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Citation: J. Appl. Phys. 110, 052017 (2011); doi: 10.1063/1.3624798

View online: http://dx.doi.org/10.1063/1.3624798

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Influence of adsorbed surface layer on domain growth in the field produced by conductive tip of scanning probe microscope in lithium niobate

Ferroelectric Laboratory, Institute of Physics and Applied Mathematics, Ural State University, 620083 Ekaterinburg, Russia

(Received 22 February 2011; accepted 9 June 2011; published online 2 September 2011)

The results of investigation of the single domain growth in electric field applied by conductive tip of the scanning probe microscope in thin plates of lithium niobate (LiNbO₃) crystals doped with MgO after various surface preparations and at various ambient conditions are presented. It has been shown that the sizes of the produced domain can exceed by several orders of magnitude the value of the tip curvature radius. The observed effect has been explained taking into account the existence of the conductive adsorbed surface layer in all experimental conditions. We have demonstrated that the domain growth decelerates with decreasing of the layer conductivity. The existence of the conductive adsorbed surface layers drastically changes the spatial distribution of electric field. In addition to strongly localized electric field, just in the vicinity of the tip there exists the field component remaining homogeneous over the distance exceeding the radius of any experimentally produced domain. The crucial role of the conductive properties of the adsorbed surface layers on the screening of the depolarization field has been revealed. Within proposed approach the domain growth is controlled by the current in the external circuit including the surface layer with low conductivity. The proposed model allows us to explain time and field dependences of the domain size for various types of surface treatment. © 2011 American Institute of Physics. [doi:10.1063/1.3624798]

I. INTRODUCTION

The rapidly developing technology of ferroelectric domain engineering by scanning probe microscopy (SPM) is supposed to be used for manufacturing of various photonic devices and for writing with record spatial density in memory devices. Various SPM modes and especially, the piezoresponse force microscopy (PFM) possess the unique spatial resolution for visualization and manipulation of ferroelectric nanodomains. These methods are widely used nowadays for creation and studying of the stable micro- and nanodomain structures.1–7

In recent decades lithium niobate LiNbO₃ (LN) crystal has become the most important object of domain engineering. It has been demonstrated that by using nanodomain engineering in ferroelectric crystals of LN family the rewritable bit storage with a data density of about ten Tbit/sq.in is achievable.8,9 These achievements stimulate renewed interest in application of SPM methods in development of the next-generation ultrahigh density rewritable electric data storage systems.

The possibility to apply locally electric field by conductive tip of SPM can be used for various applications. The realization of this method requires the detail knowledge of domain formation and growth in strongly inhomogeneous electric field. The number of recent publications is devoted to experimental study of the domain growth under such conditions in order to obtain the temporal and voltage dependences of the domain sizes.10–13 The obtained results were interpreted as an activation process in inhomogeneous field induced by conductive SPM tip.

The calculated local value of spatially nonuniform electric field induced by SPM tip in ferroelectric with free surface strongly decreases with increase of the distance from the tip.10 Within commonly used theoretical consideration of the domain growth this result sets the limit of the domain size below one micron for all investigated ferroelectrics. Nevertheless, it has been revealed that the experimentally observed maximum sizes of the domains exceed essentially the theoretically predicted ones.10,12,14 Moreover, it must be pointed out that the field and time dependences of the domain sizes measured in the same materials by different authors essentially differ. It is reasonable to attribute such discrepancies to uncontrolled properties of the adsorbed surface layers existing under ambient conditions.

It has been shown experimentally that the polarization reversal is very sensitive to the ambient humidity.12 This behavior has been attributed to the formation of the water layer on the ferroelectric surface. It has been proposed that the water meniscus formed between the tip and sample surface leads to change of the capacitance thus influencing the domain sizes. It has been demonstrated that under the same parameters of the switching pulses at low humidity (in dry nitrogen atmosphere) the domain sizes are smaller relative to domain sizes observed at ambient conditions.12

We undertook the systematical study of the influence of the adsorbed surface layers with different conductivity on growth of individual domains under the action of electric field produced by conductive tip of SPM. The effect was studied in
thin single crystals of MgO doped LiNbO$_3$. Piezoresponse force microscopy was used for visualization of the formed stable domains.

II. EXPERIMENT

The studied samples represent the single-domain plates of single-crystalline congruent LN doped by 5% weight of MgO (MgO:LN) with thickness about 50 $\mu$m. The samples were cut normal to the polar axis and thinned by lapping and polishing. The preparation of the thin samples allows decreasing of the switching voltage.

The MgO:LN plate with sputtered uniform Ni electrode on the bottom polar surface was glued by conductive epoxy to the metal disk. The top polar surface was polished and the sample thickness was measured by optical profiler Wyko NT1100 (Veeco Instruments, USA). The metal disk was grounded during switching and domain visualization by SPM. The initial single-domain state of the sample was carefully controlled by PFM. The local switching was carried out by application of the electric field on Z$^+$ top surface using conductive SPM tip.

The scanning probe at NanoLaboratory NTEGRA Aura (NT-MDT, Russia) was used for polarization reversal and domain visualization in PFM mode. We have used the cantilevers DCP11 and DCP20 (NT-MDT, Russia) with conductive diamond-like coating. The domains were produced under application of the single rectangular pulse with duration from 100 $\mu$s to 50 s and amplitude from 50 V to 200 V. The modulation voltage with amplitude 7.5 V and frequency 12.2 kHz was applied during PFM measurements. The phase of piezoelectric response signal was used for obtaining the domain image. The scanning time was about 10 min.

We have compared the domain sizes obtained in the same conditions in one and the same sample after surface treatment by three different procedures. The first treatment represented the cleaning by acetone for preparation of the hydrophobic surface state. The second treatment represented the cleaning by de-ionized water with subsequent drying in ambient conditions. This leads to formation of the adsorbed water layer. The third treatment representing the plasma etching was used as the most effective surface cleaning method. The switching and domain imaging were carried out under ambient conditions and in vacuum $5 \times 10^{-3}$ Torr produced in the SPM chamber by zeolite pump.

The typical PFM images of the inverted stable domains for various pulse durations and surface treatments with pulse voltage amplitude equal to 100 V are presented in Fig. 1. It is seen that domain sizes and shapes obtained under the same pulse duration essentially depend on the surface treatment procedure. The largest domains with hexagonal shape are observed for the surface treatment by de-ionized water. Such regular shape is typical for domains produced in congruent LN by application of the uniform electric field. The smaller and nearly round-shape domains were obtained for surface treatment by acetone and plasma etching.

The essential diminishing of the domain sizes for switching in vacuum as compared to switching under ambient conditions for the same pulse duration was revealed in the sample treated by de-ionized water. This effect was almost absent after sample treatment by acetone cleaning.

The domain size was characterized by effective domain size $r_{ef}$ in the sample treated by acetone on the pulse amplitude for various pulse durations are presented in Fig. 2.

The smallest size of stable domain for plasma etching and acetone treatment is about 120 nm, and for water treatment is about 250 nm. It is necessary to point out that the shortest field pulse which leads to formation of the stable domains is about 40 ms for all surface treatments. After application of the shorter pulses the domains disappear before PFM scanning.

The dependences of $r_{ef}$ of the domains formed under ambient conditions after various surface treatments on the pulse duration are presented in Fig. 3. It is seen that for the same pulse duration the largest domain sizes are obtained after sample treatment by de-ionized water. The smallest domain sizes were observed after sample treatment by plasma etching.

It is important to mention that the formation of the stable domain was achieved only for the pulse duration exceeding
40 ms. The independence of the critical pulse duration on the surface treatment demonstrates the bulk origin of this effect.

III. DISCUSSION

The most important experimental fact is that the sizes of the produced domains exceed by several orders of magnitude the value of the tip radius. In this case the estimation showed that the applied electric field produced by tip at the domain wall is much below the coercive field for MgO:LN (about 6 kV/mm) (Ref. 10).

The obtained results can be explained if we take into account the existence of the conductive adsorbed surface layer. In this case the spatial distribution of the applied electric field differs essentially as compared to the usually considered situation.10 Due to existence of the conductive layer there exists the field component remaining homogeneous over the distance exceeding the radius of any experimentally produced domains in addition to strongly localized electric field just in the vicinity of the tip. Such assumption allows us to explain the creation of the domains with radii up to several microns.10,12,14

The new small domain appeared under the application of the strong field in the vicinity of the SPM conductive tip. Let us consider its growth at the distances far from the tip where the field produced by the tip is negligible. The domain growth in this region is caused by the spatially uniform switching field due to existence of the low-conductive adsorbed surface layer. It is important that high resistivity of the layer leads to realization of “current limited switching” with constant value of the switching current.15

The obtained experimental results can be explained assuming that we produced the through domains and the backswitching effect is negligible. In this case, it is reasonable to propose that the domain sizes after application of the switching pulse with given duration are equal to the sizes of the growing domain at given time interval equal to pulse duration. Under this assumption we can apply the approach developed and experimentally verified in Refs. 16–18, which takes into account the retardation of the screening of depolarization field during domain growth. In this case the sideways domain wall motion and domain shape are essentially dependent on the screening efficiency of the depolarization field produced by bound charges of arising domains. The ineffective screening leads to deceleration of the wall motion. The termination of wall motion is observed in the limiting case of completely ineffective screening.19–22

Let us consider the sideways growth of isolated circular domain of radius \( r(t) \) for current limited switching at the distances far from the tip.

The wall can move when the switching field \( E_s(r,t) \) exceeds effective threshold field \( E_{th} \):

\[
E_s(r, t) \geq E_{th}
\]

For isolated domain the switching field at the domain wall averaged along the polar direction \( E_s(r,t) \) is given by the following expression23

\[
E_s(r, t) = E_{ex} - \left[ E_{dep} - E_{scr}(r, t) \right] L(r)
\]

where \( E_{ex} = U/d \), \( U \) is applied voltage, \( d \) is thickness of the sample, \( E_{dep} = 2P_s/\varepsilon \varepsilon_0 \), \( E_{scr} \) is the screening field, \( L(r) \) is the depolarizing factor which allows to take into account the dependence of the field on the domain sizes.

For \( r << d \) we have used the following approximation of the dependence of the depolarizing factor on the domain radius:

\[
L(r) = K \frac{r}{d}
\]

where \( K \) is the coefficient.

The difference between the depolarizing and screening fields has pronounced physical meaning.15 It represents the residual depolarizing field \( E_{rd}(r,t) \), which hinders the domain growth.

\[
E_{rd}(r,t) = E_{dep} - E_{scr}(r,t)
\]

The screening field \( E_{scr} \) is characterized by the surface charge density \( \sigma(r,t) \):

\[
\sigma(r, t) = \int_0^r I(t)d\tau / A(r,t)
\]

where \( I \) is the switching current, which is constant and independent on the applied voltage for considered case, \( A(r,t) = \pi r^2(t) \) is the area of the switched domain.

\[
E_{rd}(r,t) = \frac{2P_s - \sigma(r,t)}{\varepsilon \varepsilon_0} = \frac{2P_s - \frac{I t}{\pi r^2}}{\varepsilon \varepsilon_0}
\]

We have considered the case of quasi-static switching process when the position of the domain wall and corresponding domain radius are determined by the condition that the switching field is equal to the threshold field:

\[
E_s(r, t) = E_{th}
\]

\[
\frac{U}{d} - \frac{1}{\varepsilon \varepsilon_0} \left( 2P_s - \frac{I t}{\pi r^2} \right) K \frac{r}{d} = E_{th}
\]

\[
\frac{K}{d} E_{dep}^2 - \Delta E_r - \frac{K}{\varepsilon \varepsilon_0 \pi d} I t = 0
\]
where \( \Delta E = \frac{U}{d} - E_{\text{th}} \)

\[
r(t) = \frac{d}{2kE_{\text{dep}}} \left( \frac{\Delta E}{E_{\text{dep}}} + \sqrt{\left( \frac{\Delta E}{E_{\text{dep}}} \right)^2 + \frac{4k^2}{E_{\text{dep}}^2} \cdot \frac{I}{\ell} \cdot \frac{d^2}{E_{\text{dep}}}} \right)
\]

For \( E_{\text{th}} << E_{\text{dep}} \), \( \Delta E << E_{\text{dep}} \) we obtain the following equation for determination of the domain radius dependence on time and applied voltage:

\[
r(t, U) = aU + bt^{0.5} - c
\]

where

\[
a = \frac{1}{2kE_{\text{dep}}} ; \quad b = \left( \frac{1}{E_{\text{dep}}} \right)^{0.5} ; \quad c = \frac{d}{2kE_{\text{dep}}}
\]

The obtained dependence has been used for fitting of the experimental data (Fig. 2 and Fig. 3). It is seen that Eq. (11) has described within experimental error the \( r(t) \) data. The values of parameter \( b \) (Table I) essentially vary for different surface treatments due to dependence of \( b \) on the resistance of the adsorbed surface layer \( R \).

\[
b(R) \sim t^{0.5} \sim R^{-0.5}
\]

It is seen that the experimental data for surface treatment by de-ionized water is well fitted by Eq. (11) for domain radius up to 1000 nm (Fig. 3). This limiting value of domain radius corresponds to the observed change of the shape of growing domain from quasi-circular to hexagonal (see Fig. 1). The isotropic domain growth leading to formation of circular domain can be attributed to stochastic nucleation at the domain wall.\textsuperscript{24,25} It means that arising of nucleus is equally probable along the whole domain boundary. It has been shown that such nucleation is realized when the residual depolarization field \( E_{rd} \) is small enough.\textsuperscript{18–20} This condition can be fulfilled in two alternative cases: (a) for complete screening of depolarization field and (b) for small domains. The latter case is realized in our experiments for \( r < 1000 \text{ nm} \). The hexagon domain shape in LN crystals is attributed to the determined nucleation at the polygon vertices due to influence of incomplete compensation of depolarization field (ineffective screening).\textsuperscript{26,27} Thus, the observed peculiarity of \( r(t) \) dependence can be attributed to the transition from stochastic to predetermined nucleation at the domain walls.

Moreover, for explanation of the presented experimental data it is important to take into account the effect of the interaction between the growing domain and earlier produced one. This effect of impediment of the domain growth allows us to explain the observed deviation of the experimental data from the theoretical dependence, Eq. (11), for distances between the walls of the neighboring domains below 2000 nm (Fig. 3).

It was revealed experimentally for all surface treatments that the domains produced by application of the pulses with duration below 40 ms have been unstable after termination of the switching pulse and disappeared before PFM scanning. The domain instability can be referred to well-known backswitching (flip-back) effect, which was studied in details.\textsuperscript{28,29} The obtained critical pulse duration is close to the “stabilization time” measured in congruent LN (Ref. 30).

The observed independence of the critical pulse duration needed for formation of the stable domain on the surface treatment can be attributed to the key role of the bulk screening effect. The growing needle-like domains have the charged domain walls. The depolarization field produced by these walls can be compensated by bulk screening only. After termination of the switching pulse the uncompensated depolarization field induces the backswitching process. The domain stabilization can be achieved for effective internal screening of the depolarization field which is independent of the surface treatment.

### IV. CONCLUSION

The investigation of the single domain growth in electric field applied by conductive tip of the scanning probe microscope in thin plates of lithium niobate (LiNbO\textsubscript{3}) crystals doped by MgO reveals domain size dependence on the type of surface treatment. The effect of growth of domains with radius exceeding essentially the tip curvature radius was studied and discussed. The observed differences in the dependences of domain radius on pulse duration for different surface treatments have been referred to variation in conductivity of the prepared adsorbed surface layers. The existence of the conductive layers drastically changes the spatial distribution of switching electric field. In addition to strongly localized field produced by the tip there exists the homogeneous field over the large distance from the tip. The existence of the adsorbed surface layer leads to “current limited switching process” when domain growth is controlled by the current in the external circuit including the low conductive layer. The wall motion in this homogeneous field is possible only for efficient enough screening of the depolarization field. The proposed quasi-static description of the isolated domain growth accounting for the retardation of the depolarization field screening allows one to explain the temporal and voltage dependences of the domain radius. The observed change of the domain shape from circular to hexagonal was referred to the transition from stochastic to determined nucleation induced by screening retardation. The independence of the critical pulse duration needed for formation of the stable domain on the surface treatment was revealed and referred to the retardation of the bulk screening process.

### ACKNOWLEDGMENTS

The research was supported in part by RFBR (Grant Nos. 10-02-96042-r-Ural-a, 10-02-00627-a, and 11-02-91066-CNRS-a); by the Ministry of Education and Science:

### TABLE I. The parameter \( b \) and relative value of the resistance of the adsorbed layer for various types of surface treatments.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Water cleaning</th>
<th>Acetone cleaning</th>
<th>Plasma etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b ), nm/ms\textsuperscript{1}</td>
<td>312</td>
<td>183</td>
<td>139</td>
</tr>
<tr>
<td>R, arb. units</td>
<td>1.0</td>
<td>2.9</td>
<td>5.0</td>
</tr>
</tbody>
</table>
(Contract 16.552.11.7020 and 02.740.11.0171) and the Program “Scientific and scientific-pedagogical personnel of innovative Russia 2009-2013” (Contract P870).


