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Effects of residual stress and interface dislocations on the ionic conductivity of yttria stabilized zirconia nano-films

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ABSTRACT

The effects of residual stress and interface dislocations on the ionic conductivity of yttria stabilized zirconia (YSZ) polycrystalline nano-films deposited onto quartz substrate via pulsed-DC magnetron sputtering are systematically studied. The residual stress of YSZ film is evaluated by a $\cos^2\alpha\sin^2\psi$ method. The X-ray diffraction data indicates that a peening-induced compressive residual stress develops in the as-deposited film, increases with film thickness, and decreases the ionic conductivity. On the other hand, a thermal-mismatch-induced tensile residual stress develops in the annealed film, increases with annealing temperature, decreases with film thickness, and enhances the ionic conductivity. Ionic conductivities higher than the YSZ bulk are measured in both the as-deposited and annealed YSZ nano-films, indicating the existence of interface enhancement effect on the ionic conductivity. A type of low-energy dislocation structure forms next to the interface by sputtering, which hinders oxygen ion diffusion along the interface and lowers the ionic conductivity.

1. Introduction

Yttria stabilized zirconia (YSZ) is the most commonly used electrolyte for solid oxide fuel cells (SOFCs), owing to its high ionic conductivity of ~0.1 S/cm at 900–1000 °C and desirable chemical stability in both oxidizing and reducing atmospheres. The ionic conductivity of YSZ electrolyte is attributed to the mobility of the oxygen ions [1–3]. But the operation temperature of YSZ is still esteemed too high to find an appropriate interconnect material and to reduce the cost of such SOFCs. In an attempt to further increase the ionic conductivity of solid electrolyte materials, many researchers focused on creating highly conductive paths along the interface as a result of ion redistribution in a space charge region. For example, Sata et al. [4] found that an increase in the interface density in multilayered CaF_2/BaF_2 strongly enhanced the ionic conductivity along the interfacial direction, particularly when the film thickness ranged between 20 and 100 nm, as compared with either bulk CaF_2 or BaF_2. It was thus attributed to the space charge regions at the interfaces.

Experimental studies on the interfacial transports of oxide ion conductors have also been performed by Kosacki et al. [5]. Enhanced conductivity in highly textured thin films of YSZ, with thicknesses between 60 and 15 nm, reaching 0.6 S/cm at 800 °C was found. Because reducing the film thickness (thus increasing the fraction of material near the interface) produced such a noticeable conductivity enhancement, the interfaces themselves would seem to play a determining role in the outstanding conductivity observed. In 2008, Garcia-Barriocanal et al. [6] reported a very high ionic conductivity, 0.014 S/cm at 357 K, of a strained, 1-nm thick YSZ film which was sandwiched between $SrTiO_3$ (STO) layers. The calculated activation energy of the conductivity of this YSZ nano-film, 0.64 eV, was much smaller than that of the YSZ bulk (1.1 eV). It was proposed that the eight orders of magnitude enhancement of the ionic conductivity might result from both the tensile strain of 7% within the YSZ film and the space-charge effects. However, much debate surrounding this report has since been drawn. Among them, Yildiz et al. [7,8] and De Souza et al. [9,10] employed computer simulations, while Korte et al. [11,12] developed a simple analytical model to address the effects of strain on the ionic conductivity. The enhancements calculated from these studies are, however, still orders of magnitude lower than that in Ref. [6].

On the other hand, Guo [13,14] argued that the claimed ionic conductivity by Garcia-Barriocanal et al. [6] lacks experimental support and that the observed conductivity enhancement could also be due to an electronic contribution from the STO substrate. According to him, the substrate contribution is a common source of artifacts in experiments on thin films. Cavallaro et al. [15] also demonstrated the electronic nature of the enhanced conductivity in their own YSZ–STO multilayers made by pulsed laser deposition (instead of high-temperature RF sputtering employed in Ref. [6]). After re-analyzing the data from Ref. [6,13] and [15], De Souza et al. [16] not only confirmed the contribution to enhanced conductivity from STO, which is

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exclusively ionic below ~540 K, but also dismissed the possibility of contribution from the space-charge effects.

Following a previous study [17] to avoid such complications, here we chose quartz, which has a much lower electrical conductivity (ρ(quartz) > 10^{17} Ω cm at room temperature) than $SrTiO_3$ ($\rho(SrTiO_3) \sim 10^{13}$ Ω cm at room temperature) [18], as the host substrate. In addition, we believe that the ionic conductivity of YSZ nano-film would obviously be affected by the microstructural defects and residual stresses inevitably formed during deposition and easily modified by subsequent annealing, especially near the interface between YSZ film and quartz substrate. Moreover, in contrast to the epitaxial films studied in most works mentioned above, polycrystalline films would be more practical in application and easier to obtain in most circumstances. This paper thus attempts to address these issues by studying the effect of residual stress on the ionic conductivity of polycrystalline YSZ nano-films sputtered on quartz, with and without post-deposition annealing.

2. Experimental details

YSZ films were grown onto quartz substrate (25 × 25 × 1 mm^3, Lindberg, Denmark) by a reactive pulsed-DC magnetron sputtering system (Saturn SV-MG01, Taiwan) using a 6 mm-thick, 3″-diameter 80Zr/20Y (mol%) alloy target (Putuo Technology, Taiwan). A vacuum of 2.67×10^{-4} Pa was obtained using a set of turbo-molecular and mechanical pumps. High-purity argon and oxygen were introduced into the system to raise the working pressure to about 0.25 Pa during deposition. The argon-to-oxygen ratio was fixed by a constant argon flow of 30 sccm and a constant oxygen flow of 5 sccm, corresponding to an oxide-mode sputtering. The cathode was powered by a pulsed-DC power supply (SPIK 2000A, Shenchang Electric Co., Taiwan) at a constant power of 200 W with a 50% duty cycle at 50 kHz. The target-to-substrate distance was 70 mm. All the substrates were cleaned with de-ionized water followed by vapor degreasing with isopropyl alcohol prior to deposition. The deposition was carried out, without substrate heating, for 257, 428, 643 and 857 s to fabricate YSZ nano-films of 30, 50, 70 and 100 nm in thickness respectively. A typical α-step (Surfcordor ET3000, Kosaka, Japan) was employed to measure the film thickness.

Phase identification was performed using grazing-incidence X-ray diffraction (GIXRD, XPert Pro MPD, PANalytical, Netherlands) with Cu Kα radiation. The residual stresses of the YSZ nano-films were determined by the $\cos^2\alpha\sin^2\psi$ method with grazing-incidence geometry [19]. The samples were pasted on an XRD specimen holder, where the specimen tilt angle ψ could be adjusted from 0° to 50°. A grazing angle of X-ray incidence was set at 1°, and the detector scanned in a two-theta range from 48.3° to 50.3° to measure the YSZ (220) peak. It should be noted that this method is indeed a direct measurement using the film to be measured as a strain gauge in its own right. It is superior to other methods including curvature measurement of a large wafer substrate both before and after film deposition, using Stoney's equation, and nanoindentation which requires a stress-free reference sample and encounters complexities due to surface roughness and substrate [20–22]. Microstructural features of the interface between the YSZ film and substrate were analyzed by a transmission electron microscope (JEM-2100, JEOL Ltd., Japan) operated at 200 kV with specimens carefully prepared using an ion-miller (691 PIPS, Gatan, USA). The ionic conductivity of the films, both before and after annealing at 800 °C for 2 h in air, was determined by an AC impedance analyzer (HIOKI 3532-50 LCR Hi Tester, Koizumi, Japan) using a four-terminal pair configuration with applied Ag paste electrodes to which leads were attached, as shown schematically in Fig. 1. The impedance values were recorded in the frequency range of 42 Hz–5 MHz at 400–600 °C (in a heating rate of 10 °C/min and a dwell time of 10 min) in air. Following the pioneering work of Bauerle [23], the film resistances were extracted from the measured complex impedance plots and the ionic conductivities were calculated accordingly. Typical examples of such complex impedance plots are shown in Fig. 2 for the annealed 30-nm-thick YSZ films, where the equivalent circuit is also shown in the inset.

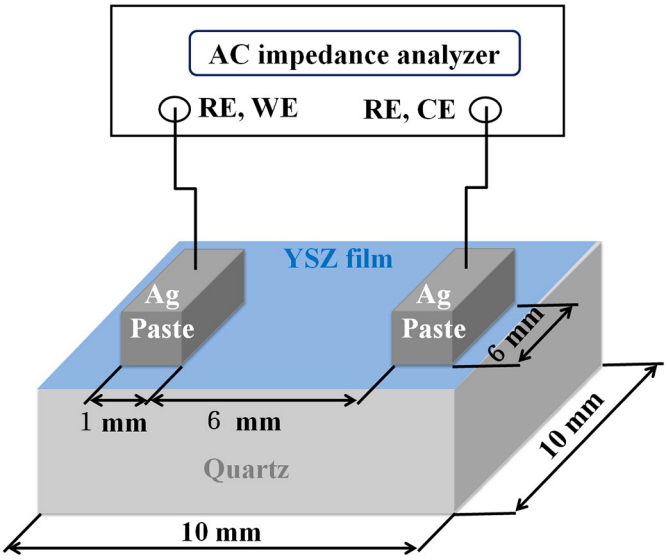

Fig. 1. A schematic showing the setup for AC impedance measurement.

3. Results and discussion

Fig. 3(a) illustrates the GIXRD patterns of polycrystalline YSZ nano-films reactively sputtered on quartz. The characteristic diffraction peaks of a cubic-YSZ phase can be identified for all the YSZ nano-films, as expected from the stabilization effect of yttria addition. It is noticed that the GIXRD patterns from the as-deposited YSZ films all show peak shifts (e.g., $\Delta 2\theta \sim -0.53°$ for the 100-nm-thick film's (220)) toward lower two-theta angles, compared to a diffraction pattern of the YSZ bulk under a stress-free condition (as shown by the broken lines, according to JCPDS 82-1246, for a stress-free $Zr_{0.8}Y_{0.2}O_{1.9}$ with a lattice parameter of $a_0 = 5.147$ Å). In contrast, the diffraction patterns shift to the other side of the standard (e.g., $\Delta 2\theta \sim 0.22°$ for the 100-nm-thick film's (220)) after annealing at 800 °C for 30 min, as shown in Fig. 3(b). It thus indicates that there exist different kinds of residual stresses in the as-deposited and annealed YSZ nano-films respectively. It is also noted that the annealed YSZ films exhibit stronger and narrower diffraction peaks than that of the as-deposited ones, implying the enhancement of crystallinity of these YSZ nano-films by thermal annealing.

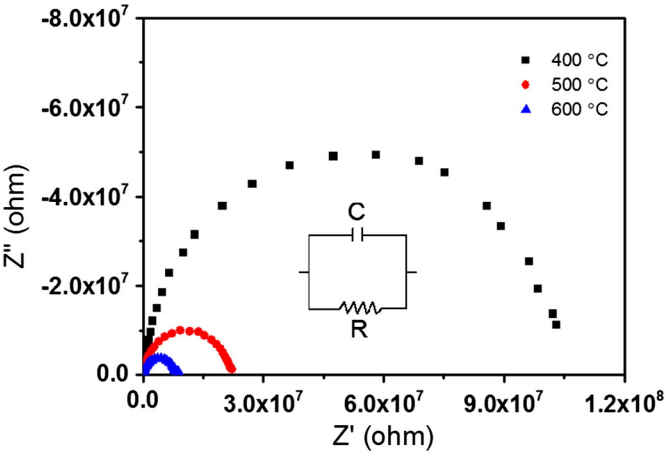

Fig. 2. Typical complex impedance plots for the annealed 30-nm-thick YSZ films, where the equivalent circuit is also shown in the inset.