

Self-nanostructuring of the chemical termination of SrTiO₃(001) substrates: templates for fabrication of functional oxide nanostructures

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Low-dimensional structures of complex oxides with a wide range of functional properties, from ferroic to catalytic properties, hold the promise to lead to a new generation of materials with unrivalled properties compared to their bulk counterparts. However, nanostructure fabrication of complex oxides is not as well-established as these of metals or semiconductors, which is partly due to the complexity of lattices and the numerous chemical elements. Moreover, the long-range order in self-assembling methods is very challenging. Therefore, new strategies are required for cost-effective fabrication of ordered oxide nanostructures. Here we report a method to fabricate functional oxide nanostructures ordered over the centimeter scale. The method is based in tailoring the chemical termination of SrTiO₃(001) substrates and exploiting the selective nucleation of functional oxides on SrO(001) and TiO₂(001) surfaces.

We have studied in detail the morphological and chemical evolution of the topmost surface of STO substrates with annealing. We recently reported that annealing of STO substrates at 1100-1200 °C causes surface diffusion of the two existing chemical terminations. As a result, TiO₂-terminated terraces separated by SrO-terminated quasi one-dimensional regions are formed [1]. Now we will show that proper annealing at higher temperature (1300 °C) under oxidizing conditions causes Sr diffusion from the bulk, resulting in atomically flat surfaces, perovskite-layered SrO terminated. Moreover, we will show that the progressive surface enrichment of SrO allows to obtain surfaces with chemical-termination separated at the nanoscale (Figure 1). Such large-area nanopatterned surfaces, stable at relatively high temperature, can be used as template to grow functional ordered nanostructures, exploiting the termination-dependent nucleation.

We will show how the intermediate chemically-organized surfaces occurring during the progressive SrO enrichment can be used as template for nanostructure fabrication of ferromagnetic oxides by chemically-driven selective nucleation. First we prove it with SrRuO₃, which is known to nucleate distinctly and preferentially on TiO₂ rather than on SrO termination of SrTiO₃(001) surfaces [1,2]. The topographic atomic force microscopy images of a treated substrate and a deposited film in Figure 2 show that SrRuO₃ nucleates exclusively on the TiO₂-termination, and thus it replicates any nanostructuring of a treated substrate.

We have also investigated the selective growth of the ferromagnetic oxides La_{2/3}Sr_{1/3}MnO₃ and CoFe₂O₄ on nanostructured substrates. The results confirm the selective growth and indicate that the method here presented offer new opportunities for the fabrication of functional low-dimension structures of complex oxides.

References:

- [1] R. Bachelet, F. Sánchez, J. Santiso, C. Munuera, C. Ocal, J. Fontcuberta, *Self-organization of the SrTiO₃(001) chemical terminations: a route for oxide nanostructure fabrication by selective growth*, Chemistry of Materials, in press (published online)
- [2] R. Bachelet, F. Sánchez, J. Santiso, J. Fontcuberta, *Reversible growth mode transition in SrRuO₃ epitaxy*, Applied Physics Letters **93**, 151916 (2008)

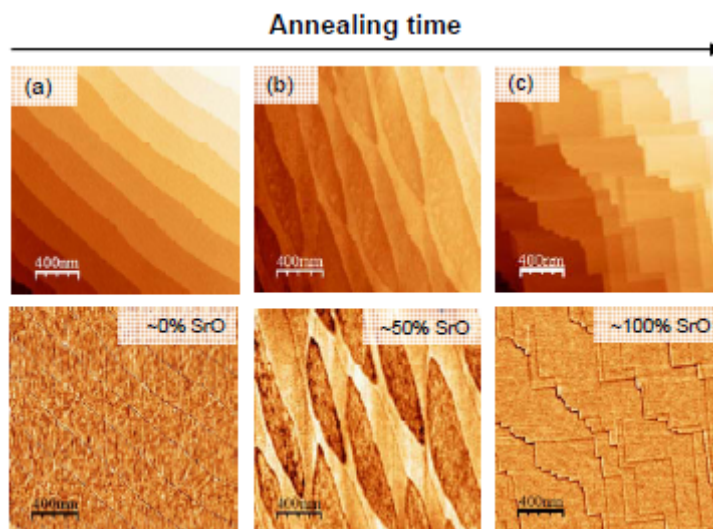
Figures:

Figure 1: AFM topographic (top panels) and phase-lag (bottom panels) images of a chemically-treated SrTiO₃(001) substrate after annealing at 1300 °C for (a) 2h, (b) 12h, and (c) 72h.

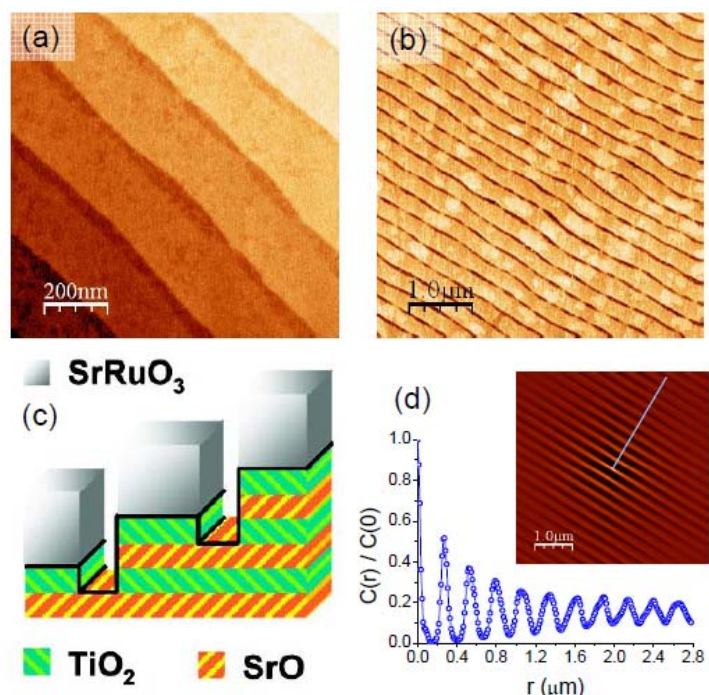


Figure 2: AFM topographic images: (a) $1 \times 1 \mu\text{m}^2$ area of bare SrTiO₃(001) substrate after annealing at 1200 °C for 2h, and (b) $5 \times 5 \mu\text{m}^2$ area of a SrRuO₃ film, 7 monolayer thick, deposited on (a). (c) Sketch of the substrate nanostructuration and the selective growth. (d) Self-correlation of (b) and the corresponding profile taken perpendicular to the steps signalling the long-range spatial order.