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Ionic properties of ultrathin yttria-stabilized zirconia thin films fabricated by atomic layer deposition with water, oxygen, and ozone

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ABSTRACT

We compared the ionic properties of yttria-stabilized zirconia (YSZ) thin films prepared by atomic layer deposition (ALD) using various oxidants including water, oxygen, and ozone. Cross-plane conductivity measurements were performed at low temperature (50 °C) and high temperature (450 °C) using AC impedance spectroscopy. As a result, we have confirmed that the conductivity of ALD YSZ films below 300 °C is greater by several orders of magnitude compared to the nano-scale YSZ thin films synthesized by other conventional techniques. Among the ALD YSZ samples, ALD YSZ fabricated using water showed the highest conductivity while ALD YSZ fabricated using ozone showed the lowest. We have analyzed this result in relation with grain morphology characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), and the chemical binding states measured by X-ray photoelectron spectroscopy (XPS).

1. Introduction

Yttria-stabilized zirconia (YSZ) is an oxide ion-conducting ceramic material and most commonly used as electrolytes in high-temperature electrochemical systems such as solid oxide fuel cells (SOFCs). YSZ exhibits good thermal and chemical stability in oxidizing/reducing environments even at elevated temperatures, while the ionic conductivity is relatively low, with a high activation energy; owing to this reason, recent efforts to fabricate YSZ as ultrathin films (thickness < 100 nm) have dramatically reduced electrolyte resistances and enabled operation of SOFCs at intermediate temperatures (<500 °C) [1–6]. Recently, atomic layer deposition (ALD) has been successfully used in the synthesis of high quality nano-scale YSZ thin films [1–8]. ALD is a modified chemical vapor deposition (CVD) technique where the substrate is alternatively exposed to gasified precursors. In each precursor cycle, films grow a maximum of 'one atomic layer' in principle, because of the self-limiting chemistry of precursor chemisorption. Therefore, the growth rate of ALD is represented as thickness per precursor cycle, which is independent of the source supply rate or deposition time. Hence, composition and thickness of films can be controlled precisely on the atomic scale. ALD YSZ is synthesized by altering the Y_2O_3 and ZrO_2 cycles. The concentration of the dopant (Y_2O_3) in ALD YSZ can be modified by changing the number of ZrO_2 and Y_2O_3 cycles. The latest studies have successfully demonstrated high performance micro-SOFCs with ultrathin ALD YSZ electrolytes where the maximum power output has been reported to be above 1.3 W/cm^2 at 500 °C [4,6]. This improved performance is not only because of the decreased ohmic loss but also because of the enhanced surface kinetics of nano-crystalline ALD YSZ [1–8].

Another interesting property of ALD YSZ electrolytes is proton conduction [9–11]. Proton incorporation and diffusion in YSZ were first reported by Wagner [12]. The proton incorporation mechanism of YSZ suggested the incorporation of water into the oxide ion vacancies as hydroxyl ions (OH^-) [9–11]. The oxide ion vacancies ($V_O^{\cdot\cdot}$) are created to maintain overall charge neutrality as the 4+ host cations (Zr^{4+}) are replaced by the 3+ dopant cations (Y^{3+}) in YSZ. Recent studies have revealed enhanced proton transport in nano-granular YSZ [9–11,13–18]; this is due to the high population of vacancies on the grain surface for compensation of space charge potentials in the vicinity of grain boundary regions [19]. Hence, water or hydroxyl groups preferentially adsorb or chemisorb onto the grain surface, which lead to high concentration of protons in nano-granular YSZ compared to micro-granular materials [13–15,17,18]. In this respect, it is reasonable that a substantial amount of protons are incorporated into ALD YSZ films comprised of nanoscale grains [9–11]. Incorporation of protons is significant at low temperatures as water or OH^- is thermodynamically stable under 100–150 °C while OH^- groups decompose and completely diffuse out as water vapor above 350 °C; therefore, the ionic conductivity at 50 °C is close to that at 350 °C where oxide ion conduction is dominant. We successfully ran micro-SOFCs with 100 nm-thick ALD YSZ displaying an open circuit voltage close to 1 V below 100 °C [11].

Our recent studies have also clarified that the water used in the ALD process as an oxidant source provides environments desirable to

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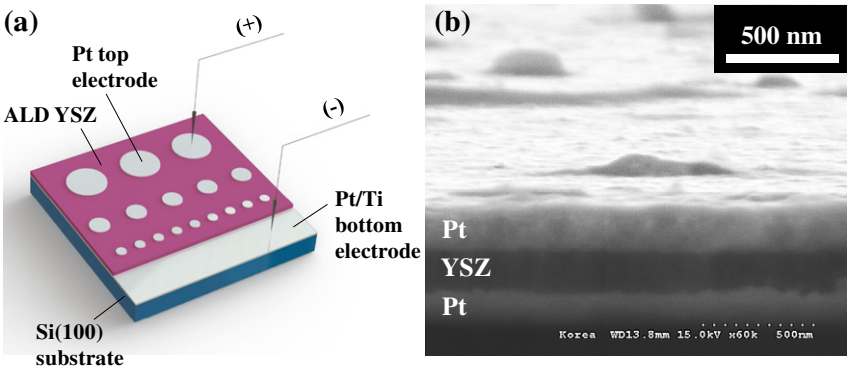

Fig. 1. (a) Schematic diagram for cross-plane impedance measurements. (b) SEM image of the ALD YSZ with sputtered dense Pt as top and bottom electrodes prepared on a Si(100) wafer for the cross-plane conductivity measurement.

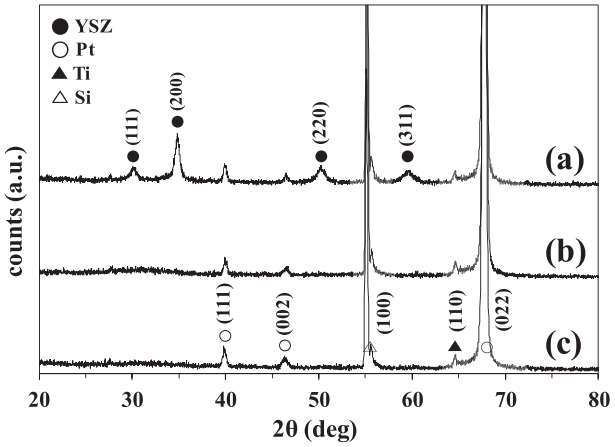

Fig. 2. XRD patterns of ALD YSZ using (a) water, (b) oxygen, and (c) ozone as oxidants deposited on a Pt-coated Si(100) wafer deposited at 250 °C.

incorporate OH^- groups or protons, which was confirmed using water isotopes (^2H_2O) and secondary ion mass spectrometry (SIMS) [9,10]. This observation provides a clue about the roles of ALD oxidants in determining chemical properties of the electrolyte films. It has been widely reported that microstructures and chemical properties of ALD films can change dramatically by switching oxidants i.e. O_2, O_3, H_2O, and H_2O_2 although the same cation precursors are used [20,21]. In this work, we have examined a variety of oxidants including water, oxygen, and ozone for the synthesis of ALD YSZ thin films and investigated the changes in the properties of the materials. As YSZ is a ceramic electrolyte, the focus lies on ionic conductivity analysis in relation with grain and crystal structures.

2. Experimental details

Film synthesis was performed in a customized thermal ALD chamber (ICOT Inc.). Tetrakis(ethymethylamido)zirconium(IV) (UP Chem.) and tris(methyl-cyclopentadienyl)yttrium(III) (Strem Chem.) were used as precursor sources for ZrO_2 and Y_2O_3, respectively. Distilled water, O_2 (20 sccm), or O_3 (20 sccm) was used as the oxidant, as proposed in the introduction, and dry nitrogen (N_2) was used as the carrier and purge gas at a flow rate of 1.0 sccm. The deposition temperature was set at 250 °C, which is reported to be the most typical for ALD YSZ [1–6,8–11]. The precursor pulsing time was 0.5 s, and the oxidant pulsing time was 3 s in case of oxygen and ozone, and 0.5 s in case of distilled water. The cycle ratio of ZrO_2 and Y_2O_3 deposition was 4:1 (ZrO_2:Y_2O_3 = 4:1); the Y_2O_3 cycle was performed in the middle of the total cycle and the resulting yttria concentration of the deposited film was 8–9 mol%.

The microstructure of the ALD YSZ films was analyzed using scanning electron microscopy (SEM, Hitachi, S-4300) and atomic force microscopy (AFM, Park Systems, XE-100). The crystallinity was analyzed by X-ray diffraction (XRD, Rigaku, DMAX-2500, Cu-Kα1 radiation λ = 1.5406 Å, scan step size 0.02°), and X-ray reflection (XRR, Rigaku, ATX-G, Cu-Kα1 radiation λ = 1.5406 Å, scan step size 0.001°) was used to measure the film roughness and density.

For cross-plane measurements of electrical conductivity, the 100-nm-thick ALD YSZ thin films were fabricated on Si(001) wafers coated

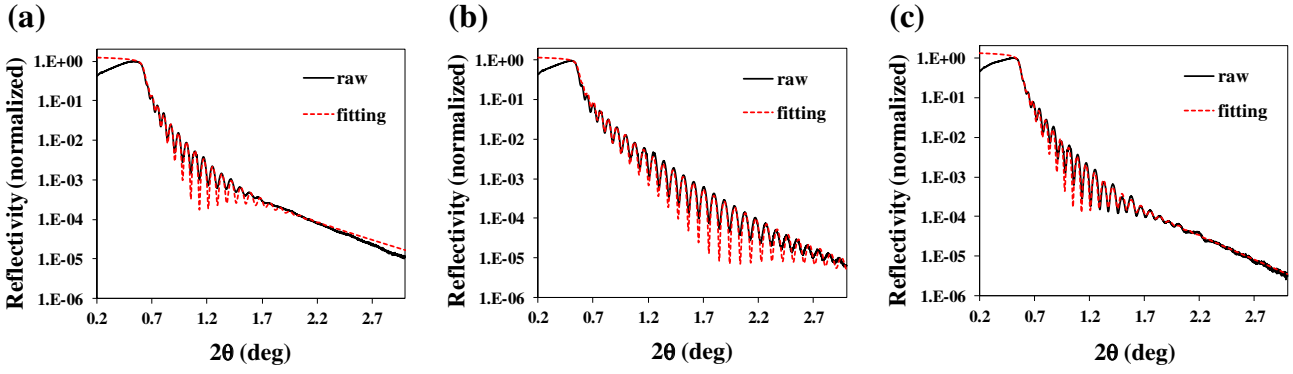

Fig. 3. XRR patterns of ALD YSZ with curve fitting prepared using (a) water, (b) oxygen, and (c) ozone as oxidants deposited on a Pt-coated Si(100) wafer deposited at 250 °C.