Wedgelike ultrathin epitaxial $BaTiO_3$ films for studies of scaling effects in ferroelectrics

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(Received 24 June 2008; accepted 29 July 2008; published online 18 August 2008)

To study ferroelectric size effects in heteroepitaxial $SrRuO_3/BaTiO_3/SrRuO_3$ capacitors, ultrathin $BaTiO_3$ layers were deposited in wedge form across $SrTiO_3$ substrates. The wedgelike films were fabricated by using either an off-center substrate-target geometry or via a moveable shutter during high-pressure sputter deposition. The crystallinity, composition, and surface roughness along wedgelike $BaTiO_3$ films were verified by x-ray diffraction, Rutherford backscattering spectrometry, and atomic force microscopy, respectively. The electrical measurements performed at 77 K showed that, despite progressive reduction in remanent polarization as the film thickness decreases even the 3.5-nm-thick $BaTiO_3$ film retains a large remanent polarization of 28 $\mu C/cm^2$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2972135]

The thickness limit for the existence of ferroelectricity in epitaxial films of complex oxides such as $BaTiO_3$ or $Pb(Zr_xTi_{1-x})O_3$ is extensively studied nowadays. The experimental and theoretical studies indicate that even ultrathin films containing only a few unit cells in the thickness direction may remain ferroelectric under appropriate electrical and mechanical boundary conditions.[1–3] In this letter, we present an experimental approach to investigate the scaling of the ferroelectric order parameter by sputtering wedgelike $BaTiO_3$ epitaxial films and fabricating nanoscale $SrRuO_3/BaTiO_3$(wedge)$/SrRuO_3$ capacitors. Our aim is to avoid possible run to run uncertainties and to prepare a large number of devices of varying thickness on a short time scale.

Wedgelike metal films have been applied to the study of giant magnetoresistance effects in metallic mutilayers and, more recently, the superconducting coupling in 0-π Josephson tunnel junctions.[4,5] There either elemental metals (e.g., Co, Fe, Cu, Au, etc.) or binary alloys (for example, Ni_xCu_{1-x} and Co_xFe_{1-x}) were deposited in a wedgelike form. Wedge-shaped MgO layers were grown by molecular beam epitaxy to study spin-dependent electron tunneling in Fe/MgO/Fe tunnel junctions.[6] For metal wedges, low roughness and a uniform composition were obtained along the wedge. We would like to point out that for a wedge-like film of a complex oxide, this task might be more challenging due to the multi-component character of the unit cell.

The $SrRuO_3/BaTiO_3/SrRuO_3$ heterostructures were grown *in situ* on $SrTiO_3$ using a high-pressure sputtering technique. More details regarding the growth method and the film characterization can be found in Refs. 7 and 8. The conductive $SrRuO_3$ layer was grown at a substrate temperature of 610 °C and an oxygen pressure of 3 mbar, while the $BaTiO_3$ films were deposited at 700 °C in 2.6 mbar pure oxygen atmosphere. The crystal structure of $BaTiO_3$ films was found to be tetragonal, with the fourfold symmetry axis orthogonal to the substrate surface. The "cube on cube" growth of such (001)-oriented films on the $SrRuO_3$-covered $SrTiO_3$ substrate was confirmed by φ-scans of the (101) reflection. Measurements of the lattice parameters showed that the $SrTiO_3$ substrate imposes a compressive in-plane strain on the $BaTiO_3$ films.[7,9,10] The films showed a rms roughness of 0.19 nm averaged over an area of 5×5 μm^2.

Next we used two different preparation methods to deposit a wedgelike $BaTiO_3$ layer on top of the $SrRuO_3$ electrode. In the first approach, the sputter target and the substrate were off-centered by several millimeters. The target was 50 mm in diameter, and the top face of our (001)-oriented $SrTiO_3$ substrates was 10×10 mm^2 in area. In the alternative approach, the linear movement of a motorized shutter during the deposition was used to obtain a wedge-shaped $BaTiO_3$ film. This shutter technique was employed in a combinatorial laser molecular beam epitaxy deposition system to prepare a gradient in composition of complex oxide films.[11] After the deposition of wedgelike $BaTiO_3$ film, either a homogeneous 20-nm-thick top $SrRuO_3$ electrode was deposited *in situ* for electrical measurements, or the $BaTiO_3$(wedge)$/SrRuO_3$ bilayer without top electrode was used to check the structural properties along the wedge. In the latter case, the thickness gradient, composition, and roughness were investigated by x-ray diffraction, Rutherford backscattering spectrometry (RBS), and atomic force microscopy, respectively.

In the case of off-center-deposited films, the thickness profile along the wedge was measured using synchrotron radiation at Hasylab (DESY). The beam width of 1 mm in combination with large flux resulted in a good lateral resolution of the thickness gradient measurements. The x-ray θ-2θ scan around the (100) peak for one position along the wedge is presented in Fig. 1(a), and the thickness profile and the out-of-plane lattice parameter extracted from these measurements are shown in the inset of Fig. 1(a). It can be seen that the film thickness has nearly linear dependence on the in-plane position. The out-of-plane lattice constant of the

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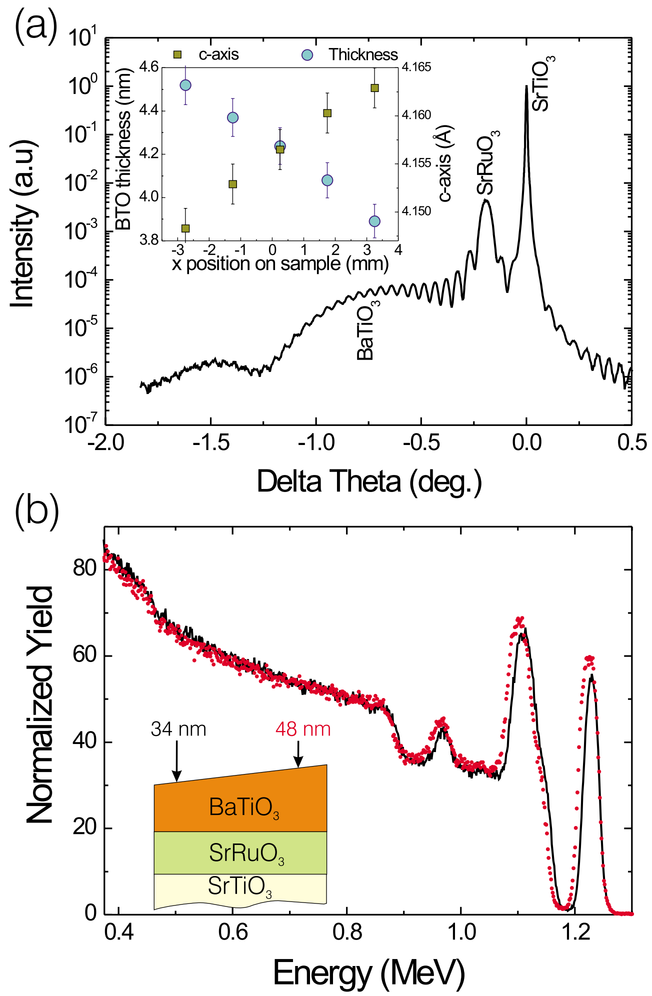

FIG. 1. (Color online) (a) X-ray synchrotron radiation measurements performed at Hasylab (DESY) for several positions along the wedgelike $BaTiO_3$ film. The inset shows the film thickness and the out-of-plane lattice parameter of the $BaTiO_3$ film as a function of position along the wedge. (b) RBS spectra of two representative sections of the wedgelike $BaTiO_3$ film demonstrating constant composition along the wedge.

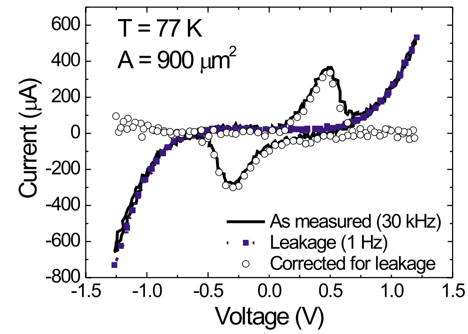

FIG. 2. (Color online) Current response of the 5.4-nm-thick ferroelectric $BaTiO_3$ capacitor with $SrRuO_3$ electrodes measured at 77 K. The black line shows the response measured at the excitation signal frequency of 30 kHz, whereas the square dots denote the current response measured at a frequency of 1 Hz. The circles show the difference between these two current-voltage curves, which represents the leakage-compensated current response. The area of the pad is $30 \times 30\ \mu m^2$.

$BaTiO_3$ film has a very slight increase in the thinner part of the wedge.

An important issue is to check whether the stoichiometry of the deposited films was preserved along the wedge. The composition of the $BaTiO_3$ film along the wedge was checked by RBS. To that end, we have chosen two sections of the sample, which are 6 mm apart and correspond to relatively thin (34 nm) and thick (48 nm) parts. The results of RBS measurements presented in Fig. 1(b) show that the Ba:Ti ratio remains unity within experimental error at these two thicknesses.

For electrical measurements, 17 groups of capacitors having various areas A ranging from 4×4 to $100 \times 100\ \mu m^2$ were fabricated using standard lithography and ion beam etching. These groups were distributed along the wedgelike film in the direction of the thickness gradient. The thickness of $BaTiO_3$ layer inside each group of capacitors was determined using the measured thickness profile. For the polarization-voltage hysteresis measurements presented in this work, we used capacitors with the area $A = 30 \times 30\ \mu m^2$.

A well known difficulty in measuring the polarization-voltage (P-V) loops for ultrathin ferroelectric films is the presence of large leakage currents which are superimposed on the displacement current. In order to reduce the leakage current, we performed the measurements of P-V loops at 77 K. These loops were recorded at a frequency of 30 kHz under an excitation signal of triangular shape using a TF Analyzer 2000 FE (aixACCT Systems). In Fig. 2, the current response of the 5.4-nm-thick $BaTiO_3$ capacitor is shown as a representative example (black solid line). The measured current is the sum of three contributions: the ferroelectric displacement current caused by the switching of the spontaneous polarization, leakage current, and dielectric displacement current. For the same set of capacitors, we measured the quasistatic current response at an excitation signal having a much lower frequency. The result obtained at 1 Hz for the 5.4-nm-thick $BaTiO_3$ capacitor is shown in Fig. 2 by square dots. Evidently, it corresponds to the leakage current contribution alone, since the displacement current can be neglected at such a low frequency. As can be seen from Fig. 2, the difference between the dynamic and quasistatic responses becomes very small at voltages above +0.7 and below −0.6 V, where the ferroelectric switching current vanishes. This feature indicates that the dielectric displacement current can be neglected in comparison with other contributions to the measured total current, which enables us to evaluate the ferroelectric switching current i_F as a difference between the currents measured at 30 kHz and 1 Hz. (This method, described in Ref. 12, is called the static leakage current compensation.) Thus determined switching current i_F is shown in Fig. 2 by circular dots. By integrating i_F over time we can further determine the switched charge $Q = \int_0^\tau i_F dt$ in the ferroelectric thin-film capacitor and evaluate the remanent polarization P_r via the standard relation $P_r = Q/(2A)$, where A is the capacitor area. The measured polarization P_r is shown in Fig. 3 as a function of the film thickness t. The magnitude of P_r decreases dramatically from about $43\ \mu C/cm^2$ at $t \cong 5.4$ nm down to $28\ \mu C/cm^2$ at $t \cong 3.5$ nm. The maximum remanent polarization in our wedgelike films agrees well with the values reported earlier for fully strained conventional $BaTiO_3$ films grown on $SrTiO_3$.[7,13] Remarkably, even at 3.5 nm thickness the $BaTiO_3$ film subjected to in-plane compressive strain remains ferroelectric and has a remanent polarization P_r larger than the spontaneous polarization $P_s = 26\ \mu C/cm^2$ of bulk $BaTiO_3$ at room temperature. This result supports the recent theoretical prediction[14] that the

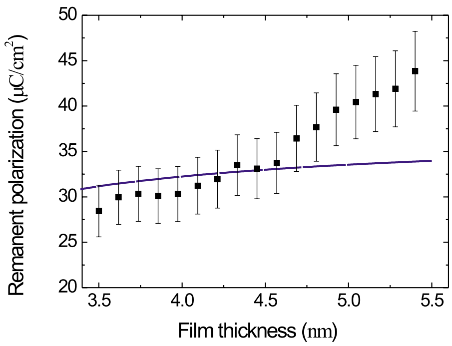

FIG. 3. (Color online) Thickness dependence of polarization in $SrRuO_3/BaTiO_3/SrRuO_3$ capacitors at 77 K. Squares show the remanent polarizations measured for an off-center-deposited wedgelike $BaTiO_3$ film. The solid line represents the theoretical dependence.

single-domain polarization state remains stable in $BaTiO_3$ films grown on $SrTiO_3$ down to very small thickness of a few nanometers. However, further scaling is needed to confirm that the critical film thickness is below 2.5 nm at 77 K, as calculated in Ref. 14.

The observed thickness dependence of P_r may be compared with the variation in spontaneous polarization P_s in $BaTiO_3$ capacitors predicted by the nonlinear thermodynamic theory.[14] Since in the studied thickness range $BaTiO_3$ films are fully strained by the thick $SrTiO_3$ substrate,[7] the polarization scaling results from the depolarizing-field effect governed by the total capacitance c_i of the screening space charge in the electrodes.[14] Taking $c_i=0.444\ \mathrm{F/m^2}$ (capacitor with two $SrRuO_3$ electrodes) and assuming the misfit strain to have the value of −2.6%, we calculated the dependence $P_s(t)$ at 77 K using the procedure described in Ref. 14, which employs the eight-order thermodynamic potential of barium titanate.[15,16] As is seen from Fig. 3, the thermodynamic theory correctly predicts a gradual reduction in polarization as the film thickness decreases, but underestimates the slope of this dependence. Stronger polarization scaling observed in $BaTiO_3$ capacitors may be due to the short-range interactions, which were not taken into account in the thermodynamic calculations.

In summary, ultrathin wedgelike $BaTiO_3$ films with constant composition along the wedge were produced for the study of size effects in ferroelectrics. By performing direct *P-V* measurements at 77 K, we found that the remanent polarization progressively reduces with decreasing thickness of the $BaTiO_3$ layer sandwiched between two $SrRuO_3$ electrodes. Nevertheless, the $BaTiO_3$ film grown on $SrTiO_3$ retains a large remanent polarization of 28 $\mu C/cm^2$ even at the thickness of 3.5 nm, which is well below the ferroelectric thickness limit of 5 nm confirmed earlier by direct *P-V* measurements.[13,17] The approach based on wedgelike films may be useful for the experimental studies of ferroelectric tunnel junctions,[18,19] as well as for the detection of the thickness limit for ferroelectricity and for the investigations of polarization retention in ferroelectric capacitors.

The authors wish to thank M. Hambe for helpful suggestions. The financial support of Hasylab through project II-05-079 and the Deutsche Forschungsgemeinschaft under Grant No. KL 1021/4-1 and the Volkswagen-Stiftung within the program "Complex Materials: Cooperative Projects of the Natural, Engineering, and Biosciences" under the project I/77 737 entitled "Nano-sized ferroelectric Hybrids" is gratefully acknowledged.

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