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Ferroelectricity in thin perovskite films

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We report on the investigation of ferroelectricity in thin tetragonal single-crystalline perovskite films of $Pb(Zr_{0.2}Ti_{0.8})O_3$ grown by off-axis rf magnetron sputtering. The local ferroelectric properties of atomically smooth films, with thicknesses ranging from a few unit cells to 800 Å, were measured using a combination of electric force microscopy and piezoelectric microscopy. The time dependence of the measured signals reveals a stable ferroelectric polarization in films down to thicknesses of 40 Å. © *1999 American Institute of Physics.* [S0003-6951(99)01932-4]

Ferroelectricity has long been viewed as a collective phenomenon associated with a spontaneous macroscopic polarization resulting from the alignment of localized dipoles within a correlation volume.[1] In this picture, the long-range electrostatic interaction along the polarization axis favors the parallel alignment of dipoles and plays an important role in the ferroelectric instability. The anisotropic character of the dipole–dipole interaction implies an anisotropic correlation volume and an energy per unit cell that is considerably higher in a perpendicularly polarized thin-film geometry than in the bulk, suggesting a finite-size effect on the ferroelectric properties. The occurrence of a size effect in thin films would have important implications for applications, since it would limit the minimum useful thickness of these materials.

Theoretical attempts have been made to calculate and predict the critical size or thickness for ferroelectricity to occur. In a mean-field Ginzburg–Landau approach,[2] the free energy of the finite system, including volume and surface terms, is computed and minimized; the order parameter describing the phase transition is the polarization vector *P*. These calculations suggest a material-dependent critical thickness and correlation volume. In the particular case of $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films, a critical thickness of $\sim$200 Å at room temperature has been predicted.[3] However, recent *ab initio* calculations predict that, with appropriate boundary conditions corresponding to short-circuit boundary conditions, ferroelectricity can occur at the monolayer level.[4]

Experimentally, reports on nanoparticles[5] and superlattices[6] are in agreement with the Ginzburg–Landau predictions. Recent results, however, indicate that a copolymer film, as thin as 10 Å, displays phase transitions attributed to bulk and surface ferroelectricity,[7] and that 100 Å $Pb(Zr_{0.25}Ti_{0.75})O_3$ thin films can sustain a ferroelectric phase.[8]

In this letter, we report on the observation of ferroelectricity at room temperature in single-crystalline perovskite $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) films, with thicknesses ranging from 800 to 40 Å (10 unit cells). The samples are atomically flat with a roughness much smaller than the average film thickness. To study the ferroelectric properties, we used a combination of local piezoelectric and electric-field microscopy. These techniques are essentially insensitive to problems as-sociated with leakage currents, which become severe in extremely thin ferroelectric films.

The PZT films used in this study were grown on metallic Nb-doped (001) $SrTiO_3$ (Nb–STO) single-crystal substrates by off-axis radio frequency (rf) magnetron sputtering. The films were prepared at a substrate temperature of $\sim$500 °C in a 160 mTorr atmosphere of O_2 and Ar (O_2/Ar:3/10). X-ray analyses reveal the growth of *c*-axis oriented tetragonal single-crystalline thin films, with a *c*-axis parameter of 4.12–4.18 Å. Rocking curves taken around the 001 PZT reflection display a full width at half maximum (FWHM) of less than 0.1°, indicative of samples with a high-crystalline quality, and θ–2θ scans taken around the 001 reflection show up to 12 orders of satellite peaks.[9] These additional peaks are related to the finite thickness of the film[10] and allow one to measure accurately the film thickness, within $\pm$5%.[11] The surface crystalline quality was checked on a 50-Å-thick film using low-energy electron diffraction (LEED), which reveals a crystalline surface and epitaxial growth.[12]

A key parameter for this work is the surface roughness of the films, which was investigated by atomic force microscopy (AFM) measurements, carried out in air and at room temperature. Figure 1 shows typical AFM data taken on films with thicknesses of 1000, 50, and 16 Å; in each case, the vertical scale is equal to the film thickness. All three films show a root-mean-square (rms) roughness of $\sim$2 Å over the 5 μm by 5 μm areas measured, indicating that these films are essentially atomically smooth. This high surface quality allows one to have a well-defined mean thickness for these films.

To examine ferroelectricity, we used an AFM equipped with a metallic tip. The experimental procedure was to start by applying a voltage between the tip and the metallic substrate to polarize a well-defined area, then we carried out piezoelectric microscopy[9,13] and electric-field microscopy (EFM)[14,15] to study the ferroelectric response of the material. In the piezoelectric technique, we measure the mechanical deformation along the (001) film direction that results from a voltage that is applied between the metallic AFM tip and the conducting Nb–STO substrate. To reduce the noise level, which is $\sim$0.03 pm for these experiments, an ac lock-in detection scheme is used, and, for the thinnest films, the signals were averaged over the written regions. In the EFM technique, we measure the residual surface charge of the ferro-

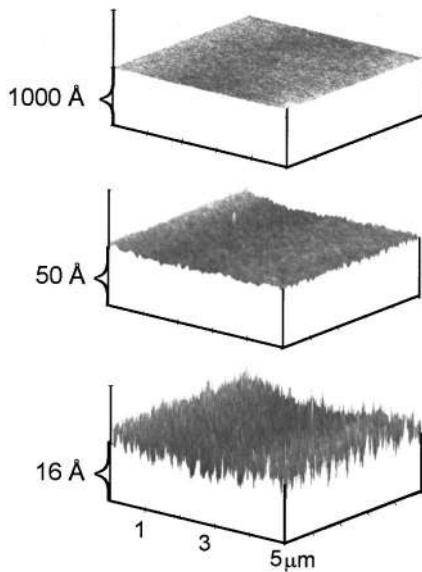[a)]Electronic mail: tybell@physics.unige.ch

FIG. 1. AFM topographic measurements of PZT film surfaces. The films, grown on (001) Nb–SrTiO$_3$ substrates, have thicknesses of 1000, 50, and 16 Å. For each sample, the z axis corresponds to the total film thickness.

electric by probing the electrostatic interaction between the metallic AFM tip and the charge distribution on the ferroelectric surface. By following the time dependence of the signals, one can rule out spurious influences due to simple electrostatic charging, as described below.

As a reference experiment, we first measured an 800-Å-thick film. Figure 2(a) shows a piezoelectric image of the film surface. The film had an original homogeneous polarization (light gray in the figure), except for some small regions (dark in the figure) polarized oppositely. The line in the image was switched using the AFM. Figure 2(b) shows the same area after switching back a part of the line to the initial polarization state. Figure 3(a) shows the time evolution of the EFM and piezoelectric signals as a function of time, with the signals having been normalized to their values at $t=0$. As can be seen, the piezoelectric signal remains constant for times of up to 180 h, the longest time we measured, demonstrating that the film is ferroelectric with a stable domain structure. In contrast, we observe that the EFM signal decays with time; due to a screening of the surface charge density. We note that the measured surface charge density at $t=0$ is much smaller than the remnant polarization P_r, typically $<10^{-3}$ P_r, with a sign that corresponds to an over-
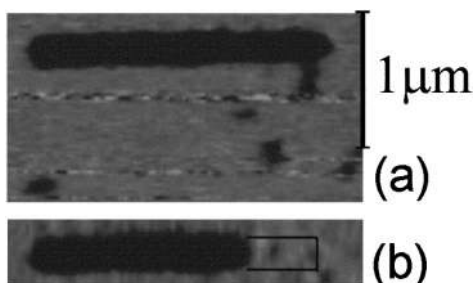

FIG. 2. Piezoelectric images of an 800 Å film surface. Originally, the polarization of the sample was uniform (light gray in the images) except for some regions [dark in (a)] polarized oppositely. In (a) a line region was switched from ''light to dark'' polarization. (b) Shows a zoom after switching back a part of the written line to its original polarization state.
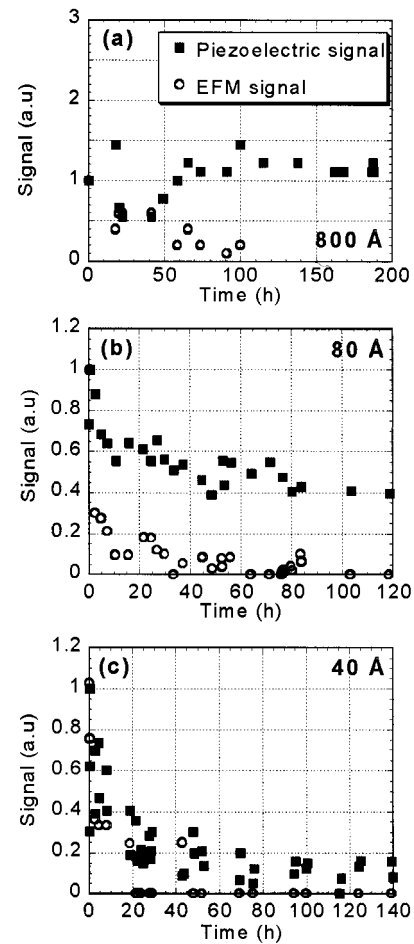

FIG. 3. Time dependencies of the EFM and piezoelectric signals measured on lines [as shown in Fig. 2(a)] on a: (a) 800-Å-thick film, (b) 80-Å-thick film, and (c) 40-Å-thick film. We notice that while the EFM signal goes to zero, the piezoelectric signal saturates at a nonzero level.

screening of the polarization.[16] This measurement reveals that the polarization field is essentially screened in our experimental conditions.

We next performed similar experiments on thinner films, with thicknesses 80 and 40 Å. Figures 3(b) and 3(c) show the time evolution of the EFM and piezoelectric signals for these films. The general trend of the data is similar to what is observed in Fig. 3(a) for the 800-Å-thick film: the piezoelectric signals saturate at nonzero levels, while the EFM signals go to zero. We note that for the 80-Å- and 40-Å-thick films, the piezoelectric signals decrease at the beginning of the measurements, which we tentatively attribute to an electrostatic coupling between the surface charge density and the tip. We believe the effect is more pronounced in these extremely thin films because the magnitude of the piezoelectric response, which scales with the film thickness, is correspondingly smaller in these very thin films. This electrostatic coupling shows that it is particularly important for these local probe studies to follow the time dependence of the signals, with particular attention to the fact that the piezoelectric signal must saturate at a nonzero level as the EFM signal goes to zero. We also remark on the magnitude of the signals we observe. The piezoelectric signal of the 40 Å film saturates at a level that is weaker than that of the 80 Å film, in qualitative agreement with the fact that the piezoelec-

modulation should decrease linearly with the film thickness. Here, however, it is difficult to quantify the absolute value of the piezoelectric response, since the measurement geometry and tip-to-tip variations make it difficult to determine accurately the magnitude of the voltage drop across the thin ferroelectric layer.[17]

Finally, we have also performed similar measurements on films with thicknesses down to 3 unit cells; for these films, however, the signal levels are comparable to the noise level of the measurement and do not allow one to draw definitive conclusions at this time.

In conclusion, we have demonstrated the growth of atomically smooth $Pb(Zr_{0.2}Ti_{0.8})O_3$ films down to thicknesses of 16 Å using off-axis rf magnetron sputtering. Through a combination of techniques, EFM and piezoelectric microscopy, and the investigation of the time dependence of these measurements, we have studied the ferroelectric properties of these films. These results are particularly striking for 40-Å-thick films, where the measurements show that a ferroelectric state is stable for over ~140 h, the duration of these measurements, in accord with recent calculations that predict ferroelectricity down to monolayer thicknesses.[4]

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[12] The LEED measurements were performed after heating the sample to ~300 °C in an oxygen atmosphere. A part of the sample, masked during the deposition, revealed the underlying $Nb–SrTiO_3$ substrate, allowing us to confirm the epitaxy.

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