Ferroelectric domain evolution with temperature in BaTiO$_3$ film on (001) SrTiO$_3$ substrate

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The evolution of ferroelectric domains in BaTiO$_3$ film on (001) SrTiO$_3$ substrate is studied at 20–120°C. The dominant domains orient in (001) plane due to strong internal strain when BaTiO$_3$ island grains are embedded in the film, most of which is of layer-by-layer growth. These domains are commonly larger than grains at 20°C, however, they are close to grain size at 60–80°C, which largely enhances the coercive field. The in-plane domains are very stable at 20°C; however, they can transform to out-of-plane domains at 40–80°C under electric field, which is likely the cause of enhanced piezoelectric response.

Domain evolution in ferroelectric materials is of great importance for both fundamental physics and applications. Many aspects of this topic are not yet fully understood. Domain nucleation, growth, and switching depend significantly on grain size, crystal orientation, thermal/epitaxial strain, and so on. It is important to clarify the coupling between them using direct imaging techniques.$^{1–4}$ For example, mesoscale flux-closure domain formation in BiFeO$_3$ and BaTiO$_3$ single crystal$^{5}$ has been investigated using scanning transmission electron microscopy (TEM) and piezoelectric force microscopy (PFM).$^{5–9}$ Compared with other ferroelectrics,$^{10}$ BaTiO$_3$ has a Curie temperature of ~120°C, which is convenient for domain evolution study.$^{4,11,12}$ Hofer and McGilly have reported the annihilation of stripe domains across the ferroelectric-paraelectric (FE-PE) phase transition in BaTiO$_3$ single crystal.$^{12,13}$ Lu et al. reported switching of polarization direction in BaTiO$_3$ epitaxial thin film using strain gradient with the tip of PFM.$^{14}$

It is important to study the dependence of in-plane (IP) domain evolution on temperature and strain in BaTiO$_3$ film.$^{1,12,13}$ If domains are larger than crystal grains at room temperature, their size will be close to the grain at a certain high temperature in ferroelectric films. It is interesting to study the ferroelectric and piezoelectric properties of this mono-domain. Besides, the strain can change electrical polarization through piezoelectricity, and recently the strain gradient is highlighted because it may switch polarization through flexoelectricity.$^5$ In a word, epitaxial/thermal strain and its gradient are important to clarify and control the various aspects in ferroelectric domain growth, such as domain nucleation, orientation, size, and boundaries.

In this paper, we report that the strain induce mainly IP a-domains in the BaTiO$_3$ films grown on (001) SrTiO$_3$ substrates. At elevated temperature, electric field can trigger transformation from a-domain to out-of-plane (OP) c-domain, leading to enhanced piezoelectric responses.

BaTiO$_3$ films and La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO, 50 nm) buffer layers are grown on commercial (001) SrTiO$_3$ substrates at 710°C and 13 Pa oxygen pressure by pulsed laser deposition (PLD). Laser energy per pulse is modulated in order to adjust the growth modes of BaTiO$_3$ films. Besides, the target’s rough surface is helpful to get the island growth of BaTiO$_3$ film. There are three samples, i.e.,1-BaTiO$_3$ (250 mJ, 300 nm thickness) with layer-by-layer growth, 2-BaTiO$_3$ (200 mJ, 200 nm thickness) with the coexistence of island and layer-by-layer growths, and 3-BaTiO$_3$ (70 mJ, 60 nm thickness) with island growth in most area. The as-grown samples are cooled to 300°C in 1000 Pa oxygen pressure with 5°C/min, and then they are fast cooled to ~30°C within 2 min. The crystal structure and strain of BaTiO$_3$ films are characterized using X-ray diffraction (XRD, Bruker D8 advanced). PFM measurements are conducted using an Atomic Force Microscope (AFM, Bruker multimode 8) with an open loop controller, a conductive AFM tip (MESP-RC, Co/Cr coating, 35 nm tip radius), and contrast mode. An ac probing voltage ($f = 41$ kHz, 1–2 V sample bias) is used here, and the lower one is used at higher temperature to insure that it is below the coercive voltage of the BaTiO$_3$ films. A heater is used to heat the sample from 20°C to 120°C with accuracy of 0.1°C.

Only diffraction peaks from (001), (002), and (003) crystal planes of SrTiO$_3$ substrate and BaTiO$_3$ films can be observed as shown in Fig. 1. There is no impurity observed within the limit of XRD. The diffraction angles of the (003) plane of 1-, 2- and 3-BaTiO$_3$ films are 70.70°, 70.12° and 69.96°, respectively, indicating small compressive strain for 1-BaTiO$_3$, mild strain for 2-BaTiO$_3$, and large compressive strain for 3-BaTiO$_3$. It is noted that the strain and the thermal expansion coefficient of BaTiO$_3$ film on SrTiO$_3$ substrate change little at 20–120°C, and thus the domain evolution with temperature mainly originated from other factors, such as the polarization change.

Figure 2 shows the topographies and PFM phases of the three samples. Atomically flat surface with <1 nm roughness is observed for 1-BaTiO$_3$ (Fig. 2(a)). The c domains with upward polarization are dominant as revealed by the OP
Fig. 2(b)) and IP PFM phases (Fig. 2(c)). By comparison, 2-BaTiO$_3$ shows a roughness of $\frac{10}{2}$ nm in the $5 \times 5 \mu m^2$ area (i.e., the 1st area) in Fig. 2(d), which suggests island growth mode. Usually, the layer-by-layer growth leads to atomic smooth surface, while the island growth generates rough surface. When the deposition condition is properly controlled, a transient between the two growth modes can be achieved, and they can even coexist in a narrow window. Here, these two growth modes coexist and their ratio can be adjusted through the subtle change of film growth rate and the surface roughness of the target. The phase angle is close to $0^\circ$ in Fig. 2(e), which is indicative of no OP domains. Indeed, domain structures are observed in the IP PFM phase (Fig. 2(f)). Most of the domains are different from the corresponding topographic features. It suggests that the strain between grains pin most domains in the (001) plane in this sample. This is different from the common domain configuration of BaTiO$_3$ single crystal, i.e., a–c stripe zigzag domain structure.\(^{6,13}\) The roughness of 3-BaTiO$_3$ increases to $\sim 15$ nm as shown in Fig. 2(g). Both OP domains (Fig. 2(h)) and IP domains (Fig. 2(i)) are clearly identified. Most domains are larger than the grain size in the corresponding topography image. Clearly, the strain between neighboring grains plays an important role in determining the domain structure.\(^4\) In the following discussion, we focus on 2-BaTiO$_3$. Its OP PFM phases (Fig. 3), IP PFM phases (Fig. 4), and phase/amplitude versus dc voltage loops (Fig. 5) of the 1st and/or its nearby areas are collected in the same heating and cooling processes at 20–120 °C, respectively.

The evolution of OP phase on temperature was shown in Fig. 3. A special feature labeled with dashed red circle is used to identify the same location. At each temperature, the $3 \times 3 \mu m^2$ and $1 \times 1 \mu m^2$ regions are polarized with $-8$ V and $8$ V sample biases upon LSMO bottom electrode, respectively, and then the PFM phases are scanned with an ac probing voltage immediately. At 20°C, the OP phase does not show obvious change between the two polarized regions in Fig. 3(a). This suggests that (1) $8$ V is not large enough to induce a- to c-domain transition or (2) the switched domain quickly relaxes back to a-domain. The following PFM phase vs. tip bias loops confirms that (2) is the case. With temperature increasing from 40°C to 60°C, the color contrast between the two polarized regions becomes more and more clear (Figs. 3(b)–3(d)), which suggests that the domains with upward or downward polarization orientations begin to stabilize. Furthermore, the phase degree of the as-grown film outside the $3 \times 3 \mu m^2$ region is close to that of the $8$ V polarized region at 60°C in Fig. 3(d). This proves that some IP domains have switched to upward orientation at $\sim 60$ °C even without external electric field, which is consistent with the upward self polarization in many as-grown BaTiO$_3$ films on (001) SrTiO$_3$ substrate.\(^{14}\) The color contrast of two
polarized regions becomes weak at 80°C (Fig. 3(e)) and then nearly disappears at 120°C (Fig. 3(f)) due to the ferroelectric-paraelectric phase transition of BaTiO$_3$.11,12

Afterward, the sample was cooled down to 60°C and then 20°C for further measurements. Fig. 3(g) proves that most domains can be switched at 60°C, and Fig. 3(h) suggests that some domains can be switched at 20°C in the 1st area by ±8 V sample biases. The OP phase behaviors after the sample cooling down (Fig. 3(h)) are different from those before its heating process (Fig. 3(a)), which is due to the multiple switching processes or the influence of ac and dc voltages on the later domain growth. To avoid this influence, a nearby 5 × 5 μm$^2$ area, which was not measured during heating and cooling processes, was measured after the sample was cooled down to 20°C, and its OP phase in Fig. 3(i) is similar to that in Fig. 3(a).

FIG. 3. The OP PFM phase of the 1st 5 × 5 μm$^2$ area in 2-BaTiO$_3$ film at (a) 20°C, (b) 40°C, (c) 50°C, (d) 60°C, (e) 80°C, and (f) 120°C during heating process and at (g) 60°C and (h) 20°C during cooling process; (i) the OP PFM phase of a nearby area at 20°C after cooling process, where the ±8 V polarized regions are marked with dashed blue/red squares, respectively.

FIG. 4. The morphology surface of a 2 × 2 μm$^2$ area in 2-BaTiO$_3$ film at (a) 20°C; its corresponding IP PFM phase at (b) 20°C, (c) 40°C, (d) 60°C, (e) 80°C, and (f) 120°C during heating process and at (g) 60°C and (h) 20°C during cooling process; (i) the IP PFM phase of another nearby area at 20°C after cooling process.
McGilly et al. thus their gradient can decompose a big domain to several
4(c)). The temperature and strain may be not homogenous;
Most importantly, in-plane domains still overwhelm the most
crystal was relatively stable below
1st area (Fig.4(a)), while the maximum length of the ferroelec-
tric domains is
1st area are in the great majority when samples were cooled
down to 60°C (Fig.4(g)) and 20°C (Fig.4(h)), respectively. Most importantly, in-plane domains still overwhelm the most
area that was not measured during heating and cooling proc-
esses, and one example is shown in Fig. 4(i).

The PFM phase/amplitude versus tip bias loops also con-
firm that the in-plane domains are less stable with temperature increasing. At each temperature, phase/amplitude loops of BaTiO3 were repeatedly measured at more than five positions but only the most typical loops were shown in Fig. 5 for con-
venient observation. It is noted that the ac sample bias and dc
tip bias were applied simultaneously during measurements with this method; the electrostatic interaction between the sample and the tip may contribute a linear slope of the PFM
amplitude as function of DC bias. The room-temperature
loops of 1- and 3-BaTiO3 are nearly symmetric in Figs. 5(a) and
5(b), while those of 2-BaTiO3 are asymmetric in Fig.
5(c). The coercive voltages, \( V_C \), are \(-3.1\) V and \(-1.2\) V at
20°C in Fig. 5(c). Domains with downward polarization exist
under \(<-3.1\) V tip bias, and they can switch to an upward
state when the tip bias is above \(-1.1\) V. However, soon after
the tip bias is removed, strain pushes the domain to be IP
again since the upward-polarization domain is just an inter-
mediate state at 20°C. By comparison, the PFM phase versus tip
bias loop measured at 40°C shows \( V_C \) values of \(-1.1\) V and
0.4 V in Fig. 5(d). The smaller \( V_C \) shift suggests that IP
domains are easier to transform to OP domains at 40°C,
mainly due to the smaller polarization at higher temperature.

Accompanying the a- to c-domain transformation induced by
electric field, the converse piezoelectric responses of
2-BaTiO3 sample shows a dramatic increase as temperature
increases. The amplitude is due to the piezoelectric
\( d_{33} \) coefficient of OP domains and the \( d_{31} \) coefficient of IP domains. The \( d_{33} \) value (i.e., about 150 pm/V) is far larger than
\( d_{31} \) (i.e., about \(-80\) pm/V) in BaTiO3 crystal.\(^16\) The amplitude at 20°C
mainly involves the as-grown IP domains, thus the depend-
ence of amplitude on tip bias is very weak in Fig. 5(c). The IP
domains become smaller, and hence, it is much easier for
them to become OP domains under tip bias at 40°C, which
can contribute to larger amplitude through their \( d_{33} \) coefficient
in Fig. 5(d). Most of IP domains can switch to OP domains
under enough tip bias and then they contribute a large increase
of amplitude at 60°C in Fig. 5(e) and 80°C in Fig. 5(f),
respectively. The piezoelectric enhancement may originate
from a-domains which can switch to c-domains under outer
electric field at an elevated temperature. However, the ampli-
tude of 2-BaTiO3 becomes very small at 120°C (Fig. 5(g))
because the FE-PE phase transition occurs and the values of
both \( d_{33} \) and \( d_{31} \) are nearly zero in the paraelectric phase. As
comparison, the amplitude of epitaxial PbZr\(_{0.8}\)TiO\(_{3}\) (PZT,
200 nm thickness) film is shown in Fig. 5(h), which suggests
that the amplitude of 2-BaTiO3 at 60–80°C is \(~70\%) am-
litude of the PZT film.

In conclusion, the strain between island grains and other
BaTiO3 films can pin most domains in (001) plane. The sizes
of most IP domains are much larger than island grains at
20°C; however, they become smaller with temperature increasing. Piezoelectric response and coercive voltage increase largely when mono-domain appears in most regions
at 60–80°C. The IP domains are very stable at 20°C; how-
ever, they are less stable and can switch to the OP when the
ferroelectric polarization becomes smaller at a higher tem-
perature. This finding is important for the understanding of
domain evolution in ferroelectric films and the engineering of high performance piezoelectric devices.

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