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# Optimisation of growth parameters to obtain epitaxial Y-doped $BaZrO_3$ proton conducting thin films

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ABSTRACT

We hereby report developments on the fabrication and characterization of epitaxial thin films of proton conducting Y-doped $BaZrO_3$ (BZY) by pulsed laser deposition (PLD) on different single crystal substrates (MgO, $GdScO_3$, $SrTiO_3$, $NdGaO_3$, $LaAlO_3$ and sapphire) using Ni-free and 1% Ni-containing targets. Pure, high crystal quality epitaxial films of BZY are obtained on MgO and on perovskite-type substrates, despite the large lattice mismatch. The deposition conditions influence the morphology, cell parameters and chemical composition of the film, the oxygen partial pressure during film growth being the most determining. Film characterization was carried out using X-ray diffraction, transmission electron and atomic force microscopies, wavelength dispersive X-ray spectroscopy and angle-resolved X-ray photoelectron spectroscopy. All films show a slight tetragonal distortion that is not directly related to the substrate-induced strain. The proton conductivity of the films depends on deposition conditions and film thickness, and for the optimised conditions its total conductivity is slightly higher than the bulk conductivity of the target material (3 mS/cm at 600 °C, in wet 5% $H_2$/Ar). The conductivities are, however, more than one order of magnitude lower than the highest reported in literature and possible reasoning is elucidated in terms of local and extended defects in the films.

## 1. Introduction

Acceptor-doped $BaZrO_3$ is one of the state-of-the-art proton conductors for use as electrolyte in proton conducting solid oxide fuel cells [1]. The main advantages are the high bulk conductivity (~10 mS/cm above 400 °C for 20%Y in $BaZrO_3$ ceramics) and the high chemical stability towards acidic gases, such as $CO_2$ [2]. $BaZrO_3$ is, however, troubled by resistive grain boundaries that limit the performance of the ceramic material [3–5].

The search for new strategies to engineer films and interfaces in oxide materials, where the control at the nanoscale may induce an improvement of the material's performance, is a very active field of research, with outstanding examples of increased oxide ion conductivity in doped $ZrO_2$ [6,7]. The formation of space charge layers [8], generally occurring at the substrate-film interface or at the grain boundary regions, intends to rationalise this experimental enhancement with the variation of the charge carriers' density, or their mobilities, at the interface, which become increasingly dominant with decreasing the thickness/particle size. Other studies rationalise such effect to tensile strain induced from the substrate to the film [9]. The reasoning behind large variations of the conductivity in nano-sized oxides depends on each case and material, and therefore demands further investigations focused to the fundamental understanding of the phenomena.

Dedicated studies of the effect of strain and related interfacial effects in epitaxially-grown proton conducting thin film oxides are relatively scarce in literature, even for the widely studied Y-doped $BaZrO_3$ (BZY). From the experimental point of view, only a few scientific communications are available, with significant differences among them. Shim et al. [10] described that highly textured 60 nm BZY film epitaxially grown on MgO (001) showed high ionic conductivity (in the order of 1 mS/cm at 200 °C), very close the bulk values reported by Kreuer [2]. Similarly, Pergolesi et al. [11] investigated epitaxial ~1 μm BZY thin films on MgO (001) that showed very high total conductivity (110 mS/cm at 500 °C), eventually matching the bulk protonic conductivity extrapolated from low temperature data [2]. They concluded that these conductivities (the highest ever reported so far for BZY) may be understood as a direct measurement of the bulk conductivity of a grain boundary free BZY *via* the fabricated epitaxial thin film. On the other hand, Bae et al. [12] describes that polycrystalline BZY films, obtained by pulsed laser deposition (PLD) on MgO (001) at 700 °C

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under various oxygen partial pressures (10–300 mTorr), exhibited a very low conductivity below 0.1 mS/cm at 650 °C, close to that reported for 30 nm nanograined BZY thin films [2].

This discrepancy of more than three orders of magnitude in the total conductivity evidences the influence of film microstructure and composition. This work will focus on the study of the effect of deposition conditions on the structure and microstructure of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ thin films, obtained by pulsed laser deposition, in the search for possible implications in the protonic conductivity. This report contains an extensive study of the structural and microstructural characterization of the films, and complemented with the electrical conductivity of the materials and a comparison with recent literature.

## 2. Experimental

The films were grown by PLD using a Compex Pro 201 KrF excimer laser ($\lambda$ = 248 nm) at 1 Hz pulse repetition rate and laser fluence 1–2 J/cm$^2$. We ablated a target of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (thereafter referred as BZY) prepared by two different methods: Ni-free and Ni-containing bulk targets. A Ni-free target was prepared by Dr. Ricote at the Colorado Fuel Cell Center (USA) by sintering a disk pellet at 1670 °C of stoichiometric BZY powder in a bed of BZY with $BaCO_3$ to avoid Ba-evaporation, as reported in [13]. The density after sintering was ~85% and the diameter was 25 mm. A second target was prepared by Dr. Manerbino at CoorsTek Inc. (USA) by preparing a pellet using solid state reactive sintering with 1 wt% NiO at 1500 °C, as described in Ref. [14]. The density after sintering was > 98% and the diameter was 24 mm. In this case the Ni addition was intended for lowering the sintering temperature, expected to minimize Ba volatilisation and preserve the cation stoichiometry to a higher degree. The deposition was carried out in oxygen partial pressures from 10 to 380 mTorr, by using either pure $O_2$, or $O_2$/Ar mixtures. Substrate temperatures were varied from 600 to 800 °C, and the heating and cooling rate was 10 °C/min. Target to substrate distance was set to 57 mm. The thickness variation was achieved by varying the number of pulses from 100 up to 15,000 pulses. Unless stated otherwise, "standard" growth conditions are the following: 500 pulses, 100 mTorr (pure $O_2$), 700 °C and Ni-free target.

The substrates examined in this study comprise commercial single crystals of MgO (001), $GdScO_3$ (GSO) (110), $SrTiO_3$ (STO) (001), $NdGaO_3$ (NGO) (110), sapphire ($1\bar{1}02$)–also called r-cut sapphire- and $LaAlO_3$ (LAO) (012) which is equivalent to the pseudocubic (001) orientation, all purchased from CrysTec GmbH (Germany). The different substrates exhibit cubic or pseudocubic lattices with a wide range of cell parameters so that film growth and properties can be explored. Table 1 shows the relative mismatch between the BZY and the selected substrates.

After deposition, the films were analysed by X-ray diffraction (XRD) using a PANalytical X'PERT PRO MRD diffractometer. Standard 2θ-ω scans from 15 to 120° were performed using a Cu tube with a W/Si parabolic mirror (with Cu $K_{\alpha1}$ and $K_{\alpha2}$ radiations). High resolution 2θ-ω scans and reciprocal space mapping of different asymmetric H0L reflections were performed using a 2-crystal monochromator (2xGe220) for selected samples and peaks. The thickness of the films was determined by X-ray reflectometry (XRR), and the surface topography explored by atomic force microscopy (AFM) using a MFP-3D Asylum instrument in tapping mode.

Sample cross sections for transmission electron microscopy (TEM) were prepared using standard grinding, cutting and ion milling procedures. Samples were afterwards examined using a FEI Tecnai G$^2$ F20 with a field emission gun (FEG) high resolution and analytical TEM/STEM operated at 200 kV. Low- and high-angle annular dark field images were acquired using inner detector acceptance angle of around 15 and 95 mrad respectively.

The average chemical composition of selected thin film samples was analysed by wavelength dispersive X-ray spectroscopy (WDS) using a Cameca SX100 apparatus. The surface and sub-surface composition was characterised by parallel angle-resolved X-ray photoelectron spectroscopy (ARXPS) using a Thermo Scientific Thetaprobe spectrometer. Spectra were acquired at 16 angles evenly spread between 22° and 78° emission angle with respect to the surface normal. The spectra were obtained with monochromatic Al Kα radiation and using a combination of low energy electrons and $Ar^+$ ions for charge compensation. The spectra were referenced based on the position of the C 1s alkyl peak from adventitious carbon, set to 284.8 eV binding energy (BE). Data treatment was performed using the Thermo Scientific Avantage software (version 5.951). The required number of independent peak fitting components was determined using primary component analysis (PCA) before peak fitting itself was performed. The separation and intensity ratio of the spin orbit pairs was fixed to the values suggested by the software and the positions and peak widths were kept constant for all angles in each sample during the peak fitting.

Selected films were prepared for electrical measurements in a 2-point 4-wire setup using both in-plane (MgO substrate) and across-plane (conducting Nb-doped STO substrate) configurations. A thin layer of Pt was first deposited by PLD, followed by painting a thicker coating with Pt ink (reference 6926 from Metalor) and afterwards firing the film at 700 °C for 30 min. The conductivity was measured using an impedance spectrometer (Zahner Zennium electrochemical workstation) in a ProboStat™ measurement cell (NorECs, Norway). Impedance spectra were recorded in the 1 MHz to 0.1 Hz frequency range with an oscillation voltage of 50 mV in various atmospheres, including humidified/dried air, air/Ar ($pO_2$ = 500 ppm), and 5% $H_2$/Ar.

**Table 1**
Summary of the lattice mismatch between selected substrates and BZY. The in-plane lattice parameters of the substrates have been calculated from our measured XRD patterns. BZY cell parameter is chosen to be 4.2017 Å [16], at room temperature. The sign of the mismatch indicates whether the strain is compressive (−) or tensile (+).

| Substrate | In-plane parameter (Å) | Structure type | Mismatch (%) |
|---|---|---|---|
| r-Cut sapphire | 3.479 | Corundum | − 16.7 |
| LAO | 3.788 | Perovskite | − 9.8 |
| NGO | 3.867 | Perovskite | − 8.2 |
| STO | 3.905 | Perovskite | − 7.0 |
| GSO | 3.968 | Perovskite | − 5.5 |
| MgO | 4.205 | Rock-salt | + 0.2% |
| BZY | 4.2017 | Perovskite | – |

## 3. Results

### 3.1. Characterization of BZY films as a function of substrate type

Fig. 1 shows the XRD patterns obtained for the film deposited on various tested substrates at standard conditions (100 mTorr of pure $O_2$, 700 °C, Ni-free target), which serves to analyse the preferential growth direction. The most intense reflections correspond to the substrate, while the reflections corresponding to BZY (00L) are marked in the graph. This shows that all the substrates (except sapphire) induce a growth of pure perovskite BZY phase with a high preferential orientation with the c-axis perpendicular to the film surface. The BZY structure is oriented on the primitive pseudocubic structure of the substrate (see a zoomed-in graph in Supplementary material), regardless of their relative mismatch. The position of the BZY peaks ($2\theta_{(002)}$ = 43.0 ± 0.1°) is roughly independent of the substrate, which means that the films are essentially relaxed, and within the expected position for reported bulk values ($2\theta_{(002)}$ = 43.02°) [16]. In the case of MgO substrate, two different targets were used to test for a possible influence of the target characteristics to the film. There is no visible difference between the films from the XRD patterns (graph available as Supplementary material). The orientation of the film deposited on r-cut sapphire was determined by General Area Detector Diffraction System and concluded to be polycrystalline (see Supplementary material for further details). The