Development of High Temperature/High Sensitivity Novel Chemical Resistive Sensor

PhD Students: Erik Enriquez, Chunrui Ma, & Shanyong Bao
PIs: Patrick Nash and Chonglin Chen (PI)
Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX 78249-1644
Phone: 210-458-6427, Email: cl.chen@utsa.edu

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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

Resistance (Ω) vs. Temperature (°C) for 4% H$_2$ and 0.1% O$_2$ with Time (S) shown. 

Sensor Structures

LBCO Thin Film

Sensing electrodes

Insulating oxide substrate

LBCO Thin Film

Sensing electrodes

Gas Sensing Measurement System

Sensor chip

AC Bridge

Computer

Inject Air (2cc/s)

Inject Air (1cc/s)

Inject Air (4cc/s)
Oxygen Deficient Double Perovskite
(LnBa)Co$_2$O$_{5+\delta}$ (Ln=Lanthanide)

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

- Ba
- Ln
- Co
- O (occupied)
- O (partial occupied)
\[(\text{La, Ba})\text{Co}_2\text{O}_{5+\delta}\]

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

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

\[\text{Rautama et al., Chem. Mater., Vol. 21, No. 1, 2009.}\]
LaBaCo$_2$O$_{5+\delta}$ Thin Film on (001)LaAlO$_3$
Transport Properties in 4%H₂ / N₂

\[ 2O^{2-} + 2Co^{3+} + Co^{4+} \leftrightarrow 2V^{\bullet \bullet}_O + 3Co^{2+} + O_2(g) \]
Transport Properties in O$_2$

$LaCoO_3$

$2Co^{3+} \leftrightarrow Co^{2+} + Co^{4+}$

$Ba^{2+} \leftrightarrow (La^{3+} Ba^{2+})(Co^{3+} Co^{4+})O_{5+\delta} \rightarrow [Co^{4+}] + [V_{o}]$

$O^{2-} + 2Co^{4+} \leftrightarrow V_{o} + 2Co^{3+} + \frac{1}{2}O_2$

$O_{ad}^{2-} \leftrightarrow 2e^{-} + \frac{1}{2}O_2$

$T \uparrow \Rightarrow [e^{-}] \uparrow \& [h] \downarrow$

Transport Properties in 4\%H_2 / N_2

(b)

4\%H_2/3\% H_2O/ N_2

Resistance(Ω)

4\times10^4

3\times10^4

2\times10^4

1\times10^4

0

ΔR(Ω/°C)

0 100 200 300 400 500 600 700

Temperature(°C)

Resistance

PF smooth of Derivative
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
Intensity (a.u.)

LBCO (100)

LBCO (200)

MgO (002)

2 Theata (Degree)

As-grown; Post annealed

(b)

Intensity

LBCO \{101\}

(b)

MgO \{101\}

Phi (degree)

2 Theata (Degree)
Substrate-induced Strain on Transport Behavior and Magnetic Properties of Highly Epitaxial \((\text{LaBa})\text{Co}_2\text{O}_{5.5+\delta}\) Thin Films
MR (%) = \left\{ \frac{[R(7T) - R(0T)]}{R(0T)} \right\} \times 100\%
Characterization of LBCO Films in O$_2$/4$\%$H$_2$+N$_2$

- 300$^\circ$C
  - 1-10mins O$_2$
  - 10-370mins H$_2$
  - more H$_2$ from 172
  - 370-410mins O$_2$
  - 410-715mins H$_2$
  - 715-720mins O$_2$

- 350$^\circ$C
  - 0-10mins O$_2$
  - 10-120mins H$_2$
  - 120-130mins O$_2$
  - 130-200mins H$_2$
  - 200-210mins O$_2$
  - 210-300mins H$_2$
  - 300-330mins O$_2$

- 400$^\circ$C
  - 0-10mins O$_2$
  - 10-140mins H$_2$
  - 140-150mins O$_2$
  - 150-252mins H$_2$
  - 252-260mins O$_2$
  - 260-318mins H$_2$
  - 318-323mins O$_2$

- 450$^\circ$C
  - 0-10mins O$_2$
  - 10-140mins H$_2$
  - 140-150mins O$_2$
  - 150-230mins H$_2$
  - 230-240mins O$_2$
  - 240-340mins H$_2$
  - 340-355mins O$_2$
LBCO Films in Other O₂/Fuel Systems

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

550°C
- 0-20 mins O₂
- 20-170 mins N₂
- 170-210 mins O₂
- 210-370 mins N₂
- 370-420 mins O₂
Future Research

• Continually study physical properties of LBCO thin films at various chemical environments (gases, pressures,

• Design and characterize the full scale (low & high temperature) chemical sensors

• Explore novel materials for the development of new sensors and transducers

• Fundamentally understand the sensing mechanisms
Publications – published/revised


• Chunrui Ma, Ming Liu, Gregory Collins, Jian Liu, Chonglin Chen,* Jie He, Jiechao Jiang, E. I. Meletis : “Thickness Effects on Magnetic and Electrical Transport Properties of Highly Epitaxial LaBaCo$_2$O$_{5.5+\delta}$ Thin Films on MgO Substrates”, *Appl. Phys. Lett.* (Suggested Minor Revision)

Publications – papers submitted


- M. Liu, C. R. Ma, E. Enriquez, H. B. Wang, C. L. Chen, Y. Lin, “Physical Properties of Highly Mixed Conductive LaBaCo$_2$O$_{5.5+d}$ Thin Films directly Integrated on Si (100)”, *Appl. Mat & Interfaces* (submitted)

- Chunrui Ma, Ming Liu, Gregory Collins, Jian Liu, Y. M. Zhang, Chonglin Chen, Jie He, Jiechao Jiang, E. I. Meletis, “Magnetic and Electrical Transport Properties of Highly Epitaxial LaBaCo$_2$O$_{5.5+\delta}$ Thin Films on Vicinal (001) SrTiO$_3$ Surfaces”, *Appl. Phys. Lett.*, (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.

• Transport property studies indicate that the physical properties of the highly epitaxial LBCO are highly dependent upon the interface strain.

• 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!