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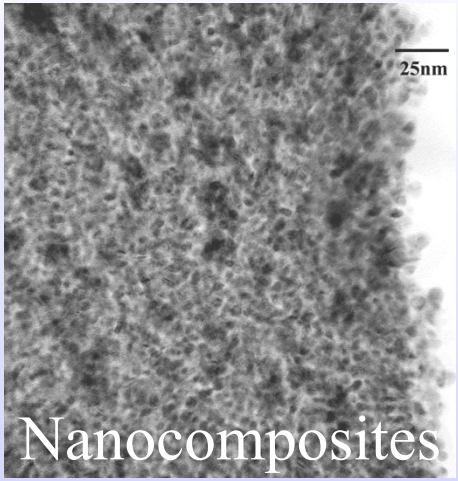

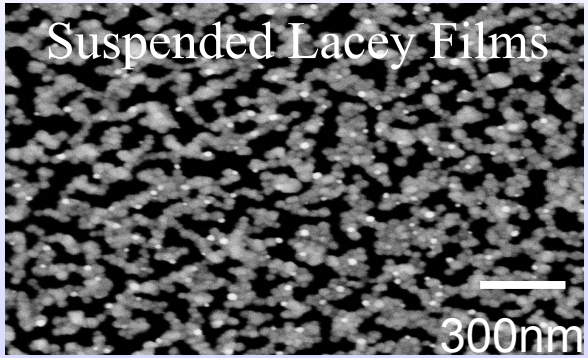

Plasmonics Based Harsh Environment Compatible Chemical Sensors

Dr. Michael A. Carpenter
College of NanoScale Science and Engineering
Energy & Environmental Technology Applications Center
University at Albany – SUNY
6/7/11

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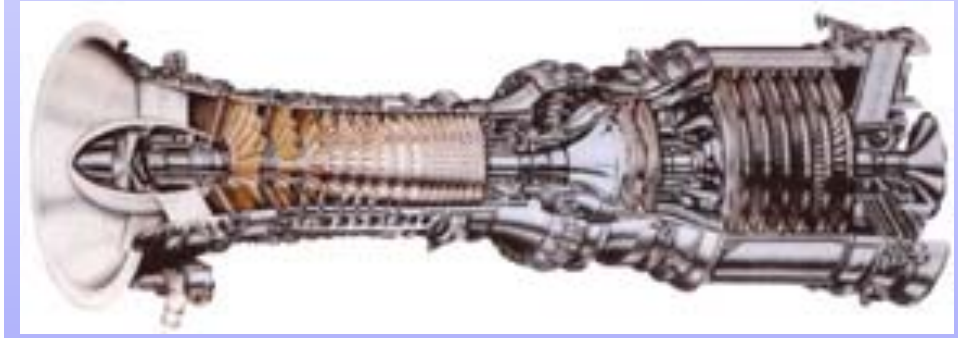
Harsh Environment Chemical Sensors

Need for new sensing technologies to meet the requirements for zero emission energy sources

Nanocomposite Materials

- Optical analysis of Au SPR bands
- YSZ, TiO_2, CeO_2 matrix materials
- 500-800°C operating environment
- SOFC, Jet engines, turbines
- CO, H_2, NO_x, R_xS



Goals of Research are Two-Fold

1. Develop prototype materials for use in next generation sensing devices
   - Sensitivity, reliability, selectivity
2. Determine fundamental material properties/dynamics/kinetics which govern the sensing mechanism

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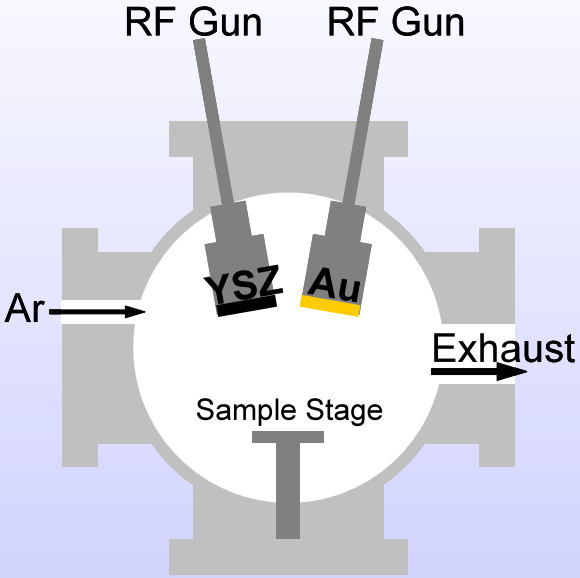
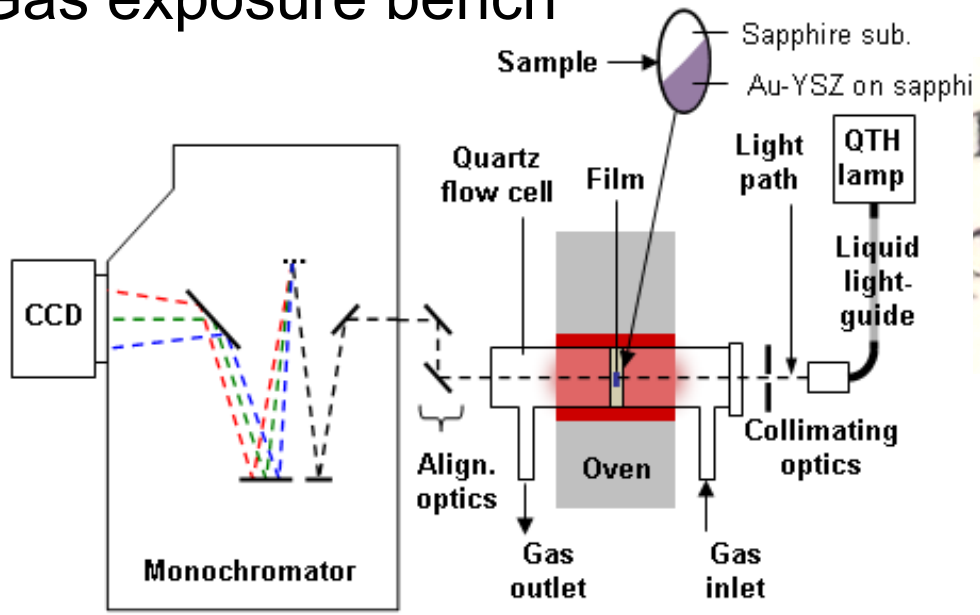
Experimental Setup



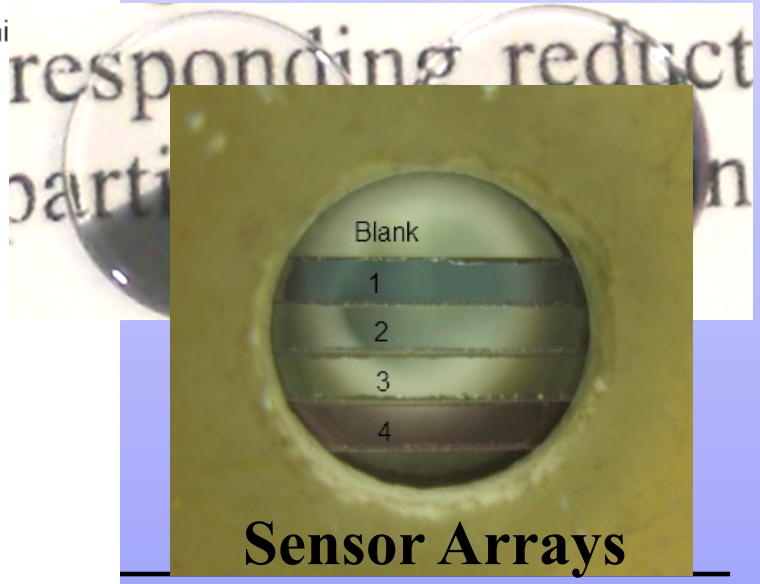
- Sample preparation
  - PVD deposition of 10 at. % Au-YSZ(TiO_2) films in 5 mtorr of Ar
  - Film thickness is varied by changing deposition time
  - Films are annealed at ~900 °C for 2 hours at 760 torr and ~1800 sccm of Ar

-MBE grown CeO_2 with implanted Au nanoparticles
-PNNL

Gas exposure bench



as-deposited post anneal



Sensor Arrays

NanoScale Science and Engineering

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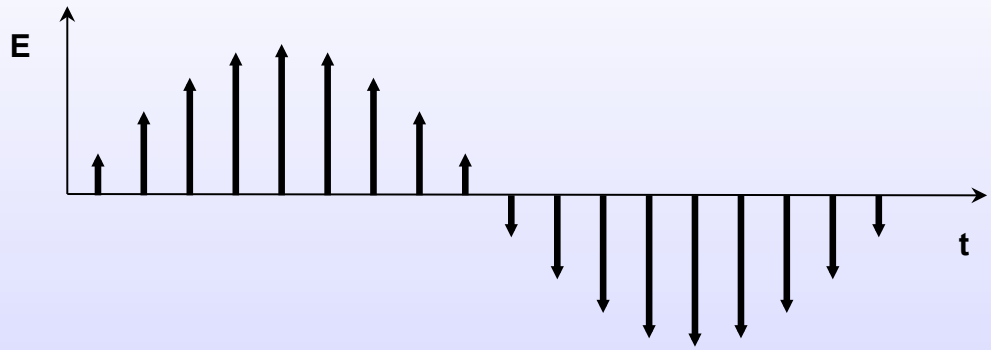
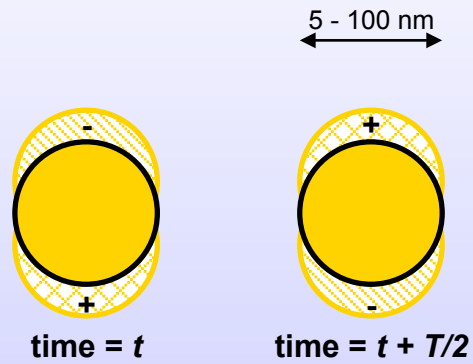
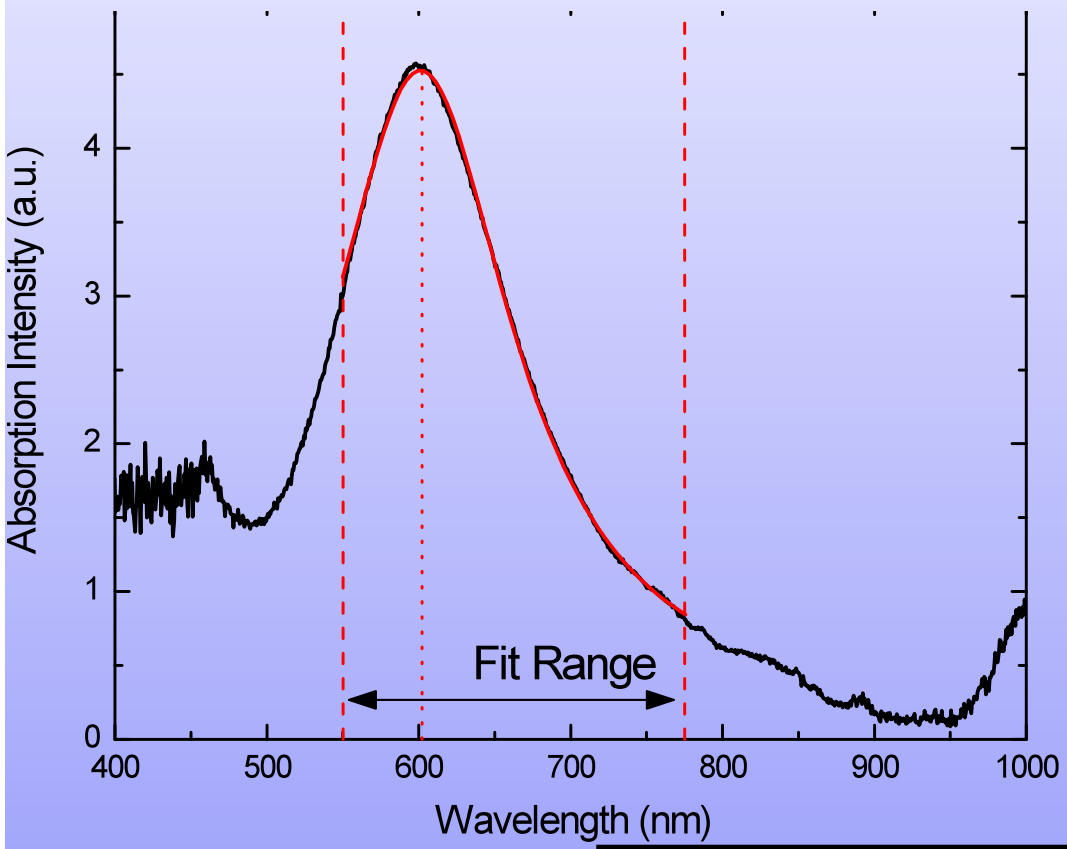
Background - Au Nanoparticles as Optical Beacons For Transduction Events







$$\Omega = \sqrt{\frac{Ne^2}{\left(1 + 2\varepsilon_m + \chi^{ib}(\Omega)\right) m_e 4\pi\varepsilon_0 R^3}}$$

Ω - SPR Frequency
N - free electron number
m_e - electron mass
ε_0 - permittivity of free space
ε_m - matrix (YSZ) dielectric constant
$\chi^{ib}(\Omega)$ - Interband trans. dielectric const.
R - particle radius

Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer, Berlin, 1995

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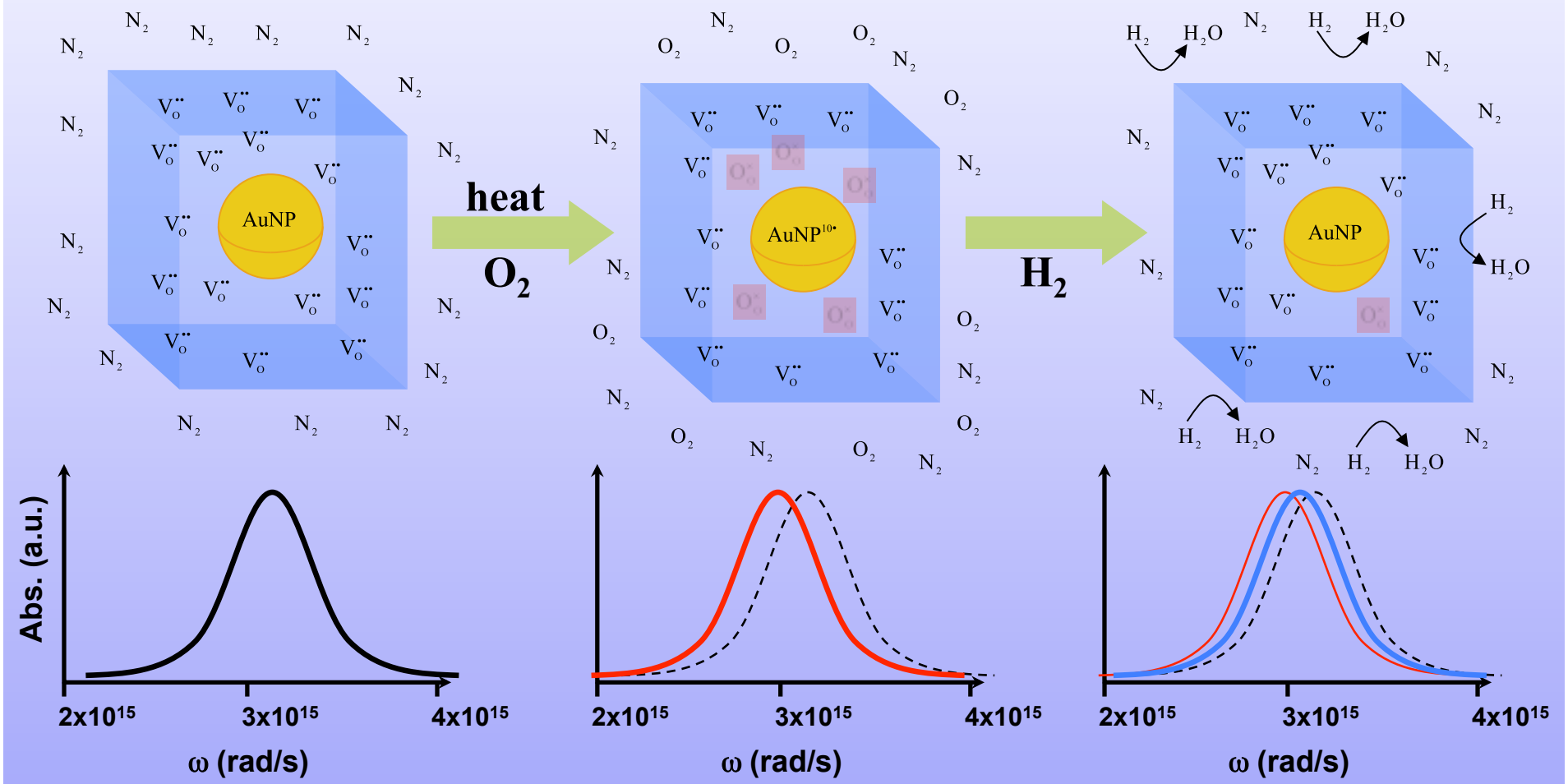
H_2 Studies

Volume cell of one AuNP and corresponding YSZ matrix in inert gas

Same volume cell exposed to a AuNP oxidizing gas

Volume cell then exposed to a AuNP reducing gas



- YSZ is an oxygen ion conductor above ~350°C

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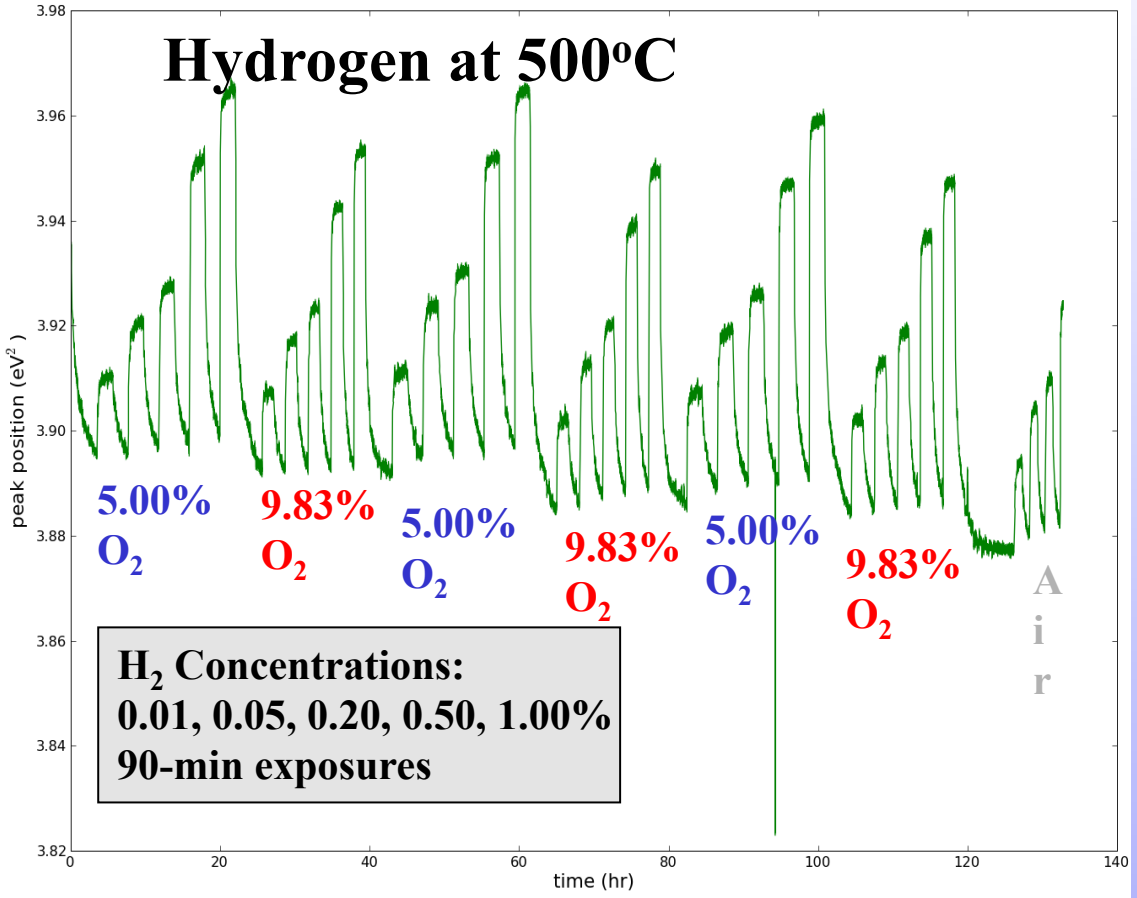
Sensing Tests on MBE grown Au-Ceria*



- Ceria is 200nm thick
- Gold is implanted to depth of ~75nm
- Post annealed to 1000°C
- Gold particle size ~30nm

$$H_2 + O^{2-} + Au^{2+} / CeO_2 \rightarrow H_2O + Au / CeO_2$$

Charge donation back to the Au nanoparticle

Blue shift of the SPR band

**In collaboration with M. Nandasiri, S. Kuchibhatla, T. Suntharampillai @ PNNL*

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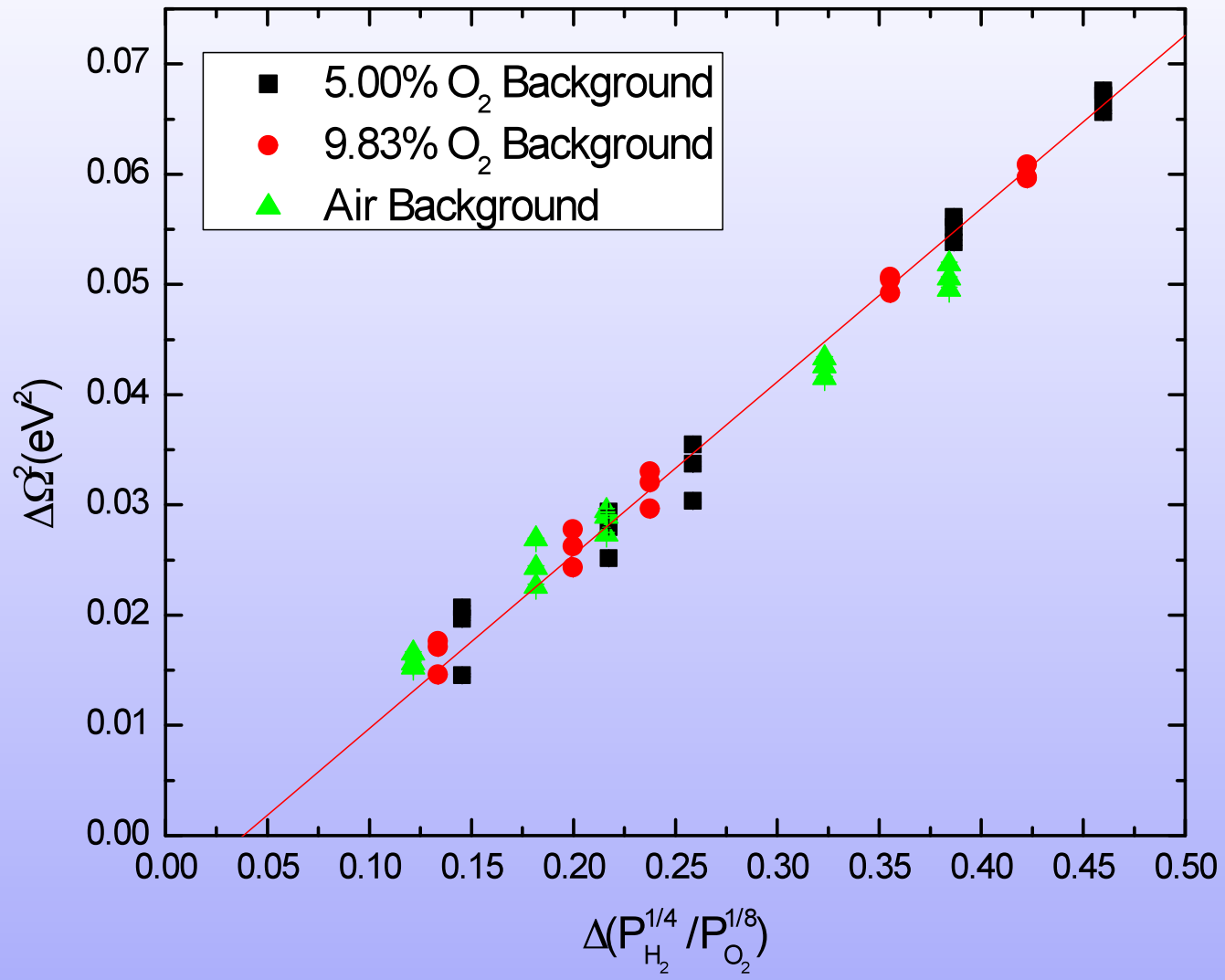

Au-CeO_2 H_2/O_2 interaction appears similar in mechanism as with Au-YSZ

Similar equilibrium charge exchange analysis as previously performed for Au-YSZ*

*Rogers, P. H.; Sirinakis, G.; Carpenter, M. A. *J. Phys. Chem. C* **2008**, *112*, 6749

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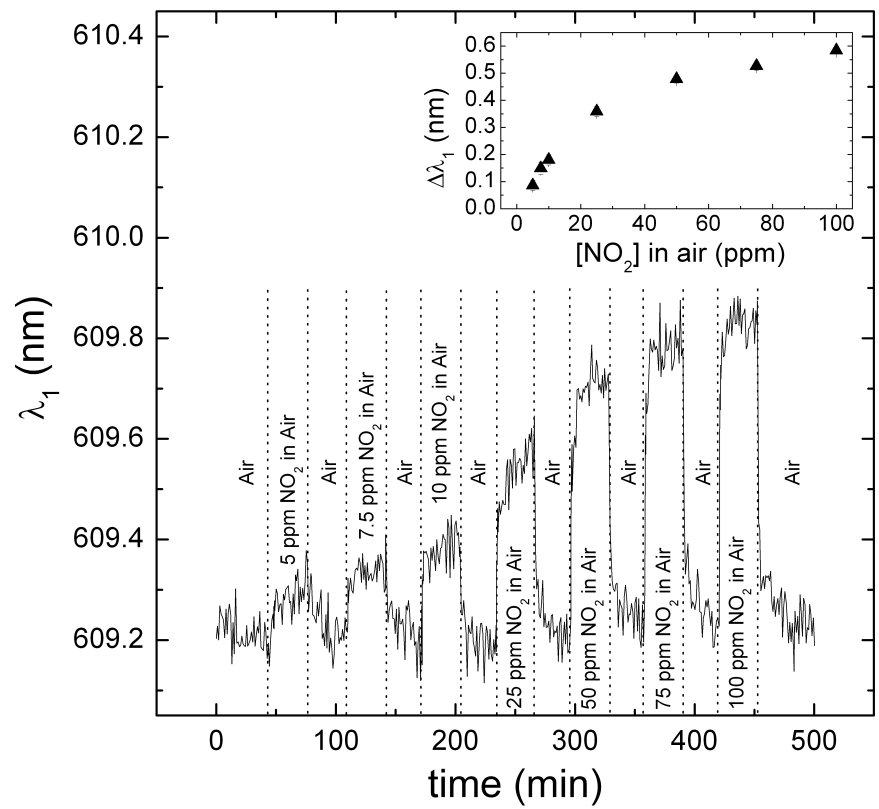
An assumption within current model is that the dielectric function is constant



$$\Omega = \sqrt{\frac{Ne^2}{\left(1 + 2\varepsilon_m + \chi^{ib}(\Omega)\right) m_e 4\pi\varepsilon_0 R^3}}$$

- **Filling oxygen vacancies likely increases polarizability of material**
- ***Dielectric function should increase as well***
- **↑ ε_m will cause red shift in SPR**
- **Vacancy filling coincides with ↓N and a red shift in SPR**

Deconvolution of ΔN and $\Delta\varepsilon_m$ requires in-situ measurement of ε_m which is of interest

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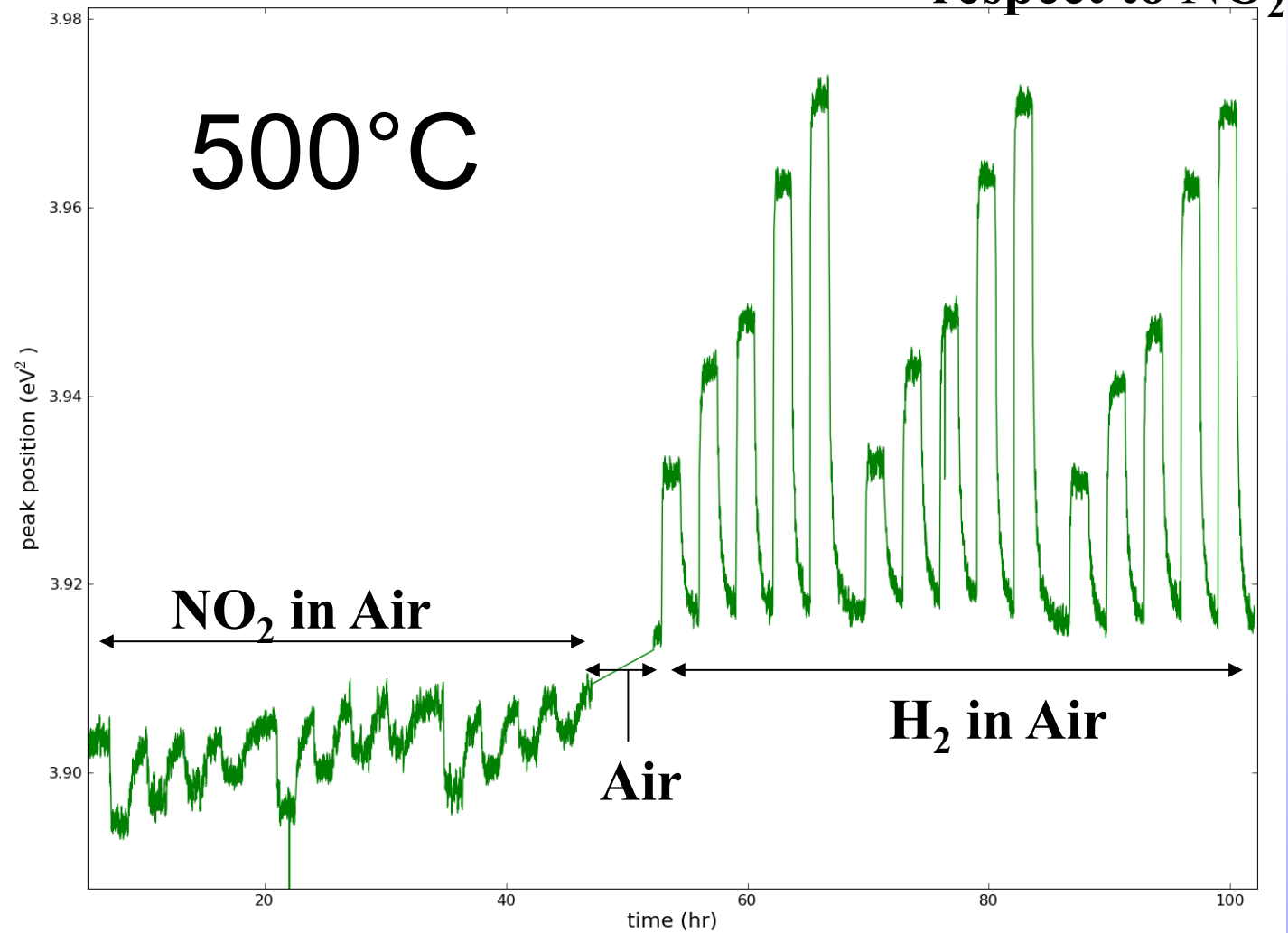
Au-CeO_2 reliability with respect to NO_2 and H_2



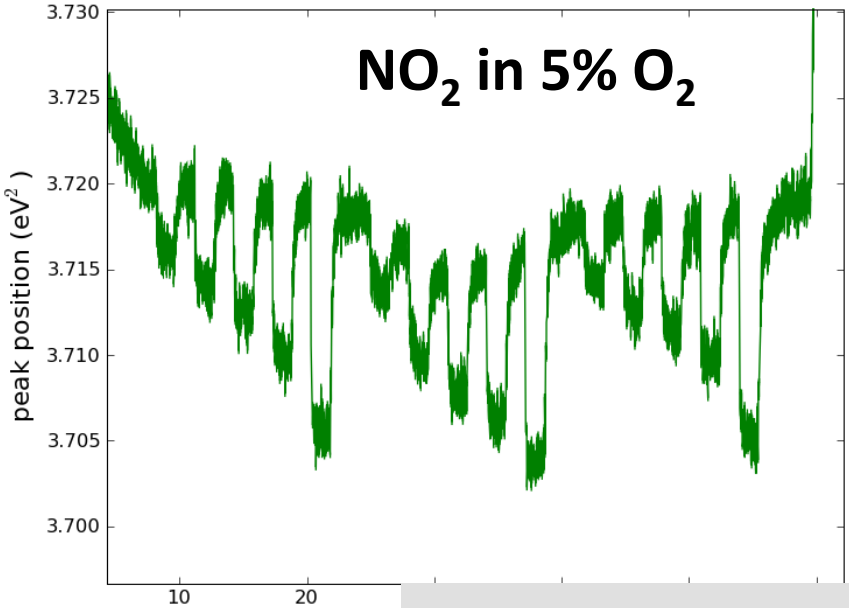
Concentrations:
NO_2:
98ppm
20
10
5

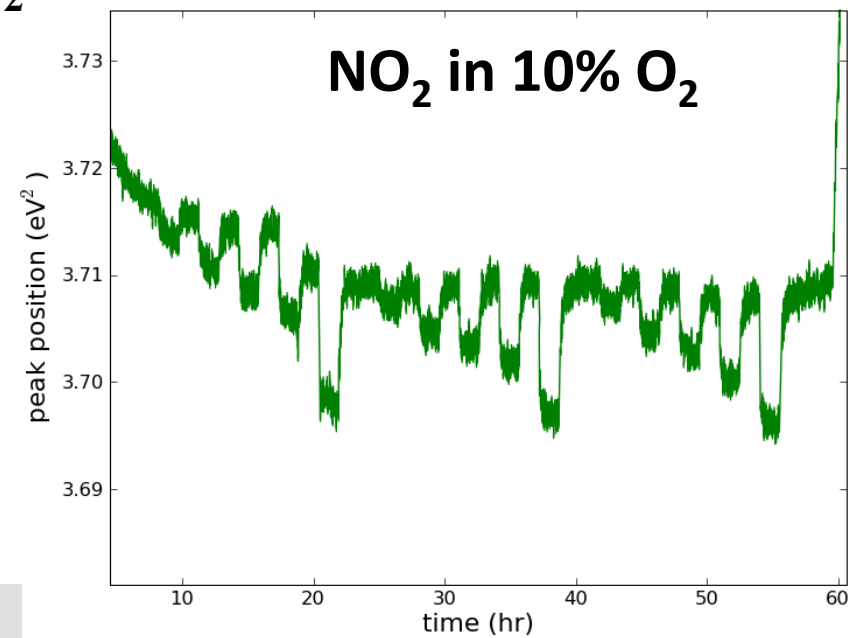
H_2:
0.01%
0.05
0.20
0.50
1.00
90-min exposures

$$NO_2 + Au / YSZ \rightarrow O^{2-} + NO + Au^{2+} / YSZ$$

Red shift of the SPR band

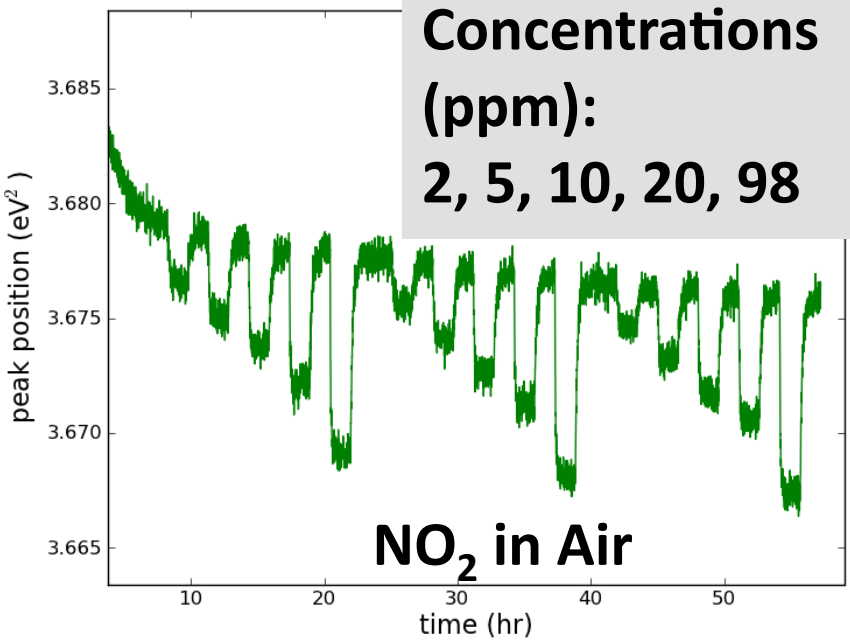
Au-CeO_2 - 500°C

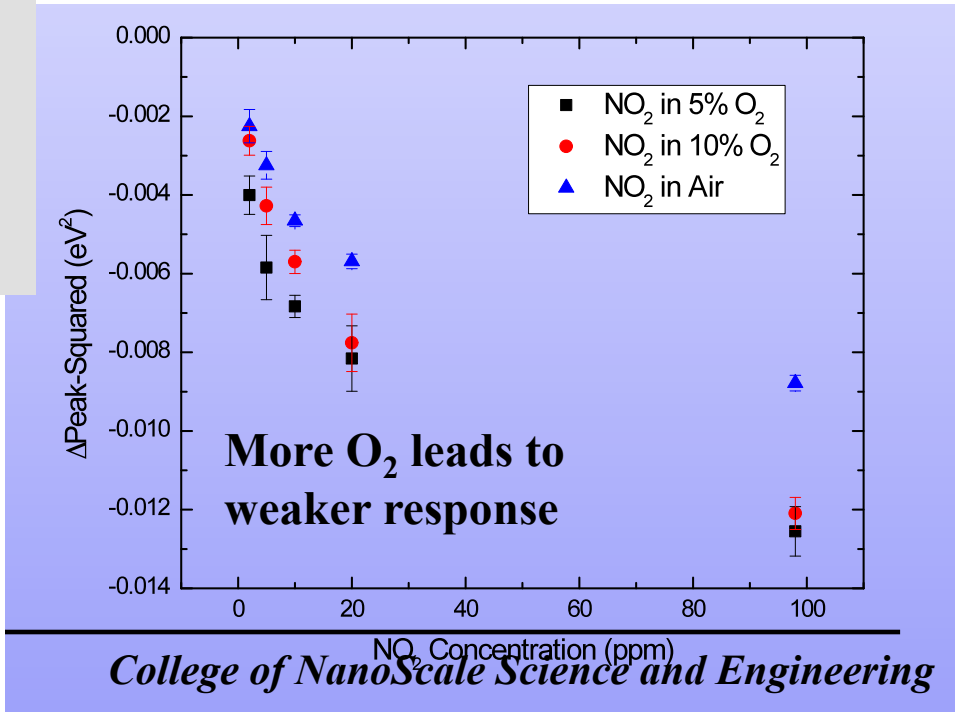




NO_2 Exposures

Concentrations (ppm):
2, 5, 10, 20, 98





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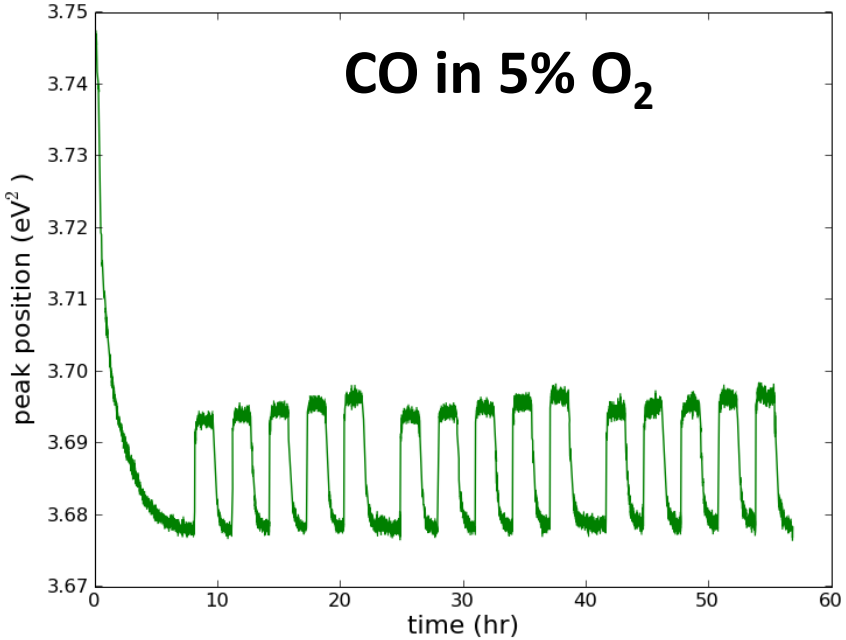
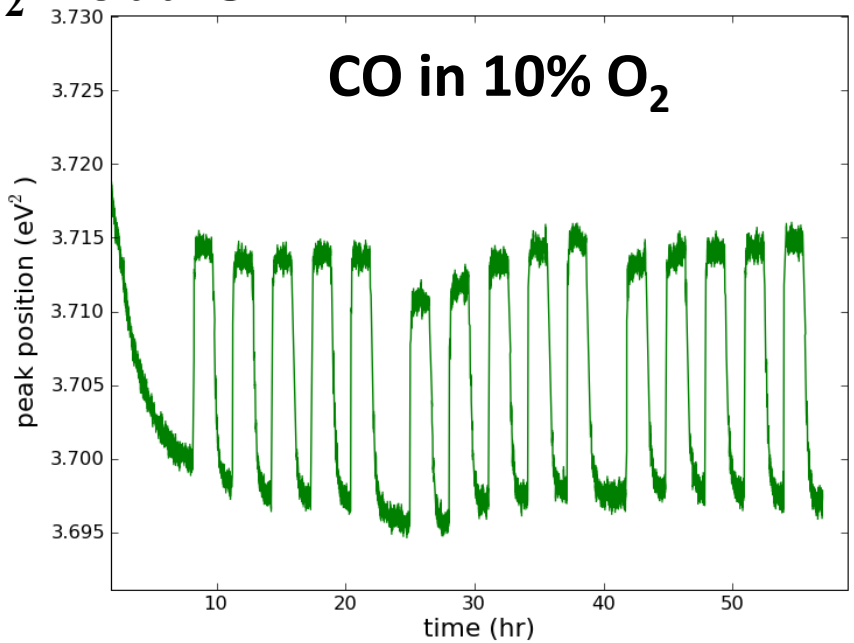
Au-CeO_2 - 500°C

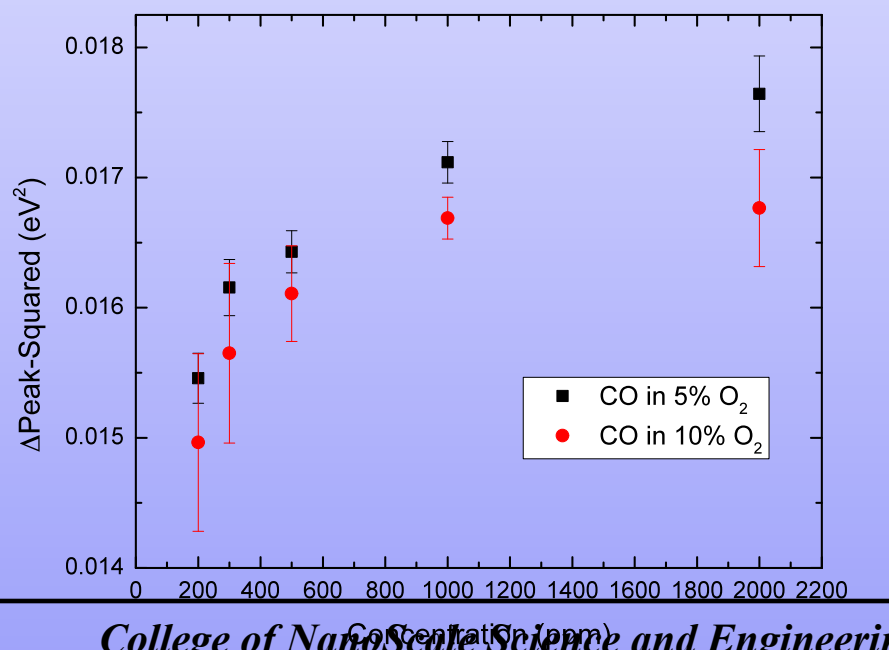




CO Exposures

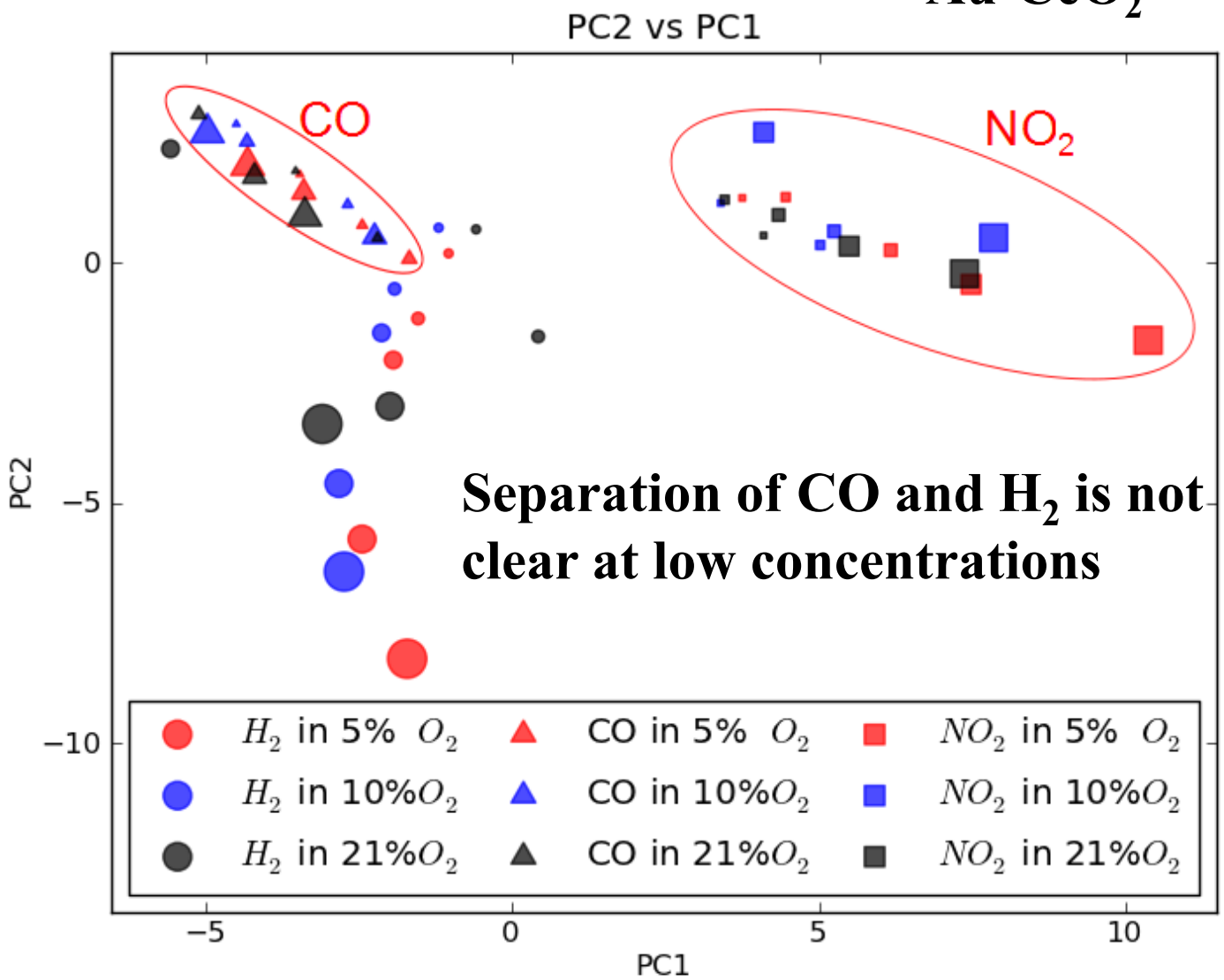
Concentrations (ppm):
200, 300, 500, 1000, 2000

- ***NOTE: CO exposure causes a blue shift, same as H_2***
- ***Selectivity challenges***



Principal Component Analysis

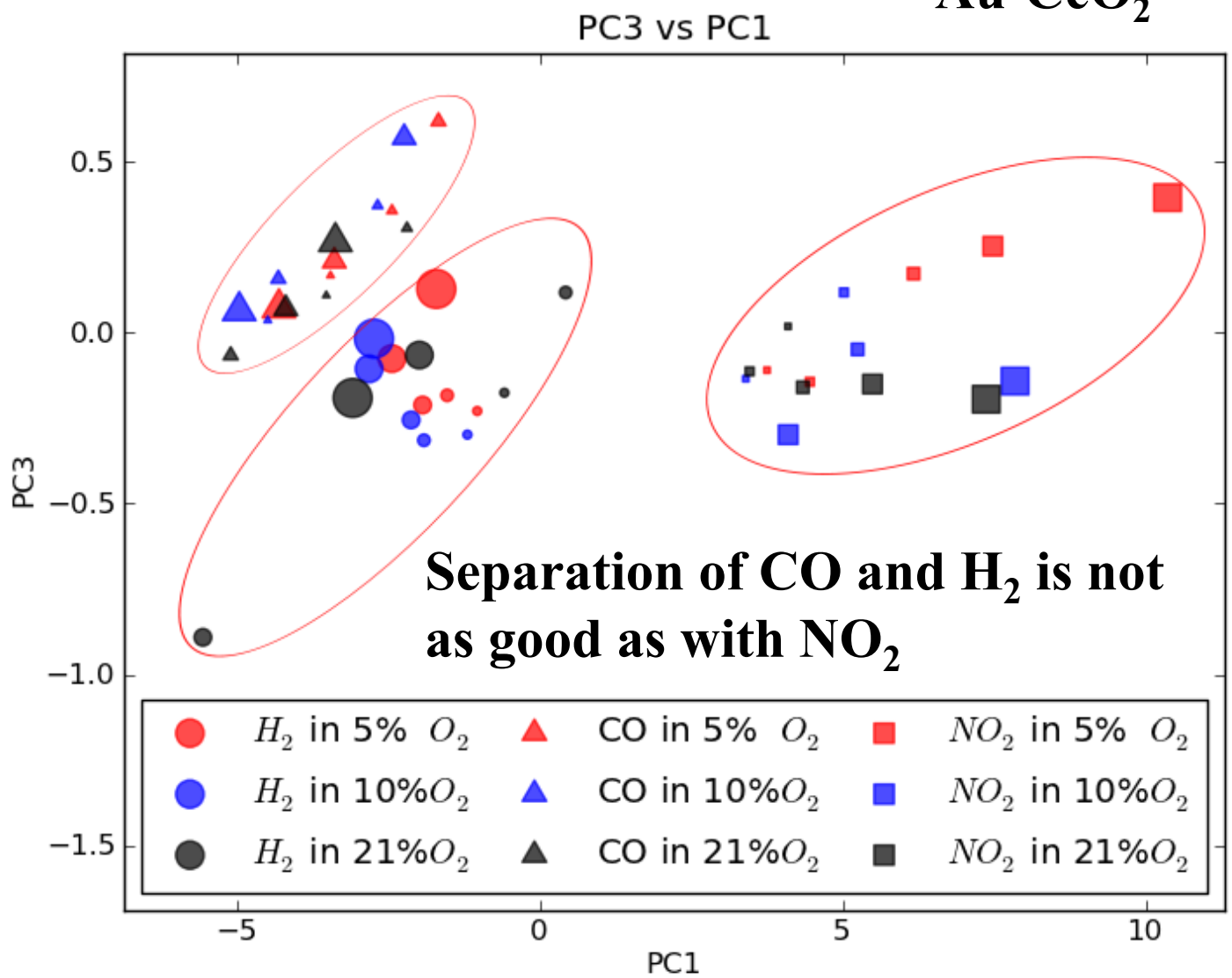
Au-CeO_2



Separation of CO and H_2 is not clear at low concentrations

Principal Component Analysis

Au-CeO_2

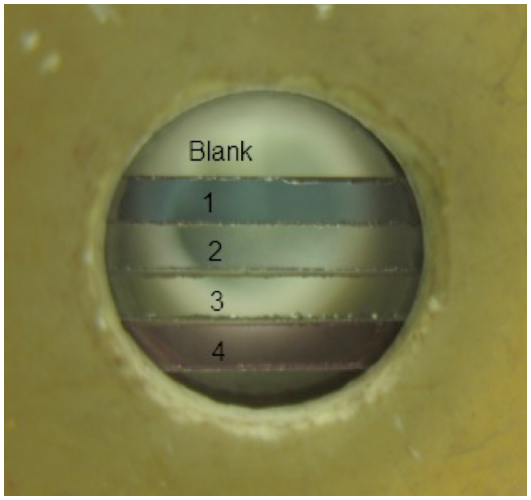


Separation of CO and H_2 is not as good as with NO_2

Sensor Array Studies

Element 1: **MBE grown CeO_2 with implanted gold**

- **Ceria is 200nm thick**
- **Gold is implanted to depth of ~75nm**
- **Post annealed to 1000°C**
- **Gold particle size ~30nm**
- **Au ~ 8 at. %**



Element 2: **PVD Au-YSZ**

- **~30nm thick Au-YSZ**
- **Au particle size ~25nm**
- **~10 at.% Au**

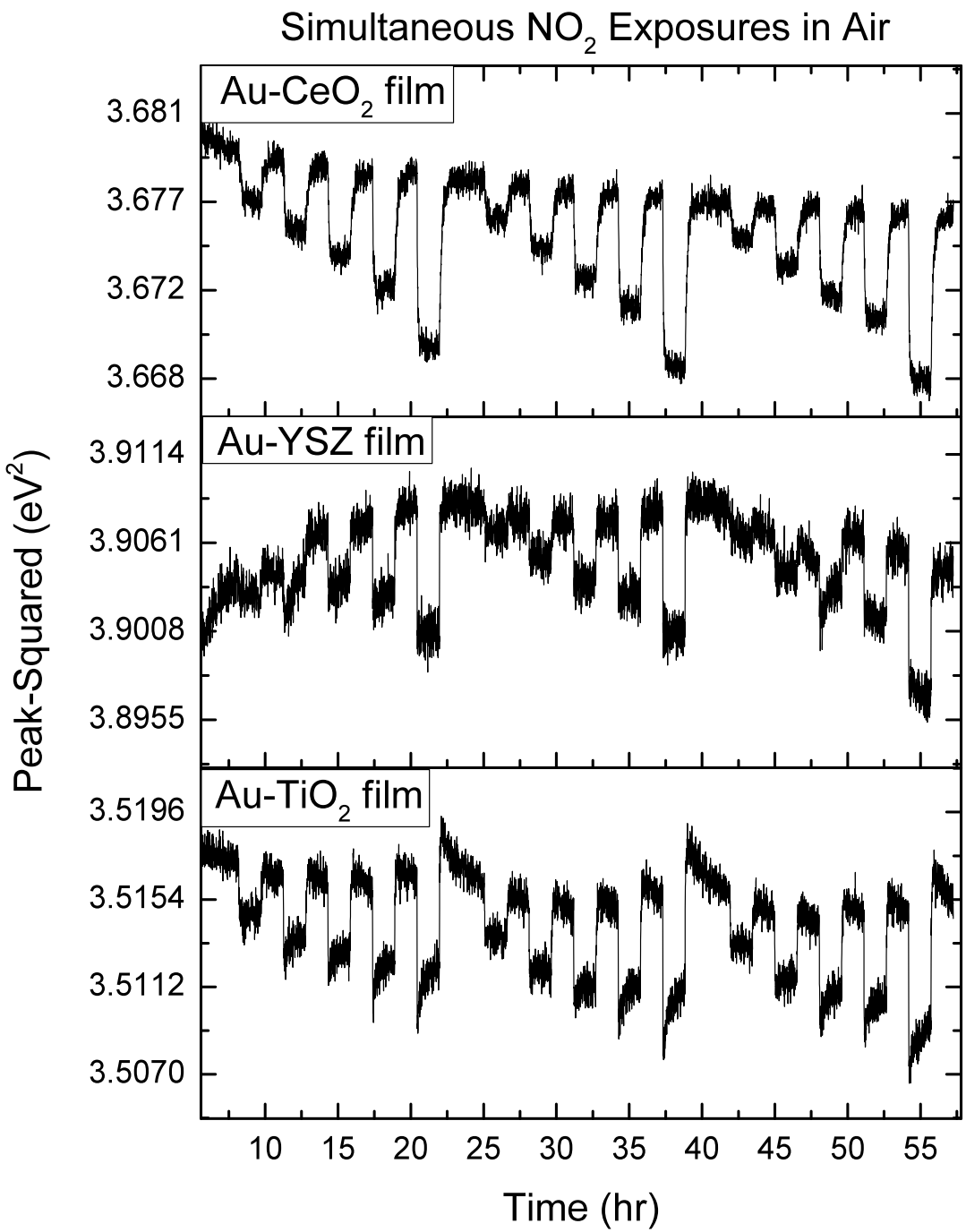
Element 3: **PVD Au-TiO_2**

- **~30nm thick Au-TiO_2**
- **Au particle size ~25nm**
- **~10 at.% Au**

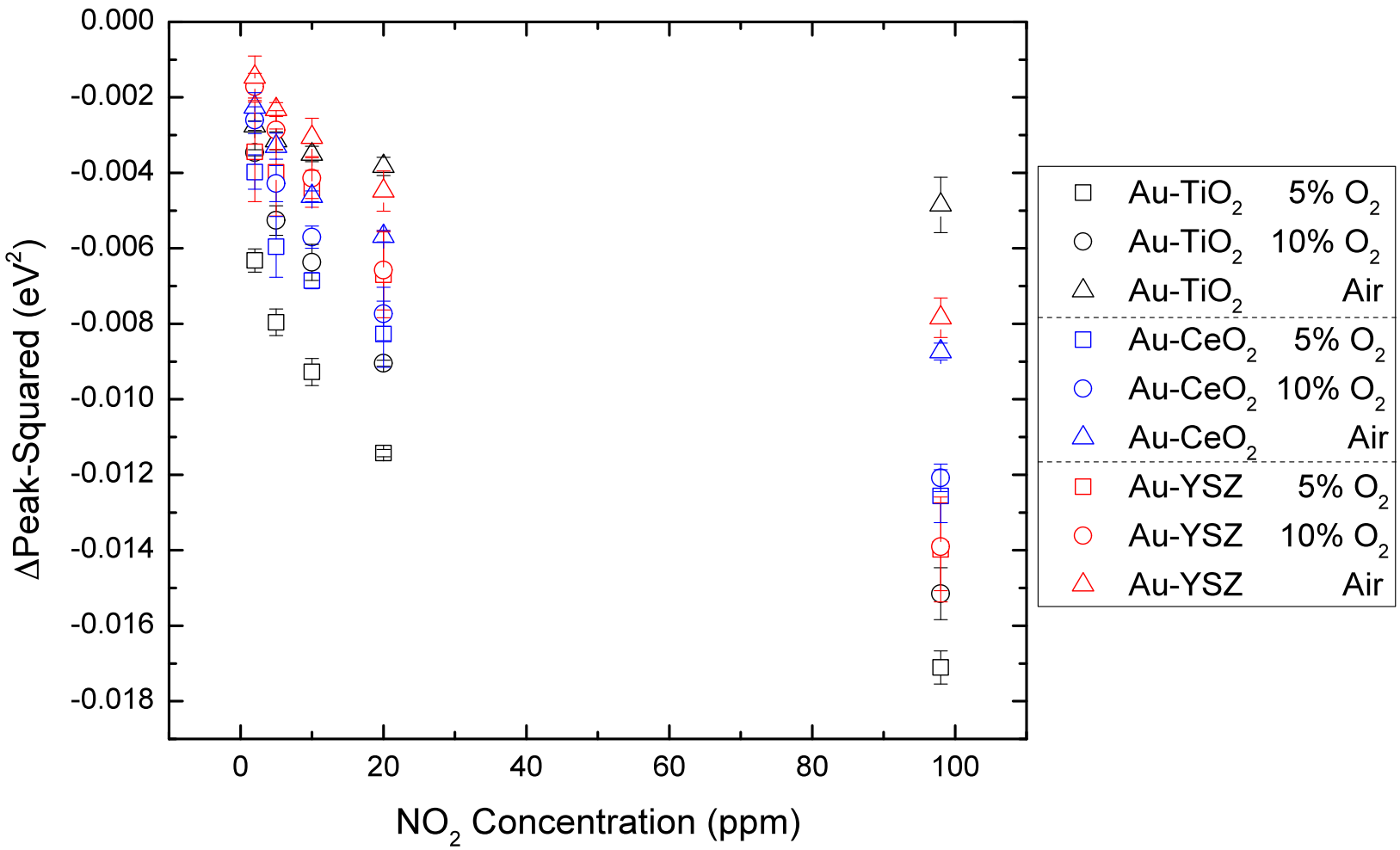
500°C	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98

- **Simultaneously Compare Sensing Characteristics**
- **PCA performed for Selectivity**
- **Detailed analysis to be completed for sensing mechanism analysis**

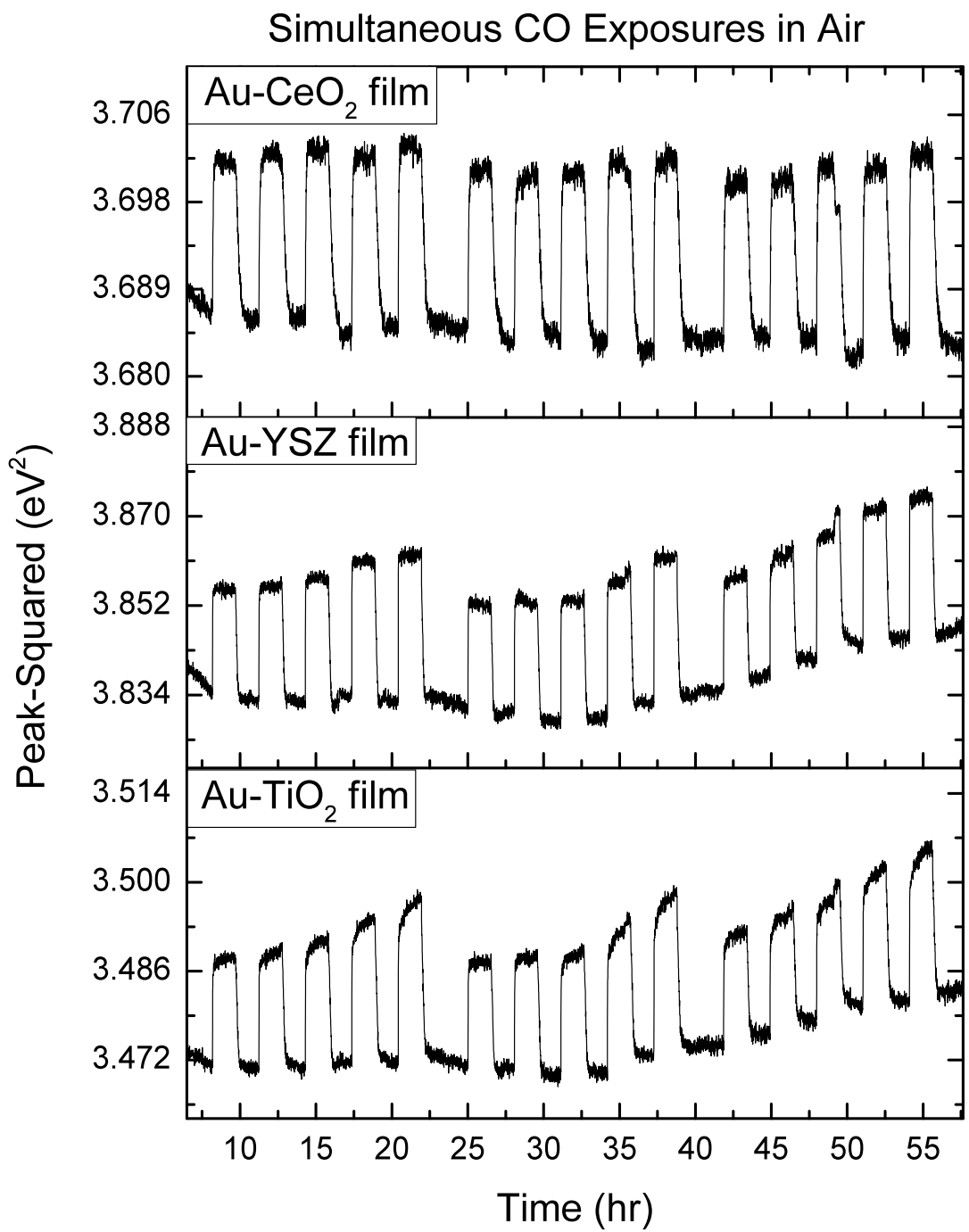
	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98



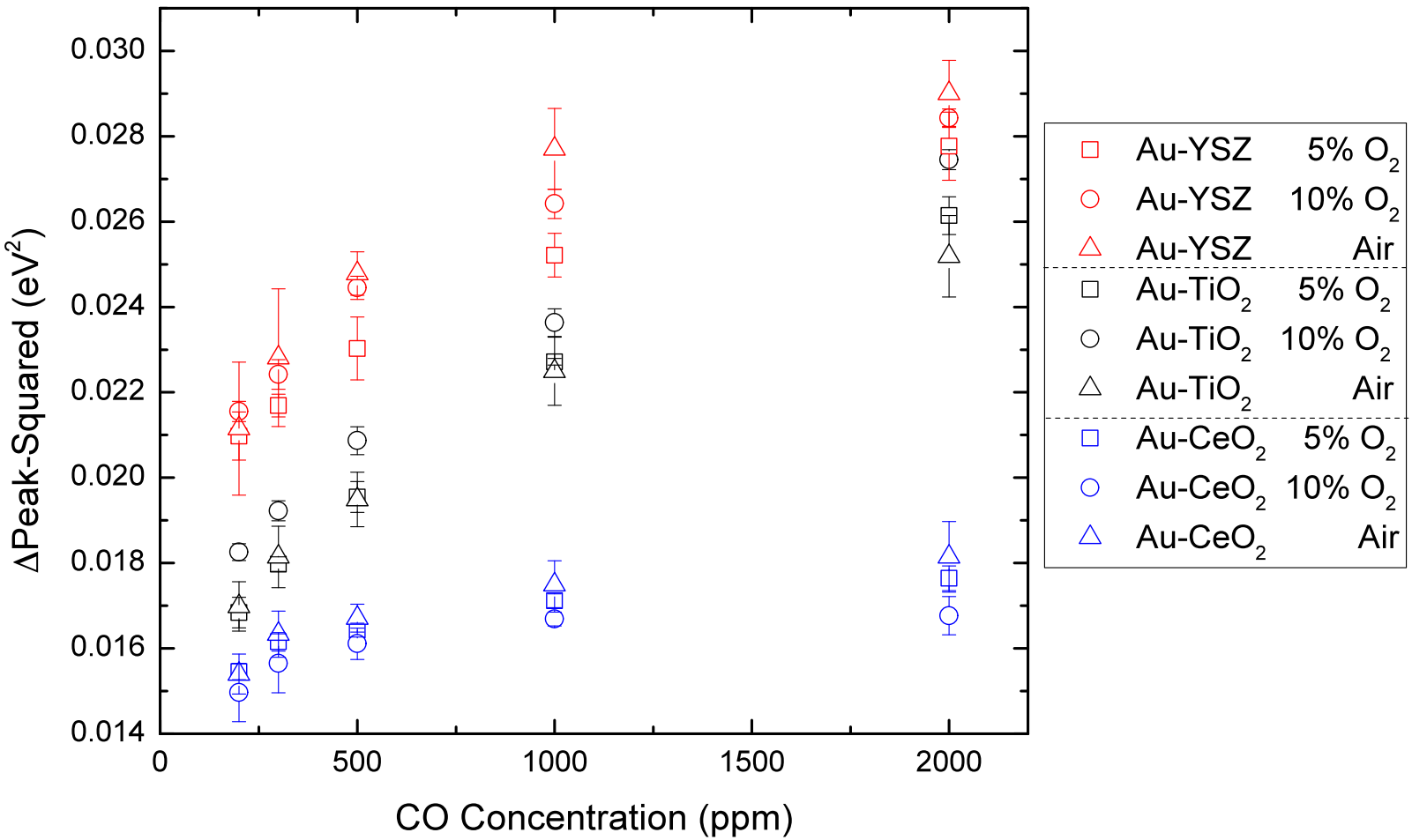
NO_2 ΔPeak position vs. Concentration



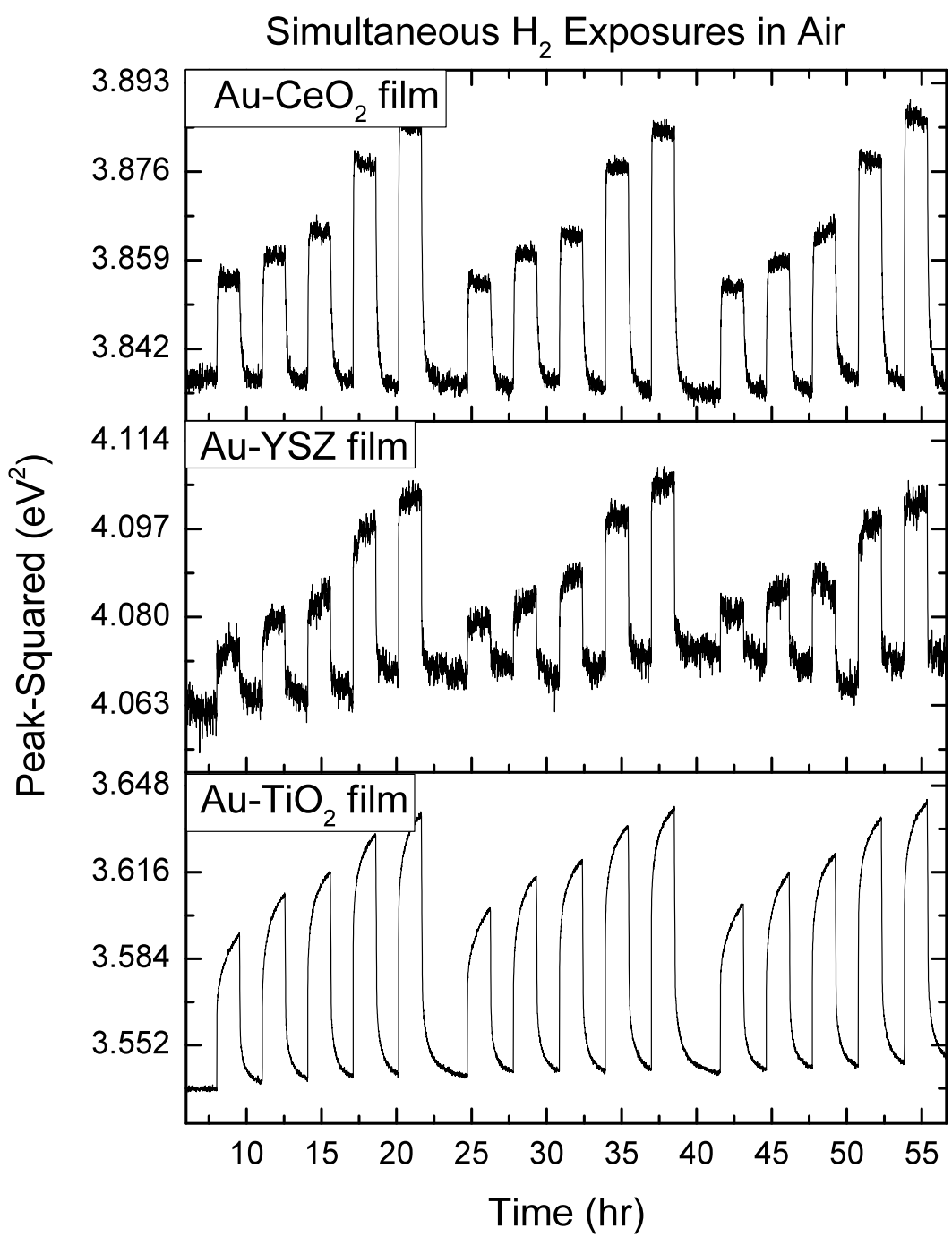
	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98



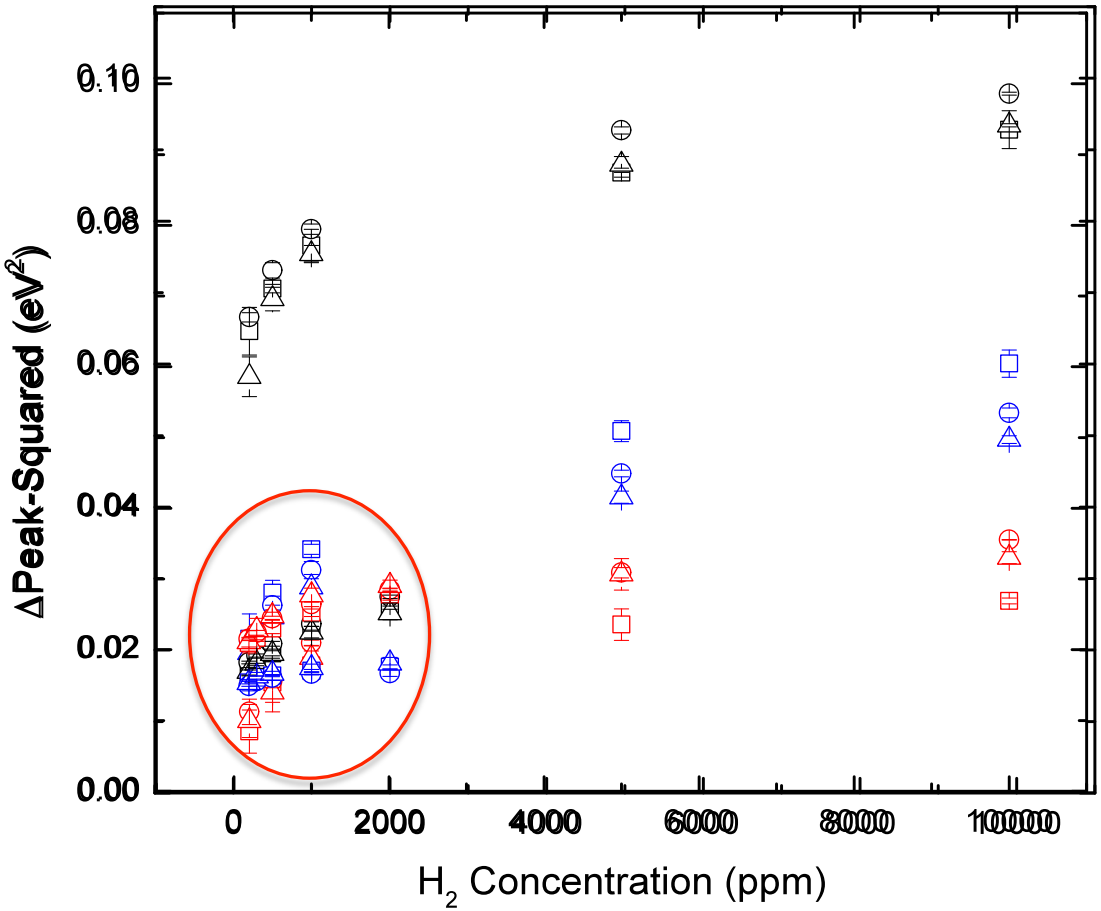
CO ΔPeak position vs. Concentration



	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98



H_2 ΔPeak vs Concentration

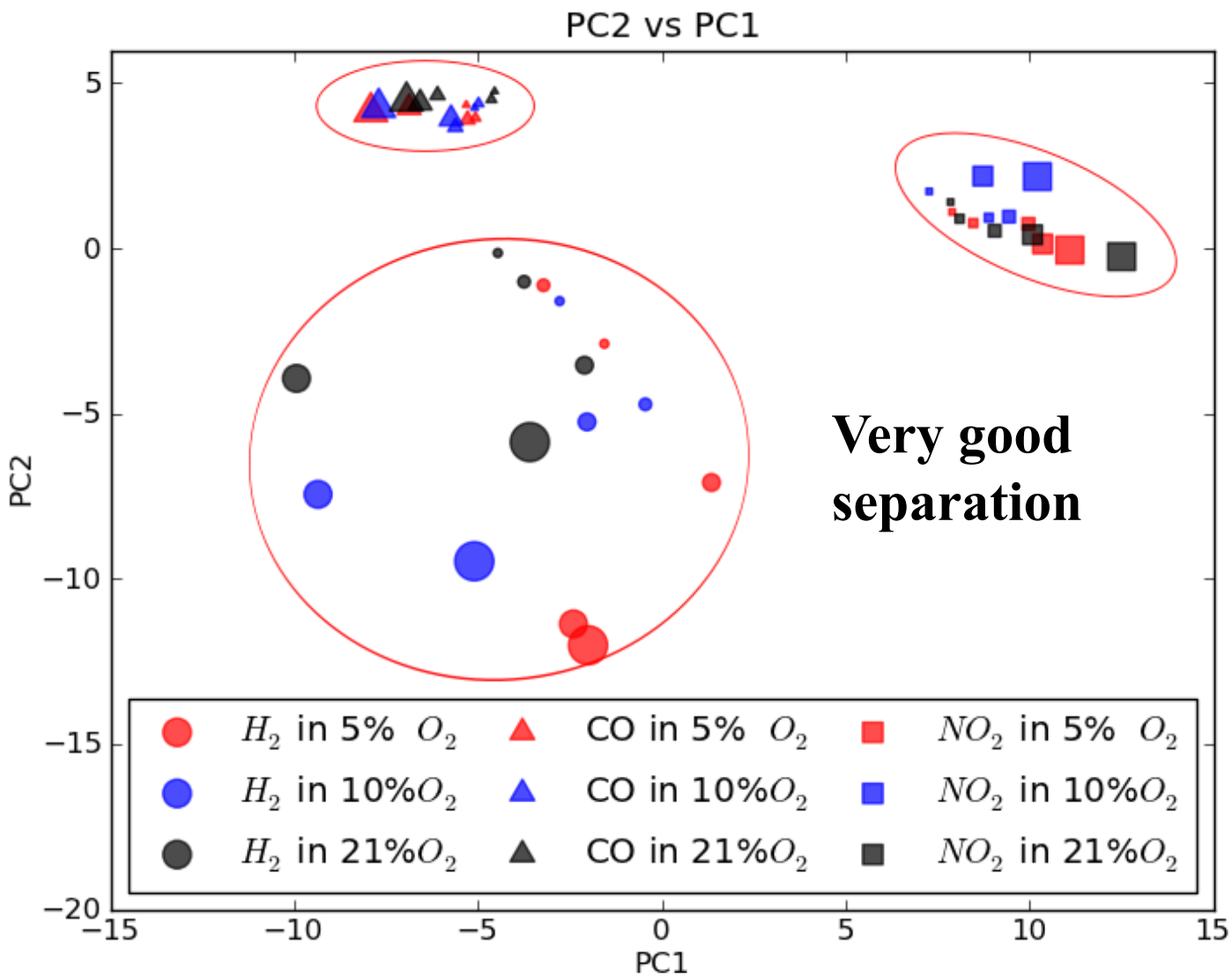


□ Au-TiO_2	5% O_2
○ Au-TiO_2	10% O_2
△ Au-TiO_2	Air
□ Au-CeO_2	5% O_2
○ Au-CeO_2	10% O_2
△ Au-CeO_2	Air
□ Au-YSZ	5% O_2
○ Au-YSZ	10% O_2
△ Au-YSZ	Air

	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98

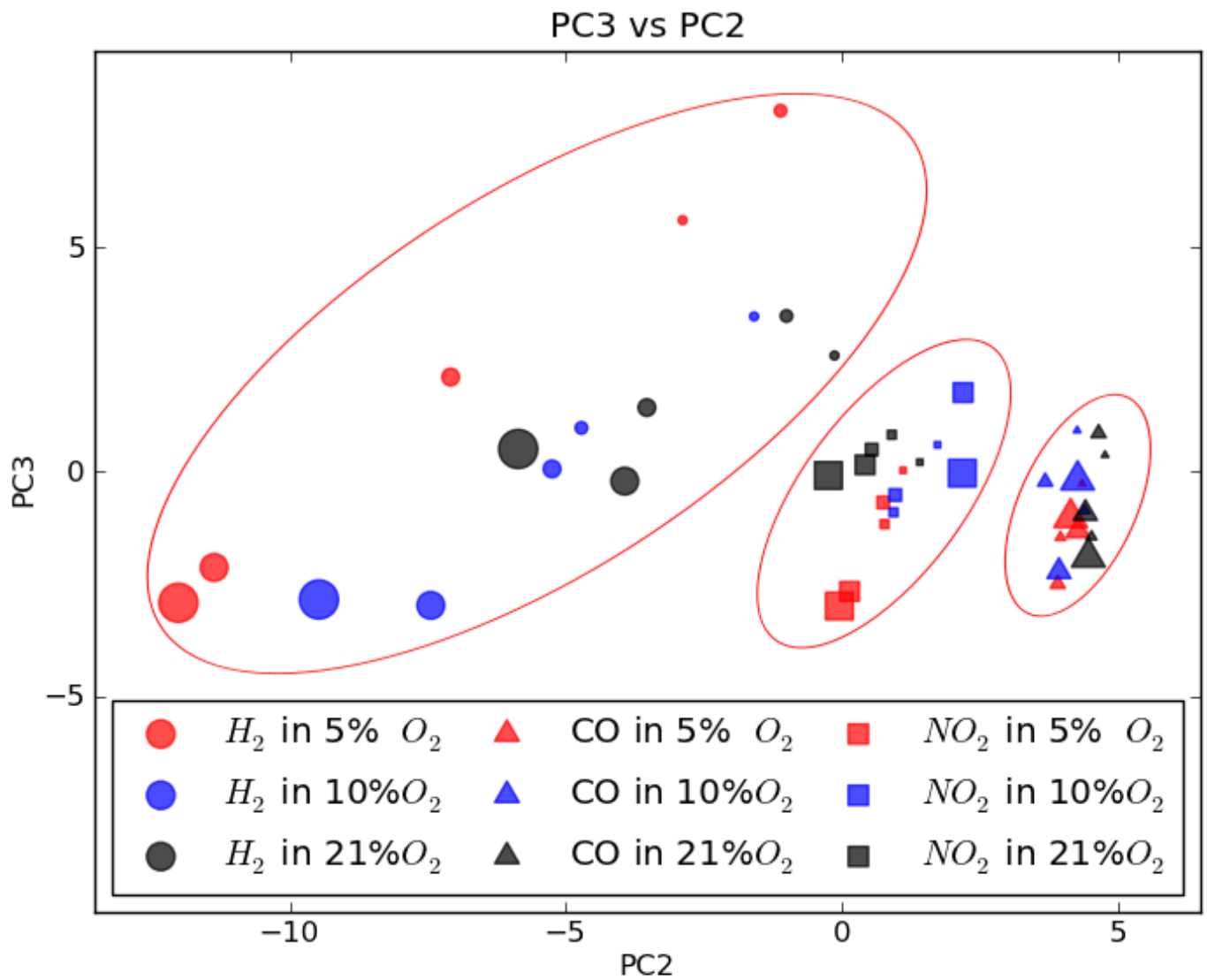
Challenging selectivity issues for CO and H_2!

PCA Analysis of Sensor Array Data

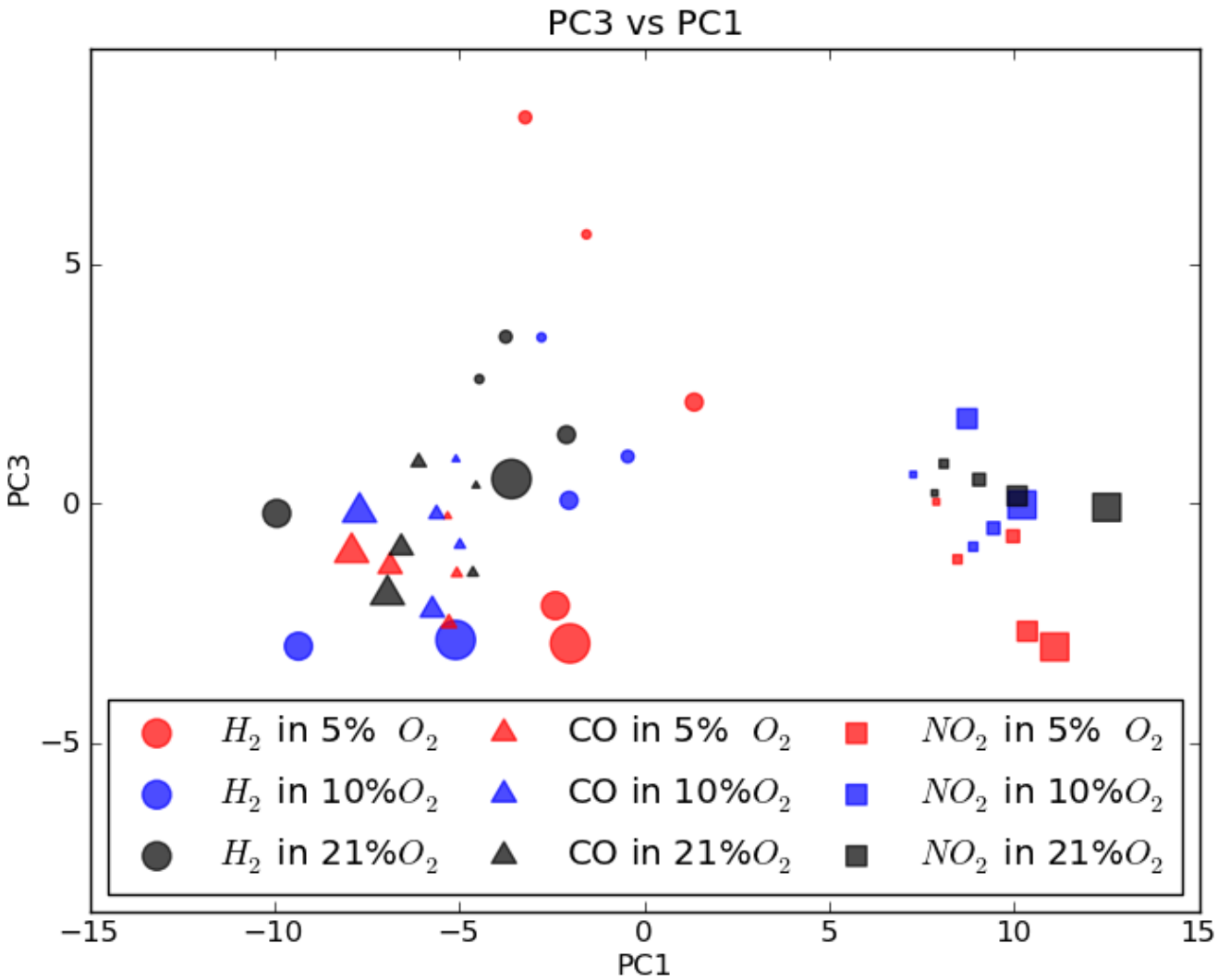


- **45 observables (5 gas concentrations, 3 target gases & 3 [O_2]**
- **~175 wavelengths used as inputs from the spectra**

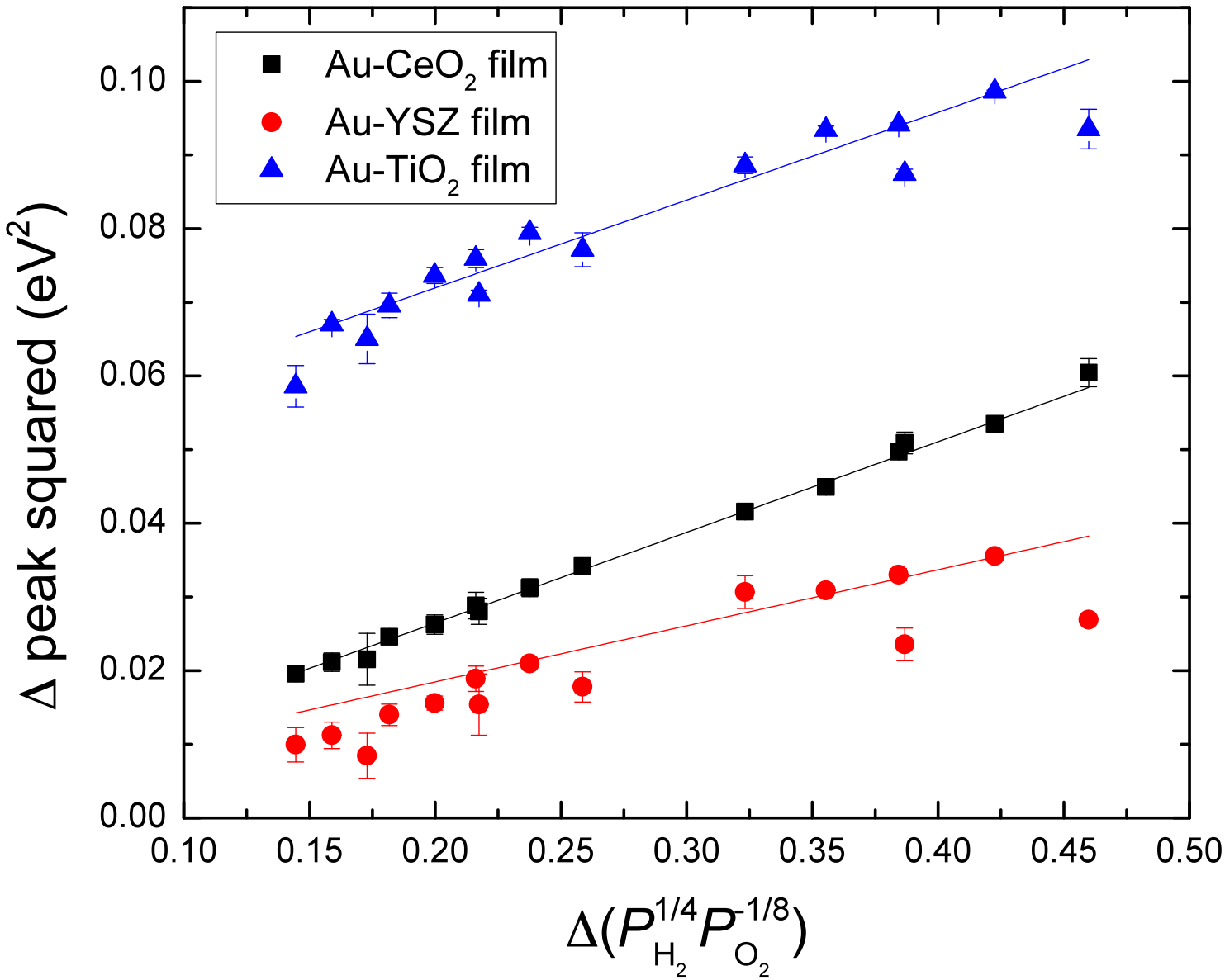
PCA Analysis of Sensor Array Data



PCA Analysis of Sensor Array Data



H_2 Sensing Mechanism

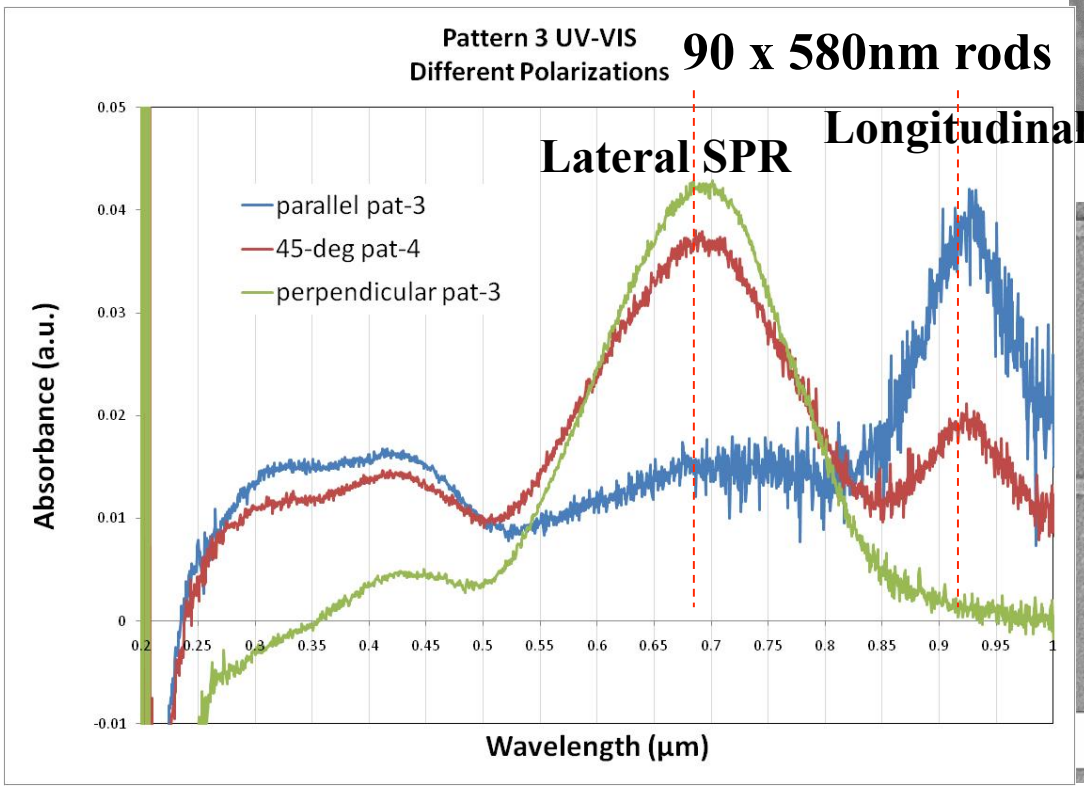


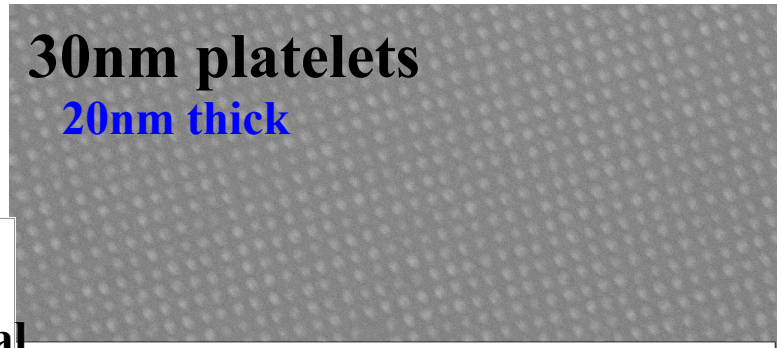
Analysis of sensing mechanism across the array is in initial stages

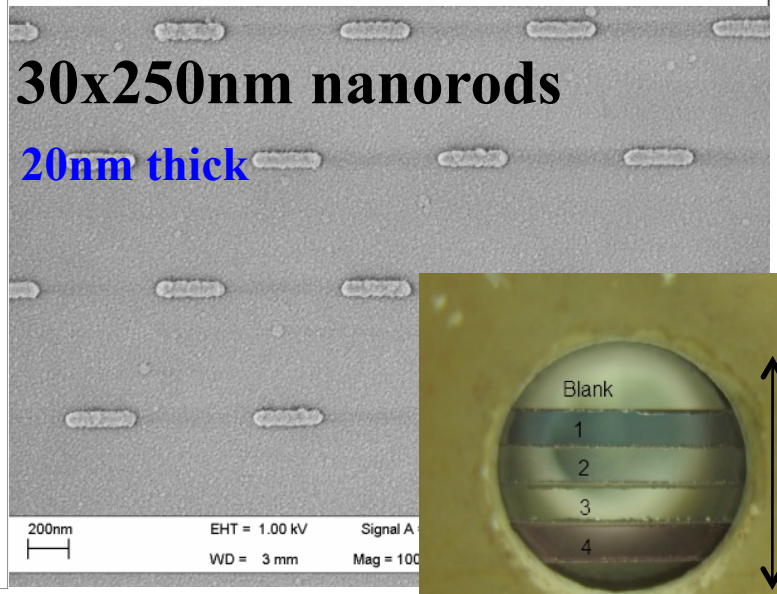
Material Control: Electron Beam Lithography of AuNPs

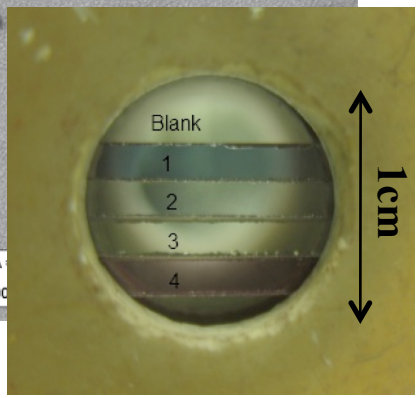
- Size and shape control
- Tune catalytic properties

Tune the optical probe signal

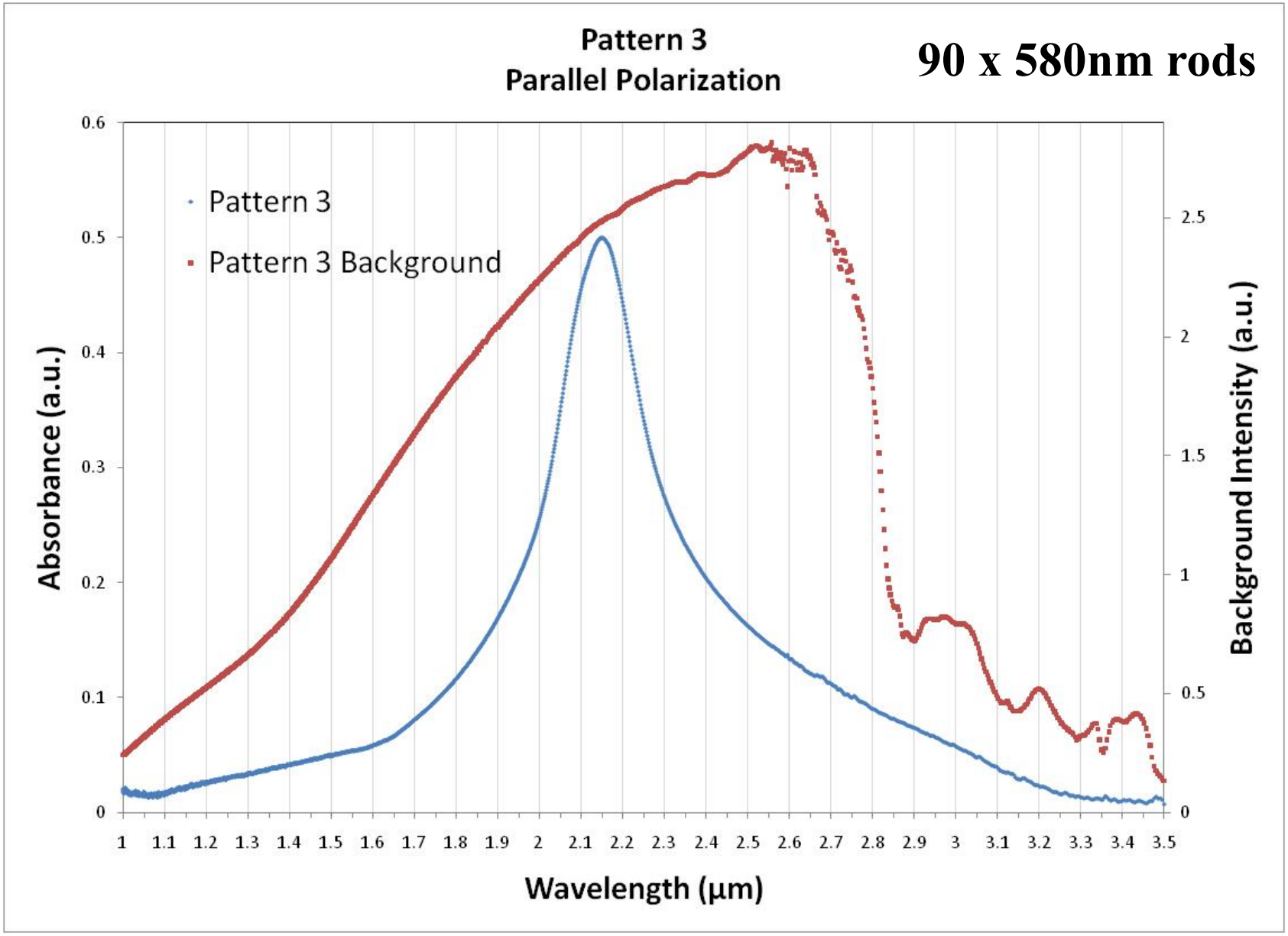








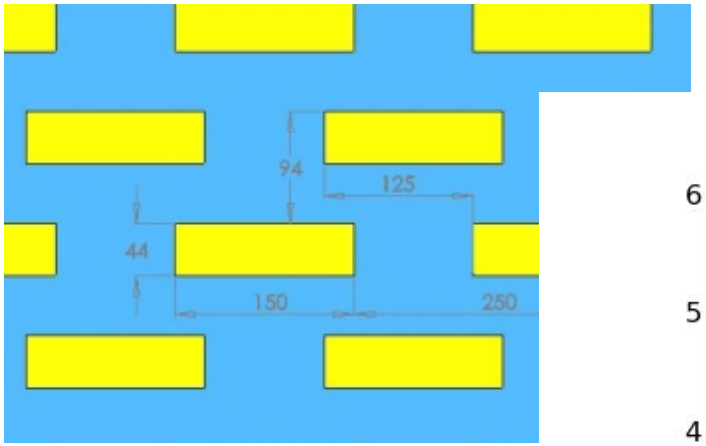
Sensing analysis with imaging spectrometer



Ebeam pattern geometry changes can tune plasmon wavelength deep in NIR and even the mid-IR

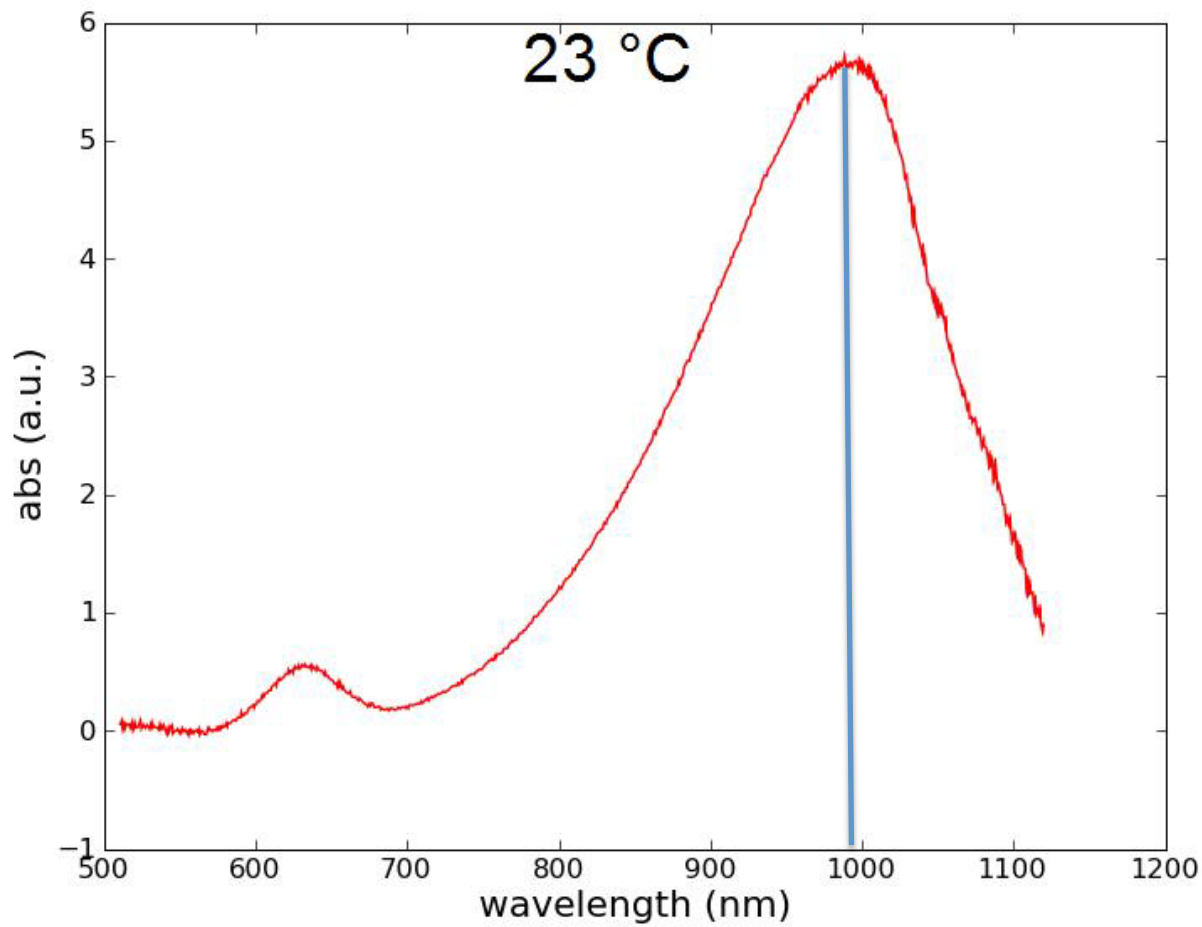
In-situ Analysis of SPR bands

Quartz—GOLD-YSZ sample



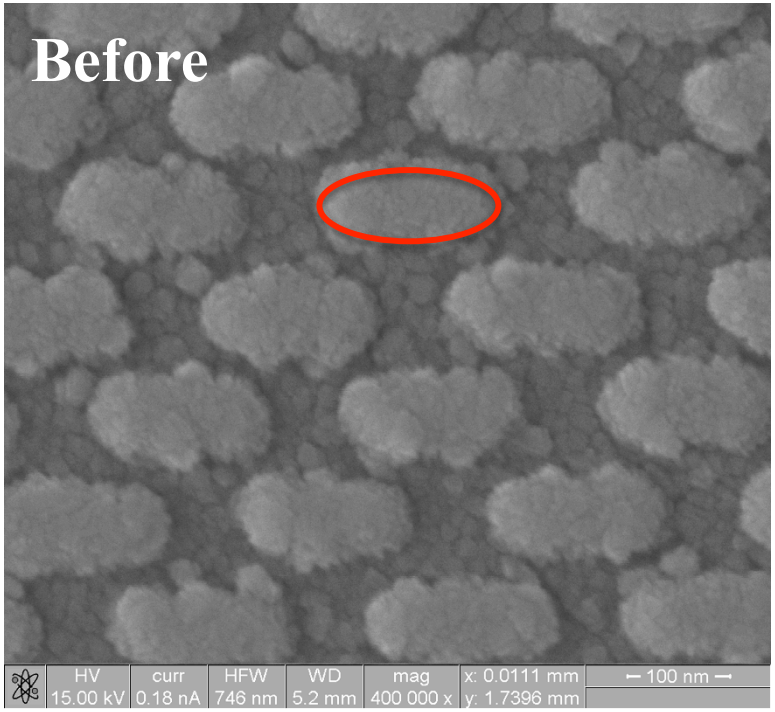
Pattern 1 44x150

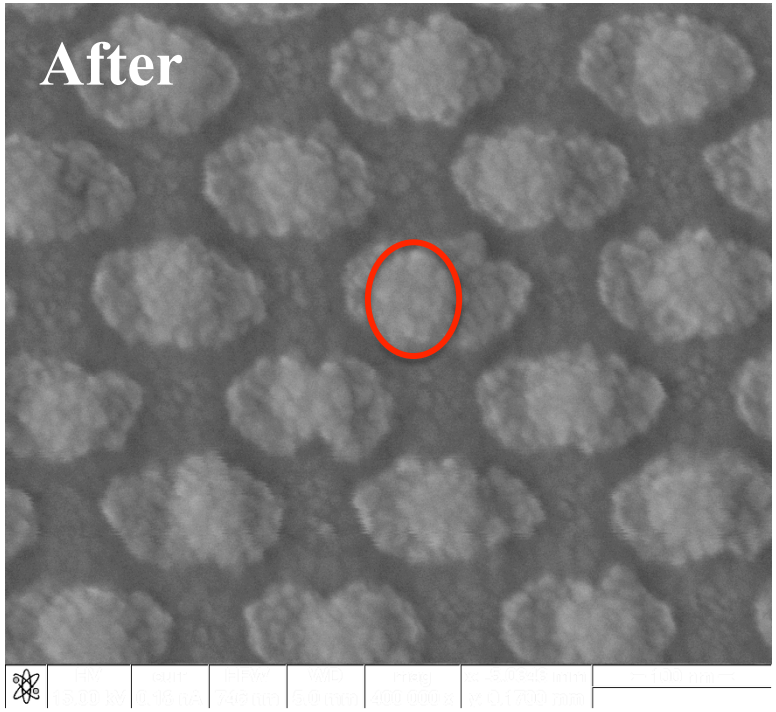
- **Thermal ramp to 800°C in argon**
- **Ramp time is ~1hr**
- **incoming light was unpolarized**



- **Rods appear stable up to ~700°C**
- **Rods clearly have a drastic change at higher temps**
- **Post analysis ESEM has been done**

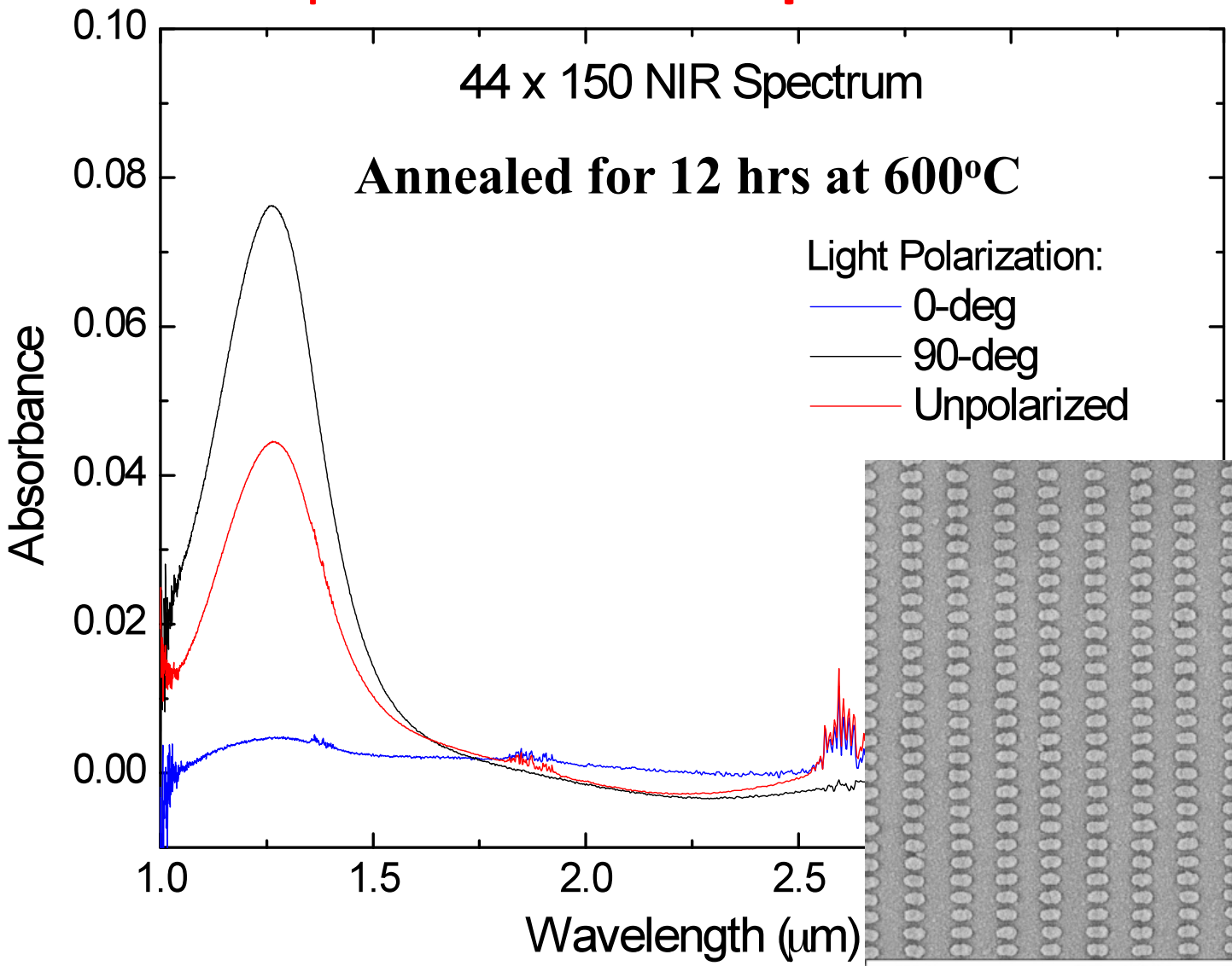
ESEM Post Analysis – 10hr anneal up to 800°C





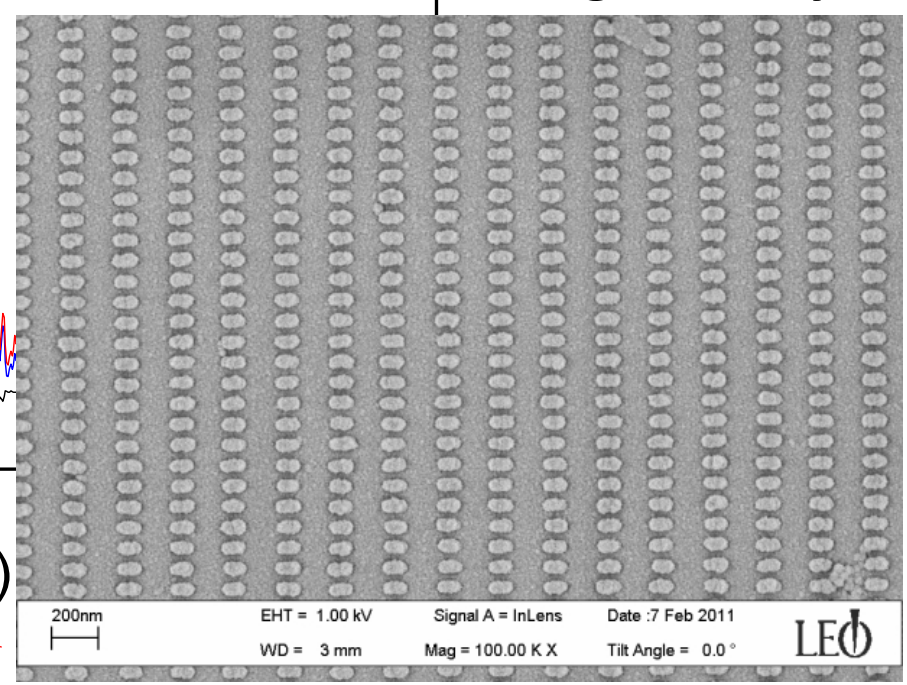
- Ebeam patterned rod sample had dramatic structural change
- Plasmon peak position blue shifts ~300nm
- Signal/noise ratio is ~50:1, high contrast, Large λ Shift

NIR Spectra – **Ebeam patterned Au on Silicon**



Si-YSZ-Au-YSZ

Spectra indicates that Au still has rod geometry



Sensing tests on ebeam samples have begun

Summary

- Efforts this past year have focused on developing a library of Au-metal oxide plasmonic sensing elements for parallel testing
- PCA analysis shows promise for selective detection of emission gases
- Demonstrated enhanced control of metal oxide characteristics – MBE
- Developed ebeam lithography techniques for depositing patterns of Au-metal oxide nanoparticle arrays
- Demonstrated thermal stability characteristics

Future Efforts

- Continue development of multi-variable sensor array development
- Enhanced sensitivity and selectivity
- Testing a Sm-doped ceria sample deposited by PNNL, enhanced oxygen ion diffusivity – array test with un-doped ceria
- Testing ebeam patterned AuNPs
- Develop understanding of sensing mechanisms across array elements

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