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Pulsed Laser Deposition of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}/\text{Zr}_{0.9}\text{Sc}_{0.1}\text{O}_2$ Bilayer Films for Fuel Cell Application

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Abstract.

Samarium doped ceria exhibits relative high conductivity of 0.1 S/cm at 700 °C and has been considered to be an attractive electrolyte for solid oxide fuel cells operating at the temperature range between 500 to 600 °C. Although the material exhibits better chemical and structural compatibility with electrodes as well as higher ionic conductivity than Yttria-stabilized Zirconia, the reduction of Ce^{4+} to Ce^{3+} induces n-type electronic conduction which tends to decrease power output of solid oxide fuel cells. The problem can be eliminated by using a barrier of thin $\text{Zr}_{0.9}\text{Sc}_{0.1}\text{O}_2$ layer deposited over SDC layer as an alternative electrolyte to improve the stability of Samarium doped ceria under reducing atmosphere.

In this work, we will report the results on the development of the Pulsed Laser Deposition (PLD) process to fabricate $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}/\text{Zr}_{0.9}\text{Sc}_{0.1}\text{O}_2$ bilayer films. Bilayer films with controlled microstructures, density, and interfacial properties were successfully grown by the PLD at various deposition temperatures on Si(100) substrates. X-ray diffraction was used to determine their crystal structures, while the cross section images of the film-film and film-substrate interfaces were examined by field-emission SEM. The film density was calculated from the index of reflection data determined by a fiber-optic spectrophotometer.

Introduction

High (~1000 °C) operating temperature is one of the main barriers for wide scale adoption of solid oxide fuel cells (SOFC) technology [1]. Therefore, most of the research works is focused on the development of intermediate temperature SOFCs operating at around 500-600 °C. To achieve the objective of low operating temperatures, a number of approaches from the viewpoint of new materials, novel processes, and unique architectures have to be re-examined.

One important step to reduce the operating temperature of SOFCs is to use thin film (around 1 micrometer) electrolytes to reduce the Ohmic loss which can be obtained by thin film deposition. Miniaturized SOFCs fabricated by thin film deposition and micromachining can bring down the operation temperatures to 300 ~ 600°C [2]. Such a small fuel cell could replace batteries in many applications where a longer operating time is needed.

Another problem that has to overcome is the low conductivity of traditional SOFC materials (e.g. yttrium-stabilized zirconia (YSZ) electrolytes) when operating at low temperatures (500-600 °C). Different materials, therefore, need to be found for that purpose. Samarium doped ceria (SDC) is being considered as an attractive electrolyte for solid oxide fuel cells operating in a temperature range of 500 ~ 600 °C [3, 4]. SDC exhibits relative high conductivity of 0.1 S/cm at 700 °C [5] and has been investigated widely over the past two decades. Although the material exhibits better chemical and structural compatibility with electrodes as well as higher ionic conductivity than YSZ,

the reduction of Ce^{4+} to Ce^{3+} induces n-type electronic conduction which tends to decrease power output of solid oxide fuel cells. The problem can be eliminated by using barriers of thin Scandium-stabilized Zirconia (ScSZ) layer deposited over SDC layer as the alternative electrolyte to improve the stability of SDC under reducing atmosphere. The ionic conductivity of ScSZ is the highest among all the ZrO_2 -based electrolytes [6], however, it is not considered as the candidate electrolyte for the intermediate temperature SOFCs since its conductivity decreases rapidly with temperature below 800°C [7]. When the bilayer SDC/ScSZ electrolyte was used, ScSZ layer acted mainly as the barrier and its layer thickness can be in the range of a few tens to a few hundreds of nanometers, therefore its relative low conductivity will not contribute significantly to the overall Ohmic loss of the bilayer SDC/ScSZ electrolyte for the SOFCs.

For the fabrication of the bilayer SDC/ScSZ electrolyte on anodic-supported SOFC, wet ceramic processes like screen printing and tape castings have been used. These processes normally require processing temperatures over 1200°C . At such high co-fired temperatures, doped ceria (i.e., SDC) reacts easily with stabilized zirconia (i.e., ScSZ) to form $(\text{Zr}, \text{Ce})\text{O}_2$ -based solid solutions which have a very low electrical conductivity [8]. Ohmic loss due to the low-conductive interfacial layer will result in poor performance of SOFCs. In addition, highly conductive cubic phase ScSZ, stabilized at high temperature, will transfer to a less conductive β -phase when ScSZ cools down below 800°C . To avoid those issues, low temperature techniques (under 800°C) such as pulsed laser deposition (PLD) are to be exploited. PLD is an emerging physical vapor deposition technique that offers better control of the film properties, such as microstructures, chemical composition, density and interfacial properties. Grain size from a few nanometers to a few micrometers can be easily prepared by selecting appropriate process parameters. Recently, an enhancement of ionic conduction was found in the nanocrystalline ScSZ, whose specific grain boundary conductivity is 1-2 orders of magnitude higher than that of the microcrystalline specimen at $700\text{--}850^\circ\text{C}$ [9]. PLD technique usually can operate at low processing temperatures, which can suppress grain growth to achieve nanocrystalline materials.

Lower temperature processes like PLD is particularly suitable for the fabrication of miniaturized SOFCs based on multilayer thin films. This method not only can deposit a dense electrolyte thin layer, but also porous anode and cathode layers, therefore possesses the potential for automation. In addition, this technique holds promise for improved quality control and integrated testing to enhance the reliability, performance and durability of the resulting product while dramatically reduces the costs.

The focus of this research is on the development of the PLD process to fabricate SDC/ScSZ bilayer films with controlled microstructures, density and interfacial properties. Si(100) wafers are used as the substrate in this study since most of the miniaturized SOFCs were built on silicon wafers by using thin film deposition and microfabrication based on lithographic methods. Results on the deposition of the bilayer films on ceramic anode electrodes, such as NiO-YSZ or NiO-SDC modified NiO-YSZ ceramic dishes, will be reported in our future communications.

Experimental

The $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC), $\text{Zr}_{0.9}\text{Sc}_{0.1}\text{O}_2$ (ScSZ) and bilayer SDC/ScSZ films were deposited by ablating either a 90 mm diameter rotating SDC target (SDC, 99.95%, from Prexair), or a ScSZ target (prepared by IFCI-NRC), or both the SDC target and the ScSZ target (one follows by the other), in an advanced deposition chamber (PVD, Inc., PLD-3000) by means of a pulsed KrF excimer laser ($\lambda = 248\text{ nm}$, Lambda Physik, LPX-210i), at a repetition rate of 50 Hz. The laser beam was focused down to a spot size of $\sim 4\text{ mm}^2$ on the target surface. The on-target laser beam fluence was adjusted to about $3 \sim 5\text{ J/cm}^2$. Silicon wafers [(100) orientation, p-type, $\rho = 10\text{--}30\ \Omega\cdot\text{cm}$] of 75 mm diameter was used as the substrates for the deposition. Before introducing a Si

wafer into the deposition chamber, it was cleaned by acetone, and isopropyl alcohol, and then etched in 2.5 % HF acid etch for five minutes to remove the native oxide. After loading the substrate, the system was pumped down to a base pressure below 2×10^{-6} Torr using a turbo-molecular pump. The substrate was then heated, under vacuum, using a programmable non-contact radiative heater. The substrate to be coated was facing the target, with a stand-off distance of 12 cm. To achieve uniform deposition over the entire substrate surface, the laser beam was rastered over the radius of the rotating target. Oxygen gas pressure was adjusted to be 5.32 Pa (40 mTorr) during deposition. The detailed information about the deposition processes has been given in our previous communication [10].

The film structure was examined by using a X-ray diffraction equipment (XRD, Philips, X-Pert MRD) with monochromatized Cu K_{α} in the θ_0 -2 θ thin film configuration, where θ_0 was fixed at 0.5° for single layer films and 3° for bilayer films. The cross-section of the deposited SDC, ScSZ and SDC/ScSZ bilayer films was investigated by Hitachi's FE-SEM S-4500 using the new super ExB filter technology. FE-SEM images were taken at a magnification of 100,000 with a 5 kV beam voltage. The refractive index at the wavelength of 633 nm was determined by spectral reflectance using a fiber-optic-based spectrophotometer (Scientific Computing International, Film Tek 3000). A generalized Lorentz oscillator model, developed by SCI, was used for curve fitting.

Results and Discussions

Figure 1 shows the XRD spectra of SDC films deposited on silicon wafers at 200 °C, 400 °C and 600 °C in 5.32 Pa of oxygen gas. SDC films crystallize to a single-phase fluorite type structure (e.g., face-centered cubic phase, PDF card # 75-0158 [11]) at substrate temperatures as low as 200 °C, while films deposited at lower substrate temperatures were mainly amorphous. The crystallized films deposited at 200 °C and 400 °C show the (111) preferential orientation, while the film deposited at 600 °C, the (200) orientation is dominated. The full-width at half maximum of the XRD peaks decreases with the deposition temperature, which indicates that the average crystallite size of the SDC phase increases with the increase in the deposition temperature according to Scherrer equation [12].

Similar to SDC films, ScSZ films crystallized to the cubic phase (PDF card # 27-0997 [11]) but at higher deposition temperatures (~ 400 °C) as shown in Figure 2. The crystallinity and average crystallite size of the ScSZ films also increases with the increase in the deposition temperature as diffraction

Figure 1: XRD spectra of SDC films deposited on silicon wafer at (a) 200 °C, (b) 400 °C and (c) 600 °C in 5.32 Pa O_2

Figure 2: XRD spectra of ScSZ films deposited on silicon wafer at (a) 200 °C, (b) 400 °C and (c) 600 °C in 5.32 Pa O_2

peaks become sharper and intenser at high temperatures. However, ScSZ does not show any preferential orientation at different deposition temperatures.

The refractive index, n , of SDC and ScSZ films deposited on Si(100) at different deposition temperatures was measured by the spectral reflectance in the 250-850 nm ranges. Figure 3 shows the index of refraction at wavelength $\lambda = 633$ nm as a function of the deposition substrate temperatures. It is interesting to note that the refractive index of SDC films increases with the substrate temperatures. In contrast, for the ScSZ films it decreases with the substrate temperatures. The Lorentz-Lorenz formula relates the refractive index (n), and the density of the film (ρ), in the following equation:

$$(n^2 - 1) / (n^2 + 2) = (4\pi / 3) \alpha_{\text{opt}} \rho / M \quad (1)$$

where α_{opt} is the infinite frequency molar polarizability and M the molar mass. Using the measured values of n for all the films and assuming, to first order, that α_{opt} does not vary with the density we can crudely estimate the relative density of films deposited at various temperatures. The optical data show that the density of SDC films increases with the increase in deposition temperature, but ScSZ films decrease with the increase of deposition temperatures. The density of 200°C and 400°C SDC films are only 63% and 70%, respectively, of the density of the 600°C SDC films. In contrast, the 200°C ScSZ film is more dense than that of the 400 °C and 600°C ScSZ films. The densities of 400 °C and 600°C film are 82% and 77%, respectively, of the density of 200 °C film. The reasons for such a different behaviour of the two materials are not clear. It may be due to the nature of the material or the target preparation processes (i.e., density, grain size of the target etc.). In order to deposit a dense and gas impermeable film, higher temperatures are required for SDC films while low temperatures are suggested for ScSZ films based on the above results.

Figure 4 shows the XRD spectra of SDC/ScSZ bilayer films deposited on silicon wafers at 200 °C, 400 °C and 600 °C in 40 mTorr O_2 process gas. The XRD spectra consist of diffraction peaks originating from both cubic SDC and ScSZ phases. Peak assignment for the SDC

Figure 3: The index of refraction, of SDC and ScSZ films as a function of deposition temperature.

Figure 4: XRD spectra of SDC/ScSZ bilayer films deposited on silicon wafers at (a) 200 °C, (b) 400 °C and (c) 600 °C in 40 mTorr O_2

top layer and the ScSZ underneath layer were shown in the figure. No additional peaks due to (Zr, Ce)O₂-based solid solutions or β -phase ScSZ were found in the diffraction pattern, which indicates that during the deposition process, no chemical reaction occurred at the interface between SDC and ScSZ. This means that PLD technique is an excellent technique for growing both highly conductive cubic ScSZ and SDC phases at very low processing temperatures. Laser deposition process can indeed stabilize the ScSZ cubic phase at low temperatures that prohibits the phase transition from more conductive cubic phase to less conductive β -phase which occurs during cooling step for most of the high temperature wet-ceramic processes. SDC layer shows strong (111) preferential orientation on the top of the cubic phase ScSZ at all temperatures, which is quite different than on Si(100) substrate where at 600 °C, (200) is dominated orientation (Figure 1). The XRD peaks for the bilayer film deposited at 200 °C are quite broad and not well-defined, indicating that the grain size of the low temperature deposited bilayer film is small and its crystallinity is poor. As the deposition temperature increases, the full-width at half maximum of the XRD peaks increases, indicating that the grain size and crystallinity of films increases with the increase in deposition temperatures.

Figure 5 shows the cross-section FE-SEM graphs of ScSZ/SDC bilayer films deposited at a temperature of 200°C, 400°C and 600°C. At 200°C, both ScSZ and SDC layers contain small grains. The SDC layer is very porous, while ScSZ layer is relatively denser. At 400°C, both SDC and ScSZ layers are quite dense. The grain size of SDC layer is significantly larger than that of ScSZ layer in the bilayer film. SDC layer has columnar-like structure with grain diameter of about 60-70 nm oriented perpendicularly to the substrate, while the grain size of ScSZ layer is around 30 nm and the grain orients randomly. At 600°C, both ScSZ and SDC layers contain columnar-like structure oriented perpendicularly to the substrate and are very dense. The grain diameter for SDC layer is about 60-70 nm while for the ScSZ film it is around 30-40 nm. The FE-SEM results are consistent with the previously described XRD and spectra reflectance results.

All the above results have clearly shown that by simply selecting the process parameters of the PLD technique, bilayer SDC/ScSZ films with various microstructures, density and interfacial properties can be deposited. It is obvious that a dense and gas impermeable layer is required for the electrolyte layer in SOFCs, therefore high deposition temperatures (i.e., 600°C) will be selected for producing a denser SDC/ScSZ bilayer. However, when considering the application for the PLD technique for the deposition of anode and/or cathode layers in SOFCs where very porous structures are desired, low deposition temperatures may be used to produce a microstructure similar to that shown in Figure 5 (a). The added flexibility of the PLD process indeed makes it a very promising technique for the fabrication of all solid-state devices based on multilayer thin films, such as the miniaturized SOFCs.

Figure 5: FE-SEM graphs of ScSZ/SDC dual-layer films deposited at a substrate temperature of (a) 200, (b) 400, and (c) 600°C in 40 mTorr of O₂.

Conclusion

PLD technique has been used in this study to deposit thin films of SDC, ScSZ and SDC/ScSZ bilayer on Si(100) substrates. By varying the deposition temperatures in 5.32 Pa oxygen process gas, SDC, ScSZ and SDC/ScSZ films with various crystallite sizes, density and interfacial properties can be grown successfully. XRD results indicate that both SDC and ScSZ films were crystallized to cubic phases (PDF card # 75-0158 for SDC and card # 75-0158 for ScSZ) at relatively low deposition temperatures ($\sim 200^{\circ}\text{C}$ for SDC and $\sim 400^{\circ}\text{C}$ for ScSZ, respectively). The density of the SDC films increases with the increase in the deposition temperature while for ScSZ it decreases with the increase in the deposition temperature. For ScSZ/SDC bilayer films, the PLD technique was able to deposit the cubic phase for both ScSZ and SDC layer. No additional XRD peaks due to (Zr, Ce) O_2 -based solid solutions or β -phase ScSZ were found. Comparing to other wet ceramic processes which require high processing temperatures, PLD method is a very promising low temperature process for the deposition of ScSZ/SDC bilayer films which is a potential electrolyte for the intermediate temperature SOFCs.

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