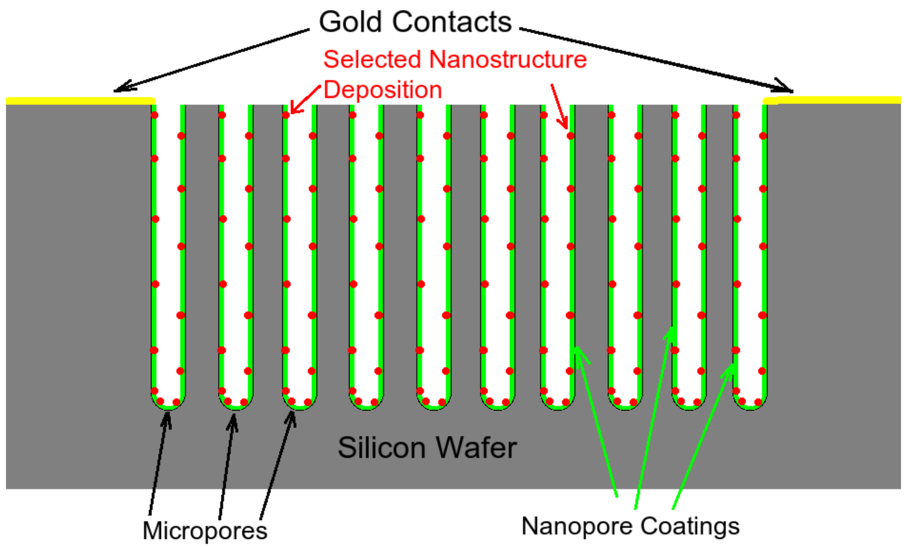
Metal Oxide Decorated Porous Interfaces for Sensor Applications: the Question of Water Interaction and Stability, Platform Diversity, and Sensitivity/Selectivity
C03-1224

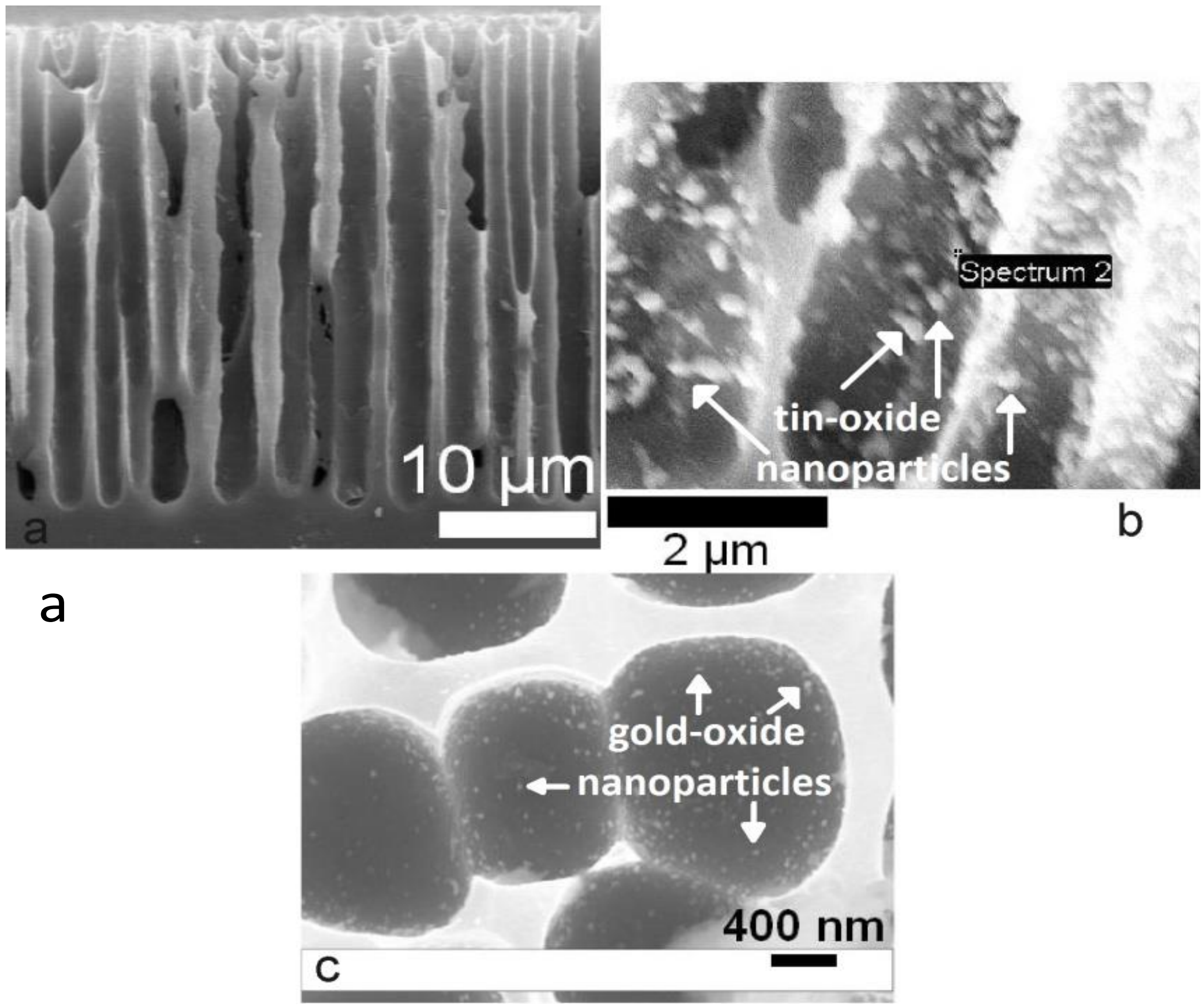
James L. Gole[+,‡]

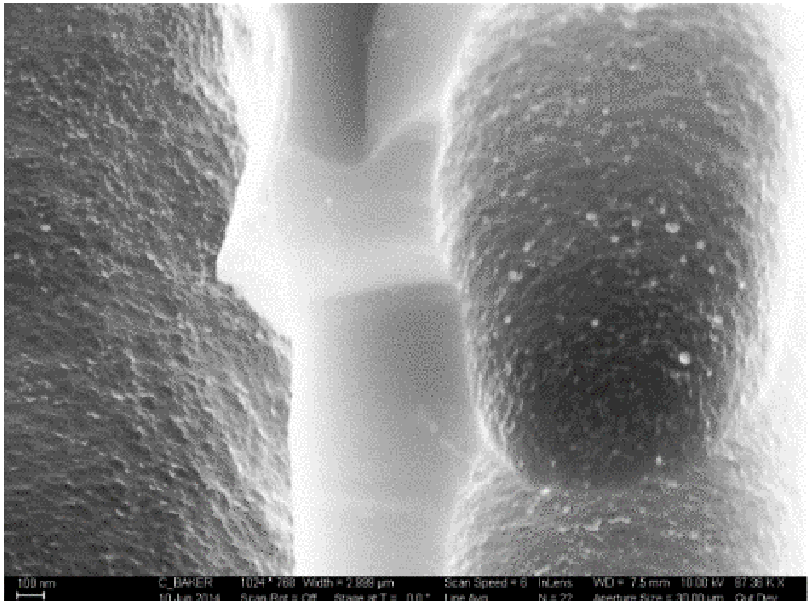
[+] School of Physics, Georgia Institute of Technology
[‡] School of Mech. Engineering, Georgia Institute of Technology
E-mail:james.gole@physics.gatech.edu. Phone: 404-874-9650

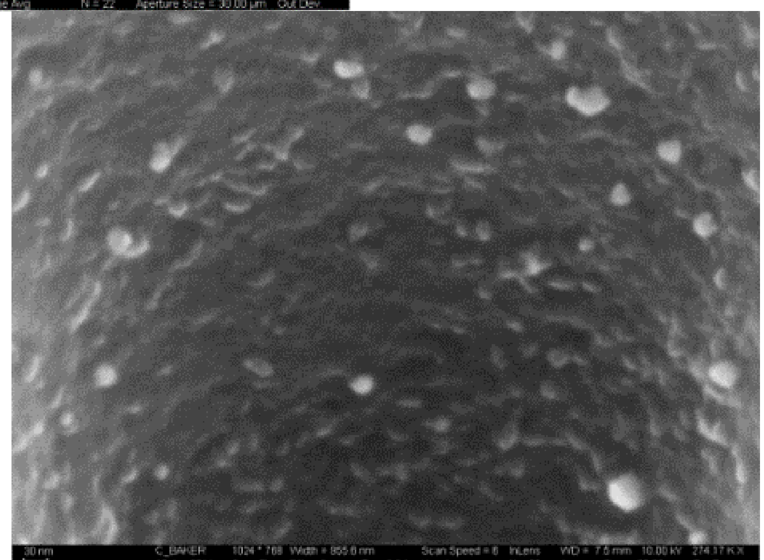
Side View of the Sensor Configuration



*Nanostructured sites easily accessed- Fickian diffusion and rapid analyte-nanostructure interaction greatly improve micropore sensitivity.
*Nanopore coating traps the nanoparticle site depositions and insures against their sintering at elevated temps.
* Exacting reproduction of the sites is not required - simply avoid cross - talk between sites by determining optimum deposition times
*Metal-based nanostructured sites rapidly oxidized > PSi. Nitration to form oxynitrides readily accomplished for both the nanoparticles and PSi.
* Configuration has been found to be stable for extended periods


10 µm
a
Spectrum 2
tin-oxide
nanoparticles
2 µm
b
a
gold-oxide
nanoparticles
400 nm
c

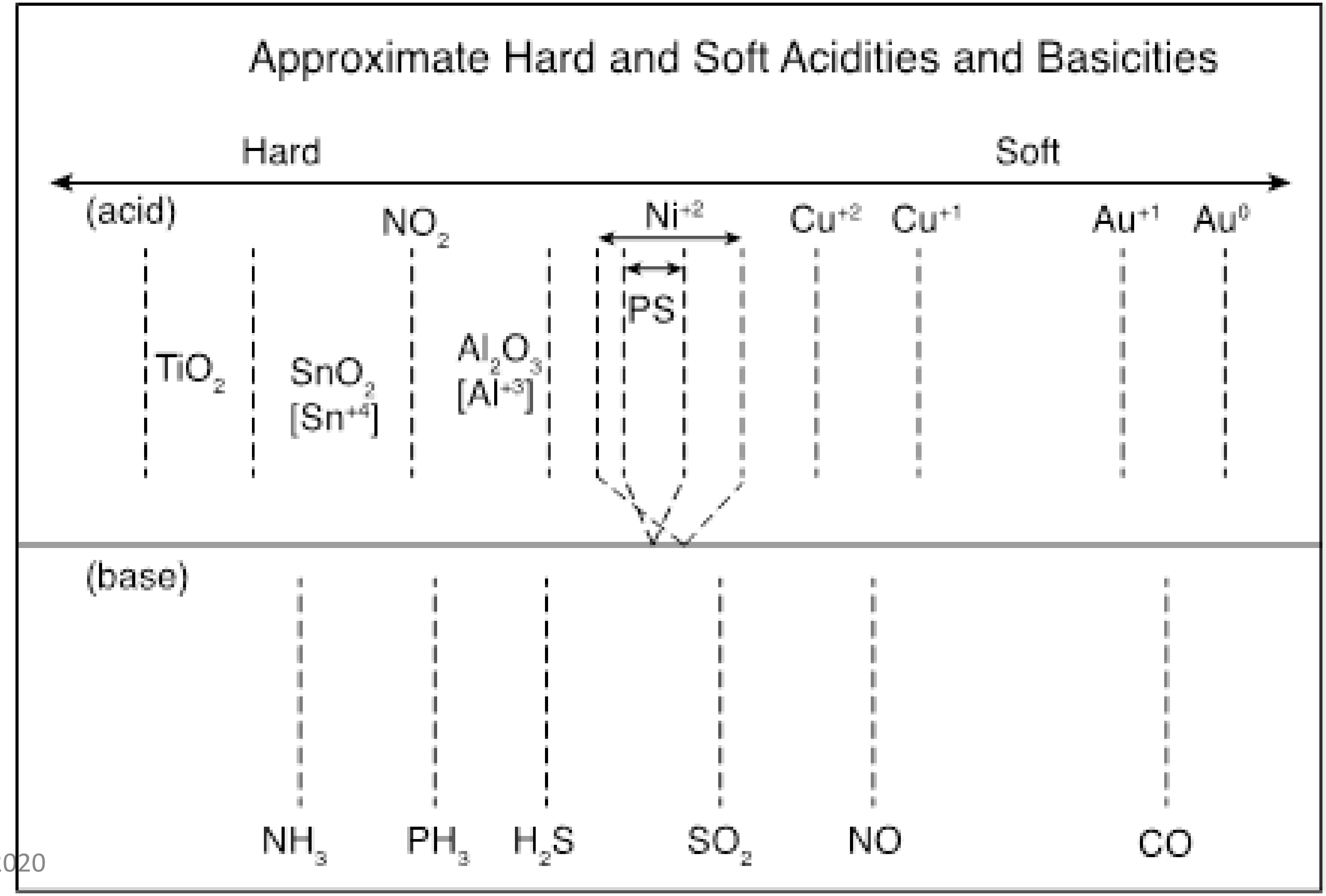

100 nm
C_BAKER
10 Jun 2014
Scan Rot = Off
Scan Speed = 6
Line Avg
InLens
N = 22
WD = 7.5 mm
10.00 kV
Aperture Size = 30.00 µm
Out Dev.


30 nm
C_BAKER
1024 * 768
10 Jun 2014
Scan Rot = Off
Stage at T = 0.0 °
Scan Speed = 6
Line Avg
InLens
N = 22
WD = 7.5 mm
10.00 kV
274.17 K X
Aperture Size = 30.00 µm
Out Dev.

Nanostructured sites provide distinctly different responses to several analytes as exemplified for an SnO_x, NiO, Cu_xO, and Au_xO decorated "p-type" PSi interface. (avoid molecular orbital matching ionic (strong acid/strong base) or covalent (weak acid/weak base) chemical bonding - focus on mismatched strong acid/weak base or strong base/weak acid physical interactions)

	SnO_x	NiO	Cu_xO	Au_xO
PH_3	2	2.5	4	5
NO	7–10	3.5	1	1.5–2
NH_3	1.5	1.5–2	2-2.5	~3
SO_2	4	(2)	1+	2

Metal Oxide – Basic Analyte Interactions
Inverse Hard/Soft Acid/Base (IHSAB) Principle
Prediction of Response Matrices



Approaches to deal with water vapor interaction and problems of stability

Pore diameter induced hydrophobicity

- For pore diam. ~ 2 nm, water vap. condensation observed @ 15% rel. humidity
- For pore diams. ~100 nm, condensation @ 90-100% RH
- Diameters preferable for PSi humidity sensors are of order 20-100 nm

IN CONTRAST

- 700-1500 nm pore diameters display negligible water condensation and minimal sensitivity to water vapor

Micropores result in pore diam. induced stability

In-situ nitration to produce hydrophobic interfaces

Demonstrated that hydrophilic TiO2 nanocolloids are readily converted to hydrophobic TiO(2x)N(x)

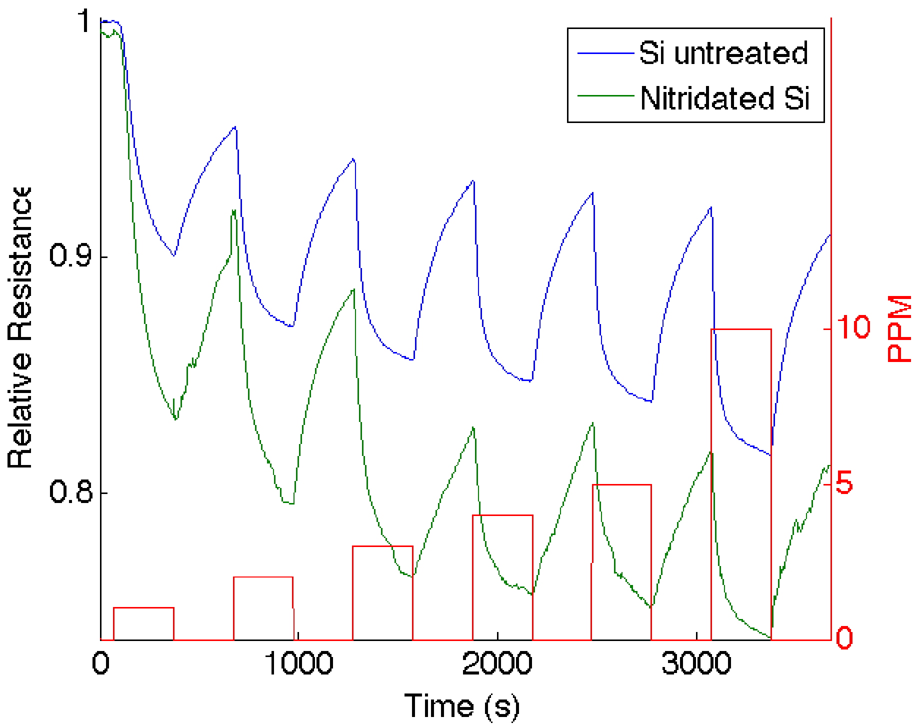
*Rapid nitration of metal oxide decorated PSi to form metal oxynitride decorated silicon oxynitride interfaces

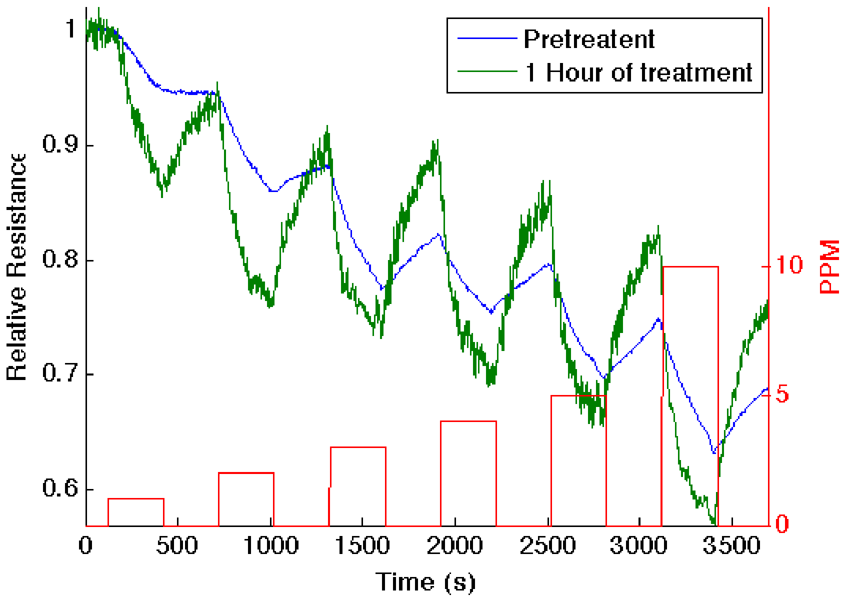
*Nitration of a metal oxide decorated PSi interface produces a high degree of hydrophobicity and thus enhances long term stability

FOR COMPARISON

*Extensive recent studies of SiO(x)N(y) films (vs. SiO2) indicate excellent long term stability

Ammonia on n-type PSi and nitrated n-type PSi (conductance increase) (< 15s ~ near saturation)



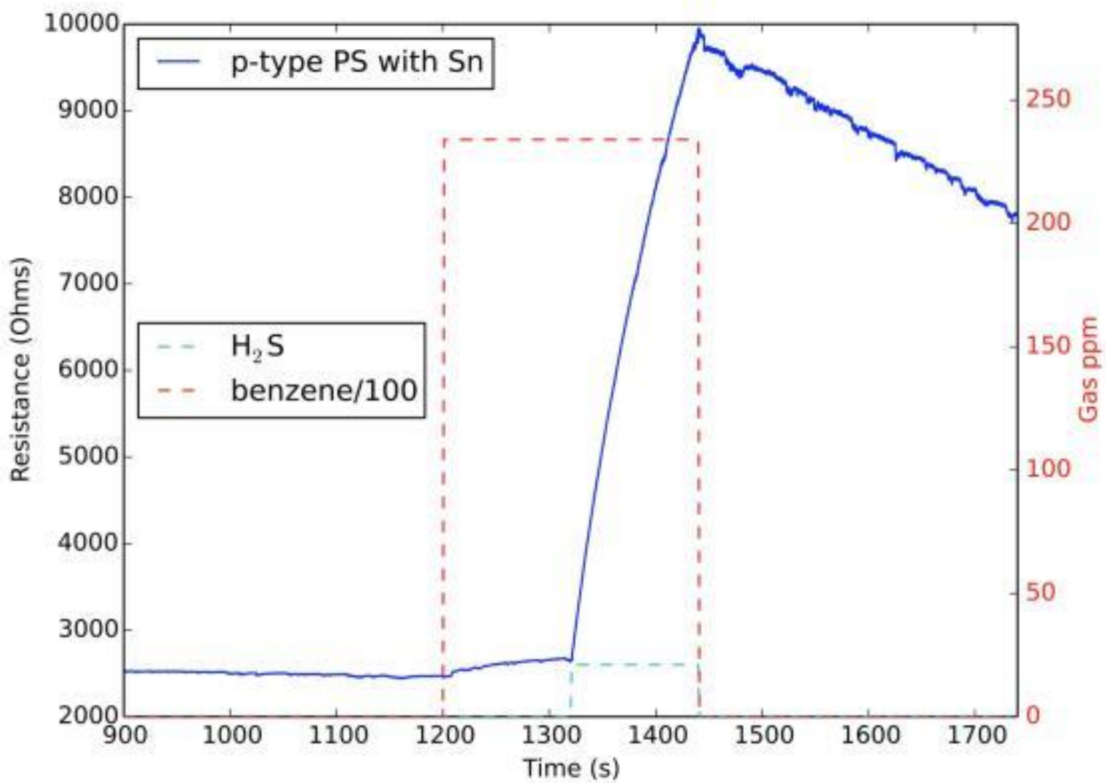


Multi-gas Interactions Sensing Considerations

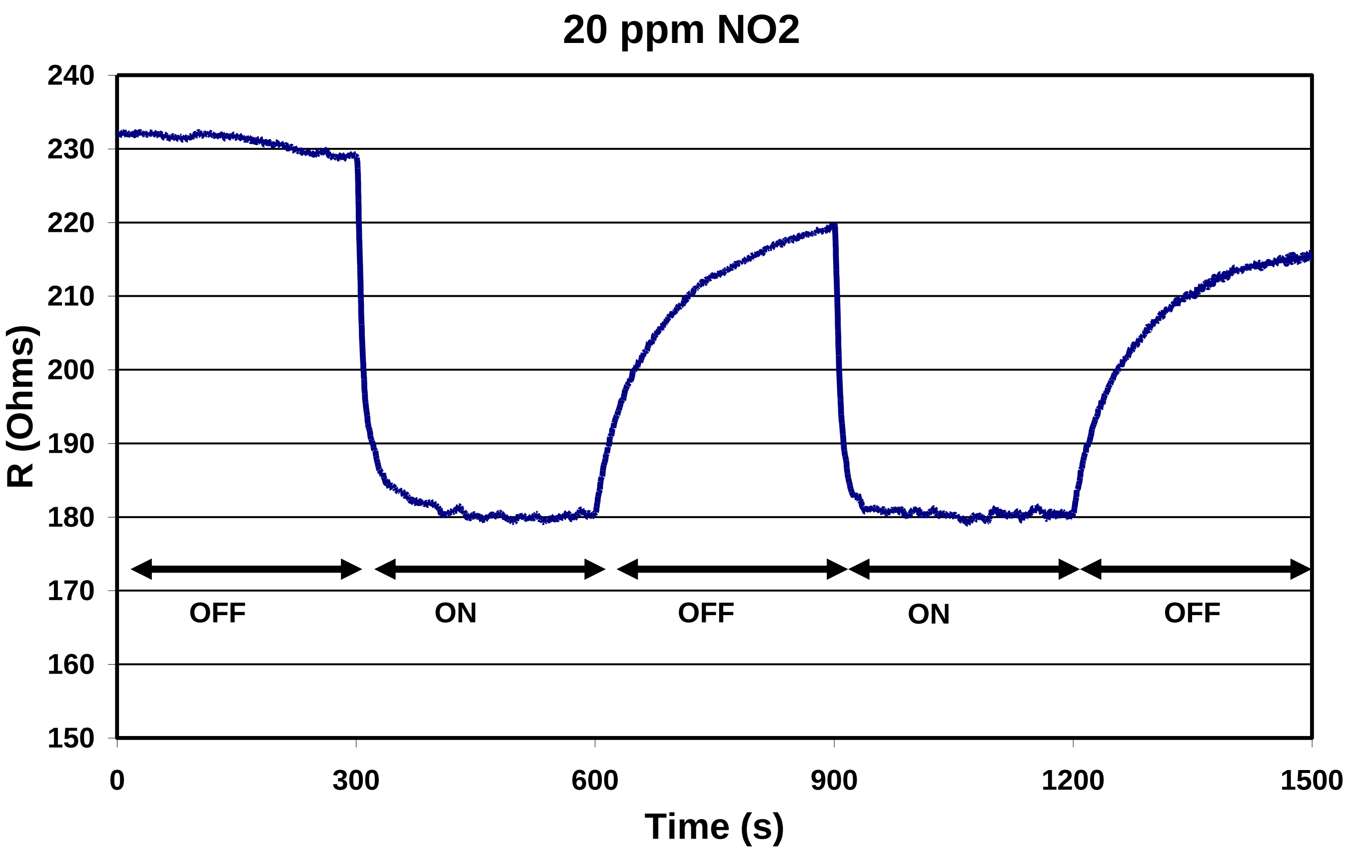
- Pore diameter induced sensitivity/selectivity
- Distinct p- and n-type PSi majority charge carrier interaction with acids and bases
- The combination of nanostructure-based detection matrices (distinct metal oxide nanostructured island site responses)
- Adsorp./desorp. isotherms (Langmuir vs. Fermi)-distinct adsorption/desorption coeffs.
- Time-dependent diffusion responses

Pore Diameter Selectivity

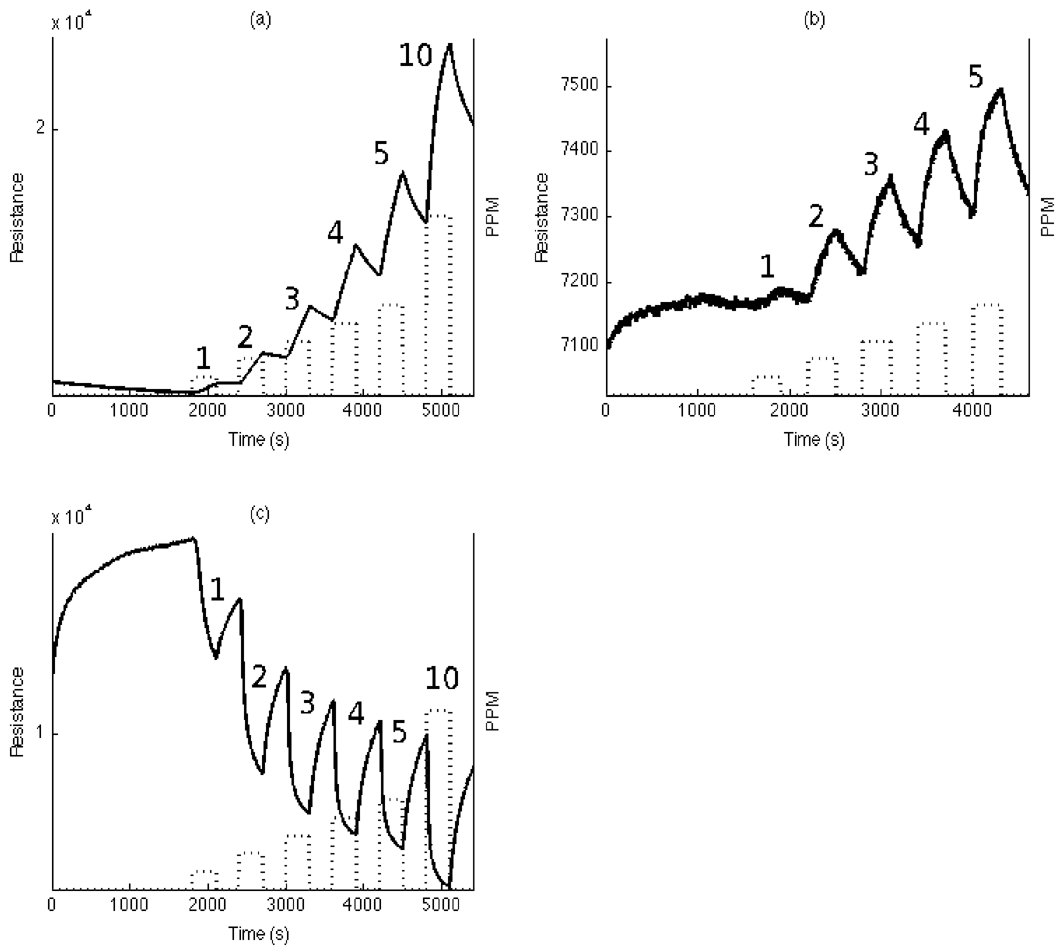
H_2S in the presence of BTEX compounds (on tin oxide decorated p-type PSi)



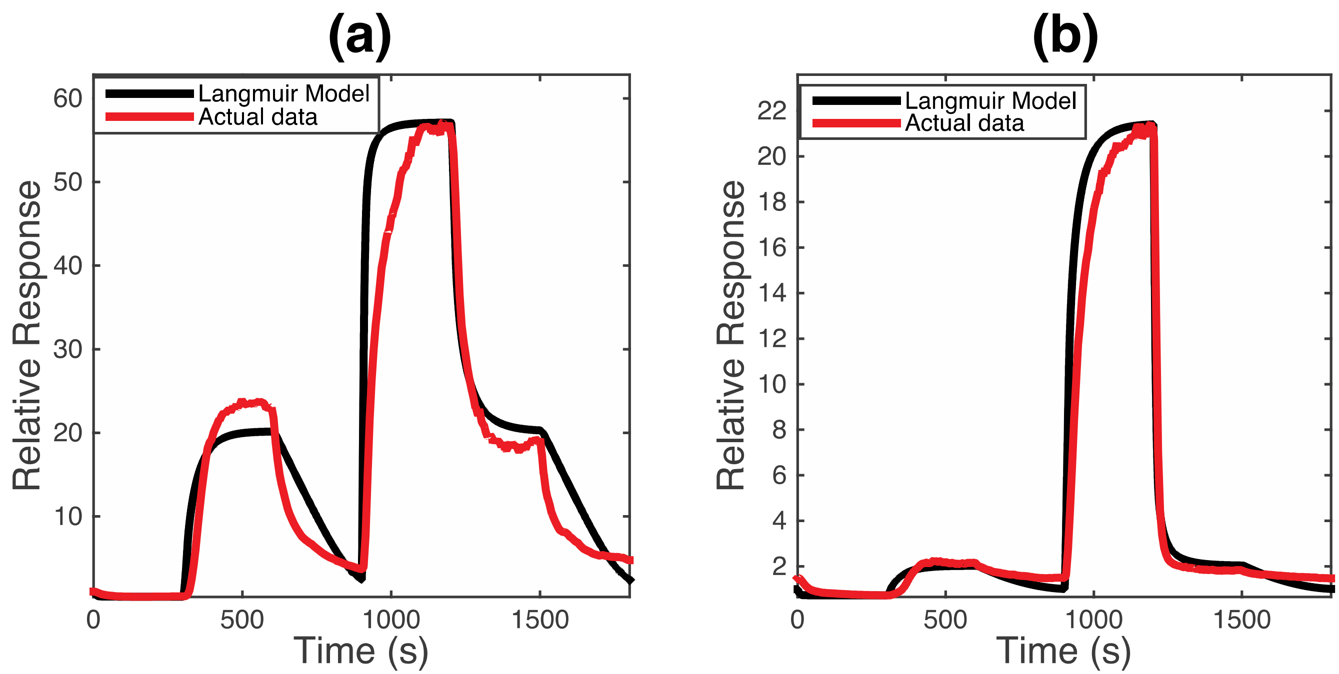
NO_2 interacting with p-type PSi (conductance increase)



NO_2 ,NO(weak acid), and NH_3 on n-type PSi



NO (weak acid) + NH_3 (strong base) mixture on p-type PSi (Langmuir model)



Response (red) of p-type (a) PSi/TiO_2 (b) PSi/Au_xO interfaces to 5ppm of NO (0 s – 300 s), NH_3 (900 s – 1200 s) and NO + NH_3 simultaneously (300 s – 600 s and 1200 s – 1500 s) compared to the simulated (black) response. **Note that the response of the mixed gas levels off to a specific value independent of which gas was first exposed to the sensor.**

NO + NH_3 mixtures (Langmuir model) (weak acid and strong base)

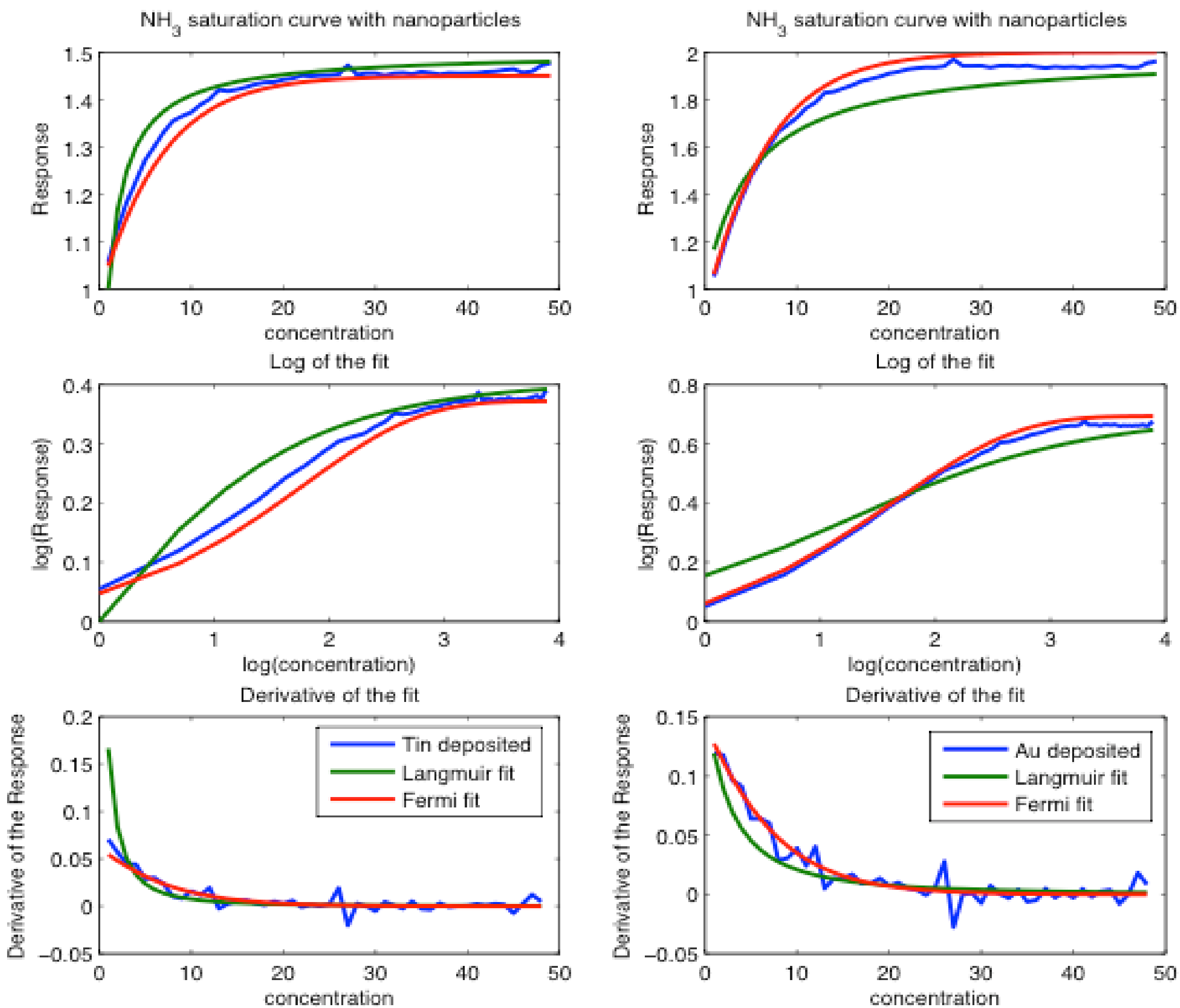
Metal Oxide	Sensitivity		Adsorption constant*	
	NO	NH_3	NO	NH_3
Au_xO	-0.27	24.76	14.4	0.47
TiO_2	-0.73	69.76	0.93	0.41
CaO	-0.21	0.527	0.21	0.377
MgO	-0.4	13.78	4.82	0.28
BaO	-0.7	2.24	0.38	0.12

- **Adsorption coefficient/desorption coefficient**
- **> 1 adsorption process dominates,,< 1 desorption process dominates**

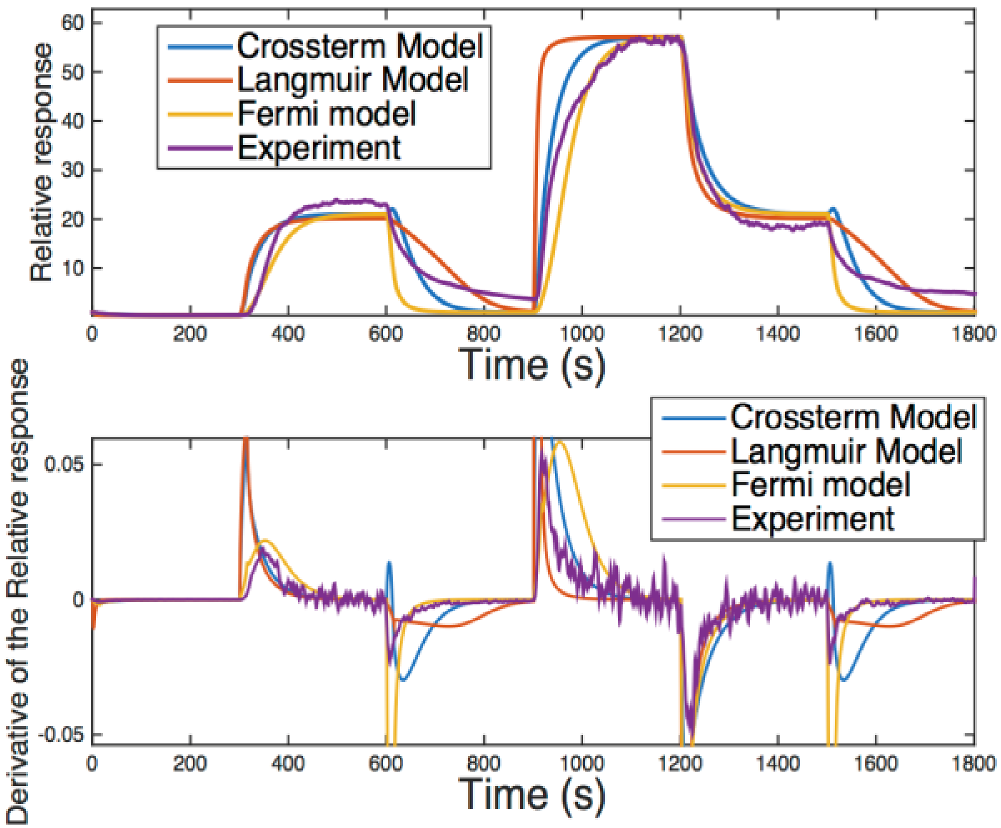
Sensor response to NH_3 is in blue. The best fits using a Langmuir model are in green and the FDF fits are in red. The fits have been checked against the log log plot (middle) and the derivative of the concentration(bottom), for higher accuracy.

(Fermi vs. Langmuir model)

On p-type PSi



Fermi model
Nitric Oxide and Ammonia
on
TiO_2/PSi (p-type)



Multi-gas Interactions
Sensing Considerations

- Pore diameter induced sensitivity/selectivity
- Distinct p- and n-type PSi majority charge carrier interaction with acids and bases
- The combination of nanostructure-based detection matrices (distinct metal oxide nanostructured island site responses)
- Adsorption/desorption isotherms (Langmuir, Fermi)
- Time-dependent diffusion responses

Metal Oxide Decorated Porous Interfaces for Sensor Applications: the Question of Water Interaction and Stability, Platform Diversity, and Sensitivity/Selectivity
C03-1224

James L. Gole[+,‡]

[+] School of Physics, Georgia Institute of Technology
[‡] School of Mech. Engineering, Georgia Institute of Technology
E-mail:james.gole@physics.gatech.edu. Phone: 404-874-9650