Temperature-Dependent Studies of Gas Sensing Materials Using MEMS Microarrays

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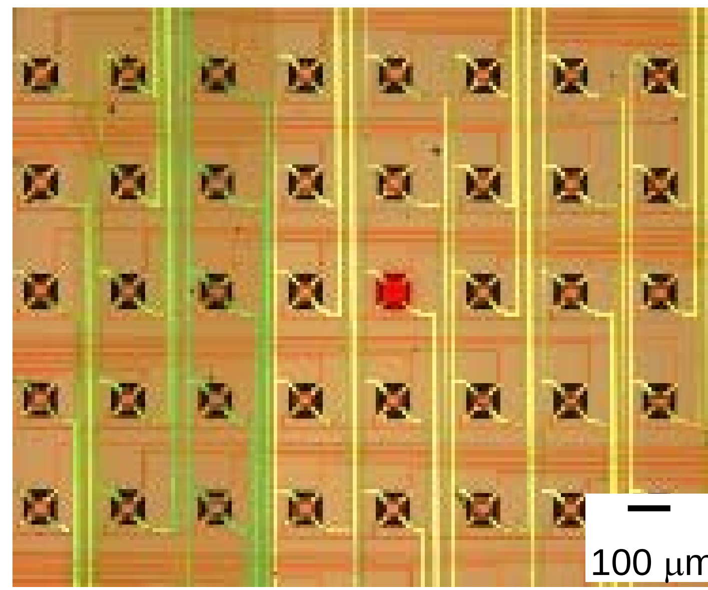
an approach for efficient studies of T-dependent phenomena using microsamples

Platforms - microhotplate arrays
Processing - T-assisted deposition/modification
Performance – T-dependent on-chip and external evaluation



Array of Microhotplates

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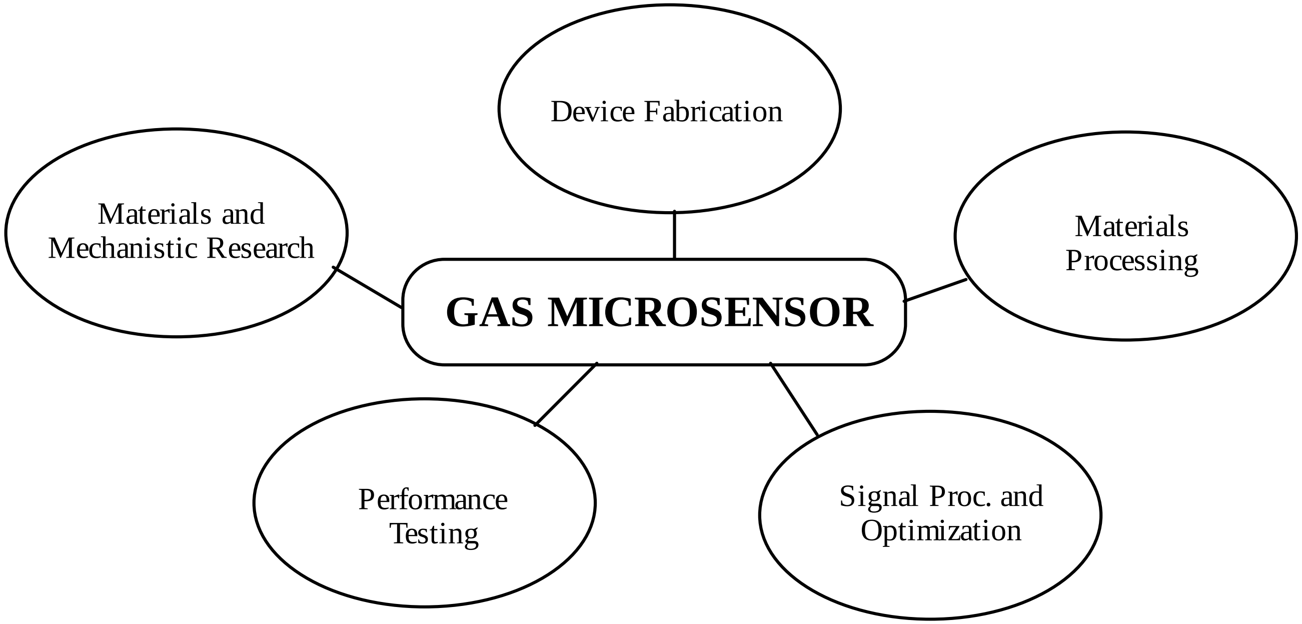
Multi-Faceted Project for Improved Sensing Performance



Performance Characteristics

- Sensitivity
- Selectivity
- Stability
- Speed

Set by customer's application-specific needs

find optimized sensing films and operating temperatures

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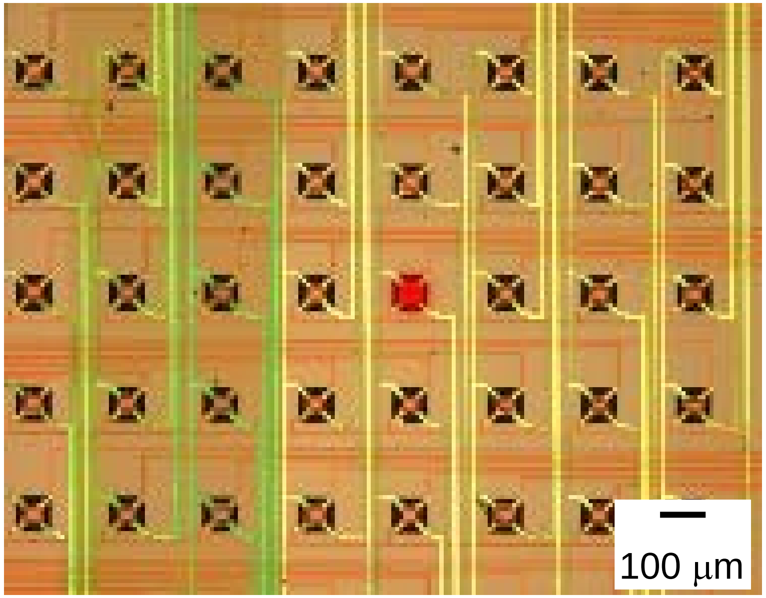
Combinatorial Science with Microsample Temperature Control



Features

- Thermally-isolated elements
- Individually-addressable
- Electronically controlled matrix of T, electrodes
- Suited for statistically-designed studies

Utility

- T-dependent growth, post-processing
- T-dep. response testing [fixed T_i, T_i (t)]
- Monitoring performance by elec. outputs
- All separate experiments
- Purposely redundant microsamples

Advantages

- Simultaneous testing
- Same “external” conditions for all microsamples
- Much faster than single-sample, serial studies

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Outline

- **Microhotplate Platform Fabrication (elements and arrays)**
- **Deposition of Gas Sensing Materials on Microelements**
- **Processing/Performance Case Studies**
- **Comments on Generalization of the Techniques**

Some Take Home Points – Opportunities and Challenges

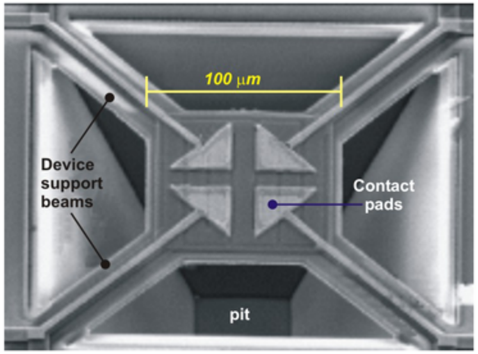
Microplatform design has great flexiblility (but platform materials limitations exist)

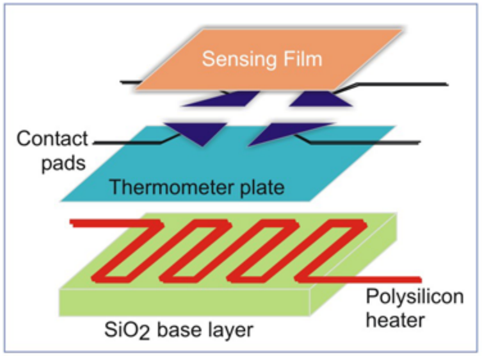
Many samples can be fabricated and studied in parallel (mainly “discrete samples” here)

Novel thermal programming with short time constants available

Certain on-chip analyses can be readily included

NIST Microhotplate (μHP) Platform





Components of a basic microhotplate element:

1. Surface electrical contacts
   - configurations: 4-point, 2-point or interdigitated
   - surface metal: Tungsten, TiN or Platinum
2. Aluminum heat conducting layer
3. Polysilicon heater
4. SiO_2 electrical isolation layers

- Functionality for T(*t*) measurements and control, and film electrical characterization
- Size: 30 - 200 μm; mass: 0.25 μg
- Temperature range: 20°C to 500 (750)°C
- Time constant: ~2 ms

Easily replicated to form arrays

Each microhotplate is individually addressable

Advantages of MEMS structures:

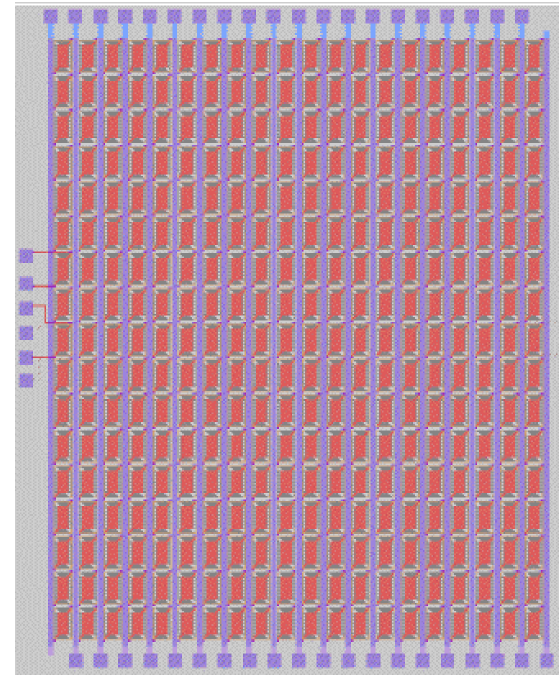
- Low cost fabrication
- Low mass
- Low energy consumption
- Novel operational modes possible

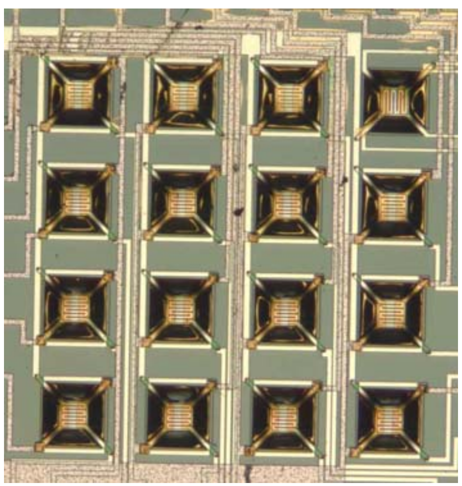
Si etching (micromachining) – enabling technology

Varied Microarray Designs

4-element array for gas microsensor prototypes

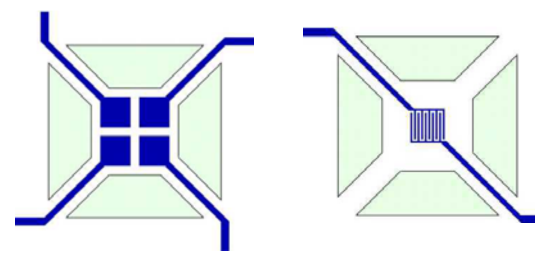
340-element array for investigating adsorbate transients and surface coverage-conductance relationships and film Deposition studies





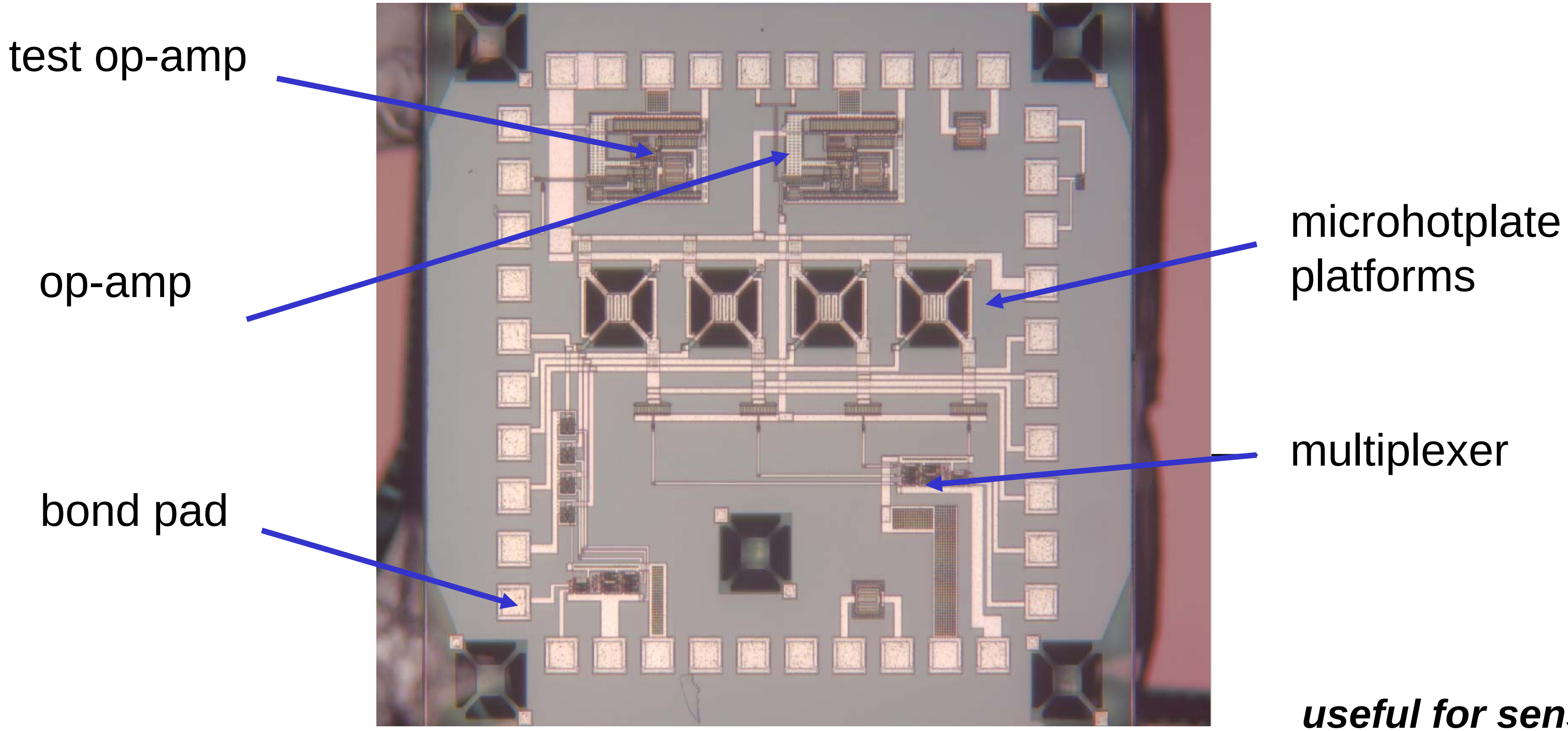
16-element array for process/property studies on sensing films

different 2- and 4-contact surface electrode designs

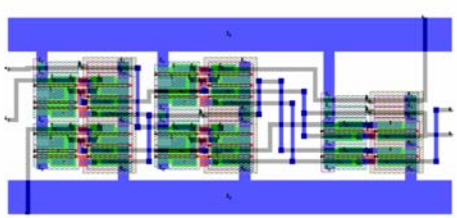


An Additional Benefit - Electronics Integration

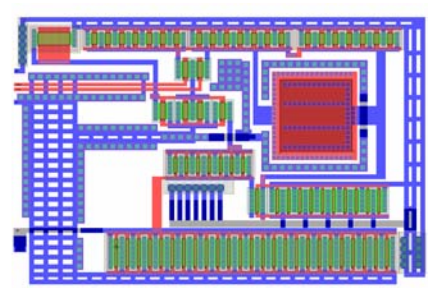
on-board circuitry to enhance capabilities



useful for sensing and microarray materials work



multiplexer layout



op-amp layout

Solid State Gas Sensing Materials

- **Transduction Mechanism**

adsorption- or reaction-induced changes in film properties

mass	temperature
electrical conductance	ionic conductance
capacitance	work function

- **Conductometric Sensing Materials**

-- Conducting polymers

-- (Semiconducting) oxides

SnO_2 **TiO_2** **ZnO** WO_3 Ga_2O_3 **Fe_2O_3**

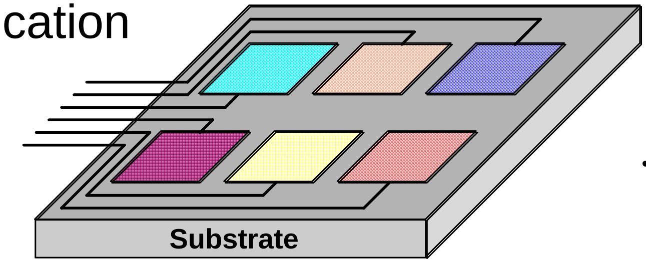
$BaSnO_3$ $LaFeO_3$ $SnWO_4$ $MnWO_4$

TiO_2-SnO_2 CuO-SnO_2 In_2O_3-SnO_2 CuO-ZnO

Gas Sensing with Conductometric Arrays

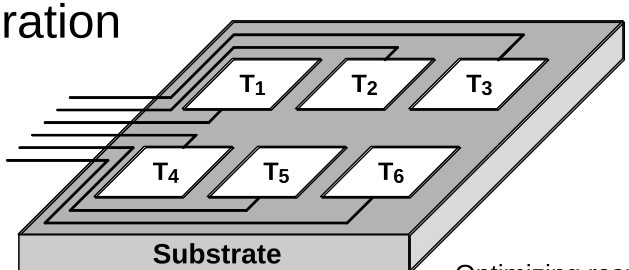
An Inherently Combinatorial Problem

Fabrication



Matching materials to target analytes

Operation



Optimizing response

Testing

Altering the conditions

tunability

Fabrication Variables

Film class
Additive type/concentration
Deposition method(s)
Processing parameters
Growth T
Thickness

Performance Variables

Operating T
Gas composition
Analyte concentrations

Application areas:
- chemical warfare agents
- space environments
- hazardous waste
- process control

Film Deposition & Processing on Microelements

Local Heating

- Thermally-activated CVD
- Sol-gel, suspension drying
- Annealing
- Thermal lithography
- Thermally-assisted imprinting

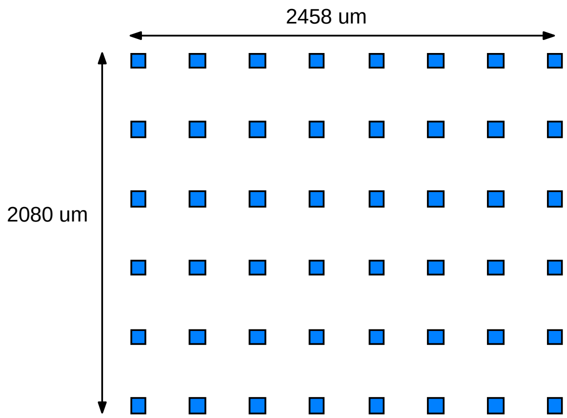
Incorporating Chemically Functional Materials

- **sensing**
- **preconcentration**
- **filtering**

Local Potential Control

- Addressable electrochemical deposition (polymers)

Masking



litho-defined shadow mask

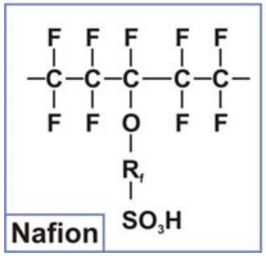
Micro-Dispensing (pipetting)

all processing done after etching and packaging (to avoid etchants and to use electrical contacts)

Polyaniline Deposition Using a Capillary Microdispensor

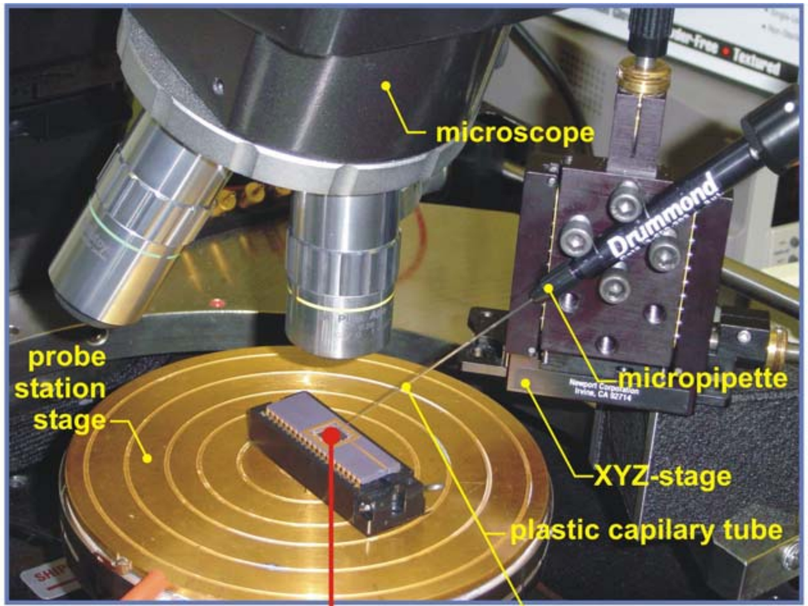
Casting solution:

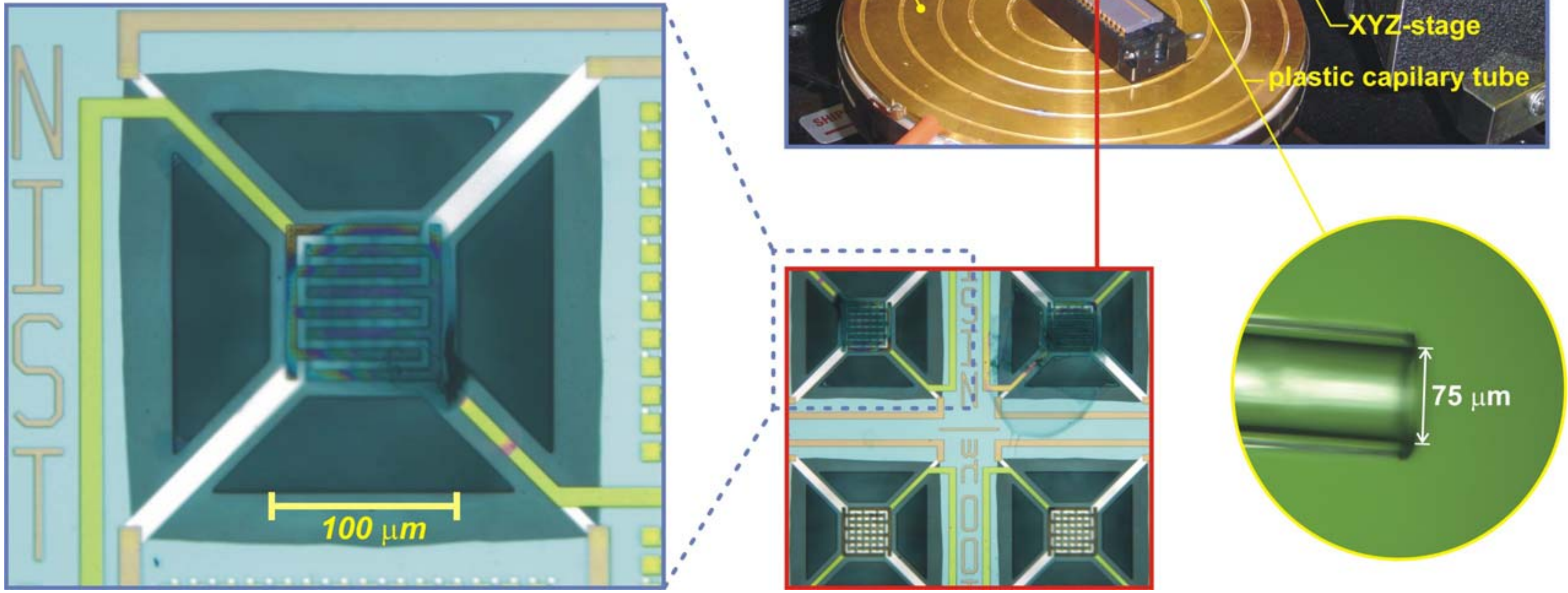
PANI + Nafion in Formic Acid



Roles of Nafion:

- improves film adhesion
- high-temperature stability
- proton source
- enhances sensor performance





(also for sol-gels)

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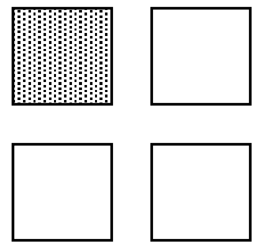
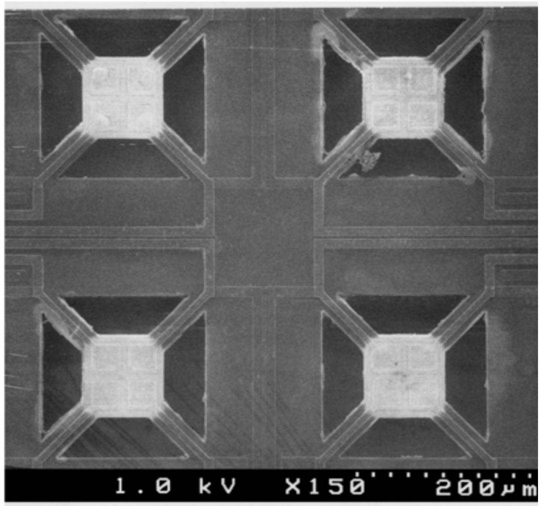
Localized, Thermally-Activated CVD

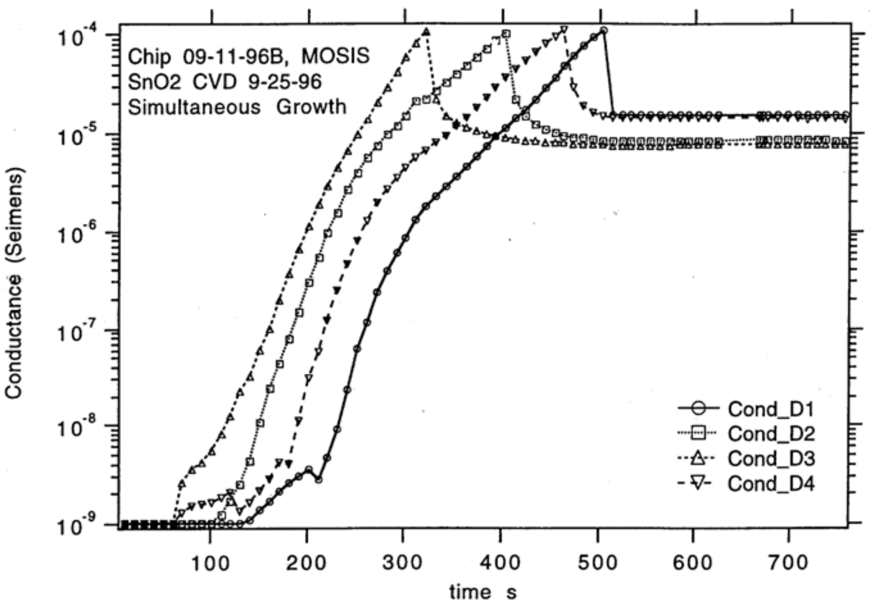
1. Site select element to be deposited on
2. Input appropriate precursor (and reactants)
3. Switch on heater to desired temperature (T)



individually addressable microhotplates in 2 x 2 array



self-lithographic deposition of SnO_2 using tin nitrate on 450 °C microhotplates
(can be same or different materials)



real time growth monitoring with electrical conductance measurements
(for CVD and other methods)

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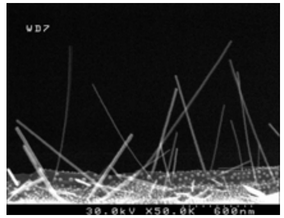
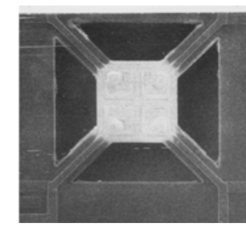
Incorporated Chemical Materials & Methods

Method | **Chemical Material**



CVD: SnO_2 TiO_2 ZnO Pt CNT

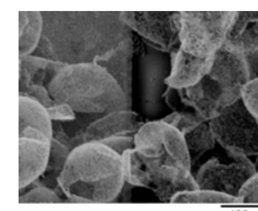
Sol-Gel: SnO_2 Fe_2O_3 TiO_2



Dried Colloidal Suspension: SnO_2 TiO_2

Masked Evaporation: catalytic metals

Heated,Calcined SiO_2/ Polymer Blends: ultrathin μspheres porous SiO_2

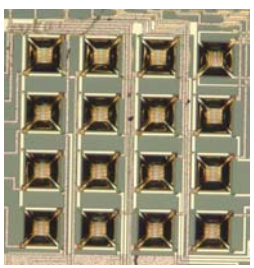


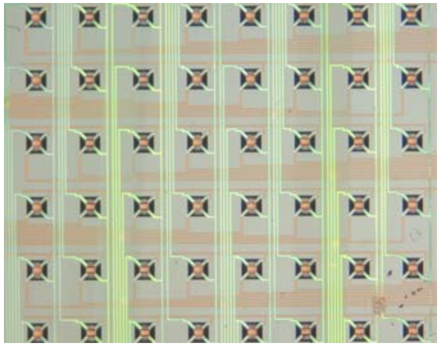
All deposition and post deposition processing at set individual microheater temperatures

Electrochemical: polypyrrole, polyaniline metals

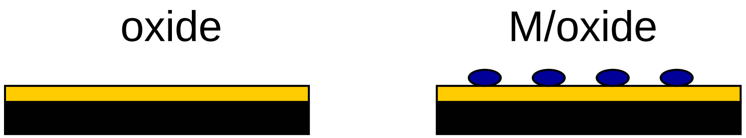
Some Case Studies

- 36-element study of performance changes from low coverage, surface-dispersed metal additives on CVD SnO_2
- 16-element study of T-dependent microstructure for CVD TiO_2
- survey discoveries of sensing films and operating T's for different applications
- Neural Network pruning ("database mining")





Oxide-Based Gas Sensing Films



- Reproducibility check by having redundant elements in columns

- <u>Same platform to process samples & evaluate sensing performance</u>

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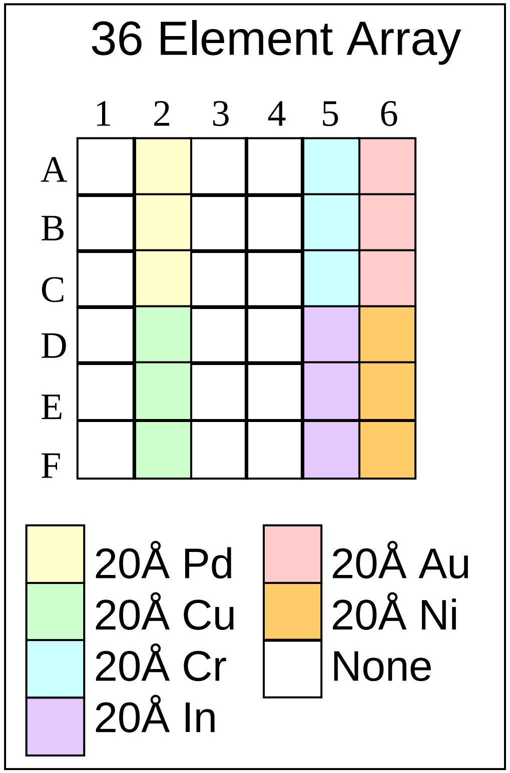
Catalytic Additive Microarray Study

Experimental Design

- Sensing Films
  - 36 Element Array
    - 1 chip/platform used
    - Seeded tin oxide deposited (Ni)
    - 6 catalytic metals deposited
    - Each metal 3 replicates
    - 18 control elements
- Gas Sensing
  - 9 gases used
  - 150 s gas pulses
  - Air flow between pulses
  - Sensing temperature 150-400 °C
  - Sensitivity calculate

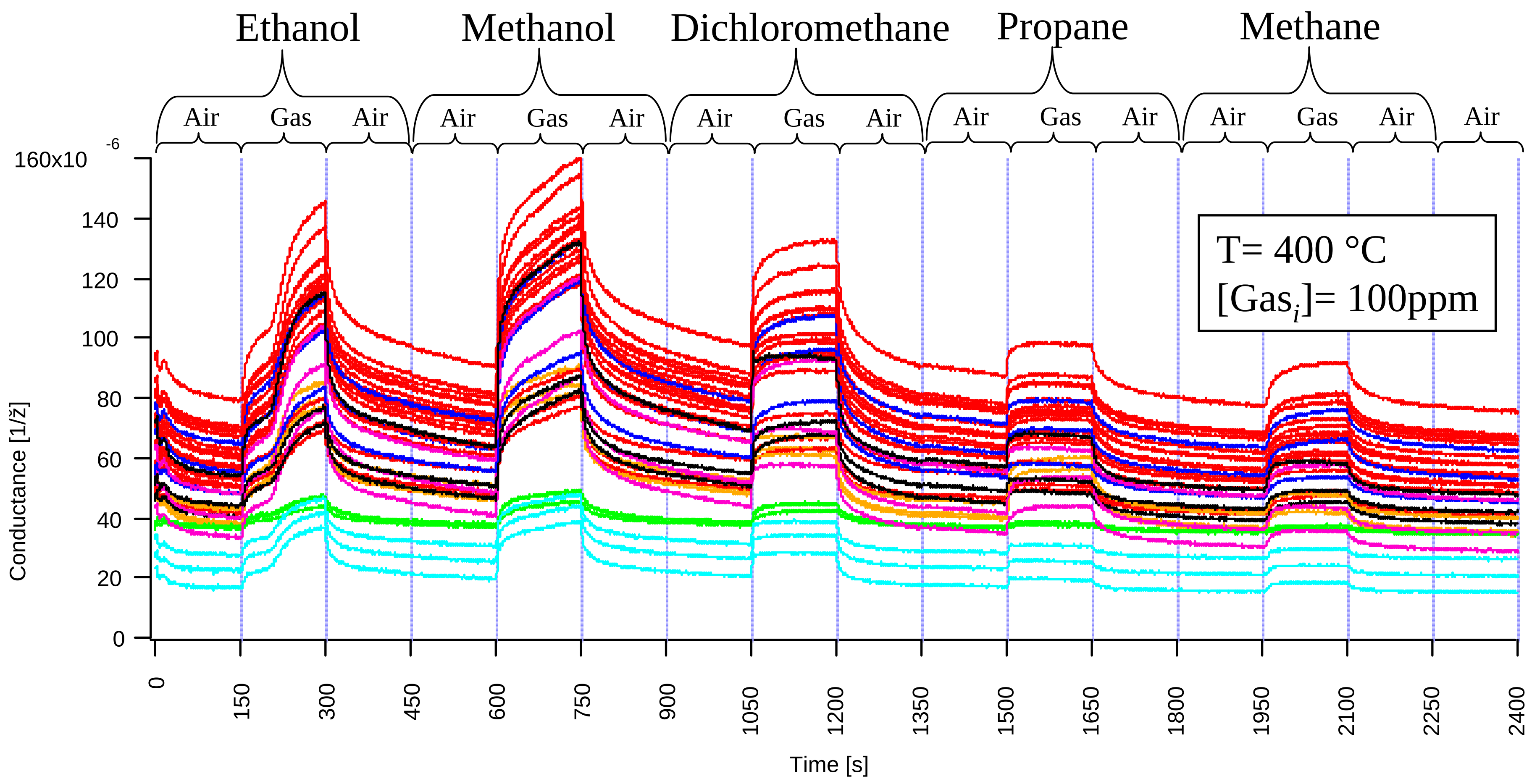
<u>Gases Used</u>

Methanol
Ethanol
Dichloromethane
Propane
Methane
Acetone
Benzene
Hydrogen
Carbon Monoxide



Fixed Temp. Sensing (FTS) Data

- Sensing response of 36 element array to 5 gases at 400 °C



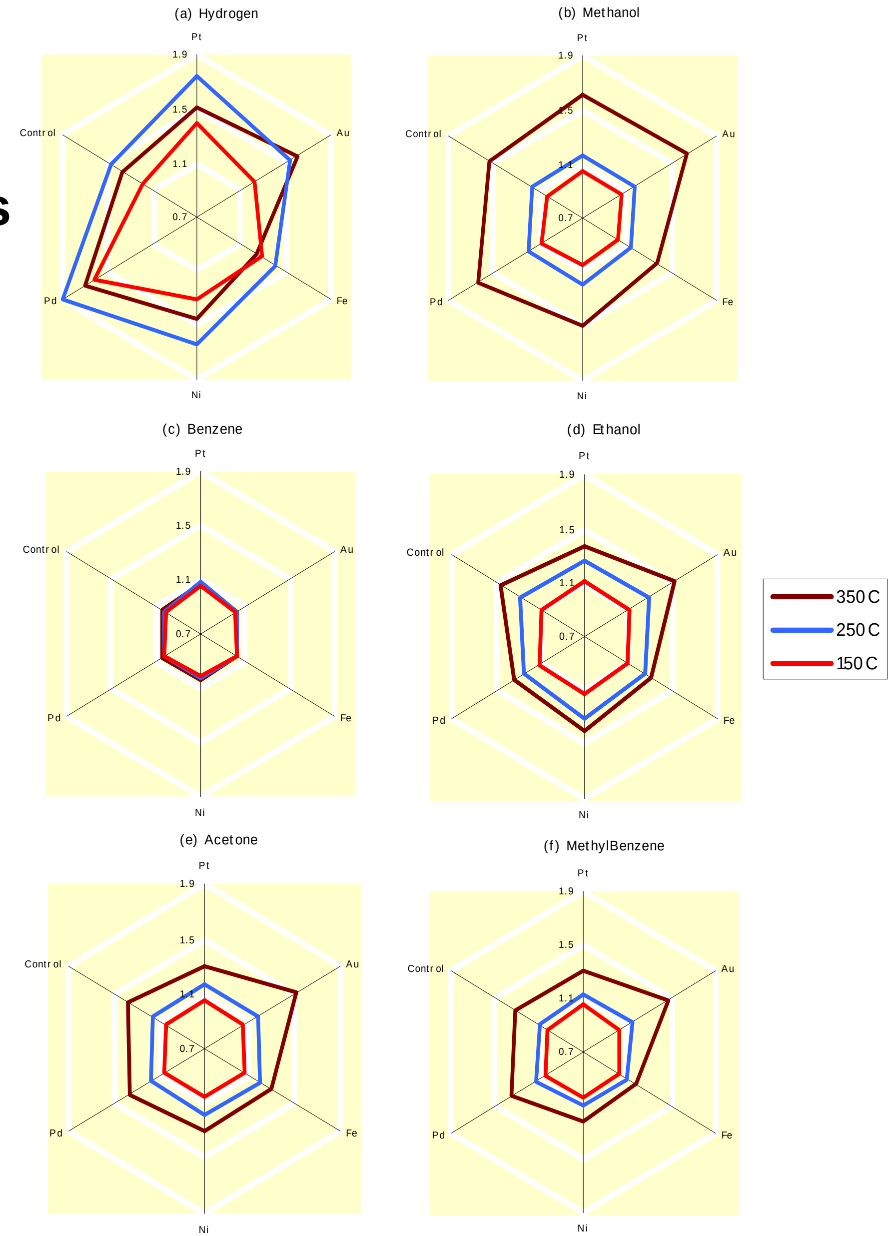
Gas Sensitivity Web Plots

SnO_2-supported catalytic additive samples (like previous 2 slides) – **additives form axes**

Multiple test-gas series

3 parametric FTS operating temperatures (150 °C, 250 °C, 350 °C)

Compresses a great deal of data and provides "shapes" for selectivity



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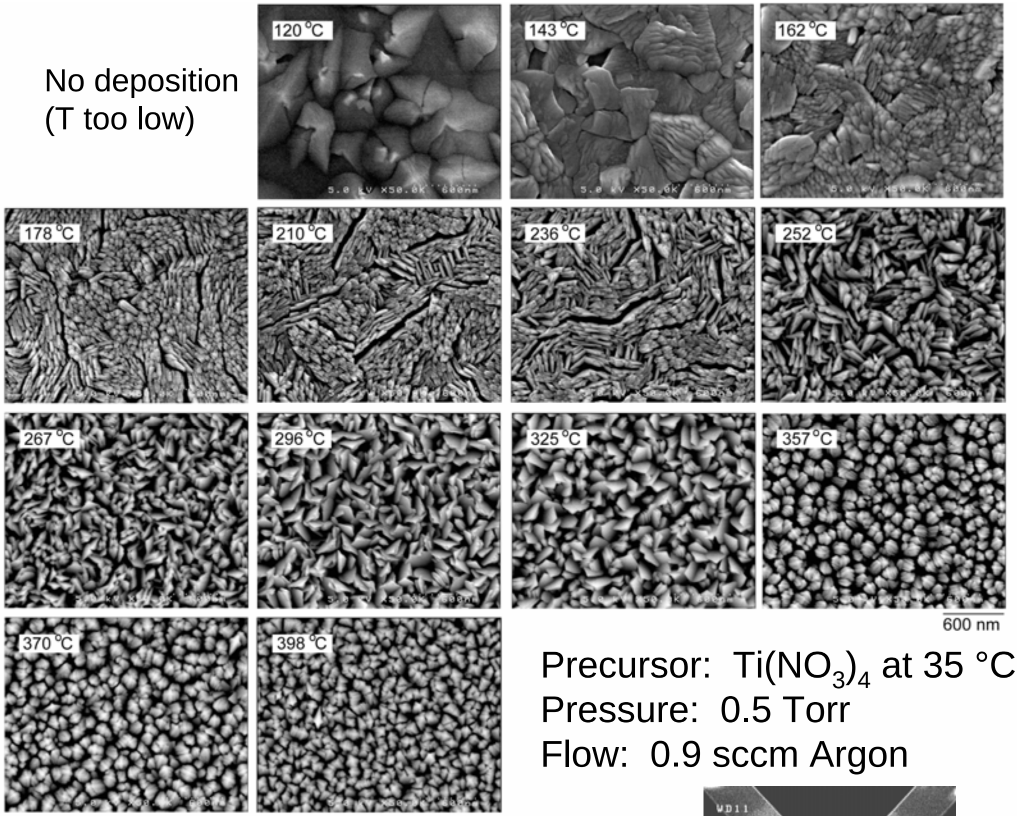
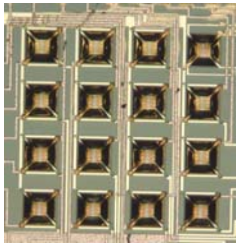
Efficient Microdevice Studies of Film Microstructure

TiO_2 Sensing Films: Microstructure Strongly Dependent on Deposition T

No deposition
(T too low)

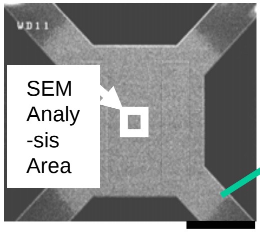


Precursor: $Ti(NO_3)_4$ at 35 °C
Pressure: 0.5 Torr
Flow: 0.9 sccm Argon

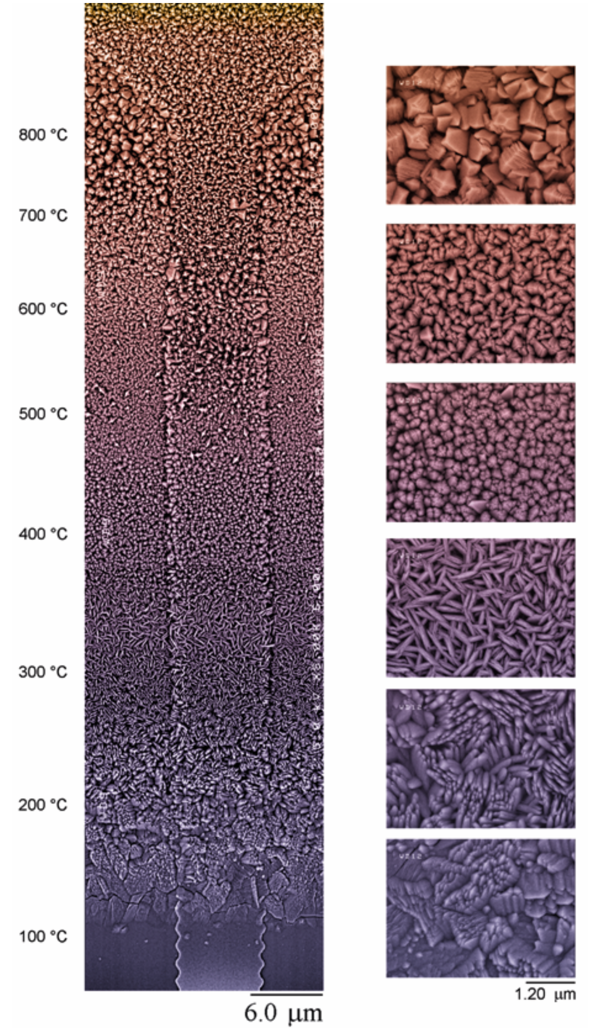


discrete samples

simpler characterization and performance evaluation



50 µm



gradient samples (hotplate leg)

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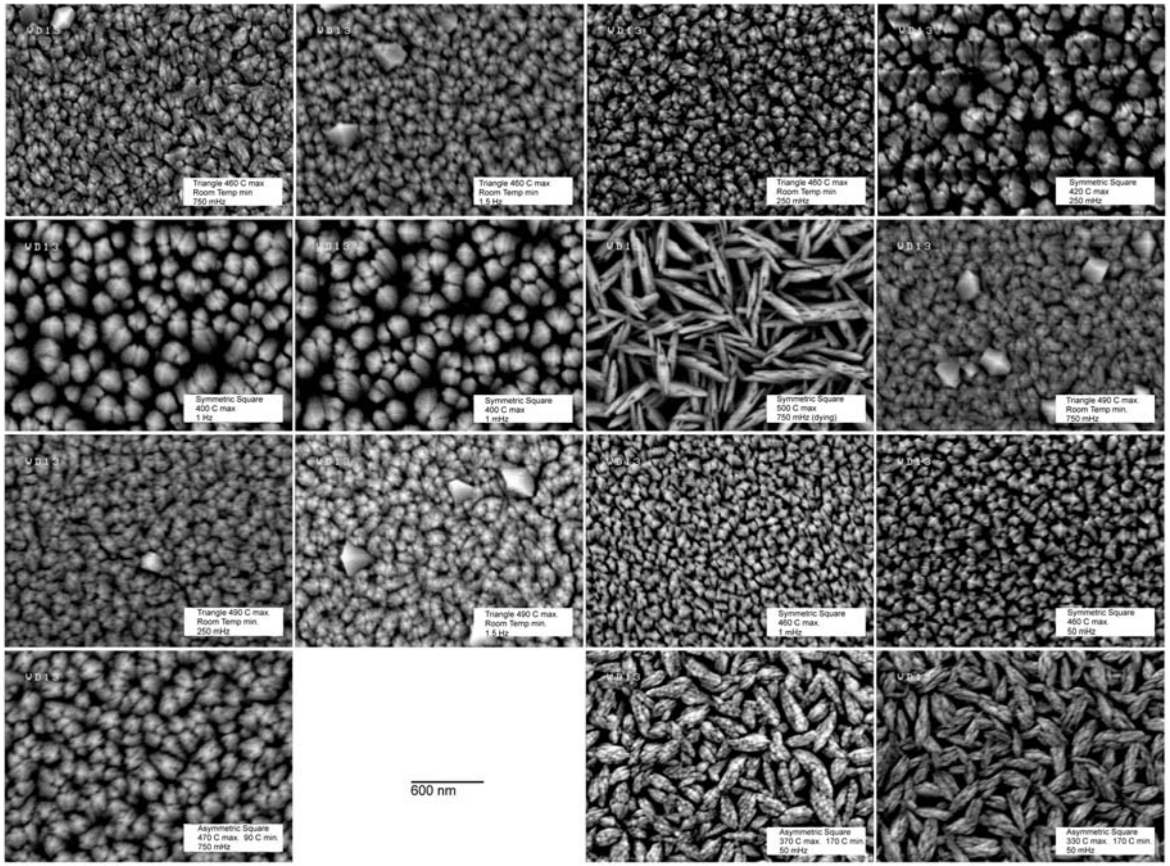
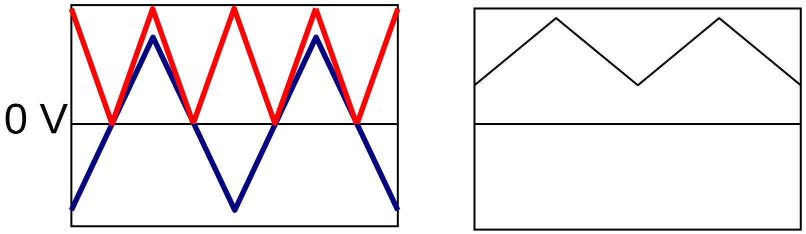
performance surveys for different applications

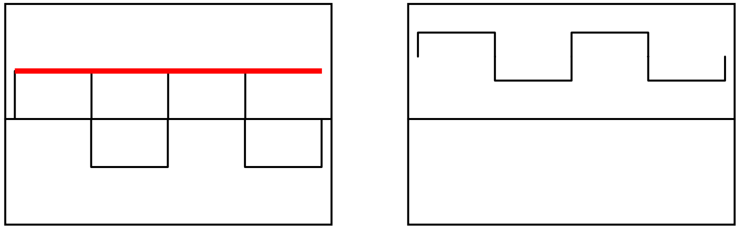
Temperature Programmed Deposition



- **T(t) during growth [deposition analogue to TPS]**
- **new microstructures can occur**



Symmetric and Asymmetric Triangle Wave



Symmetric and Asymmetric Square Wave

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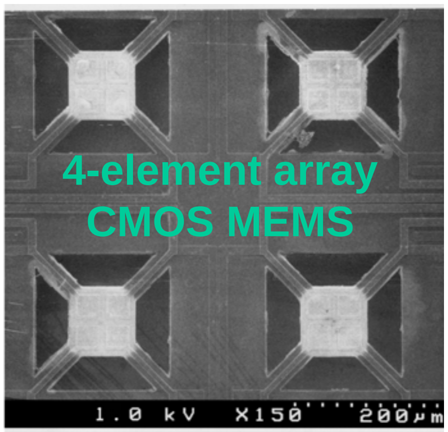
Solid State, Low Power Microsensors for Detecting CW Agents

#1 SnO_2 #2



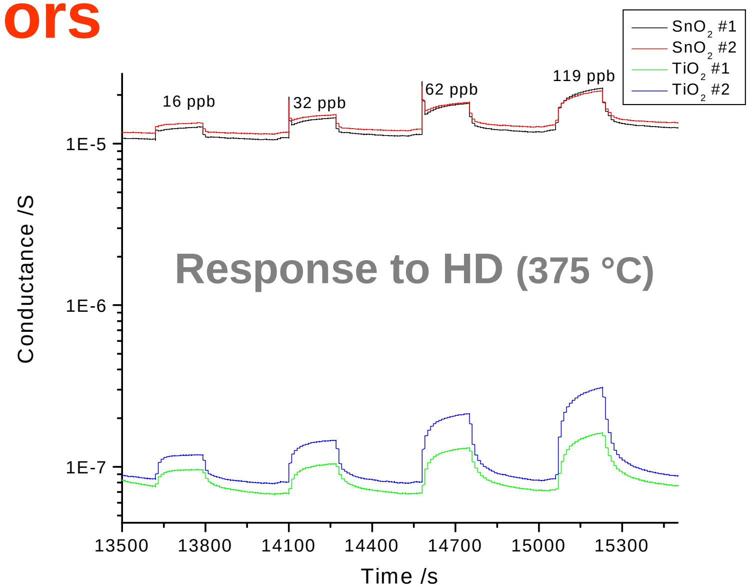
#1 TiO_2 #2

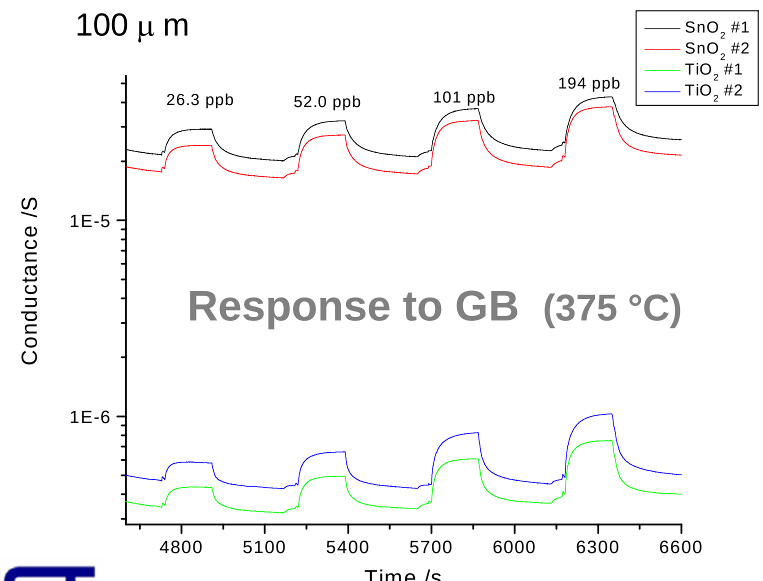
100 μ m

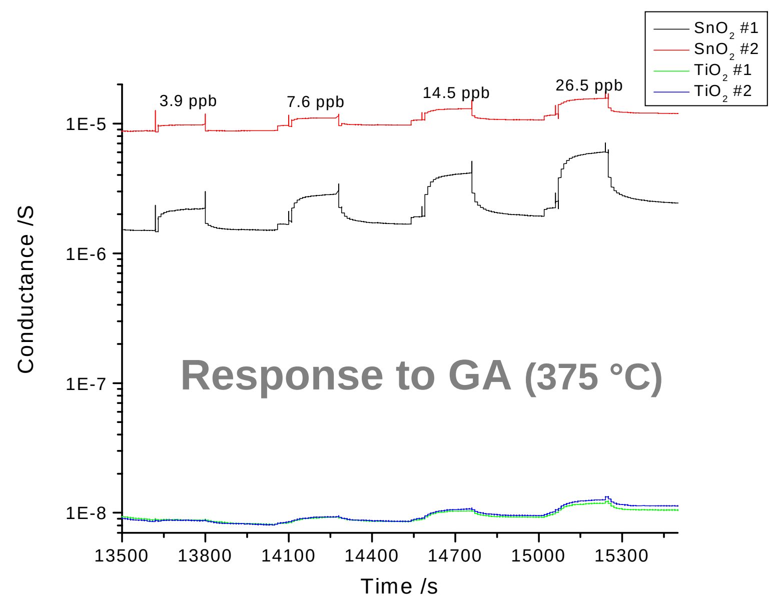
tin nitrate CVD

titanium isopropoxide CVD

600 nm







(and, temperature programming for faster agent recognition)

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ANN Pruning: Most Useful Analytical Data

Classification and Concentration Prediction of CW Agents by ANN Modeling of MHP Sensor Array: Minimal set of Sensors and Temperatures

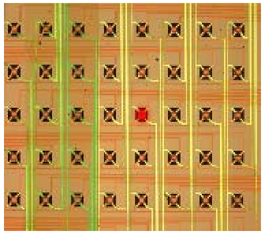
(C – Classification of the CW Agents, Concentration Prediction: GA – Tabun, GB – Sarin CE – Chloro-Ethyl-Ethyl-Sulfide, HD – Sulfur Mustard)

classify

concent.

Temp	20	44	68	93	117	141	165	190	214	238	262	286	311	335	359	383	407	432	456	480
Sn1	C	C		C																
Sn2	C	C	C		C															C
Ti1						C		C												
Ti2																		C		C
Sn2						GA	GA													
Ti1							GA	GA		GA										
Ti1	GB			GB	GB			GB			GB		GB	GB	GB					
Ti2	GB			GB		GB	GB	GB	GB	GB										
Sn1			CE									CE	CE	CE						
Sn2			CE	CE							CE	CE	CE							
Ti1																		CE		
Ti1							HD	HD						HD						
Ti2								HD								HD				

On-Chip vs External Characterization



On-Chip: electrical conductance
capacitance
temperature (by power or tcr)

External: µ-pyrometry
µ-FTIR
µ-Raman
NSOM

Advantages

- inexpensive
- fast at each element
- can multiplex

- optical snapshot of whole array
- high info content
- can see gradients (e.g. - T)

Disadvantages

- gradients averaged
- surface-bulk decoupling (for fast ΔT)

- costly instruments
- array-technique compatibility
- analytical complications (e.g. emissivity)

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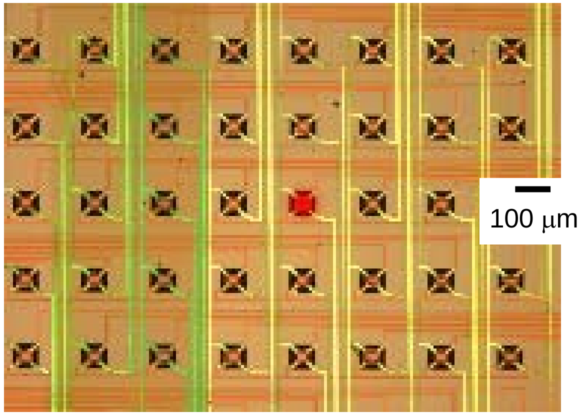
Closing Thoughts

- Versatile microplatform with electronically controlled T for microsample studies



- Examples of processing and on-chip characterization (for gas sensing materials)

- Considerable potential for widespread application in combinatorial materials science

- Materials processing and characterization issues to be dealt with to fully generalize utility

  [Biosystems, Catalysis, Coatings, Electronics, Photovoltaics, Polymers]

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