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Low Temperature Synthesis of Sub-micrometer Yttria-doped Barium Zirconate Thin Films by Modified Chemical Solution Deposition Technique

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Yttria-doped barium zirconate (BZY) electrolyte films with sub-micrometer thickness were prepared using a modified chemical solution deposition (CSD) technique at very low sintering temperature of 800°C without sintering aid. Pure perovskite BZY phase without barium carbonate associated with low calcination temperature was successfully obtained with no obvious barium (Ba) evaporation to deviate the stoichiometry composition. This cost effective and scalable method for BYZ, as compared to the other reported vacuum-based thin film deposition techniques such as pulsed laser deposition (PLD) or atomic layer deposition (ALD), is potentially applicable in the fabrication of high quality electrolyte for nano-thin film micro solid oxide fuel cells operating at temperature below 500°C.

Introduction

Solid oxide fuel cells (SOFCs) are known for their efficient electrochemical energy conversion process. The typical operating temperature of SOFCs is well above 750°C, which has confined the selection of materials and imposed difficulties such as long start-up time and poor durability of materials. Currently, the focus of research has been on the low to intermediate temperature SOFC (400-700°C) in order to address the issues caused by the high operating temperature .

In the attempt to reduce the operating temperatures, the primary issues to be addressed are the high electrolyte Ohmic resistance and slow electrode polarization (1). This is because both the ion conduction through ceramic oxide electrolytes and the electrochemical reactions occurring at the electrodes are thermally activated processes. To lower the Ohmic resistance of the electrolytes, one can either to decrease its thickness or use alternative electrolyte materials with better ionic conductivity in the lower temperature range. In search of alternate electrolyte materials, proton conducting ceramics, specifically perovskite oxides, have drawn ever growing attention in the past decades (2). These materials show proton conduction upon exposure to hydrogen and/or water vapor by Grotthus mechanism with low activation energy (0.45-0.65 eV) compared to oxygen ionic conductors (2), and can be suitable for application at low to intermediate temperatures. Another advantage of using proton-conducting electrolyte is that the water generation is on the cathode side which avoids fuel dilution at the anode side.

The state-of-the-art proton conducting ceramic electrolytes are yttria-doped barium cerate (BCY) and yttria-doped barium zirconia (BZY). Although BCY shows the highest protonic conductivity, it decomposes to barium carbonate (BaCO_3) and ceria (CeO_2) in

carbon dioxide (CO₂)-containing atmosphere and therefore has poor chemical stability (3). On the other hand, BZY is known for its better chemical stability under operating condition with satisfactory protonic conductivity (1×10^{-2} S/cm at 450°C) (4). The issue for fabrication of BZY is the poor sinterability that requires very high sintering temperature to ensure a dense and gas-tight electrolyte. As per the literature report, the least sintering temperature for BZY is 1400 °C with spark plasma sintering without addition of sintering aid (5). Even through with the use of sintering aids such as copper oxide, zinc oxide, lithium nitrate, the lowest reported sintering temperature was still at 1325°C (6-8). The major impediments to the fabrication of BZY electrolyte are the deviation of stoichiometry due to Ba evaporation at high sintering temperature, as well as the presence of BaCO₃ second phase during sintering. Although the sintering aid reduces the sintering temperature, its presence also deteriorates the conductivity of BZY due to formation of the second phase and/or segregation at the grain boundaries.

In order to deal with these issues, we have developed a method based on a modified chemical solution deposition (CSD) technique for fabrication of BYZ thin films, which allows the formation of pure phase BZY films at very low sintering temperature of 800°C without sintering aid. CSD is known for capable of the formation of both amorphous and crystalline film (9) and is able to synthesize dense and sub-micrometer thickness film. This process employs several organic materials with their special properties to achieve desired film thickness without defects. Presently various thin film deposition techniques such as ALD, PLD are employed to fabricate thin film electrolyte for micro-SOFCs for the application in low-to-intermediate temperature range. These techniques need sophisticated infrastructure creating significant obstacles to the technological application, up-scalability and commercialization. On the other hand, CSD technique requires simple arrangement for processing. Therefore, this technique is reliable for the commercialization of micro-SOFC.

We have deposited a dense 320 nm-thick BZY film on a silicon substrate without formation of undesirable BaCO₃ phase. The highest processing temperature of 800 °C was the lowest ever reported temperature without use of sintering aid.

Experimental

Preparation of Chemical Solution for BZY

The flow chart for the preparation of BZY solution is presented in Figure 1. Y-nitrate and Zr-acetate were first mixed stoichiometrically to formulate the Y-Zr composite solution, followed by addition of distilled water, ethanol, acetylacetone, and N,N-dimethylformamide (DMF). In a separate beaker, Ba-acetate was dissolved in acetic acid at 110°C. These two solutions were then mixed together and became turbid after mixing. Transparent solution was obtained with the addition of few drops of ammonium hydroxide; pH of the solution was adjusted to 4. The cation concentration of the solution was 0.625 M.

Deposition of BZY Solution and Sintering

Silicon (100) wafer was used as a supporting substrate for the deposition of BZY thin films. The silicon substrate surface was cleaned with acetone, isopropanol and water, and

then spin coated with the BZY solution at the speed of 3000 rpm for 30 seconds in air atmosphere. The coated substrate was placed on a hot plate to bake at 450°C for 5 minutes. The procedure of coating followed by baking was repeated for 6 times to form one layer of BYZ film. After baking, the film was placed in a box furnace at 450 °C and heated up at 10°C/min to 700°C for 30 minutes, followed by heating to 800°C for 2 hours for sintering. After sintering, the film was cooled to room temperature at a rate of 10°C/min.

Figure 1. Flow chart of solution preparation.

Characterizations of Solution and Sintered Films

The stability of the solution was characterized by Fourier transformed infrared (FTIR) spectroscopy in transmittance mode in the range of 4000 to 500 cm^{-1} at room temperature. The weight loss characteristic of the solution was determined through thermogravimetric analysis (TGA, TA Instruments Q500 Thermogravimetric Analyzer) in the temperature range of 20 to 800°C with a heating rate of 10°C/min in air atmosphere. The crystallinity of the sintered film was characterized by x-ray diffraction (XRD, PANalytical Empyrean system) in the 2θ range of 20-80° using $\text{CuK}\alpha$ radiation with a step size of 0.01°. The microstructure of the sintered films was observed by field-emission scanning electron microscope (FESEM, (FE-SEM, JEOL JSM-7600 F, operating voltage 15 kV).

Results and Discussion

Optimization of BZY Solution

One of the challenges to deposit sub-micrometer BYZ film with CSD is to ensure good adhesion between the film and the substrate, which depends on the good wetting of

the solution with substrate. Therefore, the wettability of the BZY solution was optimized with non-aqueous solvents. The primary solvent of this solution is was acetic acid which has surface tension of 25.71 mN/m at 30°C (10). In the mixed solution, the presence of water was necessary to ensure complete dissolution of Y-nitrate and to facilitate network formation through partial hydrolysis. However, since the surface tension of water is 71.21 mN/m (11) at 30°C, which is too high to wet the silicon substrate, we added ethanol which has lower surface tension of 21.41 mN/m at 30°C (10) to the solution. The ratio of water and ethanol was maintained in such a way that the mixture gives similar value of surface tension with that of acetic acid. Another purpose of addition of ethanol was to facilitate hydrolysis.

Figure 2. FTIR spectra of the fresh solution and 2 months old solution.

A film with good wetting characteristic may get disrupted due to the stress generated during solvent evaporation with heat treatment. The film after deposition acts like a viscoelastic solid which entraps solvent in the pores of the network of inorganic cations along with organic moieties. As the solvent evaporates, capillary contraction occurs and generates high capillary pressure, causing differential pressure in the whole network. To reduce this pressure make it uniform throughout the network, DMF as drying control chemical agent (DCCA) was used to help in increasing the pore radius within the network of the cations, thereby decreasing the stress (12). Acetylacetone has been added as chelating agent to form good network of cations.

In order to maintain the stability of the solution over time, the pH value of the solution was adjusted to 4 by adding ammonium hydroxide. Without pH adjustment, the solution cannot be stable for more than 3 to 4 hours. The stability of the solution was confirmed by taking FTIR spectrum for the fresh solution and 2 month after it was formulated. As presented in Figure 2, both the functional group region and the finger print region remained unchanged, meaning the solution remained stable after formulated for 2 months.

Selection of Processing Temperature

In order to identify the lowest processing temperatures required for high quality BYZ thin films, the mass loss of the organic substances in the solution with temperature was characterized via TGA. As shown in Figure 3, the major mass loss occurred around 83°C, which is close to the boiling point (78.37°C) of ethanol. The boiling temperatures for other organics in the solution are 153, 118 and 140°C for DMF, acetic acid, and acetylacetone, respectively. Therefore, these substances along with water might have evaporated. The total weight loss up to 153°C is 68.2%, which means most of the organics in the solution have been evaporated. Another temperature where a good amount of weight loss occurred was 330°C; here the amount of weight loss is 6.70%. This temperature is high enough for condensation reaction, and the organics and water generated due to condensation reaction are expected to be removed. Above 330°C, no significant weight loss was observed up to 800°C. Therefore, any temperature between 330 and 800°C can be chosen for partial removal of organic substances and occurrence of partial pyrolysis. Since the complete crystallization of the film may cause grain growth commonly occurring at low temperature leading to the island formation of solids instead of formation of film, the complete removal of organic matters is not desirable. In order to delay complete crystallization of the film, we purposefully bake the spin-coated solution directly at 450°C for only 5 minutes to allow partial pyrolysis keeping some organic in the film; the purpose is to keep the film in the disordered state, i.e., in the amorphous stage.

Figure 3. Mass loss profile of the solution to determine processing temperature.

The temperature range of 450-700°C is generally attributed to condensation, structural rearrangement and crystallization (13). At this stage formation of islands on the substrate is obvious if heating rate is not judiciously controlled. Basically the island formation in solid state occurs due to surface diffusion and evaporation-condensation method at low temperature; these two methods have lower activation energy, compared to volume diffusion, at lower temperature. These processes facilitate grain growth and

modification of grain growth instead of movement of particle centres; therefore density of the film does not improve. At higher temperature volume diffusion predominates over surface diffusion, thereby leading to densification (14). The relative temperature range for all the processes varies due to the nature (i.e., grain size, amorphous or crystalline, composition, impurity, etc.) of the particular materials. The fast heating rate suppresses the low temperature processes. Therefore, fast heating rate directly initiates high temperature processes which lead to densification of the film. In the present study, we maintained a heating rate of $10^{\circ}\text{C}/\text{minute}$ to suppress the low temperature processes; normally this much slow heating rate produces crystal in this temperature range (15). The presence of organics also helps to suppress low temperature processes.

In order to obtain the lowest possible sintering temperature, the film was sintered at various temperatures above 450°C . Experiment results showed the film sintered at 800°C did not have unwanted BaCO_3 phase and any residual carbonaceous materials. Therefore 800°C was chosen as final sintering temperature. The outcome of the films sintered at these two temperatures is discussed in the next section.

Microstructure and Crystallinity of Sintered BZY Thin Film

Figure 4 shows the microstructure and XRD result for BYZ film sintered at 700°C for 30 minutes. The XRD result showed the retention of amorphous phase along with BaCO_3 , and undesirable phase was observed on the surface of the BYZ. Both the cross sectional and surface images showed that the film was not fully sintered. Figure 5 shows SEM images and XRD profile of the film sintered at higher temperature of 800°C for 2 h.

Figure 4. Thin film heat treated at 700°C for 30 minutes (a) Cross-sectional SEM image, (b) surface SEM image, and (c) XRD pattern.

XRD patterns showed good crystallinity of BYZ without the presence of BaCO_3 , and the SEM images showed the film was dense and sintered without cracks or defects. It is likely the retention of amorphous phase have helped in sintering at this low temperature, as well as the dissociation of BaCO_3 to BaO may have initiated reactive sintering to assist the formation of a dense film. No delamination was observed, indicating a good adhesion with the substrate was also obtained.

Figure 5. Thin film heat treated at 700°C for 30 minutes followed by 800°C for 2 hours. (a) Cross-sectional SEM image, (b) surface SEM image, and (c) XRD pattern.

Conclusion

Thin film of BZY electrolyte materials has been successfully fabricated via modified CSD process with carefully controlled temperature profile for sintering. A dense, crack-free sub-micrometer BYZ thin film was successfully obtained. The addition of several organic compounds with their significant properties allowed the formation of a stable solution. The FTIR result revealed that the solution is stable for at least 2 months. TGA study has successfully provided the information for selection of proper heat treatment profile by a partial pyrolysis at 450°C, followed by sintering at 800°C for 2 hours. The resulted film showed no presence BaCO_3 and exhibited good crystallinity, where the 800°C sintering temperature is the lowest ever reported. As compared to the sophisticated vacuum-based thin film deposition process such as ALD or PLD that are often used for electrolyte fabrication for silicon-based micro-SOFCs, this process can be potentially low cost and more scalable one, which can facilitate the commercialization of such devices.

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