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Lanthanum silicate thin films for SOFC electrolytes synthesized by magnetron sputtering and subsequent annealing

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ABSTRACT

Thin films of La and Si with Si/(La + Si) atomic ratios ranging from 0.36 to 0.44 were produced by magnetron sputtering in pure Ar. For all compositions, the apatite-like $La_{9.33}Si_6O_{26}$ phase was formed during annealing in air at 900 °C. A preferential orientation was developed during annealing of the films with higher silicon content while formation of oxide impurities was detected for the films with less silicon. Silicon segregation to the thin film/substrate interface was observed after annealing for thin films with higher Si/(La + Si) atomic ratios. The higher ionic conductivity values were obtained with the films with lower silicon content (2.81×10^{-3} Scm^{-1} at 800 °C for the film with Si/(La + Si) atomic ratio of 0.36). This film presented the lower activation energy E_a (0.94 eV).

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are receiving ever-increasing attention because they are among the most efficient fuel cell electricity generators besides they are environmentally friendly. At present, their most common electrolyte is yttria stabilized zirconia (YSZ) which exhibits high oxide ion conductivity at temperatures in the range 850°–1000 °C [1]. The commercial implementation of SOFCs has been hindered by these high operating temperatures which require the use of expensive materials to avoid deterioration of the cell components. Current developments concentrate mainly on increasing the durability and lowering the cost of the final product. The goal is to develop intermediate temperature Solid Oxide Fuel Cells, IT-SOFCs, that may operate at lower temperatures (500°–800 °C) without incurring performance losses [2–4]. Several solutions were proposed to achieve that purpose such as reducing the thickness of the electrolyte layer and/or developing new electrolyte materials with higher oxygen ion conductivities at relatively low temperatures [5–7]. Consequently, research into ceramic solids displaying high oxide ion conductivity at intermediate temperatures for application as solid electrolytes of IT-SOFCs has been gathering momentum over the past few decades, with a range of materials studied [2–4,8–11]. Recently, apatite-type lanthanum silicates have been considered promising candidates due their high oxide ion conductivities and low activation energies at moderate temperatures [3,7,12,13]. These apatites have compatible thermal expansion coefficients with current electrode materials and they can be obtained from rather cheap raw materials [10]. Their more interesting characteristic which provides new opportunities to optimize their properties as fuel cell electrolyte is related with the wide range of substitution possibilities on both the La and Si sites due to the flexibility of the apatite structure in accommodating a range of ion sizes [7,11,14–16]. It has been established that the high ionic conductivities are caused by oxygen interstitial migration along a sinusoidal-like pathway leading to interstitial-type conduction mechanisms [17,18]. Thus, to achieve high levels of anionic transport, non-stoichiometry in terms of oxygen excess and/or cation vacancies is required, with the latter causing Frenkel-type defects formation [10,11,14,19].

Traditionally, these materials are produced by solid state methods involving high processing temperatures (≥1400 °C) [20–23]. An alternative to prepare this kind of materials is the use of magnetron sputtering owing to the versatility of this technology as well as the ability to control composition and morphology [24,25]. Magnetron sputtering is a powerful processing technique for the synthesis of homogeneous thin layers with improved mechanical and physical properties. Moreover, the low thickness of the electrolyte produced by sputtering will compensate resistive losses associated with the electrolyte ohmic resistance at lower working temperatures of IT-SOFCs. Sputtering has already been applied to produce thin electrolyte films of YSZ [26–29], ceria [30,31], lanthanum gallate [31,32], bismuth oxide [33] and also apatite-type lanthanum silicates [34–37].

In this paper, we present results of a study concerning the synthesis and characterization of apatite-type lanthanum silicate thin films. Two metallic targets of La-20 at.%Si and pure Si were sputtered by DC magnetron sputtering in order to obtain thin films with a chemical composition centered on the stoichiometric composition of the

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$La_{9.33}Si_6O_{26}$ compound (Si/(La + Si) atomic ratio = 0.39). The thin films were deposited in pure argon atmosphere and they were subsequently submitted to a post-annealing treatment at 900 °C for 1 h for promoting the apatite formation by oxidation of the surface. The thin films were structural and morphological characterized in the as-deposited state and after annealing. The electrical properties of the heat-treated layers were determined.

2. Experimental procedures

La–Si thin films were deposited by magnetron sputtering on glass slides, AISI M2 steel substrates and Al_2O_3 pellets by co-sputtering of a Si (200 mm × 100 mm × 10 mm) and a La–Si composite target with 20 at.% Si (200 mm × 100 mm × 10 cm) in pure argon (99.99%). The experimental device was a 55-liter sputtering chamber pumped down by a diffusion pump allowing to reach a base vacuum of about 10^{-4} Pa. The targets were positioned facing each other on opposite sides of the substrate holder axis, resulting in a target to substrate distance of 140 mm. Power regulation was performed in all depositions using DC Advanced Energy Pinnacle + supplies. The La–Si and Si target powers were varied from 390 to 480 W and 650 to 780 W, respectively, keeping the total power at about 1150 W. All experiments were carried out for 1 h at a deposition pressure of 0.32 Pa of Ar (60 sccm) with rotating substrates (5 rpm). Neither bias nor intentional heating of the films was used during deposition. Thermal treatments of the films were carried out at 900 °C in air using a tubular furnace. The films were heated at 20 °C/min and maintained at annealing temperature for 1 h.

The thickness of the films was measured using a Perthometer PRK profilometer with a Perthometer S4P electronic module allowing an accuracy of about 50 nm. The elemental composition was determined by electron probe microanalysis (EPMA). The structure was analyzed by X-ray diffraction (XRD) using a Phillips diffractometer in Bragg-Brentano configuration with Co(Kα) radiation and by micro-Raman spectroscopy using a Renishaw RA100 Raman analyser equipped with an argon laser as excitation source (514.5 nm wavelength). The laser power applied was of approximately 10 mW and the measurement time varied between 30 and 90 s. The morphology of the cross-section and surface topography of the La–Si thin films were examined with a JEOL scanning electron microscope (SEM) equipped with an EDAX energy dispersive spectrometer (EDS). The observed samples were coated with a thin gold layer to improve electrical conduction. The electrical properties of the films were measured by AC impedance spectroscopy (HP4284A precision LCR meter, 20 Hz–1 MHz) using a four-terminal pair configuration with Pt electrodes painted on top of the films deposited on the Al_2O_3 pellets to act as electrical contact. The distance between the Pt electrodes was 5 mm. Measurements were performed in the temperature range 450–1000 °C with a step of 50 °C.

3. Results and discussion

The Si/(Si + La) atomic ratio in the as-deposited La–Si films was varied by changing the deposition power applied to the targets while keeping the same total power. The chemical composition and thickness of the films are compiled in Table 1 as a function of the power applied to the targets. The Si/(Si + La) atomic ratio in the stoichiometric apatite-like lanthanum silicate phase ($La_{9.33}Si_6O_{26}$) is close to 0.39. In order to study the effect of this parameter on the ionic conductivity, thin films with Si/(Si + La) atomic ratio centered on this value were deposited in this work. As a result, two films exhibit excess Si (Si/(Si + La) = 0.43 and 0.44), two films exhibit excess La (Si/(Si + La) = 0.36 and 0.37) and one as the same Si/(Si + La) atomic ratio as $La_{9.33}Si_6O_{26}$. The coating thickness measured by profilometry varies between 4.0 to 4.5 μm corresponding to deposition rates between 0.067 and 0.075 μm/min, respectively. Oxygen contamination in the range 2 to 9 at.% was determined by EPMA.

Table 1
Chemical composition and thickness of the as-sputtered thin films as a function of the power applied to the targets.

Si(Si + La) power ratio	Chemical composition [at.%]			Si/(Si + La) atomic ratio	Thickness [mm]
	La	Si	O		
0.57	58.4	32.8	8.8	0.36	4.5
0.60	59.1	35.2	5.7	0.37	4.4
0.62	59.9	38.1	2.0	0.39	4.5
0.65	54.7	40.7	4.6	0.43	4.0
0.67	54.5	42.0	3.5	0.44	4.2

Two XRD patterns representative of the as-deposited films are shown in Fig. 1 as well as tentative deconvolutions of the diffraction peaks using Pseudo-Voight function. Both patterns can be fitted with three large peaks in the 2θ range between 20 and 50°. Using the Scherrer equation a grain size of 1.5 nm was found for both films, showing that the as-deposited films are quasi-amorphous. The peaks centered near 2θ = 29.2 and 36.5° were already reported by Oliveira et al. [37] for as-sputtered La–Si thin films with Si/(Si + La) ratios of 49.0, 45.6 and 43.2%. The diffraction peak centered near 2θ = 31.8° was also reported by Oliveira et al. [37] but only after annealing of La–Si films with a Si/(La + Si) atomic ratio of 43.2% at 873 K for 1 h. This peak was attributed by the authors to the formation of hexagonal La_2O_3 during the annealing process. In our case, the La_2O_3 peak is already present in the as-deposited films and should be due to the formation of a surface oxide layer. Using the Scherrer formula a grain size of 3.5 to 4 nm was found for the oxide phase.

Fig. 2 a), b) and c) shows cross-section SEM micrographs of the as-deposited films with Si/(La + Si) atomic ratio of 0.37, 0.39 and 0.43. The films exhibit a columnar morphology, rather dense and compact, with a good adhesion to the Al_2O_3 substrate. No damaged interfaces are observed between the films and the substrates. These micrographs confirm the thickness values compiled in Table 1. The cross-section SEM images of the annealed thin films with the same atomic ratio are displayed in Fig. 2 d), e) and f). The micrographs reveal crack-free and good adhesion coatings. Moreover, a more heterogeneous but still rather dense and compact morphology is observed. According to the literature [38] the subsequent oxidation at high

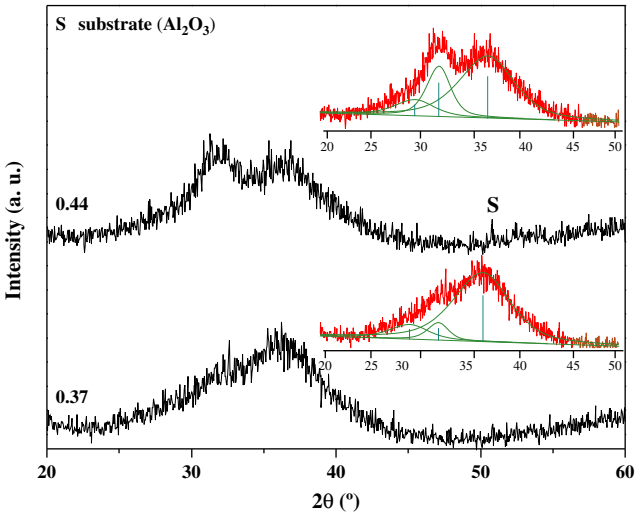

Fig. 1. XRD patterns of the as-deposited La–Si films with Si/(La + Si) atomic ratios of 0.37 and 0.44.