BL-2A/2023G006

High Surface Electron-Proton Mixed Conduction of $BaCe_{0.7}Ru_{0.1}Y_{0.2}O_{3-\delta}$ Thin Film

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1 Introduction

Proton conducting ceramic fuel cell (PCFC) operating at medium temperature (MT) range of 300~600°C is highly attractive because the operating temperature become lower than solid oxide fuel cell using YSZ ceramic electrolyte. To realize this PCFC, an anode electrode with high reaction activity in MT range are required. In particular, the development of anode electrode material with electron-proton mixed conduction is the most important subject for the avoidance of the triple-phase boundary issue and the expansion of electrode reaction area.

In this study, we attempted to realize a practical mixed conduction of $BaCe_{0.7}Ru_{0.1}Y_{0.2}O_{3-\delta}$ (BCRY) thin film in order to generate large amounts of oxygen vacancies, which are responsible for electron carrier and proton storage.

2 Experiment

BCPY thin films were deposited on MgO (100) single-crystal substrates heated to 550~700 °C by RF magnetron sputtering. The RF power of the ceramic target was fixed at 30 W. The Ar gas flow rate and deposition pressure were kept at approximately 3.0 sccm and 4.0×10^{-3} Torr, respectively. The thickness was ~100 nm.

The crystal structure was confirmed using X-ray diffraction (XRD). The valence state and O-H bond were characterized by X-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES), respectively, which are installed at the undulator beamline BL-2A in the Photon Factory at KEK. The conductivity in in-plane was characterized by AC impedance method using and an amplifier (Solatron 1296) and a frequency response analyzer (Solatron 1260) in MT range region under dry and wet atmosphere ($p(H_2O)$=2.3 kPa).

3 Results and Discussion

Figure 1(a) shows the XRD patterns of the BCRY thin films prepared at various substrate temperature (T_{sub}) and bulk ceramic. The prepared thin films exhibit highly c-axis orientation and its intensity increases with increasing T_{sub}.

Figure 1(b) shows the Ce $3d_{5/2}$ XAS spectra of as-deposited and wet-annealed BCRY thin films. The existences of the mixed valence states of Ce^{3+} and Ce^{4+} were estimated using Gaussian fitting. In particular, the Ce^{3+} (~17.2%) ratios are closely related to the oxygen vacancies ($V_{\ddot{O}}$) concentration. The $V_{\ddot{O}}$ concentrations in as-deposited and wet-annealed films by defect chemical calculation were δ~0.11 and ~0.09, respectively [1].

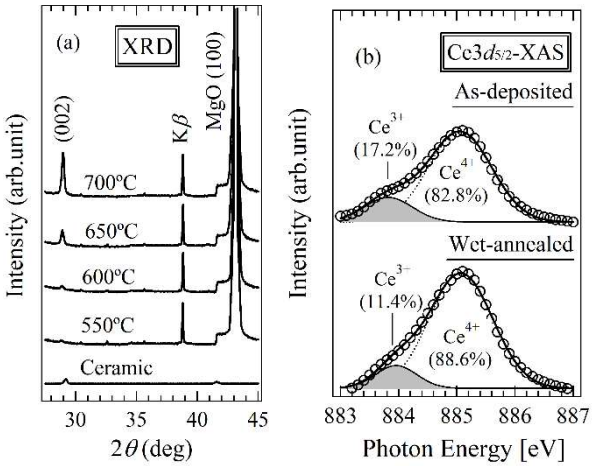

Fig.1: (a) XRD patterns of BCRY thin films prepared at various T_{sub}. (b) Ce $3d_{5/2}$-XAS spectra of as-deposited and wet-annealed BCRY thin films.

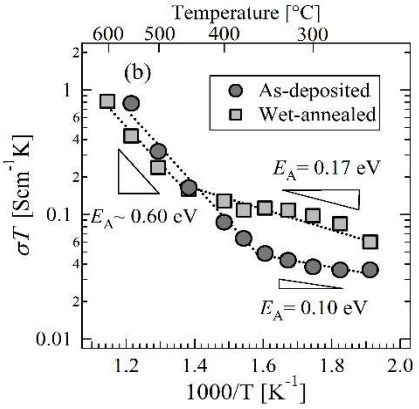

Fig.2: Arrhenius plots of the conductivities of BCRY thin films.

Figure 2 shows the Arrhenius plots of the electrical and ionics conductivities. In particular, the wet-annealed thin film exhibits higher conductivity than the as-deposited film between 225 and 400 °C. Additionally, the wet-annealed thin film has a low E_A of ~0.17 eV, although the E_A of as-deposited film is ~0.10 eV. These results may suggest that the wet-annealed thin film has electron-proton mixed conduction in the temperature range [1].

References

[1] N. Kaneda *et al.*, Jpn. J. Appl. Phys. **64** (2025) 02SP28.

Research Achievements

1. R. Kaneko, T. Yamada, R. Morizane, N. Kaneda, R. Tabuchi, G. Notake, D. Shiga, H. Kumigashira, and T. Higuchi, "Resistive Control of b-Axis Oriented VO_2 Thin Film by Lithium Ions Diffusion from $LiCoO_2$ Buffer Layer". Jpn. J. Appl. Phys. **64** (2025) 02SP30.

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