Gallium Oxide Nano-structures for High Temperature Sensors

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OUTLINE:

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- Experiments:
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  - Characterization
  - Sensor Testing
- Results and Discussion:
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  - Tungsten (W)-doped Ga$_2$O$_3$ Films (PVD)
  - Sensor Performance
- Summary & Future Work
INTRODUCTION
Introduction

3 main combustion products:

- CO
- O₂

These two gases provide a measure of the completeness of combustion

- NOₓ

This gas measures the main controllable pollutant from the combustion

- Types of Oxygen Sensors
  1. Potentiometric:
     - YSZ sensor based on Nernst Principle
  2. Amperometric:
     - YSZ sensor based on Polarographic Oxygen Pumping
  3. Semiconducting Metal Oxides
     - TiO₂, Ga₂O₃, SnO₂, based on Defect Induced Conductance Variation
Gallium Oxide

- 5 Polymorphs: α, β, γ, ε, and σ
- Wide band gap (>5 eV) semiconductor
- High thermal and chemical stability (T_m: 1725 °C)
- Due to a high melting point and stable structure, it is one of the most suitable materials for high temperature gas sensing.
- Doping with appropriate metallic ions can improve semiconducting properties for gas sensing.
- Gallium Oxide has demonstrated oxygen sensing properties at high temperatures >700 °C
- < 700 °C Ga-oxide exhibits sensitivity to reducing gases (CO, H₂)

Sensing Mechanism is governed by the following equation:

\[ \sigma = \exp\left(-\frac{E_A}{kT}\right)P_{O₂}^m \]

Where:
- \( E_A \): Activation Energy
- \( T \): Temperature
- \( \sigma \): Electric Conductivity
- \( P_{O₂} \): Partial Pressure of Oxygen
- \( k \): Boltzmann Constant
- \( m \): Parameter determined by the defects and the type of carrier
Goals & Objectives

• Objective 1: To fabricate high-quality pure and doped Ga$_2$O$_3$ based materials and optimize conditions to produce unique architectures and morphology at the nano scale

• Objective 2: Derive the structure property relationships at the nanoscale dimensions and demonstrate enhanced high temperature oxygen sensing and stability

• Objective 3: To promote research and education in the area of sensors and controls

• Goal: Design the high temperature oxygen sensors (employing Ga$_2$O$_3$ nanostructures)
EXPERIMENTS
Materials

Gallium Oxide (Ga$_2$O$_3$) Target: 99.99% Pure
Tungsten (W) Target: 99.99% Pure

Substrates:
Sapphire (Al$_2$O$_3$): (0001)
Silicon (Si): (001)
Fabrication – Thin Films

RF magnetron sputtering

Deposition Conditions

**Fixed:**
- Base pressure $\sim 10^{-6}$ Torr
- Powers: $\text{Ga}_2\text{O}_3 \rightarrow 100$ W
- Target-Substrate distance: 7 cm
- Sputtering gas: Argon + $\text{O}_2$

**Variables:**

Sample set 1:
Tungsten Target Power (50 to 100 W)
Substrate Temperature = 500 °C

Sample set 2:
Target Powers = const; Substrate temperature varied from RT to 800 °C
Testing and Experimentation
Results and Discussion
Ga$_2$O$_3$ - Chemical Analysis

Ga$_2$O$_3$ Sputtered Films exhibit deficit in gallium atomic percentage when substrate deposition temperature is lower than 200 °C. Ratio of 2-Ga to 3-O was obtained for the rest of the tested temperatures.
Nanocrystalline Structure was achieved under β-phase structure with the corresponding wide band gap of ~5 eV.

Grain size evolution with increasing deposition temperature, 500 °C ideal temperature for crystallization.

Structural Analysis - Intrinsic Ga₂O₃ Films
W-Doped Ga$_2$O$_3$

- Co-sputtering films (W/ Ga$_2$O$_3$) demonstrated crystallization of β- Ga$_2$O$_3$ structure (monoclinic)
- No WO$_3$ formation
- Increasing sputtering power, is proportional to increasing W-content
W-Doped Ga$_2$O$_3$

- Achieving full surface crystallinity W-doped Ga$_2$O$_3$ film at 800 °C, while only β- Ga$_2$O$_3$ phase is presented for all films. Grain formation is initialized at 600 °C.
Heat Treatment of Ga$_2$O$_3$ Based Films

β-phase is stable for all films after annealing; however, surface morphology suffer porous formation for W-doped films.
Thermal Stability

Pure Ga$_2$O$_3$ As-deposited

W-50W 500 °C As-deposited

W-50W 800 °C As-deposited

1 hr 15 hr

500 nm
H$_2$ Sensitivity by Optical Absorption

Absorbance Spectra (Ar & Ar-H$_2$)

Absorbance Spectra (Ar & Ar-Air)
Hot Gas Exposure

- Ga$_2$O$_3$ Films demonstrated sensing properties to Hydrogen and Oxygen at 600 °C. The higher the H$_2$ content, the higher the optical response.
W-doped films showed being sensible to H₂ and O₂.

O₂ sensitivity increased from 10% to 15% of O₂ into Ar, but decrease again at 20%.

Sensitivity to gases was optimum in Ar environment, but small-to-non response in a mixture of Ar+Air.
Oxygen Sensor Characteristics

- $\beta$-Ga$_2$O$_3$ showed oxygen sensitivity at 700 °C,
- As an n-type semiconductor the resistance of the film increased in the presence of oxygen.
Oxygen Sensor Characteristics

W-doped Ga$_2$O$_3$ films demonstrated improved time response, by reducing sensitivity of the sensor. W-doped films showed p-type semiconductor behavior.
Comparison of W-doped $\text{Ga}_2\text{O}_3$ vs. Pure $\text{Ga}_2\text{O}_3$ Films

<table>
<thead>
<tr>
<th></th>
<th>W-doped $\text{Ga}_2\text{O}_3$</th>
<th>Pure $\text{Ga}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response Time</td>
<td>~25 Seconds</td>
<td>~65 Seconds</td>
</tr>
<tr>
<td>Recovery Time (s)</td>
<td>~130 Seconds</td>
<td>~120 Seconds</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>~3.1</td>
<td>~134</td>
</tr>
<tr>
<td>Base Resistance</td>
<td>4.3E+09 $\Omega$</td>
<td>2.5E+06 $\Omega$</td>
</tr>
<tr>
<td>Max/Min Resistance</td>
<td>1.3E+09 $\Omega$</td>
<td>3.3E+08 $\Omega$</td>
</tr>
</tbody>
</table>

Sensitivity can be expressed as the following equation:

$$S = \frac{R_g}{R_b}$$

Where:

$S$: Sensitivity of the Sensor  
$R_g$: is the electrical resistance at different analyte gas partial pressures  
$R_b$: is the resistance of the baseline when Ar was used
Future Work

- Testing cross-sensitivity behavior of Ga$_2$O$_3$ and W-Ga$_2$O$_3$ films at high temperature
- Test sputtering films inside a combustion chamber to evaluate the actual sensorial characteristics inside energy systems.
Impact

Journal Publications:

Conference Presentations:
1. International Materials Research Congress (IMRC) August 11-August 15, 2014
3. AVS International Symposium, October 28 – November 2, 2012 Tampa, FL
6. AVS International Symposium, October 27 – November 1, 2013 Tampa, FL

Education & Training:
1. Ernesto J. Rubio: PhD (Full)
2. A.K. Narayana Swamy: PhD (part of dissertation)
4. Abhilash Kongu: MS (non-thesis)
Summary and Conclusion

- Pure Ga$_2$O$_3$ and W-doped Ga$_2$O$_3$ films were fabricated and analyzed
- All films demonstrated the stable β-phase (monoclinic) of Ga$_2$O$_3$
- Ga$_2$O$_3$ films demonstrate to have structural and morphological stability, regardless the time of heat/exposure, while W-doped films performed morphological changes after initial thermal exposure with no further change afterwards.
- Pure Ga$_2$O$_3$ and W-doped Ga$_2$O$_3$ films demonstrated to be sensitive to oxygen at high temperatures, with improved time of response with the inclusion of tungsten
- W-doped Ga$_2$O$_3$ films showed optical sensor properties to O$_2$
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