

Domain structure of epitaxial SrRuO₃ thin films on miscut (001) SrTiO₃ substrates

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The microstructure of epitaxial SrRuO₃ thin films grown on vicinal (001) SrTiO₃ substrates with miscut angle of 1.9° and miscut direction of 12° away from [100] direction was studied using transmission electron microscopy (TEM). Cross-section as well as plan-view TEM studies revealed that these films are single domain with the in-plane epitaxial orientation relationship of SrRuO₃[001]//SrTiO₃[010] and SrRuO₃[110]//SrTiO₃[100]. This result is in contrast to the previous studies of the SrRuO₃ thin films grown on exactly (001) SrTiO₃, which are composed of two types of [110] domains with nearly the same volume fraction. The occurrence of these different domain structures is attributed to the step-flow growth of the film on the substrate surface due to the miscut.

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SrRuO₃ is a conductive magnetic oxide, which is paramagnetic at room temperature¹ and ferromagnetic below 160 K.² Recently, epitaxial thin films of SrRuO₃ have attracted considerable attention because of its important electrical and magnetic properties, such as high-perpendicular remnant magnetization and large magneto-optical constant³ which make this material very useful for making various electronic and optic devices. Furthermore, (Pb,Zr)TiO₃ ferroelectric and BaSrTiO₃ high dielectric constant capacitors with SrRuO₃ thin film electrodes exhibit superior fatigue and leakage characteristics.^{4,5} Epitaxial SrRuO₃ thin films have been successfully grown on different substrates by different methods, such as 90° off-axis sputtering,⁶ molecular beam epitaxy,⁷ and pulsed laser ablation.⁸

SrRuO₃ thin films grown on (001) SrTiO₃ and (001) LaAlO₃ substrates have different magnetic properties. For example, thin films formed on (001) SrTiO₃ and (001) LaAlO₃ show different coercive behavior at low temperature,³ and thin films grown on miscut (001) SrTiO₃ substrate show a strong anisotropic magnetoresistance, whereas those grown on (001) LaAlO₃ substrate show identical magnetoresistance behavior in two orthogonal directions.⁹ It is well known that the properties of perovskite oxide devices depend strongly on the surface morphology and the microstructure of the thin films. Therefore, a major challenge in heteroepitaxial perovskite devices is to explore the growth mechanisms in order to produce high quality epitaxial thin films. The deposition conditions and the choice of substrates play a key role in determining the microstructure and the properties of the thin films, thus, making it possible to deliberately control the surface morphology, domain structure, and properties of thin films.

SrRuO₃ has a GdFeO₃ type pseudo-cubic perovskite structure.¹⁰ At room temperature, it is an orthorhombic phase with the space group of Pbnm (No. 62) and lattice parameters $a = 5.5670 \text{ \AA}$, $b = 5.5304 \text{ \AA}$, and $c = 7.8446 \text{ \AA}$.¹¹ All

the planes and directions of SrRuO₃ referred to in this work are based on the orthorhombic unit cell. SrTiO₃ has a cubic perovskite structure with the space group of Pm3m and lattice constant of $a = 3.905 \text{ \AA}$.¹² When SrRuO₃ is deposited on (001) SrTiO₃ substrate, the film can grow epitaxially with its (001), (110), or (110) planes parallel to the SrTiO₃ (001) surface. Therefore, there are six possible domain structures based on the possible interfacial structural models of SrRuO₃/SrTiO₃ as shown schematically in Fig. 1. For clarity, the pseudo-cubic perovskite unit cell of SrRuO₃ is shown in the figure with orthorhombic indexing of the unit cell directions. The SrRuO₃ film can grow with its (110) plane parallel to the SrTiO₃ (001) surface with an in-plane orientation relationship with respect to the SrTiO₃ substrate of either SrRuO₃[001]//SrTiO₃[010] and SrRuO₃[110]//SrTiO₃[100] (mode X), or SrRuO₃[001]//SrTiO₃[100] and SrRuO₃[110]//SrTiO₃[010] (mode Y). The SrRuO₃ film can also grow with its (110) plane parallel to the (001) surface of SrTiO₃ with an in-plane orientation relationship of either SrRuO₃[001]//SrTiO₃[010] and SrRuO₃[110]//SrTiO₃[100] (mode X'), or SrRuO₃[001]//SrTiO₃[100] and SrRuO₃[110]//SrTiO₃[010] (mode Y'). It is also possible that the SrRuO₃ film grows along its [001] axis normal to the (001) surface of SrTiO₃, with an in-plane orientation

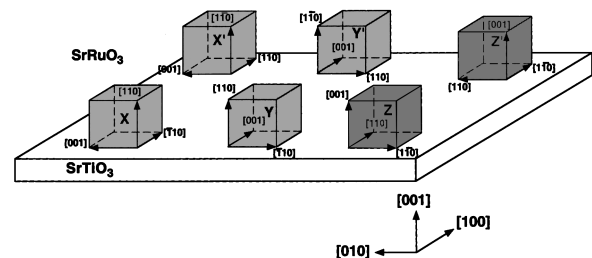


FIG. 1. Schematic diagram showing six possible growth modes of SrRuO₃ thin film on the (001) substrate of SrTiO₃. Note that while the pseudo-cubic perovskite unit cell of SrRuO₃ is drawn, the cell directions are indexed based on the orthorhombic unit cell.

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relationship of either $\text{SrRuO}_3[100]/\text{SrTiO}_3[110]$ and $\text{SrRuO}_3[010]/\text{SrTiO}_3[1\bar{1}0]$ (mode Z), or $\text{SrRuO}_3[100]/\text{SrTiO}_3[110]$ and $\text{SrRuO}_3[010]/\text{SrTiO}_3[110]$ (mode Z'). If the above six growth modes are simultaneously formed during the process of film growth, then the six domain structures will coexist in one thin film. Among the six types of domains in the film, X(X')-, Y(Y')-, and Z(Z')-type domains can be distinguished by means of conventional transmission electron microscopy (TEM), while the difference between the X (Y or Z) and X' (Y' or Z') is not distinguishable by the same techniques due to the pseudo-cubic characteristic of the SrRuO_3 structure. In the present work, we only classify the domains as three types (X, Y, and Z).

In order to investigate the effect of substrate miscut on domain structures and properties, SrRuO_3 thin films were grown on (001) SrTiO_3 substrates with different miscut angles and directions and studied by a variety of analytical methods, such as x-ray diffraction and atomic force microscopy.^{13,14} In our previous work, we reported the microstructure of SrRuO_3 thin films on exact (001) SrTiO_3 substrates.¹⁵ It was found that SrRuO_3 thin films grown on exact (001) SrTiO_3 consist of both the X- and the Y-type domains with nearly the same volume fraction. In this letter, we report the TEM studies of the SrRuO_3 thin films on a vicinal (001) SrTiO_3 substrates.

SrRuO_3 thin films on a vicinal (001) SrTiO_3 substrate, with a miscut angle (α) of 1.9° and miscut direction (β) of 12° away from the in-plane $[100]$ direction, were deposited by 90° off-axis sputtering. Here α is defined as the angle between the surface normal and the crystallographic $[001]$ direction of SrTiO_3 , while β is defined as the angle between the projection of the surface normal onto the (001) plane and the in-plane $[100]$ direction.¹³

The cross-sectional slices for TEM studies were obtained by cutting the $\text{SrRuO}_3/\text{SrTiO}_3$ heterostructural samples along the $[100]$ direction of SrTiO_3 and then gluing the cut slides face-to-face by joining the SrRuO_3 surfaces. Plan-view and cross-section TEM specimens were prepared by mechanical grinding, polishing, and dimpling, followed by Ar-ion milling at 5 kV. Electron diffraction patterns and dark-field images were recorded in a Philips CM12 electron microscope operated at 120 kV in the EMAL at the University of Michigan.

Figure 2(a) is a dark-field image of a cross-sectional sample, formed by the (111) reflection of a SrRuO_3 film, viewed along the $[010]$ direction of SrTiO_3 . Similar to the previous TEM observations of the SrRuO_3 thin film grown on exact (001) SrTiO_3 substrate,¹⁵ the film studied in this work has a smooth surface and a sharp interface between the film and the substrate and maintains a uniform thickness of about 100 nm over the entire specimen. The occurrence of bright and dark parts in the image indicates that the film consists of two types of domains. Figures 2(b) and 2(c) are selected area electron diffraction (SAED) patterns taken from the two SrRuO_3 domains of different types [corresponding to the regions marked A and B in Fig. 2(a)], for which the electron beam direction is parallel to the $[010]$ axis of SrTiO_3 . Figure 2(b) is identified to be the $[110]$ zone electron diffraction pattern of SrRuO_3 . According to this diffraction pattern, the (110) plane of the film is parallel to the

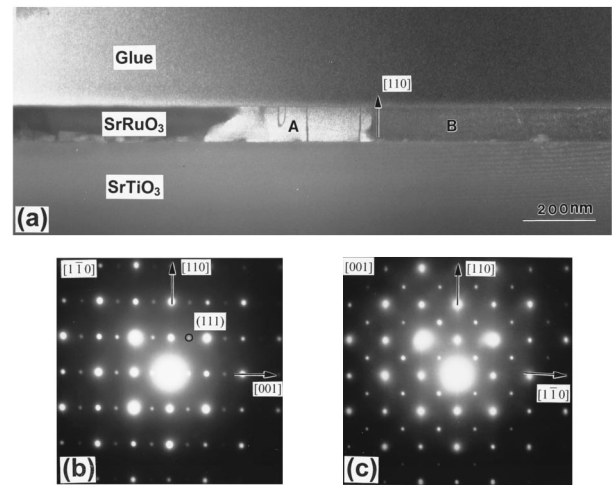


FIG. 2. (a) Dark-field image formed by the (111) reflection of SrRuO_3 showing two types of domain structures (bright and dark). (b) and (c) SAED patterns from the bright and dark regions showing the $[110]$ and $[001]$ zone of SrRuO_3 , respectively.

(001) surface of SrTiO_3 , while the $[001]$ direction of the SrRuO_3 film lies in the film plane, indicating a Y-type domain structure in this region. In contrast, Fig. 2(c) is the $[001]$ zone electron diffraction pattern of SrRuO_3 , in which the (110) plane is parallel to the SrTiO_3 (001) surface, while the $[1\bar{1}0]$ direction lies in the film plane, indicating an X-type domain structure. The TEM studies of cross-sectional specimens cutting from different region of the same film revealed that the film grown on the vicinal (001) SrTiO_3 substrates mainly consists of the X-type domain and that the small Y-type domains only occasionally be observed.

The microstructure and the size distribution of X and Y types of domains in the film were investigated in plan-view samples of the same film. Micrographs in Figs. 3 and 4 were taken from different areas of the same plan-view specimen. Figure 3(a) is a SAED pattern showing the $[110]$ zone electron diffraction patterns of the SrRuO_3 film. Figure 3(b) is a dark-field image formed using a weak reflection marked by "X" in Fig. 3(a). Comparing the diffraction pattern in Fig. 3(a) with the electron diffraction pattern of the SrTiO_3 substrate, it has been found that the specimen area in Fig. 3(b) has a crystallographic orientation of the X-type domain structure shown in Fig. 1. From detailed TEM studies of plane-view specimens prepared from different parts of the same SrRuO_3 film, it can be concluded that the X-type domains in the SrRuO_3 film form a continuous matrix with a small amount of islands of either Y- or Z-type domains. This is shown in Fig. 4. Figure 4(a) shows a SAED pattern taken from the same plan-view specimen as in Fig. 3. It is a superposition of SAED patterns generated from domains of all the three types shown in Fig. 1. The weak reflection marked by "X", "Y", and "Z" in Fig. 4(a) belong to domains of X, Y, and Z type, respectively. Figures 4(b), 4(c), and 4(d) are dark-field images formed by these three weak reflections, respectively. The white contrast in Fig. 4(b) represent X-type domains, while the black contrast represent the mixture of Y- and Z-type domains, which are bright in Figs. 4(c) and 4(d), respectively. The fine dark lines in Figs. 3(b) and 4(b) are antiphase boundaries of SrRuO_3 . It should be pointed out that the Y- and Z-type domains were only occasionally ob-

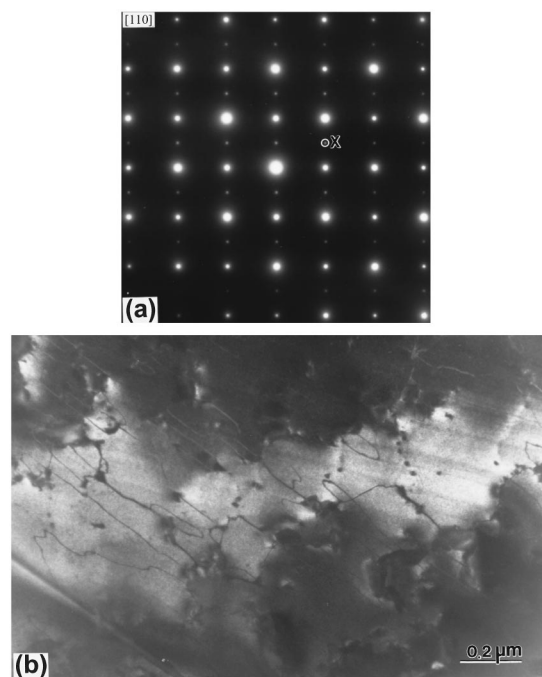


FIG. 3. (a) SAED pattern from a plan-view specimen showing [110] zone of SrRuO₃. (b) Dark-field image using weak reflection marked by "X" in (a), showing one purely X-type domain.

served. However, the previous x-ray diffraction studies using a four-circle diffractometer¹³ showed that the as-grown film on the vicinal (001) SrTiO₃ substrate consists of a single domain (the X-type domain) structure. The reason for this inconsistency is so far unclear, based on the present studies.

The present TEM investigations of the SrRuO₃ thin films deposited on the vicinal (001) SrTiO₃ show that the film consists of a matrix domain of the X-type with some small islands of the other-type domains. The previous TEM investigations¹⁵ showed that the SrRuO₃ thin films grown on exact (001) SrTiO₃ substrate are composed of both X- and Y-type domains with nearly the same volume fraction. The volume fraction of X-, Y-, and Z-type domains presented in the SrRuO₃ films grown on exact and vicinal (001) SrTiO₃

TABLE I. The volume fraction of X-, Y-, and Z-type domains in the SrRuO₃ films grown on exact and vicinal (001) SrTiO₃ substrates.

Substrate orientation	X-domain (vol. %)	Y-domain (vol. %)	Z-domain (vol. %)
Exact (001)	~50%	~50%	0
Vicinal (001)	>95%	<5%	≪1%

substrates is summarized in Table I, based on the TEM observations. The different domain structures observed in the SrRuO₃ thin films grown on the exact and vicinal (001) SrTiO₃ substrates reveal that the surface morphology of the substrate has a strong effect on the SrRuO₃ thin film growth. This effect may be ascribed to the influence of the periodic step-terrace structure of the miscut substrate surface on the growth mechanism of the film.¹³ However, the understanding of the underlying mechanisms, such as preferential formation of a particular kind of domain structure needs further detailed studies on the microstructure of the films grown on substrates with different miscut angles and directions, and especially the study of films grown at different deposition conditions such as growth temperature, growth rate, cooling rate, and oxygen pressure.

In conclusion, the SrRuO₃ thin films deposited by 90° off-axis sputtering on the vicinal (001) SrTiO₃ show a different domain structure compared to those grown on exact (001) SrTiO₃ substrate. The film on miscut (001) SrTiO₃ substrate consists of some small regions of Y- and Z-type domains embedded in a matrix domain which has the X-type domain orientation. These studies reveal that a miscut of the (001) SrTiO₃ substrate along the [100] direction has a strong influence on the microstructure of the SrRuO₃ film. Further studies of domain configurations and interfacial atomistic structures of thin films grown at different conditions are necessary to understand the underlying mechanisms of the effect.

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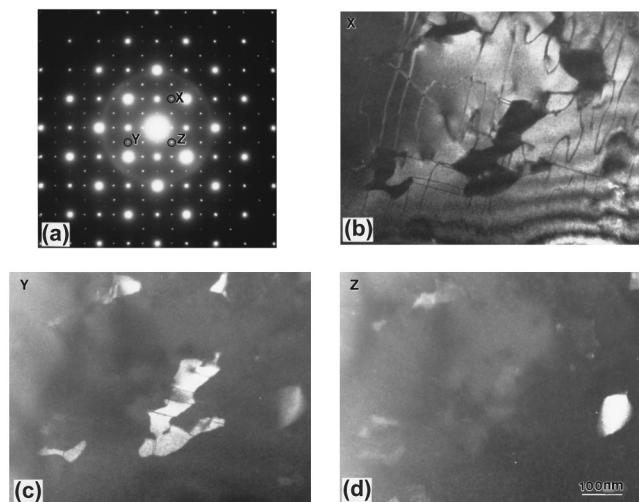


FIG. 4. (a) SAED pattern from the same plan-view specimen as that shown in Fig. 3. (b), (c), and (d) dark-field images using X, Y, and Z reflections, respectively, showing small amount of Y- and Z-type domains existing as islands within the dominant X-type domain.

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