T2R2 東京科学大学 リサーチリポジトリ
Science Tokyo Research Repository

論文 / 著書情報
Article / Book Information

Title	Parallel syntheses and thermoelectric properties of Ce-doped SrTiO_3_ thin films
Author	Y. F. Yamada, A. Ohtomo, M. Kawasaki
Journal/Book name	Applied Surface Science, Vol. 254, No. 3, pp. 768-771
Issue date	2007, 11
URL	http://www.journals.elsevier.com/applied-surface-science/
DOI	http://dx.doi.org/10.1016/j.apsusc.2007.04.089
Note	このファイルは著者（最終）版です。 This file is author (final) version.

Powered by T2R2 (Science Tokyo Research Repository)

Parallel syntheses and thermoelectric properties of Ce-doped $SrTiO_3$ thin films

Y. F. Yamada[a], A. Ohtomo[a,b,*], M. Kawasaki[a,c]
[a]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan.*
[b]*PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan.*
[c]*CREST, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan.*

Abstract

Thermoelectric properties of single crystalline $Ce_xSr_{1-x}TiO_3$ films ($0 \leq x \leq 0.5$) have been studied by using combinatorial pulsed-laser deposition. Temperature gradient method was used for identifying an optimum growth temperature for $SrTiO_3$ homoepitaxial growth, at which both oxygen stoichiometry and persisting layer-by-layer growth mode could be accomplished. Electrical conductivity (σ) and Seebeck coefficient (S) were measured at room temperature for the composition-spread films grown at the optimized temperature and found to be considerably higher than those reported for bulk poly-crystalline compounds. Hall measurement revealed that carrier density linearly increased with increasing x, suggesting that a trivalent Ce ions substituted divalent Sr ions to supply electrons. A maximum power factor ($S^2\sigma$) was obtained for the x = 0.2 film, being 7 and 14 μW/(K^{2}cm) at 300 and 900 K, respectively.

PACS: 73.50.Lw, 73.61.Le, 81.15.Fg

Keywords: $SrTiO_3$, thermoelectric, combinatorial chemistry, conductivity, Seebeck effect, thin films, pulsed-laser deposition

***Corresponding author**: Akira Ohtomo (2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan; Phone: +81-22-215-2088; Fax: +81-22-215-2086; E-mail: aohtomo@imr.tohoku.ac.jp)

1. Introduction

Combinatorial chemistry has been developed in many fields of materials research and recent technological advancements have enabled to perform fast experimentations in optimization of synthesis parameters and improvement of materials properties [1,2]. In the field of oxide electronics, composition-spread technique combined with pulsed-laser deposition (PLD) has been successfully applied for parallel synthesis of various composition films and rapid characterizations of their physical properties [3]. Some of the most challenging materials targets that can be efficiently explored by the virtue of this technique would be high-T_c superconductors and thermoelectric (TE) materials, especially important classes for global energy saving protocol. Recent discoveries of new TE materials based on oxides have attracted revival attention and established new materials design for substantial increase in materials properties [4,5], which can be accelerated with the use of combinatorial technologies [2].

Transition-metal oxides are emerging candidates of TE materials since large power factor (PF = $S^2\sigma$) was found in hole-doped cobaltates, exhibiting extremely large Seeback coefficient (S) despite high conductivity (σ) [4]. Spin and orbital degrees of freedom play a key role for substantial enhancement of S, which is thought to arise from larger entropy transfer associated with hole transport from $Co^{4+}[3d(t_{2g})^5]$ to $Co^{3+}[3d(t_{2g})^6]$ sites [4,6]. In the framework of this model, TE properties of $La_xSr_{1-x}TiO_3$ have also been studied, in which free electrons carry large entropy due to a mixed valence configuration of $Ti^{3+}[3d(t_{2g})^1]$ and $Ti^{4+}[3d(t_{2g})^0]$ [7], being an electronic analogy to cobaltate system. Due to large effective mass in addition to above-mentioned advantage, relatively

large PF values are reported to be 36 μW/(K^{2}cm) at 300 K [7] and 5 μW/(K^{2}cm) at 900 K [8] for $La_{0.02}Sr_{0.98}TiO_3$ and $SrTi_{0.98}Nb_{0.02}O_3$ bulk single crystals, respectively.

In this paper, we have studied composition dependences of the TE properties in the composition-spread films consisting of $CeTiO_3$ (CTO) and $SrTiO_3$ (STO) grown by using combinatorial PLD. We found that S and σ values evaluated at room temperature were considerably larger than those reported for bulk poly-crystalline samples [9] and PF had a maximum at x = 0.2. We further grew a single-composition $Ce_{0.2}Sr_{0.8}TiO_3$ film, in which the PF was as large as 7 and 14 μW/(K^{2}cm) at 300 and 900 K, respectively.

2. Experiment

All films discussed in this paper were grown in a pulsed-laser deposition chamber with an oxygen flow of 1×10^{-6} Torr and with using a KrF excimer laser operated under a constant condition (2 Hz and 3 J/cm^2) and a semiconductor laser heating system. Using temperature gradient method [10], we first investigated the growth temperature (T_g) dependence of growth mode and sheet resistance (R_s) for STO homoepitaxial film. The T_g was monitored by a pyrometer with an emissivity set at 0.35. Using the intensity oscillation of reflection high-energy electron diffraction (RHEED), film thickness was regulated to be approximately 100 nm. The R_s was measured by a low-impedance electrometer through a micro-four probe (0.05-mm-diameter WC tips placed every 0.1-mm-distance) at room temperature [See Fig. 1(a)]. Then, 100 nm-thick composition-spread $Ce_xSr_{1-x}TiO_3$ films ($0 \leq x \leq 0.5$) and the single-composition $Ce_{0.2}Sr_{0.8}TiO_3$ film were grown at

830°C on (100) STO and $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrates. A STO single crystal and a sintered body having prescribed composition of $(STO)_{0.5}$-$(CTO)_{0.5}$ were used to make the films. Epitaxial structure of the films was characterized by a concurrent x-ray diffraction apparatus [11]. The σ and Hall coefficient (R_H) were measured with a four probe method below room temperature, whereas the σ and S were measured by a steady state method at temperatures raging from 300 K to 1000 K.

3. Results and discussion

Figure 1(a) illustrates our procedure for optimizing the PLD growth condition. Temperature gradient method enables to grow a film at a wide range of T_g while surface reaction obeys different kinetics of oxidation and crystallization at local T_g [12,13]. In Fig. 1(b), a drastic decrease in R_s seen at T_g = 830°C (indicated by arrow) is attributed to the formation of oxygen vacancies. When the film is grown at this T_g, the persisting RHEED intensity oscillations can be observed [Fig. 1(c)], being consistent with the previous study [12]. This preparatory experiment is important to optimize T_g for the layer-by-layer growth of solid-solution films based on perovskite titanate and to achieve good crystallinity and nearly ideal oxygen stoichiometry, simultaneously [14]. In this study, therefore, all the $Ce_xSr_{1-x}TiO_3$ films were grown at 830°C.

The concurrent x-ray diffraction measurements confirmed that all the composition-spread films grown on the STO and LSAT substrates were single-phase perovskites. The out-of-plane lattice constants of the films slightly increased with increasing x from 0 to 0.5 (approximately 0.2 %

for the films grown on STO). The in-plane lattice constants remained same as those of the substrates up to x = 0.25 and 0.5 for LSAT and STO substrates, respectively. These results are reasonable if we take into account the facts that the lattice volume of bulk $Ce_xSr_{1-x}TiO_3$ increases with x [9] and the lattice constant of LSAT [3.867 Å (pseudo-cubic)] is smaller than STO (3.905 Å).

The composition dependences of electronic properties for $Ce_xSr_{1-x}TiO_3$ film grown on the LSAT substrates is summarized in Fig. 2. The σ systematically increases with x, which arises mostly from increase in carrier density ($-1/R_He$). As shown in the insert of Fig. 2(b), the carrier density linearly increases with increasing x, indicating that Ce^{3+} ion substituting Sr^{2+} ion introduces a free electron in Ti 3*d* state. This result is consistent with the fact that formation energy of $Ce^{3+}Ti^{3+}O_3$ is much lower than that of either $Ce^{2+}Ti^{4+}O_3$ or $Ce^{4+}Ti^{2+}O_3$ at an appropriate oxidation condition. Hall mobility ($-R_H\sigma$) is nearly constant, exhibiting a weak maximum at $x \sim 0.2$.

Figure 3(a) shows the composition dependence of σ and S measured for a film grown on the STO substrate. The magnitude of σ values is nearly equal to those in the film grown on LSAT. The S is found to be negative for all compositions, and to systematically decreases with increasing x, similar to those obtained in doped STO crystals [7,8,15,16]. Compared with the data reported for bulk poly-crystalline samples (indicated by dashed lines) [9], no significant deference is seen, but σ is considerably larger in our films due to better crystallinity and grain-boundary free nature. Figure 3(b) shows the composition dependence of PF, nearly constant in a range of x from 0.1 to 0.4.

Judging from the results shown in Fig. 2(c) and Fig. 3(b), one can expect better thermoelectric

properties at $x \sim 0.2$ in the present system. Therefore, we further studied the temperature dependences of S and σ for single-composition $Ce_{0.2}Sr_{0.8}TiO_3$ film grown on the STO substrate, which is shown in Fig. 4. Room temperature values of S and σ are -70 μV/K and 1.3×10^3 S/cm, respectively, which are large than those of the composition-spread film (See open symbols in Figs. 3). With increasing temperature, the absolute value of S systematically increases, whereas σ decreases, resulting in small, but continuous increase in PF by a factor of 2 as temperature increases from 300 K to 900 K.

4. Conclusion

Using combinatorial pulsed-laser deposition, systematic study of TE properties in $Ce_xSr_{1-x}TiO_3$ films has been efficiently carried out. Temperature gradient method enabled us to optimize growth temperature in single experimental run. Composition-spread technique allowed high-throughput characterizations of crystalline structure and thermoelectric properties, leading to rapid establishment of their composition dependences. We found that the present system has comparable TE properties to other electron-doped STO systems.

References

[1] H. Koinuma, I. Takeuchi, Nature Mater. **3** (2004) 429.

[2] X.-D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W. G. Wallace-Freedman, S.-W. Chen, P. G. Schultz, Science **268** (1995) 1738.

[3] T. Fukumura, M. Ohtani, M. Kawasaki, Y. Okimoto, T. Kageyama, T. Koida, T. Hasegawa, Y. Tokura, H. Koinuma, Appl. Phys. Lett. **77** (2000) 3426.

[4] I. Terasaki, Y. Sasago, K. Uchinokura, Phys. Rev. B **56** (1997) R12685.

[5] M. Lee, L. Viciu, L. Li, Y. Wang, M. L. Foo, S. Watauchi, R. A. Pascal Jr., R. J. Cava, N. P. Ong, Nature Mater. **5** (2006) 537.

[6] W. Koshibae, K. Tsutsui, S. Maekawa, Phys. Rev. B **62** (2000) 6869.

[7] T. Okuda, K. Nakanishi, S. Miyasaka, Y. Tokura, Phys. Rev. B **63** (2001) 113104.

[8] S. Ohta, T. Nomura, H. Ohta, K. Koumoto, J. Appl. Phys. **97** (2005) 034106.

[9] M. Onoda, M. Yasumoto, J. Phys.: Condens. Matter. **9** (1997) 5623.

[10] T. Koida, D. komiyama, H. Koinuma, M. Ohtani, M. Lippmaa, M. Kawasaki, Appl. Phys. Lett. **80** (2002) 565.

[11] M. Ohtani, T. Fukumura, M. Kawasaki, K. Omote, T. Kikuchi, J. Harada, H. Koinuma, Appl. Phys. Lett. **80** (2002) 2066.

[12] A. Ohtomo, H. Y. Hwang, cond-mat/0604117.

[13] A. Tsukazaki, A. Ohtomo, M. Kawasaki, Appl. Phys. Lett. **88** (2006) 152106.

[14] A. Ohtomo, J. Nishimura, Y. Murakami, M. Kawasaki, Appl. Phys. Lett. **88** (2006) 232107.

[15] H. Muta, K. Kurosaki, S. Yamanaka, J. Alloys Compd. **350** (2003) 292.

[16] H. Obara, A. Yamamoto, C.-H. Lee, K. Kobayashi, A. Matsumoto, R. Funahashi, Jpn. J. Appl. Phys. **43** (2004) L540.

Figure Captions

Fig. 1. (a) Schematic illustration of temperature gradient method during PLD growth and room-temperature resistivity measurement with using a micro-four probe. (b) Growth temperature dependence of sheet resistivity for a homoepitaxial STO film, exhibiting a critical transition at 830°C (indicated by arrow). (c) Persisting RHEED intensity oscillations during STO homoepitaxial growth at 830°C in an oxygen flow of 1×10^{-6} Torr.

Fig. 2. Composition dependences of (a) conductivity σ, (b) carrier density $-1/R_H e$, and (c) Hall mobility $-R_H\sigma$ at 300 K for $Ce_xSr_{1-x}TiO_3$ films grown on the LSAT substrate. Inset depicts linear-scale plot of (b). Dashed line is calculated by assuming electronic compensation with Ti 3*d* electrons of positive charge in Ce^{3+} ions at Sr^{2+} site.

Fig. 3. Composition dependences of (a) conductivity σ (left ordinate) and Seebeck coefficient S (right ordinate), and (b) power factor (PF = $S^2\sigma$) at 300 K for $Ce_xSr_{1-x}TiO_3$ films grown on the STO substrate. The data reported for sintered bulk samples are indicated by dashed lines [9]. Open symbols refer to those plotted in Fig. 4

Fig. 4. Temperature dependence of conductivity σ (left ordinate) and Seebeck coefficient S (right ordinate) for a single-composition $Ce_{0.2}Sr_{0.8}TiO_3$ film grown on the STO substrate.

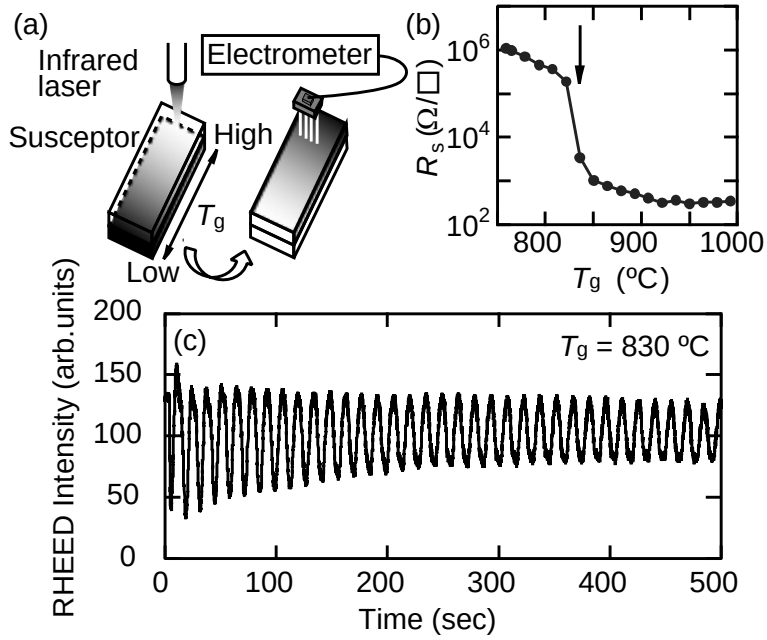

Fig. 1. Y. F. Yamada, A. Ohtomo, M. Kawasaki

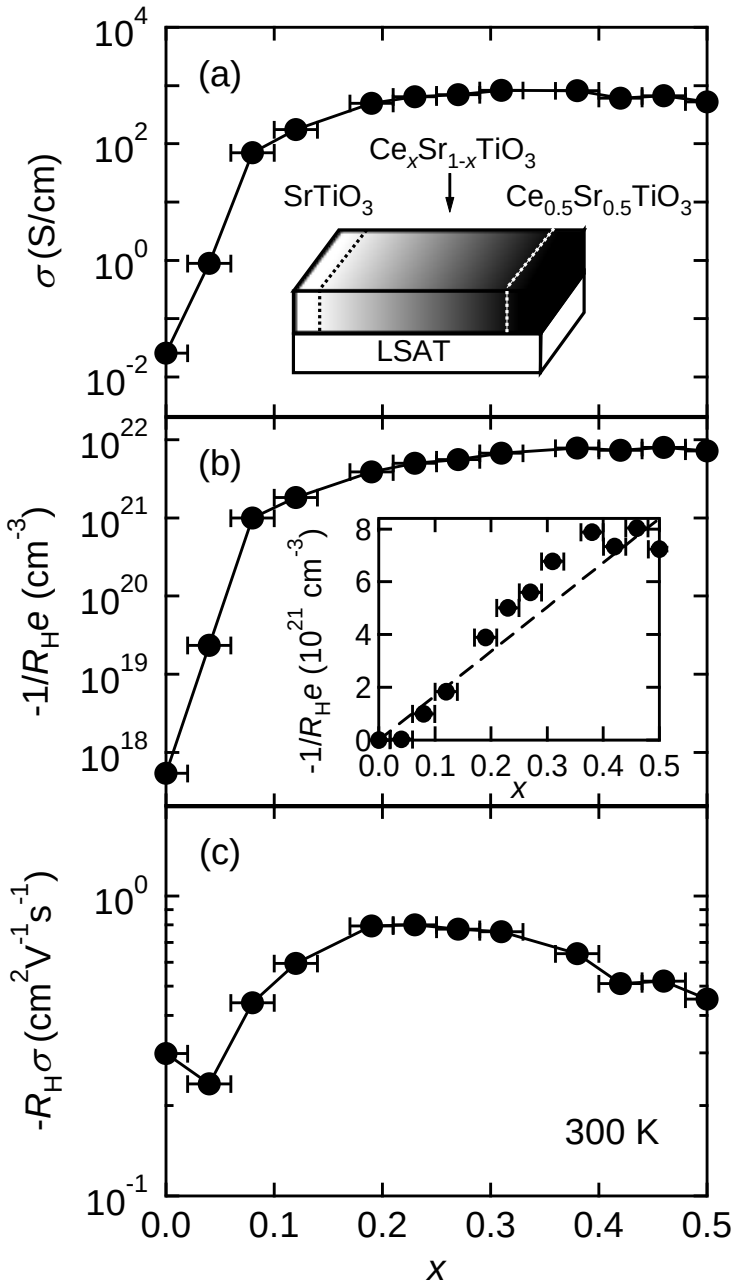

Fig. 2. Y. F. Yamada, A. Ohtomo, M. Kawasaki

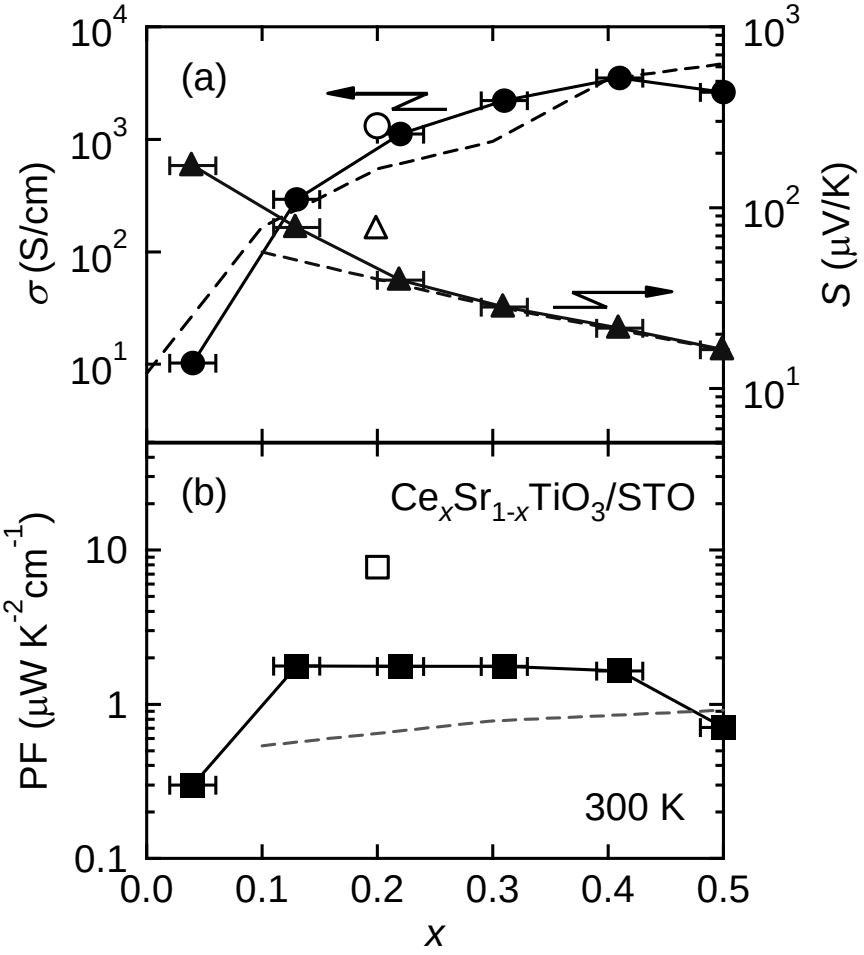

Fig. 3. Y. F. Yamada, A. Ohtomo, M. Kawasaki

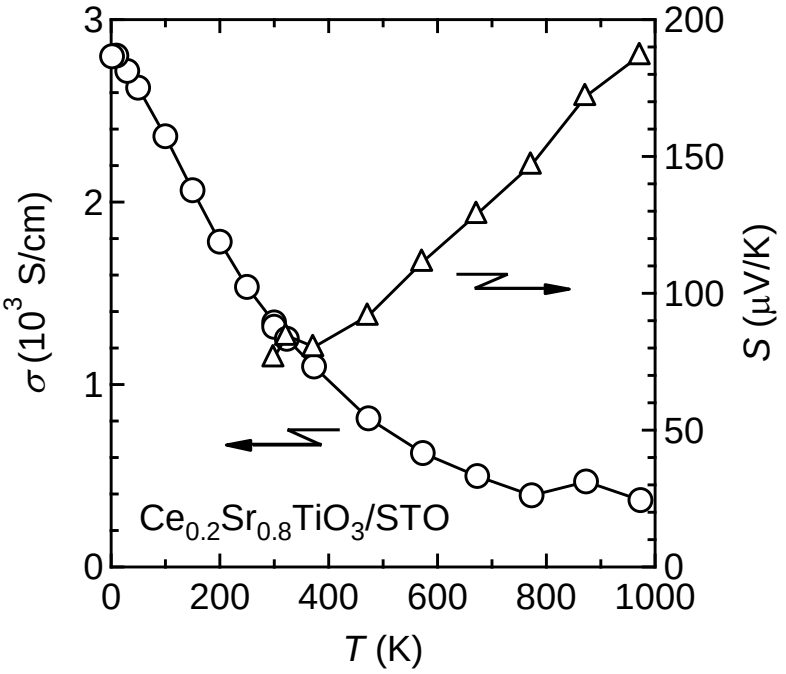

Fig. 4. Y. F. Yamada, A. Ohtomo, M. Kawasaki