Ultramicroscopy 000 (2017) 1–12

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Structure and chemistry of epitaxial ceria thin films on yttria-stabilized zirconia substrates, studied by high resolution electron microscopy

Robert Sinclair[a,*], Sang Chul Lee[a,*], Yezhou Shi[a,b,c], William C. Chueh[a,b,c]

[a] Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA
[b] Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA
[c] Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

ARTICLE INFO

Article history:
Received 24 August 2016
Revised 15 December 2016
Accepted 28 December 2016
Available online xxx

Keywords:
Aberration-corrected TEM
Environmental TEM
Electron energy loss spectroscopy
In situ high resolution electron microscopy
Epitaxial ceria thin films
Yttria-stabilized zirconia substrates

ABSTRACT

We have applied aberration-corrected transmission electron microscopy (TEM) imaging and electron energy loss spectroscopy (EELS) to study the structure and chemistry of epitaxial ceria thin films, grown by pulsed laser deposition onto (001) yttria-stabilized zirconia (YSZ) substrates. There are few observable defects apart from the expected mismatch interfacial dislocations and so the films would be expected to have good potential for applications. Under high electron beam dose rate (above about 6000 $e^-/Å^2s$) domains of an ordered structure appear and these are interpreted as being created by oxygen vacancy ordering. The ordered structure does not appear at lower lose rates (ca. 2600 $e^-/Å^2s$) and can be removed by imaging under 1 mbar oxygen gas in an environmental TEM. EELS confirms that there is both oxygen deficiency and the associated increase in Ce^{3+} versus Ce^{4+} cations in the ordered domains. *In situ* high resolution TEM recordings show the formation of the ordered domains as well as atomic migration along the ceria thin film (001) surface.

1. Introduction

Ceria (CeO_{2-x}) is an interesting material from the technological and scientific points-of-view. In particle form it has applications as catalysts, particularly for electrochemical hydrogen oxidation [1,2] and thermochemical water splitting [3,4]. It also can be used as a support material for metal nanoparticles to promote their catalytic activity of, and use for, the carbon monoxide oxidation reaction [5,6]. As a thin film, it can be employed as an electrode for solid-oxide fuel cells especially in combination with yttria-stabilized zirconia (YSZ) [2,7–9] as discussed here.

Ceria has the fluorite crystal structure whereby the oxygen anions form a simple cubic array with the cerium cations in half of cubic interstices in a face centered cubic (FCC) arrangement. Thus the space group is Fm $\bar{3}$m. Substitution on cation sites is employed to increase ionic conductivity [10,11], through the introduction of oxygen vacancies to compensate for a charge disparity for trivalent or divalent cations. Oxygen vacancies can also form intrinsically in CeO_{2-x} as a proportion of the cerium can be triply rather than quadruply charged [12,13]. The role of oxygen vacancies is critical to the oxygen ion transport in this material and hence its ionic conductivity.

There are many notable transmission electron microscopy (TEM) investigations of ceria largely associated with its catalytic activity (e.g. ref [14–17]). Both high resolution imaging to show the structure [14,18] and electron energy loss spectroscopy (EELS) to establish the cerium ionization state through the M_5/M_4 peak ratio [19] have been effectively employed. In the present paper we concentrate on the structure of ceria thin films grown epitaxially on isomorphous yttria-stabilized cubic zirconia (YSZ) substrates. Amongst other findings, it will be seen that in some circumstances an ordered structure is created which we demonstrate is likely associated with anion vacancy ordering. Such a structure would be detrimental to the ionic conductivity as the vacancies would be more trapped in this structure and not able to move about so freely to assist oxygen ion diffusion.

* Corresponding authors.
E-mail addresses: bobsinc@stanford.edu (R. Sinclair), sclee99@stanford.edu (S.C. Lee).

http://dx.doi.org/10.1016/j.ultramic.2017.03.015
0304-3991/

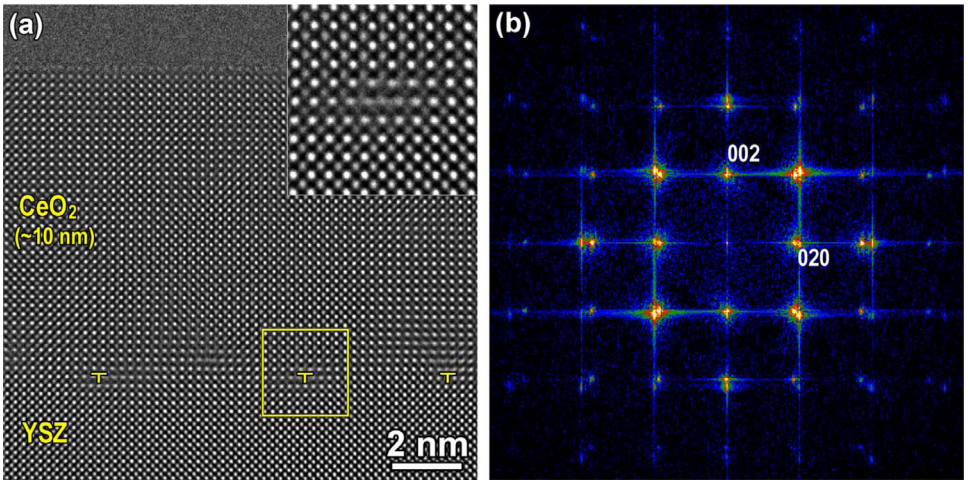

Fig. 1. (a) NCSI high resolution image of an epitaxial pure ceria thin film (10 nm) on the (001) YSZ substrate. Interfacial dislocations, seen as extra terminating planes in the YSZ, are indicated. Inset shows high magnification view of the boxed area in the image showing an individual interfacial dislocation. Any orthogonal dislocations present in the foil do not normally manifest themselves in such images, as known previously [29]. (b) FFT of the image in (a) showing the reflections of both phases in the epitaxial relationship.

2. Materials and methods

Ceria thin films were deposited by pulsed laser deposition onto YSZ (001) single crystal substrates (CrysTec, Germany). The as-received substrates have steps and terraces due to miscutting by 0.05°. They are sonicated in isopropanol for 15 min prior to annealing in 99.999% Ar at 1250 °C for 12 h to produce atomically-flat terraces on YSZ before inserting into the vacuum chamber (PLD/MBE 2300, PVD products). The step heights are of the order of 0.25 nm (half the unit cell dimension as determined atomic force microscopy (AFM)). The substrate was held at 500 °C in 0.5 mTorr (6.6×10^{-4} mbar) 99.999% O_2, and ceria or samarium (Sm^{3+}) doped ceria (20 at% doping) targets were ablated by a KrF (λ=248 nm) excimer laser with the laser spot focused to approximately 5 mm^2 on the target. The energy of the pulse was calibrated to be 80 mJ and a repetition rate of 1 Hz was used. Further details are given elsewhere [20]. Under these conditions the deposition rate is approximately 0.008 nm/pulse.

Cross-section specimens for TEM were prepared by modification of a standard method [21]. The cut pieces were glued and mechanically ground and polished to 15 µm thickness and ion-milled to electron transparency using a Gatan PIPS II System. A 5 kV argon ion beam was used to create a hole in the center of the specimen with an incident angle of 5°. Then, the argon ion energy was reduced gradually to 0.1 keV to remove any surface amorphous layer.

Electron microscopy was carried out using a FEI Titan 80–300 environmental TEM (ETEM) equipped with a spherical aberration corrector for the imaging (objective) lens, a monochromator and the X-FEG high brightness electron gun. Typical resolutions are sub 0.1 nm for the images and 0.1–0.2 eV for the monochromated EELS (0.7–0.8 eV for a non-monochromated beam). Most of the images shown here were obtained at 300 kV using negative spherical coefficient imaging (NCSI) conditions (Cs=−13 µm) [22–24], and were recorded on a Gatan OneView high frame rate camera. For electron irradiation experiments, the electron dose rate ($e^-/Å^2s$) was measured from the fluorescent screen current, which had been calibrated for the instrument using an analytical TEM holder with a Faraday cup. Dose rates between 2600 and 15,000 $e^-/Å^2s$ were employed (10 A/cm^2≡6,200 $e^-/Å^2s$). ETEM experiments were performed in the same microscope using oxygen gas of research grade 6.0 (99.9999%) purity (Praxair Inc.). The gas pressure was adjusted to 1.0 mbar for this experiment. Image simulations were performed using a JEMS program based on the multislice method. STEM–EELS observations were carried out by operating the microscope in scanning mode without the monochromator. Spectra were collected using a C2 aperture size of 50 µm, camera length of 38 mm, entrance aperture of 2.5 mm, and a dispersion of 0.1 eV/pixel. This corresponds to convergence and collection semi-angles of 9.3 and 18.7 mrad, respectively. The STEM probe size was approximately 0.5 nm. Quantitative data were obtained following background subtraction by a power law method using Gatan Digital Micrograph software (version 2.11).

3. Results

3.1. General observations

Fig. 1(a) shows a typical aberration-corrected image of the thin film structure (10 nm of deposited pure ceria) in the [100] orientation. It has been found by X-ray diffraction and cross-section TEM [20,25] that the ceria grows epitaxially onto the YSZ substrate, remaining coherent up to a critical thin film thickness of 3.5 nm, beyond which coherency is lost by the formation of a regular array of dislocations at the interface [20], thereby becoming semi-coherent. In Fig. 1(a) the square lattices of the projected fluorite structures are clearly seen in both film and substrate, and the unit cell dimensions are close to those in the bulk state (i.e. 0.511 nm for YSZ and 0.541 nm for ceria). Measured lattice parameters of ceria from the images and fast Fourier transformation (FFT) in Fig. 1(b) are 0.542 nm along both the in-plane and out-of-plane directions. The measured angles for the $(04\bar{4})$ FFT reflections from the $(00\bar{4})$ spots are 45.0° and 45.1° for the ceria and YSZ reflections respectively. Both the FFT and corresponding measurements on the images yield identical in-plane and out-of-plane YSZ lattice parameters (0.511 nm) within experimental uncertainty (0.001 nm). The FFT of the image shows the epitaxial relationship of the two phases with slightly different lattice constants. The dislocations at the interface are also indicated.

Fig. 2 shows a thickness/defocus (Δf) tableau of simulated images for the ceria. For the imaging conditions used here (spherical aberration coefficient: −13 µm; semi-angle of beam convergence: 0.2 mrad; defocus spread: 4.5 nm), the best match between the experimental and calculated images is at around 11 nm specimen thickness (i.e. 20 ceria unit cells) and so this thickness is used for further simulations. This is a reasonable value for typical cross-section specimen preparation using the polishing and ion milling method. Moreover, our imaging conditions are similar to those of Jia and Urban [23] who noted that the point spread function is

Please cite this article as: R. Sinclair et al., Structure and chemistry of epitaxial ceria thin films on yttria-stabilized zirconia substrates, studied by high resolution electron microscopy, Ultramicroscopy (2017), http://dx.doi.org/10.1016/j.ultramic.2017.03.015