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Two-dimensional vacancy trapping in yttria doped ceria

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ABSTRACT

Thin film processing methods offer a number of means to investigate and engineer ion conduction in solid electrolytes. In this work, we present fabrication and characterization of Y-doped CeO_2 thin films where the Y-dopants were distributed homogeneously or were condensed into increasingly concentrated layers, to the limit of alternating layers of pure Y_2O_3 and pure CeO_2. Both the entire film thickness and net Y-concentration were kept constant such that only the spatial distribution of dopants was altered. Space charge regions formed at interfaces between regions with varying vacancy concentrations, yielding vacancies trapped within two-dimensionally arranged accumulation regions. A Gouy–Chapman model was implemented in order to further investigate the distribution of the accumulated oxygen vacancies in the space charge regions of pure CeO_2 layers. Comparison of the measured activation energy of conduction indicates that in films with intermediate dopant condensation, conduction occurred predominantly by vacancies trapped in the Y-containing layers. Conversely, in the film composed of alternating layers of Y_2O_3 and CeO_2, vacancies trapped in the CeO_2 space charge regions became significantly conductive, thus providing a means to determine the properties of vacancies in ceria that are trapped near dopants.

1. Introduction

Ceria (CeO_2) based materials are promising oxygen ion conductors for electrolytes in solid oxide fuel cells (SOFCs) [1–4]. The addition of aliovalent oxides into CeO_2 creates oxygen vacancies as Ce^{4+} is substituted by lower-valence solute cations, e.g., Y^{3+}. Oxygen ion conduction in Y-doped CeO_2 ($Ce_{1-x}Y_xO_{2-\delta}$ or YDC) and other cubic fluorite solid electrolytes occurs via a highly thermally activated vacancy mechanism [5]. Because of this, SOFCs and other devices based on ion conduction in ceria are normally required to operate at high temperatures (>600 °C) for sufficient performance. A tempting way to improve low temperature conductivity of electrolytes is to increase the vacancy concentration by adding more dopants. Unfortunately, oxygen ion conductivity in doped CeO_2 reaches a maximum value at a dopant concentration of about 15 to 20%, with increased dopant concentration yielding decreased conductivity [6,7].

A simple model of vacancies independently hopping through the crystal lattice is not able to fully interpret the non-monotonic relationship between oxygen ion conductivity and dopant concentration. Defect association between Y'_{Ce} (or the analogous species for other dopants) and $V_O^{\cdot\cdot}$ at high dopant concentration is a widely accepted explanation [8–11]. The positively charged oxygen vacancies in defect associates, such as ($Y'_{Ce} - V_O^{\cdot\cdot}$), become trapped near the randomly distributed dopant atoms in the lattice due to both Coulombic attraction to the negatively charged dopant site and, at least in some cases, local lattice strain effects. The association decreases oxygen vacancy mobility, leading to reduced ion conductivity.

Recently, several reports summarized in Ref. [12] have suggested that nanostructured multilayers can have a significant effect on the conductivity. Sata et al. observed an increase of F^- ion conductivity by two orders of magnitude as the interfacial spacing of heterostructures decreased from 215 nm to 8 nm in BaF_2/CaF_2 multilayers [13]. This enhancement was explained by ion redistribution in space charge regions where F^- ions were transferred from BaF_2 to CaF_2 [14]. The F^- site vacancies left in the BaF_2 layers significantly increased the total ionic conductivity as the layer thicknesses became comparable to the size of the space charge regions. For systems involving oxygen ion conductors, past reports involving multilayers have typically investigated doped conductors such that the space charge regions are inconsequentially small, defect concentrations are fixed, and atomic structural features such as lattice strain and/or dislocations are instead envisioned as means to alter the mobility of the existing defects [15–17]. These results have proven difficult to repeat [18,19]. In this work, we take an alternative approach, and use nanoscale control over the composition as a means to study the association between dopants and ionic defects.

Here, we study $Ce_{0.95}Y_{0.05}O_{2-\delta}$ thin films where the Y-dopants are distributed homogeneously or are condensed into increasingly concentrated two-dimensional layers, to the limit of alternating layers of pure CeO_2 and pure Y_2O_3, as shown in Fig. 1. We take advantage of a

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novel film deposition technique developed recently that allows creation of fluorite structured films with composition controlled through the thickness at the nanometer level [20]. The use of ceria-based rather than zirconia-based materials in this study is to avoid any issues related to non-cubic phase formation. Y-dopant is used in part since the fluorite-equivalent lattice parameter of Y_2O_3 is somewhat close to that of ceria [21], and thus vacancy trapping in the space charge layer may be modeled to first order by simple Coulombic interaction. The total film thickness and the net Y-dopant content are kept constant so that only the distribution of the dopants within the film is altered. Space charge regions form at regions within films with modulated composition due to a created vacancy concentration gradient, yielding vacancies trapped within two-dimensionally arranged accumulation regions. A study using molecular dynamics simulations reported that the activation energy of oxygen ion diffusion in similarly heterodoped YSZ [22] should increase to correspond to the dopant concentration in the doped layer. Structures at the limit of pure yttria and pure zirconia layers, where distinctly different behaviors would be expected, were not examined. In this work, the combined effects of dopant condensation and interfacial defect redistribution on oxygen ion conduction in $Ce_{0.95}Y_{0.05}O_{2-\delta}$ films are discussed.

2. Experimental

A multi-target, custom-built reactive magnetron sputtering machine (PVD Products, Wilmington, MA) was used to deposit oxide thin films. Single element targets of Ce and Y (ACI Alloys, San Jose, CA) were sputtered in an oxygen-rich environment to create oxidized films. No evidence of reduced phases or cation species was found by X-ray diffraction (XRD) or X-ray photoelectron spectroscopy (XPS). In the operation of a typical film deposition, the base pressure of the sputtering chamber was roughly 1.33×10^{-5} Pa (10^{-7} Torr). The total working gas flow rate was held constant at 20 sccm with a working pressure of 1.33 Pa (10 mTorr) and an argon to oxygen ratio of 9:1. Substrates were electrically grounded, rotated, and heated to 650 °C. The deposition rate from each target was adjusted via the RF sputtering power applied.

$Ce_{1-x}Y_xO_{2-\delta}$ films were produced by simultaneously sputtering from the Ce and Y targets. Further details on this fabrication process, including calibration of the film composition and deposition rate, can be found in Ref. [20]. Films with modulated composition were created by using computerized control to modulate the power applied to each target and/or toggling of target shutters. Films fabricated by this technique have exhibited atomically sharp interfaces, and growth rates are typically $\approx 1\ \mathrm{nm \cdot min^{-1}}$ [23]. Taken together, compositional modulation through the thickness at the single nanometer scale is enabled.

Compositional modulations are likely to be metastable; however, the diffusion of Y dopants into neighboring undoped CeO_2 layers during film deposition and subsequent conductivity measurement is highly unlikely to be an issue in this work. A calculation of the diffusion length of Y cations in doped ceria at 650 °C shows why this is so. Cation diffusion in fluorite-structured oxide ceramics at 650 °C is extremely slow with diffusion coefficients on the order of $10^{-26}\ \mathrm{m^2/s}$ [24]. The total time for all film deposition and conductivity measurements was less than 35 h, and for only a portion of this time were the samples at the maximum 650 °C. Nevertheless, we overestimate the diffusion length of Y cations after 35 h at 650 °C to be about 0.7 Å. Diffusion of the Y dopants through the films, therefore, is not a concern over the experimental time scales of this work.

The surface chemical compositions of $Ce_{1-x}Y_xO_{2-\delta}$ films were measured by a Perkin Elmer 5400 XPS system with an X-ray source emitting at 1253.6 eV. XPS measurements correspond to the elemental composition of the sample surface down to at most about 5 nm [25]. A pass energy of 89.45 eV was applied in the survey scans, while for high resolution scans, it was 35.75 eV. The obtained spectra were deconvoluted using XPSPEAK 4.1 software. XRD measurements were performed on a Rigaku Ultima IV diffractometer (Cu Kα radiation) using a typical θ–2θ geometry to determine the orientations of the films and Al_2O_3 substrates. The modulated composition in $Ce_{1-x}Y_xO_{2-\delta}$ films was visualized using transmission electron microscopy (TEM) (JEOL JEM-2010F) to verify that the desired structures were created. Focused ion beam/scanning electron microscopy (Zeiss AURIGA 60 FIB–SEM) was utilized to prepare the cross-sectional TEM samples.

The cation compositions through the films were also measured using depth-profiling time-of-flight secondary ion mass spectrometry (TOF-SIMS) on a TOF-SIMS IV system (ION-TOF GmbH; Münster, Germany). Material removal was carried out by sputtering with a Cs^+ beam at 5 kV with ion current of 20 nA over a rastered area of 500 μm × 500 μm. A 25 kV Bi^+ beam operated in a "high-current bunched mode" was applied to analyze over a central region with a rastered area of 150 μm × 150 μm. The depth profile was obtained in a non-interlaced mode in which the sputtering beam operated for 1 s and then paused for 0.5 s before operating the Bi^+ analysis beam and then repeating this cycle. Since the samples are relatively nonconductive, an electron flood gun provided charge compensation.

Single crystal Al_2O_3 substrates (10 mm × 10 mm × 0.5 mm) with (0001) orientation were used for the growth of all samples. Although other substrates such as $SrTiO_3$ and Si could provide a much better crystallographic compatibility with $Ce_{1-x}Y_xO_{2-\delta}$ films, electrical conduction through the substrate may confuse the interpretation of experimental results [26–28]. Platinum interdigitated electrodes were fabricated on the top surface of the films by UV-photolithography

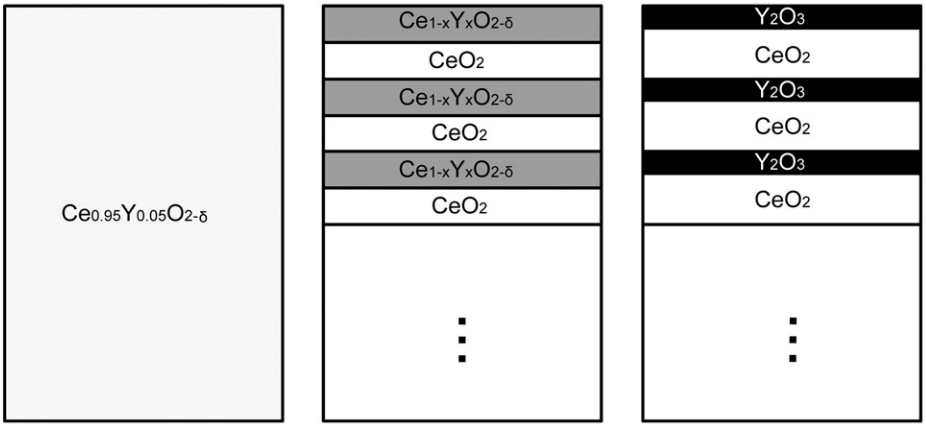

Fig. 1. Schematic diagram of the structures of $Ce_{0.95}Y_{0.05}O_{2-\delta}$ films with modulated composition. The Y-dopant concentration x in $Ce_{1-x}Y_xO_{2-\delta}$ layers is gradually increased while keeping the net Y-dopant concentration of the whole film at a constant 5% by adjusting the relative thickness ratio between CeO_2 and Y-containing layers.