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A study on properties of yttrium-stabilized zirconia thin films fabricated by different deposition techniques

Jun Yeol Paek [a], Ikwhang Chang [b], Joon Ho Park [a], Sanghoon Ji [b], Suk Won Cha [a], *

[a] *School of Mechanical and Aerospace Engineering, Seoul National University, Gwanakro 599, Gwanak-gu, Seoul 151-744, Republic of Korea*
[b] *Graduate School of Convergence Science and Technology, Seoul National University, 864-1 Iui-dong, Yeongtong-gu, Suwon-city, Kyunggi-do, Republic of Korea*

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ABSTRACT

This paper investigates the micro-structural, chemical and crystalline properties of yttrium-stabilized zirconia (YSZ) thin films by using pulsed laser deposition (PLD), atomic layer deposition (ALD) and sputter. Atomic ratio of Y:Zr of YSZ thin films fabricated by three different deposition methods was adjustable. ALD YSZ with smaller grains has high density compared to PLD YSZ and sputter YSZ. On the other hand, the low crystallinity of ALD YSZ can be supplemented by annealing process. From these experimental results, ALD YSZ thin film has the characteristics that satisfy requirements for using an electrolyte of thin film solid oxide fuel cells.

1. Introduction

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 (SOFCs) 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]. However, for all such applications of conventional SOFC, 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) developing alternative electrolyte materials with high ionic conductivity; (2) decreasing the thickness of the electrolyte [8]. As the next-generation electrolyte material, a large body of research on yttrium-stabilized zirconia (YSZ) has been established. YSZ is a very attractive material because of its high ionic conductivity and high chemical stability. Due mainly to these advantages, YSZ is the most popular solid electrolyte material for SOFCs and high temperature electrochemical sensor [9]. Moreover, research on SOFCs which use a thin film electrolyte for reducing the ohmic resistance has been conducted [10]. If the thickness of the electrolyte is small, the degradation in the performance SOFC resulting from ohmic loss can be compensated [11]. Kerman et al. reported that thin film SOFC is capable of delivering higher power densities at a lower temperature (<500 °C), measuring 1.037 W/cm^2 at 500 °C [12]. Actually, research has shown that the performance of SOFC is sensitive to the electrolyte's thickness [13–15]. However, reducing the thickness of the electrolyte alone would effectively take full advantage of the ohmic resistance reduction. Not only the thickness but the dense and pinhole-free structure of the electrolyte is also important [16]. If the structure of the electrolyte is porous and a defect occurs, short-circuits can be formed, resulting in zero cell performance.

In order to achieve the small thickness and pinhole-free structure, many thin film deposition techniques have been researched. Typical deposition methods are pulsed laser deposition (PLD), atomic layer deposition (ALD) and sputter. PLD, one of the physical vapor deposition techniques, is a common technique for the deposition of thin films of complex oxide. The principle of PLD is that the laser hit the target and target particle ejected by laser

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* Corresponding author. Tel.: +82 2 880 1700; fax: +82 2 883 1513.
E-mail address: swcha@snu.ac.kr (S.W. Cha).

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deposit on substrate by forming laser plume. The advantages of the PLD technique are usually summarized as follows: (1) thin films of complex stoichiometry can be produced from a bulk target; (2) PLD is a pulsed process by which the number of particles arriving at the substrate can be controlled easily with the number of pulses and the fluence [17]. Therefore, PLD is used for the deposition of materials for a wide range of applications, ranging from biocompatible thin films to cathodes for Li-ion batteries and electrolytes of thin film SOFCs [18]. ALD is one of the several chemical vapor deposition (CVD) techniques. In case of ALD, it relies on alternate pulsing of the precursor gases and vapors onto the substrate surface and subsequent chemisorptions or surface reaction of the precursors [19]. ALD can form a thin film stably, resulting in making a dense thin film structure and the increase in thickness is constant in each deposition cycle. These advantages make the ALD method attractive for micro electronics for the manufacture of next-generation integrated circuits [20]. Sputter is the most typical deposition technique. The sputter process involves the physical vaporization of atoms from a surface by momentum transfer from bombarding energetic atomic-sized particles. The advantages of sputter technique are as follows: (1) any material can be sputtered and deposited (i.e. an element, alloy, metal or compound); (2) sputtering conditions can easily be reproduced from run to run; (3) there is little radiant heating in the system compared to vacuum evaporation. Because of these advantages, sputtering technique can apply to deposit single and multi-layer metal conductor and compound conductor films [21].

Research about the optimum conditions for YSZ deposition based on a variety of techniques have been conducted [9,22,23]. However, a comparison of properties between thin films deposited by many deposition techniques has not been extensively conducted. Therefore, the primary purpose of this study is to investigate the properties of YSZ thin films deposited by sputter, ALD and PLD, respectively, in terms of crystallinity, morphology, composition and surface roughness. From this data, the best YSZ deposition technique is expected to be identified (Fig. 1).

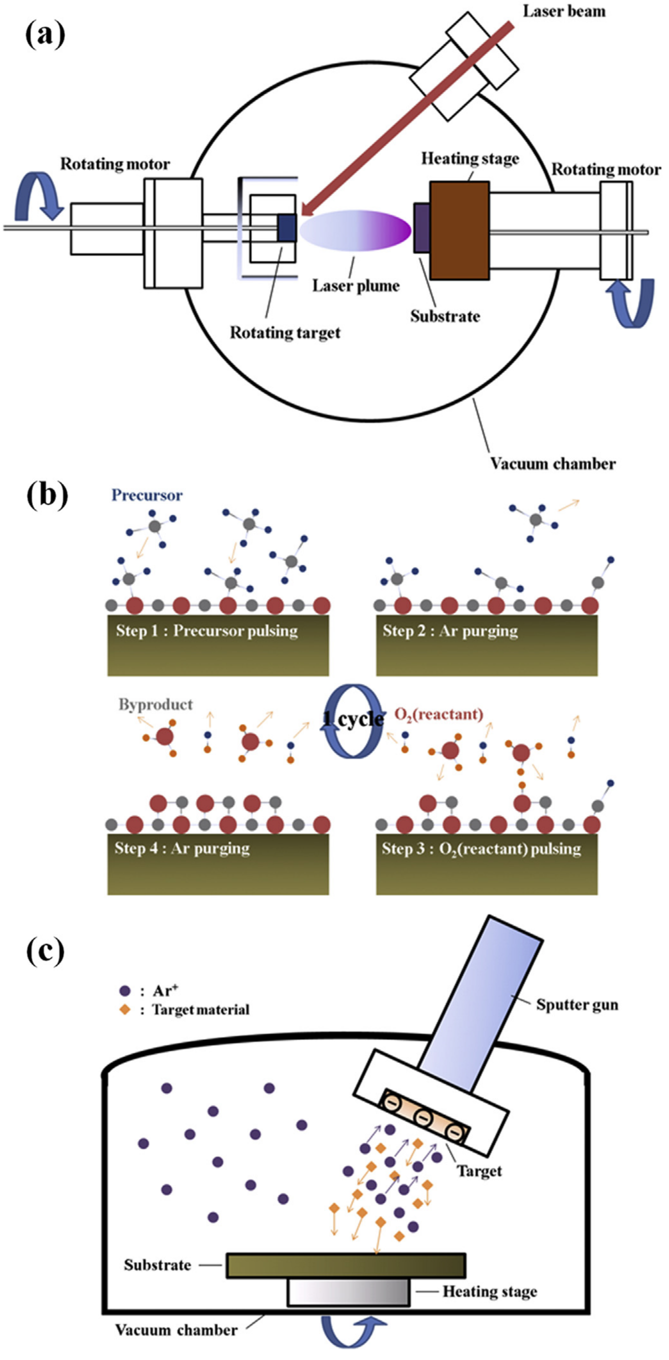

Fig. 1. The scheme of (a) PLD (b) ALD (c) sputter.

2. Experimentals

2.1. Preparation of the thin films

2.1.1. Pulsed laser deposition (PLD)

A vacuum chamber (Korea Vacuum Tech. Ltd) which includes a turbomolecular and rotary pump was utilized. These pumps can create a chamber pressure of 0.01 mbar (high vacuum). A silicon wafer chip (1 cm × 1 cm) was attached onto the substrate using silver paste (Pyro-Duct 597-A, Aremco Products Inc.). The YSZ thin film was deposited onto the silicon wafer. A sintered zirconium oxide (−8 mol% Y_2O_3, 99.95% purity) pellet (Part #: SYSZ1D10T3N5, RND Korea Company.) was used as a target. Thin films were grown using a 248 nm KrF excimer laser (Lamda Physik, Germany). The laser was operated at a repetition rate of 6 Hz and a fluence of 1.2 J/cm^2. The oxygen partial pressure in the PLD chamber was 0.013 mbar (10 mTorr) and the substrate temperature was 800 °C. The TSD was 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.

2.1.2. Atomic layer deposition (ALD)

YSZ thin films deposited by ALD were fabricated by co-deposition of zirconia and yttria using a commercial ALD system (model: Plus 100-TWR, Quros Co. Korea). A silicon wafer chip was attached onto the substrate using mask. Tetrakis (dimethylamido) zirconium, $Zr(NMe_2)_4$ and tris (methylcyclopentadienyl) yttrium, $Y(MeCp)_3$ were used as precursor of zirconium and yttrium. Ar gas was used as purging gas and O_2 gas was used as oxidant. Monolayer deposition was conducted by repeating the sequence: (1) precursor pulse (3 s); (2) purging (20 s); (3) oxidant pulse (1 s); (4) purging (10 s). The temperatures of canisters with charged precursors were 40 °C and 180 °C and the line temperatures were 65 °C and 210 °C for zirconium and yttrium. The chamber temperature was 250 °C. Before the deposition, the pressures of the line and chamber were set to 0.031 mbar (23 mTorr) to minimize impurities during the deposition process.

2.1.3. Sputter

A silicon wafer chip (1 cm × 1 cm) was used as substrate. A sintered zirconium oxide (−8 mol% Y_2O_3, 99.99% purity) was used