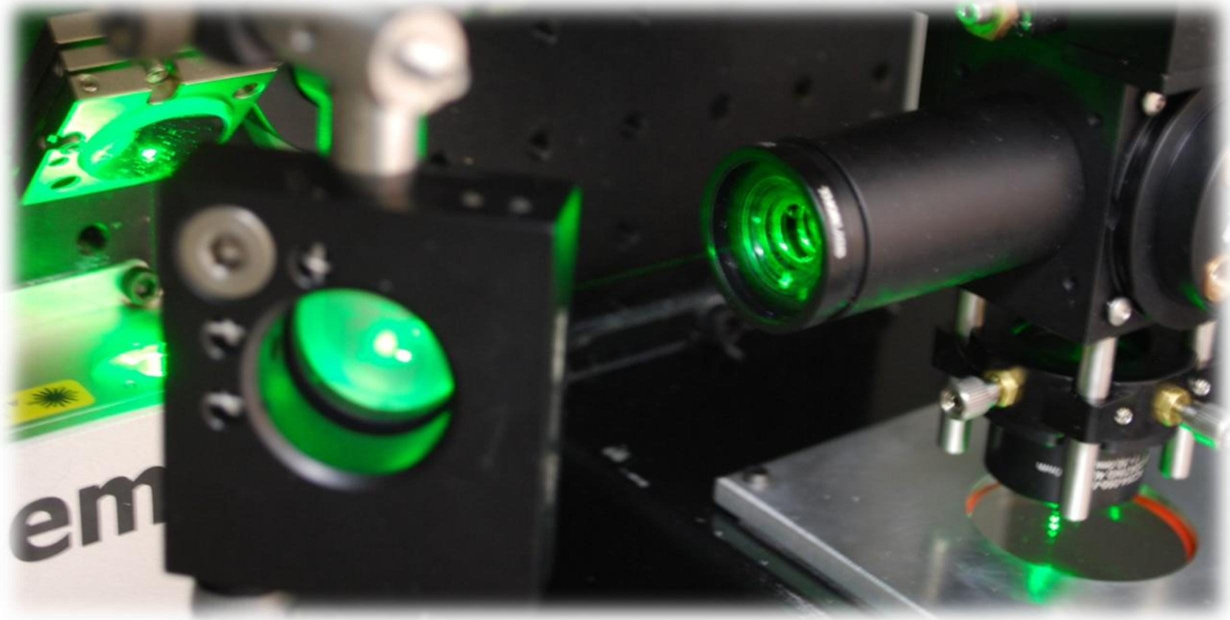

Optical Thin Films for High Temperature Gas Sensing in Advanced Coal Fired Power Plants

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Paul Richard Ohodnicki, Jr.
Chemistry and Surface Science Division

NETL-RUA
Regional University Alliance

U.S. DEPARTMENT OF ENERGY

Acknowledgement and Disclaimer

This work was funded by the Cross-Cutting Technologies Program at NETL and managed by Robert Romanosky (technology manager) and Patricia Rawls (technical monitor).

Overview of Presentation

- Sensors Needs for Energy Production and Energy Efficiency
- Motivational Work on SnO_2
- Recent Work on TiO_2 and Au Incorporated TiO_2 Films
- Optical Response Sensitivity Modeling
- Future Plans

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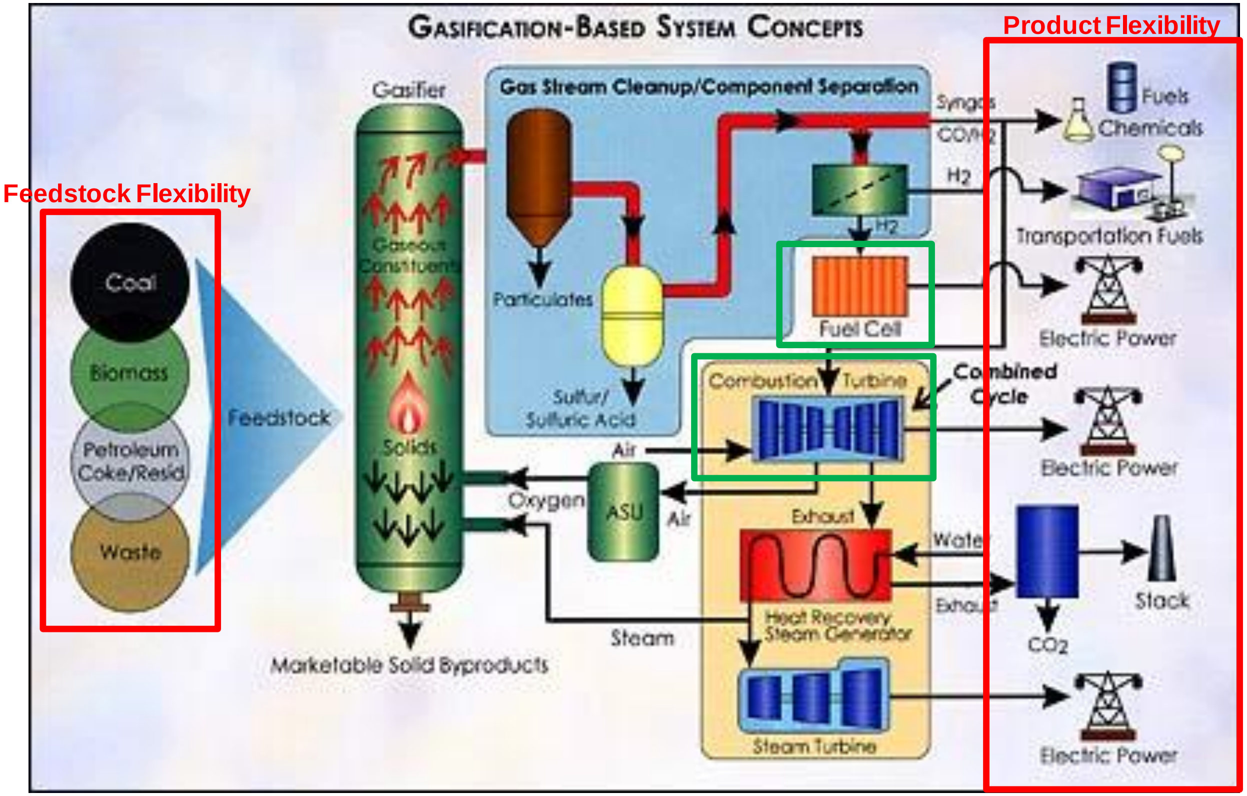
Harsh Environment Sensor Needs for Energy Production and Energy Efficiency

Advanced Fossil Energy Technologies

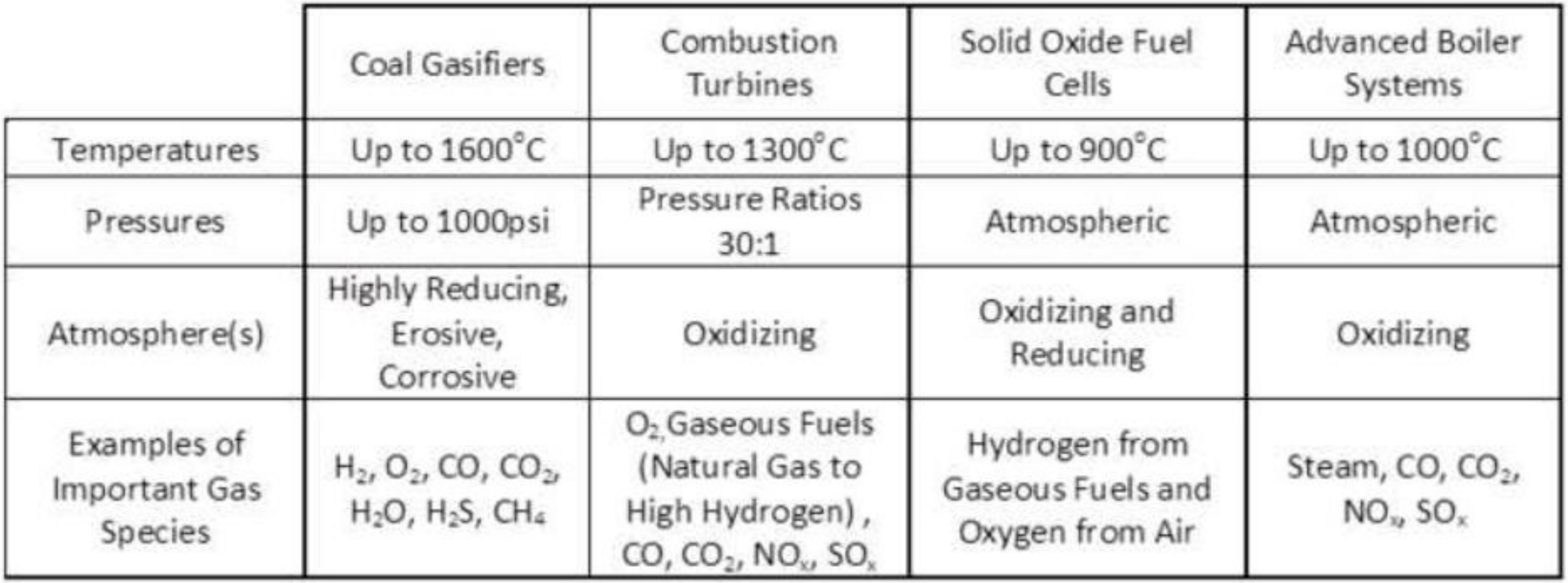


http://www.fossil.energy.gov/programs/powersystems/gasification/howgasificationworks.html

Coal-Based Power Plants of the Future are Highly Complex Making Sensors and Controls of Crucial Importance.

Advanced Fossil Energy Technologies

Table of Relevant Harsh Environments in Advanced Fossil Energy Technologies



	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
Examples of Important Gas Species	H_2, O_2, CO, CO_2, H_2O, H_2S, CH_4	O_2 Gaseous Fuels (Natural Gas to High Hydrogen) , CO, CO_2, NO_x, SO_x	Hydrogen from Gaseous Fuels and Oxygen from Air	Steam, CO, CO_2, NO_x, SO_x

A Wide Range of Gas Species are of Interest for Relevant Applications. In General, Functional Sensor Layers Must Be Capable of Operating in Extreme Conditions (T, P, corrosive).

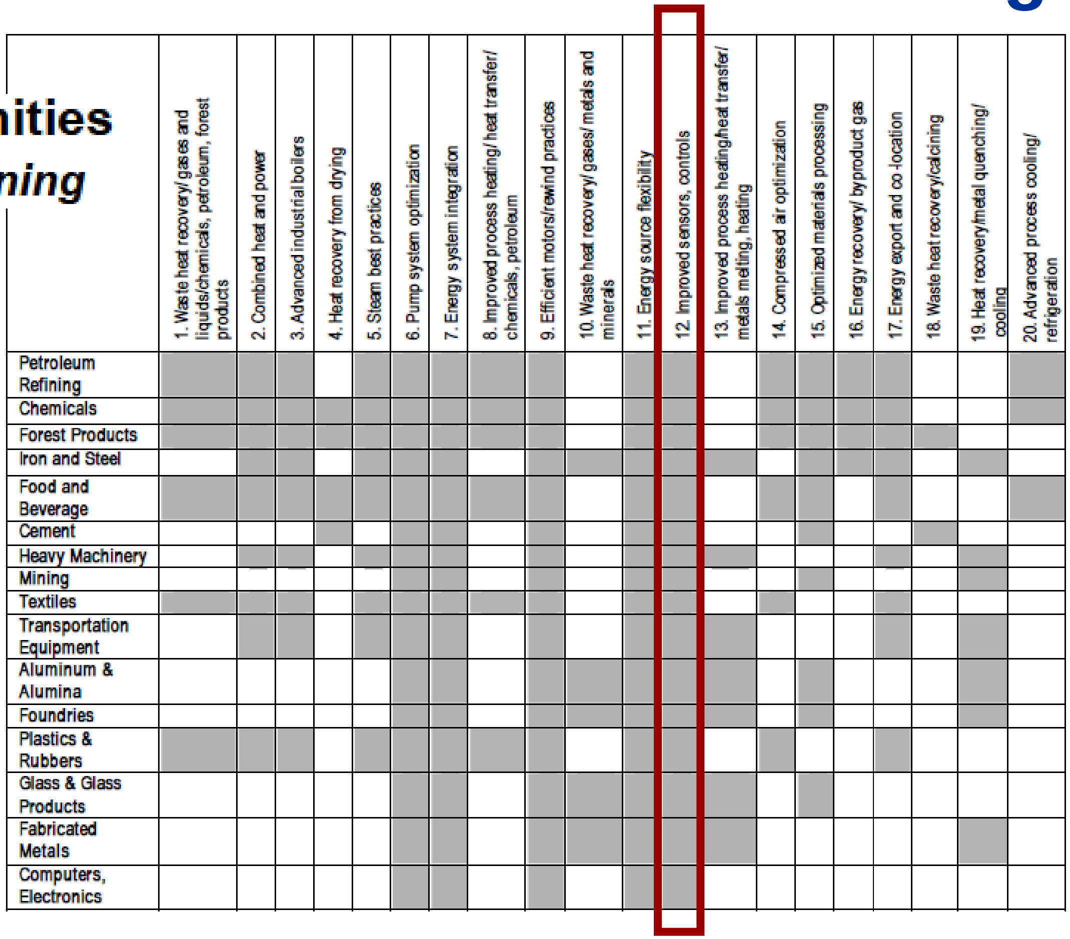
Opportunities for Efficient Domestic Manufacturing

Energy Use, Loss and Opportunities Analysis: *U.S. Manufacturing & Mining*

Prepared by Energetics, Incorporated and
E3M, Incorporated for the
U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
Industrial Technologies Program

December 2004

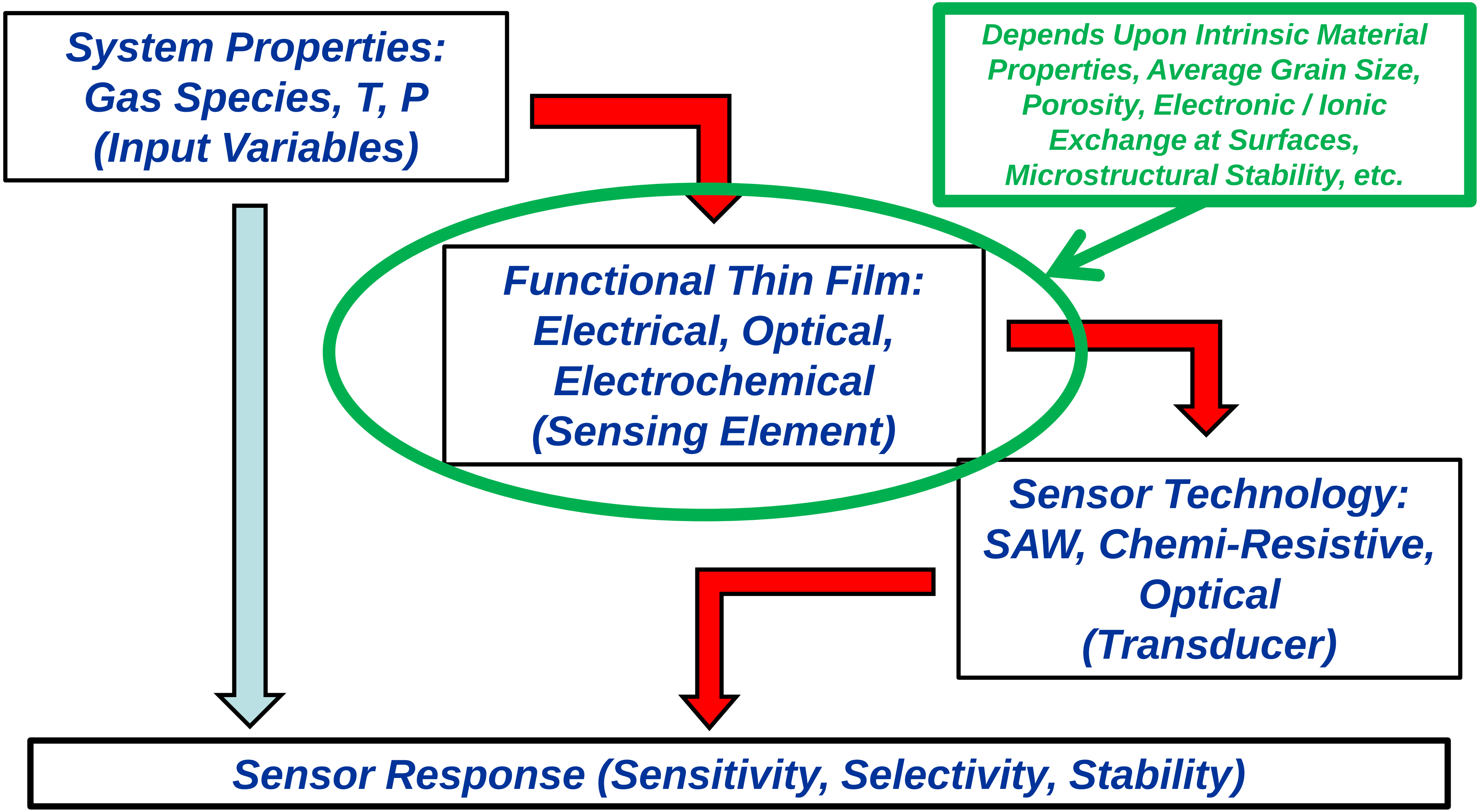
Improved Sensors & Controls was Listed as #12 of the Top 20 Opportunities for Energy Efficiency Improvements.



	1. Waste heat recovery/ gases and liquids/chemicals, petroleum, forest products	2. Combined heat and power	3. Advanced industrial boilers	4. Heat recovery from drying	5. Steam best practices	6. Pump system optimization	7. Energy system integration	8. Improved process heating/ heat transfer/ chemicals, petroleum	9. Efficient motors/rewind practices	10. Waste heat recovery/ gases/ metals and minerals	11. Energy source flexibility	12. Improved sensors, controls	13. Improved process heating/heat transfer/ metals melting, heating	14. Compressed air optimization	15. Optimized materials processing	16. Energy recovery/ byproduct gas	17. Energy export and co-location	18. Waste heat recovery/calcining	19. Heat recovery/metal quenching/ cooling	20. Advanced process cooling/ refrigeration
Petroleum Refining	■	■	■		■	■	■	■	■		■	■		■	■	■	■			■
Chemicals	■	■	■	■	■	■	■	■	■		■	■		■	■	■	■			■
Forest Products	■	■	■	■	■	■	■	■	■		■	■		■	■	■	■	■		
Iron and Steel		■	■		■	■	■		■	■	■	■	■		■	■	■		■	
Food and Beverage	■	■	■	■	■	■	■	■	■		■	■		■	■		■			■
Cement				■		■	■		■		■	■			■			■		
Heavy Machinery		■	■		■	■	■		■		■	■	■				■		■	
Mining						■	■		■		■	■			■				■	
Textiles	■	■	■		■	■	■	■	■		■	■		■			■			
Transportation Equipment		■	■		■	■	■		■		■	■	■				■		■	
Aluminum & Alumina						■	■		■	■	■	■	■		■				■	
Foundries						■	■		■	■	■	■	■		■				■	
Plastics & Rubbers	■	■	■		■	■	■	■	■		■	■		■			■			
Glass & Glass Products						■	■		■	■	■	■	■		■					
Fabricated Metals						■	■		■	■	■	■	■						■	
Computers, Electronics						■	■		■		■	■								

Sensors and Controls are Also Important for Improving Efficiency of Major Domestic Manufacturing Industries.

Thin Film Functional Sensor Layers in Harsh Environment Sensing Applications



System Properties:
Gas Species, T, P
(Input Variables)

Depends Upon Intrinsic Material Properties, Average Grain Size, Porosity, Electronic / Ionic Exchange at Surfaces, Microstructural Stability, etc.

Functional Thin Film:
Electrical, Optical, Electrochemical
(Sensing Element)

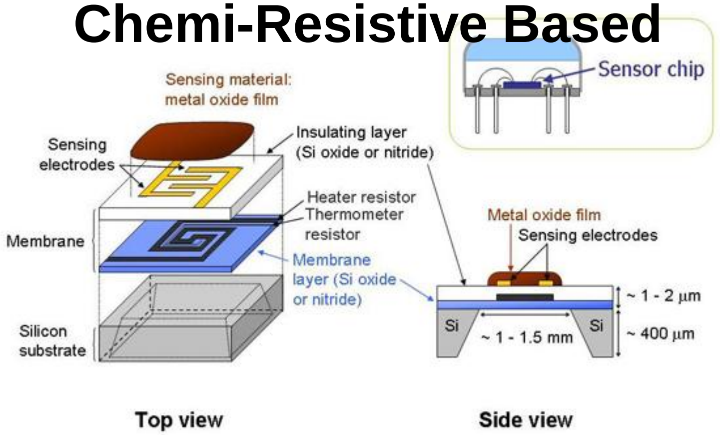
Sensor Technology:
SAW, Chemi-Resistive, Optical
(Transducer)

Sensor Response (Sensitivity, Selectivity, Stability)

High Temperature, Harsh Environment Gas Sensing

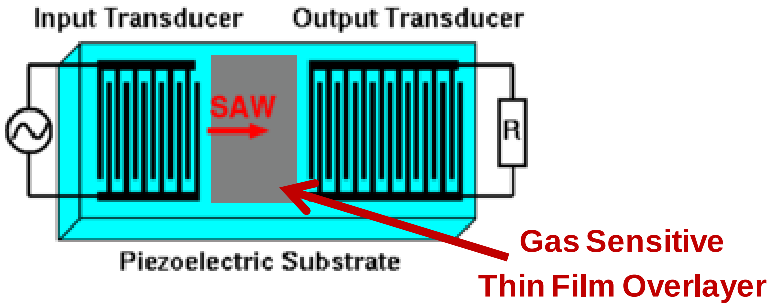
NETL In-House R&D
Regional University Alliance
Advanced Sensor Materials

Chemi-Resistive Based



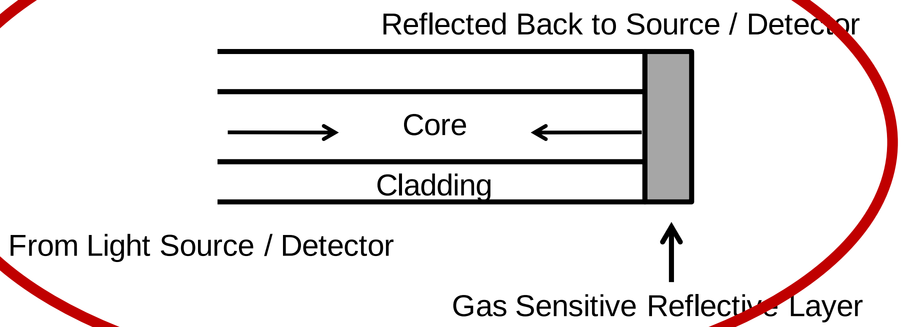
Prof. Alex Star, U. Pitt.

Surface Acoustic Wave Based



Prof. David Greve, CMU

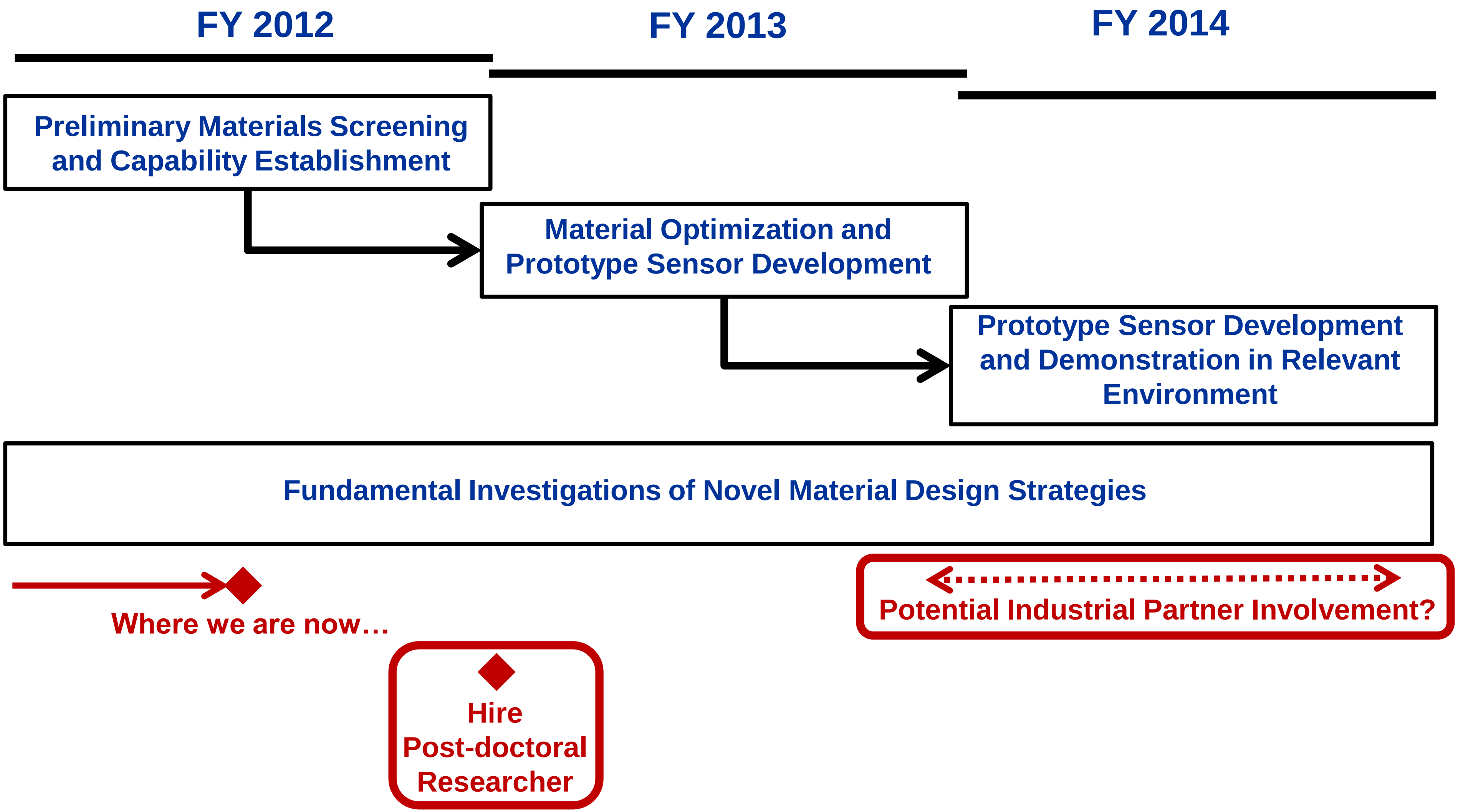
Optical Waveguide Based



Paul Ohodnicki, NETL ORD

Many Harsh Environment Sensing Platforms are Based on In-Situ Monitoring of Electrical or Optical Property Changes in Functional Thin Film Layers.

Advanced Sensor Materials Project Timeline



FY 2012

FY 2013

FY 2014

Preliminary Materials Screening and Capability Establishment

Material Optimization and Prototype Sensor Development

Prototype Sensor Development and Demonstration in Relevant Environment

Fundamental Investigations of Novel Material Design Strategies

◆ Where we are now…

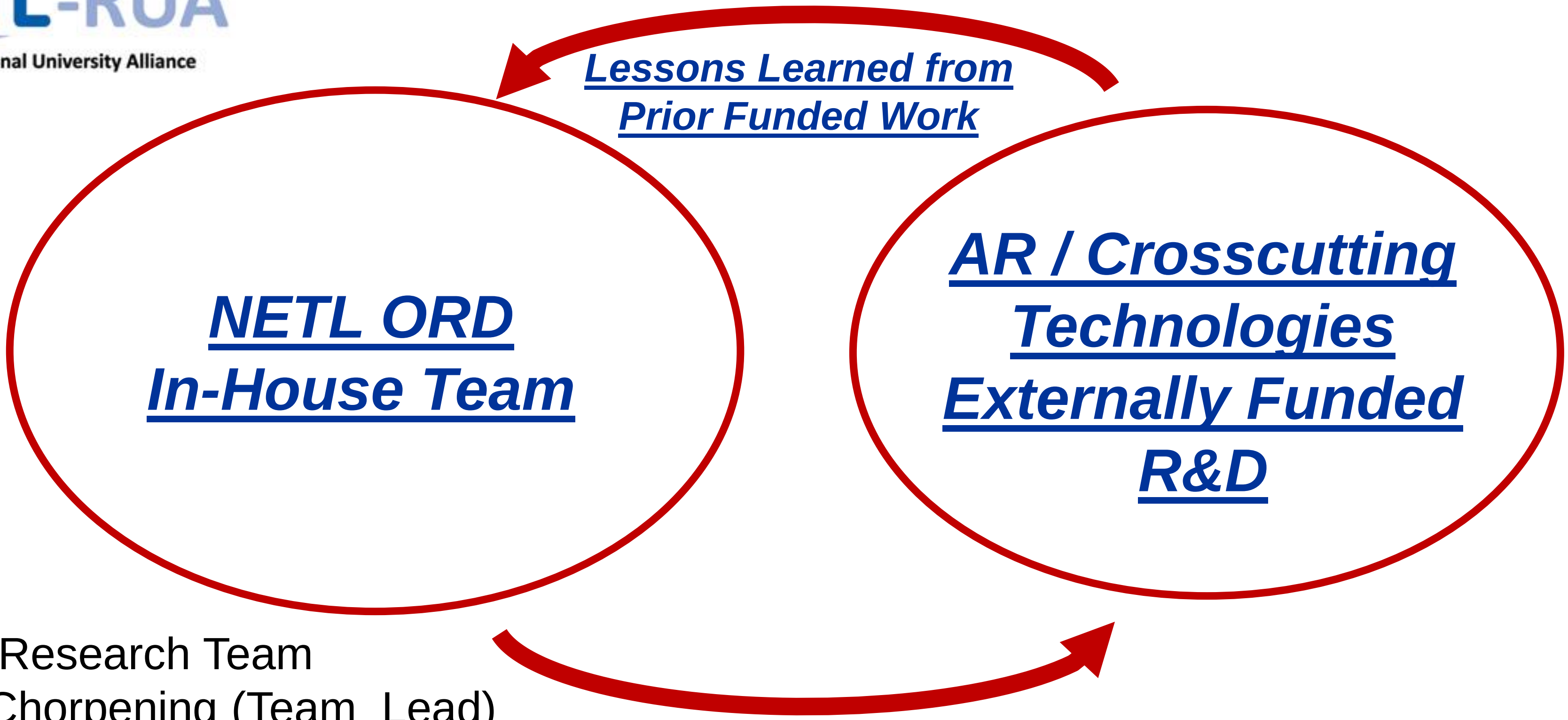
Potential Industrial Partner Involvement?

◆ Hire Post-doctoral Researcher

We are Attempting to Identify Useful and Novel Material Approaches and to Help Bridge the Well-Known "Valley of Death".

Interactions with Externally Funded Projects

Access to Resources Established By
Past / Present NETL Funded Work



Lessons Learned from
Prior Funded Work

NETL ORD
In-House Team

AR / Crosscutting Technologies Externally Funded R&D

ORD Interactions to Provide
Perspective or Technical Support

In-House Research Team
- Ben Chorpening (Team Lead)
- Paul Ohodnicki (PI, Sensor Materials)
- Thomas Brown (Materials Testing System)
- John Baltrus (Fundamental Material Studies)
- Mike Buric (Sensor Design and Modeling)
- Steve Woodruff (Sensor Design)

Relevant NETL In-House / RUA Facilities

Metal Oxide Film Deposition

NETL Pittsburgh In-House Facilities:

1) *Sol-Gel Synthesis : Spin Coating*
2) *Sol-Gel Synthesis : Dip Coating*

Carnegie Mellon University Facilities:

1) *Reactive Sputter Deposition*

Ambient Chemical / Structural Characterization

NETL Pittsburgh In-House Facilities:

1) *X-ray Diffraction*
2) *Scanning Electron Microscopy*
3) *X-ray Photoelectron Spectroscopy w/ Depth Profiling Capability*

Carnegie Mellon University Facilities

1) *Advanced Thin Film X-ray Diffraction*
2) *Transmission Electron Microscopy*
3) *Atomic Force Microscopy*

Ambient Optical / Electronic Property Characterization

NETL Pittsburgh In-House Facilities:

1) *UV / Visible Optical Spectrometer + Optical Modeling*
2) *Flourometer*
3) *Electrochemical Testing Setup (EIS, Cyclic Voltammetry)*
4) *Four-Point Probe Sheet Resistance Measurement Setup*

In-Situ Optical Property and Structural / Chemical Characterization AVAILABLE

NETL Pittsburgh In-House Facilities:

1) ***UV / Visible Optical Transmission and Reflection at High Temperatures in Flowing Gas at Ambient Pressure***
2) ***High-Temperature, Non-ambient X-ray Diffraction***
3) ***High-Temperature XPS Reaction Chamber***
4) ***Temperature Programmed Reduction / Oxidation***

In-Situ Optical / Electrical Property Characterization IN PROGRESS

NETL Pittsburgh In-House Facilities:

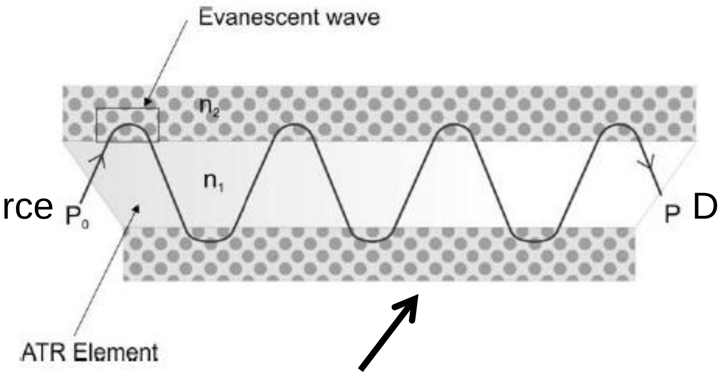
1) ***Additional Optics for Expanded Wavelength Transmission at High Temperatures in Flowing Gas at Ambient Pressure***
2) ***High Temperature Electrical Resistance***
3) ***More Sophisticated Gas Delivery System***
4) ***Higher Pressure (up to 500-1000psi) Reaction Chamber for In-Situ Measurements***

NETL-RUA
Regional University Alliance

Sensor Material Fabrication and Characterization Capabilities Available at NETL and Through the Regional University Alliance.

Motivational Work in the Literature

Evanescent Waveguide Based Sensors Use Gas-Sensitive Optical Absorption of Thin Film Coatings



From Light Source

To Detector

Gas Sensitive Cladding

Thin Film Sensitive Cladding Layer with Environment Dependent Optical Absorption

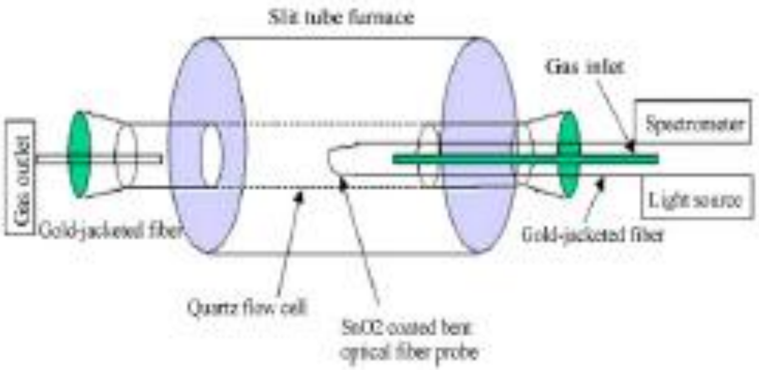


Fig. 1. A diagram of the testing system for investigating the optical properties o sol–gel derived silica optical fibers.

Talanta 77 (2009) 953–961

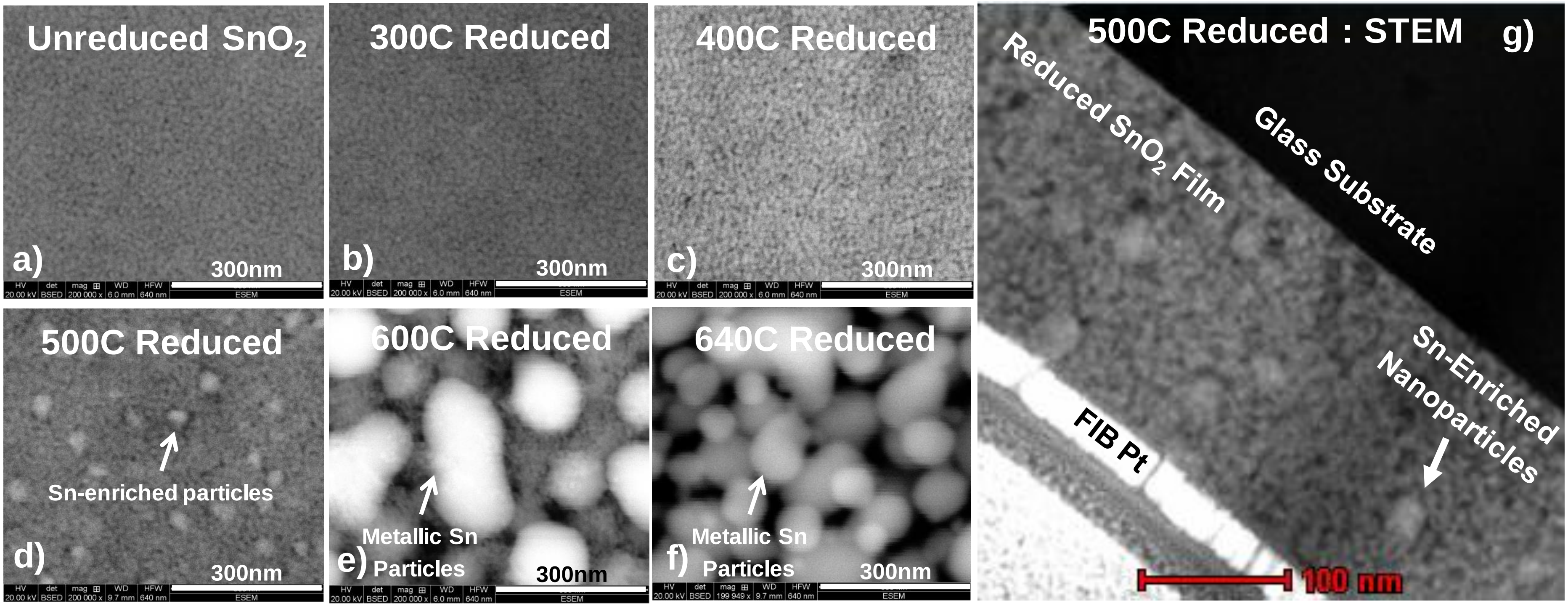
Optical fiber evanescent wave absorption spectrometry of nanocrystalline tin oxide thin films for selective hydrogen sensing in high temperature gas samples

Qiangu Yan[a,*], Shiquan Tao[a,b,*], Hossein Toghiani[a]

[a] *Dave C. Swalm School of Chemical Engineering, Box 9595, Mississippi State University, MS 39762, United States*
[b] *Department of Mathematics, Chemistry and Physics, WTAMU, Box 60787, West Texas A&M University, Canyon, TX 79016, United States*

A Recent Reference Reported Selective, High Temperature H_2 Sensing up to 800°C Using SnO_2 Deposited on Optical Fibers In an Evanescent Wave Optical Absorption Based Sensor

First Investigation: SnO_2



Formation of Sn-enriched Nanoparticles is Observed at Reduction Temperatures of Approximately 500ºC and Above.

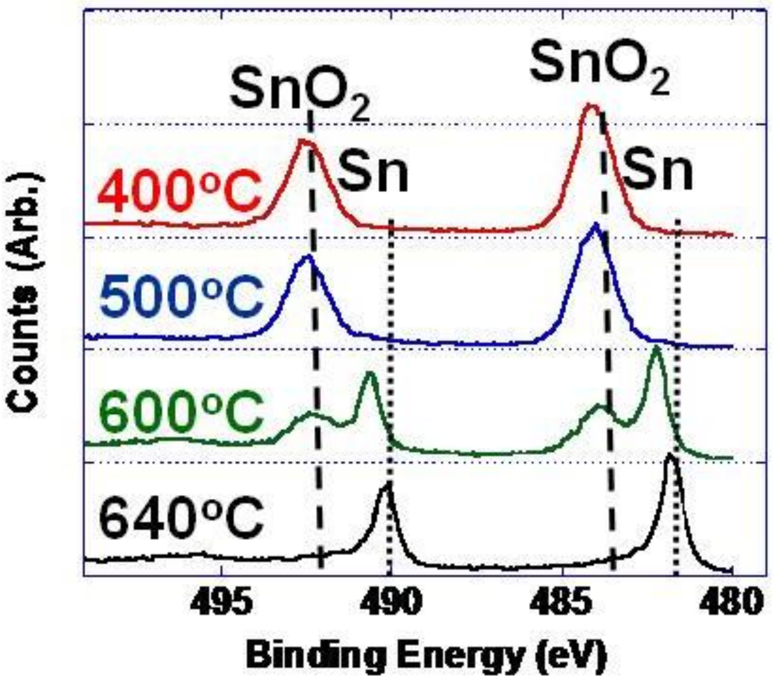
Cross-Sectional TEM Data Shows that the Sn-Enriched Nanoparticles are Found Embedded Throughout the Reduced SnO_2 Film.

Manuscript Accepted By Thin Solid Films to be Published Soon.

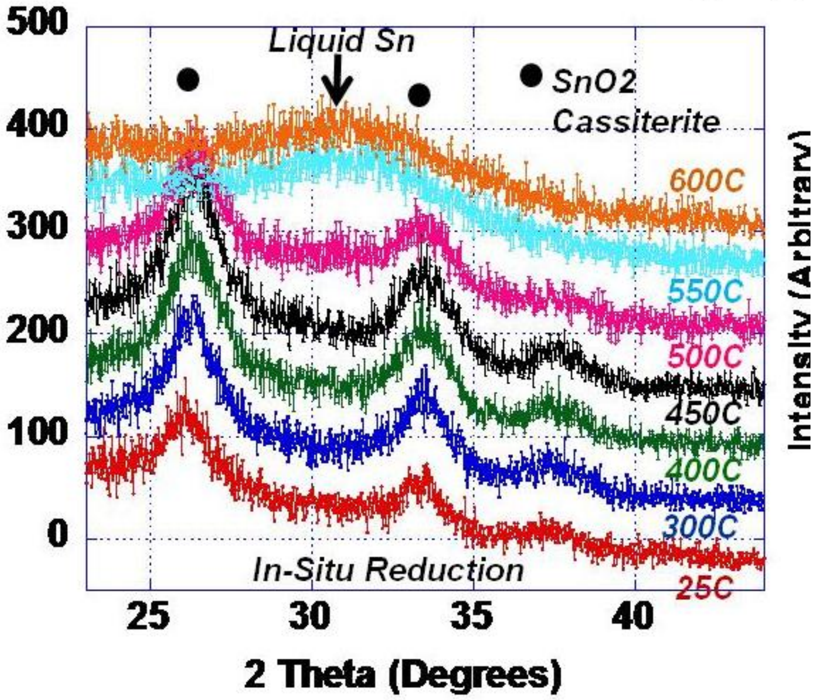
XPS and XRD Reduction Experiments of SnO_2 Films

XPS Reduction Experiment Using HighTemperature XPS Reaction Chamber and High Temperature X-ray Diffraction Experiments.

XPS Sn3d5 Spectra after Sputtering Away ~25nm

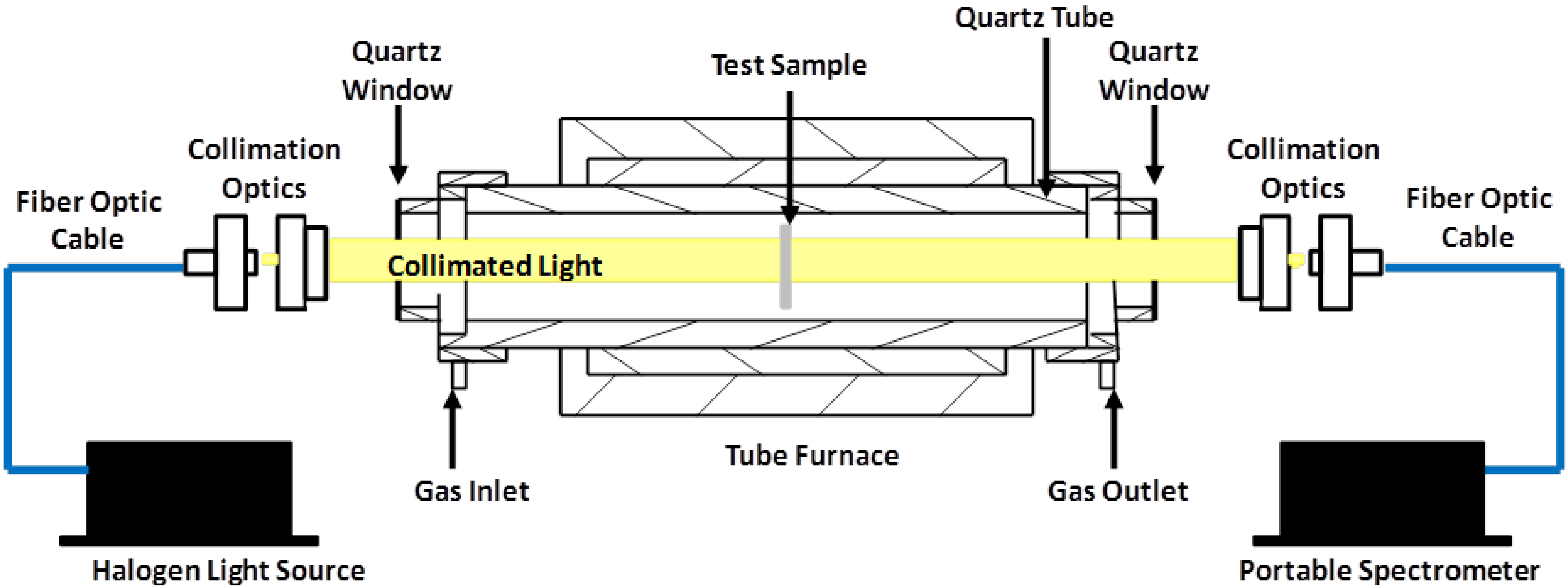


In-Situ Glancing Incidence XRD (4% H_2 / N_2)



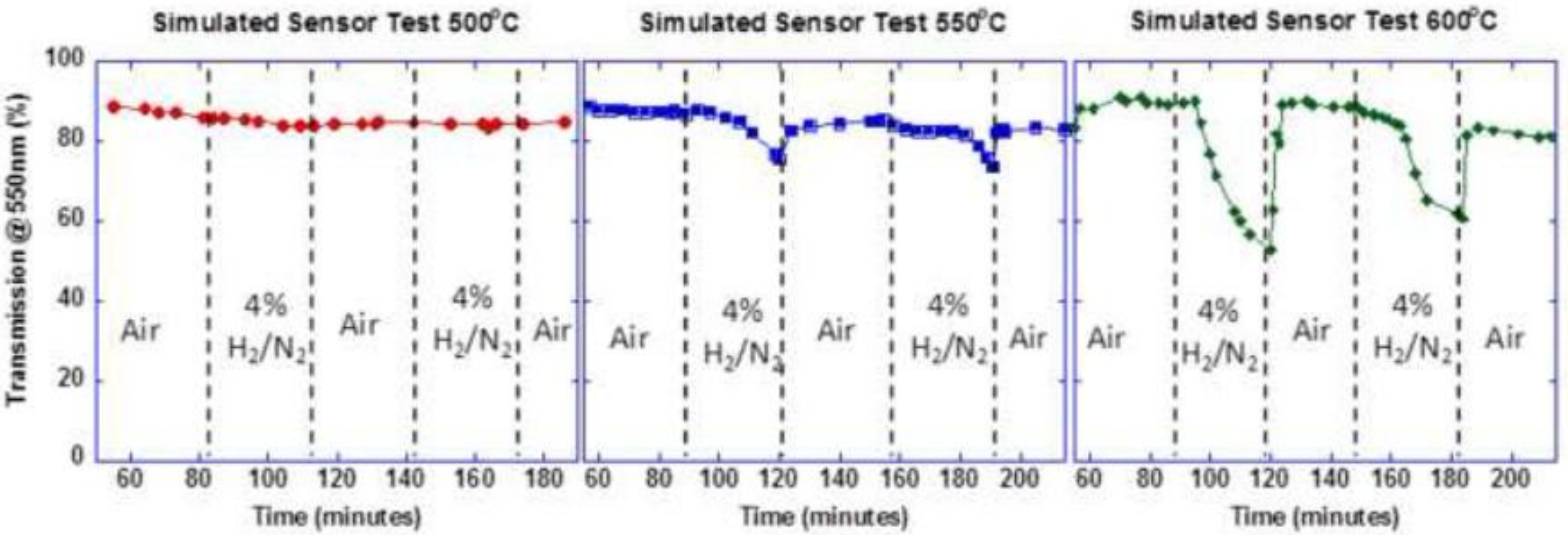
X-ray Photoelectron Spectroscopy Following High Temperature Gas Exposure Treatments Can Be Used to Probe Changes in Oxidation State.

Custom Set-up for Simulated Optical Sensing



A Key Piece of Equipment for Our Work is a Custom Designed Testing System for Monitoring Optical Property Changes at High Temperatures in Response to Changing Gas Atmospheres.

Simulated Optical Sensor Response



A Significant Reduction in Transmission Upon Exposure to 4% H_2/N_2 is Observed at Temperatures Where Reduction of the Film is Expected to Occur Based on Ex-Situ and In-Situ Characterization Techniques.

Lessons Learned from SnO_2 Film Studies

1) SnO_2 is Not Expected to Be a Good Candidate for High Temperature Sensing in Reducing Conditions Due to a Tendency for Bulk Film Reduction @ T > ~500°C.

2) Measured Changes in Transmission are Proposed to Be Associated with Liquid Sn-Nanoparticle Formation, Growth, and Eventually Coalescence Upon Full Film Reduction.

3) Prior Work Done on SnO_2 Thin Films Deposited on Optical Fibers Should Re-Explore Interpretation of Data Considering the Possibility of Film Reduction.

4) STANDARD MATERIALS USED FOR GAS SENSING AT LOW TEMPERATURES MAY NOT BE RELEVANT FOR HIGH TEMPERATURES, HIGH PRESSURES, AND HARSH ENVIRONMENTS

TiO_2 Films Exhibit Improved High T Stability

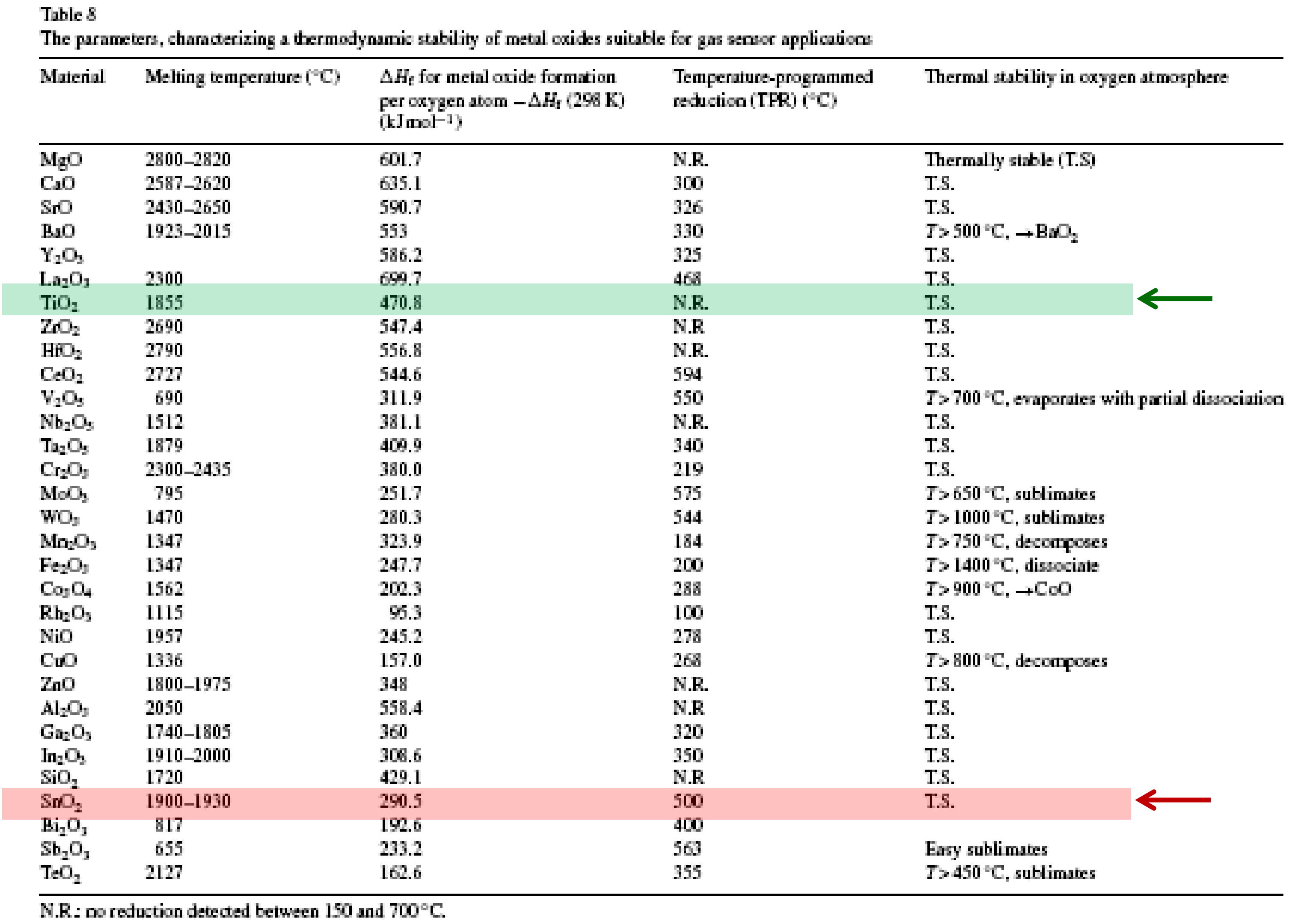


Table 8

The parameters, characterizing a thermodynamic stability of metal oxides suitable for gas sensor applications

Material	Melting temperature (°C)	ΔH_f for metal oxide formation per oxygen atom $-\Delta H_f$ (298 K) (kJ mol^{-1})	Temperature-programmed reduction (TPR) (°C)	Thermal stability in oxygen atmosphere
MgO	2800–2820	601.7	N.R.	Thermally stable (T.S)
CaO	2587–2620	635.1	300	T.S.
SrO	2430–2650	590.7	326	T.S.
BaO	1923–2015	553	330	$T > 500$ °C, → BaO_2
Y_2O_3		586.2	325	T.S.
La_2O_3	2300	699.7	468	T.S.
TiO_2	1855	470.8	N.R.	T.S.
ZrO_2	2690	547.4	N.R	T.S.
HfO_2	2790	556.8	N.R.	T.S.
CeO_2	2727	544.6	594	T.S.
V_2O_5	690	311.9	550	$T > 700$ °C, evaporates with partial dissociation
Nb_2O_5	1512	381.1	N.R.	T.S.
Ta_2O_5	1879	409.9	340	T.S.
Cr_2O_3	2300–2435	380.0	219	T.S.
MoO_3	795	251.7	575	$T > 650$ °C, sublimates
WO_3	1470	280.3	544	$T > 1000$ °C, sublimates
Mn_2O_3	1347	323.9	184	$T > 750$ °C, decomposes
Fe_2O_3	1347	247.7	200	$T > 1400$ °C, dissociate
Co_3O_4	1562	202.3	288	$T > 900$ °C, → CoO
Rh_2O_3	1115	95.3	100	T.S.
NiO	1957	245.2	278	T.S.
CuO	1336	157.0	268	$T > 800$ °C, decomposes
ZnO	1800–1975	348	N.R.	T.S.
Al_2O_3	2050	558.4	N.R	T.S.
Ga_2O_3	1740–1805	360	320	T.S.
In_2O_3	1910–2000	308.6	350	T.S.
SiO_2	1720	429.1	N.R	T.S.
SnO_2	1900–1930	290.5	500	T.S.
Bi_2O_3	817	192.6	400	
Sb_2O_3	655	233.2	563	Easy sublimates
TeO_2	2127	162.6	355	$T > 450$ °C, sublimates

N.R.: no reduction detected between 150 and 700 °C.

Korotcenkov, G. (2007). "Metal oxides for solid-state gas sensors: What determines our choice?" Materials Science and Engineering: B 139(1): 1-23.

Prior Work: Au Nanoparticle Incorporated Oxides

An Optical Absorption Peak Associated with the Gold Nanoparticles Shifts to Lower Wavelengths in Reducing Atmospheres.

Gold Nanoparticle-Doped TiO_2 Semiconductor Thin Films: Gas Sensing Properties**

By *Dario Buso, Michael Post, Carlo Cantalini, Paul Mulvaney,* and *Alessandro Martucci**

Adv. Funct. Mater. 2008, 18, 3843–3849

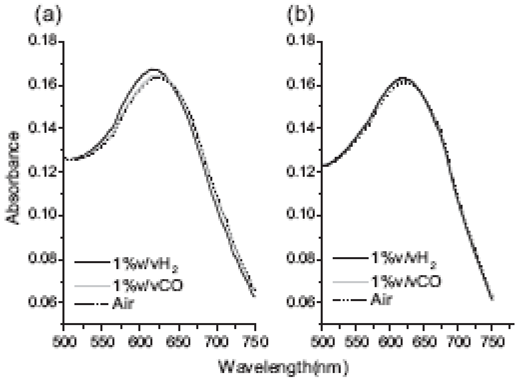


Figure 3. Optical absorbance spectra of films annealed at 400 °C (a) and 500 °C (b) measured in air (dotted line) and during exposure to 1% v/v CO (gray line) and 1% v/v H_2 (black line) at 360 °C operative temperature. The figure highlights the effect of gas exposure on the SPR frequencies of Au NPs (500–750nm region).

Au / TiO_2

Optical hydrogen sensitivity of noble metal–tungsten oxide composite films prepared by sputtering deposition

Masanori Ando[a,*], Rupert Chabicovsky[b], Masatake Haruta[a]

Sensors and Actuators B 76 (2001) 13–17

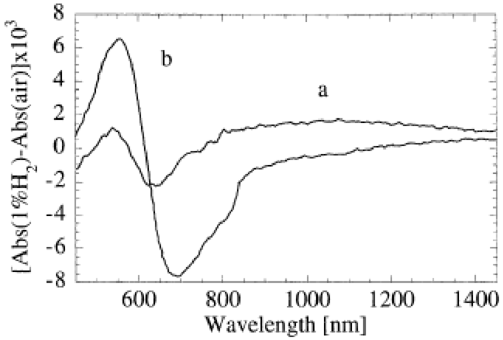


Fig. 8. Difference spectra obtained by subtracting the absorption spectra of the Au–WO_3 composite film in fresh air from those in air containing 1 vol.% H_2 at temperatures of: (a) 200°C; (b) 250°C.

Au / WO_3

Plasmonic Based Kinetic Analysis of Hydrogen Reactions within Au–YSZ Nanocomposites

Nicholas A. Joy, Charles M. Settens, Richard J. Matyi, and Michael A. Carpenter*

dx.doi.org/10.1021/jp11228h | J. Phys. Chem. C XXXX, XXX, 000–000

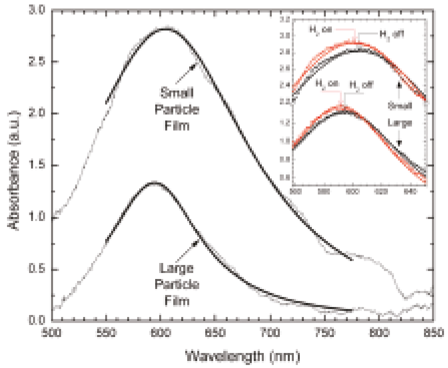


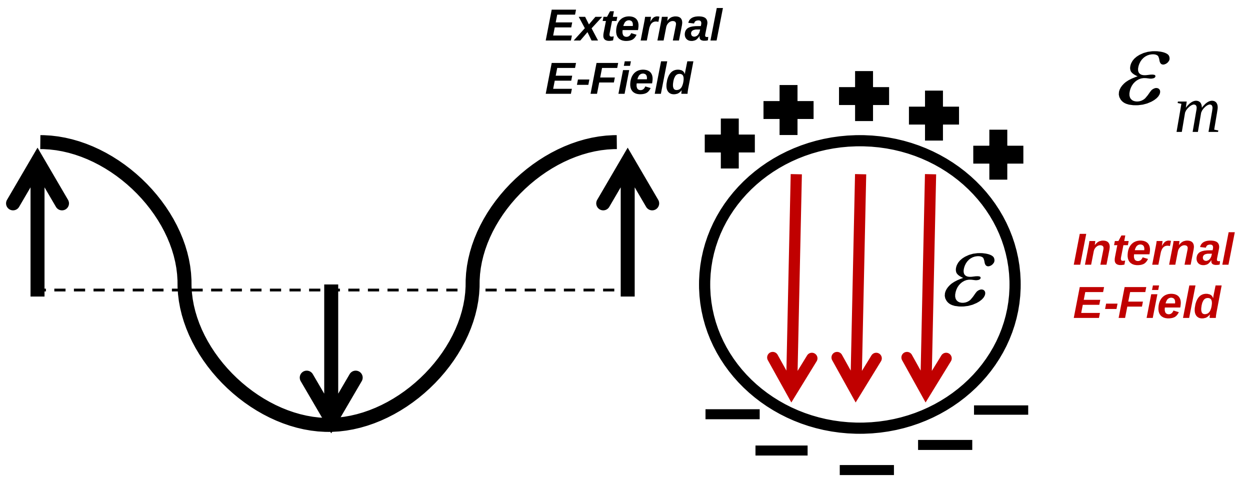
Figure 2. Example of the LSPR absorption spectra acquired during the experiment and the corresponding Lorentzian fits. The inset illustrates the ~3–5 nm peak shift upon gas exchange.

Au / YSZ

In a Number of Recent References, Au Nanoparticle Incorporated Metal Oxide Thin Films Have Shown Enhanced Gas Sensing Response Relative to Base Metal Oxide Thin Films.

Surface Plasmon Resonance Based Sensing

Localized Surface Plasmon Resonance in Noble Metal Nanoparticles is Associated with the Free Electrons



$$\sigma_{ABS} = \left(\frac{18\pi}{\lambda}\right)\frac{\varepsilon_m^{3/2}\,\mathrm{Im}[\varepsilon]}{\mathrm{Im}[\varepsilon]^2 + \left(2\varepsilon_m + \mathrm{Re}[\varepsilon]\right)^2}$$

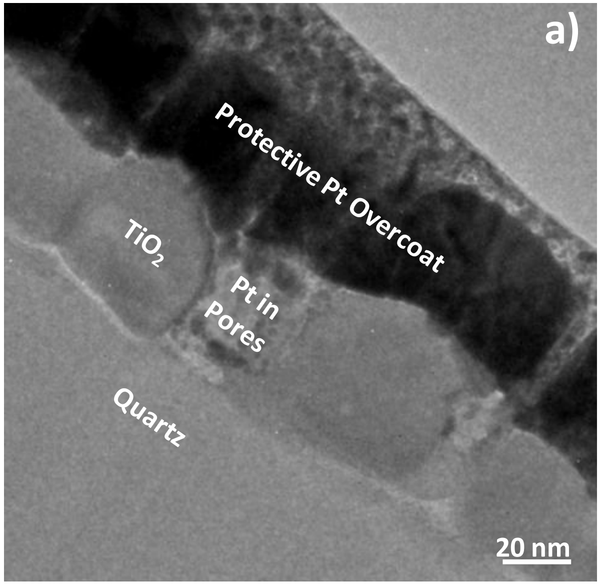
A Peak in Absorption Occurs if:

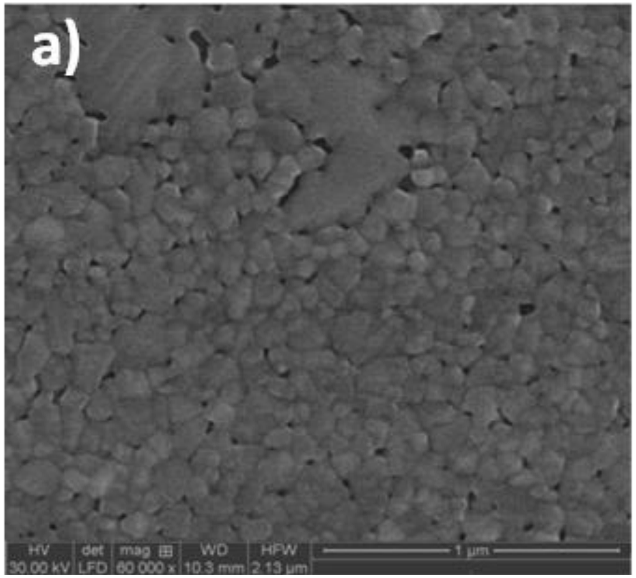
Re[ε]□-2 ε_m

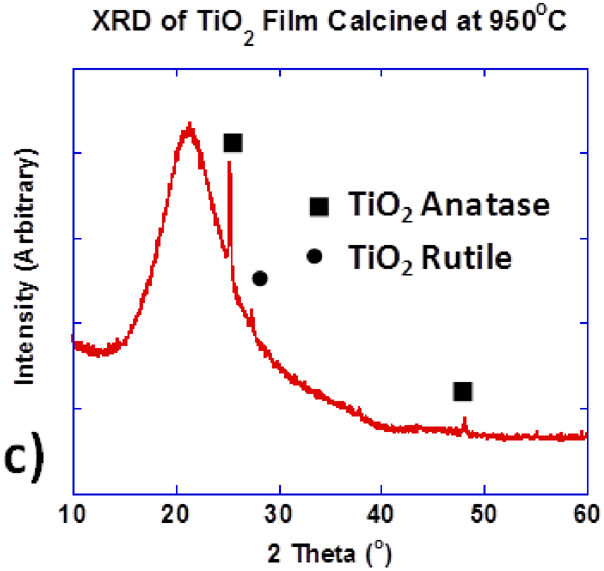
Froelich Condition

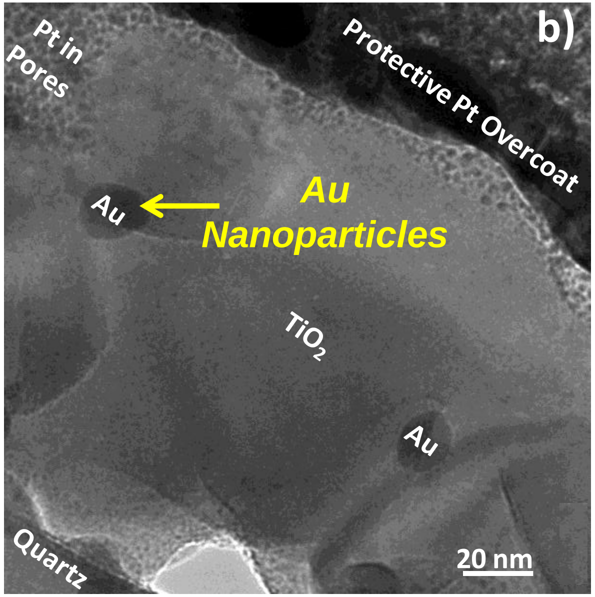
Surface Charges Create an Internal Field that Acts as a Restoring Force on Displaced Charge Carriers Resulting in an Oscillation with an Associated Resonance

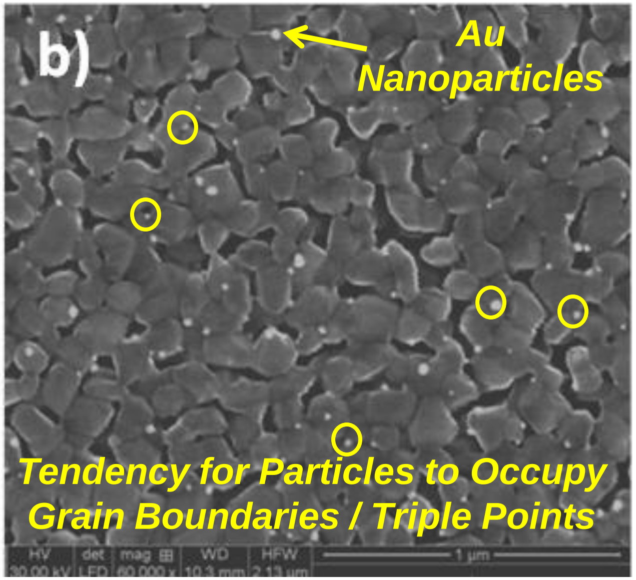
Sol-Gel Deposited TiO_2 and TiO_2 / Au Thin Films

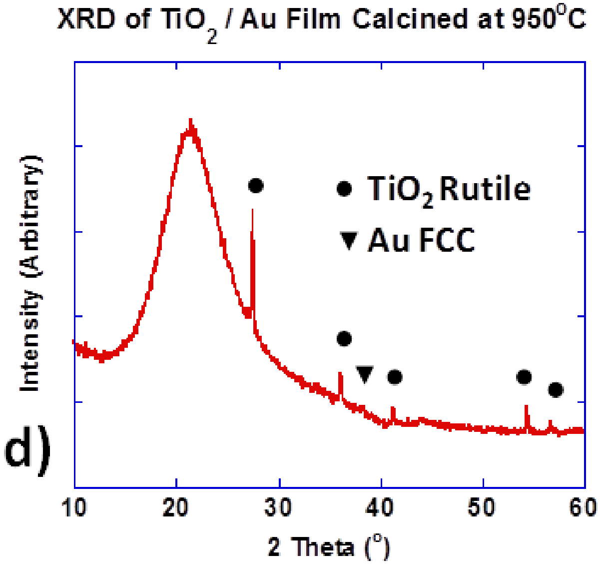




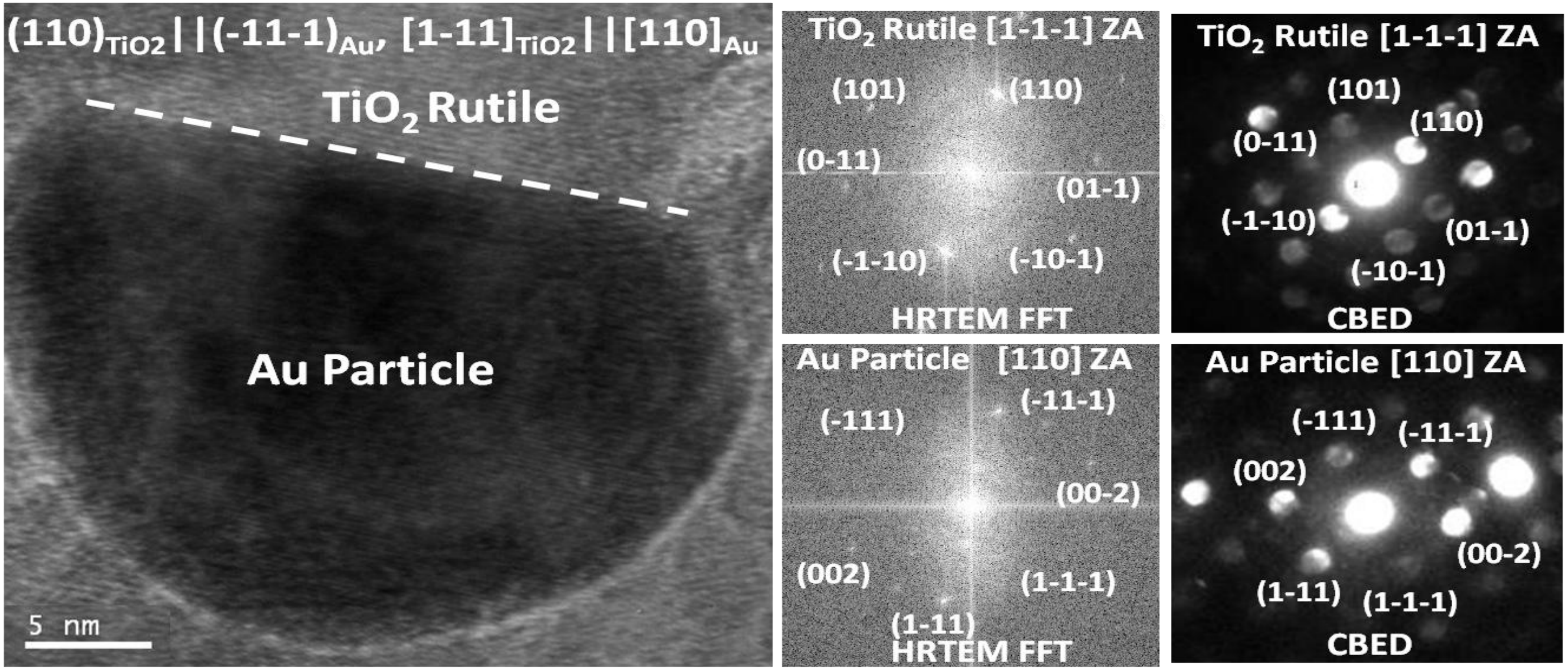








Detailed Microstructure of TiO_2 / Au Thin Films



S. Sivaramakrishnan, "Interfacial properties of epitaxial gold nanocrystals supported on rutile titanium dioxide", PhD Thesis, Materials Science and Engineering, University of Illinois at Urbana-Champaign, 2010.

Au Nanoparticles Tend to Have a Specific Crystallographic Orientation Relationship with the Underlying TiO_2 Rutile Matrix.

$\{110\}_{TiO_2}||\{111\}_{Au}$, $\langle 111\rangle_{TiO_2}||\langle 110\rangle_{Au}$ ➔ Most Commonly Observed Here

$\{110\}_{TiO_2}||\{111\}_{Au}$, $\langle 001\rangle_{TiO_2}||\langle 110\rangle_{Au}$ ➔ Reported to Be the Most Stable (Observed Occasionally)

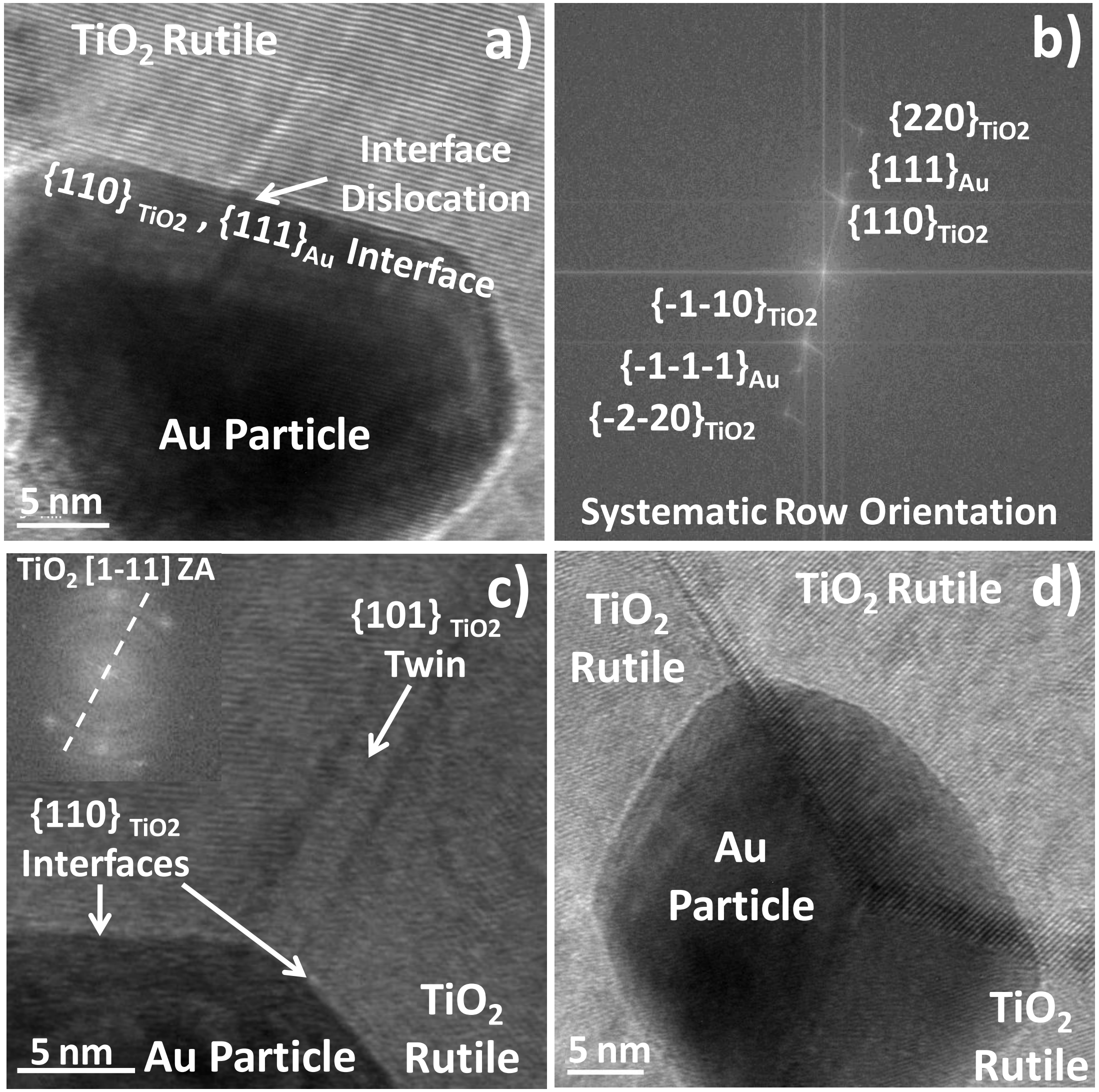
Detailed Microstructure of TiO_2 / Au Thin Films

Dislocation Observed in Systematic Row Orientation

FFT Illustrating $\{110\}_{TiO_2} \parallel \{111\}_{Au}$

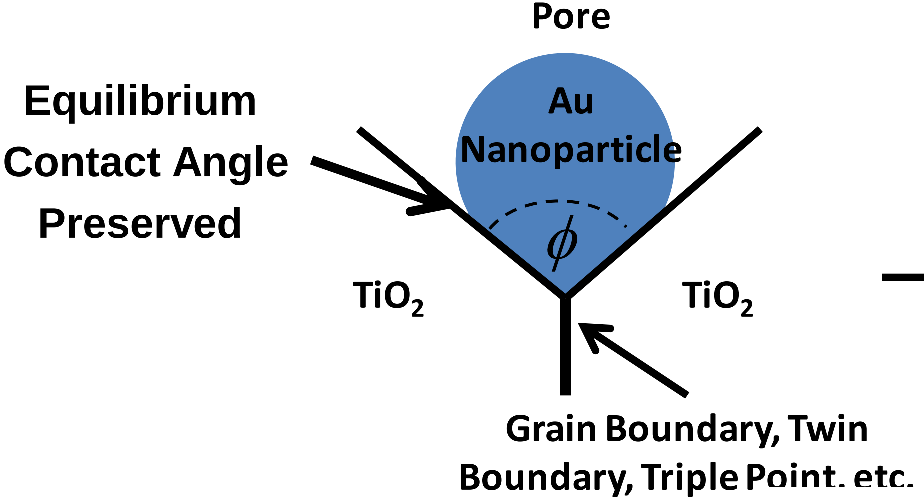
{101} TiO_2 Twin Boundary

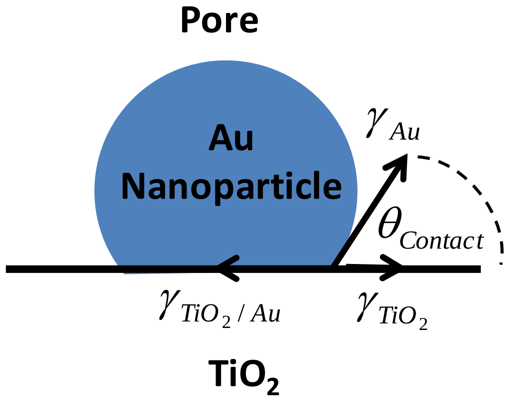
Triple Point Between Three TiO_2 Grains



Au Nanoparticles Tend to Occupy Specific TiO_2 Rutile Microstructural Sites.

Surface Energy Modeling in the Au / TiO$_2$ System





$$\phi = \pi$$

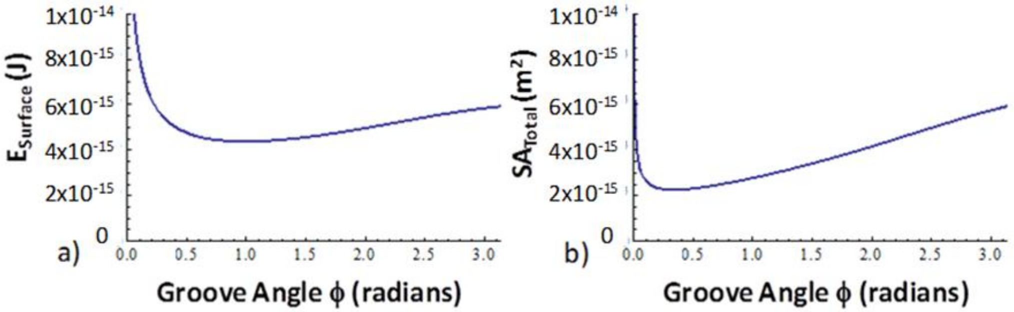
$$\gamma_{Au} = \gamma_{Au\{111\}} \approx 1.283 J/m^3$$

$$\gamma_{TiO_2} = \gamma_{TiO_2\{110\}} \approx 0.33 J/m^3$$

$$\gamma_{TiO_2/Au} = \gamma_{TiO_2\{110\}/Au\{111\}} \approx 0.61 J/m^3$$

$$E_{Surface} = \gamma_{Au} SA_{SphereCap} + (\gamma_{TiO_2/Au} - \gamma_{TiO_2}) SA_{Groove}$$

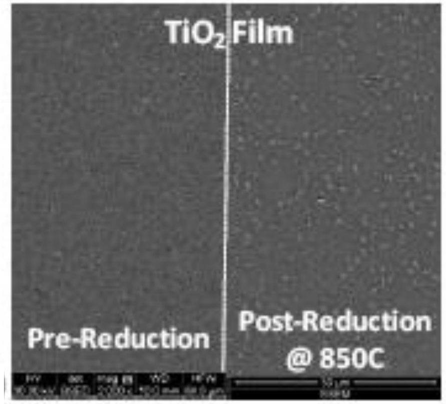
$$\left(\frac{E_{Surface}(\phi = \pi) - E_{Surface}(\phi = 3\pi/4)}{k_B T}\right) \approx 70{,}500 @ T = 950^\circ C$$

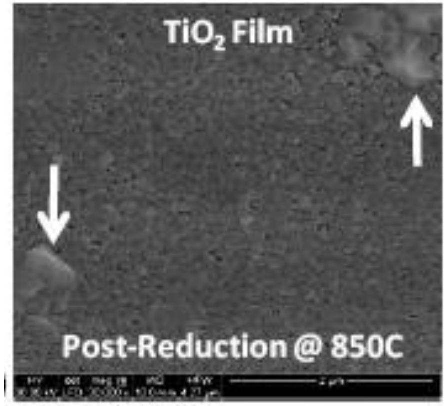


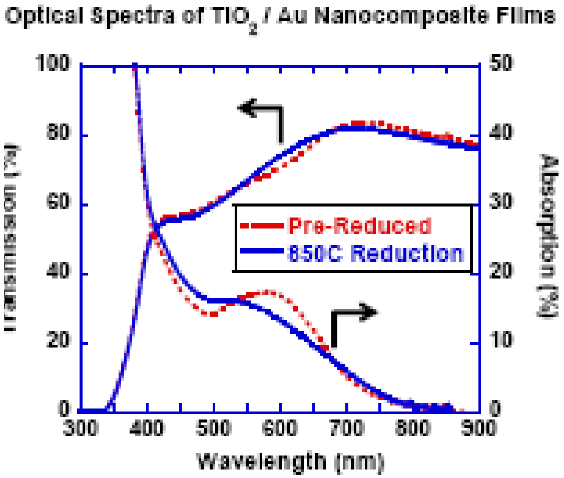
S. Sivaramakrishnan, "Interfacial properties of epitaxial gold nanocrystals supported on rutile titanium dioxide", PhD Thesis, Materials Science and Engineering, University of Illinois at Urbana-Champaign, 2010.

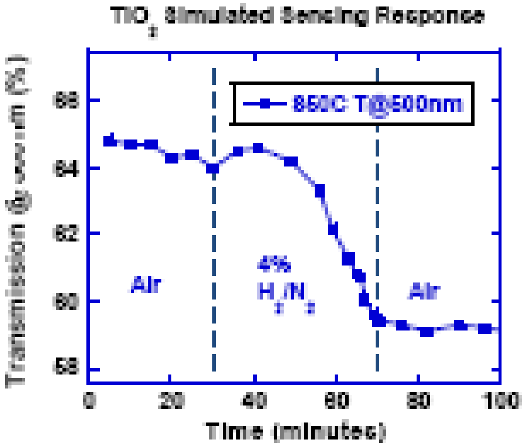
Reduction in Surface Energy For a Given Au Nanoparticle Volume Can Explain a Strong Tendency for Nanoparticles to Occupy Grain Boundaries, Twin Boundaries, or Triple Points.

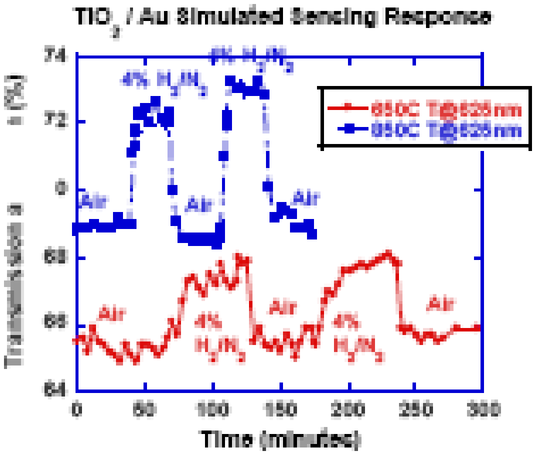
Simulated Sensing Responses at High Temperatures

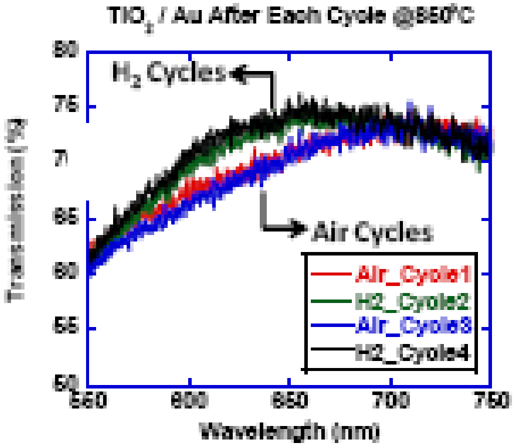










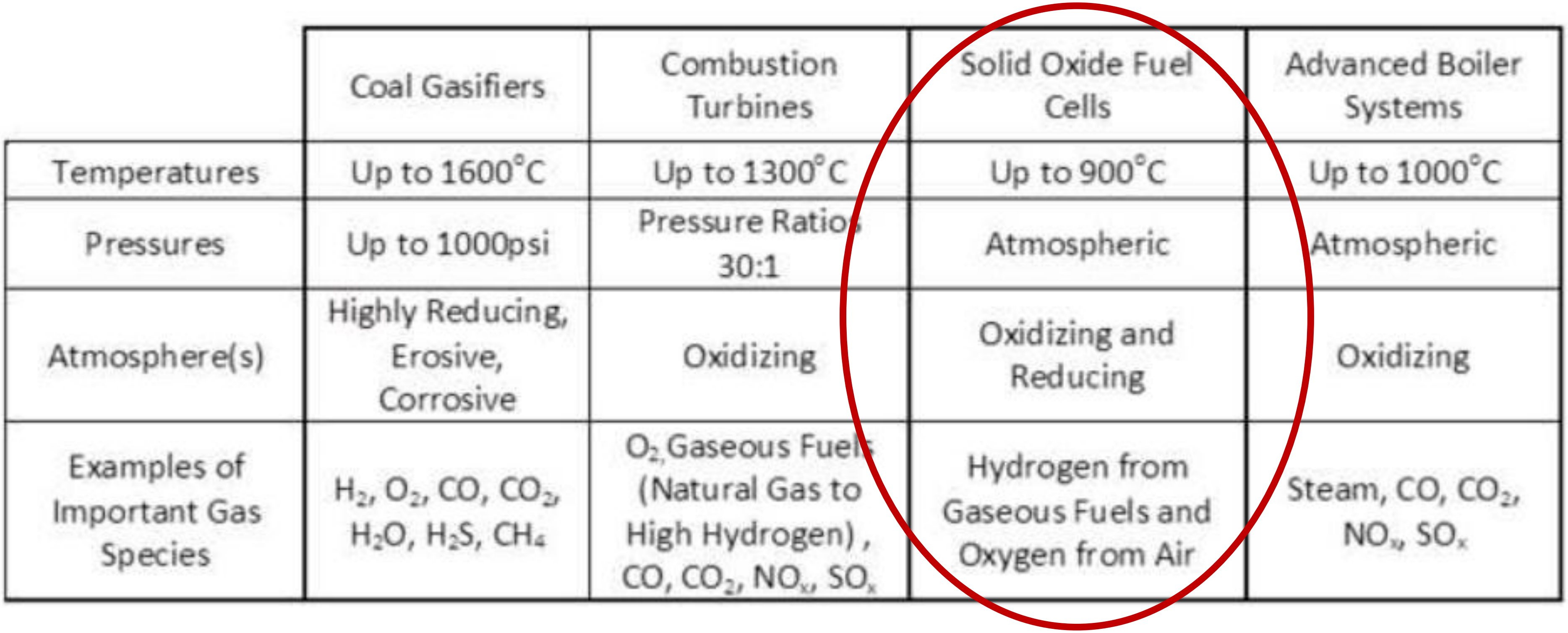


The TiO_2 / Au Film Shows a Potentially Useful Optical Response at Temperatures as High as T=850°C But Not for the Base TiO_2 Film.

1) **Rapid Response Rate, Particularly at High Temperatures Such as 850°C.**
2) **Reversible Response for Multiple Cycles.**

Advanced Fossil Energy Technologies

Table of Relevant Harsh Environments in Advanced Fossil Energy Technologies

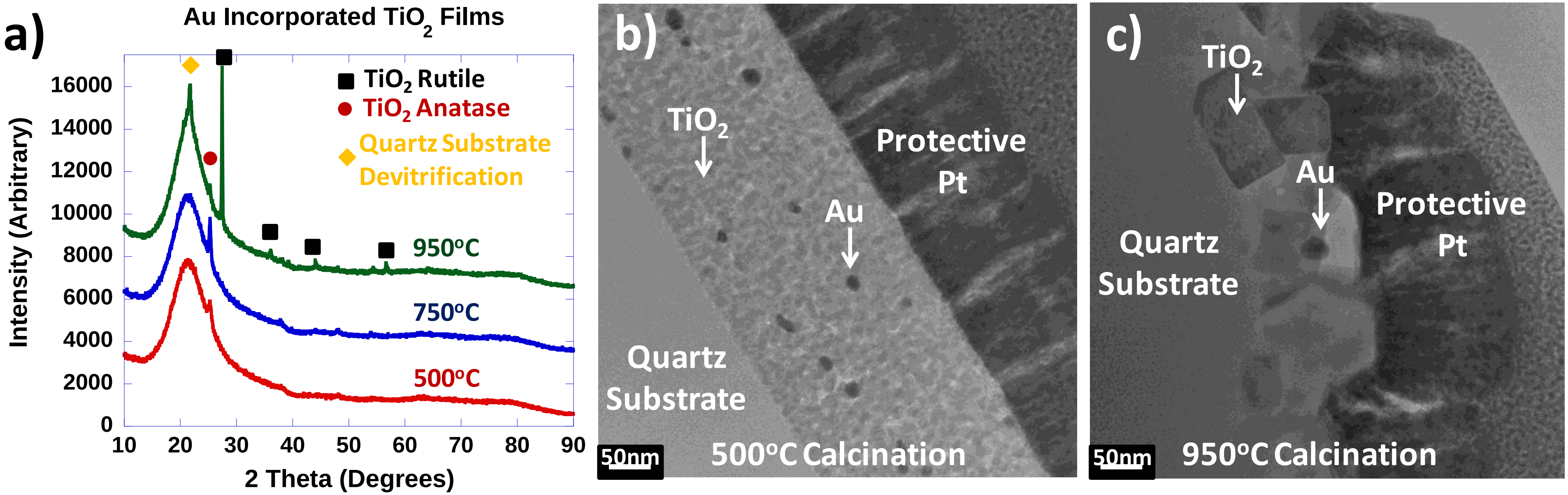


	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
Examples of Important Gas Species	H_2, O_2, CO, CO_2, H_2O, H_2S, CH_4	O_2 Gaseous Fuels (Natural Gas to High Hydrogen) , CO, CO_2, NO_x, SO_x	Hydrogen from Gaseous Fuels and Oxygen from Air	Steam, CO, CO_2, NO_x, SO_x

Au / TiO_2 Films Have Potential Application in High Temperature H_2 Sensing for Solid Oxide Fuel Cells.

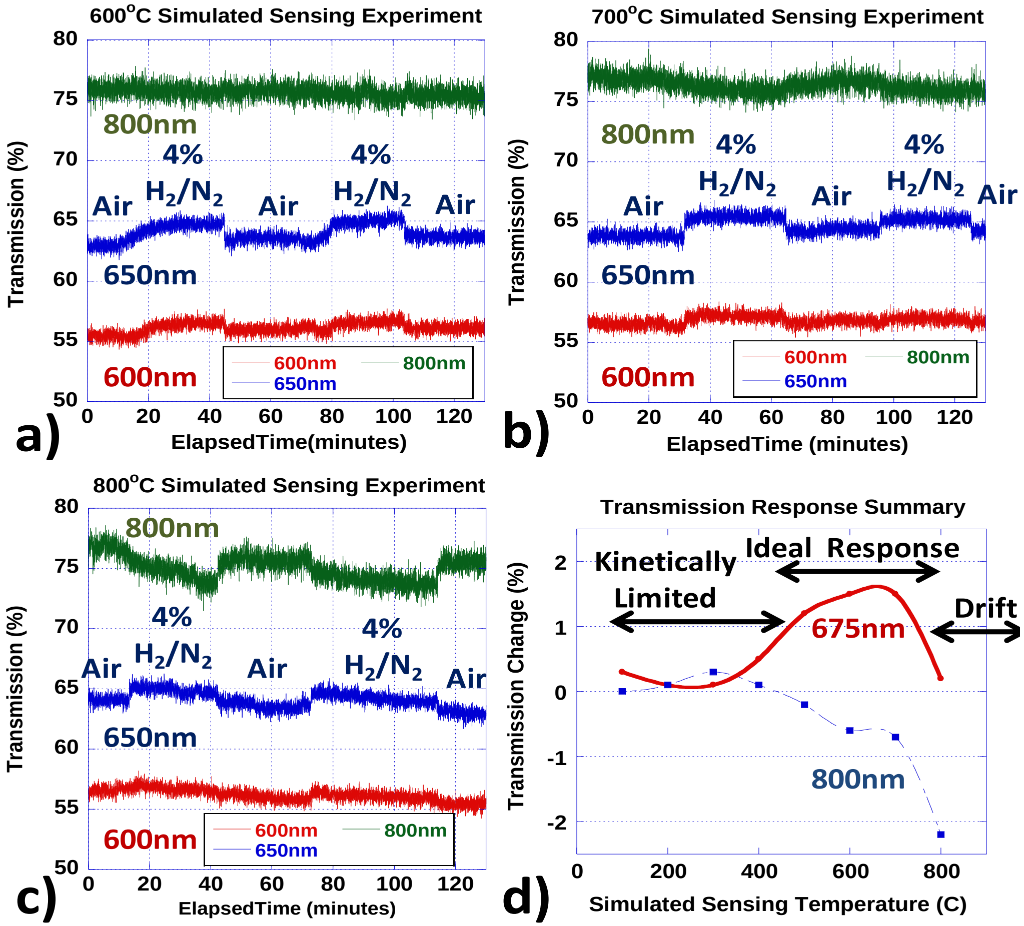
Potential Relevance to Other Applications Needs Investigated.

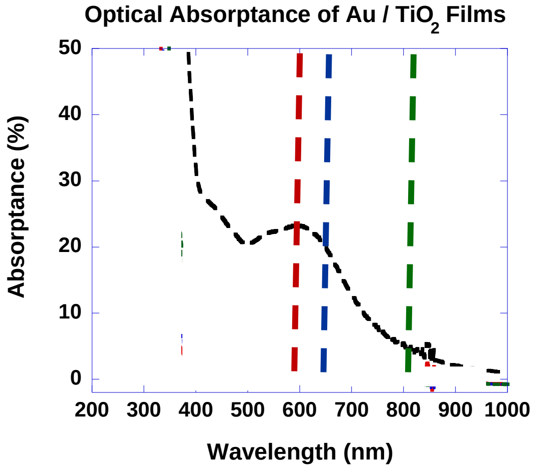
More Detailed Studies of Au / TiO_2 Films



A Dramatic Difference in Microstructure is Observed for the Highest and Lowest Temperature Calcination Treatments. Some Evidence for Substrate Devitrification is Also Observed.

More Detailed Studies of Au / TiO_2 Films



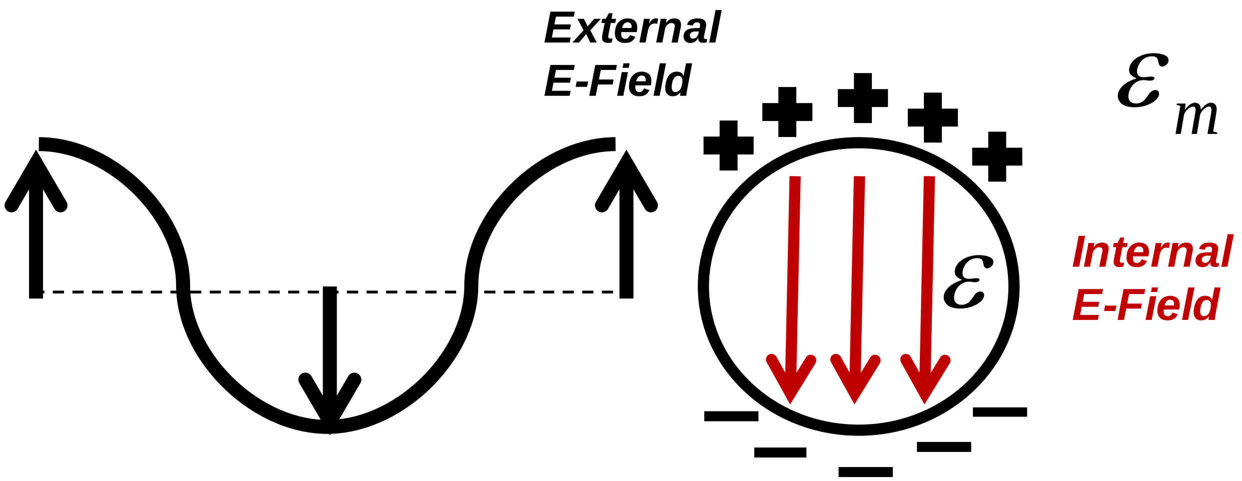


Why is the Largest Response Observed at 650nm?

Simulated Sensing Experiments Show an Optimal Window for High Temperature H_2 Response Ranging from Approximately 500-800°C.

Surface Plasmon Resonance Based Sensing

Localized Surface Plasmon Resonance in Noble Metal Nanoparticles is Associated with the Free Electrons



$$\sigma_{ABS} = \left(\frac{18\pi}{\lambda}\right)\frac{\varepsilon_m^{3/2}\,\mathrm{Im}[\varepsilon]}{\mathrm{Im}[\varepsilon]^2 + (2\varepsilon_m + \mathrm{Re}[\varepsilon])^2}$$

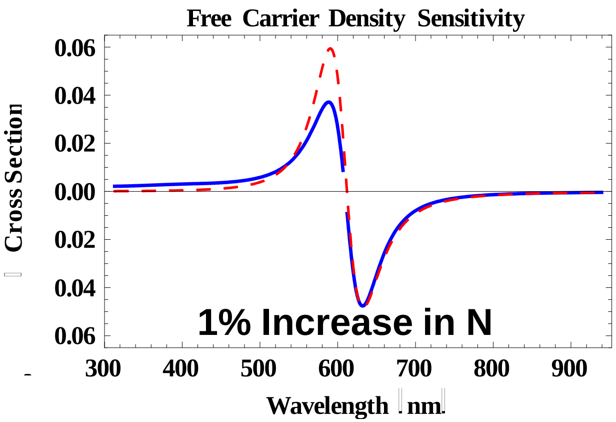
A Peak in Absorption Occurs if:

Re[ε]□-2 ε_m

Froelich Condition

Surface Charges Create an Internal Field that Acts as a Restoring Force on Displaced Charge Carriers Resulting in an Oscillation with an Associated Resonance

Comparison of Model with Literature Results



Theoretical Modeling

Optical hydrogen sensitivity of noble metal–tungsten oxide composite films prepared by sputtering deposition

Masanori Ando[a,*], Rupert Chabicovsky[b], Masatake Haruta[a]

Sensors and Actuators B 76 (2001) 13–17

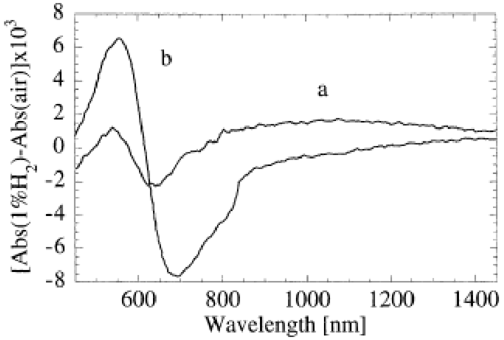


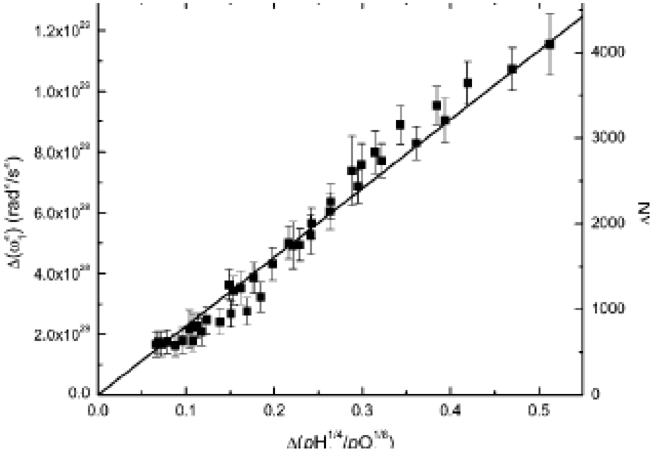
Fig. 8. Difference spectra obtained by subtracting the absorption spectra of the Au–WO_3 composite film in fresh air from those in air containing 1 vol.% H_2 at temperatures of: (a) 200°C; (b) 250°C.

Direct Observations of Electrochemical Reactions within Au–YSZ Thin Films via Absorption Shifts in the Au Nanoparticle Surface Plasmon Resonance

J. Phys. Chem. C 2008, *112*, 6749–6757

Phillip H. Rogers, George Sirinakis, and Michael A. Carpenter*

College of Nanoscale Science and Engineering, The University at Albany—State University of New York, 255 Fuller Road, Albany, New York 12203



Experimentally Reported Observations Consistent With LSPR Modeling

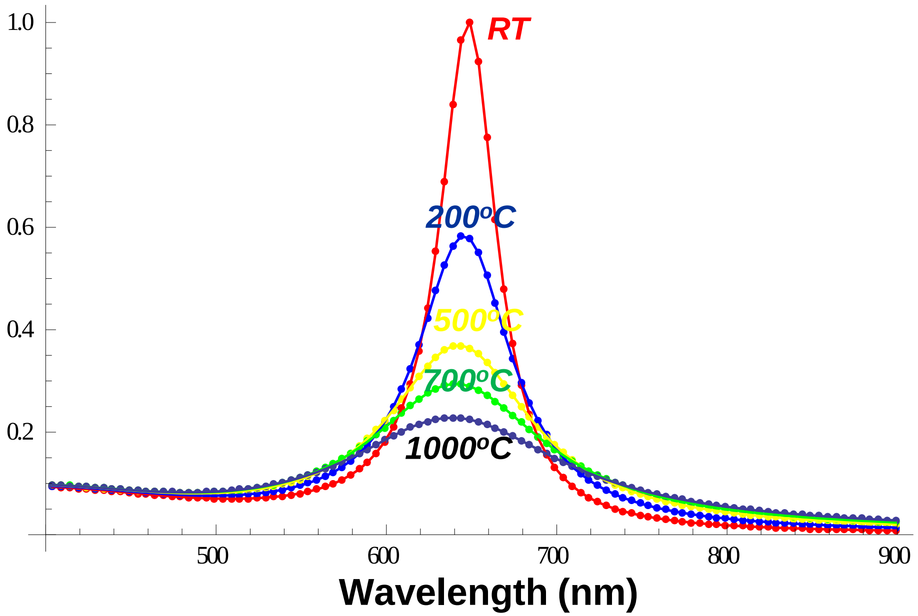
Qualitative Change in Optical Absorption is Similar to Published Results

Defect Chemistry was Linked with Ratios of H_2 to O_2 Partial Pressure.

Experimental Results in Literature Strongly Suggest Direct Interactions Between the Oxide and the Gas Atmosphere Followed by Charge Transfer Reactions with the Au Nanoparticles.

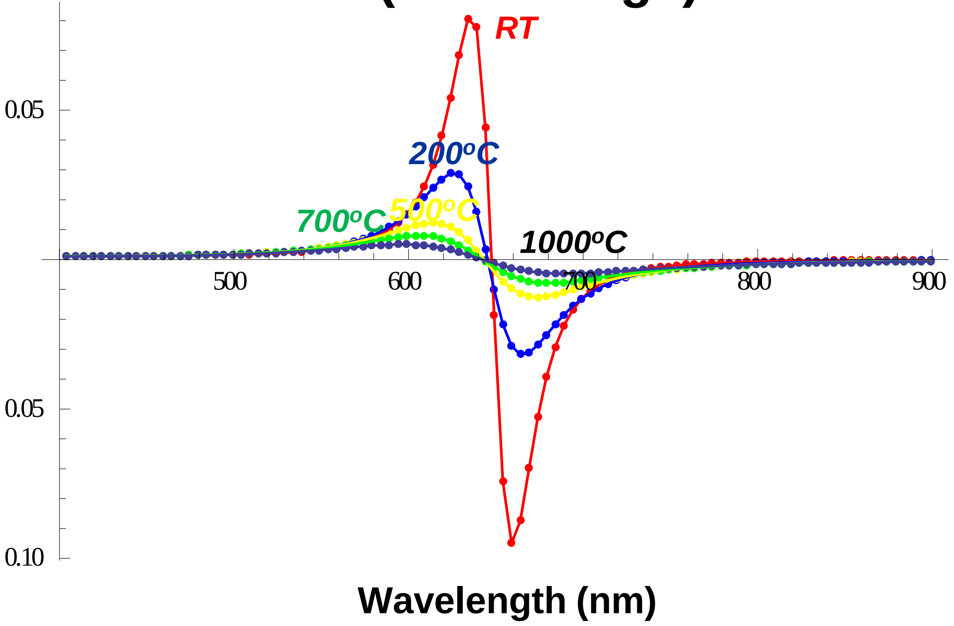
Temperature Dependence of Sensitivity

Normalized Absorption Cross Section



Au Free Carrier Sensitivity

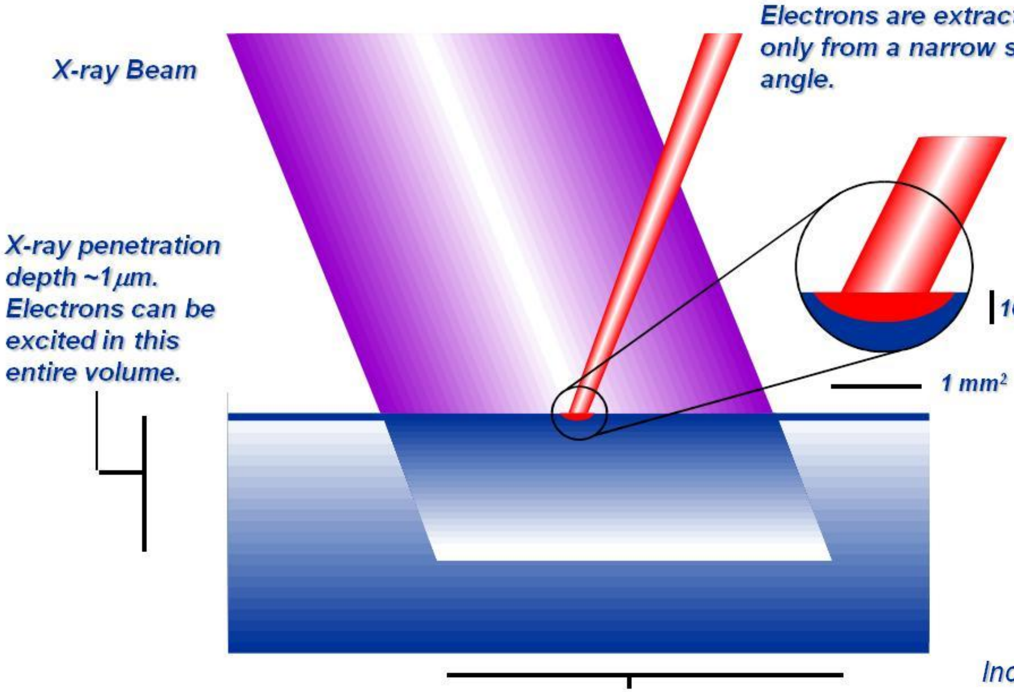
(1% Change)



Broadening of the Absorption Peak is Observed at High Temperatures Due to Increased Free Electron Scattering in Au. Shifts Are Also Observed.

The Result is a Decrease in Peak Sensitivity and a Shift in Peak Wavelength.

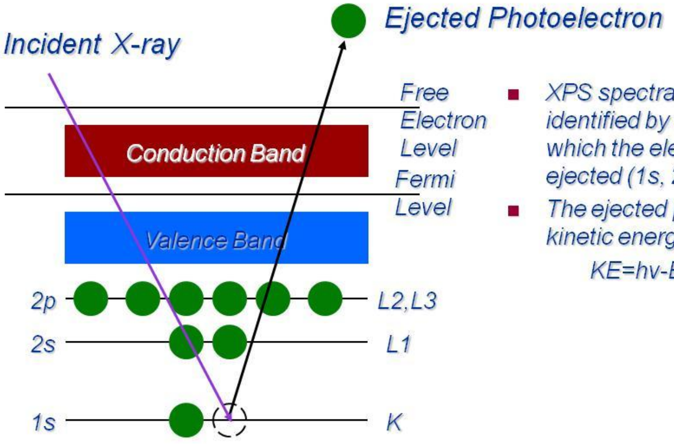
X-ray Photoelectron Spectroscopy



Electrons are extracted only from a narrow solid angle.

X-ray penetration depth ~1 μm. Electrons can be excited in this entire volume.

X-ray excitation area ~1x1 cm^2. Electrons are emitted from this entire area



- *XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).*
- *The ejected photoelectron has kinetic energy:*

  $KE = h\nu - BE - \Phi$

XPS Experiments with Au/TiO_2

Work Performed by John Baltrus, NETL

Trial 1

Pretreat with O_2, 20 min, 600 C

- Δ Ti $2p_{3/2}$ – Au $4f_{7/2}$ = 375.25 eV

Treat with 10% H_2/Ar, 20 min, 640 C

- Δ Ti $2p_{3/2}$ – Au $4f_{7/2}$ = 374.80 eV

Trial 2

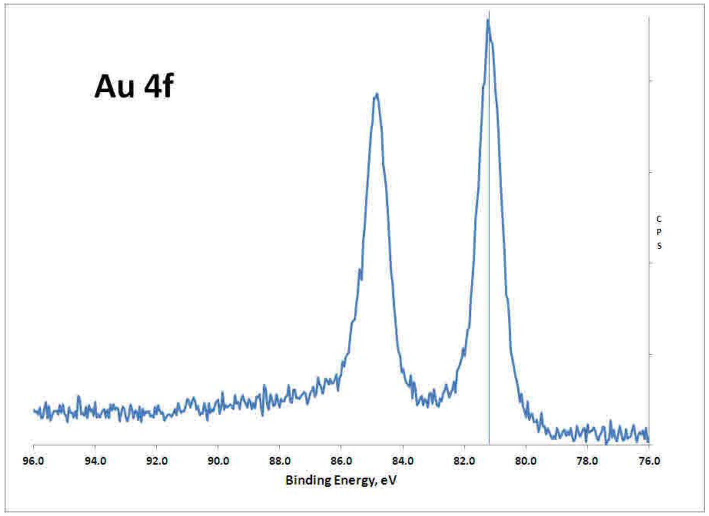
No Pretreatment

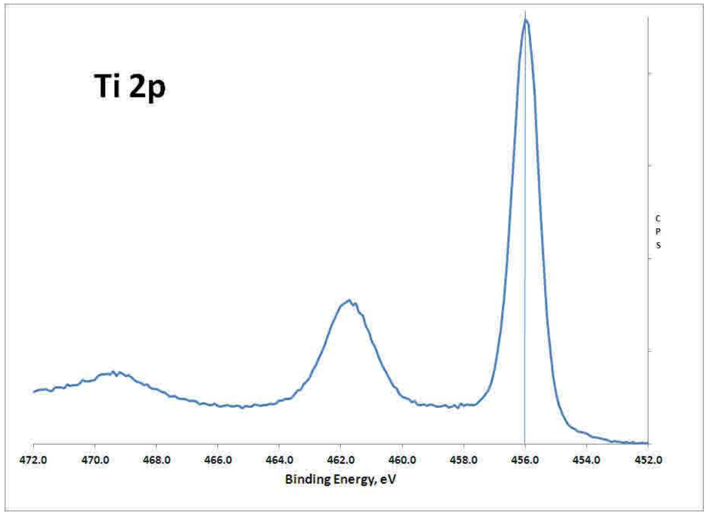
- Δ Ti $2p_{3/2}$ – Au $4f_{7/2}$ = 375.20 eV

Treat with 10% H_2/Ar, 20 min, 640 C

- Δ Ti $2p_{3/2}$ – Au $4f_{7/2}$ = 374.80 eV

A decrease in ΔB.E. is consistent with injection of electrons into the conduction band of TiO_2 relative to Au.





Lessons Learned from TiO_2 and Au / TiO_2 Studies

1) Au-Incorporated Metal Oxides Such as TiO_2 Display Improved Optical Gas Sensing as Compared to Base Metal Oxides.

2) A Temperature Window of Optimal Gas Sensing Response is Observed at Temperatures Between ~500-800ºC.

3) Theoretical Simulations Demonstrate a Broadening of the Absorption Peak at High Temperatures and Illustrate Why there is a Wavelength Dependent Absorption Response.

Future Work

1) We Will Continue Performing a Combination of Fundamental Materials Investigations and Applied Research in this Area.

2) A Number of Material Design Strategies Will Be Pursued.

3) Fundamental and Applied Investigations of High Temperature Gas Sensor Materials are Important for Fossil Energy Applications.

Thank you!

Our Recent Publications in this Area:

1) P. R. Ohodnicki, C. Wang, S. Natesakhawat, J. P. Baltrus, and T. D. Brown, Journal of Applied Physics, 111 064320 (2012).
2) P. R. Ohodnicki, J. P. Baltrus, S. Natesakhawat, B. Howard, and T. D. Brown, Accepted for Publication, Thin Solid Films (2012).
3) P. Ohodnicki et al., Under Review, Journal of Applied Physics, 2012.

Questions or Comments?

Please contact:

Paul.ohodnicki@netl.doe.gov

412-386-7389

EXTRA SLIDES

Sensor Applications in the Aerospace Industry

D. Senesky et al, IEEE Sensors Journal, Vol. 9, No. 11, November 2009

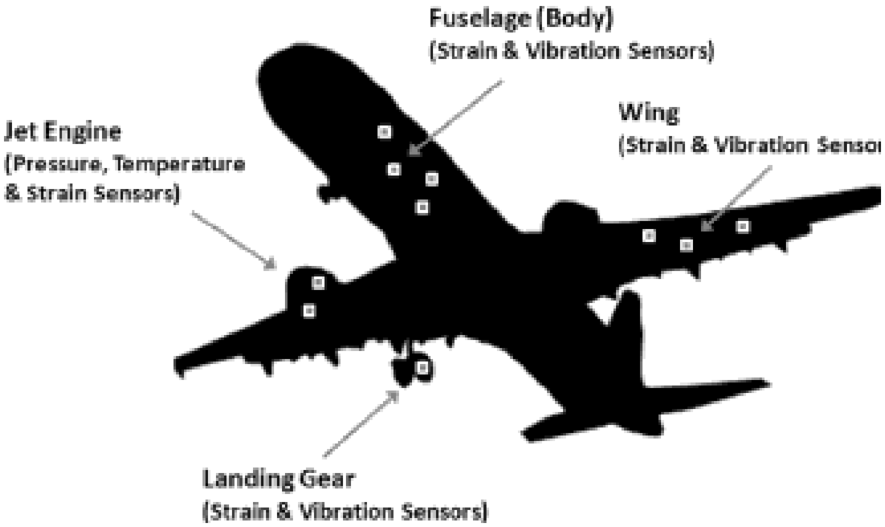


Fig. 1. Schematic representation of the possible locations and types of se
sors to be used for real-time health and performance monitoring of aerospac
systems.

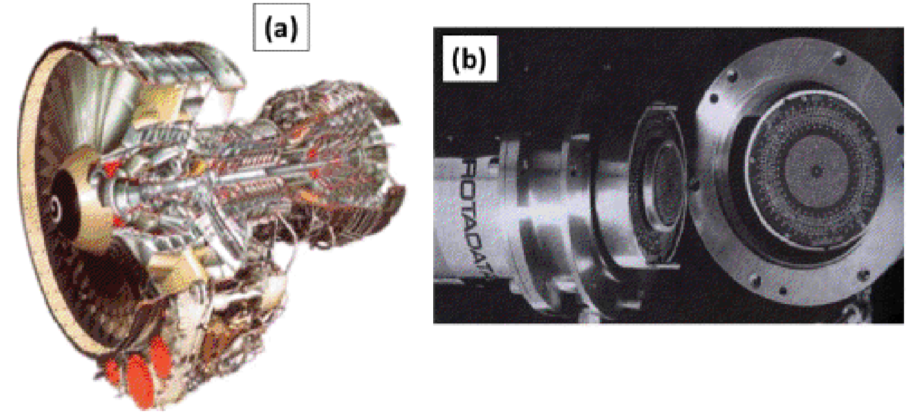


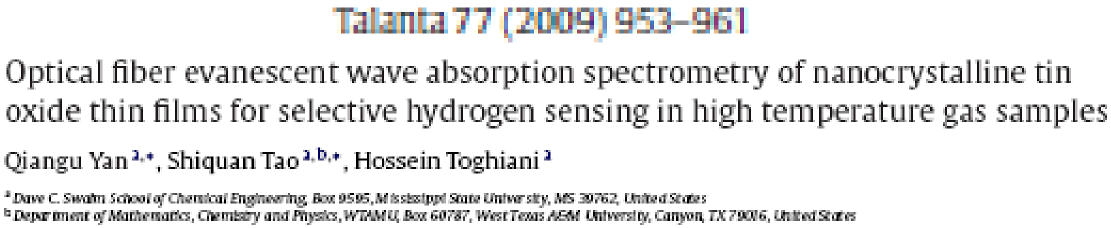
Fig. 3. Schematic image of a jet engine composed of complex systems such as air intake, compressor, combustion chamber, turbine, and exhaust duct [21]. Image of an optical measurement system (Rotodata) that utilizes digital telemetry for diagnostic instrumentation of turbine engines [22].

Careful Control of Air / Fuel Ratio Improves Efficiency and Reduces Emissions

Temperatures up to 1000ºC are Relevant in the Gas Turbine Combustion Environment

High Temperature Harsh Environment Sensors are Also Relevant for Jet Engine Monitoring in the Aerospace Industry

SnO$_2$ Optical Absorption for H$_2$ Exposure at High T



Talanta 77 (2009) 953–961

Optical fiber evanescent wave absorption spectrometry of nanocrystalline tin oxide thin films for selective hydrogen sensing in high temperature gas samples

Qiangu Yan[a,*], Shiquan Tao[a,b,*], Hossein Toghiani[a]

[a] Dave C. Swalm School of Chemical Engineering, Box 9595, Mississippi State University, MS 39762, United States
[b] Department of Mathematics, Chemistry and Physics, WTAMU, Box 60787, West Texas A&M University, Canyon, TX 79016, United States

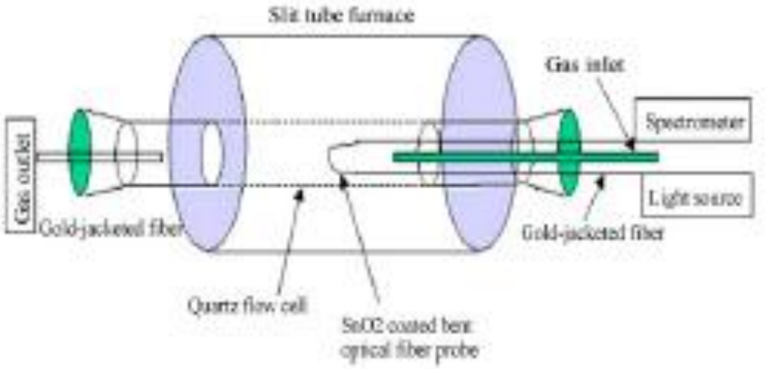


Fig. 1. A diagram of the testing system for investigating the optical properties o sol–gel derived silica optical fibers.

(1)

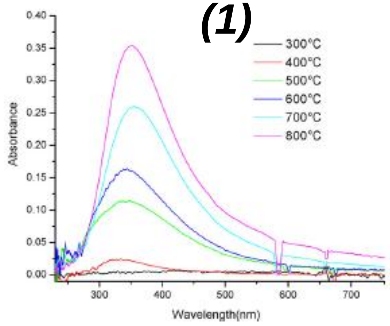


Fig. 5. UV–vis absorption spectra of a SnO$_2$ thin film optical fiber sensor response to a 1 vol% H$_2$–N$_2$ flow under different temperatures.

(2)

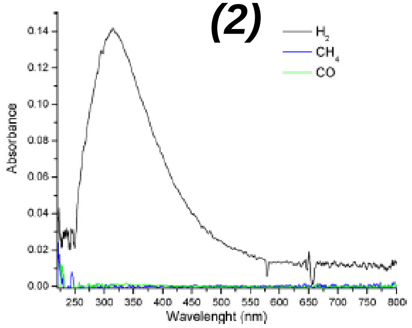
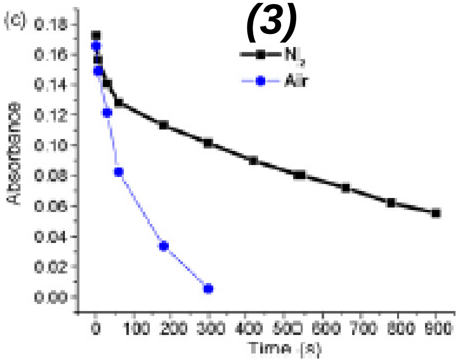
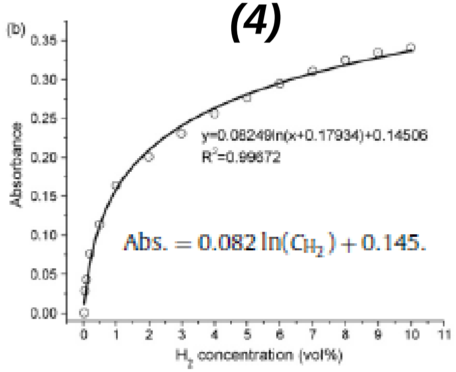


Fig. 4. UV–vis absorption spectra of a SnO$_2$ thin film optical fiber sensor response to 1 vol% H$_2$, 5 vol% CH$_4$ and 5 vol% CO in N$_2$ flows at 600 °C, respectively.

(3)



(4)



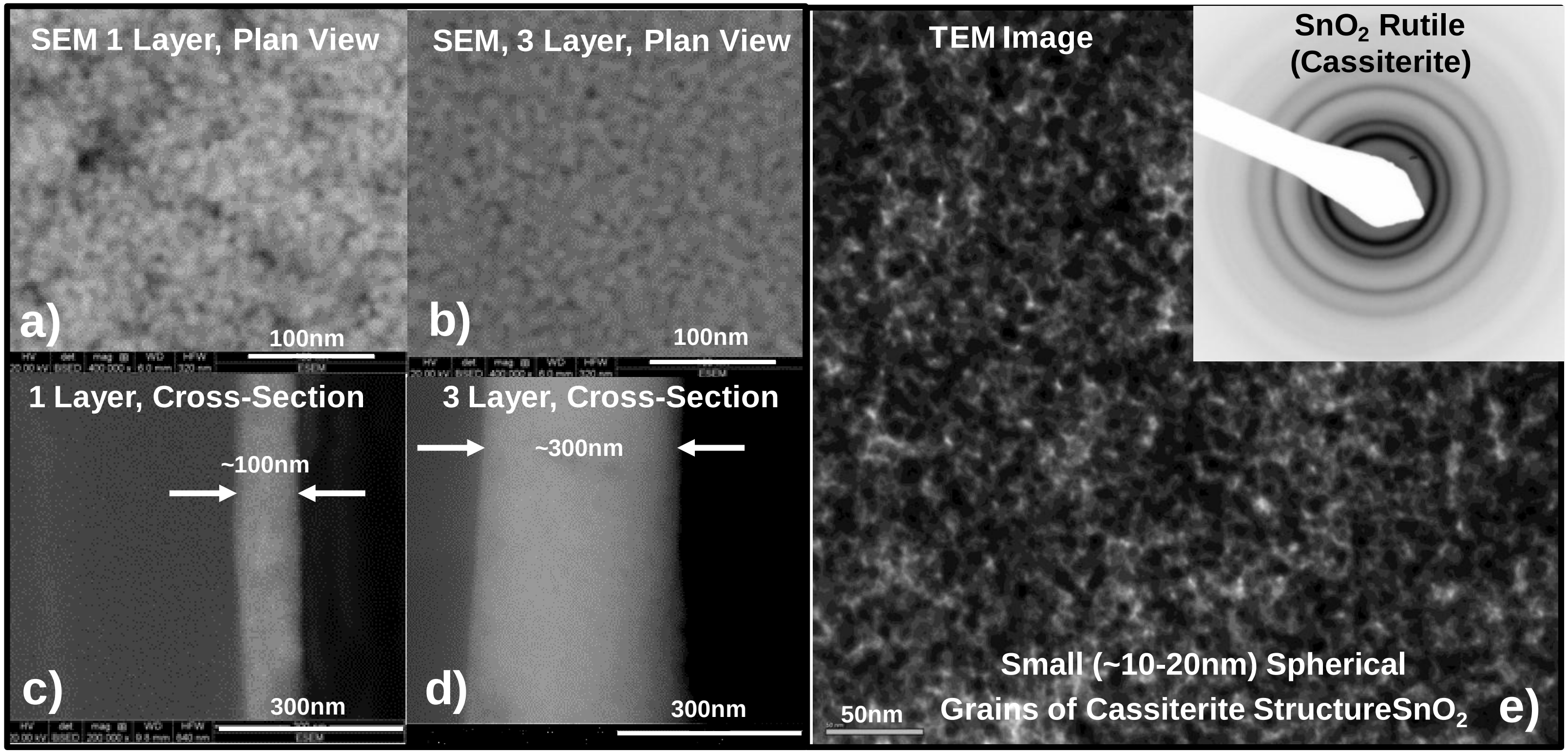
$$\text{Abs.} = 0.082\ \ln(C_{H_2}) + 0.145.$$

Examples of Observations Reported by the Authors of This Work:

1) Increasing Absorption with Increasing Temperature
2) Selectivity to H$_2$ as Compared to CH$_4$ or CO
3) Transformation is Reversible, Recovery Time Shorter in Air Atmosphere vs. N$_2$
4) Logarithmic Relationship Between H$_2$ and Absorbance at Fixed Temperature

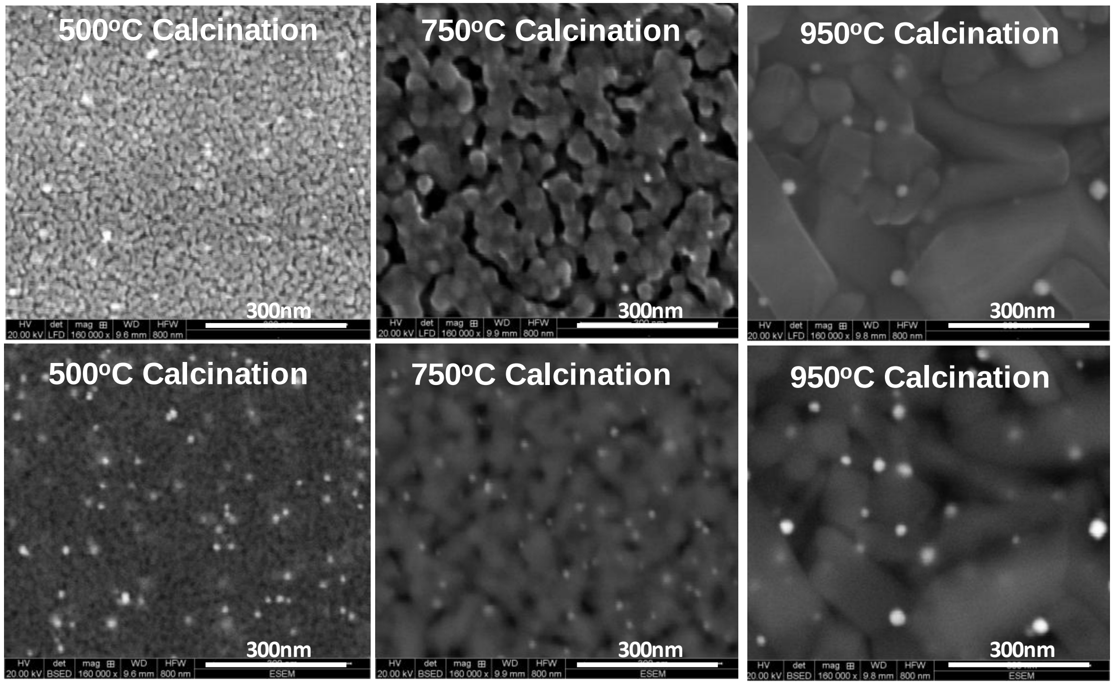
First Investigation : Detailed Study of SnO_2 Film Interactions with High Temperature H_2 Environment

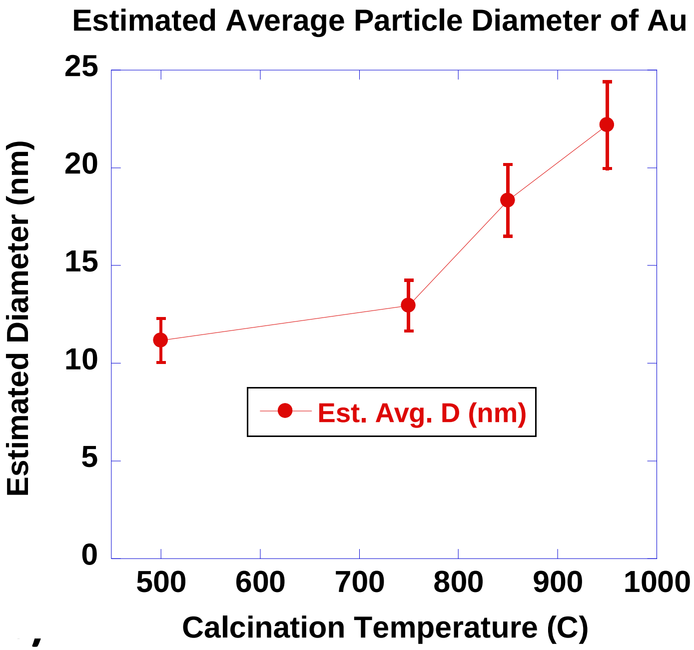
Sol-Gel Deposition: Sn(IV)-isopropoxide (10% w/v) in isopropanol (72 vol%) and toluene (18 vol%) Spin-Coated 1, 2, and 3-Layer Films



Original Films were Calcined @ 500^{o}C and Deposited on Float Glass Substrates with Limited Temp. Stability (~600^{o}C).

More Detailed Studies of Au / TiO_2 Films

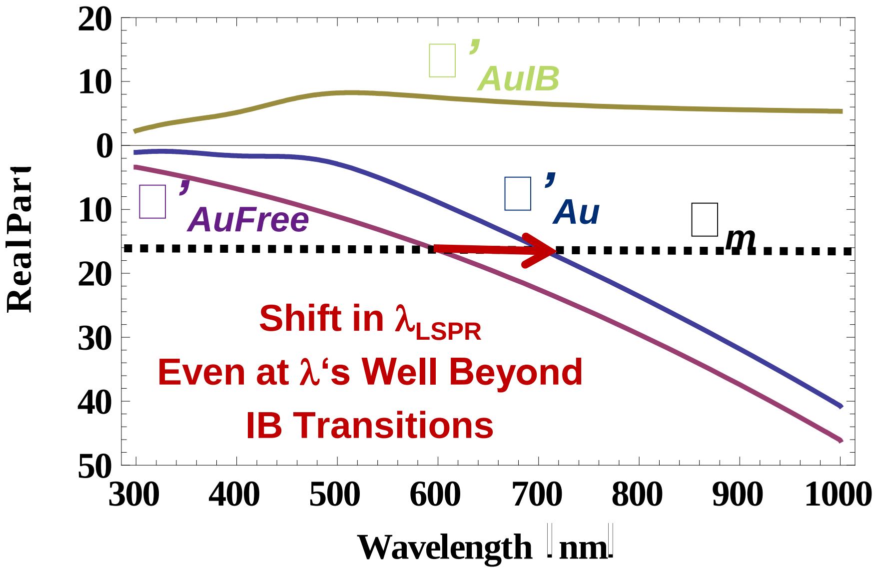




A Series of New Au / TiO_2 Films were Prepared Using Similar Deposition Techniques for Investigation as a Function of Calcination Temperature and Simulated Sensing Temperature.

Optical Constants of Au Nanoparticles

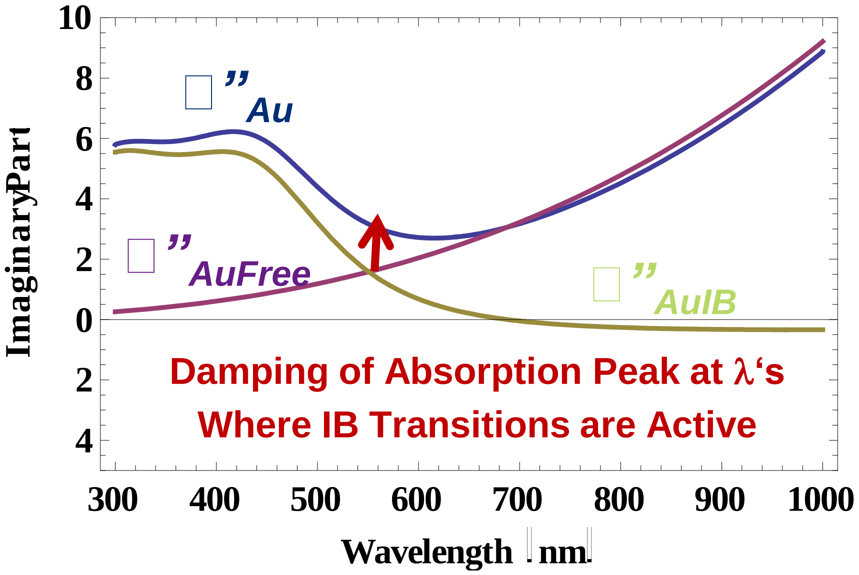
$$\epsilon_{Au} = \epsilon_{AuFree} + \epsilon_{AuIB} = \left(1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}\right) + \epsilon_{AuIB} \qquad \omega_p = \sqrt{\frac{Ne^2}{m^*\epsilon_0}}$$



Shift in λ_{LSPR}

Even at λ‘s Well Beyond

IB Transitions



Damping of Absorption Peak at λ‘s

Where IB Transitions are Active

Interband Electronic Transitions Significantly Modify the Optical Constants of Au as Compared to the Damped Free Electron Theory.

Room Temp. Sensitivity of Au LSPR Absorption Peak

$$\epsilon_{Au} = \epsilon_{AuFree} + \epsilon_{AuIB} = \left(1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}\right) + \epsilon_{AuIB} \qquad \omega_p = \sqrt{\frac{Ne^2}{m^* \epsilon_0}}$$

$$\sigma_{ABS} = \sigma_{ABS}(\varepsilon_m, \Gamma, N, \lambda) = \left(\frac{18\pi}{\lambda}\right) \frac{\varepsilon_m^{3/2}\,\mathrm{Im}[\varepsilon]}{\mathrm{Im}[\varepsilon]^2 + \left(2\varepsilon_m + \mathrm{Re}[\varepsilon]\right)^2}$$

Γ = Damping Coefficient Related to the Effective Resistivity of Au

N = Carrier Density of Free Electrons of the Au Nanoparticle

ε_m = Dielectric Constant / Refractive Index of Matrix Phase

Three Primary Materials Constants Can Interact with the Ambient Environment Resulting in Modifications of the LSPR Absorption Peak.

Temperature Dependence of Sensitivity

How is Sensitivity Affected at Extreme Temperatures (e.g. 900ºC)?

$$\epsilon_{Au} = \epsilon_{AuFree} + \epsilon_{AuIB} = \left(1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}\right) + \epsilon_{AuIB} \qquad \omega_p = \sqrt{\frac{Ne^2}{m^*\epsilon_0}}$$

$$\sigma_{ABS} = \sigma_{ABS}(\varepsilon_m, \Gamma, N, \lambda) = \left(\frac{18\pi}{\lambda}\right)\frac{\varepsilon_m^{3/2}\,\mathrm{Im}[\varepsilon]}{\mathrm{Im}[\varepsilon]^2 + (2\varepsilon_m + \mathrm{Re}[\varepsilon])^2}$$

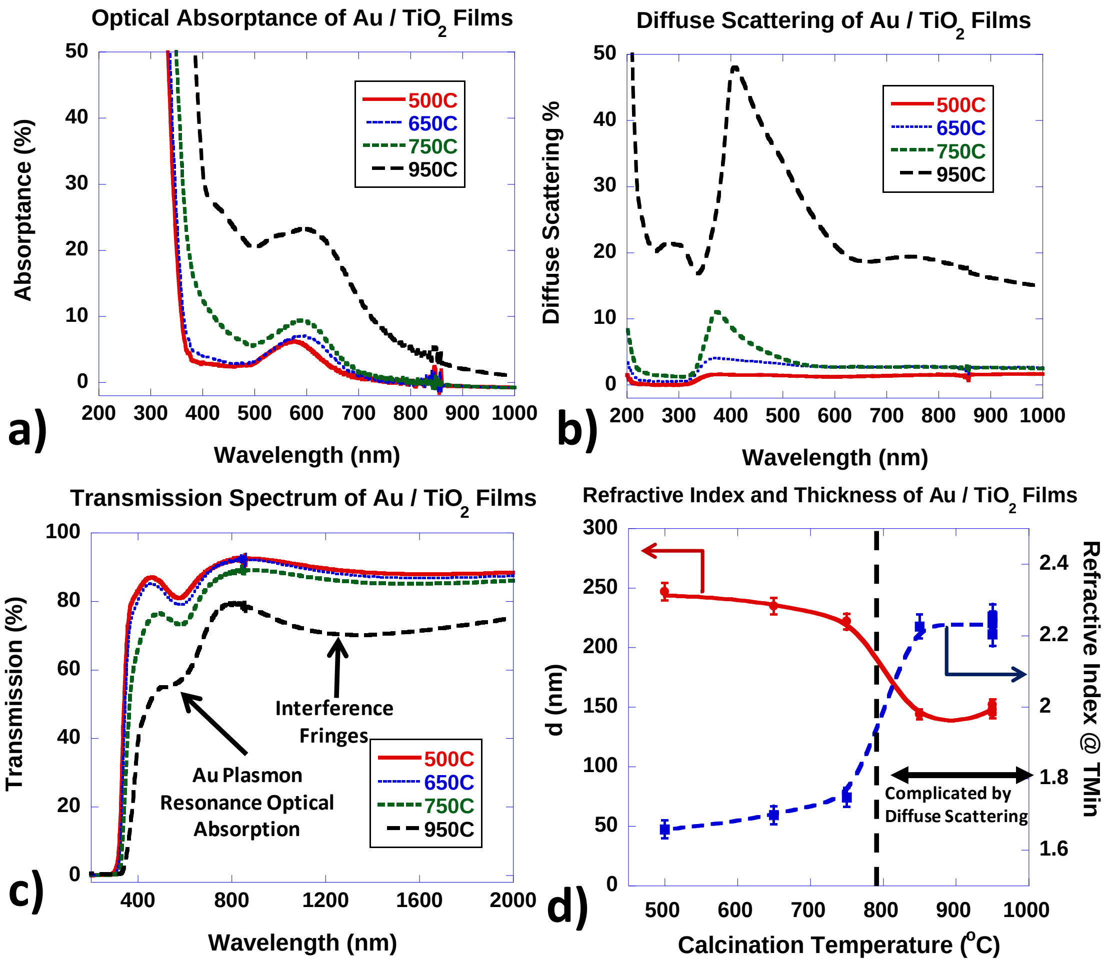
Γ ➔ **Can Be Extracted From Experimentally Measured Resistivity Values of Au as a Function of Temperature**

N ➔ Can Be Directly Linked with the Thermal Expansion of Au Assuming the Total Number of Free Electrons is Constant

ε_m ➔ **Can Be Estimated from the Temperature Dependence of Optical Constants of TiO_2**

The Three Primary Material Constants all Have an Intrinsic Temperature Dependence that Impact the Measured LSPR Absorption Peak

More Detailed Studies of Au / TiO_2 Films



Optical Absorptance of Au / TiO_2 Films

Diffuse Scattering of Au / TiO_2 Films

Transmission Spectrum of Au / TiO_2 Films

Refractive Index and Thickness of Au / TiO_2 Films

Systematic Trends in LSPR Absorption, Film Thickness, and Refractive Index are Observed with Increasing Calcination T

Opportunities in Existing Coal Based Plants

FUEL COSTS
$39 Million/Year @
9,500 BTU/kw-hr,
$1.25/million BTU's

Non Fuel O&M COSTS
$6 Million/Year
(10 - 20% of total costs)

Total Fuel + O&M Budget
$45 Million - Avg. 500 MW Unit

Gaseous emissions

POWER

3,285,000,000 kw-hr/yr
@75% Capacity Factor

Solid wastes

Analysis for Year 2000

- 1% improvement in **EFFICIENCY**
  - $390,000 savings in fuel
  - $4.1 million for entire installed fossil capacity
- **Approximately 1% REDUCTION in greenhouse gases and solid wastes**

- 1% increase in **AVAILABILITY**
  - Yields 33 million kw-hr/yr added generation for a 500MW plant
  - Approximately $2 million in sales (at $60/1000kw-hr)
  - An additional 5,000 MW of power for entire installed fossil capacity

http://www.netl.doe.gov/technologies/coalpower/advresearch/pubs/G3-ICMS%20Presentation%20080707f1b.pdf

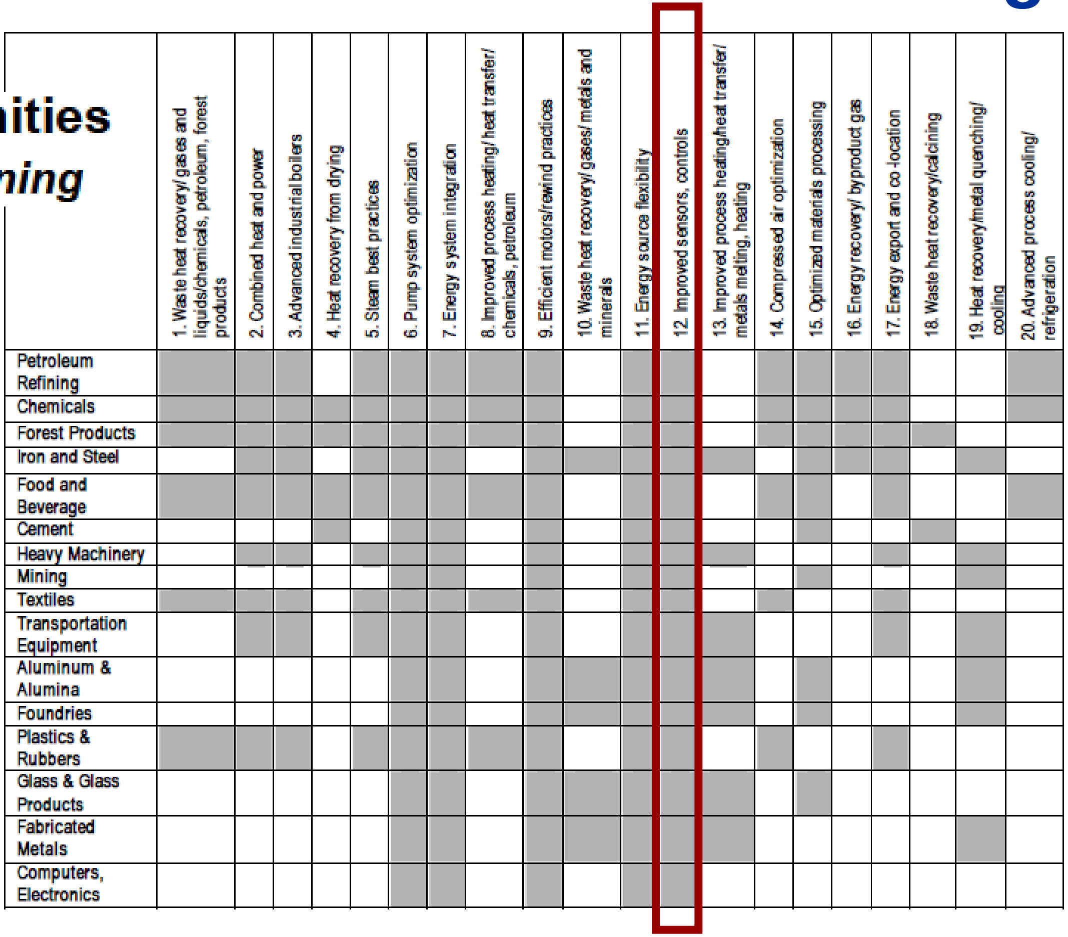
Even for Existing Coal Based Plants, the Opportunity for Sensors and Controls to Improve Efficiency is Great.

Opportunities for Efficient Domestic Manufacturing

Energy Use, Loss and Opportunities Analysis: *U.S. Manufacturing & Mining*

Prepared by Energetics, Incorporated and
E3M, Incorporated for the
U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
Industrial Technologies Program

December 2004



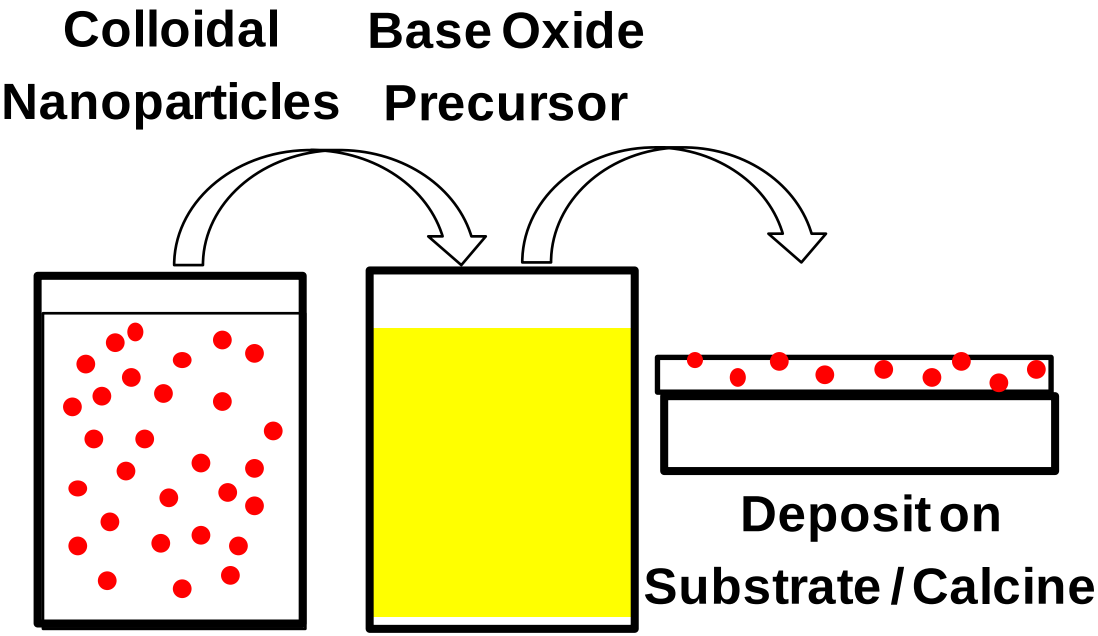
	1. Waste heat recovery/ gases and liquids/chemicals, petroleum, forest products	2. Combined heat and power	3. Advanced industrial boilers	4. Heat recovery from drying	5. Steam best practices	6. Pump system optimization	7. Energy system integration	8. Improved process heating/ heat transfer/ chemicals, petroleum	9. Efficient motors/rewind practices	10. Waste heat recovery/ gases/ metals and minerals	11. Energy source flexibility	12. Improved sensors, controls	13. Improved process heating/heat transfer/ metals melting, heating	14. Compressed air optimization	15. Optimized materials processing	16. Energy recovery/ byproduct gas	17. Energy export and co-location	18. Waste heat recovery/calcining	19. Heat recovery/metal quenching/ cooling	20. Advanced process cooling/ refrigeration
Petroleum Refining	■	■	■		■	■	■	■	■		■	■		■	■	■	■			■
Chemicals	■	■	■	■	■	■	■	■	■		■	■		■	■	■	■			■
Forest Products	■	■	■	■	■	■	■	■	■		■	■		■	■	■	■	■		
Iron and Steel		■	■		■	■	■		■	■	■	■	■		■	■	■		■	
Food and Beverage	■	■	■	■	■	■	■	■	■		■	■		■	■		■			■
Cement				■		■	■		■		■	■			■			■		
Heavy Machinery		■	■		■	■	■		■		■	■	■				■		■	
Mining						■	■		■		■	■			■				■	
Textiles	■	■	■		■	■	■	■	■		■	■		■			■			
Transportation Equipment		■	■		■	■	■		■		■	■	■				■		■	
Aluminum & Alumina						■	■		■	■	■	■	■		■				■	
Foundries						■	■		■	■	■	■	■		■				■	
Plastics & Rubbers	■	■	■		■	■	■	■	■		■	■		■			■			
Glass & Glass Products						■	■		■	■	■	■	■		■					
Fabricated Metals						■	■		■	■	■	■	■						■	
Computers, Electronics						■	■		■		■	■								

Improved Sensors & Controls was Listed as #12 of the Top 20 Opportunities for Energy Efficiency Improvements.

Sensors and Controls are Also Important for Improving Efficiency of Major Domestic Manufacturing Industries.

Synthesis of Au Incorporated TiO_2 Thin Films

Ti (IV) – Isopropoxide, Isopropanol, and Glacial Acetic Acid



Wet Chemistry Based Techniques (Sol-Gel)

Wet Chemistry Based Deposition Techniques Allow for the Addition of a Functional Second Phase Such as Au Nanoparticles.