Structural Secrets of Multiferroic Interfaces

H. L. Meyerheim,[1,*] F. Klimenta,[1] A. Ernst,[1] K. Mohseni,[1] S. Ostanin,[1] M. Fechner,[1] S. Parihar,[1]
I. V. Maznichenko,[2] I. Mertig,[1,2] and J. Kirschner[1]
[1]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*
[2]*Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany*

(Received 2 October 2010; published 23 February 2011)

We present an experimental and theoretical study of the geometric structure of ultrathin $BaTiO_3$ films grown on Fe(001). Surface x-ray diffraction reveals that the films are terminated by a BaO layer, while the TiO_2 layer is next to the top Fe layer. Cations in termination layers have incomplete oxygen shells inducing strong vertical relaxations. Onset of polarization is observed at a minimum thickness of two unit cells. Our findings are supported by first-principles calculations providing a quantitative insight into the multiferroic properties on the atomic scale.

DOI: 10.1103/PhysRevLett.106.087203 PACS numbers: 68.35.Ct, 68.37.Ef, 73.20.At, 75.70.Rf

In recent time there has been a considerable amount of research activity that is directly aimed at controlling magnetism with electric fields. An attractive possibility is the one that involves the use of bulk multiferroics [1]. The obtained magnetoelectric coupling in complex multiferroic oxides is, however, weak [2].

An alternative but challenging approach is based on interfacial magnetoelectric coupling via multiferroic interfaces consisting of a ferroelectric (FE) and a ferromagnetic (FM) component. Indeed, theory has predicted the possibility of significant changes in the interfacial magnetization and spin polarization in a ferromagnet in response to the ferroelectric polarization state across the interface [3–5]. Control and manipulation of magnetism and spin polarization through interfacial magnetoelectric coupling has been clearly demonstrated by ferroelectric tunnel junctions with ferromagnetic leads [6]. A successful realization of ferroelectric control of spin polarization prepares the ground for the use of interface effects for low-power-consumption spintronic devices [7].

In this context, the $BaTiO_3/Fe(001)$ interface represents an archetype system in which the classical FE film is combined with the FM electrode in an almost perfect lattice match (misfit 1.4%). Surprisingly, current knowledge is limited to theoretical predictions, while quantitative information on growth, film, and interface structure is not available so far. This situation calls for a proof of principle that ferroelectric films can be grown epitaxially on a ferromagnetic substrate. Thorough analysis of the thickness-dependent geometric structure of the $BaTiO_3/Fe(001)$ epitaxial system is required.

In this study we elucidate several important structural properties of the $BaTiO_3/Fe(001)$ interface, which go far beyond current wisdom. In contrast to common assumptions we find that ultrathin $BaTiO_3$ films are characterized by the presence of complete unit cells terminated by a BaO layer, schematically written as: $(BaO\text{-}TiO_2)_m/Fe$. Furthermore, the FE film shows the Stranski-Krastanov growth mode in which after deposition of the first unit cell ($m = 1$), island growth is observed. The onset of polarization is characterized by the movement of the first Ti atom in the direction away from the Fe surface. It is observed for films with $m > 1$ only. Our experimental observations are interpreted in detail using first-principles calculations providing quantitative estimates of the multiferroic properties at this interface.

Surface x-ray diffraction (SXRD) experiments were carried out *in situ* in an ultrahigh vacuum x-ray diffractometer. The Fe(001) single crystal was cleaned by standard methods leading to a surface characterized by large terraces and almost free of contaminants. Using a KrF (248 nm) excimer laser, $BaTiO_3$ films were grown by pulsed laser deposition at room temperature followed by annealing for 10 min. at 600 °C. After this preparation a $c(2 \times 2)$ superstructure pattern with respect to the primitive Fe(001) surface unit cell was observed by low-energy electron diffraction and SXRD. The stoichiometry of the films was proven by Auger-electron spectroscopy and SXRD (vide infra). Several films were prepared in this way, whose coverage were 0.8, 1.6 and 2.7 monolayers (MLs). We refer to one ML as one complete unit cell composed of a TiO_2-BaO double layer. In the following we discuss samples characterized by film thicknesses of 1, 2, and 3 $BaTiO_3$ units cells, which are labeled as 1BTO, 2BTO, 3BTO, respectively.

A multilayer x-ray optics focused the x rays from a rotating anode generator (Co-$K\alpha$ radiation, $\lambda = 1.79$ Å) on the sample surface aligned for total reflection conditions of the incoming beam. Integrated intensities [$I(hkl)$] were collected by rotating the sample about its surface normal. The structure factor amplitudes ($|F(hkl)|$) are derived by applying instrumental correction factors to $I(hkl)$ [8].

Figure 1 shows the observed (symbols) and calculated (lines) structure factor amplitudes for 1,2, and 3BTO along q_z, the momentum transfer normal to the sample surface. Reflection indices are related to the primitive Fe(001)

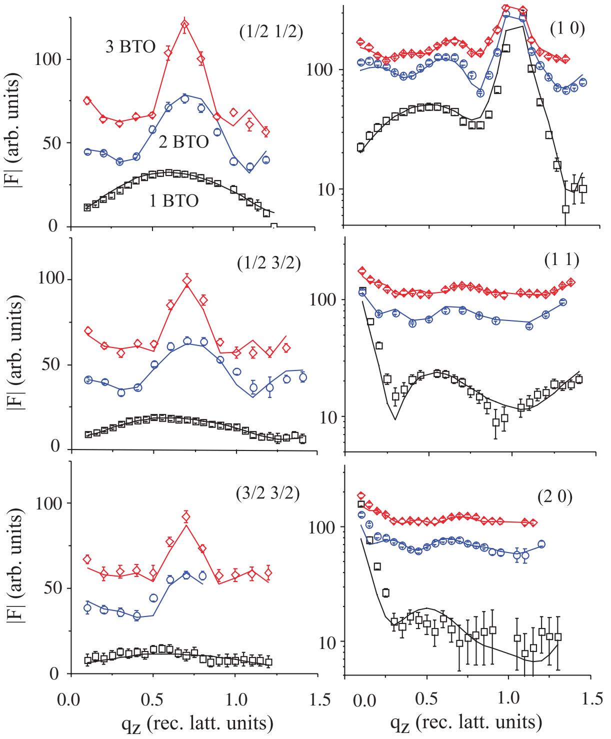

FIG. 1 (color). Experimental (symbols) and calculated (lines) structure factor amplitudes for 1BTO (black), 2BTO (blue) and 3BTO (red) films on Fe(001). Curves are shifted for clarity.

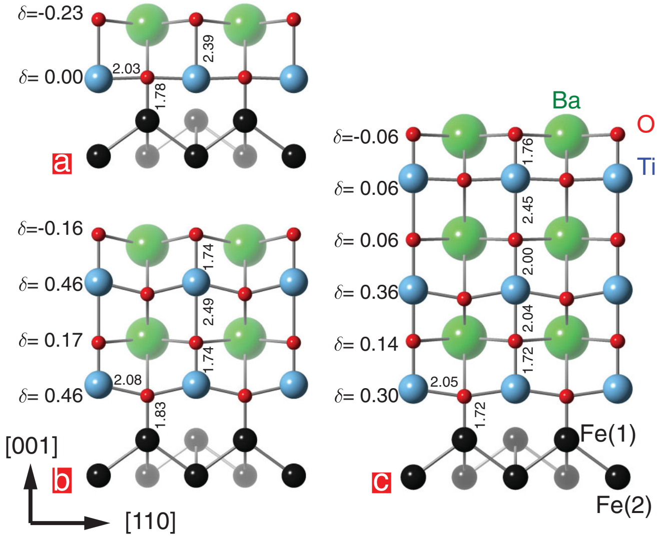

FIG. 2 (color). Model of the $BaTiO_3$/Fe(001) structure. (a)–(c) side view for films with 1, 2, and 3 unit cells of $BaTiO_3$. Red, green, blue and black spheres correspond to O, Ba, Ti and Fe atoms, respectively. Experimental distances and vertical displacements (δ) between oxygen and the Ti (Ba) atoms are given in angstrom units.

surface unit cell. Error bars represent the standard deviations (1σ) derived from the counting statistics and the reproducibility of symmetry equivalent reflections (≈ 5–10%). Clearly, increasing the film thickness leads to a more rapid intensity variation along q_z and to an overall intensity enhancement.

In general, the data sets consist of 100–150 symmetry independent reflections (plane group *p4mm*) along 3 fractional order rods (left) and three integer order crystal truncation rods (right, log-scale). Very good fits could be achieved quantified by the unweighted residuum (Ru) [9]. Excellent values in the range of $\text{Ru} = 0.10$–0.13 were obtained in general. Because of the high structural symmetry only the z coordinates of the atoms are free parameters, thereby limiting the number of fitting parameters to at most 12 in the case of 3BTO.

Figures 2(a)–2(c) show the refined $BaTiO_3$/Fe(001) interface structure in side view, for the 1BTO, 2BTO, 3BTO samples, respectively. Atomic species are represented by the different sizes and colors as labeled. The orientation relation between BTO and Fe(001) is characterized by $[110]_{\text{BTO}} \parallel [100]_{\text{Fe}}$ keeping the *p4mm* plane group symmetry as derived from the symmetry equivalence of the reflections. Several important results can be summarized: (i) Within the experimental accuracy of about 10 percentage points we find that layers are stoichiometric. Growth proceeds in the Stranski-Krastanov mode, i.e., after the completion of an (almost) filled first layer, subsequent layers form islands (not shown in detail in Fig. 2). (ii) All films are terminated by a BaO layer, while a TiO_2 layer is adjacent to the Fe(001) surface where the bonding is mediated between the O atoms atop of the Fe atoms. Although the latter has been theoretically predicted previously [3], model structures assuming a symmetric termination by TiO_2 layers on both sides of the magnetic tunnel junction can be ruled out. (iii) For the lowest coverage sample (1BTO) we determine $\delta_{(\text{Ti-O})} = 0$ and $\delta_{(\text{Ba-O})} = -0.23$ Å (the parameter δ defines the relative vertical displacement between the cation and the plane of oxygen atoms). Thus, the TiO_2 layer is flat within the experimental uncertainty $\Delta\delta \approx 0.10$ Å. The Ba atom is below the level of oxygen atoms ($\delta < 0$).

In clear contrast, for 2BTO we find a strong outward shift of the Ti atoms within the first and second unit cell given in both layers by $\delta_{(\text{Ti-O})1,2} = 0.46$ Å, which is considerably larger than in bulk $BaTiO_3$ (0.11 Å). This remarkable result represents a direct proof for the so far only theoretically predicted lower limit of $m = 2$ for the onset of the formation of an interface dipole [10]. There is also a positive shift of Ba in the first cell $\delta_{(\text{Ba-O})1} = 0.17$ Å, but a negative shift of Ba for the film-terminating BaO layer $[\delta_{(\text{Ba-O})2} = -0.16$ Å$]$ similar to 1BTO. The same trend is found in 3BTO, although the atomic displacements in the top unit cell are smaller as compared to 2BTO, which might be related to the partial coverage of the surface in this sample (2.7 MLs).

To gain further insight into the complex thickness-dependent structural details we have carried out first-principles simulations of the $BaTiO_3$/Fe(001) interface using the Vienna *ab initio* simulation package (VASP), well known for providing precise total energies and forces [11], and a self-consistent Korringa-Kohn-Rostoker Green function method specially designed to treat semi-infinite layered systems [12]. The calculations were performed within the density functional theory in the generalized gradient approximation [13].

To model the $BaTiO_3/Fe(001)$ biferroic system, within a slab geometry, we used the seven monolayer thick 2×2 supercell of Fe(001) (with the four Fe atoms per each monolayer) covered by the L-unit-cell thick $BaTiO_3(001) - c(2 \times 2)$ structure ($L = 1,2,3$). A 2-nm-vacuum layer separates the slabs along [001]. The in-plane Fe lattice parameter of the substrate was set to the experimental value. The two Fe MLs and all $BaTiO_3$ adlayers in this asymmetric slab were relaxed using the $6 \times 6 \times 4$ k point Monkhorst-Pack [14] mesh. The ionic relaxation was performed within the spin-polarized mode, starting from the ferromagnetic or, alternatively, from the antiferromagnetic configuration in the Fe layers, until the forces were less than 1.2×10^{-2} eV/Å. To calculate the electronic charge density as well as the local magnetic moments, we used the tetrahedron method with a k mesh of $12 \times 12 \times 8$ points for each completely relaxed atomic configuration.

The calculations confirm that the $TiO_2/Fe(001)$ interface configuration is energetically preferred by approximately 2 eV per unit cell over the BaO/Fe(001) interface. Oxygen atoms of the TiO_2 layer are located atop the Fe atoms forming a very strong chemical bond as is evident by the short Fe-O distances in the range between 1.78–1.83 Å. Similar values were recently found by SXRD for the Fe-O bonds in the $p(1 \times 1)$ structure of O/Fe(001) [15] and theoretically predicted for the multiferroic $Fe/BaTiO_3$ interface [4].

As a consequence of the $TiO_2/Fe(001)$ interface formation thin $BaTiO_3$ films on Fe(001) are always terminated by a BaO layer, since they grow in complete unit cells. Growth of complete cells is attributed to the requirement of charge neutrality throughout the whole film. Charge neutrality is also the driving force for the formation of atomic relaxations. The proof for this statement is seen in Fig. 3 showing the (normalized) calculated charge distribution for the 1BTO sample in the (010) plane for the shift kept fixed at $\delta = 0$ (left) and the experimentally obtained value of $\delta = -0.23$ Å (right), respectively. A flat isocharge surface is only achieved by inward relaxation of the large Ba atoms as experimentally observed. For the unrelaxed ($\delta = 0$) surface, however, the isocharge surface is not homogeneous and consequently not neutral.

The complex interface and surface geometry of thin $BaTiO_3$ films on Fe(001) as observed in our experiment can be linked to the presence of an incomplete oxide coordination around the cation at the oxide/Fe(001) interface and at the film surface. First layer Ti atoms have only five oxygen neighbors instead of six in the bulk. Similarly, Ba in the top BaO layer is surrounded by only eight oxygens (12 in the bulk). This induces strong atomic relaxations.

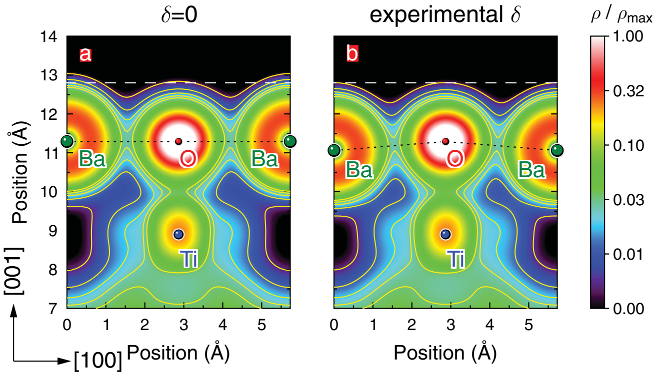

FIG. 3 (color). Calculated charge density of $BaTiO_3$ with unrelaxed atomic positions (left) and with experimentally obtained vertical atomic shift $\delta = -0.23$ Å (right). The flat isocharge surface (depolarization of the surface) is achieved by inward relaxation of the large Ba atom relative to oxygen.

The detailed structure of the BTO films is strongly influenced by two determining factors, namely, the strong bond between the O and the Fe atoms at the interface and the top BaO layer relaxation. In the 1BTO sample, the outward relaxation of the oxygen atom in the BaO layer leads to a large interlayer Ti-O distance (2.39 Å) corresponding to a weak interlayer Ti-O bond. The TiO_2 layer remains flat in which Ti atoms are in a fourfold planar environment with oxygen atoms located at a distance of 2.03 Å [see Fig. 2(a)].

The situation significantly changes beginning with 2BTO [Fig. 2(b)]. This is the thinnest film in which completely coordinated Ti (in the 2nd unit cell) and Ba (in the 1st unit cell) exist, which is linked to the onset of polarization. Values of δ become strongly positive except for the top BaO layer. This combination of relaxations results in a sequence of alternating vertical Ti-O distances (1.74, 2.49, 1.74 Å). In consequence, the film structure is composed of two $BaTiO_3$ unit cells, in which the $BaO\text{-}TiO_2$ bond within each unit cell is strong, but in which the bond between the unit cells is relatively weak. The trend is confirmed by the structure of the 3BTO sample [Fig. 2(c)].

The multiferroic interface properties were also investigated by calculating the dependence of the total energy change (ΔE) and the magnetic moments at the interface for different polarizations ($P\uparrow$, $P\downarrow$) as outlined in Fig. 4. The inset shows ΔE for $\delta_{(\text{Ti-O})1} = 0.30$ Å, 0.00 Å and -0.30 Å, corresponding to a simulated switching from $P\uparrow$ via $P = 0$ to $P\downarrow$ based on the experimentally derived atomic coordinates. Note, that simultaneously all other δ values were also inverted except that for the top BaO layer to preserve the surface charge neutrality. Displacements δ_i for $P\uparrow$ and $P\downarrow$ are shown for all atoms in Fig. 4 as blue triangles and squares, respectively.

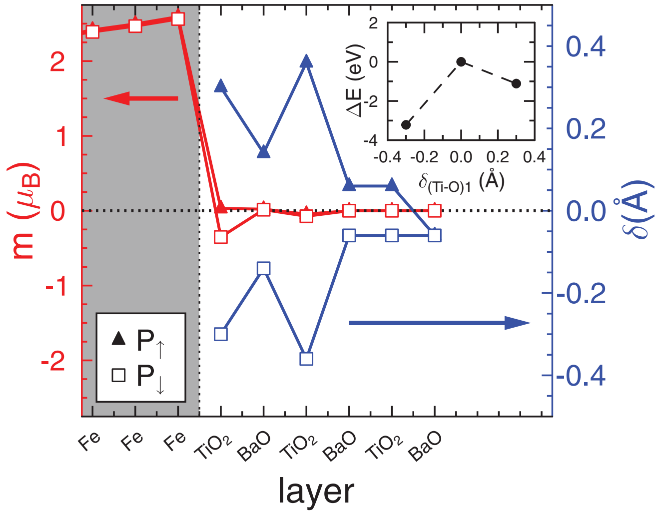

FIG. 4 (color). Calculated layer resolved magnetic moments (red symbols) and vertical displacements (blue symbols) for $P\uparrow$ (triangles) and $P\downarrow$ (squares) for 3BTO. The inset shows the change of total energy (ΔE) versus $\delta_{(\mathrm{Ti-O})1}$ (for details see text).

The simulation shows that besides the state $P\uparrow$ which is realized in our 3BTO sample there exists a state $P\downarrow$ which is even lower in energy by $\Delta E \approx 2$ eV than $P\uparrow$. The gain of energy can be related to the missing domain wall nearby the surface. Both states are lower in energy than the state with $P = 0$ which could be interpreted as a saddle point between $P\uparrow$ and $P\downarrow$ indicating the possibility of permanent switching of P. Moreover, we observe a change of the induced magnetic moment in the first layer Ti atom from $m_{\mathrm{Ti1}} = 0.03\ \mu_B$ for $P\uparrow$ to $m = -0.35\ \mu_B$ for $P\downarrow$. The magnetic moment of the surface Fe atoms is much less affected. We find $m_{\mathrm{Fe1}} = 2.59\ \mu_B$, and $m_{\mathrm{Fe1}} = 2.56\ \mu_B$ for $P\uparrow$ and $P\downarrow$, respectively.

Comparison with the previous theoretical models of Duan *et al.* [3] and Velev *et al.* [5] assuming a BTO film terminated by TiO_2 layers between Fe electrodes, our experimental data point to a larger polarization. For the 2BTO and 3BTO film the Ti-O displacements equal to $\delta = 0.30$–0.46 Å (see Fig. 2) as compared to values slightly below 0.1 Å in Refs. [3,5] for comparable film thicknesses. As a result of the larger distance of the Ti atom from the Fe surface we find that m_{Ti1} is almost quenched for $P\uparrow$ while it is $m = -0.18\ \mu_B$ in Ref. [3]. Also the polarization dependence is considerably larger ($\Delta\mu_{\mathrm{Ti}} = 0.38\ \mu_B$ versus $0.22\ \mu_B$ in Ref. [3]).

In conclusion, our quantitative structural analysis in combination with first-principles calculations has provided deep quantitative insight into the physical properties of the multiferroic $BaTiO_3$/Fe(001) interface. We find that $BaTiO_3$ films grow in complete unit cells and that the interface to the Fe(001) substrate is formed by a TiO_2 layer involving a BaO surface layer. Both termination layers contain cations with incomplete oxygen shells (fivefold versus sixfold Ti and eightfold versus twelvefold Ba) inducing strong vertical relaxations and causing a complex hierarchy of vertical interatomic distances. In the limit of only one unit cell film thickness the polarization in the TiO_2 layer is suppressed ($\delta = 0$).

Based on the quantitative atomic positions we have shown that the $BaTiO_3$/Fe(001) heterojunction is multiferroic in nature. We find a significant multiferroic effect as a result of the substantial polarizations as measured by the relative Ti-O displacements in the $\delta = 0.3$–0.4 Å range. A change in polarization from $P\uparrow$ to $P\downarrow$ goes in parallel with an energy gain of $\Delta E \approx 2$ eV via a barrier indicating the possibility of switching the polarization permanently. The induced magnetic moment in the first layer Ti atom increases from $m_{\mathrm{Ti1}} = +0.03\ \mu_B$ to $m_{\mathrm{Ti1}} = -0.35\ \mu_B$, in the latter case corresponding to antiferromagnetic coupling. The results open a pathway to the experimental realization of magnetoelectric coupling via multiferroic interfaces, a new tool to control magnetism by electric fields.

We thank F. Weiss for technical support. This work is supported by the DFG through SFB 762.

---

*hmeyerhm@mpi-halle.mpg.de

[1] T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature (London) **430**, 541 (2004).
[2] N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[3] C.-G. Duan, S. S. Jaswal, and E. Y. Tsymbal, Phys. Rev. Lett. **97**, 047201 (2006).
[4] M. Fechner, I. V. Maznichenko, S. Ostanin, A. Ernst, J. Henk, P. Bruno, and I. Mertig, Phys. Rev. B **78**, 212406 (2008).
[5] J. P. Velev, C.-G. Duan, K. D. Belashenko, S. S. Jaswal, and E. Y. Tsymbal, J. Appl. Phys. **103**, 07A701 (2008).
[6] V. Garcia, M. Bibes, L. Bocher, S. Valencia, F. Kronast, A. Crassous, X. Moya, S. Enouz-Vedrenne, A. Gloter, and D. Imhoff *et al.*, Science **327**, 1106 (2010).
[7] R. Ramesh, Nature Mater. **9**, 380 (2010).
[8] E. Vlieg, J. Appl. Crystallogr. **30**, 532 (1997).
[9] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).
[10] C.-G. Duan, R. F. Sabirianov, W.-M. Mei, S. S. Jaswal, and E. Y. Tsymbal, Nano Lett. **6**, 483 (2006).
[11] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
[12] M. Lüders, A. Ernst, W. M. Temmermann, Z. Szotek, and P. J. Durham, J. Phys. Condens. Matter **13**, 8587 (2001).
[13] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[15] S. S. Parihar, H. L. Meyerheim, K. Mohseni, S. Ostanin, A. Ernst, N. Jedrecy, R. Felici, and J. Kirschner, Phys. Rev. B **81**, 075428 (2010).