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Short communication

Epitaxial pore-free gadolinia-doped ceria thin films on yttria-stabilized zirconia by RF magnetron sputtering

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Abstract

A thin film of gadolinia-doped ceria (GDC) grown on (001) single crystal of yttria-stabilized zirconia (YSZ) was produced by RF magnetron sputtering using a stoichiometric target. Films deposited at room temperature showed columnar porosity which changed to equiaxed on annealing at 1150 °C. It is shown that films deposited at 500 °C were epitaxial, uniform in thickness, pore-free and remained dense after annealing at 1150 °C. This method can be used to attain reproducible control over important characteristics of the film such as structure, composition, orientation, thickness and morphology.

Keywords: A. Films; B. Interfaces; Gadolinia-doped CeO_2; Yttria-stabilized zirconia (YSZ)

1. Introduction

A great deal of interest has recently emerged in the development of multi-component oxide films to study their properties for potential use in various applications including, but not limited to, solid-state electrochemical devices such as solid oxide fuel cells (SOFC), oxygen pumps and sensors [1,2], and automotive emission control devices for oxygen storage and release [3,4]. Arguably the most common methods to deposit such films are powder based, such as screen printing from a paste or spin coating from slurry, followed by sintering at an elevated temperature, typically 1300 °C and above [5,6]. The widespread use of these conventional techniques even to this day owes it to their simplicity and ease by which they can be employed, although it is extremely challenging to get films with reproducible thickness, microstructure, phase and stoichiometry. High sintering temperatures make matters worse leading to films with compositional gradients and undesirable reaction products at the film/substrate interface. While performing experimental studies and measurements on such systems, the effect of variations in film characteristics such as porosity and interfacial reaction products are often neglected. Although this might be an acceptable practice in some cases, such variations in film characteristics can lead to complicated effects (e.g., effect of porosity and interfacial reaction product on electrical conductivity in SOFC) which are hard to characterize. [7] CVD [8,9] processes have been employed to mitigate some of the problems listed above, but these processes suffer from challenges such as complex reactor design and the fact that process parameters (temperatures and precursor vapor pressures) have to be carefully controlled to get the desired film characteristics. Furthermore, low temperature CVD might yield amorphous films which might have to be annealed at a high temperature to get the desired crystalline phase [8,9]. Hence, there remains a challenge to produce multi-component ceramic films by techniques which can minimize compositional and structural variability without substantial compromise on ease and simplicity of the process.

The last decade or so has seen a shift toward thin film deposition techniques for the development of multi-component oxide thin films. Several methods such as molecular beam epitaxy (MBE) [1,10] and reactive sputtering [2,11] have been employed which are superior to conventional methods in not only that they provide control over film characteristics but also eliminate the high-temperature sintering step. These methods,

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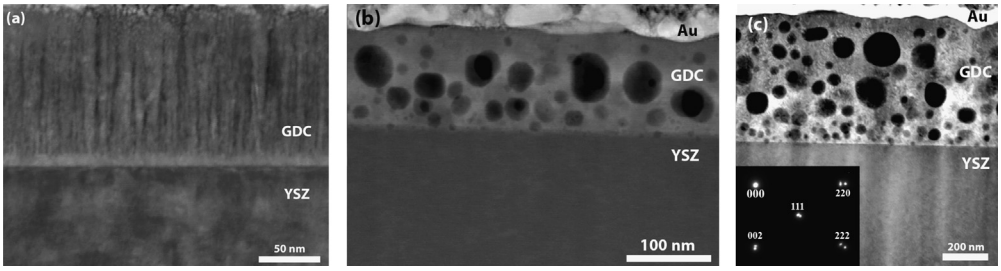

Fig. 1. (a) A dark-field STEM image of a GDC film on YSZ-(001) single crystal deposited at room temperature (RT), (b) a dark-field STEM image of a GDC film on YSZ-(001) single crystal, deposited at the same time along with the one in (a), followed by annealing at 1150 °C for 2 h, and (c) a dark-field STEM image of a thicker film deposited at room temperature and later annealed at 1125 °C for 25 h. The SAD pattern in the inset ((with [1$\bar{1}$0] zone axis) shows that the film is epitaxial.

however, require high substrate temperature (~600–650 °C) [1,2] and careful control of partial pressures of chamber gases to get reproducible films with well defined structure, orientation and compositional homogeneity. Furthermore, in some cases, a post deposition anneal in air is necessary to get the desired structure and stoichiometry [11]. It is therefore imperative to investigate alternative thin film deposition processes in which the desired structure and composition is attained in a single step at much lower substrate temperatures.

In the present work, high quality gadolinia-doped ceria (GDC) films on yttria-stabilized zirconia (YSZ) (001) substrates have been prepared by RF magnetron sputtering from a stoichiometric target. Both GDC and YSZ, owing to their high ionic conductivities at elevated temperatures, have been the focus of extensive research in the solid oxide fuel cell (SOFC) technology area [5,12]. GDC thin film on YSZ has also been identified as a barrier layer to stop the interfacial reaction of perovskite cathodes and YSZ electrolyte [5,13]. The GDC/YSZ couple presented here is not intended to be a fuel cell component per se; rather it can be useful in studying intrinsic effects in the couple not complicated by structural and compositional variability. The process employed in this work gives reproducible control over important characteristics of the film such as structure, composition, orientation, thickness and morphology. In films which are deposited by conventional techniques (such as screen printing or spin coating followed by annealing) there are several uncontrolled variables such as compositional homogeneity, orientation, morphology etc. If, for example, ac impedance spectroscopy measurements are made on such a system, there could be multiple equivalent circuits (due to a large number of uncontrolled variables) leading to the same macroscopic response. The couple produced by our process has reduced number of unknown variables, hence making modeling of equivalent circuits more reliable. This makes our GDC/YSZ couple amenable to fundamental studies such as oxygen reduction kinetics and effectiveness as a barrier layer for SOFC applications, and stability of films in various temperature and gas environments for automotive emission control devices.

2. Experimental procedure

GDC thin films were deposited on YSZ-(001) single crystal substrates using a Discovery 18 DC/RF magnetron sputter deposition system (Denton Vacuum, Moorestown, NJ). The GDC targets were prepared from stoichiometric powder ($Ce_{0.89}Gd_{0.11}O_{1.95}$) having a specific surface area of 35–47 m^2/g (purchased from Nextech Materials, Columbus, OH). The powder was cold pressed into discs and sintered at 1350 °C to a final diameter of 3 in. and a thickness of 0.125 in. Then the sintered disc was mounted in a copper backing cup by Sputtering Target Manufacturing Co., LLC (Westerville OH). Sputtering Target Manufacturing has since been purchased by Kurt J. Lesker Company. Single crystal 8 mol% YSZ substrates with a (001) surface orientation were purchased from MTI Corporation (Richmond, CA). The substrates were 5.0 × 5.0 × 0.5 mm in dimension and chemically polished to < 5 Å surface roughness.

The GDC films were sputtered at a power of 60 W for 1–4 h in an Ar atmosphere (5 mTorr) at two different substrate temperatures (room temperature and 500 °C). Following deposition, the films were annealed in air at 1125–1150 °C for 2–25 h in a box furnace. Scanning Transmission Electron Microscopy (STEM) was used to characterize the phase, morphology and the microstructure of the film. STEM samples were prepared by focused ion beam (FIB: FEI Helios, FEI Company, Hillsboro OR) and imaging was performed on a FEI Tecnai F-20 and Philips CM200 microscopes (FEI Company, Hillsboro OR).

3. Results and discussion

Fig. 1(a) shows a high angle annular dark-field (HAADF) STEM image of a film after deposition at room temperature (RT). As evident in the micrograph, RT deposition led to a columnar grained microstructure. This type of microstructure is well known for films deposited at a temperature less than $0.3T_m$, T_m being the melting point [14]. Due to the screening effect of large grains and their impingement upon each other, significant columnar porosity was observed between grains. The film, however, was crystalline as confirmed by x-ray diffraction (XRD), and had the same structure as the substrate (fluorite). Furthermore, analysis by x-ray fluorescence spectroscopy (XRF) revealed that the film had the same chemical composition as that of the sputtering target and the starting powder from which the target was made. Contrast in HAADF-STEM depends on the atomic number (Z) as well as the atomic density [15]. As the film is porous, although having a higher Z

than the substrate, it does not appear brighter. The bright band along the GDC/YSZ interface is predominantly GDC as confirmed by energy dispersive spectroscopy (EDS), and dense, which is expected during early stages of film deposition. Fig. 1(b) shows a dark-field STEM image of the film which was annealed at 1150 °C after RT deposition. The columnar grains disappeared, giving rise to significant equiaxed porosity having an area fraction of ~30% (using ImageJ image analysis software). A thicker film annealed for a longer time (1125 °C for 25 h) showed similar behavior (Fig. 1(c)). Electron diffraction showed that the film was epitaxial ($(001)_{GDC}//(001)_{YSZ}$ and $[1\bar{1}\,0]_{GDC}//[1\bar{1}0]_{YSZ}$), as revealed by separation of higher order diffraction spots in the SAD pattern (inset in Fig. 1(c)). Since GDC is not volatile at 1150 °C, this porosity must have formed by pore coarsening and coalescence, leading to stabilization of larger pores. Such porosity was also observed by Mai et al. upon sintering of a layer of GDC (deposited by reactive sputtering) on YSZ at 1080 °C for 3 h [13]. The columnar porosity in Fig. 1(a) coarsens to the equiaxed porosity in Fig. 1(b) by a mechanism similar to the one during sintering. In polycrystalline films, the surface of the film and the grain boundaries act as sinks for vacancies. Since our films are single crystalline, the only available sink for vacancies is the film surface. A close look at Fig. 1(b) shows that the big equiaxed pores are concentrated in the middle of the film, while the film is denser near the surface. This means that the part of the film near the surface densifies by vacancy exchange with the surface. The part of the film in the middle, however, does not have that luxury and hence it densifies by vacancy exchange with the existing pores, causing them to coarsen.

Fig. 2 shows a dark-field STEM image of a GDC film deposited at 500 °C, together with a selected area diffraction (SAD) pattern in the inset. The film was uniform in thickness and epitaxial ($(001)_{GDC}//(001)_{YSZ}$ and $[1\bar{1}0]_{GDC}//[1\bar{1}0]_{YSZ}$) as revealed by separation of higher order diffraction spots in the SAD pattern, and there was no evidence of any porosity as compared with the film deposited at RT. This means that there is significant atomic mobility at 500 °C to cause the requisite atomic rearrangement for densification of the microstructure and also the absence of the bright higher-density band along the GDC/YSZ interface which was visible in the film deposited at RT. The thickness of the film was ~50 nm which is significantly smaller than that of the film deposited at room temperature (~120 nm), even though the same deposition parameters (60 W, 5 mTorr Ar, 1 h) were used. The thickness difference can be attributed to the fact that room temperature deposition does not allow the requisite densification leading to a film with higher apparent thickness.

Fig. 3 shows a low magnification dark-field STEM image of the film deposited at 500 °C and annealed at 1150 °C, together with a high magnification bright-field STEM image with the corresponding selected area diffraction (SAD) pattern with the [100] zone axis (inset in Fig. 3(b)). The film was uniform in thickness, epitaxial and in comparison to the film deposited at RT and later annealed, this film was free from any porosity. A closer look at the GDC/YSZ interface (for both the films as-deposited at 500 °C and annealed) reveals a periodic array of misfit dislocations (Figs. 2 and 3(b)). The spacing of this dislocation array is consistent with that for unit edge dislocations having a Burgers vector of the type $(a/2)\langle 110\rangle$.

Fig. 4 shows normalized Ce and Zr EDS intensity profiles taken across the interface before and after annealing. Although an increase in the apparent width of the interface is seen after annealing, such levels of broadening by interdiffusion are expected at that annealing temperature as diffusivity of Ce in YSZ is higher by orders of magnitude at 1150 °C as compared to that at 500 °C [16]. The interfacial structure, however, is not

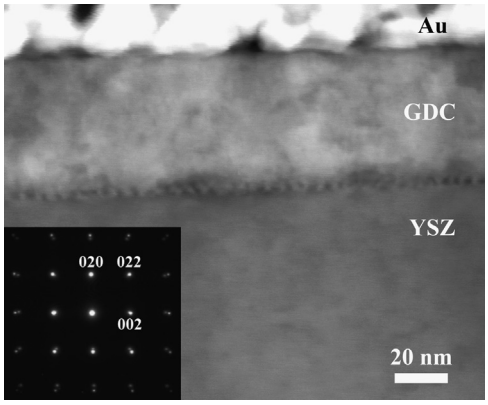

Fig. 2. A dark-field STEM image of a GDC film on YSZ-(001) single crystal deposited at 500 °C. The periodic contrast at the interface is due to dislocations and the SAD pattern in the inset has a [100] zone axis.

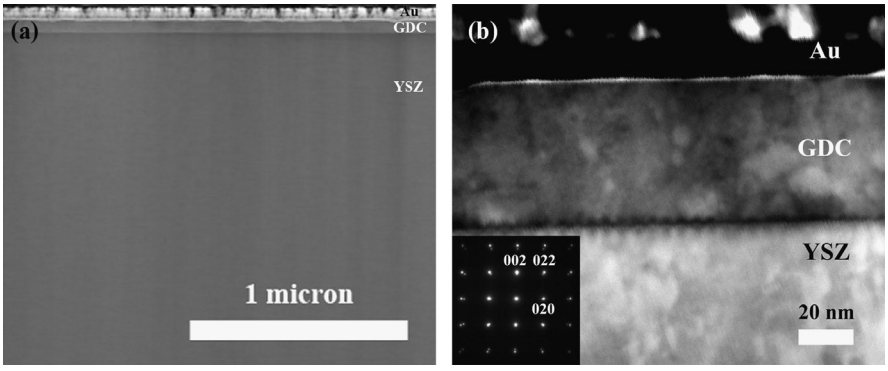

Fig. 3. (a) A low magnification dark-field STEM image of a GDC film on YSZ-(001) single crystal, deposited at the same time along with the one in Fig. 2, followed by annealing at 1150 °C for 2 h, and (b) a bright-field STEM image showing periodic contrast at the interface due to dislocations, with the SAD pattern in the inset (with [100] zone axis).

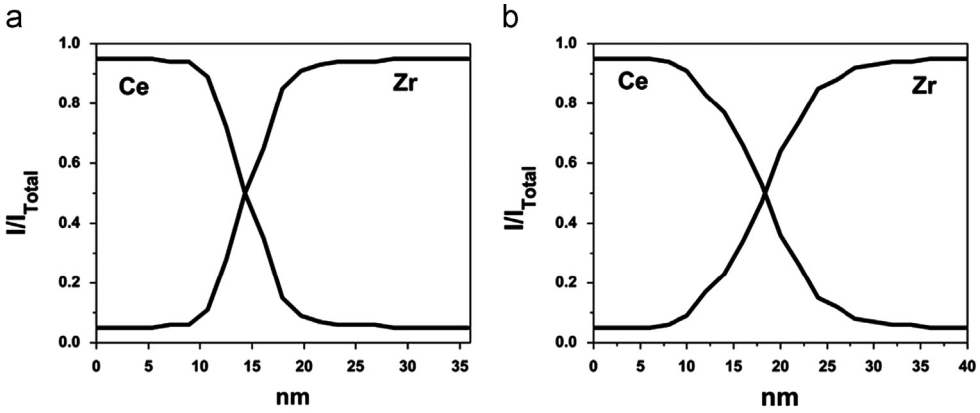

Fig. 4. Normalized Ce and Zr EDS intensity profiles (a) before annealing, and (b) after annealing at 1150 °C, for the GDC film deposited at 500 °C.

expected to change significantly with a 2 h anneal at 1150 °C. It is pertinent to mention here that the post deposition anneal was done to compare the microstructural evolution in the films deposited at room temperature and 500 °C. Films deposited at 500 °C are already dense (as compared to the ones deposited at room temperature) and have the desired structure and stoichiometry. The annealing treatment does not change the structure but rather serves to emphasize the stability of these films and the interface at such high temperatures.

4. Conclusions

In this work, GDC thin films were successfully deposited on YSZ single crystal substrates by RF magnetron sputtering from a stoichiometric target. The films were epitaxial, pore-free, and uniform in thickness when deposited at 500 °C. Annealing at 1150 °C did not impart any significant change to the properties of the film and its interfacial structure. The dense epitaxial GDC/YSZ couple can be employed in understanding intrinsic effects in the couple not complicated by structural and compositional variability that might be present in films produced by conventional deposition techniques.

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