High Proton Conductivity in Highly Defected Perovskite-type Oxide Thin Films

Yuji Zenitani, Takashi Nishihara, Tetsuya Asano, Hideaki Adachi, Akihiro Itou, Hiroki Takeuchi, Saifullah Badar and Eiji Fujii

Panasonic Corporation
Advanced Technology Research Laboratories,
3-4, Hikaridai, Seika-cho, Soraku-gun, Kyoto, 619-0237, Japan
Phone: +81-774-98-2538 E-mail: zenitani.yuji@jp.panasonic.com

Abstract

We demonstrate that epitaxially grown BZY thin films with large concentrations of ionic defects can exhibit high bulk proton conductivity with minimal temperature dependence. Its activation energy for proton conduction was 0.04 - 0.09 eV, significantly below the typical value for BZY thin film of approximately 0.5 eV. These new BZY films could be advantageous for high efficiency and low temperature operation of electrochemical energy devices.

1. Introduction

Proton conduction in metal oxides is advantageous to realize low temperature operation of solid-oxide fuel cells (SOFCs) and other electrochemical devices such as solid oxide electrolysis cells (SOECs) owing to higher mobility of protons than oxide ions and most of other constituent ions. Among all of the oxide proton conductors, BaZr_{1-x}Y_xO_{3-δ} (BZY) has so far exhibited the highest conductivity [1,2]. Yet its activation energy for proton conduction is still high and thus the proton conductivity at low temperature, particularly lower than 500°C, sharply drops with decreasing temperature. Therefore, achieving high proton conductivity in solids at much lower temperatures remains a central goal in the field of proton conductors [3].

In this paper, we show our discovery that epitaxially grown BZY film subsequently annealed under vacuum exhibited several orders of magnitude higher proton conductivity with minimal temperature dependence than hitherto reported. This minimal temperature dependence clearly indicates that the protons transport in almost barrier-less pathway, which is manifested by activation energy of only 0.04 eV.

2. Experiments

We prepared the epitaxially-oriented BZY thin films by means of radio-frequency (RF) reactive sputtering using BaZr_{1-x}Y_xO_{3-δ} (x = 0.1, 0.3, and 0.5) targets on magnesium oxide (MgO) single-crystalline substrates. The crystallinity of a sputtered BZY thin film can be controlled through the deposition temperature and the growth atmosphere. We annealed the thin-film specimens under vacuum (0.1 Pa, 1000°C) and then exposed them to an argon-hydrogen atmosphere (95% argon, 5% hydrogen) in a furnace for the conductivity measurements.

3. Results and Discussions

The X-ray diffraction (XRD) patterns of the as-grown specimen (x = 0.3) (Fig. 1) indicate that the BZY film has a tetragonally distorted perovskite-type crystal structure with a = 4.221 Å and c = 4.278 Å and epitaxially grew on the MgO (100) substrate in a (001) orientation. The lattice constants of the vacuum-annealed BZY film were slightly reduced by approximately 0.1 - 0.2% and the cubic volume decreased by approximately 0.6%.

The chemical compositions of the as-grown specimen and vacuum-annealed and subsequent hydrogen-treated BZY specimen were determined using electron-probe micro-analysis (EPMA; Table I). The compositions of both the samples are largely deviated from the stoichiometry of BaZr_{1-x}Y_xO_{3-δ}. Particularly barium content is significantly less than stoichiometry. Extended X-ray absorption fine
structure (EXAFS) measurements, which were performed to elucidate the crystal fine structure around the yttrium atoms, confirmed that most of yttrium atoms substituted for the Zr$^{4+}$ sites (Fig. 2). This led us to the conclusion that the BZY films incorporated large amount of vacancies in A-site and O-site of the perovskite-type structure. In spite of such high degree of deficiencies, the crystalline structure of BZY thin films was retained and no secondary phase was formed (see Fig. 1). Such highly defected crystalline structure is not thermodynamically stable by itself, but the single crystalline phase was retained in the epitaxial thin film by epitaxial stabilization.

Fig. 3 shows the electrical conductivity of the as-grown and annealed BZY thin films measured using electrochemical impedance spectroscopy (EIS) in the in-plane direction (that is, parallel to the thin-film surface). The conductivity of the vacuum-annealed specimen at 600°C was approximately three orders of magnitude higher than that of the as-grown specimen. The activation energy for proton conductivity in hydrogen was approximately 0.04 eV for the vacuum-annealed specimen, which is less than 10% of the value for the as-grown specimen (0.54 eV). The resistance was inversely proportional to the film thickness (Inset of Fig. 3), indicating that the measured conductivity is not associated with the surface or the interface but indeed represents bulk conductivity.

We performed electrical motive force (EMF) measurements of the vacuum-annealed BZY thin-film (x = 0.3) to verify the nature of the charge carrier. The EMF was measured using a single-chamber configuration equipped with platinum and gold electrodes with different electro-catalytic activities toward the hydrogen oxidation reaction (Inset of Fig. 4). A voltage developed upon the introduction of oxygen gas reached 260 mV (Fig. 4). Simultaneous EIS measurement showed the conductivity of the film to be ~ 0.33 S/cm, corresponding to the value shown in Fig. 3. This result unambiguously verifies that the observed high conductivity of the annealed specimen in Fig. 3 is indeed protonic. The mechanism behind the occurrence of such high proton conductivity remains to be clarified, but is most likely related to the fact that the BZY thin film was highly off-stoichiometry and incorporated high density of vacancies.

3. Summary
We have demonstrated that BZY thin films containing a large number of ionic defects (barium deficiencies and oxide-ion vacancies) with intact crystal structure can be produced using RF sputtering. The resulting thin-film specimens display improved proton conductivities with as low activation energy as ~ 0.04 eV upon heat treatment under vacuum and in the presence of hydrogen. This low activation energy results in much higher proton conductivity than previously reported especially at low temperature, e.g. 0.14 S/cm at 100°C. This discovery holds promise to realize low temperature SOFCs at or below 100°C as well as any other solid state electrochemical devices utilizing SOECs at low temperature.

References