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Initial Stage Nucleation and Growth of Epitaxial $SrRuO_3$ Thin Films on (0 0 1) $SrTiO_3$ Substrates

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Abstract. We have investigated the initial stage nucleation and growth of epitaxial $SrRuO_3$ thin films grown on both polished (as received) and buffered HF (BHF) etched single crystal (0 0 1) $SrTiO_3$ substrates by 90° off-axis sputtering. Atomic force microscopy indicates a dramatic difference in the initial stage growth of $SrRuO_3$ films on the two substrates. The films on polished substrates nucleate as rectangular islands, which merge together to form a continuous film as the thickness increases. Complete coverage is obtained at film thickness of $\sim 20\,nm$. In contrast, the film on BHF etched substrate nucleates as finger-shaped islands at the step sites and continues to grow by adatom diffusion to the step sites. Complete coverage is obtained at a film thickness of $\sim 10\,nm$. This difference in the initial stage nucleation is attributed to the difference in surface morphology and termination layer of the two substrates. However, the thicker films on both as received and BHF etched substrates have identical surface morphologies. Such studies on the initial stage nucleation will also help us understanding the growth kinetics and development of surface morphology and interfaces in multilayered perovskite thin film heterostructures and devices.

Keywords: perovskite thin films, intial stage nucleation, vicinal $SrTiO_3$ substrates, growth mechanisms, surface termination

Epitaxial thin films of perovskite oxides exhibit a wide range of electrical, magnetic, and optical properties. They consequently have great potential for device applications, such as high-T_c Josephson tunnel junctions [1,2], ferroelectric non-volatile memories [3], and spin dependent tunneling [4] in magnetic oxides [5]. The properties of these devices are very sensitive to the growth mechanisms, surface morphology and domain structure of the thin films. Therefore, controlled growth on an atomic scale becomes an important issue, as often times there is little reproducibility in the growth and properties of films on the same kind of substrate.

The growth mechanisms of the films depend largely on the surface morphology, termination layer [6], crystal structure and lattice mismatch of the substrate. Therefore, controlling the surface morphology and chemistry of the substrates will ensure run-to-run reproducibility. Furthermore, the coverage of ultra thin films and barrier layers is a crucial issue in many perovskite heterostructure devices such as high-T_c SNS Josephson junctions and spin polarized tunneling devices. One approach to control the surface morphology and chemistry of the substrate is to employ surface treatments such as annealing or chemical etching of the substrate. Some evidence has been found that annealing single crystal $SrTiO_3$ substrates in oxygen [7] can produce a periodic step-terrace pattern with mixed SrO and TiO_2 termination layers on the substrate surface. Chemically etching the $SrTiO_3$ substrates also produces uniform steps of single unit cell height with a purely TiO_2 terminated surface [8,9]. The terraced surface, which results from these surface treatments, offers a reproducible template surface for atomically regulated growth of epitaxial thin films.

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In this study, we have compared the initial stage growth of $SrRuO_3$ thin films on both etched and as-received (polished) (0 0 1) $SrTiO_3$ substrates (miscut angle $\approx 0.1°$). $SrTiO_3$ is a cubic perovskite with a lattice parameter of 0.3905 nm. $SrRuO_3$ is a distorted perovskite with a pseudocubic lattice parameter of 0.393 nm in the bulk material, and thus, has a close lattice match with $SrTiO_3$. The isotropic metallic oxide $SrRuO_3$ is an attractive material to study because of its potential device applications and excellent structural and chemical compatibility with other technologically important oxides such as $Pb(Zr_{1-x}Ti_x)O_3$-based ferroelectrics [10].

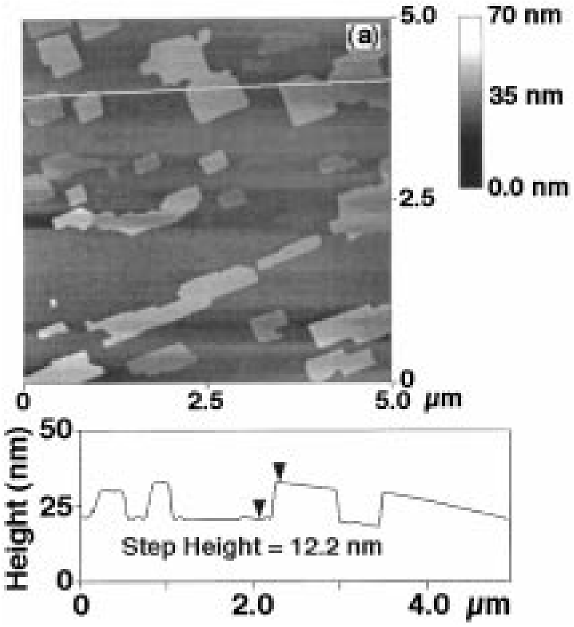
The growth of thick (100 nm–300 nm) $SrRuO_3$ films on both exact and miscut (0 0 1) $SrTiO_3$ substrates has already been studied and controlled [11–13]. It has been shown that on 0° miscut or exact (0 0 1) $SrTiO_3$ substrates with no preferred step structure, the $SrRuO_3$ film nucleates as numerous two dimensional islands and grows by adding material to the circumference of these laterally growing islands. Such a growth mechanism is known as two-dimensional nucleation. In contrast, the periodic steps exposed on the surface of miscut (0 0 1) $SrTiO_3$ substrates, act as preferential nucleation sites for the film adatoms, which leads to a step-flow growth of the film [14].

The miscut angle (α) of the single crystal (0 0 1) $SrTiO_3$ was determined by reflecting a He-Ne laser beam off the sample surface in conjunction with four circle x-ray diffraction. The surface of the untreated or polished substrate is very flat and featureless with a root mean square (RMS) roughness of 0.18 nm over a $5\,\mu m \times 5\,\mu m$ scan area. The commercially polished substrates are known to have mixed SrO and TiO_2 termination layers. Furthermore, this top layer of the polished substrate may be damaged due to polishing and hence, the surface morphology differs from substrate to substrate, which limits the reproducibility of growth of the $SrRuO_3$ thin films. In order to obtain a more reproducible template surface some of the as-received substrates were chemically etched in a buffered HF (BHF) solution that preferentially etches the SrO atomic plane leaving behind a TiO_2 terminated $SrTiO_3$ substrate surface [8,9]. The BHF etched $SrTiO_3$ substrate surface shows atomically flat terraces with well defined uniform steps of unit cell (0.4 nm) height.

The $SrRuO_3$ thin films were deposited on both the polished and etched (0 0 1) $SrTiO_3$ substrates from a 2-inch diameter stoichiometric composite target using a 90° off-axis sputtering technique [15,16]. The films were deposited at 600°C in an operating pressure of 200 mTorr (60%Ar/40%O_2). After deposition, the chamber was vented with oxygen to a pressure of 300 Torr and the samples were then cooled down to room temperature. The $SrRuO_3$ films were deposited using a shadow mask technique. The mask was held at a height of $\sim$ 1 mm above the surface of the substrate such that half of the substrate was under the shadow of the mask. The $SrRuO_3$ films thus grown had a thickness gradient with the film thickness increasing from $\sim$ 0 nm at one end to 100 nm at the other end, which is left exposed by the mask. The film adatoms diffuse onto the region of the substrate in the shadow of the mask with the amount of deposition decreasing as one goes further away from the exposed region. Thus, different stages of nucleation can be studied using a single sample.

The $SrRuO_3$ films grown on the two substrates were characterized by tapping mode atomic force microscopy (AFM). Images were taken across the entire range of each sample to observe growth behavior. Figure 1(a) shows the AFM image from a very thin region ($\sim$ 3 nm nominal thickness) of a $SrRuO_3$ film deposited on the polished substrate. The film in this region shows rectangular islands $\sim$ 12 nm in height scattered over the $5\,\mu m \times 5\,\mu m$ scan area. The film is not fully covered as indicated by the highly non-uniform thickness of the film in this region. The top surface of the rectangular columns is extremely flat and featureless. No layering or steps are observed on the top surface of these columns.

As the thickness of the film increases to $\sim$ 15 nm, the rectangular islands begin to merge together as shown in Fig. 1(b). At this stage the film coverage is still only $\sim$ 80%. In this stage, the top surface of the columnar structures begins to show step-terrace features with $\sim$ 0.8 nm (2-unit cell high) steps as shown in the section analysis of Fig. 1(b). Eventually, as the thickness of the film increases further, all the columnar features merge together and provide complete coverage at a nominal film thickness of $\sim$ 20 nm. The features on top of the columns are much more pronounced and the steps are clearly visible at this stage. The film grows by a combination of two-dimensional nucleation and step-flow as seen in the thick films [12]. Figure 2 shows the AFM image from a thick region of the film on a polished substrate, clearly showing a two-dimensional circular island and



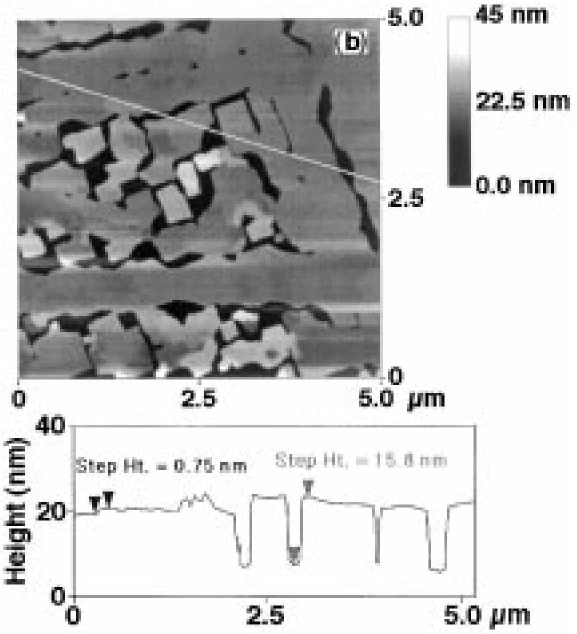


Fig. 1. The development of SrRuO$_3$ film surface morphology on a polished (001) SrTiO$_3$ substrate. (a) ~ 3 nm thick SrRuO$_3$ film and (b) ~ 15 nm thick film. The section analysis shown below the AFM images corresponds to the line scan along the line shown in the images.

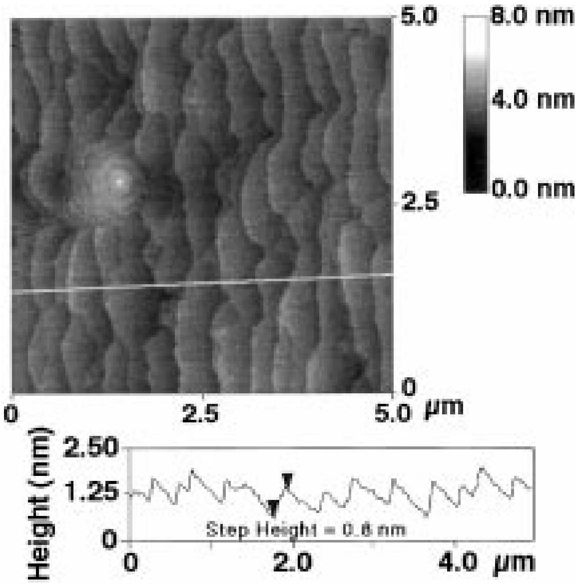


Fig. 2. The surface morphology of ~ 70 nm thick SrRuO$_3$ film on a polished (001) SrTiO$_3$ substrate. The section analysis shown below the AFM image corresponds to the line scan along the line shown in the image.

step-flow growth. As seen in the section analysis in Fig. 2, the atomically flat terraces on the island are separated by steps of about 0.4–0.8 nm in height, which corresponds to one or two unit cells of SrRuO$_3$.

In contrast to the polished substrate, the surface of an etched substrate shows a periodic step terrace structure and has TiO$_2$ as its terminating atomic plane [6,9]. Figure 3 shows the growth of SrRuO$_3$ and development of film surface morphology on the etched substrate. The AFM image of a very thin region (~ 1 nm) of the film shown in Fig. 3(a), indicates that the film nucleates at the step sites as expected and grows along the step edges, resulting in ''finger'' shaped islands that are scattered along the steps. Thus, the film grows more in the lateral directions than on the polished substrate. Therefore, at this stage the film has better coverage and is smoother with an RMS surface roughness of 0.26 nm over the scan area. As the thickness of the film increases to ~ 6 nm, the coverage is better as the islands begin to coalesce, as shown in Fig. 3(b). At this stage the film coverage is ~ 80%. The steps on the film surface are multiple unit-cell high (~ 3–4 unit cell high). The step height on the film surface is

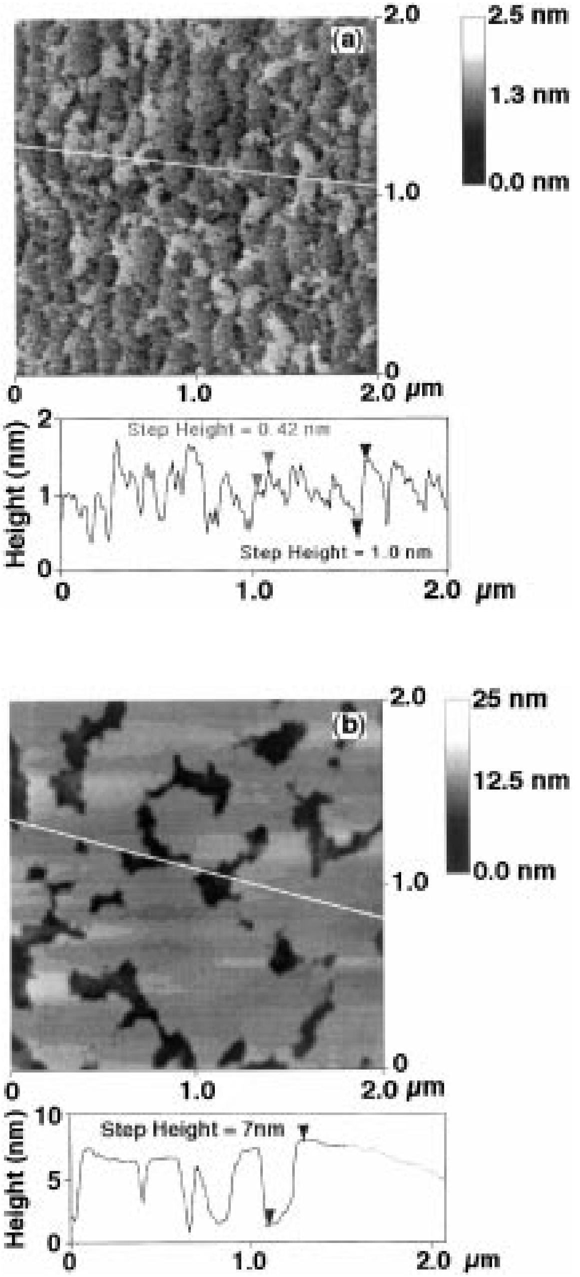


Fig. 3. The development of $SrRuO_3$ film surface morphology on a BHF etched (001) $SrTiO_3$ substrate. (a) $\sim$ 1 nm thick $SrRuO_3$ film and (b) $\sim$ 6 nm thick film. The section analysis shown below the AFM images corresponds to the line scan long the line shown in the image.

lower than that on the film grown on the polished substrate.

As the film thickness is further increased to $\sim$10 nm, the coverage is complete and the film surface consists of regular terraces separated by atomic steps. The morphology of the film at this stage is very similar to that grown on a as polished substrate, shown in Fig. 2. The film then continues to grow by step-flow and some two-dimensional nuclei are also observed on the terraces. In some regions spiral growth patterns were observed indicating screw-dislocation mediated growth. Such growth spirals might nucleate at corresponding dislocations on the substrate surface. Thus, while the initial stage growth mechanism of the film is dramatically different on the etched and polished substrates, the growth morphology of thick films is identical on both substrates.

This difference in the initial stage growth mechanism is attributed to the difference in surface energy of the substrate and kinetics of the film growth on the two different substrates. Depending on 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 $SrRuO_3$. Therefore, the film surface can display both SrO and RuO_2 terminations, both of which are electrically neutral. Such mixed terminations, resulting in half-unit cell high steps, have been observed on our thicker ($\sim$ 3000 A) films [12].

In summary, a dramatic difference is observed in the initial stage of film growth on an etched substrate and that on a polished (untreated) substrate. However, at increased film thickness ($\geq$ 100 nm), films grown on both substrates have identical surface morphologies. These results indicate that substrate surface morphology and termination layer can have a large influence on the initial stage film growth and properties of ultra-thin films and superlattices, where coverage and nanoscale control of interfaces and roughness are critical technology issues. For instance, such atomic scale control of growth mechanisms is essential to obtain uniform coverage of barrier layers in high-T_c SNS Josephson junctions and magnetic tunnel junctions where the junction properties are sensitive to the barrier layer thickness. The $SrRuO_3$ films grown on the BHF-etched substrate show more uniform coverage than films grown on the polished substrate. Thus, it is evident that such surface pretreatment of substrates could be beneficial to the performance of devices using such ultra-thin films. Secondly, the growth of thicker films

($\geq 100\,\text{nm}$) is not influenced by substrate pretreatments, especially chemical etching. Furthermore, such studies on the initial stage nucleation will also help understand the growth kinetics and development of surface morphology in the growth of perovskite oxide thin films.

Acknowledgments

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