Surface & Coatings Technology xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Deposition of yttria-stabilized zirconia thin films by high power impulse magnetron sputtering and pulsed magnetron sputtering

Steffen Sønderby [a,b,*], Asim Aijaz [a], Ulf Helmersson [a], Kostas Sarakinos [a], Per Eklund [a]

[a] *Department of Physics, Chemistry and Biology, IFM, Linköping University, SE-581 83 Linköping, Sweden*
[b] *Danish Technological Institute, Tribology Centre, Teknologiparken, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark*

ARTICLE INFO

Article history:
Received 23 September 2013
Accepted in revised form 4 December 2013
Available online xxxx

Keywords:
HiPIMS
HPPMS
Pulsed DCMS
SOFC
YSZ
Substrate bias

ABSTRACT

Yttria-stabilized zirconia (YSZ) thin films were reactively sputter-deposited by high power impulse magnetron sputtering (HiPIMS) and pulsed direct current magnetron sputtering (DCMS). The use of substrate bias voltage was studied in both modes of deposition as a process parameter to promote the growth of dense and less columnar films. Films were deposited on both Si(100) and NiO–YSZ fuel cell anodes. The texture, morphology and composition of the deposited films were investigated with regard to their application as thin electrolytes for solid oxide fuel cells (SOFCs). Independent of the deposition mode the films were found to be stoichiometric. The application of substrate bias voltage had opposite effects on texture and crystallinity of films deposited by pulsed DCMS and HiPIMS. Films deposited by pulsed DCMS became highly crystalline and <220> textured at high bias voltage whereas bias applied to HiPIMS deposited films disrupted crystal growth leading to deterioration of crystallinity. Comparing film morphology, it was found that pulsed DCMS films were columnar and contained voids regardless of the applied substrate bias. When depositing by HiPIMS a window of operation at a bias voltage of −25 V to −50 V was found in which it is possible to deposit non-columnar thin films without voids and cracks as desired for SOFC applications.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Yttria-stabilized zirconia (YSZ) is the most commonly used material for solid oxide fuel cell (SOFC) electrolytes [1] as it is an adequate ionic conductor, has a low electronic conductivity, and is relatively cheap to process compared to other electrolyte materials. The ionic conductivity in the stabilized zirconia system is due to the mobility of O^{2-} vacancies created when substituting Zr^{4+} by Y^{3+} in the cationic network. However, the ionic conductivity of state-of-the-art YSZ based electrolytes is only sufficient at elevated temperatures (800–1000 °C) which results in increased reactivity of cell core components, drastically limited lifetimes and requires the use of expensive interconnect materials [2]. Therefore, the reduction of the operation temperature to an intermediate temperature range (500–750 °C) is a key objective in SOFC research. Among the possible routes to achieving lower operation temperatures, reduction of the electrolyte thickness in order to reduce the overall resistance is promising [3,4].

YSZ electrolytes are typically fabricated by screen printing or spraying techniques followed by subsequent sintering [5] which are ideal for low-cost fabrication with high throughput. However, these methods are not suitable for producing dense and thin (a few μm in thickness) YSZ electrolytes. The latter can be achieved by synthesizing YSZ thin films employing a variety of chemical and physical methods [6] such as pulsed laser ablation (PLD) [7,8] chemical vapor deposition (CVD) [9], atomic layer deposition (ALD) [10], spin coating [11] and magnetron sputtering [12–17]. An issue often encountered when depositing YSZ thin films by physical vapor deposition techniques (PVD) (e.g., magnetron sputtering) at relatively low synthesis temperatures is the formation of underdense and columnar microstructures. Such microstructures are unfavorable as they may result in internal leakage in the cell leading to decreased open cell potential. Therefore, an undesirable extra manufacturing step in the form of post-deposition annealing is often required to eliminate pores in such films [6]. Reports on cell tests performed on SOFCs containing magnetron sputtered electrolytes with a columnar structure have shown an electrochemical performance comparable to or worse than cells containing tape cast electrolytes and not a significant improvement as would be expected from the reduced electrolyte thickness [18,19]. This lack of performance is related to leaks in the electrolyte due to the columnar morphology. In contrast, Nédélec et al. have deposited electrolytes without visible continuous columnar structure and has achieved significant improved electrochemical performance at low temperatures [20].

High power impulse magnetron sputtering (HiPIMS) is a PVD-based technique for thin film deposition. Inherent to this technique is a relatively large fraction of ionization of the sputtered material with energies up to several 10s of eV that have been shown to provide added means for controlling the microstructural evolution during film growth [21].

* Corresponding author at: Department of Physics, Chemistry and Biology, IFM, Linköping University, SE-581 83 Linköping, Sweden. Tel.: +45 7220 2795; fax: +45 7220 1550.
E-mail address: stso@dti.dk (S. Sønderby).

0257-8972/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.12.001

ARTICLE IN PRESS

The latter has been, for instance, shown to favor the growth of dense films at relatively low growth temperatures and to suppress columnar microstructure giving rise to globular film morphology [22]. This is what is desired in the fabrication of thin film electrolytes for SOFC. Therefore, the goal of the present study is to explore the potential of HiPIMS for the synthesis of dense YSZ films and to establish the effect of the HiPIMS on the film morphology. Films are also synthesized by pulsed direct current magnetron sputtering (DCMS), for reference. As previous studies have shown that the substrate bias is a crucial parameter in order to obtain dense films suitable for SOFC application [20], the bias voltage has been varied between depositions. Coatings are deposited on both Si and NiO–YSZ anodes for SOFC applications and the morphological and structural features of the films are investigated.

2. Experimental details

Experiments were performed using a 50 mm diameter, 3 mm thick Zr/Y (82:18 wt.%) target (purity 99.9%, excluding Hf) equipped in a circular magnetron source placed in a cylindrical stainless steel vacuum chamber. Prior to depositions, the chamber was evacuated by a turbo molecular pump to a background pressure in the order 10^{-4} Pa. Ar gas (purity 99.9997%) was used as the sputtering gas while O_2 gas (purity 99.9995%) was used as the reactive gas. Ar and O_2 gas flows were controlled by electronic mass flow controllers while the total process pressure was controlled by a gate valve. A constant Ar partial pressure of 660 mPa was used while the O_2 partial pressure was ~40 mPa. Before depositions, characterization of the reactive process was performed by measuring the variations of the target voltage as a function of O_2 partial pressure. The change in discharge voltage was highly dependent on the target race track depth. Even though pulsed DCMS and HiPIMS depositions were carried out at the same average power an O_2 flow of ~6 sccm was needed to poison the target in the case of pulsed DCMS while only ~3 sccm was needed in HiPIMS. Films were deposited at working points that correspond to the transition zone between metallic and oxidic mode seeking to optimize the film growth rate. Si(100) wafers, cut into approximately 1×1 cm^2 pieces were coated by films with thicknesses smaller than 0.5 μm and used for structural characterization and compositional analysis. NiO–YSZ SOFC anodes of size up to 5×5 cm^2 were coated with films with thicknesses 0.6–1 μm and used to assess the morphological and structural features of the films. The NiO–YSZ anodes were supplied by Forschungszentrum Jülich GmbH (Germany) and were manufactured by reverse sequential tape casting of a thin anode on top of a thicker anode support and subsequently co-fired. The anode support was not optimized with respect to mechanical strength and was therefore too brittle to be used in cell testing experiments. For all depositions, the substrates were placed on a stationary substrate holder at a distance of 7 cm from the target surface and no intentional substrate heating was used. The depositions were made reactively by pulsed DCMS as well as HiPIMS. In both of the cases, an average power of 150 W was used. In the case of pulsed DCMS, the power to the cathode was applied by a pulsed DC plasma generator (ENI RPG-50) operating at a frequency of 150 kHz with 40% duty cycle. In the case of HiPIMS, the power to the cathode was applied in the form of unipolar pulses having a frequency of 500 Hz and a width of 35 μs resulting in a duty cycle of 1.75%. The power was supplied by a pulsing unit (SPIK 1000A, Melec) fed by an MDX 1 K direct current generator (Advanced Energy) operated in constant power mode. The time-dependent discharge voltage and discharge current were monitored on a Tektronix TDS 520C oscilloscope. During the depositions, the energy of the depositing flux was tuned by applying a negative pulsed bias potential to the substrate using a pulsing unit (home-design) operating at a frequency of 200 kHz. The range of the substrate bias potential was chosen, in steps of 25 V, from −75 V to floating potential (no bias). In order to achieve comparable film thicknesses for characterization purposes, deposition times were adjusted to account for the lower deposition rates obtained as the bias voltage was increased and when HiPIMS was employed.

The crystalline phases and texture of the deposited films were determined by means of X-ray diffractometry (XRD). Measurements were performed in Bragg–Brentano (θ–2θ) with a Bruker D8 Discover diffractometer using Cu*K*α radiation. Pole figures were acquired in the tilt-angle (χ) range 0–84° and the azimuth-angle (φ) range 0–360° with steps of 3° using a PANalytical Empyrean diffractometer. Scanning electron microscopy (SEM) was used to determine the film morphology as well as film thickness. SEM imaging was performed with a Nova 600 nanoSEM from FEI and a Zeiss EVO LS25. Both systems were equipped with an energy dispersion X-ray spectroscopy (EDX) module which was used to determine the film composition. The latter was also studied by means of Rutherford backscattering spectroscopy (RBS) using a 2 MeV $^4He^+$ ion beam from a Van de Graff accelerator and a scattering angle of 161°. The experimental RBS data were simulated with the SIMNRA software [23]. RBS was used to assess the global composition of the thin films. However, as the atomic mass of zirconium and yttrium are close they cannot be discriminated by RBS. EDX was therefore applied to estimate the ratio Zr and Y content. The Zr/Y ratio was then used to calculate the atomic composition based on the RBS measurement. Due to overlapping ZrL and YL lines in the EDX spectrum a calibration first needed to be done by performing EDX measurements on the applied sputtering target with a known composition.

3. Results and discussion

Fig. 1.a shows θ–2θ X-ray diffractograms of films deposited on Si (100) by HiPIMS at different bias voltages at otherwise identical conditions. The corresponding diffractograms for films grown by pulsed DCMS are seen in Fig. 1.c. For all the deposited films, the observed peaks correspond to cubic YSZ (ICDD JCP2 No. 30-1468). For films deposited by HiPIMS (Fig. 1.a) at floating potential, −25 V and −50 V

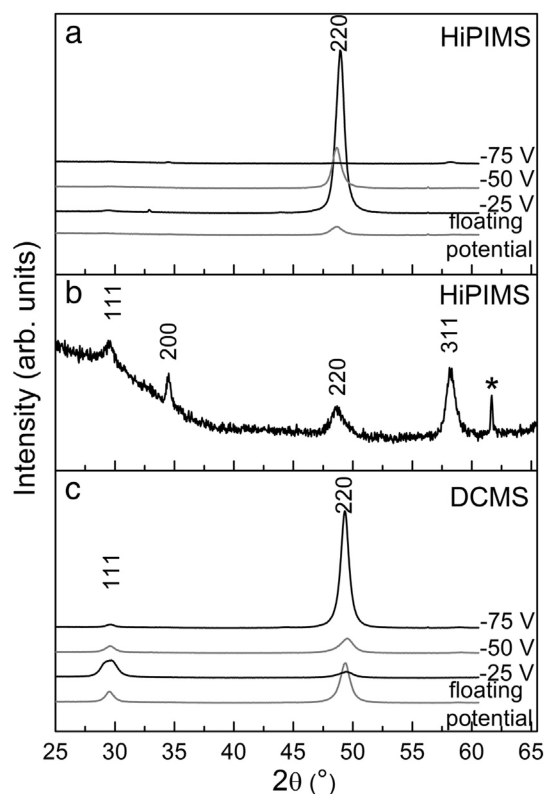

Fig. 1. XRD θ–2θ scans of: (a) HiPIMS deposited films, (b) close-up of film deposited by HiPIMS at −75 V bias, and (c) films deposited by pulsed DCMS. Asterisk marks the Si (004) CuKβ substrate peak.

Please cite this article as: S. Sønderby, et al., Surf. Coat. Technol. (2013), http://dx.doi.org/10.1016/j.surfcoat.2013.12.001

Download English Version:

https://daneshyari.com/en/article/8028156

Download Persian Version:

https://daneshyari.com/article/8028156

Daneshyari.com