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Full Length Article

Preparation of p-type semiconductor perovskite $La_{1-x}Sr_xCoO_3$ films and their p–n heterostructure devices

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ABSTRACT

Semiconductor $La_{0.67}Sr_{0.33}CoO_3$ thin films has been investigated as function of oxygen atmosphere during film growth in pulsed laser deposition. While amount of oxygen greatly depends on an oxygen atmosphere during film growth, in condition of oxygen atmosphere from 4 Pa to 100 Pa, the carrier in $La_{0.67}Sr_{0.33}CoO_3$ thin films were found to be positive, exhibiting p-type conduction. Furthermore, we prepared (p)-$La_{0.67}Sr_{0.33}CoO_3$/(i)-CeO_2/(n)-$InGaZnO_x$ heterostructure devices and investigated electrical properties. These results showed rectifying behavior was clearly observed in heterostructure at room temperature. The sharp increase of current with voltage, when voltage exceeds diffusion potential, indicates the conductive resistance was small. p-type semiconductor $La_{0.67}Sr_{0.33}CoO_3$ thin films and their p–n heterostructure devices with rectifying behavior may aid in the development of various semiconductor devices such as three terminal transistors, light emitted diode (LED) and solar cell.

1. Introduction

Perovskite oxides are useful as modern electronic materials and, because of their diverse physical properties, including dielectric properties [1], ferroelectric properties [2], superconductivity [3], colossal magnetoresistance [4], ferromagnetism [5], and multi-ferroelectricity [6], their possible uses are continuously being explored for the development of new devices. The p–n heterostructure has been widely used as a basic element in various semiconductor devices such as three-terminal transistors, light-emitting diodes (LEDs), or solar cells [7–11]. In particular, materialization of plane emission is expected in LEDs with p–n heterostructures. Consequently, p–n heterostructures are of great interest in terms of their practical applications and in relation to applied physics. Moreover, p–n heterostructures made of oxides are expected to operate at high temperatures where conventional p–n heterostructures cannot be used. Consequently, a great deal of research has been devoted to the development of p–n heterostructures of oxide materials. Whereas p-type perovskite semiconductors are limited to $La_{1-x}Sr_xCoO_3$ [12], $La_{1-x}Sr_xMnO_3$ [7,8], $SrTi_{1-x}Fe_xO_3$ [13], $SrTi_{1-x}In_xO_3$ [14], $LaRhO_3$ [15,16], and the like, many n-type oxide semiconductors are known. In perovskite oxides such as $La_{1-x}Sr_xCoO_{3-\delta}$, where La^{3+} is partially replaced by Sr^{2+}, when $\delta = 0$ there are mixture of Co^{3+} and Co^{4+} in the crystals, and this mixture is responsible for electrical conduction in the $La_{1-x}Sr_xCoO_{3-\delta}$ system [12]. Therefore, the electrical characteristics of p-type semiconductors consisting of thin films of $La_{1-x}Sr_xCoO_{3-\delta}$ would be expected to be highly dependent on the nature of the oxygen atmosphere present during film growth. To prepare semiconductor p–n heterostructures, high-quality p-type semiconductor thin films are required. In this study, we elucidated the structural and electrical properties of p-type semiconductor thin films of $La_{0.67}Sr_{0.33}CoO_3$, prepared a p–n heterostructure, and investigated the effect of an insulating layer on the current–voltage characteristics.

2. Experiments

The films were grown on single-crystal $SrTiO_3$ (001) substrates by conventional pulsed-laser deposition using a single-phase $La_{0.67}Sr_{0.33}CoO_3$ polycrystalline target. The target chemical composition of the films was $La_{0.67}Sr_{0.33}CoO_3$ ($a_p = 0.3856$ nm) [17], which gives the large electrical conductivity, a small lattice mismatch for $SrTiO_3$ ($a_p = 0.3905$ nm) of less than 1.5%, and a large Hall

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mobility of more than 3 cm^2/Vs [12]. The single-phase $La_{0.67}Sr_{0.33}CoO_3$ powders and polycrystalline targets were prepared by conventional solid-state reactions. A stoichiometric mixture of high-purity $SrCO_3$, La_2O_3, and Co_3O_4 powders was milled, pressed, pre-sintered, and finally sintered at 1273 K for 24 h. During film growth, the $SrTiO_3$ (001) substrates were heated to 700 °C, and the oxygen partial pressure was controlled at 1 Pa to 100 Pa. The ArF excimer laser (λ = 193 nm) that we had used a repetition rate of 8 Hz and a fluence of ~1.2 $J\,cm^{-2}$ $pulse^{-1}$ at the target surface. All the films in this study were approximately 300-nm thick. The phase and crystallinity of the films were examined by x-ray diffraction (the out-of-plane and asymmetric in-plane XRD). The current–voltage response and carrier-transport properties of the samples were determined at room temperature by the Hall measurement method (Resitest 8300; Toyo Corp., Tokyo).

3. Results and discussion

3.1. Semiconductor perovskite $La_{1-x}Sr_xCoO_3$ films

Epitaxial growth of the $La_{0.67}Sr_{0.33}CoO_3$ films on the $SrTiO_3$ (001) substrates in an oxygen atmosphere at 40 Pa was confirmed by the out-of-plane XRD. The out-of-plane XRD pattern of a $La_{0.67}Sr_{0.33}CoO_3$ film grown at 700 °C is shown in Fig. 1(a). The (00*l*) reflections, which correspond to (00*l*) reflections in an perovskite lattice, appeared exclusively in these patterns, suggesting that the $La_{0.67}Sr_{0.33}CoO_3$ films had grown epitaxially. Asymmetric in-plane XRD measurements also showed diffraction from the (220) planes, and a four-fold symmetry was distinctly observed by the ϕ scan, as shown in Fig. 1(b). In addition, reflection high-energy electron diffraction (RHEED) from the films showed streaky patterns. Taken together, the out-of-plane XRD patterns, asymmetric in-plane XRD, and RHEED patterns confirmed that the films grew epitaxially on the $SrTiO_3$ (001) substrates and had a high crystal quality.

A typical atomic-force microscopy (AFM) image of a 300 nm thick film of $La_{0.67}Sr_{0.33}CoO_3$ grown on an $SrTiO_3$ (001) substrate is shown in Fig. 2. The calculated average roughness *Ra* was 0.72 nm. The image also shows that the $La_{0.67}Sr_{0.33}CoO_3$ film had a flat surface and there were no higher precipitate to induce electrical micro-short-circuits and concentrations of the electric field. These results indicated that the $La_{0.67}Sr_{0.33}CoO_3$ films had flat surfaces and were suitable for use as base-side layer in p–n heterostructures.

The semiconducting properties, such as the mobility and carrier concentration, of the $La_{0.67}Sr_{0.33}CoO_3$ system are largely dependent on the amount of oxygen present [12]. In conventional pulsed-laser deposition, the atmosphere during film growth is a reducing condition, unlike sintering in an oxygen atmosphere for bulk preparation. It is difficult to accurately determine the amount of oxygen δ in thin films of $La_{0.67}Sr_{0.33}CoO_{3-\delta}$ due to small volume. To regulate the amount of oxygen in thin films of $La_{0.67}Sr_{0.33}CoO_{3-\delta}$, we prepared thin films of $La_{0.67}Sr_{0.33}CoO_3$ in atmospheres with oxygen partial pressures of 1–100 Pa during film growth. Oxygen was expected to be introduced into the $La_{0.67}Sr_{0.33}CoO_3$ system in atmospheres when high partial pressures of oxygen were present during film growth. We prepared thin films in atmospheres with partial pressures of oxygen of 1, 2, 4, 10, 20, 40, or 100 Pa during film growth under otherwise identical conditions, and we investigated their semiconducting properties at room temperature. The dependence of the carrier concentration and the mobility on the oxygen atmosphere during film growth is shown in Fig. 3. The carrier concentrations for films grown in atmospheres of oxygen partial pressure 4, 10, 20, 40, or 100 Pa were 2×10^{20}, 1.5×10^{20}, 7×10^{20}, 1.5×10^{21}, and 7×10^{20} cm^{-3}, respectively, and the corresponding mobilities were 0.75, 0.9, 0.8, 1.0, and 1.2 $cm^{-2}\,V^{-1}\,s^{-1}$, respectively. The carriers in $La_{0.67}Sr_{0.33}CoO_3$ thin films were found to be positive and the films exhibited p-type conduction; at oxygen partial pressures of more than 4 Pa, definite p-type semiconducting properties were obtained. The mobilities of the thin films were smaller than those found in the corresponding bulk material. An improvement in the mobility by post-annealing could not be confirmed. A degradation in crystallinity might be responsible for the changes in semiconductor properties, such as the mobility. The carrier concentration and mobility were dependent on the oxygen atmosphere during film growth, and their values at oxygen partial pressures of 4 Pa–100 Pa were larger than those obtained at lower oxygen partial pressures. In oxygen atmospheres of less than 2 Pa, no distinct n-type or p-type semiconductor was produced. To elu-

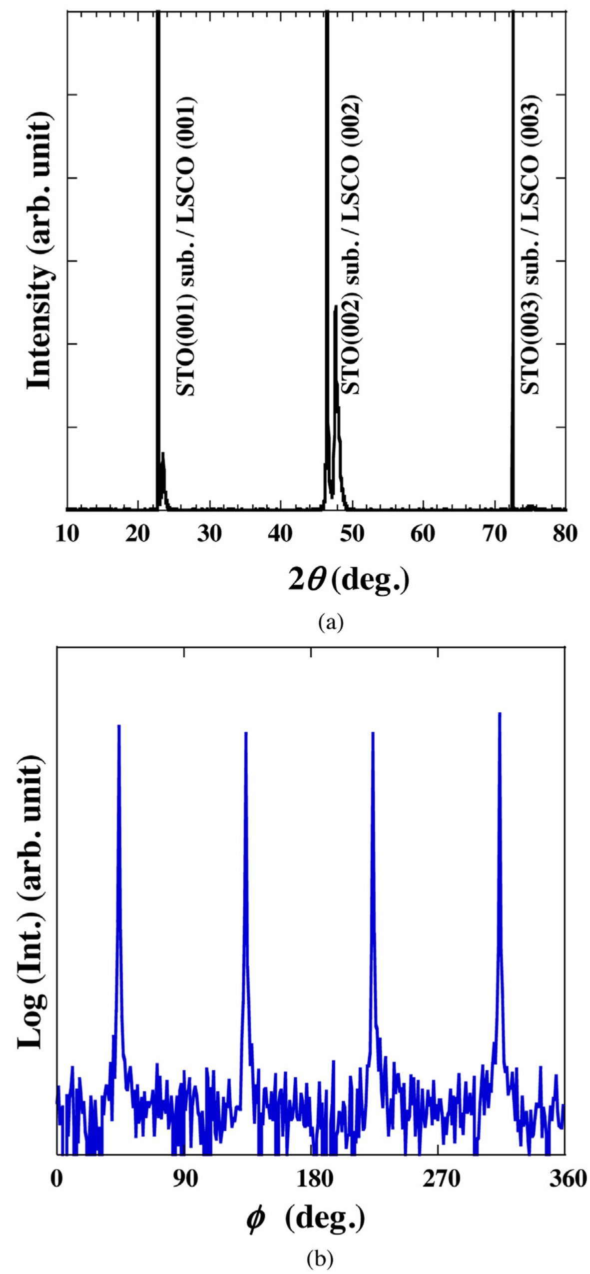

Fig. 1. (a) The out-of-plane XRD pattern of a $La_{0.67}Sr_{0.33}CoO_3$ thin film on a $SrTiO_3$ (001) substrate. The (00*l*) reflections, which correspond to (00*l*) reflections in an ideal perovskite lattice, appeared exclusively in these patterns, showing that the $La_{0.67}Sr_{0.33}CoO_3$ films had grown epitaxially. (b) A ϕ scan pattern of the $La_{0.67}Sr_{0.33}CoO_3$ thin film on the STO (001) substrate with an incident angle of 0.3°. Asymmetric in-plane XRD measurements showed that a four-fold symmetry was distinctly observed.