PHYSICAL REVIEW B **73**, 073401 (2006)

Giant step bunching from self-organized coalescence of $SrRuO_3$ islands

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(Received 20 October 2005; revised manuscript received 21 December 2005; published 6 February 2006)

Step bunching develops in the epitaxy of $SrRuO_3$ on vicinal $SrTiO_3(001)$ substrates. We have investigated the formation mechanisms and we show here that step bunching forms by lateral coalescence of wedgelike three-dimensional islands that are nucleated at substrate steps. After coalescence, wedgelike islands become wider and straighter with growth, forming a self-organized network of parallel step bunches with altitudes exceeding 30 unit cells, separated by atomically flat terraces. The formation mechanism of step bunching in $SrRuO_3$, from nucleated islands, radically differs from one-dimensional models used to describe bunching in semiconducting materials. These results illustrate that growth phenomena of complex oxides can be dramatically different to those in semiconducting or metallic systems.

DOI: 10.1103/PhysRevB.73.073401 PACS number(s): 68.55.−a, 81.07.−b, 68.47.Gh, 68.37.−d

The perovskite $SrRuO_3$ (SRO) has a high electrical conductivity and becomes ferromagnetic below around 150 K. It has a high chemical stability and a low lattice mismatch with other transition metal oxides, being an excellent candidate as an electrode in ferroelectric memories. These devices require multilayered structures and, therefore, an accurate control of surface morphology. For the epitaxial growth of SRO, (001)-oriented $SrTiO_3$ (STO) single crystals are the most suitable substrates.[1–4] Even on low-miscut angle $(\sim 0.1^\circ)$ vicinal STO surfaces, SRO growth can proceed by step flow mechanisms.[2–4] The film surface morphology is then defined by smooth terraces separated by steps ~ 0.4 nm high. However, the transport properties of SRO films are better (lower residual resistivity) when vicinal substrates (miscut angle around 2°) are used. These films, in contrast with the deposited on nominally exact substrates, show bunched steps (steps having a height of more than one lattice unit cell).[5] In spite of the importance of the surface morphology, the process of bunching formation in SRO films is unknown. Concerning other oxides, bunching after annealing has been reported in some vicinal single crystals,[6] whereas much less attention has been addressed to oxide films. To date, research on bunching has been mainly done with metallic or semiconducting materials.[7]

The number of monolayer steps in a bunch is generally between two and ten,[7–9] depending on the system (layer and substrate materials) and formation conditions. Bunching of more than ten monolayers (ML) is less likely, but it has been found in some systems,[10,11] and even bunching involving more than 20 ML has been reported also.[12,13] To explain bunching formation, both thermodynamic and kinetic origins have been proposed.[7,14–17] Irrespectively of the proposed origin, the general belief is that bunching forms, as terraces progressively disappear, due to differences in the velocity of the flowing steps, and therefore models are essentially one dimensional (1D).[14,15] In this paper, we report on the formation mechanism of step bunching in SRO films grown on vicinal STO substrates. The bunching is of giant size (even more than 30 ML per bunch) and, unexpectedly, forms from the nucleation and coalescence of wedgelike islands. With subsequent growth, islands become wider and straighter up to transforming into well-defined terraces. Thus bunching formation cannot be described as a 1D process. Here we describe and discuss experimental observations that provide a new view on bunching process.

SRO thin films were grown at 750 °C on vicinal STO $(\sim 2^\circ$ miscut along a [100] direction) by pulsed laser deposition. The growth rate was ~ 0.18 Å/pulse as deduced from proper calibration using x-ray reflectivity. The nominal thickness (t) of the films ranges from 1.7 to 100 nm. Another film, $t=75$ nm, was grown at a much lower rate $(\sim 0.042$ Å/pulse) by reducing the laser pulse energy. Atomic force microscopy (AFM) working in the tapping mode was used to characterize the surface of substrates and films. The films are epitaxial, single domain,[18] and ferromagnetic below 150 K. Additional details of the deposition conditions, as well as information on epitaxial nature, lattice strain, and magnetotransport properties can be found elsewhere.[18,19]

The morphology of a $t=100$ nm SRO film is shown in Fig. 1. There are straight steps, running along the [100] direction, and defining terraces of a quite uniform width around 170 nm. We recall that, for a miscut of $\sim 2^\circ$, the terraces had to be only 11.3 nm wide if the steps were 1 ML

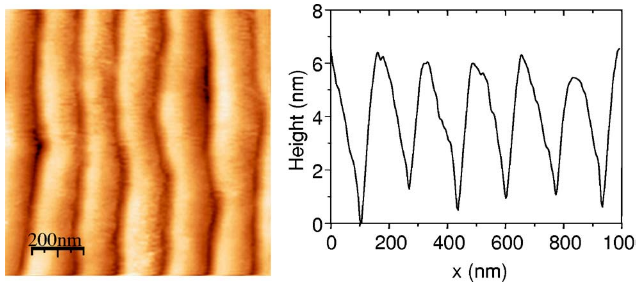

FIG. 1. (Color online) AFM topographic images of a film $t=100$ nm. The one-dimensional height profile was taken perpendicularly to the steps.

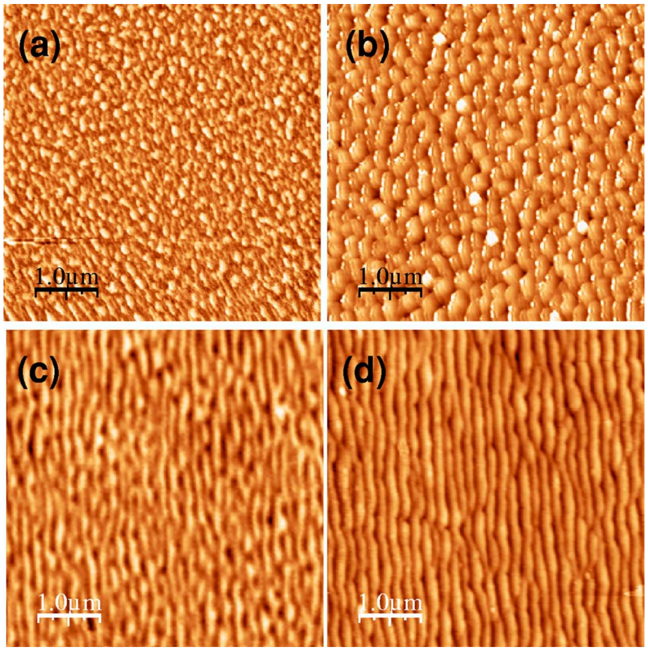

FIG. 2. (Color online) AFM topographic images of films (a) $t=1.7$ nm, (b) $t=5$ nm, (c) $t=22$ nm, and (d) $t=100$ nm.

high (the out-of-plane lattice parameter of the strained films is 0.396 nm). Therefore, the terraces must be separated by bunches of around 15 ML (unit cell) steps, as height profiles confirm (right panel). A bunch of 15 unit cells is unusually high, so bunching can be properly called giant. To exclude any possible pre-existing bunching in the substrate, we studied the morphology of STO substrates after annealing at 800 °C (a temperature slightly higher than the one used to grow the films) during 2 h. The surface showed terraces separated by atomic steps, and thus it is concluded that the SRO giant bunching develops during the film growth.

As mentioned above, if step bunching arises from differences in step velocity, since giant step bunching necessarily requires an important amount of deposited material to form, a progressive change in the terraces width with nominal film thickness should be observable. Aiming to eventually monitor terrace widening, a series of SRO films having various thicknesses (1.7 to 100 nm) were grown. Interestingly enough, instead of smooth terraces, islands were found in the nanometric films. The lateral dimensions of the islands in the $t=1.7$ nm film [Fig. 2(a)] are 100–150 nm; we notice that this corresponds roughly to about ten times the width of the substrate terraces, thus implying that the islands cover several substrate terraces. Thus, early stages of growth—on vicinal STO substrates—do not show the step flow growth mechanism but rather the nucleation and three-dimensional growth mechanism. As the film thickness increases, the islands grow in size until they merge. Indeed, in the $t=5$ nm film, they have just merged [Fig. 2(b)]. The islands tend to have an oval shape, with their long axis roughly parallel to substrate steps and with varied short axes up to around 300 nm long. As the thickness increases further, there is a progressive lateral coalescence of islands, which thus becomes definitely elongated [Fig. 2(c)], until forming almost perfect terraces with fairly straight edges around 170 nm apart [Fig. 2(d)].

The absence of a gradual terrace widening evidenced by the growth progression illustrated in Fig. 2 was unexpected. In order to get some insight, we have analyzed higher resolution AFM images (Fig. 3) of the thinnest films. The three-dimensional view [Fig. 3(a)] of the surface morphology of the $t=1.7$ nm film emphasizes the island shape. They have a triangular contour (see encircled island in Fig. 3) and a wedgelike section. We note that the islands have a relatively flat surface, forming (see the height profile) an angle of about 2°—as expected for (001) facets—with the substrate average surface. Therefore, the front edges of the islands shall be formed by bunches of several monolayers. Indeed, the presence of several single unit cell steps (see the arrows in the height profiles) can be appreciated in the figure. Moreover, some faceting can be observed at the sides. The shape of the islands is sketched in Fig. 3(c).

To get insight on the progressive transformation of these islands into terraces, we examined [Fig. 3(b)] the islands, in the $t=5$ nm film, after they just merged. Similar to earlier stages [Fig. 3(a)], some single-atomic steps in the (001) surfaces, as the one marked by an arrow in the height profile,

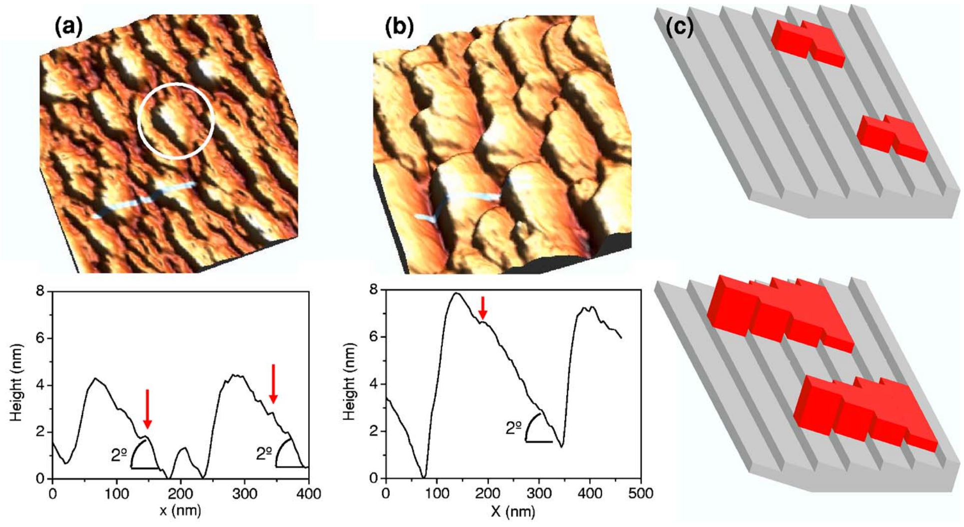

FIG. 3. (Color online) AFM topographic images (1×1 μm^2, three-dimensional view) of films (a) $t=1.7$ nm and (b) $t=5$ nm. The one-dimensional height profiles correspond to the lines marked in the images. The arrows indicate the presence of single steps on the (001) facets. (c) (bottom) Sketch of the wedgelike islands shown in (a); (top) a proposed early stage of growth.

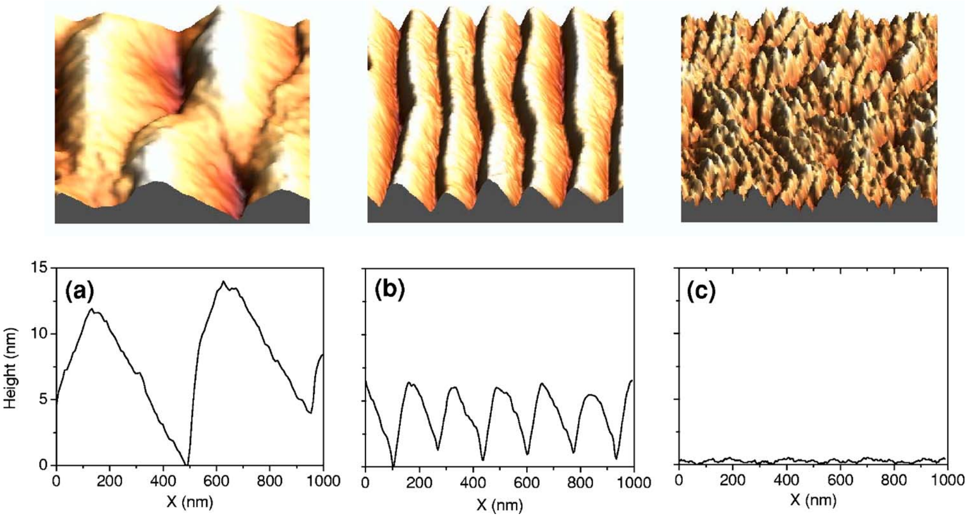

FIG. 4. (Color online) AFM topographic images ($1\times 1\ \mu m^2$, three-dimensional views) of films grown at (a) 0.042 Å/pulse on 2° miscut STO, (b) 0.18 Å/pulse on 2° miscut STO, and (c) 0.18 Å/pulse on 0.5° miscut STO. The corresponding one-dimensional height profiles are taken perpendicularly to the steps.

can be appreciated. The bunched steps are now taller, because the number of steps in the wedgelike islands increased progressively until they merged with other islands; the longer the islands are perpendicular to the steps, the higher is the number of unit cell steps in the bunch. Later, during lateral coalescence, bunching size becomes progressively more uniform (as the width of the terraces does) until a quasiequilibrium state is reached when bunching size remains constant as edges straighten.

Li *et al.*[20] investigated the epitaxy of CaF_2 on Si(111) and observed the nucleation of two-dimensional (2D) plates at the substrate steps. We propose that 2D plates can form if the chemical potential for adatom incorporation to a nucleated plate island is lower than that for the incorporation to the substrate steps. Under this assumption, the growth on vicinal substrates with very narrow terraces, should favor the formation of wedgelike islands extending through several substrate terraces, as observed. We illustrate our model in Fig. 3(c). In the top panel, we sketch an earlier growth stage: the lower chemical potential for the adatom incorporation at preformed 2D plates promotes its growth extending to more than one substrate terrace. In the bottom panel, subsequent growth leads to 2D plates covering several substrate steps. Notice that this is just what is experimentally observed in Fig. 3(a).

We also note in Fig. 3(b) that there is some step meandering, thus excess edged energy is accumulated. Thus, increasing nominal thickness, i.e., after incorporation of much more atoms to the film, the steps edges are expected to relax and thus becoming straighter. Indeed this is confirmed by the topographic images of thicker films [see Figs. 2(c) and 2(d)]. A self-organized network of parallel step bunches can be clearly appreciated in the $t=100$ nm film. The step-to-step distances in bunched films can provide information about the bunch formation.[16] Therefore, we analyzed these distances in the $t=5$ nm and the $t=100$ nm films by line-scanning the AFM images along much lines perpendicular to steps. The histogram of the $t=5$ nm film showed a broad distribution which reflects the finite size of the 2D plates and the correspondingly long length of the step profile. In contrast, in the $t=100$ nm film, steps are well straight and the terrace width distribution (Δl) is narrow; maximum widths are below 300 nm. Interestingly, for this well-ordered bunched structure, the distribution fits well to a Gaussian function, the average distance l_0 (determined from the fit) is 178 nm, and the ratio $\Delta l/l_0$ is ~ 0.35. We note that such a Gaussian distribution with $\Delta l/l_0 \sim 0.3$ has been predicted, and experimentally observed; in the presence of a repulsive interaction between steps; broader distributions occur for noninteracting steps.[7,21] However, in spite of this similarity we should stress that in SRO the terrace width is controlled by the size of the initial islands. The Gaussian distribution and its narrow width suggest universality beyond the interactions that determine the fluctuations of steps and meandering.

It follows from the previous description that the density of the initial 2D plates determines the bunch size. Therefore, it could be expected that the growth of films under lower adatom supersaturation shall produce a lower density of nucleus, even when nucleation takes place at the steps, and consequently its size and that of bunches, shall be larger. To test this hypothesis, we grew a film, $t=75$ nm, at much lower rate (~ 0.042 Å/pulse). The bunching [Fig. 4(a)] is certainly of giant size, with some steps around 14 nm high (it means they are constituted by around 35 atomic steps), twice that in the case of the films of similar thickness grown at the high rate (0.18 Å/pulse) [Fig. 4(b)]. Comparison of Figs. 4(a) and 4(b) demonstrates that the density of nucleated islands determines the bunching size. On the other hand, since wedgelike islands extend to several substrate terraces, their formation should be relevant in vicinal substrates with terraces narrow enough; this explains that step bunching disappears when films are grown on nonvicinal or low-vicinal substrates. The AFM image of a SRO film grown on 0.5° miscut STO at 0.18 Å/pulse [Fig. 4(c)] illustrates the absence of bunching in films on low-vicinal substrates. Moreover, Fig. 4 demonstrates that steps from 1 to above 35 atomic unit cells can be engineered in SRO films.

Finally, we would like to remark that substrate termination can affect surface diffusivity and thus the initial growth of SRO.[4] Varying the substrate miscut, not only the width of terraces but also its morphology can differ; in a vicinal substrate, the atomic termination could be different from that of the singular one and thus the adatom mobility and nucleation rate could be also different. But it is also clear that these effects, if relevant, are modulated by miscut angles and thus our observation and conclusion are still well established. To discriminate between purely topological effects (terrace widths and miscut angle) or other eventually accompanying effects would require the control of atomic termination in vicinal substrates. To the best of our knowledge, this control has been demonstrated in singular or moderately vicinal $SrTiO_3$ substrates but not yet on strongly vicinal (2°) substrates.

In conclusion, the formation mechanisms of giant step bunching in SRO films have been investigated. Terraces separated by bunched steps form from nucleation and self-organization of wedgelike islands. This is a 2D process that contrasts with the 1D bunching formation process commonly invoked in semiconducting and metallic systems. It thus follows that the 1D models so far used to describe bunching may not be as general as commonly accepted. Finally, we have shown that the bunch size can be controlled either by substrate miscut or by growth rate and thus these bunched structures could be used as tailored templates to grow one-dimensional wires of other materials.

Financial support from the MEC of the Spanish Government (Project Nos. NAN2004-9094-C03 and MAT2005-5656-C04) and FEDER is acknowledged.

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