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Kinetics of nanodomain growth in ferroelectric artificial superlattices

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We report the kinetics of nanoscale domain growth in ferroelectric $PbZrO_3/PbTiO_3$ artificial superlattices. Ferroelectric superlattices behave as single ferroelectric materials with only 180° domain structure (monodomain). Domain size increases linearly with the pulse voltage, and is linearly dependent on the logarithmic value of the pulse duration. It was found that ferroelectric superlattices have a relatively high activation field for domain growth and enhanced domain stability, resulting in a long-term retention behavior of more than one month.

Keywords: Ferroelectric materials; Domain kinetics; Piezoresponse force microscopy; Artificial superlattices

Significant interest in the artificial superlattice of perovskite oxide has developed over the last decade as superlattices have the potential to create novel materials with enhanced physical properties or new functionality [1–6]. The formation of an artificial superlattice for ferroelectricity offers opportunities to manipulate ferroelectric properties and expand the functionality of these materials [4–6]. Recent experimental and theoretical studies have revealed that ferroelectric superlattices have intriguing structural and electronic properties that are closely related to their domain structures [6–10]. The domain morphologies of ferroelectric superlattices have features that depend on the stacking periods [8,9]. For example, 180° periodic nanostripe domain structures were observed at relatively large periods, while monodomain-like structures appeared at ultrashort-stacking periods. Such domain morphologies are critical to domain engineering for practical applications. In an earlier study, we reported that the ultrashort-period ferroelectric superlattice was more advantageous than nanodomain engineering due to its prototype supercell with only two polarities along up and down directions and the resulting domain structures were comprised of only 180° domain boundaries [10]. Even though the kinetics of domain wall motion (domain growth) in nanodomain engineering of ferroelectrics has practical implications in scanning probe microscopy (SPM)-based applications, such as high-density data storage, few experimental studies of the domain dynamics of superlattices have been performed.

In terms of electronic device miniaturization and the development of nanotechnology, nanoscale characterization of local ferroelectric properties has been a key issue. Various characterizations of ferroelectric materials at the nanoscale, such as visualization and manipulation of the domain structure, domain reversal and domain growth, have been provided by piezoresponse force microscopy (PFM) [11,12]. Recently, in situ transmission electron microscopy and time-resolved X-ray microdiffraction studies have provided direct and accurate information on the dynamics of ferroelectric switching, which complements PFM measurements [13,14].

Following nanodomain engineering via superlattices, i.e. the formation of nanoscale domains, the kinetics of the domain growth in nanoscale superlattices have been

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investigated with an ultrashort stacking period, e.g. a two-unit-cell $PbZrO_3$/two-unit-cell $PbTiO_3$ (PZO_2/PTO_2), by PFM. Nanoscale domain formation as a function of the applied pulse voltage and time for the domain growth (domain wall motion) was specifically investigated. The domain wall motion is reported in terms of the electric field dependence of the domain wall velocity and inhomogeneous electric field distribution in the sample beneath the PFM tip. The domain wall velocity of the ferroelectric superlattice is proportional to exp $(-\delta/E)$ (Merz's law), where δ is the activation field and E is the applied electric field [15]. The superlattices showed a relatively high activation field for domain growth and enhanced domain stability, resulting in long-term retention greater than one month (i.e. 42 days).

Artificial PZO/PTO superlattices were fabricated on a $(La_{0.5},Sr_{0.5})CoO_3$(LSCO)/MgO (100) substrate by multi-target pulsed laser deposition (PLD, $\lambda = 248$ nm, KrF excimer laser). Epitaxial PZO and PTO layers with the same number of unit cells were alternately deposited at 500 °C with a 100 mtorr oxygen ambient after epitaxial growth of LSCO to form a bottom electrode on the MgO substrate. The stacking period was varied from one unit cell of the PTO layer and one unit cell of the PZO layer (i.e. PZO_1/PTO_1) to PZO_{100}/PTO_{100}. In our previous work, maximum polarization of the superlattice was obtained at a stacking period of PZO_2/PTO_2. Additionally, the formation of the superlattice structure was also confirmed by X-ray diffraction analysis with the appearance of satellite peaks near the main diffraction peak [16]. Only a single peak of the (0 0 1) domain structure was observed in reciprocal space mapping (data not shown), indicating that PZO/PTO superlattices have a perfect single c-axis domain and tetragonal structure. For the microscopic aspects of domain growth and switching of 50 nm thick PZO_2/PTO_2 superlattices, the PFM domain imaging and study of domain growth were performed with a PFM system consisting of a commercial scanning probe microscope (Seiko, SPA 300), a low-pass filter and a lock-in amplifier (Stanford Research System, SR830).

A key parameter for estimating and manipulating ferroelectric domains is the film surface roughness. Figure 1a shows the topography of the 50 nm thick PZO_2/PTO_2 superlattice. The root-mean-square (rms) roughness over a 4 μm × 4 μm surface was ~0.4 nm, indicating that the films were atomically smooth. A highly smooth and uniform surface is advantageous for effective writing or imaging of ferroelectric domains in SPM-based applications. The ferroelectric domain structure and switching behavior in artificial PZO/PTO superlattices were elucidated by forming the polarized domains using PFM. Figure 1b shows the piezoresponse images of the polarized domain patterns written by alternately applying +10 V and −10 V DC to the LSCO bottom electrode over four successive scans. In sequence, the written areas were 4, 3, 2 and 1 μm^2. The tip was electrically grounded while scanning to enable writing. In Figure 1b, the dark region represents the positively polarized area (positive domain with the polarization vector oriented upward) written by applying +10 V, while the negative domain with polarization oriented toward the bottom electrode written by −10 V appears as a bright region. As

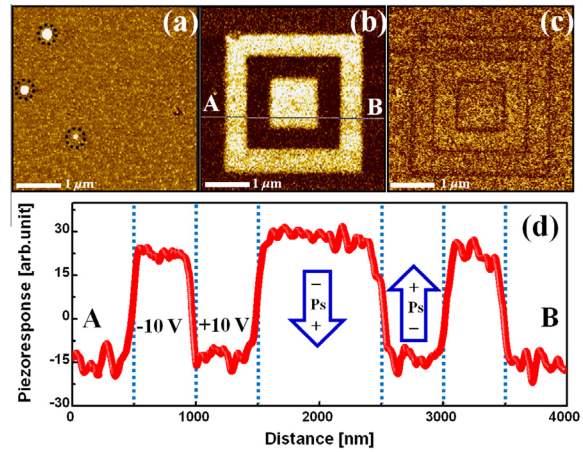

Figure 1. (a) Topographic image of a 50 nm thick PZO_2/PTO_2 superlattice showing 0.42 nm rms roughness over a 4 μm × 4 μm area. Dust particles are at the left of the image (dotted circle). (b) The piezoresponse and (c) amplitude images of the patterned domain with various polarized areas. (d) Cross-sectional piezoresponse profile of the polarized domain across the A–B line in (b).

observed in the well-defined domain image, each region produces a uniform piezoresponse, indicating a homogeneous polarization state. The image contrast was also clearly observed, implying ferroelectric polarization reversal. Figure 1d shows a cross-section profile of the piezoresponse domain image along the A–B line, as indicated in Figure 1b. The piezoresponse signal of the positive domain (polarized by +10 V) was equal to that of the negative domain (−10 V), suggesting a single polarization with opposite polarity. The abrupt transition from a positive domain to a negative domain was also observed in Figure 1d.

Furthermore, piezoresponse images revealed the absence of the a-domain and 90° domain boundary. Note that the ultrashort stacking-period superlattices have only a single c-axis orientation, e.g. a monodomain-like domain, even throughout the 200 nm sample thickness. Based on these results, PZO/PTO superlattices with ultrashort stacking periods (i.e. PZO_1/PTO_1 and PZO_2/PTO_2) may act as a single-component system with a single ferroelectric domain structure, even though the superlattice consists of alternating ferroelectric and antiferroelectric layers. Recent first-principles studies on ultrashort-period $KTaO_3/KNbO_3$ showed that the polarization in the B-site modulation superlattice is more sensitive to the variations in composition and atomic configuration than that in the A-site modulation superlattice, such as the $BaTiO_3/SrTiO_3$ superlattice, since the B-site modulation breaks the translational symmetry of the oxygen octahedron [17]. Sepliarsky et al. also predicted the anisotropy in correlation of each P_Z (polarization along the modulation direction) and P_X (the in-plane component of the polarization) through the B-site modulation superlattice via molecular-dynamics simulation and revealed that the superlattice acts as a single artificial ferroelectric structure at short modulation lengths [18].

It is necessary to consider the amplitude images in detail in order to understand the polarized domain struc-