Development of a Batch Fabrication Process for Chemical Nanosensors: Recent Advancements at NASA Glenn Research Center

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http://www.grc.nasa.gov/WWW/sensors/

OUTLINE

- Background

- Previous Work

- Experimental

- Results and Discussion

- Summary

- Acknowledgements

Integration of Micro Sensor Combinations into Small, Rugged Sensor Suites
Example Applications: AEROSPACE VEHICLE FIRE, FUEL LEAKS, EMISSIONS, ENVIRONMENTAL MONITORING, CREW HEALTH, SECURITY

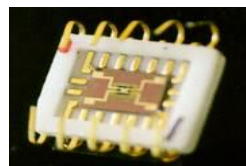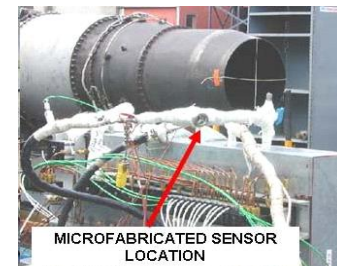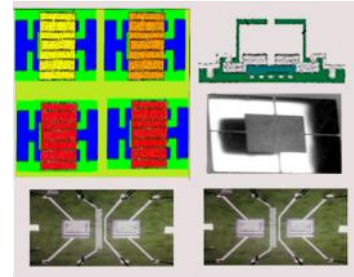**Multi Species Fire Sensors for Aircraft Cargo Bays and Space Applications**

Environmental monitoring (ISS Whitesand Testing)

"Lick and Stick" Space Launch Vehicle Leak Sensors with Power and Telemetry
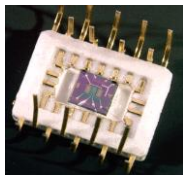
Aircraft Propulsion Exhaust High Temperature Electronic Nose
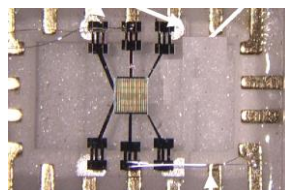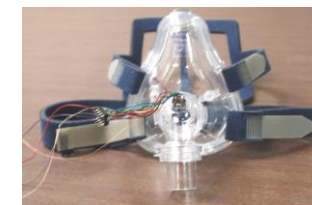
Oxygen Sensor

SiC Hydrocarbon Sensor

H2 Sensor

Nanocrystalline Tin Oxide NOx and CO Sensor

Sensor Equipped Prototype Medical Pulmonary Monitor

Hydrazine EVA Sensors (ppb Level Detection)

MEI Makel Engineering Inc.

BACKGROUND

- Fabrication of operational sensors from nanostructures is less mature than MEMS sensors.

- No matter how good the sensor, if you cannot make contact with the sensor, then the device will be ineffective.

- Micro-nano integration/contacts
  - Major question for nanostructured based sensors: how are the nanostructured materials integrated into a micro/macro structure
    - Cost effectiveness, time-efficient, controlled electrical contact

- Typical standard method of deposition of nanostructures onto a sensor platform
  - Disperse in suspension and deposit on a substrate
    - Simple but difficult to reproduce
    - Inability to mass produce sensors in a controllable way.

BACKGROUND

- Manual methods generally involve repeatability issues e.g.
  - Density of the nanorod or nanowire materials
  - Quality of the contact
  - Limited alignment
  - Device contacts are random and uncontrolled, rather than reproducible and uniform.
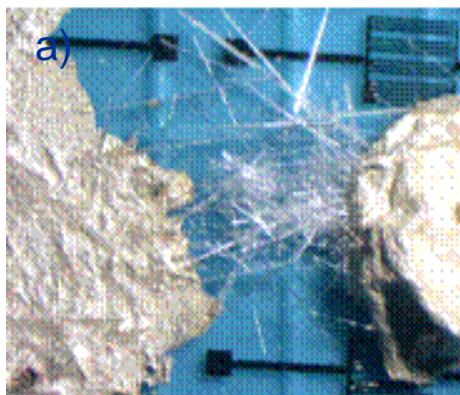
a) nanorods contacted with the substrate via a silver epoxy

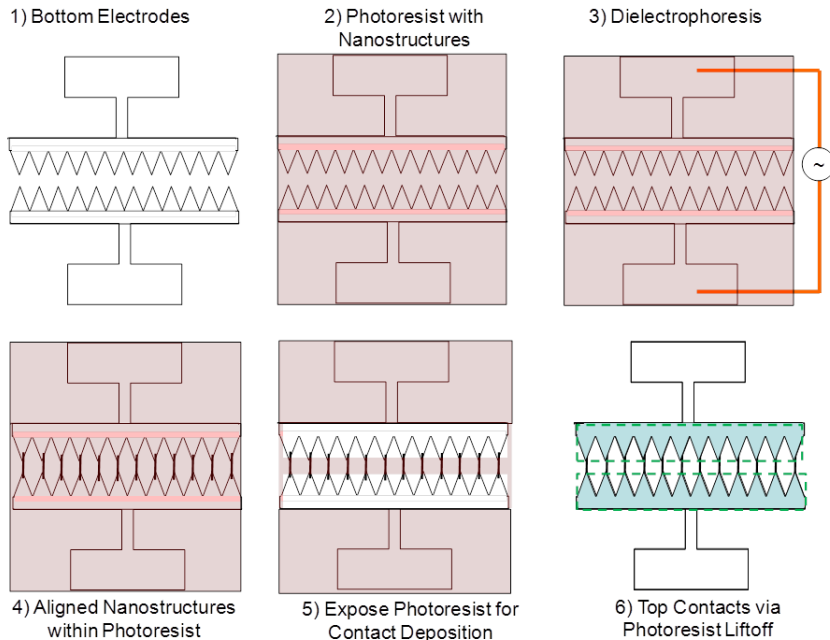b) nanorods precipitated onto substrate between two electrodes

BACKGROUND

- Attempts to control orientation and alignment of nanostructures on microdevices:
  - AFM or laser tweezers
    - Labor-intensive
    - Not viable for mass production
  - e-beam lithography
    - High-end processing
    - Limited to nanodimensional linewidths (standard microfabrication techniques require larger linewidth resolutions)
  - Langmuir-Blodgett method
    - Slow compression of dispersed nanostructures in organic solution on substrate until desired structure is achieved.
    - Range of materials is limited
  - Superlattice nanowire pattern transfer (SNAP)
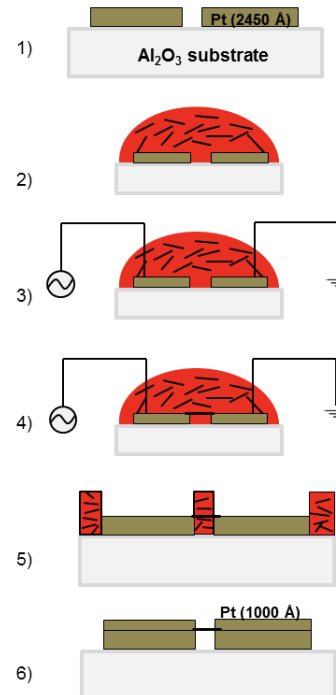   - Range of materials is limited.

PREVIEW WORK

- ## Integration of standard microfabrication techniques with the alignment of nanostructures

a)

1) Bottom Electrodes
2) Photoresist with Nanostructures
3) Dielectrophoresis
4) Aligned Nanostructures within Photoresist
5) Expose Photoresist for Contact Deposition
6) Top Contacts via Photoresist Liftoff

b)

Pt (2450 Å)
Al$_2$O$_3$ substrate
Pt (1000 Å)

Fabrication steps of the alignment and deposition process. **a)** Top view and **b)** side view.

1) Deposit opposing sawtooth patterns on a substrate using standard photolithographic techniques.
2) Coat the electrodes with a photoresist mixture containing nanostructures.
3-4) Use the sawtooth electrodes and dielectrophoresis to align the nanostructures.
5) Expose the electrodes while the nanostructures are held in place with photoresist.
6) Deposit the top metallic layer over the bottom sawtooth electrode pattern leaving nanostructures buried in the electrodes and complete photoresist removal. The dotted line is an alternate pattern for the top metallic layer that broadly covers the bottom electrodes in a rectangle, rather than the sawtooth electrode pattern.

G.W. Hunter, et.al. Nanostructured Material Sensor Processing Using Microfabrication Techniques, Sensor Review 32/2 (2012) 106-117.   *Patent pending

PREVIOUS WORK

- Advantages of this approach

  – Through control of photoresist density and nanostructure concentration/dispersion, different densities of nanostructures can be obtained

  – Length of nanostructures are affected by AC frequency used for alignment

  – Improved electrical contacts

    • Nanostructures are buried in a metallic contact "sandwich"

  – Incorporation of nanomaterials into standard photolithographic processing procedures
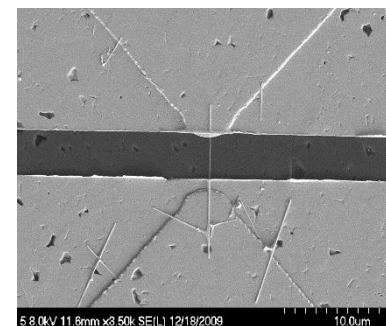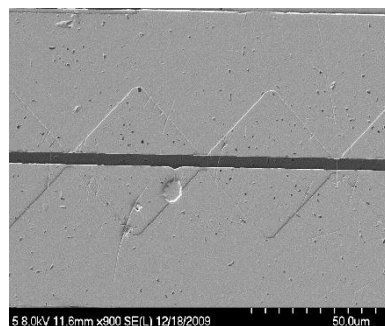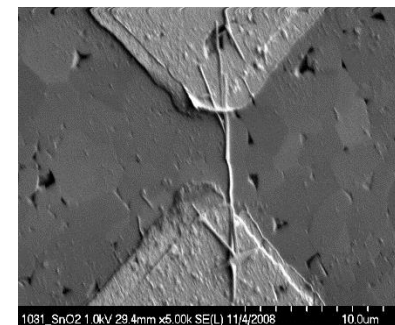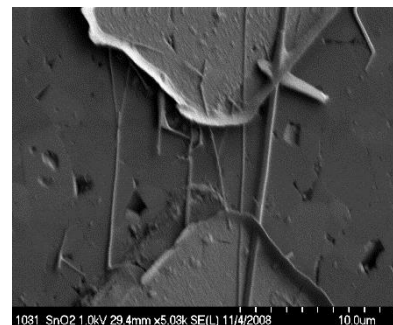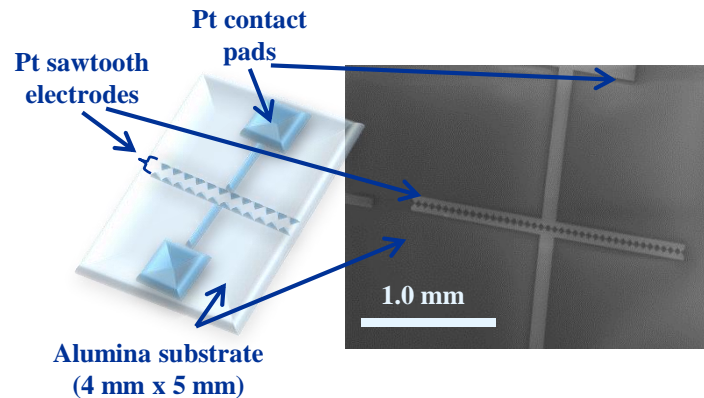
Pt sawtooth electrodes

Pt contact pads

Alumina substrate (4 mm x 5 mm)

1.0 mm

G.W. Hunter, et.al. Nanostructured Material Sensor Processing Using Microfabrication Techniques, Sensor Review 32/2 (2012) 106-117.   *Patent pending

PREVIOUS WORK

- ## Motivation:
  - Build a SnO_2-based sensor for H_2 and hydrocarbons that can operate at room temperature as well as high temperatures.
  - SnO_2 is an n-type wide band gap (~3.6 eV) semiconductor.
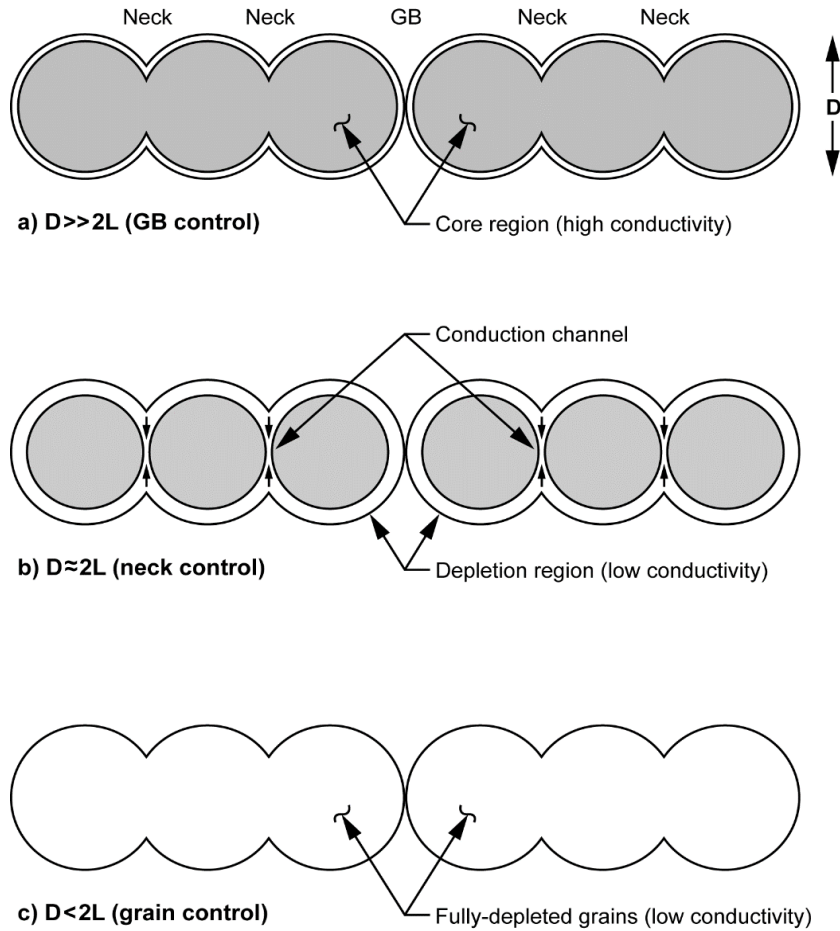 - Sensors usually operate above 200°C due to their reaction mechanism.

Schematic representation of the reactions occurring at the surface of an n-type semiconductor metal oxide
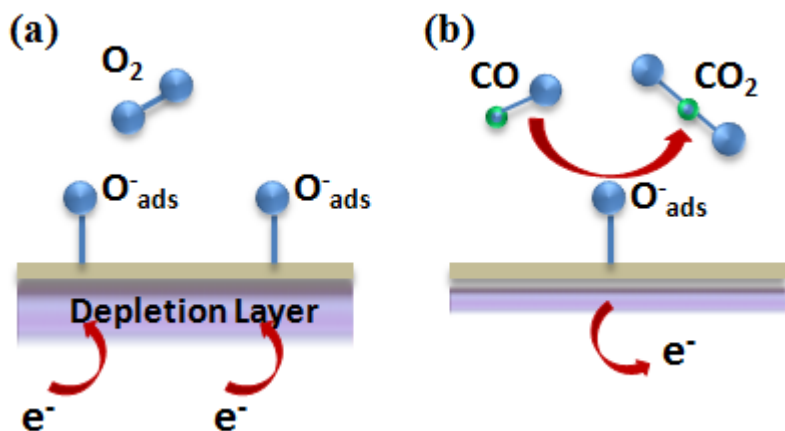
(a) Adsorption of oxygen at the surface creates surface-acceptor sites that immobilize conduction band electrons from the near surface region, creating a depletion layer.

(b) Reducing gases, such as CO, remove surface bound oxygen atoms, releasing the immobilized electrons, reducing the thickness of the depletion layer.

PREVIEW WORK

Three mechanisms of conductance in metal-oxide gas sensitive materials:

a) D>>2L (GB control)
Core region (high conductivity)

b) D≈2L (neck control)
Conduction channel
Depletion region (low conductivity)

c) D<2L (grain control)
Fully-depleted grains (low conductivity)

A. Rothschild and Y. Komen. The effect of grain size on the sensitivity of nanocrystalline metal-oxide gas sensors, J. App. Phys. **95**, 6374 (2004).

- The shaded part shows the core region and the unshaded part shows the depletion layer and GB = grain boundary.
- a) D >> 2L, the conductance, which is higher in the non-depleted core region, is controlled by grain boundaries.
- b) D ≈ 2L, where necks between coalesced primary grains control the conductance.
- c) D < 2L, when the grains are small enough to be fully depleted the conductance is grain controlled [4]

When the SnO_2 crystallite size is comparable with or less than 2L (~ 6 nm), where L is the depth of the space-charge layer, the sensitivity can be greatly increased.

PREVIOUS WORK

- Dielectrophoretic alignment approach extended for use with other nanomaterials.
    - Porous SnO_2 nanorods via templated approach
        - Room temperature methane detection
        - High temperature methane detection (up to 500°C)
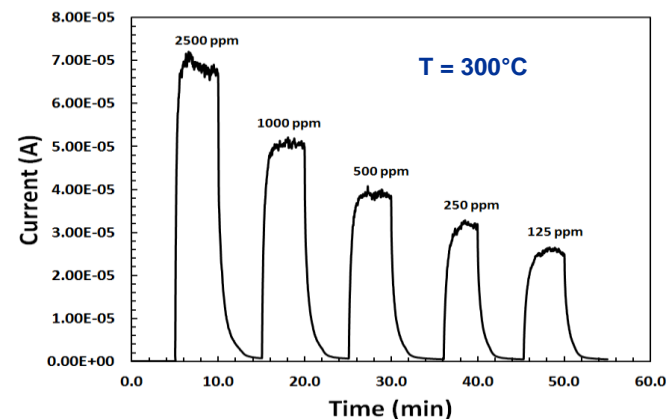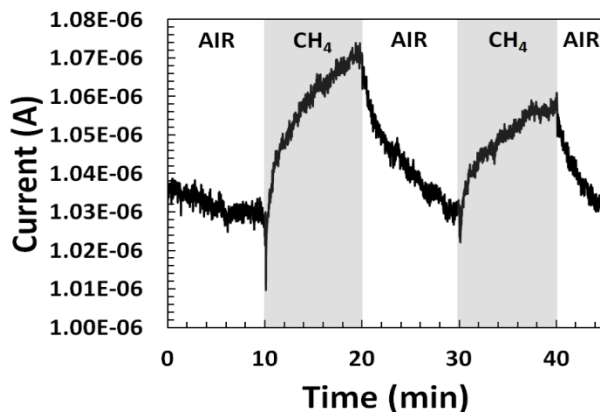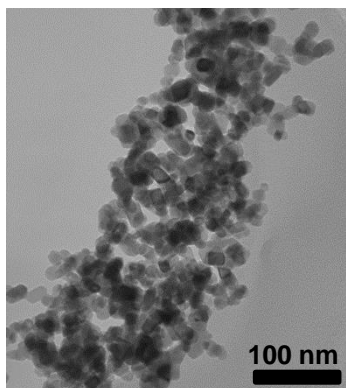
Concentration	Temperature					
(ppm)	25 (°C)	100 (°C)	200 (°C)	300 (°C)	400 (°C)	500 (°C)
2500	0.58	4.8	40	86.25	41	30
1000	-	3.6	30.3	62.5	28.3	13.5
500	-	2.8	21	47.5	25.7	14
250	-	2.2	16.3	40	22.3	13.5
125	-	1.6	11.7	32.13	20.3	12.5

A. Biaggi-Labiosa, et.al. A Novel Methane Sensor Based on Porous SnO2 Nanorods: Room Temperature to High Temperature Detection, Nanotechnology 23 (2012) 455501.   *Patent pending

EXPERIMENTAL

- **<u>Goal</u>**: Mass production of sensors with uniformly controlled properties.
  - Broader applications

- Commercial MWCNTs (NanoLab) were used for the proof-of-concept.
  - Diameter 15±5 nm
  - Length 5-20 µm
  - S1805 photoresist solution concentration 2 mg/mL

- Array of paired patterned Pt electrodes on a 2" alumina wafer.
  - Electrical connection in such a way that a field applied to one set of electrodes is simultaneously applied to the full array on the wafer.
  - Distance between opposing sawtooth electrodes ~1-2 µm
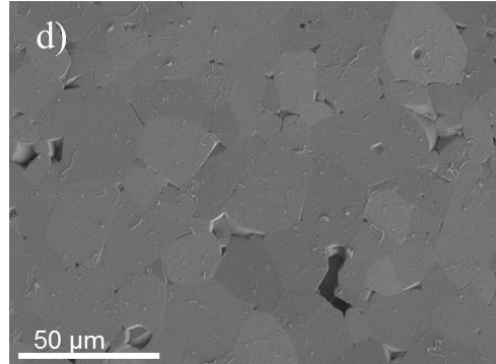 - 20 MHz, 10 V_{p-p}, 0 V_{offset} for 20 min
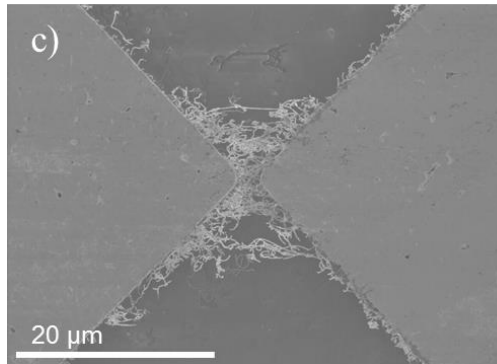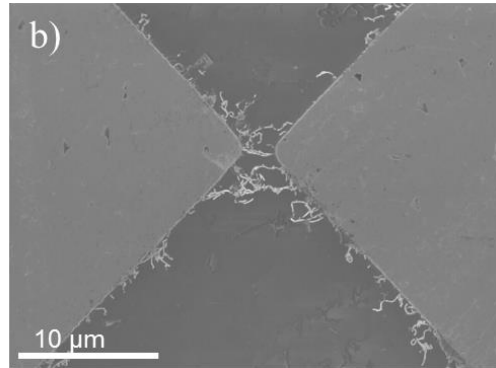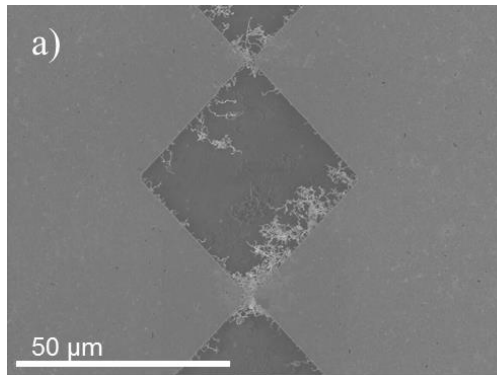
RESULTS AND DISCUSSION

- Design
  - There are 16 patterns, each with 146 opposing sawtooth electrodes for a total of 2336 electrodes.
  - Can be separated into individual sensors.

Probe contact

Probe contact

40
30
20
14
12
10
8
6
4
2
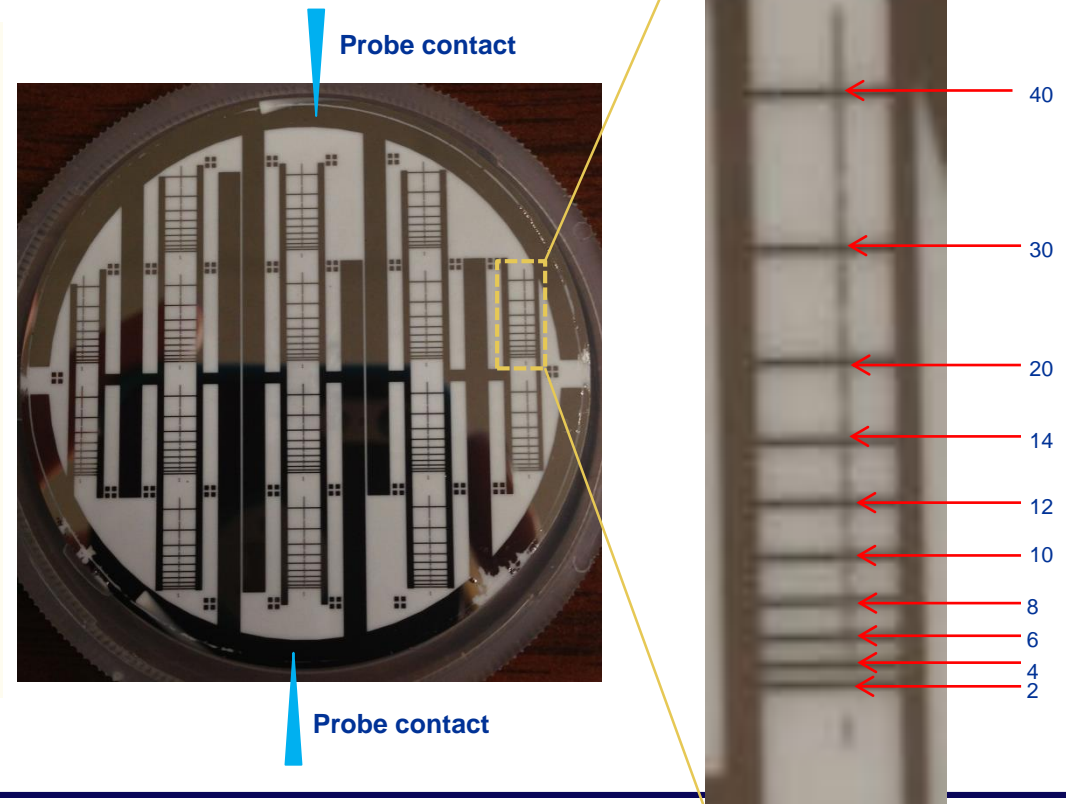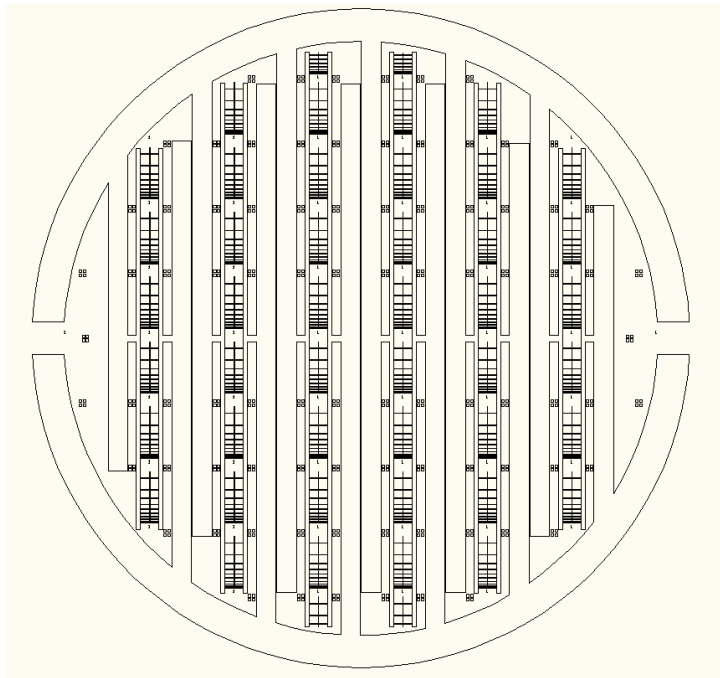
RESULTS AND DISCUSSION

- ## Proof-of-concept
  - ### SEM images of aligned MWCNTs on the whole wafer

a) Lower magnification to show alignment on more than one sawtooth electrode.

b) Alignment of a few nanotubes between opposing electrodes.

c) Alignment of more nanotubes between opposing electrodes.

d) Image of alumina substrate showing that there are no nanotubes (or a little amount) demonstrating that the nanotubes are found between opposing electrodes.

Managed to obtain alignment on 2313 of the 2336 electrodes for a **99% yield**.

SUMMARY

- Standardized approach to chemical sensors processing using nanostructures.

  – Integration and alignment of nanostructures with microfabrication methods.

- Mass production of sensors with uniformly controlled properties.

- Approach addresses significant barriers in integrating nanotechnology with microsensors, such as

  – Deposition control

  – Contact robustness

  – Simplified processing

SUMMARY

- Resulting sensors can be used in applications where presently microsensors are used.

- Further refinement of the DEP and photoresist suspension are planned to increase and to better control the yield for each paired contact pattern.

- Current work in applying mass production approach with metal oxide nanostructures.

ACKNOWLEDGEMNTS

- Dr. Gary Hunter, Laura Evans, Gordon Berger and Dr. Jennifer Xu

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  — José M. González
  — Michelle Mrdenovich
  — Christopher Hampton

- Dr. Lawrence G. Matus and Dr. Mary V. Zeller for helpful discussions.

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QUESTIONS