Smallest 90° domains in epitaxial ferroelectric films

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Periodic ferroelectric-ferroelastic 90° domain patterns with an unprecedented small domain periodicity of 27 nm were observed in thin $PbTiO_3$ films grown on $DyScO_3$ substrates. These patterns contain the narrowest possible *a* domains (6 nm wide) that allow to preserve the lateral coherence in the films, producing highly ordered patterns visible by x-ray diffraction. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2783274]

The synthesis of self-organized ferroelectric nanostructures could lead to very large storage density and further device miniaturization,[1,2] and has clear advantages over artificial patterning. However, in order for the ferroelectric bits to be addressable, these structures have to be periodic.[3–5] Controlling the size and increasing the coherence of the ferroelectric patterns are still a challenge. Here we show that nanometric periodic domain patterns with a large coherence length can be obtained, as predicted by the theory,[6] by growing ferroelectric thin films epitaxially on an adequate substrate. A nearly perfect lattice match between the film and the substrate at the growth temperature, which promotes domain formation as the only relaxation mechanism, as well as low-miscut substrates, with long atomically flat terraces, have made this possible.

In the simplest and most common case of tetragonal ferroelectric thin films grown on cubic substrates, the orientation of the polarization in the ferroelectric film depends on the relationship between the lattice parameters of the film (a, c) and the substrate (a_s). If $a_s \lesssim a$, the film will grow with c and, thus, the polarization, out of plane (c phase). Such films would (if no or bad electrodes are present) split into 180° domains in order to decrease the depolarizing fields.[7,8] These domains will form periodic stripe patterns,[9] similar to those found on ferromagnetic thin films.[10] In this scenario, the electrostatic energy is responsible for domain formation. Conversely, if $a_s \simeq c$, the film will grow with c in-plane (a phase) and in-plane a_1/a_2 domains can form. Here only elastic considerations dictate the domain scaling.[6,11]

For intermediate situations ($a < a_s < c$), the film will usually consist of domains of c and a phases in a ratio such as to fit the substrate, and both elastic and depolarization effects compete with each other, as a function of thickness, temperature, or electrode material.[6,11–16] Finding the right choice of film and substrate, which imposes enough strain without causing misfit dislocations is quite important, but it was, un-

til recently, difficult. Here we show that this is now possible by combining ferroelectric $PbTiO_3$ (PTO) with the recently introduced $DyScO_3$ (DSO) as a substrate.[17]

Several films with thickness of about 30 nm were grown by pulsed laser deposition[18] on DSO substrates with low-miscut angle ($\approx 0.05°$), provided by CrysTec GmbH. In some of these films, a 30 nm thick electrode layer of $SrRuO_3$ was also deposited in between the substrate and the PTO layer. At room temperature, PTO is tetragonal with $a = 3.90$ Å and $c = 4.15$ Å, while DSO is orthorhombic with a pseudocubic lattice parameter of $a_s \approx b_s = 3.95$ Å.[17] There is, however, a very good lattice match of the two at the growth temperature, and thin films of PTO can be grown with essentially zero strain, thus minimizing the appearance of defects. Only as the films cool down through T_C do strains develop and increase. At room temperature, the strain between PTO and DSO is such that the elastic energy lies near the critical boundary for the appearance of a/c domains,[6] and thus, competition effects between depolarization and elastic energy are easily observed. Indeed, as a function of thickness (d), we have observed a transition from depolarization-dominated, 180° domains[18] ($d=5$ nm) to strain-dominated, 90° domains ($d \approx 30$ nm). We report here that in these latter films, the width of the a domains is the smallest possible in order to keep the films' horizontal coherency. The reduced amount of defects allows the self-organization of these domains in very regular $c/a/c$ patterns.

Figure 1 shows a synchrotron x-ray diffraction (XRD) area scan around the $(100)_c$ reflection of the substrate. XRD was performed in standard reflection geometry and in grazing incidence geometry (GID) at the wiggler W1 beamline in Hasylab (DESY-Hamburg). The intensity modulation along the $[H00]_c$ direction is clearly visible. Scans around other reflections, both in plane and out of plane, have shown that the modulation is present throughout reciprocal space with a spacing of $\Delta H \approx 0.014$, corresponding to a real-space wavelength of $\Lambda = 0.395$ nm$/\Delta H \approx 28$ nm. Similar satellites, with periodicities of 29 ± 2 nm, were observed in all 30 nm thick films, with and without electrode bottom layer. The Bragg peak corresponding to the relaxed (bulk) c lattice parameter

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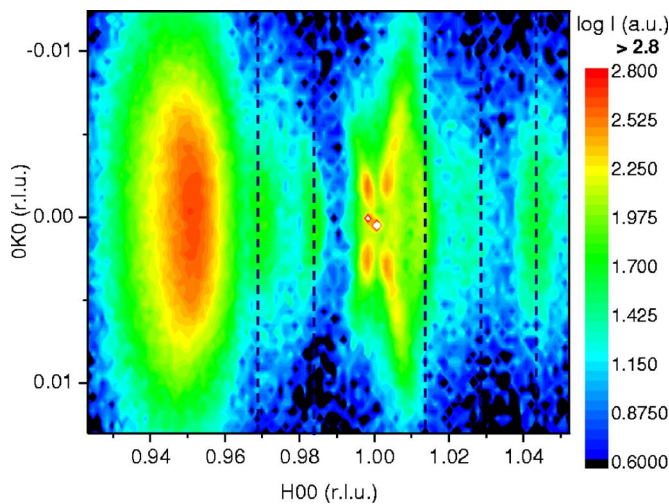[a]Author to whom correspondence should be addressed. Electronic mail: b.noheda@rug.nl

FIG. 1. (Color online) Reciprocal space map in the in-plane ($HK0$) scattering plane, around the $(100)_c$ reflection of the substrate (at $H=1$), obtained by synchrotron XRD in GID geometry at a wavelength $\lambda = 1.26515$ Å. 1 r.l. $= 2\pi/3.95$ Å^{-1}. The four twin peaks that appear around the substrate peak correspond to the SrRuO$_3$ buffer layer. A gradient of lattice parameters is observed in the c domains ($H \approx 1.01$), which will be reported in detail elsewhere (Ref. 19).

FIG. 2. (Color online) (a) AFM image of a 28 nm thick PbTiO$_3$ film on DyScO$_3$. The growth morphology (mounds) shows unit-cell steps and a rms roughness of 3.7 Å (full z scale is 3 nm). (b) Horizontal line scan of the fast fourier transform of a larger 4×4 μm^2 AFM image of a similar 28 nm thick PbTiO$_3$ film on DyScO$_3$ with a SrRuO$_3$ buffer layer. 1 and 2 indicate the domain and mound periodicities, respectively.

of PbTiO$_3$ can be observed in the in-plane scan (at $H = 0.952$), showing the presence of a domains.

Figure 2(a) shows an atomic force microscopy (AFM) image of a 28 nm thick film of PTO on DSO. It can be seen that the film grows as atomically flat islands, or mounds,[20] in agreement with the two-dimensional electron diffraction patterns observed by *in situ* reflection high energy electron diffraction (RHEED) during growth. The figure also shows narrow dip stripes running through the film, the width of which is below the resolution limit of the AFM tip ($\sim$9 nm). Films grown on a SrRuO$_3$ electrode buffer layer show similar morphology. A Fourier analysis of one such film [see Fig. 2(b)] gives a value of 30 nm for the periodicity of the stripes (1) and 150 nm for the periodicity of the growth mounds (2). A third periodicity of 525 nm (not visible in Fig. 2) is also visible and corresponds to the substrate terraces. By combining these results with transmission electron microscopy (TEM) images (Fig. 3), we can show that the narrow stripes are a grid of ultrathin a domains running between larger c domains. This morphology is a miniaturized version of that observed in thicker PZT layers.[14,15]

A TEM image of one of the films, taken with a 300 kV Philips CM300ST-FEG microscope, is shown in Fig. 3(a). The total periodicity (Λ) extracted from the TEM images is 27 nm, in good agreement with the diffraction data of the same film (Fig. 1). As explained, during cooling after the film growth, the mismatch between the a lattice parameter of PTO and that of pseudocubic (110)-DSO increases from 0 at the growth temperature to $\sim$1.3% at room temperature. The fraction of a domains needed to compensate this mismatch, in the absence of defects, can be simply estimated by imposing that $N_c a + N_a c = N a_s$, where N_a and N_c are the number of unit cells in the a domain and c domain, respectively, and N is the total number of unit cells in one wavelength. This leads to a fraction of unit cells in the a domain of $N_a/N = (a_s - a)/(c - a) \approx 0.20$, in good agreement with the experimentally observed ratio. This quantity was defined in the seminal works by Pompe and co-workers[6,13] as the coherency strain
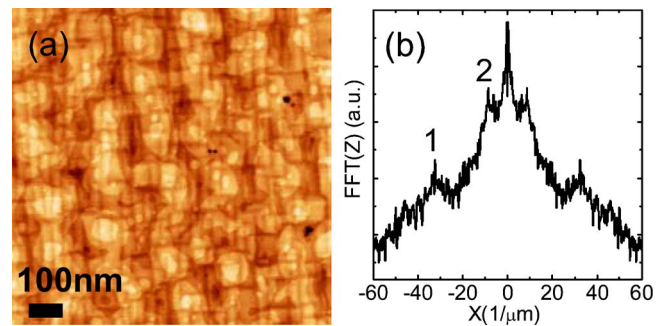
(e_r). The stability limit for the existence of a domains at large thicknesses predicted by these works is $e_r \approx 0.215$, implying that PTO on DSO is close to the critical line that separates the stability of c/c (180°) domains from a/c (90°) domains. But for small enough thickness, the strain energy is not large enough to favor ferroelastic domain wall formation. Following these authors, for PTO on DSO, the transition from 180° to 90° domains should take place at around 10 nm, which is consistent with our observations.

One of the most interesting features of the TEM images is the strong tendency for the a domains to have the same width of 14–16 unit cells (6–7 nm). Constant or discretized
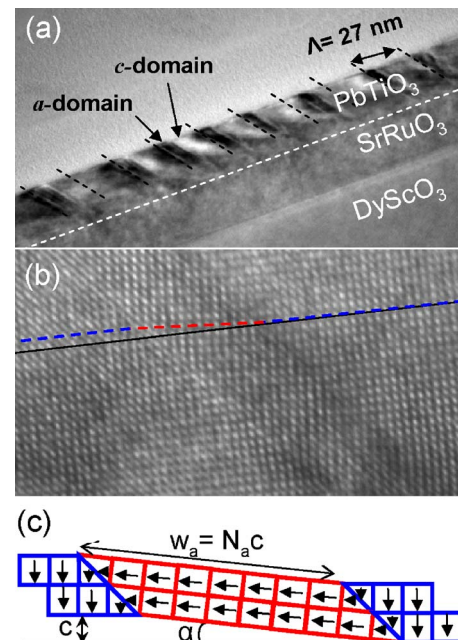

FIG. 3. (Color online) (a) TEM image of a 30 nm thick film of PbTiO$_3$ with a SrRuO$_3$ buffer layer on DyScO$_3$. The dashed lines indicate the wall positions for perfect registration. Disruptions of this periodicity exist but are local, probably due to the steps of the substrate or other defects. (b) TEM image around an a-domain band. The dashed lines show the coherent connection between two c domains mediated by the narrow a domain. A sketch of the $c/a/c$ chain is shown in (c). Note that close to the interface, where the film has to attach to the (flat) substrate, this simple picture does not hold. There, the strains at the interface due to the clamping of the a domain will tend to reduce the width of this domain in a way that will depend on the elasticity of the substrate (Ref. 22). This also introduces a large degree of disorder in the a domains compared to that of the c domains.

(but bigger) widths of the a domains can be found in the literature,[13–15,21] suggesting that they may be a general (but, as far as we know, unexplained) feature of a/c domains. High resolution TEM helps here to clarify their origin [see Fig. 3(b)]. The tilt angle α between the a and c domains, as measured from these images, is 3.8°, a bit larger than the 3.5° expected for bulk PbTiO$_3$.[22] Figure 3(b) shows that, except at the proximity of the interface (where distortions are introduced by clamping to the substrate),[22] the width of an a domain is such that the coherence of the neighboring c domains is preserved. There is, therefore, a minimum possible size of the a domain in order to maintain lateral coherence (collinearity of the atomic planes in adjacent c domains), that is, $w_a^{min} = c/\sin\alpha$ [Fig. 3(c)]. For PTO, $w_a^{min} \sim 6.2$ nm, in good agreement with the values observed in the TEM images. This analysis implies that, in general, in a tetragonal film that shows lateral coherence, the width of the a domains must be a multiple of w_a^{min}. This conclusion is independent of the substrate as long as dislocations and other defects that can induce domain nucleation are avoided.

Since $N_a/N = e_r$, the existence of a minimum size for the a domains implies also the existence of a minimum size for the domain wavelength. In our case, $\Lambda = Na_s = 29.6$ nm for the domain periodicity, again in very good agreement with the one observed in all the 30 nm thick films ($\Lambda = 27–31$ nm). It is worth emphasizing that continuum theories such as Kittel's law[10,11] predict that the domain period scales as the square root of the film thickness. Kittel's law has been observed to work for epitaxial films with 180° domains[9] and for freestanding films with 90° domains.[23] Our preliminary results on films with different thicknesses indicate that $\sim$27 nm is, indeed, a lower bound for the a/c periodicity, which cannot be further reduced by decreasing the film thickness.

To conclude, for PTO on DSO, as in many other systems,[13–15,21] the 90° a/c domains appear in the form of wide c domains separated by narrow a stripes. We show that the condition of horizontal coherency forces the a domains to adopt discrete sizes, which depend only on the tetragonality of the ferroelectric film. We have achieved the narrowest (6–7 nm) possible a domains as well as the shortest $c/a/c$ domain periodicity (27–31 nm) that are possible in order to preserve horizontal coherency in the film. The small periodicity (large storage density) makes these films potentially interesting for ferroelectric memories, in which the narrow a domains would act as spacers between two ferroelectric bits.

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