SPECTROSCOPIC AND MICROSCOPIC ANALYSIS OF WO3 THIN FILMS

Felicia Speranta Manciu

Department of *Physics*

University of Texas at El Paso

OUTLINE

- Motivation and Objectives
- Sample Preparation and Characterization Techniques
- Results and Discussion
- Conclusions

MOTIVATION and OBJECTIVES

- The H_2S emission for coal gasification plants must be effectively monitored, controlled, and removed
- Tungsten oxide (WO_3) is a promising material for gas sensor applications among others
- Important properties for a gas sensor: → Sensitivity
  → Selectivity
  → Stability
- Analyzing structural, microscopic, and spectroscopic WO_3 to completely asses the properties and quality of the material to meet expected standards for its use in coal gasification.

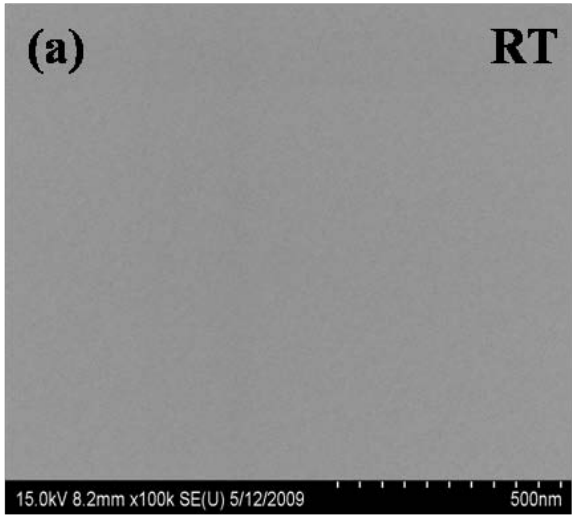
SAMPLE PREPARATION

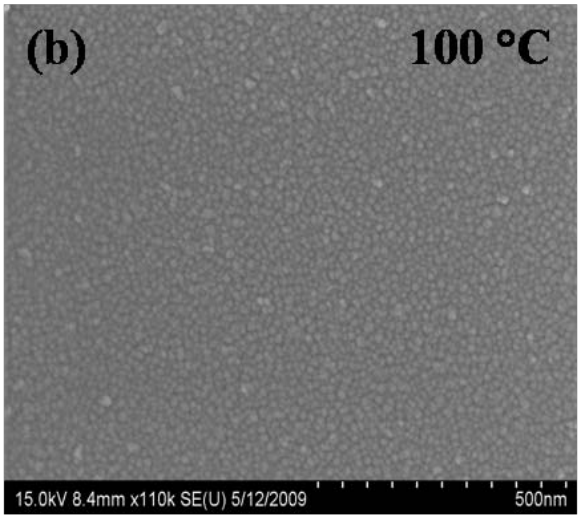
- WO_3 thin films were grown by RF magnetron sputtering
- 4 sets of samples grown with different parameters were analyzed
- Common parameters: → Base pressure: ~ 10^{-6} Torr
  → Substrate distance: 8 cm
  → Initial power: 40 W
- Ar introduced into vacuum chamber to ignite plasma
- Pre-sputtering for 10 min. with shutter closed
- Power to 100 W, O_2 into chamber into chamber
- Reactive deposition for 30 or 60 min on Si substrate or sapphire.

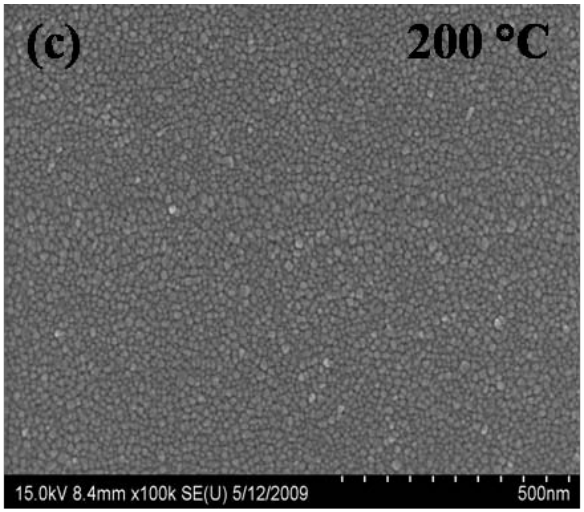
TECHNIQUES

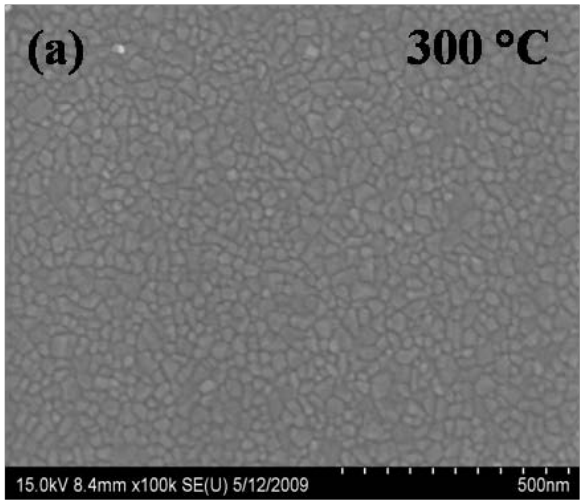
- Scanning Electron Microscopy → Hitachi S-4800 Field Emission Scanning Electron Microscope
- X-ray Diffraction → Bruker D8 Advance
- Raman Spectroscopy → WITec confocal Raman system
- Fourier Transform Infrared Spectroscopy → Bruker IFS 66v FTIR system

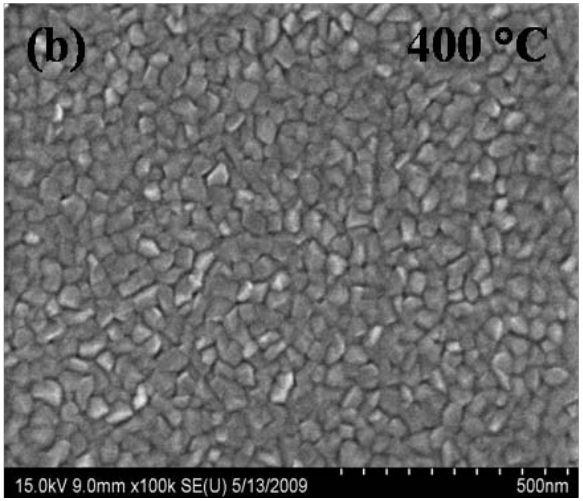
RESULTS – SEM

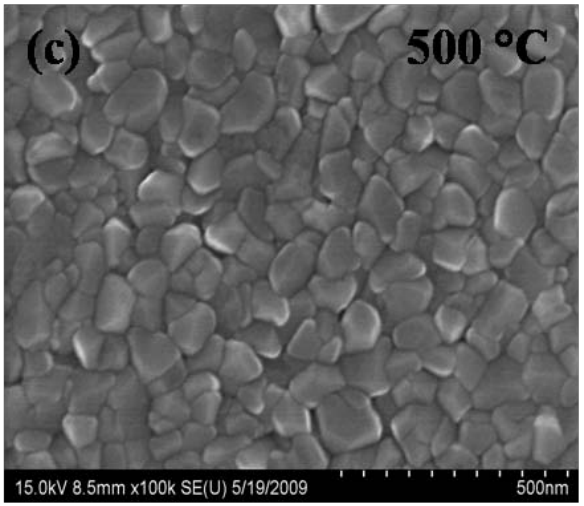




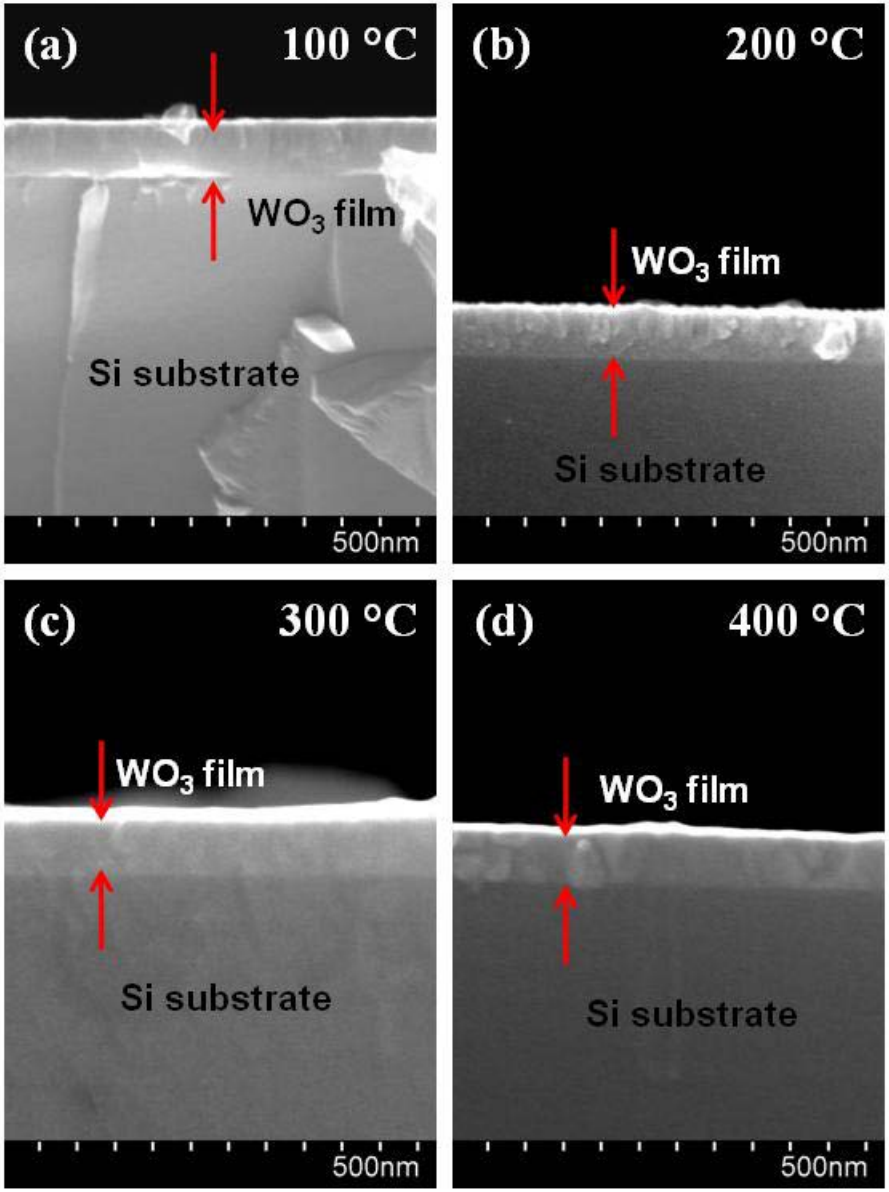








Increasing particle size with increasing Si substrate temperature



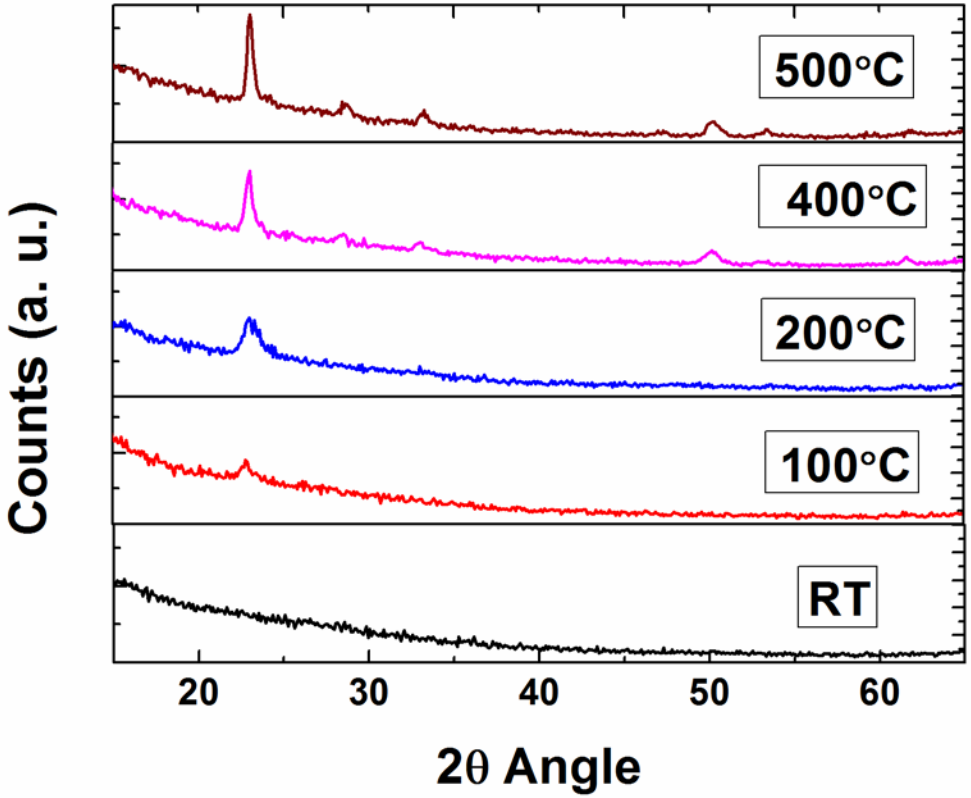
- Analysis of cross-sectional SEM images of WO_3-Si interfaces indicates

→ WO_3 film thickness of ~ 80 nm

→ WO_3 films grow as columnar structures on Si surfaces

→ no reaction leading to compound formation at the Si-WO_3 interface even at the highest temperature (500 ^oC)

RESULTS – X-ray DIFFRACTION



- The intensity of the peak at 23.1°, corresponding to diffraction from (002) planes of WO_3, increases with increasing temperature

→ An increase in the average crystallite-size

→ A preferred orientation of the film along (002) for temperatures ≥200 °C, while minimizing the strain-energy in the WO_3 film on the Si(100) surface.

RESULTS – STRUCTURAL PROPERTIES OF WO_3

- A dependent structure of WO_3 was previously observed

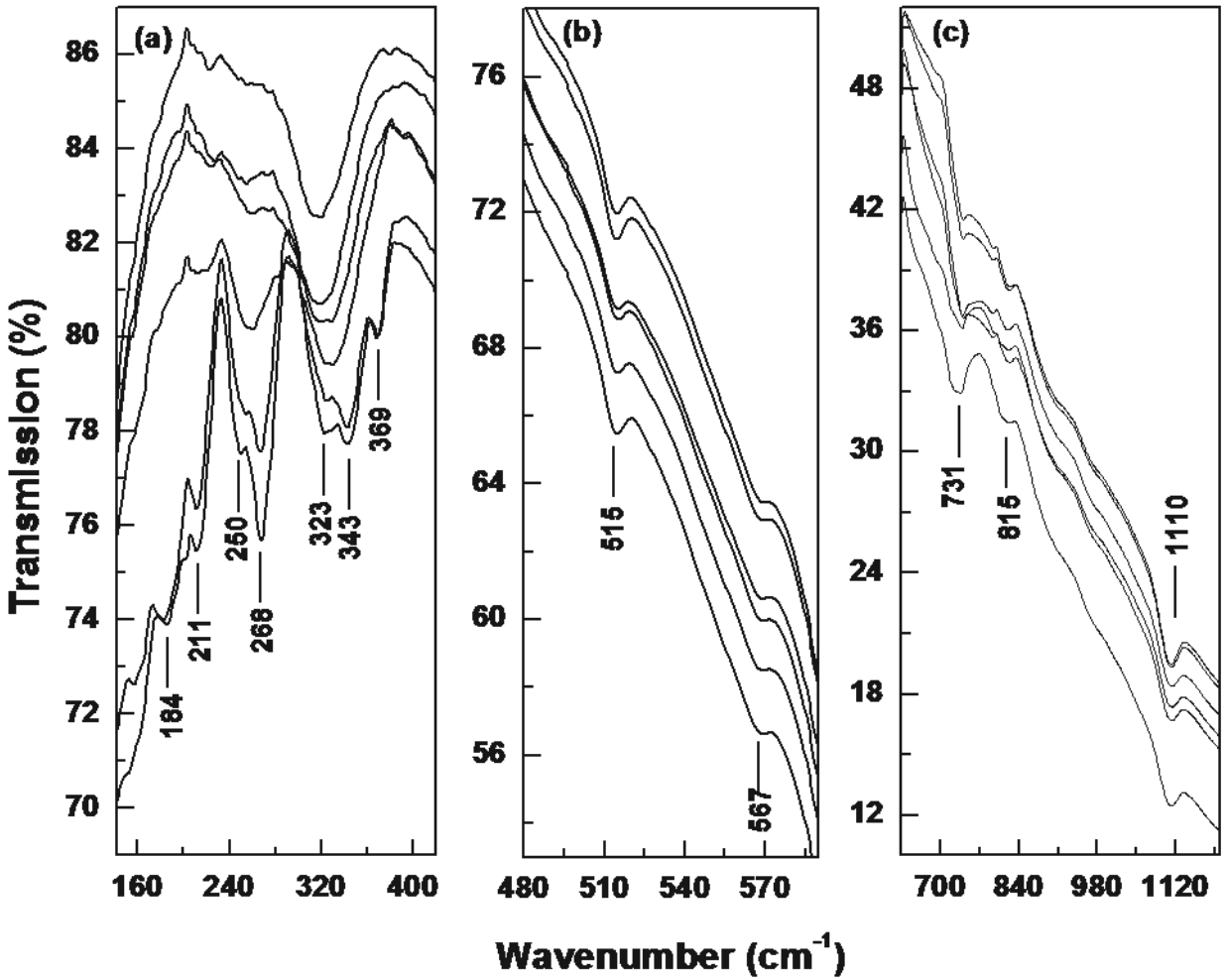
→ Triclinic from -25 – 30 °C

→ Monoclinic from 30 – 330 °C

→ Orthorhombic from 330 – 740 °C

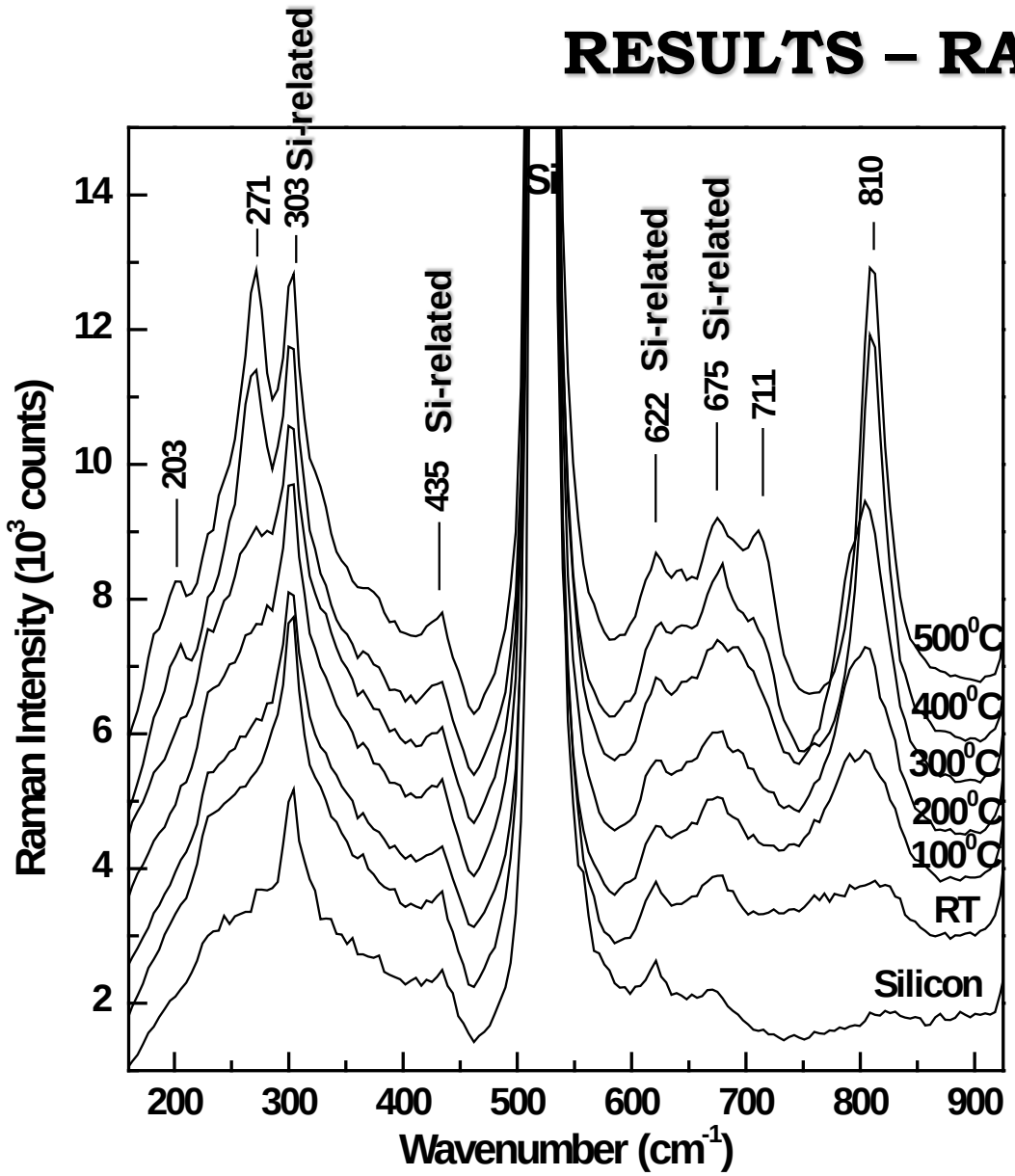
→ Tetragonal from 740 – 1437 °C

RESULTS – FTIR



- Increased intensity with higher temp.
- 515 and 567 cm^{-1} symmetric Si – O –Si vibrations
- 731 and 815 cm^{-1} W – O stretching
- 1110 cm^{-1} antisymmetric Si – O – Si vibration

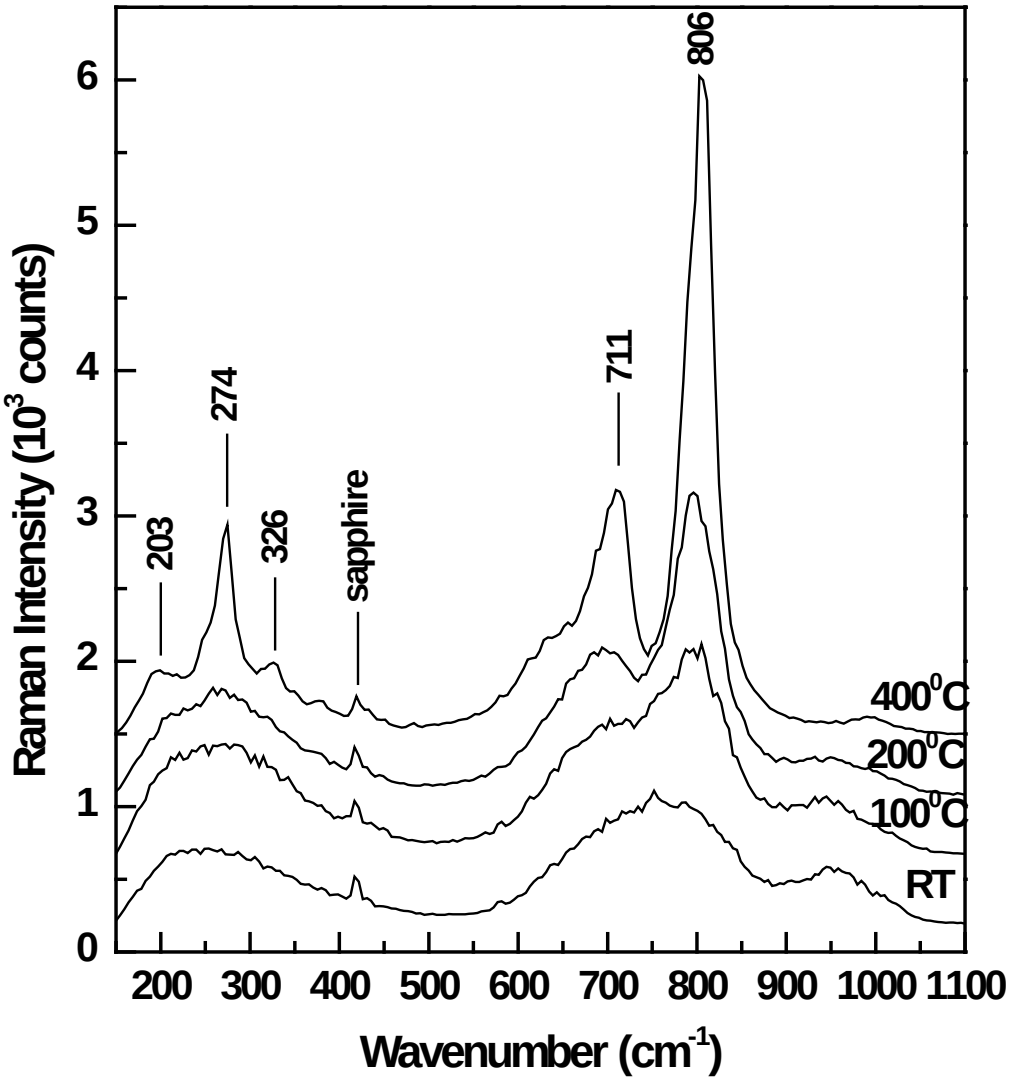
RESULTS – RAMAN



o-WO_3	m-WO_3
203	
	242
253	
271	273
303	
	326
374	
636	638
713	716
807	806

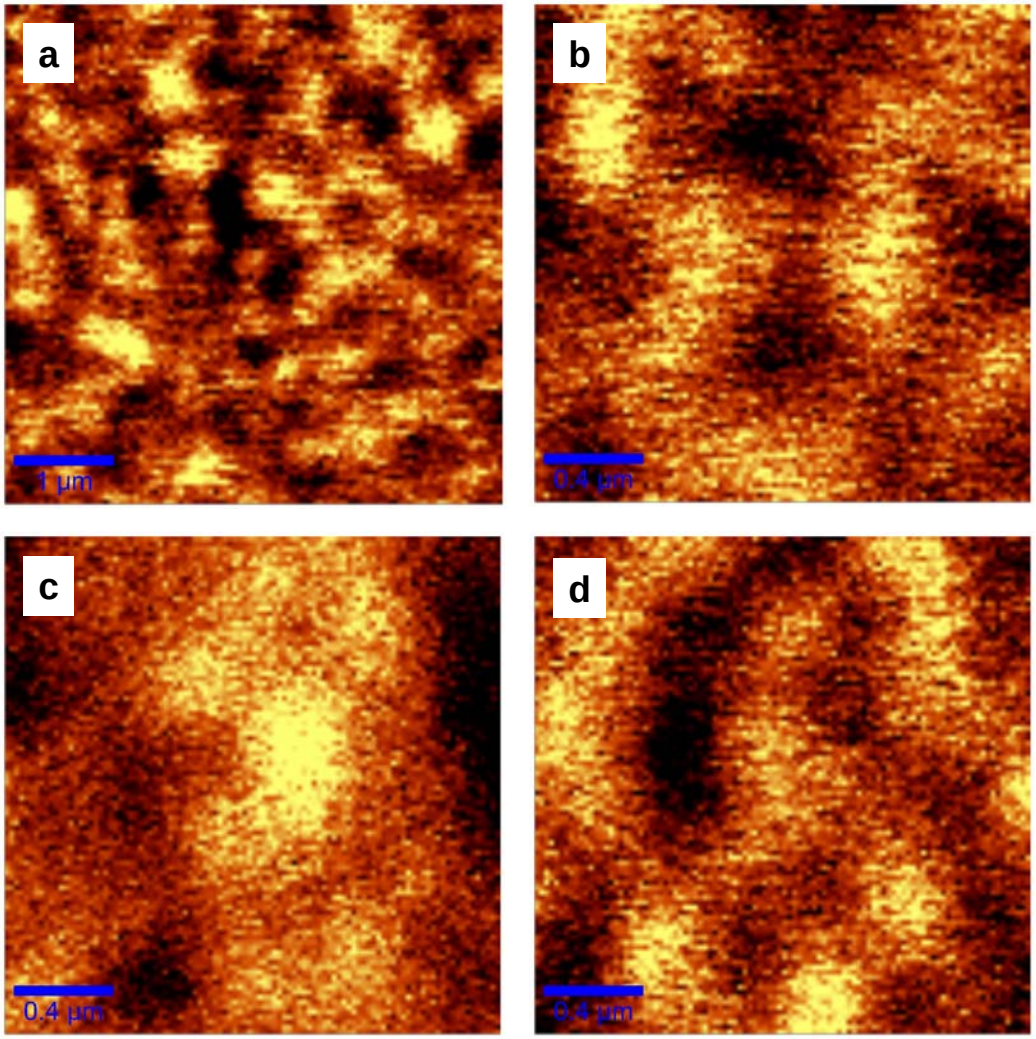
- The peaks at 203 and 303 cm^{-1} reveal a "possible" structural phase transition to orthorhombic
- 203 cm^{-1} vibration → strain

RESULTS – RAMAN



- Peak revealed at 326 cm^{-1} → still monoclinic structure
- Vibration at 203 cm^{-1} → presence of a strained phase
- Completely amorphous structure at RT

RESULTS – CONFOCAL RAMAN MAPPING

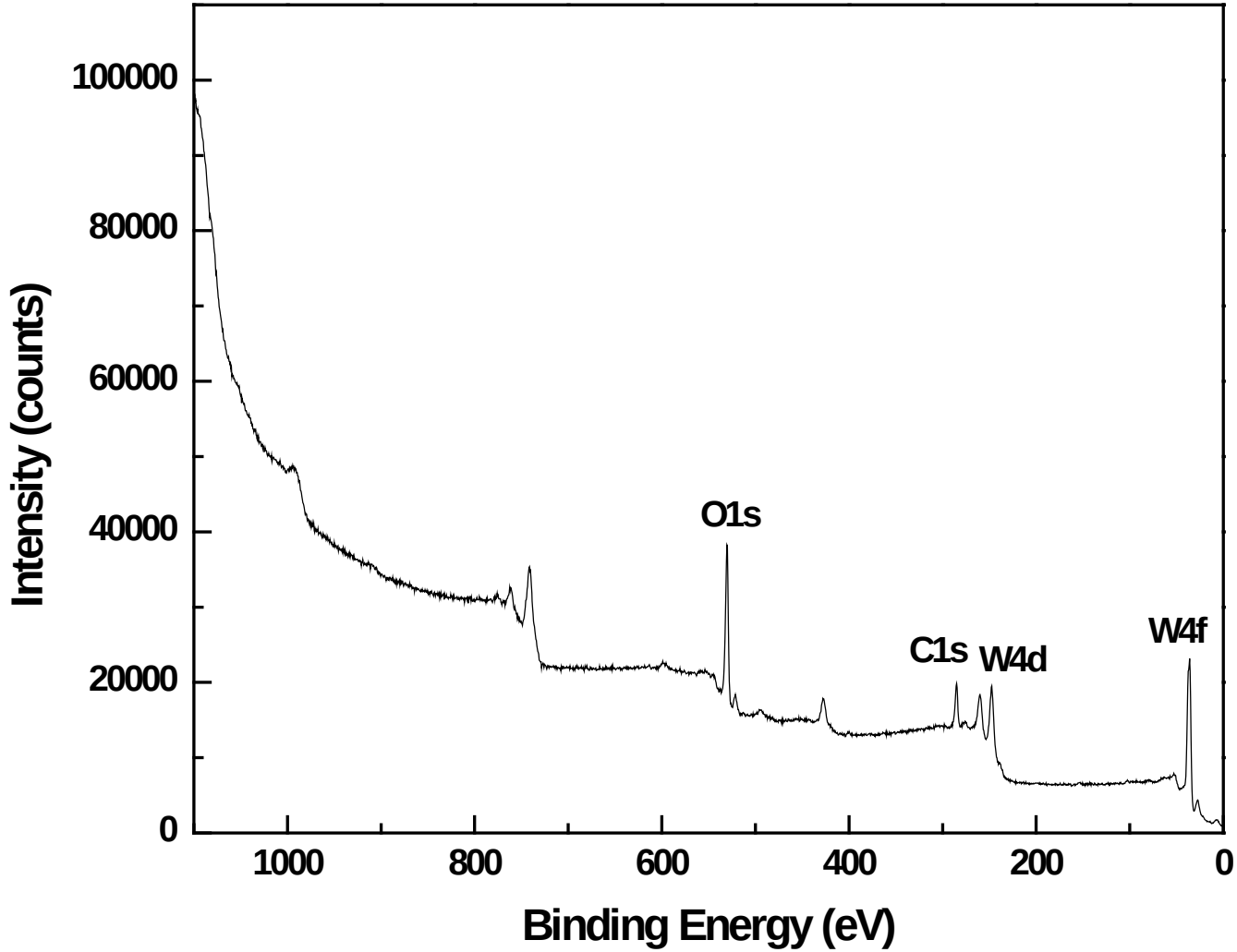


- Measurements at the surface of the samples

(a) and (b) → 400 °C
(c) and (d) → 500 °C

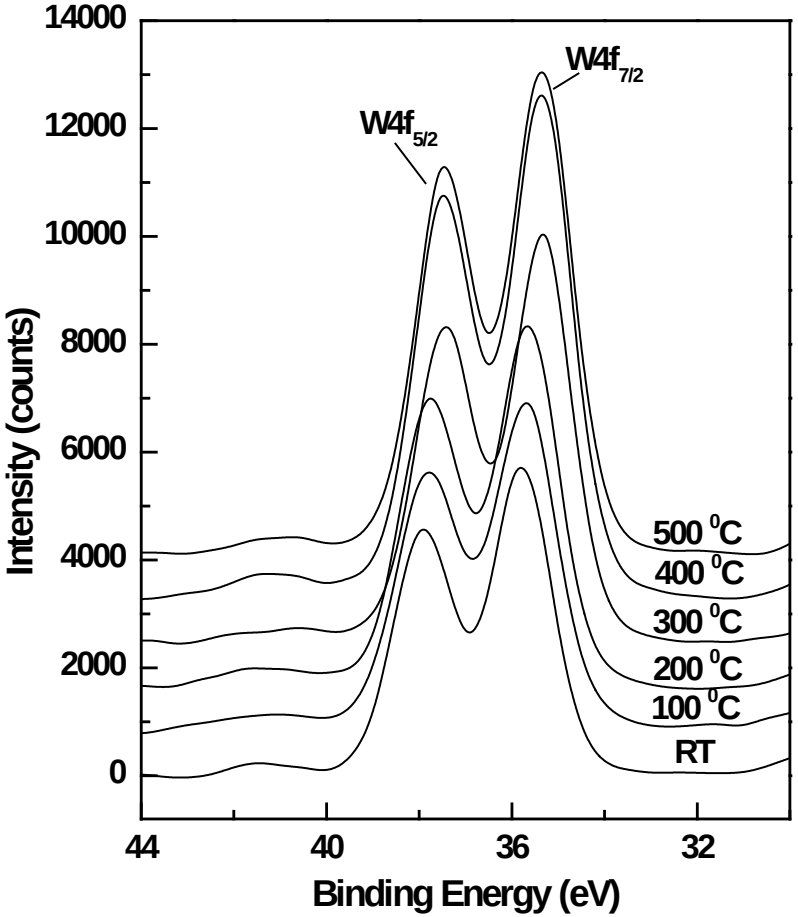
- Darker areas: monoclinic structure
- Lighter areas: strained phase

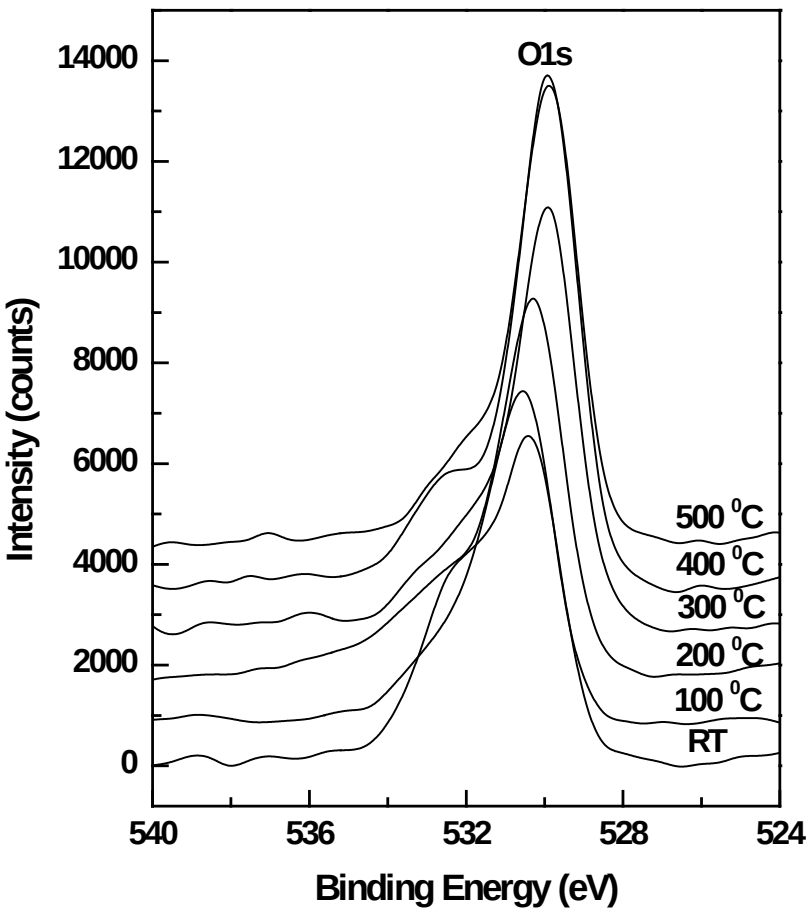
RESULTS – XPS



- The survey scan shows primary components: W and O, some adsorbed C

RESULTS – XPS





Narrow scan measurements:

Doublet peaks: W $4f_{7/2}$ at 35.8 eV,
W $4f_{5/2}$ at 37.9 eV.

Peak at 530.4 eV → metal oxide form
Weak shoulder at 532.4 eV → surface oxygen contamination

RESULTS – XPS

- Calculation of the peak areas of O 1s and W 4f core levels

Electron level	Sensitivity factor
O 1s	0.63
W 4f	2.0

- Over-stoichiometric ratio of oxygen to tungsten atomic concentration of 3.2 ± 0.1 at room temperature

- Ratio observed to decrease slightly with increasing temperature
  → continuing crystallization process

CONCLUSIONS

- Monoclinic phase in all samples above 100 °C, amorphous structure below 100 °C

- Small variations in growing process leads to changes in the morphology of the samples
  - → Increased crystallinity at higher temperatures
  - → Strained phase in some high temp. samples
  - → Dominant over the monoclinic phase

- The films surface maintain the stoichiometry of WO_x, with x slightly over 3 at room temperature, and approaching 3 as temperature increases

Optical Spectroscopy & Microscopy Laboratory

Peer reviewed articles

• Tungsten Oxide (WO3) Thin Films for Application in Advanced Energy Systems, Satya K. Gullapalli, Felicia S. Manciu, Jose L. Enriquez, and Chintalapalle V. Ramana, *Journal of Vacuum Science and Technology A*, accepted (2010).

• Spectroscopic Analysis of WO3 Thin Films, Felicia S. Manciu, Jose L. Enriquez, William G. Durrer, Young Yun, Chintalalpalle V. Ramana, and Satya K. Gullapalli, *Journal of Materials Research*, submitted (2010).

Conference presentations

• Jose L. Enriquez (graduate student)

2010: Presentation at Building Partnerships and Pathways to Address Engineering Grand Challenges Workshop (El Paso, TX)

2009: Presentation at 2009 Texas Section APS Meeting (San Marcos, TX)

• Satya K. Gullapalli (graduate student)

2009: Presentation at the American Vacuum Society 56th International Symposium & Exhibition (San Jose, CA).

Students supported under this grant

• Jose Luis Enriquez, graduate student in Department of Physics, UTEP

• Satya K. Gullapalli, graduate student in Department of Mechanical Engineering, UTEP

• Francisco Pineda, graduate student in Department of Mechanical Engineering, UTEP

• Rama Shesha Vemuri, graduate student in Department of Mechanical Engineering, UTEP

• Jose M. Mares, graduate student in Department of Mechanical Engineering, UTEP

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Thank You