

The influence of oxygen deficiency on the thermoelectric properties of strontium titanates

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We report oxygen reduction in bulk strontium titanate substrates when a thin film was deposited in an oxygen-deficient environment. The oxygen diffusion occurred at moderate temperatures and oxygen pressures, which were not enough to produce detectable oxygen vacancies without the film deposition. In order to identify the reduction, we used a series of different annealing conditions and various substrates and performed comparative studies regarding thermoelectric properties before and after removing the films. Our experimental results suggest that the measurements of material properties of thin films on SrTiO₃ single crystal substrates need to be performed carefully due to its strong susceptibility to oxygen deficient conditions. © 2008 American Institute of Physics.

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Direct thermal to electrical energy conversion using solid-state thermoelectric systems is very attractive due to many advantages over conventional systems. However, the current thermoelectric materials based on bismuth telluride and semiconductors do not provide enough efficiency comparable to that of current energy conversion systems.¹ It is primarily due to the strong correlation among thermoelectric parameters— S , σ , and k , where they are thermopower (or Seebeck coefficient), electrical conductivity, and thermal conductivity, respectively—changing one parameter favorably often induces adverse influence on others. Particularly, it has been extremely difficult to increase $S^2\sigma$ [often called as a power factor (PF)].²

Recently, it was reported that a monolayer of SrTiO₃ (STO) at the interface between TiO₂ and STO exhibited both large electrical conductivity and thermopower, resulting in a huge PF, ~ 25 times larger than that of bismuth telluride alloys. It appears that the highly conducting layer ($\sigma \sim 10^3 \Omega^{-1} \text{cm}^{-1}$), which originated from a high carrier concentration ($\sim 10^{21} \text{cm}^{-3}$), did not degrade the thermopower ($\sim 1 \text{mV/K}$).³ It is suggested that the extraordinary properties were due to the existence of two-dimensional electron gas confined within one unit-cell thick interface.³ On the other hand, a large sheet carrier density ($\sim 10^{17} \text{cm}^{-2}$) has been reported for the interface between two electrically non-conducting LaAlO₃ (LAO) and STO, which could be interpreted as an unphysical carrier density of $\sim 1.7 \times 10^{22} \text{cm}^{-3}$ over a 60 nm thick conducting layer.⁴ While it is possible to ascribe the high carrier density to oxygen vacancies created in the thin layer of STO, electronic reconstruction was also suggested as a feasible explanation for the conduction at the LaO–TiO₂ interface.⁴ To understand this interface activity, it is instructive to describe the perovskites in terms of their constituting AO and BO₂ layering sequence. In STO, the SrO and TiO₂ layers are charge neutral, but the charge states in the LAO are (LaO)⁺ and (AlO₂)⁻, respectively. Conse-

quently, a polarity discontinuity could arise at the LAO-STO interface, which gave rise to such electrical conduction. These remarkable electrical properties of interfaces have attracted considerable attention from several research groups.^{5–11} Recently, photoluminescence¹⁰ and Shubnikov de Haas oscillation¹¹ studies suggested the origin of the very large carrier densities, observed at LAO-STO interfaces grown at low oxygen pressures, could be due to the oxygen deficiency. While the origin of the extraordinary properties is still in debate, in this letter, we present the possibility of creating oxygen vacancies in STO substrates during pulsed laser deposition (PLD) processes, which could shed light on revealing the origin of the extraordinary behavior, by systematically measuring the thermopower and sheet resistance of a series of samples grown at different conditions. Furthermore, we offer a methodology to reduce the reduction of the STO substrate by inserting a thin, epitaxially strained layer of LAO.

We deposited Sr_{1-x}La_xTiO_{3- δ} ($\delta > 0$) (SLTO) films using a PLD method on various substrates including $\sim 500 \mu\text{m}$ thick STO (100), with and without thin LAO layers, and $\sim 500 \mu\text{m}$ thick DyScO₃ (DSO) (110), NdGaO₃ (NGO) (110), LAO (100), and (LaAlO₃)_{0.3}–(Sr₂AlTaO₆)_{0.7} (LSAT) (100) substrates. The La concentration x was measured to be $\sim 2\%$ by Rutherford backscattering spectroscopy. First, we deposited $\sim 100 \text{nm}$ thick SLTO on STO substrates at $\sim 2 \times 10^{-7}$ Torr and 450 °C. The whole sample became very dark and the sheet resistance was measured to be only $\sim 12 \Omega$. When we attribute all electrical conduction to the film, the resistivity of the film is too low to be realistic. On the contrary, without any deposition, the annealing process did not change the color of the STO substrates and the sheet resistance cannot readily be measured due to a high resistance and Schottky barriers with metal contacts. Note that stoichiometric STO is an insulator with $\sim 3.2 \text{eV}$ bandgap at room temperature. It is obvious that the film deposition process played an important role in creating oxygen vacancies in the STO substrates. This led us to deposit epitaxial 10 nm LAO films, as an oxygen-diffusion barrier, on STO sub-

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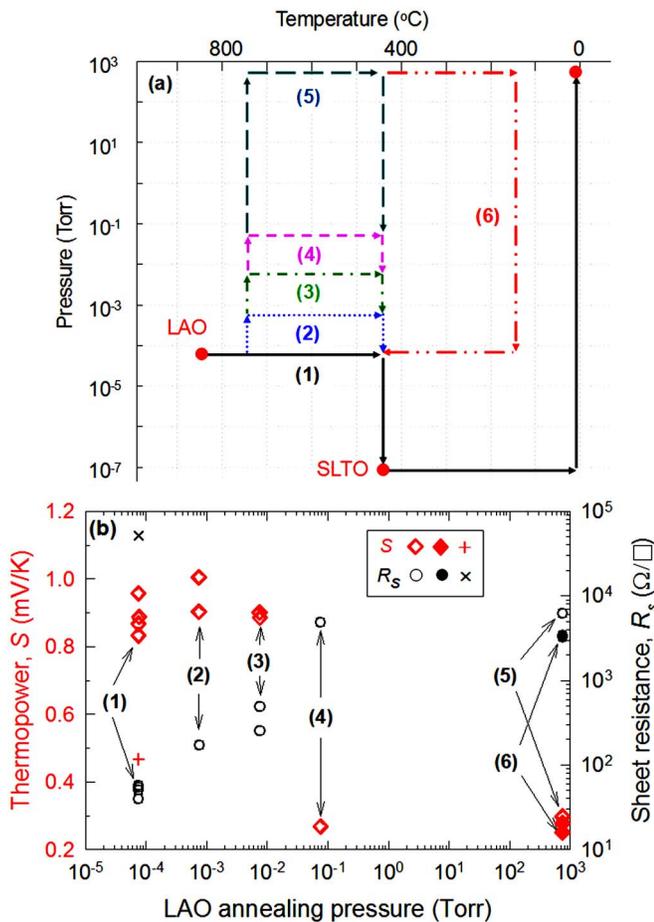


FIG. 1. (Color online) (a) Upper panel: temperatures and pressures of LAO and SLTO deposition processes. LAO-STO substrates were annealed at different oxygen pressures and temperatures prior to SLTO depositions as indicated by (1)–(6). (b) Lower panel: sheet resistance (\circ , \bullet) and thermopower (\diamond , \blacklozenge) when 50 nm thick SLTO films were deposited on LAO-STO substrates. The properties of an as-grown LAO-STO substrate was indicated by + (thermopower) and \times (sheet resistance).

strates at 850 °C and $\sim 0.75 \times 10^{-4}$ Torr prior to the deposition of the SLTO film. Subsequently, the samples were annealed at higher oxygen pressures immediately after the LAO deposition in order to suppress any possible oxygen vacancies that could have been created during the LAO deposition processes. Note that LAO does not get reduced due to the invariant Al^{3+} state as opposed to the mixed valence Ti^{3+} and Ti^{4+} states in STO. The LAO annealing conditions are indicated in Fig. 1(a). For example, (2) in Fig. 1(a) indicates the sample was exposed to $\sim 0.75 \times 10^{-3}$ Torr oxygen pressure during the annealing process from 750 to 450 °C. At 450 °C, the deposition chamber was evacuated until the pressure became $\sim 10^{-7}$ Torr for the SLTO depositions.

The thermopower and sheet resistance of a 10 nm thick LAO layer on the STO substrate, without depositing any SLTO films, were, respectively, small and large as they are indicated by “+” and “ \times ” in Fig. 1(b). It would be from either the oxygen reduction in the STO substrate or the conducting LAO–STO interface. However, only 50 nm thick SLTO deposition, using a condition indicated by (1) in Fig. 1(a), brought a significant increase in thermopower [indicated by diamonds in Fig. 1(b)] as well as an approximately three-order magnitude reduction in sheet resistance [indicated by circles in Fig. 1(b)]. When we exposed LAO-

TABLE I. Thermopower (S) and electrical resistivity (ρ) of bulk STO (F1–F4 and Y1–Y3) and SLTO (YL1 and YL5) after oxygen reduction processes with various pressures, temperatures, and times. YL1 and YL5 represent $\text{Sr}_{0.99}\text{La}_{0.01}\text{TiO}_3$ and $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$, respectively. The results indicated by F1–F4 were adopted from Frederikse *et al.*^a. The S and ρ measurements were performed at ~ 300 K.

Sample	Pressure (Torr)	Temp. (°C)	Time (h)	S ($\mu\text{V}/\text{K}$)	ρ (m Ω cm)
F1	5×10^{-5}	1200	240	890	2000
Y1	10^{-6}	1000	24	772	552
F2 ^b	10^{-4}	900	72	770	400
F3	10^{-1}	1000	28	750	350
Y2	1.5×10^{-7}	1000	24	719	271
F4 ^b	5×10^{-5}	1200	240	600	80
Y3	8.5×10^{-7}	1200	24	522	29
YL1	400	6.7
YL5	167	0.78

^aReference 16.

^bTitanium was used for F2 (0.002 mg) and F4 (0.1 mg) as oxygen getters.

deposited STO substrates to more oxygen prior to the SLTO deposition [(2)–(6) in Fig. 1], the resistance was increased even with the same SLTO deposition process. Interestingly, the large thermopower was maintained until the oxygen annealing pressure of $\sim 10^{-2}$ Torr notwithstanding considerable changes in the sheet resistance. Suddenly, the annealing process in more oxygen environment brought abrupt decrease in thermopower with substantial increase in the sheet resistance [(4)–(6) in Fig. 1(a)]. This would suggest that the annealing process at higher oxygen pressure suppressed oxygen vacancies or/and increased the oxygen-diffusion barrier height in the STO substrates.

The measured properties are determined by the relative magnitudes of the properties from the film, substrate, and interface. In this case, we can consider two conductive paths, the SLTO film and the substrate in parallel as the LAO is not an electrical conductor. The measured total thermopower and total sheet resistance can be expressed as^{12,13}

$$S_{\text{total}} = \left(\frac{S_{\text{substrate}}}{R_{\text{substrate}}} + \frac{S_{\text{SLTO}}}{R_{\text{SLTO}}} \right) / \left(\frac{1}{R_{\text{substrate}}} + \frac{1}{R_{\text{SLTO}}} \right), \quad (1)$$

$$\frac{1}{R_{\text{total}}} = \frac{1}{R_{\text{substrate}}} + \frac{1}{R_{\text{SLTO}}}, \quad (2)$$

where R and the subscript indicate sheet resistance and the conducting path, respectively. The interface contribution to the total sheet resistance would be very small even if it has high electrical conductivity as the sheet resistance is inversely proportional to the thickness (t) of the conducting layer ($R_s = \rho/t$). For example, the sheet resistance of one unit cell (~ 0.3905 nm) layer with 10^{21} carriers/cm³ would be ~ 25 000 Ω . This resistance is much larger than R_{total} for the cases of (1)–(3) in Fig. 1, even if such conducting layer is present. From Eq. (1), the total thermopower becomes only a SLTO property when the resistance of the substrate is significantly larger than that of the SLTO. For the samples [(5)–(6) in Fig. 1], whose substrates went through strong oxidation processes, the sheet resistance of R_{SLTO} can be estimated to be equal to or larger than ~ 5000 Ω . When $R_{\text{total}} \ll R_{\text{SLTO}}$ (~ 5000 Ω) [(1)–(3) in Fig. 1], $S_{\text{total}} \approx S_{\text{substrate}}$ from Eq. (1) and $R_{\text{total}} \approx R_{\text{substrate}}$ from Eq. (2). This would mean the large thermopower was due to the substrate. In fact, as shown in Table I, the thermopower of oxygen-deficient STO is large

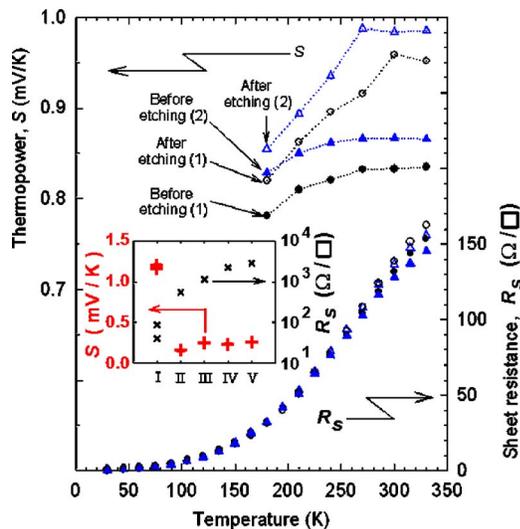


FIG. 2. (Color online) Thermopower (upper plots) and sheet resistance (lower plots) of two samples [(1) circles and (2) triangles] before (filled plots) and (hollow plots) after removing the film. Inset: The thermopower (+) and sheet resistance (\times) after the SLTO was deposited on (I) STO, (II) DSO, (III) NGO, (IV) LAO, and (V) LSAT substrates.

and comparable to the values obtained in this study [(1)–(3) in Fig. 1]. When $R_{\text{substrate}}$ became as large as R_{SLTO} [(4)–(6) in Fig. 1], the SLTO film properties were no longer negligible. This would explain the sudden drop of the thermopower as the thermopower of La-doped STO is smaller than that of undoped ones (see Table I and Okuda *et al.*¹⁴).

The origin of the thermoelectric properties was further investigated by removing only the films and subsequently measuring the substrate properties. Two samples were prepared using the growth condition of (1) in Fig. 1(a). First, we ground off approximately 175 and 200 μm of the back side of the samples in order to investigate the diffusion depth. Their sheet resistances were increased from 51.3 and 50.6 into 131.5 and 128.2 Ω , respectively. If the substrates were homogeneously reduced, the resistivity of the removed portion can be estimated to be approximately several $\Omega\text{ cm}$, which matches that of the large-thermopower bulk sample (F1 in Table I). Then, the SLTO film was removed by using a mixture of nitric and fluorine- and chlorine-based acids.

Figure 2 shows the thermopower (upper plots) and sheet resistance (lower plots) of the two samples [(1) circles and (2) triangles] before (filled plots) and after (hollow plots) removing the film. The thermopower of both samples was increased by the etching, but the change in the sheet resistance was negligible. Note that the etching process did not produce any notable changes in the electrical property of a bare stoichiometric-STO single crystal. The increase in thermopower would be because the thermopower of SLTO is smaller than that of reduced STO. The small difference in the sheet resistance can be ascribed to the large contrast in the thickness of each conductive path ($R_s = \rho/t$). As the resistivity of the substrate is estimated to be approximately several $\Omega\text{ cm}$, the thickness of the conductive portion in the substrate could be up to $\sim 500\text{ }\mu\text{m}$. Furthermore, we measured thermoelectric properties after SLTO was deposited at 450 $^\circ\text{C}$ and $\sim 2 \times 10^{-7}$ Torr on $\sim 500\text{ }\mu\text{m}$ thick nonconducting DSO, NGO, LAO, and LSAT substrates in addition to STO sub-

strates, as shown in the inset of Fig. 2. The thicknesses of the SLTO films were $\sim 170\text{ nm}$ except one on the DSO substrate ($\sim 100\text{ nm}$ thick SLTO). We observed a large thermopower and low sheet resistance only from the samples grown on STO substrates. The thermopower of all other samples was low and more or less the same, $\sim 0.2\text{ mV/K}$, although the lattice mismatches between the substrates and the film were less than $\sim 2\%$. These properties might be influenced by strains due to the lattice mismatch.¹⁵ Nevertheless, we conclude that the properties of the sample on the STO substrate are dominantly from substrate as other substrates do not reduce to become electrically conductive.

In summary, we noticed that the film deposition process could easily reduce STO substrates. It suggests the thermoelectric property measurements of thin films or interfaces could have been strongly influenced by the substrate rather than interfaces or films. The large thermopower could be a result from a very small number of oxygen vacancies in the STO substrate, which would produce a relatively high resistivity. However, the substantial oxygen diffusion depth kept the sheet resistance of the STO substrate small. This brought dominant effects over the properties of the interface and film on the measurements. Finally, these experimental results strongly suggest careful analysis during any study of material properties of thin films on STO single crystal substrates is crucial due to its strong susceptibility to oxygen deficient conditions.

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¹A. Majumdar, *Science* **303**, 777 (2004).

²D. M. Rowe, *Thermoelectrics Handbook* (CRC, Boca Raton, 2006).

³H. Ohta, S. Kim, Y. Mune, T. Mizoguchi, K. Nomura, S. Ohta, T. Nomura, Y. Nakanishi, Y. Ikuhara, M. Hirano, H. Hosono, and K. Koumoto, *Nat. Mater.* **6**, 129 (2007).

⁴A. Ohtomo and H. Y. Hwang, *Nature (London)* **427**, 423 (2004).

⁵N. Nakagawa, H. Y. Hwang, and D. A. Muller, *Nat. Mater.* **5**, 204 (2006).

⁶M. Huijben, G. Rijnders, D. Blank, S. Bals, S. Aert, J. Verbeeck, G. Tendeloo, A. Brinkman, and H. Hilgenkamp, *Nat. Mater.* **5**, 556 (2006).

⁷S. Thiel, G. Hammerl, A. Schmehl, C. Schneider, and J. Mannhart, *Science* **313**, 1942 (2006).

⁸W. Siemons, G. Koster, H. Yamamoto, W. A. Harrison, G. Lucovsky, T. H. Geballe, D. H. A. Blank, and M. R. Beasley, *Phys. Rev. Lett.* **98**, 196802 (2007).

⁹A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. Maan, W. van der Wiel, G. Rijnders, D. Blank, and H. Hilgenkamp, *Nat. Mater.* **6**, 493 (2007).

¹⁰A. Kalabukhov, R. Gunnarsson, J. Börjesson, E. Olsson, T. Claesson, and D. Winkler, *Phys. Rev. B* **75**, 121404R (2007).

¹¹G. Herranz, M. Basletic, M. Bibes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzic, J. M. Broto, A. Barthelemy, and A. Fert, *Phys. Rev. Lett.* **98**, 216803 (2007).

¹²T. Koga, S. B. Cronin, M. S. Dresselhaus, J. L. Liu, and K. L. Wang, *Appl. Phys. Lett.* **77**, 1490 (2000).

¹³H. W. Hillhouse and M. T. Tuominen, *Microporous Mesoporous Mater.* **47**, 39 (2001).

¹⁴T. Okuda, K. Nakanishi, S. Miyasaka, and Y. Tokura, *Phys. Rev. B* **63**, 113104 (2001).

¹⁵J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, *Nature (London)* **430**, 758 (2004).

¹⁶H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, *Phys. Rev.* **134**, A442 (1964).