ABSTRACT

Understanding Atomic Structure and Structural Evolution of Perovskite Oxides at the 2-D Limit: From Surface to Thin Film

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Perovskite oxide materials for the wide array of properties that make them candidate materials for application ranging from catalysis, to electronics, to beyond-Moore computation. As many of these oxides share similar structures they can be combined in a seemingly-endless number of ways to produce the desired properties for a given application. Understanding of their surface structures and interface formation during growth however, is an area not given enough attention, especially in a class of materials that relies heavily on interfaces to produce its unique properties. The objective of this dissertation is to present theories and tools for probing and understanding the atomic structure of perovskite materials at the 2-D limit (i.e. surfaces and thin films).

In this dissertation the applicability of Pauling's rules to prediction and determination of oxide surface structures is presented. Examples of solved surface reconstructions on $SrTiO_3$ (1 0 0), (1 1 0), and (1 1 1) are considered as well as nanostructures on these surfaces and a few other ABO_3 oxide materials. These rules are found to explain atomic arrangements for reconstructions and thin films just as they apply to bulk oxide materials. Using this data and Pauling's rules, the fundamental structural units of reconstructions and their arrangement are discussed.

Pauling's rules are applied to the $SrTiO_3$ (1 1 1) surface to solve the atomic structures of two reconstructions, $(\sqrt{7} \times \sqrt{7})R19.1°$ and $(\sqrt{13} \times \sqrt{13})R13.9°$. These structures were determined using a combination of density functional theory and scanning tunneling microscopy data and APW+lo density functional theory minimizations and simulations. These reconstructions belong

to the same structural family made up of an interconnected, single layer of edge-sharing TiO_6 and $TiO_5[]$ octahedra. This family is found to include the previously-solved (2 × 2)a reconstruction. This reconstruction family and the calculations of surface energies for different hypothesis structures also shed light on the structure of Schottky defects observed on these reconstructed $SrTO_3$ (1 1 1) surfaces.

Moving from surfaces to thin films, growth of strontium cobalt oxide thin films by molecular beam epitaxy, and conditions necessary to stabilize different defect concentration phases are reported. In situ X-ray scattering is used to monitor structural evolution during growth, while in situ X-ray absorption near-edge spectroscopy is used to probe oxidation state and measure changes to oxygen vacancy concentration as a function of film thickness. Experimental results are compared to kinetically-limited thermodynamic predictions, in particular, solute trapping, with semi-quantitative agreement. Agreement between observations of dependence of cobaltite phase on oxidation activity and deposition rate, and predictions indicates that a combined experimental/theoretical approach is key to understanding phase behavior in the strontium cobalt oxide system.

To facilitate studies of thin film structure, a portable metalorganic gas delivery system was designed and constructed to interface with an existing molecular beam epitaxy chamber at beamline 33-IDE of the Advanced Photon Source. This system offers the ability to perform in situ X-ray measurements of complex oxide growth via hybrid molecular beam epitaxy. Performance of the hybrid molecular beam epitaxy system while delivering metalorganic source materials is described. The high-energy X-ray scattering capabilities of the hybrid molecular beam epitaxy system are demonstrated both on oxide films grown solely from the metalorganic source, and ABO_3 oxide perovskites containing elements from both the metalorganic source and a traditional effusion cell.