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Sputter-deposited 20 mol% gadolinia-doped ceria films on 8 mol% yttria-stabilized zirconia tapes for improved electrochemical performance

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ABSTRACT

20 mol% Gd-doped ceria (20GDC) films on poly-crystalline 8 mol% yttria-stabilized zirconia tapes (8YSZt) were rf-sputtered through a lab-made 20GDC oxide target and investigated with regard to the oxygen non-stoichiometry, chemical composition, and morphology of the films. The as-deposited 20GDC dense films with various oxidation states of Ce ions were obtained by the deposition conditions of 200 W. The interpretation of chemical states of cerium (Ce) in the as-deposited 20GDC films showed the mixing tetravalent (Ce^{4+})/trivalent (Ce^{3+}) states of Ce_4O_7 phase. After the annealing process in air at 900 °C for 2 h, results of X-ray diffraction and X-ray photoelectron spectroscopy showed that the fully oxidized 20GDC phase with a cubic fluorite structure was obtained. Columnar grain features of annealed films were examined normal to ⟨200⟩ of 8YSZ substrates by quantitative transmission electron microscopy techniques. The conductivity measurement results provided that the sputtered-20GDC films on 8YSZ tape can be used as solid electrolytes for improved electrochemical performance in a solid oxide fuel cell system at the operation temperatures of 500 – 700 °C.

1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device that can efficiently transfer chemical energy to electric power without associated mechanical energy loss [1–2]. 8 mol% Y_2O_3 stabilized ZrO_2 (8YSZ) is the most mature material as electrolyte in SOFCs, which usually operated at elevated temperature (over 800 °C). Nevertheless, several issues, such as the thermal mismatch between ceramics, electrode sintering, carbon coking on electrodes, interfacial interdiffusion, and cell sealing, should be prevented and conducted carefully [2–3]. In order to reduce the operation temperature from 800 °C to 500 °C while maintaining the higher power generation efficiency, the current researches have mainly focused on the development of a thin-film electrolyte (<10 μm) [4–7] and electrolyte materials with a sufficient conductivity [7–9] to decrease the resistance of the cells.

Nowadays, several doped ceria oxides are acceptable as the electrolyte materials for intermediate temperature (IT) SOFCs [10–12]. In the aspect of conductivity, 20 mol% Gd-doped ceria (20GDC) performed about one order of the magnitude greater than that of 8YSZ, especially at the temperature lower than 600 °C [13]. However, the main problem with GDC is the partial reduction of Ce^{4+} to Ce^{3+} at an elevated temperature in a reducing atmosphere, such as in the anode compartment of a SOFC. Therefore, to fabricate a protective layer, such as 8YSZ layer, between anode and GDC electrolyte layer is a possible way to prevent the mentioned reduction problem [14–15].

In our previous works, we have investigated the material characteristics and electrical behaviors of GDC films on Al_2O_3 substrates prepared by radio frequency (rf) magnetron sputtering from an alloy target and an oxide target [16–18]. The purpose of the present study is to examine the characteristics of GDC films on 8YSZ tapes prepared by rf sputtering for the development of electrolyte layers for IT-SOFCs. Films characterization and electrical behaviors were accomplished by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (FETEM), X-ray photoelectron spectroscopy (XPS) and alternating current (AC) impedance.

2. Experimental details

Before sputtering process, dense and poly-crystalline 8 mol% yttria-stabilized zirconia tapes (8YSZt) in a thickness of around 200 μm manufactured by Holy Stone Enterprise Company Ltd. were cut into 2 cm × 2 cm squares as the substrates. Before deposition, 8YSZt substrates were cleaned in acetone with a 30-min-ultrasonic bath, rinsed in de-ionized water for 15 min, and finally dried at 105 °C. 20GDC thin films were deposited on 8YSZ tapes by rf magnetron sputtering from a lab-made 20GDC oxide target in pure Ar flow. The target is 7.5 cm in diameter and around 600 μm in thickness. The detailed target fabrication and homogeneity examination can be referred from our previous work [18]. The base pressure of the deposition chamber was 8×10^{-4} Pa. During deposition, the total pressure was maintained constant at 1.13 Pa.

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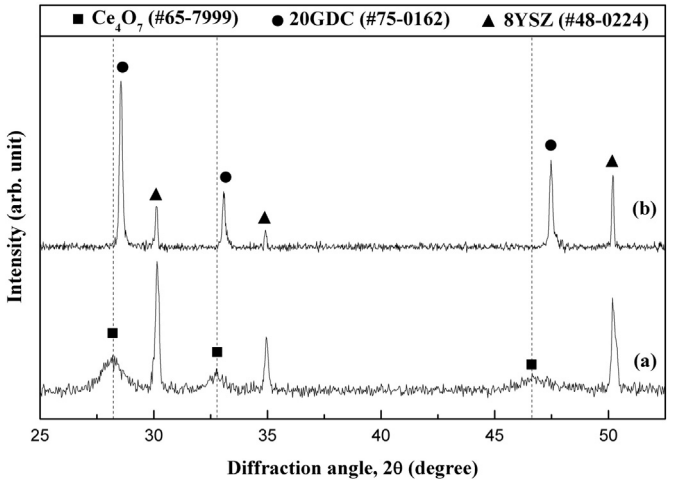

Fig. 1. XRD patterns of (a) as-deposited and (b) 900 °C-annealed 20GDC films on 8YSZt samples.

The rf power applied to the oxide target and the target-to-substrate distance was 200 W and 7.5 cm, respectively. While the flow rate of Ar working gas was maintained at 10 sccm. After the deposition of GDC film process, all the samples were subjected to a heat-treatment at 900 °C for 2 h in atmosphere condition.

Possible crystalline phases of as-prepared and annealed 20GDC films were examined by X-ray diffractometry (XRD, X′ Pert Pro, PANalytical Co., Netherlands) in grazing incidence geometry in 2θ model with a Cu K_α radiation of $\lambda = 1.5405$ Å. Chemical compositions of 20GDC films were investigated by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe). The X-ray source was performed at 10 kV and 20 mA while the main chamber pressure was maintained at 2×10^{-7} Pa. All XPS data presented herein were acquired using a monochromatized Al Kα line 1486.6 eV, and were recorded at constant pass energy of 50 eV with giving a resolution of 0.5 eV. The photoelectrons were collected at an electron take-off angle of 60°. Peak positions were then calibrated with respect to the C1s peak at 284.6 eV from the adventitious hydrocarbon. Cross-sectional and plane views of prepared films were observed by a field emission scanning electron microscope (FESEM, LEO Instrument, Cambridge, UK) and operating at 5 kV. Prior to SEM analyses, conductive Pt layer deposited by sputter coater was made for the prevention of surface charge on the samples. Film thickness was directly measured from the cross-sectional SEM image. Interfacial microstructure was investigated by quantitative FETEM (JEOL 2000FX, acceleration voltage of 200 kV). The composition of annealed

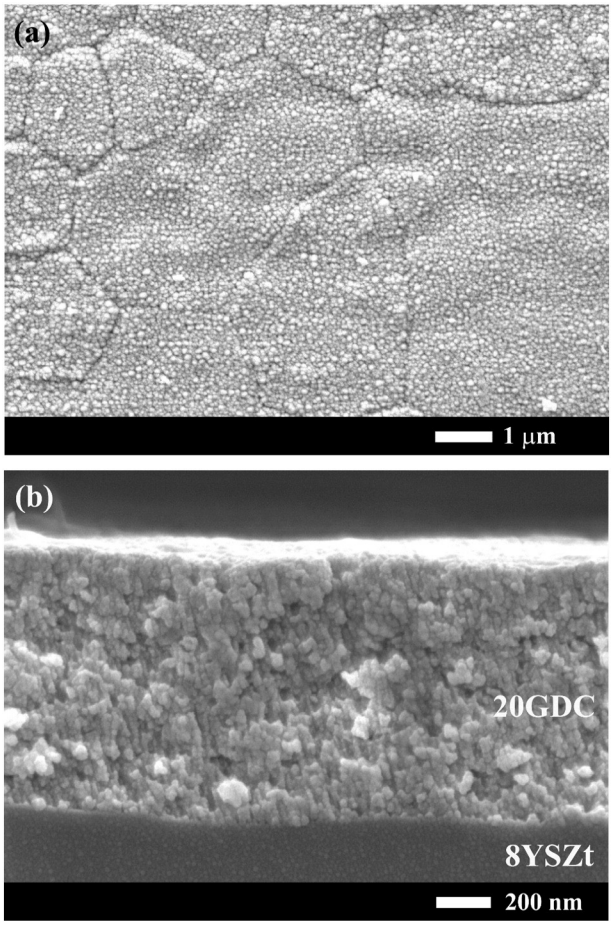

Fig. 3. SEM images of 900 °C-annealed 20GDC/8YSZt samples (a) plane view and (b) cross section.

20GDC films was evaluated by energy-dispersive X-ray spectroscopy (EDS) analyses using a statistical student-distribution method, which considers the distribution of Ce and Gd contents in each sample as a normal distribution [18].

Impedance spectroscopy for total conductivities of samples was measured by Sloarton 1260 AC impedance analyzer at temperatures ranging from 500 °C to 700 °C. Both sides of the samples were screen-printed using Heraeus CL11-5100 Pt ink (Resistance: 28.03 mΩ/sq.) and was annealed at 900 °C for 1 h to burn out the organic solvents.

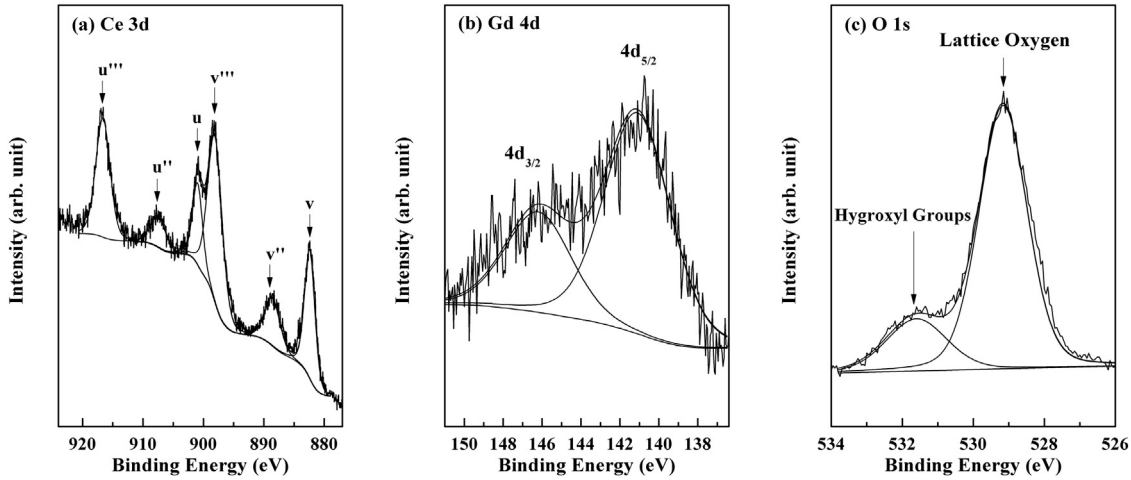

Fig. 2. XPS spectra of (a) Ce 3d, (b) Gd 4d, and (c) O 1s core levels for the 900 °C-annealed 20GDC films on 8YSZt samples.

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