Reducibility of Co at the $La_{0.8}Sr_{0.2}CoO_3/(La_{0.5}Sr_{0.5})_2CoO_4$ hetero-interface at elevated temperatures

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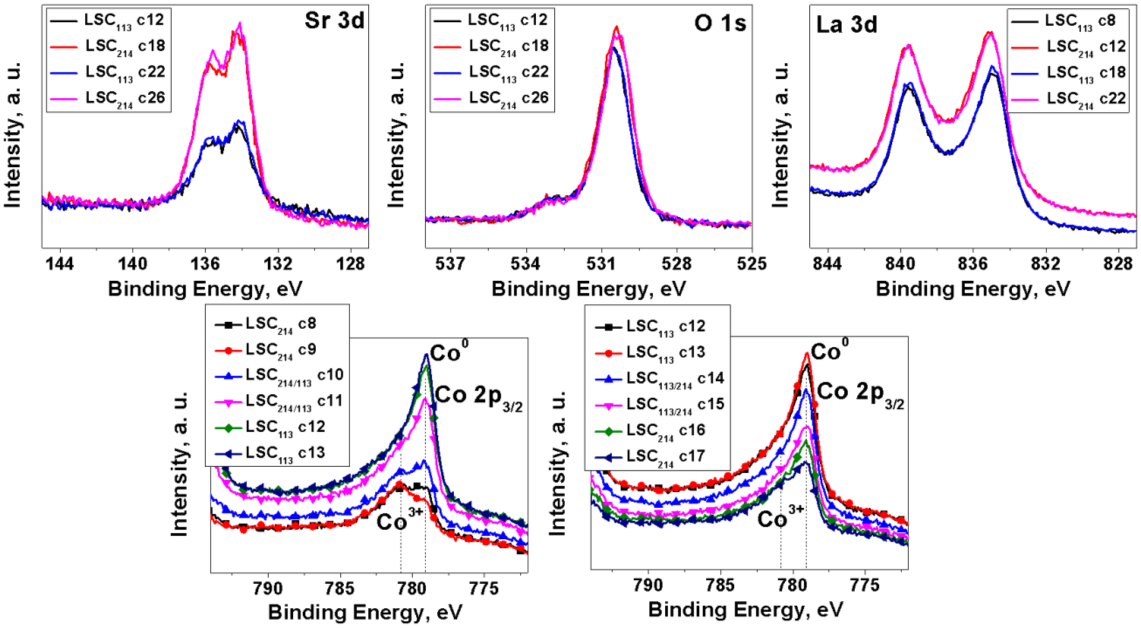

Figure S1. Typical O 1s, Sr 3d, La 3d and Co 2p XPS core-level spectra obtained from different LSC_{113} and LSC_{214} layers within the multilayer (ML) structure at room temperature. At sputtering cycles c12 and c22 the high Co/(La+Sr) ratio comes from LSC_{113} layers in ML. At sputtering cycles c18 and c26 the low Co/(La+Sr) ratio comes from LSC214 layers in ML. Co 2p spectra are presented for different sputtering cycles, denoted as c8-13 (left) and c12-17 (right) in the legends, showing the gradual change of the peak shape going from LSC_{214} to LSC_{113}, and from LSC_{113} to LSC_{214}, respectively.

In addition to reduction of Co, sputtering with Ar^+ ions could lead to formation of other chemical artefacts. This process is usually accompanied by the shift of binding energy of cation core-levels and broadening of the peaks as the sputtering progresses into the material. However we did not find any such effects of sputtering. The La or Sr peaks remain unchanged during the sputtering; only peak intensity variations related with chemical composition changes were observed (Fig. S1). Within LSC$_{113}$ and LSC$_{214}$ phases all the element photoelectron emission peaks keep the same core-level binding energy position, emission intensity and shape. Moreover the binding energies of all the peaks are unchanged across the whole ML cross-section. A small shift of around 0.1 eV is detected for La core-level peak within LSC$_{113}$ and LSC$_{214}$ layers, and this shift can be related to the different coordination number of A-site cation in the perovskite phase and the rocksalt layer in the Ruddlesden-Popper phase.

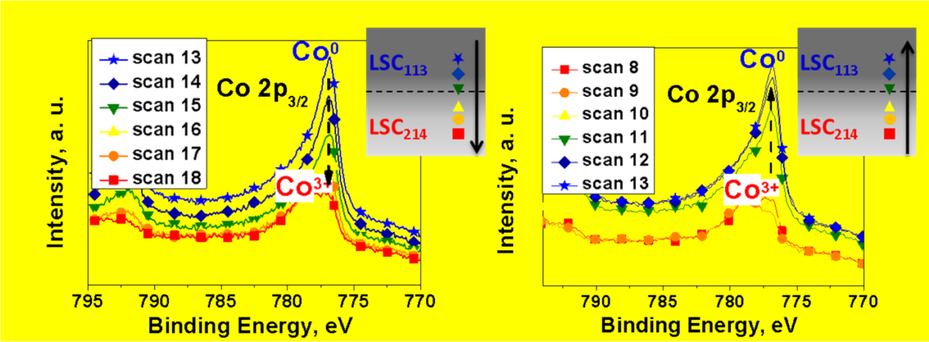

Figure S2. Evolution of Co 2p photoelectron spectra during the sputtering of LSC$_{113/214}$ multilayer structure at room temperature. As it can be seen the Co 2p peaks for different LSC$_{214}$ layers (scan 8 and scan 18) have very similar shape. The same situation takes place in case of LSC$_{113}$ layers.

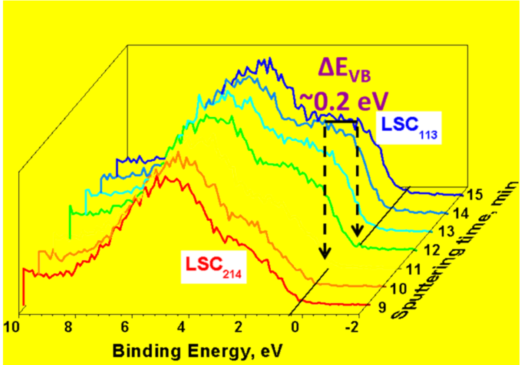

Figure S3. Evolution of the valence band spectra across the LSC$_{113/214}$ interface within the multilayer structure recorded at room temperature.

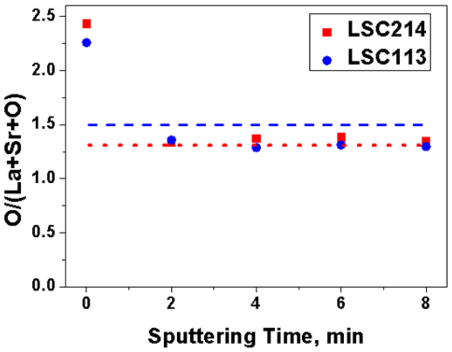

Figure S4. O/(La+Sr+Co) content for single phase LSC_{113} and LSC_{214} sputtered at 250 °C. Dashed and dotted lines indicate the stoichiometric O/(La+Sr+Co) ratio for LSC_{113} and LSC_{214}, respectively.

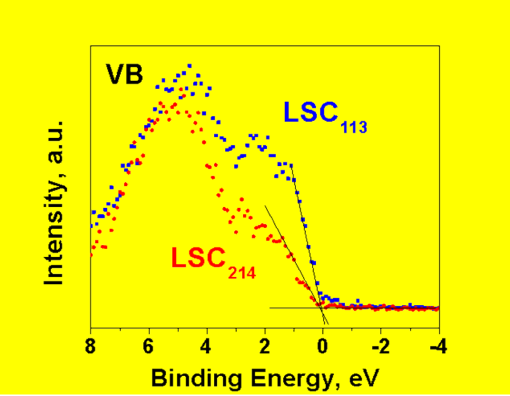

Figure S5. Valence band spectra of single phase LSC_{113} and LSC_{214} films recorded at 250 °C by XPS.