Abnormal Domain Growth in Lithium Niobate with Surface Layer Modified by Proton Exchange

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Formation of abnormal domain shapes was studied in single crystalline LiNbO3 with surface layer modified by proton exchange. It has been shown that the isolated domain shape is very sensitive to the electric field: 1) three-rayed stars and concave polygons appear in low field, 2) hexagonal domains form in moderate field, 3) oriented domain rays grow in high field. The transformation from concave to convex polygon and the fast growth of narrow domain rays in front of the growing domain wall were investigated. The obtained abnormal behavior was attributed to non-effective external screening of depolarization field caused by artificial dielectric layer.

Keywords Lithium niobate; domain kinetics; polarization reversal; proton exchange; surface modification; domain shape; one-dimensional domain growth

I. Introduction

The self-organized formation of quasi-regular nanodomain patterns is very important both for understanding the domain structure evolution with high spatial resolution, and for creation of the nanoscale domain structures with controlled geometry, which is still problem challenging domain engineering in ferroelectrics. Recently appeared nanodomain engineering requires qualitatively new methods for production of the stable tailored domain structures with submicron periods which will allow to construct the new types of nonlinear optical devices for coherent light operation [1, 2].

It has been shown that the self-organized domain evolution can be realized under highly non-equilibrium switching conditions which are characterized by completely ineffective screening of depolarization field thus preventing classical sideways domain growth [3]. Polarization reversal in this case is governed by correlated nucleation effect leading to formation of quasi-regular domain structures consisting of isolated nanodomains [4, 5]. One of the possible ways to achieve these conditions can be satisfied by fabrication of the artificial surface dielectric layers using various methods. Recently, it has been shown that congruent lithium niobate (CLN) with PE surface layers demonstrates the original scenario of domain structure evolution during polarization reversal resulting in formation of self-assembled micro- and nanodomain patterns [4, 6].

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The proton exchange (PE) is a very popular and well elaborated technique widely used for integrated and nonlinear optical applications [7]. PE in CLN represents the partial substitution of Li by H in the surface layer prepared by annealing of the sample in acid [8, 9].

The dependence of the shape of growing isolated domains in CLN on the switching conditions has been demonstrated experimentally [10–12]. The variety of the domain shapes predicted for switching in non-equilibrium conditions arisen due to retardation of the depolarization field screening has been found experimentally. In this paper, we present the systematical experimental study of the domain shape evolution in uniform slow increasing field using in situ visualization of the domain evolution in CLN single crystals with PE layers on both polar surfaces.

II. Experiment

Both polar surfaces of the 0.5 mm thick CLN wafer cut perpendicular to polar axis were subjected to PE procedure which was carried out in benzoic acid with 1% lithium benzoate at 300°C. Different exposures resulted in formation of so-called \( \beta_2 \) non-ferroelectric phase in the surface layers with thickness ranged from 0.5 to 3.0 \( \mu \)m [13].

It has been shown experimentally that the modified layers possess a step-like profile of refractive indices [14], thus representing well-defined uniform dielectric surface layers. Such layers are just appropriate for studying the influence of the uniform artificial surface dielectric gap on the domain evolution in CLN.

The experimental setup based on polarizing microscope Carl Zeiss LMA 10 was used for in situ visualization of the domain kinetics during polarization reversal. The switching pulse of the external electric field was applied using uniform liquid electrodes (saturated LiCl aqueous solution) in order to invoke the polarization reversal of the studied CLN samples. The designed waveform of applied electric field (switching pulse) consisted of three stages: 1) rising front with a rate of \( 2 \div 2.2 \text{ kV/(mm·s)} \) from zero to \( 20 \div 21.5 \text{ kV/mm} \) (slightly below the nominal threshold field of CLN), 2) main switching stage with slowly increasing field at a rate of \( 0.5 \div 0.7 \text{ kV/(mm·s)} \) up to \( 22 \div 23 \text{ kV/mm} \), 3) falling front with a rate of \( 2 \div 10 \text{ kV/(mm·s)} \) to zero field. Polarization reversal mostly occurred at the second stage of the switching pulse.

Switching current was measured for integral characterization of the polarization reversal. The switching current data were recorded simultaneously with the series of instantaneous domain patterns.

III. Results and Discussion

Typical shape of the switching pulse waveform and corresponding switching current for polarization reversal in CLN sample with 3-\( \mu \)m-thick PE layers on both polar surfaces are presented in Fig. 1. One can see that the polarization reversal occurred mostly at the second stage of the switching pulse. The switching current data can be divided in two basic inputs: 1) smooth monotonically increasing part demonstrating ohmic-like behavior and 2) noisy part consisting of the number of individual current spikes corresponding to fast rearrangements of the domain structure. The latter input represents the typical behavior for CLN when the polarization reversal is accompanied by jump-like motion of the domain walls strictly oriented along Y crystal directions [15, 16]. Although the switching current started to grow at the external field about 8 kV/mm (Fig. 1), the optically visible domains
Figure 1. The waveform of applied external field and typical switching current data measured during polarization reversal in CLN with PE surface layers. (See Color Plate XII)

appeared in the electroded area only at 20.9 kV/mm, which is just close to the well-known value of the threshold field for CLN (21 kV/mm) [5, 15, 17].

It has been found that in contrast with CLN crystals with classical hexagon domain growth [15, 17], the geometry of nucleated domains as well as dynamics of domain wall motion in PE-modified CLN samples crucially depend on the value of applied electric field (Figs. 2, 3). Formation of the isolated domains with three various shapes was revealed: 1) three-rayed stars and concave polygons appeared in low field range from 20.9 to 21.2 kV/mm (Fig. 2a), 2) hexagonal domains formed in moderate field range from 21.3 to 22.5 kV/mm (Fig. 2b), and 3) oriented domain rays started to grow in high field above 22.6 kV/mm (Fig. 2c).

Polarization reversal in CLN sample with 3 µm thick PE layers started at 20.9 kV/mm by formation and growth of domains representing the three-rayed star shape (Figs. 2a and 3a). It must be pointed out that the rays of the domain stars are oriented strictly along Y directions. The detail analysis of the set of instantaneous domain images allows us to extract the field dependence of the sideways domain wall shift (distance from the star center) (Fig. 4).

It is seen that at low field range the longitude growth of the star rays along Y+ direction prevails with the average velocity about 7.1 ± 0.2 µm/s. In this case the domain walls are strictly oriented along Y directions (Fig. 5a) and the domain shape does not change.

In moderate fields the shape of existing domain stars begins to change. The process of the shape transformation occurs through essential acceleration of the growth of three convex vertices along Y− directions (the average velocity about 4.7 ± 0.2 µm/s) and essential deceleration of the longitude growth of the star rays along Y+ direction with the average velocity about 2.2 ± 0.2 µm/s (Fig. 4). The change of domain wall orientation was caused

Figure 2. Instantaneous domain patterns corresponding to different domain shapes appeared in CLN with PE surface layers in various field ranges: (a) low field (21.2 kV/mm), (b) moderate field (21.7 kV/mm), (c) high field (22.5 kV/mm). In situ visualization by polarizing microscopy.
Figure 3. Transformation of the isolated domain shape in increasing electric field in CLN with PE surface layers. *In situ* visualization by polarizing microscopy.

Figure 4. Time dependence of the domain wall shift in $Y^+$ (diamonds) and $Y^-$ (circles) directions for switching in slowly increasing electric field in CLN with PE surface layers. (See Color Plate XIII)

Figure 5. Scheme of the domain shape transformation for switching in slowly increasing electric field in CLN with PE surface layers.
by growth prevalence of three convex vertices (Fig. 5b). The process of transformation to regular hexagon is obtained at 21.9 kV/mm. In this case the distance from the domain center to all vertices became equal (Figs. 4 and 5c). The different stages of domain shape transformation are demonstrated in Fig. 3.

Finally, the further increasing of the external field above 22.5 kV/mm led to the instability of the domain wall shape and arising of individual strictly Y-oriented narrow domain rays (Fig. 2c). Their growth velocities (longitude growth of the domain ray along $Y^+$ direction) ranged from 20 to 60 $\mu$m/s exceed essentially the sideways wall motion velocity of hexagon domain.

### IV. Explanation

The observed behavior can be easily explained in terms of competition between switching rate and screening efficiency [15, 18]. The former is determined by the value of the acting field, while the latter strongly depends on the thickness of the surface dielectric layers. The thicker the modified PE layers are, the less effective the fast external screening of depolarization field is resulting in suppression of the conventional domain walls sideways motion [5].

The growth of the isolated domain in LN is based on the predetermined nucleation mechanism, which means that the generation of the steps (2D nucleation) along the wall is spatially inhomogeneous [15, 19]. During domain growth the switching field at the wall is decreased due to incomplete screening of depolarization field. For polygon domains the screening retardation leads to formation of the field singularities at the vertices leading to increase of the step generation rate. Thus, in LN crystal with $C_{3v}$ symmetry the predetermined nucleation at three Y non-adjacent polygon vertices must be realized. The generated steps propagated by 1D nucleation along the existing domain wall in three Y directions. The classical hexagon shape is obtained when the step propagation rate exceeds essentially the step generation rate.

For highly non-equilibrium switching conditions, the step propagation can be completely suppressed and step generation at the three vertices being the only switching mechanism leads to growth of domain rays in three $Y^+$ directions (Figs. 2a and 3a). Thus, the growth of three-rayed domain stars is observed in low fields. Increasing of the applied field stimulates the step propagation, thus the velocity of wall motion in $Y^-$ direction increases in moderate field range (Fig. 3).

The various effects of loss of the domain wall shape stability are observed when switching is realized under highly non-equilibrium conditions. The uncompensated depolarization field suppresses the domains broadening by the sideways motion. Nevertheless, the alternative mechanism of the broadening through formation of “fingers” representing rays oriented along Y direction can be observed. The individual fingers have been generated by perturbation at the domain wall (Fig. 2c) [20].

### V. Conclusion

In conclusion, the growth of isolated domains was studied in the single crystals of CLN with surface layers modified by proton exchange. Evolution of the domain structure in uniform electric field was studied in situ using conventional polarizing microscopy. It has been shown that the geometry of nucleated domains as well as dynamics of domain wall motion crucially depend on the value of applied electric field. Three regimes corresponding to growth of: 1) three-rayed domain stars, 2) hexagonal domains, and 3) irregularly shaped
domains with fingers, were distinguished and quantitatively characterized. The observed domain shape transformations were attributed to the changes of the ratio between step generation and step propagation rates. It has been confirmed that non-effective external screening of depolarization field plays the crucial role in formation and growth of domains in ferroelectrics with artificial surface dielectric layers.

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