Gallium Oxide Nanostructures for High Temperature Sensors

Ramana Chintalapalle (PI)
Mechanical Engineering, University of Texas at El Paso
Students: Ernesto Rubio (PhD); S.K. Samala (MS)

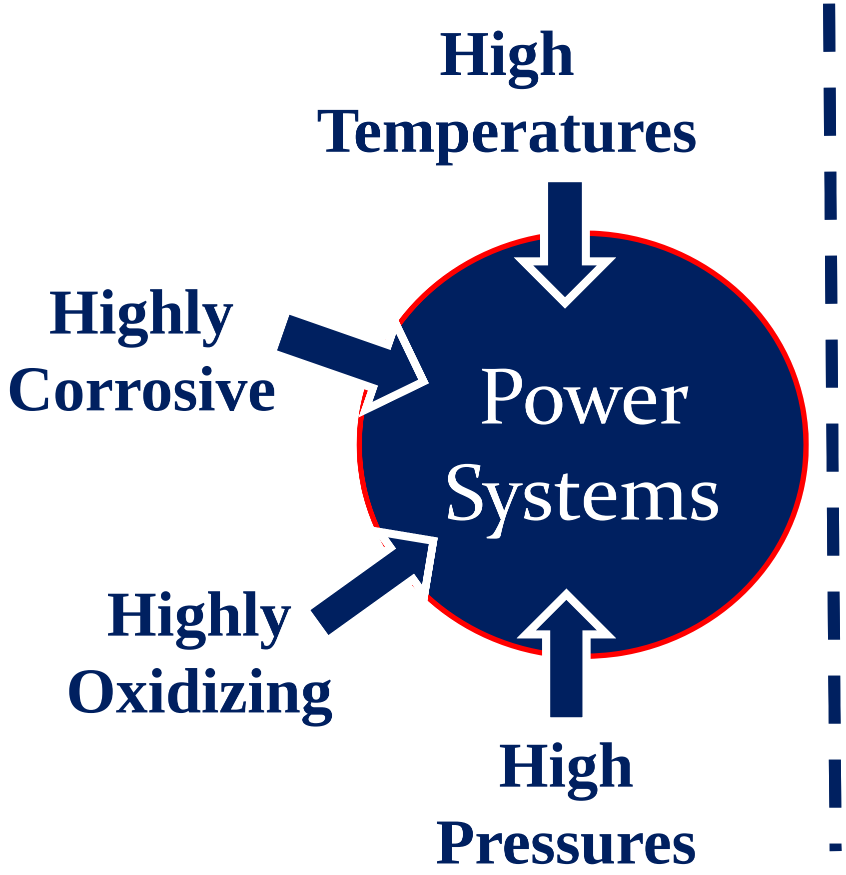
Program Manager:
Richard Dunst, NETL, DOE
Project: DE-FE0007225
Project Period: 10/01/2011 to 12/31/2014

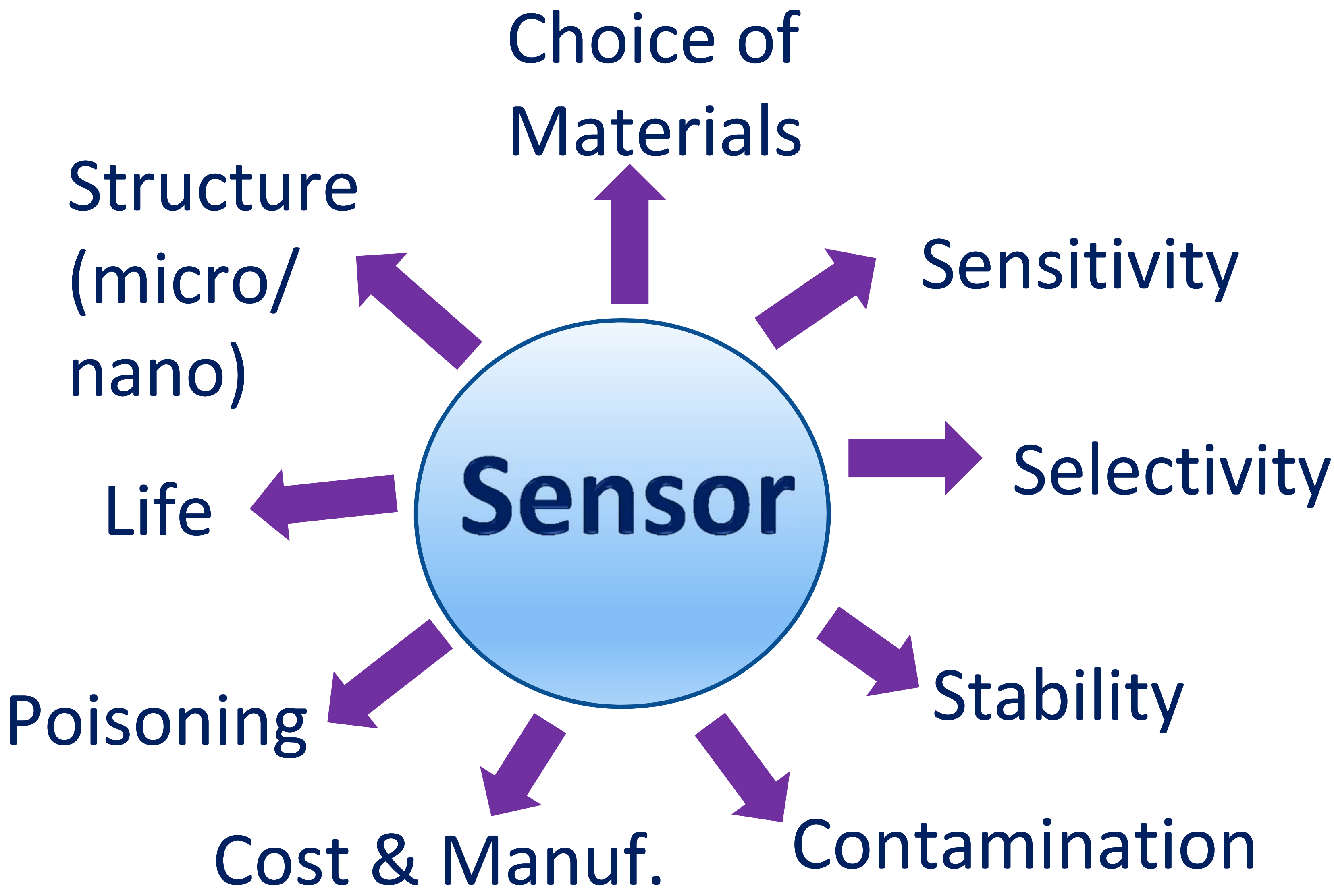
Outline

- ❖Introduction
- ❖Research Objectives
- ❖Experiments
- ❖Results
  - ❑Intrinsic Ga_2O_3
  - ❑Tungsten (W)-doped Ga_2O_3
- ❖Summary & Outlook

Introduction

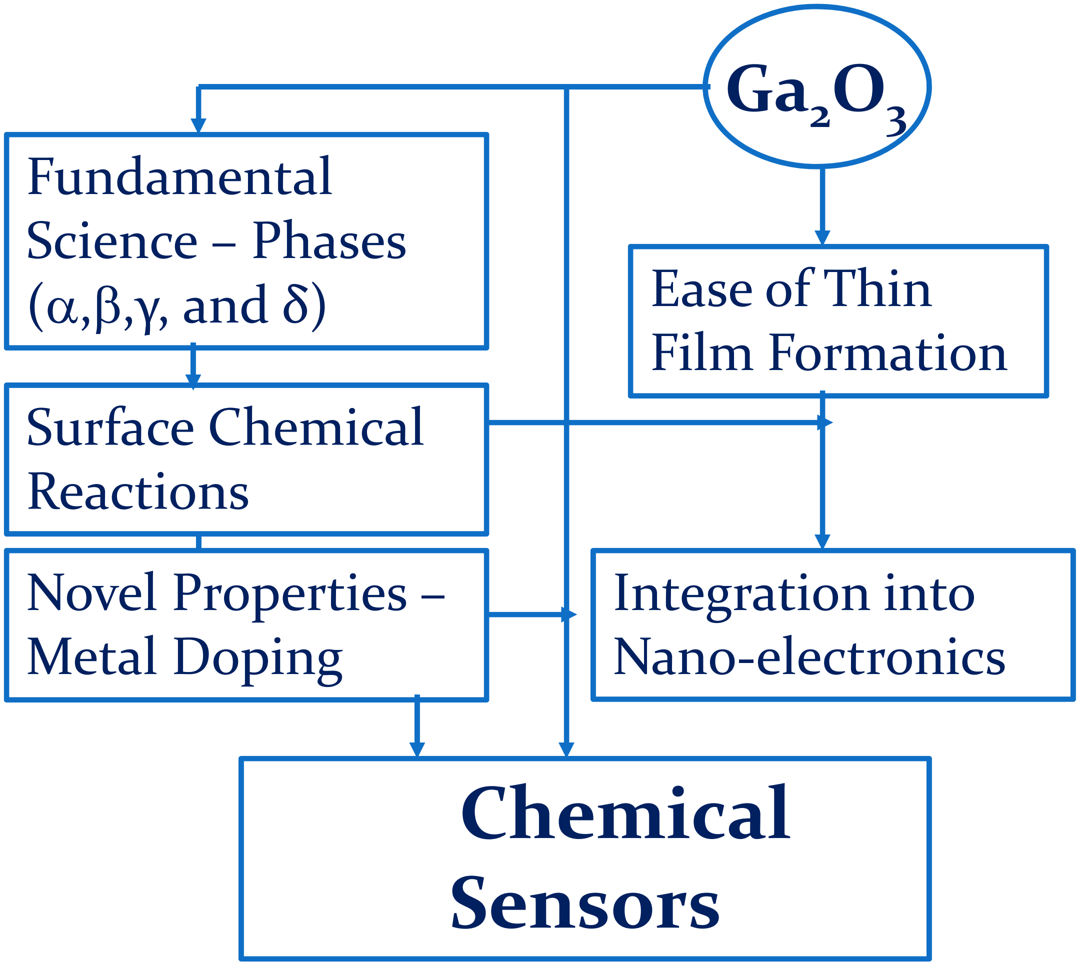
Challenging Environment in Power Systems




Choice of Materials
Structure (micro/ nano)
Sensitivity
Selectivity
Life
Sensor
Poisoning
Stability
Cost & Manuf.
Contamination

Oxygen Sensors and Controls

Gallium Oxide (Ga_2O_3)



- ♦ Wide band gap (>5 eV) semiconductor
- ♦ High thermal and chemical stability (T_m: 1725 ^oC)
- ♦ One of the most suitable materials for high temperature gas sensing

Sensing Mechanism

At T≥700 °C, defects → equilibrium with surrounding atmosphere → n type conductivity → depends on oxygen partial pressure

Electrical conductivity

Activation energy

$$\sigma = \sum_i pO_2 \exp\left(\frac{-E_A}{k_B T}\right)$$

Oxygen partial pressure

Boltzmann constant

Temperature

At T< 700 °C, Ga-oxide exhibits sensitivity to reducing gases (CO, H_2)

Project Objectives and Goals

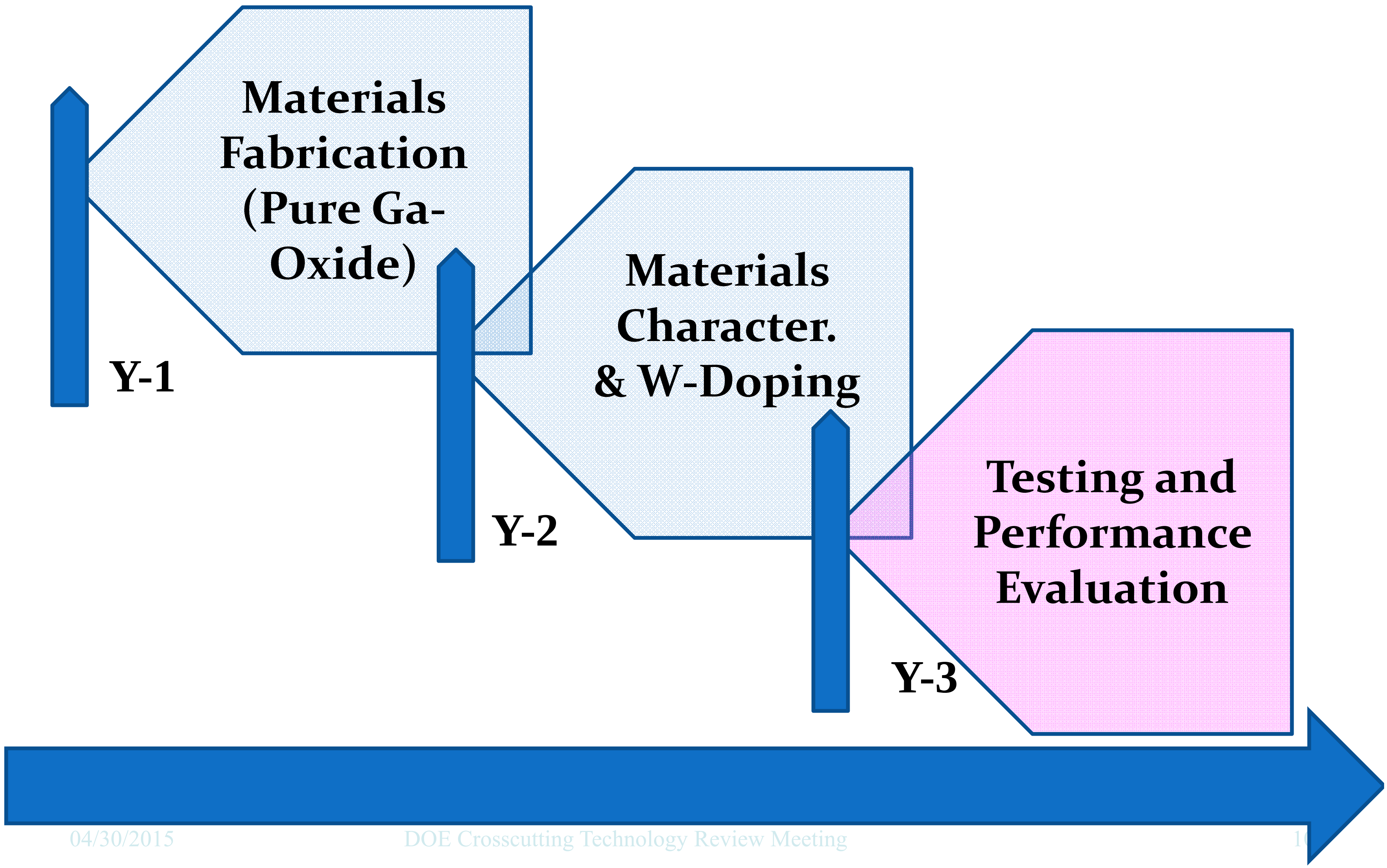
Objective 1: To fabricate high-quality pure and doped Ga_2O_3-based materials and optimize conditions to produce unique architectures and morphology at the nano scale

Objective 2: Derive the structure-property relationships at the nanoscale dimensions and demonstrate high-temperature oxygen sensing (faster response) 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-based nanostructures)

Project Work Plan



Experiments

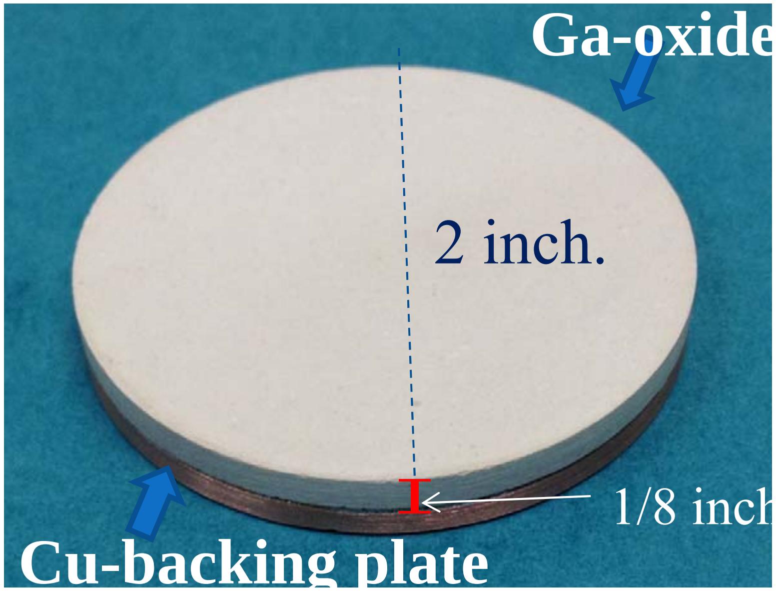
Materials

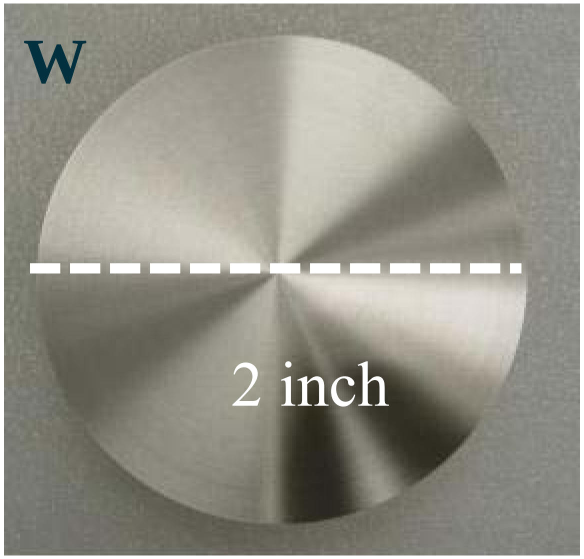
Target (for Deposition)

Ga_2O_3 & W

Substrate(s):

- Si(100)
- Alumina





Fabrication – Thin Films

- RF magnetron sputtering
- Deposition Conditions

Fixed:

- Base pressure ~10^{-6} Torr

- Powers: $Ga_2O_3 \rightarrow 100$ W

- Target-Substrate distance: 7 cm

- Sputtering gas: Argon + O_2

Variables:

Sample set 1 (Intrinsic):

Substrate Temperature: RT-500 ˚C

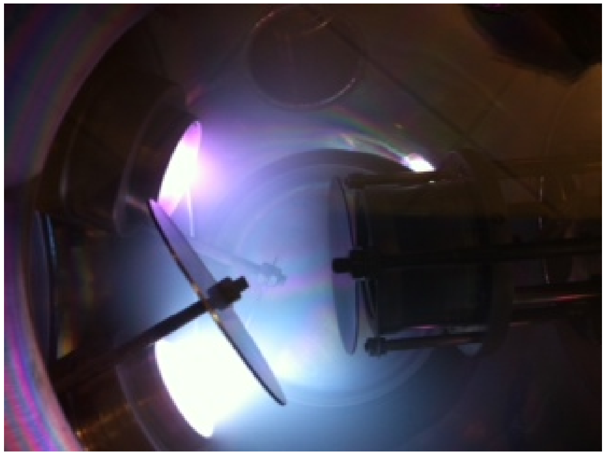
Sample set 2 (W-Doped):

Tungsten Target Power (50 to 100W)

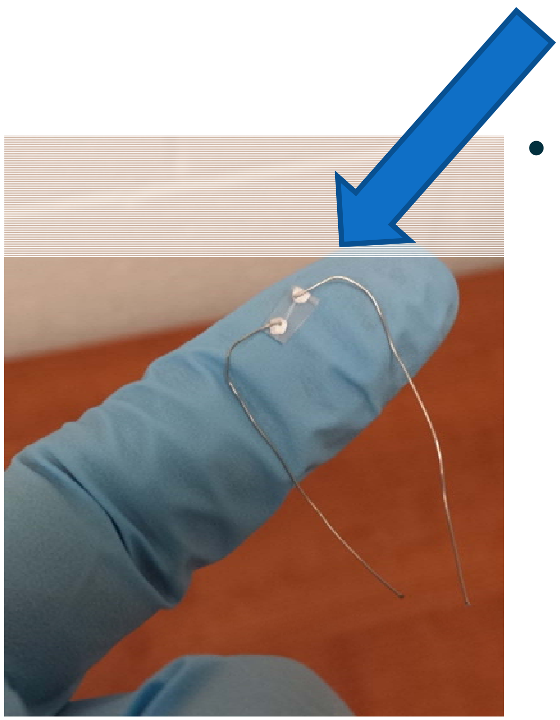
Substrate Temperature = 500 ˚C

Sample set 3 (W-Doped):

Target Powers = const.; Substrate temperature varied from 500 to 800˚C

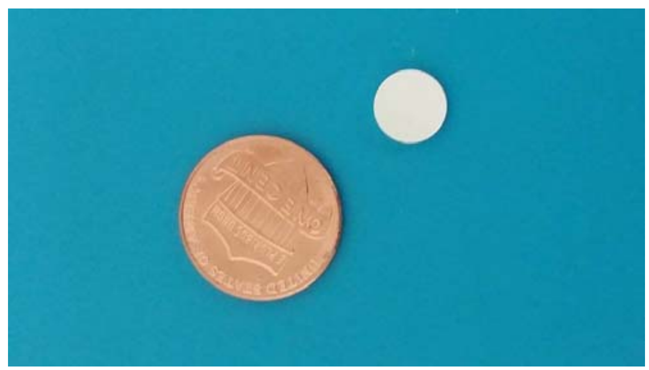


Sensors and Sample Matrix



- Extremely thin (~50 nm) samples
- Two silver electrodes attached on the surface

- ~200 nm thick Ga-oxide
- 200 nm thick Pt interdigited electrodes
- Spacing: 100 µm

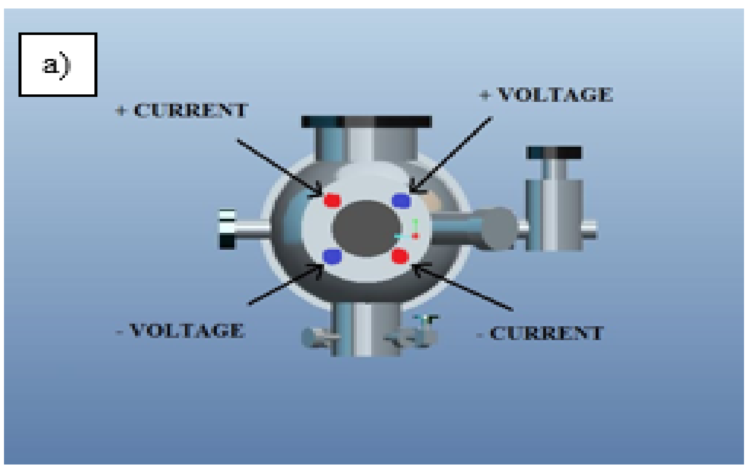


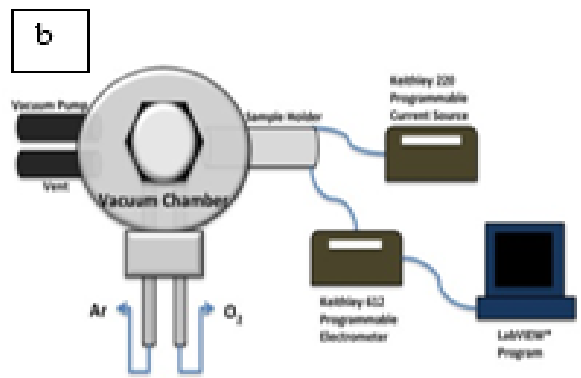
- Bulk (ceramic pellets)
- Electrical Impedance

Sensor Performance - Electrical

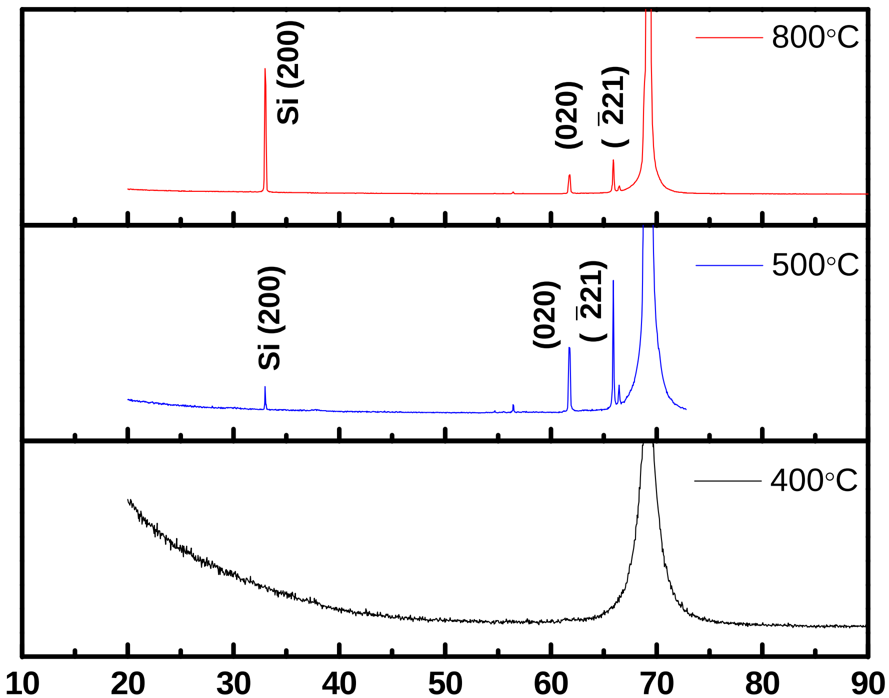
- Oxygen introduced and partial pressures of oxygen were varied
- Evaluation at temperatures ≥ 700 °C

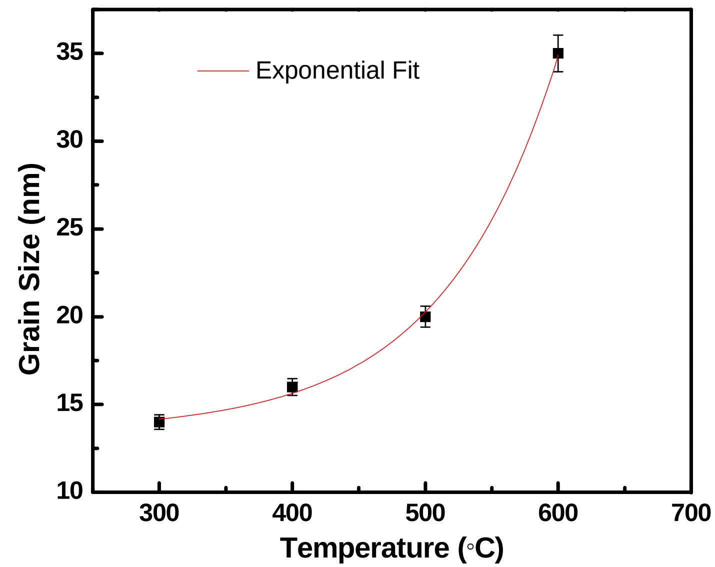
- Constant current





Crystal Structure





500 °C is favorable/critical to provide sufficient energy for Ga_2O_3 film crystallization (β-phase)

$L = L_o \exp(-\Delta E/k_B T)$

L: Average size

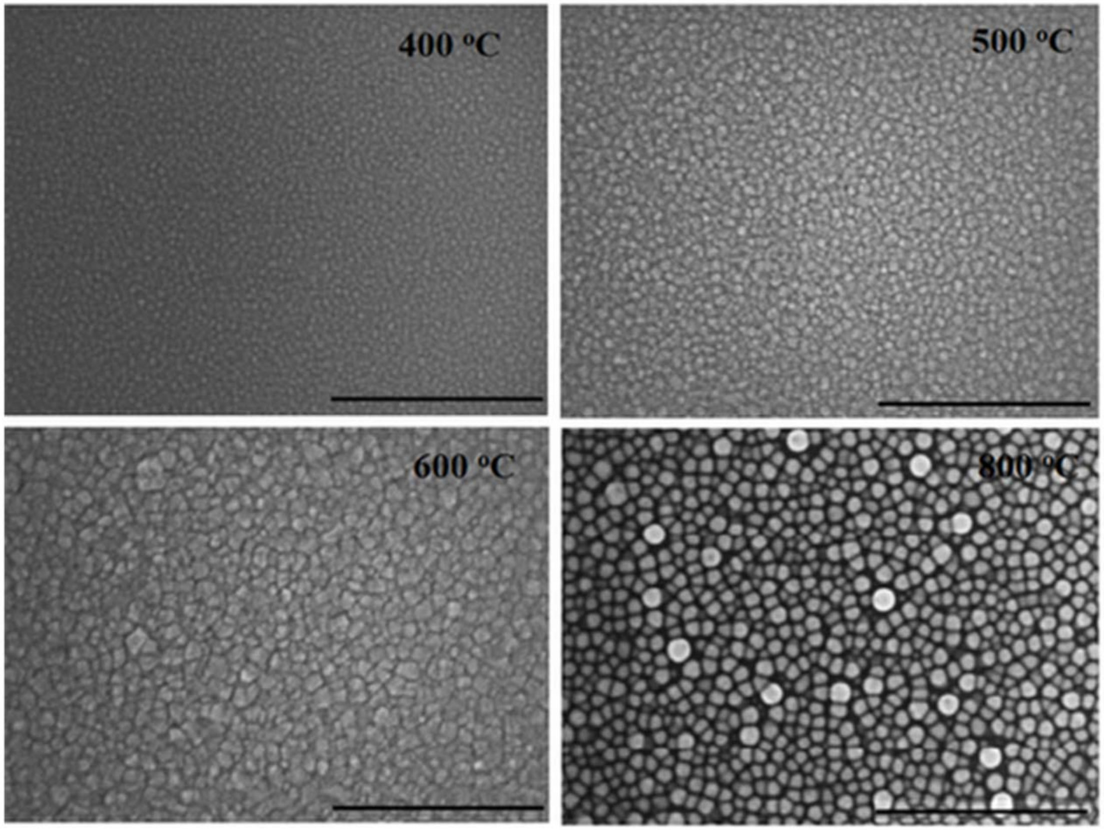
L_0: Pre-exp. factor (film, substrate materials)

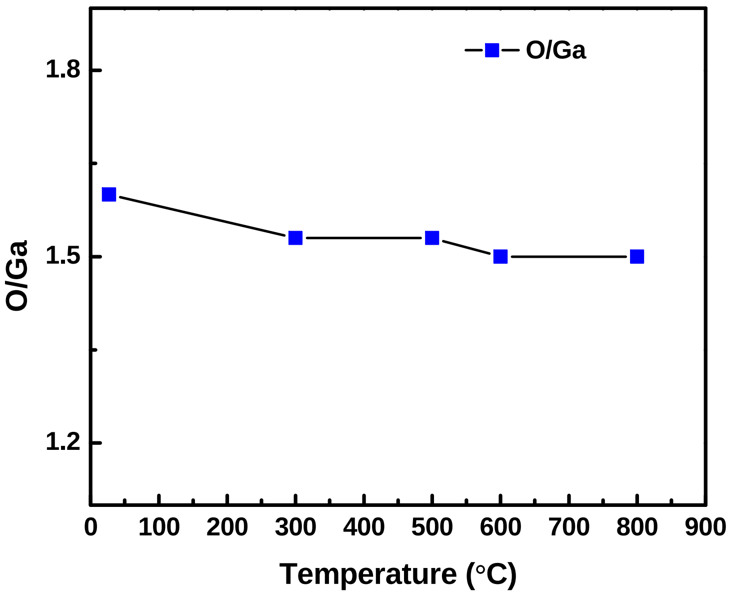
ΔE: Activation energy,

k_B: Boltzmann constant and

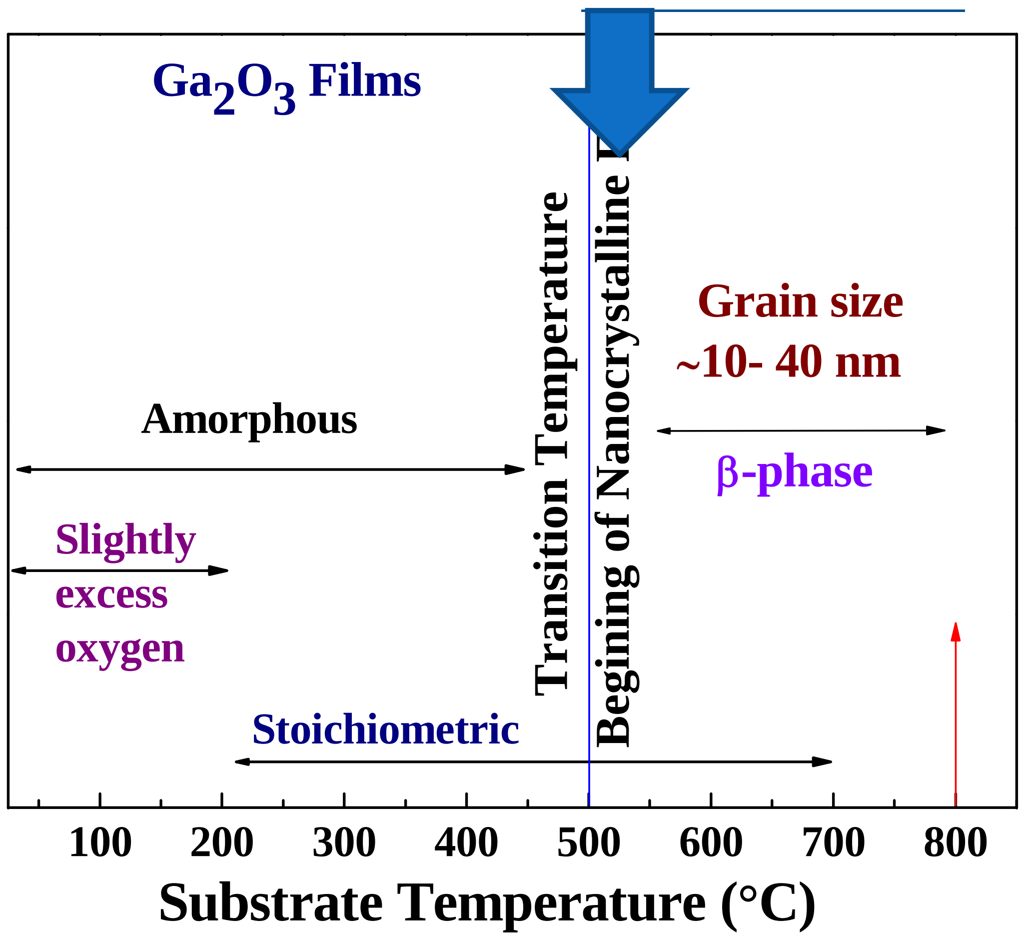
T: Absolute temperature.

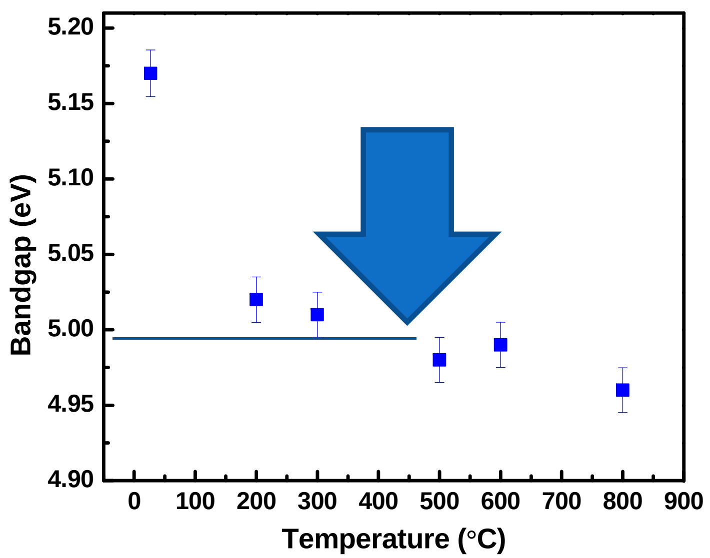
Morphology & Composition





Microstructure & Electronic Properties





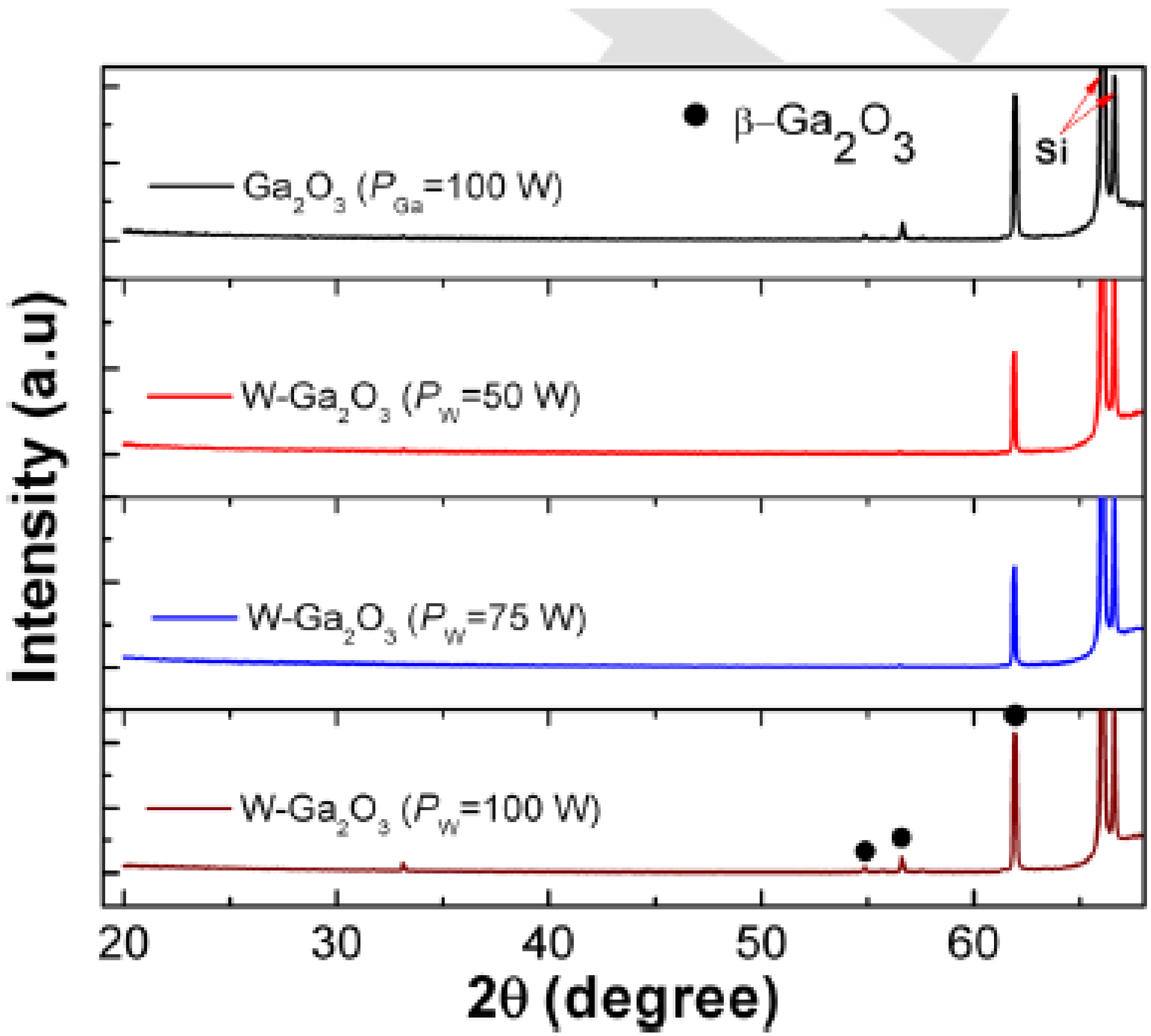
Tungsten Doping

W-Doped Ga-Oxide

t = 200 nm

W-Power (Watts)	W-Content (Atomic %)
0	0
50	5
75	10
100	15

Crystal Structure – Power dependence



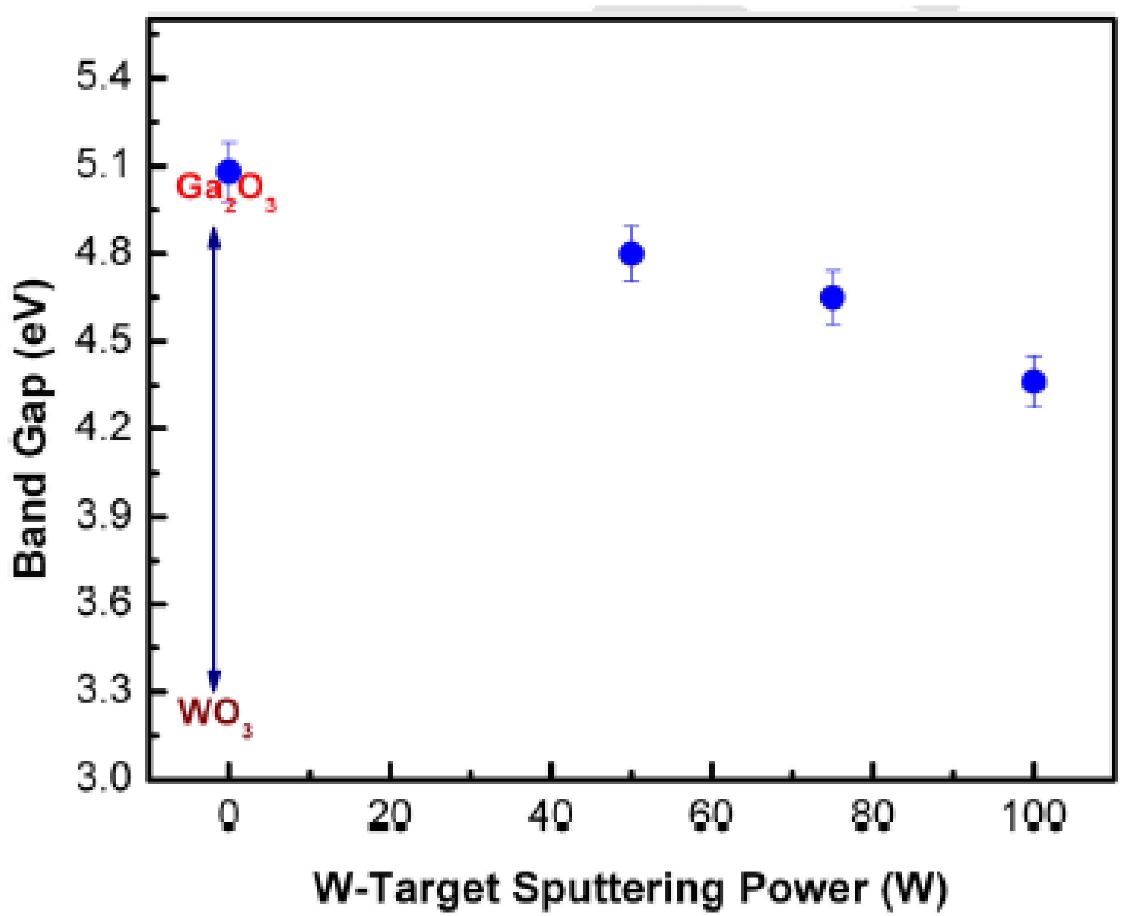
500 C

Only Ga-oxide phase is present

No secondary phase formation

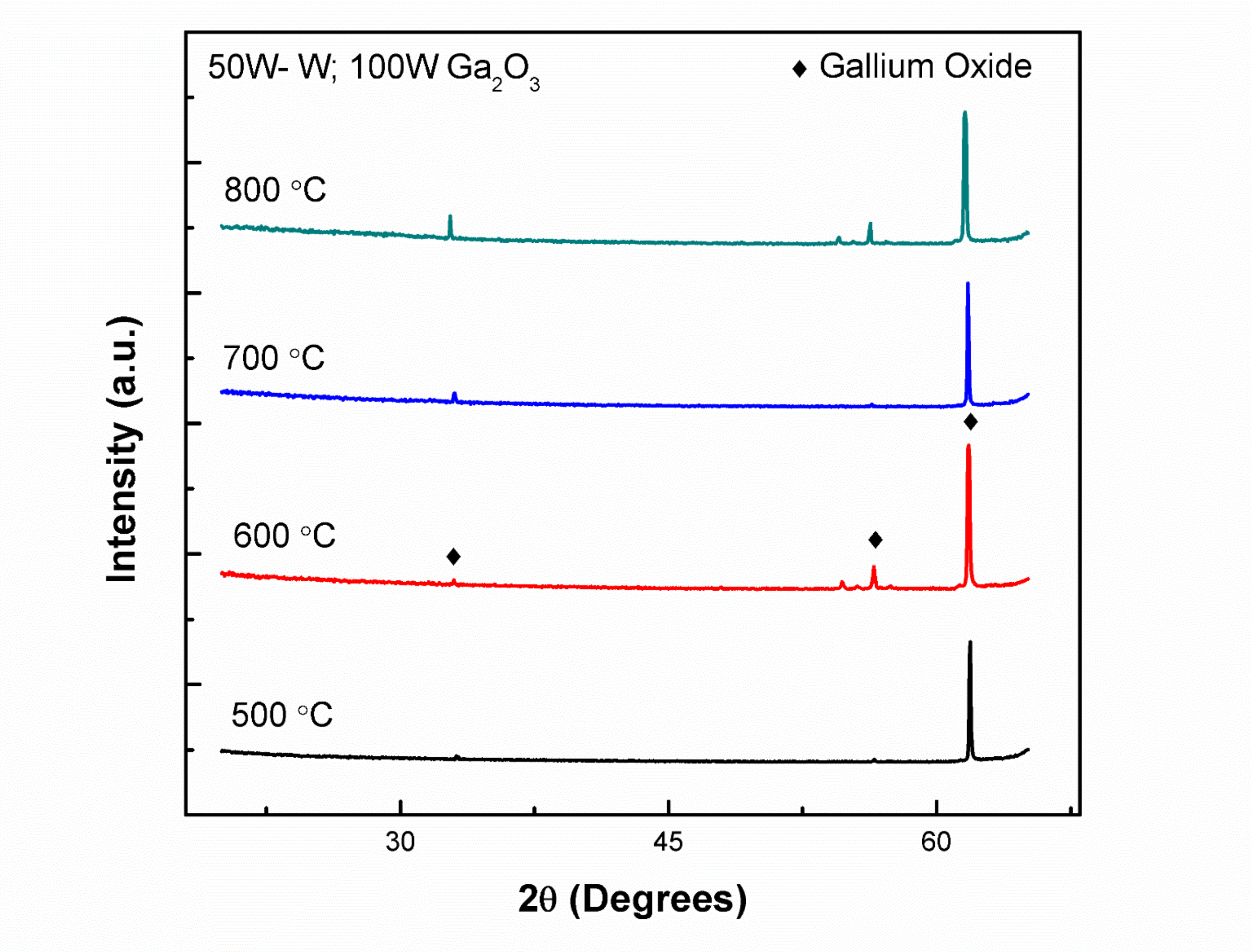
Band Gap (Power dependence)

Reduction by ~0.75-1.00 eV with the inclusion of tungsten into Ga-oxide films!



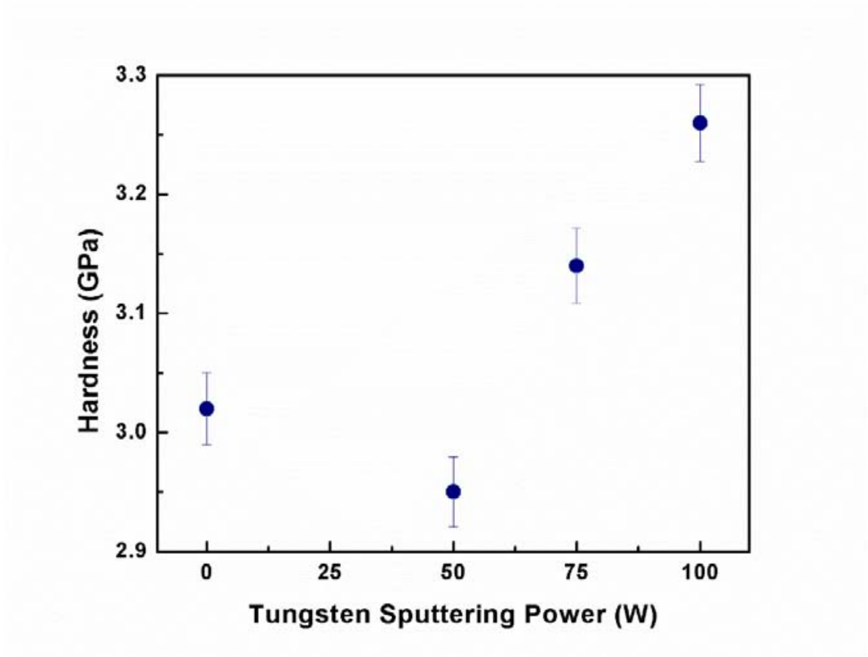
E.J. Rubio and C.V. Ramana, *Appl. Phys. Lett.* **102**, 191913 (2013).

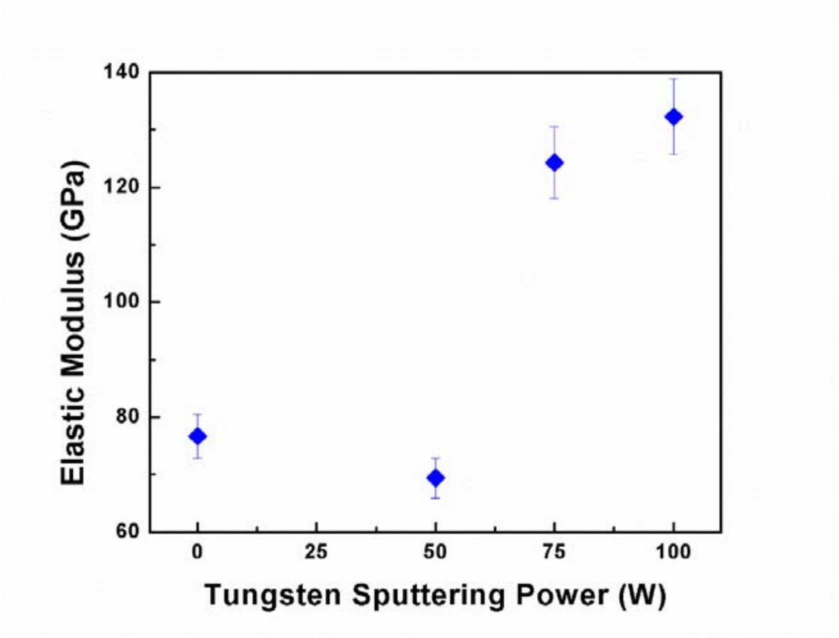
Crystal Structure – (Temp. Dependent)



Only β-phase presented for all films.

Mechanical Characteristics

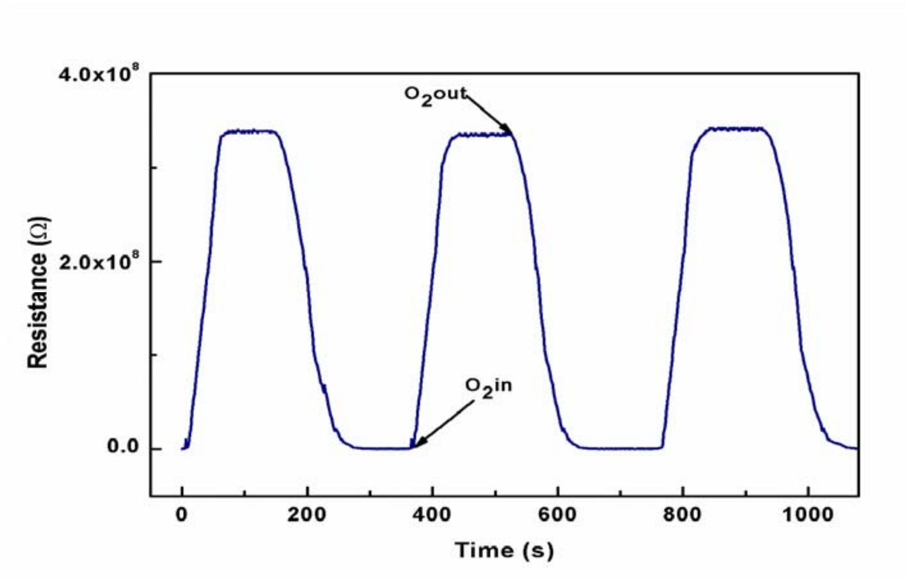




Hardness & Elastic Modulus increases with W-content

Can be tolerant and impact resistant

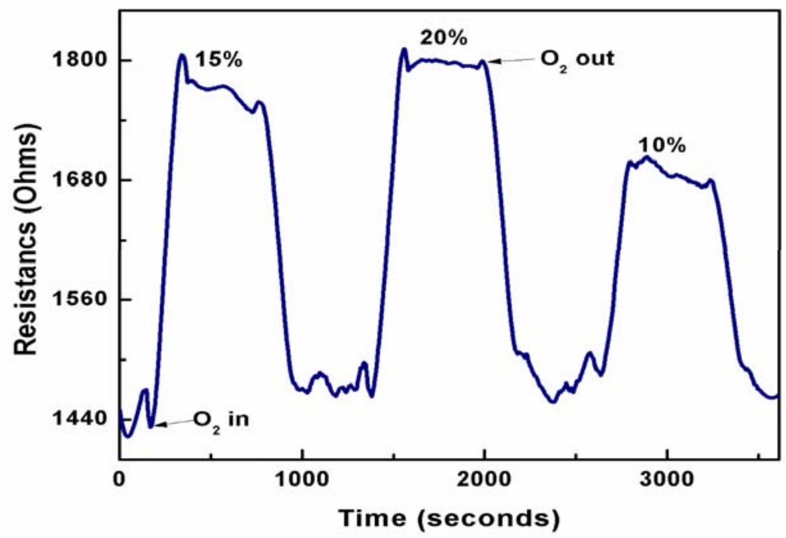
Oxygen Sensor Characteristics



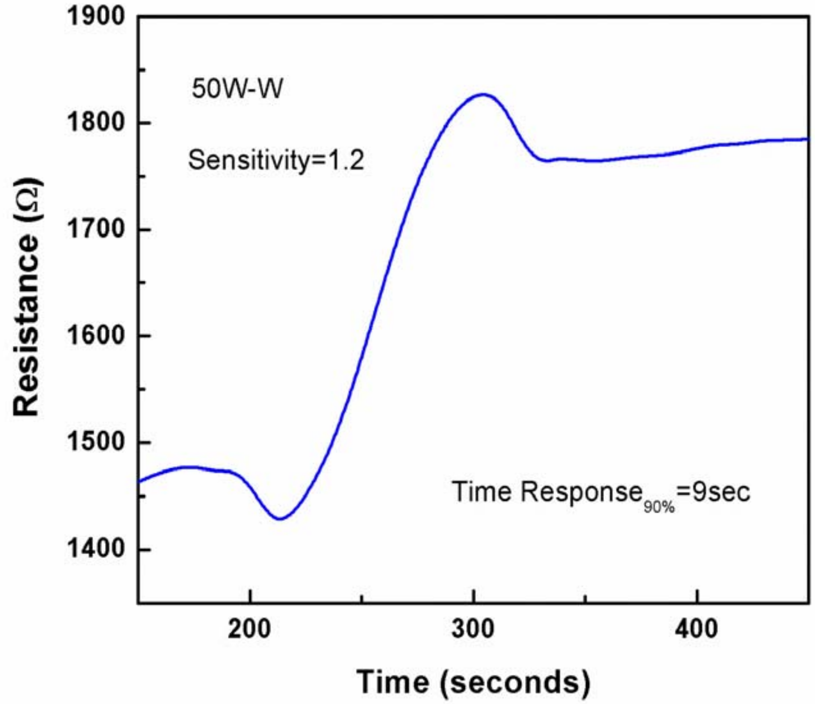
Intrinsic Ga_2O_3 films
Time response: 62 sec

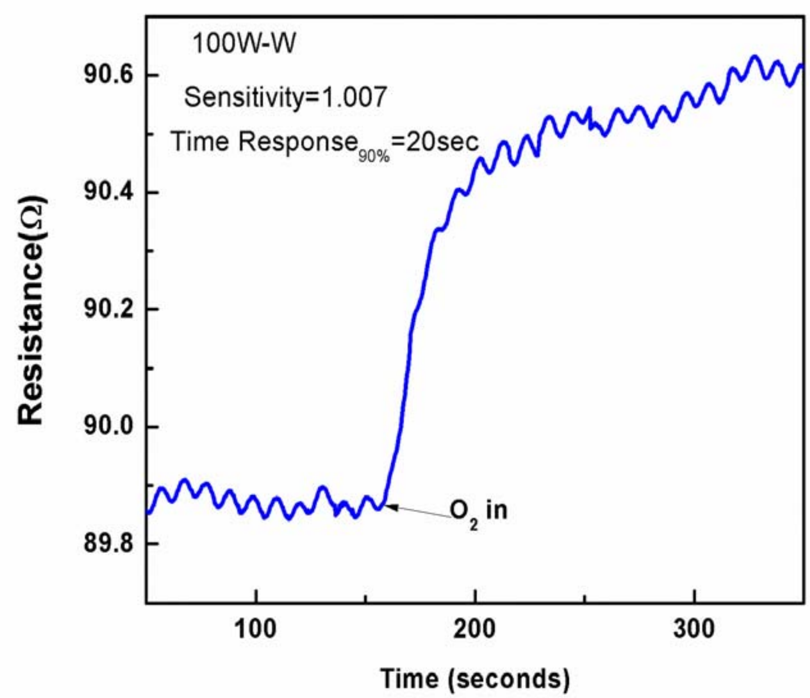
Oxygen Sensor Characteristics

W (5 at%) - doped
Ga_2O_3 films



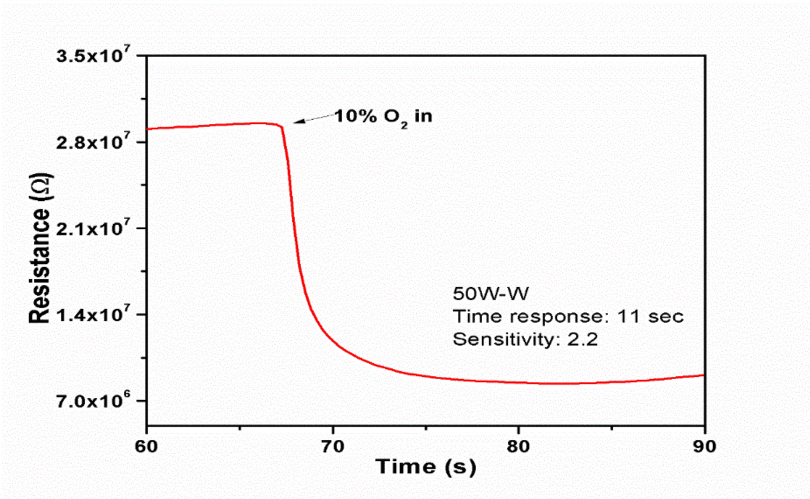
- Ga_2O_3 based films showed oxygen sensitivity at 700 °C,
- As an n-type semiconductor the resistance of the film increased in the presence of oxygen.
- Time response was drastically improved with the incorporation of tungsten

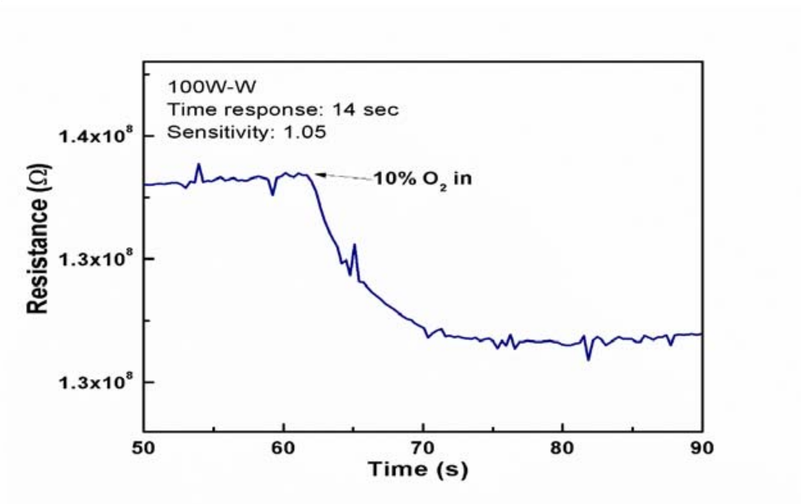


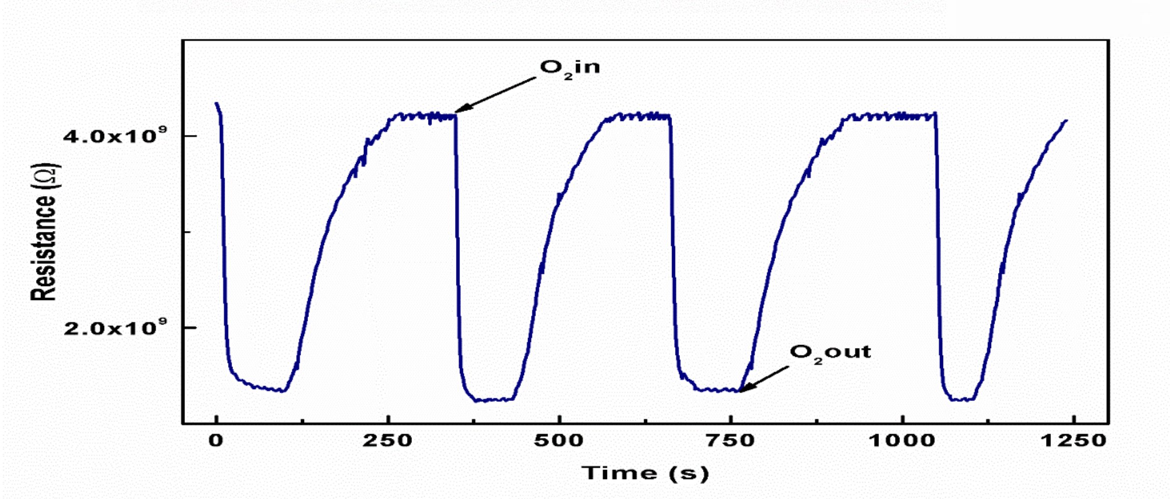


- Increasing W-content reduces sensitivity of the sensors
- Time response is increased with increasing W-content
- Stability of the electrical properties is reduced with increasing W-content

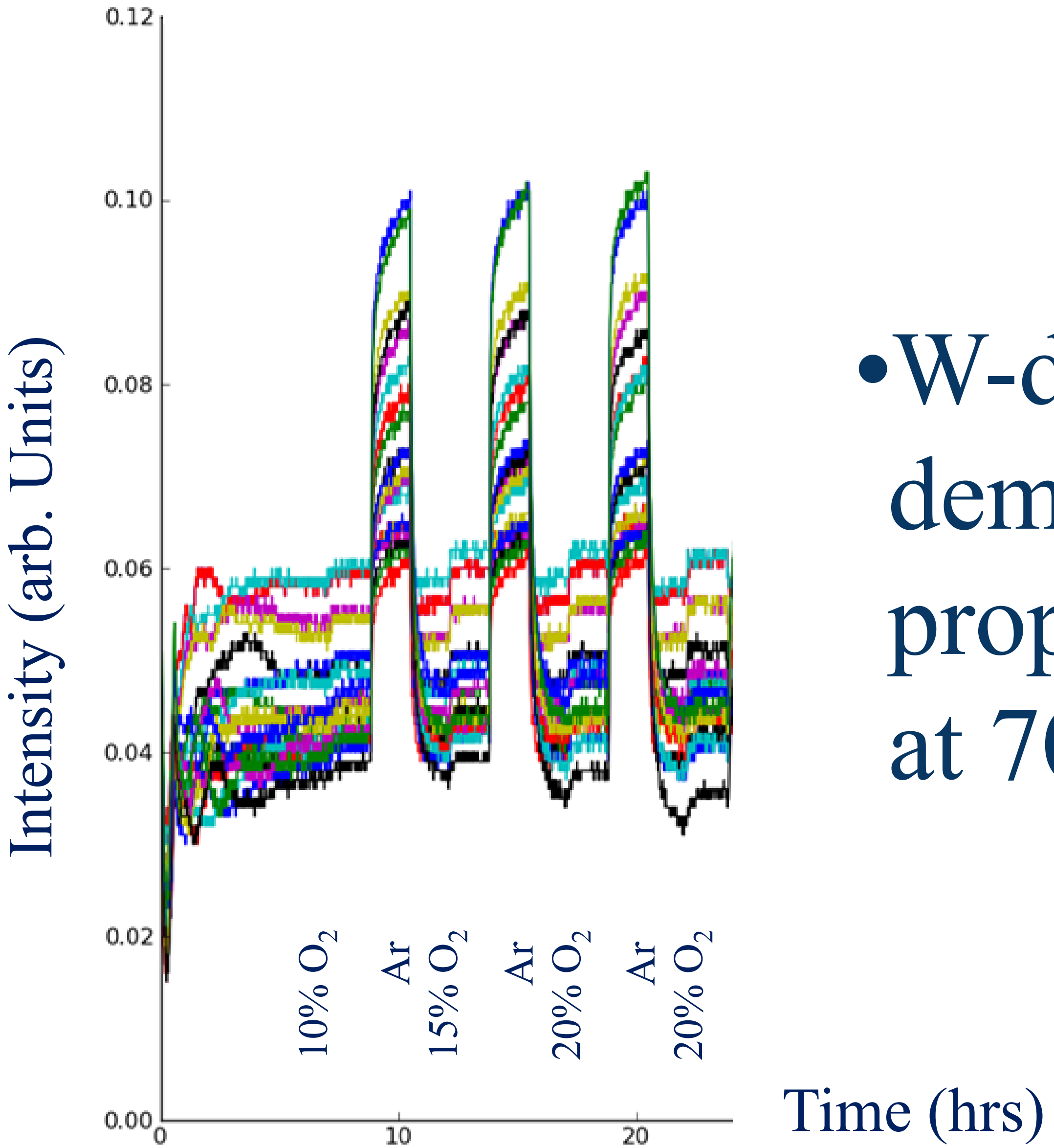
Two Probe Oxygen Sensor Characteristics





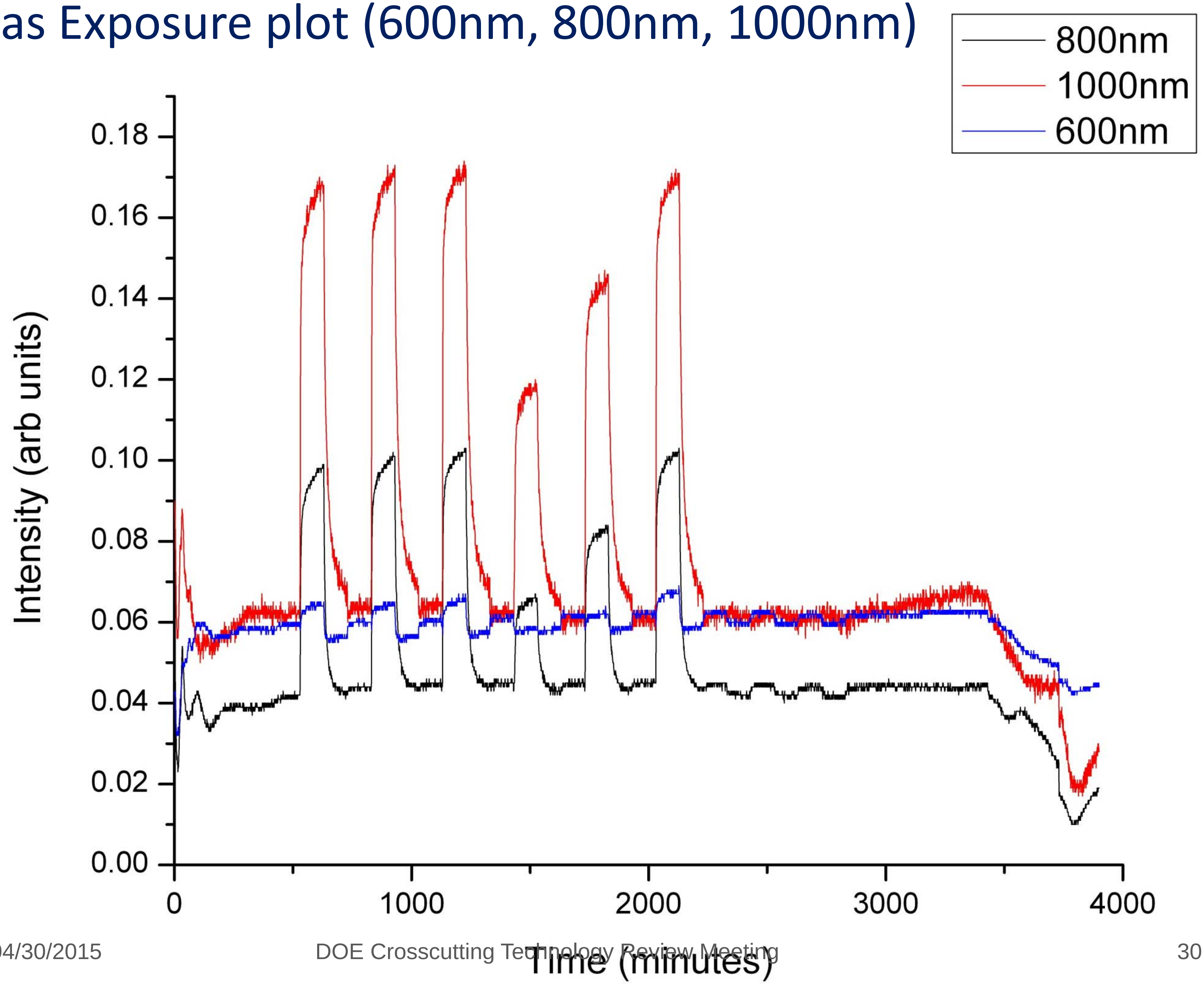


Hot Gas Exposure (600-700 nm)

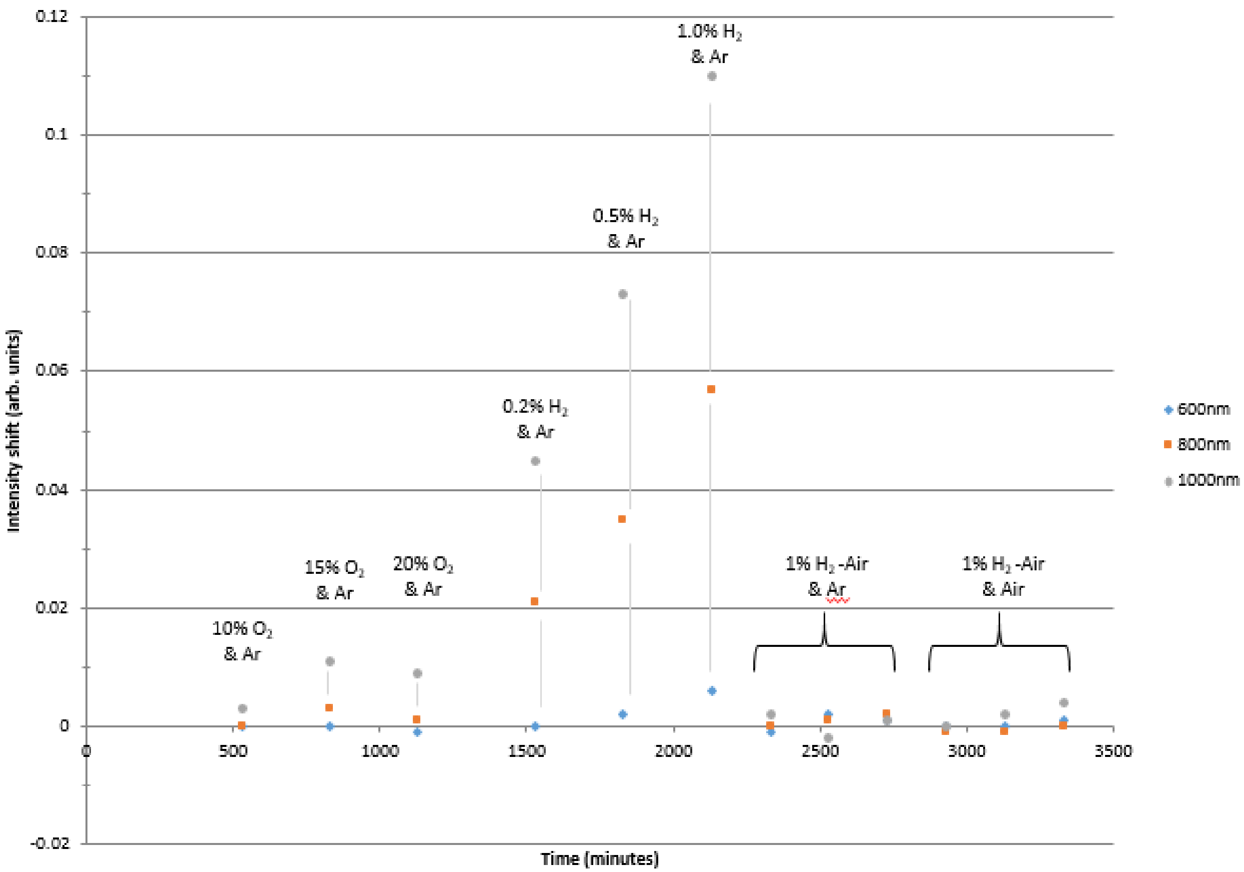


- W-doped Ga-oxide demonstrated sensing properties to oxygen at 700 °C.

Gas Exposure plot (600nm, 800nm, 1000nm)

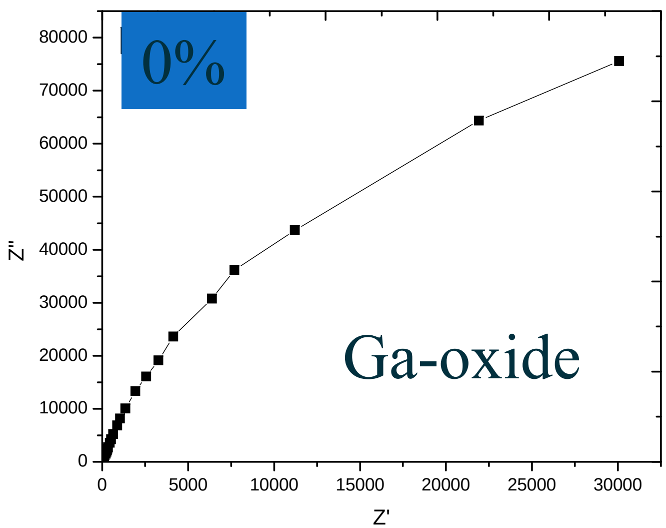


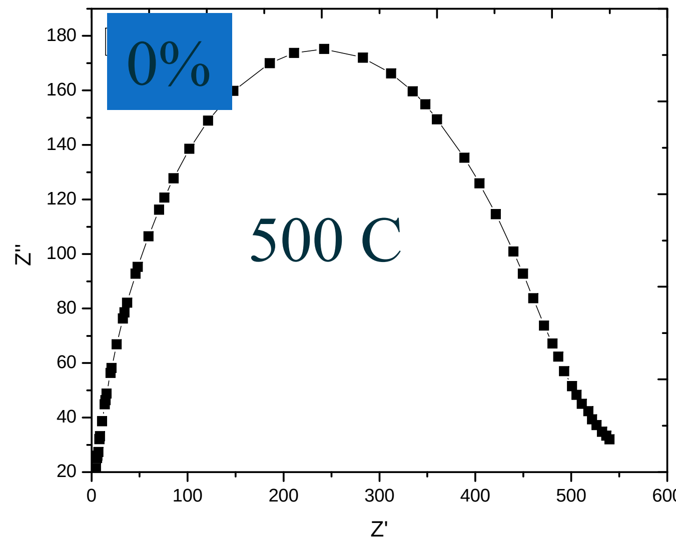
Intensity vs. Gas Exposure Summary

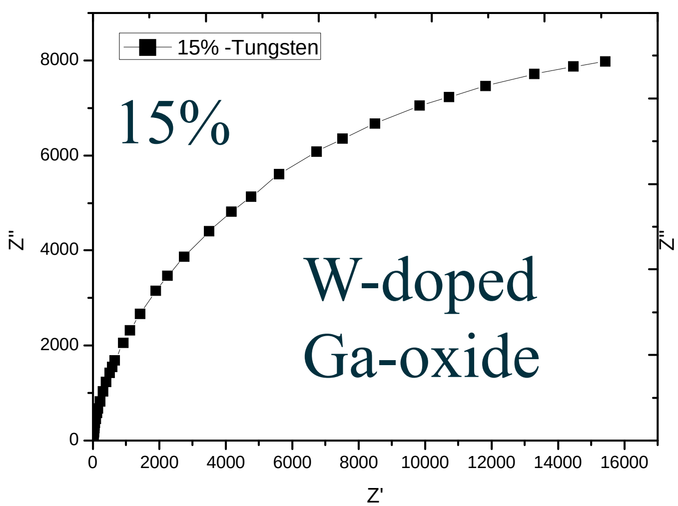


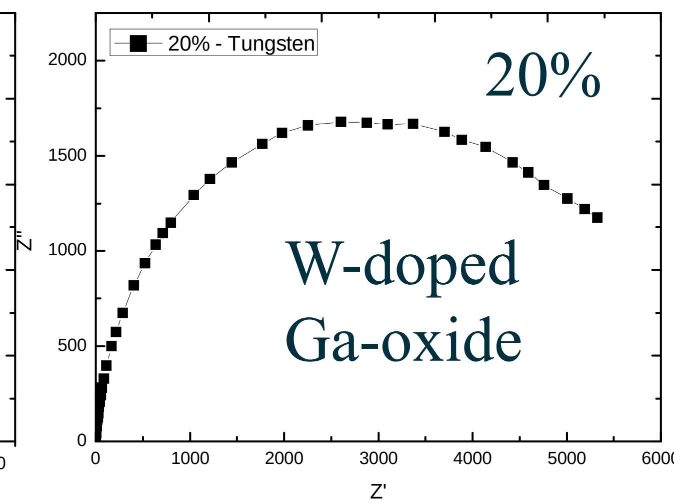
- ❖W-doped films showed being sensible to H_2 and O_2.
- ❖O_2 sensitivity increased from 10% to 15% of O_2 into Ar, but decrease again at 20%
- ❖Sensitivity to gases was optimum in Ar environment, but small-to-non response in a mixture of Ar+Air

Electrical Impedance Analyses

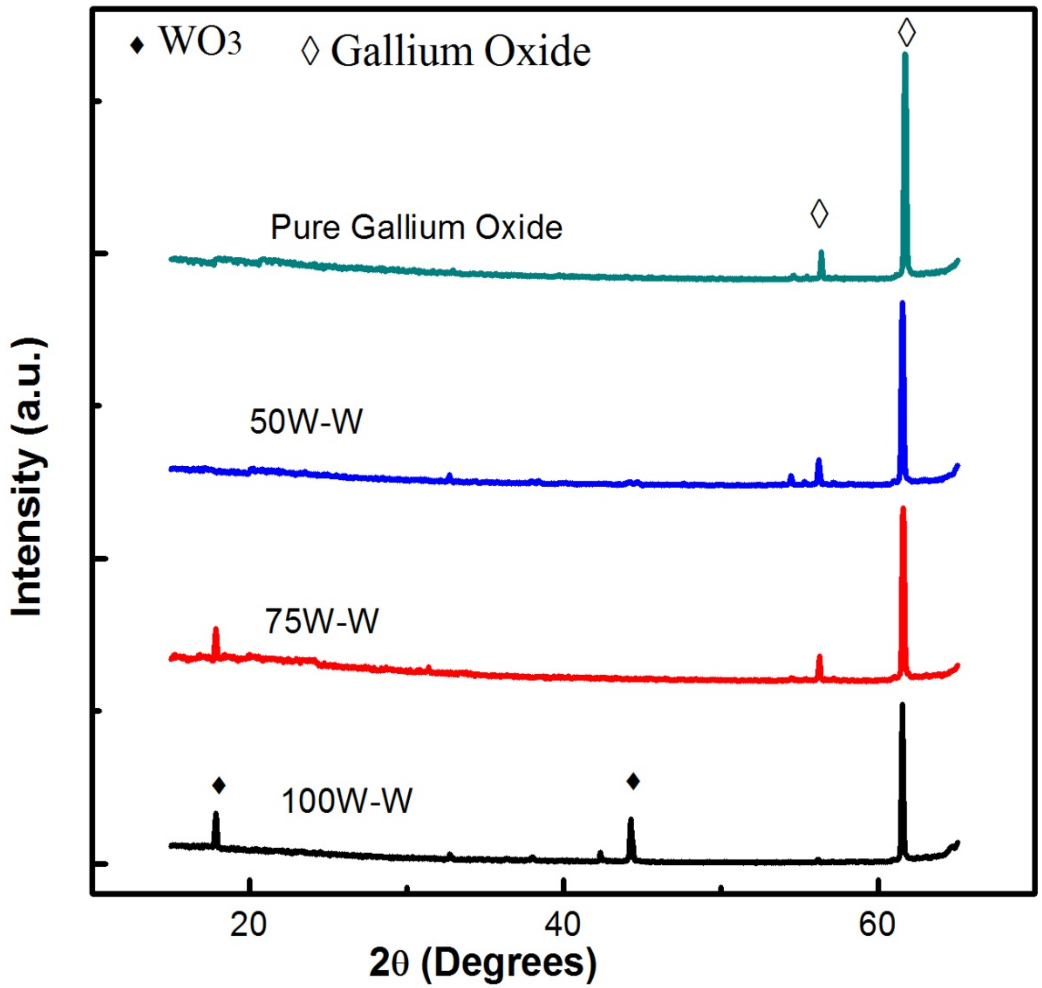






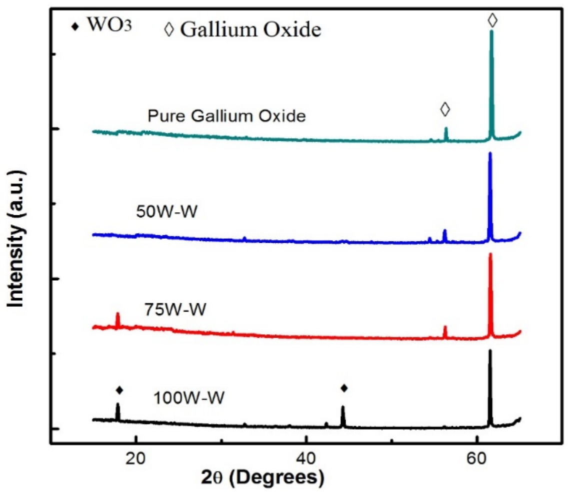


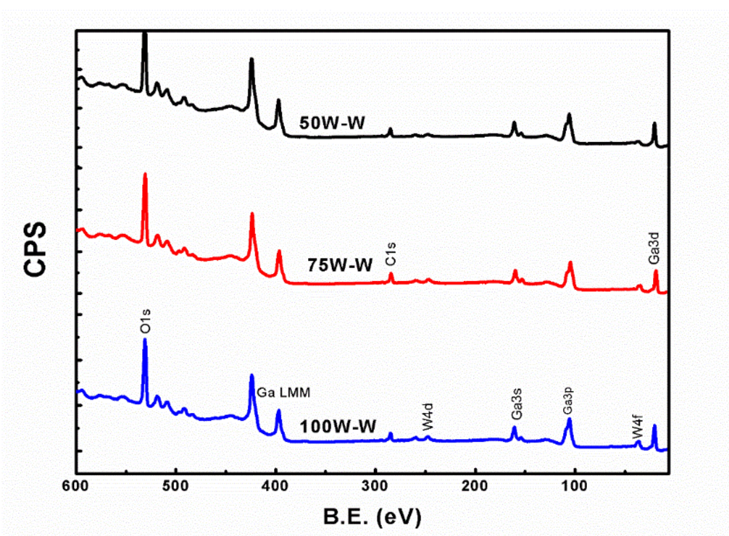
Crystal Structure – (after annealing)



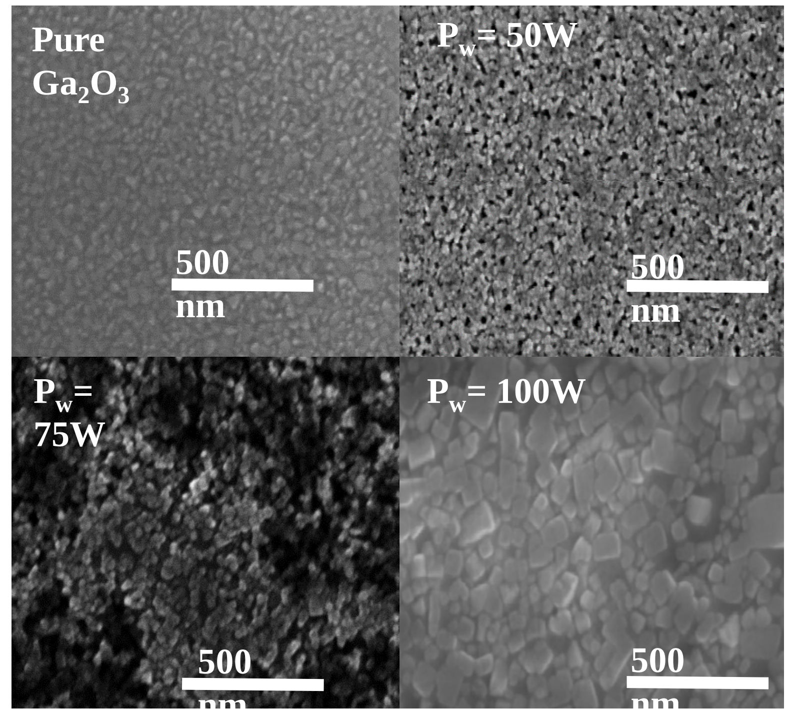
Deposition Temperature T_s=500 °C; Annealing Temperature T_a=700 °C for 30 min

Heat Treatment

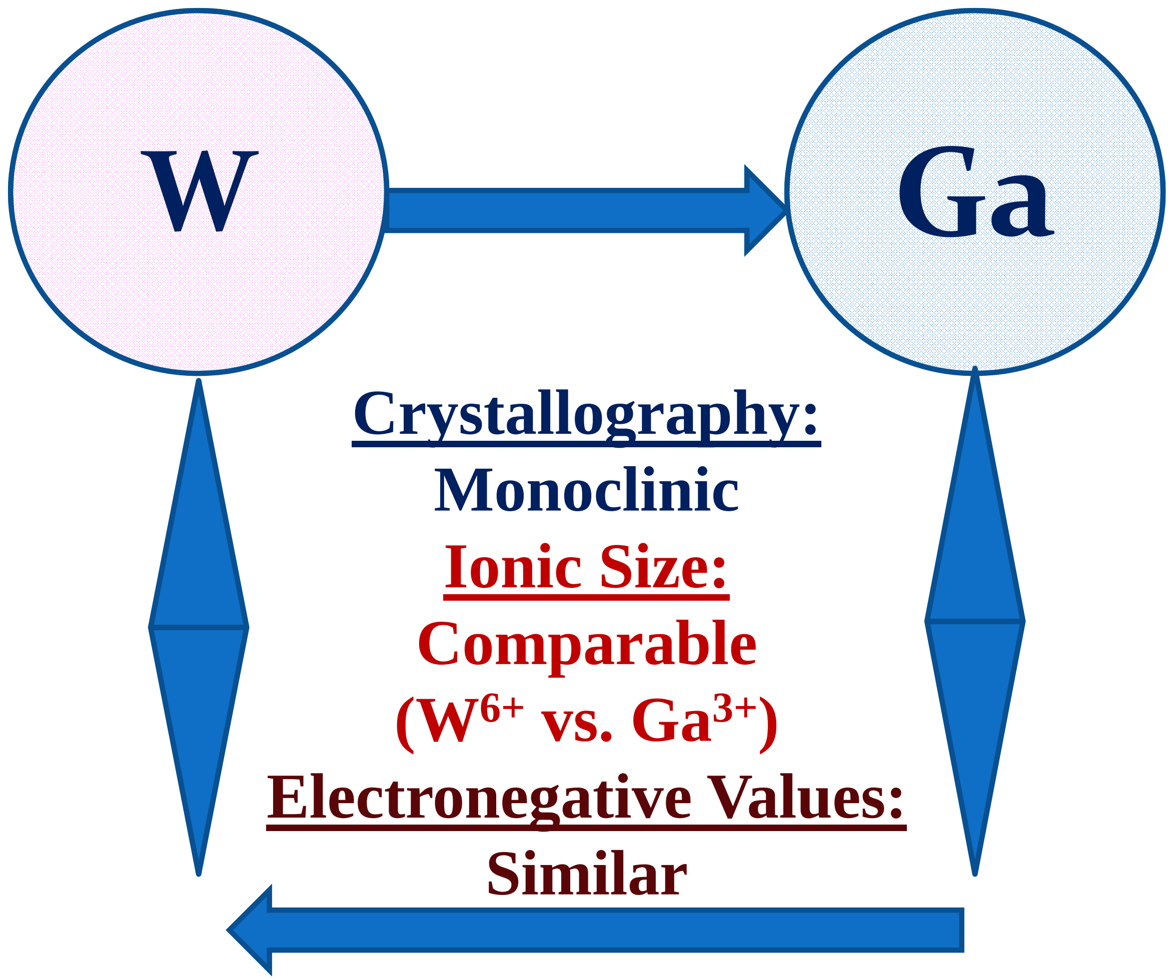




- β-phase is stable for all films after annealing
- surface morphology suffer porous formation for W-doped films. Evidence of W-self diffusion



How does it work?



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. Two others (under preparation)

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)

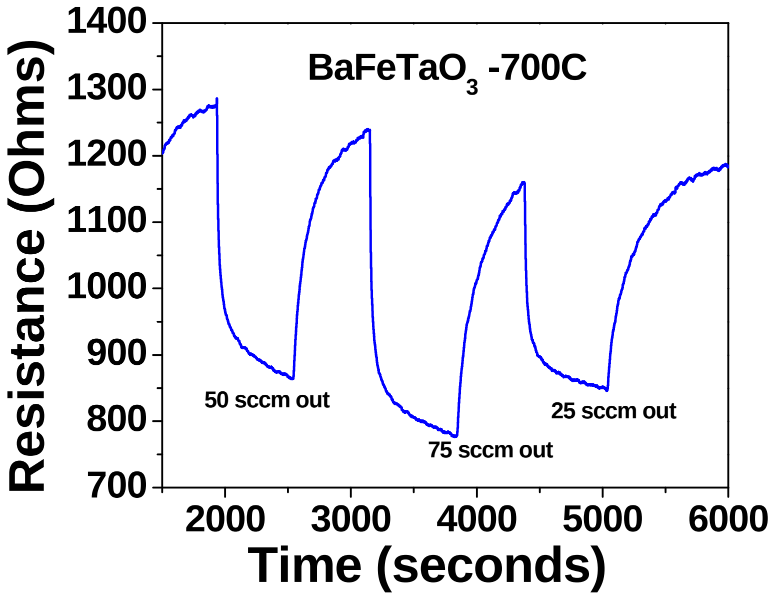
Conference Presentations:

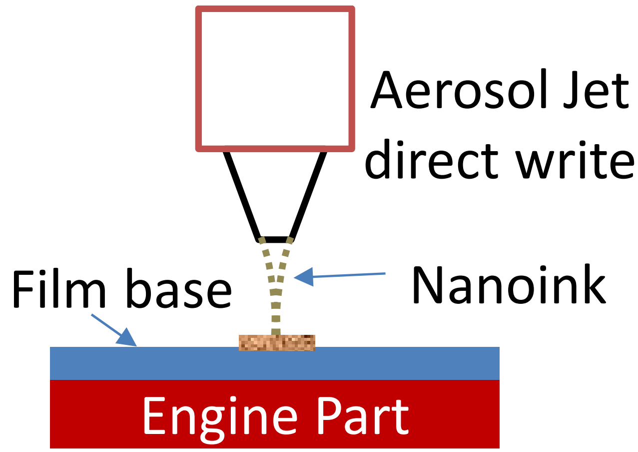
1. International Materials Research Congress (IMRC) – to be presented (2015)
2. Southwest Energy Symposium, 2015, El Paso, TX
3. TMS – 2014; ICMCTF - 2015
4. ICMCTF-2013, San Diego, CA
5. AVS International Symposium, 2012
6. Southwest Energy Symposium, March 24, 2012, El Paso, TX

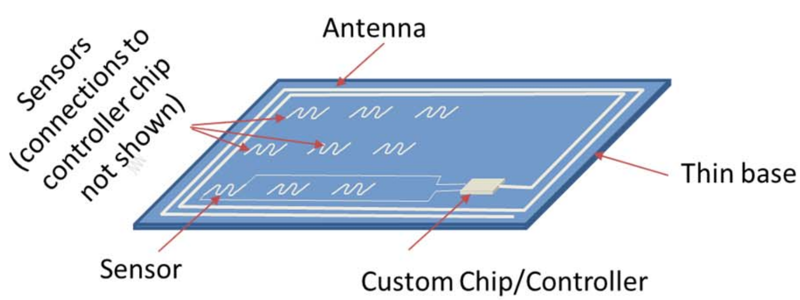
Summary and Conclusions

- Optimum conditions were established to fabricate Ga_2O_3 and W-doped Ga_2O_3 with the stable β-phase (monoclinic)
- Intrinsic Ga_2O_3 and W-doped Ga_2O_3 demonstrated to be sensitive to oxygen at high temperatures, with improved time of response for W-incorporation

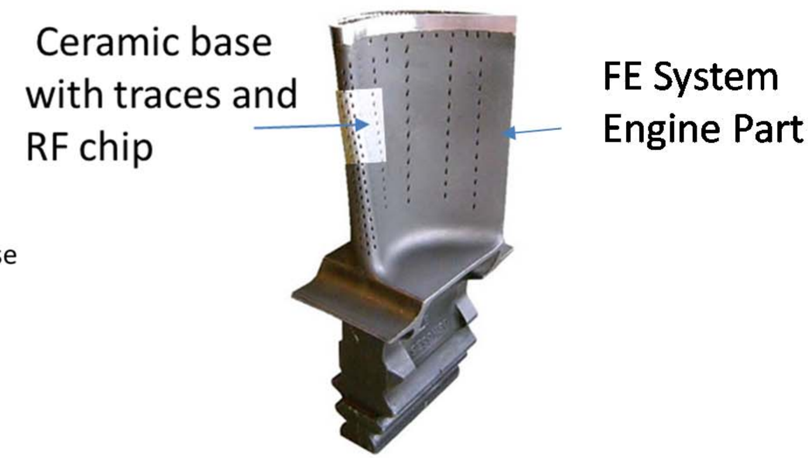
Future Work





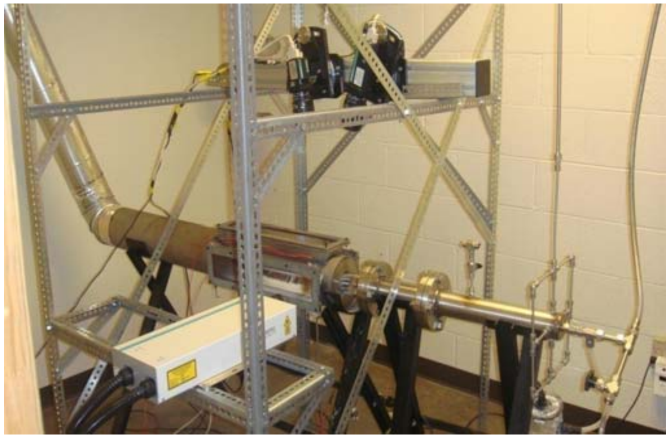


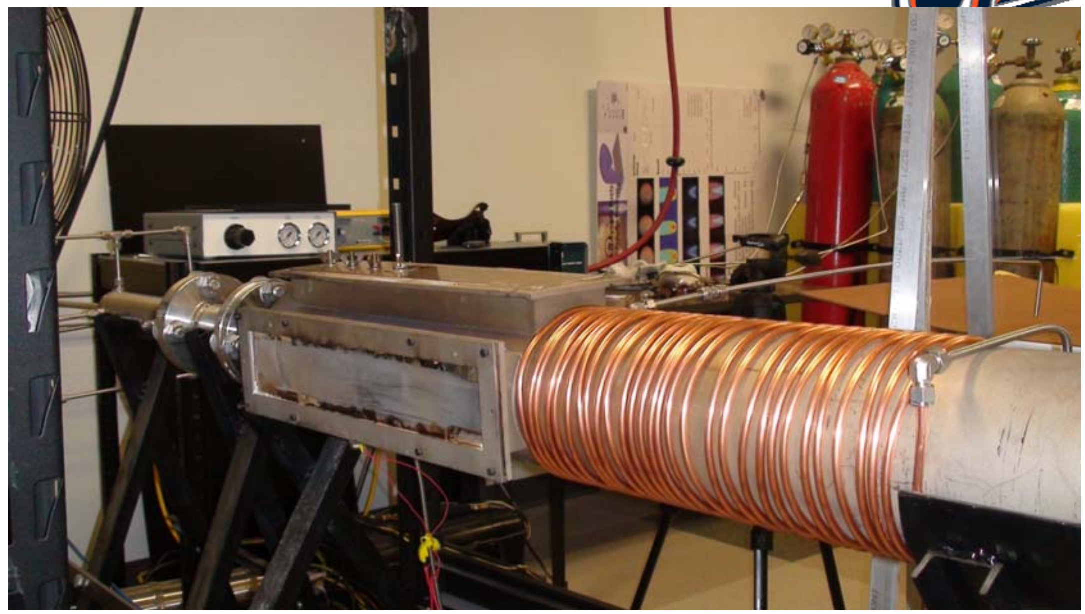
Sensor Sysem

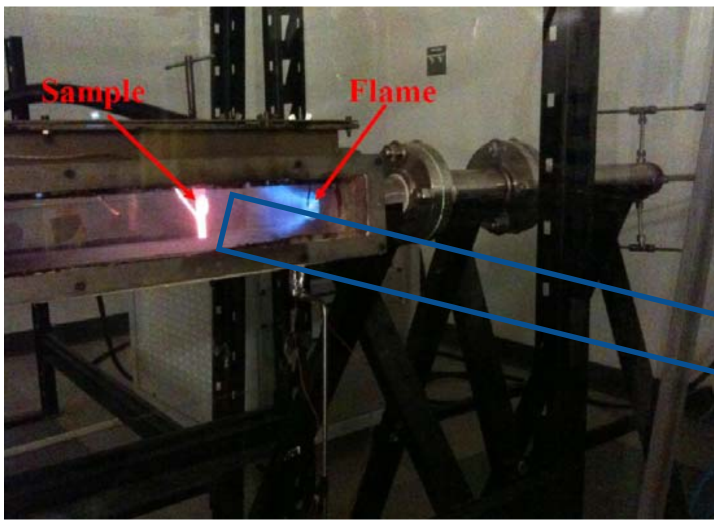


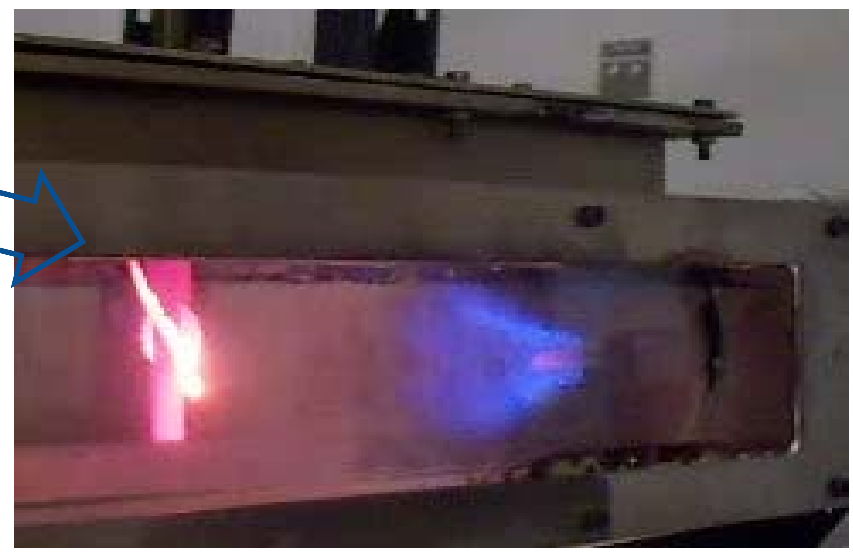
Final Objective

Future Work









Acknowledgements

- DOE-NETL
- EMSL/PNNL, Richland, WA
- Michael Carpenter (SUNY)

THANK YOU!