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Author(s): E. L. Brosha, B. W. Chung, F. H. Garzon

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ELECTROCHEMICAL STUDIES OF PEROVSKITE MIXED CONDUCTORS

Eric L. Brosha, Brandon W. Chung, and Fernando H. Garzon.
Electronic and Electrochemical Materials and Devices Group
Los Alamos National Laboratory, Los Alamos, N.M. 87545

Research into the growth of high-quality single crystal thin films of high transition temperature (T_C) superconductors have stimulated interest in other perovskite metal oxides with a variety of physical properties.¹ Thin films of perovskite materials are among the major focal research areas for optical, sensor, electronic, and superconducting applications.¹ Two lanthanum-based oxygen/electronic conducting perovskite oxides of particular interest for high temperature fuel cell electrodes and interconnects and for other electrochemical applications such as oxygen separation devices are $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-y}$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$. The La-based perovskites are valuable for these technologies because they reduce interfacial resistances by eliminating the need for a three phase contact area (gas, metal electrode, electrolyte).² In addition, these oxides may also serve a valuable role as novel catalysts or catalytic supports; however, little is known about what catalytic properties they may possess.

Fundamental study of the electrochemical, diffusional oxygen transport, and surface catalytic properties of these materials can be greatly simplified if the complications associated with the presence of grain boundaries and multiple crystallite orientations can be avoided. Therefore, single crystals of these La-based perovskites become highly desirable. In this work, we report the structural and electrical properties of highly oriented thin films of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ grown on single crystal Y-ZrO₂ substrates. An addition, we have demonstrated growing, *in situ*, epitaxial multilayer perovskite/fluorite/perovskite configurations for fundamental fuel cell modeling.

Experimental

We have deposited films by using a 90° off-axis radio-frequency (RF) magnetron sputtering^{3,4} technique from a single 2-inch-diameter, hot-pressed stoichiometric target of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ and $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ (purchased from SSC) on Y-ZrO₂ (200)-oriented substrates. We also deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ in a multilayer configuration on epitaxial YSZ on SrTiO₃ (100). In a typical deposition, a 1cm² substrate was fastened to a heater box using silver paint, and the substrate heater temperature was measured using thermocouple and/or IR camera. The substrate heater was maintained at a temperature of 650°C-700°C. All of the depositions were carried out at an RF power of 100W. Typical total pressures were between 40 and 42 mTorr (60% argon and 40% oxygen). After the depositions, the chamber was flooded with pure oxygen to a pressure of 5 Torr, then the films were allowed to cool to room temperature.

For each of the films, x-ray diffraction (XRD) data was taken for structure and texture analysis. The XRD measurements were made with a Siemens D5000 diffractometer fitted with a $\text{CuK}\alpha$ source. We used Rutherford Backscattering spectroscopy (RBS) to study the composition

and deposition rate of films. Scanning tunneling microscopy (STM) was used to image the free surfaces of the epitaxially grown films for studies of surface microstructures. A Schlumberger 1260 frequency response analyzer was used to obtain AC impedance spectroscopy data.

Results and Discussion

Figures 1a and 1b are XRD patterns for $\text{La}_{0.84}\text{Sr}_{0.16}\text{MO}_3$ (LSMO) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CO}_3$ (LSCO) sputtered thin films. The principal orientation is pseudo-cubic [110]; however, a small amount (<1%) of pseudo-cubic [100] orientation is present in both films. By varying temperature, heater position, and Ar/O_2 pressure, it was also possible to obtain a principal pseudo-cubic [100] orientation or a mixture of both orientations. Figures 2a and 2b are XRD patterns of the rocking curve of the (110) reflection and the phi-scan of the (310) reflection for the LSCO film in Figure 1b. These data indicate that the sputtered films exhibit a high degree of crystallinity and in-plane orientation. Similar rocking curve widths and oriented phi-scans were obtained for the LSMO thin films.

The surface microstructures of the LSMO and LSCO depositions were examined by STM. The images indicated an island growth mechanism with plateaus present within the islands. Most significantly, LSCO and LSMO films sputtered on YSZ single crystals revealed a typical root-mean-square roughness of 17 to 40Å.

The capability of growing smooth oriented thin films is necessary in order to grow oxide materials in multilayer configurations.⁵ One useful configuration, for fundamental electrochemical device modeling, is a LSMO/YSZ multilayer grown *in situ* on SrTiO_3 . Figure 3 is an XRD trace of such a multilayer film. A 5000Å thick [200] oriented YSZ film was first grown on [100] SrTiO_3 followed by a 2500Å thick [110]-pseudocubic oriented LSMO film on the YSZ layer. The excellent epitaxy, evident in this XRD trace, shows that an all single-crystal thin-film fuel-cell model can be fabricated for fundamental electrochemical study.

For electrical AC response characterization, an 8000Å-thick oriented LSMO film was grown on single crystal YSZ substrate; for comparison, a 1 micron thick polycrystalline LSMO film was prepared by sputtering onto a 1cm² polycrystalline tetragonal zirconia substrate. For both the single crystal and polycrystalline samples, a small 2mm² platinum electrode was then sputtered onto the LSMO film and a platinum counter electrode was sputtered to completely cover the zirconia side. Platinum wire was bonded to the electrodes and both substrates were placed into a furnace under flowing oxygen. Figures 4a and b are AC impedance data taken under polarizing and non-polarizing conditions for the two LSMO films at the conditions of 1 atm PO_2 and 500°C. Figure 5 is the current-voltage data for the two films taken at these same conditions. XRD analysis indicated that heating the single crystal films above 600°C would lead to recrystallization. The frequency range for these measurements was 1MHz to 100mHz with an amplitude of 50mV. The equivalent circuit used to model the data is shown in each figure as well. Although, for this work, the system remains underdetermined, we do see a simplification in the equivalent circuit for the

polarization, these trends are not observed in the polycrystalline sample. This preliminary data tends to suggest that the presence of grain boundaries in the film/substrate dominate the electrochemical response.

Conclusions

We have demonstrated that high quality, fully dense, and smooth thin films of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-y}$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$ can be grown on single crystal YSZ substrates via off axis RF magnetron sputtering. In addition, epitaxial, multilayer perovskite/fluorite/perovskite configurations can be grown *in situ*. Preliminary AC impedance analysis indicates that these films may be utilized to simplify equivalent circuit modeling for fundamental electrochemical study of working fuel cell devices.

Acknowledgments

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REFERENCES

- ¹J. T. Cheung, P. E. D. Morgan, D. H. Lowndes, X. Y. Zheng, and J. Breen. Appl. Phys. Lett. **62**, 2045 (1993); and references therein.
- ²N.Q. Minh. J. Am. Ceram. Soc., **76**, 563 (1993); and references therein.
- ³C. B. Eom, J. Z. Sun, K. Yamamoto, A. F. Marshall, K. E. Luther, S. S. Laderman, and T. H. Geballe, Appl. Phys. Lett. **53**, 595 (1988).
- ⁴C. B. Eom, J. Z. Sun, B. M. Lairson, S. K. Streiffer, A. F. Marshall, K. Yamamoto, S. M. Anlage, J. C. Bravman, T. H. Geballe, S. S. Laderman, R. C. Taber, and R. D. Jacowitz. Physica C, **171**, 354 (1990).
- ⁵R.J. Houlton, D.W. Reagor, M.E. Hawley, K.N. Springer, Q.X. Jia. C.B. Mombourquette, F.H. Garzon, and X.D. Wu to be published in the IEEE Transactions on Applied Superconductivity Proceedings of the Applied Superconductivity Conference - Boston MA., October 1994.

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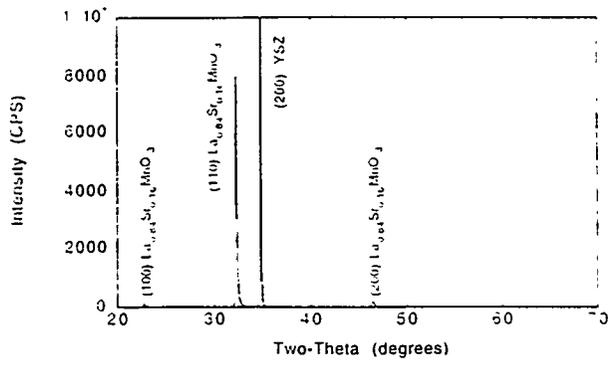


Figure 1a. XRD pattern of a $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ thin film grown on Y-ZrO_2 [100].

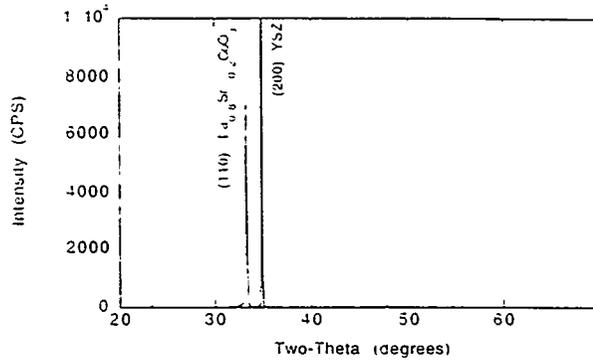


Figure 1b. XRD pattern of a $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ thin film grown on Y-ZrO_2 [100].

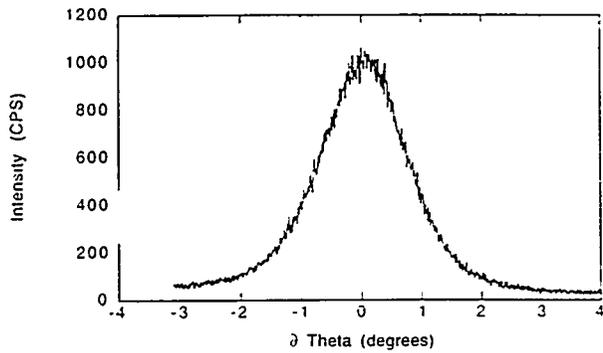
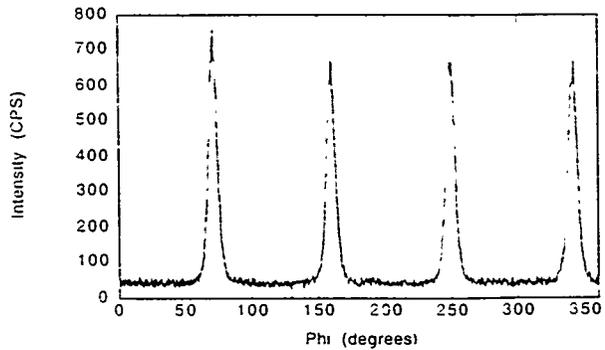


Figure 2a. XRD rocking curve of the (110) reflection of a $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ thin film grown on Y-ZrO_2 [100].

Figure 2b. XRD phi-scan of the (310) reflection of a $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ thin film grown on Y-ZrO_2 [100].



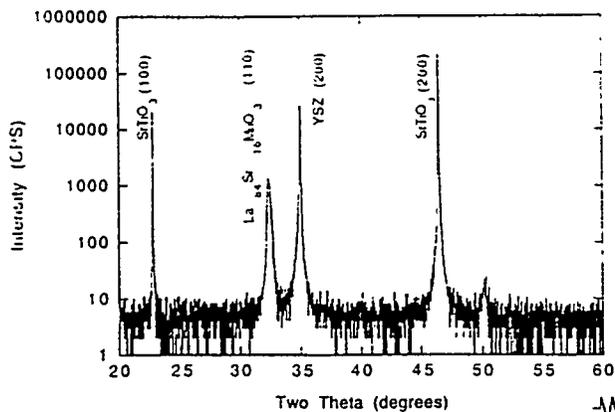


Figure 3. XRD pattern of a $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ [110] / YSZ [100] / SrTiO_3 multilayer stack configuration.

Figure 4a. AC impedance characterization, 1MHz-0.1Hz and 50 mV amplitude, of an oriented $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ [110] thin film grown on Y-ZrO₂ [100]. AC data was taken under polarizing and non-polarizing conditions at 1 atm PO₂ and 500°C. Frequency decreases from left to right. Inset: expanded view. Top: equivalent circuit model used to model this data.

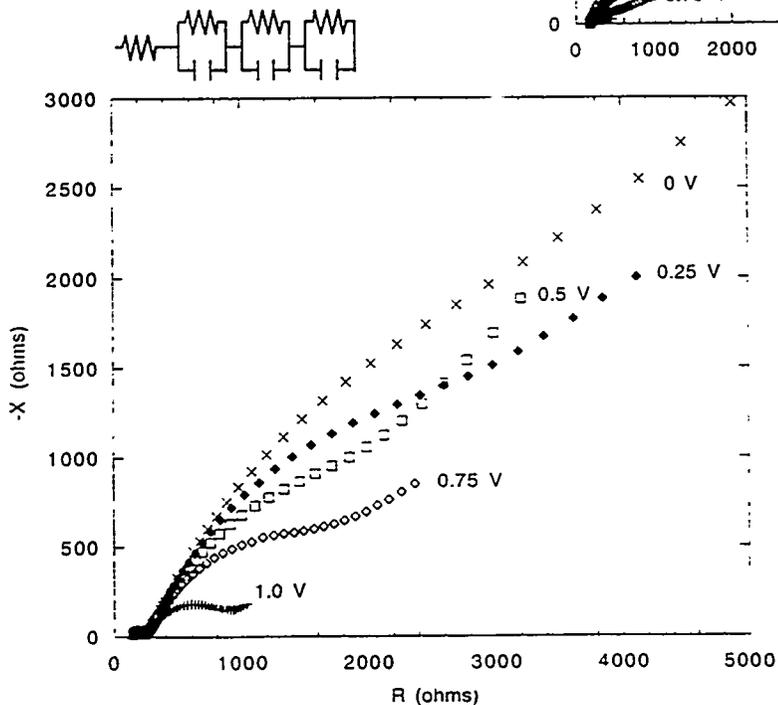
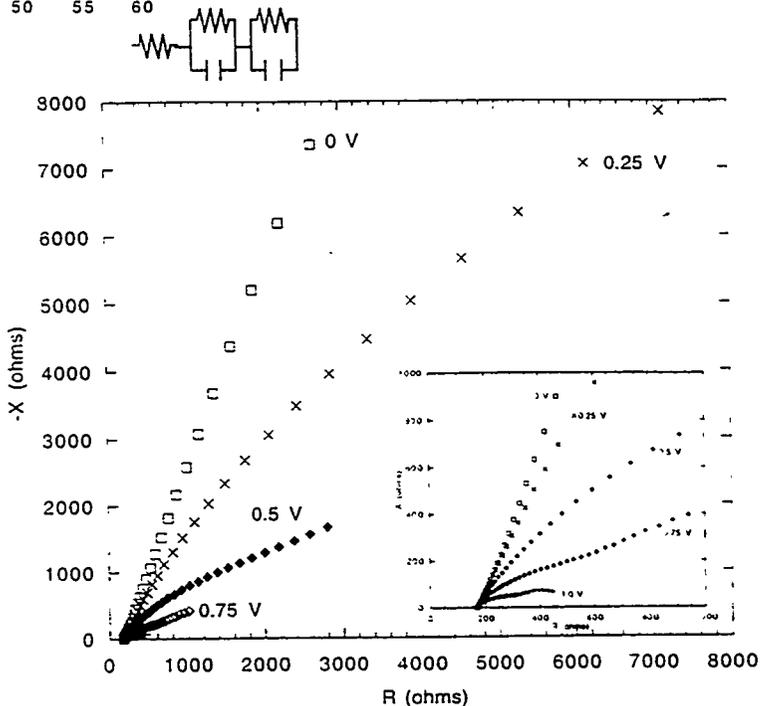


Figure 4b. AC impedance characterization, 1MHz-0.1Hz and 50 mV amplitude, of a polycrystalline $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ thin film sputtered on TZP. AC data was taken under polarizing and non-polarizing conditions at 1 atm PO₂ and 500°C. Frequency decreases from left to right. Top: equivalent circuit model used to model this data.