Thickness dependence of the conductivity of thin films (La,Sr)FeO$_3$ deposited on MgO single crystal

Majid Mosleh*, Nini Pryds, Peter Vang Hendriksen

Department of Fuel Cells and Solid State Chemistry, Risø National Laboratory, Technical University of Denmark, DK-4000 Roskilde, Denmark

Abstract

Thin films of La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ of different thicknesses have been deposited on single crystal MgO substrate by pulsed laser deposition (PLD). The deposited films are characterized by XRD before and after annealing, by scanning electron microscopy (SEM) for morphological characterization and by the Van der Pauw (VDP) technique for determination of the conductivity. The temperature dependence of the conductivity in air for samples of different thickness has been investigated. The electrical conductivity of the films increases with increasing film thickness but the conductivity of all films is less than the value of the bulk material. The apparent conductivity versus temperature shows a maximum at a certain temperature ($T_{\text{max}}$). This characteristic temperature ($T_{\text{max}}$) decreases as the film thickness increases and reaches the value for bulk for thicker films. All of the samples show the same activation energy of the conductivity in the low temperature limit.

Keywords: Lanthanum strontium ferrite (LSF); Perovskite; Oxygen membrane; Electrical conductivity; Van der Pauw (VDP) technique; Pulsed laser deposition (PLD); Thin film

1. Introduction

Mixed ionic and electronic conducting materials can be used in solid oxide fuel cells and in ceramic membranes for gas separation including oxygen separation and partial oxidation of methane to syn?gas in a membrane reactor. One group of promising materials with high oxygen conductivity and high chemical stability in reducing atmosphere for use as oxygen membranes is the lanthanum strontium ferrites (La$_{1-x}$Sr$_x$FeO$_3$). Both electronic and ionic conductivity of La$_{1-x}$Sr$_x$FeO$_3$ has been reported by Patrakeev and co-workers [1–3].

While the bulk transport properties of La$_{1-x}$Sr$_x$FeO$_3$, are well studied, less is known about the properties of La$_{1-x}$Sr$_x$FeO$_3$ thin films. It has been found that the microstructure and the electrical properties of thin films are different from the properties reported for the bulk material with the same composition. Pardo et al. [4] have studied the electrical conductivity of epitaxial thin films of Sr$_2$Fe$_2$O$_{13-\delta}$ deposited on single crystal NdGaO$_3$ and the dependency of the conductivity on the film thickness. The conductivity of the films was found to increase with decreasing film thickness.

The objective of this work is to study the conductivity of La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ deposited on a MgO single crystal and its dependence on the film thickness. MgO was chosen as substrate to avoid reaction between the substrate and the film and to avoid any contribution from the substrate conductivity.

2. Experimental

(La$_{0.6}$Sr$_{0.4}$)$_{0.99}$FeO$_3$ (LSF64) powders were prepared using the glycine nitrate process (GNP). The synthesised powder was calcined at 900°C for 24 h. The resultant powders were ball-milled in ethanol for 1 week and subsequently dried. The targets for the PLD were prepared by pressing the powder initially uniaxially followed by isostatic pressing. The pressed targets were then sintered in air at 1200°C for 20 h. The X-ray diffraction (XRD) analysis shows that after sintering, the target becomes well crystalline with a structure consist only of La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$.

The samples were irradiated with 20 ns laser pulsed from a KrF excimer laser at 248 nm with a fluence of 4 J/cm$^2$. During the deposition the substrate temperature was kept around 750°C and an oxygen background pressure of 10 Pa. The ablated material was collected on the substrate located at a distance of 88 mm from the target.

To study the variation of conductivity with film thickness, the deposition is carried out with variable deposition time under...
the same deposition conditions. The thicknesses of the films were determined by comparing energy dispersive spectrometry (EDS) determined in a scanning electron microscope (SEM) with Monte Carlo simulations [5]. The structure of the films was determined by X-ray diffraction (XRD) using Bragg–Brentano geometry with a STOE & CIE θ/θ powder diffractometer equipped with an energy-dispersive Kevex detector. The radiation used was Cu Kα. The morphology and the microstructure of the deposited films were investigated by SEM, imaging and cross-sectioning of the films was performed on a Zeiss 1540XB CrossBeam field emission scanning electron microscope (FESEM) equipped with a focused ion beam (FIB) column and a gas injection system (GIS).

3. Results and discussions

Fig. 1 shows the XRD patterns of the target material together with the deposited layer after different deposition times. The XRD patterns were originally recorded in the range $2\theta = 20–90^\circ$ but for the comparison of the peak position and the line broadening the XRD data are shown with a $2\theta$ scan from $20^\circ$ to $35^\circ$.

The formation of a perovskite structure at all deposition time was confirmed by these measurements. The peak positions are close to those of the target and the corresponding ICDD-card files for $\La_{0.6}\Sr_{0.4}\Fe_{1-\delta}$. The LSF64 films on the single crystal MgO(1 0 0) show the reflections at 22.8$^\circ$ and 46.6$^\circ$ (not shown here) for all films, which can be identified with the (0 1 2) and (0 2 4) orientation, respectively.

The substrate, MgO, has a cubic structure with lattice parameter $a = 0.4216$ nm while bulk $\La_{0.6}\Sr_{0.4}\Fe_{1-\delta}$ has a perovskite structure with a rhombohedral structure (space group: $R \bar{3} c$) and lattice parameters $a = 0.55273$ nm and $c = 1.3421$ nm. It has a pseudo-cubic lattice parameter 0.3897 nm, equal to the $d$-spacing of the (0 1 2) planes. The lattice mismatch between the film and the substrate defined as $e = (a_{\text{sub}} - a_{\text{bulk}})/a_{\text{sub}}$, is thus 7.6% for LSF64(0 1 2) on MgO(1 0 0). The LSF64 film on MgO(1 0 0) substrate is thus under tensile strain.

For films thicker than 130 nm other peaks than the (0 1 2) and the (0 2 4) were observed. However, the intensity of these peaks are much lower then for the (0 1 2) so the (0 1 2) orientation is still the predominant one. The vertical lines in Fig. 1 indicate the peak positions of the target material. It should be noted that the (1 1 0) plan of the LSF64 is in fact composed of two peaks at 32.2$^\circ$ and at 32.5$^\circ$, which belong to the (1 1 0) and the (1 0 4) plans, respectively. However, these peaks could not be distinguished.

The X-ray diffraction profiles of the films show both a peak shift and line broadening. The inter-planar spacing was calculated for the (0 1 2) planes from the X-ray results and is plotted in Fig. 2. The inter-planar spacing increases with the increase of the film thickness up to a film thickness of 130 nm where after it is almost constant. From the XRD data, it is also observed that the full width at half maximum (FWHM) decreases with an increase in film thickness and approaches a minimum value at a deposition time of 20 min (film thickness ~130 nm). As the film thickness increases further, the width of the peaks increases.
The conductivity of the films was measured with help of the Van der Pauw (VDP) technique in air at different temperatures. The measurements were first performed during heating from room temperature to 950°C. The temperature was then kept at 950°C until a steady state is reached. The temperature was then decreased down to room temperature and the measurements were performed again on the heat-treated samples.

Fig. 3 demonstrates the variation of the conductivity of each film over time at 950°C. At this temperature the oxygen content of the films equilibrates fast, so the change in the conductivity is attributed to the change in the microstructure of the films. For films thinner than 66 nm, for example, a film of thickness 33 nm, we found a strong reduction of the conductivity from 49 S/cm to 4.1 S/cm. For the film with thickness 66 nm the conductivity first increases from 33 S/cm to 47 S/cm, then decreases to the steady state value of 29 S/cm. For films thicker than 66 nm, the conductivity increases until steady state is reached. One can see that as the film thickness increases from 33 nm to 650 nm, the steady state conductivity increases from 4.1 S/cm to 60 S/cm. However, the conductivity for the thickest film is still far from the equilibrium bulk value, which at this temperature is 99 S/cm [1].

The dependence of the total conductivity ($\sigma$) on the temperature in air is presented in Fig. 4 for all samples as determined in the cooling runs after the long time equilibration at 950°C (cf. Fig. 3).

Fig. 4 shows a thermally activated behaviour below 650°C followed by a maximum and a decreasing to 950°C. This reduction of total conductivity with increasing temperature is observed in all films in the high temperature region and is due to the loss of oxygen from the perovskite. A similar behaviour has been reported in several perovskite ceramics [6,7].

It is clearly seen that the conductivity increases rapidly as a function of film thickness up to the 130 nm thick film until it approaches a constant value.

The linear dependence of $\log (\sigma T)$ versus $1/T$ in the low temperature range allows us to determine activation energy ($E_{ac}$) for each sample. This behaviour is consistent with the Arrhenius relation [6]. The activation energy is found to be constant, equal to 0.307 ± 0.02 eV. The results from Fig. 4 are summarized in Table 1. As seen from Table 1, the peak temperature and the conductivity change significantly with changing the film thick-
Fig. 7. Scanning electron micrograph of the synthesised LSF64 before (left) and after (right) the conductivity measurements for thinnest film and thickest film.

ness especially for films less than 130 nm in thickness. The peak temperature (denoted as $T_{\text{max}}$), which corresponds to maximum conductivity decreases as the film thickness increases. Above 130 nm, $T_{\text{max}}$ decreases very slowly and reaches a minimum around 580 $^\circ$C which is close to the value found for bulk samples.

Fig. 5 demonstrates the variation of the conductivity as a function of the film thickness at 950 $^\circ$C. One can see that for films thicker than 130 nm, the conductivity slowly approaches the value for the bulk material. A possible explanation of the thickness effect on the conductivity is the change in the crystallite size without any effect on crystal orientation.

In order to investigate the effect of the heat treatment on the film crystallinity, XRD measurements of the heat-treated samples were taken right after the conductivity measurements. An XRD pattern of a heat-treated sample is compared to the “as prepared” in Fig. 6. The heat-treated samples still had the (0 1 2) orientation. It should be noted that we have not observed any new peaks, which can indicate any reaction between film and substrate. All the observed peaks belong either to the LSF64 or to the MgO substrate. However, there is a slight shift in peak position towards the lower angles, which probably reflects a change in oxygen stoichiometry in the sample.

The effect of heat treatment on the morphology of the films was investigated by SEM (see Fig. 7). Fig. 7 shows SEM pictures of the samples before and after the heat treatment (the micrographs to the left are the one before heat treatment). As for the thin films, it was observed that the films contain a continuous uniform layer and triangular shape particulates of about 200–500 nm in diameter on the top of the layer. The existence of these two distinct components in the produced coatings—thin uniform layer of LSF64 and triangular shape particulates on the top was confirmed by the EDS measurement technique during the thickness determination [5]. In that case, the measurement of the conductivity reflects the average conductivity of the film and the triangular shape particulates on the top. The thin film changed drastically after the heat treatment and has a totally different microstructure (see the top right micrograph in Fig. 7). After heat treatment it seems as if the film ceases to be continuous and only partially covers the substrate plane with a connected chain of deposited materials. The observed changes in apparent conductivity with time (Fig. 3) are therefore caused by the morphological/microstructural changes occurring during heat treatment. When the thin films break up and form holes, the measurements are no longer valid, due to tortuosity. In that case the measurements will underestimate the microscopic conductivity of the film, i.e. the measured conductivity over time reflects the film morphology rather than a change in material conductivity.

For the thick films samples SEM images (Fig. 7) show that during the conductivity measurements at 950 $^\circ$C the shape of the grains changes and the size of the grains increases. For the thick films expressing the results of the conductance measurements the conductivity is warranted, as the film is continuous and flawless.

4. Conclusions

Thin films of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ (LSF64) of different thicknesses have been prepared by pulsed laser deposition on MgO single crystal substrates. The Van der Pauw technique was used to investigate the effect of film thickness on total conductivity. The total apparent conductivity of the thin layer of LSF64 on MgO single crystal was found to increase with increasing film thickness. It seems that as the film becomes thicker the conductivity will asymptotically reach a value close to bulk. All of the samples are found to have the same activation energy of the conductivity. The observed thickness dependence of the conductivity reflects different tendencies to re-crystallize and re-shape during heat treatment.
Acknowledgments

The conductivity cell was designed by Dr. Nikolaos Bonanos. We are grateful to him and to Dr. Jørgen Bilde-Sørensen and Dr. Jesper Knudsen for SEM pictures.

References