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Chemical Solution Deposition of Transparent and Metallic $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ Films Using Topotactic Reduction

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Metallic and transparent $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films were prepared by the chemical solution deposition (CSD) method using topotactic reduction processing. The use of Si powder as the reducing agent was facile and allowed easy manipulation. It was observed that metallic (resistivity at 300 K ~2.43 mΩ cm) and transparent (~80% transmittance at visible light) $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films could be obtained with an annealing temperature of 900°C, which was significantly lower than the hydrogen reduction temperature (~1400°C). The successful preparation of metallic and transparent $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films using CSD has provided a feasible route for depositing other perovskite-structured functional layers on $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films using this low-cost all CSD method.

I. Introduction

TRANSPARENT conducting oxide (TCO) films are unusual materials that are both electrically conductive and visually transparent, and are widely used as transparent electrodes for liquid crystal displays, organic light emitting diodes, and solar cells. Perovskite-type oxides represent an important class of materials because they possess many excellent physical properties.[1–5] In order to fabricate devices based on perovskite materials, it is desirable to obtain perovskite-structured TCO films, which have a similar structure to the functional layers, allowing for improved performance or novel functionalities.[6–8]

$La_{1-x}Sr_xTiO_3$ films can be both metallic and transparent, which is a characteristic of filling-control behaviors. As reported by Tokura *et al.*,[9] the conductivity of $La_{0.5}Sr_{0.5}TiO_3$ is the highest in the $La_{1-x}Sr_xTiO_3$ system. Moreover, Cho *et al.*[10] and Wu *et al.*[11] found that pulsed laser deposition (PLD)-derived $La_{0.5}Sr_{0.5}TiO_3$-based films were metallic and transparent, enabling them be used as transparent conductors.

Chemical solution deposition (CSD) is a very useful method for film growth that has been widely used in various fields and for different types of films, such as ferroelectric films, magnetic films, and superconducting films. CSD is considered as a facile route for large area films that is low-cost and easy manipulate.[12] However, there have been no reports about CSD for $La_{0.5}Sr_{0.5}TiO_3$ films. The difficulties in fabricating metallic and transparent $La_{0.5}Sr_{0.5}TiO_3$ may be attributed to the following causes: first, it is difficult to obtain Ti^{3+}-based organic precursors; second, in order to convert Ti^{4+} ions into Ti^{3+} ions, a reducing atmosphere and a high annealing temperature need to be used.

In this article, we report on CSD for $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films using topotactic reduction. Topotactic reduction for oxides can be defined as follows: within some specific temperature range and by using a reduction agent, the products inherit their orientations from the reagent crystals, but the oxygen content will be decreased because there is preferential out-diffusion of oxygen atoms while other elements are not changed. In previous topotactic reduction experiments, the commonly used reducing agent is CaH_2 powders.[13,14] In this paper, we choose Si powders as the reducing agent, because it is cheap and can be manipulated in air. The results showed that metallic and transparent $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films could be obtained when the annealing temperature was 900°C, which was much lower than for H_2-reduction processing (~1400°C).[15]

II. Experimental Procedure

First, $La_{0.5}Sr_{0.5}TiO_{3.25}$ films were prepared using the CSD method. La-acetate (Alfa Aesar, 99.9% purity, Ward Hill, MA), Sr-acetate (Alfa Aesar, 99% purity), and Ti-*n*-butoxide (Alfa Aesar, 99% purity) were dissolved in propionic acid and stirred for more than 20 h in order to obtain a well-mixed precursor solution. Then, the films were prepared using spinning coating with a rotation speed of 5000 rpm and a deposition time of 60 s. The substrates were (*h*00)-oriented $LaAlO_3$ (LAO) single crystals. The as-deposited films were baked at 300°C for 30 min; in order to get the desired film thickness, the spin coating and baking processes were repeated three times, giving a film thickness of about 200 nm. Finally, the baked films were annealed at 950°C in air for 20 h. The obtained $La_{0.5}Sr_{0.5}TiO_{3.25}$ film is defined here as sample S_{air}.

In order to obtain metallic $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films, topotactic reduction was carried out. Several S_{air} samples were separately sealed in a quartz tube using Si powders as the reducing agent. In order to avoid the evaporation of Si onto the samples, Al_2O_3 powder was used as a blocking layer. Then, the samples were annealed at various temperatures from 500° to 900°C. A schematic illustration of the topotactic reduction process is shown in Fig. 1. Electronic dispersion spectroscopy was carried out and it was observed that the evaporation of Si onto the samples was completely blocked. Here, we define the samples annealed at different temperatures as samples $S_{subscript}$, where the subscript is the annealing temperature.

X-ray diffraction (XRD, Almelo, Netherlands) using a Philips X'pert Pro diffractometer with CuK_α radiation was carried out to examine the crystallization and orientation both out-of-plane and in-plane. Field emission scanning electronic micros-

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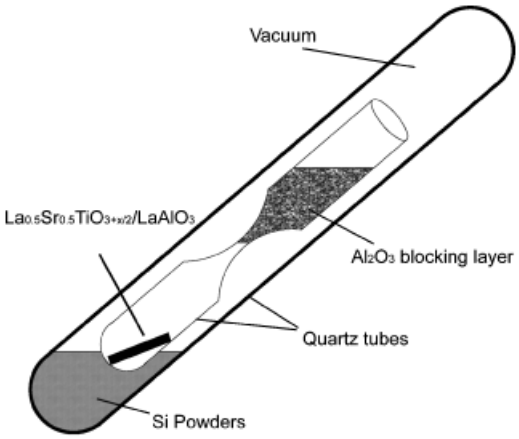

Fig. 1. Schematic illustration of topotactic reduction.

copy (FE-SEM, FEI Sirion 200 type, Hillboro, OR) was used to determine the film thickness. Atomic force microscopy (AFM, Park Scientific Instruments Autoprobe CP type, Sunnyvale, CA) was carried out to investigate the microstructure. Transmittance of the derived films was measured using an automated scanning monochromator (Varian-designed Cary-5E type, Belmont, WA, Australia). The resistivity data were obtained using a physical properties measurement system (PPMS, quantum designed) with a standard four-point probe method.

III. Results and Discussions

In order to compare the transport properties between hydrogen reduction and topotactic reduction samples, the temperature dependence of the resistivity ($\rho-T$) was also measured for several samples derived from hydrogen reduction processing, as is shown in Fig. 2. It can be observed that for the 900°C annealing temperature, the resistivity is reduced gradually with annealing time. Moreover, for the samples with annealing times <10 h, the $\rho-T$ shows semiconductor-like characteristics within the whole measured temperature range, while the sample with a 20 h annealing time is metallic within 192–350 K, and then becomes semiconductor-like within the 5–192 K range. The metal-semiconductor transition can be attributed to the antiferromagnetic transition, as previously reported.[16] Additionally, even when the temperature was increased to 1000°C using a 10%H_2–Ar annealing atmosphere, although the resistivity is obviously decreased, the resistivity is rather high as compared with the PLD-derived films.[10,11] The above results suggest that it is difficult to obtain low resistance $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films when the annealing temperature is lower than 1000°C under hydrogen atmosphere, because the oxygen atoms are difficult to be pulled out of the lattice due to low reactivity under these conditions.

Figure 3(a) contains the XRD patterns of the prepared $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films made by topotactic reduction. The XRD pattern of the S_{air} sample is also shown for comparison. It can be seen that all films are highly (h00)-oriented. Additionally, from Fig. 3(b) it can be seen that the lattice constant is gradually increased with the annealing temperature, which indicates that the oxygen content is gradually decreased in $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films. The out-of-plane orientation was evaluated by rocking-curve measurements, and the in-plane orientation was evaluated by phi-scans. The results showed that the full width at half-maximum (FWHM) from the rocking-curve measurements and phi-scans is about 2° and 4°, respectively. The decreased oxygen content suggests that the filling factor n (where $n=0.5-2x$)[16] is gradually increased with increasing annealing temperature, which indicates that the carrier concentration is increased due to the conversion of Ti^{4+} into Ti^{3+}.

Figure 4 presents the AFM results for some typical $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films prepared by topotactic reduction. It can be seen

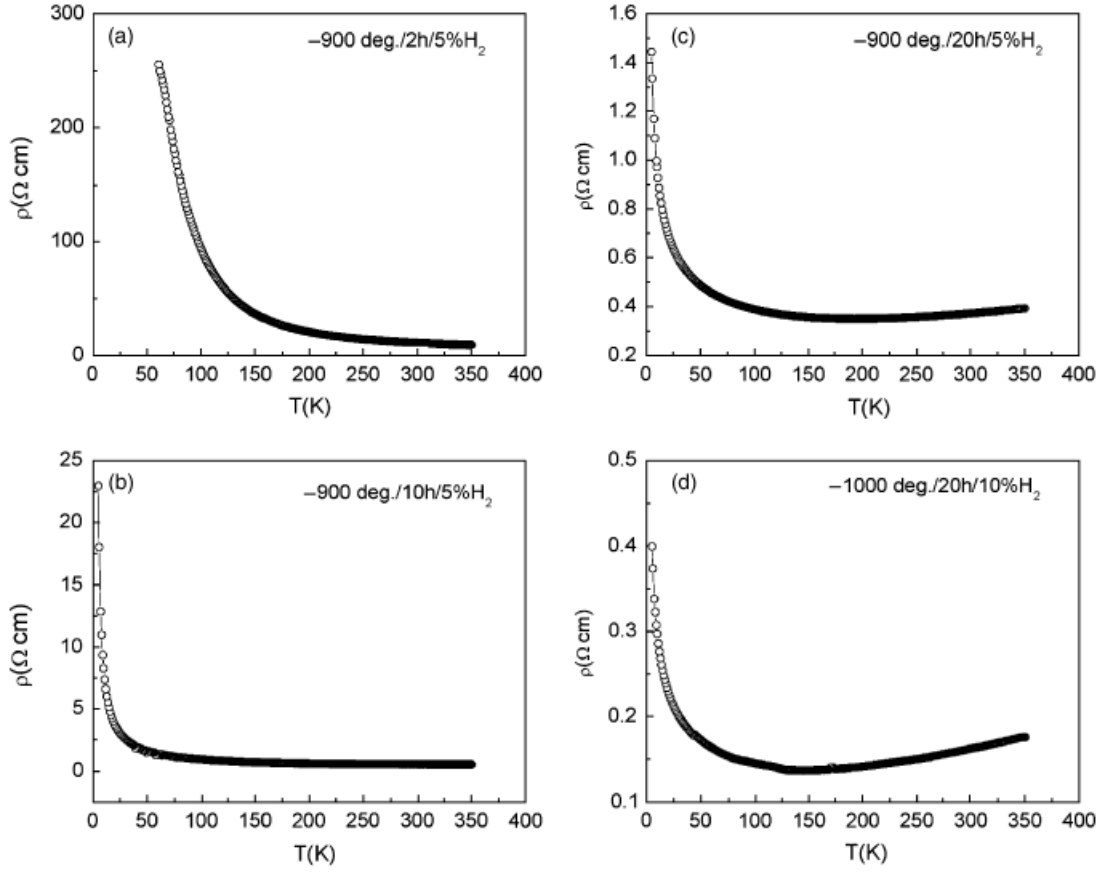

Fig. 2. $\rho-T$ results of some $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films prepared by hydrogen reduction. The reducing conditions are labeled in the plots. (a) $SH_{900\text{-}2h}$ (b) $SH_{900\text{-}10}$ (c) $SH_{900\text{-}20}$ (d) $SH_{1000\text{-}20}$

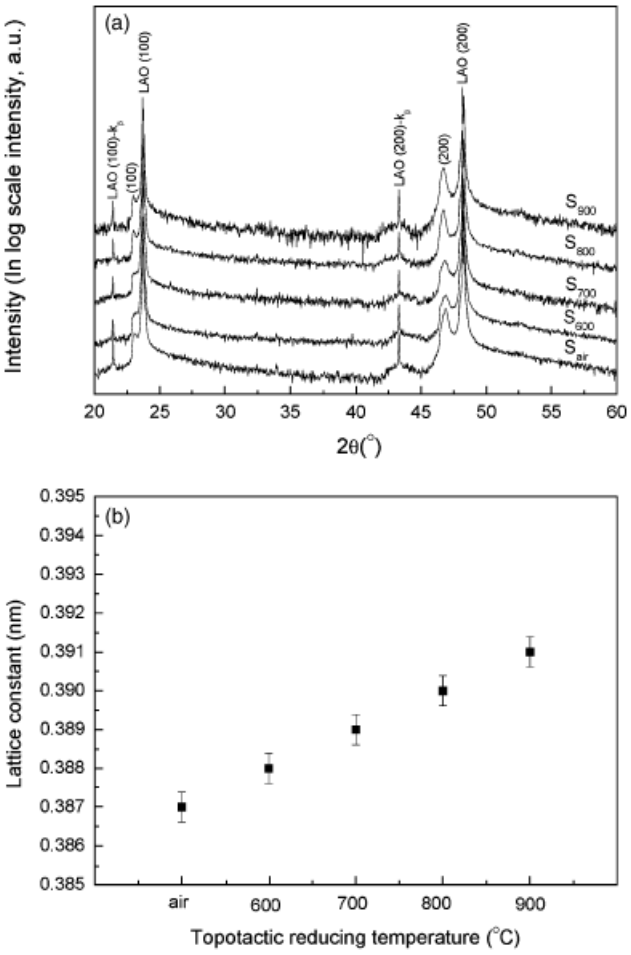

Fig. 3. (a) X-ray diffraction results on some $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films prepared by topotactic reduction. The corresponding reduction temperature can be obtained from the sample description. (b) Relationship between the lattice constants of the derived films and the topotactic reduction temperature.

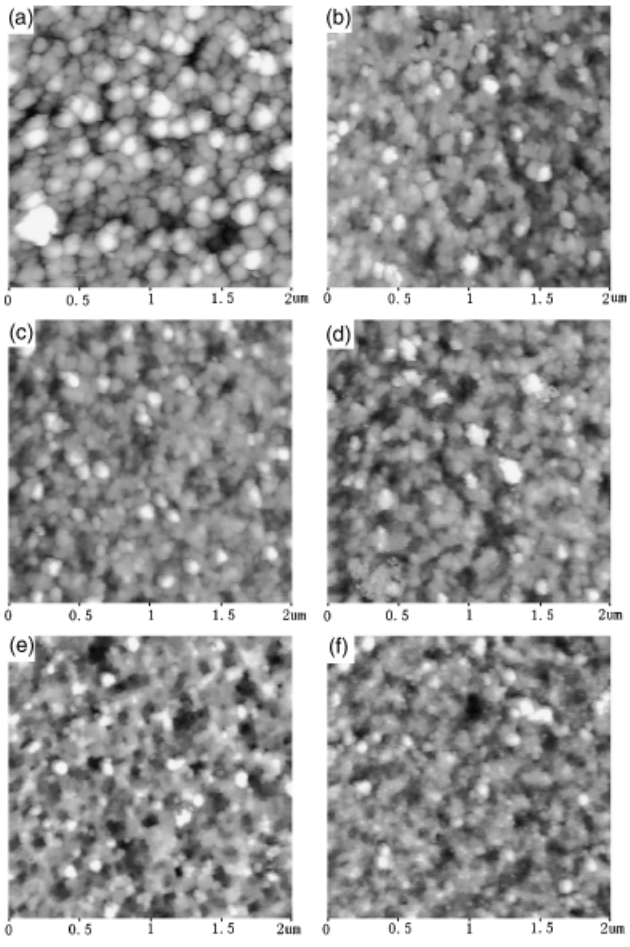

Fig. 4. AFM results on some $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films prepared by topotactic reduction: (a) S_{air}; (b) S_{600}; (c) S_{700}; (d) S_{800}; (e) S_{900}; (f) $S_{900–40\ h}$.

that the grain size is reduced with increasing annealing temperature, which is different from the typical grain growth mode. In general, the grain size should be increased with increasing annealing temperature due to the improvement of atomic diffusion.[17] However, in topotactic reduction processing, the oxygen atoms are gradually pulled out from the perfect $La_{0.5}Sr_{0.5}TiO_{3.25}$ lattice, which will lead to rupture of the bonds, resulting in decreased grain size.

Figure 5 contains the ρ–T results for some typical $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films obtained by topotactic reduction. It can be seen that the sample S_{600} is semiconductor-like within the measured temperature range of 5–390 K. The sample S_{800} is metallic in the whole measured temperature range, but behaves as a semiconductor at lower temperatures. With the annealing temperature increased to 900°C, the samples are metallic within all the measured temperature ranges, and the resistivity at 300 K is ~2.43 mΩ cm. Moreover, when the annealing time is increased from 2 to 20 h, the resistivity is gradually decreased, which can be clearly seen from the results for the samples $S_{900–10\ h}$ and $S_{900–20\ h}$. When the annealing time is prolonged from 20 to 40 h, the resistivity does not vary. It is suggested that in perovskite titanium oxides, the grain boundary plays a very important role in the determination of resistivity.[18] The resistivity is increased with decreasing grain size. Combined with the AFM and ρ–T results, it is concluded that the invariability of the resistivity for samples annealed for more than 20 h should be attributed to the competition effects between oxygen content and grain size.

Table I contains the room temperature (at 300 K) resistivity of some typical samples derived from hydrogen reduction and topotactic reduction processing in order to give a comparison. It can be seen that topotactic reduction processing is a feasible method for obtaining low resistance $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films with a low annealing temperature, whereas this is impossible with hydrogen reduction processing.

In order to study the transport properties for the topotactic reduction samples, the ρ–T results were fitted using different models, as shown in Fig. 6. It was previously reported that the ρ–T can be well fitted using the thermal activation model for $R_{1-x}A_xTiO_3$.[16] However, in our experiments, ρ–T cannot be well fitted using a thermal activation model within the whole measured temperature range. As a typical example, Fig. 6(a) shows the ρ–T fitting of the sample S_{600}, and it is found that the thermal activation model, $\rho \sim \exp(T_0/T)$ where T_0 is the activation energy, can only be well fitted within the temperature range of 230–390 K, whereas at lower temperatures the variable range hopping (VRH) model, $\rho \sim \exp(T_0/T)^{1/4}$, is suitable. The obtained T_0 is 543 meV and 2.76×10^6 K for the thermal activation and the VRH model, respectively. The obtained fitting parameters are similar to the previously reported results for $R_{1-x}Ca_xTiO_{3+y/2}$ ceramics.[16] The crossover in the ρ–T behavior is attributed to decreasing thermal energy with decreasing temperature.[19] The difference between our samples and the $R_{1-x}A_xTiO_3$ samples suggests that Ti-site disorder plays a different role as compared with R-site doping effects, because in our samples the disorder is related to a change in the Ti^{3+}/Ti^{4+} ratio due to the different reduction temperature, while in the $R_{1-x}A_xTiO_3$ samples the disorder is of the R-site type due to A-doping on the R-site.

For samples showing metallic behaviors as shown in Fig. 6(b), it can be observed that the ρ–T can be well fitted by $\rho = \rho_0 + AT^2$, where ρ_0 is the residual resistivity and A is a coefficient related to the square of the specific heat γ^2. The fitting

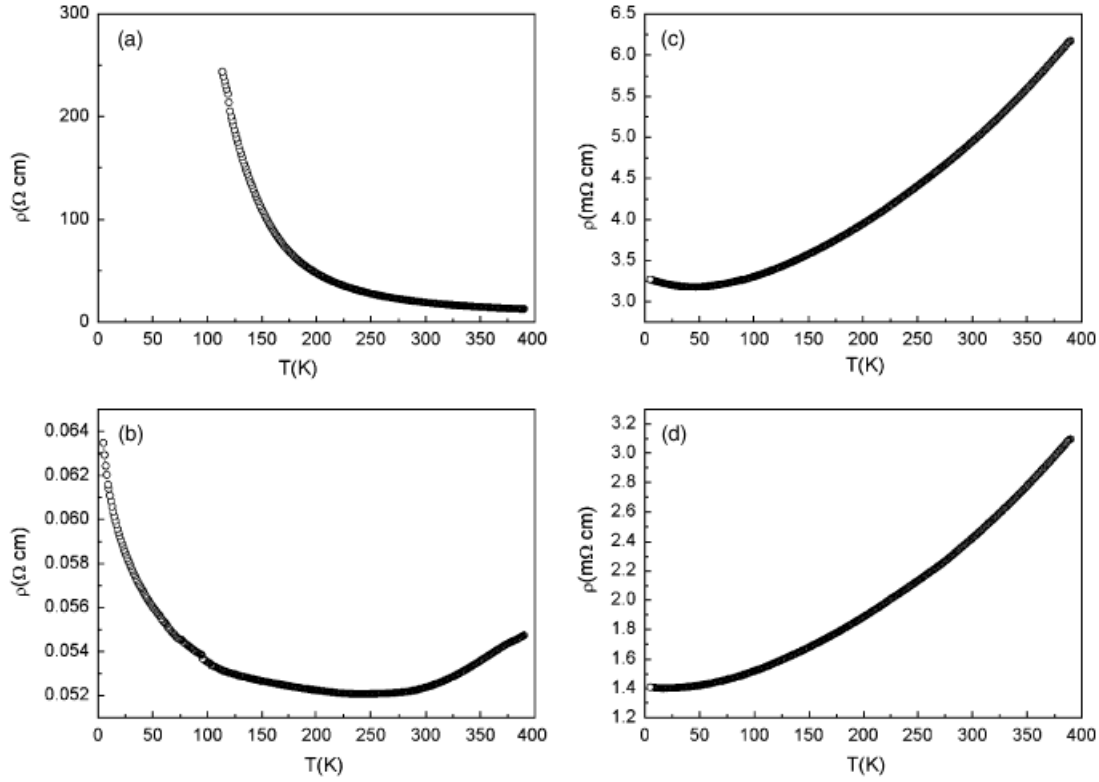

Fig. 5. ρ–*T* results for some $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films prepared by topotactic reduction: (a) S_{600}; (b) S_{800}; (c) $S_{900-10\ h}$; (d) S_{900}.

parameters of ρ_0 and A for two typical metallic samples S_{900-10} and S_{900} are 3.1 and 1.4 mΩ cm, 2.0×10^{-8} and 1.1×10^{-8} Ω cm/K^2, respectively. The obtained fitting parameters of ρ_0 and A are similar to the previous reported results with $\rho_0 \sim 10^{-4}$ Ω cm and $A \sim 10^{-9}$ Ω cm/K^2,[9] which suggests that the sample results are credible and can be attributed to the Fermi-liquid system.

For TCO, the visible transmittance is a very important property. In our experiments, it was observed that the transmittance does not vary with reduction temperature or time. Figure 7 shows the transmittance results for two typical samples, and it can be seen that the topotactic reduction processing does not change the transmittance in any obvious way. The S_{900} sample shows about 80% transmittance, which can be considered as high enough for TCO. Combined with the optical and transport properties, it is suggested that the number of electrons in the *d* band excited by the visible light is small, but that the T^{3+}/Ti^{4+} mixed valence is enough to induce a metallic behavior. It is recognized that if the density of states (DOS) near/at the Fermi level is high, photons could easily excite the carriers to higher levels, resulting in low transmittance. Combined with our experimental results, that is, the obtained $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films

Table I. Comparison of Room Temperature (300 K) Resistivity Between Some $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ Films Prepared by Hydrogen and Topotactic Reduction Processing

Sample	Reducing method	Reducing time (h)	Reducing temperature (°C)	$\rho_{330\ K}$ (Ω cm)
$SH_{900\text{-}2\,h}$	5%H_2–Ar	2	900	10.9
$SH_{900\text{-}10\,h}$	5%H_2–Ar	10	900	0.53
$SH_{900\text{-}20\,h}$	5%H_2–Ar	20	900	0.37
$SH_{1000\text{-}20\,h}$	10%H_2–Ar	20	1000	0.16
S_{600}	Topotactic	20	600	19.1
S_{700}	Topotactic	20	700	0.56
S_{800}	Topotactic	20	800	0.05
S_{900}	Topotactic	20	900	2.43
$S_{900\text{-}10\,h}$	Topotactic	10	900	4.96

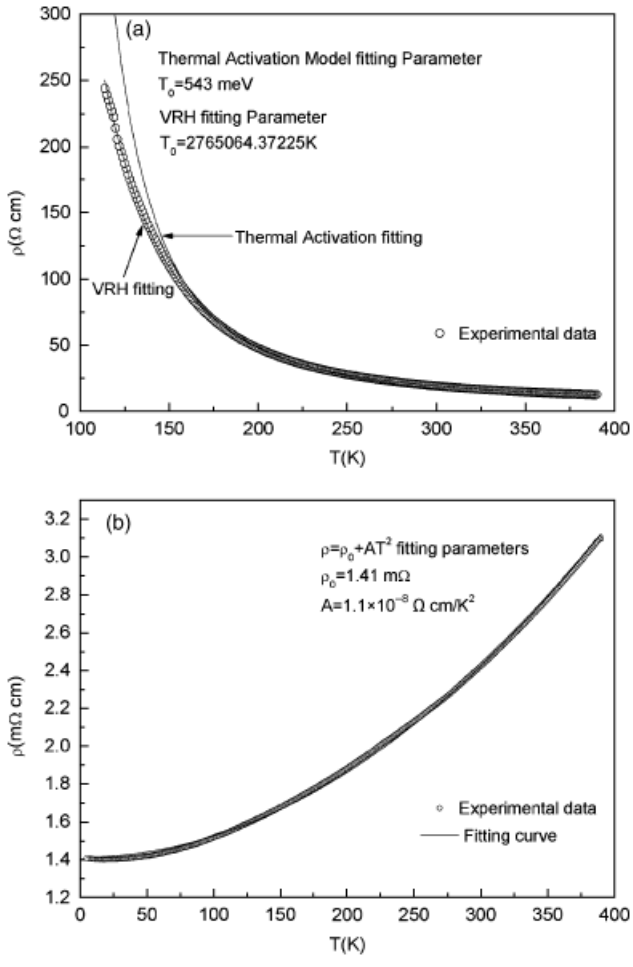

Fig. 6. (a) ρ–*T* fitting of results for S_{600}; (b) ρ–*T* fitting results for S_{900}.

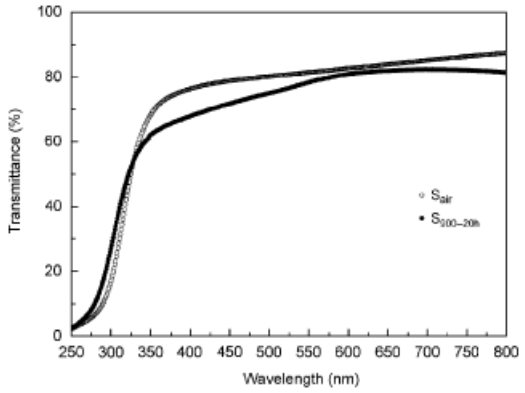

Fig. 7. Transmittance versus wavelength curves for two typical films.

can have metallic characteristics with high transmittance, it can be reasonably believed that the Ti compounds should have lower DOS in the *d* bands near/at the Fermi level because of the proximity of the empty Ti^{4+} configuration, which will result in excellent optical transparency in the visible range.[10]

IV. Conclusion

CSD is a facile method for preparing films and was used to fabricate $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films by topotactic reduction processing using Si powders as the reducing agent. It was observed that metallic and transparent $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films could be obtained at 900°C using topotactic reduction, which was significantly lower than the hydrogen reduction temperature (~1400°C). By tuning the annealing temperature, the transport properties could be easily tuned whereas the transmittance did not vary. The results suggest that it is possible to obtain Ti^{3+}-containing metallic perovskite materials using Ti^{4+} precursors in CSD by topotactic reduction. The success in obtaining metallic and transparent $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films provides a feasible route for depositing a functional perovskite layer on $La_{0.5}Sr_{0.5}TiO_{3+x/2}$ films using an all chemical solution method.

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References

[1]I. Hamberg and C. G. Granqvist, "Evaporated Sn-Doped In_2O_3 Films: Basic Optical Properties and Applications to Energy-Efficient Windows," *J. Appl. Phys.*, **60** [11] R123 (1986).

[2]Q. Z. Liu, H. F. Wang, F. Chen, and W. Wu, "Single-Crystalline Transparent and Conductive Oxide Films with the Perovskite Structure: Sb-Doped $SrSnO_3$," *J. Appl. Phys.*, **103** [9] 093709 (2008).

[3]H. Kim and A. Pique, "Transparent and Conducting Sb-Doped SnO_2 Thin Films Grown by Pulsed-Laser Deposition," *Appl. Phys. Lett.*, **84** [2] 218 (2004).

[4]M. F. A. M. van Hest, M. S. Dabney, J. D. Perkins, D. S. Ginley, and M. P. Taylor, "Titanium-Doped Indium Oxide: A High-Mobility Transparent Conductor," *Appl. Phys. Lett.*, **87** [3] 032111 (2005).

[5]G. Haacke, "Transparent Conducting Coatings," *Ann. Rev. Mater. Sci.*, **7**, 73–93 (1977).

[6]C. H. Ahn, J. M. Triscone, and J. Mannhart, "Electric Field Effect in Correlated Oxide Systems," *Nature*, **424**, 1015–8 (2003).

[7]K. Dörr, "Ferromagnetic Manganites: Spin-Polarized Conduction Versus Competition Interactions," *J. Phys. D*, **39** [7] R125–50 (2006).

[8]B. N. Mbenkum, N. Ashkenov, M. Schubert, M. Lorenz, H. Hochmuth, D. Michel, M. Grundmann, and G. Wagner, "Temperature-Dependent Dielectric and Electro-Optic Properties of a ZnO–$BaTiO_3$–ZnO Heterostructure Grown by Pulsed-Laser Deposition," *Appl. Phys. Lett.*, **86** [9] 091904 (2005).

[9]Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, T. Arima, K. Kumagai, and Y. Iye, "Filling Dependence of Electronic Properties on the Verge of Metal-Mott-Insulator Transition in $Sr_{1-x}La_xTiO_3$," *Phys. Rev. Lett.*, **70** [14] 2126–9 (1993).

[10]J. H. Cho and H. J. Cho, "Optical Transparency of Metallic $La_{0.5}Sr_{0.5}TiO_{3+\delta}$ Thin Films," *Appl. Phys. Lett.*, **79** [10] 1426 (2001).

[11]W. B. Wu, F. Lu, K. H. Wong, G. Pang, C. L. Choy, and Y. H. Zhang, "Epitaxial and Highly Electrical Conductive $La_{0.5}Sr_{0.5}TiO_3$ Films Grown by Pulsed Laser Deposition in Vacuum," *J. Appl. Phys.*, **88** [2] 700–3 (2000).

[12]X. B. Zhu, Y. P. Sun, H. C. Lei, X. H. Li, R. Ang, B. C. Zhao, W. H. Song, D. Q. Shi, and S. X. Dou, "Growth of $Ca_3Co_4O_9$ Films: Simple Chemical Solution Deposition and Stress Induced Spontaneous Dewetting," *J. Appl. Phys.*, **102** [10] 103519 (2007).

[13]Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter, and W. Paulus, "Infinite-Layer Iron Oxide with a Square-Planar Coordination," *Nature*, **450**, 1062–5 (2007).

[14]S. Inoue, M. Kawai, Y. Shimakawa, M. Mizumaki, N. Kawamura, T. Watanabe, Y. Tsujimoto, H. Kageyama, and K. Yoshimura, "Single-Crystal Epitaxial Thin Films of $SrFeO_2$ with FeO_2 "Infinite Layers"," *Appl. Phys. Lett.*, **92** [16] 161911 (2008).

[15]M. Janousch, G. I. Meijer, U. Staub, B. Delley, S. F. Karg, and B. P. Andreasson, "Role of Oxygen Vacancies in Cr-Doped $SrTiO_3$ for Resistance-Change Memory," *Adv. Mater.*, **19** [17] 2232–5 (2007).

[16]T. Katsufuji, Y. Taguchi, and Y. Tokura, "Transport and Magnetic Properties of a Mott-Hubbard System Whose Bandwidth and Band Filling are Both Controllable: $R_{1-x}Ca_xTiO_{3+y/2}$," *Phys. Rev. B*, **56** [16] 10145–53 (1997).

[17]C. V. Thompson, "Grain Growth in Thin Films," *Ann. Rev. Mater. Sci.*, **20**, 245–68 (1990).

[18]M. Higuchi, K. Aizawa, K. Yamaya, and K. Kodaira, "Electrical Properties of $Sr_{1-x}La_xTiO_3$ ($0 \leq x \leq 0.10$) Single Crystals Grown by the Floating Zone Method," *J. Solid State Chem.*, **92** [2] 573–7 (1991).

[19]N. F. Mott, "The Transition to the Metallic State," *Philos. Mag.*, **6** [62] 287–309 (1961). □