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Preparation and characterization of rf-sputtered Sr-doped lanthanum cuprate thin films on yttria-stabilized zirconia substrates

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Abstract

Sr-doped lanthanum cuprate of the composition of $La_{1-x}Sr_xCuO_{2.5-\delta}$ exhibits both good electrical and ionic conductivities. Thus, $La_{1-x}Sr_xCuO_{2.5-\delta}$ (LSCu) may be a potential material for the application of electrode material for high operating temperature fuel cell, catalyst or sensor material. However, the perovskite LSCu was present in a narrow range of $0.15 \leq x \leq 0.25$. Due to the structural stability of LSCu is strongly affected by the valence state of copper ions in the material, the control of chemical composition, and the oxygen partial pressure during deposition and heat-treatment plays an important role on the synthesis of LSCu film. For the LSCu film preparation, the composition of target materials, sputtering atmosphere, and heat-treatment temperature were carefully studied.

The LSCu thin film was deposited on a YSZ substrate by rf sputtering under a pressure of 5 mTorr with a 120 W rf power. A single tetragonal perovskite phase was obtained when the sample was subjected to heat-treatment at more than 500 °C in air for 2 h. However, a second phase was formed when the specimen was heat-treated at 800 °C. The electrical conductivity of LSCu film was about 131 S/cm when the specimen was heat-treated at 500 °C. The structure of LSCu was identified by X-ray diffraction (XRD). The chemical composition of LSCu films was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES), and X-ray photoelectron spectroscopy (XPS). The surface morphologies and the thicknesses of the LSCu films were examined by scanning electron microscopy (SEM). The electrical conductivities were investigated by four-point probe technique.

Keywords: Lanthanum cuprate; Scanning electron microscopy; Electrical conductivity

1. Introduction

Recently, the perovskite oxides were widely investigated as electrode materials for solid oxide fuel cells, catalysts, superconductors, and sensor materials due to their mixed conductivity [1–6]. Among them, the Sr-doped lanthanum cuprate, $La_{1-x}Sr_xCuO_{2.5-\delta}$ (LSCu), exhibits a good electrical conductivity of about 2000 S/cm and a high oxygen vacancy concentration of about 17%. Therefore, the perovskite LSCu may contribute potential applications for oxygen sensor and electrode material of solid oxide fuel cell. It has been investigated that, the lanthanum cuprate cannot be synthesized in the ambient atmosphere. On the contrary, a high oxygen partial pressure of 0.2–1 kbar is needed for the lanthanum cuprate synthesis [7,8]. Such a high synthesis oxygen partial pressure may limit the application for the application of this material. In this study, the lanthanum cuprate was stabilized by strontium doping. The Sr-doped lanthanum cuprate, $La_{1-x}Sr_xCuO_{2.5-\delta}$, is present in a narrow range of $0.15 \leq x \leq 0.25$. With 15% of strontium addition, the LSCu was formed in orthorhombic perovskite. And the tetragonal perovskite LSCu was present as the strontium addition in a range of 20–25% [9–11]. The tetragonal perovskite LSCu exhibit a symmetry for which $a \approx 2\sqrt{2}a_p$ and $c \approx a_p$ (a_p is the lattice parameter of the primitive cubic perovskite) and shows a higher structural stability and electrical conductivity than that of orthorhombic phase [6]. Therefore, for the tetragonal perovskite LSCu thin film fabrication, the chemical composition control plays an important role on the LSCu

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synthesis. For this reason, the LSCu thin film was fabricated by rf-sputtering in this study.

For the applications of oxygen sensor and solid oxide fuel cell elecrode material, the yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte material [2,12–15]. Hence, the LSCu thin film in this study was prepared on the polished YSZ substrate.

2. Experimental procedure

The 8 mol% yttria-stabilized zirconia flakes with a thicknesses of 0.6 mm were used as substrate for LSCu film deposition. All the LSCu films were grown by rf magnetron sputtering from a LSCu target with a composition of La:Sr:Cu = 72.5:27.5:100. For the target preparation, an appropriate amount of La_2O_3 (Alfa, 99.99%), $SrCO_3$ (Merck), and CuO (Riedel-deHaën, 99.7%) powders were adequate mixed by ball-milling. After the powder mixture was calcined at 800 °C for 20 h in air, it was compressed into plates with 63.5 mm in diameter by cold isostatically pressed at 200 MPa. And the compacted powder mixtures were sintered at 1030 °C for 20 h in air. The LSCu deposition was carried out under the pressure of 5 mTorr after pre-sputtering for 10 min. The Ar and O_2 flow rates were set at 10 and 30 sccm, respectively, to contribute the LSCu perovskite oxide fabrication. The rf power was 120 W and the distance between the substrate and the target was 60 mm. After rf-sputtered, the specimens were heat-treated at 400–800 °C in air for 2 h. The structure and the degree of crystallization of LSCu films were examined by X-ray diffraction (XRD) traces (GID: Rigaku D/MAX2500) using Cu $K\alpha_1$ radiation at a scanning rate of 2/min covering a 2θ range from 20 to 70°. The chemical composition of the LSCu film was determined by ICP-AES (Kontron S-35). The valence state of the copper ions in LSCu was analyzed by XPS (VGESC A210), and the binding energy is referenced to C 1s (binding energy = 284.9 eV). The morphology and cross-section of the LSCu film were observed using field-emission SEM (Hitachi S4200). The electrical conductivities measurements of the LSCu films were examined by four-point-probe technique.

3. Results and discussion

3.1. Structural characterization

In order to prepare pure phase tetragonal perovskite Sr-doped lanthanum cuprate by rf sputtering, the chemical composition of LSCu target was prepared in an atomic ratio of La:Sr:Cu = 72.5:27.5:100. Also, the Ar and O_2 flow rates were set at 10 and 30 sccm to provide appropriate oxygen source. After the deposition, the XRD pattern of the as-deposited LSCu film on YSZ substrate is shown in Fig. 1(a). Except for the YSZ peaks, no LSCu peak was observed. This result suggests that the as-deposited LSCu film exhibited

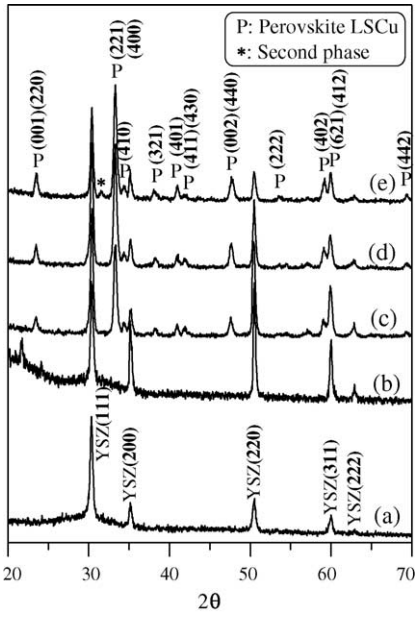

Fig. 1. X-ray patterns of LSCu films deposited on YSZ substrate after heat-treated at various temperatures: (a) as-deposited; (b) 400 °C; (c) 500 °C; (d) 700 °C and (e) 800 °C.

amorphous structure on the YSZ substrate. Subsequently, the as-deposited LSCu film was heat-treated at the temperature range from 400 to 800 °C. For the LSCu film heat-treated at 400 °C, the reflections representing YSZ were still present as shown in Fig. 1(b). For the LSCu films heat-treated at 500 and 700 °C, the tetragonal perovskite LSCu phase were observed as shown in Fig. 1(c) and (d). However, a small amount of second phase was observed when the specimen was heat-treated at 800 °C as shown in Fig. 1(e). Comparing the LSCu(2 2 1)(4 0 0)/YSZ(1 1 1) relative intensities of the samples heat-treated at various temperatures, the relative intensity increased with increasing heat-treated temperature. This result shows that the crystallization of the perovskite LSCu film increases with increasing heat-treated temperature from 500 to 800 °C.

3.2. SEM micrographs of LSCu films

The surface morphologies of the LSCu films deposited on polished substrates with various heat-treatment temperatures was observed by SEM and shown in Fig. 2. Without heat-treatment, no obvious crystallization was observed on the surface of LSCu as-deposited film (Fig. 2(a)). This result is consistent with the XRD analyses (Fig. 1(a)). After the LSCu film was heat-treated at high temperatures (500–800 °C) for 2 h, the crystallization of amorphous LSCu occurred. At 600 °C, nano-sized grains with average grain size of 100–300 nm were observed in Fig. 2(b). When the LSCu film was heat-treated at 700 °C, grain growth was enhanced and larger grains (200–600 nm) were found. The grain size of the LSCu film increased with increasing heat-treatment temperature. As the heat-treatment temperature was raised to 800 °C, the