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The effects of substrate surface structure on yttria-stabilized zirconia thin films

Jun Jiang [a,*], Daniel Clark [b], Weida Shen [b], Joshua L. Hertz [a,b]

[a] Department of Materials Science and Engineering, University of Delaware, 201 DuPont Hall, Newark, DE 19716, USA
[b] Department of Mechanical Engineering, University of Delaware, 126 Spencer Laboratory, Newark, DE 19716, USA

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ABSTRACT

Thin film properties can be controlled to a large degree by the substrate upon which the film is grown. The substrate surface can affect the film's crystal phase and microstructure and, thereby, many other properties. In this study, yttria-stabilized zirconia films on single crystal MgO and Al_2O_3 substrates with polished, ion cleaned, or milled surfaces were studied. The different substrate surfaces influenced the thin films' microstructures and ionic conductivities. The increased roughness of the milled surfaces led to significant decreases in both the crystallinity and the ionic conductivity of the films. Ion cleaning of the substrate surface immediately before deposition did not affect the conductivity of films on MgO substrates but led to conductivity reductions by a factor of about 4 on sapphire substrates.

1. Introduction

Solid electrolytes exhibiting high ionic conductivity are of prime importance to solid oxide fuel cells (SOFCs), solid state batteries, and permeation membranes [1]. The common electrolyte material yttria-stabilized zirconia (YSZ) does not offer sufficient ionic conductivity for many applications until the temperature reaches 800–1000 °C [1,2], and such high operating temperature decreases the device efficiency and longevity. Compared with YSZ bulk, nanoscale YSZ thin films look promising, as they have been reported (with some controversy) to exhibit highly improved ionic conductivity [3–5]. A number of techniques have been used for YSZ thin film fabrication, including sol–gel [6] and powder methods [7]. Physical vapor deposition methods, including evaporation [5,8], sputtering [4,9,10], and pulsed laser deposition [3,11–14] are the most common for YSZ thin film fabrication, especially nanoscale films.

We recently reviewed the research on nanoscale YSZ thin films and found that the reported ionic conductivity varied from as low as 10^{-4} S/cm to as high as 1 S/cm at 500 °C, a range of 4 orders of magnitude [15]. The highest conductivity of nanoscale YSZ thin film was reported by Sillassen et al. [4] at more than 3 orders of magnitude higher than that of YSZ bulk. Increased conductivities have been attributed to a YSZ/substrate interface structure with high oxygen ion mobility [3,4], lattice strain [4,16] or space charge effects [5]. Reduced conductivities, as reported by Guo [11] and Navickas [13], were attributed to the blocking effect of grain boundaries, which become increasingly significant as the grain size decreases. As further evidence for this hypothesis, Navickas et al. [13] found that the conductivity of columnar YSZ thin films was nearly one order of magnitude higher when measured with current perpendicular to the substrate relative to an in-plane measurement.

In our previously reported experimental results, we found [16] that YSZ thin films achieved epitaxial growth on sapphire (0 0 0 1), orienting in (1 1 1) directions. While 100 nm thick films exhibited similar conductivity to a YSZ single crystal, when the thickness was 6 nm, the conductivity increased by 1–1.5 orders of magnitude. However, when deposited on MgO (1 0 0) substrates, nominally identical films had poor crystallinity and variable texture, and the conductivity decreased to significantly below that of the single crystal [17].

In this study, the effects of different MgO and sapphire substrate surfaces on the electrical properties of sputtered YSZ thin films are investigated. The MgO and sapphire substrates used offer two kinds of surfaces: one is polished to a roughness less than 1 nm, while the other is mechanically milled. The milled surface is visibly much rougher and, unlike the polished side, presents a wide range of surface termination crystallographic planes. In addition to these as-purchased surfaces, the polished surfaces can

* Corresponding author at: Department of Mechanical Engineering, University of Delaware, 126 Spencer Laboratory, Newark, DE 19716, USA. Tel.: +1 3022765155.
E-mail address: jiangjun@udel.edu (J. Jiang).

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be ion cleaned within the deposition chamber by applying an RF bias in pure argon, effectively sputtering clean the substrate. Since ion cleaning is performed within moderate vacuum soon before deposition, it is intended to enable presentation of a chemically pristine surface to the initial film deposition. Specifically, the surface can be free from adventitious carbon, moisture, and resilient inorganic contaminants. Structurally, ion cleaning might create different surface morphology and roughness [18]; chemically, ion cleaning might clean the surface of impurities and/or adjust the surface stoichiometry, in particular by creating oxygen deficiency [19]. Ion cleaning may also introduce atomic surface damage, compressive stresses, or amorphization through shot peening [20]. These differences in surface structure and chemistry are believed to influence the microstructure and electrical properties of the YSZ thin films. Below, we use these various surfaces in order determine the effect of substrate surface on the structure and electrochemical properties of nanoscale YSZ thin films.

2. Experiment

YSZ thin films were fabricated by reactively co-sputtering single element, metallic Zr and Y targets. The deposition pressure was 1.33 Pa (10 mTorr) with a composition of 9:1 Ar:O_2, and the gas flow rate was held constant at 20 sccm. The substrate temperature during deposition was 650 °C. The power output was 200 W for the Zr target and 70 W for the Y target, which gave a deposition rate of 32 nm h^{-1} and a dopant concentration of about 9 mol% as verified by energy dispersive spectroscopy and X-ray photoelectron spectroscopy. More details about the sample fabrication were reported previously [21]. The film thickness was 50 nm for all samples.

Single crystal MgO (1 0 0) and sapphire (0 0 0 1) (MTI Corporation) were used as the substrates. The substrates were polished on one side and milled on the other side by the manufacturer. Before being loaded into the vacuum chamber, the substrates were rinsed sequentially with acetone, isopropanol, and DI water and then blown dry with filtered air to remove organic residues and other contamination.

For some samples, the polished surface was further ion cleaned by applying an RF bias to the substrate within the sputtering chamber before beginning the film deposition. The total power output from the RF source for the ion cleaning was 100 W and the chamber contained 1.33 Pa (10 mTorr) of 99.999% pure Ar. The milling rate for oxide materials under these conditions was roughly 2.4 nm min^{-1}. Ion cleaning was performed for 30 or 60 min, removing approximately 72 nm and 144 nm, respectively, from the surface. Deposition occurred immediately after the surfaces were ion-cleaned, with the substrates remaining in the chamber in vacuum during this time.

X-ray diffraction (XRD) (Rigaku Ultima IV) using θ–2θ plane reflection geometry with Cu Kα radiation was performed to determine the films' orientations. Atomic force microscopy (AFM) (NTEGRA Prima) was used to quantify the roughness of the substrate surfaces. Interdigitated platinum electrodes with total length 681 mm, electrode spacing and finger width 25 μm, and thickness 200 nm were prepared using lift-off photolithography. Conductivity was measured using impedance spectroscopy (Alpha-A, Novocontrol Technologies) over the frequency range 1 Hz–3 MHz at temperatures between 300 °C and 650 °C in flowing dry air. Impedance spectra were analyzed by equivalent circuit analysis using Zview software (Version 3.3, Scribner Associates). Before the conductivity measurement of YSZ thin films, bare MgO and sapphire substrates with identical electrodes were measured to ensure the film resistances were at least one order of magnitude less than that of the substrates. This test helps to eliminate erroneous results due to possible current leakage through the substrate [22].

3. Results and discussion

Fig. 1 shows the surface morphology of the milled surface of an Al_2O_3 substrate as measured by AFM. The surface morphology of the milled MgO substrate was substantially similar. The roughness (R_A) calculated from the AFM images was around 116 nm. Sputtering is well known to provide very uniform, conformal coatings as long as the surface does not have reentrant features or high aspect ratio topographical features [23]. As seen in the height profile, the surface topographic features are all at relatively low angle. Thus, films sputtered onto this surface are expected to be continuous. The polished and ion cleaned surfaces were also measured, however the roughnesses were immeasurably low, below 1 nm, and could not be reliably quantified.

XRD patterns for 50 nm thick YSZ films deposited on the MgO (1 0 0) and Al_2O_3 (0 0 0 1) substrates with various surface treatments are shown in Fig. 2. As shown in Fig. 2(a), films deposited on MgO have different orientations depending on the surface treatment. Specifically, films deposited on polished MgO have strong (1 1 1) texture, while films on an ion cleaned MgO surface have

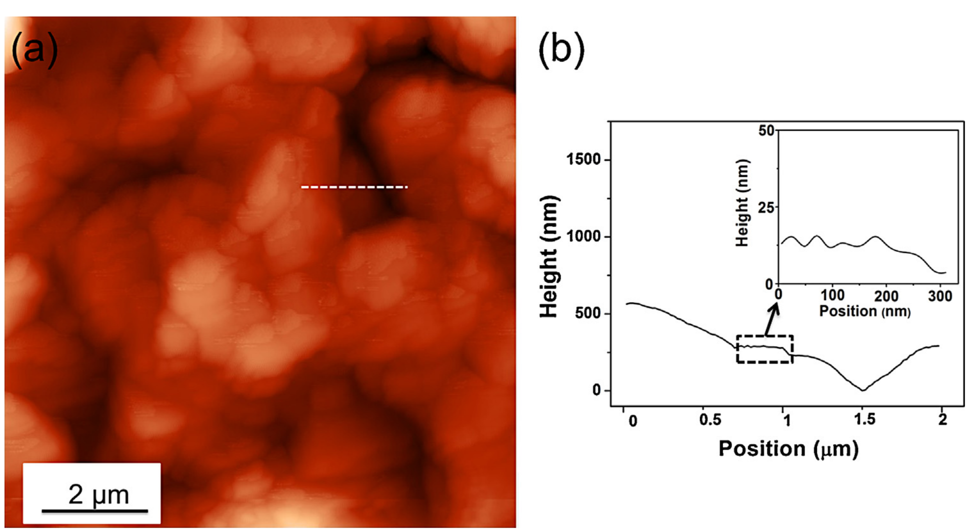

Fig. 1. (a) AFM image of milled surface of Al_2O_3 and (b) height profile along the path indicated with a dashed line. In part (a), height is indicated by shade where the scale from black to white is 800 nm.