



UNIVERSITY  
OF WOLLONGONG  
AUSTRALIA

University of Wollongong  
Research Online

---

Faculty of Engineering - Papers (Archive)

Faculty of Engineering and Information Sciences

---

2008

# Chemical solution deposition of LaMnO<sub>3</sub>-based films for coated conductors

Dongqi Shi

*University of Wollongong, dongqi@uow.edu.au*

Xuebin Zhu

*University of Wollongong, xuebin@uow.edu.au*

Jung Ho Kim

*University of Wollongong, jhk@uow.edu.au*

Hechang Lei

*Institute of Solid State Physics*

Lin Wang

*University of Wollongong*

*See next page for additional authors*

<http://ro.uow.edu.au/engpapers/3798>

---

## Publication Details

Shi, D., Zhu, X., Kim, J., Lei, H., Wang, L., Sun, Y., Zeng, R. and Dou, S. X. (2008). Chemical solution deposition of LaMnO<sub>3</sub>-based films for coated conductors. In 8th European Conference on Applied Superconductivity (EUCAS 2007), 16-20 September, Brussels, Belgium. *Journal of Physics*, 97 102054-1-102054-6.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library:  
[research-pubs@uow.edu.au](mailto:research-pubs@uow.edu.au)

---

**Authors**

Dongqi Shi, Xuebin Zhu, Jung Ho Kim, Hechang Lei, Lin Wang, Yuping Sun, Rong Zeng, and S. X. Dou

# Chemical solution deposition of LaMnO<sub>3</sub>-based films for coated conductors

D Q Shi<sup>1,\*</sup>, X B Zhu<sup>1,2</sup>, J H Kim<sup>1</sup>, H C Lei<sup>2</sup>, L Wang<sup>1</sup>, Y P Sun<sup>2</sup>, R Zeng<sup>1</sup>, S X Dou<sup>1</sup>

<sup>1</sup> Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

<sup>2</sup> Key Laboratory of Materials Physics, Institute of Solid State Physics, Hefei 230031, P. R. China

**Abstract** LaMnO<sub>3</sub>-based films were prepared using the chemical solution deposition method. It was found that the films on perovskite oxide single crystal substrates are highly (h00)-oriented when the annealing atmosphere is oxygen or air; however, when the substrate is yttrium-stabilized ZrO<sub>2</sub>, only the La<sub>1-x</sub>Na<sub>x</sub>MnO<sub>3</sub> films are highly (h00)-oriented, and other LaMnO<sub>3</sub>-based films are (110)-oriented. Under a reducing annealing atmosphere, the atmosphere must be wet in order to create a suitable oxygen partial pressure to crystallize the LaMnO<sub>3</sub>-based films. After annealing under a wet reducing atmosphere the LaMnO<sub>3</sub>-based films are (110)-oriented when the films are directly deposited on Ni tapes; however, when SrTiO<sub>3</sub>-buffered Ni tapes are used, the LaMnO<sub>3</sub> films are (h00)-oriented, which is suitable for subsequent growth of YBCO. The results suggest that it is possible to tune the orientation of buffer layers using suitable templates, which can widen the selection of buffer layers for coated conductors in the all metallorganic deposition approach.

## 1. Introduction

In recent years, RE123 (RE: rare earth) based high temperature superconductor (HTS) tapes, which are also called 2<sup>nd</sup> generation HTS tapes or coated conductors, have been widely studied due to their higher current-burden capacity and suitability for applications in higher magnetic fields as compared with Bi2223-based HTS tapes.

Currently, two types of routes have been considered as very promising methods for realization of large-area applications: ion beam assisted deposition (IBAD) and rolling assisted biaxially textured substrates (RABiTS). In RABiTS processing, the buffer layers and the superconducting films can be prepared using chemical solution deposition (CSD), which is called the all metalorganic deposition (MOD) method. Since the all MOD method is based on non-vacuum processing, this method has the potential for low costs. Moreover, it has been reported that coated conductors have been successfully prepared with critical currents as large as 200A/cm-width at 77K and self-field by the all MOD method [1].

In all MOD processing, the buffer layers play a very important role. First, the buffer layers should be effective in blocking the interdiffusion between the superconducting films and the Ni-based

---

\* Corresponding author: Dongqi Shi; e-mail: dongqi@uow.edu.au

substrates; secondly, the biaxial texture of the substrates can be transmitted to the superconducting films through the buffer layers.

Many types of materials have been used as buffer layers, including pyrochlore structured  $\text{La}_2\text{Zr}_2\text{O}_7$ ,  $\text{Gd}_2\text{Zr}_2\text{O}_7$ , fluorite structured  $\text{CeO}_2$ , perovskite structured  $\text{SrTiO}_3$ , and so on [2]. Among these,  $\text{LaMnO}_3$  (LMO)-based materials are considered to make very excellent buffer layers for coated conductors and are especially attractive because of their potential applications as single buffer layers[3, 4]. Moreover, it has been reported[5,6] that a Sr-doped  $\text{LaMnO}_3$  layer can be used as a conductive buffer layer, which can effectively transmit electric current from the superconducting film to the Ni-based tapes and protect the coated conductor if superconductivity is lost.

In this article, we report our recent results on the preparation of LMO-based films using CSD, in order to increase our understanding of the all MOD approach to coated conductors using LMO-based buffer layers.

## 2. Experimental procedures

The substrates in this work were purchased Ni tapes and oxide single crystal substrates. Before the spin coating for LMO-based films, the substrates were cleaned ultrasonically in acetone, methanol, and deionized water; then they were annealed at  $900^\circ\text{C}$  under  $\text{N}_2 - 4\%\text{H}_2$  for Ni tapes and at  $1000^\circ\text{C}$  in air for oxide single crystal substrates in order to obtain a well-defined surface.

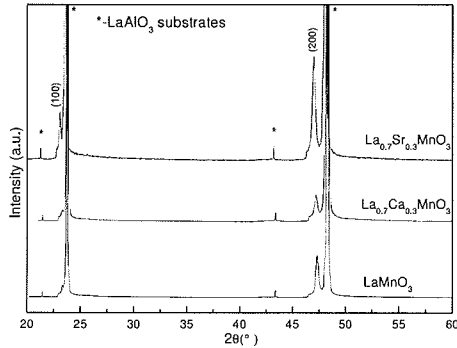
The precursors for the LMO-based solution were all acetate salts. For example, the  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) solution was prepared using La-acetate (Alfa Aesar, 99.9% in purity), Sr-acetate (Alfa Aesar, 99% in purity), and Mn-acetate (Alfa Aesar, 99% in purity). The acetate salts were dissolved in propionic acid at  $70^\circ\text{C}$  and stirred at this temperature for 20 minutes using a magnetic stirrer, and then stirred at room temperature for more than 20h in order to obtain a well-mixed precursor solution. The solutions were diluted only by propionic acid down to 0.2M. At this stage, the solutions could be kept in air without significant deterioration for more than 3 months.

The deposition of LMO-based films was conducted using a spin coater with a rotation speed of 4000rpm over a time of 60s. The deposited films were then dried at  $300^\circ\text{C}$  for 30 minutes in air or  $\text{N}_2 + 4\%\text{H}_2$  atmosphere. The dried films were annealed at different temperatures using different atmospheres, as described below. The spin coating, drying, and annealing processes were repeated several times in order to obtain thicker LMO-based films.

The typical thickness was about 100nm that was checked using an ellipsometer. The crystallization quality, as well as the out-of-plane and in-plane orientation, was characterized by x-ray diffraction (XRD) using  $\text{CuK}_\alpha$  diffraction. Field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) were carried out to investigate the microstructure of the derived samples.

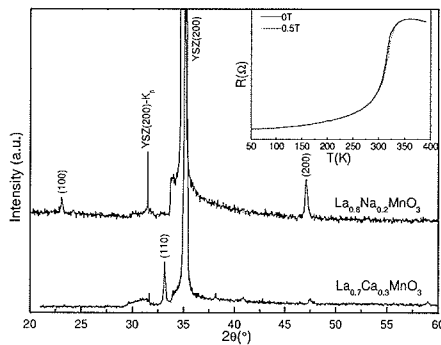
## 3. Results and discussion

Figure 1 shows the XRD results on LMO,  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (LCMO), and LSMO films on  $\text{LaAlO}_3$  substrates using annealing at  $900^\circ\text{C}$  in an air atmosphere. It can be seen that all the three films are highly (h00)-oriented without any undesired diffraction peaks. The out-of-plane and in-plane orientations were examined by rocking curve and  $\Phi$ -scanning measurements. The results show that the full width at half maximum (FWHM) is less than  $0.5^\circ$  and  $1.5^\circ$  for the rocking curve and  $\Phi$ -scanning results, respectively, indicating the excellent biaxial texture of the LMO-based films. The above results suggest that the highly (h00)-oriented LMO-based films can be easily prepared by annealing under air using CSD methods. The results on LMO-based films on  $\text{SrTiO}_3$  single crystal substrates are same as these for  $\text{LaAlO}_3$  substrates. Because of large lattice misfit between LMO and Ni ( $\sim 9.5\%$ ), it is difficult to directly deposit LMO on Ni-based tape. However, due to small lattice misfit between LMO and YBCO ( $\sim 1.5\%$ ) and the stability of LMO, LMO is very suitable as a cap layer for YBCO deposition.



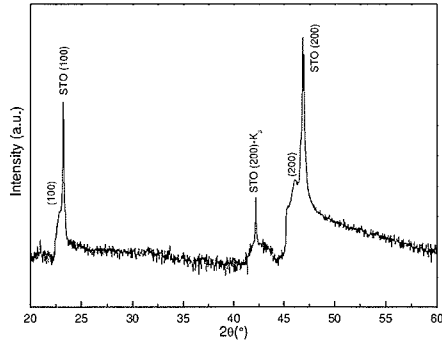
**Figure 1.** XRD results on LMO-based films on  $\text{LaAlO}_3$  substrates annealed under air.

Guided by our experience on  $\text{CeO}_2/\text{YSZ}/\text{CeO}_2$  ( $\text{Y}_2\text{O}_3$ )-based buffer layers, we deposited LMO-based films on YSZ single crystal substrates. Figure 2 contains XRD results on the LMO-based films on YSZ substrates that were annealed at  $900^\circ\text{C}$  in an oxygen atmosphere. It can be seen that the LCMO/YSZ is (110)-oriented, which is unsuitable for subsequent growth of YBCO films; however, the  $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$  (LNMO)/YSZ is highly (h00)-oriented, and the temperature dependence of the resistance, R-T, is shown in the inset of figure 2. It clearly suggests that the LNMO/YSZ behaves like epitaxial  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  films [3], which indicates that the LNMO is suitable for subsequent YBCO films.



**Figure 2.** XRD results on LCMO and LNMO films on YSZ substrates; the inset contains the R-T results under 0 and 0.5T field for the LNMO/YSZ film.

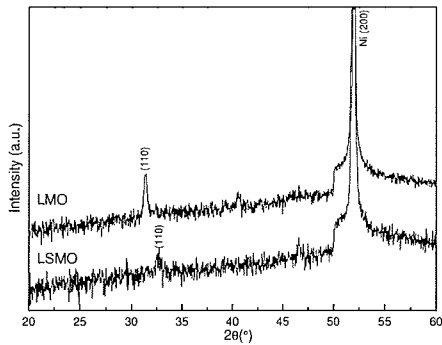
In order to fabricate the LMO-based films on Ni tapes, a reducing atmosphere is needed in order to protect the Ni tapes from oxidation. First, we prepared LMO-based films on  $\text{LaAlO}_3$  single crystal substrates under a reducing atmosphere. The results showed that when the annealing atmosphere was dry  $\text{N}_2 - 4\%\text{H}_2$  the LMO-based films could not be crystallized, indicating that the oxygen partial pressure was too low. In order to improve the oxygen partial pressure in the annealing processing,  $\text{N}_2 - 4\%\text{H}_2$  gas was bubbled through three water-containing bottles at  $25^\circ\text{C}$ . Figure 3 contains the typical XRD results for a LMO film on a  $\text{SrTiO}_3$  substrate. It can be seen that the film is highly (h00)-oriented, which indicates that the wet annealing atmosphere is positive for LMO-based films under a reducing annealing gas.



**Figure 3.** XRD spectrum of a LMO film on a SrTiO<sub>3</sub> single crystal substrate, after annealing under a wet reducing atmosphere.

From the above results, it can be observed that the LMO-based films are easily crystallized by annealing under oxygen. However, when a dry reducing annealing atmosphere is used, the LMO-based films cannot be crystallized due to the low oxygen partial pressure. When annealing is done under a wet reducing atmosphere, the extra oxygen partial pressure from the decomposition of water is positive for LMO-based films. Based on our analysis, we prepared LMO-based films on Ni tapes using an annealing atmosphere of wet N<sub>2</sub> - 4%H<sub>2</sub>.

Figure 4 contains the XRD results for LMO and LSMO films on Ni tapes that were annealed at 900°C using wet N<sub>2</sub> - 4%H<sub>2</sub>. It can be seen that the two films are (110)-oriented, without any other undesired phases. XRD results for LMO-based films on Ni tapes that were annealed using the same wet reducing atmosphere but different annealing temperatures from 650°C to 950°C are all (110)-oriented, indicating that the annealing temperature plays a trivial role in determining the orientation of LMO-based films.

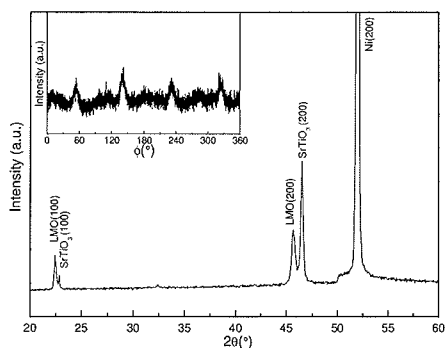


**Figure 4.** XRD spectra of LMO and LSMO films on Ni tapes, with annealing under a wet reducing atmosphere.

The above results show two characteristics: first, when perovskite single crystal substrates are used, the LMO-based films are highly (h00)-oriented, regardless of whether an oxidating or wet reducing atmosphere is used; second, under a wet reducing atmosphere, the LMO-based films are (110)-oriented when the substrates are Ni tapes. Besides the lattices parameter misfit between film and substrate, it is known that the orientation of films is roughly dependent on two important factors: the surface energy of the film and the interface energy between the film and the substrate. As for the LMO-based films on perovskite oxide single crystal substrates, the above results strongly suggest that the interface energy is the dominant factor. However, for the LMO films on Ni tapes that possess a different crystal structure, when the LMO-based films are annealed under a wet reducing atmosphere, the films are oxygen deficient. It has been reported that the (110) plane of LMO has the lowest oxygen ratio as compared with the (100) and (111) planes. That means that the surface energy of the (110)

plane may be the lowest when the LMO films are annealed under a wet reducing atmosphere. Combined with the experimental results, this suggests that the interface energy and the surface energy synchronously may also play a role in determining the orientation of LMO-based films on Ni tapes. Addition to the large lattices misfit between LMO and Ni substrate, it is suggested to tune the orientation of LMO films by using different templates.

Based on the above analysis, we investigated whether the orientation of LMO films could be changed when the Ni tapes were buffered by perovskite films. Figure 5 contains the XRD spectrum of a LMO film on a SrTiO<sub>3</sub> buffered Ni tape. The detailed processing parameters of CSD for SrTiO<sub>3</sub> buffer layers can be found elsewhere [7,8]. It is interesting to find that the LMO and SrTiO<sub>3</sub> films are both highly (h00)-oriented. The result suggests that the orientation of LMO films can be effectively tuned through insertion of a SrTiO<sub>3</sub> layer. The in-plane orientation was characterized by a  $\Phi$ -scanning measurement, and the result is shown in the inset of Figure 5. It can be seen that the LMO has an in-plane orientation although there are some undesirable LMO domains with other orientations. The FE-SEM and AFM results show that the LMO/SrTiO<sub>3</sub>/Ni buffer layers are dense and flat, with a root-mean-square roughness of less than 10 nm, indicating that the buffer layers were suitable for subsequent growth of YBCO films.



**Figure 5.** XRD spectrum of LMO film on CSD-derived SrTiO<sub>3</sub>/Ni substrate. The inset contains the  $\Phi$ -scan of the LMO layer.

Systematic research on the effects of humidity in the annealing atmosphere and of dopants at Mn sites, as well as effects on the subsequent growth of YBCO films, is currently being carried out and will be reported elsewhere.

#### 4. Conclusions

Chemical solution deposition was used to prepare LaMnO<sub>3</sub>-based films. The results showed that under an oxygen or air annealing atmosphere, the LaMnO<sub>3</sub>-based films were highly (h00)-oriented, when perovskite oxide single crystal substrates were used; however, when YSZ substrates were used, only La<sub>1-x</sub>Na<sub>x</sub>MnO<sub>3</sub> films were highly (h00)-oriented. When a wet reducing atmosphere was used for annealing, all the LaMnO<sub>3</sub>-based films were highly (h00)-oriented on perovskite oxide single crystal substrates; however, the LaMnO<sub>3</sub>-based films were (110)-oriented when Ni tapes were used as substrates. By using Ni tapes buffered with perovskite SrTiO<sub>3</sub> films, the orientation can be tuned to highly (h00)-oriented, which is suitable for subsequent growth of YBCO films.

#### Acknowledgements

This work was funded by the Australian Research Council under Project No. DP 0666771, and also supported by the National Key Basic Research Program of China under Contract No. 2006CB601005 and the Foundation of the Chinese Academy of Sciences under Contract No. O64N161294.

#### References

- [1] Parans M, Paranthaman M, Sathyamurthy S, Heatherly L, Martin P M, Goyal A, Kodenkandath T, Li X, Thieme C L H, Rupich M W 2006 *Physica C* 445–448 529
- [2] Bhuiyan M S, Paranthaman M and Salama K, 2006 *Supercond. Sci. Technol.* **19** R1
- [3] Aytug T, Paranthaman M, Zhai H Y, Christen H M, Sathyamurthy S and Christen D K, 2002 *J. Mater. Res.* 17 2193
- [4] Kim K, Paranthaman, Norton D P, Aytug T, Cantoni C , Gapud A A, Goyal A and Christen D K 2006 *Supercond. Sci. Technol.* 19 R23
- [5] Aytug T, Paranthaman M, Kang B W, Sathyamurthy S, Goyal A, and Christen D K 2001 *Appl. Phys. Lett.* **79** 2205
- [6] Aytug T, Paranthaman M, Thompson J R, Goyal A, Rutter N, Zhai H Y, Gapud A A, Ijaluola A O and Christen D K 2003 *Appl. Phys. Lett.* **83** 3963
- [7] Zhu X B, Liu S M, Hao H R, Tong P, Wang C X, Song W H, Sun Y P, Shi K, Sun Z Y, Chen S and Han Z 2004 *Scripta Materialia* **51** 659
- [8] Zhu X B, Chen L, Liu S M, Song W H, Sun Y P, Shi K, Sun Z Y, Chen S and Han Z 2004 *Physica C* 415 57