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Ion conductivity of low-Y_2O_3-content yttria-stabilized zirconia

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Abstract

In this work, we discuss ion conductive character of low-Y_2O_3-content (below 8 mol%) yttria-stabilized zirconia (YSZ) crystallized into high-symmetric phase (cubic and/or tetragonal phases). We analyzed impedance response from ultra-thin YSZ films in metal/insulator/metal (MIM) capacitor measured at ~441°C. It is expected that a characteristic kink on Nyquist-diagram is correlated to the conductivity of inner grain of the YSZ. The conductivity still exhibits the highest value at certain Y_2O_3 content, but it is suggested that the Y_2O_3 content is shifted to the low content side. While the activation energy for ion conduction is monotonically reduced with decreasing Y_2O_3 content.

1. Introduction

YSZ is a typical ion conductor and its ion conductivity is stable against wide range of oxygen pressure [1]. Therefore, YSZ is one of promising candidates for solid electrolyte material in solid oxide fuel cell (SOFC) [2]. It is well known that the ion conductivity and its activation energy exhibit the highest and lowest values at around 8 mol%, respectively [3,4]. This is related to that YSZ with less than 8 mol% Y_2O_3 forms thermodynamically stable monoclinic phase [5] with low ion conductivity.

On the other hand, the lowering operation temperature of SOFC has been proposed from the viewpoint of durability, lifetime and cost [6]. To obtain high ion conductivity at relatively low temperature, thinning of the electrolyte is one of feasible approaches. Here, we focus on that the stability of YSZ structure in high-symmetric phase (cubic and tetragonal phases) is enhanced by thinning due to surface energy contribution [7]. This modulation of YSZ stability suggests that high-symmetric YSZ with lower Y_2O_3 content might be available for thinner electrolyte of SOFC. Although a few works (e.g. the conductivity of 3 mol% tetragonal YSZ [8] and ion conductivity of poly-crystallized thick YSZ around 1000°C [9]) have been reported, ion conductive character of high-symmetric YSZ with lower Y_2O_3 content in the relatively lower temperature range is still unclear.

Therefore, in this work, we surely stabilized low Y_2O_3 content YSZ into high-symmetric phase by thinning YSZ films down to ~10 nm and tried to systematically analyze their ion conductive characters.

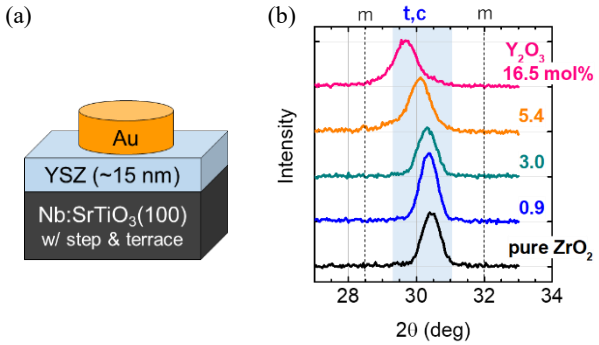

Fig. 1(a) Schematic image of fabricated MIM capacitor. Atomically flat STO substrate is effective to suppress local leakage pass of electron current in YSZ film. The area of Au electrode is ~7000 μm^2. **(b)** XRD spectra from 15-nm-thick YSZ films after impedance measurement at high temperature (θ-2θ scan). CuKα line was used as incident X-ray. "m", "t" and "c" denotes reflection peak angle assigned to monoclinic, tetragonal and cubic phase, respectively. All samples including pure ZrO_2 are crystallized into high-symmetric phase (cubic and/or tetragonal).

2. Experiment

We fabricated Au/ultra-thin YSZ/$SrTiO_3$ (STO) capacitor (**Fig. 1(a)**) as follows. As an electrode and substrate, we used heavily Nb-doped (~10^{19} /cm^3) single crystal STO with atomically flat (100) surface. After chemical cleaning of STO substrate by alcohol, ~15 nm thick amorphous YSZ films were deposited on the STO substrate by rf-sputtering (co-sputtering of ZrO_2 and Y_2O_3). YSZ films were crystallized by following rapid thermal annealing in N_2 atmosphere at 500°C for 30sec. Then, Au electrodes were deposited on YSZ films by thermal evaporation in vacuum chamber. The impedance measurement of ultra-thin YSZ films were carried out in the frequency range of 10^2~10^6 Hz in the temperature range of 30~441°C in vacuum chamber with pressure of 10^{-1}~10^{-3} Pa.

Y_2O_3 content in YSZ films and thickness of YSZ films was determined by X-ray photoelectron spectroscopy and X-ray reflectivity measurement, respectively. We also confirmed the crystal structure of YSZ films by XRD after the impedance measurement. All YSZ films were crystallized into high-symmetric phase as shown in **Fig. 1(b)**. Although it is possible that YSZ(100) epitaxially grows on STO(100)

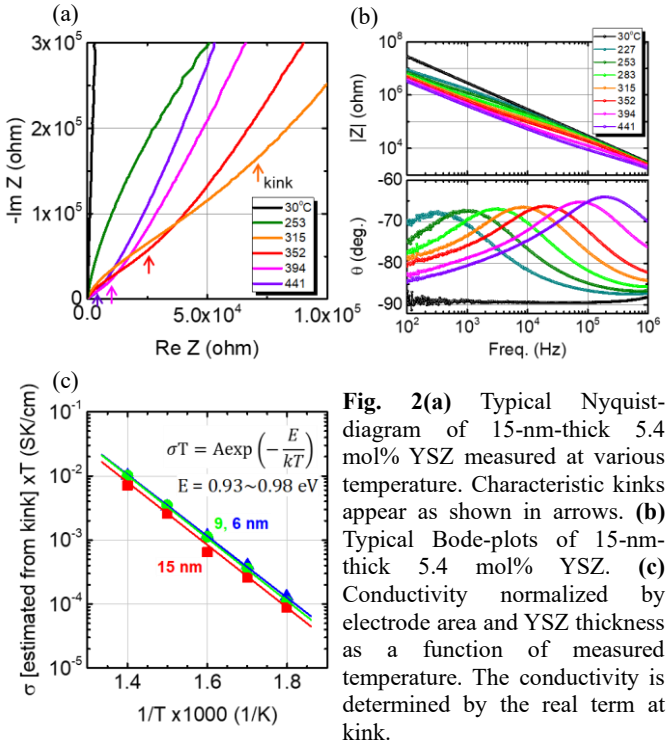

Fig. 2(a) Typical Nyquist-diagram of 15-nm-thick 5.4 mol% YSZ measured at various temperature. Characteristic kinks appear as shown in arrows. **(b)** Typical Bode-plots of 15-nm-thick 5.4 mol% YSZ. **(c)** Conductivity normalized by electrode area and YSZ thickness as a function of measured temperature. The conductivity is determined by the real term at kink.

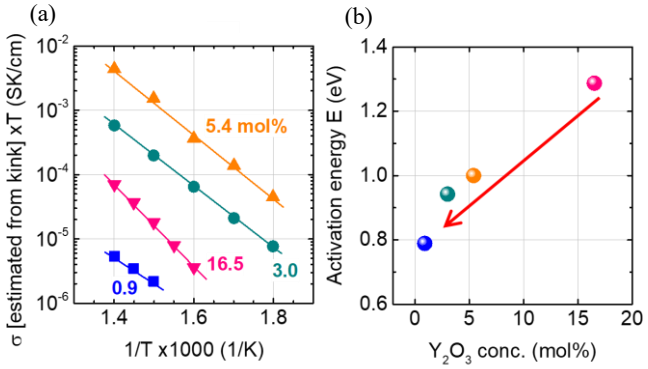

Fig. 3(a) Ion conductivity of YSZ with various Y_2O_3 content estimated from the kink as a function of measured temperature. The conductivity of pure ZrO_2 could not be estimated in the measured temperature range. The conductivity still exhibits the highest value at a certain Y_2O_3 content around 5.4 mol% in this temperature range. **(b)** Activation energy estimated from the slope in (a). The activation energy is clearly reduced with decreasing Y_2O_3 content.

with large 2D tensile strain (~7%) [10], the YSZ films in this work seem poly-crystallized. The lattice constant estimated from the assigned peak in Fig. 1(b) also implies that the YSZ films are not so strained.

3. Results and discussion

3.1 Impedance characteristics of ultra-thin YSZ films

Figure 2(a) shows typical Nyquist-diagram of 15-nm-thick 5.4 mol% YSZ measured at various temperature. Instead of well-known semi-circle, a characteristic kink, which corresponds to local maximum of θ on Bode-plot shown in **Fig. 2(b)**, appears on the diagram. It may be due to a large capacitive component of electron response and/or a high resistive one in ion conduction pass of MIM capacitor. It is reasonable that the resistance determined from Re Z at the kink on Nyquist-diagram corresponds to bulk conductivity of YSZ, since the conductivity is well normalized by the thickness as shown in **Fig. 2(c)**. Furthermore, the YSZ films are so thin that grain boundary might not be formed in direction to the film thickness and that the conductivity may be attributed to inner grain.

Based on the relationship of $\sigma T = Aexp(-E/kT)$, the activation energy E for the ion conduction is estimated to be ~1.0 eV. The fact that this activation energy is in good agreement with reported ones [3,4] also supports the validity of estimation of the inner grain conductivity.

3.2 Y_2O_3 content dependence of ion conductivity

Figure 3(a) shows the relationship between inner-grain conductivities of 15-nm-thick YSZ with various Y_2O_3 content and measured temperature. The 5.4 mol% YSZ has the highest conductivity in this temperature range. The activation energy evaluated from the slope in Fig. 3(a) is shown as a function of Y_2O_3 content in **Fig. 3(b)**. In the range down to 0.9 mol% at least, the activation energy looks monotonically decreased with decreasing Y_2O_3 content. This suggests that the binding energy for defect association included in the activation energy depends on Y_2O_3 content even in such a low Y_2O_3 content, which is in contrast to that at high temperature region [9].

On the other hand, in spite of excluding the lower-side content limit caused by monoclinic phase formation, the conductivity of YSZ still has the peak at certain content. This suggests that the effective conductivity of high-symmetric YSZ is simply described by two mechanisms. One decreases the conductivity with increasing Y_2O_3 content, which corresponds to the activation energy term. The other increases the conductivity and is related to the pre-factor term A. This may correspond to the effective density of oxygen vacancy. It means that the peak Y_2O_3 content of high-symmetric YSZ surely shifts from 8 mol% to lower.

4. Conclusions

The activation energy for ion conduction of ultra-thin low-Y_2O_3-content YSZ with high-symmetric structure is monotonically reduced with decreasing Y_2O_3 content. While the conductivity exhibits the highest value with certain Y_2O_3 content, but it expected to be less than 8 mol%.

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