

LA-UR- 94-3935

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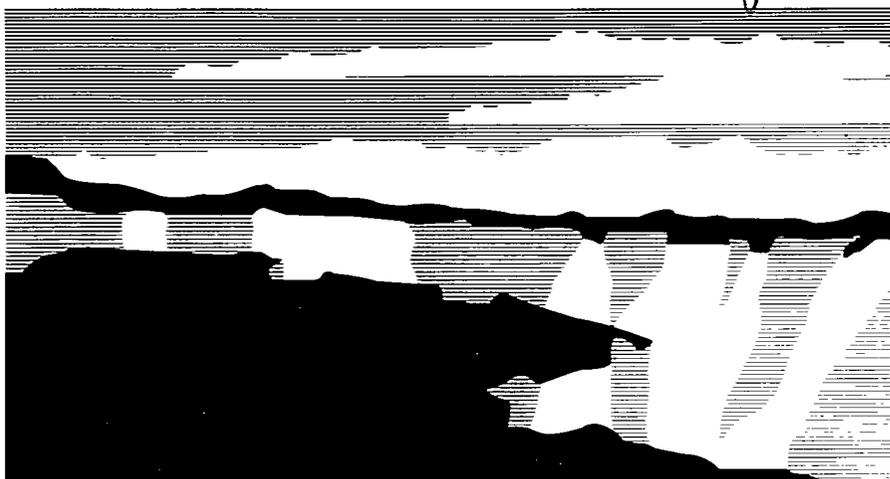
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Submitted to: Materials Research Soc., Boston, MA
Nov. 28 - Dec. 2, 1994

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VAPOR DEPOSITION OF THIN-FILM Y-DOPED ZrO₂ FOR ELECTROCHEMICAL DEVICE APPLICATIONS

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ABSTRACT

The growth of high-quality, pin-hole free, yttrium doped ZrO₂ thin films is of great interest for a variety of electrochemical applications such as fuel cells and oxygen gas separation devices. In the work, we have grown polycrystalline thin films of fully stabilized Y-ZrO₂ on thick porous Al₂O₃ substrates in multilayer La_{1-x}Sr_xMEO₃/YSZ/La_{1-x}Sr_xMEO₃ (ME = Mn, Co) configurations using a combination of single-target RF magnetron sputtering and electron beam physical vapor deposition techniques. The structure and morphology of these films have been studied using X-ray diffraction, and Scanning Electron Microscopy techniques. The ionic conductivity of the thin films has been measured using AC impedance analysis.

INTRODUCTION

Solid oxide electrolytes based on yttria-stabilized zirconia (YSZ) is widely used in applications such as oxygen sensors, solid oxide fuel cells, oxygen pumps, electrocatalytic reactors, and electrochemically driven oxygen separation membranes. However, bulk YSZ is used in these applications. This requires high operating temperatures in order to minimize ohmic loss. One alternative of overcoming this problem is to use a thin film of the electrolyte. The thin films of YSZ would exhibit lower resistance and hence greater oxygen flux at similar temperatures, enabling their use at reduced operating temperatures. Thus, there has been increased recent interest in thin films of stabilized zirconia [1-4]. In order to make thin-film solid oxide electrolyte applicable, it is necessary to establish a method for forming thin films on porous substrates.

In this study, we report the structure, morphology, and conductivity of the thin films of La_{1-x}Sr_xMEO₃/YSZ/La_{1-x}Sr_xMEO₃ (ME = Mn, Co) deposited on porous alumina substrates.

EXPERIMENTAL

We have deposited La_{0.8}Sr_{0.2}CoO₃ and La_{0.84}Sr_{0.16}MnO₃ films by using 90° off-axis radio-frequency (RF) magnetron sputtering [5] from a single 2-inch-diameter, hot-pressed stoichiometric target (purchased from Seattle Specialty Ceramics) on porous alumina substrates (purchased from Coors Ceramics with approximate porosity of 20%). The substrate heater was maintained at a temperature of 700°C during the deposition of La-based perovskite oxides. All of the depositions of perovskites were carried out at an RF power of 100W with total pressure of 40 mTorr (75% argon and 25 % oxygen). The electron beam physical vapor deposition technique was used to produce thin films of yttria-stabilized zirconia (YSZ) on La_{1-x}Sr_xMEO₃ (ME = Mn, Co) layers. All the depositions were carried out with ZrO₂ doped with 7.3 mole percent yttrium (purchased from International Advanced Materials) at a substrate temperature of 800°C. The top layer of La-based perovskite oxides were produced using the same condition as the bottom layer to form a single cell. Figure 1 shows the top view of the cell observed with an optical microscope. The cells were demonstrated to be open circuit at room temperature.

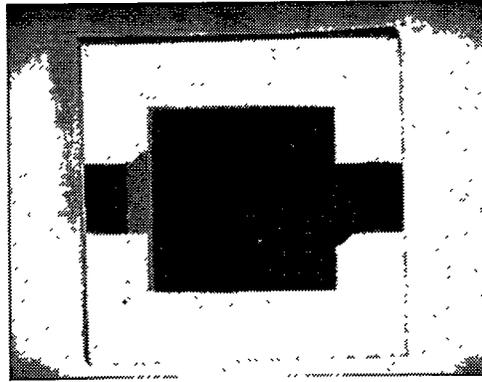


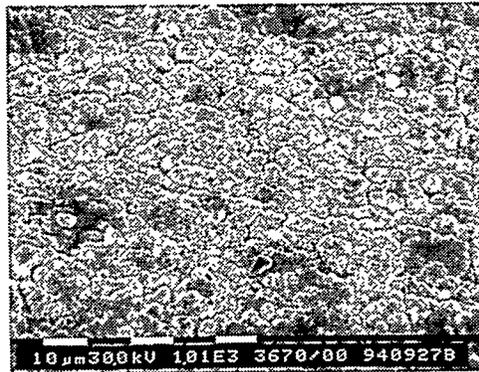
Figure 1. The top view of the multilayer device (1cm \times 1cm)

We employed X-ray diffraction and Scanning Electron Microscopy techniques to study structure and morphology of these films. The ionic conductivity of the YSZ thin films has been measured using AC impedance analysis using Solartron 1260 Frequency Response Analyzer in the frequency range between 0.1 Hz and 1 MHz.

RESULTS AND DISCUSSION

The thickness and stoichiometry of La-based perovskite oxides were obtained using Rutherford backscattering spectroscopy (RBS). The thickness of the perovskite oxides was between 16 and 18 μm (deposition rate of 2000 $\text{\AA}/\text{hour}$). The compositions of the films were revealed to be close to the nominal values. The thickness of deposited YSZ was between 14 and 15 μm as determined by profilometer. Using energy dispersive spectroscopy (EDS), the yttrium concentration in zirconia was found to be 6.5 mole percent.

Fig. 2 shows a representative scanning electron micrograph of the deposited layers. The yttria-stabilized zirconia (YSZ) was shown to grow with similar surface morphology without visible pinholes on both $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ and $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ layers. However, the surface morphology of La-based perovskite oxide layers were found to be different. The $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ films were more dense and granular than the $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ films.



(a)

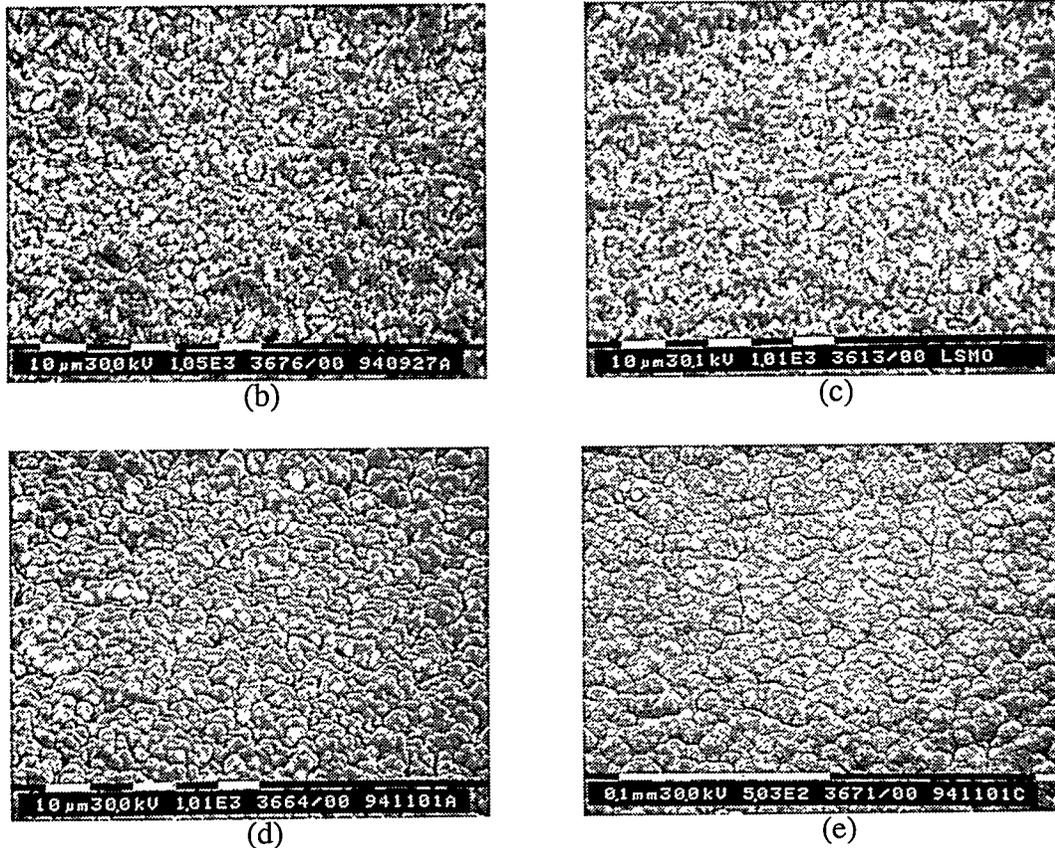
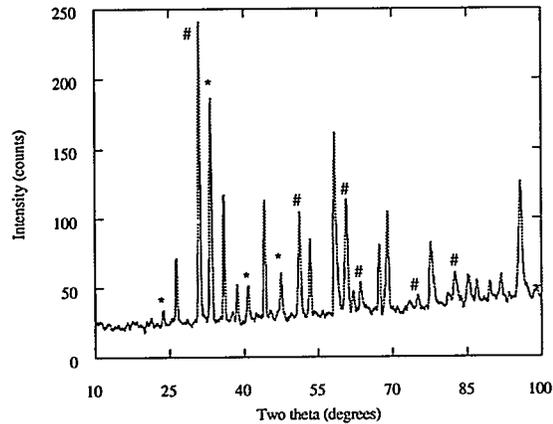


Figure 2. SEM micrograph of (a) YSZ layer, (b) $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ on Al_2O_3 , (c) $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ on YSZ, (d) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ on Al_2O_3 , and (e) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ on YSZ.

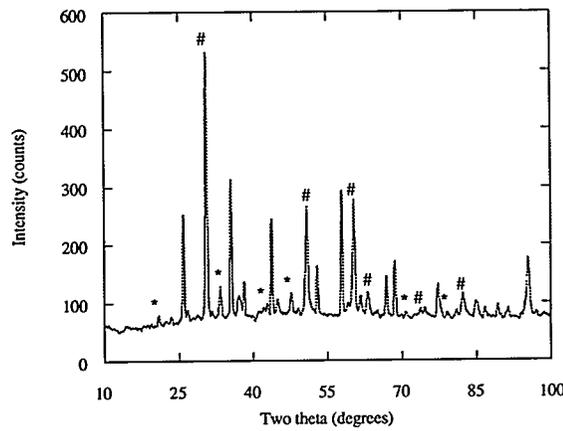
The x-ray diffraction patterns of a multilayer $\text{La}_{1-x}\text{Sr}_x\text{MEO}_3/\text{YSZ}/\text{La}_{1-x}\text{Sr}_x\text{MEO}_3$ (ME = Mn, Co) depositions are shown in fig. 3. The diffraction patterns of yttrium doped zirconia layers on $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ and $\text{La}_{0.84}\text{Sr}_{0.16}\text{CoO}_3$ were both assigned to cubic zirconia. The X-ray diffraction analysis indicates that $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ films are grown with rhombohedral structure while $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ films are shown to grow with cubic perovskite structure. However, after the AC impedance measurements at various temperature, the x-ray diffraction pattern of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ shows splitting of (111) peak indicating crystallographic transition to rhombohedral perovskite structure. Table I shows parameters obtained from x-ray analyses.

Table I. Structural parameters for YSZ thin film

	after deposition	after measurement
YSZ/ $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$	5.05Å	5.08Å
YSZ/ $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$	5.08Å	5.09Å



(a)



(b)

Figure 3. X-ray diffraction patterns of multilayers. (a) $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3/\text{YSZ}/\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$; (b) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3/\text{YSZ}/\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$. * $\text{La}_{1-x}\text{Sr}_x\text{MEO}_3$ (ME=Mn, Co), # YSZ.

The AC impedance measurements were done under open circuit condition on multilayers. The real and imaginary parts of the complex impedance are plotted in the complex plane and shown in Fig. 4 in the temperature range between 800°C and 300°C. The AC impedance data were interpreted using an equivalent circuit model shown in figure 4. The offset from the origin is indicative of the presence of a purely resistive path at high frequency. The equivalent circuit is tentatively proposed to represent a simple model that simulates the experimentally observed frequency dispersion in fig. 4. It is comprised of a resistance at high frequency in series with parallel combinations of resistance, constant phase angle capacitive elements, and Warburg [6] impedances. The resistance at high frequency may be associated with the total YSZ electrolyte resistance. The total YSZ electrolyte conductivity obtained from the complex plane is shown in Fig. 5.

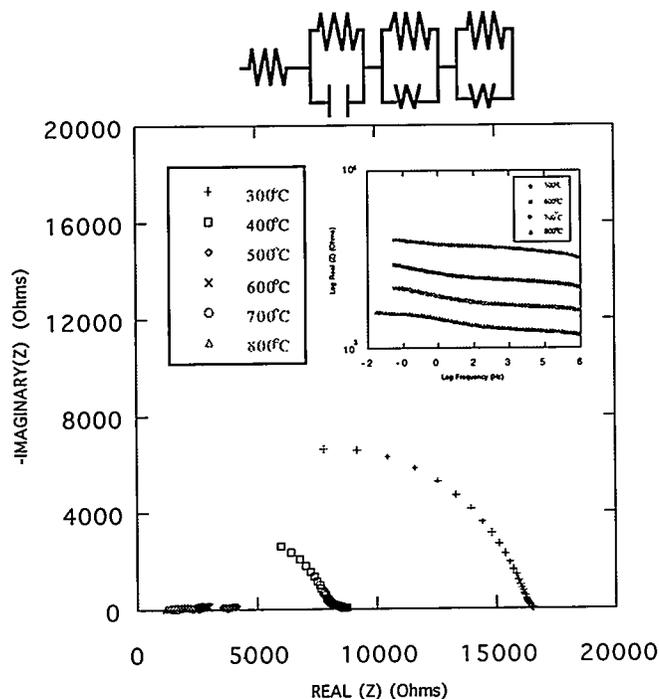


Figure 4. Frequency dispersion characteristic for $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3/\text{YSZ}/\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ multilayer with a proposed equivalent circuit model

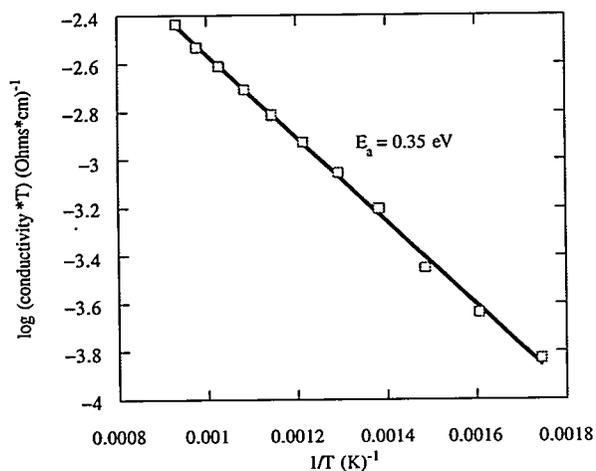


Figure 5. Arrhenius plot for the conductivity of YSZ thin film electrolyte.

CONCLUSION

We have demonstrated that highly dense, pin-hole free, thin films of yttria-stabilized zirconia can be formed on thick porous Al_2O_3 substrates in multilayer $\text{La}_{1-x}\text{Sr}_x\text{MEO}_3/\text{YSZ}/\text{La}_{1-x}\text{Sr}_x\text{MEO}_3$ (ME = Mn, Co) configurations using RF magnetron and electron beam physical vapor deposition techniques. The structure and morphology

of each layer of these films have been studied. Cracks and pinholes were not detected with a scanning electron microscope. The ionic conductivity of the film of YSZ showed low activation energy of 0.35eV.

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