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# Atom Probe Tomography Characterization of Engineered Oxide Multilayered Structures

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The high temperature operation of solid oxide fuel cells (SOFC) is one of the main challenges we have to overcome, especially for commercializing SOFC for portable power generating applications [1]. Solid state electrolytes with enhanced oxygen ionic conductivity at low and intermediate temperatures are needed to lower the operating temperature of SOFC [2]. Thus, there is an ongoing need to develop new electrolytes or modify existing electrolytes to enhance the ionic conductivity. Recently, oxide multilayer hetero-structures with enhanced ionic conductivity stimulated a great interest as SOFC electrolytes [3]. Here, we investigate the influence of engineered nano-scale interfaces on the ionic conductivity of doped ceria and zirconia multilayer thin film electrolytes by utilizing state-of-the-art characterization techniques including atom probe tomography (APT).

The multilayer thin films with alternative layers of samaria doped ceria (SDC) and scandia stabilized zirconia (ScSZ) were grown using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) to understand the effect of nano-scale interfaces on oxygen ionic conductivity through these films. The number of layers in the SDC/ScSZ multilayer thin films was varied from 2 to 20 by keeping the total film thickness constant at 140 nm. Oxygen ionic conductivity measurements were carried out as a function of temperature on well characterized samples using four probe surface impedance spectroscopy. Although these measurements demonstrate significantly higher ionic conductivity in multilayer thin films in comparison to a single layer thin film or bulk polycrystalline materials, the mechanisms associated with the enhanced ionic conductivity through nano-scale interfaces is not well-understood. Elemental inter-diffusion and dopant segregation across multiple interfaces could play important roles in the oxygen ionic conductivity through these hetero-structures. As such, we carefully characterized the structural and chemical properties of the materials utilizing various bulk and surface sensitive capabilities including x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). In particular, the interfaces in multilayer thin films were carefully characterized using APT to study the elemental distributions along with the elemental inter-diffusion and dopant segregation at the interfaces.

Laser assisted APT can provide quantitative three-dimensional chemical analysis of dielectric materials with lateral and depth resolutions in the order of 0.2-0.3 nm and chemical sensitivity up to parts-per-million levels with field-of-view on the order of $100 \times 100 \times 100$ nm$^3$ [4, 5]. Although conventionally APT has been extensively used to characterize metals and alloys, it is comparatively in its infancy in characterizing oxides and insulators especially composites consisting of heterogeneous structure [6]. Oxide multilayer structures add additional

complications to the characterization of the doped ceria/zirconia multilayers. We have used APT to map the elemental distribution in these films and interfaces and Fig.1 shows 3-D reconstruction of APT experiments carried out parallel to the interfaces and perpendicular to the interfaces along with the XPS depth profiling of these multilayer thin films.

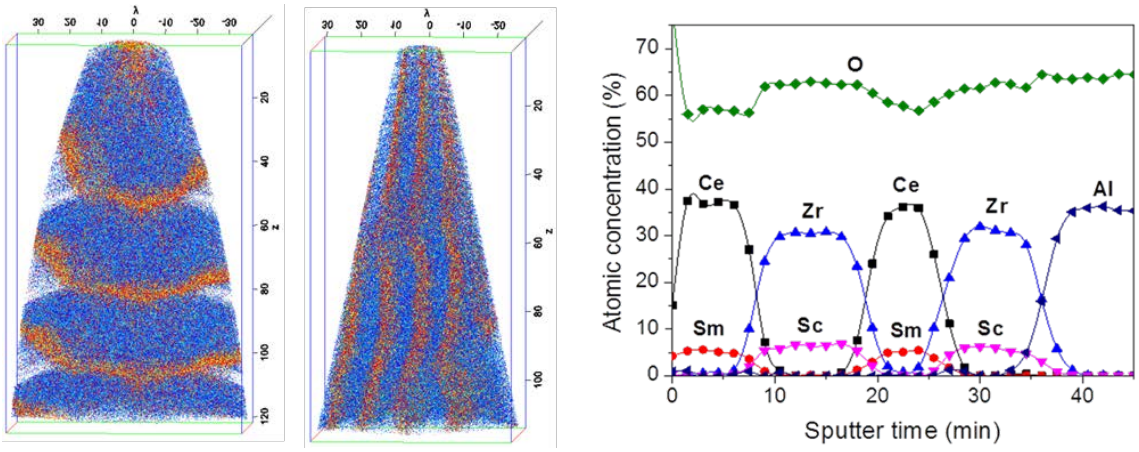


Fig. 1: Three dimensional reconstructions of APT data (Red ions correspond to $CeO_2$ layer and blue ions correspond to $ZrO_2$ layer) along with the XPS depth profiles of SDC/ScSZ multilayer thin films.

The APT reconstructions demonstrate asymmetric tip shape evolution and artifacts associated with trajectory aberrations and we carried out level set model calculations to explain these artifacts [7]. The asymmetric evolving shape predicted by the level set model will be qualitatively compared with the experimental data collected by aligning the hetero-structured interfaces perpendicular and parallel to the tip axis.

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