

## Supporting Information for

### “Oxygen Partial Pressure during Pulsed Laser Deposition: Deterministic Role on Thermodynamic Stability of Atomic Termination Sequence at SrRuO<sub>3</sub>/BaTiO<sub>3</sub> Interface”

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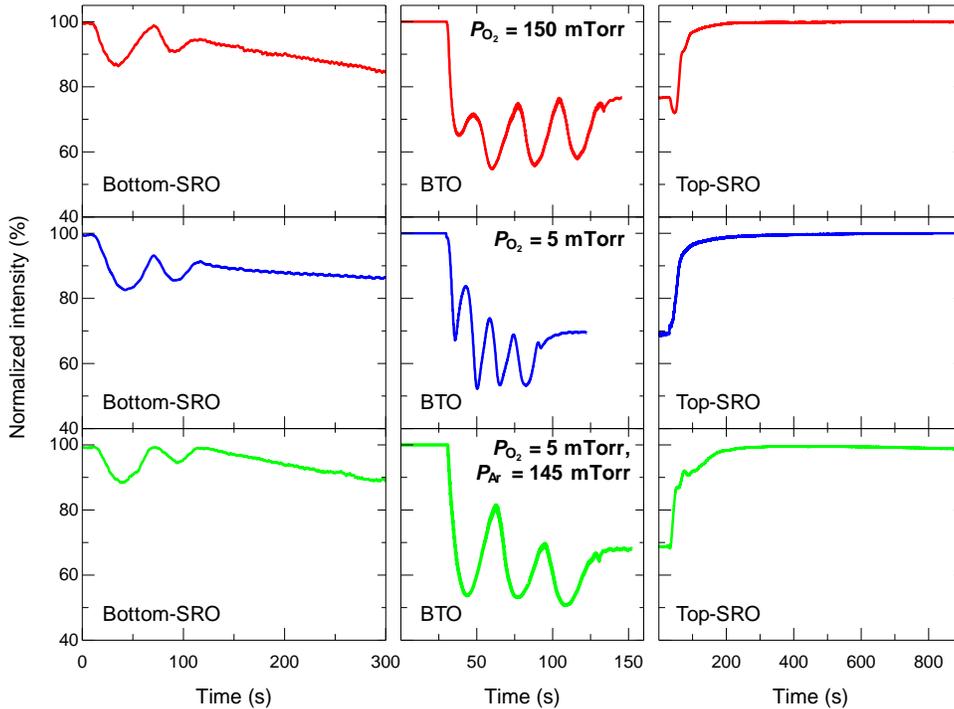
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## I. RHEED monitoring of the SRO/BTO/SRO heterostructure growths.



**Figure S1.** Time-dependent reflection high-energy electron diffraction (RHEED) intensity profiles of the specular spot during SrRuO<sub>3</sub>/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> (SRO/BTO/SRO) growths under  $P_{O_2} = 150$  mTorr (red),  $P_{O_2} = 5$  mTorr (blue), and O<sub>2</sub>/Ar mixed atmosphere (green).

The growths of SrRuO<sub>3</sub>/BaTiO<sub>3</sub>/SrRuO<sub>3</sub> (SRO/BTO/SRO) heterostructures were monitored by using *in situ* reflective high-energy electron diffraction (RHEED). **Figure S1** shows the intensity profiles of a specular spot of RHEED during the growths of bottom-SRO, BTO, and top-SRO layers. The BTO layers were grown under three total background gas pressure ( $P_{total}$ ) and oxygen partial pressure ( $P_{O_2}$ ) conditions; 1) a pure oxygen atmosphere with  $P_{total} = P_{O_2} = 5$  mTorr (upper), 2) a pure oxygen atmosphere with  $P_{total} = P_{O_2} = 150$  mTorr (middle), and 3) an argon and oxygen (O<sub>2</sub>/Ar) mixed atmosphere with  $P_{O_2} = 5$  mTorr and  $P_{total} = 150$  mTorr (lower). The background atmospheres for bottom- and top-SRO layers were fixed to  $P_{total} = P_{O_2} = 100$  mTorr. The bottom SRO layers show a standard growth mode tradition from layer-by-layer mode

to step-flow growth mode at first few layers.<sup>1</sup> Please note that the slight intensity decrement of bottom-SRO occurs because the electron beam was focused on the substrate surface and gets out of focus the more layers are grown. For the top SRO growths, the RHEED intensity profiles show a slight difference at the initial stage depending on the growth conditions, which may be related to the imperfect surface of BTO layer. However, all the RHEED intensity profiles of top-SRO layers saturated during the further growth, indicating a standard step-flow growth mode.

## II. Methodology for calculating relative BaTiO<sub>3</sub> surface stabilities

The evolution of BTO surface stability can be described in terms of the surface Gibbs free energy for different surface structures and background atmospheres.<sup>2,3</sup> The surface Gibbs free energy of the  $i$ -th termination of BTO ( $\Omega^i$ ) can be written as

$$\Omega^i = \Delta E^i - n_{\text{Ba}}\mu_{\text{Ba}} - n_{\text{Ti}}\mu_{\text{Ti}} - n_{\text{O}}\mu_{\text{O}} , \quad (\text{S1})$$

where  $\Delta E^i$  is the relative total energy of the heterostructure surface except for the fixed region that limits atomic relaxation as a bulk-like region per surface area;  $n_{\text{Ba}}$ ,  $n_{\text{Ti}}$ , and  $n_{\text{O}}$  denote the numbers of Ba, Ti, and O atoms in the surface per surface area, respectively; and  $\mu_{\text{Ba}}$ ,  $\mu_{\text{Ti}}$ , and  $\mu_{\text{O}}$  are their corresponding chemical potentials, respectively. For convenience, we measured the chemical potentials for each species with respect to their standard states at 0 K, for example,  $\Delta\mu_a = \mu_a - E_a^{\text{std}}$ . The reference state for oxygen is O<sub>2</sub> gas, such that  $E_{\text{O}}^{\text{std}} = E_{\text{O}_2}^{\text{gas}}/2$ . The reference states for cations are their respective bulk elemental phases. In addition, we can impose constraints on the chemical potentials of each atom species and the formation energy of bulk BTO,  $\Delta G_f(\text{BTO})$ :

$$\Delta\mu_{\text{Ba}} + \Delta\mu_{\text{Ti}} + 3\Delta\mu_{\text{O}} = \Delta G_f(\text{BTO}) . \quad (\text{S2})$$

If we combine eq S1 and eq S2, we can express  $\Omega^i$  with the chemical potentials of Ba and O as variable:

$$\Omega^i = \phi^i + \Gamma_{\text{Ba}}^i \Delta\mu_{\text{Ba}} + \Gamma_{\text{O}}^i \Delta\mu_{\text{O}} , \quad (\text{S3})$$

where  $\phi^i = \Delta E^i - n_{\text{Ti}}E_{\text{BTO}}^{\text{bulk}} + \Gamma_{\text{O}}E_{\text{O}}^{\text{gas}}/2 + \Gamma_{\text{Ba}}E_{\text{Ba}}^{\text{bulk}}$ ,  $\Gamma_{\text{Ba}} = -(n_{\text{Ba}} - n_{\text{Ti}})$ , and  $\Gamma_{\text{O}} = -(n_{\text{O}} - 3n_{\text{Ti}})$ . Note that all of these coefficients are intrinsic properties for each termination and

independent of chemical environment. With the simple assumption of bulk-like ( $1 \times 1$ ) surface termination, the surface Gibbs free energies of the  $\text{TiO}_2$ - and  $\text{BaO}$ -terminated BTO surfaces can be written simply as

$$\Omega^{\text{TiO}_2} = \phi^{\text{TiO}_2} + \Delta\mu_{\text{Ba}} + \Delta\mu_{\text{O}} \text{ and} \quad (\text{S4})$$

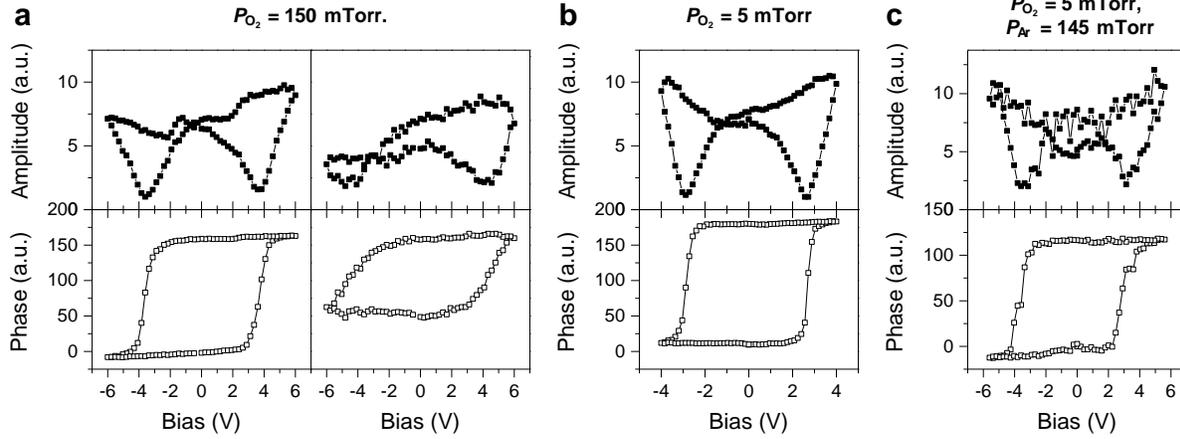
$$\Omega^{\text{BaO}} = \phi^{\text{BaO}} - \Delta\mu_{\text{Ba}} - \Delta\mu_{\text{O}} , \quad (\text{S5})$$

respectively. eq S3 and eq S4 demonstrate that decreasing  $\Delta\mu_{\text{O}}$  monotonically decreases the surface energy difference  $\Omega^{\text{TiO}_2} - \Omega^{\text{BaO}}$ , making the  $\text{TiO}_2$ -terminated BTO surface more stable. For quantitative investigations of the relative BTO surface Gibbs energy, we summarize the important thermodynamic parameters from our DFT calculations and previous experiments in Table S1.

Table S1: Thermodynamic parameters for obtaining the relative surface Gibbs free energy of BTO. The values are obtained from the generalized gradient approximation (GGA) with the on-site  $U$  Perdew–Burke–Ernzerhof (PBE) scheme and from the published thermodynamic data<sup>4</sup> at room temperature.

	Values	Note
$E_{\text{Ba}}^{\text{bulk}}$	-1.87 eV	GGA-PBE
$E_{\text{O}_2}^{\text{gas}}/2$	-4.71 eV	Exp.
$E_{\text{BTO}}^{\text{bulk}}$	-11.81 eV	GGA-PBE
$\phi^{\text{TiO}_2} - \phi^{\text{BaO}}$	6.73 eV	GGA-PBE & Exp.

### III. Ferroelectric polarization switching properties of SRO/BTO/SRO heterostructures



**Figure S2.** The amplitudes and phases from piezoresponse force microscopy (PFM) hysteresis loops of BTO films grown under (a)  $P_{\text{total}} = P_{\text{O}_2} = 150$  mTorr, (b)  $P_{\text{total}} = P_{\text{O}_2} = 5$  mTorr, and (c)  $\text{O}_2/\text{Ar}$  mixed atmosphere ( $P_{\text{total}} = 150$  mTorr and  $P_{\text{O}_2} = 5$  mTorr).

The ferroelectric polarization switching properties of ultrathin BTO layers grown under three different background atmospheres were investigated by piezoelectric force microscopy (PFM). It was reported that the interface termination sequence at SRO/BTO interface affects ferroelectric properties. In particular, the formation of  $\text{BaO-RuO}_2$  interface termination sequence at SRO/BTO generates pinned interface electric dipole which significantly disturbs the ferroelectric polarization stability in the ultrathin limit.<sup>5</sup> The interface termination sequence-dependent ferroelectric polarization properties can be found in our BTO films also.<sup>6</sup> Figure S2 shows the ferroelectric polarization switching of our BTO films measured by PFM. For  $P_{\text{O}_2} = 150$  mTorr case, both switchable (left, Figure S2a) and pinned ferroelectric polarization switching (right, Figure S2a) were found due to the coexistence of  $\text{SrO-TiO}_2$  and  $\text{BaO-RuO}_2$  interface termination sequences. On the other hand, for  $P_{\text{O}_2} = 5$  mTorr and  $\text{O}_2/\text{Ar}$  mixed atmosphere cases, clear ferroelectric polarization switching were observed due to uniform  $\text{SrO-TiO}_2$  termination

sequences at SRO/BTO interfaces (Figure S2b and S2c, respectively). Please note that the switchable ferroelectric polarization requires at least 3.5 unit cells (uc) thickness of BTO layer. The 2.5 uc-thick BTO films do not exhibit ferroelectricity for both  $P_{O_2} = 5$  mTorr and O<sub>2</sub>/Ar mixed atmosphere cases.

## Supporting Information References

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