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| **Title** | Domain growth kinetics in lithium niobate single crystals studied by piezoresponse force microscopy |
| **Authors(s)** | Rodriguez, Brian J., Nemanich, R. J., Kingon, A. I., et al. |
| **Publication date** | 2005-01 |
| **Publication information** | Rodriguez, Brian J., R. J. Nemanich, A. I. Kingon, and et al. “Domain Growth Kinetics in Lithium Niobate Single Crystals Studied by Piezoresponse Force Microscopy.” American Institute of Physics, January 2005. https://doi.org/10.1063/1.1845594. |
| **Publisher** | American Institute of Physics |
| **Item record/more information** | http://hdl.handle.net/10197/5350 |
| **Publisher's version (DOI)** | 10.1063/1.1845594 |

APPLIED PHYSICS LETTERS **86**, 012906 (2005)

# Domain growth kinetics in lithium niobate single crystals studied by piezoresponse force microscopy

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(Received 7 September 2004; accepted 11 November 2004; published online 23 December 2004)

The kinetics of sidewise domain growth in an inhomogeneous electric field has been investigated in stoichiometric $LiNbO_3$ single crystals by measuring the lateral domain size as a function of the voltage pulse magnitude and duration using piezoresponse force microscopy. The domain size increases linearly with the voltage magnitude suggesting that the domain size is kinetically limited in a wide range of pulse magnitudes and durations. In spite of that, the written domains exhibit strong retention behavior. It is suggested that the switching behavior can be described by the universal scaling curve. Domain kinetics can be described as an activation process by calculating the field distribution using the charged sphere model under the assumption of an exponential field dependence of the wall velocity. The activation energy is found to be a function of the external field. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1845594]

Ferroelectric domain engineering by scanning probe microscopy (SPM) is a rapidly evolving technology that can be used for the development of high-density data storage, nonlinear optical devices and ferroelectric lithography.[1–7] Nanoscale domain patterns may also enable new approaches to fabrication of molecular structures for biological and chemical sensors. The key issues in SPM domain engineering are writing resolution and domain stability which depend both on the domain growth kinetics and on the domain size in the thermodynamically equilibrium state. A theory of equilibrium domain formation under the tip-generated electric field has been developed by Molotskii.[8] However, stable domain patterns can be produced not only by fabricating equilibrium domains. Domains can exist in a metastable nonequilibrium state infinitely long after being stabilized via the screening effects or by lattice defects. These nonequilibrium domains can be generated as a result of a kinetic switching process when an applied voltage pulse is shorter than the time necessary for a domain to reach the true equilibrium state. This type of switching allows fabrication of much smaller domains and improvement of SPM writing resolution which is critical for increasing the data recording density and for decreasing the feature size in lithography. In spite of the importance of detailed investigation of domain switching kinetics in SPM, so far it was addressed in a very few special cases.[9–11]

Piezoresponse force microscopy (PFM) has been shown to be an ideal tool to create and to characterize nanoscale domains by inducing local polarization reversal. In contrast to a switching pattern in a macroscopic ferroelectric capacitor where a number of domains nucleate at the electrodes, in PFM, the electric field concentrated directly below the tip results in nucleation of a single domain at the tip-surface junction. Subsequent evolution includes forward domain propagation along the polar axis toward the bottom interface as well as lateral domain growth. In this letter, we report the detailed analysis of the process of sidewise domain growth in PFM and interpret it in terms of the inhomogeneous distribution of the tip-generated field. It is shown that the 180° domain wall kinetics in PFM can be described as an activation process with an activation field being a function of the applied field. In addition, the obtained results show that the domain size is kinetically limited in a wide range of the pulse magnitudes and duration.

In this study, we used a *z*-cut 850-nm-thick crystal of stoichiometric lithium niobate (SLN). An indium tin oxide (ITO) electrode was deposited on a $+z$ surface of the sample by magnetron sputtering. The SLN sample was mounted with its $-z$ surface upward on the 0.5-mm-thick congruent lithium niobate substrate using organic adhesive. Conductive silver paste was used to establish electrical contact with the bottom ITO electrode. Domain switching was performed by applying a negative bias to the uncoated $-z$ surface using a conductive probing tip. To address the growth evolution of the domains, they have been fabricated and measured as a function of both pulse magnitude and pulse duration.

All measurements were performed using a commercial atomic force microscope (Park Scientific Instruments Autoprobe M5). A computer-controlled Keithley 236 Source Measure Unit was used to apply switching voltage pulses to the SLN sample via a Pt coated Si cantilever (5 N/m force constant, MikroMasch). The same tip was used for domain imaging in the piezoresponse mode by applying a 10 kHz modulation voltage of 2.5 V rms.[12]

Figure 1 shows the PFM amplitude and phase images of an array of nine domains fabricated by applying negative 10 ms voltage pulses of various magnitudes in the range from 20 to 70 V. The PFM contrast is the same across the

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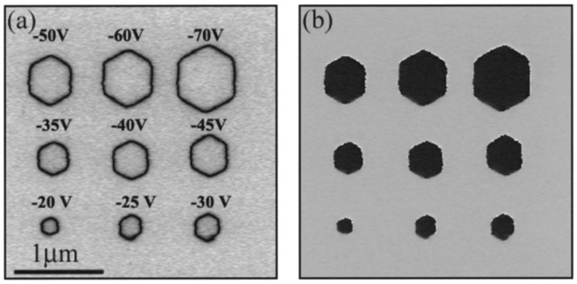

FIG. 1. PFM (a) amplitude and (b) phase images of ferroelectric domains fabricated by 10 ms voltage pulses of various amplitudes.

180° domain boundaries, which appear as dark lines in the amplitude image, suggesting that the fabricated domains extend from the top to the bottom interface. The fabricated domain array did not show any sign of decay 800 min after writing. The smallest stable domain that could be written was found to be ~150 nm (by a 12.5 V, 10 ms pulse). Presumably, smaller domains can be fabricated with shorter pulse duration. However, it is interesting to note that the width of the domain wall is ~65 nm. Therefore, it is likely that the minimum size of the domain in lithium niobate crystals being limited by the domain wall width will not pass below the 100 nm mark.[13] The domain width value seems to be too high compared to the first-principle calculations of 180° domain walls suggesting that their width may be just 1–2 unit cells.[14] However, it is consistent with the results of x-ray synchrotron imaging of domains in lithium niobate and lithium tantalate crystals, which showed significant broadening of the 180° domain walls as well as with theoretical estimations of the wall width in these materials based on experimentally measured coercive fields.[15,16] Note that situation may be different in ultrathin crystals.[2]

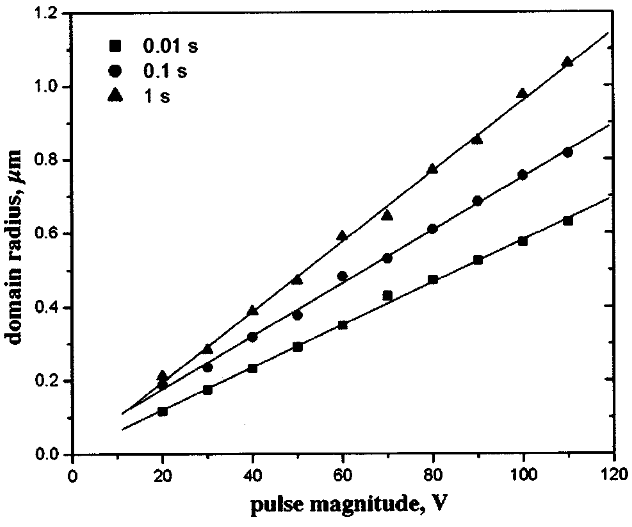

FIG. 2. Domain radius vs pulse magnitude for three different pulse durations.

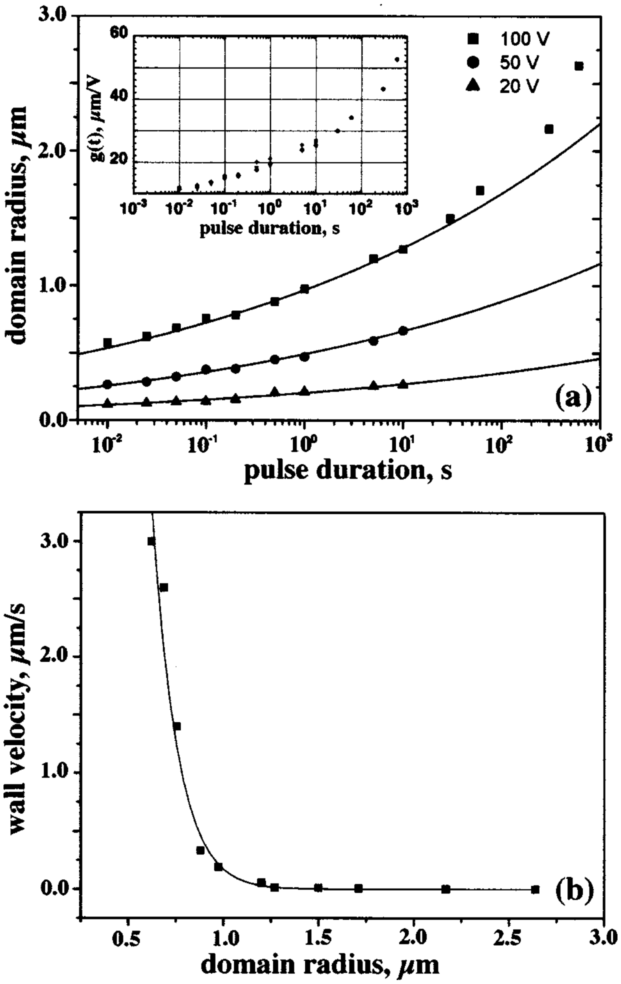

FIG. 3. (a) Domain radius vs the pulse duration for various pulse magnitudes. Inset shows a scaling curve $g(t)=r(V,t)/V$ calculated using all data points from (a); (b) domain wall velocity as a function of domain radius for the pulse amplitude of 100 V. The data are fitted using Eqs. (1) and (2).

Figure 2 shows the domain radius as a function of the pulse magnitude for various pulse durations. Variations in domain size did not exceed 8% for domains below 1 μm and 4% for larger domains. It can be seen that, in contrast to fabrication of domains in bulk lithium niobate crystals which showed a power law voltage dependence of domain size with subsequent saturation,[17] in our case the domain radius does not appear to saturate but follows a linear voltage dependence.[18] This behavior suggests that the domains represent different stages of the switching kinetic process and do not correspond to the equilibrium state domains.[8] This conclusion is further supported by the time dependence of the domain radius shown in Fig. 3(a) for three different pulse amplitudes. Again, there is no saturation in domain size with time. Notably, results shown in Figs. 2 and 3 suggest that the kinetics of the sidewise domain growth can be described by a scaling curve $g(t)=r(V,t)/V$ illustrated in Fig. 3(a). It will be shown in a forthcoming paper that this universal scaling behavior is directly related to the field dependence of domain wall velocity and field distribution inside the material. Here, we analyze the kinetics of the sidewise domain growth using the classical activation model of wall motion in the tip-generated field assuming a weak indentation regime.[19]

According to the Miller and Weinreich model,[20] the sidewise growth of the domain develops as an activation process via nucleation at the existing 180° domain wall. This nucleation process determines the exponential field dependence of the wall velocity. To calculate the tip-generated field distribution the tip was modeled as a charged sphere with radius $R$ at the distance $\delta$ from the sample surface. The normal component of this electric field at a section of the 180° domain wall with the sample surface at a distance $r$ from the tip is calculated using an expression for the electric potential from Mele:[4,21]

$$E(r) = \frac{C_t V_t}{2\pi\varepsilon_0\sqrt{\varepsilon_c\varepsilon_a} + 1}\sqrt{\frac{\varepsilon_a}{\varepsilon_c}}\frac{R+\delta}{[(R+\delta)^2 + r^2]^{3/2}}, \tag{1}$$

where $C_t$ and $V_t$ are the tip capacitance and bias, respectively, and $\varepsilon_a$ and $\varepsilon_c$ are the dielectric constants along the nonpolar and polar axes of the sample, respectively. In the present study, we used the following values: $R=50$ nm, $\delta=1$ nm, $\varepsilon_a=85$, and $\varepsilon_c=30$. The tip capacitance was calculated to be $1.6\times10^{-17}$ F. The data in Fig. 3 were fitted using the following expression for the time dependence of the domain radius:

$$t = \int \frac{dr}{v(r)} = \int \frac{dr}{e^{-\alpha/E(r+r_0)}}, \tag{2}$$

where $\nu(r)$ is a local wall velocity and $\alpha$ is the activation field. The meaning of the fitting parameter $r_0$ can be understood as follows. Underneath the probing tip, the generated field is much larger than the local coercive field and the domain growth develops as a nonactivated process. The spatial inhomogeneity of the external field results in a transition from the nonactivated to the activated process.[8] Therefore, $r_0$ can be considered as the domain radius at which the activation type of the wall motion begins. The $r_0$ value was found to be 17 nm for the applied voltage of 20 V and 110 nm for the 100 V voltage. The activation energy was found to decrease with an increase in the applied voltage from $\sim 2\times10^3$ kV/cm for 20 V to $\sim 50$ kV/cm for 100 V. It should be noted that a strong decrease of the external field with the distance from the tip as well as nonlocal tip effect might result in a different mechanism of domain wall motion that may explain a less adequate fitting of $r(t)$ for large ($r > 1.5$ $\mu$m) domains in Fig. 3(a).

Finally, the instantaneous local wall velocity has been extracted from the time dependence of the domain radius as described in Ref. 11. Figure 3(b) shows that $\nu(r)$ fits well to $\nu(r)\sim\exp[-\alpha/E(r+r_0)]$ where the local electric field $E(r)$ is calculated using Eq. (1), thus supporting an activation mechanism of the wall motion.

In summary, the domain growth kinetics in the tip-generated electric field has been investigated in lithium niobate single crystals using piezoresponse force microscopy. For the used range of pulse magnitude and duration, the lateral domain size did not saturate, suggesting that the domain size is kinetically limited. In spite of that, the written domains exhibit strong retention behavior. The sidewise domain growth can be well approximated by calculating the lateral field distribution in the charged sphere model under the assumption of an exponential field dependence of the wall velocity. The activation field is found to be a function of the external field. The measured growth kinetics is different from that observed by SPM in bulk crystals, reflecting the complicated nature of the ferroelectric domain formation and stabilization process in the inhomogeneous electric field.

This work was supported by Bilateral US-Israel Science Foundation, National Science Foundation (Grant No. DMR02-35632 and Grant No. 0403871, NIRT on Nanopatterned Polar Surfaces) and U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC. Support from ORNL Laboratory Research and Development funding is acknowledged (S.V.K.). The authors are thankful to J. D. Waldrep for designing the TestPoint Program used in this study.

[1] T. Hidaka, T. Maruyama, I. Sakai, M. Saitoh, L. A. Wills, R. Hiskes, S. A. Dicarolis, and J. Amano, Integr. Ferroelectr. **17**, 319 (1997).
[2] K. Fujimoto and Y. Cho, Appl. Phys. Lett. **83**, 5265 (2003).
[3] Y. Cho, K. Fujimoto, Y. Hiranaga, Y. Wagatsuma, A. Onoe, K. Terabe, and K. Kitamura, Appl. Phys. Lett. **81**, 4401 (2002).
[4] G. Rosenman, P. Urenski, A. Agronin, Y. Rosenwaks, and M. Molotskii, Appl. Phys. Lett. **82**, 103 (2003).
[5] K. Terabe, M. Nakamura, S. Takekawa, K. Kitamura, S. Higuchi, Y. Gotoh, and Y. Cho, Appl. Phys. Lett. **82**, 433 (2003).
[6] K. Terabe, S. Takekawa, M. Nakamura, K. Kitamura, S. Higuchi, Y. Gotoh, and A. Gruverman, Appl. Phys. Lett. **81**, 2044 (2002).
[7] S. V. Kalinin, D. A. Bonnell, T. Alvarez, X. Lei, Z. Hu, J. H. Ferris, Q. Zhang, and S. Dunn, Nano Lett. **2**, 589 (2002).
[8] M. Molotskii, J. Appl. Phys. **93**, 6324 (2003).
[9] K. Terabe, M. Nakamura, S. Takekawa, K. Kitamura, S. Higuchi, and T. Togashi, Mater. Sci. Technol. (to be published).
[10] M. Abplanalp, Ph.D. thesis, ETH Zurich, 2001.
[11] T. Tybell, P. Paruch, T. Giamarchi, and J.-M. Triscone, Phys. Rev. Lett. **89**, 097601 (2002).
[12] *Nanoscale Characterization of Ferroelectric Materials: Scanning Probe Microscopy Approach*, edited by M. Alexe and A. Gruverman (Springer, Berlin, 2004).
[13] This conclusion is further supported by the domain writing experiments in the same sample using a special probe with a high aspect ratio that generates a strongly localized electric field compared to the conventional PFM probe that showed the smallest domain size of about 120 nm.
[14] J. Padilla, W. Zhong, and D. Vanderbilt, Phys. Rev. B **53**, R5969 (1996).
[15] S. Kim, V. Gopalan, and B. Steiner, Appl. Phys. Lett. **77**, 2051 (2000).
[16] S. Kim, V. Gopalan, and A. Gruverman, Appl. Phys. Lett. **80**, 2740 (2002).
[17] A. Agronin, Y. Rosenwaks, and G. Rosenman, Appl. Phys. Lett. **85**, 452 (2004).
[18] For pulse duration of 10 ms this linear behavior holds at least up to 250 V.
[19] S. V. Kalinin, A. Gruverman, J. Shin, A. P. Baddorf, E. Karapetian, and M. Kachanov, cond-mat/0406383.
[20] R. C. Miller and G. Weinreich, Phys. Rev. **117**, 1460 (1960).
[21] E. J. Mele, Am. J. Phys. **69**, 557 (2001).