, by Award No.REC-005 of the U.S. Civilian Research&Development Foundation for Independent States of the Former Soviet Union (CRDF), and by TRW Foundation, CNOM.

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