Electrical resistivity anomaly in (Pr$_{1-y}$Y$_y$)$_{1-x}$Ca$_x$CoO$_3$ epitaxial films (M=Y, Gd) fabricated by pulsed laser deposition


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Electrical resistivity anomaly in (Pr$_{1-y}$M$_y$)$_{1-x}$Ca$_x$CoO$_3$ epitaxial films (M=Y, Gd) fabricated by pulsed laser deposition

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(Pr$_{1-y}$M$_y$)$_{1-x}$Ca$_x$CoO$_3$ epitaxial films (M=Y, Gd) have been successfully fabricated by pulsed laser deposition on the single crystal substrates with different lattice constant. The polycrystalline bulk of this material shows a first-order metal-insulator (MI) transition below the critical temperature. Although $\rho(T)$ of all the as-grown films shows a semiconducting behavior at entire temperature range, an anomalous $\rho(T)$ upturn with wide hysteresis can be clearly seen for the film grown on the SrLaAlO$_3$ (SLAO) substrate, which applied the in-plane compressive stress to the film. Such anomaly in $\rho(T)$ is interpreted as a sign of the first-order phase transition related with the spin-state (SS) transition, which was observed in the polycrystalline bulk. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0). [http://dx.doi.org/10.1063/1.4942558]

I. INTRODUCTION

The perovskite cobaltites RECoO$_3$ (RE=rare-earth element and Y) show a spin-state (SS) transition of Co$^{3+}$ ions from a low spin state (LS; $t_{2g}^6e_g^0$, $S=0$) to a high spin state (HS; $t_{2g}^4e_g^2$, $S=2$) with increasing temperature, followed by the formation of the metallic state of the intermediate spin state (IS; $t_{2g}^2\sigma^+\sigma^-$, $S=1$) at higher temperatures.$^1$ The temperature induced SS transition indicates a small energy difference $\delta E$ between the crystal-field splitting and Hund coupling energy.$^2,3$ The hole-doped systems such as La$_{1-x}$Sr$_x$CoO$_3$ generally show a temperature stable phase with itinerant cobalt states, which result presumably from the mixed IS Co$^{3+}$/LS Co$^{4+}$ or HS Co$^{3+}$/LS Co$^{4+}$ configurations, and undergo a ferromagnetic ordering at low temperatures. Most interestingly, some Pr-based cobaltites exhibit a pronounced first-order transition to a low-temperature phase of weakly paramagnetic character and reduced conduction. This effect was revealed for the first time on Pr$_{0.5}$Ca$_{0.5}$CoO$_3$ at $\sim$ 90 K by the step-like resistivity jump and concomitant anomalies in the magnetic susceptibility, heat capacity, lattice dilatation and photoemission spectroscopy.$^4,5$ The mechanism of the transition was tentatively ascribed to a spin state crossover from the itinerant cobalt states to an ordered mixture of localized LS Co$^{3+}$ and LS Co$^{4+}$ ($t_{2g}^5e_g^0$, $S=1/2$) states. Similar metal-insulator (MI) transition was evidenced also in the less doped Pr$_{1-x}$Ca$_x$CoO$_3$ ($\chi=0.3$) under higher hydrostatic pressures and in the (Pr$_{1-x}$RE)$_{1-x}$Ca$_x$CoO$_3$ system ($0.2<x<0.5$) with a partial substitution of Pr by smaller RE cations such as Sm, Eu, and Y under ambient pressure.$^7,8$ This peculiar transition appeared to be conditioned not only by the presence of both Pr and Ca ions, but also by a larger structural distortion of the CoO$_6$ network, depending on the average ionic radius and size mismatch of perovskite A-site ions.$^9$ Furthermore, the critical temperature $T_{MI}$ was found

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to decrease in a quadratic dependence of applied magnetic field, so that the transition could be completely suppressed in very high fields.\textsuperscript{10}

An alternative scenario explaining the nature of such specific transition was proposed on the basis of electronic structure calculations exploiting the temperature dependence of the structural experimental data for \(\text{Pr}_0.5\text{Ca}_{0.5}\text{CoO}_3\),\textsuperscript{11} in which the formal cobalt valence should change below \(T_M\) from mixed-valence \(\text{Co}^{3.5+}\) towards pure \(\text{Co}^{3+}\) with strong preference for the LS state and, concomitantly, the praseodymium valence should increase simultaneously from \(\text{Pr}^{3+}\) towards \(\text{Pr}^{4+}\). The theoretical hypothesis about the crucial role of variable praseodymium valence was experimentally supported by the observations of a Schottky peak in the low temperature specific heat of \((\text{Pr}_{1−y}\text{Y}_y)_0.8\text{Ca}_{0.2}\text{CoO}_3\) \((y=0.075\text{ and }0.15)\),\textsuperscript{12} and by the x-ray absorption near-edge structure (XANES) spectra at the \(\text{Pr} L_3\) edge directly.\textsuperscript{13–16}

It is widely desirable to use a single crystal or an epitaxial film for the physical investigation. In the \(\text{La}_{1−x}\text{Sr}_x\text{CoO}_3\) system, single crystals and thin films have been fabricated and investigated.\textsuperscript{17–19} In the epitaxial thin film, the electrical conduction and the spin state change depending on the film thickness and fabrication condition.\textsuperscript{19} However, for the \((\text{Pr}_{1−x}\text{M}_x)_1−\text{Ca}_x\text{CoO}_3\) system with the simultaneous MI and SS transition, only polycrystalline bulk materials have been investigated experimentally in the previous studies and there is no investigations using a single crystal or an epitaxial film because of the difficulty of the fabrication.

When the material is prepared in the thin film form, the physical properties are sensitive to crystal structure, metallic composition, oxygen content \textit{etc}, mainly depending on the lattice mismatch between the substrate and the material. Thin films experience a stress due to mismatch of the lattice and the thermal expansion to the substrate, in addition to the intrinsic internal stress. In particular, the interface between the film and the substrate can play an important role, giving rise to boundary regions with different structures and affecting the transport and magnetic properties due to the induced strain especially in very thin films. The strain in the epitaxial thin films can be easily manipulated by the film thickness and the lattice parameter of the substrate material. For example, in the \(\text{RNiO}_3\) thin film, which shows the bandwidth controlled MI transition, the transition temperature, \(T_M\), was increased (decreased) by tensile (compressive) in-plane strain.\textsuperscript{20} The strain effect is attributed to an increase (decrease) of the Ni-O-Ni bond angle, which affects to films in the same way as the bulk under higher pressure.\textsuperscript{21} Thin films of these materials have potential for various applications such as the use in resistive switches and phase-change memory.

In the present work, we fabricated the \((\text{Pr}_{1−y}\text{M}_y)_{1−x}\text{Ca}_x\text{CoO}_3\) epitaxial films \((\text{M}=\text{Y, Gd})\) by pulsed laser deposition (PLD) on the single crystal substrates with different lattice constant. We investigated the electrical resistivity anomaly, which seemed to be related with the spin-state transition shown in the bulk materials.

II. EXPERIMENTAL PROCEDURE

\((\text{Pr}_{1−y}\text{Y}_y)_{1−x}\text{Ca}_x\text{CoO}_3\) (PYCCO) and \((\text{Pr}_{1−y}\text{Gd}_y)_{1−x}\text{Ca}_x\text{CoO}_3\) (PGCCO) thin films were prepared by the PLD method using a fifth harmonic wave of YAG laser with \(λ=213\text{ nm}\) and a repetition rate of 10 Hz. The pulse duration is 5 ns and the power is 18 mJ. \((\text{Pr}_{0.8}\text{Y}_{0.2})_0.8\text{Ca}_{0.2}\text{CoO}_3\) and \((\text{Pr}_{0.8}\text{Gd}_{0.2})_0.8\text{Ca}_{0.2}\text{CoO}_3\) polycrystalline targets with nominal composition were prepared by a standard solid-state reaction. \(\text{Pr}_6\text{O}_{11}\), \(\text{Y}_2\text{O}_3\), \(\text{Gd}_2\text{O}_3\), \(\text{CaCO}_3\), \(\text{Co}_3\text{O}_4\) raw powders with purity higher than 99.9\% were used as starting materials. The powders were mixed, calcined at 1000°C for \(12\text{ h}\), pressed into pellets with a diameter of \(20\text{ mm}\) and a thickness of \(5\text{ mm}\) and then sintered at \(1200°C\) for \(48\text{ h}\) in flowing oxygen gas. Powder X-ray diffraction analysis revealed that the sintered targets were a single phase. The target and the substrate were mounted in the vacuum chamber and were rotated at the speed of 7 rpm and 3 rpm, respectively, to reduce non-uniform erosion and to deposit uniformly. The deposition was carried out for 1 - 4 hours in a pure oxygen atmosphere of 0.1 to 1.0 Torr and at a substrate temperature of 600°C and the film thickness was measured to be about 50–100 nm. The films were grown on \((001)\) oriented \(\text{SrTiO}_3\) (STO: \(a=0.3905\text{ nm}\), \(\text{LaAlO}_3\))\(_{0.3}$$\text{Sr}_2\text{AlTaO}_6$$\(_{0.7}\) (LSAT: \(a=0.3868\text{ nm}\)), \(\text{LaAlO}_3\) (LAO: \(a=0.3790\text{ nm}\)) and \(\text{SrLaAlO}_4\) (SLAO: \(a=0.3756\text{ nm}, c=1.2636\text{ nm}\)) single crystal substrates. The pseudo cubic lattice parameter of the \((\text{Pr}_{1−y}\text{Y}_y)_{1−x}\text{Ca}_x\text{CoO}_3\) bulk \((x=0.4, y=0.2)\) is \(a=0.3775\text{ nm}\) and the lattice mismatch using
FIG. 1. The relation between the lattice parameters of the \((\text{Pr}_{\sub{0.8}}\text{Y}_{\sub{0.2}})_{\sub{0.6}}\text{Ca}_{\sub{0.4}}\text{CoO}_3\) and those of the used single crystal substrates.

The relation of \(\varepsilon = (a_{\text{PYCCO}} - a_{\text{sub}})/a_{\text{sub}}\) is +3.4% for STO, +2.5% for LSAT, +0.4% for LAO and -0.5% for SLAO. The relation of the lattice parameters between the material and the substrates is shown in Fig. 1, in which the in-plane tensile stress is applied to the film grown on the STO, LSAT and LAO substrates and the in-plane compressive stress is applied in the film grown on the SLAO substrate. The chemical composition of the grown films was measured by electron probe microanalysis (EPMA), in which the measured composition of \((x, y)\) of the film was decreased to \((0.3, 0.13)\) from the nominal composition of \((0.4, 0.2)\) for the PYCCO sample. To clarify the crystalline quality of the grown films, X-ray diffraction analyses of \(\theta-2\theta\) and \(\phi-2\theta\) scans were performed, both of which identified the out-of-plane and in-plane alignments, respectively. The electrical resistivity \(\rho(T)\) was measured on cooling and heating runs in the 10 - 300 K range by a standard four-probe method for the as-grown films and heat-treated films under high-pressure oxygen gas (2.0 MPa) at 600°C for 3 h.

III. RESULTS AND DISCUSSION

Figure 2 shows the out-of-plane XRD patterns \((\theta-2\theta\) scan) of the PYCCO films fabricated on the STO and SLAO substrates. The PYCCO films display clear \((00l)\) reflections of the pseudo cubic structure with no indications of impurities or miss-orientation together with the strong \((00l)\) reflections from the substrates. These results demonstrate the out-of-plane orientation of PYCCO thin films on the substrates.

Figure 3 presents the \(\phi-2\theta\) azimuth scan for the PYCCO film, fabricated on the SLAO substrate. Four sharp peaks of the \((002)\) reflections were observed every 90 deg. and the in-plane alignment can be confirmed, which were also confirmed for the films grown on the other substrates. These results suggest that the PYCCO films are epitaxial films grown on the substrates.

Figure 4 shows the \((002)\) intensity of the out-of-plane XRD patterns of the PYCCO films on the STO substrate, as a function of the film thickness, \(d\). The diffraction peak angle of the films decreases with increasing film thickness, \(d\), and shifts toward the peak position for the bulk crystal. These results suggest that the out-of-plane lattice constant of the epitaxial films on the STO substrate is smaller than that of the bulk crystal and approaches the lattice constant of the bulk material. This is because the tensile stress was induced in the film surface due to the positive lattice mismatch \(\varepsilon = +3.4\%\), and then was relaxed with increasing film thickness. On the other hand, for the films grown on the SLAO substrate, the \((002)\) peak was found at \(2\theta=47.70°\) for the \(d=100\) nm film (not shown), which was the lower angle than that of the bulk crystal \((2\theta=47.21°)\). In this case, the in-plane compressive stress is induced in the film surface because of negative lattice mismatch \(\varepsilon = -0.5\%\).

Figure 5(a) shows the temperature dependence of the electrical resistivity, \(\rho(T)\), of the as-grown PYCCO films grown on each substrate. The thickness of each film was about 50 nm. \(\rho(T)\) of the target bulk is also shown in the figure, in which \(\rho(T)\) shows a jump with about two orders of magnitude at \(T_{\text{MI}}=140\) K on the cooling run, and shows a sharp drop at \(T_{\text{MI}}=150\) K with a hysteresis. The absolute value of \(\rho(T)\) on the heating run was larger than that on the cooling run.
FIG. 2. The out-of-plane XRD patterns (θ-2θ scan) of the PYCCO films grown on the (a) STO and (b) SLAO substrates in the case of the target composition of \((x=0.4, \ y=0.2)\).

run above \(T_{MI}\). The irreversibility in \(\rho(T)\) might come from the occurrence of micro cracks created by the large volume contraction and expansion passing through the transition temperature.\(^4\) On the other hand, the \(\rho(T)\) curves for all the as-grown films show a semiconducting behavior without pronounced anomaly, the absolute \(\rho(T)\) values change depending on the substrate used, and no irreversibility is detectable after the cooling and heating runs for the films grown on the STO, LSAT and LAO substrates. Nonetheless, one may notice a distinct behavior of the film grown on the SLAO substrate, namely the anomalous inflection point at 170 K and a wide hysteresis in \(\rho(T)\) below this temperature that are seen in more detail Figure 5(b), where an alternative plot of \(\log(\rho) vs. T^{-1/4}\), commonly used for variable range hopping (VRH), is displayed. To understand this observation, we refer to the fact that MI transition can be induced in polycrystalline \(\text{Pr}_{1-x}\text{Ca}_x\text{CoO}_3\) \((x=0.3)\) under high hydrostatic pressures and the critical temperature \(T_{MI}\) increases with increasing pressure.\(^7\) The compression stress in the present PYCCO film on SLAO substrate seems to have analogical effect to
FIG. 3. The in-plane XRD patterns ($\phi$-2$\theta$ scan) of the PYCCO film fabricated on the SLAO substrate in the case of the target composition of ($x$=0.4, $y$=0.2).

the hydrostatic pressure. In this sense, the anomalous $\rho(T)$ upturn followed by a hysteresis region is likely a sign of a similar first-order phase transition.

A question arises why the MI transition in the film grown on the SLAO substrate is less pronounced compared to the bulk material. This is unexpected, especially in view of the fact that actual mismatch conditions seem to be much in favor of the transition. Firstly, the out-of-plane lattice constant of the film, 0.3820 nm, at room temperature (see Figure 6 below) combined with the in-plane $a$=0.3756 nm imposed by SLAO substrate illustrates some deformation of the PYCCO structure, but the unit cell volume remains exactly same as for bulk material. This is a signature that

FIG. 4. The (002) intensity in the out-of-plane XRD patterns of the PYCCO films, as a function of the thickness of the film in the case of the target composition of ($x$=0.4, $y$=0.2).
FIG. 5. Temperature dependence of the electrical resistivity, $\rho(T)$, at the cooling and heating runs: (a) The log$\rho$ vs. $T$ plot for the as-grown (AG) PYCCO films on different substrates; (b) An alternative log$\rho$ vs. $T^{-1/4}$ plot with linear low-temperature trend demonstrating the viability of the VRH scenario. The data shown by dashed lines refer to PYCCO films grown on LAO and SLAO substrates, after a heat-treatment (HT) in high-pressure oxygen gas at 600°C for 3 h.

film is likely well developed on the substrate without cracks. Secondly, it can be anticipated that the unit cell of PYCCO is shrank at the MI transition to the same extent as it is in the bulk material, 1.0% in volume or 0.3% in linear dimensions.\textsuperscript{22} Therefore, the deformation energy comprised in the film at room temperature will be removed below the transition to the low-temperature phase. There should be evidently another reason for the less pronounced anomaly at $T_{MI}$. It is worth mentioning that early experiments on prototypical compound Pr$_{0.5}$Ca$_{0.5}$CoO$_2$ revealed a critical sensitivity of the MI transition to any oxygen deficiency. To check such hypothesis, the PYCCO films grown on the each substrate were post-annealed under high-pressure oxygen gas (2.0 MPa) at 600°C for...
3 h. The resistivity data on two samples with minimum film/substrate mismatch were added to the results on as-grown samples in Figures 5(a) and 5(b). For the film grown on the SLAO substrate, the anomalous $\rho(T)$ upturn disappeared in the oxygenized sample and some irreversibility in the cooling and heating runs arose. These changes suggest that, contrary to our expectation, the first-order phase transition vanished by the heat treatment. For the film grown on the LAO substrate, the absolute $\rho(T)$ value was only slightly increased by the post annealing.

Figure 6 presents the lattice constant $a$ determined by out-of-plane measurements and the electrical resistivity at 300 K, $\rho(300 \text{ K})$, of the as-grown films on each substrate, as a function of lattice mismatch $\varepsilon$. The thickness of each film was about 50 nm. The out-of-plane lattice constant $a$ monotonically decreases with increasing lattice mismatch $\varepsilon$, which suggests that the film was extended in plane due to the tensile stress for the positive $\varepsilon$ value. The $\rho(300 \text{ K})$ value takes a minimum around $\varepsilon=0$, which is a reasonable trend. Namely, the deformation of CoO$_6$ octahedra due to the lattice mismatch affects the electron transport in the film.

Figures 7(a) and 7(b), respectively, show the temperature dependence of the electrical resistivity, $\rho(T)$; the $\log \rho \text{vs.} T$ plot and the alternative $\log \rho \text{vs.} T^{-1/4}$ plot at the cooling and heating runs of the as-grown (Pr$_{1-y}$Gd$_y$)$_{1-x}$Ca$_x$CoO$_3$ (PGCCO) films on each substrate. $\rho(T)$ of the heat-treated PGCCO films grown on the LAO and SLAO substrates are also shown. All the films, of which the thickness was about 100 nm, were confirmed to be epitaxial films by XRD analysis. $\rho(T)$ of the target bulk is also shown in the figures, in which $T_{MI}$ was 70 K and 80 K on the cooling and heating runs, respectively. $\rho(T)$ of all the as-grown films shows a semiconducting behavior at entire temperature range. Similarly to the PYCCO film, an anomalous $\rho(T)$ upturn with a wide hysteresis can be clearly observed only for the as-grown film on the SLAO substrate, which is interpreted as a sign of the first-order phase transition. However, the $\rho(T)$ upturn seems to remain after the heat treatment as can be seen in Fig. 7(b). For the thinner PYCCO film on SLAO substrate about 50 nm in thickness shown in Fig. 5, the transition was clearly suppressed by the heat treatment under the high-pressure oxygen gas, where the heat treatment removed the stress. On the other hand, in the present thicker PGCCO film on SLAO substrate with 100 nm in thickness, the heat treatment made only much smaller change. The appearance of the anomalous $\rho(T)$ upturn and the relaxation after the heat treatment change depending on the film thickness.
FIG. 7. Temperature dependence of the electrical resistivity, $\rho(T)$, at the cooling and heating runs: (a) the log$\rho$ vs $T$ plot and (b) the alternative log$\rho$ vs $T^{-1/4}$ plot for the as-grown (AG) PGCCO films on different substrates. The data shown by dashed lines refer to the heat-treatment (HT) PGCCO films grown on LAO and SLAO substrates after the heat treatment in high-pressure oxygen gas at 600°C for 3 h.

IV. SUMMARY

The $(\text{Pr}_{1-y}\text{Y}_y)_{1-x}\text{Ca}_x\text{CoO}_3$ (PYCCO) and $(\text{Pr}_{1-y}\text{Gd}_y)_{1-x}\text{Ca}_x\text{CoO}_3$ (PGCCO) films have been fabricated by pulsed laser deposition (PLD) method on the single crystal substrates with different lattice constants, and their crystallographic and electrical properties have been investigated. The important experimental results and conclusions are summarized as follows.

(1) The obtained films have been confirmed to be epitaxial films grown on the single crystal substrates with different lattice constants by XRD measurements.
The electrical resistivity, $\rho(T)$, of all the as-grown films shows a semiconducting behavior at entire temperature range. However, the anomalous $\rho(T)$ upturn with a wide hysteresis can be clearly observed only for the films grown on the SLAO substrate, which applied the in-plane compressive stress. The $\rho(T)$ anomaly of the thin PYCCO film 50 nm in thickness on SLAO vanished after the heat treatment in high-pressure oxygen gas. On the other hand, the $\rho(T)$ upturn of the thick PGCCO film 100 nm in thickness on SLAO seems to remain after the heat treatment.

The anomaly in $\rho(T)$ is interpreted as a sign of the first-order phase transition accompanied by the spin-state transition, which was observed in the polycrystalline bulk.

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