Step velocity tuning of SrRuO$_3$ step flow growth on SrTiO$_3$

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Taking advantage of vicinal (001) SrTiO$_3$ substrates with different mean terrace widths, the heteroepitaxial growth of SrRuO$_3$ in the step flow mode has been mapped as a function of mean step velocity. Transition between stable and unstable step flow is shown to occur at a well-defined critical step velocity, with a step bunching instability observed below this threshold. The ability to pass from unstable to stable step flow during growth upon increasing the mean step velocity is demonstrated. This result is discussed in terms of a stress-based driving force for step bunching in competition with an effective step-up adatom current.

When considering the use of complex oxides in solid state electronic devices, a core issue is the control of the interfaces regarding both their structure and chemical nature. Sharpness of the interfaces at single-layer level is for example a requisite for well-defined barriers in magnetic tunnel junctions [1]. Similar high-end control of atomic termination and oxidation state between heteroepitaxial oxide films allows for the obtention of a confined electron gas at the interface [2, 3]. First step towards optimal interface quality is to start from a substrate with a homogeneous surface termination, like the single-terminated (001) SrTiO$_3$ substrate exhibiting only TiO$_2$ planes after suitable preparation [4, 5]. Next, a two-dimensional (2D) growth mode will often be preferred to limit the development of surface roughness. In this way, the pulsed Laser deposition (PLD) technique is able to build on the quality of the substrate surface to obtain fully strained films with the target stoichiometry, as has been shown in particular for SrRuO$_3$ growth on SrTiO$_3$ [6, 7].

Going the 2D growth route, an appealing scheme is to start from a vicinal surface and to control both the atomic step positions and surface termination during growth in the so-called step flow mode [8]. The latter is usually achieved through proper tuning of deposition temperature ($T$) and flux ($F$) with respect to the substrate mean terrace width ($L$). In this work, we studied the heteroepitaxy of SrRuO$_3$ on TiO$_2$-terminated SrTiO$_3$ substrate as a model system, for which step flow growth is readily achieved [6] while being found unstable against step bunching [9, 10]. In Ref. 9 and 10, the origin of this instability has been traced back to a strain-driven attractive interaction between steps [11], with a model being proposed to account for the transition between stable and unstable step flow. However, a comprehensive experimental study of this transition as a function of growth parameters is found lacking, in particular going from unstable to stable step flow. Focusing on $F$ as tunable growth parameter, we show experimentally that the mean step velocity $V = FL$ of the flowing step train determines the stability of this growth mode for a strained layer, with a reversible transition evidenced at a critical velocity value. For a fixed temperature, we mapped SrRuO$_3$ growth as a function of mean step velocity, by varying the deposition flux and using (001) SrTiO$_3$ vicinal substrates with different mean terrace widths.

![Image](337x468 to 423x554)

**FIG. 1.** $4 \times 4 \mu m^2$ AFM topographs of SrRuO$_3$ films grown at $610^\circ C$ in the step flow mode with mean step velocities (a) $V = 10.2$ nm/s and (c) $V = 8.3$ nm/s. Mean terrace width of SrTiO$_3$ substrate is 120 nm (a,b), 150 nm (c,d) and 250 nm for inset of (c). Height histograms taken on a $1 \times 1 \mu m^2$ area of image (a) and on the whole image in (c) are displayed in (b) and (d), respectively. The height is normalized to the one of a strained SrRuO$_3$ unit cell (see text).

Substrates of SrTiO$_3$ were prepared according to an established procedure [4, 5] to ensure their chemical termination to be TiO$_2$. The mean terrace width varies from 65 nm to 370 nm, corresponding to miscut angles from $0.06^\circ$ to $0.3^\circ$. The substrates were systematically characterized with atomic force microscopy (AFM) in contact mode prior to their introduction into the growth chamber, in particular to check the single atomic termination through the friction contrast. From X-Ray diffraction (XRD) and AFM mean terrace width values are obtained with a relative accuracy better than 10%. Thin films of SrRuO$_3$ 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/cm² 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 [12].

Inset of Fig. 1(c) is a 4 nm step bunches, which are not straight but curved as seen on the AFM image. Single steps are still found on the terraces in between the step bunches, which are not straight but curved as seen on the AFM image.

Figure 1 shows AFM topographs of typical morphologies observed after SrRuO₃ growth in the stable step flow regime (a,b) and in the step-bunching instability region (c,d). Height histograms are given in (b,d), with the height normalized to the single-step height of 0.395 nm found for our strained SrRuO₃ films. While after stable step flow all terraces are separated by single steps, after 8.7 nm-step flow in the unstable regime step bunches comprised of 3 to 4 steps are clearly seen in the histogram. Single steps are still found on the terraces in between the step bunches, which are not straight but curved as seen on the AFM image. Inset of Fig. 1(c) is a 4 × 4 μm² topograph of a film grown with the same parameters as for the one of Fig. 1(c) but on a SrTiO₃ substrate with 250 nm-wide terraces instead of 150 nm. Flux has been adjusted to get the same step height of 0.395 nm for our strained SrRuO₃ films. After while stable step flow all terraces are separated by single steps, after 8.7 nm-step flow in the unstable regime step bunches comprised of 3 to 4 steps are clearly seen in the histogram. Single steps are still found on the terraces in between the step bunches, which are not straight but curved as seen on the AFM image.

A similar bunched morphology is found for both films, with roughly the same number of steps in the bunches and thus a bunch separation scaling with initial terrace width.

The drastic change between stable step train (Fig. 1(a)) and unstable step bunches (Fig. 1(c)) is obtained for a rather small increase of deposition flux and thus of mean step velocity. Moreover, all bunched morphologies are already well developed after deposition of 8.7 nm of strained SrRuO₃. These observations point to a sharp transition from stable to unstable step flow, which was further investigated through varying both deposition flux and substrate mean terrace width. Noting that a bunched morphology gives an increased surface roughness, the latter parameter has been chosen to trace the transition. Results are plotted as a function of mean step velocity in Fig. 2 with the root mean square (rms) roughness measured from 4 × 4 μm² AFM images. A clear transition from stable step flow and roughness around 0.2 nm to unstable one and roughness close to 0.4 nm is found with a critical step velocity V* = 9 nm/s. We checked explicitly that upon increasing the deposition flux further on substrates with the largest terrace widths, typically above 200 nm, monolayer-high islands are observed on the terraces with a growth dominated by island nucleation and coalescence [8].

The origin of the experimentally observed sharp transition can be captured in the step velocity model accounting for strain effects introduced in Ref. [8]. In the absence of step interactions, step flow can be stabilized against step bunching due to a preferred incorporation of diffusing adatoms to the ascending step edges. A characteristic length ℓs can be defined for adatom incorporation to a step from the upper terrace, often traced back to an excess energy barrier for diffusion over the step edge. The ratio f s = ℓs/(L + ℓs) then measures the strength of the incorporation asymmetry, assuming instantaneous attachment from the lower side of a step edge. In a step train picture, a fraction (1 + f s)/2 of all the adatoms diffusing on a given terrace will eventually attach to the ascending step edge, while the remaining (1 − f s)/2 will be incorporated at the descending step, for an effective adatom current in the step-up direction. Now considering step interactions, it has been shown that for a strained film there is an attractive interaction between steps in addition to the classical elastic repulsion, and all strained step trains could thus be thermodynamically unstable against step bunching [11]. Introducing these interactions in a step velocity model, the competition between stabilizing step-up adatom current and attractive interaction between steps results in a critical step velocity V* for step flow, below which step bunching occurs [9, 10].
\[ V^* = \frac{\Omega^2 \pi^2 \alpha_1 c_0 D}{k_B T f_s L \ell_s} \]  

(1)

Here \( \Omega \) is the area of the surface unit cell, \( \alpha_1 \) is the elastic constant measuring the strength of the attractive interaction between steps \([11]\), \( c_0 \) the equilibrium concentration of adatoms in the vicinity of a straighth step, \( D \) adatom diffusion coefficient, and \( k_B \) the Boltzmann constant. As factors promoting an increase of \( V^* \) and thus step bunching, the mass transfer coefficient expressed through \( c_0 D/k_B T \) is found alongside \( \alpha_1 \) given that the driving force for step bunching does not require actual growth and is present even for vanishing deposition flux. This is at variance with the term \( f_s L \ell_s \) stemming from the kinetics of the flowing step train with an effective step-up adatom current. For a weak attachment barrier \( f_s L \sim \ell_s \) and the critical step velocity does not depend on mean terrace width \( L \), while for moderate or strong barrier \( V^* \) increases with decreasing \( L \).

Looking at our data, the fact that a transition from unstable to stable step flow can be detected at \( V^* = 9 \) nm/s for a wide range of mean terrace widths especially around the transition points at a small barrier for incorporation at a descending step, i.e. the \( \ell_s << L \) case. For example, the growth of SrRuO\(_3\) at \( V = 8.3 \) nm/s is found unstable for \( L = 150 \) nm and \( L = 250 \) nm (Fig. 1(c)), while going to the smaller terrace width \( L = 120 \) nm the step flow is already stabilized at \( V = 10.2 \) nm/s (Fig. 1(a)). Still an asymmetry of incorporation between both sides of a step has to be invoked otherwise the step train would be always unstable with respect to step bunching \([11]\).

In order to demonstrate the ability to pass from unstable to stable step flow through the tuning of step velocities, first a SrRuO\(_3\) layer was grown in the step bunching regime up to 17 nm thickness with \( V = 7.7 \) nm/s, followed by 48 nm of stable step flow at \( V = 10.9 \) nm/s. The mean terrace width of the SrTiO\(_3\) substrate was 180 nm, and the deposition flux \( F \) was changed by tuning the Laser repetition rate. As seen in Figure 3 final morphology is a smooth step train with only single steps. In several places an in-phase meandering of steps can be observed which is a signature of a flowing step train with effective step-up adatom current. For example the close-up in Fig. 3(c) shows step edge profiles of neighboring steps aligned along the dotted line. According to Ref. 10 step bunching only occurs above a critical thickness which increases with terrace width, so that a transient stability region is found for step flow up to this thickness. As all the bunched morphologies are here well developed already for 8.7 nm deposited SrRuO\(_3\), the critical thickness should be lower than this value. We thus believe the step flow growth observed for \( V > V^* \) to be outside the transient region. Added support for a persistent step flow is given by the fact that a bunched morphology is fully turned into a step train with equidistant steps upon growth at \( V > V^* \) (Fig. 3), which would not be expected if step flow was ultimately unstable in this step velocity region. It should be noted that the instability does not initially proceed through the bunching of straighth steps as step meandering is seen on all our bunched films (see Fig. 1(c)). While the interplay between step bunching and step meandering is non trivial to address theoretically in particular as for the attractive interaction between steps \([13, 14]\), such morphologies have already been reported for the step flow growth of metals on vicinal surfaces \([13]\).

In conclusion, we demonstrated the ability to tune the growth mode of SrRuO\(_3\) on (001) SrTiO\(_3\) from stable to unstable step flow with formation of step bunches through the control of the mean step velocity. This parameter sums up the effects of deposition flux (Laser repetition rate) and substrate mean terrace width, stressing the importance of the latter and thus of substrate preparation. A critical step velocity \( V^* = 9 \) nm/s below which step bunching occurs was found at 610°C and is independent of mean terrace width. \( V^* \) is expected to increase with increasing temperature as the adatom incorporation asymmetry which stabilizes the step train against step bunching is a decreasing effect with temperature. As the repetition rate and thus the mean step velocity can be adjusted during growth it opens the possibility for in situ growth mode manipulation in order to control the film step structure, the latter being monitored for example with grazing incidence electron diffraction or optical reflectometry techniques. This is of particular interest for the elaboration of oxide superlattices where maintaining a stable step flow going from one layer to the next through a proper tuning of deposition flux is one possible way to ensure smooth interfaces between layers.

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[8] In the case of PLD growth, a transient supersaturation of hyperthermal species coming from the target is created on the surface during each Laser pulse. Step flow is achieved when all deposited atoms are eventually incorporated at pre-existing steps. When stable immobile islands are formed on the terraces, growth proceeds through island nucleation and coalescence possibly mixed with step flow depending on terrace width and deposition parameters. Such islands can be detected with AFM after deposition, provided the deposition is not stopped exactly at layer completion in the case of perfect layer-by-layer growth.
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