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Time-dependent conduction current in lithium niobate crystals with charged domain walls

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We present the experimental study of the increase and decrease of the abnormal conduction current appeared during polarization reversal at elevated temperatures (120–250 °C) in stoichiometric and MgO doped lithium niobate single crystals. It is shown that the conduction current is caused by existence of the through charged domain walls. The time dependence of the conduction current has been measured in low electric field immediately after partial switching. The maximal value of the conduction current in crystal with through charged domain walls is of 4–5 orders of magnitude higher than in initial single domain state. The activation energy is 1.1 eV.
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The recent interest in the abnormally high electrical conductivity along the ferroelectric domain walls[1–6] is due to the possible applications of this effect in high-density memory storage and reconfigurable nanoscale electronic circuits.[2] It is important to point out that the strong increase of the bulk conductivity in the vicinity of the charged domain walls (CDW) has been revealed in seventies in the single crystals of semiconductor-ferroelectric SbSI and has been investigated both theoretically[7–10] and experimentally.[11,12] The effect has been attributed to the increase of the free carrier density near CDW.[7–10] Recently, the effect has been studied intensively both in thin film multiferroics and ferroelectrics[1,4] and in the bulk single crystals of $BaTiO_3$ (Ref. 6) and $LiNbO_3$ (LN).[5,13,14] The conduction current (j_c) measurements were made usually by macroscopic electrodes[5,11,12] and by conductive tip of the atomic force microscope.[1,13,15]

The strong increase of the bulk conductivity during the poling process induced by formation of CDW has been revealed in MgO doped LN (MgOLN).[5] Recently, the strong increase of the conductivity along CDW during illumination of MgOLN with photoactive light has been demonstrated using high resolution conduction AFM method.[13]

The single crystals of LN family are widely used for nonlinear optical applications.[16] Moreover, LN crystals can be studied as the model ferroelectrics due to: (1) simple domain structure with only 180° domain walls, (2) high quality wafers available, (3) ability to apply various nondestructive methods of the domain visualization with sub-micron spatial resolution,[17,18] and (4) possibility to increase the bulk screening efficiency by heating and doping.

In this paper we present the experimental study of the abnormal increase and decrease of j_c appeared during polarization reversal in stoichiometric lithium niobate (SLN) and MgOLN crystals at elevated temperatures (120–250 °C). The choice of these representatives of LN family is caused by their lower coercive field and higher bulk conductivity as compared to the conventional congruent LN.

LN crystals of two different compositions were studied: the commercially available Z-cut wafers of SLN single crystals from SAES Getters (Italy) and congruent LN doped with 5 mol. % MgO from Yamaju Ceramics (Japan). The typical sample dimensions were $1 \times 20 \times 20\,\mathrm{mm}^3$. Both polar surfaces of the wafer were polished to optical grade.

The external electric field was applied using evaporated or DC magnetron sputtered 100-nm-thick Cr electrodes. Z-polar surface was covered completely by solid electrode, whereas the array of circular electrodes with diameter 2 mm and period of 2.5 mm was deposited on Z+ polar surface.

The scheme of experimental setup for polarization reversal at elevated temperature and subsequent measurement of j_c in low field is presented in Fig. 1(a). The sample was fixed by pressure contacts in Teflon bath with silicone oil (Fig. 1(b)). The oil temperature was maintained constant in the range from 100 °C to 200 °C using coil connected with solid-state relay and proportional-integral-derivative controller OVEN TPM-151 operating in pulse-width modulation mode with pulse-repetition interval 1 s. The temperature was measured by K-type thermocouple.

The commutation circuit with three relays controlled by NI PCI-6251 multifunctional data acquisition board (designated as "Switch" in Fig. 1(a)) was used for fast reconnection of the sample from polarization switching circuit to j_c measurement circuit. The commutation time was about few milliseconds.

The voltage signals for polarization reversal were generated by NI PCI-6251 board and amplified by high-voltage amplifier TREK 20/20C (TREK, Inc., USA). Precision series resistor (200 Ω) was used for measurement of the current during polarization reversal. The experimental setup allowed us to realize *in situ* visualization of the domain structure evolution using Carl Zeiss LMA10 polarizing microscope with spatial resolution about few microns.

The circuit for conduction current measurement included the picoamperemeter Keithley 6487 (Keithley Instruments, Inc., USA) controlled by computer using IEEE-488.2

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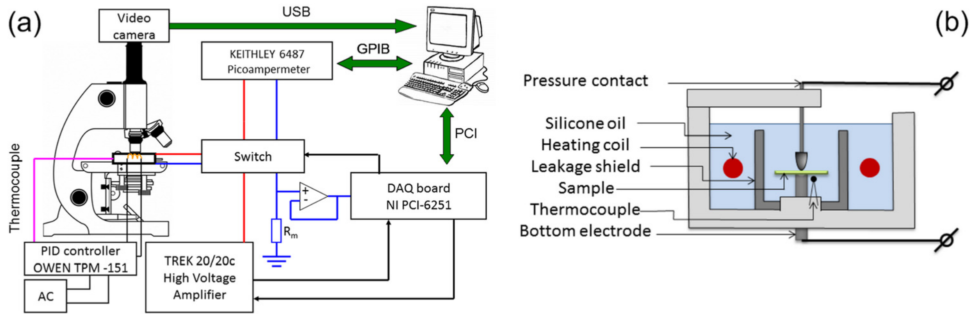

FIG. 1. (a) Experimental setup for polarization reversal and subsequent j_c measurement. (b) Teflon bath with the silicone-oil-immersed sample holder.

(General Purpose Interface Bus, GPIB) interface and external signal generator Agilent 33210A (Agilent technologies, USA). The internal analogous low-pass filter of the picoamperemeter allowed us to reduce the noise level of the measured j_c.

The time dependence of j_c was recorded just after partial polarization reversal. Thus, the experimental procedure can be divided in two subsequent stages (Fig. 2).

At the first stage the unipolar rectangular pulse of high field was applied to the single circular electrode on Z+ surface connected to the high voltage amplifier through the switching circuit. The current and the set of instantaneous domain images were *in situ* recorded during switching. The amplitude and the length of the switching pulse were adjusted to obtain partial polarization reversal of the electrode area. For MgOLN samples the pulse amplitude ranged from 1.5 to 1.8 kV/mm and for SLN from 2 to 3 kV/mm. The same pulse duration about 5 s was used for all experiments.

At the beginning of the second stage the sample was commutated to j_c measurement circuit (Fig. 2). The low voltage rectangular pulses with amplitude 10 V (unipolar pulse or series of bipolar rectangular pulses with period ranged from 1 to 10 s) were applied.

After partial switching and recoding of j_c the electrodes were removed by Chrome Etch N^{o}1 (Technic, France). The selective chemical etching in hydrofluoric acid (HF) for 2–5 min at room temperature was used for revealing of the static domain patterns. The surface reliefs corresponding to the domain pattern at both polar surfaces and Y cross-section were visualized by Olympus BX51 optical microscope using dark field mode (Fig. 3).

The obtained high increase of the current at the end of the switching stage has been attributed to the dominance of

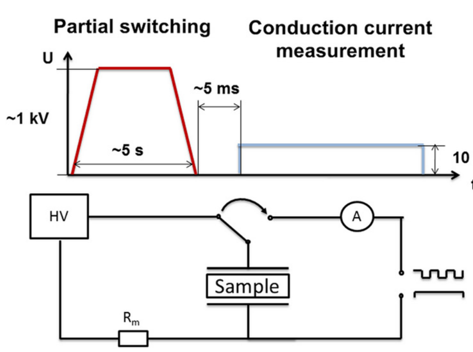

FIG. 2. Waveforms of high-voltage pulse for partial polarization reversal and low-voltage pulse for j_c measurement.

j_c input (Fig. 4). In this case the measured charge was from 10 to 100 times larger than the polarization reversal charge for the switched area covered by electrode. The analysis of the domain images (Z+ and Z-views, and Y cross-section) and their comparison with the current data demonstrated that the high j_c appeared at the moment, when the through CDW was formed (Fig. 3). Thus, the delay time between the start of the switching process and the appearance of the high j_c corresponds to the time, which is necessary for domain growth through the sample.

Increase and subsequent decrease of j_c recorded just after partial polarization reversal in SLN have been revealed (Fig. 5(a)). It has been found that the maximal value of j_c in multidomain state with through charged domain walls is of 4–5 orders of magnitude higher than in initial single domain state. The time dependences of j_c for both processes have been successively fitted by exponential law. The temperature

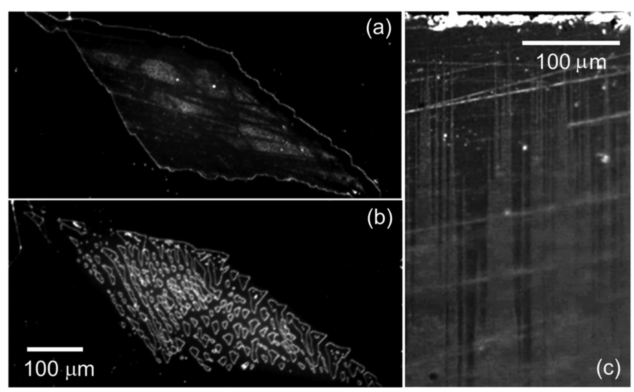

FIG. 3. The domain structure images on polar surfaces (a) Z+, (b) Z−, and (c) on Y-cross section in MgOLN after partial polarization reversal. Optical microscopy in dark field mode after selective chemical etching.

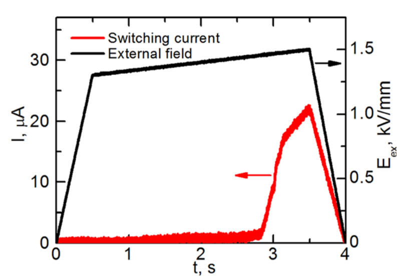

FIG. 4. Waveform of the external field pulse and corresponding switching current in MgOLN. T = 250 °C.

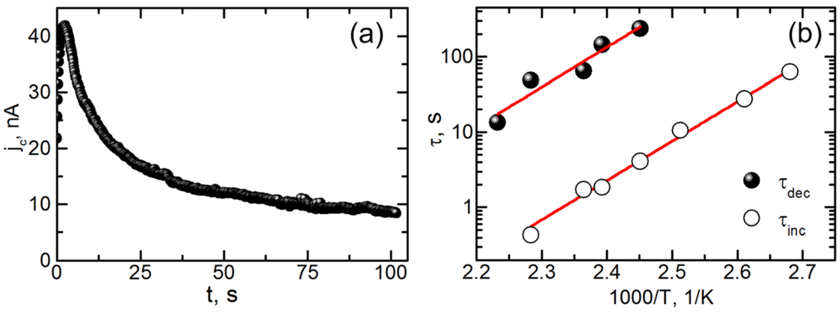

FIG. 5. (a) j_c measured just after partial polarization switching (T = 150 °C). (b) Temperature dependence of j_c time constants for current increase (τ_{inc}) and current decrease (τ_{dec}) in SLN. Experimental points fitted by Arrhenius law.

dependence of the extracted time constants allowed us to reveal the value of activation energy for both processes equal to 1.1 ± 0.1 eV (Fig. 5(b)).

The input of j_c was studied at different stages of the polarization reversal process. j_c maxima were measured in MgOLN during application of the series of 5 s rectangular pulses with period about 100 s needed for sufficient decrease of j_c (Fig. 6). The observed j_c value was negligibly low after the first and the second pulses. The current maximum increased essentially after subsequent four pulses and decreased drastically during further switching (Fig. 6). Negligible j_c was observed after the last pulse.

The obtained increase and decrease of the abnormally high j_c are due to time variation of the conductivity along the through CDW. The bulk screening of the depolarization field produced by the bound charges existing at the CDW leads to the charge accumulation. The formation of the space charge region results in increase of j_c caused by appearance and growth of the "conductive layer" in the bulk. The subsequent decrease of j_c can be attributed to the capture of the free charges at the deep traps.[19,20] The obtained value of the activation energy for both j_c increase and decrease can be attributed to conductivity related to lithium vacancies.[19,20]

The increase and decrease of j_c maximum during switching by pulse series are caused by increase and decrease of the area of the newly appeared through conductive layers. This behavior is qualitatively similar to the switching current obtained during conventional polarization reversal process.

Conduction current was measured during polarization reversal at elevated temperatures (120–250 °C) in stoichiometric and MgO doped lithium niobate single crystals. Comparison of j_c data and domain images revealed on polar surfaces and Y-cross-section allowed us to reveal that the abnormally high j_c appeared at the moment when the through charged domain walls were formed. The time dependence of j_c was measured in low field immediately after partial polarization reversal by high electric field. The exponential increase and subsequent exponential decrease of j_c were revealed. It was shown that the maximal value of j_c in multidomain state with through charged domain walls was of 4–5 orders of magnitude higher than in the initial single domain state. The value of the activation energy 1.1 eV was extracted from the temperature dependence of the time constants for j_c increase and decrease. The input of j_c was studied during switching by pulse series at different stages of the polarization reversal process. The increase and decrease of j_c maximum were caused by increase and decrease of the area of the newly appeared through conductive layers. It was proposed that j_c increase was caused by the charge accumulation in the vicinity of the charged domain wall. The subsequent j_c decrease was attributed to the capture of the free charges at the deep traps.

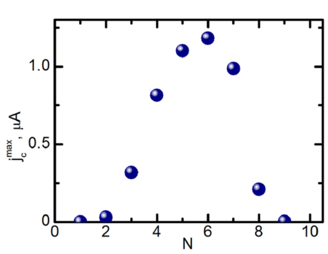

FIG. 6. Dependence of j_c maximum on the number of the switching pulses in MgOLN. T = 150 °C.

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[1]J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y.-H. Chu, A. Rother, M. E. Hawkridge, P. Maksymovych, P. Yu, M. Gajek, N. Balke, S. V. Kalinin, S. Gemming, F. Wang, G. Catalan, J. F. Scott, N. A. Spaldin, J. Orenstein, and R. Ramesh, Nat. Mater. **8**, 229 (2009).
[2]J. Seidel, J. Phys. Chem. Lett. **3**, 2905 (2012).
[3]E. A. Eliseev, A. N. Morozovska, G. S. Svechnikov, V. Gopalan, and V. Ya. Shur, Phys. Rev. B **83**, 235313 (2011).
[4]P. Maksymovych, A. N. Morozovska, P. Yu, E. A. Eliseev, Y.-H. Chu, R. Ramesh, A. P. Baddorf, and S. V. Kalinin, Nano Lett. **12**, 209 (2012).
[5]K. Mizuuchi, A. Morikawa, T. Sugita, and K. Yamamoto, J. Appl. Phys. **96**, 6585 (2004).
[6]T. Sluka, A. K. Tagantsev, P. Bednyakov, and N. Setter, Nat. Commun. **4**, 1808 (2013).
[7]B. M. Vul, G. M. Guro, and I. I. Ivanchik, Ferroelectrics **6**, 29 (1973).
[8]B. V. Selyuk, Ferroelectrics **6**, 37 (1973).
[9]G. M. Guro, I. I. Ivanchik, and N. F. Kovtonyuk, Sov. Phys. Solid State **10**, 100 (1968).
[10]G. M. Guro, I. I. Ivanchik, and N. F. Kovtonyuk, Sov. Phys. Solid State **11**, 1574 (1970).
[11]A. A. Adonin and A. A. Grekov, Sov. Phys. Solid State **16**, 364 (1974).
[12]A. A. Grekov, A. A. Adonin, and N. P. Protsenko, Ferroelectrics **13**, 483 (1976).

[13]M. Schröder, A. Haußmann, A. Thiessen, E. Soergel, T. Woike, and L. M. Eng, Adv. Funct. Mater. **22**, 3936 (2012).
[14]I. S. Baturin, D. S. Chezganov, A. A. Esin, A. R. Akhmatkhanov, and V. Ya. Shur, "Charged domain wall conductivity in lithium niobate and lithium tantalate single crystals at elevated temperatures," *Abstract Book of 11th European Meeting on Ferroelectricity (EMF-2011)* (The Institute for Solid State Chemistry Bordeaux, 2011), pp. 2C–3O.
[15]S. Farokhipoor and B. Noheda, Phys. Rev. Lett. **107**, 127601 (2011).
[16]R. L. Byer, J. Nonlinear Opt. Phys. Mater. **6**, 549 (1997).
[17]P. S. Zelenovskiy, M. D. Fontana, V. Y. Shur, P. Bourson, and D. K. Kuznetsov, Appl. Phys. A **99**, 741 (2010).
[18]E. Soergel, Appl. Phys. B **81**, 729 (2005).
[19]V. M. Fridkin, *Ferroelectric Semiconductors* (Consultants Bureau, New York, 1980).
[20]A. M. Prokhorov and Y. S. Kuz'minov, *Physics and Chemistry of Crystalline Lithium Niobate* (Hilger, New York, 1990).