Conference Paper

Dielectric Permittivity Enhancement by Charged Domain Walls Formation in Stoichiometric Lithium Niobate

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Abstract

We present an experimental study of contribution of charged domain walls into dielectric permittivity of lithium niobate. It has been shown that formation of dense structure with spike-like domains leads to order of magnitude increase of permittivity, which gradually decreases with time. The decrease rate accelerates under DC bias. Dielectric permittivity decreases linearly with a logarithm of frequency. The obtained results were explained considering vibration of the steps on the charged domain walls.

Keywords: dielectric relaxation, ferroelectrics, domain structure

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1. Introduction

In the recent years, a growing attention is paid to the modification of the property of the ferroic materials by the domain walls engineering. These intrinsic interfaces are considered as an alternative to the conventional chemical doping to achieve structure tailorability at the nanoscale. It is possible to create, displace, and erase the charged domain walls (CDW) by the application of the external electric field, which implies the possibility to build real-time reconfigurable devices. Currently, the influence of CDW on the conductivity [1], dielectric permittivity [2], and piezoelectric coefficient [3] of ferroelectrics has been revealed. It has been shown that the bulk properties can be effectively modified by formation of the high density of the domain walls [3].

The contribution of domain walls to dielectric permittivity of ferroelectrics was intensively studied for the last twenty years. The vibration of the domain walls in the AC electric field leads to additional polarization response. The model considered the pinning of the DWs on the randomly distributed defects (initially developed for the magnetic materials [4]) was successively applied to describe the nonlinear dielectric response in lead zirconate-titanate (PZT) thin films [5, 6]. Similar effect was proposed for explanation of frequency dispersion of nonlinear dielectric response in relaxor ferroelectrics, where vibration of the interface boundary analogous to DW vibration was considered [7]. Two main results of the mentioned papers [5-7] should be outlined: the Rayleigh law field dependence and the inversed logarithm frequency dependence

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of the dielectric permittivity. The discrimination between the vibrational and stationary inputs of CDW to dielectric permittivity is still under discussion [2].

In this work, we present an experimental study of the time evolution of dielectric response of the CDWs measured immediately after polarization reversal in lithium niobate $LiNbO_3$ (LN). It was shown earlier, that CDWs changed drastically the LN dielectric behavior. The CDWs response was considered as a result of the reversible motion of the domain wall steps [8, 9]. Recently, the significant enhancement of the CDWs contribution into dielectric permittivity under superbandgap UV illumination has been demonstrated [10].

The free carriers have to screen the bound charges at the CDW in order to compensate the depolarization field. Thus, two charge subsystems formed across the CDW: bound charges and the screening charges of opposite sign. The external field can displace these systems, leading to dielectric response.

Just after polarization reversal the next important processes take place: screening of the residual depolarization field by the free charges, localization of this charge on the deep traps, and domain wall pinning on the defects. All these processes have a significant influence on the mobility of the charge subsystems; thus, it is very important to investigate the time evolution of the CDW dielectric response.

2. Methods

The near stoichiometric lithium niobate (SLN) single crystals were used as a model material for studying of the dielectric permittivity enhancement by CDW due to lower coercive fields as compared with conventional congruent LN crystals.

The samples represented 0.5-mm-thick rectangular plates with a size 10x15 mm^2 cut using automated dicing saw Disco DAD 3220 (Disco, Japan) from commercial available Z-cut wafers (SAES Getters, Italy). Both polar sample surfaces were polished to the optical grade and covered by chromium electrodes deposited by magnetron sputtering. The array of 2-mm-diameter circular electrodes was formed on the Z+ surface using shadow mask, whereas Z- surface was completely covered by solid electrode.

The sample was immersed into circulating bath thermostat for precise temperature control. Pure silicone oil was used as a heat transfer liquid to prevent surface breakdown during polarization reversal and suppress parasitic leakage during impedance measurements. The electrical connections to the sample were secured by the pressure contact. The sample holder was completely covered by the grounded metal shield to prevent electrostatic interference.

The commutation system allowed us to connect the sample to the high-voltage amplifier TREK 20/20C (TREK Inc., USA) or to the impedance bridge QuadTech RLC 7600 (IET Labs Inc. USA) with a time lag below 5 ms.

At the beginning of the experimental procedure, the switching pulse was applied to the sample through the high-voltage amplifier with simultaneous measurement of the switching current as a voltage drop on the 200 kΩ series resistor. The sample was connected to impedance bridge immediately after polarization reversal. The excitation

AC voltage with an amplitude U_{AC} = 1 V and the frequency F swept continuously from 100 Hz to 100 kHz was superimposed with DC bias and applied to the sample in order to measure the impedance |Z| and the phase angle θ Open\short compensation was performed to exclude cable and test fixture influence.

In view of the fact that an overall response of the sample was composed of the bulk and the domain walls inputs, we extracted the CDW contribution assuming the simple parallel connection of these two subsystems. The bulk response was measured before poling in the single domain state: ε_{33} = 29, loss tangent below 0.001.

Dielectric constant (ε_{dw}′) and dielectric loss (ε_{dw}″) components of the complex dielectric permittivity were calculated from the impedance of the domain walls data according to the following formula:

$$\varepsilon_{dw} = \varepsilon'_{dw} + i\varepsilon_{dw}" = \frac{\sin\theta_{dw}}{\omega C|Z|_{dw}} - i\frac{\cos\theta_{dw}}{\omega C|Z|_{dw}} \qquad (1)$$

where $\omega = 2\pi$F and C is capacitance of the measuring circuit without ferroelectric crystal inside (consisting from two evaporated electrodes only).

The obtained domain structure was visualized by optical microscopy after selective HF etching.

3. Results

We used the conventional electrical poling technique at elevated temperature (145°C) to create a domain structure with a high CDW concentration. It was shown earlier that during partial polarization reversal at these conditions the quasi-periodic assembly of the needle-like domains grew from Z+ to Z- polar surface, thus forming «head-to-head» CDWs [11]. The switching current shown in the Figure 1 has a significant leakage contribution – the total charge exceeds by the order of magnitude the full polarization reversal charge for the given electrode area (Fig. 1a). The linear current-voltage characteristic was measured at the trailing edge of the switching pulse (Fig. 1b). This leakage contribution was previously attributed to the conductivity through the CDWs that interconnected the polar surfaces [12, 13]. *Ex situ* visualization of the domain structure on the Y section allowed us to measure the average CDW inclination angle as 0.7° (Fig. 1c).

Immediately after partial polarization reversal the CDW contribution into dielectric permittivity is rather high, especially at low frequencies (Fig. 2). The ε_{dw}′ reaches the value 300 at 100 Hz that is an order of magnitude higher than the bulk value. This extremely high enhancement can be explained while taking into account the CDWs displacement. Although magnitude of the electric field used during impedance measurement is three orders of magnitude lower than macroscopic threshold field, the small displacement of the individual steps on the charged wall is still feasible, due to small activation field for the kink motion at the charged domain wall.

It was shown that the ε_{dw}′ decreased significantly with time at rate depending on DC bias value (Fig. 3). Whereas there is slight variation of the initial value of CDWs response (the domain structures is partially irreproducible), each curve was normalized

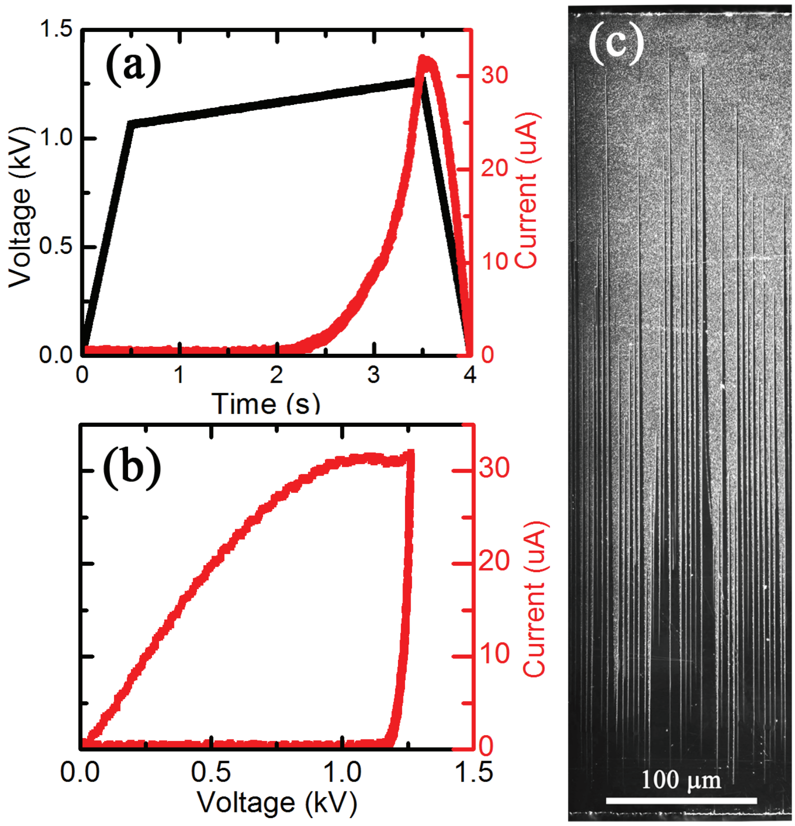

Figure 1: (a) Time dependence of the switching current. (b) The same data in the current-voltage axes. (c) Visualized domain structure on Y-section (optical microscopy after selective HF etching). SLN, 145°C.

by maximum value. It is clearly seen, that although decrease of ε_{dw}' was observed even without DC bias, the effect is more pronounced under DC bias. The similar behavior has been recently reported in the PZT thin films [14].

In the framework of the proposed model, the decrease of the response can be explained by CDW structure stabilization. Screening of the bound charges by the free carriers, subsequent localization of these carriers on the deep traps, domain walls pinning by the defects, and redistribution of the individual steps along the CDW lead to increase of the activation field for the nucleation. Thus, the effective displacement of the wall in given AC electric field decreases. External DC bias accelerates the transition of CDW to the energetically favorable position, thus increasing the ε_{dw}' decrease rate.

It is important to note that the CDW dielectric response decreases linearly with a logarithm of frequency (Fig. 4). This dependence is in a good agreement with a proposed model [4, 6]. Decreasing of the switched polarization with increasing of the switching pulse frequency is a well-known effect during the hysteresis loop measurement, attributed to limited value of the DW velocity. The observed decrease of dielectric response can be explained by applying of this statement to the micro-scale vibrations of the steps on the CDW.

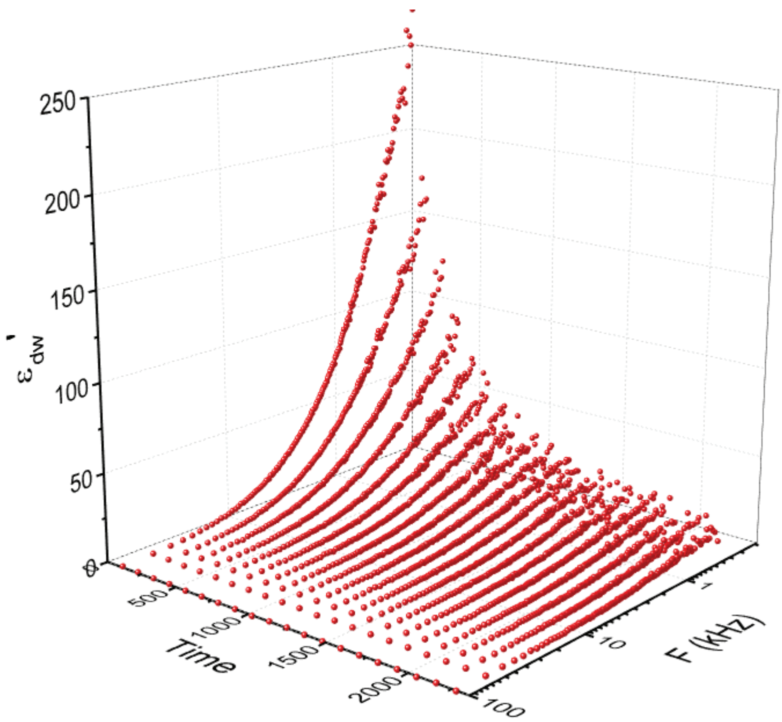

Figure 2: Time dependence of the CDW contribution into dielectric permittivity at different frequencies. SLN, 145°C, DC bias 200V/mm.

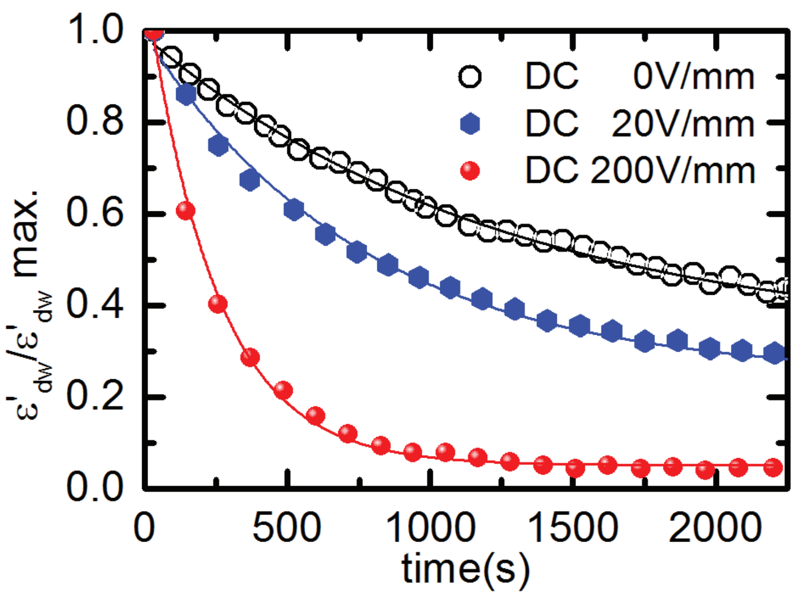

Figure 3: Time dependences of the CDW contribution into dielectric permittivity for various DC bias. Each curve was normalized by the maximum value. SLN, 145°C, f = 500 Hz.

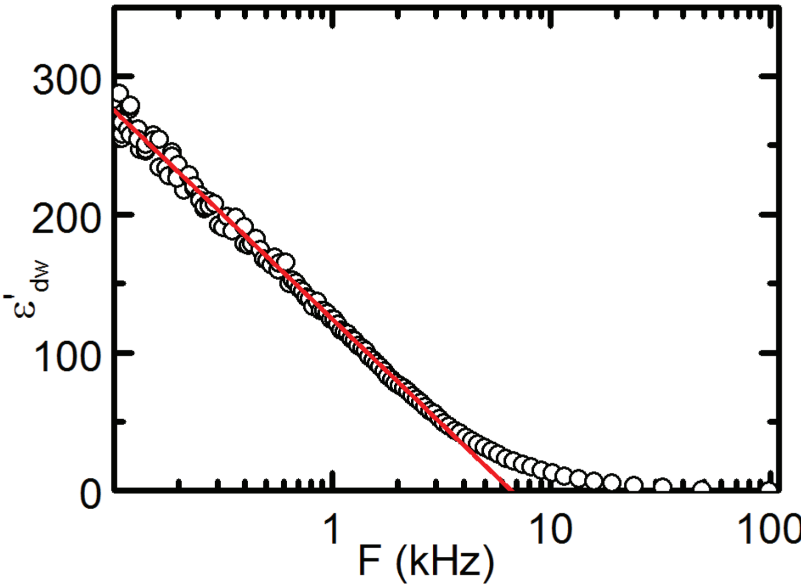

Figure 4: Frequency dispersion of the CDW input to dielectric permittivity. SLN, 145°C, DC bias 0 V/mm.

4. Conclusion

The dielectric permittivity enhancement by charged domain walls formation has been studied in stoichiometric lithium niobate. It has been shown that the vibration of individual steps on the charged domain walls leads to strong dielectric response immediately after polarization reversal. Stabilization of the domain structure leads to decrease of this response during time. Acceleration of the decrease rate under DC bias can be attributed to intensification of the stabilization process. The obtained inverse logarithm frequency dependence is in a good agreement with proposed model based on domain wall pinning on randomly distributed defects.

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