

SURFACE OXYGEN NONSTOICHIOMETRY DEPENDS NON-MONOTONICALLY ON BIAXIAL STRAIN IN ULTRATHIN CERIA FILMS

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Strain engineering provides a 'dopant-free' alternative to tailor the electronic, defect chemical and catalytic properties of mixed ion and electron conducting (MIEC) oxides. By perturbing the crystallographic symmetry of an oxide, strain can dramatically alter both the position and degeneracy of electronic energy levels, which directly impact the defect chemistry of the oxide. In this work, we employed ambient pressure X-ray photoelectron spectroscopy (APXPS) to probe the valence and core levels of ultra thin films of cerium oxide, a prototypical MIEC, subject to an elastic strain. Coherently strained CeO₂ films were grown on atomically flat (001) Y_{0.16}Zr_{0.84}O_{1.92} (5.5 % compressive strain) and SrTiO₃ (2.1 % tensile strain) single crystal substrates. Aberration-corrected transmission electron microscopy revealed an CeO₂/substrate interface free of cation diffusion and devoid of misfit dislocations. While equilibrium theory predicts that a coherently ceria/YSZ interface is unlikely because of the large lattice mismatch, we demonstrate a stable, redox active coherent ceria film up to 3 nm in thickness on YSZ.

Surface sensitive APXPS performed at 450°C and 550°C under various oxygen partial pressures revealed that the surfaces of the strained ultrathin oxide films, both compressive and tensile, exhibited higher surface polaron concentration (and by extension, oxygen vacancies) compared to the bulk-like, unstrained films. This remarkable result is at odds with the conventional view that the reduction enthalpy decreases monotonically with strain. We systematically performed depth resolved XPS measurements on films of different thicknesses to deconvolve strain effect on the surface redox capacity from that of substrate induced chemical and electrostatic effects. We hypothesize that elastic biaxial strain has a two-pronged effect on the redox capacity. By its coupling with oxygen chemical potential through chemical expansion, tensile and compressive strain will have a monotonic effect on the oxygen nonstoichiometry. However, the symmetry breaking induced by the tetragonal distortion – irrespective of compression or tension - predisposes the oxide away from cubic symmetry. In turn, this favors the reduced oxide (3+ oxidation state of Ce) in its hexagonal sesquioxide environment. The latter effect leads to a non-monotonic dependence of redox properties on biaxial strain.

This work expands our understanding of the behavior of highly strained MIEC oxide films under catalytically relevant conditions. The knowledge of non-monotonic oxygen nonstoichiometry dependence could be extremely useful for strain-engineered heterolayers for memristive applications and surface coatings for pseudocapacitive energy storage.