ABSTRACT

Defect-induced Behavior in Complex Oxides

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Complex oxides show great potential for future devices as they offer functionalities beyond what can be delivered by conventional semiconductors. Among the complex oxides, the ABO_3 perovskite oxides are the most studied and engineered in the form of thin films and heterostructures. This thesis applies powerful synchrotron-based X-ray characterization tools, combined with theoretical methods, to study defect-induced behaviors in perovskite-type complex oxides. These investigations primarily focused on strontium titanate ($SrTiO_3$ or STO), with the goal of understanding and controlling several key defects in this material, as it plays a central role as a widely used substrate in the growth of complex oxide thin films and heterostructures for oxide-based devices.

First, oxygen vacancy defects were studied. A strategy for using vacuum annealing to engineer a two-dimensional electron gas (2DEG) on the STO (0 0 1) surface was explored. *In situ* soft X-ray spectroscopy characterization of the evolving electronic structure and spatial distribution of doped electrons across a gradient of oxygen vacancies on a TiO_2-terminated STO (0 0 1) single crystal revealed the formation of 2DEG near the surface.

Quantitative band diagrams were developed to describe the gradual 2DEG formation along the lateral gradient of oxygen vacancies. The engineering of oxygen vacancy defects was extended to cobaltite thin films grown on (0 0 1)-oriented STO substrates. Soft X-ray spectroscopy of short-period $SrCoO_x$:$SrTiO_3$ superlattices and a $Sr(Co,Ti)O_x$ alloy grown by oxide molecular beam epitaxy (MBE) showed that the strategic *placement* of the Co and Ti cations with highly different oxygen affinities could be used to engineer the oxygen coordination environments of the Co cations. This work demonstrated the use of interfaces to control the spatial arrangement of oxygen vacancies and also the electronic structure.

Next, STO (0 0 1) surfaces were studied using first principles density-functional calculations of TiO_2 double-layer (DL) STO (0 0 1) surface reconstructions. Several new TiO_2-DL STO (0 0 1) surface reconstructions with $(\sqrt{5} \times \sqrt{5})R26.6°$ (RT5) and $(\sqrt{10} \times \sqrt{10})R18.4°$ (RT10) periodicities were predicted on the basis of favorable surface energies within a convex hull construction mapped across different compositions. Furthermore, a modified convex hull that takes into account the surface dissolution energies emphasized the glass-like structure of real STO (0 0 1) surfaces, composed of multiple TiO_2-DL reconstructions with generally higher TiO_2 adlayer coverages that possess short-range order but no long-range order.

Finally, the role of the Ti-rich STO (0 0 1) surface on the initial stages of oxide MBE was studied using *in situ* surface X-ray diffraction. (0 0 1)-oriented STO substrates prepared using a standard etch-and-anneal method were found to have TiO_2-DL surface terminations under the growth conditions, modeled as mixtures of $(\sqrt{13} \times \sqrt{13})R33.7°$

(RT13) and $(\sqrt{2} \times \sqrt{2})R45.0^{\circ}$ (RT2) reconstructions. Time-resolved SXRD measurements were performed during the growth of individual LaO and TiO_2 monolayers on the TiO_2-DL-terminated (0 0 1) STO substrates using opposite deposition sequences (i.e., LaO-TiO_2 and TiO_2-LaO). Here, despite showing differences in the evolution of island sizes and distributions, final surface morphologies, and timescales across the different deposition sequences, the TiO_2 adlayer on each of the bare STO substrates was found to diffuse towards the surface, leading to TiO_2-DL surface terminations in the films.

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