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Interface control of ferroelectricity in a full oxide capacitor toward ultrathin limit

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Atomic-scale synthesis of artificial oxide heterostructures offers new opportunities to create novel states that do not exist in nature. The main challenge is to obtain a correct sequence of atomic layers with proper precision, which warrants the desirable abrupt interface. Here, we demonstrate synergetic experimental and theoretical approaches to attaining abrupt oxide interfaces by tuning a key thermodynamic parameter. We fabricated prototypical full oxide ferroelectric $SrRuO_3/BaTiO_3/SrRuO_3$ (SRO/BTO/SRO) capacitors by pulsed laser deposition (PLD). Contrary to the commonly assumed *unit-cell-by-unit cell* growth, the top interface of the BTO layer usually has a mixture of BaO and TiO_2 terminations. Using the first principle calculations, we examined thermodynamic stability of different surface terminations of BTO. Accordingly, by tuning oxygen partial pressure, we realized abrupt BTO top interface with TiO_2 termination. The interface-controlled BTO exhibits a robust ferroelectricity down to 2.5 unit cells (u.c.) thickness— a theoretical limit that to date remains experimentally elusive.

During the last few decades, atomic-scale oxide engineering has advanced significantly. There are important developments, including PLD with *in-situ* reflection high energy electron diffraction (RHEED) and the numerous computation methods, such as the first-principles calculations.[1–5] These advancements opened doors to design new classes of oxide heterostructures and have paved ways to explore novel emerging phenomena.[6–10] The illustrative examples include two-dimensional electron gas in the insulating systems,[11–13] interface superconductivity,[14,15] topological effects,[16] magneto-electric coupling,[17,18] and ferroelectric polar vortices.[19] Such emerging properties, discovered through materials-by-design, stem from abrupt interfaces with an appropriate sequence of atomic layers.[9,20]

However, the task of creating desirable interface structures through atomic control is still challenging, even for simple perovskite oxides. To form an abrupt interface, a high temperature growth is usually required to obtain sufficient adatom mobility.[21] But it simultaneously can induce entropy-driven disordered structures, e.g., anion/cation vacancies,

inter-diffused interfaces or other complex phases.[22] Most oxide fabrication techniques, such as PLD and sputtering, cannot control individual constituent elements, making it difficult to determine the exact termination. Even with reactive molecular beam epitaxy, where individual constituents can be controlled, the intended atomic stacking sequence are often not consistent with the actual layering sequence.[23,24] In addition, there have been many reports on surface reconstructions,** which will hinder securing abrupt interfaces.

We will focus on ferroelectric (FE) heterostructure as an ideal platform to explore the importance of thermodynamic parameters for obtaining correct interface terminations. Since FE properties strongly depend on local charge distributions,[25,26] they are significantly affected by interface details, including polarization screening,[27] chemical bonding,[5,28] and ferrodistortive cation off-centering.[29] Among such complicated issues, the simplest yet very important issue is the critical thickness, at which ferroelectricity of a single FE layer becomes unstable. For a $PbTiO_3$ film, it was experimentally confirmed by X-ray scattering that the FE layer could be stable down to 3 u.c.[30] However, in real FE capacitor capped between two metallic electrodes, such a small FE critical thickness value has not yet been confirmed as conclusive. Recent studies on SRO/BTO/SRO capacitors showed that, when the SRO/BTO interface had mixed terminations, pinning dipoles were made and their critical thickness could become about 20 u.c. or above.[25] This value is much larger than other theoretical predictions with ideal interfaces (usually 2.5 – 6.5 u.c.,[27,31]), pointing to the importance of the abrupt interface in the FE heterostructures. Here, we perform synergetic experimental and theoretical investigations on how a thermodynamic parameter can affect microscopic interfacial properties and resulting macroscopic functionalities.

Let us think about a prototypical all oxide SRO/BTO/SRO heterostructure. As illustrated in **Scheme 1**, there are two kinds of atomic layers for BTO termination, i.e. BaO or TiO_2. Since RuO_2 are thermally unstable during deposition, the bottom SRO layer always have the SrO termination,[32] thereby the BTO layer will start with TiO_2 layer. With the

commonly assumed *unit-cell by unit-cell growth* mode, the growth of the BTO layer should end with top BaO termination. Then the top interface should have BaO-RuO_2 sequence, which makes the capacitor configuration asymmetric (right side of Scheme 1). On the other hand, many calculations of the FE critical thickness were performed on the symmetric configuration with TiO_2 terminations for both top and bottom BTO surfaces (left side).[27,31]

The fully-strained SRO/BTO/SRO heterostructures were fabricated by PLD on atomically smooth TiO_2-terminated $SrTiO_3$(001) substrates. The thicknesses of bottom and top SRO electrodes were fixed at 20 nm. During the BTO film growth, the oxygen partial pressure (P_{O2}) was set at 5 mTorr or 150 mTorr. The BTO film thicknesses (t_{BTO}) were controlled by observing the high pressure RHEED intensity oscillations. In the ideal layer-by-layer growth mode, the number (n) of the RHEED oscillations signified a BTO layer with t_{BTO} = n u.c.. However, we found that relative instability of the BaO surface at 5 mTorr could induce a half-unit-cell BTO layer (details are described in Figures S1 and S2 in *Supporting Information*). In this case, we denote the film thickness by t_{BTO} = (n-0.5) u.c..

When the BTO layer was grown at P_{O2} = 150 mTorr, two kinds of interfaces coexist at the top SRO/BTO interface. Using the scanning transmission electron microscope (STEM), we probed their atomic structure. **Figure 1**a shows the cross-sectional high-angle annular dark field (HAADF) image, viewed along [100] zone axis. It always displays an atomically sharp BTO/SRO bottom interface only with SrO-TiO_2 interface. On the contrary, SRO/BTO top interface becomes highly inhomogeneous, as displayed in the dashed squares. In Figure 1b and 1c, we present the magnified HAADF images and intensity profiles along the *B*-site cations, respectively. Note that the intensity of Ti peaks is lower than those of Ru peaks due to the smaller atomic number. Four (three) TiO_2 layers imply that the BTO film thickness is 3.5 u.c. (3 u.c.). The resulting SrO-TiO_2 (RuO_2-BaO) interface will make the corresponding capacitor configuration symmetric (asymmetric). The mixed BTO termination was confirmed repeatedly in the other regions (details are described in Figures S3 in *Supporting Information*).

Due to the mixed termination, local FE responses varied significantly. Using lithography techniques, we fabricated capacitors with diameters of 500 nm (see the Experimental Section). We measured their FE polarization hysteresis loops by using piezoresponse force microscopy (PFM).[33] For some capacitors, PFM signals indicate a normal ferroelectric switching. Namely, the curve has ~180° of phase difference and a clear butterfly-shaped amplitude loop (Figure 1d). The effective piezo-response (PR) also shows a clear FE-like hysteresis loop (Figure 1f). In other capacitors, FE polarizations become strongly pinned along one direction. Namely, the amplitude and phase loops show the clear signals only for upward polarization direction (Figure 1e). The PR loop clearly indicates a pinned polarization state, which suppresses the loop and moves it downward (Figure 1f). The existence of mixed BTO termination and the large fluctuation of locally pinned FE switching behavior tellingly implies a close relationship between interface termination and ferroelectricity.[25,26]

To obtain further insights on growth conditions, we investigated how thermodynamic parameters can affect stability of BTO surface theoretically.[34,35] We performed first-principles density-functional-theory (DFT) calculations on surface Gibbs free energies of BaO- and TiO_2-terminated surfaces (see details in Section III, Supporting Information). Since we were comparing the relative stabilities of simple BaO- and TiO_2-terminated surfaces, we did not consider nonstoichiometric surface reconstructions, such as (2 × 1) and ($\sqrt{5} \times \sqrt{5}$)*R*26.6°.[34] **Figure 2**a illustrates a phase diagram of stable termination surfaces under $\Delta\mu_{Ba}$ and $\Delta\mu_O$, which are Ba- and O-chemical potentials, respectively. The region surrounded by the dashed (solid) line indicates the stability region of a homogeneous phase at 0 K (1000 K). Outside the region, secondary phases, such as BaO_2 and Ti_2O_3, will be formed. At 0 K, the BaO-terminated surface has a lower Gibbs free energy. As temperature increases, the stability region moves left and enters into the TiO_2-termination region. At 1000

K, close to our film growth temperature, both surfaces with TiO_2- or BaO-termination could be possible (Figure 2b), but the stability region for BaO-termination is quite narrow (Figure 2a). It has been widely accepted, based on the *unit-cell by unit-cell growth* model, that a BTO film on SrO-terminated SRO layer should have a BaO-terminated surface. However, our calculations indicate that a perfect BaO-terminated surface is very difficult to obtain around 1000 K.

Therefore, to obtain an abrupt top interface in the SRO/BTO/SRO heterostructure, it would be more plausible to search for the top TiO_2 termination for BTO. By using STEM and supporting X-ray results (see Figrue S1 in Supporting Information), we confirmed that there was no secondary phase formation. As suggested in Figure 2b, our growth condition (i.e. P_{O2} = 150 mTorr) for mixed terminations would be quite close to the thermodynamic boundary between TiO_2- and BaO-terminations. The bar under Figure 2b shows how P_{O2} can vary $\Delta\mu_O$. With decreasing P_{O2}, $\Delta\mu_O$ becomes more negative. It thus enters deeply into the stability region of TiO_2-termination. Based on this theoretical guideline, we fabricated the FE heterostructures using lower P_{O2} (i.e = 5 mTorr).

The heterostructure grown at P_{O2} = 5 mTorr has an abrupt BTO top interface and the symmetric capacitor configuration (shown in Scheme 1, left side). **Figure 3**a and 3b show high-resolution HAADF images of the heterostructure grown at P_{O2} = 5 mTorr. Contrary to Figure 1a, these STEM images show atomically abrupt interfaces along the lateral dimension over 50 nm. The BTO layer has TiO_2 terminations for both top and bottom interfaces. The intensity profile along the solid box in Figure 3b also confirms the symmetric SrO-TiO_2 interface termination sequences (Figure 3c). As a result, the heterostructure attains t_{BTO} = 3.5 u.c., as emphasized in enlarged image in Figure 3d.

The uniformness of the BTO interfaces was further confirmed by surface X-ray scattering studies that we conducted. Since the STEM provides information only in a local region, we performed the X-ray scattering measurements and coherent Bragg rod analysis

(COBRA). We used a heterostructure with 3 u.c. of SRO top and bottom electrodes and 3.5 u.c. of BTO film, grown with P_{O2} = 5 mTorr. The COBRA electron density mapping (Figure 3e) tells us that the symmetric SrO-TiO_2 interface terminations can exist uniformly at least in the length scale of ~30 μm (i.e. size of X-ray beam spot).

Our BTO capacitors with symmetric interfaces have FE critical thickness of 2.5 u.c.. **Figures 4**a and 4b displays STEM images of symmetric capacitors with t_{BTO} = 3.5 and 2.5 u.c., respectively. Using PFM, we obtained clear FE-like hysteresis curves in forty BTO capacitors with t_{BTO} = 3.5 u.c.. A representative PFM result shows a symmetric butter-fly-shaped amplitude hysteresis and a phase loop with ~180° of difference (Figure 4c). For BTO capacitors thicker than 3.5 u.c., we also observed similar PFM signals. To exclude extrinsic effects, such as surface charging or oxygen reactions under the probe tip, we also measured coercive voltage-dependence of the PFM signals with *ac* voltage-modulation.[36–38] Our study also confirmed that the PFM signals should originate from the intrinsic FE properties (See experimental details in Section V, Supporting Information). The FE signatures disappear for BTO capacitors with t_{BTO} = 2.5 u.c. (Figure 4d). This critical thickness value agrees well with the earlier DFT calculations by G. Gera *et al*.,[27] and its smallness also indicates that our BTO capacitors should have little electrostatic surface instability.

The stability of oxide termination layer is much more sensitive to thermodynamic parameters than that of the bulk counterpart. During the film growth, its surface is always open to chemical environment. Numerous nonstoichiometric structures are also easy to be formed depending on temperature and oxygen pressure.[35] However, up to this point, most thermodynamic stability studies on complex oxide heterostructures has focused on bulk materials,[39] not on their termination layers. Most significantly, our simple synergic theoretical and experimental approach of tuning thermodynamic parameters can be used to secure correct stoichiometric surface terminations for abrupt oxide interfaces.

In summary, we pioneered a new approach to manipulating interface structures of SRO/BTO/SRO heterostructures *via* controlling a thermodynamic parameter. To uncover the critical thickness of the ferroelectric BTO layers, we realize the symmetric interface with abrupt TiO_2 termination samples proposed by materials-by-design. We succeeded at proving the theoretically predicted thickness by the charge distribution effect at the interface beyond the Thomas-Fermi capacitor[27]; namely, the critical thickness in the real capacitor geometry is decreased to 2.5 unit cells. Our research suggests that the atomic control will serve as a useful tool to exploring emergent properties of oxide heterostructures and functional devices.

Experimental

Film fabrication: The SRO/BTO/SRO heterostructure were grown *in-situ* using PLD technique onto $SrTiO_3$ (001) substrates with miscut less than 0.1°. Commercial stoichiometric BTO and SRO ceramic target (Shinkosha Co., Ltd.) were used. KrF excimer laser (248 nm, COMPex pro, Coherent) was used for ablating SRO or BTO ceramic targets. Deposition temperature was kept in 700℃ during whole growth. High quality ultrathin BTO epitaxial films with 5 mTorr and 150 mTorr of P_{O2} conditions were grown. The thicknesses of both SRO layers were 20 nm. For electrical measurements of the BTO layer, capacitor devices with diameter form 500 nm to 10 μm were fabricated using the e-beam lithography and ionic milling.

PFM measurements: The ferroelectric polarization switching properties were measured using atomic force microscopy (AFM) machine, Cypher (Asylum), at room temperature. Commercially available Cr/Pt coated probe tip with ~40N/m of spring constant and with ~400 kHz of resonance frequency (Tap300E, Budget Sensors) was. The contact resonance frequency was found to be at 1.2 – 1.3 MHz. The high spring constant and contact resonance frequency will minimize the possible effects from non-piezoelectric response, such as

electrostatic force.[38,40] The effective piezoresponse were obtained by convoluting PFM amplitude and phase, namely $A*\cos(\theta+\phi)$. A is the PFM amplitude, θ is the PFM phase and ϕ is the additional phase offset, which come from the instrumental circumstances. Note that ϕ values were adjusted to make total phase located between 0^{o} and 180^{o}. Most of the PFM data showed 180^{o} phase difference between maximum and minimum signals, so that the choice of ϕ did not affect our argument.

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[1] J. M. Rondinelli, N. A. Spaldin, *Adv. Mater.* **2011**, *23*, 3363.
[2] J. M. Rondinelli, N. A. Spaldin, *Phys. Rev. B* **2010**, *82*, 1.
[3] J. He, A. Borisevich, S. V. Kalinin, S. J. Pennycook, S. T. Pantelides, *Phys. Rev. Lett.* **2010**, *105*, 227203.
[4] M. Stengel, N. A. Spaldin, *Nature* **2006**, *443*, 679.
[5] M. Stengel, D. Vanderbilt, N. A. Spaldin, *Nat Mater* **2009**, *8*, 392.
[6] N. Feature, *Nature* **2009**, *459*, 28.
[7] J. Mannhart, D. G. Schlom, *Science* **2010**, *327*, 1607.
[8] P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, J.-M. Triscone, *Annu. Rev. Condens. Matter Phys.* **2011**, *2*, 141.
[9] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, Y. Tokura, *Nat Mater* **2012**, *11*, 103.
[10] J. Chakhalian, A. J. Millis, J. Rondinelli, *Nat Mater* **2012**, *11*, 92.
[11] A. Ohtomo, H. Y. Hwang, *Nature* **2004**, *427*, 423.
[12] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, S. V Kalinin, *Science* **2009**, *324*, 1421.
[13] V. Garcia, S. Fusil, K. Bouzehouane, S. Enouz-Vedrenne, N. D. Mathur, a Barthélémy, M. Bibes, *Nature* **2009**, *460*, 81.
[14] N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, J. Mannhart, *Science* **2007**, *317*, 1196.
[15] Y. Kozuka, M. Kim, C. Bell, B. G. Kim, Y. Hikita, H. Y. Hwang, *Nature* **2009**, *462*, 487.
[16] D. Doennig, W. E. Pickett, R. Pentcheva, *Phys. Rev. B* **2014**, *89*, 121110.
[17] S. M. Wu, S. A. Cybart, P. Yu, M. D. Rossell, J. X. Zhang, R. Ramesh, R. C. Dynes, *Nat. Mater.* **2010**, *9*, 756.

[18] V. Garcia, M. Bibes, L. Bocher, S. Valencia, F. Kronast, A. Crassous, X. Moya, S. Enouz-Vedrenne, A. Gloter, D. Imhoff, C. Deranlot, N. D. Mathur, S. Fusil, K. Bouzehouane, A. Barthélémy, *Science* **2010**, *327*, 1106.
[19] A. K. Yadav, C. T. Nelson, S. L. Hsu, Z. Hong, J. D. Clarkson, C. M. Schlepütz, A. R. Damodaran, P. Shafer, E. Arenholz, L. R. Dedon, D. Chen, A. Vishwanath, A. M. Minor, L. Q. Chen, J. F. Scott, L. W. Martin, R. Ramesh, *Nature* **2016**, *530*, 198.
[20] N. Nakagawa, H. Y. Hwang, D. A. Muller, *Nat. Mater.* **2006**, *5*, 204.
[21] C.-H. Lee, N. D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J. A. Mundy, L. F. Kourkoutis, Y. Nie, M. D. Biegalski, J. Zhang, M. Bernhagen, N. A. Benedek, Y. Kim, J. D. Brock, R. Uecker, X. X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D. A. Muller, I. Takeuchi, J. C. Booth, C. J. Fennie, D. G. Schlom, *Nature* **2013**, *502*, 532.
[22] W. S. Choi, C. M. Rouleau, S. S. A. Seo, Z. Luo, H. Zhou, T. T. Fister, J. A. Eastman, P. H. Fuoss, D. D. Fong, J. Z. Tischler, G. Eres, M. F. Chisholm, H. N. Lee, *Adv. Mater.* **2012**, *24*, 6423.
[23] J. H. Lee, G. Luo, I. C. Tung, S. H. Chang, Z. Luo, M. Malshe, M. Gadre, A. Bhattacharya, S. M. Nakhmanson, J. A. Eastman, H. Hong, J. Jellinek, D. Morgan, D. D. Fong, J. W. Freeland, *Nat. Mater.* **2014**, *13*, 879.
[24] Y. F. Nie, Y. Zhu, C.-H. Lee, L. F. Kourkoutis, J. a. Mundy, J. Junquera, P. Ghosez, D. J. Baek, S. Sung, X. X. Xi, K. M. Shen, D. a. Muller, D. G. Schlom, *Nat. Commun.* **2014**, *5*, 4530.
[25] H. Lu, X. Liu, J. D. Burton, C. W. Bark, Y. Wang, Y. Zhang, D. J. Kim, A. Stamm, P. Lukashev, D. A. Felker, C. M. Folkman, P. Gao, M. S. Rzchowski, X. Q. Pan, C. B. Eom, E. Y. Tsymbal, A. Gruverman, *Adv. Mater.* **2012**, *24*, 1209.
[26] X. Liu, Y. Wang, P. V. Lukashev, J. D. Burton, E. Y. Tsymbal, *Phys. Rev. B* **2012**, *85*, 1.
[27] G. Gerra, a. Tagantsev, N. Setter, K. Parlinski, *Phys. Rev. Lett.* **2006**, *96*, 107603.
[28] C. G. Duan, R. F. Sabirianov, W. N. Mei, S. S. Jaswal, E. Y. Tsymbal, *Nano Lett.* **2006**, *6*, 483.
[29] J. M. Pruneda, V. Ferrari, R. Rurali, P. B. Littlewood, N. A. Spaldin, E. Artacho, *Phys. Rev. Lett.* **2007**, *99*, 1.
[30] D. D. Fong, *Science* **2004**, *304*, 1650.
[31] J. Junquera, P. Ghosez, *Nature* **2003**, *422*, 506.
[32] G. Rijnders, D. H. A. Blank, J. Choi, C.-B. Eom, *Appl. Phys. Lett.* **2004**, *84*, 505.
[33] S. Jesse, A. P. Baddorf, S. V. Kalinin, *Appl. Phys. Lett.* **2006**, *88*, 21.
[34] A. M. Kolpak, D. Li, R. Shao, A. M. Rappe, D. a. Bonnell, *Phys. Rev. Lett.* **2008**, *101*, 1.
[35] W. A. Saidi, J. M. P. Martirez, A. M. Rappe, *Nano Lett.* **2014**, *14*, 6711.
[36] M. Andrä, F. Gunkel, C. Bäumer, C. Xu, R. Dittmann, R. Waser, *Nanoscale* **2015**, *7*, 14351.
[37] E. Strelcov, Y. Kim, J. C. Yang, Y. H. Chu, P. Yu, X. Lu, S. Jesse, S. V. Kalinin, *Appl. Phys. Lett.* **2012**, *101*, DOI 10.1063/1.4764939.
[38] N. Balke, P. Maksymovych, S. Jesse, A. Herklotz, A. Tselev, C. Eom, I. I. Kravchenko, P. Yu, S. V Kalinin, *ACS Nano* **2015**, *9*, 6484.
[39] J. H. Song, T. Susaki, H. Y. Hwang, *Adv. Mater.* **2008**, *20*, 2528.
[40] S. Jesse, A. P. Baddorf, S. V Kalinin, *Nanotechnology* **2006**, *17*, 1615.