

Control of Epitaxial Orientation and Anisotropic Transport Properties in Layered Cobaltite Thin Films

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We have investigated the control of crystal orientation in layered cobaltite β - A_x CoO₂ (A =Sr and Ca) and misfit-type Ca₃Co₄O₉ thin films and succeeded in the growth of epitaxial films with c axis orientation perpendicular and parallel to the substrate surface by rf-planar magnetron sputtering. Anisotropic transport properties (parallel to the CoO₂ layers \parallel and perpendicular to the CoO₂ layers \perp) were measured using the epitaxial films with c axis parallel to the film plane. The resistivity parallel to the CoO₂ layers ρ_{\parallel} for the β - A_x CoO₂ is as low as a few m Ω cm at room temperature and shows metallic behavior. Large anisotropic nature was observed in misfit-type Ca₃Co₄O₉ epitaxial films and the ratio ranged from 40 to 80. As for thermoelectric properties, relatively isotropic nature was observed in the Seebeck coefficient. Parallel Seebeck coefficients S_{\parallel} for layered cobaltite thin films are approximately 50 μ V/K for A_x CoO₂ and 110 μ V/K for Ca₃Co₄O₉ at room temperature, and the perpendicular S_{\perp} for both materials are about half of S_{\parallel} .

Key words: Layered cobaltites, Thermoelectric properties, Thin films, Anisotropic transport properties

1. INTRODUCTION

Layered cobaltites have been investigated extensively in recent years because of their potential use in thermoelectric energy conversion devices. The large thermoelectricity was first discovered in Na_{0.5}CoO₂ [1], and since then many reports have been made on new materials with similar structure such as Ca₃Co₄O₉ [2, 3], Bi₂Sr₂Co₂O₉ [4], TlSr₂Co₂O₉ [5], and so on [6–9]. Crystal structure of layered cobaltites consists of alternate stacking of two kinds of layers along c axis. One is the CdI₂-type conducting CoO₂ layer and the other is the insulating block layer. The insulating layer is unique for each cobaltite and strongly relates to the degree of anisotropy in whole material. The crystal structure of Na_xCoO₂ is considered to be primitive because the insulating layer is a simple Na monolayer. Another layered cobaltites, such as Ca₃Co₄O₉ or Bi₂Sr₂Co₂O₉, have a rock-salt type insulating block layer consisting of three or four atomic layers of rock-salt structure. The square rock-salt layers and the triangular CoO₂ layers form different sublattices individually and two lattice constants exist along b axis, which causes so-called misfit-type structure.

It is considerably worth studying in detail on anisotropic transport properties in layered cobaltites, in order to clarify the origin of their unusual thermoelectricity. However, few studies of thermoelectricity along the perpendicular direction to the CoO₂ layers (i.e. along the c axis) are reported because available single crystals of most layered cobaltites are too thin (<500 μ m) to measure physical properties along the c axis [1,10]. Furthermore primitive

thermoelectric cobaltite Na_xCoO₂ has reactive alkaline element in the major constituents and so instable in air. In this experiment, we tried to handle alkaline-free composition, and we investigated simple chemical composition in alkaline-earth cobalt oxides A-Co-O (A =Sr and Ca).

Meanwhile, thin-film processing is effective not only for device application but also for the growth of metastable phases [13]. In addition, the growth orientation can be controlled by adjusting growth parameters, which enables aligned crystal with large dimension along the c axis [14].

Here we report on the thin-film preparation of layered cobaltites in simple A-Co-O (A =Sr and Ca) chemical composition. We succeeded in the syntheses of three compounds of metastable Sr_xCoO₂, Ca_xCoO₂ and misfit-type Ca₃Co₄O₉, and also succeeded in the control of crystal orientation and measurement of anisotropic nature between parallel and perpendicular directions to CoO₂ layers.

2. THIN FILM PREPARATION

Thin films were prepared by an rf-planar magnetron sputtering. We used composite A-Co-O targets with A/Co ratio of 0.5-1.0. Sputtering deposition was carried out onto c -plane (0001), a -plane (11 $\bar{2}$ 0) and m -plane (1 $\bar{1}$ 00) of sapphire substrates concurrently in a mixed atmosphere of Ar and O₂ (20-30%) with 5 Pa total pressure. The substrates were heated at 600-700°C during the deposition. Thickness of all films was maintained at 1000 Å. After the

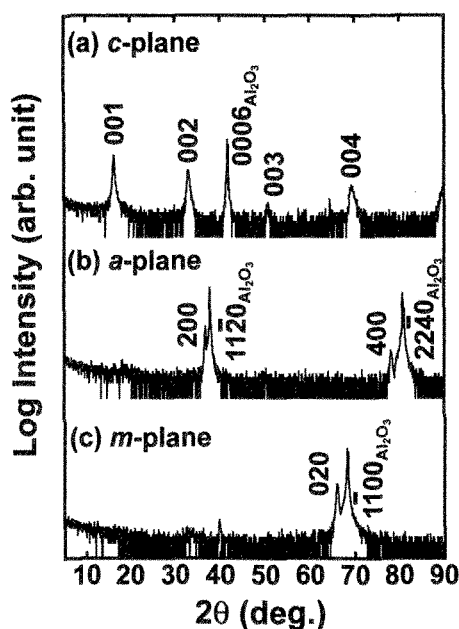


Fig.1: XRD patterns of Ca_xCoO_2 thin films on (a) *c*-plane, (b) *a*-plane and (c) *m*-plane sapphire substrates.

deposition, samples were slowly cooled down to room temperature in an oxidizing atmosphere at a rate of 5 °C/min. The color of the films was metallic black and the cationic composition (A/Co) of the films, measured by an energy dispersive x-ray spectroscopy (EDX), was ranged from 0.4 to 0.8 depending on the target composition.

3. FILM PROPERTIES

3.1 Crystallographic Characterization

It was found that two types of layered cobaltites were synthesized in A-Co-O films. One is conventional misfit-type $\text{Ca}_3\text{Co}_4\text{O}_9$, and the other is A_xCoO_2 with primitive structure, which is the metastable phase obtained previously by an ion-exchange method [11,12]. Fig.1 and Fig.2 show the XRD patterns for Ca_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ films grown on *c*-plane, *a*-plane and *m*-plane of sapphire substrates, respectively. Almost the same patterns as Fig.1 were observed for Sr_xCoO_2 films. The series of peaks in Fig.1 (a) corresponds to the period of 5.41 Å, while the period estimated from Fig.2 (a) is 10.8 Å. The period of 5.41 Å indicates the successful creation of alkaline-free primitive Ca_xCoO_2 structure isomorphous with ion-exchanged metastable Ca_xCoO_2 [11] by the sputtering processing. The period of 10.8 Å in Fig.2 (a) confirms the formation of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase having a almost doubled *c*-axis period of Ca_xCoO_2 .

In-plane alignment of films was investigated by the reciprocal space mapping and the heteroepitaxial growth of all A_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ films on sapphire substrates was confirmed. It was also proved that the grown phase in both A_xCoO_2 films is a monoclinic

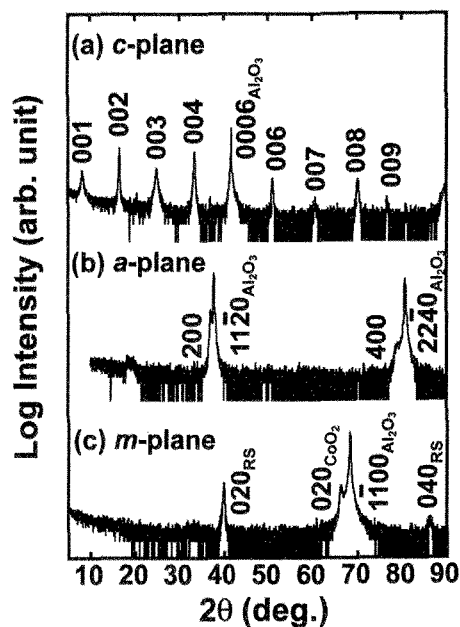


Fig.2: XRD patterns of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on (a) *c*-plane, (b) *a*-plane and (c) *m*-plane sapphire substrates.

β -phase [16], not a hexagonal γ -phase. Thus the indices of reflections are assigned as shown in Fig.1 and Fig.2. The epitaxial relation of both β - A_xCoO_2 and misfit-type $\text{Ca}_3\text{Co}_4\text{O}_9$ films on *c*-plane sapphire is $(001)[100]_{\text{film}} \parallel (0001)[11\bar{2}0]_{\text{Al}_2\text{O}_3}$.

From Fig.1 (b) and (c) as well as Fig.2 (b) and (c), *a* axis orientation perpendicular to *a*-plane and *b* axis orientation perpendicular to *m*-plane of sapphire substrates were confirmed, respectively. Especially, for *b*-axis oriented $\text{Ca}_3\text{Co}_4\text{O}_9$ film as shown in Fig.2 (c), two series of reflections were observed, due to the misfit structure along *b* axis, namely reflection from insulating rock-salt (RS) sublattice and from conducting CoO_2 sublattice [11]. It was found that both substrates (*a*-plane

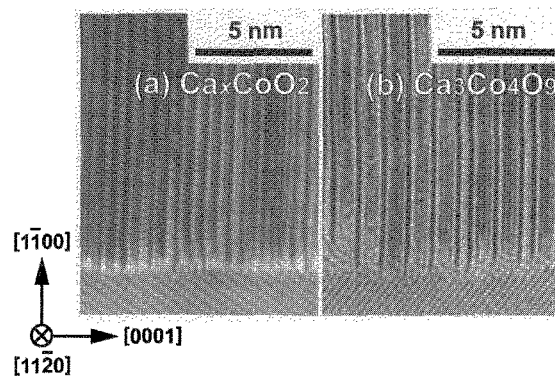


Fig.3: Cross-sectional TEM images of (a) Ca_xCoO_2 and (b) $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on *m*-plane sapphire substrates. Crystallographic directions of sapphire are shown besides the images.

and *m*-plane of sapphire) resulted in the formation of layered cobaltites with layer structure perpendicular to the substrate surface. In these substrates, the crystallinity of the film on *m*-plane of sapphire seems superior to that on *a*-plane sapphire. So the anisotropic nature of the layered cobaltite films was evaluated using the films prepared on *m*-plane of sapphire substrates.

Cross-sectional transmission electron micrographs of Ca_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ films on *m*-plane were taken with the incident beam parallel to $[11\bar{2}0]$ of sapphire and are shown in Fig.3. Well-ordered pile-ups of layered structure were observed for both films, which indicates that the CoO_2 layers are grown perpendicular to the substrate surface and uniquely aligned in the film plane. The pitch of stripes was evaluated to be approximately 5.5 Å in Fig.3 (a) and 10.8 Å in Fig.3 (b). In $\text{Ca}_3\text{Co}_4\text{O}_9$ film (Fig.3 (b)), a small amount of intergrowth structure was observed, which have the period of about half of regular one, i.e. intergrowth of Ca_xCoO_2 layers. The epitaxial relation of the both Ca_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ films on *m*-plane in the out-of-plane direction is $[010]_{\text{film}} \parallel [1\bar{1}00]_{\text{Al}_2\text{O}_3}$. As for in-plane relation, tilted *c* axis of monoclinic lattice for β - Ca_xCoO_2 and misfit-type $\text{Ca}_3\text{Co}_4\text{O}_9$ is not parallel to the *c* axis of sapphire but the normal axis of the CoO_2 layers is parallel, namely $[001]_{\text{film}} \parallel [0001]_{\text{Al}_2\text{O}_3}$. In the similar way, the epitaxial relation of the films on *a*-plane of sapphire was determined to be $[100]_{\text{film}} \parallel [11\bar{2}0]_{\text{Al}_2\text{O}_3}$ for out-of-plane and $[001]_{\text{film}} \parallel [0001]_{\text{Al}_2\text{O}_3}$ for in-plane geometry [17].

In the epitaxial layered cobaltite thin films on *m*-plane sapphire, two distinct directions, parallel to CoO_2 layers (\parallel) and perpendicular to CoO_2 layers (\perp), exist in the film plane. Thus, anisotropic transport properties can be investigated by choosing the measuring direction.

3.2 Electric Properties

Electric resistivity was measured for the rectangular (approximately 5mm × 1mm) samples along the direction parallel (ρ_{\parallel}) and perpendicular (ρ_{\perp}) to the CoO_2 layers with four-terminal Au electrodes deposited on the film surface. Fig. 4 shows the temperature dependence of the resistivity for Sr_xCoO_2 , Ca_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ films on *m*-plane sapphire substrates. Parallel resistivity ρ_{\parallel} of both Sr_xCoO_2 and Ca_xCoO_2 films has a low value in the order of few $\text{m}\Omega\text{cm}$ at room temperature and shows metallic behavior in the measured temperature range down to 10 K. On the other hand, perpendicular resistivity ρ_{\perp} is about ten times larger than ρ_{\parallel} , whereas the temperature dependence is still metallic. This behavior is quite different from that for films on *a*-plane sapphire substrates, which exhibit higher resistivity and semiconductive behavior [17].

Larger anisotropic nature was observed in the

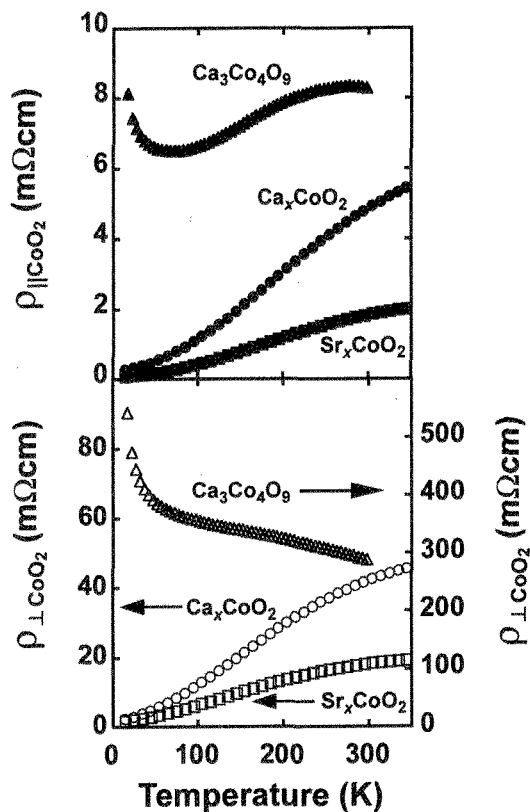


Fig.4: Temperature dependence of electric resistivity parallel to the CoO_2 layers (upper) and perpendicular to the CoO_2 layers (lower) in Sr_xCoO_2 , Ca_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on *m*-plane sapphire substrates.

$\text{Ca}_3\text{Co}_4\text{O}_9$ film on *m*-plane of sapphire. Parallel resistivity ρ_{\parallel} is 8-10 $\text{m}\Omega\text{cm}$ at room temperature, almost twice of that of β - Ca_xCoO_2 , and shows metallic behavior in the temperature range from 300 K to 50 K, whereas semiconductive behavior is observed below 50 K. Perpendicular resistivity ρ_{\perp} is much higher and exhibits semiconductive nature in the whole measuring temperature range. The ratio $\rho_{\perp}/\rho_{\parallel}$ increases from 40 at 300 K to 80 at 10 K. The result obtained using the present orientation-controlled $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film is almost consistent with that in $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystal [2], except for the slight difference in curvature of ρ_{\perp} -T curves. The difference may be caused by the mixed contribution of $\text{Ca}_3\text{Co}_4\text{O}_9$ and the existing intergrowth of Ca_xCoO_2 phase as found in the TEM image (Fig.3 (b)).

3.3 Thermoelectric Properties

Seebeck coefficients for the rectangular-shaped samples (approximately 4 mm × 1 mm) were measured by a steady-state method using a standard reference of constantan wire. A sapphire substrate of the same rectangular dimension was attached just close to the reference wire in order to match the thermal conduction

with the sample. The measurement was made possible for perpendicular Seebeck coefficients S_{\perp} of layered cobaltites thin films, owing to the large c axis dimension in the b axis oriented epitaxial thin films on m -plane sapphire. The temperature dependences of the Seebeck coefficients for β - $A_x\text{CoO}_2$ and misfit-type $\text{Ca}_3\text{Co}_4\text{O}_9$ are shown in Fig. 5. Seebeck coefficients parallel to the CoO_2 layers (S_{\parallel}) for both Sr_xCoO_2 and Ca_xCoO_2 are around $50 \mu\text{V/K}$ at room temperature and decreased monotonically with the decrease of temperature. Perpendicular Seebeck coefficients S_{\perp} at room temperature were around $20 \mu\text{V/K}$, which is about a half of S_{\parallel} , and also decreased as the temperature is lowered. Misfit-type $\text{Ca}_3\text{Co}_4\text{O}_9$ films shows large S_{\parallel} of about $110 \mu\text{V/K}$ and S_{\perp} of about $40 \mu\text{V/K}$. The temperature dependence of Seebeck coefficients of S_{\perp} and S_{\parallel} show similar tendency as β - $A_x\text{CoO}_2$. From the present study using the orientation-controlled cobaltite films, properties of Seebeck coefficients (S_{\perp}) perpendicular to the CoO_2 layers were demonstrated for the first time and the value was found to be about a half of S_{\parallel} parallel to the CoO_2 layers.

4. SUMMARY

We have prepared epitaxial thin films of primitive layered cobaltite $A_x\text{CoO}_2$ with A elements occupied only by the alkaline-earth Sr and Ca, and misfit-type cobaltite $\text{Ca}_3\text{Co}_4\text{O}_9$. The crystal orientation of the film could be controlled by the surface plane of the sapphire substrates used. In the epitaxial films on a -plane and m -plane sapphire, CoO_2 layers grew perpendicularly to the substrate surface and two unique orientations parallel (\parallel) and perpendicular (\perp) to the CoO_2 layers intersect in the film plane. Measurement of anisotropic properties was achieved by considering the transport direction and large anisotropy was confirmed in electric resistivity while more isotropic nature in the Seebeck coefficients. The

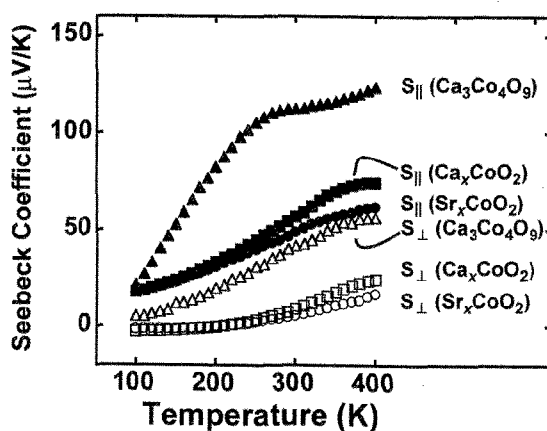


Fig.5: Temperature dependence of Seebeck coefficient in Sr_xCoO_2 , Ca_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on m -plane sapphire substrates. Measurements were performed in both parallel S_{\parallel} and perpendicular S_{\perp} directions in respect to CoO_2 layers.

present thin-film processing using sputtering, which is capable of fabricating metastable phase, has potential advantage in search for thermoelectric materials of higher performance and in basic research such as anisotropic transport properties.

ACKNOWLEDGMENTS

The authors would like to thank Prof. T. Kajitani, Dr. Y. Ono, Dr. Y. Miyazaki of Tohoku University, and Prof. I. Terasaki and Dr. S. Okada of Waseda University for their useful discussions. They also wish to thank Dr. K. Ohnaka for the continuous encouragements.

REFERENCES

- [1] I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, R12685-87 (1997).
- [2] A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau, and J. Hejtmanek, *Phys. Rev. B* **62**, 166-75 (2000).
- [3] Y. Miyazaki, K. Kudo, M. Akoshima, Y. Ono, Y. Koike, and T. Kajitani, *Jpn. J. Appl. Phys.* **39**, L531-33 (2000).
- [4] R. Funahashi, I. Matsubara, and Satoshi Sodeoka, *Appl. Phys. Lett.* **76**, 2385-87 (2000).
- [5] S. Hebert, S. Lambert, D. Pelloquin, and A. Maignan, *Phys. Rev. B* **64**, 172101 (2001).
- [6] W. Shin and N. Murayama, *J. Mater. Res.* **15**, 382 (2000).
- [7] R. Funahashi, I. Matsubara, H. Ikuta, T. Takeuchi, U. Mizutani, and S. Sodeoka, *Jpn. J. Appl. Phys.* **39**, L1127-29 (2000).
- [8] I. Terasaki, I. Tsukada, and Y. Iguchi, *Phys. Rev. B* **65**, 195106 (2002).
- [9] A. Maignan, S. Hebert, D. Pellouin, C. Michel, and J. Hejtmanek, *J. Appl. Phys.* **92**, 1964-67 (2002).
- [10] G. Peleckis, T. Motohashi, M. Karppinen, and H. Yamauchi, *Appl. Phys. Lett.* **83**, 5416-18 (2003).
- [11] B. L. Cushing and J. B. Wiley, *J. Solid State Chem.* **141**, 385-91 (1998).
- [12] R. Ishikawa, Y. Ono, Y. Miyazaki, and T. Kajitani, *Jpn. J. Appl. Phys.* **41**, L337-39 (2002).
- [13] H. Minami, K. Itaka, H. Kawaji, Q. J. Wang, H. Koinuma, and M. Lippmaa, *Appl. Surf. Sci.* **197-198**, 442-47 (2002).
- [14] H. Matsuda, H. Sakakima, H. Adachi, A. Odagawa, and K. Setsune, *J. Mater. Res.* **17**, 1985 (2002).
- [15] C. Fouassier, G. Matejka, J. -M. Reau, and P. Hagenmuller, *J. Solid State Chem.* **6**, 532-37 (1973).
- [16] Y. Ono, R. Ishikawa, Y. Miyazaki, Y. Ishii, Y. Morii, and T. Kajitani, *J. Solid State Chem.* **166**, 177-81 (2002).
- [17] T. Kanno, S. Yotsuhashi, and H. Adachi, *Appl. Phys. Lett.* **85**, 739 (2004).
- [18] H. Adachi, T. Kanno, and S. Yotsuhashi, *Proc. ICT 2004* (to be published).

(Received December 23, 2004; Accepted February 15, 2005)