

## Strain-induced single-domain growth of epitaxial SrRuO<sub>3</sub> layers on SrTiO<sub>3</sub>: A high-temperature x-ray diffraction study

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Temperature dependent structural phase transitions of SrRuO<sub>3</sub> thin films epitaxially grown on SrTiO<sub>3</sub>(001) single crystal substrates have been studied using high-resolution x-ray diffraction. In contrast to bulk SrRuO<sub>3</sub>, coherently strained epitaxial layers do not display cubic symmetry up to ~730 °C and remain tetragonal. The cause of this behavior is believed to be the compressive strain in the SrRuO<sub>3</sub> layer due to the lattice mismatch with SrTiO<sub>3</sub> substrate due to lattice mismatch. The tetragonal symmetry during growth explains the single domain growth on miscut SrTiO<sub>3</sub> substrates with step edges running along the [100] or [010] direction. © 2007 American Institute of Physics. [DOI: 10.1063/1.2771087]

Thin films of the perovskite SrRuO<sub>3</sub> have attracted considerable interest due to their low room temperature resistivity and small lattice mismatch with a range of functional oxide materials.<sup>1-3</sup> In order for SrRuO<sub>3</sub> to grow coherently on a single crystal substrate, matching of layer in-plane lattice parameter to that of a substrate is required. The mismatch between in-plane lattice parameters of a film and the substrate introduces strain which affects the structural and electrical properties of the SrRuO<sub>3</sub> layer.

X-ray and neutron diffraction studies on bulk SrRuO<sub>3</sub> show that at room temperature the SrRuO<sub>3</sub> structure possesses an orthorhombic *Pbnm* symmetry with  $a=5.5670$  Å,  $b=5.5304$  Å, and  $c=7.8446$  Å, similar to other ABO<sub>3</sub> perovskite compounds, and is isostructural with GdFeO<sub>3</sub>.<sup>4</sup> The orthorhombic phase can be obtained by rotation of BO<sub>6</sub> (RuO<sub>6</sub>) octahedra counterclockwise about the [010]<sub>cubic</sub> and [001]<sub>cubic</sub> directions and clockwise rotation about the [100]<sub>cubic</sub> direction of an ABO<sub>3</sub> cubic perovskite. At around 550 °C, the orthorhombic structure transforms into a tetragonal one with the space group *I4/mcm*.<sup>5</sup> In the tetragonal unit cell, RuO<sub>6</sub> octahedra are rotated only about the [001]<sub>cubic</sub> ABO<sub>3</sub> direction. At even higher temperatures of about 680 °C, tetragonal SrRuO<sub>3</sub> transforms into a cubic structure with a standard perovskite space group *Pm3m* where no rotations of RuO<sub>6</sub> octahedra are observed.<sup>5</sup>

Maria *et al.*,<sup>6</sup> reported thin RuO<sub>6</sub> films grown on SrTiO<sub>3</sub>(001) substrates undergo an orthorhombic to tetragonal (*O-T*) structural phase transition at a somewhat lower temperature of ~350 °C. They also measured a tetragonal to cubic (*T-C*) phase transition temperature of ~600 °C, but this was obtained from a bulk SrRuO<sub>3</sub> sample. The suggested transitions imply that SrRuO<sub>3</sub> exhibits cubic symmetry during film synthesis, which is typically in the range of 600–700 °C.<sup>6</sup> Since the *T-C* transition was observed on a powder SrRuO<sub>3</sub> sample, which does not represent conditions

of commensurate strained layer growth, it is still unclear what crystal symmetry strained epitaxial SrRuO<sub>3</sub> layer possesses during growth under constrained geometries imposed by the substrate.

The only experiment that could clarify the presence of one or the other symmetry is to measure the structure of a SrRuO<sub>3</sub> layer at high temperatures, under the conditions that it is normally deposited on single crystal substrates. To see the *T-C* transition in a thin oriented SrRuO<sub>3</sub> film is difficult, because it involves just a slight rotation of the RuO<sub>6</sub> octahedra along the [001]<sub>cubic</sub> ABO<sub>3</sub> axis where only light oxygen atoms are involved. Using SrRuO<sub>3</sub> powder diffraction pattern simulations we established that the SrRuO<sub>3</sub>(211) diffraction peak is very sensitive to oxygen rotation and is absent in the cubic symmetry. In this letter, capitalizing on this insight, we report a study of temperature-dependent structural transition of SrRuO<sub>3</sub> films coherently grown on SrTiO<sub>3</sub>(001) substrates by high-resolution x-ray diffraction using laboratory as well as synchrotron radiation sources.

Thin film samples were grown by two different methods: molecular beam epitaxy (MBE) and pulsed laser deposition (PLD). The samples were grown in the same vacuum chamber with a background pressure of 10<sup>-9</sup> Torr. The MBE grown samples are deposited in an oxygen pressure of 10<sup>-5</sup> Torr and at a temperature of 700 °C. All films were grown on TiO<sub>2</sub> terminated SrTiO<sub>3</sub> substrates.<sup>7</sup> Samples were grown at a rate of about 1 Å/s from separate Ru and Sr sources. Typical thicknesses of the films range from 200 to 300 Å. During growth, reflection high energy electron diffraction is used to monitor the morphology of the samples. For PLD a 248 nm wavelength KrF excimer laser was employed with typical pulse lengths of 20–30 ns. The energy density on the target is kept at approximately 2.1 J/cm<sup>2</sup>. Films were deposited with a laser repetition rate of 4 Hz, with the substrate temperature at 700 °C.

X-ray diffraction (XRD) measurements were performed using a PANalytical X'Pert materials research diffractometer

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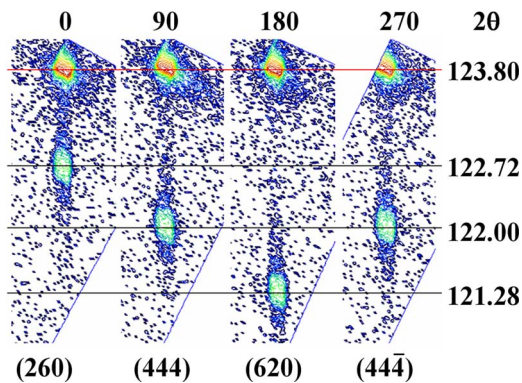


FIG. 1. (Color online) Room temperature reciprocal space maps of the  $\text{SrTiO}_3(204)$  and  $\text{SrRuO}_3(260)$ ,  $(444)$ ,  $(620)$ , and  $(44-4)$  Bragg reflections. The fact that the  $(260)$  and  $(620)$  peak positions are different from the  $(444)$  and  $(44-4)$  positions indicates an orthorhombic unit cell.

in high-resolution mode at the Stanford Nanocharacterization Laboratory as well as a synchrotron source at beamline 7-2 at the Stanford Synchrotron Radiation Laboratory. For temperature dependent structural analysis an Anton-Paar hot stage was used.

The XRD results demonstrate that grown  $\text{SrRuO}_3$  films exhibit  $(110)$  out-of-plane orientation with  $(100)$  and  $(-110)$  in-plane orientations along the  $[100]$  and  $[010]$  directions of the  $\text{SrTiO}_3$  substrate. Reciprocal lattice maps taken at room temperature using symmetrical and asymmetrical reflections confirm that the  $\text{SrRuO}_3$  layers are grown in a fully coherent fashion with respect to the underlying  $\text{SrTiO}_3(001)$  substrate and exhibit a slightly distorted orthorhombic unit cell with the angle  $\gamma$  between the  $[100]$  and  $[010]$  directions being less than  $90^\circ$ , a distortion that was also reported by Gan *et al.*<sup>8</sup> Coherently grown  $\text{SrRuO}_3$  is compressively strained along the  $[-110]$  and  $[001]$  directions. The in-plane compressive stress introduces out-of-plane strain that elongates the  $\text{SrRuO}_3$  unit cell along the  $[110]$  direction. Such constrained in-plane geometry distorts the  $\text{SrRuO}_3$  lattice from the ideal orthorhombic structure.

Figure 1 shows reciprocal lattice maps from the  $(260)$ ,  $(444)$ ,  $(620)$ , and  $(44-4)$  reflections together with the  $\text{SrTiO}_3(204)$  reflections of a single domain  $\text{SrRuO}_3$  layer. The difference in  $\text{SrRuO}_3(260)$  and  $(620)$  atomic plane spacings represents a dissimilarity in the  $a$  and  $b$  lattice parameters typical for the orthorhombic structure. In contrast, the tetragonal structure with  $a=b$  should show identical positions for the  $(260)$  and  $(620)$  Bragg reflections. In reciprocal space, the transition from the orthorhombic to the tetragonal structure leads to an increase of the distance between  $\text{SrRuO}_3(260)$  and  $\text{SrTiO}_3(204)$  peaks, while the distance between the  $\text{SrRuO}_3(620)$  and  $\text{SrTiO}_3(204)$  peaks will decrease.

In order to examine the  $O-T$  transition, temperature-dependent XRD scans were performed along the  $l$  direction. As can be seen from Fig. 2, the distance between  $\text{SrTiO}_3(204)$  and  $\text{SrRuO}_3(620)$  peaks decreases as temperature increases. Above  $\sim 450^\circ\text{C}$ , the  $\text{SrRuO}_3(620)$  peak position reaches the same value as  $\text{SrRuO}_3(260)$  completing the transition to the tetragonal structure. The inset of Fig. 2 shows the  $\text{SrRuO}_3(221)$  peak intensity as a function of temperature. The disappearance of this peak at higher temperatures further proves the presence of a tetragonal phase with an  $O-T$  transition temperature of  $\sim 310^\circ\text{C}$ . The reported

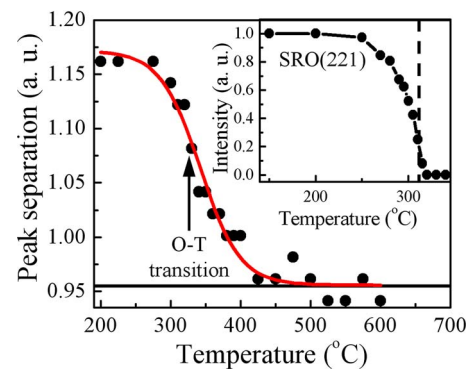


FIG. 2. (Color online) Distance between  $\text{SrTiO}_3(204)$  and  $\text{SrRuO}_3(620)$  peaks in the reciprocal space as a function of temperature indicating an orthorhombic to tetragonal transition. The inset shows the disappearance of  $\text{SrRuO}_3(221)$  peak as the symmetry of the film changes to tetragonal. The black horizontal line indicates the separation between the  $\text{SrTiO}_3(204)$  and  $\text{SrRuO}_3(444)/(44-4)$  peak positions (see Fig. 1).

transition temperature for thin  $\text{SrRuO}_3$  films is significantly lower than that of bulk  $\text{SrRuO}_3$ . The source of this effect is not clear, but can be related to the local epitaxial strain induced by the layer-substrate lattice mismatch. The negative in-plane biaxial strain and the resulting positive out-of-plane strain may promote the tetragonal  $\text{SRO}$  phase over the orthorhombic one at lower temperatures. The discrepancy between the  $O-T$  transition temperatures reported in this study and by Maria *et al.* can be attributed to the different sample preparation conditions as well as to the fact that their analysis was mainly based on bulk  $\text{SrRuO}_3$  samples.<sup>6</sup>

Finally, temperature dependent x-ray diffraction measurements of the  $\text{SrRuO}_3(211)$  diffraction peak were performed using synchrotron radiation. The  $\text{SrRuO}_3(211)$  peak intensity as a function of temperature is shown in Fig. 3. While the peak intensity gradually decreases indicating the rotation of the oxygen atoms, it does not vanish up to temperatures of  $\sim 730^\circ\text{C}$ .

The results unambiguously demonstrate that a  $\text{SrRuO}_3(110)$  layer grown coherently on  $\text{SrTiO}_3(001)$  substrate does not undergo a tetragonal to cubic transition and remains tetragonal at temperatures up to  $730^\circ\text{C}$ .<sup>9</sup> The tetragonal unit cell allows us to explain single domain growth of  $\text{SrRuO}_3$  films on miscut  $\text{SrTiO}_3$  substrates. In step flow growth mode, growing species tend to attach to the steps due to a diffusion length which is larger than the terrace length of the substrate. For a tetragonal unit cell, where  $c > a=b$ ,  $\text{SrRuO}_3$  will tend to align its  $c$  axis along the steps.

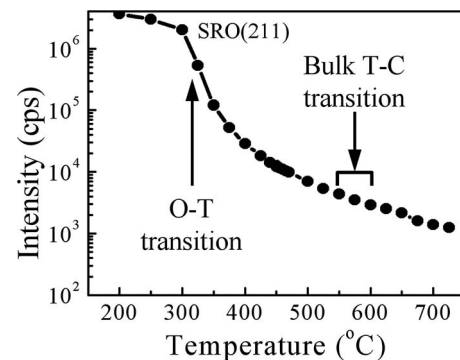


FIG. 3. Intensity of the  $\text{SrRuO}_3(211)$  peak as a function of temperature. The nonzero intensity indicates  $\text{SrRuO}_3$  possesses a tetragonal symmetry up to  $730^\circ\text{C}$ .

If the step edges run only along the SrTiO<sub>3</sub> [100] or [010] directions a single domain SrRuO<sub>3</sub> layer is formed. On the other hand, if the step edges run along the direction rotated by some angle from [100] or [010] directions, SrRuO<sub>3</sub> will attach to steps with its longer unit cell axis parallel to the steps resulting in twinned structure due to the serrated nature of the step edge, as was already observed by Gan *et al.*<sup>10</sup> SrRuO<sub>3</sub> layers on substrates with low miscut angles exhibit twinned structures due to the large length of the substrate terraces compared to the diffusion length of SrRuO<sub>3</sub>, which results in a 2-dimensional island growth. In this regime, SrRuO<sub>3</sub> tetragonal unit cell aligns randomly along the [100] and [010] directions of the SrTiO<sub>3</sub> substrate.

In summary, we have established the mechanism of single domain growth of epitaxial SrRuO<sub>3</sub> layers on single crystal SrTiO<sub>3</sub> substrates. We show that at room temperature SrRuO<sub>3</sub> films exhibit a distorted orthorhombic structure with an angle  $\gamma$  between the [100] and [010] directions being less than 90°. At a temperature of  $\sim 310$  °C, the SrRuO<sub>3</sub> layer undergoes a structural phase transition from orthorhombic to tetragonal. In contrast to the structural studies done on bulk SrRuO<sub>3</sub> samples, strained SrRuO<sub>3</sub> films do not show a structural phase transition from tetragonal to cubic and remain tetragonal up to temperatures of  $\sim 730$  °C.

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<sup>9</sup>Our results indicate that the unit cell of epitaxial SrRuO<sub>3</sub> layer at high temperatures is slightly distorted from perfect tetragonal with  $\gamma < 90^\circ$ . Future study is under way to determine precise unit cell parameters and bond angles of the observed high temperature tetragonal SrRuO<sub>3</sub> phase.

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