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Creation of periodical domain structure by local polarization reversal in planar waveguide produced by soft proton exchange in $LiNbO_3$

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The paper presents the results of an experimental study of the local polarization reversal and creation of domains by a biased tip of scanning probe microscope (SPM) in lithium niobate single crystals of congruent composition with a surface layer modified by soft proton exchange (SPE). The depth dependence of H+ ions concentration in the SPE-modified layer measured by confocal Raman microscopy demonstrates a sufficient composition gradient. The creation of isolated domains and stripe domain structures has been done by two switching modes: (1) point switching by field application in separated points and (2) line scanning switching by motion of the biased tip being in contact with the sample surface. For point switching for pulse durations less than 10 s, the logarithmic dependence of the domain diameter on the pulse duration was observed. The change of the dependence to a linear one for pulse duration above 10 s has been attributed to the transition from the stochastic step generation at the domain wall to the deterministic one at the domain vertexes. The periodical structure of stripe domains was created in SPE CLN planar waveguides by scanning at elevated temperature. The revealed switching regime suppresses electrostatic interaction of neighboring domains and leads to a significant improvement of the domain structure regularity. The creation of the stable periodical domain structure with submicron periods in SPE CLN planar waveguides was demonstrated.

Keywords: Scanning probe microscopy; piezoelectric force microscopy; periodical poling; composition gradient.

1. Introduction

Ferroelectric crystals are widely used in acoustics,[1] microelectronics[2] and optics.[3] Domain engineering[4,5] has been developing rapidly in recent years — a field of knowledge that studies methods of creation of domain structures of the specified geometry in ferroelectrics for practical use.

One of the most widely used ferroelectric crystals is lithium niobate ($LiNbO_3$). The well-developed technology of Czochralski process makes it possible to obtain big size high-quality congruent lithium niobate (CLN) single crystals. The CLN wafers possess high values of piezoelectric and nonlinear optical coefficients,[6] as well as a high phase-transition temperature which make it possible to create different devices for nonlinear and integrated optics.[7]

Optical waveguides in the CLN crystals are created for applications in telecommunications and integrated optics.[8] One of the most popular methods of creating optical waveguides in CLN is proton exchange.[8] In this case, the change of refraction index in the near-surface layer of a CLN plate is realized by the replacement of lithium ions with protons. Benzoic acid (C_6H_5COOH, BA) is used usually as a source of protons. Addition of lithium benzoate (C_6H_5COOLi, LB) into benzoic acid leads to deceleration of the exchange process and creation of waveguides with preserved ferroelectric properties. The modified process is named soft proton exchange (SPE).[9,10]

The creation of periodic domain structures (PDSs) in CLN single crystals makes it possible to use the effect of the quasi-phasematching[11,12] to implement the second harmonic generation and optical parametric oscillation with record-high efficiency. The most widespread method of creating PDS is the application of an external electric field using the periodical electrodes created by photolithography.[5] Recently, new methods of PDS creation by local polarization reversal have been developed: by scanning of sample's surface with the focused beam of electrons or ions,[13,14] as well as by using biased conductive tip of a scanning probe microscope (SPM).[15] It should be noted that the creation of optical waveguides with a PDS for wavelength conversion has an important practical application and requires deep study of the domain structure kinetics in SPE CLN waveguides.

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In this paper, we present an experimental study of creation of isolated domains by local switching in SPE CLN planar waveguides using a conductive tip of an SPM. We also demonstrate the creation of periodical domain structure with a submicron period in SPE CLN.

2. Experimental

The 0.5-mm-thick CLN plates, cut perpendicular to the polar axis and polished to the optical quality, were used. The area of the studied sample plates was $15 \times 10\,\text{mm}^2$.

The SPE was carried out in benzoic acid with the addition of lithium benzoate. The sample was fixed at the top part of a zirconium container (Fig. 1(a)). The container was annealed in 10^{-3} millibar vacuum at 110°C for 1 h to decrease the influence of adsorbed water. The following manipulations were carried out in the glove box with dry air. The mixture of benzoic acid and 3.0% of lithium benzoate was placed in the lower part of the container (Fig. 1(a)). The container was closed and pumped down to 10^{-3} millibar. After heating up to 300°C the container was turned over (Fig. 1(b)) and the sample was dived into the liquid proton source. The SPE duration ranged from 12 h to 72 h. After completing of the proton exchange the container was turned over and cooled down to the room temperature (Fig. 1(c)). The rate of temperature changes did not exceed 5°C/min.

As a result of the SPE the nonuniform composition $H_xLi_{1-x}NbO_3$ appeared in the near-surface layer. The depth dependence of the H^+ concentration ($C(z)$) near the surface was extracted by confocal Raman microscopy (CRM) using a confocal Raman microscope Alpha 300 AR (WiTec, Germany), equipped with a solid-state laser with a wavelength of 488 nm and a power of up to 27 mW and a diffraction grating with 1800 lines/mm, which provided a spectral resolution of $1.2\,\text{cm}^{-1}$. The spatial resolution for the 100× objective was about 300 nm.

The intensity of the measured Raman spectrum line at $3492\,\text{cm}^{-1}$, corresponding to vibrations of the OH group, is proportional to the concentration of H^+ ions.[16] The maximum intensity of this line was determined by fitting the measurement results with the Lorentz function. This study has shown that SPE process has led to formation of a modified surface layer with inhomogeneous distribution of H^+ ions and the depth up to 4 μm for the 72 h SPE process (Fig. 2).

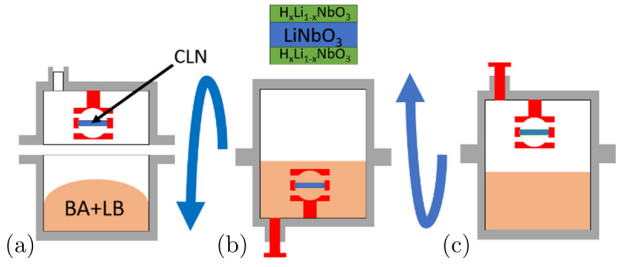


Fig. 1. Stages of the proton exchange: (a) Assembling of a cell, (b) the proton exchange, (c) completion of the proton exchange.

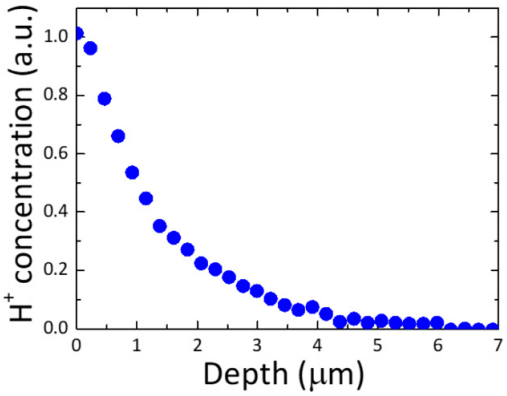


Fig. 2. Depth dependence of relative concentration of H^+ ions in the near-surface layer of SPE CLN sample. The SPE was carried out for 72 h at 300°C with 3.0% fraction of lithium benzoate.

It is known that the composition gradient in the crystal can be considered as a source of the internal bias field,[17] which can lead to formation of PDS[18,19] and significant decrease of the threshold field for domain nucleation and growth.[20]

The domains at the sample surface were imaged by piezoelectric force microscopy (PFM) with a resolution of about 30 nm using Ntegra Aura SPM (NT-MDT, Russia) with an HA_NC/W2C silicon probe (ScanSens, Germany) covered by a conductive carbon-tungsten coating. The piezoelectric response was measured under the action of an alternating modulating voltage between the tip and the lower electrode with an amplitude $U_{\text{mod}} = 3$–5 V and a frequency $f_{\text{mod}} = 20\,\text{kHz}$ below the resonant frequency of the tip-sample system.

The imaging of the domain structure in the bulk was carried out by the CRM based on the measurement of the spatial distribution of the shifts of the $581\,\text{cm}^{-1}$ E(TO_8) and $872\,\text{cm}^{-1}$ $A_1(LO_4)$ lines in the Raman spectrum during 2D scanning.[21] The spatial resolution was about 500 nm.

The creation of isolated domains and domain structures has been done by local polarization reversal using the same SPM. The voltage pulses with amplitude from 50 V to 300 V and duration from 1 ms to 100 s were applied to the tip in an atmosphere with a controlled relative humidity of 25%. The switching was realized at room and elevated temperatures up to 100°C. The heating and cooling rates did not exceed 5°C/min. The voltage pulses were generated using an NI-6251USB data acquisition board (National Instruments, USA) and amplified using a Trek-677B high-voltage amplifier (TREK, USA). Two switching modes were used: (1) point switching by field application in separated points and (2) line scanning switching by motion of the biased tip being in contact with the sample surface. For the point switching the probe was taken away from the sample surface before the pulse was completed. Isolated domain chains with different distances between voltage application points were recorded.

3. Results and Discussion

3.1. *Point switching*

It was found that during point switching in the samples with an SPE duration less than 48 h, the switched domains were not observed in the whole range of voltages and durations due to complete backswitching under the action of residual depolarization field. All further studies were carried out in the samples with the SPE durations of 48 h and 72 h.

The dependencies of the effective diameter of the point domains on the duration and amplitude of the voltage pulse were analyzed (Fig. 3). It was supposed that the domain wall terminates its motion at the point where the local value of the applied field is equal to the threshold field value for domain wall motion. The obtained voltage dependence of the domain diameter was fitted by the following equation[22]:

$$r(U_{\text{tip}}) = \sqrt{a\left(\frac{U_{\text{tip}}}{E_{\text{th}}}\right)^{2/3} - R_{\text{tip}}^2}, \quad (1)$$

where U_{tip} is the applied voltage, R_{tip} is a tip curvature radius, E_{th} is a threshold field for domain wall motion, C is the capacitance of the tip, ε_0 is the vacuum permittivity, ε is the permittivity of the sample, $a = (CR_{\text{tip}}/2\pi\varepsilon_0(1+\varepsilon))^{1/3}$.

The resulting threshold voltage value for the pulse duration of 1 s is about 50 V (Fig. 4).

For circular domains appeared for pulse durations less than 10 s, the logarithmic dependence of the domain radius

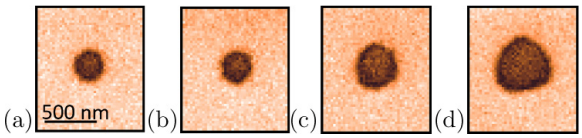


Fig. 3. PFM images of isolated domains obtained by point switching at a voltage of 200 V and different pulse durations: (a) 10 ms, (b) 100 ms, (c) 10 s, (d) 100 s. The SPE was carried out for 72 h at 300°C with 3.0% fraction of lithium benzoate.

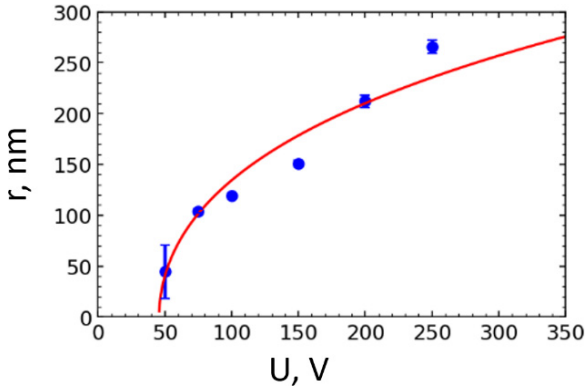


Fig. 4. Dependence of the domain radius on the applied voltage at a pulse duration of 1 s. The SPE was carried out for 72 h at 300°C with 3.0% fraction of lithium benzoate. Experimental points are fitted by Eq. (1).

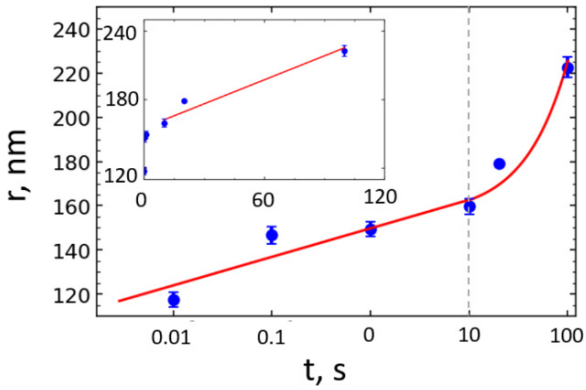


Fig. 5. Dependence of the effective domain radius on the pulse duration at a voltage of 200 V. The proton exchange was carried out for 72 h at 300°C with 3.0% fraction of lithium benzoate.

on the pulse duration was observed, which is typical for local switching in uniaxial ferroelectrics (Fig. 5).[23] With a pulse duration above 10 s, the dependence became linear (Fig. 5, inset). The observed effect can be attributed to the transition from the stochastic step generation at the domain wall to the deterministic one at the domain vertexes.[22,24]

The dependencies of the sizes and shape of point domains in the chain on the period were investigated. It was shown that the circular domain shape was distorted for domain periods less than 500 nm (Fig. 6(a)) and the domain diameter decreased with period decreasing (Fig. 7).

The reduction of size of point domains in a chain was related to: (1) reducing the domain switching field due to the contribution of the depolarizing field created by the previous domain in the chain, (2) partial backswitching under the action of the depolarizing field of the created domain. The first effect manifests itself in a decrease in the size of domains in

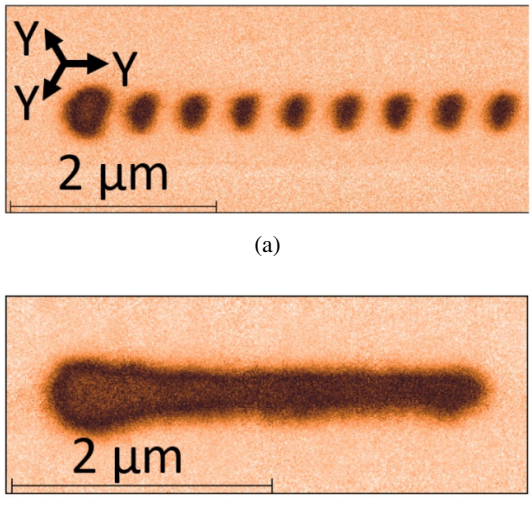


Fig. 6. PFM images of the domains produced by point switching with different periods, nm: (a) 500, (b) 150. The SPE was carried out for 72 h at 300°C with 3.0% fraction of lithium benzoate.

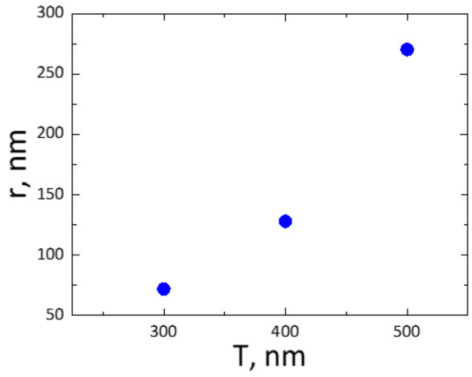


Fig. 7. The dependence of the effective domain radius on the chain period.

the chain compared to the first domain, and the second one — in a distortion of the domain shape.[25]

For periods below 300 nm, the domains merging leads to formation of a stripe domain with a width of about 150 nm, which does not depend on the period (Fig. 6(b)).

3.2. *Periodical poling*

The periodical structure of stripe domains was created in SPE CLN planar waveguides by line scanning switching along the Y crystallographic direction (Fig. 8).

The domain width essentially decreases with distance from the start point of scanning process and stabilizes at the distance above 2 μm (Fig. 8). The minimal domain width equal to 100 nm was obtained for 150 V. The discrete switching leading to formation of the chain of isolated domains was obtained at the lower voltages.

The voltage dependence of the stabilized width of the stripe domains was approximated by Eq. (2) (Fig. 9). In this case, the threshold voltage was 130 V, and the domain width reached 250 nm for voltage 300 V and scanning rate 1 μm/s.

$$w(U_{\text{tip}}) = \sqrt{a\left(\frac{U_{\text{tip}}}{E_{\text{th}}}\right)^{\frac{2}{3}} - R_{\text{tip}}^2}. \tag{2}$$

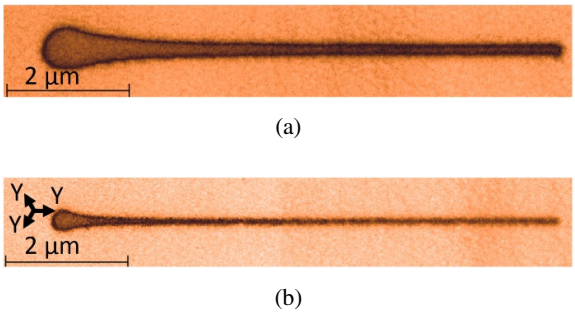


Fig. 8. PFM images of the stripe domains created by line scanning switching at different voltages: (a) 270 V, (b) 150 V. The scanning rate is 1 μm/s. The SPE was carried out for 72 h at 300° C with 3.0% fraction of lithium benzoate.

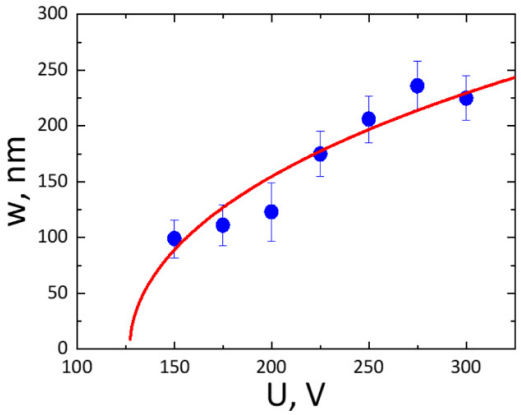


Fig. 9. Voltage dependence of the stabilized width of stripe domains created by line scanning switching.

The created domain structure is stable. It was found that with repeated imaging after 90 min, no noticeable changes in the width of the created domain were observed (Fig. 10).

The PDS was produced by line scanning switching. Each stripe domain was created by a pair of scanning motions along the same line: from left to right and from right to left immediately after it.

It was impossible to obtain PDS with submicron period at room temperature, which is caused by the electrostatic domain interaction, previously revealed for point switching. It is known that the interaction can be reduced for switching at the elevated temperatures, due to acceleration of bulk screening and decrease of the threshold field.[20] It was shown that the line switching at the elevated temperatures leads to significant improvement in the regularity of the domain structure with submicron periods (Fig. 11).

The performed studies made it possible to choose the optimal switching parameters: voltage 200 V, temperature 85° C, using which it was possible to create a stable PDS with a period of 500 nm in samples with a proton exchange duration of 48 h and 72 h (Fig. 11).

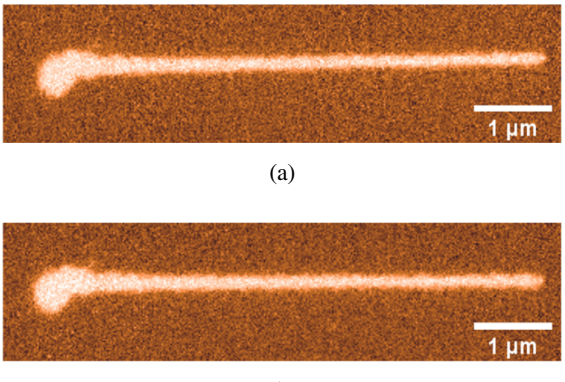
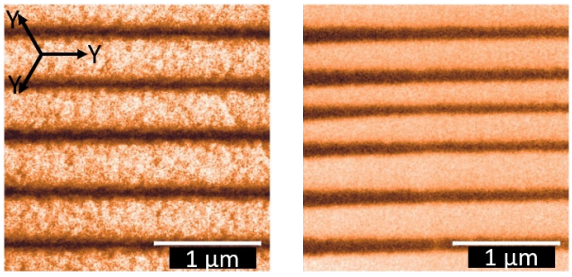


Fig. 10. PFM images of isolated stripe domain: (a) Immediately after switching, (b) 90 min after switching. The SPE was carried out for 72 h at 300° C with 3.0% fraction of lithium benzoate.



(a) (b)

Fig. 11. PFM images of periodic domain structures created by line scanning with a period of 500 nm at 85°C. Domain width is 150 nm. Duration of proton exchange: (a) 48 h, (b) 72 h, at a temperature of 300°C with a fraction of lithium benzoate 3.0%.

CRM imaging was used for measurement of the PDS depth. The achieved depth above 5 μm exceeds sufficiently the depth of the SPE waveguide. This allows us to assume that the created PDS can be used for realization of effective nonlinear optical interactions in SPE waveguides.

The creation of PPLN with SPE waveguides has been published in Refs. 9 and 13. In Ref. 9 the authors created SPE waveguide in the PPLN sample with period ranged from 18 μm to 20 μm. In Ref. 13 the PDS was produced by focused ion beam irradiation of the sample with SPE waveguides and the period of 2 μm was achieved. The submicron periods achieved in this paper open the way for realization of the backward second harmonic generation and mirrorless backward optical parametric oscillation in a waveguide.

4. Conclusion

We have carried out experimental study of the local switching and creation of isolated domains by a biased tip of SPM in lithium niobate single crystals of congruent composition with a surface layer modified by SPE. The depth dependence of H^+ ions in the surface layer modified by SPE was measured by CRM. It has shown that SPE process for the 72 h at 300°C has led to formation of the surface layer with a depth of about 4 μm and sufficient composition gradient.

The creation of isolated domains and stripe domain structures has been done by local polarization reversal using the SPM. Two switching modes were used: (1) point switching by field application in separated points and (2) line scanning switching by motion of the biased tip being in contact with the sample surface.

It was found that in the samples with a proton exchange duration less than 48 h, the switched domains were not observed in the whole range of applied voltages and pulse durations.

It was shown that the dependence of the diameter of the isolated domains on the pulse duration can be described by the model in which the domain wall stops at the point where the local value of the applied field is equal to the threshold field for the wall motion.

It was shown that for point switching for pulse durations less than 10 s, the logarithmic dependence of the domain diameter on the pulse duration was observed, which is typical for local switching in uniaxial ferroelectrics. The linear dependence was obtained for pulse duration > 10 s. The observed effect has been attributed to the transition from the stochastic step generation at the domain wall to the deterministic one at the domain vertexes.

The reduction of size of point domains in a chain was related to: (1) reducing the domain switching field due to the contribution of the depolarizing field created by the previous domain in the chain, (2) partial backswitching under the action of the depolarizing field of the created domain. The first effect manifests in a decrease in the size of domains in the chain compared to the first domain, and the second one — in a distortion of the domain shape.

The periodical structure of stripe domains was created in SPE CLN planar waveguides by scanning along the Y crystallographic direction. The possibility of obtaining stable domain structure with submicron periods was demonstrated by switching at elevated temperature which allowed to suppress electrostatic interaction of neighboring domains and led to a significant improvement in the regularity of the domain structure.

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