



공학석사학위논문

A study on electrochemical properties of yttrium doped barium zirconate electrolyte by pulsed laser deposition for thin film solid oxide fuel cell

펄스 레이저 증착법으로 제작한 이트륨이 도핑된 바륨 지르코네이트를 전해질로 하는 박막 고체산화물 연료전지의 전기화학적 특성 분석

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Abstract

This paper researches the optimum deposition condition of yttrium-doped barium zirconate (BZY) through a change in the parameters of pulsed laser deposition (PLD) such as oxygen partial pressure in chamber, substrate temperature, target-substrate distance, laser power by conducting an analysis of the structural and morphological properties of BZY thin films. As the oxygen partial pressure and target-substrate distance increase, the BZY thin films show a tendency to be porous. has porous structure. If the substrate temperature increases, the crystallinity of thin films increases. Also, PLD has optimum target-substrate distance that deposition rate is set to maximum by changing oxygen partial pressure and laser power. From these data, thin film solid oxide fuel cells (SOFCs) that have variety of thickness in BZY electrolyte are fabricated by PLD and sputter. As thickness of BZY increases, the performance of cell increases because the root-mean-square (RMS) roughness that influences the activation of electrochemical reaction increases.

Keywords : Pulsed Laser Deposition(PLD), Yttrium-doped barium zirconate(BZY), thin film solid oxide fuel cells, proton conductor, electrochemical properties.

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1. Introduction

1.1 Background

Renewable energy sources have taken the center stage as an alternative to fossil fuel because pollutants associated with renewable energy sources can be minimized and the resources are not limited in the way that fossil fuels are. Of renewable energy sources, fuel cells are widely thought as the best energy because of their high conversion efficiency and stable output [1]. Of all types of fuel cells, solid oxide fuel cells (SOFC) technologies have received much attention during recent decades as the next-generation of power sources because it has high efficiency, high volumetric energy density, high specific power and superior fuel flexibility [2-5]. For all such applications of conventional SOFC, however, the operating temperature must be 700°C or above. Therefore, SOFCs need a long start-up time and have severe restrictions on the scope of application, requiring bulky thermal shielding and material stability [6,7]. A lower operating temperature would allow a greater flexibility in the choice of materials, compact stack design and superior start-stop capabilities. In order to achieve a reduction in the operating temperature, the following researches have been conducted: (1) decreasing the thickness of the electrolyte (2) developing alternative electrolyte materials with high ionic conductivity [8]. First, research on SOFCs which use a thin film electrolyte for reducing the ohmic resistance has been conducted [9]. If the thickness of the electrolyte is small, the degradation in the performance SOFC resulting from ohmic loss can be compensated [10]. Kerman et al. reported that thin film SOFC is capable of delivering higher power densities at a lower temperature (<50 0°C), measuring $1.037 \text{W/cm}^2 \text{at} 500$ °C [11]. Actually, research has shown that the performance of SOFC is sensitive to the electrolyte's thickness [12-14]. Second, hydrogen ion conductor (proton conductor) has received much attention as next-generation electrolyte material. To operate a thin film SOFC at a low temperature, an electrolyte conducting hydrogen ion (proton conductor) is helpful to use as the electrolyte of low temperature thin film SOFCs as compare with a conventional oxygen-ion conducting electrolyte. The performance of a SOFC using an oxygen ion conductor can be reduced under operation and the selection of different composition elements is restricted due to the high-temperature operation.[15] In contrast, SOFCs based on proton conductor offer several advantages. First, the lower activation energy for proton than for oxygen ion transport implies that the ionic conductivity of proton conductors is independent to the temperature. This characteristic of proton conductors potentially exhibits higher ionic conductivities at intermediate or low temperatures. Second, the fuel will not be diluted during the operation of the fuel cell because the water is produced not on the fuel side but the cathode compartment of the SOFCs.[16,17]

The recent research on proton conductor demonstrated that a solid electrolyte composed of ABO₃-type perovskite material has

better hydrogen ion conductivity than any other electrolyte.[18] Among the ABO₃-type perovskite materials, acceptor-doped perovskites of the general formula of ABO₃. such as yttrium-doped barium cerate (Y-doped BaCeO₃, BCY), and yttrium-doped barium zirconate (Y-doped BaZrO₃, BZY) are known as next-generation proton-conducting electrolytes due to their high levels of ionic conductivity. In reality, barium affiliated perovskite proton conductor has high conductivity at low temperature as shown in figure 1.1. BCY, known as one of the most promising materials among proton conductors due to its low internal resistance, has been shown to decompose into barium carbonate and ceria upon exposure to carbon dioxide at high temperature.[19] On the other hand, BZY has sufficient chemical stability due to its low reactivity with carbon dioxide, even if the internal resistance is higher than that of BCY.[20] Shim et al. fabricated freestanding fuel cells employing a few tens of nanometers thick BYZ electrolytes deposited by both atomic layer deposition and pulsed laser deposition (PLD) techniques on micromachined silicon substrates [21]. Kang et al. investigated a porous anodic alumina oxide (AAO) based thin film fuel cell with BYZ electrolyte membrane and non-porous Pd anode [22]. Kim et al. produced and assessed the 3-D crater patterned fuel cell architecture with BYZ electrolyte deposited by PLD, using the nonlithographic nanospherical patterning (NSP) method [23].



Figure 1.1. Proton conductivities of various oxides as calculated from data on proton concentrations and mobilities [20]

1.2 Pulsed Laser Deposition (PLD)

Pulsed Laser Deposition (PLD), one of the physical vapor deposition (PVD), has become a standard technique for the production of thin films of complicated stoichiometry or sandwich structure.[24,25] The principle of PLD is as shown in the figure A target in a vacuum chamber is irradiated by laser with 1.2. nanosecond pulses that can remove the material particles from target. The removal of material during high intensity laser irradiation leads to the formation of a plasma called plume. This plume expands in a flow perpendicular to the surface and is collected on a suitable substrate in a holder system. PLD has many advantages. First, thin films of complex stoichiometry can be produced from a bulk target of almost same stoichiometry. Second, the chemical properties of thin films can be controlled by changing the composition of gas in the PLD chamber, substrate temperature and type of substrate. Also, the number of particles arriving at the substrate can be controlled precisely with the number of pulses and the laser fluence. The variation of choosing the experimental condition means that PLD offers a high flexibility to produce the various type of thin films. Finally, PLD has cost-effectiveness. Many PLD chamber can be used by single laser source by controlling laser path with reflector.[26]



Figure 1.2 The scheme of PLD mechanism

1.3 Objective of the present study

The primary purpose of this study is to investigate the effects of the parameters associated with pulsed laser deposition such as oxygen partial pressure in chamber, substrate temperature, target-substrate distance, laser power and frequency in terms of surface and cross-sectional morphology, crystallinity and composition. From this data obtained, the optimum PLD condition of BZY thin film can be obtained. Also, the variety of thickness in BZY electrolyte was acquired by carrying the PLD process time. Thin film SOFCs with different electrolyte thicknesses marked a difference in terms of open circuit voltage (OCV) and performance behavior.

2. Experimental

2.1 Preparation of the thin films

BZY thin films were fabricated by a pulsed laser deposition technique. A vacuum chamber (Korea Vacuum Tech. Ltd) which includes a turbomolecular and rotary pump was utilized. These pumps can create a chamber pressure of 10^{-5} bar (high vacuum). A silicon wafer chip (1cm × 1cm) was attached onto the substrate using silver paste (Pyro-Duct 597-A, Aremco Products Inc.). BZY thin film was deposited onto the silicon wafer. A sintered BaZr_{0.8}Y_{0.2}O₃₋₆pellet (Part #: PS-TBaZr301-33AE, Praxair Inc.) was used as a target. Thin films were grown using a 248 nm KrF excimer laser (Lambda Physik, Germany). The laser was operated at a repetition rate of 6 Hz and a fluence of 1, 1.5, 2 and 2.5 J/cm². The oxygen partial pressure in the PLD chamber was 0.013 bar (10 mTorr), 0.13bar (100mtorr) and 0.26bar (200mtorr). And the substrate temperature was varied between 2 5° and 600° . The deposition time is 30 minutes for all of BZY thin films. The heating rate and cooling rate of the substrate were 30 $^{\circ}C/min$ and -10 $^{\circ}C/min$, respectively so as to minimize the structural and distinguishing change of the deposited thin film when heating and cooling. The TSD was varied in the range of 4-6 cm (at an interval of 0.5 cm). In order to achieve a uniform thickness distribution of the deposited thin films and minimize damage to the target, rotation of the target and scanning of the laser beam along the target diameter were applied.

2.2 Characterization techniques

Symmetric Θ -2 Θ diffraction measurements were performed on BZY thin films by means of X-ray diffractometer (XRD: PANalytical, Netherland). The scan range at 2 Θ was 20°- 80° and the radiation used was Cu Ka. A morphological analysis of the samples was performed using a field emission scanning electron microscope (FESEM: Carl Zeiss Supra 40, Germany). Before using the FESEM, Pt sputtering (5nm thickness) on the sample surface was conducted to improve the electrical conductivity of the surface of the sample and to obtain a clear image of the sample surface. The deposition rate and cross-sectional morphology were analyzed using a focused ion beam (FIB: Quanta 3D FEG, Netherland). After Pt deposition onto the sample surface, a hole 8 μ m \times 1 μ m \times 0.3 μ m in size was made to investigate the cross-section. A root-mean-square (RMS) roughness analysis was conducted using scanning probe microscope (SPM: Seiko instrument SPA-400, Japan). The composition of the BYZ film was analyzed under the X-ray photoelectron microscope (XPS; KRATOS AXIS-His, Japan).

2.3 Cell fabrication and analysis of electrochemical properties

Every BYZ thin film was deposited by the PLD process. A 248nm KrF excimer laser (Lambda Physik) with the energy density of 1.5J/cm² per pulse was used to ablate the target with pulse frequency of 6Hz in a 20mTorr O₂ atmosphere. The substrate temperature was set to 600 °C during deposition and the heating/cooling temperature rate were +30 °C/min and -10 °C/min, respectively. The target-to-substrate distance was set as 6cm. The thickness of electrolyte was varied from 930nm to 1340nm by controlling the deposition time. The deposition rate was approximately 0.16~0.17 Å/pulse. Prior to making a single fuel cell stack, BYZ thin film was deposited on the silicon (100) wafer as in the condition mentioned above.

AAO based cells were fabricated to measure the performance level. The performance test set up scheme and the fabricated cell image are each shown in figure 2.1. (a) and (b). A dense Pt anode was deposited on the AAO (Synkera Technology Inc.) substrate of 1cm X 1cm area and of 100µm thickness with 80nm pores by DC sputtering of 200W power at 5mTorr Ar and room temperature. The thickness of the anode was approximately 300nm. On this anode laver, BYZ electrolyte membrane is formed with various thicknesses, in accordance with the above-mentioned PLD process conditions. The surface area of the BYZ electrolyte was adjusted to 8mm X 8mm through a mask. The porous Pt cathode was sputtered on the BYZ electrolyte with 100W DC-power under 90mTorr Ar and room temperature. The cathode of 1mm² active area was patterned through a shadow mask with 9square holes. Electric contact between the anode and the custom-made metal ring was generated by using silver paste, while the cathodic current was collected via a micro-probe. Ceramic adhesive (Aremco Products Inc., CP4010) was used to prevent leakage of the hydrogen toward the cathode.

The cell test method is shown in figure 1. The dry hydrogen of 20sccm was supplied to the anode side while the cathode was exposed to atmospheric environment for air-breathing. Potentiodynamic polarization and alternating current (AC) impedance were measured by using the electrochemical testing system (Solatron Analytical, 1260/1287).



Figure 2.1. The scheme of cell test set-up

3. Results and discussion

3.1 Substrate temperature and oxygen partial pressure in chamber

Control factors in order to analyze the effect of oxygen partial pressure and substrate distance are target-substrate distance (5cm), laser fluence (1.5J/cm^2) and frequency(6Hz)

3.1.1 Surface and cross-sectional morphology

Surface and cross-sectional morphology of BZY thin film deposited in different substrate temperature and oxygen partial pressure is shown in figure 3.1 and figure 3.2. Control factors when fabricating BZY thin films are target-substrate distance (5cm), laser fluence (1.5J/cm²) and frequency (6Hz). Figure 3.1 and figure 3.2 show that the structure of BZY thin film is set to be porous if oxygen partial pressure increases. This phenomenon implies that the number of oxygen molecules between the target and substrate is a critical factor related to the growth of the thin film. Due to the increase in the number of oxygen molecules between the target and the substrate as the oxygen partial pressure increases, the collisions between ejected BZY ultrafine particles (nearly vapor) and the oxygen molecules increase. If there is no oxygen molecule between the target and the substrate (oxygen partial pressure is small), there are virtually no collisions before the BZY particles reach the substrate and the BZY can be deposited on the substrate as a uniform background film. When the oxygen partial pressure increases, however, the BZY particles can undergo many collisions. Through these collisions, nucleation and growth of these BZY particles to form larger particulates can occur before their arrival at the substrate.[27] The fact that the particulate size increases as the number of collisions increases strongly suggests that the particulates are formed from ultrafine particles instead of liquid droplets. Given that the growth mechanism is conducted by diffusion, the residence time of a BZY particle in air controls the size of the particulate. The longer the residence time, as is the case with an increased oxygen partial pressure, the larger the particulate of BZY. Also, structure of BZY thin film becomes dense if substrate temperature increases. This phenomenon implies that the BZY particulates in thin film are relocated by thermal energy in order to minimize the binding energy among other particulates (dense structure). Also, the particles arriving to the substrate surface have not enough energy for any mitigation if substrate temperature is low, thus they stick mostly next above the particulate deposited already. This phenomenon can bring about firming significant voids.



Figure 3.1. Surface morphology of BZY thin film deposited by PLD in different substrate temperature and oxygen partial pressure in chamber



Figure 3.2 Cross-sectional morphology of BZY thin film deposited by PLD in different substrate temperature and oxygen partial pressure in chamber

3.1.2 Crystallinity

The crystallinity of BZY thin film can be changed if substrate temperature changes as shown in figure 3.3. Figure 3.3 shows that, up to 400°C, no BZY peaks can be seen. Although BZY thin films deposited from 25 to 400°C my by partially crystallized, fully crystallized diffraction patterns were not observed. On the other hand, perovskite peaks are present in the diffraction pattern at temperatures higher than 500°C. This phenomenon implies that active crystallization occurs between 400°C and 500°C. When thermal energy of atoms is low (substrate temperature is low), the vapor species have a low surface mobility and will be located at a different position on the surface. The low mobility of the species prevents full crystallization of the films. On the other hand, the increase of substrate temperature causes the diffusion of atoms deposited on the substrate and accelerates the migration of atoms to the position that minimizes the binding energy between atoms [28]. Hence, the particles with higher thermal energy are able to form a crystal structure.



Figure 3.3. X-ray diffraction pattern of BZY thin films deposited by PLD at temperature from 25° and 600°



Figure 3.4 Generalized BZY thin film structures as a function of substrate temperature and oxygen partial pressure

3.2 Target-substrate distance (TSD)

Control factors in order to analyze the effect of TSD are oxygen partial pressure in chamber (10mtorr), substrate temperature (60 0° C), laser fluence (1.5J/cm²) and frequency(6Hz)

3.2.1 Deposition rate

The cross-sectional morphology and the thickness of BZY are presented in Figures 3.5 (a) and (b), respectively. The maximum thickness was noted at 4.5 cm. As the TSD increases, the thickness of BZY thin film gradually decreases. If the TSD is shorter than 4.5 cm, likewise, the thickness decreases (as shown in Fig. 3.5 (b)). This result shows that the specific effects of the TSD and the number of oxygen molecules between the target and the substrate are interrelated. Although the oxygen partial pressure is significantly low (10mtorr), the number of oxygen molecules is increased as the target-substrate distance increases. In other words, the exposure time of BZY atoms to oxygen molecules increases with an increase of the TSD. Due to the increased collisions between the laser-produced plume and the oxygen molecules, the plume dimension decreases as the TSD increases. Dyer et al.[29] shows that the relationship between the length of the plume (L) and the scaling parameter (E/P_0) , where E is the laser-pulsed energy and P_0 is the oxygen partial pressure, for the plume range is as follows:

$$L = \left(\frac{E}{P_0}\right)^{\frac{1}{3\gamma}} \quad \dots \qquad (1)$$

Here, γ is the ratio of the specific heat of the elements in the plume (-0.786). For an oxygen partial pressure of 10 mtorr and a laser-pulsed energy of 1.5 J/cm², the length of the plume corresponds to approximately 4.442 cm.

When the TSD is much smaller than L, the proportion of BZY particles ejected from the substrate to the air in the PLD chamber is increased, as the kinetic energy of BZY particles is very high such that some BZY particles cannot be deposited on the substrate. On the other hand, As the TSD increases, the proportion of the smaller particulates that reach the substrate decreases and a few larger particulates appear, denoting a merge during flight from the target to the substrate.[30] Once the substrate is located far beyond L, the adhesion to the substrate of ejected matter, including the particulates and atomic species, is poor.



Figure 3.5. (a) Cross-sectional image of BZY thin films prepared by FIB at a target-substrate distance is 4.5cm (b) Thickness of BZY thin films with respect to the target-substrate distance.

3.2.2. Crystallinity

Figure 3.6 shows X-ray diffraction patterns of BZY thin films deposited at different target-substrate distances. The preeminent peaks at 30° and 70° correspond to Si(100) and Si(110), respectively. According to figure 3.6, the Si(100) peak at 4.5cm is smaller than any other TSD, as the thickness of BZY thin film at 4.5cm is high such that the Si(100) phase cannot be shown. The tetragonal-phase crystal structure of the films is indicated by the small splitting of the BZY (110) peak.[31] As shown in figure. 6, the diffraction peaks corresponding to BZY shifts decrease with an increase in the distance between the target and substrate; that is, a decrease in the crystallization of the BZY thin films occurs. This phenomenon can be explained as follows: when the BZY particles arrive at the substrate surface during the PLD process, their kinetic energy is transferred to local heating or to the scattering of the previous layers of the film. This phenomenon implies that the kinetic energy of particles arriving at the substrate plays an important role in building the structure of thin films. Also, when the particles hit the substrate at a low amount of kinetic energy (from a long distance), no significant energy is supplied to the previous film layer. On the other hand, when the particles hit the substrate with a high amount of kinetic energy (from a short distance), the increase in the local energy allows initial and arriving particles to relocate in order to minimize the binding energy. Therefore, the particles with higher kinetic energy are able to form a crystal structure which is dense and adheres better to the substrate, exhibiting lower internal stress in the perovskite structure.



Figure 3.6. X-ray diffraction pattern of BZY thin films deposited at (a) 5cm (b) 4.5cm (c) 4cm.

3.2.3. Surface morphology

The surface morphology of BZY thin films with respect to the TSD is shown in Figure 3.7. It is believed that the grain size of BZY particles and the surface morphology become large and porous with an increase of the TSD, as shown in Figure 3.7. This phenomenon implies that the number of oxygen molecules between the target and substrate is a critical factor related to the growth of the thin film. Due to the increase in the number of oxygen molecules between the target and the substrate as the TSD increases, the collisions between ejected BZY ultrafine particles (nearly vapor) and the oxygen molecules increase. If there is no oxygen molecule between the target and the substrate, there are virtually no collisions before the BZY particles reach the substrate and the BZY can be deposited on the substrate as a uniform background film. When the TSD increases, however, the BZY particles can undergo manv collisions. Through these collisions, nucleation and growth of these BZY particles to form larger particulates can occur before their arrival at the substrate. The fact that the particulate size increases as the number of collisions increases strongly suggests that the particulates are formed from ultrafine particles instead of liquid droplets. Given that the growth mechanism is conducted by diffusion, the residence time of a BZY particle in air controls the size of the particulate. The longer the residence time, as is the case with an increased TSD, the larger the particulate of BZY.



Figure 3.7. Surface morphology of BZY thin films deposited at target-substrate distances of (a) 4cm (b) 5cm (c) 6cm

3.3 Laser fluence

Figure 3.8 shows thickness of BZY thin film by changing laser fluence of PLD. Control factors in order to analyze the effect of laser fluence are oxygen partial pressure (10mtorr), substrate temperature (600°C) and TSD (4cm). The number of laser pulses is sustained to 7200 pulse fairly. As shown in Figure 7, the deposition rate is proportional to laser fluence. The BZY thin film thickness of 1, 1.5, 2, and 2.5J/cm² were 95nm, 149nm, 266nm and 619nm, respectively. This phenomenon implies that laser fluence and the number of ejected particles of target is interrelated. If the laser that has large fluence hits the target directly, the number of ejected particles increases.. So, the number of particles that reach the substrate increases. And, the adhesion to the substrate of ejected particles can increase because the kinetic energy of particles is high when laser fluence is high. As shown in equation (1), the laser fluence is proportional to the length of plume when P and y in the formulae is constant.[29] If the laser fluence increases, the plume intensity on the substrate is stronger in a fixed TSD condition. Consequently, the deposition rate of thin films sharply increases as the laser fluence increases.



Figure 3.8. Thickness of BZY thin films deposited at different laser fluence

3.4 Electrochemical properties of thin film solid oxide fuel cell

From these data obtained above, thin film solid oxide fuel cell was produced on the basis of AAO substrate and the application of BZY electrolyte with various thicknesses.

Figure 3.9 shows the cross-sectional image of thin film solid oxide fuel cell with BZY electrolyte in thickness of 930nm, 1240nm and 1340nm, respectively. Anode structure with dense platinum layer was formed between AAO substrate and electrolyte. The thickness of anode is about 250nm. Cathode structure with porous platinum layer was formed on the electrolyte. The thickness of cathode is approximately 200nm. As shown in figure 3.9, BZY electrolytes deposited by PLD technique have columnar grain growth.

Figure 3.10 indicates the potentiodynamic polarization of the AAO based thin film solid oxide fuel cells characterized at 450° C with different thickness of BZY electrolyte. 930nm-thick BZY cell shows approximately 0.81V of OCV. This value is lower than the theoretical one obtained from the Nernst equation (1.23V).[32] On the other hand, 1340nm-thick BZY cell indicates about 1.1V, very close to the theoretically expected value. In order to analyze the polarization, it is assumed that the gas leakage from metal ring or the sealant is negligible factor. Furthermore, it is generally known that the temperature of 450° C is little possibility of electronic conduction of BZY electrolyte.[23] So, the main reason

that OCV value of 930nm-thick BZY electrolyte cell is lower than theoretical value is the gas leakage and short-circuit phenomenon caused by defect of BZY electrolyte.[12,23]



Figure 3.9 Cross-sectional image of thin film solid oxide fuel cell with BZY electrolytes in thickness of (a) 930nm (b) 1240nm and (c) 1340nm



Figure 3.10 I–V polarization curve of AAO based thin film solid oxide fuel cell equipped with different thickness of BZY electrolyte.

If electrolyte has defect, anode and cathode are in contact through defect, bringing about electronic conduction. Also, the porous structure of the substrate causes the selective nucleation and growth of the grain, leading to propagation of the pinholes and void.[33] The grains are tendency to merge as the film becomes thicker and the defects become gradually clogged.[12] As shown in figure 3.10, therefore, it can be concluded that at least 1340nm thickness is required when fabricating thin film solid oxide fuel cell with BZY electrolyte on the PLD conditions mentioned above. Furthermore, the OCV increases as thickness of BZY electrolyte increases because the pinhole and crack in BZY electrolyte can be clogged as thickness of BZY electrolyte increases. The area specific resistance (ASR) values measured by the electrochemical impedance spectroscopy(EIS) with 0.1V DC potential were $0.17 \Omega \cdot \text{cm}^2$, $0.21 \Omega \cdot \text{cm}^2$, $0.22 \Omega \cdot \text{cm}^2$ for 930nm-, 1240nm- and 1340nm-thick BZY cell, respectively. This phenomenon indicates that the thicker BZY electrolyte has long proton conducting path. Although the ASR value increases as thickness of BZY electrolyte increases, the power density of BZY electrolyte cell increases to 7mW/cm², 13mW/cm² and 21mW/cm² as the BZY layer goes thicker as shown in figure 3.10. This phenomenon is because the structural defect causing the leakage current; the pinhole within the electrolyte was not entirely clogged in 930nm-and 1240nm-thick BZY cells. Furthermore, a cell with thicker electrolyte has rougher surface.[14] Figure 3.11 shows the analyzed result of the electrolyte surface topography in the BZY cells. During the measurement, the size of scan area is set as 30um Х 30µm and scan rate of 0.3Hz. The root-mean-square (RMS) roughness of the 930nm-, 1240nm- and 1340nm-thick BZY cell is 71nm, 78.4nm and 82nm, respectively as shown in figure 3.12. This phenomenon implies that the thicker electrolyte is formed, the rougher surface is formed. This tendency is generally observed in thin films that are formed in physical vapor deposition (PVD) technique such as sputter and PLD. If the rougher surface of BZY electrolyte layer is formed as shown in figure 3.11, it can lead to an increase of the effective reaction area at cathode/electrolyte interface called triple phase boundary (TPB).[14,23,34] The increase of the electrochemical active interfacial area enhances the electrochemical performance of the fuel cell as shown in figure 3.10.



Figure 3.11 Surface topography of the cells with (a) 930nm- (b) 1240nm- and (c) 1340nm-thick BZY electrolyte



Figure 3.12 The RMS roughness value of the electrolyte surface

4. Conclusion

PLD has many primary parameters such as oxygen partial pressure, substrate temperature, target-substrate distance and laser fluence. So, the analysis on properties of BZY thin films by changing these parameters has been conducted. If oxygen partial pressure in chamber increases, the grain size of BZY thin films becomes large and structure of thin films become porous because of the number of collisions between oxygen molecules and BZY particles. And, the BZY thin film becomes crystalline if the substrate temperature is 500° C and above. This is because the BZY particles is diffused and relocated in order to minimize the binding energy between atoms. As the target-substrate distance increases, the grain sizes of BZY particles increases and the surface of BZY thin films show a tendency to become porous. As the target-substrate distance decreases, on the other hand, the structure of BZY thin films becomes crystalline and the deposition rate generally increases. When the target-substrate distance is shorter than the length of the plume, the deposition rate is decreased due to the reflection phenomenon of BZY atoms from the substrate, resulting from the large kinetic energy of If the laser fluence increases, the deposition rate atoms. increases because the number of ejected particle increases. So, many particles can reach the substrate. Moreover, the adhesion to the substrate of BZY particles can increase because the kinetic energy of particles increases as the laser fluence is high. From these data, the AAO substrate-based thin film solid oxide fuel cell employing BZY electrolyte is successfully fabricated. The solid oxide fuel cell with BZY electrolyte in thickness of 1340nm conducts the maximum performance, approximately 1.1V of OCV and 21mW/cm² of peak power density. From these data, the pinhole and crack can be clogged if the electrolyte layer is thick. It is verified that low-thickness BZY electrolyte layer cause the pinholes and triggered the decreases of the OCV and performance from the leakage in cases of thin film solid oxide fuel cells. If the thickness of BZY electrolyte increases, moreover, the RMS roughness of surface increases. This phenomenon results in increasing the effective reaction area at cathode/electrolyte interface called TPB. The increases of the effective reaction area can enhance the electrochemical performance of the fuel cell.

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국문 초록

펄스 레이저 증착법으로 제작한

이트륨이 도핑된 바륨 지르코네이트를

전해질로 하는 박막 고체산화물 연료전지의

전기화학적 특성 분석

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고체산화물 연료전지는 효율이 높고 에너지 밀도가 높은 장점 이 있지만 작동 온도가 700℃ 이상의 고온이기 때문에 작동 준비 시간이 길고 물질의 안정성, 연료의 기밀성 등에서 단점을 드러 낸다. 이와 같은 단점을 보완하기 위해 많은 연구가 진행되고 있는데 첫 번째로는 박막 고체산화물 연료전지의 연구이다. 박 막 고체산화물 연료전지는 전해질의 두께를 nm 단위로 얇게 제 작하여 낮은 온도에서도 낮은 저항을 보여서 높은 성능을 나타낼 수 있는 연료전지이다. 두 번째로는 수소이온전도체의 연구이다. 기존에 사용되고 있는 산소이온전도체와는 달리 낮은 온도에서도 높은 성능을 낼 수 있고 작동 도중에 성능강하가 거의 일어나지 않는다는 장점이 있다. 그래서 이 연구에서는 박막 증착법 중의 하나인 펄스 레이저 증착법의 여러 변수들(챔버 내 산소 분압, 기판 온도, 타겟과 기판 사이의 거리, 레이저 파워) 에 따른 이트 륨이 도핑된 바륨 지르코네이트(BZY, 수소이온전도체) 박막의 특 성을 분석하였다. 챔버 내의 산소 분압이 높을수록 BZY 박막의 구조가 다공성 구조가 되는 경향을 보였다. 그리고 기관의 온도 가 높아지면 BZY 박막의 결정성이 증가하는 경향을 보였다. 타 겟과 기판 사이의 거리(TSD) 측면에서 봤을 때 챔버 내 산소 분 압과 레이저 파워에 의해 가장 증착률이 높은 TSD가 존재하였 고 TSD가 작을수록 박막의 결정성이 높아지고 박막 표면의 구 조가 치밀한 구조가 되는 것을 확인할 수 있었다. 이 데이터를 토대로 BZY를 전해질로 하는 박막 고체산화물 연료전지를 제작 하여 성능을 평가하였다. 그 결과 BZY 박막이 두꺼울수록 성능 이 높게 나오는 것을 확인할 수 있었다. 이는 전해질의 pinhole 을 없애서 short-circuit을 막는 것이 성능 향상에 중요한 역할을 하는 것을 알 수 있었다. 또한 전해질의 두께가 두꺼우면 표면 의 거칠기가 증가하는데 이는 전기화학적 반응이 일어날 수 있는 계면의 면적이 증가하여 성능 향상에 역할을 하였다는 것을 알 수 있었다.

주요어 : 고체산화물 연료전지, 이트륨이 도핑된 바륨 지르코네이 트, 펄스 레이저 증착법, 전기화학적 특성, 수소이온 전 도체

학 번 : 2012-20671

감사의 글

RECL에 배정되어 어색하게 자기소개를 했던 적이 엊그제 같 은데 어느덧 2년이 흘렀습니다. 시간은 빠르게 지나갔지만 많은 추억이 있습니다. 엠티에서 태풍 볼라벤을 맞고 우울하게 보낸 것, 처음 간 해외 학회 발표에서 실수한 것, 보름 동안 갔었던 하 와이 등 많은 기억이 남습니다. 우선 2년 동안 부족한 저를 지도 해 주시고 이끌어 주셨던 차석원 교수님께 감사드립니다. 그리고 석사과정 동안 제 연구에 많은 도움을 주신 연료전지 팀 익황형, 훈이형, 준호형, 상훈이형, 윤호형, 구영이형, 태현이, 성민이, 승 탁이 에게 모두 감사드립니다. 그리고 하이브리드 팀 창우형, 호 원이형, 종렬이, 현섭이형, 종대, 기영이, 희윤이 에게도 모두 감 사드립니다. 연구실의 모든 분들 덕분에 석사과정을 잘 보낼 수 있었던 것 같습니다. 마지막으로 지난 28년 간 저를 아껴주시고 키워주시고 힘들 때마다 힘이 되어주신 부모님께 감사의 말씀 드 립니다. 이 은혜에 보답할 수 있도록 졸업 후 매사에 최선을 다 하고 효도할 수 있도록 하겠습니다. 감사합니다!!!