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Polarization Reversal by Tip of Scanning Probe Microscope in SBN

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Abstract

We present the results of experimental study of the influence of initial domain state on the shape and size of isolated domains created by the conductive tip of scanning probe microscope during local polarization reversal in relaxor ferroelectric strontium barium niobate doped with nickel and cerium. The domain radius was found to increase with increasing voltage and time and depend on the initial polarization direction. Circular domains of the opposite sign were found to appear due to polarization backswitching. The obtained results can be used for practical applications of domain and domain wall engineering in ferroelectrics.

Keywords: relaxor ferroelectrics, strontium barium niobate, polarization reversal, scanning probe microscopy, domain shape

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1. Introduction

Relaxor ferroelectrics (relaxors) possess unique properties interesting from both fundamental science and practical application points of view. Strontium barium niobate $Sr_xBa_{x-1}Nb_2O_6$ (SBN) single crystals possessing high electrooptic, nonlinear-optic, piezoelectric, and pyroelectric properties [1] are known as a model relaxors for both experimental and theoretical studies. The improvement of the above mentioned properties can be achieved by the creation of the controlled domain structures. The understanding of the domain shape and domain evolution is thus important for the improvement of functionality of tailored domain patterns.

Local polarization reversal in ferroelectrics by application of dc voltage using conductive tip of scanning probe microscope (SPM) is one of the most promising methods for the creation of microdomain arrays in ferroelectrics. This technique consists of application the local electric field and visualization of the created domains with nanometer spatial resolution. A large amount of papers are devoted to the investigation of the local polarization reversal in various ferroelectrics, such as lithium niobate [2-4], but domain kinetics in relaxors is still insufficiently studied.

It is well known that the relaxor characteristics are strongly dependent on the prehistory (in non-ergodic state), and the sequence of the application of electric field and temperature change are important, as well as the initial domain state. However, the

known studies of the local reversal polarization in SBN crystals [5-7] have not taken into account the influence of the initial domain structure.

In this work, we present the study of the influence of the initial domain state on the shape and sizes of the isolated domain during local polarization reversal in SBN crystals doped by Ce and Ni.

2. Methods

The studied relaxor single crystals $Sr_{0.61}Ba_{0.39}Nb_2O_6$ doped with 0.004% CeO_2 (SBN61:Ce) and 0.01% Ni_2O_3 (SBN61:Ni) were grown by modified Stepanov technique [8]. The 0.5 and 1.0-mm-thick plates were cut perpendicular to the polar axis and polished. Freezing temperature T_f (temperature of transition from ferroelectric to relaxor phase) was between 66 and 79°C and Burns temperature T_B (temperature of transition from relaxor to paraelectric phase) was about 81-85°C in these crystals. The polarization reversal was performed at room temperature in ferroelectric phase (i.e., at $T<T_f$).

Three types of the initial domain structures have been used for the investigation: (1) "as-grown", (2) "nanodomain", and (3) "single domain" states. As-grown structure appeared after sample polishing without any application of an electric field. Nanodomain structure was created by thermal depolarization using zero-field cooling from 200°C ($T > T_B$). Single domain state was created by slow in-field heating under constant external field ranged from 400 V/mm (for SBN61:Ce and SBN61:Ni) to 500 V/mm (for SBN61:Ni only). Samples were slowly heated, annealed at 200°C during 2 hours, slowly cooled, and left at room temperature for 10 h under dc field. The heating and cooling rates were about 5 K/min.

For all initial domain structures the polarization reversal has been done by application of *dc* voltage pulses [10] with amplitudes ranged from 1 to 150 V and duration – from 0.1 to 1024 s via conductive SPM tip. Resulting static domain structure was visualized by piezoresponse force microscopy (PFM) using scanning probe microscope Asylum MFP-3D (Oxford Instruments, UK) with silicon NSC-18 tips (MikroMash, Estonia). The tips had platinum conductive coating and typical radius of curvature of about 25 nm.

It is known that the polar component of the field produced by the tip is essentially nonuniform (Fig. 1). The field distribution in ZX plane has been calculated by the following equation [11]:

$$E_{ZX} = \frac{C_t U_{sw}}{2\pi\varepsilon_0\gamma\left(\sqrt{\varepsilon_c\varepsilon_a}+1\right)} \frac{z/\gamma - z_0}{\left[(x-x_0)^2 + (y-y_0)^2 + (z/\gamma - z_0)^2\right]^{3/2}}, \quad (1)$$

where C_t is the capacitance of the probe (2), ϵ_a and ϵ_c are the dielectric constants along the polar and nonpolar axes, respectively, and U_{sw} is the switching voltage, $\gamma = \sqrt{\varepsilon_c/\varepsilon_a}$.

$$C_t = 4\pi\varepsilon_0 r_{tip} \frac{1+\sqrt{\varepsilon_c\varepsilon_a}}{1-\sqrt{\varepsilon_c\varepsilon_a}} log \frac{2}{1+\sqrt{\varepsilon_c\varepsilon_a}}, \quad (2)$$

where r_{tip} is the radius of tip curvature.

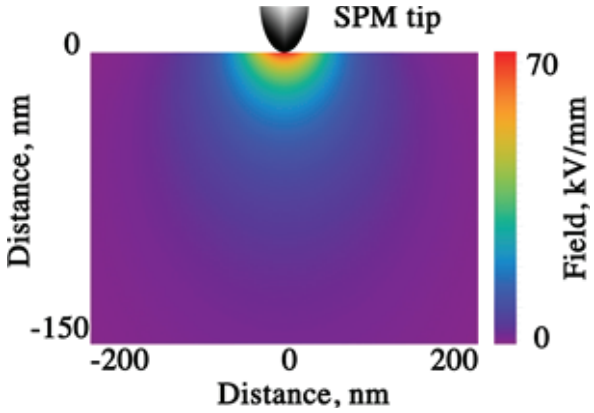

Figure 1: The calculated ZX distribution of the field, produced by SPM tip in contact with the polar surface of SBN61 (ϵ_c = 900, ϵ_a = 450, r_{tip} = 25 nm, U_{sw} = 100 V).

Two ways of pulse application for polarization reversal were performed: (1) "with withdrawal", when the voltage pulse ends simultaneously with tip withdrawal from the sample surface, and (2) "without withdrawal", when the pulse ends in about 0.1 s before the tip withdrawal.

It should be mentioned that the sizes of the formed domains depend on the relative humidity of the environment. It could be explained by the presence of water layer at the surface and appearance of the water meniscus in the vicinity of the tip [12, 13]. Our experiments were performed at the relative humidity 35±5 %.

One more parameter, which influences the domain size, is a distance between isolated domains in the created array [14]. We considered the case, when the field produced by the first domain did not affect the polarization reversal of the neighboring one. This distance was measured experimentally by adjusting the distance between subsequent positions of the tip, for which all domains in array produced with the same switching parameters have approximately the same size. The 10-μm-distance was chosen for low voltage pulses (10-50 V) and the 15-μm-distance was chosen for high voltage amplitudes (60-150 V). Afterwards, the stability of the produced domain structures was studied by serial PFM scanning of the array.

3. Results

In this work, all three initial domain states were investigated. It was shown that the as-grown domain structure represented a fractal-type 3D maze (Fig. 2a) with fractal dimension D = 1.7 for SBN61:Ce and D = 1.8 for SBN61:Ni. Thus obtained D > 1.5 indicates that formation of as-grown domain structure is a correlated process. The Fourier analysis of the structure revealed that it is quasiperiodic with the averaged period 200-300 nm.

Thermal depolarization leads to the formation of nanodomain structure, which pattern is changed slowly and after several days becomes very similar to the as-grown one. To create the artificial domains we applied dc electric field immediately after thermal depolarization.

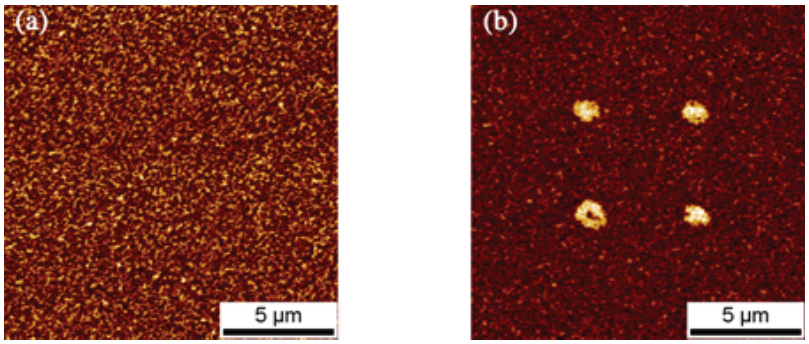

Figure 2: (a) As-grown domain structure; (b) domains formed by voltage pulse with tip withdrawal in as-grown structure. SBN61:Ni. U_{sw} = 50 V, t = 1 s.

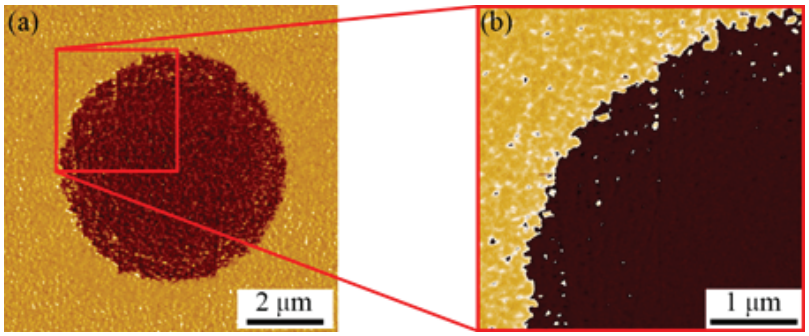

Figure 3: Typical circular shape of the domain formed by voltage pulse with tip withdrawal in SBN61 in nanodomain state. U_{sw} = 100 V, t = 1 s.

The "single domain" state obtained after referred procedure was typically instable. The most stable state has been achieved after exposure to the electric field of 500 V/mm during 12-16 hrs. Switching of this state was investigated by PFM.

3.1. As-Grown Domain State

Application of rectangular pulses with U_{sw} = 50 V and t = 1 s with tip withdrawal led to formation of irregular shape domains (Fig. 2b). It should be noted that the first domain (lower left) is larger than its neighbors due to interaction between domains produced at the distance 5 μm from each other. It is known that the depolarization field produced by existing domain decreases the applied field value in its vicinity.

3.2. Nanodomain State

The formation of circular domains was attempted for nanodomain state (Fig. 3a). We hypothesized that the domain wall shape (Fig. 3b) was determined by the presence of nanodomains, which merged with the moving wall driven by applied field. We stress that random position of the steps at the domain wall generated by merging (Fig. 3b) is equivalent to stochastic nucleation [15, 16].

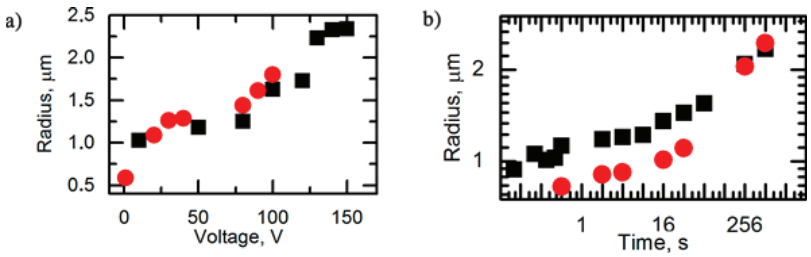

Figure 4: The dependences of the averaged domain radius on (a) voltage and (b) pulse duration for nanodomain state: SBN61:Ce (red circles); SBN61:Ni (black squares). (a) t_{sw} = 1 s, (b) U_{sw} = 100 V.

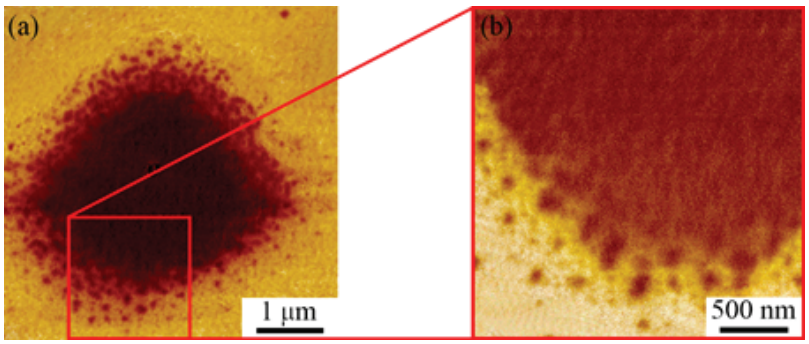

Figure 5: Typical domain shape obtained in SBN61:Ce in single domain state by dc voltage pulse with the tip withdrawal.

It is shown that the nanodomain state is very sensitive to the application of a weak field during domain visualization by piezoresponse force microscopy. Switching of nanodomains at the surface was obtained even for driving amplitude as small as 300 mV. The main feature of nanodomain state is related to the ability to produce domains by application of the electric field of both polarities.

The time (Fig. 4a) and voltage (Fig. 4b) dependences of the domain radius have been obtained for nanodomain state in SBN61:Ni and SBN61:Ce. Similar dependences have been obtained for both samples.

3.3. Single Domain State

The irregular domain shape was obtained also for single domain state (Fig. 5a). Nanodomains have been observed in a wide layer in front of the moving domain wall ("broad domain boundary", BDB [16]). The BDB in single domain state is essentially wider (about one micron) (Fig. 5b) as compared to the case of nanodomain state (about 200 nm) (Fig. 3b).

Fast relaxation of the artificially created domain structure was observed in both samples in single domain state. Domain structure formed by U_{sw} = 100 V and t_{sw} = 1 s disappeared with relaxation time of about 12 min (Fig. 6).

Typical shape of the domain formed by application of dc voltage U_{sw} = 50 V and t_{sw} = 1 s without tip withdrawal in SBN61:Ce is shown in Fig. 7a. A backswitched domain was observed in the center of the formed domain. The backswitching occurred due to injection of charge carriers from the tip and ineffective screening of the initial field. The

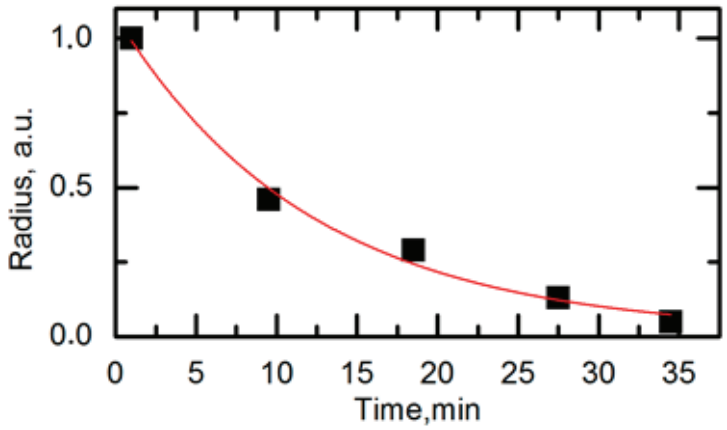

Figure 6: Relaxation of the radius of domain formed in SBN61:Ni in single domain state by dc voltage pulse with tip withdrawal. U_{sw} = 100 V, t_{sw} = 1 s. Experimental points fitted by exponential decay.

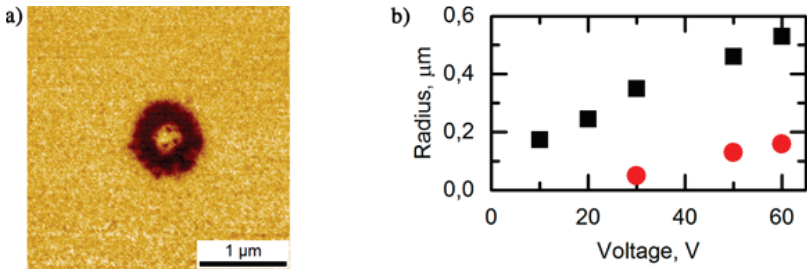

Figure 7: Backswitching of the domain formed by application dc voltage without tip withdrawal in SBN61:Ce in single domain state: (a) domain shape for U_{sw} = 50 V and t_{sw} = 1 s; (b) voltage dependence of the averaged domain radius for U_{sw} = 100 V and t_{sw} = 32 s (black squares) and averaged radius of backswitched domain (red circles).

size of backswitched domain increased with increasing of the applied voltage (Fig. 7b). Detailed explanation of the backswitching effect observed by SPM in ferroelectrics can be found elsewhere [17]. In order to understand the detailed mechanism of polarization backswitching in relaxors, further measurements are needed.

4. Conclusions

The influence of the initial domain state on the parameters of isolated domains created by local polarization reversal by the conductive tip of scanning probe microscope was studied in SBN single crystals doped with Ce and Ni. It was demonstrated that the domain shape strongly depended on the initial domain structure and domain radius increased with increasing amplitude and duration of the voltage pulse. Circular domains of the opposite sign were found to appear due to polarization backswitching. The obtained relations between the domain shape and the initial domain structure can be used for domain engineering and domain wall engineering in relaxor crystals [18].

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