Gallium Oxide Nano-structures for High Temperature Sensors

Ernesto Rubio (Ph.D); S.K. Samala (MS)

C.V. Ramana (PI)

Mechanical Engineering, University of Texas at El Paso

Program Manager:

Richard Dunst, NETL, DOE

Project: DE-FE0007225

Project Period: 10/01/2011 to 09/31/2014

OUTLINE:

- Introduction
- Research Objectives
- Experiments:
  - Fabrication
  - Characterization
  - Sensor Testing
- Results and Discussion:
  - Pure Ga_2O_3 Films (PVD)
  - Tungsten (W)-doped Ga_2O_3 Films (PVD)
  - Sensor Performance
- Summary & Future Work

INTRODUCTION

Introduction

3 main combustion products:

- CO
- O_2

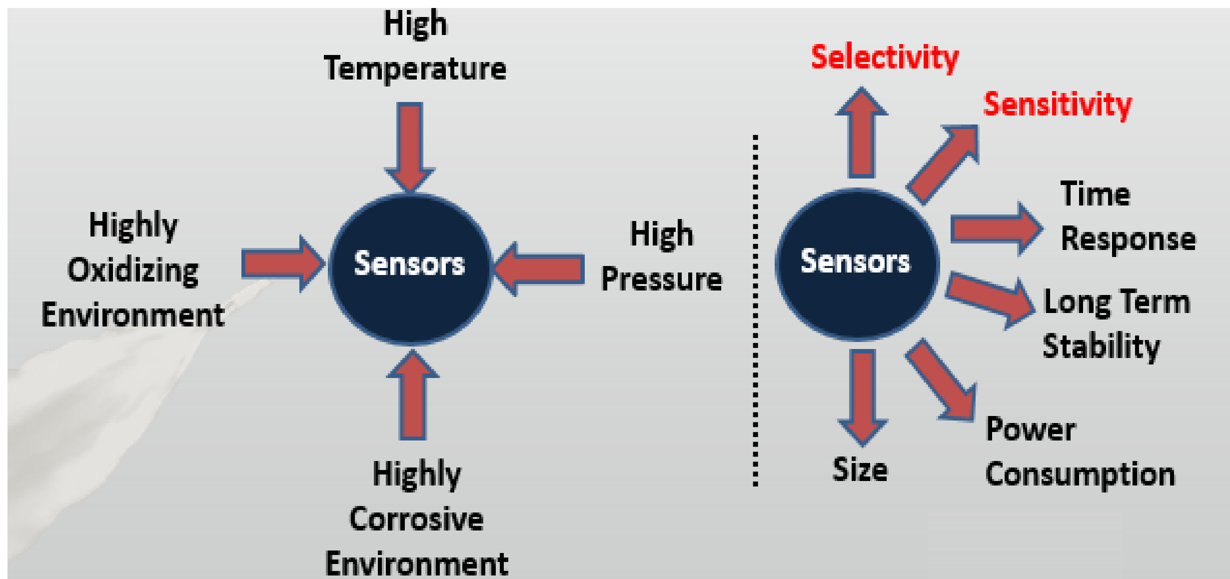
These two gases provide a measure of the completeness of combustion

- NO_x

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
   - TiO_2, Ga_2O_3, SnO_2, 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, H_2)

❖ Sensing Mechanism is governed by the following equation:

$$\sigma = \exp\left(\frac{-E_A}{kT}\right) P_{O_2}^{m}$$

Where:

E_A= Activition Energy
T= Temperature
σ= Electric Conductivity
P_{O2}= Partial Pressure of Oxygen
k= Boltzman Constant
m= Parameter determine by the defects and the type of carrier

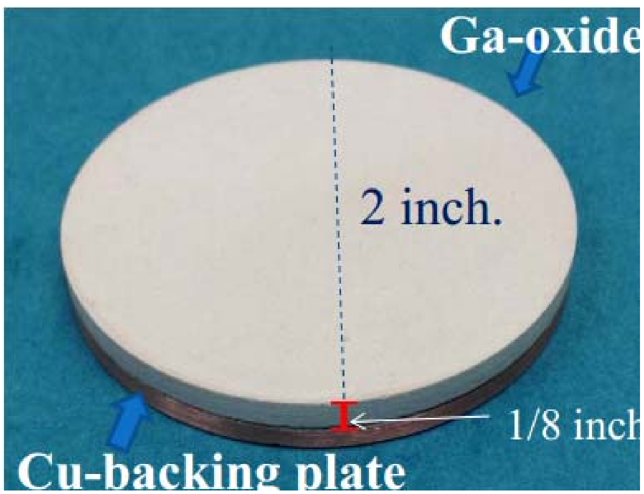
Goals & Objectives

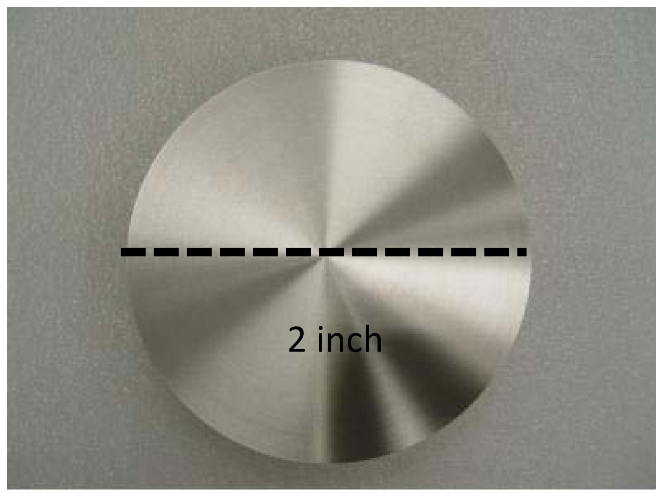
- Objective 1: To fabricate high- quality pure and doped Ga_2O_3 based materials and optimize conditions to produce unique architectures and morphology at the nano scale
- Objective 2: Derive the structure property relationships at the nanoscale dimensions and demonstrate enhanced high temperature oxygen 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_2O_3 nanostructures)

EXPERIMENTS

Materials

Gallium Oxide (Ga_2O_3) Target: 99.99% Pure
Tungsten (W) Target: 99.99% Pure





Substrates:

Sapphire (Al_2O_3): (0001)
Silicon (Si): (001)

Fabrication – Thin Films

RF magnetron sputtering

Deposition Conditions

Fixed:

- Base pressure ~10^{-6} Torr
- Powers: Ga_2O_3 → 100 W
- Target-Substrate distance: 7 cm
- Sputtering gas: Argon + O_2

Variables:

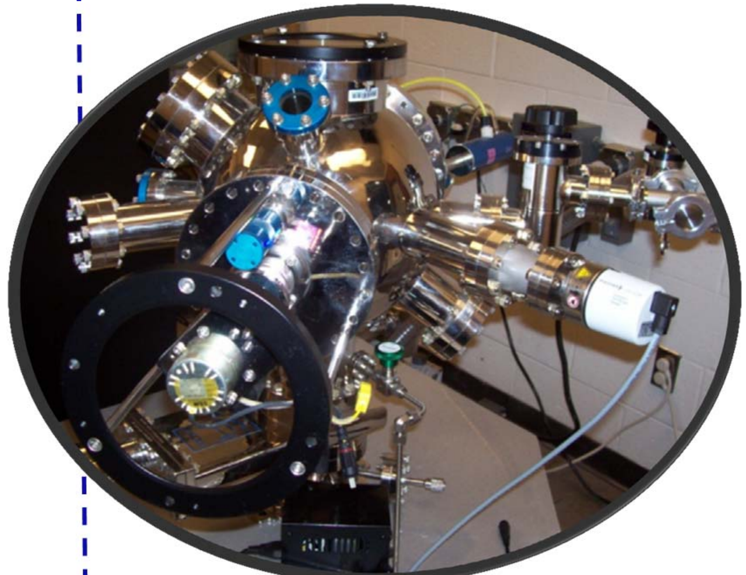
Sample set 1:

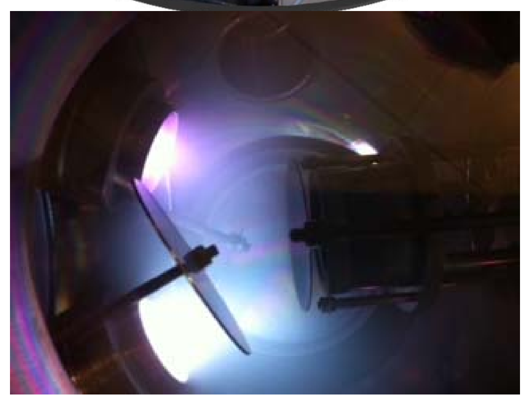
Tungsten Target Power (50 to 100W)

Substrate Temperature = 500 ˚C

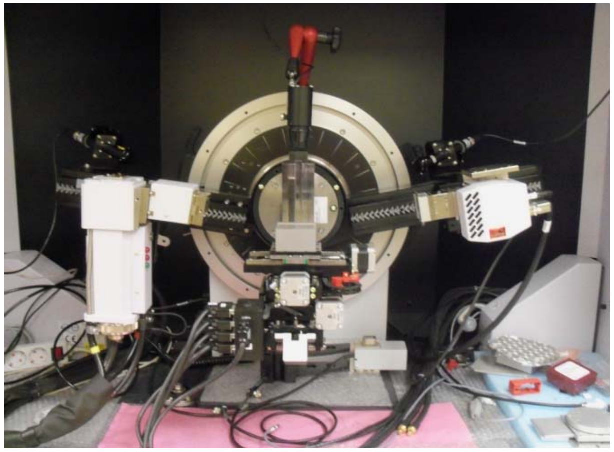
Sample set 2:

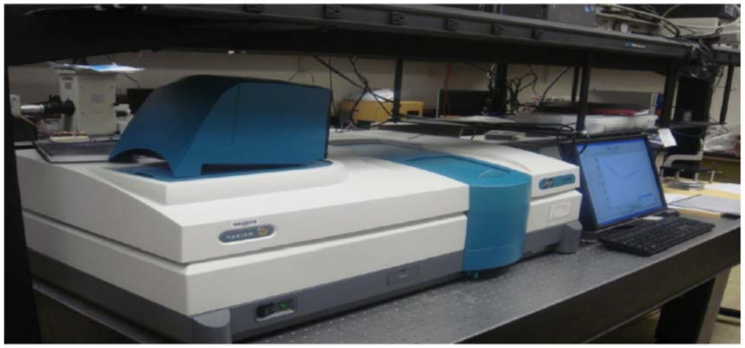
Target Powers = const; Substrate temperature varied from RT to 800 ˚C





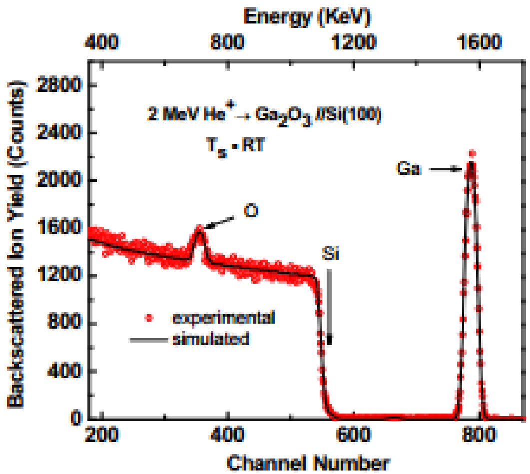
Testing and Experimentation



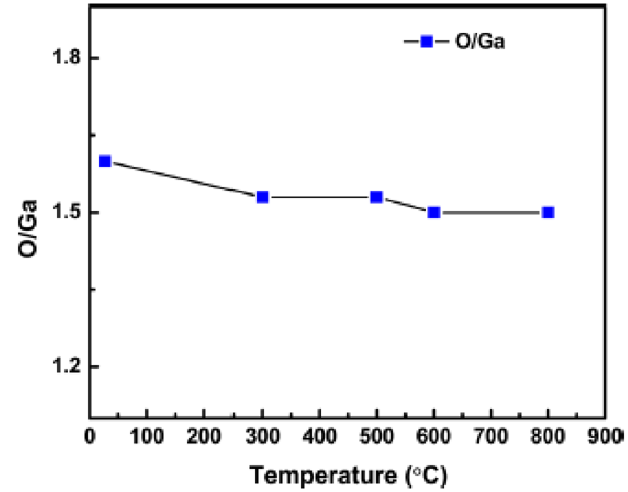


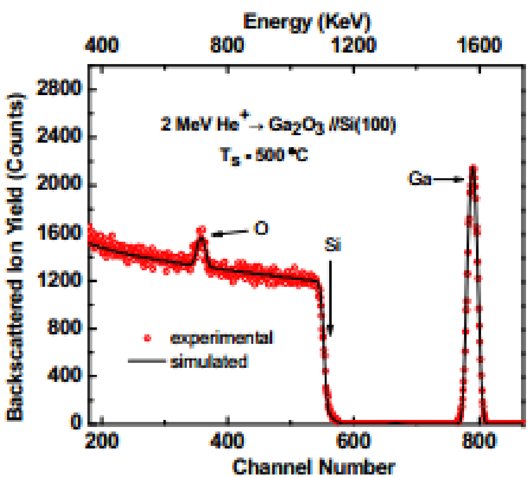
Results and Discussion

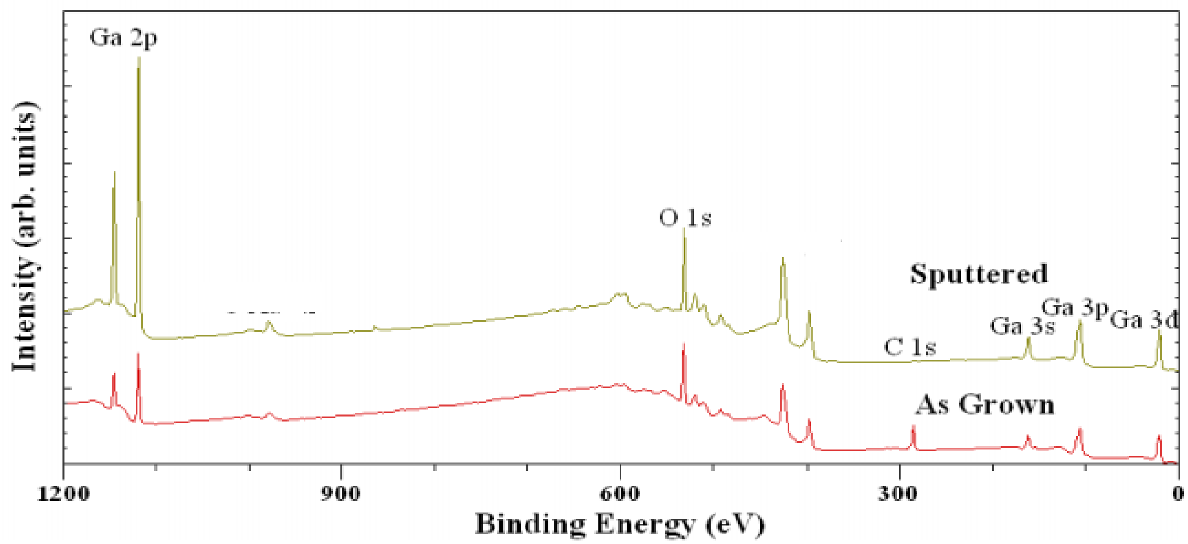
Ga_2O_3 - Chemical Analysis



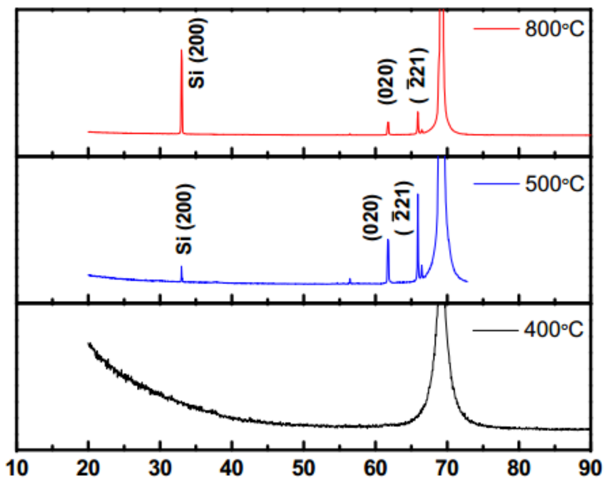
Ga_2O_3 Sputtered Films exhibit deficit in gallium atomic percentage when substrate deposition temperature is lower than 200 °C. Ratio of 2-Ga to 3-O was obtained for the rest of the tested temperatures.



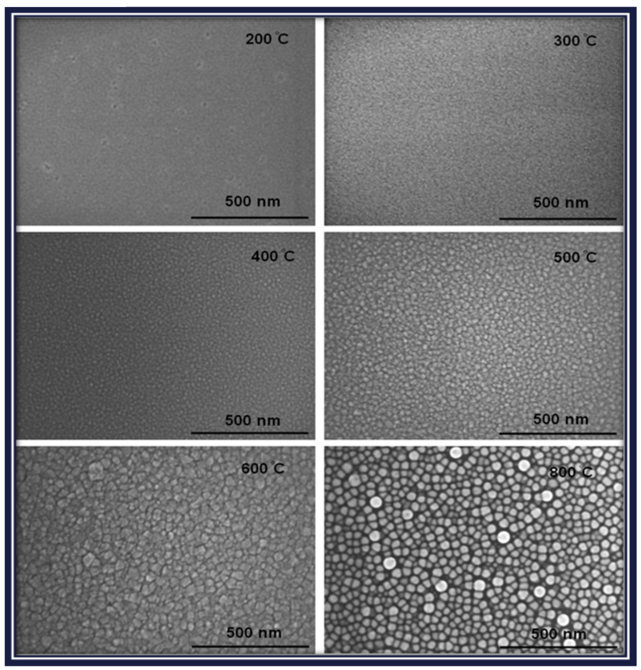




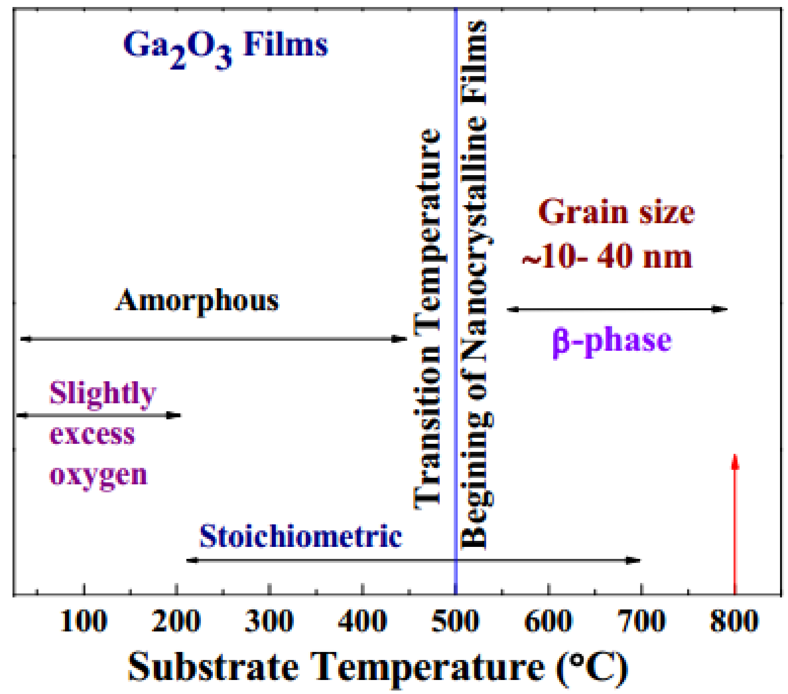
Structural Analysis - Intrinsic Ga_2O_3 Films



Nanocrystalline Structure was achieve under β-phase structure with the corresponding wide band gap of ~5 eV.

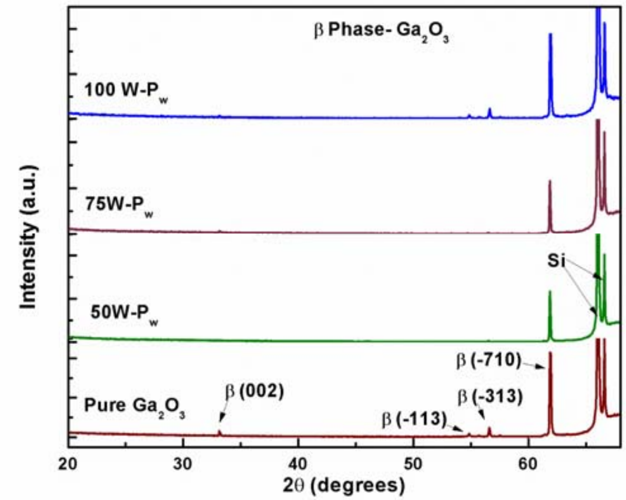


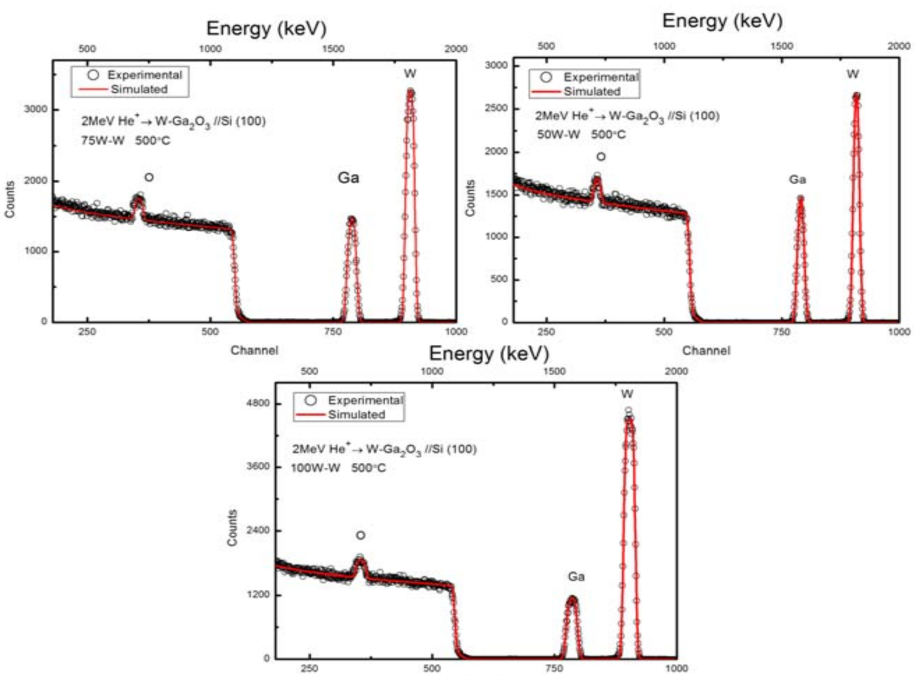
Grain size evolution with increasing deposition temperature, 500 °C ideal temperature for crystallization

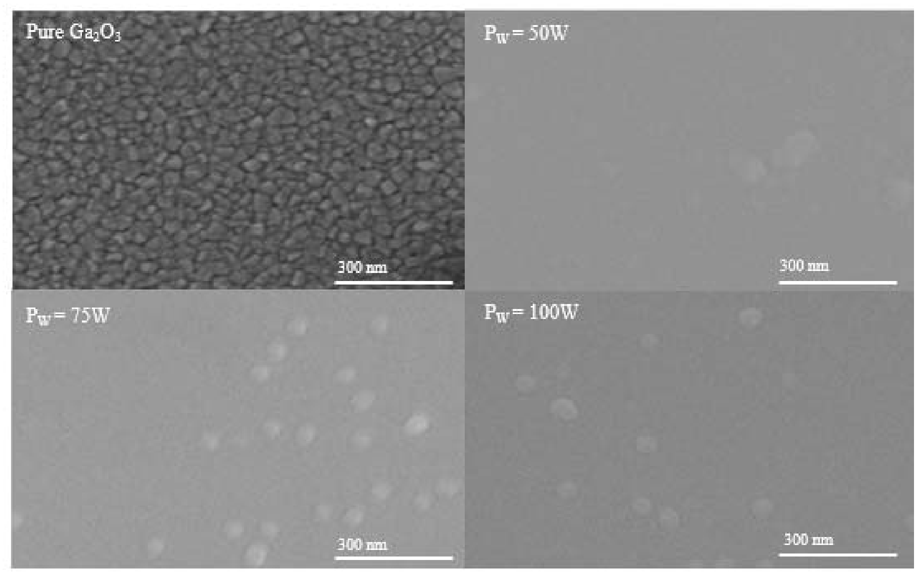


W-Doped Ga_2O_3

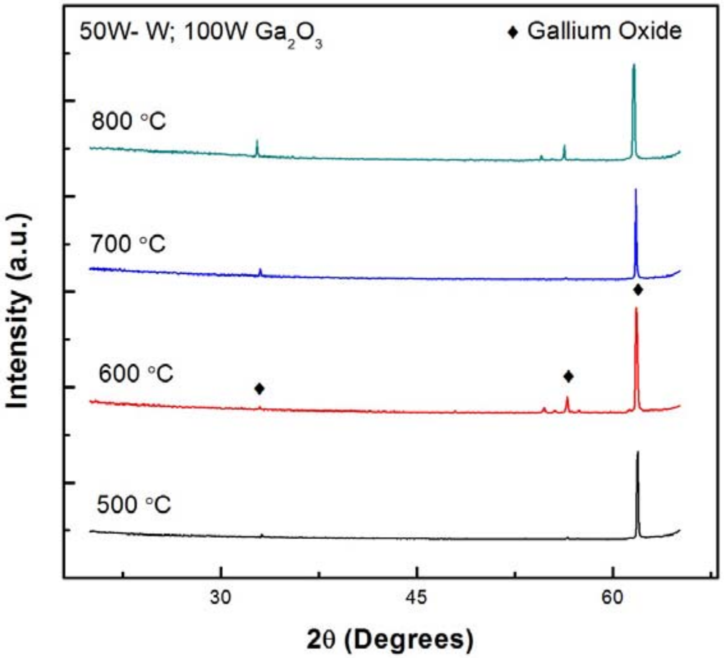
- Co-sputtering films (W/ Ga_2O_3) demonstrated crystallization of β- Ga_2O_3 structure (monoclinic)
- No WO_3 formation
- Increasing sputtering power, is proportional to increasing W-content



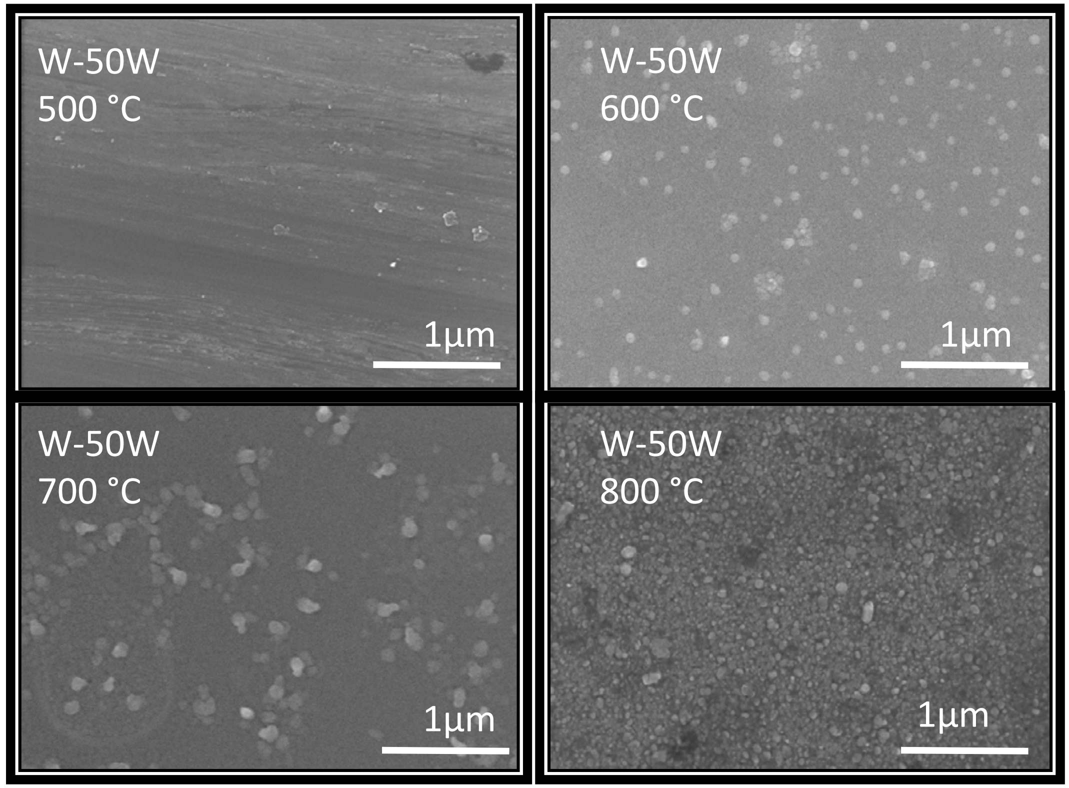




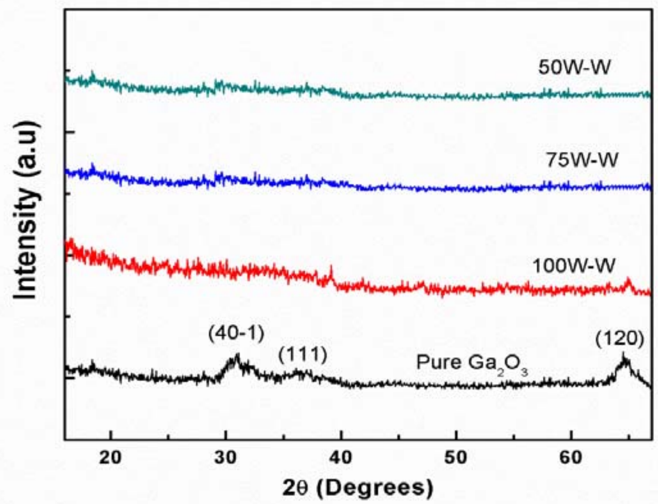
W-Doped Ga_2O_3

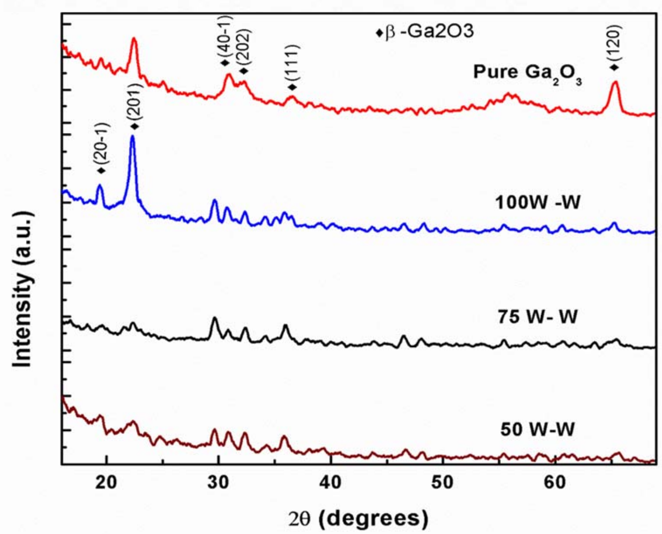


- Achieving full surface crystallinity W-doped Ga_2O_3 film at 800 °C, while only β- Ga_2O_3 phase is presented for all films. Grain formation is initialized at 600 °C.

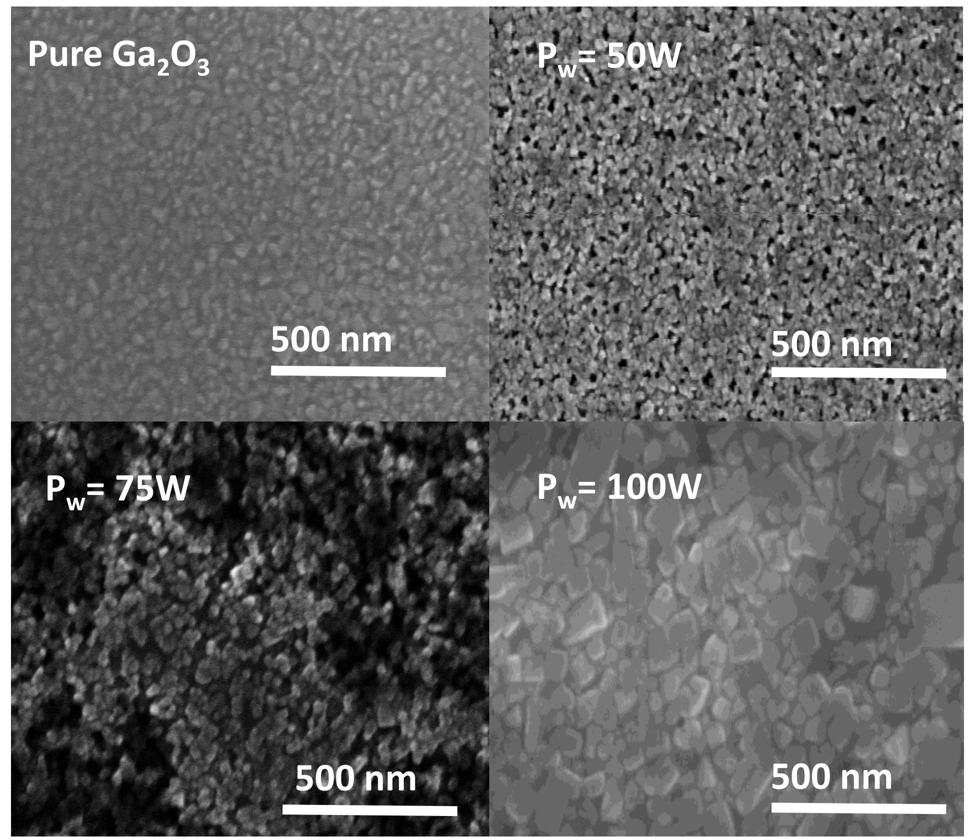


Heat Treatment of Ga_2O_3 Based Films

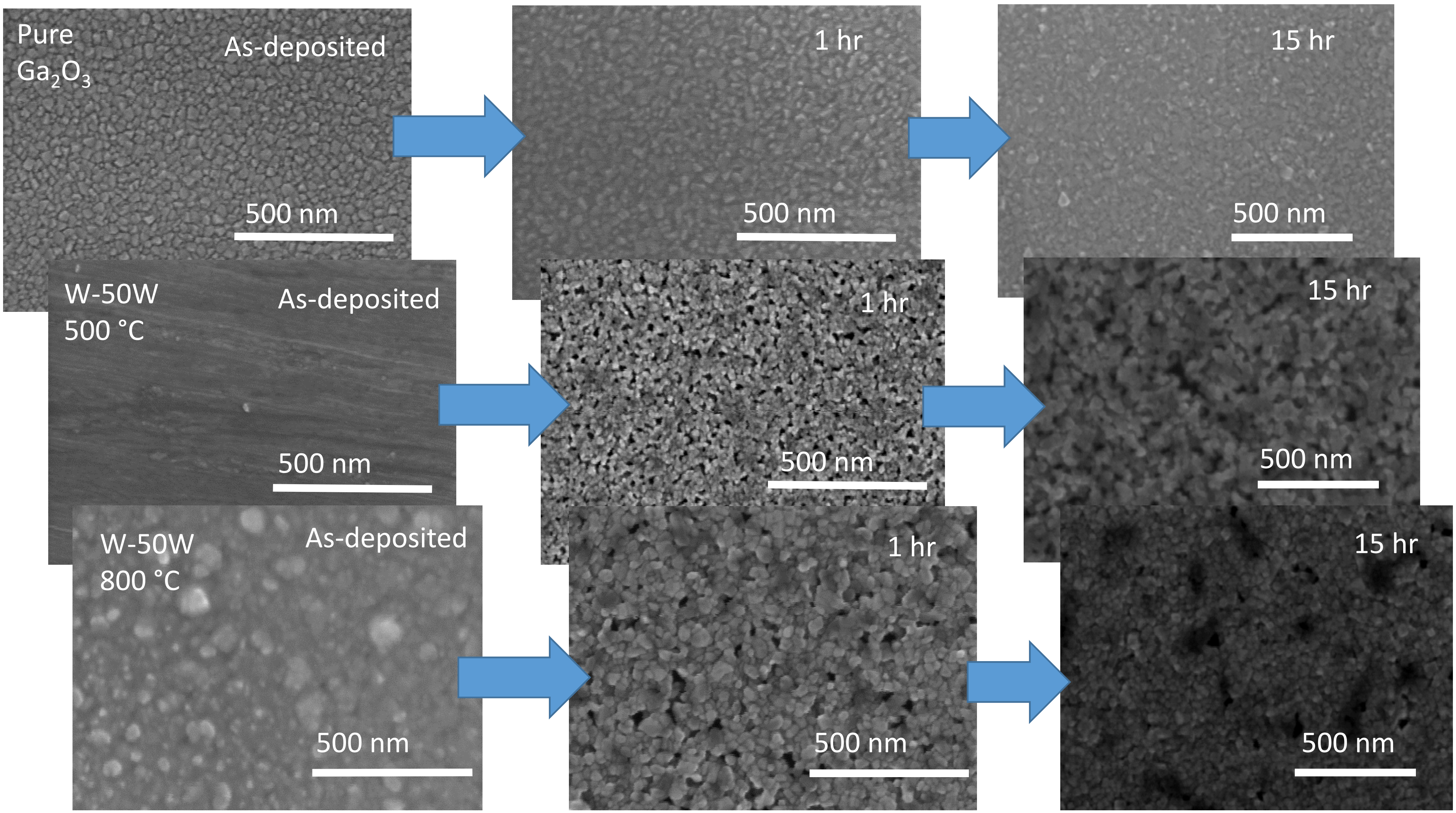




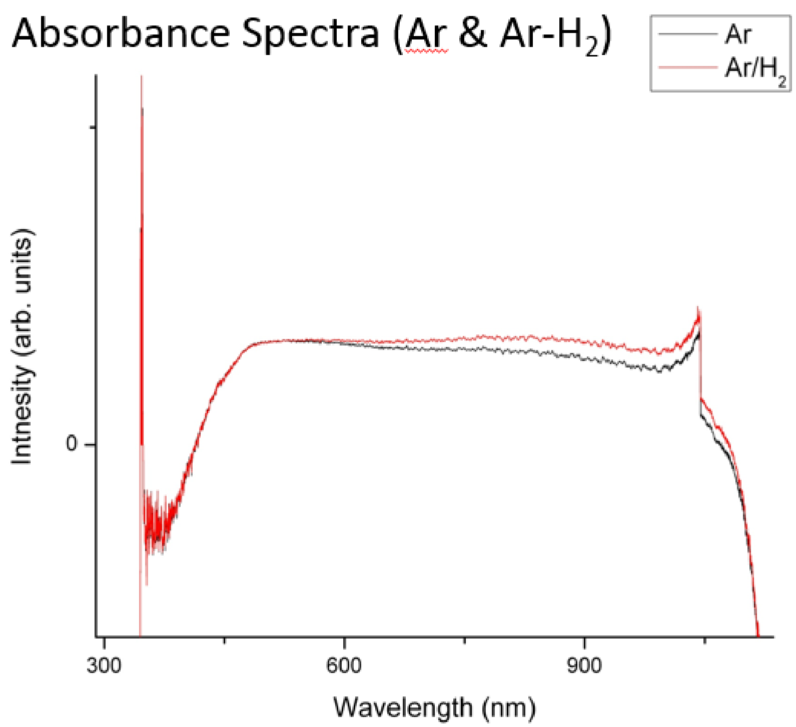
β-phase is stable for all films after annealing; however, surface morphology suffer porous formation for W-doped films

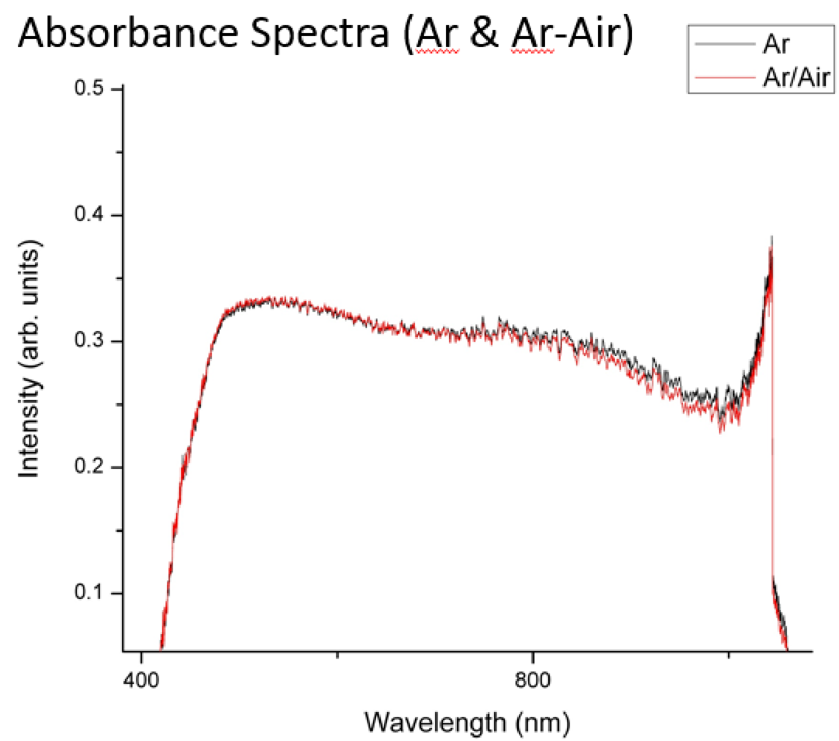


Thermal Stability



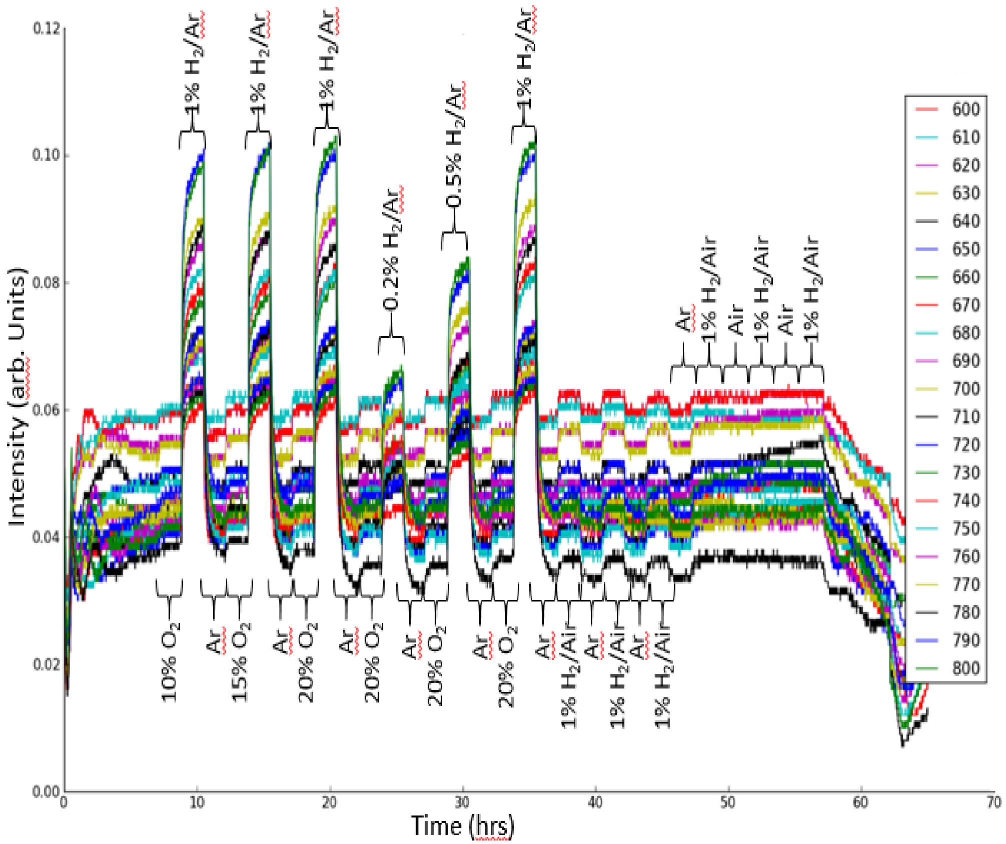
H_2 Sensitivity by Optical Absorption

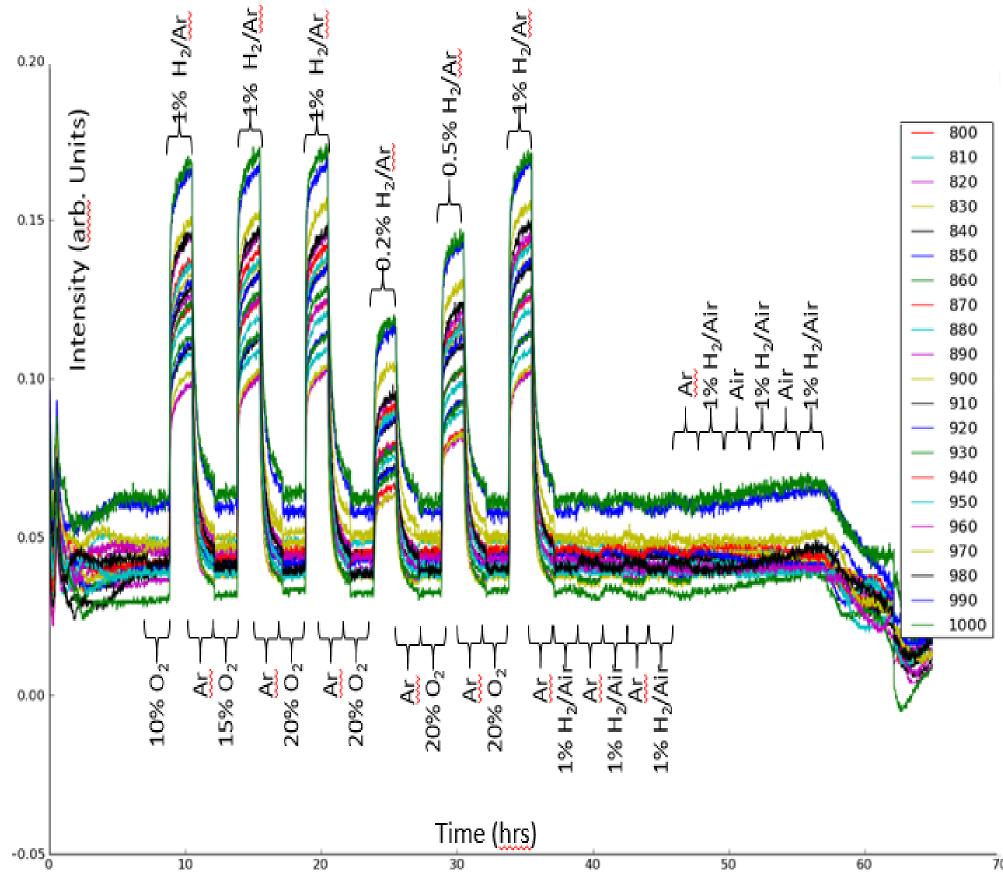




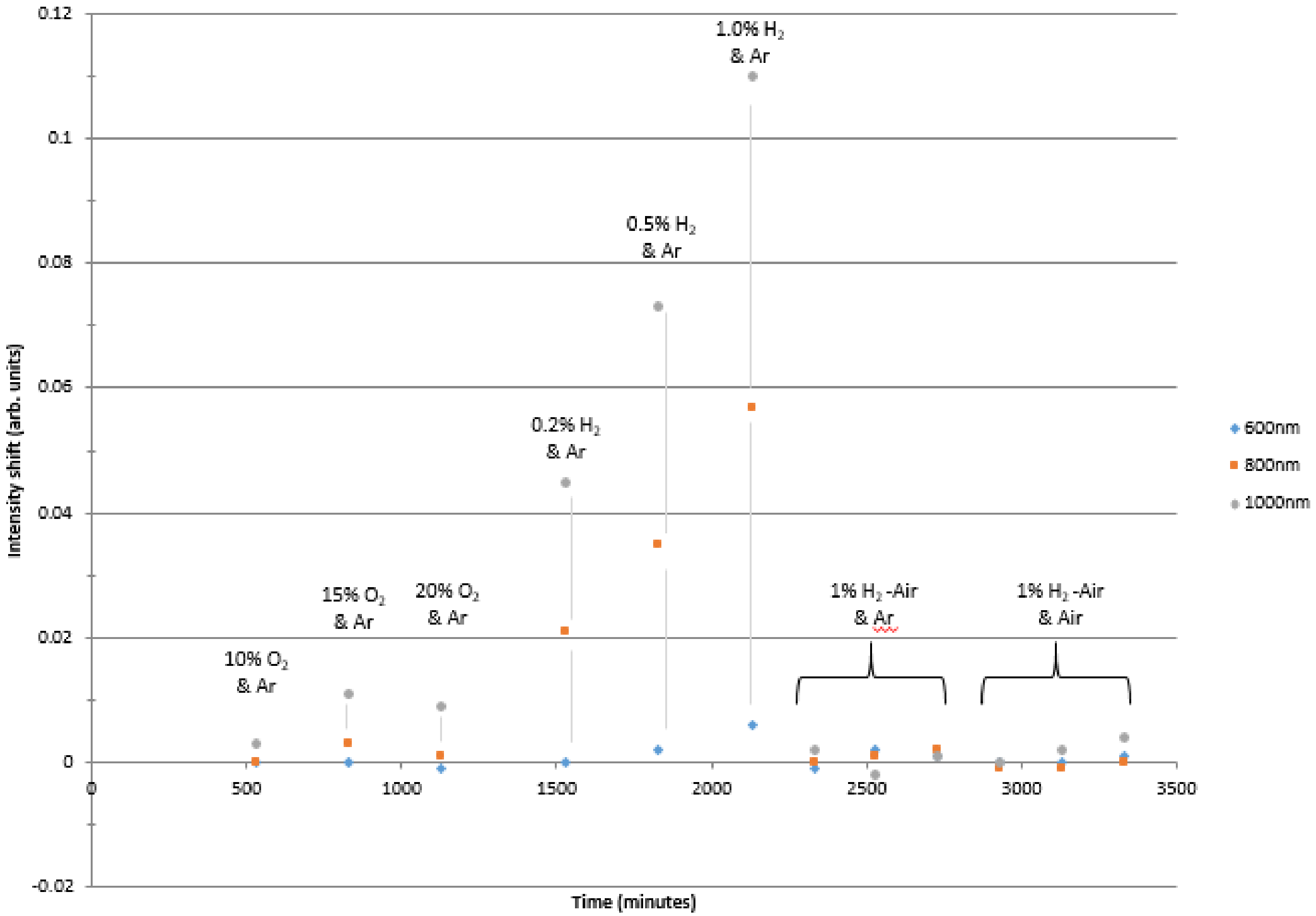
Hot Gas Exposure

- Ga_2O_3 Films demonstrated sensing properties to Hydrogen and Oxygen at 600 °C. The higher the H_2 content, the higher the optical response.



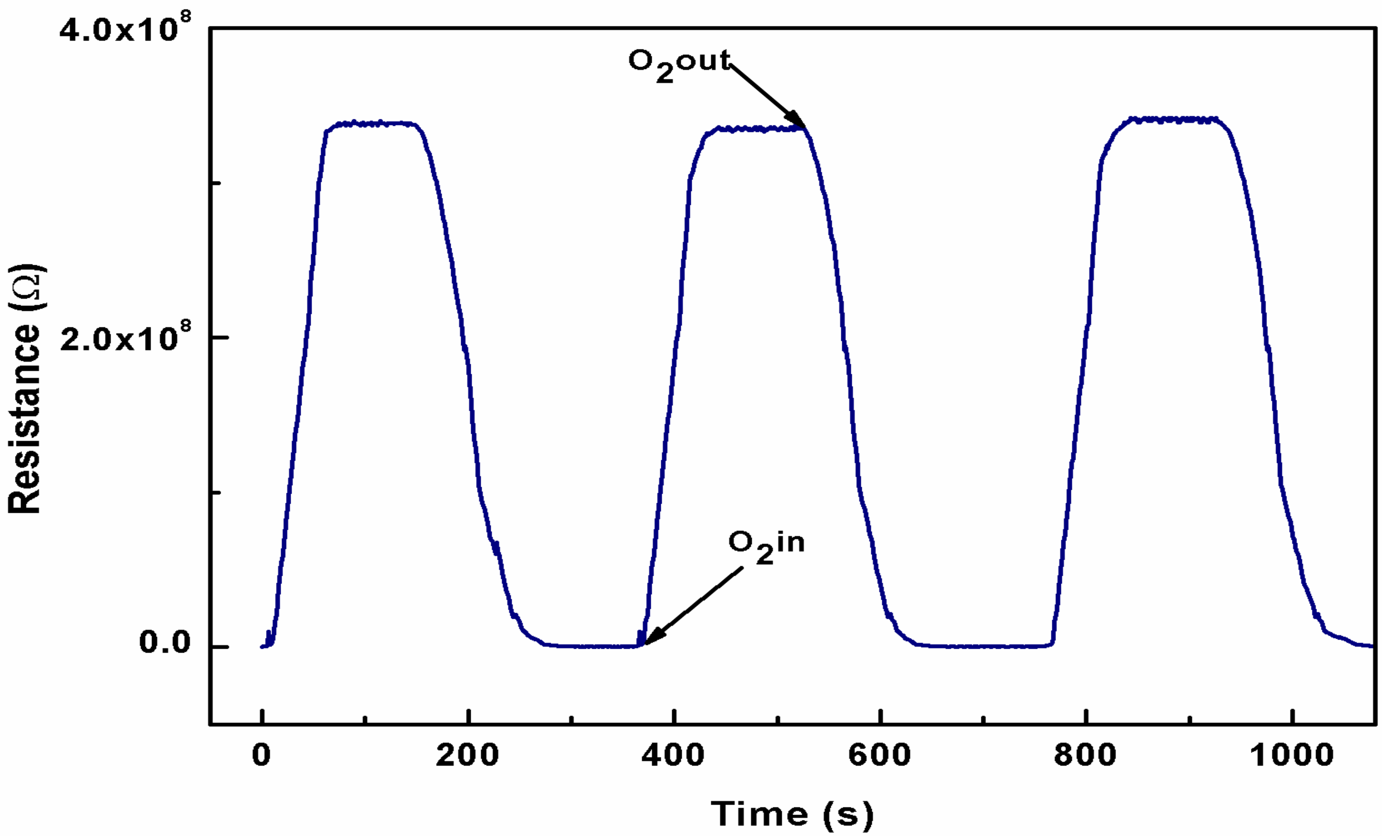


Intensity vs. Gas Exposure Summary



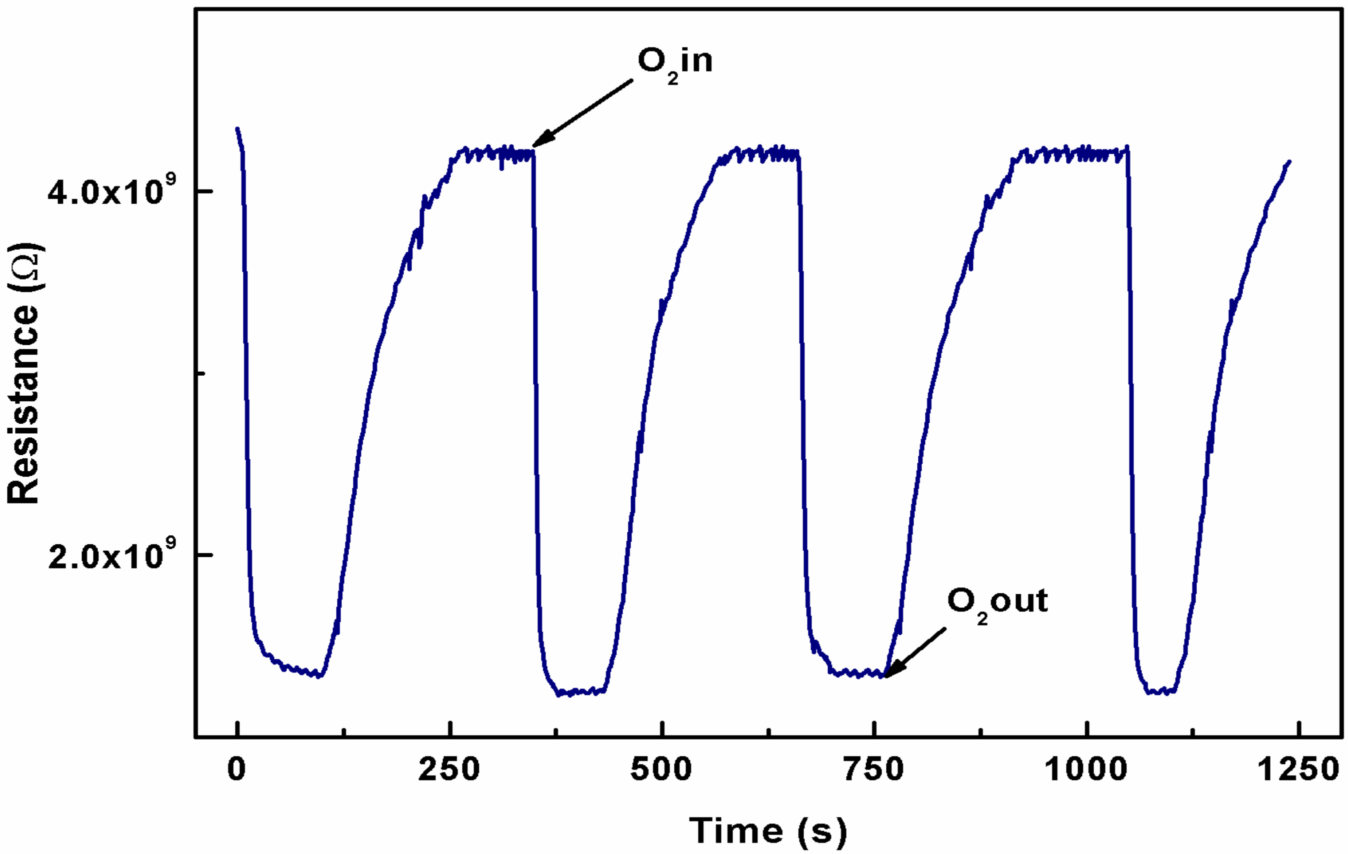
- ❖ W-doped films showed being sensible to H_2 and O_2.
- ❖ O_2 sensitivity increased from 10% to 15% of O_2 into Ar, but decrease again at 20%
- ❖ Sensitivity to gases was optimum in Ar environment, but small-to-non response in a mixture of Ar+Air

Oxygen Sensor Characteristics



- β-Ga_2O_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_2O_3 films demonstrated improve time response, by reducing sensitivity of the sensor. W- doped films showed p-type semiconductor behavior

Comparison of W-doped Ga_2O_3 vs. Pure Ga_2O_3 Films

	W-doped Ga_2O_3	**Pure Ga_2O_3**
Response Time	~25 Seconds	~65 Seconds
Recovery Time (s)	~130 Seconds	~120 Seconds
Sensitivity	~3.1	~134
Base Resistance	4.3E+09 Ω	2.5E+06Ω
Max/Min Resistance	1.3E+09Ω	3.3E+08Ω

Sensitivity can be expressed as the following equation:

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

Where:

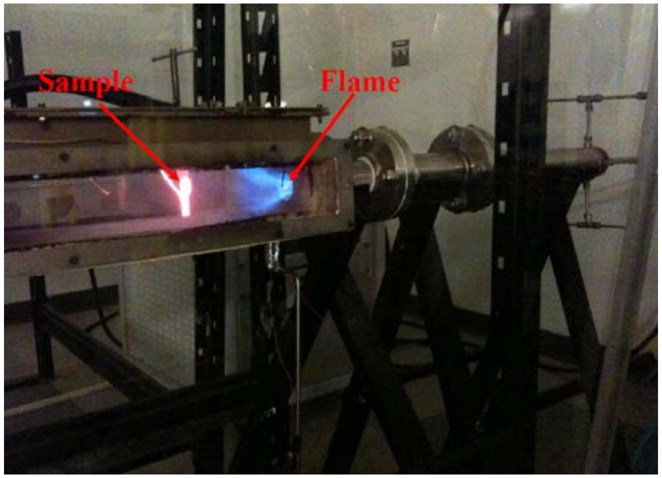
S: Sensitivity of the Sensor

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_2O_3 and W-Ga_2O_3 films at high temperature
- Test sputtering films inside a combustion chamber to evaluate the actual sensorial characteristics inside energy systems.



Impact

Journal Publications:

1. E.J. Rubio and C.V. Ramana, Appl. Phys. Lett. 102 , 191913 (2013).
2. A.K. Narayana Swamy, E. Shafirovich, and C.V. Ramana, Ceram. Inter. 39, 7223 (2013).
3. S.K. Samala, E.J. Rubio, M. Noor-A-Alam, G. Martinez, S. Manandhar, V. Shutthanandan, S. Thevuthasan, and C.V. Ramana, J. Phys. Chem. C 117 , 4194 (2013).
4. CV Ramana, EJ Rubio, CD Barraza, A Miranda Gallardo, Samantha McPeak, Sushma Kotru, JT Grant, J. Appl. Phys. **115**, 043508 (2014).

Conference Presentations:

1. International Materials Research Congress (IMRC) August 11- August 15,2014
2. International Conference on Metallurgical Coatings and Thin Films, April 29 – May 3, 2013, San Diego, CA
3. AVS International Symposium, October 28 – November 2, 2012 Tampa, FL
4. Southwest Energy Symposium, March 24, 2012, El Paso, TX
5. International Conference on Metallurgical Coatings and Thin Films, April 28 – May 2, 2014, San Diego, CA
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 disseration)
3. Sampath K. Samala: MS (thesis)
4. Abhilash Kongu: MS (non-thesis)

Summary and Conclusion

- Pure Ga_2O_3 and W-doped Ga_2O_3 films were fabricated and analyzed
- All films demonstrated the stable β-phase (monoclinic) of Ga_2O_3
- Ga_2O_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_2O_3 and W-doped Ga_2O_3 films demonstrated to be sensitive to oxygen at high temperatures, with improved time of response with the inclusion of tungsten
- W-doped Ga_2O_3 films showed optical sensor properties to O_2

Acknowledgments

- DOE-NETL
- Richard Dunst
- EMSL/PNNL, Richland, WA.
- SUNY- Prof. Michael Carpenter