Gallium Oxide Nanostructures for High Temperature Sensors

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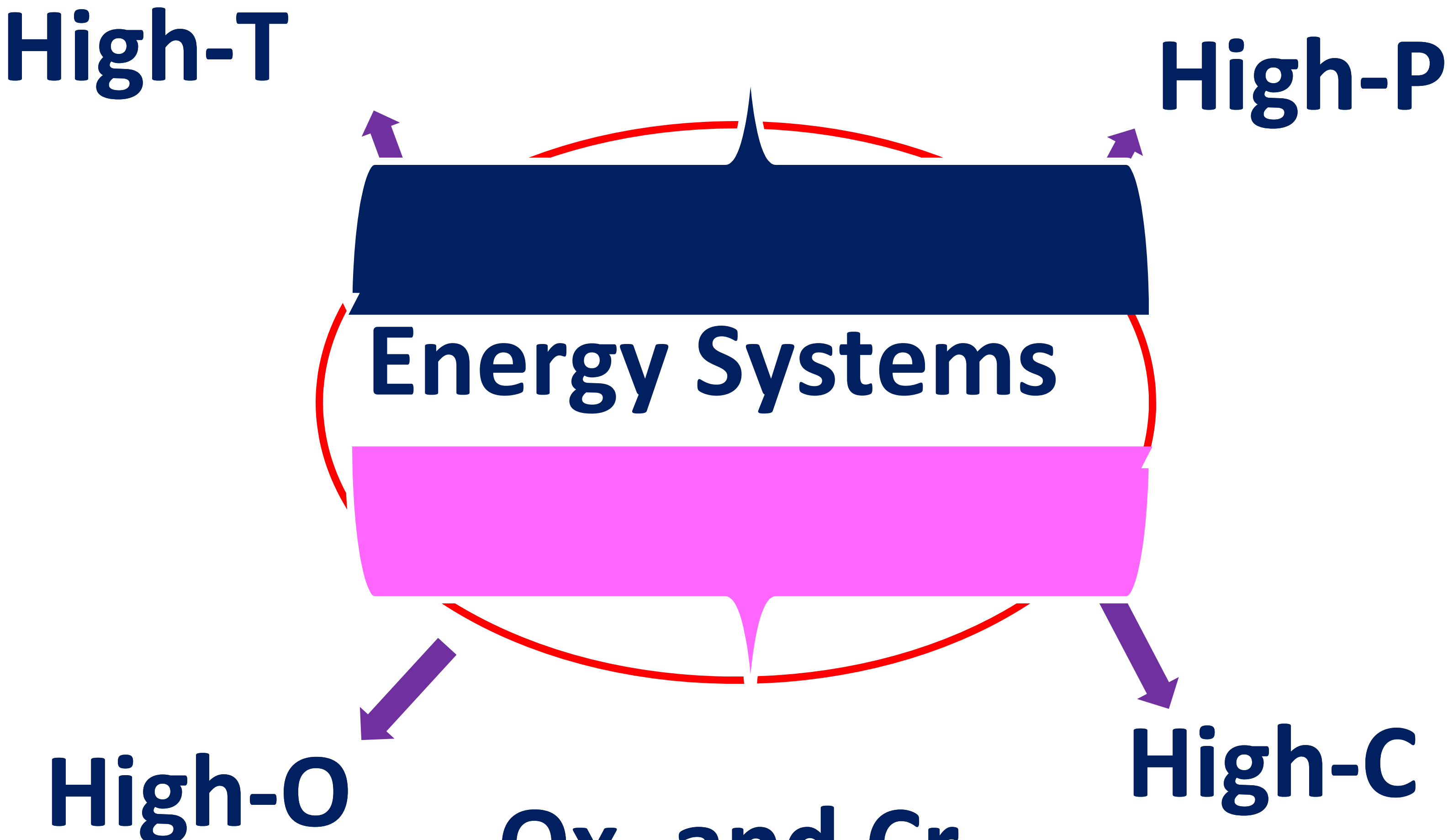
Project: DE-FE0007225
Project Period: 10/01/2011 to 09/31/2014

Outline

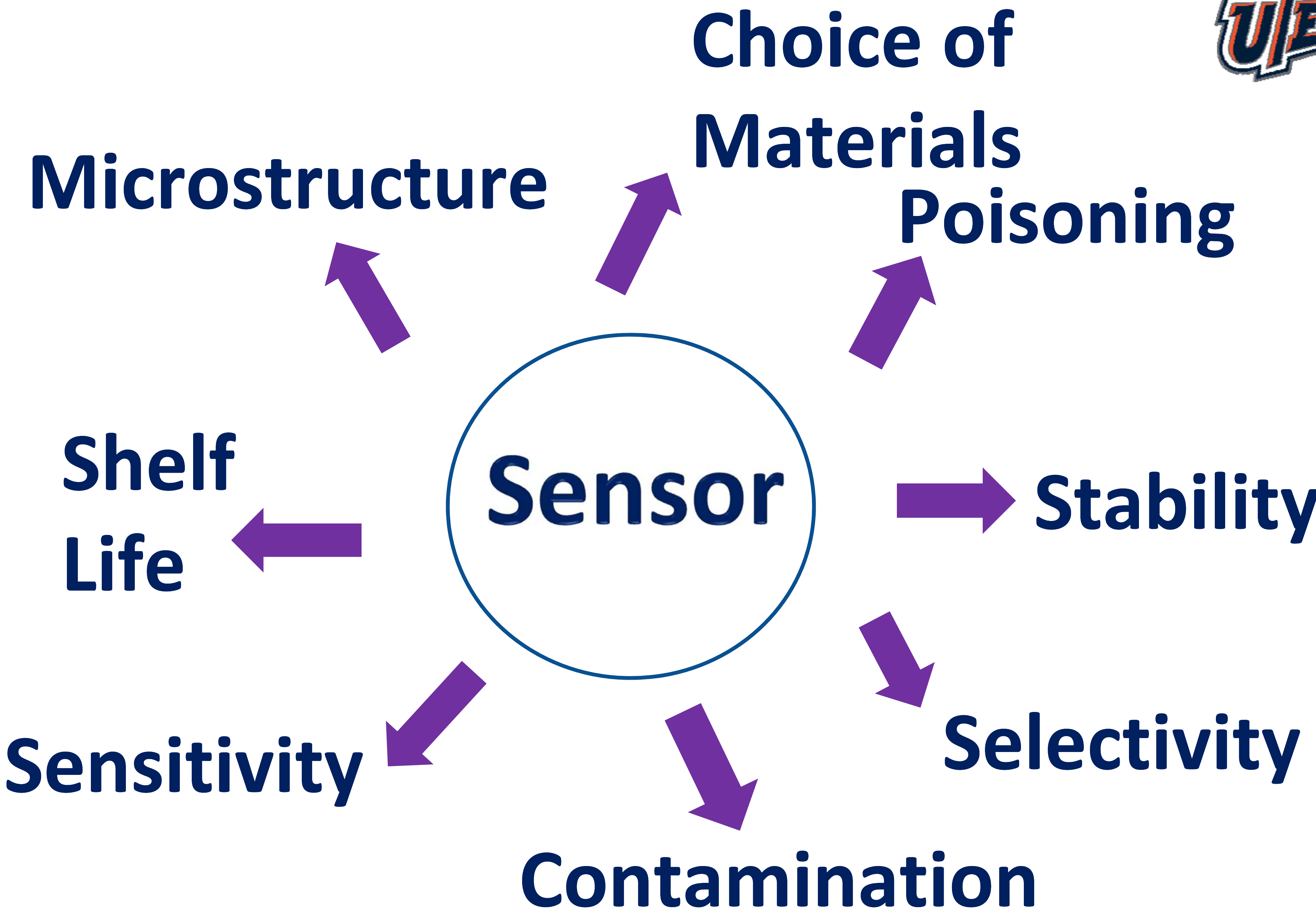
- Introduction
- Research Objectives
- Experiments
  - ► Synthesis
  - ► Characterization
- Results and Discussion
  - ► Pure Ga_2O_3 Thin Films
  - ► W-doped Ga_2O_3 Thin Films (Physical Methods)
- Summary & Future Work

Introduction

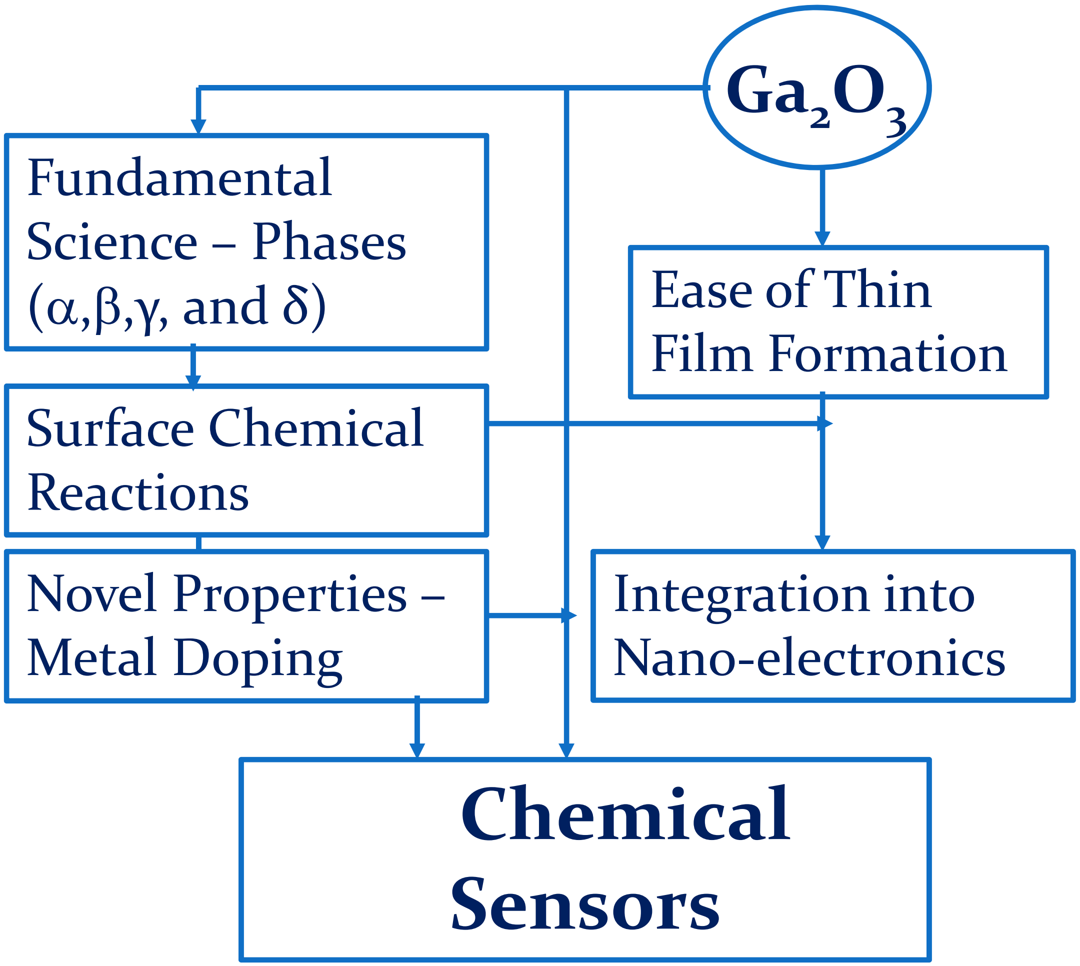
T,P Tolerance



Ox. and Cr. Resistance


Choice of Materials
Microstructure
Poisoning
Shelf Life
Sensor
Stability
Sensitivity
Selectivity
Contamination

Gallium Oxide (Ga_2O_3)



♦ 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.

Sensing Mechanism

At $T > 700\ ^{o}C$, defects → equilibrium with surrounding atmosphere → n type conductivity → depends on oxygen partial pressure

$$\sigma = \sum_i P_{O_2} \exp\left(\frac{-E_A}{k_B T}\right)$$

Electrical conductivity

Activation energy

Oxygen partial pressure

Boltzmann constant

Temperature

At $T < 700\ ^{o}C$, Ga-oxide exhibits sensitivity to reducing gases (CO, H_2)

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 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-based nanostructures)

Experiments

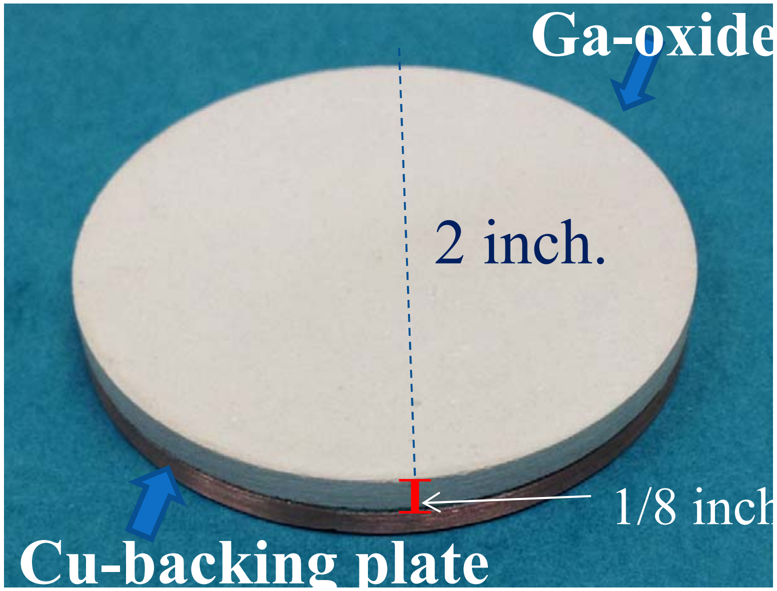
Materials

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→100 W

- Target-Substrate distance: 7 cm

- Sputtering gas: Argon + O_2

Variables:

Sample set 1 (Intrinsic):

Substrate Temperature: RT-500 ˚C

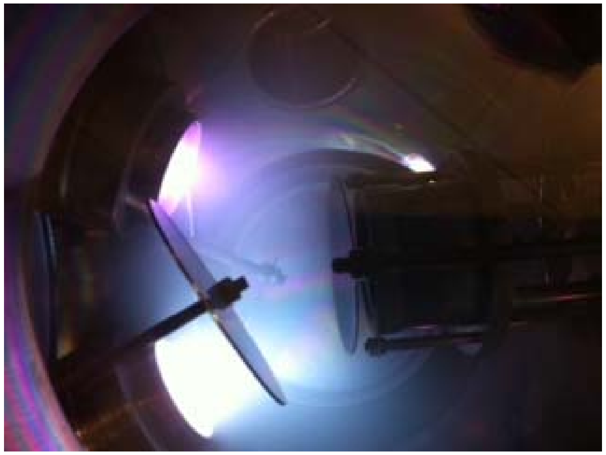
Sample set 2 (W-Doped):

Tungsten Target Power (50 to 100W)

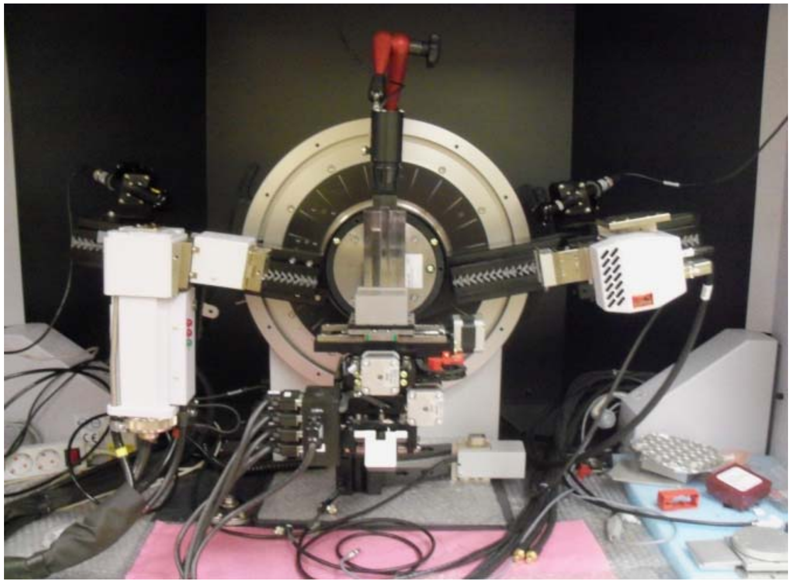
Substrate Temperature = 500 ˚C

Sample set 3 (W-Doped):

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



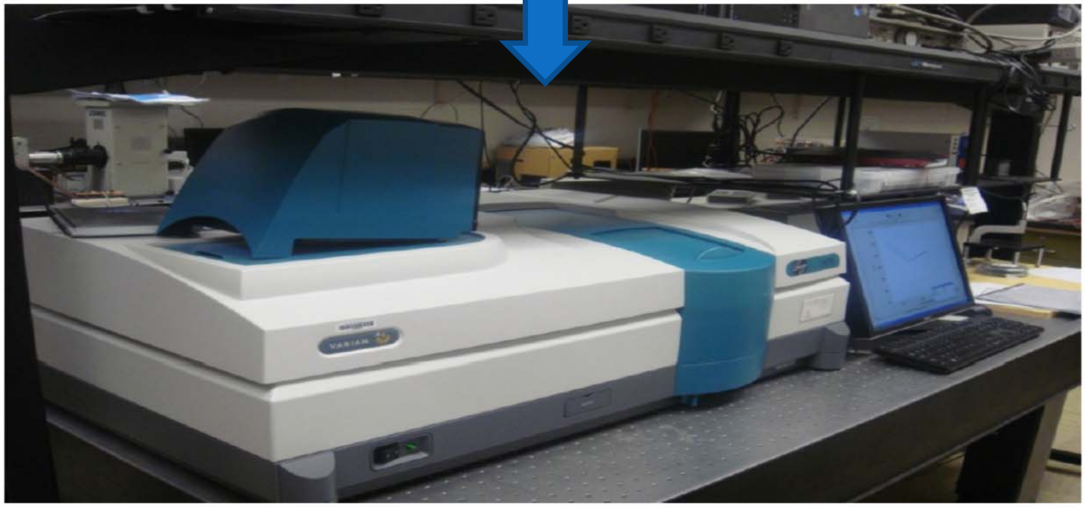
Characterization

Characterization (cont.)

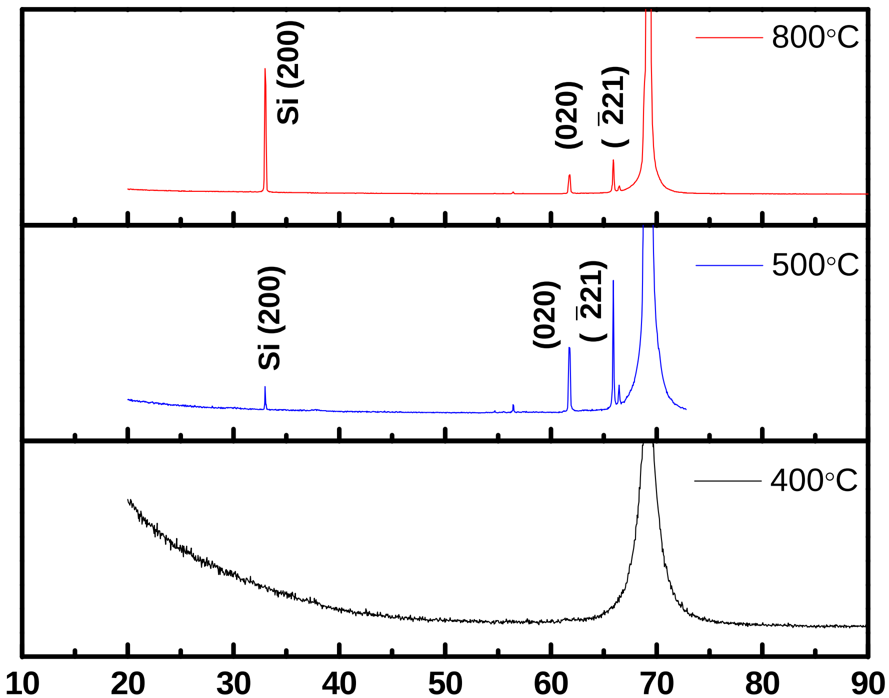
High Temperature Furnace for annealing process

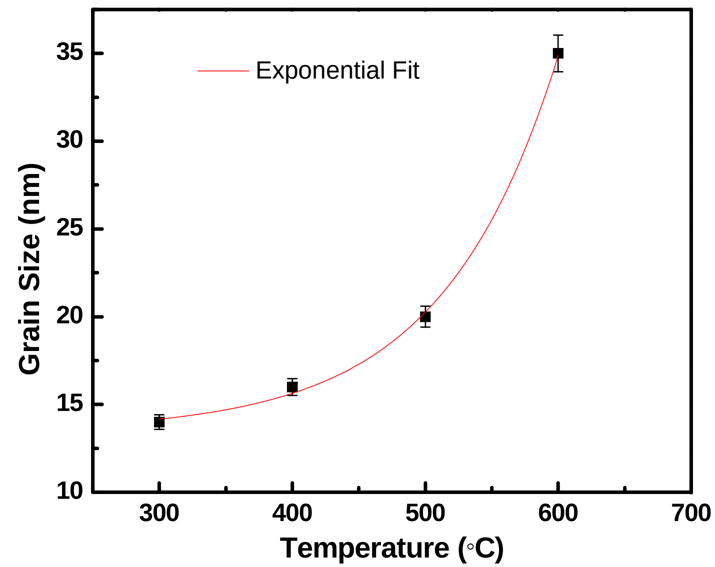
UV-vis-Spectrophotometry



Results and Analysis

Crystal Structure





500 °C is favorable 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

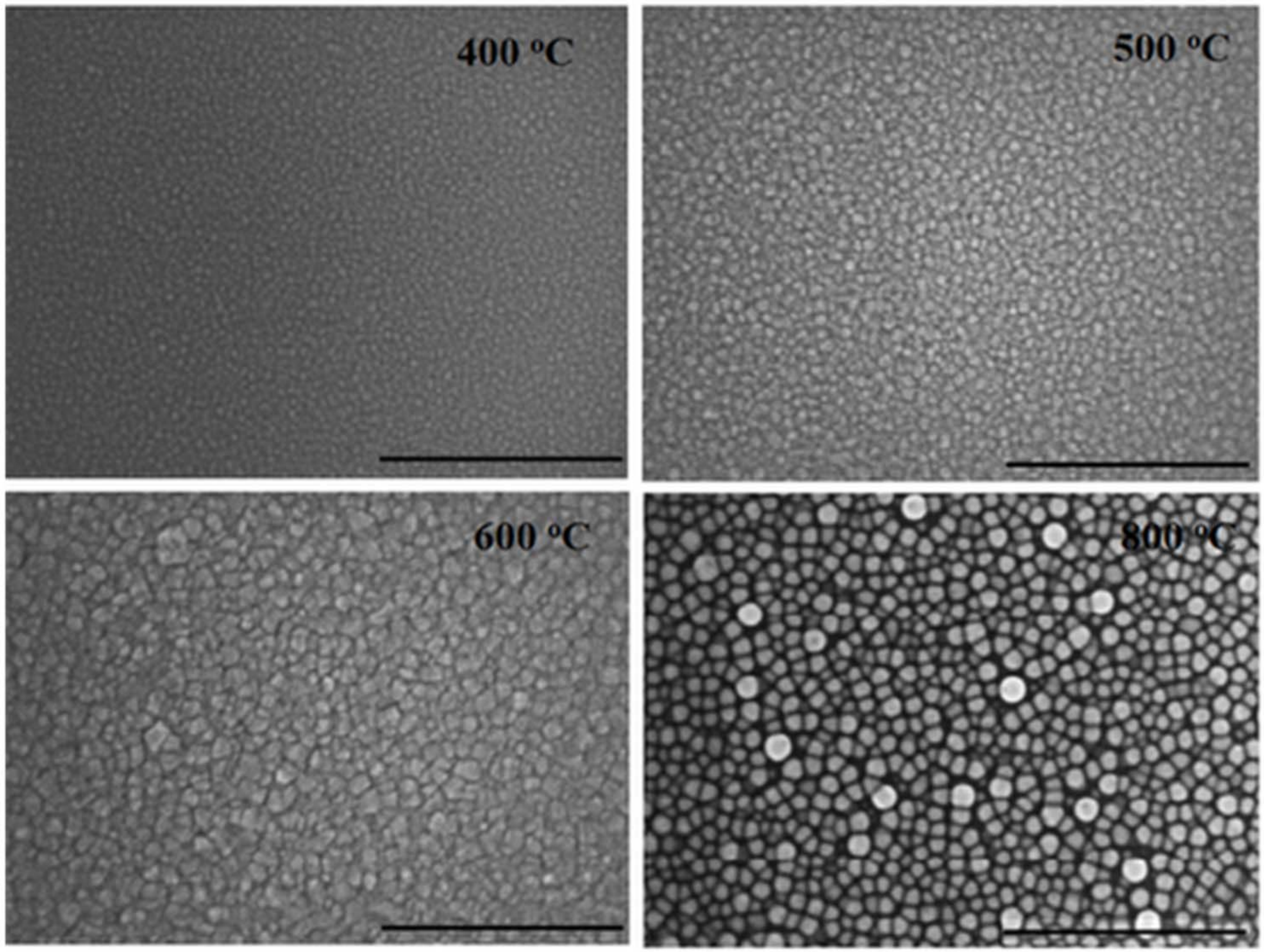
(film, substrate materials)

ΔE: Activation energy,

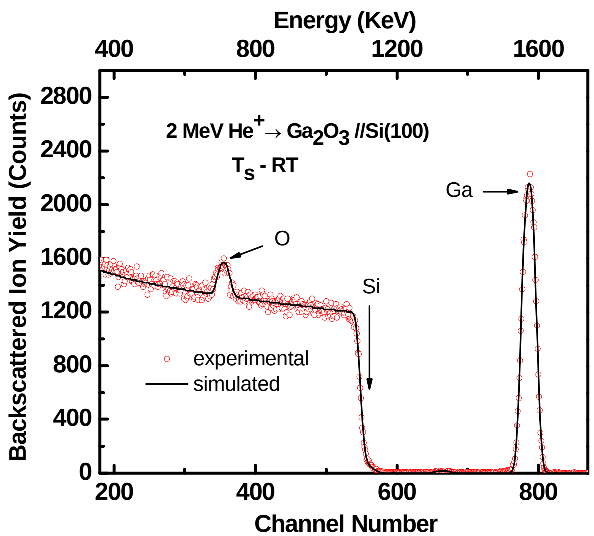
k_B: Boltzmann constant and

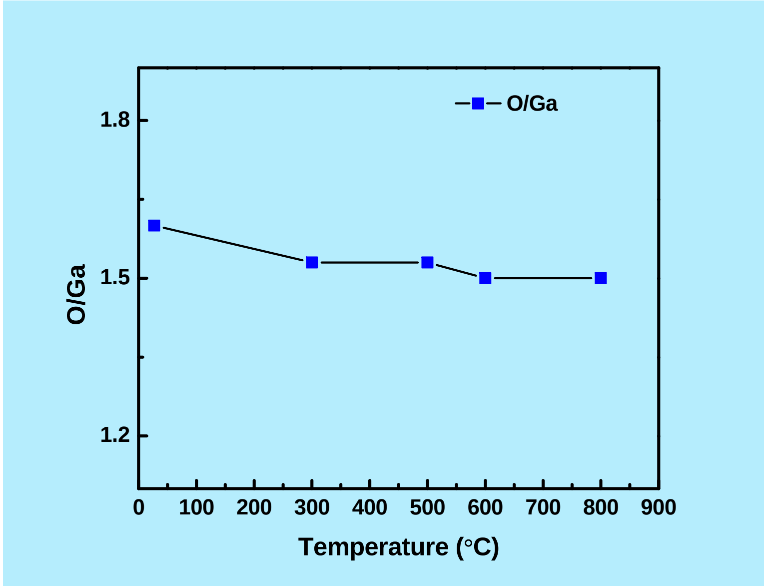
T: Absolute temperature.

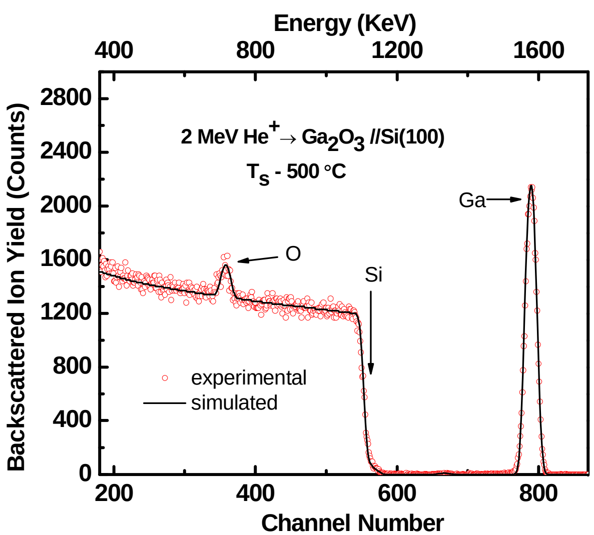
Morphology

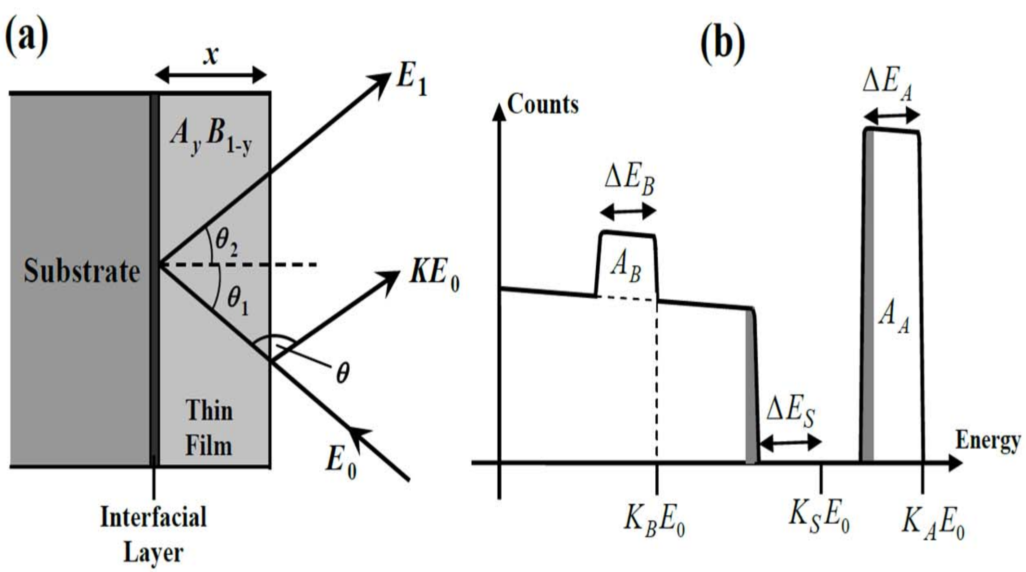


Composition - RBS

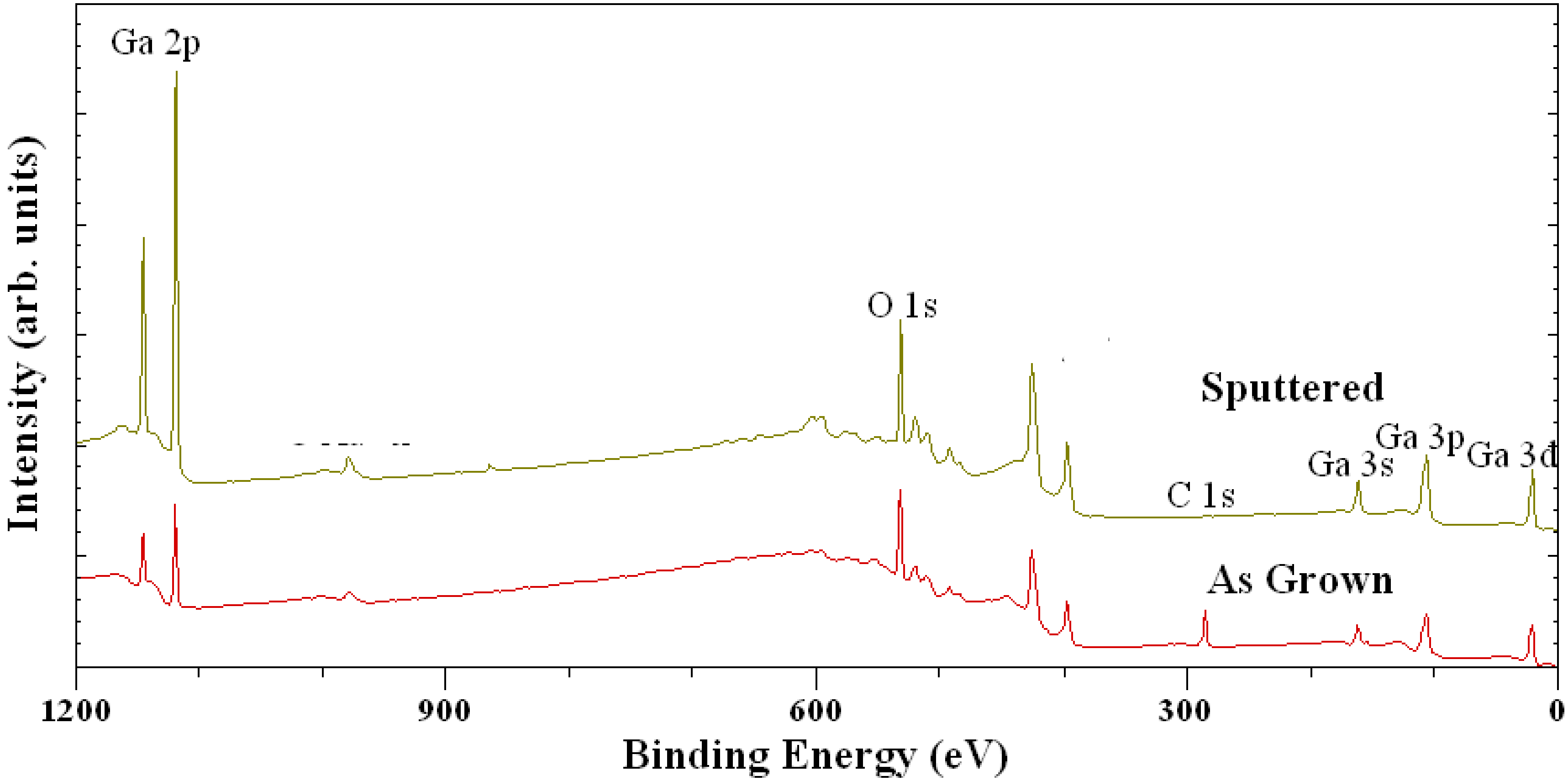








Composition - XPS

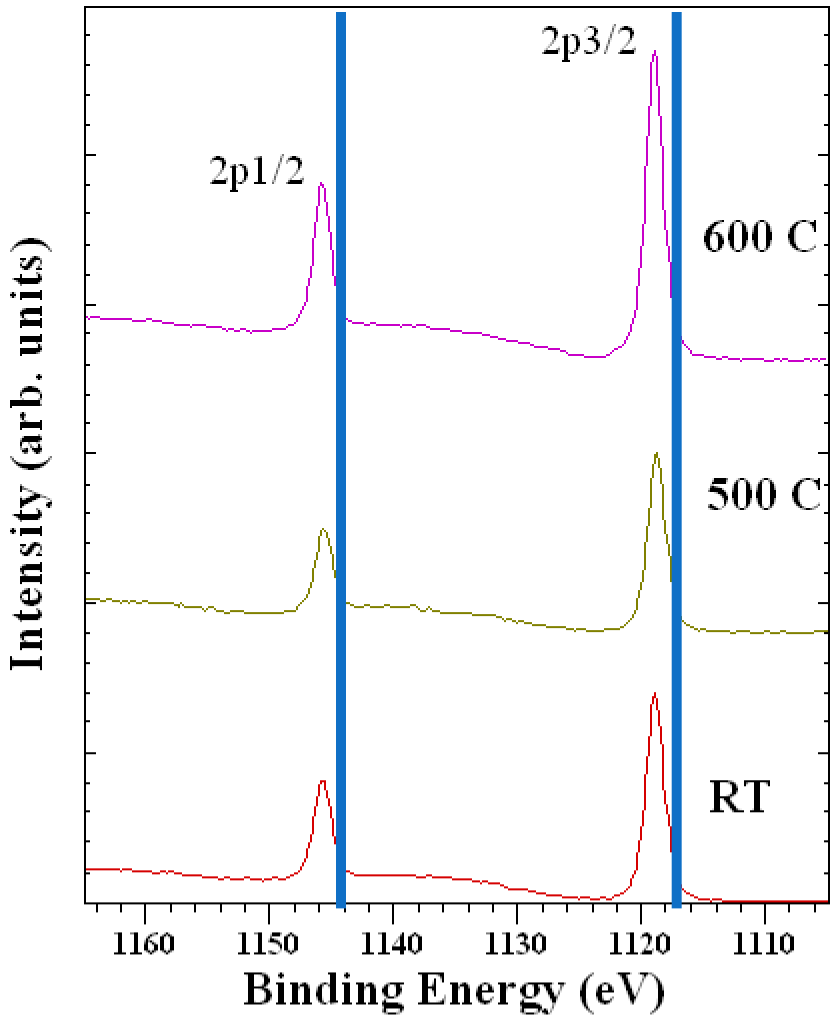


Ga 2p peak

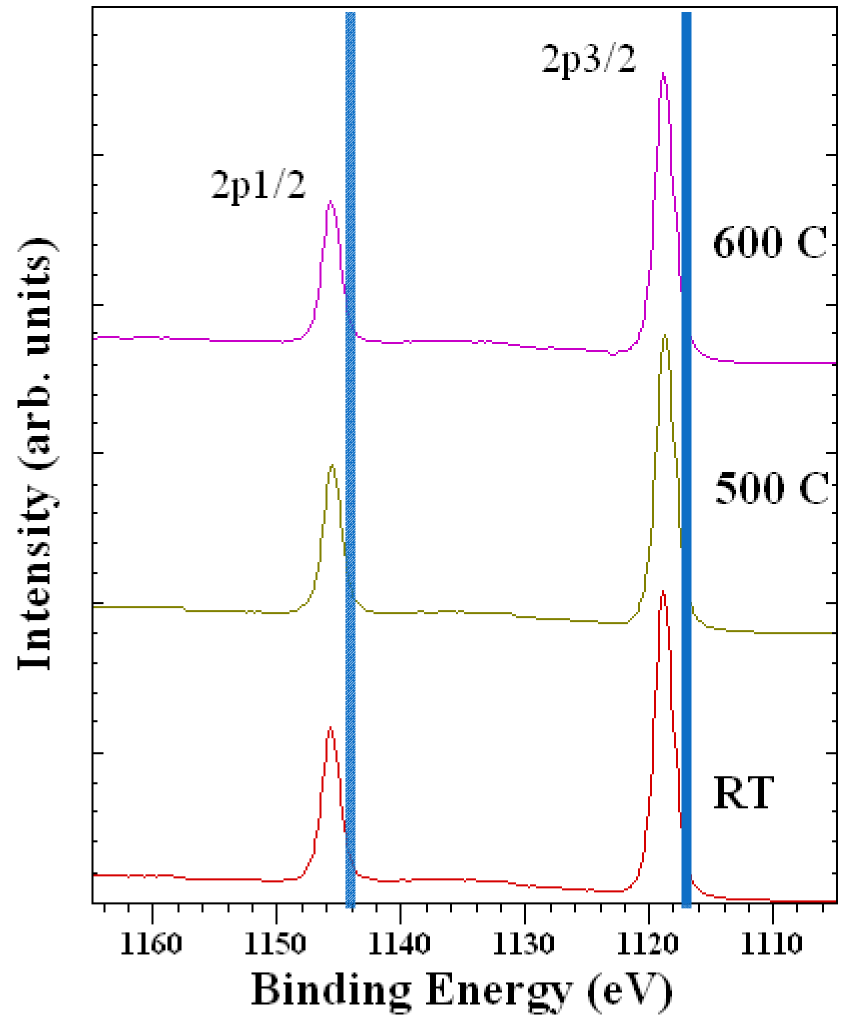
Chemical Shift in Ga 2p BE – ~1118 eV; ~1145 eV

Original Ga 2p BE – 1117eV; 1144 eV (represented by blue lines)

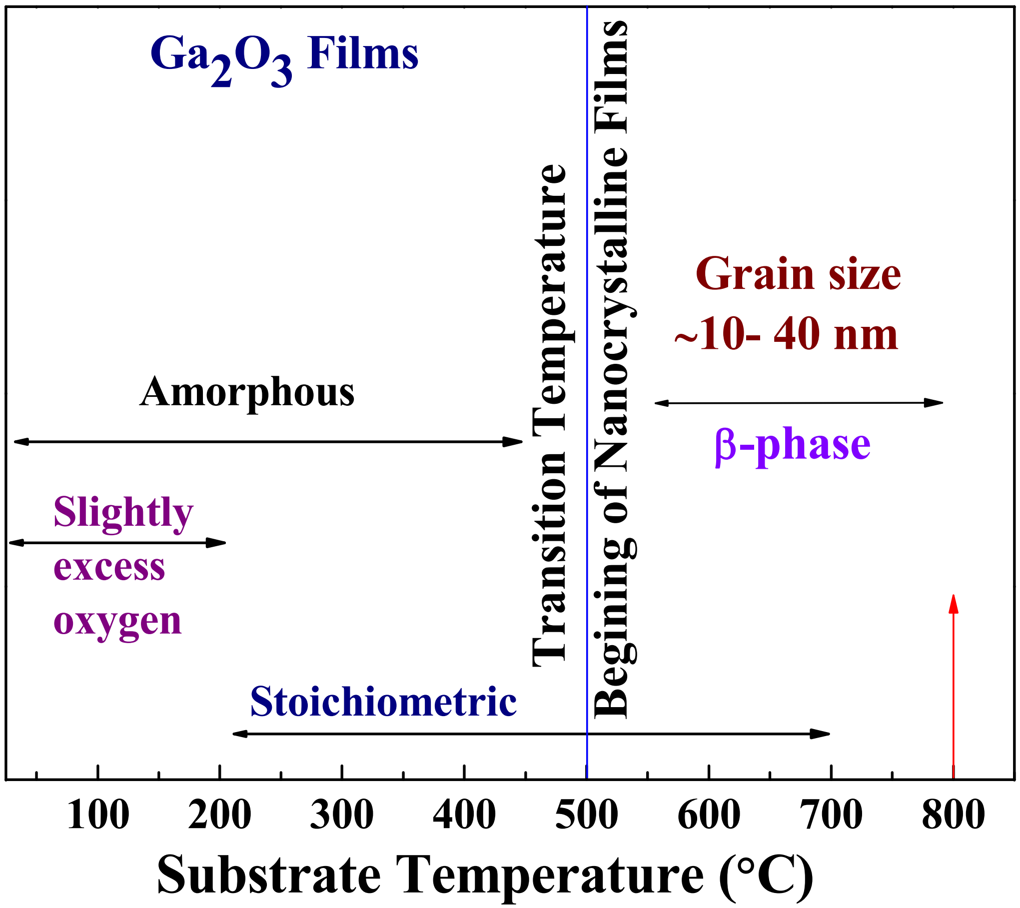
- As Grown



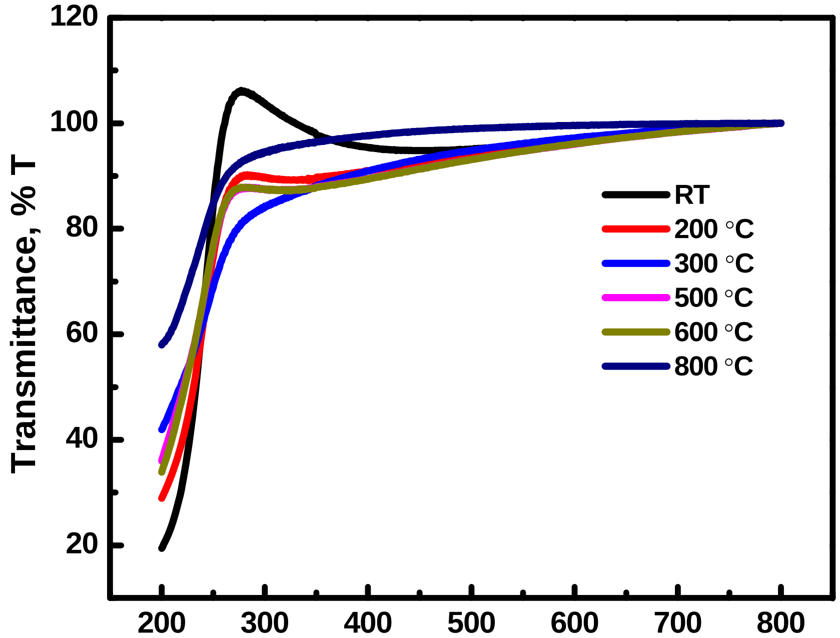
- Sputtered

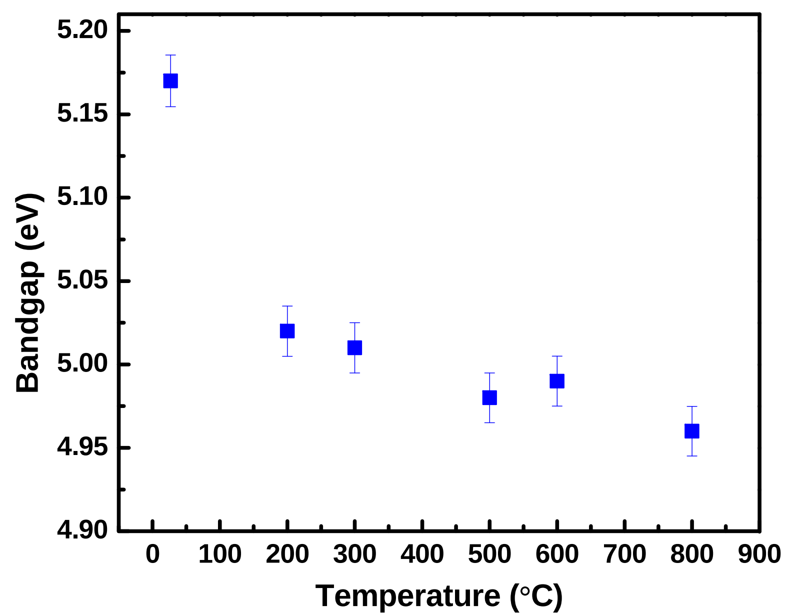


Microstructure – Phase Diagram



Electronic Properties





$(\alpha h\nu) = B\ (h\nu - E_g)^{1/2}$

$h\nu$: energy of the incident photon,

α: absorption coefficient,

B: absorption edge width parameter,

E_g:band gap.

$\alpha = [1/t]\ln[T/(1-R)^2]$

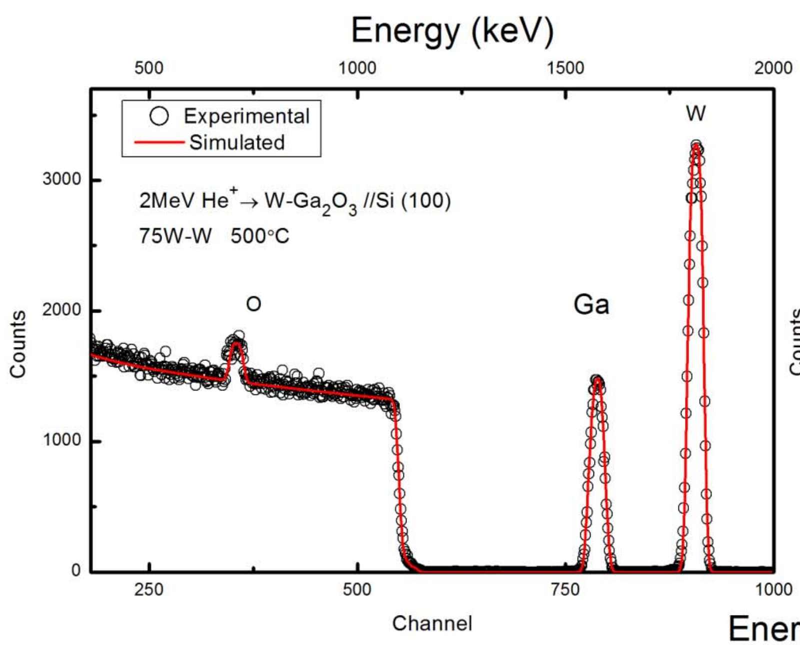
T: transmittance

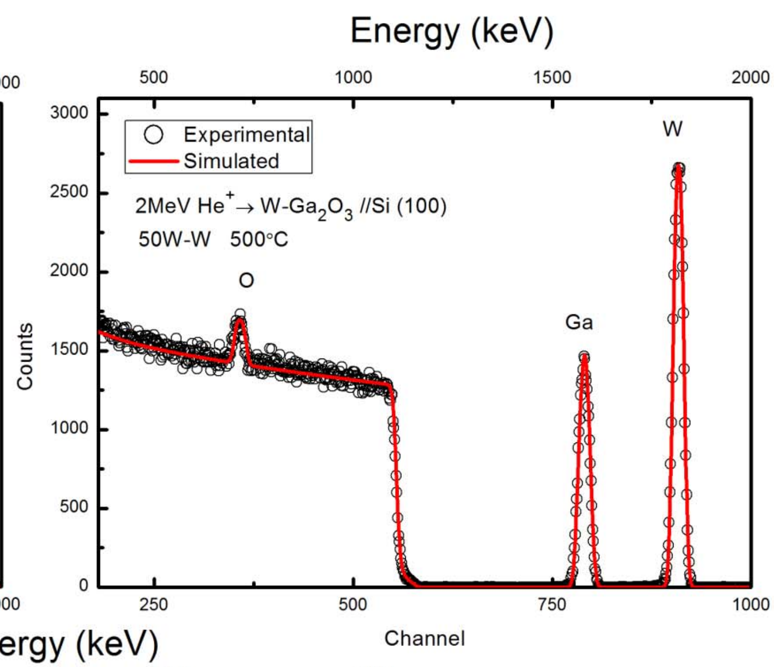
R: reflectance

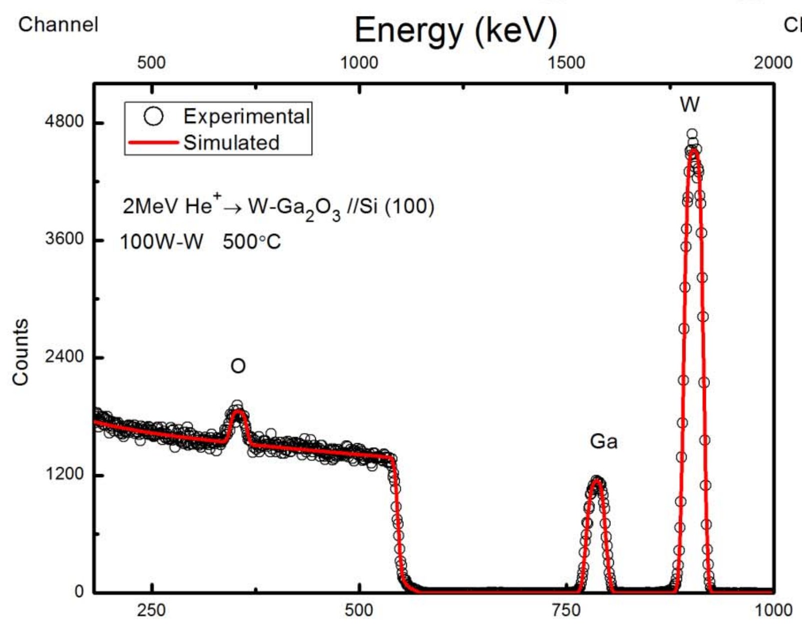
t : film thickness

Tungsten Doping

Chemical Composition (RBS)

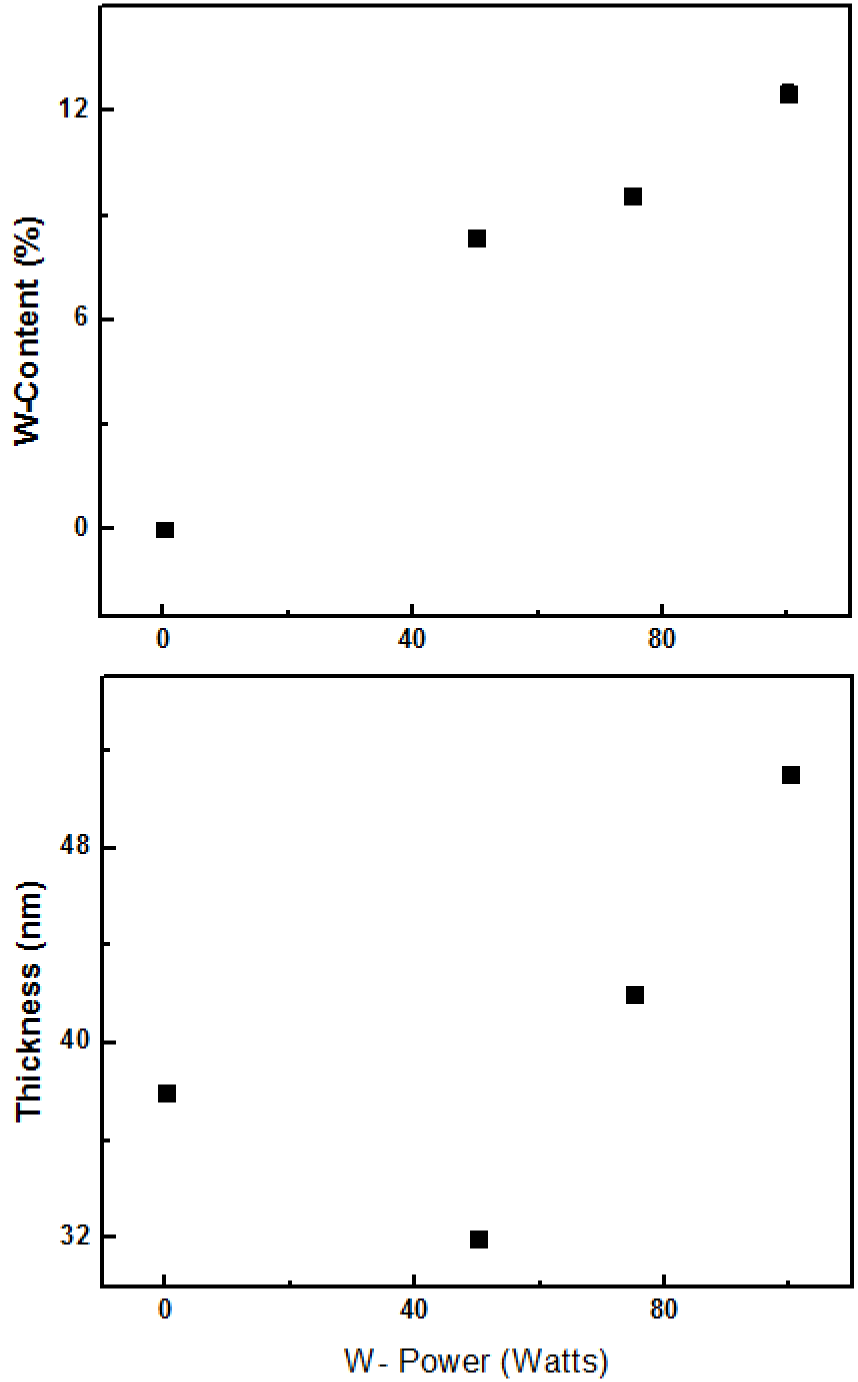




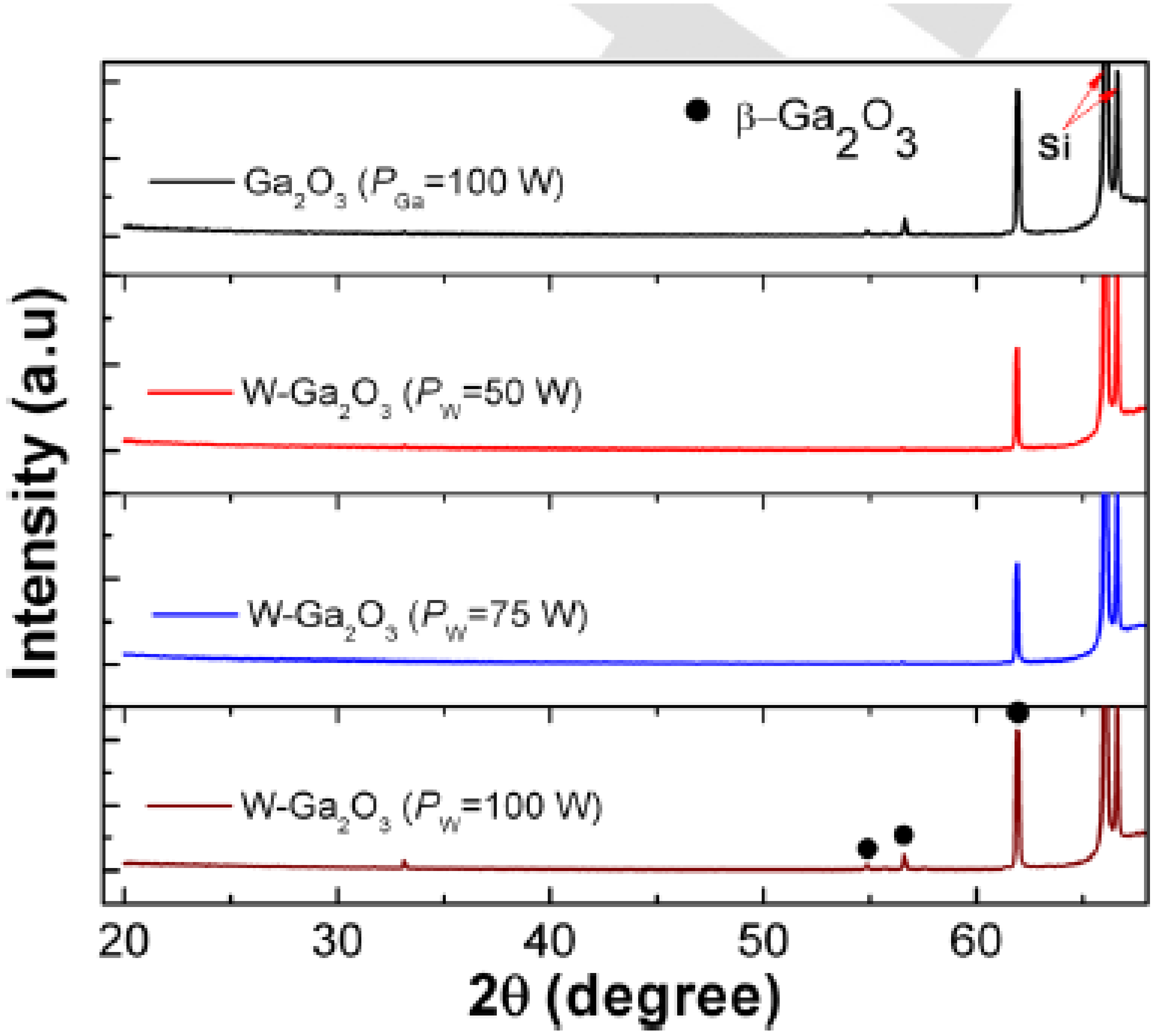


W-Doped films

W-Power (Watts)	W-Content (Atomic %)	Thick -ness
0	0	38 nm
50	8.35	32 nm
75	9.58	42 nm
100	12.5	51 nm



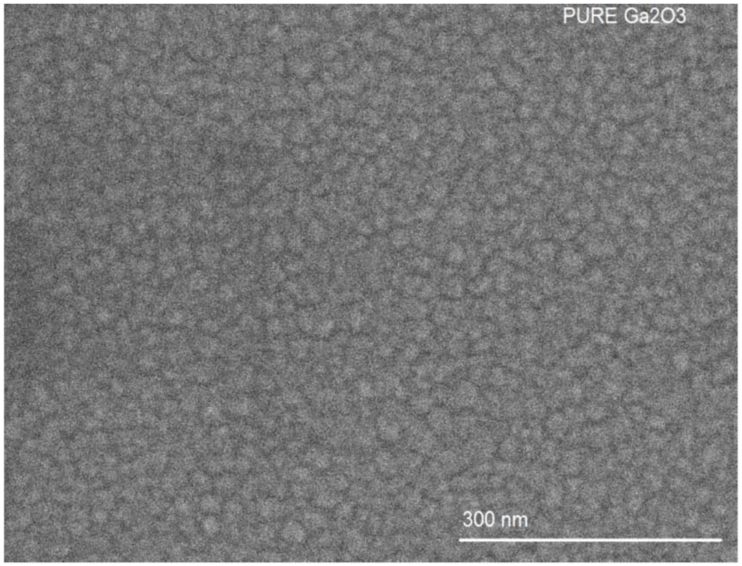
Crystal Structure – Power dependence

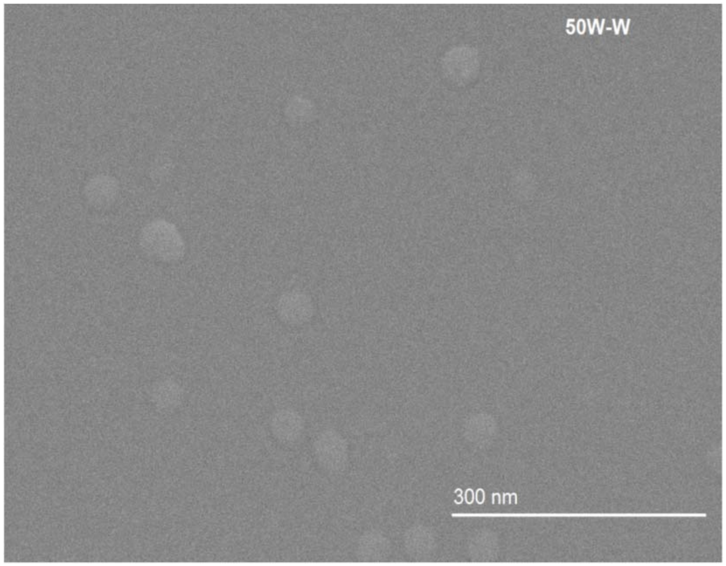


Only Gallium oxide phase is present

No secondary phase formation

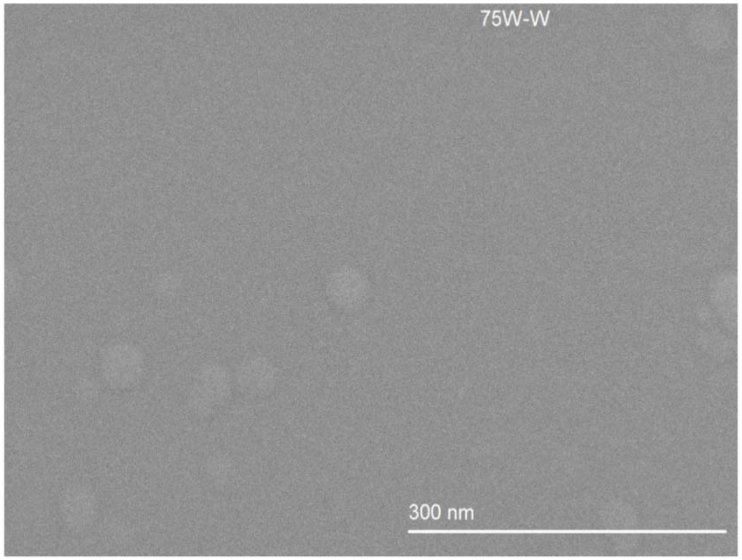
Morphology (Power Dependent)

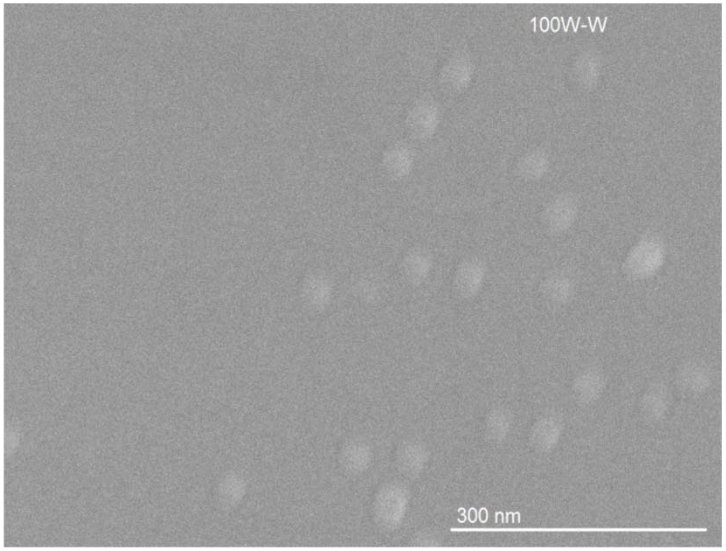




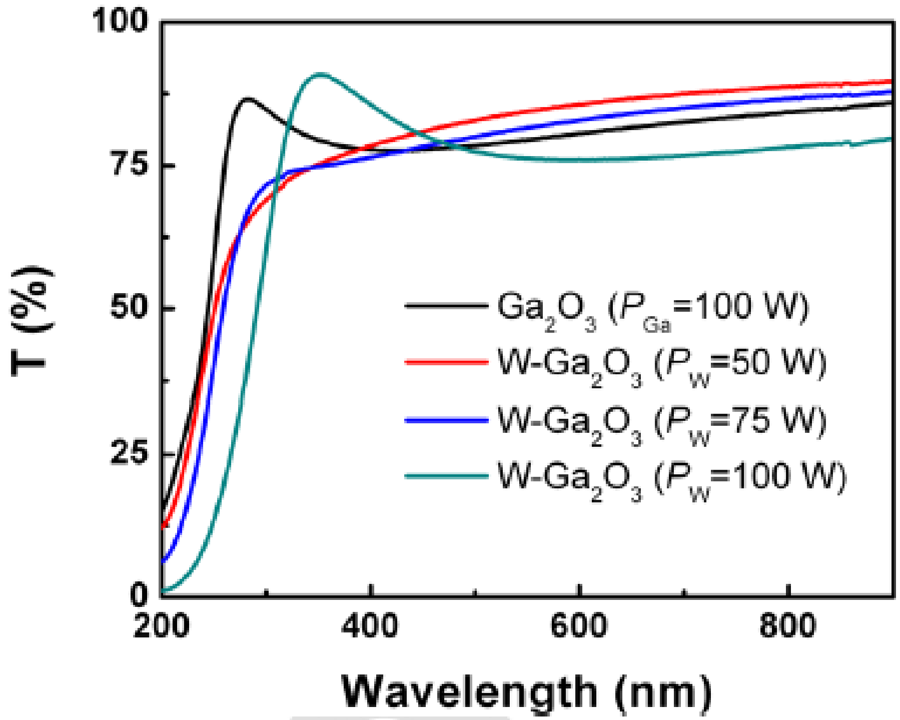
Pure Gallium Oxide Films show grains throughout the surface, and W-doped films avoid crystallites complete growth

T_S=500°C

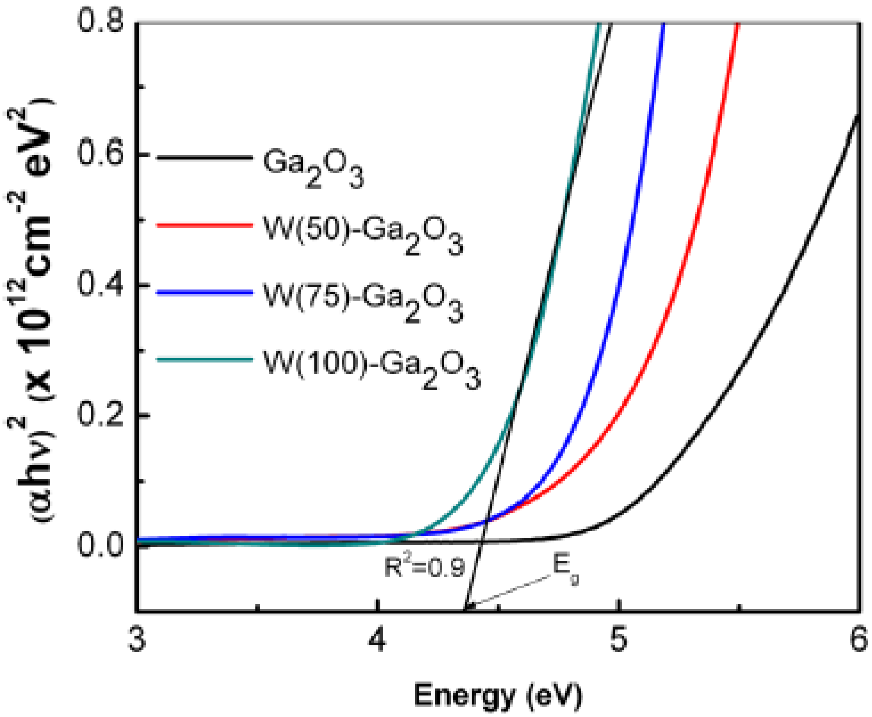




Optical Properties

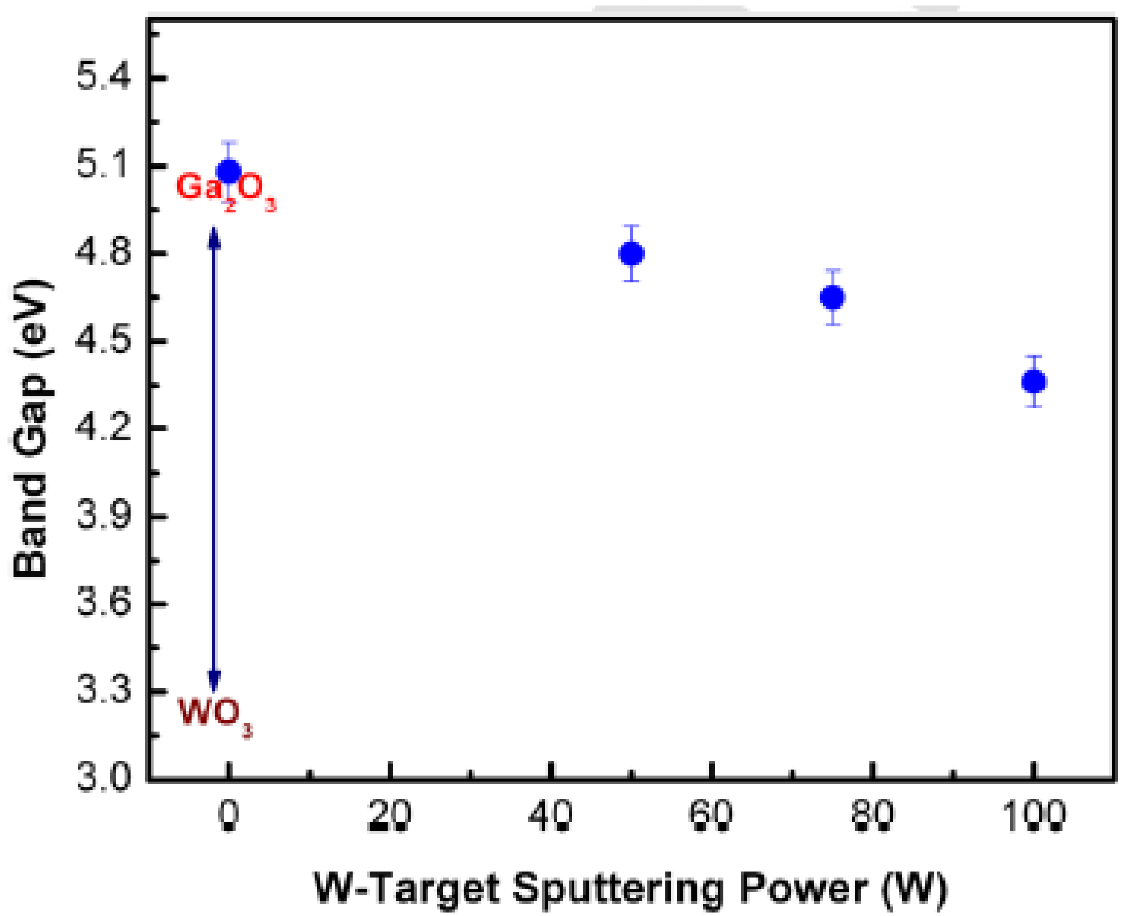


t_{dep}= 30min



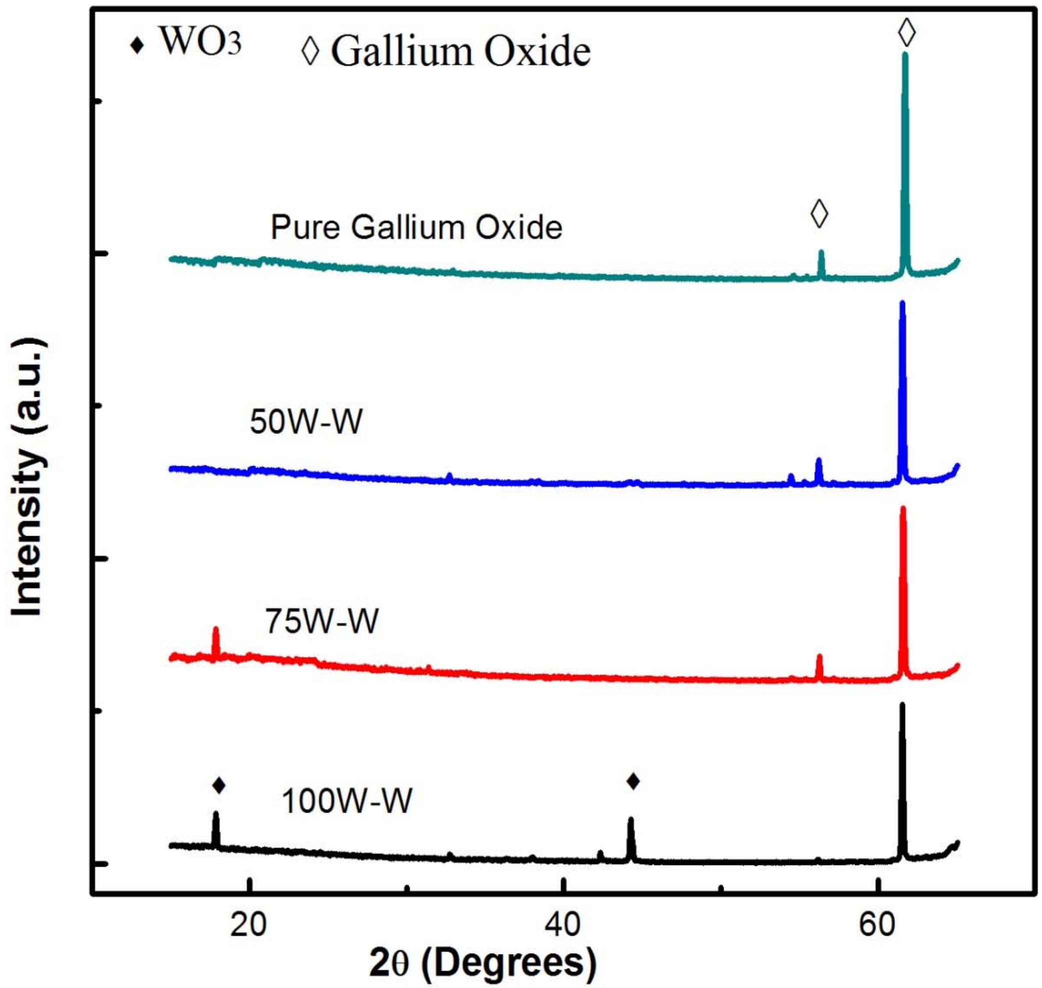
Band Gap (Power dependence)

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



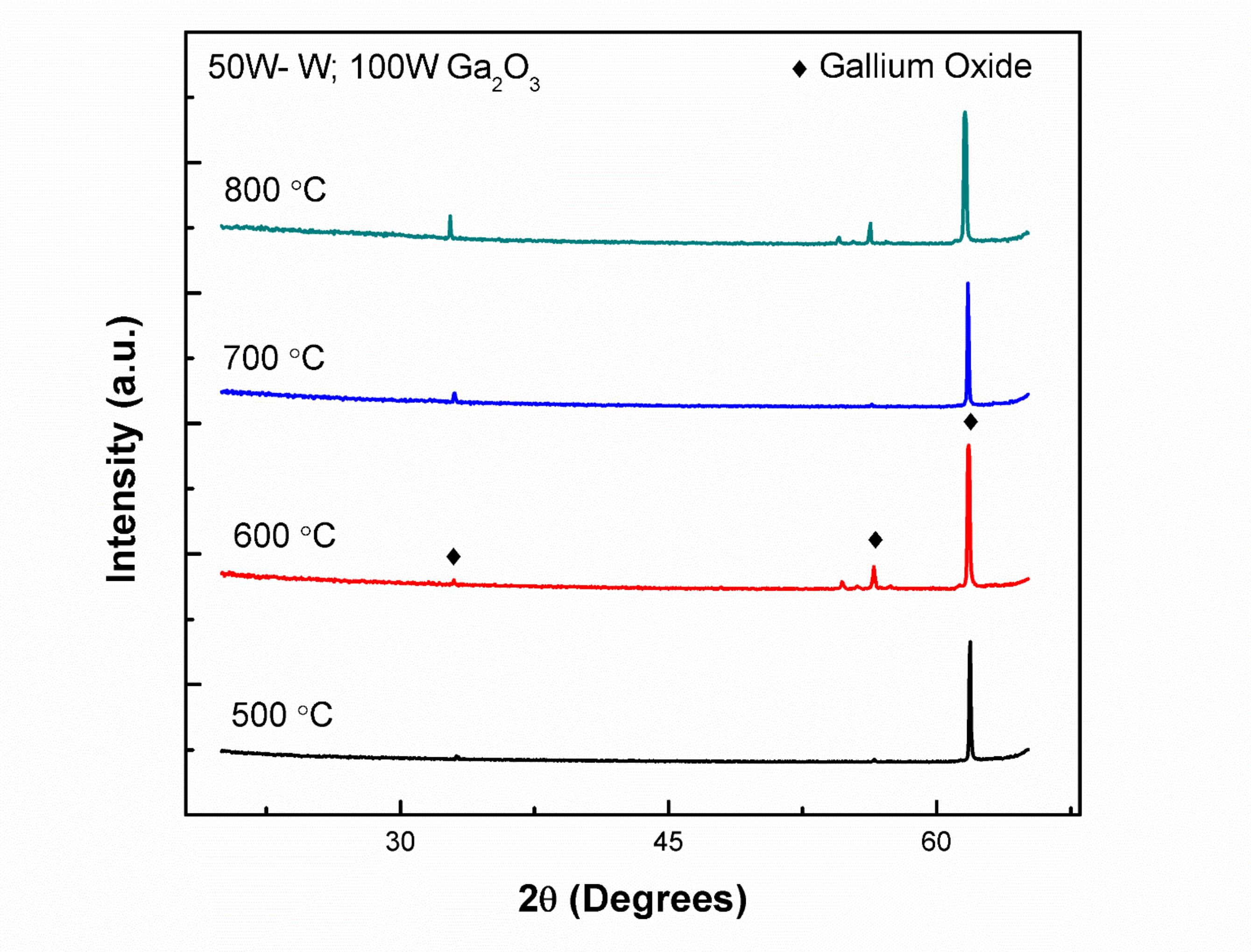
E.J. Rubio and C.V. Ramana, *Appl. Phys. Lett.* **102**, 191913 (2013).

Crystal Structure – (after annealing)



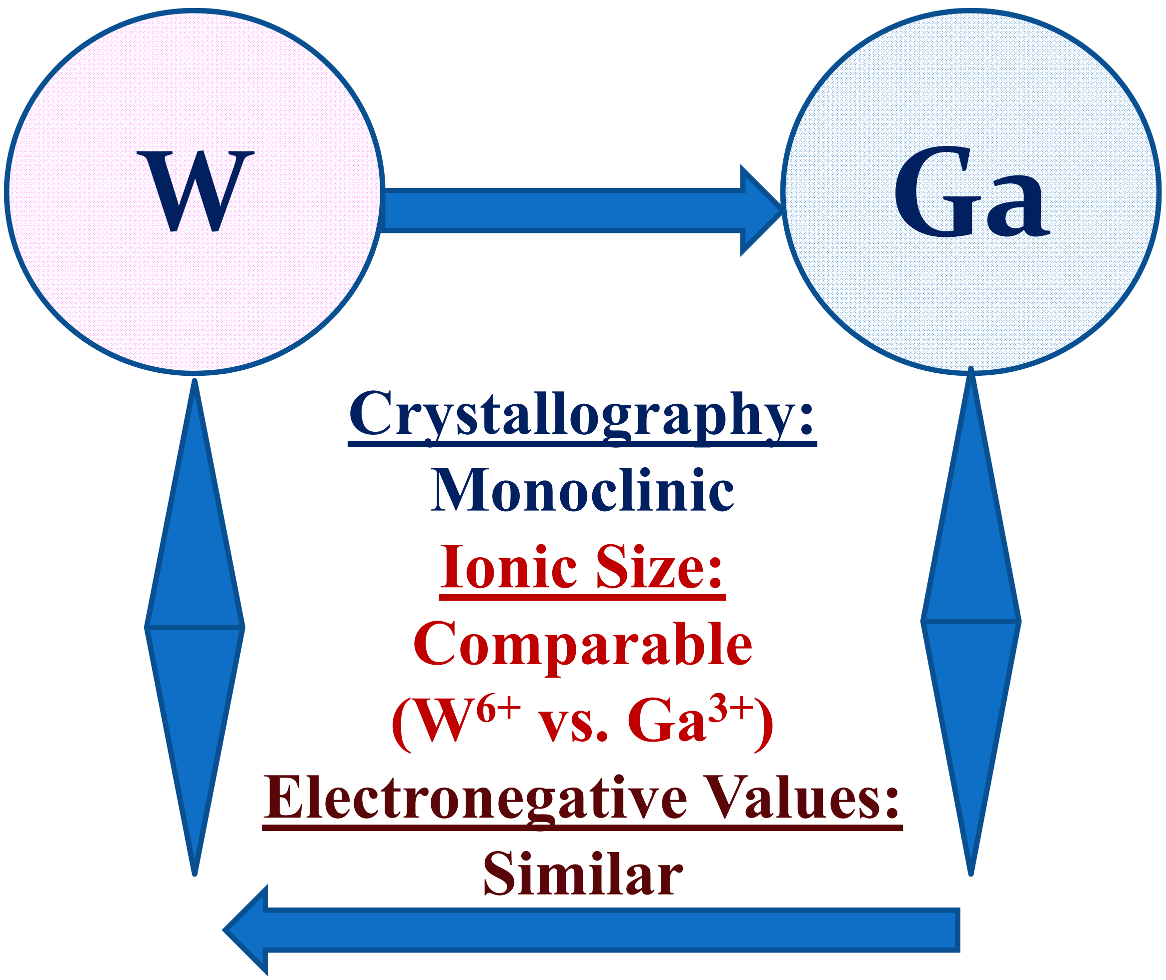
Deposition Temperature T_s=500 °C; Annealing Temperature T_a=700 °C for 30 min

Crystal Structure – (Temp. Dependent)



Only β-phase presented for all films.

Why 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)

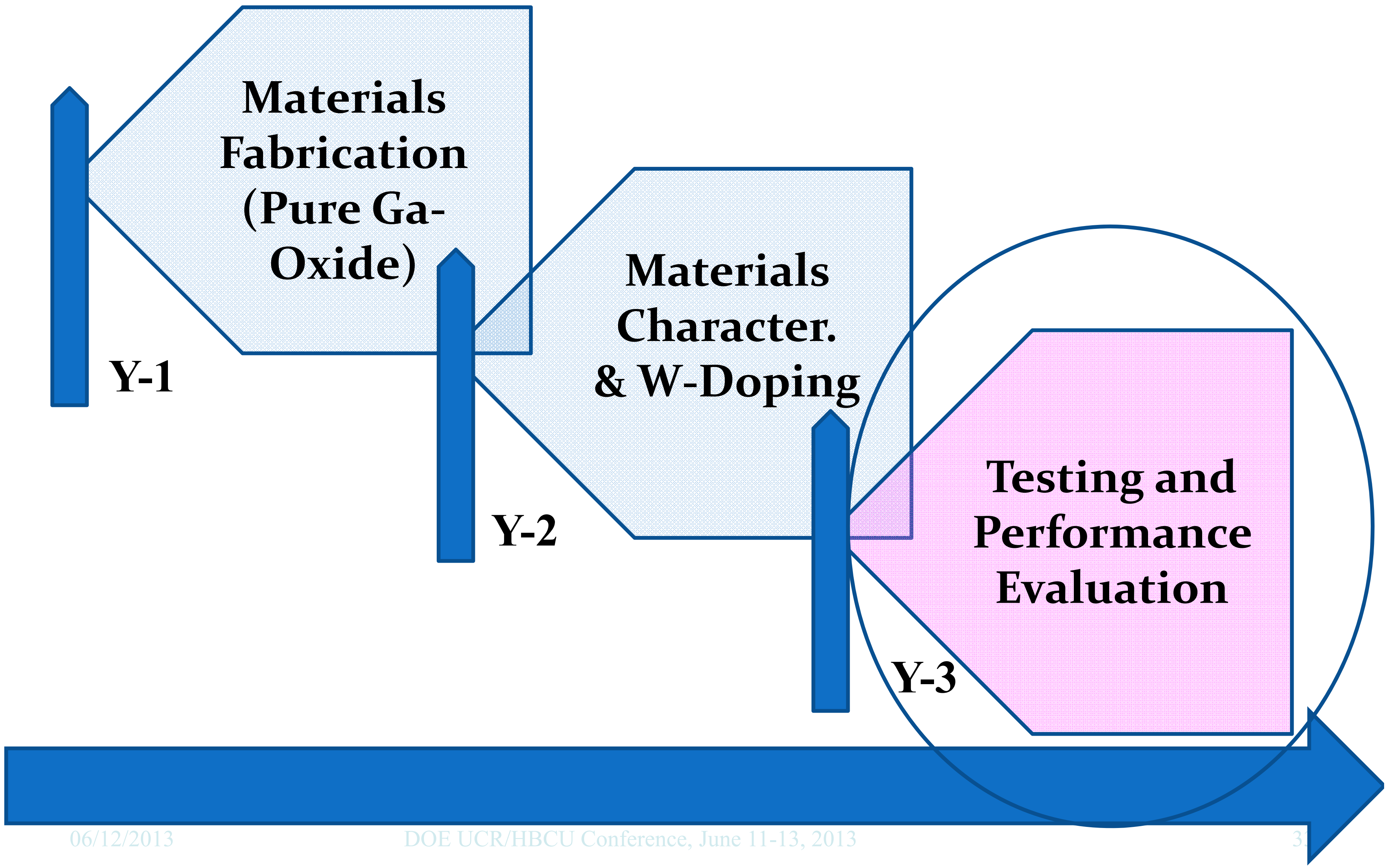
Education & Training:

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:

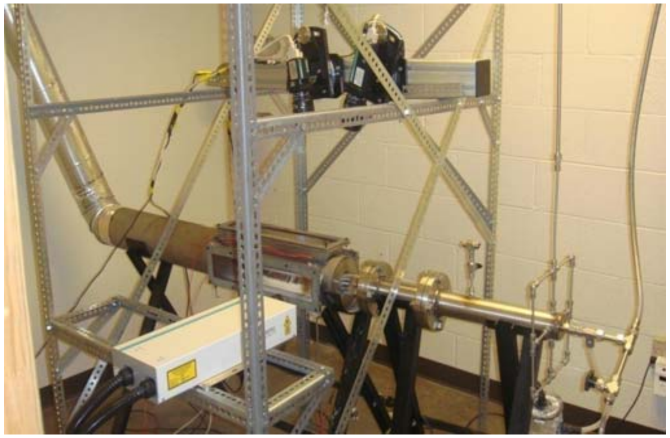
1. International Materials Research Congress (IMRC) – to be presented
2. International Conference on Metallurgical Coatings and Thin Films, April 29 – May 3, 2013, San Diego, CA
3. AVS International Symposium, October 28 – November 2, 2012 Tampa, FL
4. Southwest Energy Symposium, March 24, 2012, El Paso, TX

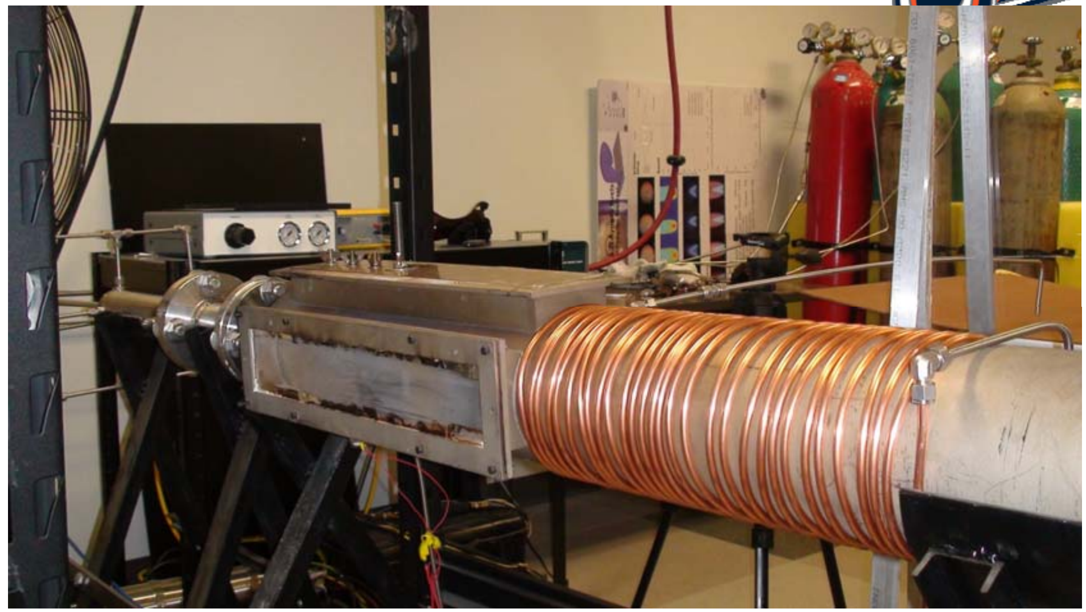
Future Work

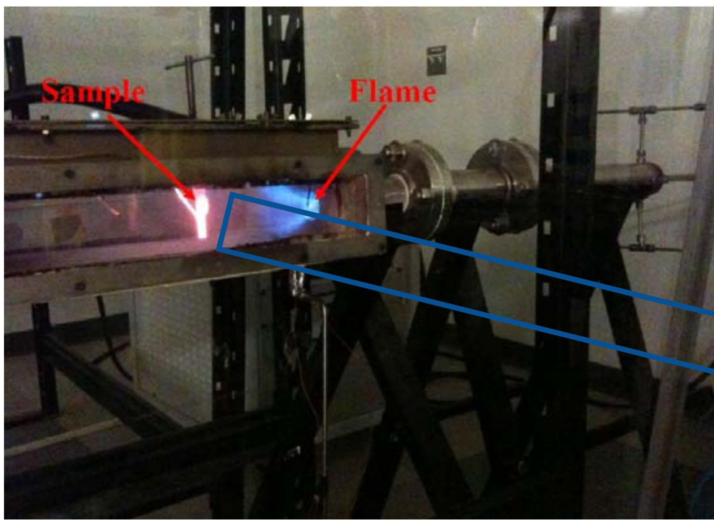


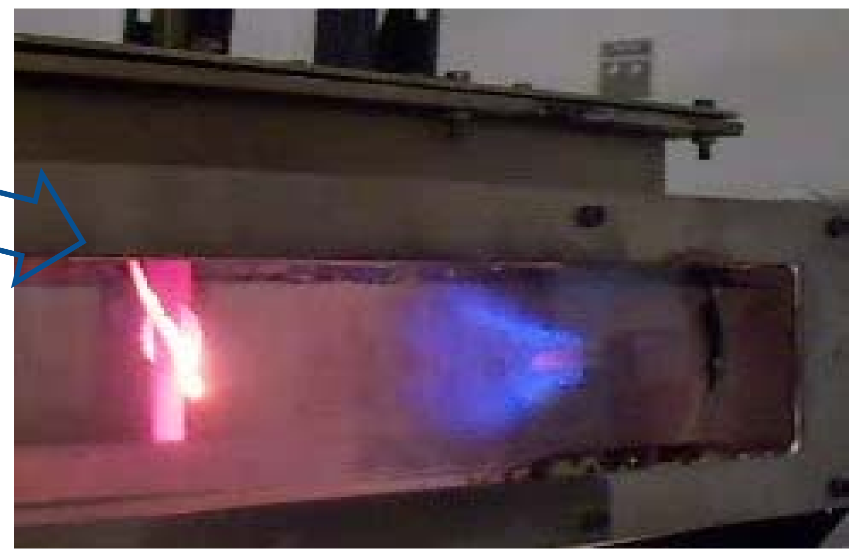
Materials Fabrication (Pure Ga-Oxide)
Y-1
Materials Character. & W-Doping
Y-2
Testing and Performance Evaluation
Y-3

Future Work









Future Work

Detailed Electrical and Sensor Characteristics (UTEP)

SUNY – Michael Carpenter (Plasmonics)

Summary & Conclusions

- Pure and W-doped Ga-oxide thin films were grown and characterized
- Experimental conditions were optimized to obtain Ga-oxide materials with wide controlled structure and morphology in a wide range
- Stability of β-phase with controlled electronic properties is demonstrated (with W-incorporation)
- Preliminary results obtained on the electrical properties are encouraging

Acknowledgements

- DOE-NETL
- Richard Dunst
- EMSL/PNNL, Richland, WA

THANK YOU!