Charged domain walls in lithium niobate with inhomogeneous bulk conductivity

V. I. Pryakhina, D. O. Alikin, I. S. Palitsin, S. A. Negashev, V. Ya. Shur

Institute of Natural Sciences, Ural Federal University, 620000 Ekaterinburg, Russia

The surface treatments by annealing in vacuum and by low energy ion irradiation have been used for inhomogeneous modification of the bulk conductivity of lithium niobate single crystals. The obtained inhomogeneous conductivity resulted in significant decreasing of external electric field in the treated volume. The inhomogeneous field distribution allowed us to obtain the polarization reversal in the bulk only, which led to formation of the domains with charged domain walls. The geometry of charged domain walls has been investigated by various methods. The proposed treatment techniques can be used for domain engineering in lithium niobate crystals.

Keywords: ion irradiation, vacuum annealing, domain structure, domain engineering

Short title: Charged domain walls in $LiNbO_3$

Corresponding author: victoria@labfer.usu.ru

1. Introduction

The recent interest to creation of the charged domain walls (CDWs) in ferroelectrics is stimulated by possibility to enhance the piezoelectric properties [1, 2] and to develop the emerging oxide electronics [3, 4] and high-density ferroelectric memory [3, 5]. The tailored stable CDWs with proper geometry and reproducible properties important for application in various ferroelectrics can be considered as a new stage of the domain wall engineering [6, 7]. The CDWs are studied actively in multiferroic and ferroelectric thin film [5, 8], as well as in bulk single crystals of $BaTiO_3$ [4] and $LiNbO_3$ (LN) [9-13]. It is necessary to point out also that LN crystals are widely used due to their outstanding electro-optical, nonlinear-optical, and piezoelectric properties and excellent mechanical stability [14, 15]. Moreover, the LN crystal is the favorite material for micro- and nanodomain engineering [16]. The control of deviations from the stoichiometry and doping allows changing essentially the main parameters characterizing the polarization reversal in the crystals of LN family [14].

It is clear that the CDWs are to arise whenever polarization reversal takes place in the bulk. One of the possible methods to initiate such switching process is application of the spatially inhomogeneous electric field, which overcomes the threshold value in the bulk only. Such situation can be realized by inhomogeneous modification of the bulk conductivity in LN crystal.

It is well known that the vacuum annealing of LN crystals at the temperatures above 600 °C leads to sufficient increase of the bulk conductivity due to increase of oxygen vacancies, which is caused by intensification of out-diffusion of the oxygen from the sample surface [17]. It is important to point out that this is a reversible process as the subsequent annealing in the oxygen atmosphere allows returning to the initial low conductive state. In this letter, we present the results of investigations of CDWs formation in LN crystals with inhomogeneous modification of the bulk conductivity produced by two methods: (1) high

temperature annealing in vacuum and (2) irradiation of the crystal polar surface by glow discharge in plasma of Ar^+ ions.

2. Experimental

The investigated samples represented 0.5-mm-thick plates of congruent LN (CLN) (CrystalTech, US) and 1-mm-thick plates of LN doped by 5 % MgO (MgO:LN) (Yamaju Ceramics, Japan) cut normal to the polar axis. The high temperature annealing in vacuum was realized in temperature range from 650 to 850 °C during 5 to 30 min. The ion irradiation of Z^+ polar surface was done during glow discharge in Ar^+ plasma with energy ranging from 2 to 5 keV (flux 0.5 μA/cm^2, fluence (1-6)·10^{17} cm^{-2}) in vacuum 10^{-4} Torr during 2 to 8 min. The irradiated sample with sides covered by silver paste was located on the metal substrate to remove the charge and to obtain out-diffusion on irradiated polar surface only. The sample temperature induced by ion radiation in used experimental conditions ranged from 500 to 800 °C.

The surface conductivity above 10^{-13} S was measured by two-probe method using picoamperemeter Keithley 6485 (Tektronix, USA). The indium electrodes were deposited on the polar surface at the distance about 10 μm. The surface conductivity was determined by linear approximation of the current-voltage characteristic measured at voltage up to 80 V. The distribution of the conductivity in the crystal bulk was measured using repeated removal from the surface the layers with thickness from 10 to 100 μm by precise polishing machine PM5 (Logitech Ltd., UK).

The spatial distribution of the electric field in the bulk of the sample was measured by optical interferometry [18, 19]. To this end, both polar Z-surfaces were covered by silver electrodes. The X surface of the samples polished at the angle 3-5 degrees was illuminated by the beam of CW He-Ne laser (λ = 633 nm) and the obtained interference patterns have been

recorded by CCD camera (Fig. 1a, b). It is assumed that the local shift of the interferometry fringes under application of the voltage ranging from 100 V to 1.6 kV due to linear electro-optical effect is proportional to $E_z(z, y)$ averaged over the whole X-direction (X size about 2-3 mm). The analysis of the recorded interference patterns allowed us to reveal the field distribution (Fig. 1c).

The polarization reversal was performed by application of the single field pulse using a cell with liquid electrolyte (saturated water solution of LiCl). The used experimental setup represented the modified Merz circuit and consisted of the data acquisition system National Instruments USB-6251 BNC and high voltage amplifier TREK 20/20C. We used three waveforms of the field pulses: (1) asymmetric triangular pulse with constant field increase rate dE/dt = 100 (V/mm·s) and field maximum E_{max} ranging from 10 to 22 kV/mm, (2) rectangular field pulse with duration 50 s and amplitude up to 22 kV/mm, and (3) the two-stage pulse waveform consisting of: (a) fast field increase from zero to E_{ch} ranging from 10 to 20 kV/mm with high ramp during 1-5 s and (b) slow field increase from E_{ch} to $E_{max} = E_{ch} + 1$ kV with slow ramp during 10-30 s. In all cases both switching current and instantaneous domain patterns were recorded.

The static domain structures were revealed by selective chemical etching in hydrofluoric acid (HF) and visualized by optical microscopy (Olympus BX51, Olympus, Japan) with lateral resolution about 500 nm. The HF treatment time less than 40 min was used to avoid the polarization reversal induced by the chemical etching [20]. The better resolution and ability to obtain the domain images at various depths were achieved using confocal Raman microscopy (CRM) (Alpha 300 AR, WiTec, Germany) with lateral and depth resolution 250 and 500 nm, respectively [21-24].

3. Results and discussion

3.1. Spatial distribution of bulk conductivity and electric field

The inhomogeneous increasing of the bulk conductivity was achieved by two alternative methods: (1) annealing in vacuum and (2) low energy ion irradiation. In both cases sufficient increase of the surface conductivity from 10^{-16}-10^{-15} Ω^{-1} in virgin LN up to 10^{-12}-10^{-10} Ω^{-1} was obtained after annealing in vacuum and up to 10^{-8}-10^{-4} Ω^{-1} after irradiation. This effect can be attributed to the lithium segregation [25].

The bulk distribution of the conductivity strongly depends on the treatment method (Fig. 2). Annealing in vacuum leads to the slight inhomogeneity of conductivity in the crystal bulk, which increased with increasing of the treatment duration. Surface irradiation by Ar^+ ions results in two processes: (1) radiation heating due to energy transfer from ions to the lattice, which leads to oxygen out-diffusion from the crystal, and (2) oxygen diffusion stimulated by radiation [26]. Similar effect was observed in LN crystals bombarded by electrons only [27, 28]. The oxygen out-diffusion leads to increase of the bulk conductivity over the oxygen vacancies. Variation of the ions energy, flux, and duration of the irradiation allows controlling the spatial distribution of the bulk conductivity.

The obtained field distribution in the crystals bulk is in good correlation with conductivity measurements (Fig. 3). The degree of field inhomogeneity estimated by the expression $(E_{max} - E_{min})/E_{max}$ is about 3 for annealing and about 30 for irradiation.

3.2. Domain structure

For visualization of the domain structure in the bulk we have used CRM to obtain the domain patterns at the different depths from the polar surfaces and optical microscopy after selective chemical etching of Y-cross-section. The significantly different geometry of CDWs has been revealed near Z^+ and Z^- polar surfaces.

High-resolution domain visualization by piezoresponse force microscopy after treatment by vacuum annealing showed a dendrite structure with average domain width about 350 nm on Z^- surface of CLN (Fig. 4b). The domains with CDWs near the Z^- polar surface represented mostly Y-oriented chains with average period about 2 μm. The oriented chain growth can be attributed to anisotropy of the bulk conductivity in CLN. The CDWs in the vicinity of Z^+ surface demonstrated quasi-periodic structure with an average period about 6 μm (Fig. 4a).

Isolated domains with unusual hexagonal shape were obtained after partial polarization reversal in ion irradiated CLN (Fig. 5). Analysis of CRM images at various depths revealed domains shrinkage near the polar surfaces and their widening in the bulk. The domain structure represented irregular hexagonal domain with CDWs with aperture about 20 μm on Z^- surface and periodical self-assembled CDWs with period about 4-6 μm and aperture about 50 μm in the vicinity of Z^+ surface.

3.3. Correlation between CDWs and field distribution

The domain growth in the crystal bulk terminates in the regions with high conductivity (about 10^{-6} Ω^{-1}) due to complete screening of external field. So, the condition that applied field exceeds the threshold value for the domain nucleation needed for realization of polarization reversal is fulfilled only in the crystal bulk (Fig. 6b, c). It was shown by us earlier that ion irradiation of MgO:LN allowed to modify almost the whole crystal bulk which led to growth of domains with CDWs in thin layer near Z^- surface [29]. This fact was confirmed by field distribution analysis (Fig. 6b).

The proposed technique of the polarization reversal after vacuum heating allowed producing the stable quasi-periodic domain patterns with CDWs with controlled geometrical parameters. This effect can be used efficiently both for investigation of CDWs properties and

for the application in domain engineering [30, 31].

4. Conclusion

It has been shown that surface treatment of LN single crystals by annealing in vacuum and by low energy ion irradiation leads to sufficient increasing of the surface conductivity due to lithium segregation and oxygen out-diffusion. The spatial distribution of the conductivity strongly depends on the treatment parameters. The obtained inhomogeneous conductivity results in significant decreasing of the electric field in the treated volume. The measured field distribution demonstrates good correlation with conductivity measurements. The inhomogeneous field distribution allowed us to realize the domain growth in the crystal bulk in the regions with low conductivity. The obtained polarization reversal in the bulk only leads to formation of the domains with CDWs. The significantly different geometry of domain patterns has been revealed in the vicinity of Z^+ and Z^- polar surfaces. The domain structure is composed of irregular hexagonal domain with CDWs with aperture about 20 μm at Z^- surface. The periodical self-assembled domain structure with CDWs with aperture about 50 μm is formed in the vicinity of Z^+ surface. The polarization reversal after vacuum heating, which has allowed us to produce the stable quasi-periodic domain structures with CDWs with controlled geometrical parameters, can be used for investigation of CDWs properties and for domain engineering in LN crystals.

Acknowledgements

The equipment of the Ural Center for Shared Use “Modern nanotechnology” UrFU was used. The research was made possible in part by the Ministry of Education and Science of the Russian Federation (contract No. 14.594.21.0011). The research was also supported by RFBR and the Government of Sverdlovsk region (grant 13-02-96041-r-Ural-a), by RFBR

(grant 13-02-01391-a) and by UrFU development program for young scientists.

References

1. Wada S, Yako K, Kakemoto H, Tsurumi T, Kiguchi T: Enhanced piezoelectric properties of barium titanate single crystals with different engineered-domain sizes. J. Appl. Phys. 2005; 98: 014109.

2. Sluka T, Tagantsev A, Damjanovic D, Gureev M, Setter N: Enhanced electromechanical response of ferroelectrics due to charged domain walls. Nat. Commun. 2012; 3: 748.

3. Catalan G, Seidel J, Ramesh R, Scott JF: Domain wall nanoelectronics. Rev. Mod. Phys. 2012; 84: 119-156.

4. Sluka T, Tagantsev A, Bednyakov P, Setter N: Free-electron gas at charged domain walls in insulating $BaTiO_3$. Nat Commun. 2013; 4: 1808.

5. Seidel J, Martin LW, He Q, Zhan Q, Chu Y-H, Rother A, Hawkridge ME, Maksymovych PYu, Gajek M, Balke N, Kalinin SV, Gemming S, Wang F, Catalan G, Scott JF, Spaldin NA, Orenstein J, Ramesh R: Conduction at domain walls in oxide multiferroics. Nat. Mater. 2009; 8: 229-234.

6. Fousek J, Cross LE: Engineering multidomain ferroic samples. Ferroelectrics. 2001; 252: 171-180.

7. Wada S: Domain wall engineering in lead-free piezoelectric materials. Ferroelectrics. 2009; 389: 3-9.

8. Maksymovych P, Morozovska AN, Yu P, Eliseev EA, Chu YH, Ramesh R, Baddorf AP, Kalinin SV: Tunable metallic conductance in ferroelectric nanodomains. Nano Lett. 2012; 12: 209-213.

9. Mizuuchi K, Morikawa A, Sugita T, Yamamoto K: Electric-field poling in Mg-doped $LiNbO_3$. J. Appl. Phys. 2004; 96: 6585-6590.

10. Schröder M, Haußmann A, Thiessen A, Soergel E, Woike T, Eng LM: Conducting

domain walls in lithium niobate single crystals. Adv. Funct. Mater. 2012; 22: 3936-3944.

11. Shur VYa, Baturin IS, Akhmatkhanov AR, Chezganov DS, Esin AA: Time-dependent conduction current in lithium niobate crystals with charged domain walls. Appl. Phys. Lett. 2013; 103: 102905.

12. Shur VYa, Rumyantsev EL, Nikolaeva EV, Shishkin EI: Formation and evolution of charged domain walls in congruent lithium niobate. Appl. Phys. Lett. 2000; 77(22): 3636-3638.

13. Eliseev EA, Morozovska AN, Svechnikov GS, Gopalan V, Shur VYa: Static conductivity of charged domain wall in uniaxial ferroelectric-semiconductors. Phys. Rev. B. 2011; 83: 235313.

14. Weis RS, Gaylord TK: Lithium niobate: summary of physical properties and crystal structure. Appl. Phys. A. 1985; 37: 191-203.

15. Volk T, Wöhlecke M: Lithium Niobate: Defects, Photorefraction and Ferroelectric Switching. Berlin, Heidelberg: Springer-Verlag; 2008.

16. Shur VYa: Nano-and micro-domain engineering in normal and relaxor ferroelectrics. In: Ye ZG. Advanced dielectric, piezoelectric and ferroelectric materials – synthesis, characterization and applications. Cambridge: Woodhead; 2008: 622-669.

17. Bordui PF, Jundt DH, Standifer EM, Norwood RG, Sawin RL, Galipeau JD: Chemically reduced lithium niobate single crystals: processing, properties and improved surface acoustic wave device fabrication and performance. J. Appl. Phys. 1999; 85: 3766-3769.

18. Shur VYa, Korovina NV, Gruverman AL: Time dependence and distribution of the internal field in lead germanate. Sov. Phys. Tech. Phys. 1985; 30: 1204-1205.

19. Shur VYa, Gruverman AL, Korovina NV, Orlova MZ, Sherstobitova LV: Spatial distribution of the internal field in lead germanate having different types of domain structure. Phys. Solid State. 1988; 30: 172-174.

20. Shur VYa, Lobov AI, Shur AG, Kurimura S, Nomura Y, Terabe K, Liu XY, Kitamura K, Rearrangement of Ferroelectric Domain Structure Induced by Chemical Etching, APL, 2005, V.87, N.2, p.022905.

21. Shur VYa, Zelenovskiy PS: Micro- and nanodomain imaging in uniaxial ferroelectrics: Joint application of optical, confocal Raman, and piezoelectric force microscopy. J. Appl. Phys. 2014; 116: 066802.

22. Zelenovskiy PS, Fontana MD, Shur VYa, Bourson P, Kuznetsov DK: Raman visualization of micro- and nanoscale domain structures in lithium niobate. Appl. Phys. A – Mater. Sci. & Proc. 2010; 99: 741-744.

23. Shur VYa, Shishkin EI, Nikolaeva EV, Nebogatikov MS, Alikin DO, Zelenovskiy PS, Sarmanova MF, Dolbilov MA: Study of nanoscale domain structure formation using Raman confocal microscopy. Ferroelectrics. 2010; 398: 91-97.

24. Shur VYa, Zelenovskiy PS, Nebogatikov MS, Alikin DO, Sarmanova MF, Ievlev AV, Mingaliev EA, Kuznetsov DK: Investigation of the nanodomain structure formation by piezoelectric force microscopy and Raman confocal microscopy in $LiNbO_3$ and $LiTaO_3$ crystals. J. Appl. Phys. 2011; 110 (5): 052013.

25. Lushkin AYe, Nazarenko VB, Pilipchak KP, Shnyukov VF, Naumovets AG: The impact of annealing and evaporation of $LiNbO_3$ crystals on their surface composition. J. Phys. D: Appl. Phys. 1999; 32: 22-28.

26. Gnaser H: Low-Energy Ion Irradiation of Solid Surfaces. Berlin, Heidelberg: Springer; 1999.

27. Klekamp A, Donnerberg H, Heiland W, Snowdon KJ: Electron bombardment induced desorption of oxygen from $LiNbO_3$. Surf Sci. 1988; 200: L465-L469.

28. Klekamp A, Snowdon KJ, Heiland W: Radiation effects and defects in solids: incorporating plasma science and plasma technology. Radiat. Eff. Defects Solids. 1989; 108:

241-249.

29. Pryakhina VI, Shur VYa, Alikin DO, Negashev SA: Polarization reversal in MgO:$LiNbO_3$ single crystals modified by plasma-source ion irradiation. Ferroelectrics. 2012; 439: 20-32.

30. Shur VYa, Rumyantsev EL, Nikolaeva EV, Shishkin EI, Batchko RG, Miller GD, Fejer MM, Byer RL: Regular ferroelectric domain array in lithium niobate crystals for nonlinear optic applications. Ferroelectrics. 2000; 236: 129-144.

31. Shur VYa: Domain engineering in lithium niobate and lithium tantalate: Domain wall motion. Ferroelectrics. 2006; 340: 3-16.

Figure captions

Fig. 1. (a) Optical scheme of the sample for obtaining the interference pattern. (b) Scheme for interferometric measurements of field distribution in the crystal bulk. (c) The interference patterns on X surface before and after application of external voltage.

Fig. 2. Surface conductivity versus depth (a) for various annealing times for temperature 850 °C and (b) for various irradiation energies.

Fig. 3. Field distribution obtained by optical interferometry: (a) after irradiation for 8 minutes with ion energy 4 keV; (b) after annealing for 15 minutes at 850 °C.

Fig. 4. Domain structure in CLN modified by annealing in vacuum (850 °C, 15 min): (a) side view Y-cross-section, visualization by optical microscopy; (b) Z^- polar surface, visualization by piezoresponse force microscopy.

Fig. 5. CRM images of domain structure in CLN modified by ion irradiation (3 keV, 8 min) at different depths from Z^- polar surface.

Fig. 6. (a) Geometry of the CDWs grown in the crystal bulk; (b), (c) electric field distribution extracted from interferometric measurements.