**Type of presentation:** Oral

**MS-14-O-3382 Real-time Observation of Vacancy Dynamics and Phase Transformation in Epitaxial LaCoO$_3$-x Thin Films and Superlattices**

Jang J.$^1$, Kim Y.$^2$, He Q.$^1$, Qiao L.$^1$, Biegalski M. D.$^1$, Lupini A. R.$^1$, Pennycook S. J.$^3$, Kalinin S. V.$^1$, Borisevich A. Y.$^1$

$^1$Oak Ridge National Laboratory, Oak Ridge, United State, $^2$Korea Basic Science Institute, Daejeon, Korea, $^3$University of Tennessee, Knoxville, United State

Email of the presenting author: jangj@ornl.gov

Transition metal oxides (TMOs) have attracted attention for solid oxide fuel cell, gas sensor and catalytic applications. [1] In many of these cases, a material functionality is dependent on the distribution and transport behavior of oxygen ions. It has recently been demonstrated that, for a static case, oxygen vacancy distribution and vacancy ordering can be characterized at an atomic scale using quantitative aberration-corrected STEM. [2] In this work, we take this approach to the next level by observing the dynamics of vacancy ordering and vacancy injection under the electron beam in LaCoO$_3$/SrTiO$_3$ (LCO/STO) superlattices and LaCoO$_3$-x thin films using high angle annular dark field (HAADF) and annular bright field (ABF) STEM. We find that while before electron beam exposure films and superlattices do not show any signs of vacancy ordering, they nevertheless contain a substantial amount of vacancies; the ordering is quickly induced by electron beam exposure (Fig.1). We can monitor vacancy ordering by tracking local interatomic spacings, and vacancy injection by tracking global average of the spacings as per Vegard's law. In (110) projection, multiple lattice distortions can be tracked simultaneously as a function of beam exposure, such as out-of-plane lattice expansion, in-plane Co shift (Fig.2), and octahedral tilt patterns in the surrounding atomic layers.

In the case of 15 u.c. LCO film, beam exposure leads to a sequence of different phases, starting from disordered perovskite LaCoO$_3$-x to a brownmillerite polytype La$_3$Co$_3$O$_8$-x (2 perovskite layers connected 1 tetrahedra layer), to eventually brownmillerite La$_2$Co$_2$O$_5$-x (alternating octahedra and tetrahedra layers in the Fig.3), which is similar to the phase evolution observed in the bulk [3]. Forming oxygen depleted layers couple in complex ways to the existing octahedral tilt system and to each other, giving rise at times to metastable intermediate states that can give us insights into oxygen transport mechanisms in this system. Kinetics of the ordering and vacancy injection, as well as implications for beam-driven material modification at an atomic scale, will be discussed.


Acknowledgement: The MSE Division, US DOE; through a user project in ORNL’s CNMS, sponsored by the SUF Division, Office of BES, US DOE; The CSGB Division, Office of BES, US DOE.
Fig. 1: HAADF images of LCO/STO superlattice along [100]pc direction (A) as-grown and (B) after electron beam exposure. (C) Atomic spacing map generated from (B) shows that lattice expansion as an indicative of vacancy accumulation develops in the each LCO blocks.

Fig. 2: HAADF images of an LCO block in LCO/STO superlattice along [110]pc direction (A) initial state and (B) after beam exposure. (C) out-of-plane La spacing map generated from (B). (D) in-plane Co-Co spacing map generated from (B). (E) schematic of structural changes in LCO block before/after Vo ordering.

Fig. 3: Sequential HAADF images and models showing the evolution of the structure (A) initial LaCoO3-x along [110]. (B) intermediate 2x1 ordering structure (C) brownmillerite 1x1 ordering structure.