Bias-assisted magnetron sputtering of yttria-stabilised zirconia thin films

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Abstract. Cubic yttria-stabilized zirconia (YSZ) thin films were deposited by reactive magnetron sputtering on NiO–YSZ fuel cell anodes under different conditions. The influence of substrate bias voltage, temperature and porosity on texture and morphology of the deposited films were investigated. Comparing film morphology of YSZ grown on NiO–YSZ anodes, it was found that films deposited on a substrate with a large porosity were columnar and contained voids regardless of the deposition parameters. It was shown that only using of anode support with very high surface quality, substrate heating up to 500 °C and pulsed substrate bias (about -30 V MF) during film deposition is necessary for deposition of non-columnar thin films without voids and cracks that may be suitable for SOFC application.

1. Introduction

Solid oxide fuel cells (SOFCs) convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. However, before fuel cell technology can gain a significant share of the electrical power market, the operation temperature needs to be reduced in order to decrease costs, improve the durability of the cells and achieve greater flexibility in the choice of material for stack construction. Application of thin film electrolytes is a way of achieving this goal. Yttria-stabilized zirconia (YSZ) is the preferred material for electrolytes in solid oxide fuel cells as it is an acceptable ionic conductor, electrical insulator, chemically inert and relatively cheap to produce.

Typically, a tape-casting method is applied for the production of the electrolyte on top of the anode support which results in electrolyte thicknesses below 50 μm [1]. However, by applying a physical vapor deposition (PVD) technique it is possible to produce thin film electrolytes with thicknesses down to a few microns and thereby lower the operation temperature of the SOFC to an intermediate temperature range of 650–800 °C [2]. Previous investigations have demonstrated deposition of YSZ thin films by techniques such as pulsed laser deposition [3], electron beam evaporation [4], atomic layer deposition [5] and magnetron sputtering [6,7].

Implementation of magnetron sputtering in large-scale SOFC manufacturing was shown by Sønderby et al. [8]. However problem often encountered when depositing YSZ thin films by magnetron sputtering at relatively low synthesis temperatures is the formation of insufficiently dense and columnar microstructures. Such microstructures are unfavorable as they may result in internal leakage in the cell leading to decreased open cell potential and electrochemical performance. Nédélec
et al. have deposited electrolytes without visible continuous columnar structure and has achieved significant improved electrochemical performance at low temperatures [9].

It is reported in the literature that bias-assisted sputtering is capable of producing films with better quality compared to normal sputtering [10]. Under optimum conditions, the positively charged Ar atoms will provide the necessary displacement energy to enhance the growth process towards layer growth. Thus, using bias the morphology of the deposited layer can be changed from porous to dense.

In the present study deposition of YSZ films by pulsed DC magnetron sputtering is carried out on SOFC NiO-YSZ anodes under the influence of substrate bias voltage. The morphology and texture dependencies of substrate bias voltage, substrate temperature and substrate type are investigated.

2. Methodology and Materials
YSZ thin films are deposited on commercial NiO-YSZ SOFC anodes (Ningbo Materials Institute of Technology and Engineering (NIMTE), China) 20 mm in diameter. To determine the influence of the structure and porosity of the anode substrate on the structure of deposited electrolyte reduced anodes composed of 60 vol.% Ni and 40 vol.% Zr$_{0.9}$Y$_{0.1}$O$_{1.95}$, made of a ceramic anode tapes 42420 and 42421 (ESL ElectroScience, USA) also used as substrates. Last substrates had a greater volume of open pores due to their reduced state. Experiments were performed using a 100 mm diameter, 8 mm thick Zr$_{0.86}$Y$_{0.14}$ target equipped in a circular magnetron source placed in a cylindrical stainless steel vacuum chamber. Before deposition substrates were cleaned by sputter etching for 10 min. In this case, the magnetron power was 200 W and negative bias voltage with amplitude of 600 V was applied to the substrate holder. After that samples were heated up to the deposition temperature approximately 500 °C. Sputtering was carried out in the oxygen-argon atmosphere at a working pressure of 0.2 Pa. Power supplies produced by Applied Electronics. Ltd. (Russia) were used for applying a voltage to the substrate and sputtering target. DC or a pulsed DC bias (MF) with a frequency of 100 kHz was applied to the substrates. Bipolar magnetron sputtering was carried out at 80 kHz with reverse pulses of 4 μs and the amplitude of 15% of the nominal negative sputtering voltage. The average discharge power was 2 kW. The distance between the magnetron target and the substrate was about 80 mm. The maximal deposition rate of stoichiometric YSZ films was 12 μm/h, which was about 70% of the film deposition rate in pure argon at the same power (17 μm/h).

X-ray diffraction (XRD) measurements in the $\theta$–$2\theta$ geometry were performed with a XRD 7000S (Shimadzu, Japan) diffractometer using CuKα radiation. Scanning electron microscopy (SEM, Hitachi TM3000, Japan) was used to determine the film morphology as well as film thickness.

3. Results and Discussion
The microstructure of the YSZ electrolyte layers deposited on NiO-YSZ anodes at different substrate temperatures and at floating potential was investigated using a SEM. Figure 1 shows micrographs taken from cross-sections.

From the viewpoint of industry applications heating of the substrate is undesirable because it complicates the equipment, extends the process of electrolyte deposition due to the additional steps of heating and cooling of the substrate and result in additional expenditure of electrical energy. But Figure 1a shows that after YSZ deposition at room temperature electrolyte delamination, i.e. debonding between the film and substrate is observed. This is due to poor adhesion and strong compressive stresses generated in the film during its growth. Poor adhesion of the film to the substrate, despite the fact that the latter was subjected to plasma pre-cleaning, may be caused by desorption of residual gas from the substrate pores during film growth due to the heating of the substrate in a magnetron discharge. Plasma cleaning removes contaminants located on the surface only, but in the case of porous substrates this is not enough. Film growth with residual stresses only aggravates the problem of insufficient adhesion. Formation of internal stresses in the films deposited by magnetron sputtering is typical [11] and caused by bombardment of a growing film by high-energy particles. In the case of magnetron sputtering, such particles can be neutral atoms scattered from the cathode, ions
of a working gas (Ar) that are generated in the discharge, and neutralized ions reflected from the cathode.

The micrographs for the deposition with substrate temperature 300 and 500°C (figures 1b and 1c) show already good layer adhesion without film delamination. This is due to the desorption of residual gas from the porous anode and adatom mobility increase with temperature increasing. The using a substrate temperature of about 500 °C from a technological point of view is preferential, since it is known that the higher the ratio between a substrate temperature during the deposition and a melting point of the material, the denser the deposited layer. Increasing the substrate temperature above 500 °C is not rational, since it leads to considerable complication of the heating system.

![Figure 1](image_url)

**Figure 1.** Cross section SEM micrographs of YSZ films deposited at room (a), 300°C (b), and 500°C (c) substrate temperature and at floating potential on NiO-YSZ anodes produced by NIMTE. Micrograph of YSZ film deposited at substrate temperature 500°C and at floating potential on Ni-YSZ anode produced from ESL ElectroScience anode tape (d).

It is interesting, the YSZ films deposited on unreduced NiO-YSZ anodes produced by NIMTE (figures 1a-1c) with sufficiently dense structure and small pore size, also possess a dense structure in which columnar crystals are practically indistinguishable. However, when depositing an YSZ film on the more porous anode, for example, produced from ESL ElectroScience anode tape (figures 1d) columnar structure of the electrolyte becomes inevitable. This is caused by the fact that initial islands of the YSZ do not attain the coalescence stage completely, thus, limiting the continuity of the deposited layer [10]. These discontinuities will have a clear negative effect on gas-tightness of deposited layers. Therefore very high surface quality of anode support is essential for the formation of thin layers of gas-tight electrolyte.
Another way of increasing adatom mobility besides heating the substrate is application of negative substrate bias voltage to draw positive ions to bombard the surface and provide energy to the film. Figures 2 and 3 show cross section and surface SEM micrographs of the YSZ films deposited at different bias voltages.

**Figure 2.** Cross section SEM micrographs of YSZ layers deposited at -30 V DC (a), -30 V MF (b), and -55 V MF (c) substrate bias on ceramic anodes. Substrate temperature was 500°C.

**Figure 3.** SEM surface pictures of YSZ layers sputtered using substrate bias on ceramic anodes. Different settings for the bias were tested: -30 V DC (a), -30 V MF (b), and -55 V MF (c). Substrate temperature was 500°C.
At DC bias voltage of −30 V applied to the substrate YSZ electrolyte (figure 2a) has a layered structure with longitudinal cracks. In addition, there is a partial or complete YSZ film delamination on some parts of the substrate surface (figure 3a). Apparently, the use of DC bias voltage during deposition of dielectric coating is not effective method due to charging of nonconductive film by positive ions. Therefore it is preferably to use RF or pulsed DC bias during the deposition of YSZ electrolyte.

At a small pulsed DC bias voltage (-30 V) YSZ film has non-columnar structure without voids and cracks (figure 2b). The film surface is clearly facetted (figure 3b), and delamination of the film from the substrate was not observed. By applying -55 V pulsed DC bias the film obtains a homogeneous and fine grained microstructure (figure 2c) but minor delaminates were observed due to the build-up of stress.

Fig. 4 shows the X-ray diffraction patterns of the YSZ films deposited without and at -30 V MF bias applied to the substrate. In all cases, the cubic YSZ film phase and metallic Ni were generally detected. No peaks of monoclinic, tetragonal or amorphous phases were detected. It should be noted that films deposited with substrate bias have broader peaks on the diffractograms indicating smaller grain size.

![X-ray diffraction pattern of the magnetron sputtered YSZ films](image)

**Figure 4.** X-ray diffraction pattern of the magnetron sputtered YSZ films: 1 – without substrate bias, 2 – at -30 V MF substrate bias. Intensities are normalized to the (111) reflection. Reflections of the Ni are marked with in asterisk. The Miller indices and peak positions for the 8 mol.% Y₂O₃-doped ZrO₂ powder reference sample (ICDD powder diffraction database entry # 030–1468) with a cubic fluorite structure are included for comparison.

Ion bombardment has been seen to increase nucleation rates and film density, to decrease the average grain-size, to inhibit formation of columns, and to control the defect density and orientation of a wide range of sputtered coating [12]. The smaller grain size of a film deposited at substrate bias than at floating potential is presumably due to the formation (by ion bombardment) of more nucleation centers.

**4. Conclusion**

It was shown that it is possible to deposit non-columnar YSZ thin films without voids and cracks by bias-assisted magnetron sputtering that may be suitable for SOFC application. The key parameters for
the formation of YSZ films with the desired characteristics are quality of substrate surface, the substrate temperature and low-energy ion bombardment of the growing film. Since the gastight YSZ film can be obtained only if its thickness significantly larger than the maximum pore size of the substrate, the substrate should not have such large defects as big voids, cracks, etc. The substrate surface to be coated should be as smooth as possible. Heating of porous substrates to a temperature above 300 °C is a prerequisite for achieving good film adhesion, while ion assisting necessary to obtain dense and non-columnar structure of films.

**Acknowledgments**

This research was carried out within the State assignment of the Institute of High Current Electronics SB RAS and under financial support of Russian Foundation for Basic Research (grant № 14-08-31679).

**References**

[1] Tucker M 2010 *J. Power Sources* **195** 4570
[2] Pederson L R, Singh P, Zhou X D 2006 *Vacuum* **80** 1066
[3] Kosacki I, Rouleau C M, Becher P F, Bentley J, Lowndes D H 2005 *Solid State Ionics* **176** 1319
[4] Karthikeyan A, Chang C, Ramanathan S 2006 *Appl. Phys. Lett.* **89** 183116
[5] Shim J H, Chao C C, Huang H, Prinz F B 2007 *Chem. Mater.* **19** 3850
[6] Smeacetto F, Salvo M, Ajitdoss L C, Perero S, Moskalewicz T, Boldrini S, Doubova L, Ferraris M 2010 *Mater. Lett.* **64** 2450
[7] Sillassen M, Eklund P, Pryds N, Johnson E, Helmersson U, Bottiger J 2010 *Adv. Funct. Mater.* **20** 2071
[8] Sønderby S, Nielsen A J, Christensen B H, Almtoft K P, Lu J, Jensen J, Nielsen L P and Eklund P 2012 *Surf. Coat. Technol.* **206** 4126
[9] Nédélec R, Uhlenbruck S, Sebold D, Haanappel V A C, Buchkremer H P, Stöver D 2012 *J. Power Sources* **205** 157
[10] Chapman B N 1980 *Glow Discharge Processes: Sputtering and Plasma Etching* (New York: John Wiley and Sons)
[11] Solov’ev A A, Sochugov N S, Oskomov K V 2010 *Phys. Met. Metallogr.* **109** 111
[12] Sillassen M B 2010 Synthesis and ionic conductivity properties of stabilized ZrO₂ thin films. PhD Dissertation. University of Aarhus. Denmark.