# Thickness-dependent structural phase transition of strained SrRuO<sub>3</sub> ultrathin films: The role of octahedral tilt

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(Received 6 June 2011; revised manuscript received 30 July 2011; published 1 September 2011)

We grew epitaxial SrRuO<sub>3</sub> (SRO) films on SrTiO<sub>3</sub> (STO) (001) substrates with SRO layer thicknesses (*t*) between 10 and 200 pseudocubic unit cells (uc). Using the square net of the cubic STO surface, we were able to epi-stabilize the tetragonal SRO phase at room temperature for ultrathin films with  $t \leq 17$  uc. On the other hand thicker films with  $t \geq 19$  uc have an orthorhombic crystal structure similar to that of bulk SRO at room temperature. With increasing temperature, the orthorhombic films undergo a structural transition to the tetragonal phase at  $T_{\text{OT}}$ . The value of  $T_{\text{OT}}$  and the orthorhombicity factor at room temperature are reduced with decreasing film thickness. We also observed half-order Bragg reflections, indicating that the tetragonal structure arises from the suppression of the tilt angle of RuO<sub>6</sub> octahedra. The observed critical thickness around  $t_c \sim 18$  uc is much larger than the recent theoretical prediction (i.e., less than 2 uc) [J. He, A. Borisevich, S. V. Kalinin, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. Lett. **105**, 227203 (2010)]. This work thus demonstrates that the lattice symmetry mismatch at the interface plays an important role in determining the structural properties of perovskite films.

DOI: 10.1103/PhysRevB.84.104101

PACS number(s): 75.70.-i, 75.70.Cn, 68.35.Ct

## I. INTRODUCTION

Controlling physical properties of functional perovskiteoxide thin films through interface engineering has been an active research field in recent years.<sup>1–3</sup> Most works have paid attention to strain, generated by the *lattice constant mismatch* at the interface between the film and the substrate.<sup>4–8</sup> By controlling the strain, researchers showed that certain physical properties such as ferroelectric phase-transition temperature<sup>4</sup> and the saturation polarization<sup>5</sup> could be enhanced. There also have been many reports claiming that strain can reveal new physical properties that do not exist in bulk materials: the multiferroicity in EuTiO<sub>3</sub> films,<sup>6</sup> the morphotropic phase boundary in BiFeO<sub>3</sub> films,<sup>7</sup> and the spin and orbital ordered state in (Nd,Sr)MnO<sub>3</sub>.<sup>8</sup> Lattice mismatch has become one of the key experimental parameters in searching for a novel behavior in oxide heterostructures.

Recently, some researchers have shifted their interests to the role of *lattice symmetry mismatch* at the interface between functional oxides.<sup>9–12</sup> Perovskite oxides are typically composed of networks of corner-sharing octahedra. In an ideal cubic perovskite oxide, such as SrTiO<sub>3</sub> (STO), the octahedra are usually connected without tilts and rotations.<sup>13</sup> However, in many perovskite oxides with lower crystal symmetry, such as (La,Sr)MnO<sub>3</sub> and SrRuO<sub>3</sub> (SRO), tilts and/or rotations of the octahedra occur.<sup>14–16</sup> It is well known that such local structural deformations in bulk perovskite oxides can significantly affect their electronic and magnetic properties.<sup>17</sup> By using two oxides with different local structural deformations, we can make symmetry-mismatched interfaces, such as (La,Sr)MnO<sub>3</sub>/STO and SRO/STO, which could be useful for tuning physical properties of oxide heterostructures and superlattices.

In recent theoretical studies, it was suggested that the lattice symmetry mismatch could create new interface properties that do not exist in bulk.<sup>9,18</sup> He *et al.* considered the role

of a lattice symmetry mismatch without invoking chemical influences by performing calculations on a model interfacial structure.<sup>9</sup> They calculated how octahedral tilt and rotation angles would be varied as a function of atomic layer numbers in (La,Sr)MnO<sub>3</sub>/STO and SRO/STO interfaces. Near the (La,Sr)MnO<sub>3</sub>/STO interface, they argued that the octahedra are not so rigid and that the interface layer could exist for several layers into the thin film.<sup>9</sup> On the other hand near the SRO/STO interface, it was argued that the rigidity is so strong that the number of interface layers could be as small as one unit cell (uc) and that the SRO layer deformation rapidly becomes bulk-like.<sup>9</sup> In addition they found that the physical properties of the SRO were more sensitive to the octahedral tilt angles compared to those of LSMO, due to its spin configuration and strong hybridization.<sup>9</sup>

Understanding the octahedral tilting and physical properties of ultrathin SRO films on STO substrate will become important scientific issues as well as application issues. First SRO has been drawing much attention due to the 4d itinerant ferromagnetism<sup>19</sup> as well as the discovery of magnetic monopole in k-space.<sup>20</sup> Second SRO film has been used as bottom electrode materials for developing various oxide heterostructures due to its high electrical conductivity, chemical stability, and atomically smooth and well-defined surfaces.<sup>21</sup> In addition the lattice constants of SRO are quite close to those of STO, which is a very popular choice for growing epitaxial perovskite-oxide heterostructures. Third recent studies on ultrathin SRO films on STO substrate revealed nontrivial electrical properties<sup>22</sup> compared to SRO bulk (or thick film) samples and proposed novel interfacial properties.<sup>3</sup> Therefore, in order to understand these intriguing physical properties and to develop next generation oxide electronics, structural properties of ultrathin SRO films on the STO substrate, accompanied by the octahedral tilting, should be investigated.

Experimentally, to date, several groups have studied epitaxial SRO/STO films with SRO layer thicknesses (*t*) of 50–130 pseudocubic uc. They found that such thick films had an orthorhombic structure at room temperature, which indicates the existence of octaherdal tilt.<sup>23–26</sup> However, experimental data on the structure of epitaxial SRO/STO films with *t* < 50 uc are not available to our best knowledge. Therefore, it would be important to investigate how the local deformation, accompanied by the octahedral tilt and rotation, can affect the structural properties of ultrathin SRO films on STO substrates.

In this paper we report our systematic investigation of the crystal structure of SRO ultrathin films on STO (001), with t between 10 and 200 uc. At room temperature, the films with  $t \leq 17$  uc have a tetragonal crystal structure, while those with  $t \ge 19$  uc are orthorhombic. From x-ray diffraction measurements, we find that all tetragonal samples do not exhibit half-order Bragg reflections that would be present in the orthorhombic phase due to the octahedral tilts. This suggests that the suppression of octahedral tilt near the SRO/STO interface could exist well beyond the theoretically predicted critical thickness of less than 2 uc.<sup>9</sup> We also find that orthorhombic films experience orthorhombic-tetragonal thermal structural transitions at  $T_{OT}$ . When t decreases from 75 uc to 25 uc, the  $T_{\rm OT}$  decreases from 315 °C to 215 °C, and the orthorhombicity factor at room temperature also decreases. Our results suggest that the octahedral tilt has a close relationship with the structural transition temperature.

### **II. EXPERIMENTS**

We fabricated epitaxial SRO films with *t* between 10 and 200 uc on TiO<sub>2</sub>-terminated STO (001) substrates. We deposited the films by pulsed laser deposition (PLD) with a KrF excimer laser. The repetition rate and fluence of the laser were 1 Hz and 2.5 J/cm<sup>2</sup>, respectively. The SRO films were grown at a temperature of 700 °C and an oxygen partial pressure of 100 mTorr. The conditions were described in more detail elsewhere.<sup>22</sup> The film thickness was controlled by monitoring the intensity oscillations of the *in situ* reflection high-energy electron diffraction (RHEED) intensity during the growth. The film thickness was further confirmed with subsequent x-ray reflectivity measurements.

To determine the crystal structure of the SRO film, we obtained x-ray reciprocal space map (XRSM). For films with  $t \ge 10$  uc, we used a commercial high-resolution x-ray diffractometer (Bruker AXS D8 with a Vantec line-detector). For thinner films, measurements were carried out at the 10C1 beamline of the Pohang Light Source (Korea). We obtained XRSM around the asymmetric {204} STO Bragg reflections with  $\phi$  angles of 0, 90, 180, and 270°. We investigated the thickness dependence of  $T_{\text{OT}}$  by measuring temperature-dependent XRSM from room temperature up to 600 °C using an Anton-Paar hot stage. Note that the linear thermal expansion coefficients of orthorhombic SRO, tetragonal SRO, and STO are approximately 20.0, 8.00, and 10.8  $\times 10^{-6}$ /°C, respectively.<sup>23</sup> The temperature was determined from the measured values of the STO lattice constants.<sup>27</sup>

## **III. RESULTS AND DISCUSSION**

The bulk crystal structure of SRO is orthorhombic with the *Pbnm* symmetry at room temperature, which becomes tetragonal above  $T_{OT}$  of 547 °C.<sup>28</sup> The difference between the orthorhombic and the tetragonal symmetry comes from the existence of octahedral tilts in the former.<sup>28</sup> Figure 1(a) shows how the epitaxial SRO film can grow on STO substrate. Note that [hk1] and [hk1]<sub>o</sub> represents the pseudocubic and orthorhombic notations, respectively. As shown in Fig. 1(a), the octahedral tilt angle is defined as  $(180^\circ-\Theta)/2$ , where  $\Theta$  is the bond angle of Ru-O-Ru along the *c*-axis. The orthorhombic SRO structure has both tilts and rotations of the RuO<sub>6</sub> octahedra, whereas the tetragonal structure allows only rotations around the [010] axis.<sup>28</sup> At room temperature, the tilt angle of bulk orthorhombic SRO is about 10°.



FIG. 1. (Color online) (a) A schematic of the epitaxial relationships of the SrRuO<sub>3</sub> (SRO) films and SrTiO<sub>3</sub> (STO) substrates. Orthorhombic uc of the SRO films are denoted in orthorhombic notation [hkl]<sub>o</sub>. (b) XRSM for the SRO film grown on STO (001) substrates with thickness of 25 pseudo cubic uc at room temperature. (c) Same for 15 uc film. The peak positions of the SRO (260)<sub>o</sub>, (444)<sub>o</sub>, (620)<sub>o</sub>, and (44-4)<sub>o</sub> reflections, corresponding to STO (204), (024), (-204), and (0-24), respectively, have different  $Q_z$  values for the 25-uc-thick sample, indicating an orthorhombic symmetry. Note that the  $Q_z$  values of the SRO reflections for the 15-uc film does not change, indicating a tetragonal symmetry. Here,  $Q_z = 4\pi \sin \theta/\lambda$  $\cos(\omega - \theta)$  and  $\lambda = 0.15406$  nm.

We observe that the lattice symmetry of the SRO film changes from orthorhombic to tetragonal with decreasing t. Figures 1(b) and 1(c) display the XRSM data in the  $Q_x - Q_z$ scattering plane for the SRO films with t = 25 and 15 uc, respectively. Note that the z direction is out of the sample surface plane. Near  $Q_z = 64.36 \text{ nm}^{-1}$ , there are strong and sharp substrate peaks. There are also weak elongated film peaks appearing at smaller  $Q_7$  values. As Fig. 1(b) shows, for the t = 25 uc film, the film peaks have different  $Q_{\tau}$  values for different azimuthal  $\phi$  angles of 0, 90, 180, and 270°, indicating that the film is orthorhombic. On the other hand, as Fig. 1(c)shows, little variation in the  $Q_z$  value is observed for the t = 15 uc film, meaning that its crystal structure should be tetragonal. This implies that the lattice symmetry change occurs at a critical thickness between 15 and 25 uc. It is important to note that, even for the 25-uc film, the  $Q_x$  values of the peaks remain the same, indicating that the in-plane lattice is fully strained.

We define the orthorhombicity factor as a/b, in order to distinguish between the orthorhombic and the tetragonal phases. From the x-ray studies we determine that the lattice parameters of the 25-uc SRO film at room temperature are a =5.582 Å, b = 5.550 Å, c = 7.810 Å, and  $\gamma = 89.29^{\circ}$ . Hence, the orthorhombicity factor is  $1.006 \pm 0.0005$ . This value is close to the reported values for 50-130 uc SRO films, which are shown as the (red) open triangular<sup>24</sup> and (brown) square symbols<sup>25</sup> in Fig. 2. On the other hand, for the 15-uc film,  $a \approx b = 5.565$  Å, c = 7.810 Å, and  $\gamma = 89.02^{\circ}$ . Thus, the orthorhombicity is  $1.000 \pm 0.0005$ . This demonstrates that we can epi-stabilize SRO films with tetragonal symmetry on STO substrate even at room temperature, which has not been possible for thicker SRO films on STO substrate.<sup>23-25</sup>

The critical thickness  $t_c$  for the orthorhombic-tetragonal lattice symmetry change was estimated by growing films

with various t from 10 uc to 200 uc. In Fig. 2(a) the black solid circles represent room temperature values of the orthorhombicity factors for films with thicknesses of 10, 15, 25, 75, and 200 uc. All of the SRO films with  $t \ge 25$  uc are orthorhombic, whereas those with  $t \le 15$  uc are tetragonal. To verify this behavior, we grew another series of SRO films with similar deposition conditions using a different PLD system.<sup>29</sup> The a/b values for the latter SRO films are included as the (green) open circles in Fig. 2(a). Our data indicate that the room temperature value of  $t_c$  for epitaxial SRO films on STO substrates is located somewhere between 17 and 19 uc.

To confirm that the orthorhombic distortion (i.e., orthorhombicity factor >1.0) comes from the octahedral tilt, we investigated half-order Bragg reflections of our SRO films with t = 17 uc and t = 67 uc. In particular, we paid special attention to the two inequivalent reflections  $(211)_0$  and  $(221)_{0}$ . First, the  $(211)_{0}$  reflection in orthorhombic notation corresponds to the  $(-0.5\ 0.5\ 1.5)$  reflection in the pseudocubic notation. These reflections come from the rotation of the RuO<sub>6</sub> octahedra along [010], so that the corresponding limiting conditions can be satisfied in both tetragonal (I4/mcm) and orthorhombic (*Pbnm*) structures.<sup>30</sup> As shown in Fig. 3(a), the  $(211)_0$  reflection appears in both samples, indicating that the octahedral rotations exist in all SRO samples and that the x-ray intensity was strong enough to measure the half-order Bragg peaks in the thinner 17 uc film. On the other hand the  $(221)_0$  reflection corresponds to the (0.5.2) half-order Bragg reflection, which is due to the tilts of the RuO<sub>6</sub> octahedra along [001], and is forbidden in the tetragonal structure.<sup>24,30</sup> As shown in Fig. 3(b), the  $(221)_0$  reflection is observed only for the SRO film with t = 67 uc but not for the film with



FIG. 2. (Color online) (a) The room temperature orthorhombicity factor, defined as a/b, as a function of the SRO film thickness. The abrupt change represents a structural phase change from orthorhombic to tetragonal structure near the thickness of 18 uc. The dashed line represents a guideline. The (red) open triangle and the (brown) open square represent the values from Ref. 24 and Ref. 25, respectively. (b) The orthorhombic to tetragonal structural transition temperature  $T_{\text{OT}}$  as a function of the SRO film thickness.



FIG. 3. (Color online) Half-order Bragg reflections of our SRO films with t = 17 uc ( $t < t_c$ ) and 67 uc ( $t > t_c$ ). *L* scan refers to the STO cubic indices. Scans along the truncation rod with (a) h = -0.5 and k = 0.5 and (b) h = 0 and k = 0.5 are shown.

t = 17 uc. These results suggest that the tetragonal structure below  $t_c$  arises when the octahedral tilts are suppressed.

An estimate of the octahedral tilt angle for the orthorhombic SRO thin films can be derived from the relationship between the orthorhombicity factor and the tilt angle:<sup>18</sup>

$$b/a = [b_{\text{oct}}/a_{\text{oct}}] \cos((180^\circ - \Theta)/2).$$

If we assume that the change in the bond-length ratio of an octahedron is negligible  $(b_{oct}/a_{oct} = 1)$ , the orthorhombicity factor is entirely determined by the tilt angle. The measured orthorhombicity factor of ~1.010 [Fig. 2(a)] corresponds to the octahedral tilt angle of approximately 8°. This value is comparable to the bulk value of about 10°, and this indicates that the octahedral tilts in the thicker films can almost attain the full bulk value.

In bulk SRO a structural transition between the orthorhombic and the tetragonal phases occurs at  $T_{\rm OT} \sim 547 \,^{\circ}\text{C}^{.28}$ For SRO films grown on STO (001) substrates, previously reported values of  $T_{\rm OT}$  were 280 °C for a 120–130-uc thick film<sup>24</sup> and 310 °C for a 50–80-uc thick film.<sup>25</sup> Although substrate-induced strain has been suggested as one possible reason for the  $T_{\rm OT}$  shift, its origin has not been fully explored.

We carried out a systematic study of the thicknessdependent shift of  $T_{\text{OT}}$  by measuring XRSM from room temperature to 600 °C. To accurately determine  $T_{\text{OT}}$ , we measured the  $Q_z$  values of the SRO (260)<sub>o</sub> and (620)<sub>o</sub> reflections as a function of temperature *T*. We also measured temperaturedependent  $Q_z$  values of STO (204) reflections to calibrate the temperature.<sup>27</sup> As shown in Fig. 4(a), the SRO (260)<sub>o</sub> and (620)<sub>o</sub> reflections for the 25-uc film are seperated below ~215 °C, indicating an orthorhombic structure. As *T* increases above 215 °C, these two peaks merge; a sign of tetragonal structure. Therefore, the peak separation  $\Delta Q_z$  values between



FIG. 4. (Color online) (a) Temperature dependent x-ray diffraction measurements: the peak positions of the SRO (260)<sub>o</sub>, SRO (620)<sub>o</sub>, and STO (204) reflections of the 25-uc film. (b) Temperature dependence of the peak separation  $\Delta Q_z$  between the SRO (260)<sub>o</sub> and the SRO (620)<sub>o</sub> reflections of the 25-uc and the 75-uc films. The gray lines represent guidelines.

SRO  $(260)_{\circ}$  and  $(620)_{\circ}$  reflections can be regarded as the order parameter for the structural transition between the orthorhombic and the tetragonal phases. Figure 4(b) displays the *T*-dependent values of  $\Delta Q_z$  for the 25-uc and 75-uc thick films. For the 75-uc film,  $\Delta Q_z$  vanishes around 315 °C. This value of  $T_{\rm OT}$  is quite consistent with those obtained for thicker films.<sup>24,25</sup> However, the  $T_{\rm OT}$  of 215 °C for the 25-uc film is much lower than any reported  $T_{\rm OT}$  value.<sup>23–25</sup>

In Fig. 4(b) note that the 25- and 75-uc films have different  $\Delta Q_z$  values at room temperature, indicating that  $T_{\text{OT}}$  is strongly dependent on the orthorhombicity factor of the film. Figure 2(b) displays  $T_{\text{OT}}$  for films with various *t*. Although we did not perform x-ray studies below room temperature, a similarity appears to exist between the *t*-dependence of the orthorhombicity factor and  $T_{\text{OT}}$ . Namely, for films with large orthorhombicity (or octahedral tilt), higher temperatures are required to make the structure change from orthorhombic to tetragonal. Since the tetragonal structure originates from suppressed octahedral tilts, it is reasonable to think that  $T_{\text{OT}}$  is closely related to the octahedral tilt. Clearly, further investigations are required to elucidate the precise relationship between  $T_{\text{OT}}$  and the octahedral tilt.

Finally, we want to point out that our experimental estimate of the critical thickness for tilt suppression near the interface  $(t_c \sim 18 \text{ uc})$  probably is an overestimate.<sup>9</sup> The x-ray data represent an average structural property throughout the sample, and one cannot rule out the possibility that a small fraction of the sample may be in orthorhombic phase even for films with  $t \leq 17$  uc. Even if we assume that about half of the sample is orthorhombic, the experimental room temperature  $t_c$  value between 17 and 19 uc suggests that suppression of the octahedral tilt can survive to at least 9 uc near the SRO/STO interface. Yet this value is still much larger than the recent theoretical prediction, which suggests that the local deformation can be sustained for as little as one uc in the SRO/STO interface.<sup>9</sup>

To understand this discrepancy in the tilt suppression between theory and experimental data, we considered three possibilities: strain relaxation, stoichiometry change, and Tdependent orthorhombicity. First, the effect of strain relaxation can be ruled out immediately. As shown in Figs. 1(b) and 1(c), both SRO film peaks are located at the same  $Q_x$ value, indicating that the lattices were fully strained along the in-plane directions. Second, stoichiometry changes in our films, e.g., oxygen vacancies and cation inter-diffusion, cannot explain the discrepancy in the tilt-suppression length either. We observed that the SRO uc volume remains nearly constant within 0.15% error bar, irrespective of the value of t. Such a negligble volume change indicates that the stoichiometry variation in our film is minimal. A third possibility is the temperature difference. The theoretical calculations were carried out for zero temperature, while the structural properties of our SRO films were measured at and above room temperature. With decreasing T, the experimental tilt-suppression length might decrease and reach the predicted value of 1-2 uc. The sharp suppression of the orthorhombicity factor a/b near 17 uc shown in Fig. 2 points to the contrary, but experimental confirmation at low T is still required to clarify the behavior of the tilt-suppression length below room temperature.

# **IV. CONCLUSIONS**

In summary we have investigated the effect of film thickness on the octahedral tilt and structural transitions in ultrathin  $SrRuO_3$  films grown on  $SrTiO_3$  (001) substrates. When the  $SrRuO_3$  films are thinner than the critical thickness of about 18 uc, the crystal structure at room temperature changes from orthorhombic to tetragonal. We show that such a crystal structural change originates from the suppression of the octahedral tilt near the substrate-film interface. In addition the film thickness influences the structural transition temperature, which seems to be correlated with the orthorhombicity factor at room temperature. These observations suggest that the thickness of an ultrathin film is another key control parameter

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- <sup>1</sup>H. Y. Hwang, Science **313**, 1895 (2006).
- <sup>2</sup>C. H. Ahn, A. Bhattacharya, M. D. Ventra, J. N. Eckstein, C. D. Frisbie, M. E. Gershenson, A. M. Goldman, I. H. Inoue, J. Mannhart, A. J. Millis, A. F. Morpurgo, D. Natelson, and J.-M. Triscone, Rev. Mod. Phys. **78**, 1185 (2006).
- <sup>3</sup>J. M. Rondinelli, M. Stengel, and N. A. Spaldin, Nature Nanotechnol. **3**, 46 (2008).
- <sup>4</sup>K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 5698 (2004).
- <sup>5</sup>S. S. A. Seo and H. N. Lee, Appl. Phys. Lett. **94**, 232904 (2009).
- <sup>6</sup>J. H. Lee, L. Fang, E. Vlahos, X. Ke, Y. W. Jung, L. F. Kourkoutis, J.-W. Kim, P. J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P. C. Hammel, K. M. Rabe, S. Kamba, J. Schubert, J. W. Freeland, D. A. Muller, C. J. Fennie, P. Schiffer, V. Gopalan, E. J. Halperin, and D. G. Schlom, Nature **466**, 954 (2010).
- <sup>7</sup>R. J. Zeches, M. D. Rossell, J. X. Zhang, A. J. Hatt, Q. He, C.-H. Yang, A. Kumar, C. H. Wang, A. Melville, C. Adamo, G. Sheng, Y.-H. Chu, J. F. Ihlefeld, R. Erni, C. Ederer, V. Gopalan, L. Q. Chen, D. G. Schlom, N. A. Spaldin, L. W. Martin, and R. Ramesh, Science **326**, 977 (2009).
- <sup>8</sup>Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
- <sup>9</sup>J. He, A. Borisevich, S. V. Kalinin, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. Lett. **105**, 227203 (2010).
- <sup>10</sup>S. J. May, J.-W. Kim, J. M. Rondinelli, E. Karapetrova, N. A. Spaldin, A. Bhattacharya, and P. J. Ryan, Phys. Rev. B **82**, 014110 (2010).
- <sup>11</sup>A. Y. Borisevich, H. J. Chang, M. Huijben, M. P. Oxley, S. Okamoto, M. K. Niranjan, J. D. Burton, E. Y. Tsymbal, Y. H. Chu, P. Yu, R. Ramesh, S. V. Kalinin, and S. J. Pennycook, Phys. Rev. Lett. **105**, 087204 (2010).
- <sup>12</sup>J. M. Rondinelli and N. A. Spaldin, Phys. Rev. B 82, 113402 (2010).
- <sup>13</sup>Note that the lattice parameters of the STO substrate are a = b = c = 3.905 Å at room temperature.

in the structural engineering of low-symmetry perovskite oxides.

#### ACKNOWLEDGMENTS

This research was supported by the National Research Foundation of Korea (NRF) grants funded by the Korean government (MEST) [Grant Nos. 2009-0080567 and 2010-0020416 (T.W.N.), 2009-0074218 (C.U.J.), 2009-0077249 (J.-S.C.)]. Y.J.K. was supported by the Korean Federation of Science and Technology Societies through the Brainpool program. The experiments at Pohang Accelerator Laboratory were done at 10C1 beamline.

- <sup>14</sup>C. W. Jones, P. D. Battle, P. Lightfoot, and W. T. A. Harrison, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 45, 365 (1989).
- <sup>15</sup>Note that orthorhombic SRO lattice parameters at room temperature are a = 5.5670 Å, b = 5.5304 Å, and c = 7.8446 Å (Ref. 14).
- <sup>16</sup>A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature **373**, 407 (1995).
- <sup>17</sup>M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
- <sup>18</sup>A. T. Zayak, X. Huang, J. B. Neaton, and K. M. Rabe, Phys. Rev. B **74**, 094104 (2006).
- <sup>19</sup>P. B. Allen, H. Berger, O. Chauvet, L. Forro, T. Jarlborg, A. Junod, B. Revaz, and G. Santi, Phys. Rev. B 53, 4393 (1996).
- <sup>20</sup>Z. Fang, N. Nagaosa, K. S. Takahashi, A. Asamitsu, R. Mathieu, T. Ogasawara, H. Yamada, M. Kawasaki, Y. Tokura, and K. Terakura, Science **302**, 92 (2003).
- <sup>21</sup>O. Auciello, C. M. Foster, and R. Ramesh, Annu. Rev. Mater. Sci.
  28, 501 (1998).
- <sup>22</sup>Y. J. Chang, C. H. Kim, S.-H. Phark, Y. S. Kim, J. Yu, and T. W. Noh, Phys. Rev. Lett. **103**, 057201 (2009).
- <sup>23</sup>J.-P. Maria, H. L. McKinstry, and S. T. McKinstry, Appl. Phys. Lett. **76**, 3382 (2000).
- <sup>24</sup>A. Vailionis, W. Siemons, and G. Koster, Appl. Phys. Lett. **91**, 071907 (2007).
- <sup>25</sup>K. J. Choi, S. H. Baek, H. W. Jang, L. J. Belenky, M. Lyubchenko, and C.-B. Eom, Adv. Mater. **22**, 759 (2010).
- <sup>26</sup>In this paper, we simply denote monoclinic structure with the angle  $\gamma$  (close to 90.0°) between the [100]<sub>o</sub> and [001]<sub>o</sub> directions as an orthorhombic structure, following the conventional notation (Ref. 24).
- <sup>27</sup>D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, Science **304**, 1650 (2004).
- <sup>28</sup>B. J. Kennedy and B. A. Hunter, Phys. Rev. B 58, 653 (1998).
- <sup>29</sup>B. W. Lee and C. U. Jung, Appl. Phys. Lett. **96**, 102507 (2010).
- <sup>30</sup>M. F. C. Ladd and R. A. Palmer, *Structure Determination by X-ray Crystallography*, (Plenum Press, New York, 1994), Chap. 4.