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Fabrication of yttrium-doped barium zirconate thin films with sub-micrometer thickness by a sol–gel spin coating method

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ABSTRACT

A modified sol–gel process was developed for the fabrication of sub-micrometer scale yttrium-doped barium zirconate (BZY) thin film at much lower processing temperatures. The film was fabricated by direct spin-coating of the sol on a Si_3N_4 passivated Si substrate, followed by low temperature thermal annealing at 1000 °C, and single BZY phase without barium carbonate residue was obtained. A 200 nm-thick thin film without obvious through-film cracks was fabricated with optimized process parameters of sol concentration and heating rate. The stoichiometry of the BZY thin film was well-controlled and no Ba evaporation was observed due to the low processing temperature. The combination of sol–gel and spin coating method can be a promising alternative to vacuum-based thin film deposition techniques for the fabrication of sub-micrometer scale BZY thin film.

1. Introduction

Proton conducting ceramics are regarded as promising electrolyte materials for low temperature solid oxide fuel cells (LT-SOFCs) due to their higher ionic conductivities and lower activation energy as compared to conventional oxygen-ion conducting electrolytes in the temperature range of 300–600 °C [1–3]. In this class of compounds, yttrium-doped barium zirconate (BZY) has attracted special attention because of its high bulk proton conductivity and excellent chemical stability [4–6]. The main drawback of BZY is its poor sinterability and large grain boundary resistance [7,8]. Therefore, in the conventional sintering process, very high heat treatment temperatures (ex., 1700 °C) are usually necessary to obtain a dense electrolyte layer. Such a high sintering temperature may lead to Ba evaporation, which is detrimental to its proton conduction. Previous research has found that Ba deficiency lowers the proton conductivity by 2 orders of magnitude in sintered pellets after high temperature sintering process [9].

Thin BZY electrolyte film is desirable for LT-SOFCs due to the reduced ohmic resistance. The most common fabrication methods are powder-based sintering, such as co-pressing [10,11] and slurry coating [12–14], but these techniques still require high sintering temperatures up to 1400 °C even by using sintering aids, and the resulted films produced are generally thicker than 10 μm to obtain pinhole-free and gas-tight electrolyte. Vacuum-based deposition techniques, such as pulsed laser deposition [15,16], atomic layer deposition [17,18], and co-sputtering [19] have been demonstrated to produce dense and high quality films in sub-micrometer to tens of nanometer scales. However, these techniques are costly and require sophisticated equipment set up, and the process is time consuming.

In this work, we demonstrated the deposition of sub-micrometer $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) thin films by an aqueous sol–gel route combined with a spin coating technique. The sol–gel method has advantages of cost effectiveness, easy control of the film composition, and lower processing temperature [20]. A systematic study was performed to investigate the process parameters including annealing temperature, sol concentration and heating rate, and the resulted phase and microstructure of the BZY thin films were characterized.

2. Experimental

2.1. Sample preparation

The BZY sol was prepared by an aqueous sol–gel synthesis route. $Ba(NO_3)_2$, $ZrO(NO_3) \cdot xH_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were used as starting salts. Citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were used as chelating agents. Stoichiometric amounts of nitrates were dissolved in deionized water, and CA and EDTA were added at a ratio of 1:0.5:1 to the total metal cations. NH_4OH was added to adjust the pH value to around 7 and produce a transparent solution. The solution was then heated at 70 °C under continuous stirring to evaporate the water. By stopping the evaporation at different points, sols for thin film deposition were obtained with different metal cation concentrations (0.5 M, 0.8 M, and 1.2 M). The remaining solution was stirred until it changed to a viscous gel. The gel was then dried in an oven at 200 °C for 3 h to produce the as-dried powders. The as-dried powders were annealed at 800 °C to 1000 °C for 2 h to investigate the temperature required for the BZY phase formation.

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A 500 μm thick Si(100) wafer with 200 nm thick Si_3N_4 coatings on both sides was used as the substrate for the deposition of film. Before deposition, the Si_3N_4/Si wafer was treated under O_2 plasma cleaning for 10 s to improve the adherence of the aqueous solution. The sol was dripped on the substrate and spun at a rate of 4000 rpm for 30 s using a G3-8 spin coater (SCS Specialty Coating Systems). The as-prepared films were dried in an oven at 150 °C for 20 min, and then annealed at 800 °C to 1000 °C in air atmosphere for 2 h with different heating rates (1 to 5 °C · min^{-1}) to obtain BZY thin films.

2.2. Characterization

The crystallinity and structural phases of the deposited films were characterized by X-ray diffraction (XRD) using a PANalytical Empyrean system. The XRD patterns were measured in the 2θ range of 20–80° with Cu Kα radiation. The microstructure of the thin film surface, cross-section and thickness were examined by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600 F, operating voltage 15 kV). The compositions of the BZY thin films were examined using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV/10 mA).

3. Results and discussion

3.1. BZY phase formation

3.1.1. Influence of annealing temperature

The XRD patterns of powders shown in Fig. 1(a) indicate the desired perovskite phase appeared at a temperature as low as 800 °C, but with small peaks that show the existence of barium carbonate residue. After annealing at 1000 °C for 2 h, all peaks corresponding to barium carbonate phases disappeared and a pure phase of BZY was obtained. The BZY films with a sol concentration of 0.8 M deposited on Si_3N_4/Si substrate (shown in Fig. 1(b)) exhibited the same trend as the powders. No additional peaks were observed in the XRD result, indicating that reaction between BZY film and substrate did not occur in this temperature range.

3.1.2. Influence of sol concentration

The effect of sol concentration on BZY phase formation was further studied. Fig. 2 shows XRD patterns of thin films deposited with sol concentrations of 0.5 M, 0.8 M and 1.2 M, all annealed at 1000 °C for 2 h. For the film deposited with a sol concentration of 0.5 M, no obvious diffraction peaks were detected. When sol concentration increased to 0.8 M, BZY phase formation was observed and for sol concentration of 1.2 M, the intensity of the diffraction peaks further increased. At a low concentration of 0.5 M, the large distance between the reacting species hindered the formation and growth of the network to form BZY. At a higher concentration up to 0.8 M, cross-linked network was formed and BZY crystalline phase appeared. The increase of the detected peak intensity with 1.2 M concentration can be attributed to the increase of the film thickness due to the higher sol viscosity [21]. Thus, sols with a concentration of 0.8 and 1.2 M were chosen for subsequent microstructure characterization and optimization.

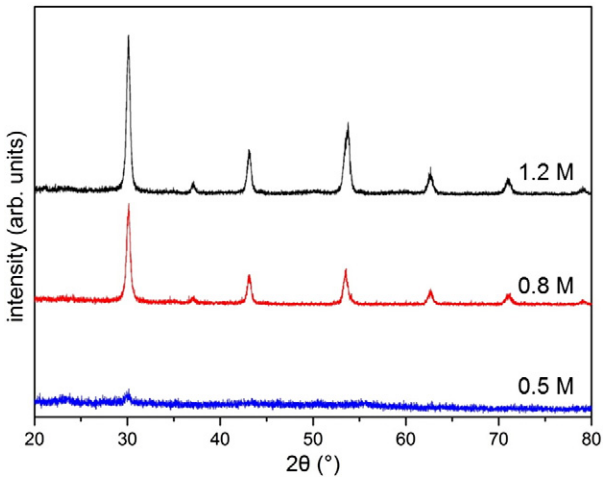

Fig. 2. XRD patterns of thin films deposited with sol concentrations of 0.5 M, 0.8 M and 1.2 M, annealed at 1000 °C for 2 h.

3.2. Thin film microstructure

3.2.1. Influence of sol concentration

Highly dense and pinhole-free thin film electrolyte is desirable for high open circuit voltages and stable cell performance during SOFC operation. Fig. 3 shows the SEM images of the surface and cross-section of BZY thin films deposited on Si_3N_4/Si substrate with sol concentrations of 0.8 M and 1.2 M, and annealed at 1000 °C for 2 h at a heating rate of 5 °C · min^{-1}. The film deposited from 0.8 M sol showed less surface cracks and better adhesion to the substrate. From cross-sectional SEM view, the film was about 200 nm thick, and no obvious through-film cracks or interconnected pores were observed. For the film deposited from 1.2 M sol, the film thickness increased to 400 nm, and through-film cracks were clearly observed. The formation of the cracks can be attributed to the large thermal stress between the BZY film and the Si_3N_4/Si substrate due to the difference in thermal expansion coefficients. Since the thicker films tend to be less tolerant to such a mismatch, 1.2 M film showed more evident cracks. Thus, the sol with a concentration of 0.8 M was selected for further experiments.

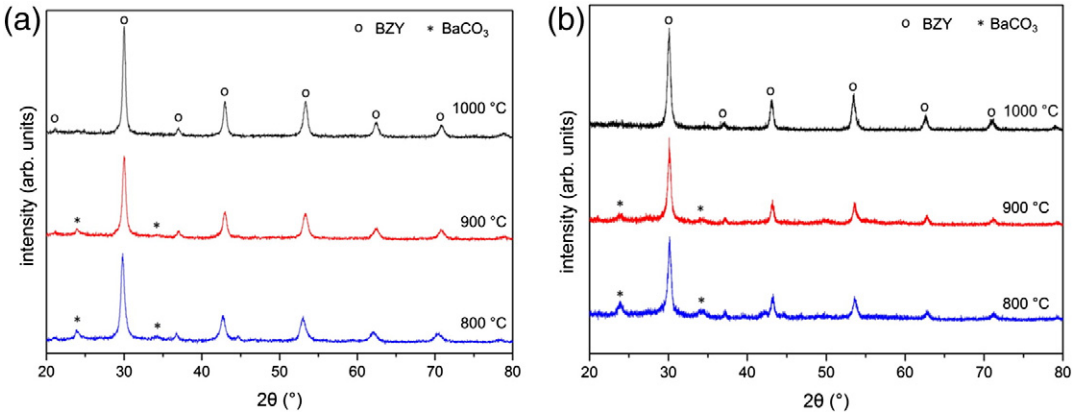

Fig. 1. XRD patterns of (a) powders and (b) thin films deposited with sol concentration of 0.8 M annealed at 800, 900, and 1000 °C for 2 h.