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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 hour, 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.

Keywords: rapid thermal processing; chemical solution deposition; yttrium-doped barium zirconate; solid oxide fuel cell; proton-conducting electrolyte.

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 hours) 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 $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (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 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 minutes 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 K α (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. Figure 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 ZrO₂ near BZY (211) peak was observed in the film sintered for 30 minutes due to insufficient reaction time. With longer

1 sintering time of 1 hour, film with pure BZY phase was obtained. Similar phenomenon was
2 observed for the film sintered at 800 °C. Thus, dwelling time of 1 hour is necessary to obtain
3 pure BZY without secondary phase. It is worth noting that no intermediate BaCO₃ phase was
4 detected for the RTP film. In comparison, as shown in Figure 2, the film heated with
5 conventional process had large amounts of intermediate BaCO₃ phase after sintering at 700 °C
6 for 30 minutes. The BaCO₃ phase still cannot be completely decomposed even after sintering for
7 longer time of 1 hour or higher temperature of 800 °C for 30 minutes. Pure BZY phase **was**
8 **formed** after sintering at 800 °C for 1 hour by conventional heating process. A possible
9 explanation is provided as follows. In conventional heating process, it is easy for BaCO₃
10 formation at the temperature range from 600 to 700 °C, which **can be** observed from the XRD
11 patterns in Figure 2. In contrast, when the film was sintered with RTP, the sintering temperature
12 directly reaches 700 °C where BZY crystallization dominates. Therefore, BaCO₃ could be
13 effectively avoided due to a much shorter time in the temperature range favoring BaCO₃
14 formation (600-700 °C). Moreover, the formed BaCO₃ may quickly react and convert to
15 perovskite BZY phase [25]. In this way, sintering with RTP can yield pure perovskite BZY
16 phase at low temperature of 700 °C.

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

retardation of crystallization to high temperature can facilitate the densification process at lower temperature, compared to other heating methods [17].

To study the relationship between microstructure and sintering temperature, the morphologies of BZY films sintered at different temperatures were observed. The studied films had a thickness around 160 nm with four-layer coating. Figure 4 (a) and (d) show SEM surface micrographs of films sintered at 700 °C and 800 °C at low magnification. Both films exhibited smooth surface morphologies without severe surface cracks, but the film sintered at 800 °C showed relatively inhomogeneous structure compared to the film sintered at 700 °C. Figure 4 (b) and (e) present high magnification SEM surface images of the sintered films. The film sintered at 700 °C had smooth microstructure and uniform grain distribution with the grain size around 20 nm. In contrast, the film sintered at a higher temperature of 800 °C was observed to have grain agglomeration and small size crack defects due to the larger thermal stress. The cross-sectional SEM images in Figure (c) and (f) indicate that both films sintered at 700 °C and 800 °C were dense without through-film cracks or interconnected pores. However, the non-uniform surface and crack defects of the film sintered at 800 °C may lead to gas leakage for the nanoscale electrolyte thin film. The film sintered at 700 °C with RTP is more desirable for electrolyte film application. Even though the one-layer coating film has a relative density of 90% determined by XRR, the thicker film after four-layer coating shows dense structure without interconnected pores, as a consequence, it may exhibit more chance to guarantee good gas tightness as electrolyte film [26, 27].

Subsequently, the composition of BZY film sintered with RTP at 700 °C for 1 hour was analyzed by XPS. From the XPS survey spectra (Figure 5 (a)), it was determined that the atomic

composition of BZY film was Ba 19.01%, Zr 14.28%, Y 4.03%, O 62.68%, which is close to the nominal value. Besides, there was no impure element detected in the film. The results showed that the low processing temperature and short heating time can maintain the composition and suppress Ba evaporation. Furthermore, the absence of BaCO₃ phase was confirmed by the narrow scan of Ba3d presented in Figure 5 (b). The Ba3d peaks showed a symmetrical nature and only one group of peaks was detected. The peak at 777.9 eV was identified as signals from Ba-O bonds [28], which is associated with perovskite BaZrO₃. No signal corresponding to BaCO₃ at higher binding energy of 779.4 eV was found, indicating the absence of BaCO₃ in the film.

4. Conclusions

Dense, homogenous and crack-free BZY thin films have been successfully fabricated by CSD method combined with RTP as sintering schedule. Crystallized BZY film without BaCO₃ impurity was obtained at the low processing temperature of 700 °C for 1 hour with well-controlled composition. To the best of the authors' knowledge, 700 °C is lower than the reported temperatures for BZY thin film fabricated by CSD. Therefore, the combination of CSD method and RTP can be a promising alternative to vacuum-based thin film deposition techniques for the fabrication of nanoscale BZY thin film. In future work, thin film conductivity measurement and fuel cell fabrication will be carried out to validate the application of the film as electrolyte for LT-SOFCs.

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3 **Figure 2.** XRD patterns of BZY thin films sintered at 600-800 °C for various time by
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5 **Figure 3.** Typical XRR curves of thin films sintered at 700 °C and 800 °C for 1 hour with RTP.

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7 at different temperatures of (a, b, c) 700 °C and (d, e, f) 800 °C.

8 **Figure 5.** XPS spectra of BZY thin film (a) survey spectra and (b) narrow-scan of Ba3d.

Figure 1
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