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## Web-like domain structure formation in barium titanate single crystals

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The evolution of ferroelectric domain structure in Remeika-grown BaTiO<sub>3</sub> crystals under an inhomogeneous electric field has been investigated using piezoresponse force microscopy. The ac imaging bias was found to affect the metastable polarization state and lead to the formation of a web-like domain structure. It is suggested that this behavior is due to the existence of subsurface domains arising in single crystals with a layered structure. © 2010 American Institute of Physics. [doi:10.1063/1.3467871]

Ferroelectric domain engineering by scanning probe microscopy can be used for the development of high-density data storage and nonlinear optical devices and may also enable approaches for the fabrication of molecular structures for biological and chemical sensors.<sup>1–4</sup> Piezoresponse force microscopy (PFM) allows for both the creation and visualization of nanoscale domains generated by an electrically-biased probe and is an established tool for investigating domain growth dynamics during polarization reversal.<sup>5,6</sup> Nanoscale domain switching by PFM is known to switch a local volume under the tip only, thus producing a nucleus in the form of half of a prolate spheroid. Domain switching occurs as the charged domain wall moves into the bulk of the ferroelectric (either head-to-head or tail-to-tail growth) resulting in a stable ferroelectric domain. Subsequent evolution includes (a) the forward domain propagation along the polar axis toward the bottom interface and (b) the lateral domain growth.

Domain growth studies in thin films<sup>7,8</sup> and single crystals<sup>9–12</sup> have led to insight into materials properties, and to a better understanding of domain growth and relaxation kinetics. Many parameters can influence the nucleation and subsequent evolution of a domain such as experimental conditions (bias magnitude and duration, temperature, humidity, etc.) and materials properties, including conductivity. In local switching experiments in an ambient environment, liquid-necks form at the tip-sample junction, increasing the contact area and influencing the lateral expansion of growing domains.<sup>13</sup> In addition, charge injection can lead to backswitching<sup>14</sup> and to the formation of double domains.<sup>15</sup>

Here, we report on PFM studies of the tip-induced domain growth and evolution in a Remeika-grown BaTiO<sub>3</sub> (BTO) crystal and on the observation of a web-like domain structure that forms under charge stabilized conditions radially away from the nucleus.

In this study, we have used ~100- $\mu$ m-thick Remeika-grown BTO to address the growth evolution of domains fabricated and measured as a function of pulse magnitude. All measurements were performed using a commercial atomic force microscope (AFM) (Park Scientific Instruments AutoProbe M5) equipped with a lock-in amplifier (Stanford Re-

search Systems, SR830). A computer-controlled Keithley 236 source measure unit was used to apply switching voltage pulses to the BTO sample via a Ti-Pt-coated Si cantilever (5 N/m force constant, MikroMasch). The same tip was subsequently used for domain imaging by applying a 10 kHz modulation voltage of 2–5 Vrms.

Figure 1 shows the topography and PFM amplitude and phase images of domains fabricated at the surface of a BTO crystal by applying voltage pulses of various magnitudes from –10 to –60 V, and 1 s duration to the AFM tip. The PFM contrast is the same across the 180°-domain boundaries, which appear as dark lines in the amplitude image, suggesting that the fabricated domains extend from the crystal surface to at least the depth of the PFM imaging volume. Note also that surface topographic features do not accelerate or impede domain wall motion or significantly affect the shape of the growing domain.

The motion of domain walls in BTO has long been a topic of interest,<sup>16</sup> and the process of sidewise motion of 180°-domain walls is well-known.<sup>17,18</sup> To gain further insight into the kinetics of the domain growth, the domain radius has been measured and plotted as a function of the pulse amplitude, as shown in Fig. 2. It can be seen that as with domain growth in other single crystal ferroelectrics such as lithium niobate and lead germanate, the domain radius depends linearly on the applied voltage, indicating a general process, independent of material, for ferroelectric domain growth dynamics in air.<sup>11</sup> This behavior suggests that the domains represent different stages of the kinetic switching process and do not correspond to equilibrium state domains. Note that imaging on the subsequent day revealed that the domains had decreased in size, and that the domains formed with pulse magnitudes of –10 and –20 V had disappeared.

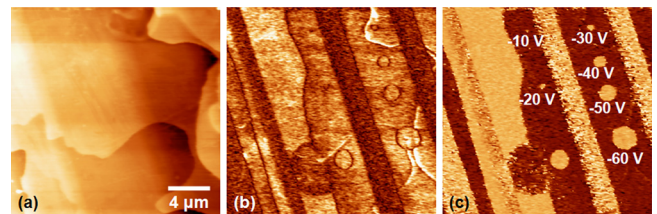


FIG. 1. (Color online) (a) Topography, PFM (b) amplitude, and (c) phase images of domains fabricated at the surface of a BTO crystal by applying 1 s voltage pulses in the range of (–10)–(–60) V to the AFM tip.

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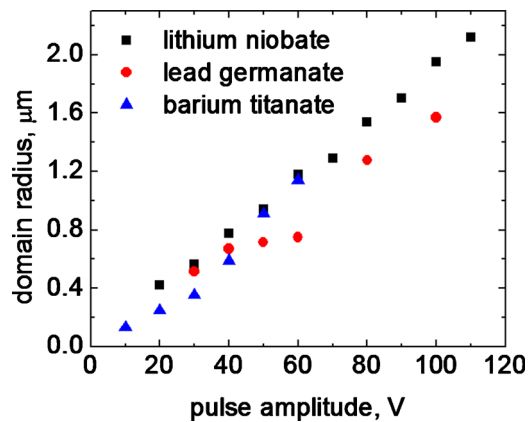


FIG. 2. (Color online) Plot of the fabricated domain radii in Fig. 1 as a function of the pulse magnitude (1 s duration) and compared with data measured on lithium niobate and lead germanate crystals.

The effects of the domain aspect ratio,<sup>19,20</sup> critical domain radii,<sup>21,22</sup> the ratio between the electrode size and the film thickness,<sup>23</sup> and thermal treatments<sup>24</sup> on domain stability have been the subject of numerous studies. In general, stable domains are ones that exceed a certain critical radius and extend through the thickness of the epitaxial film or crystal, although subsurface layers, defects, and charge injection can play a role in domain stabilization. In particular, for BTO, Gruverman *et al.*<sup>25</sup> found that domains smaller than 50 nm decayed after the removal of the dc field, and Eng *et al.*<sup>26</sup> reported that domains larger than 250 nm were stable in the absence of a dc bias. These results are in good agreement with the calculated critical radius for domain stability in BTO of 74–100 nm.<sup>22</sup> Note that the formation of domains by ferroelectric domain breakdown is not favorable in BTO crystals due to the high dielectric constant of BTO.<sup>22</sup>

Domains fabricated in this study with  $-10$  and  $-20$  V pulses decayed rapidly from initial radii of  $\sim 250$  nm and 500 nm, respectively, and while larger domains were more stable, they became smaller after scanning with ac bias overnight. That these domains decayed despite surpassing the critical radius range suggests an incomplete polarization screening of the switched domains on their polar surfaces (assuming that the domains extend through the whole sample thickness). An additional factor that might affect the stability of the switched domains is the ac bias applied during the imaging process.

To explore the role of the ac imaging bias on the formation and stability of domains fabricated by a PFM tip, a single  $-50$  V, 1 s pulse was applied to the BTO surface in a predominantly  $c$ -axis oriented area. Figure 3 shows the formation of an unusual web-like domain structure which

evolves with each cycle of imaging. In Fig. 3(a), a PFM phase image taken 10 min after the application of the pulse is shown. A double domain is visible, which has been observed in other materials, including lithium niobate—an effect generally attributed to the presence of a water layer at the crystal surface and to charge injection.<sup>13,15</sup> Further imaging results in the formation of an increasingly visible web-like domain structure surrounding the initially formed domain [Fig. 3(b), after 20 min]. The boundaries of the domains become sharper after 50 min [Fig. 3(c)], and can be seen clearly at higher resolution after 80 min [Fig. 3(d)]. Upon continuous imaging, the branches keep growing, shrinking the meshes until the entire web-like structure transforms into a single, completely switched domain [Fig. 3(e), after 18 h].

It should be noted that the web-like structure has not been found when retracting the tip after switching. In other words, the ac bias applied to the PFM tip while imaging plays a crucial role in the formation and evolution of this structure. Unlike the switching shown in Fig. 1, the domain structure shown in Fig. 3 does not have equal PFM amplitude contrast across the curved  $180^\circ$  domain boundaries, suggesting the presence of surface domains which do not extend to the depth of the PFM imaging volume. Note that no in-plane response from these surface domains is observed.

Due to the periodical oscillations of temperature at the crystallization front, the Remeika growth technique is known to produce layered variations in stoichiometry in BTO crystals. These variations could lead to surface layers having domain structure that is different from the bulk with a high concentration of domains of opposite polarity—an effect known as domain branching.<sup>27</sup> Furthermore, layered variations in stoichiometry could result in random-field defects in the surface layer, which would break the equivalence between opposite domains in terms of their response to the external electric field. Formation of the web-like structure can thus be explained as an effect of the ac bias which favors the growth of one domain over the opposite one during PFM imaging.

Labyrinthine and meandering fingerprint-like domain structures have been observed in the  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$  (PMN-PT) relaxor system,<sup>28</sup> lead germanate,<sup>29</sup> and lithium niobate.<sup>30</sup> However, in the present study, the observed domain structure in BTO is not engineered via dc-bias- or temperature-induced phase transitions, but rather through the application of an ac-bias, suggesting an additional route for tailoring domain-structured surfaces.

Plausibility of the proposed model is supported by direct PFM observation of the subsurface domain structure [Fig. 4(a)]. Here, small, irregular domains with a weak PFM signal can be seen superimposed on a much larger domain near

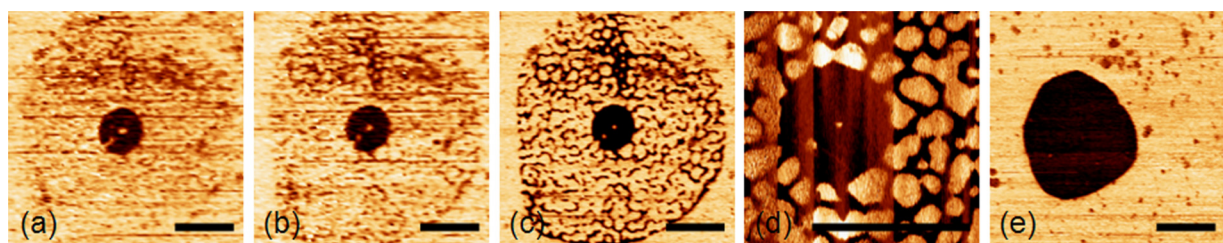


FIG. 3. (Color online) [(a)–(e)] PFM phase images showing the evolution of the fabricated domain structure (a) 10 min following the application of a  $-50$  V, 1 s pulse, and (b) 20 min, (c) 50 min, (d) 80 min, and (e) 18 h after the application of the voltage pulse, respectively. Each scale bar represents  $2 \mu\text{m}$ . The contrast indicates a  $180^\circ$  phase shift between domains.

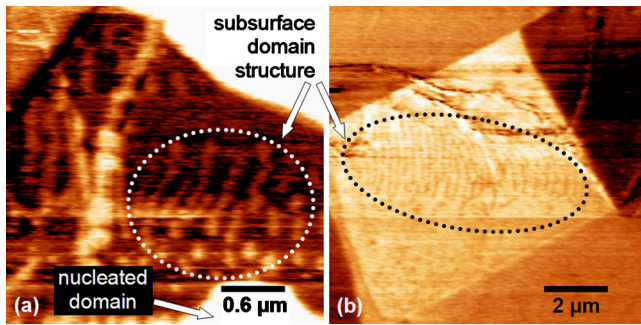


FIG. 4. (Color online) PFM images of a BTO crystal surface demonstrating subsurface domain structure. (a) Subsurface domains which evolved during imaging after the application of a voltage pulse. (b) Subsurface domain structure on top of an existing bulk domain.

a  $180^\circ$ -domain boundary of a domain nucleated by the application of a voltage pulse. In several instances, a domain structure consisting of small, curved, branching nanodomains have been visualized on top of as-grown domains [Fig. 4(b)].

The observed domain structure resembles the etch patterns of incompletely poled BTO crystals as reported by Hooton and Merz.<sup>31</sup> Similar domain structures are also visible by electron backscattering diffraction.<sup>32</sup> The formation of the subsurface domains observed in this study may be a manifestation of the free energy reduction via domain branching. In principle, such antiparallel domains could also be related to charge accumulation at the interface between the bulk crystal and a surface layer.

In summary, the formation of a web-like domain structure has been observed by PFM in barium titanate single crystals. This type of domain structure is attributed to the effect of an ac bias applied during PFM imaging, suggesting an additional route for tailoring domain-structured surfaces. It is proposed that the observed structure can be induced in crystals with layered variations in stoichiometry and random-field defects. Application of the PFM imaging bias favors the growth of the subsurface domains in one direction, effectively suppressing their growth in the opposite direction. The obtained result, which illustrates the effect of the imaging process on domain stability, may be of importance not only for local PFM switching experiments, but of general relevance to switching studies in layered heterostructures where extended electrodes are utilized.

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