

Dependence of defect chemistry and surface composition on the crystal orientation for LaSrCoO_4 dense thin films

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1. Introduction

Ruddlesden-Popper (RP) phase oxides, $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$, are attractive as potential reversible oxygen electrode materials for reversible Solid Oxide Cells.^{1, 2} One reason for this is the ability of RP phase oxides to accommodate both interstitial oxygen defects and oxygen vacancies because of their layered structure, which render them stable over large range of oxygen partial pressures.³ Furthermore, some RP phase oxides were reported to exhibit highly anisotropic oxygen incorporation and diffusion, with the oxygen incorporation kinetics on the (ac)-plane about two-three orders of magnitude faster than on the (ab)-plane^{1, 2, 4, 5}. Therefore, controlling the crystal orientation may be one way to tune the oxygen reduction and evolution kinetics.^{1, 2, 4, 5} In addition, hetero-interfaces, surface electronic structure, and surface chemistry can also greatly impact the reaction kinetics. However no prior work has been performed on understanding the surface structure and chemistry of RP oxides under varying conditions of temperature and oxygen environment. The objective of this work is to study the impact of crystal orientation on the non-stoichiometry, surface composition and surface electronic structure, and how the variation of these properties leads to different reactivities on LaSrCoO_4 (LSC_{214}) model system.

2. Experiment

Epitaxial LSC_{214} film with (001) and (100) out of plane orientation were synthesized by Pulsed Laser Deposition on single crystal SrTiO_3 (STO) (001) and SrLaAlO_4 (SLAO) (100) substrates. The in-plane and out-of-plane lattice parameters are determined through High Resolution X-ray Diffraction (HR-XRD). In-situ X-ray Photoelectron Spectroscopy (XPS) was used to determine the Co valence state at various temperatures. Lattice parameters and Co valence states were interpreted together to infer the relative oxygen non-stoichiometry in these differently oriented films.

3. Results and Discussion

Fig. 1 shows the Co 2p photoelectron spectra that we measured and analyzed to identify the Co valence state from room temperature (RT) up to 700 °C, in vacuum. There is only negligible change in the spectra over temperature on LSC_{214} (100)/SLAO film, which indicates that any change in the Co valence state and oxygen non-stoichiometry on this material is beyond the detection limit of our measurements. On the other hand, for LSC_{214} (100)/STO film, we found significant reduction of the Co, as evidenced by the appearance of the Co^{2+} satellite peak^{6, 7} at around 786 eV at 600°. This result suggests a difference in the oxygen non-stoichiometry of these differently oriented films, with an enhanced formation of oxygen vacancies near the surface of the LSC_{214} (100)/STO film.

The c-axis lattice parameters in RP phase oxides are strongly sensitive to the oxygen non-stoichiometry.^{8, 9} To explain the difference between the Co valence state on LSC_{214} (001)/STO and LSC_{214} (100)/SLAO, we varied the oxygen non-stoichiometry of the films by annealing them

in air to 800 °C and in ultra-high vacuum to 700 °, and measured the corresponding in-plane and out of plane lattice parameters of the films, particularly the c parameter.

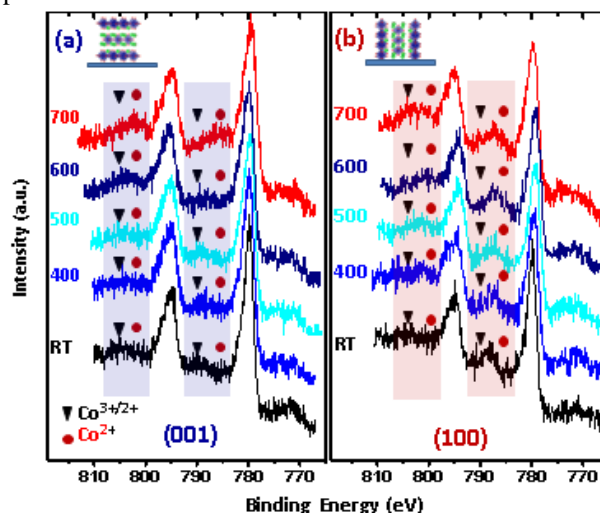


Fig.1: Co 2p region of the photoelectron spectra on (a) LSC_{214} (001) and (b) LSC_{214} (100) from room temperature up to 700°C. Satellite peaks (Sat.) represent the presence of Co^{2+} oxidation state in addition to the Co^{3+} state. The Co 2p spectra shows enhanced formation of Co^{2+} on the LSC_{214} (001) films compared to the LSC_{214} (100) at elevated temperatures.

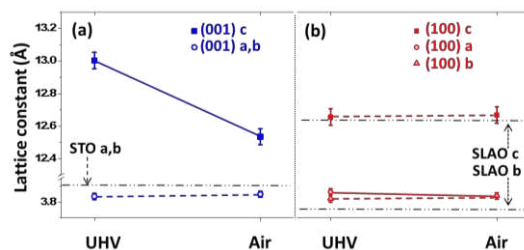


Fig. 2: Variation of lattice parameter for (a) LSC_{214} (001)/STO and (b) LSC_{214} (100)/SLAO films upon UHV annealing and Air annealing. The data points connected by solid line and dash line are corresponding to out of plane lattice parameter and in-plane lattice parameter respectively

As shown in Fig. 2, for LSC_{214} (100)/SLAO, whose c-axis is parallel to the surface, the c-axis lattice parameter was found to be fixed by the substrate and showed negligible difference between the films annealed in UHV and in air. On the other hand, for LSC_{214} (100)/STO, whose c-axis was perpendicular to the surface and could vary freely, the c-axis lattice parameter was found to be significantly greater in the film annealed in UHV compared with the one annealed in air. These results demonstrate that the oxygen non-stoichiometry known for bulk PR oxides does not hold true for RP thin films with different epitaxial relations to substrates. Especially if the c-axis is constrained by the substrate, significant deviations from bulk oxygen nonstoichiometry can prevail. Therefore, such constraint over the c-axis can potentially impact the oxygen exchange kinetics on LSC_{214} and related compounds.

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