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Anomalous domain inversion in $LiNbO_3$ single crystals investigated by scanning probe microscopy

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Ferroelectric domains were written in lithium niobate ($LiNbO_3$) single crystals by applying voltage pulses to the tip of a scanning force microscope. The generated domains are subsequently imaged by piezoresponse force microscopy. As it has been previously observed not only full domains but also doughnut-shaped ones arise from tip-based domain formation. In this contribution, we present our experiments which were carried out with 10-20 μm thin $LiNbO_3$ single crystals. We show that by choosing appropriate writing parameters, domains of predetermined shape (full or doughnut) can be reliably generated. In addition to the duration and the amplitude of the voltage pulse the moment of the retraction of the tip from the sample surface was found to be a crucial parameter for reproducible domain formation. © *2011 American Institute of Physics*. [doi:10.1063/1.3623775]

INTRODUCTION

The generation of ferroelectric domain patterns in lithium niobate ($LiNbO_3$) single crystals is of major importance since these materials have turned out to be most promising for nonlinear optical applications.[1] Such applications require the controlled patterning of the samples with ferroelectric domains in the sub-to-few-μm range. This is generally performed by locally applying an electric field exceeding the coercive field to the sample, a method known as electric field poling (EFP). If the required size of the individual domains is larger than 1 μm, EFP can be accomplished using structured electrodes and thus applying a spatially structured electric field to the sample. For patterns with individual domains of about 1 μm or smaller, this technique fails, and one possible alternative for domain formation is sequential local poling with the help of the tip of a scanning force microscope (SFM). This will be termed SFM-based domain formation in the following.

In recent years, a wealth of experimental and theoretical investigations of SFM-based domain formation have been published.[2–4] Interestingly, only a few publications were concerned about a feature very relevant for practical use, namely the effect of anomalous domain inversion,[5–12] first observed ten years ago by Abplanalp *et al*.[5] The effect can be described very briefly: SFM-based domains are occasionally observed to exhibit a doughnut-like shape. This shape, however, contradicts the expectations based on the electric field from the SFM-tip. For the explanation of this phenomenon it has been proposed that the center either maintains its original polarization during the voltage pulse (due to ferroelastoelectric switching[5]) or poles back after the application of the voltage pulse (due to an electric field either caused by charges injected from the tip[7,8] or caused by non-stoichiometric defects[9]).

A detailed analysis of the phenomenon of anomalous domain inversion in SFM-tip-based domain formation has been published some time ago by Kholkin *et al*. investigating relaxor crystals of solid solutions $PbZn_{1/3}Nb_{2/3}O_3PbTiO_3$, a material mostly known for its giant piezoelectric effect.[10] Shortly after, Liu *et al*. performed the first experiments using lithium niobate single crystals[9] and finally Kan *et al*. reported experiments once again on $LiNbO_3$, explicitly focusing on the growth and the decay of the domains.[11]

We re-approached the subject of anomalous domain inversion in order to investigate in more detail the possibilities for controllable SFM-based domain formation in $LiNbO_3$ crystals, with the aim of preventing the formation of doughnut-like shaped domains. This issue is of importance for any application that might utilize SFM-based domain patterns.

The experiments were carried out with a commercial scanning force microscope (Solaris, NT-MDT) and domains were generated by applying voltage pulses to the SFM tip. In addition to altering the pulse parameters we changed the load of the tip in order to check for a possible influence of the local pressure at the sample surface on the shape of the generated domains. We also observed an additional parameter, that was not taken into account until now, and which turned out to be relevant for reliable domain formation of a predefined shape: the moment of retraction of the tip from the sample surface. The tip can either be retracted during the voltage pulse, or after the voltage pulse (but before moving the tip to a new position), or not at all. For our investigations we varied the following parameters (termed "writing parameters" below): (1) pulse duration τ, (2) pulse amplitude U, (3) load of the tip F, (4) the moment when the tip is retracted from the sample surface, or waiting time T_{wait}, at the center position of the just-written domain before moving to a new position. A schematic of the different recipes utilized for domain formation is shown in Fig. 1.

The systematical investigation of the influence of the individual writing parameters on the domain shape was performed with a custom-designed script. This allowed us to automatically write a grid of domains, varying any two of the writing parameters. We could thereby directly investigate

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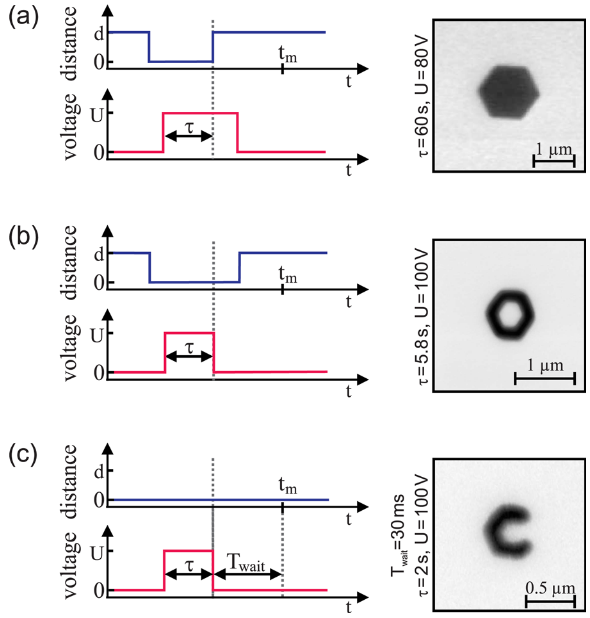

FIG. 1. (Color online) Differently shaped domains controllably generated in a SLN sample. In (a) the tip was retracted to a distance of $d \approx 3\mu$m with the voltage U still applied to it, in (b) the tip was kept at the central position after the voltage pulse and retracted only later, and in (c) the tip was not retracted at all, but moved toward the right to a new position at the moment t_m after a waiting time T_{wait}.

their influence on the domains generated. Such a grid of typically 10×10 domains will be termed "poling map'' in the following.

Imaging of the generated domain patterns was performed by piezoresponse force microscopy (PFM), applying 14 V_{pp} to the tip at a frequency of ≈ 40 kHz. The read-out of the PFM signal was performed with a lock-in amplifier (SRS 830, Scientific Instruments) recording the in-phase output channel. We used conductive, diamond-coated probes (DCP 11 from NT-MDT) with spring constants of the cantilever between 2 and 20 N/m and a nominal tip radius of 50-70 nm. The tips were found to maintain their radius after the generation of the first poling map, i.e. after a first degradation to a radius of ≈ 100 nm the tip radius remained unchanged. This was verified by measuring the lateral resolution obtained in the PFM images recorded after every generation of a poling map.

The samples used to investigate anomalous domain inversion were mm^2 sized lithium niobate ($LiNbO_3$) single crystals with a thickness of 10-20 μm. The use of single crystals takes advantage of the homogeneity of the whole sample and thus allows for reproducible results irrespective of the exact position on the crystal surface. We used $LiNbO_3$ crystals of different compositions: congruent and stoichiometric ones (CLN and SLN), some of them doped with magnesium (5% Mg:CLN and 1.3% Mg:SLN).

Figure 1 shows three types of domains that could be reproducibly fabricated in SLN crystals using the writing parameters indicated in the figure. To obtain the different domain shapes we varied the moment the tip was, if at all, retracted from the sample surface to a distance of $d \approx 3$ μm before moving it to a new position at the moment t_m:

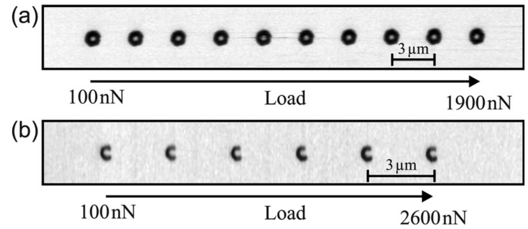

FIG. 2. Generation of o and c domains in a SLN sample applying various loads to the tip. The domains were written with voltage pulses of (a) $\tau = 60$ s, $U = 100$ V for the o domains and (b) $\tau = 1.5$ s, $U = 95$ V and an additional waiting time of $T_{wait} = 20$ ms for the c domains.

(a) For a muffin-shaped domain ("• domain") the tip was retracted from the sample surface while the voltage pulse was still applied. Grounding of the tip occurred only when the tip was at a distance d from the sample surface.
(b) For a doughnut-shaped domain ("o domain") the tip was retracted only after the voltage pulse but before moving it to a new position. The grounded tip was thus kept in contact with the sample surface directly after the voltage pulse.
(c) For a croissant-shaped domain ("c domain") the tip was at no time retracted from the sample surface. The grounded tip was moved to a new position subsequent to a predefined waiting time T_{wait} after the voltage pulse.

The recipes described above for fabricating domains of different types are the result of an extensive investigation analyzing poling maps generated with all possible combinations of the four writing parameters (τ, U, F, and T_{wait}). Regarding the reproducibility of the domain shape it can be stated that: recipe (a) reliably generates • domains, (b) results in o domains if the pulse duration τ is not too long, and for (c) both τ and T_{wait} are crucial for obtaining c domains (to be discussed in detail below).

In order to understand these results, we first investigated the generation of anomalously switched domains in $LiNbO_3$ in view of ferroelastoelectric switching.[5] In this model the size of the central area that kept its polarization should depend on the load F of the tip. Sections of two poling maps are shown in Fig. 2 where we varied the load of the tip by more than one order of magnitude. The o domains seen in Fig. 2(a) were generated with voltage pulses of $\tau = 60$ s and $U = 100$ V. The load of the tip was varied between 100 and 1900 nN. No change of the outer and the inner diameter of the o domains could be observed. As for the c domains (Fig. 2(b)) generated by voltage pulses of $\tau = 1.5$ s and $U = 95$ V together with a waiting time $T_{wait} = 20$ ms again no effect of the load, now varied between 100 and 2600 nN, could be observed. We therefore conclude that ferroelastoelectric switching in $LiNbO_3$ thin samples is not dominant.

The other model for anomalous domain inversion presumes local back-poling after the voltage pulse by an electric field between the grounded tip and charges inside the sample. The latter can either result from: (i) corona charges injected from the tip during the voltage pulse,[7] or (ii) non-stoichiometric defects generating an internal field,[9] or (iii) polarization charges originating from the head-to-head (or tail-to-tail) domain wall inside the sample.[10] This last mechanism requires the formation of surface domains, i.e., domains of limited depth not reaching the rear face of the sample, which is quite probable in the case of sample thicknesses of more than few microns. Note that all three mechanisms described above might also simultaneously take place and will have the very same impact on the anomalous domain inversion when presuming local back-poling is its origin. In the following, we will present our investigations on the formation of differently shaped domains as previously described and analyze the results using the model of local back-poling.

First, we will discuss the formation of • domains. They are reliably generated when retracting the tip during the voltage pulse. The tip is only grounded later, when it is at a distance $d \approx 3\ \mu$m from the sample surface (Fig. 1(a)). Due to the large distance only a small, widespread electric field builds up and no local back-poling occurs. The generation of • domains turned out to work best in SLN and Mg:SLN. In these two materials the generated domains become as large as 3 μm for extended pulse durations τ and beyond a certain size showed the hexagonal shape, which is typical for $LiNbO_3$. Also in CLN and Mg:CLN • domains could be written, however, in CLN they turned out to be extremely small (on the order of only 100 nm). We attribute this behavior to the difference of the coercive field which is $\approx 2\,$kV/mm in Mg:SLN, $\approx 6\,$kV/mm in Mg:CLN and SLN, and $\approx 21\,$kV/mm in CLN.[13] Since our samples have thicknesses of $> 10\,\mu$m, the application of moderate voltages ($\leq$ 100 V) to the tip is thus not sufficient for the generation of large domains in CLN.

The ○ domains could only be generated in SLN crystals. In the context of the local back-poling model, this can be explained as follows assuming charge-injection: in the Mg-doped crystals the dark conductivity is much larger,[14] and therefore a local charge distribution inside the crystal rapidly decays and back-poling does not take place. Note that the fact that ○ domains could not be created in Mg:CLN contradicts the mechanism assuming non-stoichiometric defects causing an internal field.[9] The impossibility of creating ○ domains in CLN is due to the large coercive field of this material: The injected charge distribution and therefore the electric field that builds up in the sample should be the same for CLN and SLN. The coercive field, however, is larger by an order of magnitude for CLN. The electric field necessary for back-poling is obviously large enough for SLN, but too small for CLN.

Finally, we consider the formation of c domains in SLN crystals. Just as in the case for the generation of ○ domains the tip stays in contact with the sample after the voltage pulse, leading to the formation of the central back-poled area. Now after a time interval T_{wait}, the grounded tip is moved to a new position, still being in contact with the sample. The electric field responsible for back-poling is thereby dragged out of the central area and the doughnut transforms into a croissant. We will now discuss this process in more detail on the basis of a poling map.

Figure 3 shows a poling map for a SLN crystal where we varied the pulse duration τ from 2 to 128 s and the waiting time T_{wait} from 0.01 to 41 s, keeping the pulse amplitude $U = 100$ V constant. Obviously, the longer the pulse duration τ the larger the domain, i.e., its outer diameter. The dependence of the size of a SFM-based domain on τ has been previously investigated.[15] It was found to follow a logarithmic behavior which is in agreement with Merz law.[13] Regarding anomalous domain inversion, we list a number of observations that can be made from this poling map:

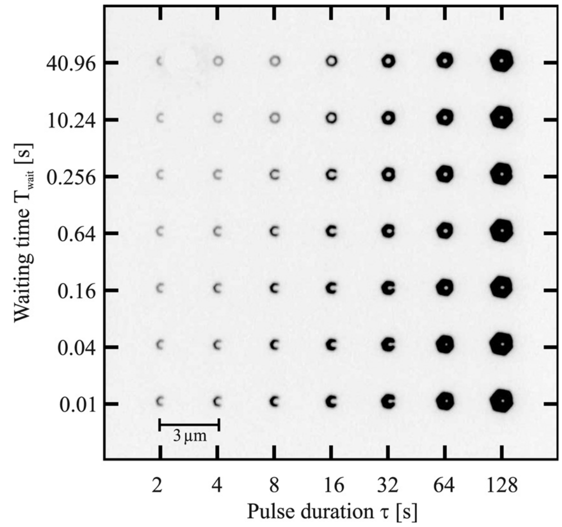

FIG. 3. Poling map on SLN for different pulse durations τ and waiting times T_{wait} for a fixed pulse amplitude of $U = 100$ V.

1. Domains generated with pulse durations $\tau \geq 64$ s do not transform into c domains, irrespective of the waiting time T_{wait}.
2. Domains generated with pulse durations $\tau \leq 32$ s transform only into c domains for short waiting times T_{wait}.
3. Domains generated with short pulse durations ($\tau = 2$ s) always transform into c domains irrespective of the waiting time T_{wait}.
4. The size of the back-poled central area is larger for shorter pulse durations τ and for longer waiting times T_{wait}.
5. The depth of the domains decreases with longer waiting times T_{wait}.

The dependencies of the domain shape on the two writing parameters τ and T_{wait} shown in Fig. 3 can be, at least qualitatively, explained by making use of well-known properties of $LiNbO_3$ and ferroelectric domains in $LiNbO_3$[16] in combination with the knowledge about their imaging by PFM[17,18] and the experience gained in SFM-based domain formation.[13,15]

From bulk poling experiments in $LiNbO_3$ it is known that the electric field necessary for back-poling is smaller for a shorter time interval between forward and backward poling.[19] This effect is caused by the incomplete relaxation of freshly poled domains.[20] In our experiment, the impact of relaxation on the obtained domain shape can be directly seen from the size of the back-poled central area. For shorter voltage pulses domain relaxation before back-poling is less complete, and therefore the back-poled area is larger.

Similarly the relaxation of the domains influences the o → c transformation. Note that in this case τ and T_{wait} add up to the time interval relevant for relaxation. Therefore domains generated with long pulse duration τ and/or long waiting times T_{wait} do not transform into c domains.

A different effect, which has the same influence on the o → c transformation as relaxation, concerns the stability of the charge distribution inside the crystal. Although $LiNbO_3$ is an insulator, the injected charge distribution spreads due to Coulomb repulsion. As a consequence, the electric field for back-poling decreases, and after a certain time back-poling cannot take place any longer. This effect would also hinder the transformation into c domains for long waiting times T_{wait}. Note that the argument regarding the spreading of the charge distribution inside the crystal is not that far-fetched: Just remember that in Mg-doped samples the dark conductivity prevents the generation of o domains.

The size of the SFM-based domains in $LiNbO_3$ is known to increase logarithmically with the pulse duration τ.[13,15] Similarly, the size of the back-poled domains increases with time, and therefore with T_{wait}. This can also be observed in the poling map. In this case, however, the dependence on T_{wait} is more complicated since the electric field is not constant over the waiting time. The electric field is decreasing with time for two reasons: the spreading of the injected charge distribution and the decrease of the injected charge distribution due to back-poling. As a consequence of this weakening of the electric field, the size of the back-poled area does not increase for any length of time, and complete back-poling does not occur.

Finally, we would like to comment on the depth of the domains. As can be seen from the poling map, domains written with pulse durations of $\tau \leq 8$ s show a reduced PFM-contrast, in particular for longer waiting times T_{wait}. A reduced PFM-contrast, however, implies that a domain is shallower than $\approx 2\ \mu$m in the case of $LiNbO_3$.[17] For the emergence of shallow domains, using these writing parameters, a number of arguments can be given. At first, one can assume that due to the shortness of the voltage pulse τ the initial domain is not deep. If so, the charged head-to-head (or tail-to-tail) domain wall is close to the sample surface, therefore contributing more importantly to the back-poling electric field. In addition, domains generated with short voltage pulses τ are back-poled more easily due to the incomplete relaxation, and they are therefore shallow since they are not completely poled back.

In conclusion, we have investigated the behavior of anomalous domain inversion by SFM-tip poling in stoichiometric lithium niobate single crystals. We could unambiguously show that for this material anomalous domain inversion is caused by charge injection, and not by ferroelastoelectric switching. In addition to the basic parameters for SFM-tip poling, i.e., the amplitude and the duration of the voltage pulse, we varied the moment the tip was, if at all, retracted from the sample surface. In this way we could deliberately generate domains of three different shapes, i.e., muffin •, doughnut o, and croissant c. The use of poling maps proved to be a very helpful tool for understanding the influence of the writing parameters on the obtained domain shape.

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[1] L. Arizmendi, Phys. Status Solidi A **201**, 253 (2004).
[2] Y. Cho, K. Fujimoto, Y. Hiranaga, Y. Wagatsuma, A. Onoe, K. Terabe, and K. Kitamura, Appl. Phys. Lett. **81**, 4401 (2002).
[3] P. Paruch, T. Tybell, and J.-M. Triscone, Appl. Phys. Lett. **79**, 530 (2001).
[4] A. Agronin, M. Molotskii, Y. Rosenwaks, G. Rosenman, B. J. Rodriguez, A. I. Kingon, and A. Gruverman, J. Appl. Phys. **99**, 104102 (2006).
[5] M. Abplanalp, J. Fousek, and P. Günter, Phys. Rev. Lett. **86**, 5799 (2001).
[6] T. Morita and Y. Cho, Appl. Phys. Lett. **84**, 257 (2004).
[7] S. Bühlmann, E. Colla, and P. Muralt, Phys. Rev. B **72**, 214120 (2005).
[8] Y. Kim, S. Bühlmann, S. Hong, S.-H. Kim, and K. No, Appl. Phys. Lett. **90**, 072910 (2007).
[9] X. Liu, K. Kitamura, K. Terabe, H. Zeng, and Q. Yin, Appl. Phys. Lett. **91**, 232913 (2007).
[10] A. L. Kholkin, I. K. Bdikin, V. V. Shvartsman, and N. A. Pertsev, Nanotechnology **18**, 095502 (2007).
[11] Y. Kan, H. Bo, X. Lu, W. Cai, Y. Liu, and J. Zhu, Appl. Phys. Lett. **92**, 172910 (2008).
[12] H. Guo, G. Cheng, S. Wang, S. Dai, S. Wu, S. Zhou, Y. Li, and Z. Du, Appl. Phys. Lett. **97**, 162902 (2010).
[13] M. Lilienblum and E. Soergel, "Determination of the coercive field of ferroelectrics by piezoresponse force microscopy," (submitted).
[14] M. C. Wengler, U. Heinemeyer, E. Soergel, and K. Buse, J. Appl. Phys. **98**, 064104 (2005).
[15] B. J. Rodriguez, R. J. Nemanich, A. Kingon, A. Gruverman, S. V. Kalinin, K. Terabe, X. Y. Liu, and K. Kitamura, Appl. Phys. Lett. **86**, 012906 (2005).
[16] T. Volk and M. Wöhlecke Lithium Niobate: Defects, *Photorefraction and Ferroelectric Switching* (Springer, Berlin, 2009).
[17] F. Johann, Y. J. Ying, T. Jungk, A. Hoffmann, C. L. Sones, R. W. Eason, S. Mailis, and E. Soergel, Appl. Phys. Lett. **94**, 172904 (2009).
[18] T. Jungk, Á. Hoffmann, and E. Soergel, New J. Phys. **10**, 013019 (2008).
[19] J. H. Ro, D. Jeong, T. Park, C. Kim, S.-B. Kwon, M. Cha, B. C. Choi, N. Yuf, S. Kurimura and G. Jeon, Mater. Sci. Eng., **B 120**, 150 (2005).
[20] V. Gopalan and T. E. Mitchell, J. Appl. Phys. **83**, 941 (1998).