Development of High Temperature/High Sensitivity Novel Chemical Resistive Sensor

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• Introduction
• Mixed Ionic/Electronic Conductive LnBaCo$_2$O$_{5.5}$ Oxides
• Full Scale Chemical Sensor Development
• Summary
OBJECTIVES & GOALS

• The objective of this research is:
  – investigate and understand the mechanisms of mixed ionic electronic conductive LaBaCo$_2$O$_{5+\delta}$ highly epitaxial thin-films
  – establish the relationship between electrochemical properties and surface/interface microstructure of the mixed conductive thin films
  – determine the overall feasibility of the LaBaCo$_2$O$_{5.5+\delta}$ based novel electrochemical devices for sensing gases in high temperature applications.

• The goals of this research are:
  – resolving and optimizing fabrication issues of highly epitaxial LaBaCo$_2$O$_{5+\delta}$ single crystalline thin films
  – establishing relationship of processing—microstructure—sensing properties—stability of the LaBaCo$_2$O$_{5+\delta}$ thin film
  – understanding the kinetics and mechanisms of redox processes on the LaBaCo$_2$O$_{5.5+\delta}$ thin films
  – demonstrating the new concept high temperature, high sensitivity, and chemically stable devices for high temperature applications.
Why LBCO?
Nanoscale ordered cobaltite LaBaCo$_2$O$_6$ thin films
Sensor Structures
Oxygen Deficient Double Perovskite (LnBa)Co$_2$O$_{5+\delta}$ (Ln=Lanthanide)

Structure of LnBaCo$_2$O$_{5+\delta}$

- Green: Ba
- Yellow: Ln
- Blue: Co
- Red: O (occupied)
- Orange: O (partial occupied)
(La, Ba)Co$_2$O$_{5+\delta}$

$Co^{2+} : Co^{3+} = \left( \frac{1}{2} - \delta \right) : \left( \frac{1}{2} + \delta \right) - - - 0 \leq \delta \leq 0.5$

$Co^{4+} : Co^{3+} = \left( \delta - \frac{1}{2} \right) : \left( \frac{3}{2} - \delta \right) - - - 1 \geq \delta \geq 0.5$

LaBaCo$_2$O$_{5+\delta}$ Thin Film on (001)LaAlO$_3$
Transport Properties in 4%H₂ / N₂

\[ 2O^{2-} + 2Co^{3+} + Co^{4+} \leftrightarrow 2V_0^{\bullet\bullet} + 3Co^{2+} + O_2(g) \]
Transport Properties in O₂

\[ \text{LaCoO}_3 \]
\[ 2\text{Co}^{3+} \leftrightarrow \text{Co}^{2+} + \text{Co}^{4+} \]
\[ \text{Ba}^{2+} \leftrightarrow (\text{La}^{3+}\text{Ba}^{2+})(\text{Co}^{3+}\text{Co}^{4+})\text{O}_{5+\delta} \leftrightarrow [\text{Co}^{4+}] + [\text{V}_O] \]
\[ \text{O}^{2-} + 2\text{Co}^{4+} \leftrightarrow \text{V}_O + 2\text{Co}^{3+} + \frac{1}{2}\text{O}_2 \]
\[ \text{O}_{ad}^{2-} \leftrightarrow 2e^- + \frac{1}{2}\text{O}_2 \]
\[ \uparrow T \quad \Rightarrow [e^-] \uparrow \& [h] \downarrow \]
Transport Properties in $4\% \text{H}_2 / \text{N}_2$
Nanoscale ordered cobaltite
LaBaCo$_2$O$_6$
Nanoscale ordered cobaltite LaBaCo$_2$O$_6$
Nanoscale ordered cobaltite LaBaCo$_2$O$_6$
Physical Properties of cobaltite LaBaCo$_2$O$_6$
Nanoscale ordered cobaltite LaBaCo2O6
Highly epitaxial nanoscale ordered cobaltite LaBaCo$_2$O$_6$ thin films
Nanoscale ordered LaBaCo$_2$O$_6$ thin films

As-grown; Post annealed

(a) 2\theta (Degree)

(b) LBCO (100) intensity
LBCO (101) intensity
MgO (002) intensity

Intensity (a.u.)

20 25 30 35 40 45 50

2 \theta (Degree)

LBCO (100)

MgO (002)

LBCO (200)

LBCO (100) intensity
LBCO (101) intensity
MgO (002) intensity

(b) 2\theta (Degree)

(b) LBCO (100) intensity
LBCO (101) intensity
MgO (002) intensity

Intensity (a.u.)

20 25 30 35 40 45 50

2 \theta (Degree)
Substrate-induced Strain on Transport Behavior and Magnetic Properties of Highly Epitaxial (LaBa)Co$_2$O$_{5.5+\delta}$ Thin Films
MR (%) = \{ \frac{R(7T) - R(0T)}{R(0T)} \} \times 100\%
Strain from Various Film Thickness
Interface Strain From Vicinal substrate

Residual Mismatching Gap

Terrace

Step

$\delta_\alpha$

$\delta_\beta$
X-ray Characterization of LBCO on Vicinal Substrate

Substrate FWHM: 0.04°
Film FWHM: 0.05°

Good Epitaxial Quality
The average width of the substrate terrace in the epitaxial LBCO thin films grown on the vicinal (001) SrTiO$_3$, and how many unit cells of the substrate SrTiO$_3$ and LaBCO ($n_s$ and $n_f$, respectively) that the average terrace can accommodate.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Terrace width (nm)</th>
<th>$N_s$</th>
<th>$N_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5$^0$</td>
<td>44.748</td>
<td>114.6</td>
<td>115.16</td>
</tr>
<tr>
<td>3$^0$</td>
<td>7.458</td>
<td>19.1</td>
<td>19.2</td>
</tr>
<tr>
<td>5$^0$</td>
<td>4.474</td>
<td>11.46</td>
<td>11.52</td>
</tr>
</tbody>
</table>

0.5 unit cell

0.1 unit cell

0.06 unit cell
The terrace width is narrower and smaller than the mean surface atom diffusion length at the growth temperature. With increasing the miscut angle, the film growth will follow the step-flow mechanism resulting in the single domain formation. The single-domain growth and small lattice-misfit strain will reduce the scattering rate of the carriers with strain lattice and domain boundaries.

Local strain from terrace is very small
Residual Mismatching Gap

The last atomic plane of the film will always occupy the terrace end by rearranging the local atomic structure.

A huge amount of interface strain energy will be generated due to the same charge repulsion at the domain boundary and interface.

Locally-strained domain will enhance strong transport electron scattering behavior, inducing the higher resistance.
Interface Strain from Different Direction of the Same Substrate

[001] 1.09% “1”  
[110] 0.6% “2”  
Compressive Strain
fig 1

![Diagram](image)

GDC/YSZ  LBCO

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![Graph](image)

$log_{10}$ 10^5 10^4 10^3 10^2 10^1 10^0

$2\theta$[deg]

LBCO(001)  LAO(001)  GDC(002)  LBCO(002)  LAO(002)  GDC(004)  LBCO(004)  LAO(004)
Figure 3

Temperature ($^\circ$C)

$E_{a}^{\text{LBCO}} = 0.49\text{eV}$

$E_{a}^{\text{PBCO}} = 0.77\text{eV}$

$K_{\text{chem}}$

$1000/T(K^{-1})$

PBCO

LBCO
LBCO Films in Other O₂/Fuel Systems

350°C
0-5mins O₂
5-65mins C₃H₈
65-80mins O₂
80-140mins C₃H₈
140-163mins O₂

550°C
0-20mins O₂
20-170mins N₂
170-210mins O₂
210-370mins N₂
370-420mins O₂
LBCO Film Reduction Property:

![Graph showing resistance over time at different temperatures](image)

- **Resistance (Ω)**
- **dR/dt (Ω·s⁻¹)**
- **Time (min)**
EBCO Film Reduction Property:

![Graph showing resistance and derivative over time](image_url)
EBCO Film Oxidation Property:

![Graph showing resistance and dR/dt over time for different temperatures.](image-url)
EBCO Film Oxidation Property:

(a) Graph showing resistance (Ω) over time (×1000 s) at different temperatures: 600 °C, 500 °C, 400 °C, 300 °C, 260 °C.

(b) Graph showing resistance (Ω) over time (×1000 s) at different temperatures: 600 °C, 500 °C, 400 °C, 300 °C, 260 °C.

(c) Graph showing resistance (Ω) over time (×1000 s) with two different reactions: H₂ and O₂.

(d) Graph showing resistance (Ω) over time (×1000 s) with different cobalt ions: Co³⁺, Co²⁺, Co³⁺.
PBCO Film Reduction Property:

![Graph showing Resistance (Ω) and dR/dt (Ω s⁻¹) vs. Time (s) at different temperatures]

- Resistance (Ω) values range from 10⁶ to 10⁹ Ω.
- dR/dt (Ω s⁻¹) values range from 10⁵ to 10⁷ Ω s⁻¹.
- Temperatures considered: 800 °C, 600 °C, 500 °C, 470 °C, 400 °C, 350 °C, 300 °C.
- Time (s) ranges from 0 to 4,000 s.
Comparison of the diffusion rates: $D(H) > D(a$-Ag$_{2+d}$S) or $D(a$-Ag$_2$Te)!
Model for diffusion of carriers

\[
\frac{c(x, t) - c_1}{c_2 - c_1} = 1 - \sum_{i=0}^{\infty} \frac{4(-1)^i}{\pi(2i+1)} \cos[\pi(2i+1) \frac{x}{L}] \exp[-\pi^2 (2i+1)^2 \frac{Dt}{L^2}]
\]

\[
\frac{\sigma_m - \sigma_1}{\sigma_2 - \sigma_1} = 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp[-(2i+1)^2 \frac{t}{\tau}]
\]

\[
\tau = \frac{L^2}{\pi^2 D}
\]

\[
\frac{\sigma_m - \sigma_1}{\sigma_2 - \sigma_1} \approx 4\pi^{-3/2} \sqrt{\frac{t}{\tau}}
\]
$d$-spacings 0.39 nm

**Planar view**

**Cross section**

**Single domain**

**Multi domains**
Future Research

• Continually study physical properties of LnBCO thin films and related materials at various chemical environments (gases, pressures, temperatures, etc.)

• Design and characterize the full scale (low & high temperature) chemical sensors, not only qualitatively but also quantitatively

• Explore novel materials for the development of new sensors and transducers (temperature, pressure, infra, etc.)

• Fundamentally understand the sensing mechanisms
Tunable interconnectivity of mesostructured cobalt oxide materials for sensing applications

- The sensor resistance change of the mesostructured cobalt oxide at different template temperatures.
Publications – published/revised


1. W. Donner, C. L. Chen, M. Liu, A. J. Jacobson, Y.-L. Lee, M. Gadre, and D. Morgan, “Epitaxial Strain-Induced Chemical Ordering in La_{0.5}Sr_{0.5}CoO_{3-d} Films on SrTiO_{3}”, *Chem. Mat.*, **23** (2011) 984


Publications – papers submitted


7. Chunrui Ma, Ming Liu, Gregory Collins, Haibin Wang, Shanyong Bao, Xing Xu, Erik Enriquez, Chonglin Chen*, and Y. Lin, “Anisotropic Strain Induced Anomalous Metal-Insulation Transition in on Highly Epitaxial LaBaCo$_2$O$_{5.5+\delta}$ Thin Films on (110) NdGaO$_3$”, *Nature Physics* (to be submitted)

8. Fransisco Ruiz-Zepeda, Chunrui Ma, Daniel B. Uribe, J. Cantu-Valle, Haibing Wang, Xing Xu, Arturo Ponce, Miguel Yacaman* and C. L. Chen*, “Nanodomain Induced Anomalous Magnetic Electronic Transport Properties of LaBaCo$_2$O$_{5.5+\delta}$ Epitxial Films”, *Chem Mat* (to be submitted)

Several other manuscripts are preparing for publication
Summary

• Mixed ionic/electronic conductive double perovskite LaBaCo$_2$O$_{5.5}$ thin films have been successfully grown on various substrates for full scale chemical sensors.

• Superfast chemical dynamic behavior was found from the symmetric cell structures.

• A new oxygen vacancy exchange diffusion mechanism was discovered from the colbaltate systems.

• Various new/interesting physical phenomena have been found and achieved in the LBCO materials.

• More experimental and theoretical works are needed to understand the superfast chemical oxidation/redox dynamics and to explore the interface physics.
Thank you very much for your attention!
Tunable interconnectivity of mesostructured cobalt oxide materials for sensing applications

- The sensor resistance change of the mesostructured cobalt oxide at different template temperatures.
Figure 3. Transmittance change of a cobalt oxide film prepared at 133 Pa of Ar. The transmittance of the film at 625 nm was monitored in dry air and 200 ppm of CO gas at 350 °C. Sensitivity is defined as \((T_{r(CO)} - T_{r(air)}) / T_{r(CO)} \times 100\), where \(T_{r(CO)}\) and \(T_{r(air)}\) are transmittance in CO gas and dry air, respectively, at 350 °C.
Hierarchically Structured Cobalt Oxide (Co$_3$O$_4$): The Morphology Control and Its Potential in Sensors

Figure 10. The alcohol sensing curve in a Co$_3$O$_4$-based sensor at 300 °C. The solid line is the response to 50 ppm alcohol and the dash line is to 1000 ppm CO, showing the selectivity of the sensor. The sensor is exposed to alcohol vapor or CO at A and for 20 s, then it is switched to dry air at B. The gas sensitivity is defined as the resistance ratio of $R_{\text{gas}}$ to $R_0$, where $R_{\text{gas}}$ and $R_0$ are the electrical resistance for the sensor in alcohol or CO and in air, respectively.