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Proton incorporation in yttria-stabilized zirconia during atomic layer deposition

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ARTICLE INFO

Article history:

Received 5 September 2013

Received in revised form

6 November 2013

Accepted 11 November 2013

Available online 8 January 2014

Keywords:

Protons

Atomic layer deposition

Yttria-stabilized zirconia

Secondary ion mass spectrometry

ABSTRACT

This work elucidated the proton-incorporation mechanism in ALD YSZ¹. Isotope ²H₂O was used as an oxidant to trace proton incorporation. The ratio of ZrO₂ to Y₂O₃ ALD cycles was varied from 1:1 to 5:1. TEM confirmed that the ALD YSZ films grew as fully crystallized columnar grains in the cubic ZrO₂ phase. SIMS indicated that the Y³⁺ and ²H⁺ concentrations were linearly correlated, indicating yttria-deposition-induced proton incorporation. XPS confirmed an appreciable amount of Y(OH)₃ proportional to the ²H⁺ content in the ALD YSZ, as was also detected by SIMS. Oxide ion vacancies created by the replacement of ZrO₂ with relatively small amounts of Y₂O₃ provided additional vacancies for proton incorporation, resulting in steeper [²H⁺]/[Y³⁺] slopes.

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1. Introduction

The presence of protons in yttria-stabilized zirconia (YSZ) has been reported by various researchers since the 1960s. The higher mobility of protons in YSZ as compared to that of oxide ions may help reduce the energy loss due to ohmic resistance across electrolyte membranes, and this characteristic has attracted the attention of scientists aiming to develop high-performance electrochemical systems including fuel cells, batteries, gas separators, and sensors [1]. Wagner et al. first reported the reasonably fast diffusion of protons through YSZ at high temperatures and proposed the use of YSZ as an

electrolyte in hydrogen sensors [2,3]. Fast diffusion of protons through nanocrystalline YSZ has recently been reported, and a decrease in grain size has been demonstrated to result in enhanced ionic conductivity [4–9]. It has also been claimed that the incorporation of water into the oxide ion vacancies and the protons orbiting the neutral oxide ions in vacant lattice spaces are responsible for the presence of protons in YSZ. This mechanism is similar to the H⁺ incorporation in doped perovskites with the general formula ABO₃ [10–12]. Oxygen vacancies are particularly likely to be found on the grain surface or along the grain boundaries in doped or undoped ZrO₂ [13]. These claims have led researchers to the conclusion that most protons reside in the inter-granular space as

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<http://dx.doi.org/10.1016/j.ijhydene.2013.11.023>

Nomenclature

$^2\text{H}^+$	deuterium or heavy hydrogen ion
$^2\text{H}_2\text{O}$	water in which deuterium is substituted for hydrogen
V_{O}^{\bullet}	oxide ion vacancy
[M]	molar concentration of ion M

Abbreviations

ALD	atomic layer deposition
YSZ	yttria stabilized zirconia
ALD YSZ	yttria stabilized zirconia film synthesized by atomic layer deposition
CVD	chemical vapor deposition
PLD	pulsed laser deposition
SIMS	secondary ion mass spectrometry
TMA	trimethyl aluminum
TEM	transmission electron microscopy
XPS	X-ray photoelectron spectroscopy

hydroxyl ions, and this conclusion has been supported by extensive experimental evidence [5,6,8,9,12,14,15]. Sakai et al. observed that fewer hydrogen isotope ions ($^2\text{H}^+$) were absorbed into 8 mol% single-crystal YSZ than onto polycrystalline YSZ at the same doping rate when annealing was performed in a $^2\text{H}_2\text{O}$ environment. Therefore, they concluded that most protons in polycrystalline YSZ existed at the grain boundaries [14]. Kim et al. demonstrated that water-incorporated solid oxide fuel cells with nanogranular 8 mol% YSZ could operate successfully at room temperature, whereas similar fuel cells that used microgranular YSZ generated almost no current with the same experimental setup [5]. They also used $^2\text{H}_2\text{O}$ to demonstrate the diffusion of protons through the YSZ electrolyte during fuel cell operation.

Atomic layer deposition (ALD) is a modified chemical vapor deposition (CVD) technique in which films are synthesized one atomic layer at a time by exposing alternating precursors. ALD YSZ films are synthesized by alternating ZrO_2 and Y_2O_3 ALD cycles, and the concentration of the dopant (Y_2O_3) can be adjusted by varying the numbers of ZrO_2 and Y_2O_3 cycles [12,16–21]. The performance of fuel cells employing nanoscale ALD YSZ electrolytes is superior to that of similar fuel cells employing YSZ fabricated using other techniques, exhibiting a power output of 0.28–1.34 W/cm² at 265–500 °C [17,20,21]. This is because the concentration of Y_2O_3 plays an important role in determining the ionic properties of YSZ, because the dopant cations (Y^{3+}) replace the host cations (Zr^{4+}) in the zirconia lattice to create empty oxygen sites or oxygen vacancies (V_{O}^{\bullet}) [21]. In the same context, controlling the number of Y_2O_3 cycles is important in ALD, as has been experimentally proven in our previous studies [18,20]. We also observed an abundance of $^2\text{H}^+$ ions in ALD YSZ synthesized using metal-organic precursors and water. These protons are presumed to reside in oxygen vacancies as hydroxyl ions [12]. Interestingly, ALD YSZ allows protons to diffuse more effectively than does YSZ synthesized by pulsed laser deposition (PLD) [12], probably because the former is fabricated in humidified environments [7,12]. Up to now, however, no rigorous study on the relationship between yttria doping and the protonation of

YSZ has been reported. Therefore, in this paper, we have elucidated the mechanism of proton incorporation into ALD YSZ using $^2\text{H}_2\text{O}$ as the source of oxidation during film production. In particular, secondary ion mass spectrometry (SIMS) was used to analyze the concentrations of trace isotopes or $^2\text{H}^+$ in relation to the doping rate.

2. Methodology

2.1. Synthesis and characterization of ALD YSZ

ALD YSZ films were synthesized using a method reported in the literature [17–21]. Tetrakis(dimethylamido)zirconium(IV) and tris(methylcyclopentadienyl)yttrium(III) were used as precursors for the ALD ZrO_2 and Y_2O_3 , respectively. As mentioned above, $^2\text{H}_2\text{O}$ was used as an oxidant. The deposition temperature was set to 250 °C, and the other process parameters and setups were the same as specified in our previous publication [21]. The ratio of ZrO_2 to Y_2O_3 ALD cycles was varied in the range of 1:1–5:1 to fabricate samples called ALD YSZ 1:1–5:1, respectively, and the thickness of the YSZ layers produced was 50 nm. For comparison, pure ZrO_2 was also deposited with $^2\text{H}_2\text{O}$. The ALD YSZ layers prepared with $^2\text{H}_2\text{O}$ were sandwiched between 20 and 30-nm-thick ALD Al_2O_3 layers made from trimethyl aluminum (TMA) and water to prevent the diffusion of $^2\text{H}^+$ ions between the layers or into air upon subsequent exposure to ambient environments. All layers were deposited consecutively without any exposure to air. A schematic structure of the sample is illustrated in Fig. 1. The microstructure and thickness of the films were evaluated using transmission electron microscopy (TEM; JEM 2100F at Korea Basic Science Institute (KBSI)). X-ray photoelectron spectroscopy (XPS; SSI S-Probe, monochromated Al K α radiation at Korea Institute of Science and Technology (KIST)) was performed for compositional analyses.

2.2. Experiments on proton diffusion

To verify that the ALD Al_2O_3 prevented $^2\text{H}^+$ ion diffusion, we fabricated 50-nm-thick Al_2O_3 layers with $^2\text{H}_2\text{O}$ on a Si wafer and carried out in-depth measurements of the concentrations of $^2\text{H}^+$ and other component cations including Al^{3+} , Zr^{4+} , and Y^{3+} using time-of-flight SIMS (TOF-SIMS: ION-TOF at the Korea Institute of Science and Technology (KIST)). The energy of the primary ion beam was set to 25 keV, with a beam current of 1 pA, and the area analyzed was 100 $\mu\text{m} \times 100 \mu\text{m}$.

3. Results and discussion

3.1. Structural characteristics of ALD YSZ

The microstructures of the ALD YSZ 1:1–5:1 and ALD ZrO_2 films were analyzed using cross-sectional TEM images. From this analysis, it was clear that all the ALD YSZ films grew as fully crystallized columnar grains regardless of the Y_2O_3 content, whereas the capping ALD Al_2O_3 layers grew with amorphous structures (Fig. 2). The measured widths of the grains were in the range of 3–20 nm. There was no substantial

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