

Control of the growth and domain structure of epitaxial SrRuO₃ thin films by vicinal (001) SrTiO₃ substrates

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We report the effect of both miscut angle (α) and miscut direction (β) of vicinal substrates on the epitaxial growth and domain structure of isotropic metallic oxide SrRuO₃ thin films. The thin films have been grown on vicinal (001) SrTiO₃ substrates with α up to 4.1° and β up to 37° away from the in-plane [010] axis. Single-crystal epitaxial (110)^o SrRuO₃ thin films were obtained on vicinal SrTiO₃ substrates with a large miscut angle ($\alpha=1.9^\circ$, 2.1° , and 4.1°) and miscut direction close to the [010] axis. Decreasing the substrate miscut angle or aligning the miscut direction close to the [110] axis ($\beta=45^\circ$) resulted in an increase of 90° domains in the plane. The films grown on vicinal substrates displayed a significant improvement in crystalline quality and in-plane epitaxial alignment as compared to the films grown on exact (001) SrTiO₃ substrates. Atomic force microscopy revealed that the growth mechanism changed from two-dimensional nucleation to step flow growth as the miscut angle increased. © 1997 American Institute of Physics. [S0003-6951(97)00715-8]

There has been considerable interest in epitaxial thin films of perovskite oxides since these materials exhibit a wide range of technologically important properties such as high-temperature superconductivity, ferroelectricity, ferromagnetism, colossal magnetoresistance,¹ and metallic conductivity. A major challenge is to prepare these materials in single-crystal epitaxial thin film form and integrate them so that these properties can be utilized in electronic, magnetic, and optical devices. Furthermore, single-crystal epitaxial thin films and heterostructures of various oxides will allow us to study the intrinsic materials behavior.

Vicinal substrates have been used to grow various high crystalline quality perovskite oxide thin films, such as YBa₂Cu₃O₇,^{2,3} (La,Sr)₂CuO₄,⁴ Ba₂Sr₂Ca_{n-1}Cu_nO₂₀₊₄,^{5,6} PbTiO₃,^{7,8} and Sr_{1-x}Ca_xRuO₃ ($0 \leq x \leq 1$).⁹ It is generally believed that the step flow growth of thin films on the vicinal substrates induces the formation of preferential domains.

In this letter, we report the effect that both miscut angle (α) and miscut direction (β) of vicinal (001) SrTiO₃ substrates have on the growth of isotropic metallic oxide SrRuO₃ thin films. SrRuO₃ is a pseudocubic perovskite and undergoes a ferromagnetic transition at 155 K. The SrRuO₃ thin films have already been used as electrodes in epitaxial ferroelectric heterostructures to improve fatigue properties.¹⁰ Due to a slightly orthorhombic distortion in SrRuO₃, it is possible to distinguish 90° domains by azimuthal x-ray scans.

The SrRuO₃ thin films were grown on both exact and vicinal (001) SrTiO₃ substrates by 90° off-axis sputtering under the conditions described in Ref. 9. The thickness of the thin films is about 2000 Å. As shown in Fig. 1, the angle between the surface normal and crystallographic [001] direction is the miscut angle α . The miscut direction, β , is defined as an angle between the projection of the surface normal onto the (001) plane and the in-plane [010] direction. (Here, $\beta=0^\circ$ is defined as the SrTiO₃ [010] direction and $\beta=45^\circ$ is de-

finied as the SrTiO₃ [110] direction in the plane.) Both α and β were determined by a four-circle x-ray diffractometer in conjunction with the reflection of a He-Ne laser beam off the sample surface. The measurement errors in α and β are $\pm 0.1^\circ$ and $\pm 2^\circ$, respectively.

The epitaxial arrangements and crystalline quality of the films were determined by a Siemens D5000 four-circle x-ray diffractometer using a Cu $K\alpha$ source. As shown in Fig. 2(a), all the SrRuO₃ films were found to be (110)^o oriented normal to the substrates with an out-of-plane lattice parameter of $d_{(110)} = 3.96 \text{ \AA}$. [The superscript *o* refers to the Miller indices based on the orthorhombic unit cell.] Grazing incidence diffraction scans consistently exhibited the in-plane lattice parameters of all the films to be $3.90 \pm 0.02 \text{ \AA}$. The in-plane lattice parameters are very close to the lattice parameters of SrTiO₃ substrates (3.905 Å), which suggests that the film-substrate interface is coherent.

The crystalline quality of the films was determined from their rocking curve widths. For films deposited on vicinal substrates, the measured full width at half maximum (FWHM) of the rocking curve for SrRuO₃ (220)^o reflection and SrTiO₃ substrate (002) reflection was the same, about 0.25°, which suggests an excellent out-of-plane alignment of the films, as shown in Fig. 2(b). These values were limited by our diffractometer's resolution. However, the films on exact (001) SrTiO₃ substrates showed broader rocking curves (FWHM $\approx 0.37^\circ$). Thus, the crystalline quality of SrRuO₃ thin films was significantly improved by using vicinal substrates.

In order to study the effect of miscut angle (α) on the in-plane domain structure, the substrate miscut angle (α) was varied from 0° to 4.1°. At the same time, the miscut direction (β) was kept relatively low ($\beta \leq 14^\circ$). Figure 3(a) shows a typical off-axis azimuthal ϕ scan of SrRuO₃ (221)^o reflection for films on 0° miscut or exact (001) SrTiO₃ substrates. Four peaks separated by 90° from each other were observed, indicating the coexistence of two (110)^o domains with in-plane epitaxial arrangement of SrRuO₃[001],[$\bar{1}\bar{1}0$]/

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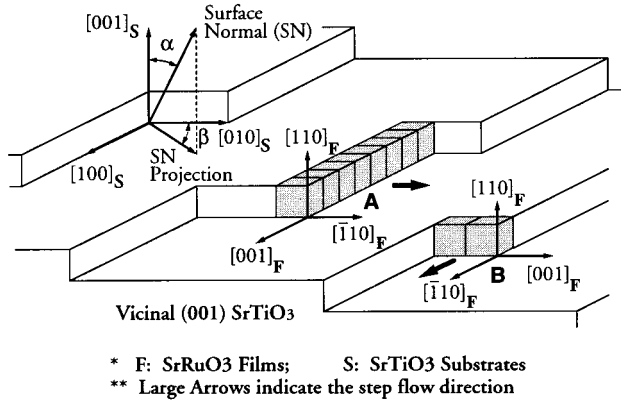


FIG. 1. Schematic diagram of a vicinal SrTiO₃ (001) substrate showing miscut angle, α , and miscut direction, β , as well as the epitaxial arrangement of two types of step flow growth of (110)^o SrRuO₃ domains.

SrTiO₃[010], and SrRuO₃[001], $[\bar{1}10]//\text{SrTiO}_3[100]$. From the integral peak intensities, we could estimate that these two domains were of approximately equal population. The FWHM of (221)^o reflections in a ϕ scan was over 4^o. This is consistent with the observed broad rocking curves for SrRuO₃ (220)^o, as seen in Fig. 2(b). The large mosaic spread in both the in-plane and out-of-plane may be due to two dimensional nucleation and subsequent three dimensional terraced-island growth as observed by both atomic force microscopy (AFM) and scanning tunneling microscopy (STM).¹¹

For vicinal SrTiO₃ substrates, the fourfold symmetry of (001) is broken by exposing the (010) and (100) planes at the surface steps, as shown in Fig. 1. For the deposition conditions used in this study, the SrRuO₃ films on (001) SrTiO₃ substrates grow more favorably in the $[110]^o$ direction than in the $[001]^o$ direction normal to the substrates. Therefore, the films grown by step flow can have two possible in-plane epitaxial arrangements depending on the direction of step flow: SrRuO₃ $[\bar{1}10]//\text{SrTiO}_3[010]$ and SrRuO₃ $[001]//\text{SrTiO}_3[100]$, or SrRuO₃ $[001]//\text{SrTiO}_3[010]$ and SrRuO₃ $[\bar{1}10]//\text{SrTiO}_3[100]$, which are marked by "A" and "B," respectively, as shown in Fig. 1. When the steps flow preferentially in one direction and no two dimensional nucleation occurs, the thin films will be single domain.

The SrRuO₃ film grown on a vicinal substrate with a small miscut angle $\alpha=0.7^o$ and $\beta=1^o$ had a two-domain in-plane texture as indicated by the two weak peaks observed at 90^o away from the two strong peaks in the ϕ scan shown in Fig. 3(b). From the integral peak intensities, the volume fraction of the second domain was calculated to be about 7%. The in-plane epitaxial arrangement of the dominant domain determined by ϕ scans was the type A shown in Fig. 1. Since β was so low, almost no SrTiO₃ (100) planes were available at the steps to allow type B step flow growth. The existence of the 90^o domains is attributed to two-dimensional nucleation on the terraces because the terrace length is larger than the critical surface diffusion length of adatoms.

The SrRuO₃ thin films on vicinal substrates with a larger miscut angle, (for example, $\alpha=1.9^o$, 2.1^o , and 4.1^o), and a miscut direction toward close to $[010]$ were found to be single domain. Figure 3(c) shows the ϕ scan for a SrRuO₃

film grown on a vicinal SrTiO₃ substrate with $\alpha=1.9^o$ and $\beta=12^o$. Two sharp peaks separated by 180^o were observed indicating that the thin film was single domain. The in-plane epitaxial relationship between this SrRuO₃ film and the SrTiO₃ substrate was also type A, as shown in Fig. 1. The FWHM of ϕ scan for SrRuO₃ (221)^o reflection was 1.7^o, which indicates a much less mosaic spread in the plane compared to the films on exact (001) SrTiO₃ substrates.

Figure 4 shows an AFM image of a single-domain SrRuO₃ film on a vicinal substrate over a 1 $\mu\text{m} \times 1 \mu\text{m}$ area. The film surface shows a step pattern with straight steps, suggesting step flow growth. No two-dimensional islands or protrusions were seen on the film. The AFM image also shows kink sites (marked by an arrow) similar to what would be expected on the substrate surface due to the miscut direction $\beta=12^o$. However, as a larger area of the (010) plane is exposed on the substrate surface, step flow along the $[010]$ direction dominates the film growth. In contrast, AFM images of SrRuO₃ films on vicinal substrates with low miscut angle ($\alpha=0.7^o$) showed a combination of step flow and two-dimensional nucleation.¹¹

We have also studied the effect of miscut direction on the domain structure by comparing the films on substrates with different β angle. The SrRuO₃ films on vicinal substrates with $\alpha=1.9^o$, 2.1^o , and 4.1^o , and $\beta \leq 14^o$ were found to be single domain. In contrast, the film deposited on a vicinal SrTiO₃ substrate with $\alpha=3.6^o$ and the miscut direction close to the $[110]$ axis ($\beta=37^o$) had a two-domain in-plane texture as indicated by the four peaks observed in the

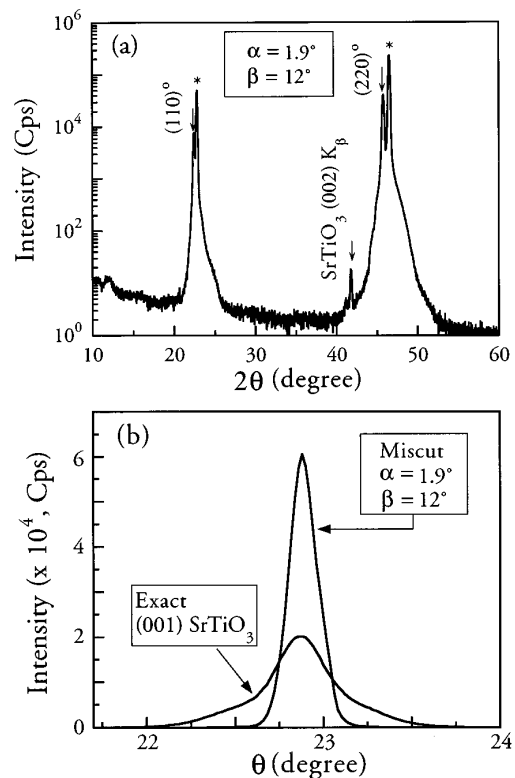


FIG. 2. (a) X-ray diffraction θ - 2θ scan of a SrRuO₃ thin film on a vicinal (001) SrTiO₃ substrate with $\alpha=1.9^o$ and $\beta=12^o$. (b) Rocking curve scans of the SrRuO₃ (220)^o reflection on an exact (001) SrTiO₃ substrate and on a vicinal (001) SrTiO₃ substrate with $\alpha=1.9^o$ and $\beta=12^o$.

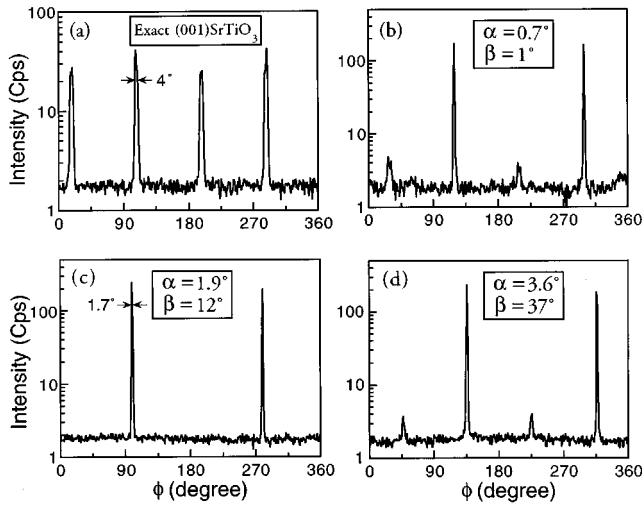


FIG. 3. In-plane azimuthal ϕ scans of the SrRuO₃ (221)^o reflection for SrRuO₃ thin films on (a) an exact SrTiO₃ (001) substrate and vicinal SrTiO₃ (001) substrates with (b) $\alpha=0.7^\circ$ and $\beta=1.0^\circ$, (c) $\alpha=1.9^\circ$ and $\beta=12^\circ$, and (d) $\alpha=3.6^\circ$ and $\beta=37^\circ$.

ϕ scan shown in Fig. 3(d). The dominant domain showed type A and the second domain showed type B epitaxial arrangement. The volume fraction of the second domain was calculated to be about 5%. We believe that the two-domain structure is induced by the high β angle.

The effect of miscut direction can be explained by the change of surface morphology of vicinal substrates. At low β angle, the area of the (010) SrTiO₃ plane exposed at the steps is much larger than the area of the (100) SrTiO₃ plane and correspondingly the thin films grow primarily by type A step flow. With increasing β , a larger area of the (100) planes is exposed at the saw-tooth shaped steps (see Fig. 1), resulting in more type B step flow growth. Thus, a two-domain structure is expected in the thin films. If the miscut were perfectly along the [110] direction of the substrate, i.e., $\beta=45^\circ$, the steps should expose both (010) and (100) planes equally as nucleation centers. Therefore, step flow of type A and type B in the [010] and [100] directions are of equal probability.

The steps on the vicinal SrTiO₃ substrate with $\alpha=3.6^\circ$ and $\beta=37^\circ$ should expose the (010) and (100) planes with the area ratio of 1:0.75, which implies that the volume fraction of the second domain in the film should be about 40%. However, from the integral peak intensities, the second domain was estimated to occupy only 5 vol. % of the thin film. Furthermore, single-domain films were obtained on vicinal substrates with β up to 14° , corresponding to an expected second-domain volume fraction of 20%. The much lower population of the second domain than the expected suggests that the step flow direction is dominated by the majority plane exposed at step edges.

In summary, we have elucidated the effect of miscut angle and direction of vicinal (001) SrTiO₃ substrates on the in-plane epitaxial arrangements, crystalline quality, and growth mechanism of SrRuO₃ thin films. Single-domain (110)^o SrRuO₃ thin films with good crystalline quality have been grown on vicinal substrates with a large miscut angle and miscut direction toward close to the [010] axis. In contrast, the films on vicinal substrates with low miscut angle

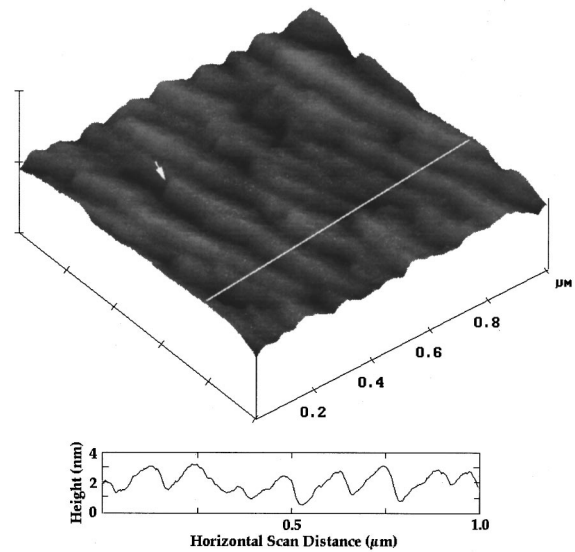


FIG. 4. AFM surface image over $1\ \mu\text{m}\times 1\ \mu\text{m}$ area for a SrRuO₃ thin film grown on a vicinal (001) SrTiO₃ substrate with $\alpha=1.9^\circ$ and $\beta=12^\circ$, the arrow marks a kink site.

and/or miscut direction close to [110] direction, had a two-domain in-plane texture and displayed a larger mosaic spread. As the miscut angle (α) is decreased, the growth mode changes from step flow to two-dimensional nucleation, resulting in an increased amount of 90° misoriented domains in the films. As β is increased, the second-domain content increases, due to step flow in two orthogonal directions. Our findings help us to better understand the growth mechanisms of perovskite epitaxial thin films, and open an avenue to grow high quality oxide thin films with controlled in-plane domain structure.

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- ¹S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, *Science* **264**, 413 (1994).
- ²D. H. Lowndes, X. Y. Zhen, S. Zhu, J. D. Budai, and R. J. Warmack, *Appl. Phys. Lett.* **61**, 852 (1992).
- ³D. G. Schlom, D. Angelmetti, J. D. Bednorz, R. Broom, A. Catana, T. Frey, Ch. Gerber, H.-J. Guntherodt, H. P. Lang, J. Mannhart, and K. A. Muller, *Z. Phys. B* **86**, 163 (1992).
- ⁴J. Kwo, R. M. Fleming, H. L. Kao, D. J. Werder, and C. H. Chen, *Appl. Phys. Lett.* **60**, 1905 (1992).
- ⁵J. N. Eckstein, I. Bozovic, D. G. Schlom, and J. S. Harris, Jr., *Appl. Phys. Lett.* **57**, 1049 (1990).
- ⁶J. Fujita, T. Yoshitake, T. Satoh, T. Ichihashi, and H. Igarashi, *IEEE Trans. Magn.* **MAG-27**, 1205 (1991).
- ⁷K. Wasa, Y. Haneda, T. Satoh, A. Adachi, S. Hayashi, and K. Setsune, *Jpn. J. Appl. Phys.* **1** **34**, 5132 (1995).
- ⁸C. D. Theis and D. G. Schlom (unpublished).
- ⁹C. B. Eom, R. J. Cava, R. M. Fleming, J. M. Phillips, R. B. van Dover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski, and W. F. Peck, Jr., *Science* **258**, 1766 (1992).
- ¹⁰C. B. Eom, R. B. van Dover, J. M. Phillips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, and R. M. Fleming, *Appl. Phys. Lett.* **63**, 2570 (1993).
- ¹¹R. A. Rao and C. B. Eom (unpublished).