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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.

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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 the 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 the oxidation state between heteroepitaxial oxide films allows for the obtention of a confined electron gas at the interface.[2,3] The first step toward 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 Refs. 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 a 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.

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 to 370 nm, corresponding to miscut angles from 0.06° to 0.3°. 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/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.[12] The thickness could thus be followed in real time taking advantage of the interferences between the light reflected from the film surface and from the film-substrate interface. XRD measurements were performed to double-check film thickness and to verify that all $SrRuO_3$ films were fully strained on $SrTiO_3$. Their unit-cell parameter perpendicular to the surface has been found to be equal to 0.395 nm, larger than the $SrRuO_3$ bulk value of 0.393 nm, thus confirming an in-plane compressive strain for the films. Unless indicated otherwise, all films are 8.7 nm thick, corresponding to 22 monolayers (ML) of strained $SrRuO_3$. The deposition flux F is taken as $F = pN_p$, with p the laser repetition rate and N_p the (fixed) amount of $SrRuO_3$ deposited per pulse, set to 0.055 ML for all depositions. Typical repetition rates were between 0.6 and 2 Hz for a flux ranging from 3.3×10^{-2} to 1.1×10^{-1} ML/s.

Figure 1 shows AFM topographs of typical morphologies observed after $SrRuO_3$ 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 $SrRuO_3$ 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 three to four 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 in the AFM image. The inset of Fig. 1(c) is a 4×4 μm^2 topograph of a film grown with the same parameters as for the

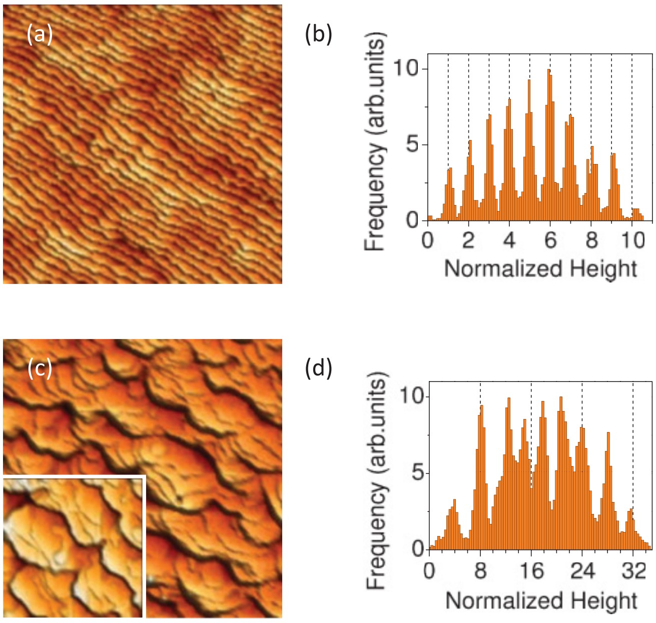

FIG. 1. (Color online) 4 × 4 μm^2 AFM topographs of SrRuO$_3$ films grown at 610 °C in the step flow mode with mean step velocities (a) $V = 10.2$ nm/s and (c) $V = 8.3$ nm/s. Mean terrace width of SrTiO$_3$ substrate is 120 nm (a,b), 150 nm (c,d), and 250 nm for the inset of (c). Height histograms taken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

one of Fig. 1(c) but on a SrTiO$_3$ substrate with 250-nm-wide terraces instead of 150 nm. Flux has been adjusted to get the same step velocity of 8.3 nm/s. 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 SrRuO$_3$. 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 μm^2 AFM images. A clear transition from stable step flow and roughness around 0.2 nm to unstable step flow 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]

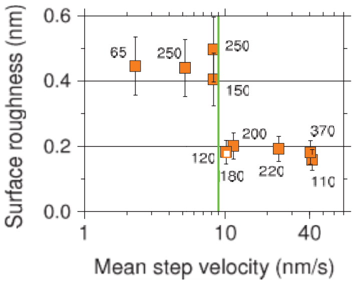

FIG. 2. (Color online) Transition from stable step flow to step bunching as seen through surface roughness. A critical step velocity materialized by the vertical line is found at $V^* = 9$ nm/s. Open square data point is for a film grown successively at $V = 7.7$ and 10.9 nm/s, the latter velocity value being the one reported in the graph. Each data point is labeled with the mean terrace width (nm) of the corresponding SrTiO$_3$ substrate.

The origin of the experimentally observed sharp transition can be captured in the step velocity model accounting for strain effects introduced in Ref. 9. 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 ℓ_s 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 $f_s \equiv \ell_s/(L + \ell_s)$ 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]

$$V^* = \Omega^2 \pi^2 \frac{\alpha_1 c_0 D}{k_B T f_s L \ell_s}. \tag{1}$$

Here Ω is the area of the surface unit cell, α_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 straight step, D is the adatom diffusion coefficient, and k_B is 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 α_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 to a small barrier for incorporation at a

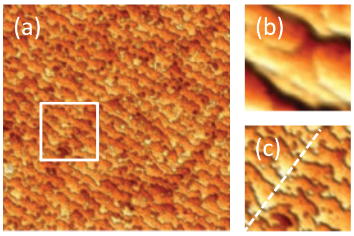

FIG. 3. (Color online) Transition *during growth* from step bunching at $V = 7.7$ nm/s (b) to stable step flow at $V = 10.9$ nm/s (a,c) through the tuning of the mean deposition flux by adjusting the laser repetition rate. AFM topographs are 4×4 μm^2 in (a) with close-ups of 1×1 μm^2 in (b,c). Image shown in (b) is for a film for which growth has been stopped in the step-bunching regime, to be compared with (c). The dotted line in (c) is a guide to the eye. The mean terrace width of the substrate is 180 nm.

descending step, i.e., the $\ell_s \ll L$ case. For example, the growth of SrRuO$_3$ at $V = 8.3$ nm/s is found to be unstable for $L = 150$ and 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 always be unstable with respect to step bunching.[11]

To demonstrate the ability to pass from unstable to stable step flow through the tuning of step velocity, 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 Fig. 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 that increases with terrace width, so that a transient stability region is found for step flow up to this thickness. As all the bunched morphologies here are 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 straight 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 nontrivial to address theoretically, in particular for the attractive interaction between steps,[13,14] such morphologies have already been reported for the step flow growth of metals on vicinal surfaces.[15]

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 the 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 that 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 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 preexisting 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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