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Rapid thermal processing of chemical-solution-deposited yttrium-doped barium zirconate thin films

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ABSTRACT

In this paper, dense and crack-free yttrium-doped barium zirconate (BZY) thin films were fabricated by chemical solution deposition (CSD) with rapid thermal processing (RTP) at low sintering temperature. BZY thin film without barium carbonate phase was obtainable after annealing at 700 °C for 1 h, which represents the lowest temperature reported in the literature. X-ray reflectivity study showed that the relative density of resultant BZY thin film was approximately 90%, indicating the effective densification of BZY at low temperature sintering by RTP. Microstructural analysis of BZY thin film showed that the film was dense, smooth and homogenous without cracks or interconnected pores. Thus, CSD method combined with RTP is promising for the fabrication of BZY electrolyte thin film due to the low processing temperature and high quality of the obtained film.

1. Introduction

Proton-conducting ceramics such as acceptor-doped perovskite-type oxides are promising electrolyte materials for low-temperature solid oxide fuel cells (LT-SOFCs) [1]. Compared to conventional oxygen ion conducting electrolytes, proton-conducting electrolytes have lower activation energy for proton conduction and higher ionic conductivities at low temperature range (<600 °C) [1–3]. Yttrium-doped barium zirconate (BZY) has been the benchmark proton-conducting electrolyte material due to its high bulk conductivity and excellent chemical stability [1,4]. In order to further improve the performance of LT-SOFCs, sub-micrometer BZY electrolyte thin films are highly desirable for minimizing the ion transportation distance and decreasing the electrolyte resistance [5,6].

Several thin film techniques such as sputtering [7], pulsed laser deposition [8–11], atomic layer deposition [12] and chemical solution deposition (CSD) [13–16] have been employed to fabricate BZY electrolyte thin films. Among them, CSD methods have the advantages of simplicity, cost effectiveness, scalability and easy control of film composition [17,18]. However, CSD usually requires relatively high processing temperature and long sintering time (up to 1000 °C for 12 h) to densify the film for the utilization of electrolyte layer [16,19]. Under such condition, barium evaporation and interfacial reaction easily occur, which can deteriorate the properties of BZY film [20,21]. Therefore, alternative sintering strategies should be exploited to address these problems. Compared to conventional heating schedule, rapid thermal processing (RTP) can facilitate the densification process in a much shorter time, thus suppressing undesired reaction processes and resulting in dense microstructure [22,23]. With fast heating rate, nucleation and crystallization processes are delayed to a higher temperature, and densification processes are facilitated prior to the onset of crystallization [24].

In this work, we fabricated $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) thin films by CSD combined with RTP as the sintering schedule to densify the films. The heating processes were optimized to obtain crystallized and dense BZY film with smooth and homogenous surface structure. In addition, systematic studies were performed to investigate thin film crystallization, microstructure, and composition.

2. Experimental

2.1. Chemical solution preparation

Barium acetate, zirconate acetate in dilute acetic acid, and yttrium nitrate were used as precursors. *N*,*N*-dimethylformamide, water and ethanol were used as solvents. Acetylacetone was added as complexing agent. After mixing the precursors and solvents, a few drops of ammonium hydroxide were added to obtain transparent solution. More details on the solution preparation can be found in our previous work [15].

2.2. Thin film fabrication

Single crystal sapphire ((0001) orientation) wafers were used as substrates for BZY thin film deposition. The substrates were spin coated

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with chemical solution at the speed of 3000 rpm for 60 s using a Laurell spin-coater (Model WS-650). After that, the coated substrates were dried on a hot plate at 300 °C for 10 min to allow pyrolysis. Subsequently, the samples were rapidly sintered in a pre-heated tube furnace. Processing time and temperature were varied for parameter optimization. For comparison, conventional sintering with ramping rate of 10 °C/min was also carried out.

2.3. Thin film characterization

The crystallinity and structural phase of the deposited films were analyzed by Grazing incidence X-ray diffraction (GIXRD) method using a PANalytical Empyrean XRD system. The XRD patterns were measured in the 2θ range of 20–80° with a constant glancing incident angle at 1°. X-ray reflectivity (XRR) measurements were carried out using the same equipment to study the density of the films. Samples were scanned in the 2θ angle of 0.2–1.0°. The XRR results were analyzed by X'Pert Reflectivity software. The surface and cross-section morphologies of films were characterized using a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F). The composition of BZY thin film was 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

The effect of sintering schedule on thin film crystallization was studied by GIXRD. Fig. 1 presents the XRD patterns of BZY thin films sintered at 600–800 °C for various time periods with RTP. The film sintered at 600 °C only exhibited a broad (110) peak, indicating that an amorphous state was formed. The polycrystalline BZY phase was formed after sintering at 700 °C. The film presented clear perovskite BZY peaks, which agree well with the standard BZY PDF card 96-720-2180. However, an extra peak corresponding to ZrO_2 near BZY (211) peak was observed in the film sintered for 30 min due to insufficient reaction time. With longer sintering time of 1 h, film with pure BZY phase was obtained. Similar phenomenon was observed for the film sintered at 800 °C. Thus, dwelling time of 1 h is necessary to obtain pure BZY without secondary phase. It is worth noting that no intermediate $BaCO_3$ phase was detected for the RTP film. In comparison, as shown in Fig. 2, the film heated with conventional process had large amounts of intermediate $BaCO_3$ phase after sintering at 700 °C for 30 min. The $BaCO_3$ phase still cannot be completely decomposed even after sintering for longer time of 1 h or higher temperature of 800 °C for 30 min. Pure BZY phase was formed after sintering at 800 °C for 1 h by conventional heating process. A possible explanation is provided as follows. In conventional heating process, it is easy for $BaCO_3$ formation at the temperature range from 600 to 700 °C, which can be observed from the XRD patterns in Fig. 2. In contrast, when the film was sintered with RTP, the sintering temperature directly reaches 700 °C where BZY crystallization dominates. Therefore, $BaCO_3$ could be effectively avoided due to a much shorter time in the temperature range favoring $BaCO_3$ formation (600–700 °C). Moreover, the formed $BaCO_3$ may quickly react and convert to perovskite BZY phase [25]. In this way, sintering with RTP can yield pure perovskite BZY phase at low temperature of 700 °C.

In order to analyze the densification behavior of the BZY thin films sintered with RTP, XRR method was employed. Fig. 3 shows typical experimental XRR curves for the BZY thin films after one-layer spin coating and subsequent sintering at 700 °C and 800 °C for 1 h with RTP. The XRR results showed that the BZY films had a thickness around 40 nm and a surface roughness about 1–2 nm after one-layer deposition. The relative densities were 90% and 93% for thin films sintered at 700 °C and 800 °C, respectively. The results indicated that RTP could be an effective way to densify BZY thin film in a short time. The rapid removal of solvent and retardation of crystallization to high temperature

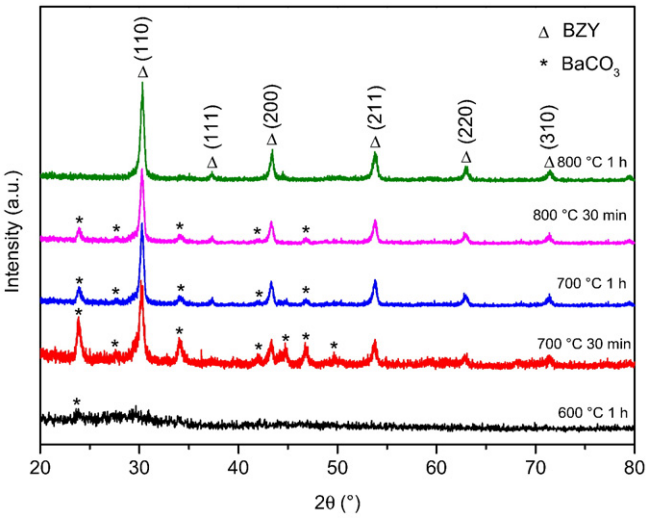

Fig. 2. XRD patterns of BZY thin films sintered at 600–800 °C for various time by conventional heating process.

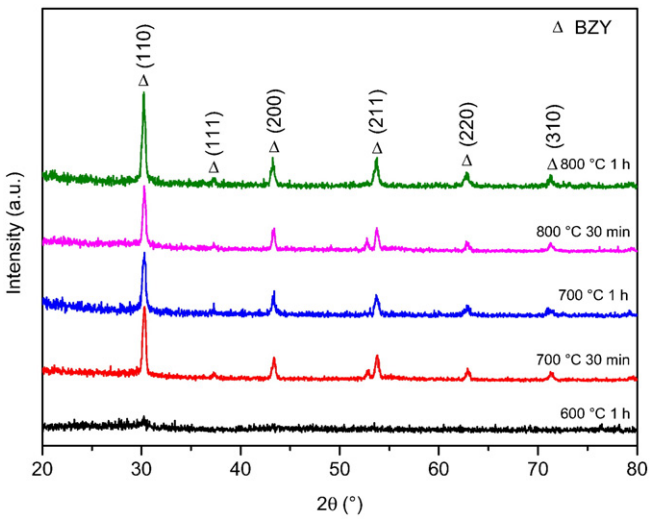

Fig. 1. XRD patterns of BZY thin films sintered at 600–800 °C for various time with RTP.

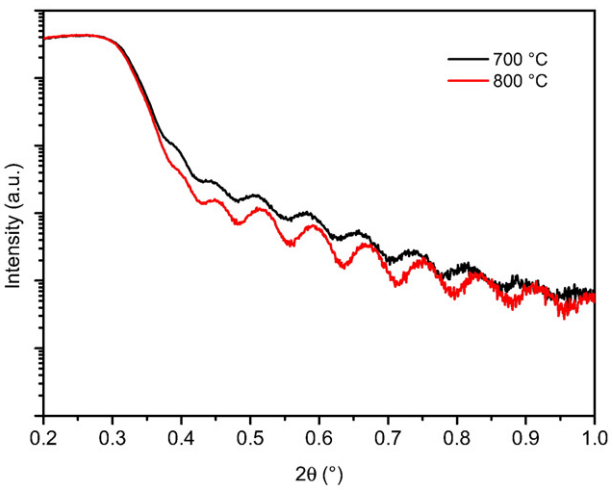

Fig. 3. Typical XRR curves of thin films sintered at 700 °C and 800 °C for 1 h with RTP.