

IV.A.24 Novel Low Temperature Solid State Fuel Cells

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Objectives

The objective of this research is to use advanced nanostructured material synthesis via optimally fabricating and fundamentally understanding the physical properties and chemical stability of multilayered structures for development of an intermediate temperature solid oxide fuel cell (IT-SOFC), and to demonstrate their advantages and unique qualities for energy device applications.

Accomplishments

- Fabricated highly mixed (ionic and electronic) conductive $\text{PrBaCo}_2\text{O}_{5+x}$ (PBCO) thin films on various substrate materials such as SrTiO_3 (STO), LaAlO_3 (LAO), NdGaO_3 (NGO), and MgO.
- Studied the electrical conductivities of the as-grown films on various substrates and simulated the nature of the conductivity.
- Investigated the interface strain effect on the film properties, in which with the increase of the temperature, the conductivity exponentially increases due to thermal activation and becomes steady around 400°C (or 670 K) probably owing to the lost of oxygen.
- Discovered that the PBCO films tensile strain on LAO and NGO substrates have excellent electrical conductivity, $\sim 10^2 \text{ S/cm}^2$, over a very broad temperature region of 300 to 1,000 K, and the films with relaxed strain on STO and MgO have relative lower electrical conductivity. In the high temperature range (higher than 400°C), tensile strained films show much better conductivity.
- Compared with the traditional electrode materials such as $(\text{La,Sr})\text{MnO}_3$ or $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$, PBCO thin films have much better electrical conductivity especially in the low temperature region.

Introduction

Perovskite oxides with high ionic conductivity have practical applications in solid oxide fuel cells, chemical membranes, and gas sensors. Among the many possible compositions with the perovskite structure, systems containing cobalt are particularly attractive systems for the electrodes due to their low electrical resistivity and high ionic conductivity. This family of cobalt containing perovskite oxides also displays many interesting physical phenomena. The oxygen-deficient ordered double perovskites $\text{RBaM}_2\text{O}_{5,+6}$ (where R is a rare earth element and $M = \text{Mn, Fe, Co}$) have been the subject of a number of investigations because of their wide ranges of stoichiometry and concomitant variable transition metal oxidation states. The low temperature structural properties of these compounds have been studied in detail and some data are available on their high temperature oxygen chemistry. Recently, with the collaboration of Professor A. Jacobson at the University of Houston, rapid surface exchange kinetics have been successfully fabricated and studied on the PBCO thin films. The epitaxial single crystalline PBCO thin films were grown on single crystal SrTiO_3 (STO) substrates and shown to have two types of domain and spin-glass interaction behavior in magneto-resistance studies.

Approach

To fabricate highly epitaxial PBCO on various oxide substrates, a KrF excimer pulsed laser deposition (PLD) system with a wavelength of 248 nm was employed to deposit the PBCO thin films on different substrate materials such as (001) STO and (001) MgO substrates. By controlling and optimizing the deposition conditions, single crystalline PBCO thin films have been achieved on the as-selected substrates and the microstructural studies from X-ray diffraction θ - 2θ scan, high-resolution synchrotron X-ray diffraction, and transmission electron microscopy (TEM) indicate that the as-growth films have good epitaxial quality. The transport properties of both the as-grown and after-annealing samples were measured by resistance measurements in the temperature range from 50 K to 450 K using the four probe method (low temperature [T] range) and impedance measurements (high T range).

Results

To understand the physical properties of materials for cathode, electrolyte, and anode applications, the focus of this study has been on the systematical characterizations of the new cathode candidate,

(Pr,Ba)CoO₃ (PBCO). Highly mixed conductive PBCO thin films have been fabricated on various substrate materials such as SrTiO₃ (STO), LaAlO₃ (LAO), NdGaO₃ (NGO), and MgO. For instance, Figure 1 is an X-ray θ -2 θ diffraction contour plot of an as-grown PBCO thin film showing that the as-grown films are predominantly *a*-oriented. The rocking curve measurement of the (200) reflection has a full width at half maximum of 0.1 deg, compared to a resolution-limited width of the STO (200) of 0.007 deg, indicating that the film on STO substrate has excellent single crystallinity and epitaxial behavior. More precise radial scan synchrotron studies performed along the STO [200] in plane direction showed that the interface relationship to be (100)_{PBCO}//(001)_{STO} and [001]_{PBCO}//[100]_{STO}. Both PBCO (200) and (004) peaks were observed, indicating that the as-grown PBCO films are *a*-axis oriented with two different domain structures in the directions parallel to the substrate surface.

The crystallinity and epitaxial quality of the as-grown films were further investigated by transmission electron microscopy. A dark field cross sectional TEM image (Figure 2 top) shows that two types of domain structures exist on the interface, which agrees with the synchrotron studies. The selected area electron diffraction (SAED) pattern taken in the area only covering the film is shown in Figure 2 (top inset). The sharp electron diffraction spots with no satellites indicate that the films have good single crystallinity. The electron diffraction pattern also confirms that the film is *a*-axis oriented with *c*-axis along the interface. High resolution cross sectional TEM studies have demonstrated that as-grown films have excellent epitaxial behavior and a sharp atomic interface, as seen in Figure 2 (bottom).

The impedance measurements on the as-grown PBCO thin films suggest that the electrical conductivities of the PBCO thin films are highly dependent upon the measuring temperature and the interface strain which induce from the lattice mismatch of the films and

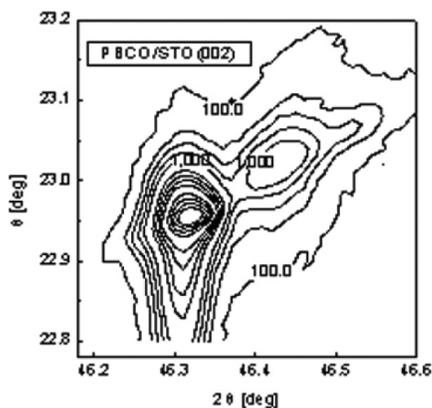


FIGURE 1. The X-ray Diffraction θ -2 θ Scans of As-Grown PBCO/STO Thin Film

substrates. The lattice mismatches between the PBCO films and substrates can be simply estimated by the standard crystal lattice parameters. It is easy to find that the PBCO films are tensile on both NGO and LAO but become strain on both MGO and STO. As seen from the Figure 3, the electrical conductivities of PBCO films on these substrates in air have been measured to determine the high temperature transport properties. With the increase of the temperature, the conductivity exponentially increases due to thermal activation and

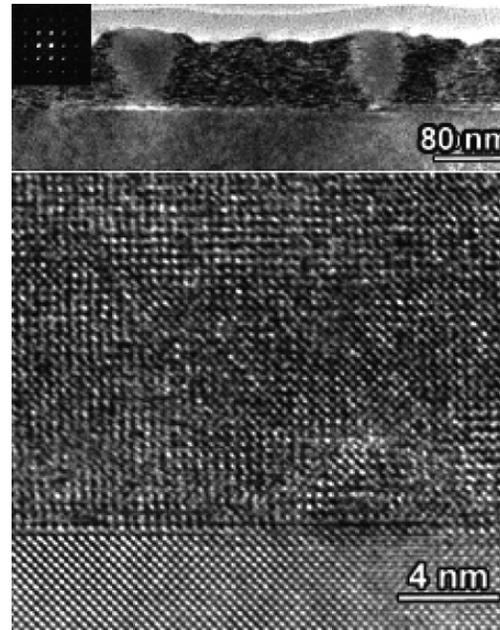


FIGURE 2. Cross Sectional TEM Studies Show the Crystallinity and Pitaxial Behavior of the As-Grown PBCO Thin Film on STO (top) and the Interface Structures of PBCO/STO

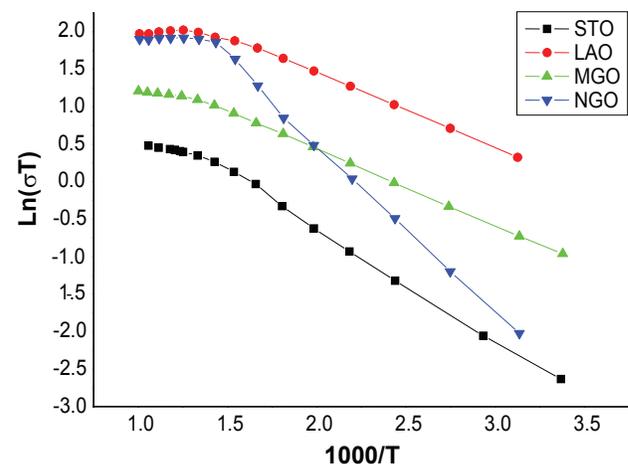
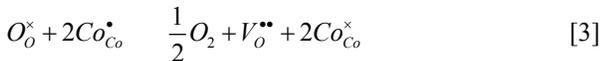
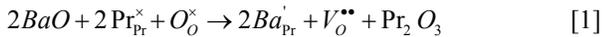


FIGURE 3. The Impedance Measurement for the PBCO Films on Various Substrates

becomes steady around 400°C (or 670 K) probably owing to the lost of oxygen. It is interesting to note that the PBCO films tensile strain on LAO and NGO substrates have excellent electrical conductivity, $\sim 10^2$ S/cm², over a very broad temperature region of 300 to 1,000 K. In contrast, the films with relaxed strain on STO and Mg, have relative lower electrical conductivity. In the high temperature range (higher than 400°C), tensile strained films show much better conductivity. Also, compared with the traditional electrode materials such as (La,Sr)MnO₃ or (La,Sr)(Co,Fe)O₃, PBCO thin films have much better electrical conductivity especially in the low temperature region.

To understand the mechanisms of the electrical conductivity and the strain effect on the physical properties, the co-PI (Professor P. Nash) has formulated a point defect model in which mobile electrons and electron holes are assumed to be localized on specific Co-site ions. Electrons localize on $\text{Co}^{2+} = \text{Co}' = \text{Co}'_{\text{Co}}$ sites and holes (small polarons) on $\text{Co}^{4+} = \text{Co}^\bullet = \text{Co}^\bullet_{\text{Co}}$. The substitution of $\text{Ba}^{2+} = \text{Ba}' = \text{Ba}'_{\text{Pr}}$ for $\text{Pr}^{3+} = \text{Pr}^\times = \text{Pr}^\times_{\text{Pr}}$ in the PrCoO₃ perovskite lattice requires charge compensation. Electroneutrality can be maintained in two ways: either by a valence change of the Co-site cation = $\text{Co}^{3+} = \text{Co}^\times = \text{Co}^\times_{\text{Co}}$ (creation of holes, electronic compensation) or by the formation of oxygen vacancies V^\bullet_{O} (ionic compensation). In general, both processes occur and compete with each other, depending on composition, oxygen partial pressure and temperature. It is assumed that the defect chemistry of PrBaCo₂O_{6-2δ} can be described by the following three reactions:



Here the oxide lattice site anion is denoted $\text{O}^{2-} = \text{O}^\times_{\text{O}}$. This system of equations provides a partial mathematical expression that substitution of Ba²⁺ for Pr³⁺ in the PrCoO₃ lattice is electronically compensated by the oxidation of $\text{Co}^\times = \text{Co}^{3+}$ cations to Co^{4+} and the formation of oxygen vacancies V^\bullet_{O} . This system of equations is completed by overall electroneutrality conditions, which can be represented by

$$[\text{Ba}'_{\text{Pr}}] + [\text{Co}'_{\text{Co}}] = [\text{Co}^\bullet_{\text{Co}}] + 2[V^\bullet_{\text{O}}] \quad [4]$$

$$[\text{Co}^\times_{\text{Co}}] + [\text{Co}'_{\text{Co}}] + [\text{Co}^\bullet_{\text{Co}}] = 1 \quad [5]$$

$$[\text{O}^\times_{\text{O}}] + \delta = 3 \quad [6]$$

It is expected that when the temperature increases or the pO₂ (O₂ pressure) decreases, the equilibrium of Equation [3] shifts to the right. As a result, oxygen vacancies V^\bullet_{O} are formed, at the expense of two holes for each V^\bullet_{O} . Therefore, a loss of lattice oxygen takes occurs when the temperature increases. This can be experimentally measured using thermogravimetry (TGA).

Conclusions and Future Directions

The focus of this study continues to be on the investigation of the physical property of PBCO on various substrate materials. The understanding of the interface behavior and ionic transport dynamics of oxygen in this new material is extremely important for the development of the fuel cell devices. Another part of the on-going research includes that the multilayered Gd:CeO₂ (GCO) and yttria stabilized zirconia (YSZ) will be fabricated (once the ordered targets arrival). The various thickness combinations of GCO and YSZ will be synthesized, and the ionic transport properties of these multilayered structures and the interface effect on the physical properties will be systematically investigated. The purpose of the YSZ layer in the multilayered structures is to block the electronic conduction to enhance the quality of the electrolyte materials and lower down the operation temperature from 800°C to 600°C. On the other hand, the fabrication and characterizations of half-cell structure from PBCO/YSZ and PBCO/GCO will be the next focusing topic to determine the best interface structures for the cathode/electrolyte interface. The fabrication and characterization of the advanced proton conductive Y_xBaCe_{1-x}O₃ (YBCO) for the anode is also planned. The physical properties and ionic transport behavior of each material (YBCO, PBCO, and multilayered GCO/YSZ structures) will be systematically studied. Various crystal structures and different crystal grain sizes will be fabricated, and the physical properties and interface phenomena of each material and the effects from interface, size, and strain will be comprehensively analyzed. The model will be used to calculate the concentrations of holes and mobile electrons, $[\text{Co}'_{\text{Co}}]$ and $[\text{Co}^\bullet_{\text{Co}}]$, respectively, from TGA data from Frontera, et al. Then, the interface phenomena in each half-cell combination can be experimentally studied and simulated by computer. The ultimate goal is to build the foundation for development of intermediate temperature SSFCs devices based on these new materials.

Acknowledgements

The authors thank Prof. Alan Jacobson at University of Houston for his support, suggestions, and helpful discussion and Prof. W. Donner and Dr. D. X. Huang for the microstructural characterizations.