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Influence of oxygen flow and film thickness on the texture and microstructure of sputtered ceria thin films

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ABSTRACT

An in depth understanding of the influence of the deposition parameters on the texture and microstructure of sputtered ceria thin films could pave the way towards the optimization of doped ceria thin films to be applied as fuel cell related electrolytes. In this work, ceria thin films were deposited at constant current using DC reactive magnetron sputtering. The influence of the oxygen flow and the film thickness on the crystallographic orientation and microstructure was studied. 200 nm thick films exhibit a change in out-of-plane orientation from random to preferential that coincides with the transition from metallic to poisoned mode. The preferential out-of-plane orientation of the films deposited in metallic mode changes from random to [200] as a function of both thickness and oxygen flow. Hence, films deposited in this mode are identified as grown under zone T conditions which agrees with scanning electron microscopy cross sections. In poisoned mode, however, a second transition is observed. The films deposited in this mode grow in zone II, but once more a change in out-of-plane orientation from [200] to random occurs when the oxygen flow is increased to higher values.

1. Introduction

The complex oxide materials used as oxygen ion conductor in traditional solid oxide fuel cells (SOFCs) demand a high working temperature of the fuel cell and as such impose strong material restrictions [1]. This limits not only the applicability of SOFCs, but also adds to the cost price. A lower operational temperature would offer the economical advantage of replacing the expensive ceramic parts of these cells by cheaper metallic alternatives. Degradation of the electrolyte, the reaction of the electrolyte with other cell components and thermal mismatch between the different parts of the fuel cell would be minimized as well [2,3].

At present, the expected performances of fuel cells are not yet proven. Especially in terms of lifetime, maintenance and reliability there are still many unknowns. One of the main drives in the current research is to lower the working temperature which would lead to a better integration of solid oxide fuel cells [4]. To do this, a better and thinner electrolyte is needed. One material meeting this demand is doped CeO_2 which has a higher ion conductivity than yttria stabilized zirconia (YSZ) at low temperatures [5,6]. By downscaling the electrolyte to a thin film (<5 μm), and therefore minimizing ohmic resistance, the structure and characteristics of the electrolyte are changed due to the occurrence of small scale or nano effects [7].

A full understanding of the influence of the deposition conditions on the texture and microstructure [8] in sputtered cerium oxide thin films could be a first incentive towards the optimization of (un)doped ceria thin films to be applied as electrolyte in conventional fuel cells [9] or battery replacements [10], and in oxygen sensors [11,12]. In this study ceria thin films were deposited by reactive magnetron sputtering [13], a physical vapour deposition technique, and their structure was characterized as a function of oxygen flow [14] and film thickness [15].

2. Experimental setup

Ceria thin films were deposited at a constant current of 0.25 A using DC reactive magnetron sputtering. A cerium target (99.5% purity; Testbourne Ltd.), 50.8 mm in diameter and 3 mm in thickness, was clamped on an unbalanced magnetron inside a rectangular cuboid vacuum chamber. The magnetron was positioned 115 mm away from a rotatable substrate holder. A shutter was installed between magnetron and substrate to sputter clean the target before each deposition. The chamber itself was pumped down to a background pressure below 3.5×10^{-4} Pa using a turbo-molecular pump and a rotary pump. The pressure was adjusted to 0.5 Pa by introducing between 33 and 37 sccm of Ar into the chamber and maintaining a pumping speed of approximately 109 L/s. Oxygen was brought directly to the substrate via a local and branched inlet to create a local higher oxygen partial pressure and thus increase film oxidation [16]. Amorphous glass substrates (26 mm × 12.5 mm) were first cleaned with distilled water and subsequently by ultrasound in methanol.

Fully transparent CeO_2 films with different textures and microstructures were obtained at different oxygen flows and thicknesses. The substrate was neither intentionally heated nor cooled. The sputtering time was chosen according to the desired thickness. The thickness of the deposited films was measured with contact

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profilometry (Taylor-Hobson Talystep), and double checked with cross section scanning electron microscopy (SEM). The deposition rate was calculated by dividing the measured thickness by the deposition time. A typical deposition rate in metallic mode is approximately 25 nm/min and decreases to a value as low as 0.6 nm/min in poisoned mode. Chemical surface analysis was performed with X-ray photoelectron spectroscopy (XPS) using monochromatic Al Kα X-rays. A pass energy of 56.1 eV was applied. An electron flood gun at 4 eV was employed. The thin film texture was determined with X-ray diffraction (XRD), based on Cu Kα radiation, in the Bragg–Brentano setup using a LynxEye Silicon Strip detector. The microstructure of the ceria thin films was assessed with a FEI Quanta 200 F scanning electron microscope applying a high voltage of 20 kV and a spot size of 3. To reduce surface charging, a thin Au film with a thickness of 20 to 40 nm was deposited before the analysis. The energy flux was measured with a passive thermal probe at the experimental conditions under which the films were deposited [17].

3. Results

3.1. Selection of the deposition conditions

The cerium oxide thin films were deposited with reactive magnetron sputtering. Cerium is DC sputtered from a metallic target and a reactive gas, oxygen in this case, is introduced into the vacuum chamber through a local and branched inlet. The intrinsic disadvantage of this process is that the oxygen does not only react with the cerium on the substrate but also with the metallic cerium target [13,18]. This causes process parameters such as the partial pressure of the oxygen gas, the discharge voltage and the deposition rate to change in a non linear fashion as a function of the reactive gas flow. Fig. 1 shows the hysteresis behaviour of the discharge voltage measured at constant current as a function of increasing and decreasing oxygen flow. Similar results were shown by Ershov et al. [19]. To ensure the stability of the measurement, every data point was measured 5 times during a 5 minute interval. In metallic mode, where the deposition rate is high because the target surface remains metallic, the oxygen flow was varied from 0 to 1.5 sccm in steps of 0.5 sccm. The voltage increase seen here can be attributed to chemisorption [20]. The transition from metallic to poisoned mode, characterized by a sudden drop in discharge voltage and deposition rate, occurs at a critical oxygen flow of 1.9 sccm. In poisoned mode, where compound formation prevails at the target surface, the flow was varied from 2.0 to 5.0 sccm. The increase of the voltage at these high oxygen flows is probably due to a change in plasma composition [21] and the overshoot in discharge voltage which occurs on returning to metallic mode along the decreasing flow curve can be connected to the disappearing anode effect [22]. Depositions were done along the increasing flow curve to study the influence of the reactive gas addition on the structure of the cerium oxide thin films. Parameters such as the discharge current (0.25 A), the target–substrate distance (115 mm) and the argon pressure (0.5 Pa) were kept constant during the depositions.

3.2. Influence of the film thickness and oxygen flow on texture and microstructure

Fig. 2 shows the XRD patterns of the ceria films grown at different O_2 flows chosen along the increasing flow curve of the above described hysteresis. According to the resulting diffraction spectra, crystalline films were obtained. The lines of the diffraction peaks correspond with those of cubic CeO_2 (JCPDS card file 34-0394) which is in line with fitting results from XPS surface analysis. The deconvolution of the Ce 3d photoemission spectra for a film deposited in poisoned mode at 5.0 sccm O_2 and for a film grown in metallic mode at 0.5 sccm O_2 is shown in Fig. 3. The Ce 3d line for cerium oxide consists of six peaks. Three spin-orbit split doublets (v/u, v″/u″ and v‴/u‴) are indicative of the presence of Ce^{+IV} and only two (v_0/u_0 and v′/u′) are indicative of Ce^{+III} [23]. The fitting was performed with a linear background and the relative binding energies according to Burroughs et al. [24]. Using the atomic percentages of the components belonging to the Ce $3d_{5/2}$ line, the oxygen deficiency (in CeO_{2-x}) was calculated. No significant difference in composition could be detected with a Student's t-test between the films deposited in metallic mode and those grown in poisoned mode. The average oxygen deficiency was determined to be 0.08.

These films have a thickness of around 200 nm. In order to more clearly visualize the texture changes occurring in the thin films, the XRD intensities were corrected for their respective thickness. The main crystallographic orientations, being [200], [111] and [220], were then determined by normalizing the net area of the intensity peaks with respect to the powder diffraction intensities. For example, the [200] fraction of crystallites is given by

$$F_{200} = \{A_{200}/I_{200}\}/\{A_{200}/I_{200} + A_{111}/I_{111} + A_{220}/I_{220}\} \quad (1)$$

with A_i being the net peak area and I_i the relative intensity given by the JCPDS card file.

The result of this calculation is shown in Fig. 4. For a 200 nm thin film, the out-of-plane orientation is not yet preferential but random in metallic mode or for low oxygen flows (see Fig. 4a). A mixture of the three main fractions, being [200], [111] and [220] is obtained. It is seen that when the oxygen flow is varied from 0.5 to 1.5 sccm, the [200] fraction decreases. Once poisoned mode is attained, the thin films grow with a [200] preferential out-of-plane orientation. The [200] fraction reaches its highest value at 2.5 sccm. As the oxygen flow is increased further, the [200] fraction abruptly decreases and becomes negligible. [111] succeeds as the highest fraction in poisoned mode at oxygen flows of 3 sccm and higher. The [220] fraction is also

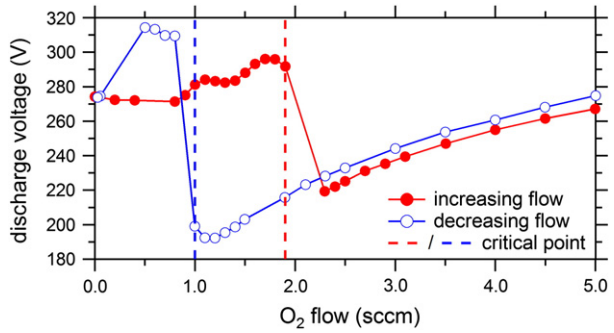

Fig. 1. Process curves of the discharge voltage as a function of increasing and decreasing O_2 flow, measured at a constant current of 0.25 A and an argon pressure of 0.5 Pa (the pumping speed was fixed at 109 L/s).

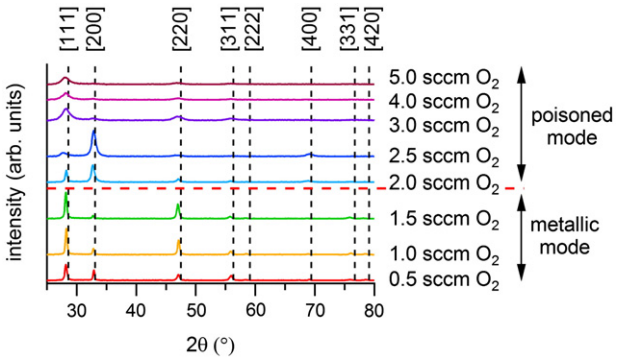

Fig. 2. XRD theta–2 theta patterns of 200 nm CeO_2 thin films deposited at different O_2 flows. The lines correspond with those of cubic CeO_2 (JCPDS card file 34-0394).