Self organization of chemical solution synthesised oxide nanostructures

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Applying nanoscale design and fabrication strategies to functional oxides is potentially promising because they posses high environmental stability and extraordinarily useful properties that expand from photocatalysis to ferroelectricity and ferromagnetism, which are highly attractive for applications in electronic, optoelectronic or biological devices. An alternative approach to the fabrications of nanostructured media by nanolithography is the formation of nanostructures by self-organization, where spontaneously ordered, large-area patterns of nanometric objects appear. In this context and although much less studied, chemical solution deposition (CSD) offers a high throughput and cost-efficient route for the generation of complex oxides capable of competing with vapour deposition techniques [1, 2].

In this work we combine ultradiluted metalorganic precursor solutions of $Ce_{0.9}Gd_{0.1}O_{2-y}$ (CGO) and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO), spin coated on top of different single crystalline substrates ($LaAlO_3$, $SrTiO_3$, Yttria-stabilized ZrO_2 (YSZ), MgO, and CeO_2 buffers deposited on YSZ), to generate 0D and 1D self-assembled strained oxide nanostructures, as a consequence of the interplay among lattice mismatch, crystallographic structure and interface and surface energies. In particular, the fluorite $Ce_{0.9}Gd_{0.1}O_{2-y}$ over $LaAlO_3$ (perovskite) heteroepitaxy results in the formation of single crystalline nanometer size nanowires, displaying two possible orthogonal orientations [3].

Different nanofabrication methods to induce self-organization of the grown nanostructures are demonstrated.

- The use of a nanoindenter at extremely low loads produces nanometer-depth indentation lines on the substrates before the growth of epitaxial CGO nanowires. A drastic change occurs due to the strain field induced by nanoindentation and the degeneracy in nanowires orientation is lifted suppressing one of the two possible orientations at the indented areas. The balance between the two orientations is restored where no deformation is present, (see Figure 1).
- Track etched polymers directly buffering low lattice mismatch single crystalline substrates have been successfully used as a novel methodology to generate assemblies of vertical LSMO nanostructures using solution methods, (see Figure 2).
- When the same methodology is used on fluorite (Gd doped-CeO_2) buffered substrates, self-assembled epitaxial horizontal and orthogonally oriented LSMO nanowires exhibiting a monoclinic crystallographic structure recently discovered for high aspect ratio manganite nanowires [4] are obtained. Self-organization and coarsening of the nanowires up to 40 μm in length is achieved through kinetic evolution at high temperatures, (see Figure 3).

This work has been supported by Nanoselect CSD200700041, Hiperchem NMP4-CT2005-516858, Xermae, Nanosuperenergy MAT2008-01022, and the MICINN. Nanoindentation was performed at the Nanotechnology Laboratory of MATGAS 2000 A.I.E.

References:

[1] J. Gutierrez *et al.*, Nat. Mater, **6** (2007) 367.
[2] M. Gibert *et al.*, Adv. Mater. **19** (2007) 3937
[3] M. Gibert *et al.*, to be published
[4] A. Carretero-Genevrier *et al.*, Adv. Mater. **20** (2008) 3672

Figures:

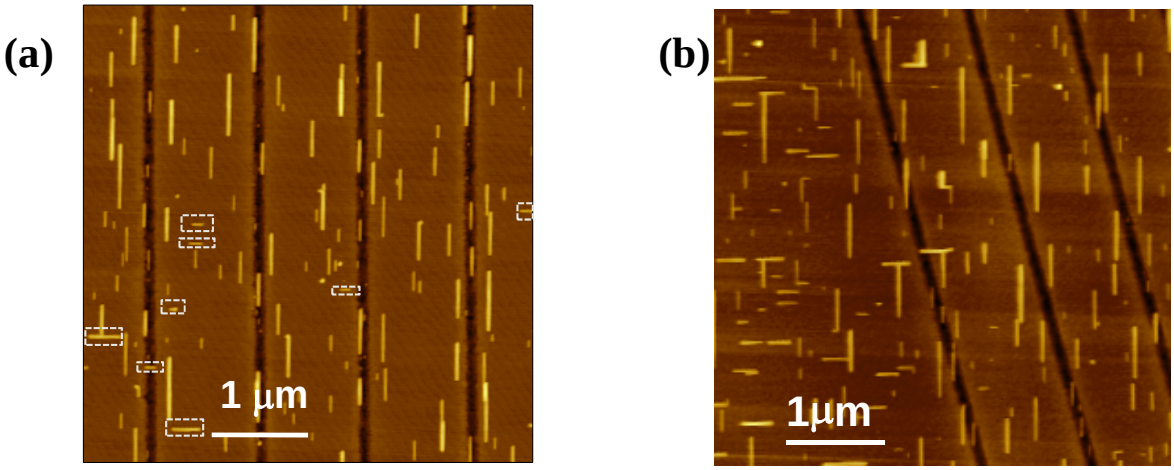

Figure 1: *(a) AFM topography image of single oriented CGO nanowires grown on a nanoindented LAO substrate; (b) outside the nanoindented area, the homogeneous distribution on both orientations is recovered*

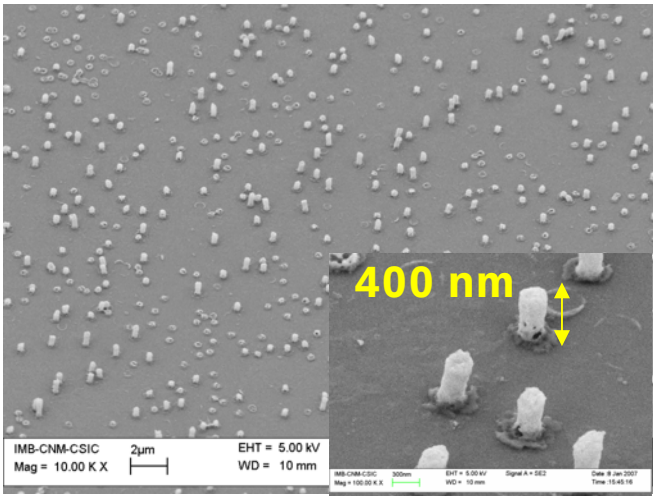

Figure 2: *FE-SEM images of vertically oriented LSMO Nanorods grown from CSD on top of a (001) STO substrate previously buffered with a track-etched polymer template*

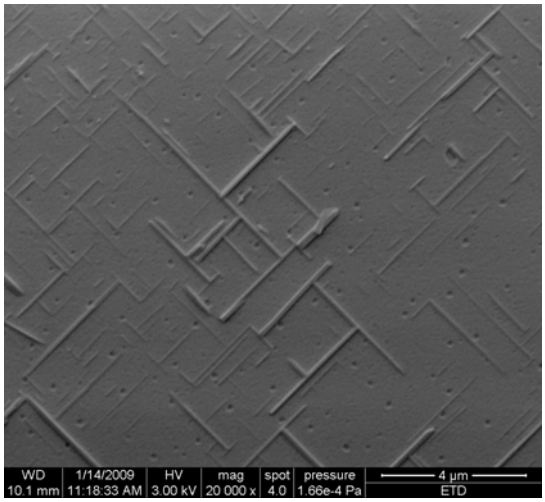

Figure 3: *FE-SEM images of self organized horizontal LSMO nanowires grown from CSD on top of a CeO_2/YSZ substrate previously buffered with a track-etched polymer template*