Study of 2D growth stability of SrRuO$_3$ on SrTiO$_3$

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Abstract. In order to control the surface roughness and chemical termination of an oxide film, a promising route is to use a vicinal substrate and to control the atomic step positions during growth in the so-called step flow mode. The stability of this mode is studied in the case of SrRuO$_3$ heteroepitaxy on SrTiO$_3$, focusing on the influence of deposition flux and substrate mean terrace width. Transitions from unstable step bunching to stable step flow and from step flow to island nucleation are observed and discussed in terms of the mean step velocity. The step bunching is traced back to a strain-based driving force in competition with a stabilizing asymmetry for incorporation of adatoms at steps. A thin film obtained after stable step flow gives a greater finite size effect than a step-bunched one, as seen by X-ray diffraction.

1. Introduction

The growth of perovskite oxides using pulsed Laser deposition (PLD) allows for the control of the surface roughness down to the atomic scale, which is a great asset in particular in the field of oxide-based electronics where interfaces play a huge part in device properties. The interface structure, in particular its sharpness and the presence of oxygen vacancies, will determine for example the magnetic coupling between layers [1] or the formation of a two-dimensional electron gas [2]. A first step to achieve such control of the interface between heteroepitaxial oxide layers is to use a substrate with homogeneous surface termination such as a TiO$_2$-terminated SrTiO$_3$ (001) substrate (STO) [3]. Then, a two-dimensional (2D) growth will often be preferred to have a low level of roughness. The PLD technique has proven the ability to build fully strained SrRuO$_3$ (SRO) films with the target stoechiometry on single-terminated STO substrates [4].

During PLD, each nanosecond-duration laser pulse brings a quantity $N_p$ of atoms to the surface, which is adsorbed as single adatoms or form small unstable clusters. These species then diffuse to stable incorporation sites, either at pre-existing step edges or through nucleation of stable islands thus forming a new layer. This transient diffusion stage is typically over before the next pulse. When all impinging atoms are able to reach the step edges, the growth proceeds in the so-called step flow mode. At variance with this 2D scenario, island nucleation on the terraces can lead to tri-dimensional (3D) growth if the nucleation of a new layer occurs before the completion of the previous one. Step flow on a vicinal surface thus appears as an optimal growth mode to control surface morphology. However, in the case of heteroepitaxy it has been shown that step flow growth can be unstable with respect to step bunching [5]. The occurence of this instability is not yet well understood in particular regarding the transition towards stable step flow upon increasing the deposition flux. In this paper, we present a study of the stability of step flow growth using SRO on vicinal TiO$_2$-terminated STO substrate as...
model system, for which step bunching has already been observed [6]. For a fixed temperature, we have mapped SRO growth as a function of deposition flux and STO mean terrace width.

2. Experimental details

Substrates of STO were prepared according to an established procedure [3,4] to ensure a TiO$_2$ chemical termination. The substrates were systematically characterized with atomic force microscopy (AFM) in contact mode prior to their introduction into the growth chamber, in particular to measure their mean terrace width ($L$). Thin films of SRO were grown on these substrates by PLD using a KrF excimer laser ($\lambda = 248$ nm) at a growth temperature of 610°C under 120 mTorr of pure oxygen atmosphere. Laser energy was set to 200 mJ and the fluence was further refined with an attenuator to get 3 J/cm$^2$ on the target. A homogenizer is used to give the laser beam a flat-top profile to avoid droplet formation on the sample surface. To ensure a good control of both film thickness and mean deposition flux, an in situ optical reflectometry technique is used [7]. Using X-ray diffraction (XRD) measurements, all SRO films were found fully strained on STO with unit cell parameter perpendicular to the surface close to 0.395 nm. The deposition flux $F$ is taken as $F = pN_p$ with $p$ the laser repetition rate and $N_p$ the (fixed) amount of SRO deposited per pulse. A repetition rate between 0.6 Hz and 10 Hz thus gives a flux ranging from $3.3 \times 10^{-2}$ ML/s to $5.5 \times 10^{-1}$ ML/s.

3. Results and discussion

Figure 1 shows 4 x 4 µm$^2$ AFM topographs of typical morphologies observed after growth of 9 nm-thick SRO films in the step bunching instability region (a), after stable step flow (b), and with island nucleation (c). The initial difference of terrace width between samples (a) and (b) is rather small, but the deposition flux was increased by about a decade, from $3.6 \times 10^{-2}$ ML/s for the bunched morphology to $3.8 \times 10^{-1}$ ML/s for the step flow sample. This huge increase of the flux stabilizes the structure, promoting an equal width for all terraces. For the same mean step velocity $FL \sim 40$ nm/s but with larger terrace width, islands are formed which can give rise to 3D growth upon further deposition.

![Figure 1: 4 x 4 µm² AFM topographs of 9 nm-thick SRO films on STO after (a) unstable step flow giving step-bunched surface, (b) stable step flow and (c) island formation. Deposition flux and substrate terrace width are given below each image. Inset of (c) is a close-up on a terrace.](image)

In the case of heteroepitaxy, the misfit parameter between the substrate and the film (~ 0.6% for SRO/STO) leads to an increase of elastic energy in the structure. There are different ways to release this energy, for example through dislocations or by gathering the steps together. Tersoff et al. [5] have expressed the elastic energy between steps as $E = \alpha_1 \ln(L) + \alpha_2 / 2L^2$, where $\alpha_1$ is linked to the stress
discontinuity at step edges, $L$ is the terrace width, and $\alpha_2$ is a dipolar interaction. The first term expresses an attractive interaction between step edges, whereas the second one points a repulsive force. These two interactions together lead to an optimal distance between steps with characteristic length $L_0 = (\alpha_2 / \alpha_1)^{1/2}$. Typically steps with $L > L_0$ will benefit from moving closer together.

On most surfaces diffusing adatoms have a higher probability to attach to ascending step edges due to an excess energy barrier for diffusion over a step, the so-called Ehrlich-Schwöbel (ES) effect. In a kinetic picture, the larger the terrace width and deposition flux, the faster this incorporation asymmetry at steps will damp terrace width fluctuations. Increasing the flux or more generally the mean step velocity is thus a stabilizing factor with respect to step bunching. Combined with the aforementioned elastic driving force, step bunching is thus expected for small deposition flux and small terrace widths with a transition to stable step flow upon increasing these parameters, as seen experimentally (figure 1). At higher temperature the instability should occur over a wider ($F,L$) range due to a decreasing ES effect with temperature. As this yields an increased adatom diffusion length, larger terrace widths can be used to obtain stable step flow without going into the island nucleation regime.

Upon closer scrutiny of the morphology shown in Figure 1 (c), all islands are found to be of one monolayer height (see inset). The adatom diffusion length is estimated of the order of 100 nm at our growth temperature, thus island nucleation is found on 370 nm-wide terraces Since our films are 9 nm thick, it is not possible at this stage to predict whether 2D growth will continue through nucleation and coalescence or if 3D growth will set in with formation of multi-layer islands.

We have elaborated two SRO films, one in the step bunching regime (60 nm thick) and the other in the stable step flow mode (50 nm thick). Figure 2 shows the XRD spectra of these two samples. The width difference of the SRO main peak comes from the thickness variation between the two thin films. To fit our data, we used a grating function corresponding to the fourrier transform of the grating mesh along the perpendicular axis, which takes into account the strained SRO parameter (0.395 nm) and the finite film thickness. This model gives a very good fit to the data for both films. The main difference between these two XRD patterns is the finite size effect which is very well defined for the step flow sample and barely visible for the step-bunched one.

![Figure 2](image)

**Figure 2**: XRD spectra of the (002) peaks of SRO (left peak) and STO (right peak) for (a) the 60 nm-thick step-bunched film and (b) the 50 nm-thick step flow sample.

The attenuation of the finite size effect in Figure 2 (a) can be related to the Root Mean Square roughness of the sample, which is higher in the case of a step bunched morphology (~ 0.4 nm) than for a step flowed sample (~ 0.2 nm). Such roughness and associated strain field can explain variations of the unit cell parameter in the near-surface region which would give a reduced size effect. XRD here allows to evidence a link between growth-induced surface morphology and film properties.
4. Conclusion

In this paper we have shown that upon increasing the deposition flux and/or the substrate mean terrace width the 2D growth of SRO on STO goes from unstable step bunching to stable step flow and finally to island nucleation and coalescence. We have evidenced an influence of surface morphology and thus of growth mode on the finite size effect as measured by XRD. This work opens the way to further studies to address the temperature dependence and the late stage of growth.

5. Acknowledgments

This work was partly supported by the French Agence Nationale pour la Recherche (ANR) under “MINOS” project.

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