Shapes of isolated domains and field induced evolution of regular and random 2D domain structures in LiNbO₃ and LiTaO₃

A. Chernykh a, V. Shur b,∗, E. Nikolaeva a, E. Shishkin a, A. Shur a, K. Terabe b, S. Kurimura b, K. Kitamura b, K. Gallo c

a Ferroelectric Laboratory, Ural State University, 51 Lenin Ave., 620083 Ekaterinburg, Russia
b Advanced Material Laboratory, National Institute for Materials Science, 305-0044 Tsukuba, Japan
c Optical Research Center, University of Southampton, Highfield, Mountbatten Bldg., SU17 1BJ Southampton, UK

Abstract

The variety of the shapes of isolated domains, revealed in congruent and stoichiometric LiTaO₃ and LiNbO₃ by chemical etching and visualized by optical and scanning probe microscopy, was obtained by computer simulation. The kinetic nature of the domain shape was clearly demonstrated. The kinetics of domain structure with the dominance of the growth of the steps formed at the domain walls as a result of domain merging was investigated experimentally in slightly distorted artificial regular two-dimensional (2D) hexagonal domain structure and random natural one. The artificial structure has been realized in congruent LiNbO₃ by 2D electrode pattern produced by photolithography. The polarization reversal in congruent LiTaO₃ was investigated as an example of natural domain growth limited by merging. The switching process defined by domain merging was studied by computer simulation. The crucial dependence of the switching kinetics on the nuclei concentration has been revealed.

Keywords: Ferroelectrics; LiNbO₃, LiTaO₃, Domains

1. Introduction

Engineerable periodically poled (PP) nonlinear optical materials are widely developed for usage in coherent light sources based on quasi-phase matching [1–3]. The poling by application of electric field to lithographically defined electrodes has been developed for domain patterning [4,5]. Lithium tantalate LiTaO₃ (LT) and lithium niobate LiNbO₃ (LN) are the most frequently used materials due to their large electro-optical and nonlinear optical coefficients. On the way from the congruent LT (CLT) and LN (CLN) to stoichiometric (Li-rich) ones SLT and SLN, the photorefractive (Li-rich) ones SLT and SLN, the photorefractive decreases and the coercive field drops by an order of magnitude [6]. Moreover, the shape of isolated domains in LT changes from triangular to hexagonal prisms. In order to choose proper conditions for domain patterning, we should know what factors influence the domain shape and how does it change during switching. Besides, shape of the isolated domains is important for developing of 2D PPLN structures.

In this paper, the detailed experimental study of the domain shape evolution during polarization reversal in LT and LN is presented. Computer simulation of isolated domain growth based on the proposed growth mechanism allows to interpret the origin of various experimentally observed domain shapes. Evolution of domain structures was investigated also for multidomain initial state both experimentally and by computer simulation. The drastic acceleration of the switching process caused by domain merging was demonstrated. The critical dependence of the main kinetic parameters on the initial concentration of isolated domains has been revealed.

2. Shapes of isolated domains

2.1. Classical domain shape in CLN, CLT and SLT

All the crystals of LN/LT family are uniaxial with 3 m symmetry in polar phase, thus, possessing the simple domain...
structure with 180° domain walls only. It was shown [7,8] that the shapes of isolated domains, formed after the application of electric field in these crystals, are regular hexagonal and triangular prisms or truncated pyramids. Usually, the investigation is carried out by observation of the domain walls at the polar surfaces. It was experimentally revealed that the shape of cross section of isolated domains by the polar surface in LN and LT are regular polygons. It was stated that in LN, only hexagonal domains with wall orientation along Y crystallographic directions are possible. While in LT, the shape drastically changes from triangular with X oriented walls in CLT to hexagonal with Y oriented walls in SLT.

There are still no publications with systematical investigation of the dependence of the domain shape on the polarization reversal conditions. We undertake the detailed investigation of the domain growth in different experimental conditions and revealed variety of shapes of isolated domains.

2.2. Experimental setup

Commercial single crystalline 0.2-mm-thick CLT and 0.5-mm thick CLN (Crystal Technology, CA), 0.9-mm-thick SLT (grown by double crucible Czochralski technique [9]) were explored. Single domain plates were cut perpendicular to the polar axis (area, 6×5 mm²). All the experiments were performed with liquid electrolyte (LiCl water solution) electrodes in rectangular field pulses at room temperature. For investigation of the role of the dielectric layer, we have carried out special experiments for switching of the samples with one of the polar surfaces coated by thin insulating film. Various insulators have been used, including silicon oil and different types of photoresist.

Static domain patterns revealed by selective chemical etching using HF based etchants were observed by optical microscope in reflected and transmitted modes. The domains have been visualized also without etching by phase-contrast optical microscopy. Moreover, the domain evolution during switching was in situ visualized by polarizing microscope in transmitted mode.

2.3. Exotic domain shapes

It was shown by systematic investigations of the switching behavior that in the samples without artificial dielectric layer, the isolated domains with classical shapes were formed in a wide range of growth rates. In contrast, it was easy to obtain the domains with unusual shapes for extremely fast switching and while using the artificial dielectric layer.

The most interesting domain shapes observed in these experiments are as follows:

1. Triangular domains in CLN (Fig. 1a).
2. Polygons with number of sides between 3 and 6, such as four- and five-sided ones with Y-oriented walls in CLN (Fig. 1b).
3. Polygons containing both X- and Y-oriented walls (Fig. 1c).

2.4. The model experiment

The polarization reversal of artificial hexagonal domain grating was carried out experimentally for further study of the domain growth mechanism. The poling procedure was as follows: a thin layer of photoresist was first deposited onto the Z−surface of a 0.3 mm thick, Z-cut wafer of CLN, and then photolithographically patterned with the hexagonal array. The orientation of the hexagonal structure was carefully aligned to coincide with the crystal’s natural preferred domain wall orientation. Poling was accomplished by applying an electric field via liquid electrodes on the polar surfaces at room temperature [10]. This hexagonal structure has a period of about 18 μm.

Two stages of the domain evolution are observed. First, formation of ideal hexagonal grating, consisting of isolated hexagonal domains, positioned under each hole in the photoresist layer. Second, appearance and subsequent growth of large domains due to merging of the neighboring isolated domains. It has been shown that the large domains appear in the vicinity of the imperfections of the photoresist layer, which provoke the merging of hexagonal domains. The subsequent nonstop fast growth of large domains is achieved through a mechanism very similar to that of step growth [11]. It must be...
stressed that the model large domains represent typical domain shapes discussed above: hexagonal (Fig. 2a), triangular (Fig. 2b) and even polygons with right angles (Fig. 2c).

2.5. Nucleation and growth model

The nucleation and growth model [11,12] was used in order to clarify the domain kinetics in CLT and CLN. This model considers the domain shape evolution as a result of elementary nucleation process. Two types of nucleation events are considered: the arising of new steps (2D nucleation) and step growth (1D nucleation). Nucleation probability in this model is determined by the local value of electric field originating from different sources, including bulk screening field, which is crucial for the compensation of residual depolarization field partially compensated by fast external screening [11,12]. As it was shown [13], the residual depolarization field diminishes the nucleation probability at the domain wall, thus, suppressing the step propagation along the wall. It is clear that within this model, the shape of individual domains is defined by the relation between these two probabilities.

2.6. Computer simulations

Computer simulation was carried out to verify the application of kinetic approach to growth of the isolated domains. The simulated polar surface was represented by regular hexagonal grating, consisting of discrete elements, shaped as equilateral equally oriented triangles, designating elementary nuclei. Filled triangles correspond to the regions with switched polarization. The filling was subjected to the following probabilistic rules:

1. Nucleation rule: any filled polygonal region grows by the appearance of discrete elements at three apices with probability $\alpha_1$. This rule corresponds to the nucleation only at three sites in crystallographically equivalent domain apexes in LN, confirmed by us experimentally.

2. Step growth rule: if two neighboring triangles are filled, the third one is filled with probability $\alpha_2$ to form enlarged circumscribing triangle with the same orientation.

The whole variety of domain shapes, observed experimentally, was obtained by varying the ratio $r = \alpha_1/\alpha_2$. The shape of the computer simulated “domain” is defined by the density of steps along the “domain wall”. Once we assume that the value of $r$ is determined by the ratio between switching rate ($1/t_s$) and bulk screening one ($1/t_{scr}$), most of experimentally observed evolution of domain shapes can be understood.

For complete screening ($r \ll 1$), the equilibrium domain growth of regular hexagons must be observed with walls oriented along Y direction. For incomplete screening ($r \sim 1$), nonequilibrium triangular domains must grow (compare Figs. 1 and 3) [11,12]. The second case is realized for polarization reversal with artificial dielectric layer. Transition of domain shape from triangular to hexagonal, observed experimentally in LT on the way from congruent to stoichiometric, can be interpreted in terms of the above discussed mechanism of domain growth. It is known that at room temperature, the bulk screening time in CLT is about 1 s whereas in SLT it is about 100 ms. For usually realized switching time ranged from 10 to 100 ms, incompletely screened depolarization field slows down the step growth. This case corresponds to $r \sim 1$ in our simulation and leads to the growth of triangular domains. On the other hand, bulk screening rate in SLT is high enough for complete screening ($r \ll 1$) for the same screening rate, thus the equilibrium growth of hexagons is obtained.

Formation of the triangular domains in CLN during very fast switching with artificial dielectric layer can be explained within the same approach also. For CLN, with the screen-
ing time about 50 ms, the incomplete screening, leading to triangle growth, can be observed only for abnormally fast switching. The artificial dielectric layer increases the value of residual depolarization field, wherefore the time, necessary for the sufficient screening of this field also increases.

3. Domain kinetics for random 2D multidomain initial state

The polarization reversal process in CLT was investigated in detail both experimentally and by computer simulation. Switching from the single-domain state in CLT starts with arising of a great number of visible small domains with a density up to 1000 mm$^{-2}$. Such behavior can be attributed to the existence of submicron needle-like invisible domains at the polar surface in the initial state[14]. Thus, contrary to the above discussed situation, the switching starts from multidomain initial state.

Two domain growth mechanisms were revealed experimentally: (1) slow growth of isolated domains (wall motion velocity, $v_s$) and (2) fast wall motion induced by domain merging. Fast wall motion velocity essentially differs in $Y^+$ ($v_f$) and $Y^-$ ($v_{sf}$) directions. Motion in three $Y^+$ directions is a result of visible step generation by merging of moving wall with small isolated domains and growth of this step along the wall (Fig. 4a). A super-mobile “zig-zag” domain walls with high step concentration form after merging of large domains leading to “super-fast” motion $v_{sf}$ in $Y^-$ directions (Fig. 4b). The velocities obtained by image processing for $E=190$ kV/cm were $v_s \sim 1 \mu$m/s, $v_f \sim 20–60 \mu$m/s, $v_{sf} \sim 130 \mu$m/s.

It was observed that the merging of two isolated triangular domains leads to very fast formation of new enlarged circumscribing triangular domain with the same orientation, thus accelerating the switching process. Similar behavior has been clearly demonstrated in the model experiment of polarization reversal on artificial hexagonal grating (Fig. 5a).

3.1. Computer simulations

The computer simulation of the domain kinetics in CLT starts from multidomain state with the given concentration of the randomly distributed elementary triangular domains. The “step growth only” model has been used. Step generation in this model has been induced by merging only. Step growth was governed by the above discussed rules. If the domain concentration is large enough, complete switching (polarization reversal in the whole sample) occurs and the main peculiarities of the domain kinetics are similar to experimentally observed ones (Fig. 5b and c).

Computer simulation reveals that the domain kinetics is strongly dependent on the concentration of the elementary domains (nuclei) in the initial state. Two qualitatively different variants of switching, corresponding to complete and incomplete polarization reversal, are obtained. The transition between these two variants occurs at critical value of the initial domain concentration $\tau_{scr}$. 

Fig. 4. Formation and motion of the “fast” and “super-mobile” domain walls, observed experimentally in CLT. Time interval between images is 40 ms.

Fig. 5. Formation and motion of the “fast” and “super-mobile” domain walls: (a) observed experimentally in CLN with artificial hexagonal domain grating (model experiment) and (b and c) simulated.
4. Conclusion

A detailed investigation of the individual domain shapes in single crystals of LN/LT family was carried out. The observed different isolated domain shapes, including triangles and hexagons, have been explained in Section 2.5. Results of computer simulation coincide with the experimental observations. The special features of domain kinetics for switching from multidomain initial state were revealed in congruent LiNbO₃. The super-fast domain evolution governed by merging of neighboring domains was investigated by computer simulation within the "step growth only" model. The crucial role of domains concentration in initial state was revealed. The achieved understanding is important for further improvement of the quality of the tailored 1D and 2D domain structures and will be very useful for a wide range of domain engineering problems.

Acknowledgements

The research was made possible in part by INTAS (Grant 03-51-6562), RFBR by Grants 04-02-16770 and 04-02-96009-p2004 Ural, by Grant 03-02-39004 of RFBR-NNSF, by Ministry of Science and Education RF by Grant A 04-2-9-240 and by Grant YP’06.01.028 of Program “Basic Research in Russian Universities”, and by Award No. EK-005-X1 of CRDF and Ministry of Education RF.

References