Growth mechanisms of epitaxial metallic oxide $SrRuO_3$ thin films studied by scanning tunneling microscopy

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(Received 23 April 1997; accepted for publication 1 July 1997)

We report the deliberately controlled growth of epitaxial metallic oxide $SrRuO_3$ thin films in three distinctly different growth modes. Scanning tunneling microscopy and x-ray diffraction indicate that the growth mechanism for films on exact (001) $SrTiO_3$ substrates is two-dimensional nucleation, which results in a two domain in-plane structure. As the miscut angle of vicinal (001) $SrTiO_3$ substrates is increased, the growth mechanism changes to step flow which leads to single domain thin films. Films on (001) $LaAlO_3$ substrates have an incoherent three-dimensional island growth due to the large lattice mismatch, resulting in a bulk-like lattice. The vast difference in the growth mechanisms of these films leads to a corresponding difference in their electrical transport and magnetic behavior. Such nanoscale control of growth mechanism, surface morphology, and domain structure can be very important in the fabrication of novel perovskite oxide devices. [S0003-6951(97)02935-5]

Epitaxial thin films and heterostructures of perovskite oxides are finding many applications in novel devices since perovskites exhibit an enormous range of electrical, magnetic, and optical properties. However, the properties of these devices are sensitive to the surface morphology and microstructure of the thin films. For instance, strong flux pinning in epitaxial $YBa_2Cu_3O_7$ (YBCO) thin films has been attributed to point defects[1] and screw dislocations.[2,3] Furthermore, atomic scale control of the surface morphology and interfaces is very important in the fabrication of SNS junctions, spin-polarized tunneling[4] in colossal magnetoresistive (CMR) manganates,[5] and other multilayered heterostructure devices. In this report, we present the deliberately controlled surface morphology, domain structure, and growth mechanisms of epitaxial metallic oxide $SrRuO_3$ thin films in three different growth modes by controlling the substrate miscut and the lattice mismatch with the film.

Among the many perovskite oxide materials, the magnetic metallic oxide $SrRuO_3$ is an attractive material to study because of its interesting electrical and magnetic properties and potential device applications. Single crystal epitaxial $SrRuO_3$ thin films have been grown[6,7] which allow us to study intrinsic anisotropic materials behavior. Furthermore, it is a conducting oxide that is chemically stable in air. Therefore, it is an ideal system for structure and growth mechanism studies by scanning tunneling microscopy (STM) at room temperature in air.

The $SrRuO_3$ thin films were deposited on exact (001) $SrTiO_3$, miscut (001) $SrTiO_3$ toward [010] and exact (001) $LaAlO_3$ substrates from a stoichiometric composite target using a 90° off-axis sputtering technique. The films were deposited at an operating pressure of 200 mTorr (60% Ar/40% O_2) and a temperature of 680 °C. After deposition, the samples were cooled down to room temperature in an oxygen pressure of 300 Torr. The thickness of the films is about 3000 Å. X-ray diffraction showed that all the films deposited on (001) $SrTiO_3$ substrates (both exact and vicinal) had a purely (110) texture normal to the substrate, with an out-of-plane lattice parameter of 3.96 Å.[8] Due to a small lattice mismatch with $SrTiO_3$ (0.64%), the in-plane lattice parameters of the films were found to be 3.91 Å which is close to the substrate lattice parameter (3.905 Å). Therefore, these films had a coherent growth resulting in a strained lattice.

On 0° miscut or exact (001) $SrTiO_3$ substrates, there is no preferred step structure on the substrate surface. Therefore, the film should nucleate as numerous two-dimensional islands on the substrate surface and grow by adding material to the circumference of these laterally growing islands. Thus, two-dimensional nucleation should be the dominant growth mechanism. Furthermore, these films should have a two domain in-plane texture because of the fourfold symmetry of the substrate surface.

The growth mechanism and surface morphology of the films was studied by both STM and atomic force microscopy (AFM). All the films were scanned such that the scan direction (one edge of the image) was parallel to the substrate [010] direction. The film deposited on an exact (001) $SrTiO_3$ substrate (miscut angle, $\alpha \approx 0.1°$) displayed a uniform distribution of multiterraced islands, indicating that the film growth was by a two-dimensional nucleation process, as expected. Figure 1(a) shows the STM image of a $0.5\ \mu m \times 0.5\ \mu m$ scan on this sample showing one such multiterraced island. The circumference of each island can be traced as a closed circular loop and no spiral patterns are observed, thus eliminating the possibility of screw dislocation growth. The presence of circular multiterraces associated with each nucleus suggests secondary nucleation taking place on the surface of already nucleated islands. The circular shape of the islands indicates that the in-plane growth rate of the films is isotropic. Consequently, these films were found to have a 90° misoriented two domain in-plane epitaxial arrangement with equal volume fractions of both domains, by azimuthal x-ray scans of off-axis (221) reflection.

The step height is found to vary between 1.8 and 4.2 Å as seen in the section analysis, in Fig. 1(b). This step height is consistent with our AFM observations and can hence be attributed to film topography. Thus, half unit cell growth is

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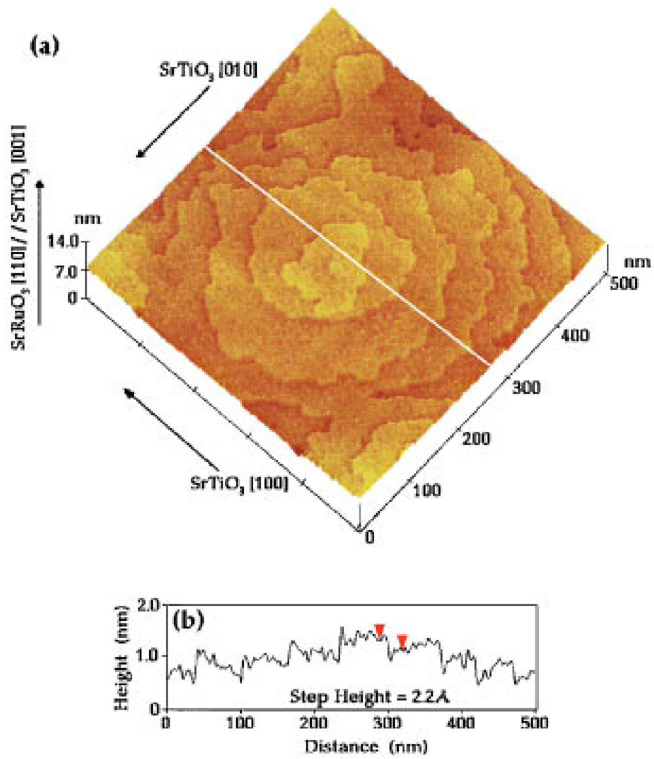

FIG. 1. (a) STM image of $SrRuO_3$ thin film showing two-dimensional nucleation on exact (001) $SrTiO_3$ substrate and (b) section analysis along the line drawn in (a).

observed in these films suggesting that the $SrRuO_3$ surface exhibits both Sr–O and Ru–O terminations. Due to the coherent growth, the film surface shows large terraces (500–2000 Å in diameter) that are atomically flat and separated by small steps varying between half and one unit cell in height. Therefore, the film surface is extremely smooth with a root mean square (rms) roughness of 4 Å over a 1 μm$\times$1μm scan area.

For vicinal substrates, if the miscut direction is along the in-plane [010] axis (represented as $\beta = 0°$), then the (010) plane of $SrTiO_3$ would also be preferentially exposed at the steps on the substrate. The exposed (010) plane would serve as a nucleation center for initiating epitaxy and growth of (110) $SrRuO_3$. Therefore, the film should grow by a step flow mechanism[9] in one direction. If the miscut angle is high enough so that the terrace width is smaller than the characteristic surface diffusion length of the film adatoms at the growth temperature, then one directional step flow can lead to the growth of single domain films.

Figure 2(a) shows a typical STM image of a $SrRuO_3$ film on a miscut $SrTiO_3$ substrate with miscut angle $(\alpha) = 2.0°$ and $\beta = 12°$. The film surface shows a periodic step pattern with straight steps, indicating step flow growth. No islands or protrusions are seen on the film. The STM image shows evidence of step bunching and half unit cell high steps can be distinguished in some of the multiple unit cell high bunched steps. The STM section analysis in Fig. 2(b) shows the bunched step height to vary between 10 and 30 Å. Due to the step flow growth, the terrace width is smaller and the step height was larger compared to the film grown by two-dimensional nucleation. Consequently, the film has a higher rms surface roughness of 8 Å over a 1 μm$\times$1 μm scan area.

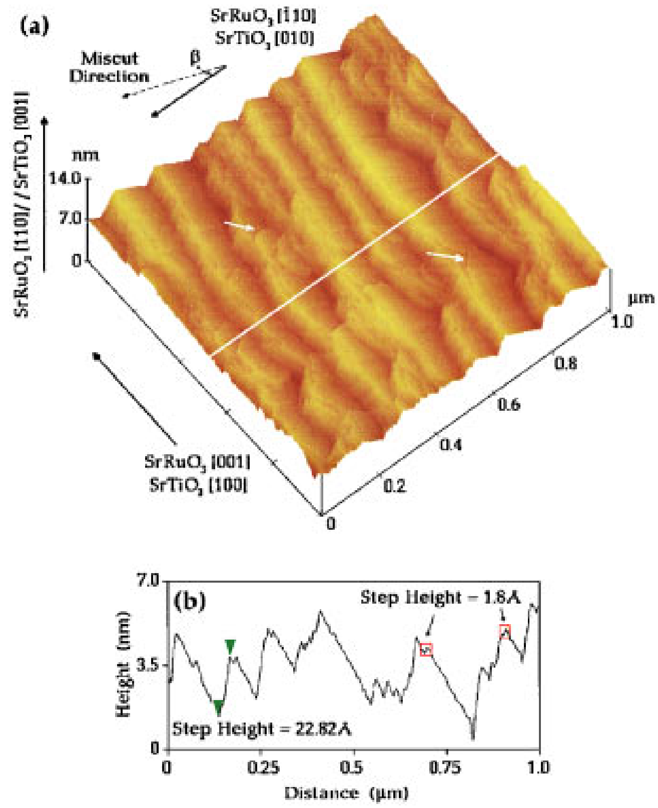

FIG. 2. (a) STM image of $SrRuO_3$ thin film on $SrTiO_3$ substrate with $\alpha = 2°$ and $\beta = 12°$. The arrows point to half and single unit cell high steps in the bunched steps, and (b) section analysis along line drawn in (a).

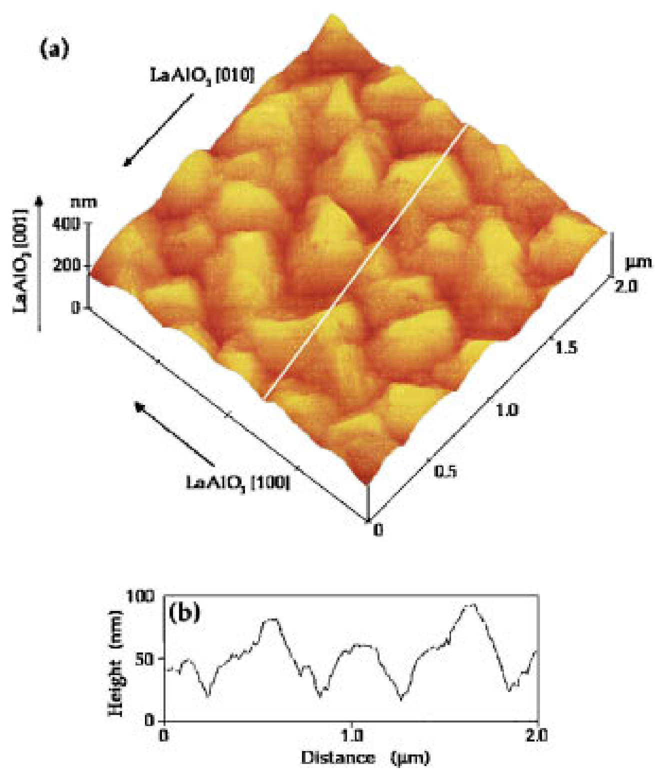

FIG. 3. (a) STM image of $SrRuO_3$ thin film showing three-dimensional island growth on exact (001) $LaAlO_3$ substrate and (b) section analysis along the line drawn in (a).

As the miscut direction is 12° away from the in-plane [010] direction, both the (010) and (100) faces of the substrate will be exposed at the kink sites with an areal ratio of approximately 5:1. The film surface also shows some kink sites similar to what would be expected on the substrate surface. However, as a larger area of the (010) face is exposed on the substrate surface, step flow along the [010] direction dominates the film growth. Consistently, x-ray azimuthal scans of off-axis peaks showed that these films were single domain with the epitaxial arrangement of $SrRuO_3[\bar{1}10]$//$SrTiO_3[010]$ and $SrRuO_3[001]$//$SrTiO_3[100]$.

As the miscut angle of the substrate is decreased the step height of the bunched step decreases and smoother films are obtained. However, if the miscut angle is too small, then the terrace width on the substrate is larger than the critical surface diffusion length of the film adatoms. As a result, the supersaturation of the adatoms reaches a critical value on the terraces and two-dimensional nucleation occurs on the terrace. The film growth then proceeds by a combination of step flow and two-dimensional nucleation resulting in meandering semicircular shaped steps. Such a surface morphology was observed by STM on a $SrRuO_3$ film by decreasing the miscut angle of the (001) $SrTiO_3$ substrate to 0.7° toward the [010] direction. The step height on the film surface varied between 4 and 12 Å. The rms roughness of the film was 5 Å over a 1 μm×1 μm scan area. Furthermore, x-ray azimuthal scans revealed a small amount (7%) of 90° misoriented domains within the plane.

An interesting feature observed in the AFM and STM images is that half unit cell high features (1.8–2.2 Å) could be distinguished, as seen in the section analysis in Figs. 1(b) and 2(b). $SrRuO_3$ is a cubic perovskite consisting of alternate layers of SrO and RuO_2 both of which are electrically neutral. Therefore, the film surface can display both SrO and RuO_2 terminations. Depending upon whether the surface termination layer of the substrate is SrO or TiO_2, the stacking sequence for the film will be bulk $SrTiO_3$–SrO–TiO_2–SrO–RuO_2-bulk $SrRuO_3$ or bulk $SrTiO_3$–TiO_2–SrO–RuO_2–SrO-bulk $SrRuO_3$. It is known that polished $SrTiO_3$ substrates exhibit both SrO and TiO_2 terminated surfaces.[10] Therefore, the $SrRuO_3$ films can display both stacking sequences leading to mismatched stacking sequences across subgrain boundaries. It is suggested that these mismatched stacking sequences can be ''healed out'' by the intercalation of a RuO_2 or SrO layer resulting in half unit cell high steps. Such nonunit cell growth has been observed in high-T_c superconductor thin films[11,12] with noncubic structures.

The films deposited on $SrTiO_3$ substrates grow in a coherent mode due to the small lattice mismatch with the substrate. However, the growth of films deposited on $LaAlO_3$ substrates is not constrained by the substrate on account of the large lattice mismatch (3.6%). Therefore, the film growth proceeds in an incoherent mode developing three-dimensional features which results in a bulk-like film lattice. Figure 3(a) shows the STM image of a $SrRuO_3$ thin film deposited on a (001) $LaAlO_3$ substrate. A very rough surface (rms roughness = 190 Å) with three-dimensional islandlike features is observed. These islands are much bigger (~5000 Å in base diameter and 1000 Å in height) compared to the features observed on the films grown on $SrTiO_3$ substrates, as seen in the section analysis in Fig. 3(b). As the lattice strain is completely relaxed, these films have a bulk-like lattice with out-of-plane and in-plane lattice parameters of 3.93 Å, as indicated by x-ray diffraction θ–2θ scans. These films display a mixture of (110) and (001) orientations normal to the substrate with both grains showing 90° domains in the plane.

Such a dramatic difference in the growth mechanisms of the films results in a corresponding difference in their magnetotransport and magnetic behavior.[13] For instance, we have already seen that the resistivity versus temperature curves of the $SrRuO_3$ films grown incoherently by three-dimensional island growth on $LaAlO_3$ substrates display a change of slope at 155 K, which indicates a ferromagnetic transition occurring at almost the same temperature as the bulk material. However, the transition occurs at slightly lower temperatures in the films deposited on $SrTiO_3$ substrates which suggests that the strain in these films suppresses the Curie temperature. Furthermore, single crystal films grown by step flow mechanism exhibit strong magnetocrystalline anisotropy. The $SrRuO_3$ $[\bar{1}10]$ direction which is a relatively easier axis for magnetization is aligned along the step flow direction whereas the harder axis, $SrRuO_3$ [001], is aligned transverse to the direction of step flow. In contrast, the two domain films grown on $SrTiO_3$ substrates by a two-dimensional nucleation mode will have essentially isotropic magnetic properties within the plane.[13]

Such nanoscale control of the surface morphology and growth mechanism can be very important in the fabrication of perovskite devices since the properties of these devices are dependent upon the surface and domain structure of the thin films. Atomically smooth film surfaces are essential to obtain sharp interfaces and optimum performance in such devices.

This work was supported by the ONR Grant No. N00014-95-1-0513, the NSF Grant No. DMR 9421947, the NSF Young Investigator Award (C.B.E.), and the David and Lucile Packard Fellowship (C.B.E.).

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