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Rapid fabrication of chemical-solution-deposited $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ thin films via flashlight sintering

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ABSTRACT

This study demonstrates the sintering effectiveness of an intense pulsed light (IPL) sintering method for the fabrication of lanthanum strontium cobaltite ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$, LSCO) thin films via xenon flashlight irradiation. LSCO thin film was coated on silicon (100) wafer via metal organic chemical solution deposition (MOCSD) methods and the flashlight irradiation process preceded instantly under ambient room temperature conditions. The properties of flashlight irradiated films were compared with thermally sintered ones as reference target. Electrical property, surface morphology, and crystallinity were observed to evaluate effectiveness of the flashlight sintering method by employing four-point probe apparatus, FE-SEM, and XRD, respectively. Considering that flashlight sintering process is procedurally accomplished in milliseconds under ambient room temperatures, this method may be able to circumvent several issues from the conventional thermal sintering process in realizing a convenient and available sintering process. The significance of this work lies in the demonstration of xenon flashlight sintering methods of perovskite oxides that are fabricated via wet chemical solution methods.

1. Introduction

Perovskite-structured oxides (ABO_3) with rare-earth materials have been widely known to possess various properties. These perovskite oxides have been broadly used as parts in memory devices, insulators, dielectric materials, charge conductors, catalysts, and superconductors [1–3]. Furthermore, some perovskite materials are considered to be valuable with regard to energy device applications due to their mixed conductivities and potential to simultaneously conduct both electrons and ions [4]. These so-called mixed ionic-electronic conductors (MIEC) [5] are comprised of various materials, including strontium-doped lanthanum cobaltites ($La_{1-x}Sr_xCoO_{3-\delta}$, LSCO), which are one of the most promising perovskite compounds (containing La and Sr cations on A-sites with Co cations on B-sites) of this type due to their desirable properties [6]. LSCOs originated from the doping of strontium to the A-site of lanthanum cobaltite ($LaCoO_3$), which had formed a pseudocubic perovskite material with a rhombohedral distortion that could be attributed to the differences of the radius between lanthanum and cobalt cations. By doping strontium divalent ions (Sr^{2+}) which could be partially substituted with lanthanum trivalent ions (La^{3+}) of the A-site, some trivalent cobalt ions (Co^{3+}) of the B-site situated near dopants should be oxidized to tetravalent ions (Co^{4+}) to compensate for any imbalance in valence and consequently produce additional extrinsic defects such as holes or vacancies that serve to promote conductivity properties. Considering the generally high thermal stability, they have been deeply investigated as candidate materials for the application of solid oxide fuel cell (SOFC) electrode [7,8]. Additionally, LSCOs are also considered to be good candidates within ferromagnetic memory devices [9,10]. By doping $LaCoO_3$ with strontium, the spin state of oxidized cobalt tetravalent ions is considered to be converted to a higher spin state, resulting in metallic ferromagnetic behavior under specific conditions. Thus, strontium substitution could yield a remarkable improvement in properties, although excessive dopant could deteriorate the structural stability or shift the crystal structure of the parent material. Over substitution of lanthanum with strontium ions could excessively increase the tolerance factor

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attributed to a difference in ionic radii and induce a rhombohedral to cubic structural transition [11]. For these reasons, a large number of related studies have shown interest with regard to controlling the stoichiometry of LSCO to match their intended purpose and due to its interesting characteristics, LSCO is an attractive perovskite oxide that has been used for a variety of purposes.

A variety of methods have been investigated with regard to the deposition of LSCO films applicable to the corresponding field, including physical vapor deposition methods such as pulsed laser deposition (PLD) [12,13], diverse methods [14–16] have also been frequently employed for the fabrication of films on various substrates such as Si, SiO_2/Si, YSZ, Al_2O_3, $SrTiO_3$, etc. Among them, solution based deposition methods possess a wide array of advantages with regard to film fabrication. These methods offer advantages such as low costs, convenient control over stoichiometry, high film purity, and large deposition areas. However, behind these advantages, additional heat treatment steps must be performed due to the nature of the wet chemical solution process to secure desirable properties of the films. Although solution based deposition methods generally require relatively low temperatures for the sintering process, fairly high temperatures (above 600 °C) and large amounts of time (at least 10 h – by considering slow ramping rate and including moderate cooling-off time) are still necessary to achieve proper depositions. Therefore, considering the overall procedures one could not easily say that the wet process is simply superior to the conventional powder sintering process or various vacuum processes. Furthermore, the thin films could inevitably encounter several issues under high temperature conditions, including interfacial issues attributed to property mismatches with the substrate, additional heat treatment steps could deteriorate the advantageous properties possessed by perovskite oxides. To resolve these issues, a millisecond flashlight sintering system was suggested as a solution [17]. In the in-house flashlight sintering system, a xenon flash lamp was usually employed with a broad wavelength ranging from 380 to 950 nm, arc plasma could also be generated by applying a high electrical current. The flashlight system possesses many advantages such as simplicity, mass producibility, and almost no environmental vulnerabilities that could be major obstacles to other methods. In a few milliseconds at room temperature under ambient air, our previous works sintered various films including printed metal nanoparticle electrodes that required very sophisticated processes [18–20].

In this study, lanthanum strontium cobaltite ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$) thin oxide films were deposited onto silicon (100) wafers with a naturally oxidized thin layer via metal organic chemical solution deposition (MOCSD) methods; a xenon flashlight with a broad wavelength range was irradiated as the sintering process. Various irradiation conditions were applied to optimize the system (including irradiation energy, time, pulse duration, and pulse quantity) and evaluate the effectiveness of the flashlight sintering method; the conventionally sintered films were also compared with the flashlight sintered films. Through the systematic experiments, microstructures, crystalline phases, and electrical properties of LSCO were investigated and well-agreed with the material properties. The results showed the dramatic decrease in heat treatment time (hours to a few seconds) while maintaining the material properties of perovskite oxides.

2. Experimental details

For the preparation of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSCO) thin films, Si (100) wafers with naturally oxidized thin layers were used as substrates and LSCO thin films were coated via MOCSD methods. Lanthanum nitrate hexahydrate [$La(NO_3)_3 \cdot 6H_2O$] (Aldrich, St. Louis, Missouri, USA), strontium acetate [$Sr(CH_3COO)_2$] (Fluka), and cobalt acetate tetrahydrate [$Co(CH_3COO)_2 \cdot 4H_2O$] (99.9%, Aldrich) were employed for precursor solutions fabrication. The amount of the cobalt precursor was gravimetrically determined, and according to the determined mole fraction of cobalt, a corresponding sum of lanthanum and strontium were also gravimetrically controlled with an appropriate molar ratio. Acetic acid [CH_3COOH] and deionized water were used as solvents by dissolving the strontium and cobaltite precursors with acetic acid, whereas the lanthanum precursor was separately dissolved in deionized water. Then, the solutions were mixed together and stirred constantly for several hours. To adjust the total concentration of the synthesized solution to 0.3 M, additional acetic acid and distilled water was added; the mixed solution was filtered several times through a nylon filter membrane (0.2 μm mesh) to eliminate any remaining precipitates or impurities which would impede proper film formation. A silicon wafer with a thickness of 300 μm was used as the substrate and the prepared solution was coated onto the silicon wafer via spray pyrolysis methods. Parameters such as the spraying time were fixed for a uniform thickness, while other factors such as the substrate temperature and substrate-nozzle distance were fixed to 150 °C and 18 cm, respectably. All coating times were fixed per the number of deposition time to unify the thickness of LSCO. The coated LSCO films were dried in an oven (200 °C) for 3 min for the procedural step.

After the coating, the subsequent process involved sintering the LSCO films via flashlight sintering method. The in-house flashlight sintering system consisted of a xenon lamp, a power supply, capacitors, a pulse controller, and a reflector. The emitted light from the xenon lamp possessed a wide wavelength range from 380 nm to 950 nm. In this study, the flashlight sintering process was divided into two steps with a preheating step and a main sintering step [21]. The preheating step focused on eliminating some of the remaining organics in the LSCO films prior to the main sintering step. After preheating, the main sintering step was performed to sinter the LSCO particles. The two steps of the flashlight sintering process involved controlling the irradiation energy (from 10 to 16 J/cm^2 per one pulse), irradiation time (10 m), pulse duration (from 10 m to 100 m), and pulse number (from #5 to #30). Also, to compare the flashlight sintering method with conventional sintering, the LSCO films were heat-treated with a halogen furnace in ambient air under various temperatures (from 400 °C to 800 °C) for 60 min at a temperature ramping rate of 2 °C/min. The heat-

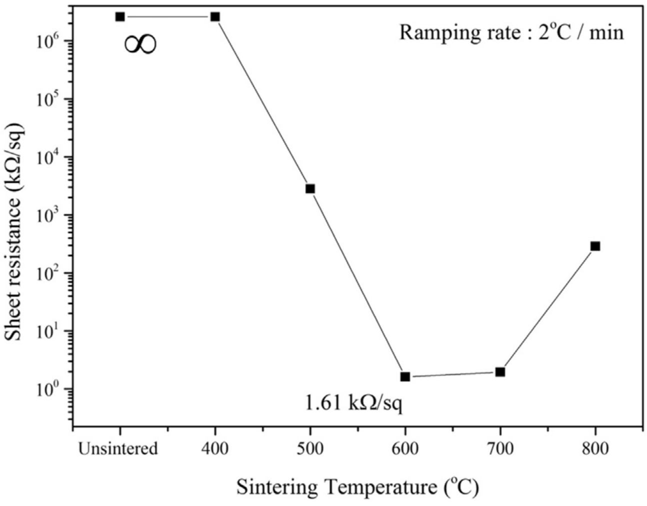

Fig. 1. Sheet resistance of thermally-sintered LSCO films as a function of sintering temperature.