Thermoelectric Properties of the Layered Cobaltite $\text{Ca}_3\text{Co}_4\text{O}_9$ Epitaxial Films Fabricated by Topotactic Ion-Exchange Method

Kenji Sugiura¹, Hiromichi Ohta^{1,2}, Kenji Nomura³, Tomohiro Saito⁴, Yuichi Ikuhara⁵, Masahiro Hirano³, Hideo Hosono^{3,6} and Kunihiro Koumoto^{1,2}

¹Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

²CREST, JST, Kawaguchi 332-0012, Japan

³ERATO-SORST, JST, in Frontier Collaborative Research Center, Mail-box S2-13, Tokyo Institute of Technology, Yokohama 226-8503, Japan

⁴Materials R & D Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

⁵Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan

⁶Frontier Collaborative Research Center, Mail-box S2-13, Tokyo Institute of Technology, Yokohama 226-8503, Japan

To clarify the thermoelectric properties of the layered cobalt oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film fabricated by the topotactic ion-exchange method [K. Sugiura *et al.*, Appl. Phys. Lett. **89**, 032111 (2006)], the electrical resistivity (ρ), Hall coefficient (R_H), and Seebeck coefficient (S) of high quality $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film were examined over the temperature range 10–1000 K. The film exhibited a low ρ of $4.0 \times 10^{-3} \Omega \text{ cm}$ and a large S of $\sim +200 \mu\text{V K}^{-1}$, which leads to the thermoelectric power factor of $1.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$, at 1000 K. Furthermore, the film exhibited good thermal stability at 1000 K in air. [doi:10.2320/matertrans.E-MRA2007864]

(Received December 10, 2006; Accepted May 22, 2007; Published July 11, 2007)

Keywords: thermoelectric properties, layered cobaltite, epitaxial film, topotactic ion-exchange method, reactive solid-phase epitaxy

1. Introduction

Thermoelectric (TE) energy conversion is one of the cleanest and environmentally compatible power generation technologies because unused heat sources are readily available, *e.g.* electric power plants, industrial factories, automobiles, and computers, and can be directly converted into electric power by utilizing the Seebeck effect of a thermoelectric material.¹⁾ The performance of TE materials is generally characterized by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. ZT corresponds to the energy conversion efficiency of a Carnot cycle.

Recently, *p*-type layered cobalt oxides including Na_xCoO_2 ($x = 0.3 \sim 1$),^{2,3)} Sr_xCoO_2 ($x \sim 0.35$)^{4,5)} and $\text{Ca}_3\text{Co}_4\text{O}_9$,^{6–8)} have attracted much attention toward the realization of oxide TE devices because of their good TE performance and advantages over state-of-the-art, high temperature TE materials, including a SiGe-based alloy⁹⁾ and $\beta\text{-FeSi}_2$,^{10,11)} in terms of chemical and thermal resistances at high-temperatures ($\sim 1000 \text{ K}$) and low toxicity. Among the layered cobalt oxides, $\text{Ca}_3\text{Co}_4\text{O}_9$ is regarded as a most promising material since it can exhibit good thermal stability at 1000 K in air. Therefore, intensive studies have been made in TE properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ to date with bulk single crystalline and polycrystalline forms.^{6–8,12–14)} The film is more favorable for practical TE applications. In particular, a high-quality epitaxial film can provide high-performance as TE device because high-quality epitaxial films can exhibit intrinsic electrical properties as bulk single crystal. Moreover, a high-quality epitaxial film is also useful to clarify some of relevant TE properties, such as Hall coefficient, of $\text{Ca}_3\text{Co}_4\text{O}_9$.

Very recently, we have developed a process for fabricating

a high-quality epitaxial film of $\text{Ca}_3\text{Co}_4\text{O}_9$ by the topotactic ion-exchange method.¹⁵⁾ $\text{Ca}_3\text{Co}_4\text{O}_9$ crystal is composed of an alternative stack of CdI_2 -type CoO_2 layer and rock-salt-type Ca_2CoO_3 layer along the *c*-axis.¹⁶⁾ The structure formula of $\text{Ca}_3\text{Co}_4\text{O}_9$ can be represented as $[\text{Ca}_2\text{CoO}_3]_x\text{CoO}_2$ ($x \sim 0.62$), but we abbreviate $[\text{Ca}_2\text{CoO}_3]_x\text{CoO}_2$ to $\text{Ca}_3\text{Co}_4\text{O}_9$ for simplicity in this paper. Figure 1(a) illustrates the crystal structure of $\text{Ca}_3\text{Co}_4\text{O}_9$ together with that of A_xCoO_2 ($A = \text{Na}, \text{Ca}$ *etc.*). Both crystals have the layered structure composed of the same CoO_2 layers. Thus, we have succeeded in fabricating high-quality epitaxial films of $\text{Ca}_3\text{Co}_4\text{O}_9$ by the topotactic ion-exchange method using the $\text{Na}_{0.8}\text{CoO}_2$ epitaxial film as a precursor (Fig. 1(b)). The fabricated $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film exhibited the high electrical conductivity, which was larger than any other value reported, below 300 K due to the enhanced carrier mobility.

From the viewpoint of the practical TE application, it is essential to clarify thermoelectric properties of the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film at high temperature ($\sim 1000 \text{ K}$). Here we report the thermoelectric properties of high-quality $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial films over the temperature range 10–1000 K. The $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film exhibited good thermal stability at 1000 K in air and a high thermoelectric performance, which was comparable to that of conventional *p*-type high temperature TE materials.

2. Experimental

The $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial films were fabricated by the topotactic ion-exchange method¹⁵⁾ using Na_xCoO_2 epitaxial film, grown by reactive solid-phase epitaxy (R-SPE) method,^{17,18)} as a precursor (see Fig. 1(b)). *Step 1:* High-quality epitaxial films of Na_xCoO_2 ($x \sim 0.8$) were grown on (0001)-face of $\alpha\text{-Al}_2\text{O}_3$ substrates by the R-SPE method and they

Fig. 1 (a) Crystal structures of layered cobalt oxides: (left) $A_x\text{CoO}_2$ ($A = \text{Na}, \text{Ca}$); (right) $\text{Ca}_3\text{Co}_4\text{O}_9$. Both crystals have CoO_2^- layer composed of edge-shared CoO_6 octahedra. (b) Flow chart of topotactic ion-exchange method to obtain $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial films. *Step 1*: The reactive solid-phase epitaxy method for $\text{Na}_{0.8}\text{CoO}_2$ epitaxial film growth. *Step 2*: Ca^{2+} -ion exchange treatment of the $\text{Na}_{0.8}\text{CoO}_2$ film. *Step 3*: Topotactic conversion into epitaxial $\text{Ca}_3\text{Co}_4\text{O}_9$.

were used as a precursor for the following ion-exchange treatment. The details of the R-SPE for the preparation of $\text{Na}_{0.8}\text{CoO}_2$ epitaxial films have been described elsewhere.^{19,20} *Step 2*: The $\text{Na}_{0.8}\text{CoO}_2$ film was heated together with $\text{Ca}(\text{NO}_3)_2$ powder at 300°C in air for 5 h to exchange Na^+ ions with Ca^{2+} ions. After that, the film was washed with distilled water for several times to remove excess $\text{Ca}(\text{NO}_3)_2$ powder attached to the film. The chemical composition ratio of $\text{Ca}:\text{Co}:\text{Na}$ in the ion-exchanged film was evaluated to be 0.32 : 1.0 : 0.01 by X-ray fluorescence (XRF, ZSX 100e, Rigaku Co.) analysis. *Step 3*: Finally, the $\text{Ca}_{0.32}\text{CoO}_2$ film was again heated with $\text{Ca}(\text{OH})_2$ powder at 800°C for 1 h in air to further incorporate Ca^{2+} -ions into the film and convert to $\text{Ca}_3\text{Co}_4\text{O}_9$.

The crystalline quality, orientation and thickness of the films were evaluated by high-resolution X-ray diffraction (HR-XRD), cross-sectional high-resolution transmission electron microscopy (HREM), and atomic force microscopy (AFM). HR-XRD measurements were conducted using a thin film X-ray diffractometer (ATX-G, Rigaku Co.). HREM observations were performed using a JEOL JEM-3000F high resolution electron microscope operating at 300 kV (JEOL Co., Tokyo, Japan.). AFM measurements were performed at room temperature with a Seiko Instruments SPI-3800N probe system. The electrical resistivity (ρ), Hall coefficient (R_H), carrier concentration (n), and Hall mobility (μ_{Hall}) of the films were measured by dc four-probe method in the van der Pauw configuration, and Seebeck coefficient (S) of

Fig. 2 (a) Cross sectional HREM image of $\text{Ca}_3\text{Co}_4\text{O}_9$ film on (0001)-face of $\alpha\text{-Al}_2\text{O}_3$ substrate fabricated by topotactic ion-exchange method. HREM lattice image is also shown together with schematic of the crystal structure. (b) Topographic AFM images of the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial films. Cross-sectional profile from a to a' is also shown.

the films was measured by a conventional steady state method over the temperature range 10–1000 K.

3. Results and Discussion

Figure 2(a) shows the cross-sectional HREM image of the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial films fabricated by the topotactic ion-exchange method. The HREM observation was made with the incident beam parallel to the $[100]$ $\text{Ca}_3\text{Co}_4\text{O}_9$ film $\parallel [11\bar{2}0]$ $\alpha\text{-Al}_2\text{O}_3$ substrate. A distinct layered lattice structure composed of the periodic stacking of the CoO_2 layers and Ca_2CoO_3 layers along the $\langle 00l \rangle$ axis is clearly observed. HR-XRD measurements revealed that the $\text{Ca}_3\text{Co}_4\text{O}_9$ was heteroepitaxially grown on the (0001)-face of $\alpha\text{-Al}_2\text{O}_3$ substrate over the entire area of the film, keeping the crystallographic orientation of $(001)[010]$ $\text{Ca}_3\text{Co}_4\text{O}_9 \parallel$

Fig. 3 Temperature dependence of (a) electrical resistivity, ρ , (b) Hall coefficient, R_H , and (c) Seebeck coefficient, S for the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film (98-nm-thick) over the temperature range 10–1000 K. The temperature dependence of ρ in the case of cooling the film from 1000 K is also shown in the inset of (a).

(0001)[1 $\bar{1}$ 00] α - Al_2O_3 .¹⁵⁾ Although an amorphous Ca-Al-O layer (*ca.* 15 nm thick) is also observed at the interface between the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial layer and the α - Al_2O_3 substrate, the amorphous layer was already formed during the R-SPE process to fabricate $\text{Na}_{0.8}\text{CoO}_2$ epitaxial film (*step 1*).²⁰⁾ The lattice constants of $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film ($a = 0.486$ nm, $c = 1.0820$ nm) were close to those of powders ($a = 0.4834$, $c = 1.0844$ nm),¹⁶⁾ suggesting that the crystalline lattice of $\text{Ca}_3\text{Co}_4\text{O}_9$ in the film had little distortion, most likely because the amorphous layer negated the lattice mismatch between the film and substrate. Figure 2(b) shows topographic AFM image of the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film. A stepped and terraced structure composed of several square-shaped domains ($\sim 1 \mu\text{m}^2$) was clearly seen, reflecting the crystal symmetry of $\text{Ca}_3\text{Co}_4\text{O}_9$ (monoclinic), and the step increment was approximately 3 nm. These results of HREM, HR-XRD and AFM measurements indicate that high-quality $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film was successfully fabricated by the topotactic ion-exchange method using $\text{Na}_{0.8}\text{CoO}_2$ epitaxial film as a precursor.

Figure 3 summarizes temperature dependence of (a) ρ , (b) R_H , and (c) S for the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film (thickness:

Table 1 Thermoelectric properties for the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film at 1000 K. The ρ , S , and $S^2\rho^{-1}$ are resistivity, Seebeck coefficient, and power factor, respectively. The values for conventional *p*-type high temperature thermoelectric materials, $\text{Si}_{0.7}\text{Ge}_{0.3}$ ⁹⁾ and $\beta\text{-Fe}_{1-x}\text{Mn}_x\text{Si}_2$ ($x = 0.06$),¹⁰⁾ are also shown for comparison.

	$\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film (present work)	$\text{Si}_{0.7}\text{Ge}_{0.3}$ [Ref. 9)] (conventional <i>p</i> -type)	$\beta\text{-Fe}_{1-x}\text{Mn}_x\text{Si}_2$ [Ref. 10)] (conventional <i>p</i> -type)
ρ (m Ω cm)	4	1–4	6
S ($\mu\text{V K}^{-1}$)	200	180–300	170
$S^2\rho^{-1}$ (mW m $^{-1}$ K $^{-2}$)	1	2–3	0.5

98 nm), which were taken in air (300–1000 K) or vacuum ($\sim 10^{-3}$ Pa, $T < 300$ K). [Note: Although the decreasing oxygen content in $\text{Ca}_3\text{Co}_4\text{O}_9$ has been observed above ~ 700 K in $P_{\text{O}_2} < 10^5$ Pa,²¹⁾ such behavior was not observed in the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film. We obtained very reliable data below 1000 K as shown in the inset of (a).] The $\rho - T$ curve (a) shows typical metallic behavior of the film. It should be noted that several transition of $\rho - T$ curve is observed at around 70 K and 600 K. Corresponding transitions are also observed in $R_H - T$ curve (b). Further, transition of $S - T$ curve is seen at around 400 K (c). As reported by Sugiyama *et al.*,²²⁾ the spin density wave is observed in $\text{Ca}_3\text{Co}_4\text{O}_9$ below 100 K. Further, spin state transition of Co ion from low-spin to intermediate- and/or high-spin occurs above ~ 400 K.²²⁾ Thus, the observed transitions at 70 K and 600 K may be assigned as formation of the spin density wave and the spin state transition, respectively.

In Table 1, TE parameters of $\text{Ca}_3\text{Co}_4\text{O}_9$ at 1000 K are compared with those of *p*-type $\text{Si}_{0.7}\text{Ge}_{0.3}$ ⁹⁾ and $\beta\text{-Fe}_{1-x}\text{Mn}_x\text{Si}_2$ ($x = 0.06$),¹⁰⁾ which are conventional *p*-type high temperature TE materials. The $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film exhibits a low ρ value of $4.0 \times 10^{-3} \Omega \text{ cm}$, which is much lower than those of the polycrystalline materials ($\sim 1 \times 10^{-2} \Omega \text{ cm}$)^{12,13)} and comparable to those of single crystals,^{6–8,14)} and a large S value of $\sim +200 \mu\text{V K}^{-1}$, reasonably agreeing with the reported values in bulk samples,^{6–8,12–14)} at 1000 K. The high TE properties may be attributed to the larger carrier mobility resulting most likely from the high crystal quality of the film.¹⁵⁾ The values of n and μ_{Hall} of the $\text{Ca}_3\text{Co}_4\text{O}_9$ film were $2.0 \times 10^{21} \text{ cm}^{-3}$ and $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, at 1000 K. From S and ρ values, the power factor ($S^2\rho^{-1}$) of the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film was evaluated to be $1.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 1000 K. These thermoelectric parameters of the film were comparable to those of conventional *p*-type high temperature TE materials, indicating that the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film fabricated by topotactic ion-exchange method can be a promising candidate to develop thin film TE devices drivable at high-temperature (~ 1000 K). For a real TE application, it is necessary to investigate the thermal conductivity (κ) of the film. Although we didn't measure κ in the present study due to the difficulty in measuring κ of the film, the low κ could be expected because the reported κ in $\text{Ca}_3\text{Co}_4\text{O}_9$ bulk single crystal ($\kappa \sim 3 \text{ W m}^{-1} \text{ K}^{-1}$)⁷⁾ is as low as that of *p*-type $\text{Si}_{0.7}\text{Ge}_{0.3}$ ($\kappa \sim 4 \text{ W m}^{-1} \text{ K}^{-1}$)⁹⁾ and $\beta\text{-FeSi}_2$ ($\kappa \sim 6 \text{ W m}^{-1} \text{ K}^{-1}$).¹¹⁾

4. Conclusion

Thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film fabricated on (0001)-face of $\alpha\text{-Al}_2\text{O}_3$ substrate by the topotactic ion-exchange method were examined over the temperature range 10–1000 K. The $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film exhibited good thermal stability and a high thermoelectric performance of $\rho = 4.0 \times 10^{-3} \Omega \text{ cm}$ and $S \sim +200 \mu\text{V K}^{-1}$, leading to the thermoelectric power factor of $1.0 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$, at 1000 K in air. These thermoelectric parameters were comparable to those of conventional p -type high temperature TE materials such as p -type $\text{Si}_{0.7}\text{Ge}_{0.3}$ and $\beta\text{-FeSi}_2$, indicating that the $\text{Ca}_3\text{Co}_4\text{O}_9$ epitaxial film fabricated by topotactic ion-exchange method can be a promising candidate to develop thin film TE devices drivable at high-temperature ($\sim 1000 \text{ K}$).

REFERENCES

- 1) T. M. Tritt, M. A. Subramanian, H. Bottner, T. Caillat, G. Chen, R. Funahashi, X. Ji, M. Kanatzidis, K. Koumoto, G. S. Nolas, J. Poon, A. M. Rao, I. Terasaki, R. Venkatasubramanian and J. Yang: in *Harvesting Energy Through Thermoelectrics: Power Generation and Cooling, special issue of MRS Bull.* **31** (2006) 188, and references therein.
- 2) I. Terasaki, Y. Sasago and K. Uchinokura: *Phys. Rev. B* **56** (1997) 12685.
- 3) M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A. Pascal Jr, R. J. Cava and N. P. Ong: *Nat. Mater.* **5** (2006) 537.
- 4) R. Ishikawa, Y. Ono, Y. Miyazaki and T. Kajitani: *Jpn. J. Appl. Phys., Part 2* **41** (2002) L337.
- 5) K. Sugiura, H. Ohta, K. Nomura, M. Hirano, H. Hosono and K. Koumoto: *Appl. Phys. Lett.* **88** (2006) 082109.
- 6) A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer and B. Raveau: *Phys. Rev. B* **62** (2000) 166.
- 7) M. Shikano and R. Funahashi: *Appl. Phys. Lett.* **82** (2003) 1851.
- 8) P. Limelette, V. Hardy, P. Auban-Senzier, D. Jérôme, D. Flahaut, S. Hèbert, R. Frèsard, Ch. Simon, J. Noudem and A. Maignan: *Phys. Rev. B* **71** (2005) 233108.
- 9) J. P. Dismukes, L. Ekstrom, E. F. Steigmeier, I. Kudman and D. S. Beers: *J. Appl. Phys.* **35** (1964) 2899.
- 10) I. Nishida: *Phys. Rev. B* **7** (1973) 2710.
- 11) H. Nagai: *Mater. Trans., JIM* **36** (1995) 365.
- 12) G. Xu, R. Funahashi, M. Shikano, I. Matsubara and Y. Zhou: *Appl. Phys. Lett.* **80** (2002) 3760.
- 13) T. Tani, H. Itahara, C. Xia and J. Sugiyama: *J. Mater. Chem.* **13** (2003) 1865.
- 14) M. Mikami, K. Chong, Y. Miyazaki, T. Kajitani, T. Inoue, S. Sodeoka and R. Funahashi: *Jpn. J. Appl. Phys.* **45** (2006) 4131.
- 15) K. Sugiura, H. Ohta, K. Nomura, M. Hirano, H. Hosono and K. Koumoto: *Appl. Phys. Lett.* **89** (2006) 032111.
- 16) Y. Miyazaki, M. Onoda, T. Oku, M. Kikuchi, Y. Ishii, Y. Ono, Y. Morii and T. Kajitani: *J. Phys. Soc. Jpn.* **71** (2002) 491.
- 17) H. Ohta, K. Nomura, M. Orita, M. Hirano, K. Ueda, T. Suzuki, Y. Ikuhara and H. Hosono: *Adv. Funct. Mater.* **13** (2003) 139.
- 18) K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano and H. Hosono: *Science* **300** (2003) 1269.
- 19) H. Ohta, S.-W. Kim, S. Ohta, K. Koumoto, M. Hirano and H. Hosono: *Cryst. Growth Des.* **5** (2005) 25.
- 20) H. Ohta, A. Mizutani, K. Sugiura, M. Hirano, H. Hosono and K. Koumoto: *Adv. Mater.* **18** (2006) 1649.
- 21) J. Shimoyama, S. Horii, K. Otzsch, M. Sano and K. Kishio: *Jpn. J. Appl. Phys.* **42** (2003) L194.
- 22) J. Sugiyama, J. H. Brewer, E. J. Ansaldo, H. Itahara, K. Dohmae, Y. Seno, C. Xia and T. Tani: *Phys. Rev. B* **68** (2003) 134423.