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Morphological and structural characterization of oxidized La-Si sputtered thin films

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High temperatures in Solid Oxide Fuel Cells (SOFCs) place stringent requirements on the cell components materials which result in high material costs for interconnects and insulation and cause the degradation of the system. The development of Intermediate Temperature SOFCs (IT-SOFCs) will require electrolyte materials with higher ionic conductivity at moderate temperatures than the conventional yttria-stabilised zirconia (YSZ) [1]. Recently, lanthanum silicates with an apatite-like structure ($La_{9,33}Si_6O_{26}$) have attracted considerable interest as potential materials for low cost electrolyte [2]. Some of these materials show conductivities at 875 K comparable to, or better than, YSZ; their high level of oxide ion mobility was related to the presence of oxygen channels along the c axis which facilitate the diffusion of the anionic species (O^{2-} for SOFCs applications) [3]. Another way to fulfil IT-SOFCs requirements is to decrease the electrolyte thickness to the micrometer range and, therefore, the ohmic drop at the electrolyte. Magnetron sputtering has already been used to synthesize thin film electrolytes for SOFCs owing to its versatility for depositing complex materials as well as its ability to control their composition and morphology [4]. The manufacturing of thin film lanthanum silicate electrolytes by magnetron sputtering, with thicknesses in the micrometer range, can be achieved through the previous deposition of La-Si films and subsequent thermal oxidation [5]. The present study focuses on the characterization of the morphological and structural changes upon oxidation of La-Si films deposited by magnetron sputtering.

The La-Si films were deposited by magnetron sputtering from pure La and Si targets (200 mm of diameter). The La target power was maintained constant at 1000 W in all depositions whereas the Si target power was varied from 400 to 750 W. All films were deposited on Al_2O_3 pellets. The substrate bias voltage was kept constant at -50 V. An Ar (99.99%) flow rate of 20 sccm, which resulted in a total pressure of about 0.4 Pa, was used in all experiments. The La-Si films were oxidised at 1175 K for 1 h in industrial air (99.995% purity) flowing through a dehumidificator. The chemical composition of the coatings was determined by electron probe microanalysis (EPMA). The cross section, surface topography and morphological features of the La-Si films were examined on a scanning electron microscope (SEM) equipped with an EDAX energy dispersive spectrometer (EDS). The structure of the coatings was studied by X-ray diffraction (XRD) in Bragg-Brentano configuration with Co(Kα) radiation and by Micro-Raman spectroscopy.

Figure 1 shows the surface and cross-section SEM micrographs of a La-Si film deposited with 49 at. % Si after thermal oxidation in industrial air for one hour at 1175 K. Besides the substrate induced features, the film surface is covered by fine grains with angular shapes (compare both halves in figure 1a) which indicate that a crystalline phase was formed as a result of the oxidation process transforming the smooth surface of the XRD amorphous as-deposited samples. As can be observed in the SEM cross sectional micrograph (see arrows on figure 1b), the thickness of the film is not uniform, higher thickness zones being observed periodically along the film cross section. As

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can be concluded from the associated backscattered electron SEM micrograph (figure 1c), the thickness increase is due to the formation of a light phase (darker regions) imbibed half way between the surface and the film/substrate interface. In some cases, the formation of this light phase gives rise to the spallation of the upper part of the film as can be observed in figure 1d. The formation of a crystalline phase upon oxidation at 1175 K for 1 h is also observed for the film with 43.2 at. % Si, as confirmed by the presence of similar fine angular grains on the surface of the film (figure 2a). Once again segregation of a light phase occur leading to a non uniform thickness (see figures 2b and 2c). However, in this case the segregated material piles up preferentially at the film/substrate interface and provokes the bending of the film and its subsequent cracking (figure 2d).

Figure 3 shows the micro-Raman spectra of the films after oxidation. The two most intense peaks of the $La_{9.33}Si_6O_{26}$ phase, associated to the vibration of the MO_4 structures, are clearly detected in both films. Besides the oxide phase, formation of silicon upon oxidation is also detected in both films, as can be concluded from the presence of the characteristic Si peaks (2TA, LO and 2TO). It is then possible to identify the light element phase detected by SEM in BSE mode as silicon and to conclude that the film after oxidation is constituted by the lanthanum silicate phase. Figure 4 shows the XRD patterns of the films after oxidation. Besides the substrate features, due to the flaking of some parts of the film, all the peaks detected for 49 at. % Si can be indexed as the lanthanum silicate apatite-like phase (figure 4a). The formation of $La_{9.33}Si_6O_{26}$ upon oxidation is also detected for the film with lower silicon content (figure 4b). However, in this case, lanthanum oxide (La_2O_3) was also formed along the oxidation process. The segregation of silicon during the oxidation process provokes a decrease of the Si content in the films. For the sample deposited with 49 at. % Si, the silicon remaining in the film is enough to react with all the La and lanthanum silicate is the only oxide formed upon oxidation. On the contrary, for the films deposited with 43.2 at. % Si, the Si remaining in the film is not enough to consume all the La upon $La_{9.33}Si_6O_{26}$ formation and the remaining La oxidizes to form La_2O_3.

In conclusion, the lanthanum silicate apatite-like phase ($La_{9.33}Si_6O_{26}$) was obtained for both La-Si films deposited by sputtering after annealing in industrial air at 1173 K for 1 h. However, silicon was segregated inside the films upon oxidation forming micrometer dimension aggregates. For the film deposited with the lower Si content, the Si remaining in the film is not enough to consume all the La upon formation of $La_{9.33}Si_6O_{26}$ and the remaining La oxidizes under the La_2O_3 phase.

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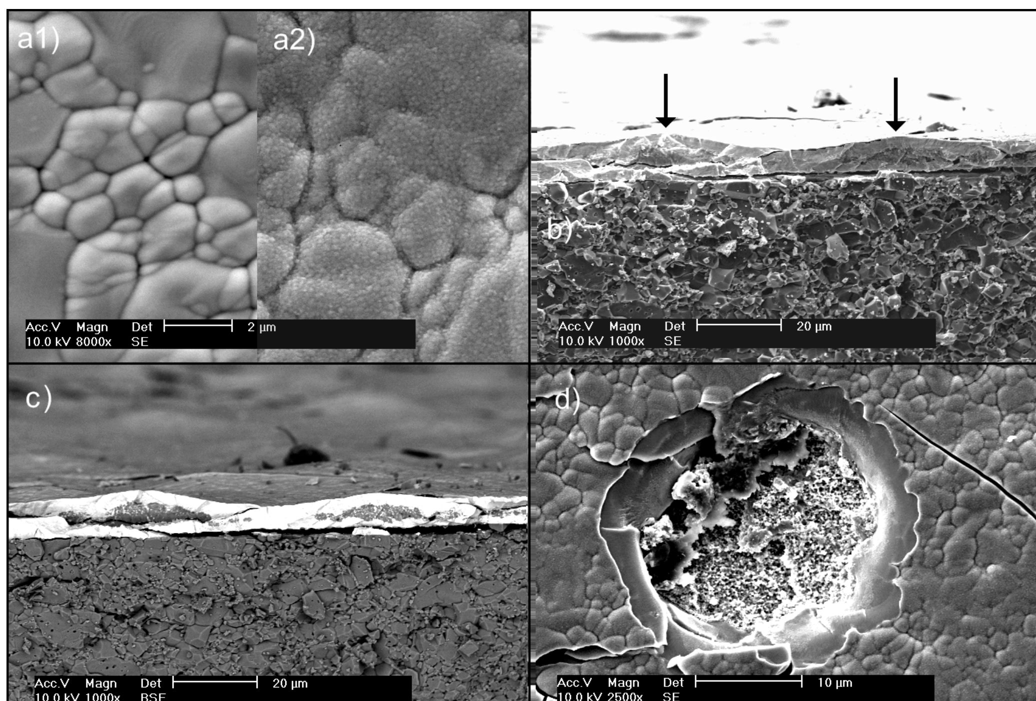

Fig. 1: SEM micrographs of the La-Si film deposited with 49 at. % Si: as-deposited (a1) and after oxidation at 1173 K in industrial air for 1 h (a2, b, c and d).

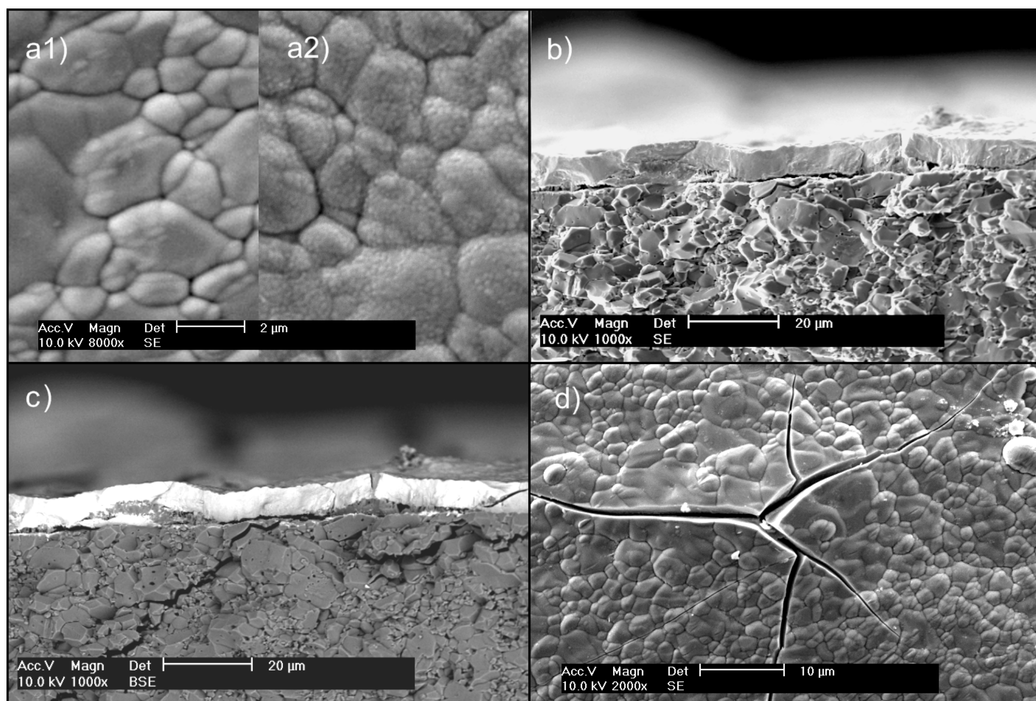

Fig. 2: SEM micrographs of the La-Si film deposited with 43.2 at. % Si: as-deposited (a1) and after oxidation at 1173 K in industrial air for 1 h (a2, b, c and d).

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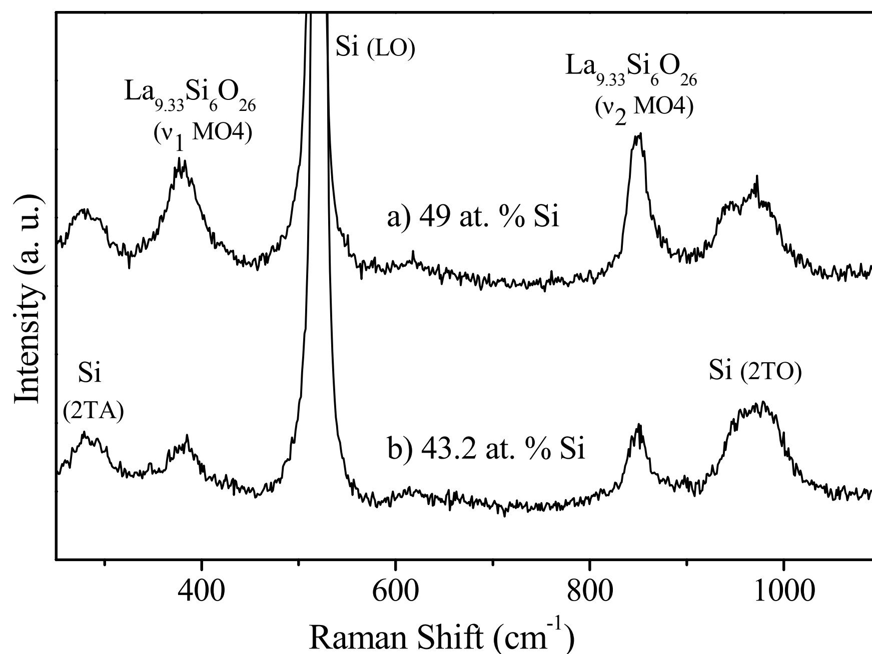

Fig. 3: micro-Raman spectra of the films deposited with a) 43.2 and b) 49 at. % Si after oxidation at 1173 K in industrial air for 1 h.

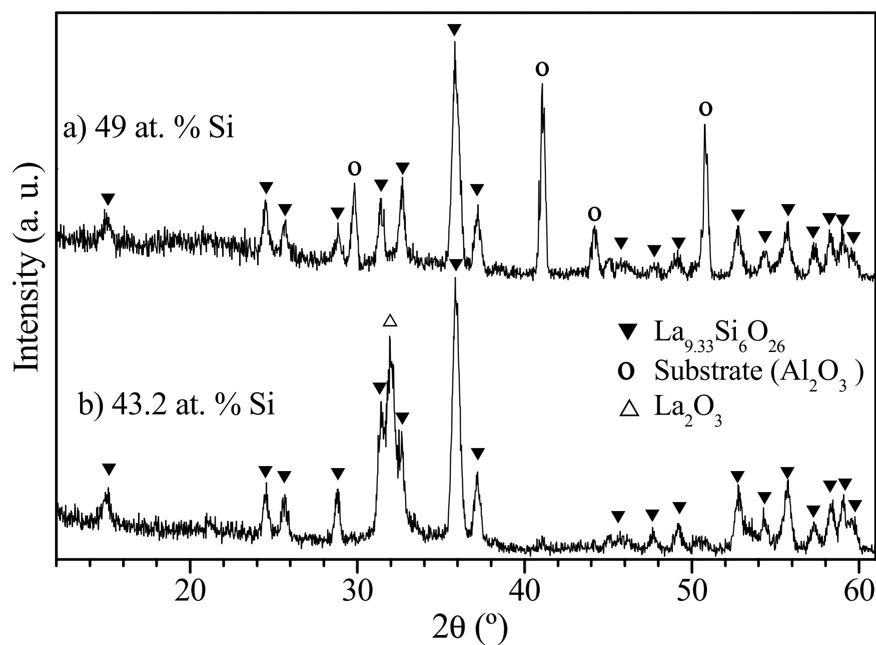

Fig. 4: X-Ray diffractograms of the films deposited with a) 43.2 and b) 49 at. % Si after oxidation at 1173 K in industrial air for 1 h.

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