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Structure and ionic conductivity of reactively sputtered apatite-type lanthanum silicate thin films

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ABSTRACT

La–Si–O thin films with Si/(La + Si) atomic ratios ranging from 0.36 to 0.43 were produced by magnetron sputtering in a reactive Ar/O discharge gas. The as-deposited films have large X-ray diffraction peak characteristic of quasi-amorphous materials and oxygen contents from 29 to 35 at.%. The Apatite-type lanthanum silicate phase was formed in all the as-deposited films upon annealing at 900 °C for 1 h. The lanthanum silicate films obtained by annealing the as-deposited films with lower Si/(La + Si) atomic ratios have a preferential orientation with the c-axis perpendicular to the substrate while low intensity diffraction peaks ascribed to $La_2Si_2O_7$ phase were detected in the films deposited with higher Si content. The preferentially oriented films have higher activation energy and lower ionic conductivity as the ionic conductivity measurements were performed in the direction perpendicular to the c-axis. The highest ionic conductivity was obtained for the film deposited with a Si/(La + Si) atomic ratio of 0.42, with a value of 1.2×10^{-2} S·cm^{-1} at 750 °C.

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1. Introduction

Apatite-type lanthanum silicate (LSO) materials have been considered potential candidates as electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFCs) [1–4]. These materials are pure anionic conductors with a high oxygen transference number across a wide range of oxygen partial pressures [5]. They also have higher oxide ion conductivity and lower activation energies at moderate temperatures than YSZ (yttrium stabilized zirconia), the most common electrolyte for SOFCs [6–8]. Contrarily to YSZ, which has a cubic symmetry and oxygen vacancy based ionic conduction, apatite-type oxide ion conductors have hexagonal structure and their high ionic conductivity is due to oxygen interstitial migration along a sinusoidal-like pathway along the c-axis direction [9–12]. As a result the LSO material conductivity is highly anisotropic [13–15] and conductivity values along the c-axis are more than one order of magnitude higher than what have been reported in the perpendicular direction. These apatites have compatible thermal expansion coefficients with current electrode materials and they can be obtained from rather cheap raw materials [16]. One of their more interesting characteristic, which provides new opportunities to optimize their properties as fuel cell electrolyte, is 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 [2,17–20].

Apatite-type lanthanum silicate materials are mostly produced by solid state methods involving high processing temperatures (>1400 °C) [21–25]. Several authors have attempted to enhance the sintering process and/or to decrease the sintering temperature [26–28]. Alternatively, these materials can be prepared as coatings [29–37] taking advantage of the low thickness of the electrolyte to compensate resistive losses at the lower working temperatures of IT-SOFCs. Magnetron sputtering is an attractive method for this purpose as it is a powerful processing technique for the synthesis of homogeneous thin layers with improved mechanical and physical properties. Thin films deposited from lanthanum-based and silicon targets by magnetron sputtering are amorphous and subsequent annealing is necessary to obtain the LSO material [32–37]. In a previous work on the production of apatite-like lanthanum silicate films by sputtering in Ar discharge gas and subsequent annealing, segregation of Si during the oxidation/crystallization of the as-deposited films was observed [37]. Segregation resulted in the pile-up of Si at preferential locations of the film substrate interface and formation of elevations resulting from film bending and even cracking, in order to accommodate the segregated material. This phenomenon was observed irrespectively of the as-sputtered film composition although with much higher frequency for the films deposited with higher Si content. Concerning the proposed application, formation of nonconductive phases at the film substrate interface will hinder the ionic conductivity of the lanthanum silicate electrolyte and downgrade its in-service performance.

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The main objectives of the present work were to study the influence of the Si/(La + Si) atomic ratio on the conductivity of the films and to prevent Si segregation during the oxidation/crystallization process by incorporating oxygen in the films during deposition. The presence of oxygen in the films prior to annealing influences the kinetics of the oxidation/crystallization process since much less oxygen has to be incorporated in the films during the annealing process for the formation of the apatite-type phase.

2. Experimental

2.1. Film deposition and annealing

La–Si–O thin films were deposited by reactive magnetron sputtering on Al_2O_3 pellets by co-sputtering of a Si (200 mm × 100 mm × 10 cm) and a La–Si composite target with 20 wt.% Si (200 mm × 100 mm × 10 cm) in an Ar (99.99%) + O_2 (99.99%) discharge gas mixture. The experimental device was a 55-liter sputtering chamber pumped down by a diffusion pump allowing reaching a base vacuum of about 10^{-4} Pa. The targets were positioned facing each other at 140 mm from the substrate holder axis. The Si target power was varied from 350 to 500 W using a Pulsed Power supply (Advanced Energy Pinacle+) with a frequency of 150 KHz and a duty time of 60%. The La–Si composite target power was varied between 450 and 650 W using a DC Advanced Energy Pinacle+ power supply. In all the depositions, the total power was kept constant to about 1150 W. The rotation speed of the substrates was 17 rpm and neither bias nor intentional heating of the films were applied. The O_2 and Ar fluxes were 6 and 34 sccm, respectively, resulting in a deposition pressure of 0.2 Pa. Annealing of the films was performed at ambient air in an electric tubular furnace at 900 °C for 1 h. A heating rate of 20 °C/min was applied.

2.2. Film characterization

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 analyzer equipped with an argon laser as excitation source (514.5 nm wavelength). The lattice parameters of the lanthanum silicate phase were calculated from the 2θ position of the XRD peaks by a least square method taking into account only well resolved peaks. The laser power applied was of 10 mW and the measurement time varied from 30 to 90 s. The morphology of the cross-section and surface topography of the La–Si–O thin films were examined with a JEOL scanning electron microscope (SEM) equipped with an EDAX energy dispersive spectrometer (EDS). 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

3.1. As-deposited films

The chemical composition and thickness of the as-deposited La–Si–O 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 ($La_{9.33}Si_6O_2$) is close to 0.39. In order to study the effect of this parameter on the ionic conductivity, two films with excess La (LSO1 and LSO2), two with excess Si (LSO4 and LSO5) and one with a Si/(Si + La) atomic ratio close to stoichiometry (LSO3) were deposited. Although the same gas mixture was used in all deposition (34 sccm of Ar + 6 sccm of O_2), slight differences in the oxygen content in the films (29.1 to 34.9 at.%) were measured.

The oxygen content values correspond to about half of the oxygen content required for formation of the stoichiometric apatite-like lanthanum silicate phase. However, the incorporation of higher amounts of oxygen in the films using higher O_2 flows was unsuccessful due to severe instabilities in the plasma. Thickness of as-deposited films varied between 3.0 and 3.8 μm, corresponding to deposition rates between 40 and 48 nm/min, respectively. These deposition rates are higher than the ones reported by Briois et al. [32] for the same kind of coatings (2.5 nm/min) using similar deposition parameters (gas composition, pressure, power density and substrate–target distance). Although several other deposition characteristics can influence the deposition rate, the higher deposition rates obtained in the present work might be the result of using a composite La–Si target instead of a La target, more prone to oxygen poisoning with consequent decrease of the sputtering yield. However and as-expected, the deposition rates obtained in this work are significantly lower than those obtained by sputtering in pure Ar discharge gas (67 to 75 nm [37]).

Two XRD patterns representative of the as-deposited films is shown in Fig. 1. Besides the Al_2O_3 substrate diffraction peaks, a single large peak centered close to $2\theta = 32.5°$ is observed. Using the Scherrer equation, a grain size of ≈1.5 nm was calculated for all the films, showing that they are quasi-amorphous. A similar range order was reported by Briois et al. [32] for La–Si–O films deposited by sputtering and by Vieira et al. [37] in a work on the deposition of La–Si films by magnetron sputtering in Ar discharge gas. In the later study the La_2O_3 phase was also detected in the as-deposited films. In the present work incorporation of oxygen in the films during the deposition process prevented the formation of La_2O_3, being homogeneously distributed across the whole films.

Fig. 2 shows cross-section SEM micrographs of the as-deposited films with Si/(La + Si) atomic ratio of 0.36 (sample LSO1) and 0.42 (sample LSO4). The films exhibit a rather dense and compact morphology, with a good adhesion to the Al_2O_3 substrate. No damaged interfaces

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

Sample	Si–La target power (W)	Si target power (W)	Chemical comp. (at.%)			Si/(Si + La) atomic ratio	Thickness [μm]
			La	Si	O		
LSO1	650	350	45.1	25.8	29.1	0.36	3.3
LSO2	600	350	43.0	24.7	32.3	0.37	3.8
LSO3	475	525	39.3	25.7	35.0	0.40	3.2
LSO4	450	550	37.4	27.7	34.9	0.42	3.0
LSO5	500	500	37.9	28.3	33.8	0.43	3.0

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