Journal of Power Sources 186 (2009) 115–122

Contents lists available at ScienceDirect

Journal of Power Sources

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

Ultra-thin nanocrystalline lanthanum strontium cobalt ferrite ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$) films synthesis by RF-sputtering and temperature-dependent conductivity studies

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ARTICLE INFO

Article history:
Received 18 August 2008
Received in revised form
22 September 2008
Accepted 23 September 2008
Available online 4 October 2008

Keywords:
Lanthanum strontium cobalt ferrite
Yttria-stabilized zirconia
Solid oxide fuel cell
Cathode
Ultra-thin film
Nanocrystalline

ABSTRACT

Nanocrystalline lanthanum strontium cobalt ferrite (LSCF) ultra-thin films with high in-plane electrical conductivity have been deposited by RF sputtering from composite targets. The films, with nominal thickness of 54 nm, are crystalline when annealed or deposited at temperatures above 450 °C. Effects of annealing temperature, annealing time, and substrate temperature on crystallization, microstructure, and room temperature lateral electrical conductivity have been systematically studied. No interfacial reaction products between the LSCF and single crystalline yttria-stabilized zirconia (YSZ) were observed from X-ray diffraction studies upon annealing until 750 °C. In-plane electrical conductivity as high as 580 S cm^{-1} at 650 °C has been observed for LSCF thin films deposited on single crystalline YSZ substrates and sputtered nanocrystalline YSZ thin films; while activation energy for conductivity were determined to be 0.15 eV and 0.10 eV for the former and latter films, respectively, in 650–400 °C range. The high in-plane electrical conductivity for the nanocrystalline LSCF ultra-thin films is likely attributed to their low level of porosity. Micro-solid oxide fuels cells using 15 nm thick LSCF films as cathodes and sub-100 nm yttria-doped zirconia thin film electrolytes have been fabricated successfully and demonstrated to achieve peak power density of 60 mW cm^{-2} at 500 °C. Our results demonstrate that RF sputtering provides a low-temperature synthesis route for realizing ultra-thin nanocrystalline LSCF films as cathodes for intermediate- or low-temperature solid oxide fuel cells.

1. Introduction

With increasing demand for energy coupled with finite reserve of fossil fuels and coals, it is imperative to develop sustainable, alternative energy sources. Hydrogen (or hydrocarbon)-fueled solid oxide fuel cells (SOFCs), with energy efficiency higher than 60% and clean emissions, represents a promising energy alternative [1]. They can be used in stationary power plants to replace coals and in automobiles to replace gasoline [2]. By taking advantage of well-established microfabrication techniques, low-cost micro-SOFCs (μSOFCs) for portable electronics have also stimulated considerable attention [3–6].

The hurdles that have yet to overcome for current SOFCs development are their high temperature operation (>900 °C) and, consequently, high cost and long-term durability issues [7]. To lower operation temperature, cathodes need special attention because they are responsible for majority of voltage loss in SOFCs [8,9]. Three approaches have usually been pursued to improve cathode performance at low temperatures: (i) using new cathode materials to replace conventional lanthanum strontium manganite (LSM) – which does not provide sufficient ionic conductivity below 800 °C [10–12]; (ii) using thinner cathode layer to reduce Ohmic resistance [11,12]; and (iii) using nanocrystalline microstructures to enhance oxygen-ion diffusion through the cathode via grain boundaries [13].

Lanthanum strontium cobalt ferrite (LSCF) has long been considered as one of the most promising cathode materials [14] for low-temperature operation due to its high mixed ionic and electronic conductivities and high electrocatalytic activity of oxygen reduction reaction that occurs on entire cathode surfaces rather than only at three phase boundaries. As a result, thin dense films could provide comparable or higher cathode performance than conventional thick porous films [15,16]. However, there are several technological and fundamental challenges for realizing LSCF thin film cathodes for SOFCs. Firstly, most of synthesis methods for LSCF thin films involve high temperature treatment (>800 °C) [13,17,18] that may lead to resistive interfacial reaction products, such as $La_2Zr_2O_7$ and $SrZrO_3$, with yttria-stabilized zirconia (YSZ) – one

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doi:10.1016/j.jpowsour.2008.09.094

of the most widely used electrolytes in SOFCs [19]. For example, it has been reported that in $La_{0.9}Sr_{0.1}MnO_3$-YSZ systems, thickness of $La_2Zr_2O_7$ reaction layer could be as high as 25 nm when treated only at 700 °C [19]. Therefore, the formation of resistive reaction layers is of particular concern for ultra-thin LSCF films when their thickness may become comparable to that of the reaction layer. Although interfacial reactions between LSCF and YSZ can be avoided by using gadolinia-doped ceria (GDC) as an interlayer [20], GDC suffers from stability in highly reducing environment [19].

Secondly, since most of the LSCF thin films that have been studied are thicker than 1 μm, it is still not well understood how LSCF thin films behave at nanoscale [4,13] and whether they could be as conductive as their bulk counterparts [14,21]. Gauckler and co-workers have recently reported on synthesis of thin-film LSCF and their transport properties [4,6,13]. Although enhanced electrochemical performance has been reported for the $La_{0.52}Sr_{0.48}Co_{0.18}Fe_{0.82}O_{3-\delta}$ ultra-thin films deposited by pulsed laser deposition [13], electrical conductivity of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ films, deposited by spray pyrolysis, that are more than one order of magnitude lower than their bulk counterpart casts concerns of possible degradation of material performance as cathodes due to nanosize effect and nanocrystallinity [4]. Finally, if LSCF were to be used for μSOFCs, a deposition technique that is compatible with Si-based microfabrication and appropriate post-deposition treatments of as-deposited thin films need to be developed [3,22].

In this report, we presented a systematic, detailed study on RF-sputtered $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ultra-thin films. To the best of authors' knowledge, although sputtering has been widely used to deposit multi-component oxides, no prior reports of sputtering of LSCF thin films exist or any data on their high temperature conductivity have been reported so far. Further, there has been no prior study on ultra-thin $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3(\delta}$ films to our knowledge. Our choice of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3(\delta}$ composition for this study is partly due to their higher electronic and ionic conductivities, lower activation energy of electronic and ionic conduction [14,21,23,24], and, significantly lower activation energy for oxygen surface exchange [15] – all as a result of higher cobalt content. A main factor that prefers $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3(\delta}$ over $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3(\delta}$ – namely, its thermal expansion mismatch with YSZ, as well as with silicon (Si) – can be partially mitigated by low heat treatment temperature and controlling their thickness and will be discussed in a later section.

Some key aspects of this paper are to demonstrate that $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3(\delta}$ ultra-thin films exhibiting (i) no interfacial reaction products of $La_2Zr_2O_7$ ad $SrZrO_3$ between LSCF and YSZ, (ii) nanocrystalline microstructures, and (iii) high in-plane electrical conductivities can be realized by RF sputtering from a $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3(\delta}$ composite target. Furthermore, we will demonstrate functional μSOFCs that utilize ultra-thin LSCF films as cathodes. Our results indicate that the LSCF ultra-thin films could be well-suited for intermediate- or low-temperature SOFC cathodes and RF sputtering provides a relatively low-temperature, microfabrication-compatible route for LSCF thin films synthesis [21].

2. Experimental procedure

RF sputtering was carried out using a custom $La_{0.6}Sr_{0.4}C_{0.8}F_{0.2}O_3$ target (from AJA International) at a gun power of 60 W. Base and Ar plasma pressure of sputtering chamber were 3×10^{-8} Torr and 5×10^{-3} Torr, respectively. Two different substrates with typical dimension of 10 mm × 10 mm × 0.5 mm were used, including (i) yttria-stabilized zirconia (YSZ) (1 0 0) substrates, and (ii) 75 nm YSZ films – sputtered from a 8% yttria-doped zirconia (from AJA International) at a gun power of 100 W and a pressure of 5×10^{-3} Torr – on 200 nm Si_3N_4 coated Si (1 0 0) substrates. Annealing was performed in ambient in a Thermolyne 21100 tube furnace. Annealing time was 2 h unless otherwise specified. Grazing incidence X-ray diffraction (XRD) and X-ray reflectivity (XRR) measurements were performed with a Scintag 2000 diffractometer using Cu Kα radiation. Microstructures were investigated by Veeco NanoMan VS atomic force microscopy (AFM) in a class 100 cleanroom and Carl Zeiss Ultra 55 field emission scanning electron microscopy (SEM). Lateral electrical conductivity at room temperature was measured by a Creative Design Engineering ResMap 168 four-point probe resistivity mapping system. High temperature lateral electrical conductivity was obtained by performing van der Pauw measurement in a home-built high temperature furnace system with an alumina sample holder and electrical assembly. Silver paste was used as the electrode contacts on four corners of the thin film samples. Four platinum leads were attached to the electrodes for independent current and voltage measurements. Further details of our high temperature probe station can be found elsewhere [25].

3. Results and discussion

To investigate crystallization behavior and to elucidate the correlation between microstructure and conductivity, sputtering was initially performed on single crystalline YSZ substrates without substrate heating. The films (referred to as LSCF/sc-YSZ thin films) were then annealed from 350 °C at every 50 °C increment until 750 °C to investigate the crystallization process. XRD was taken after every annealing step. Fig. 1 shows evolution of the diffraction patterns taken from the as-deposited amorphous LSCF films, with thickness of 54 nm, on YSZ single crystalline substrates upon sequential annealing. As seen in Fig. 1, the films were amorphous when annealed at 400 °C. After annealing at 450 °C, a peak appears at ~33.1° (2-theta). Peaks at ~23.1°, ~40.7° and ~47.2° also appear

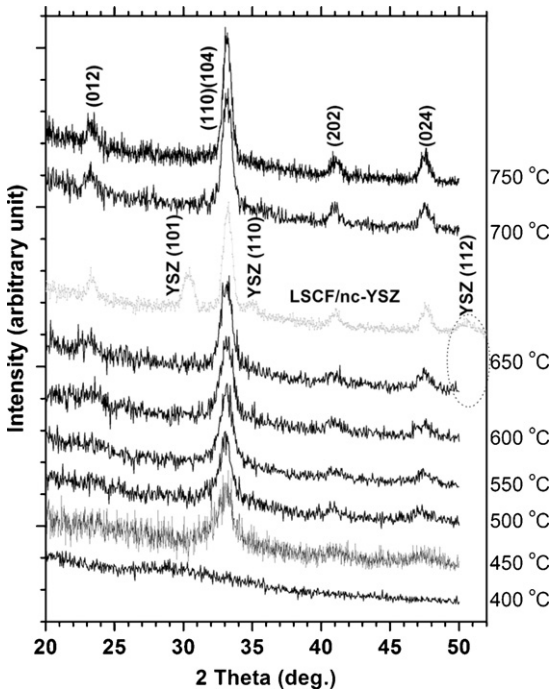

Fig. 1. XRD patterns (black lines) of amorphous LSCF/sc-YSZ thin films annealed at 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, and 750 °C. Light gray lines are XRD patterns taken from LSCF/nc-YSZ-film annealed at 650 °C.