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Strain-induced ferroelectric domain ordering in $PbTiO_3/PbZr_{0.9}Ti_{0.1}O_3$ and tricolour $PbTiO_3/SrTiO_3/PbZr_{0.2}Ti_{0.8}O_3$ superlattices

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Introduction

Periodic domain patterns occur in ferroelectric materials because of the competition between polarization, strain and electric field. The functional properties of ferroelectric materials are highly influenced by their domain structure. In particular 180° stripe domains of alternate up and down polarizations may often occur in very thin ferroelectric films in order to minimize the depolarizing field. Studies of the intrinsic domain structure in such films can contribute to the understanding of ferroelectricity at the nanoscale. In this context, our approach is the development of new thin ferroelectrics by building ferroelectric superlattices (SL) to explore the effect of strain on the domain pattern. Recently we have experimentally demonstrated the existence of 180° stripe domains in tricolour superlattices $PbTiO_3/SrTiO_3/PbZr_{0.2}Ti_{0.8}O_3$ (PT/STO/PZT 20-80) [Hubault 11] grown on (001) $SrTiO_3$ substrates. The insertion of STO layers in the ferroelectric SLs induces a strong decrease of the tetragonality, which we could be caused either by the existence of a depolarizing field or by a polarization rotation produced by a change in the symmetry of these heterostructures. In this framework, we want to determine if the polar vector in the 180° stripe domains is tilted away from the surface normal, as reported in ultrathin films of PT [Catalan 06].

Experimental set-up

In order to investigate the in-plane polar structure, reciprocal space maps in the HK0 zone were achieved using grazing incidence diffraction. The satellite reflections around the (100), (010) and (110) were measured at different values of the grazing angle (between 0.27° and 0.6°). The analysis of the in-plane distribution of the satellites, due to the 180° stripe domain structure, enables us to determine the orientation of the polarization. Measurements collected at different grazing angles provide a way to probe the domain structure along the growth direction. For these measurements, the energy was fixed to 10 keV.

Four samples were investigated: three tricolour PT/STO/PZT 20-80 superlattices and one bicolour PT/PZT 20-80.

Results

We present in **Figure 1** different reciprocal space maps recorded in the HK0 zone maps for a $[PT_{10}/STO_2/PZT_9]_{20}$[1] tricolour superlattice. Each reciprocal space map shows in-plane satellites, whose period Λ (Λ = 85 Å) is consistent with the polar modulation measured around specular reflections in the laboratory. From these measurements, we can conclude that the polarization in the domain structure has both in-plane and out-of-plane components. From the analysis of these maps we demonstrate that the SLs present a fourfold in-plane symmetry. These first results are in agreement with the existence of a rotational phase characterized by a polarization rotation away from the normal. To our knowledge, this is the first time that this domain structure is observed in superlattices. Our measurements are in good agreement with the results reported by Catalan et al. [Catalan, 06] for ultrathin films of PT (5 nm thick), which is the unique publication on the existence of a rotational phase in PT thin films.

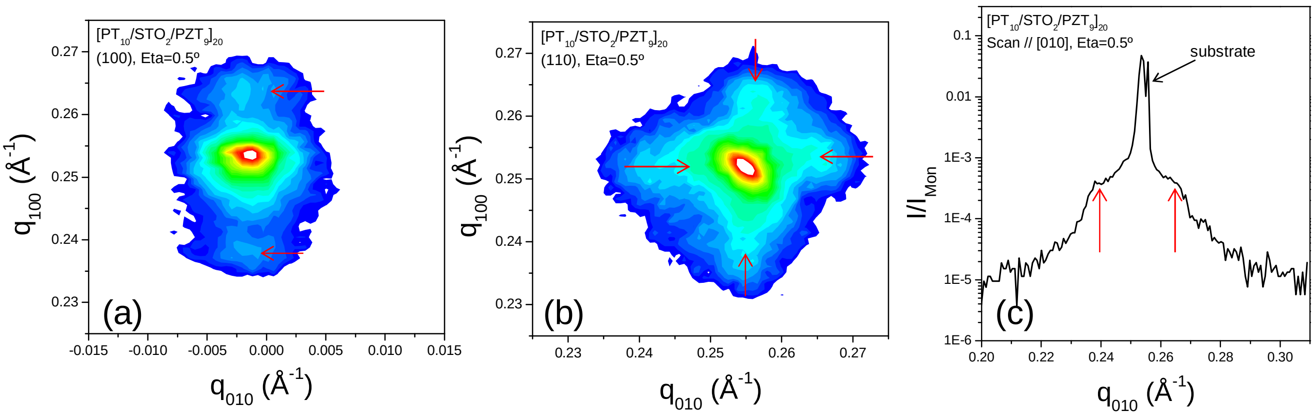

Figure 1. *Logarithmic reciprocal space maps measured for the $[PT_{10}/STO_2/PZT_9]_{20}$ tricolour superlattice, around the (a) (100), (b) (110) reflections and (c) the diffraction profile along the [010] direction. The grazing angle is 0.5°. The arrows indicate the satellite peaks.*

Figure 2 presents the diffraction profile recorded around the (100) reflection for different grazing angles (0.277° and 0.5°). These measurements clearly indicate that the in-plane modulation is weaker for the smaller grazing angle. The evolution of the diffraction profile versus the grazing angle suggests that the stripe domain structure diminished in the few unit cells at the top layer of the superlattice.

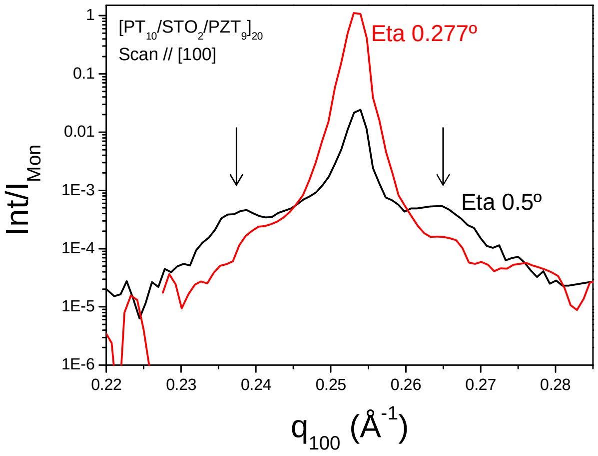

Figure 2. *Diffraction profile along the [100] direction measured for the $[PT_{10}/STO_2/PZT_9]_{20}$ tricolour SL at different grazing angles (0.277° and 0.5°). The arrows indicate the satellite peaks.*

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[1] This superlattice is composed of 20 periods, each consisting of 10 unit cells of PT, two of STO and 9 of PZT 20-80, which we designate as $[PT_{10}/ STO_2/PZT_9]_{20}$.

A bicolour $[PT_2/PZT_2]_{20}$ superlattice was also measured in order to determine if a 180° domain structure could be observed in a superlattice made of ultrathin PT and PZT 20-80 layers. In this sample, we have not detected the presence of the in-plane satellite peaks around the (001) reflection. As no stripe domain structure occurs in this bicolour superlattice, we confirm that the STO layer plays the key role for obtaining a stripe domain structure, thus reserved to tricolour SLs.

We investigated the $[PT_7/STO_7/PZT_7]_{15}$ SL in order to study the influence of the STO layer thickness. Unfortunately, the miscut angle of the substrate prevented us from obtaining reliable measurements.

The $PbTiO_3/PbZr_{0.9}Ti_{0.1}O_3$ superlattices were not measured owing to a lack of time.

These first measurements have clearly demonstrated the existence of a polar nanodomain structure whose polarization has both in-plane and out-of-plane components. Additional investigations are now required to demonstrate the monoclinic symmetry associated with this rotational ferroelectric phase.

References

[Hubault, 11] C. Hubault *et al.*, Appl. Phys. Lett. 99, 052905 (2011)
[Catalan, 06] G. Catalan *et al.*, Phys. Rev. Lett.96, 127602 (2006)