Ceramic Nano-heterostructures by Materials Design: Platforms for Sensing and Biomedical Applications

Sheikh Akbar (akbar.1@osu.edu)
Department of Materials Science and Engineering
Ohio State University, Columbus, OH, USA

Students: Sehoon Yoo, Carmen Carney, Mike Rausher, Huyong Lee, Ben Dinan, Haris Ansari, Derek Miller, Zhiyun Niu, Janine Walker, Mohamad Al-Hashem, Priyanka Karnati

Sponsors: NSF, DOE, NASA, AFOSR, Industries

CISM
Center for Industrial Sensors and Measurements
A National Science Foundation Center

BPS – Feb 7, 2021

THE OHIO STATE UNIVERSITY

Combustion Gas Sensors at CISM (1996-2004)

Specifications	CO	O_2	NO_x (total)	HCs	CO_2
Applications	Domestic Aerospace Automotive Air quality Glass	Ceramic Kiln Utility Heat-treating Automotive Glass	Automotive Utility Aerospace Air quality Glass	Automotive Utility Aerospace Air quality	Automotive Domestic Food Corrosion Air quality
Temp. Range (°C)	RT - 1000	600 - 1400	200 - 1000	400 - 1000	25 - 800
Concentration Range	35 ppm - 5%	2 ppm – 21%	100-1000 ppm	1 ppm - 2%	400 ppm-10%
Sensitivity	10 - 1,000*	38.35 mV/dec***	38.35 – 153.4 mV/dec	2 – 100*	76.7 mV/dec
Response Time**(ms)	1000 - 10,000	< 1000	2000 - 20,000	10 - 1000	10 - 1000
Interference	≤1% to [_] ppm of H_2, H_2O, NO_X, C_2H_5OH, C_XH_Y	≤1% to [_] ppm of CO, C_XH_Y	≤5% to [_] ppm of CO, H_2, O_2, C_XH_Y	≤1% to [_] ppm of CO, H_2O, C_XH_Y	O_2, H_2O, NO_X
Poisoning	in SO_X, soots	soots	in SO_X, soots	SO_X, soots	SO_X, soots
Reproducibility (%)	< ± 2	< ± 2	≤ ± 2	< ± 2	< ± 2
Stability (%/year)	< 2	< 2	≤ ± 2	< 2	< 2
Lifetime-(min hrs)	45,000	100,000	50,000	100,000	50,000
Power Requirements	DC/battery	DC/battery	DC/battery	DC/battery	DC/battery

* Resistance normalized by resistance in the absence of the sensing gas.

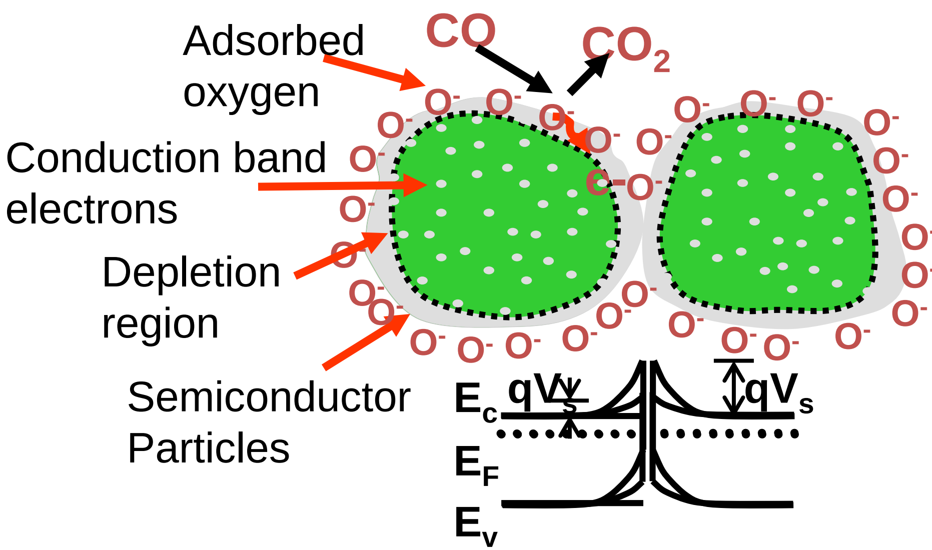
** Response time defined as the time to achieve 90% of the final change in the sensor signal.

*** Nernst slope (RT/nF; 1<n<4; 38.35 mV/decade for n=4 and 153.4 mV/decade for n=1) at 500 C

CISM
Center for Industrial Sensors and Measurements
A National Science Foundation Center

The Ohio State University

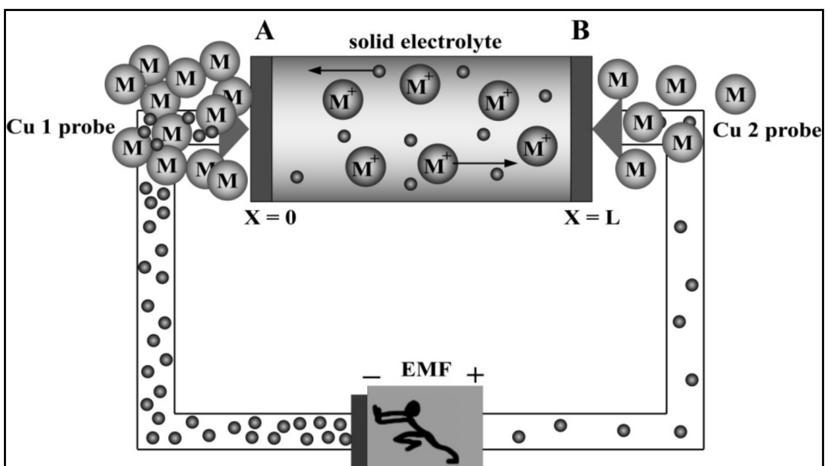
Resistive and electrochemical type sensors



Resistive sensors

$$\sigma = \sigma_o \exp\left(-\frac{qV_s}{kT}\right)$$

C.O. Park and S.A. Akbar,
J. Matls. Sci., 38, 4611(2003).



Electrochemical sensors

Nernst equation

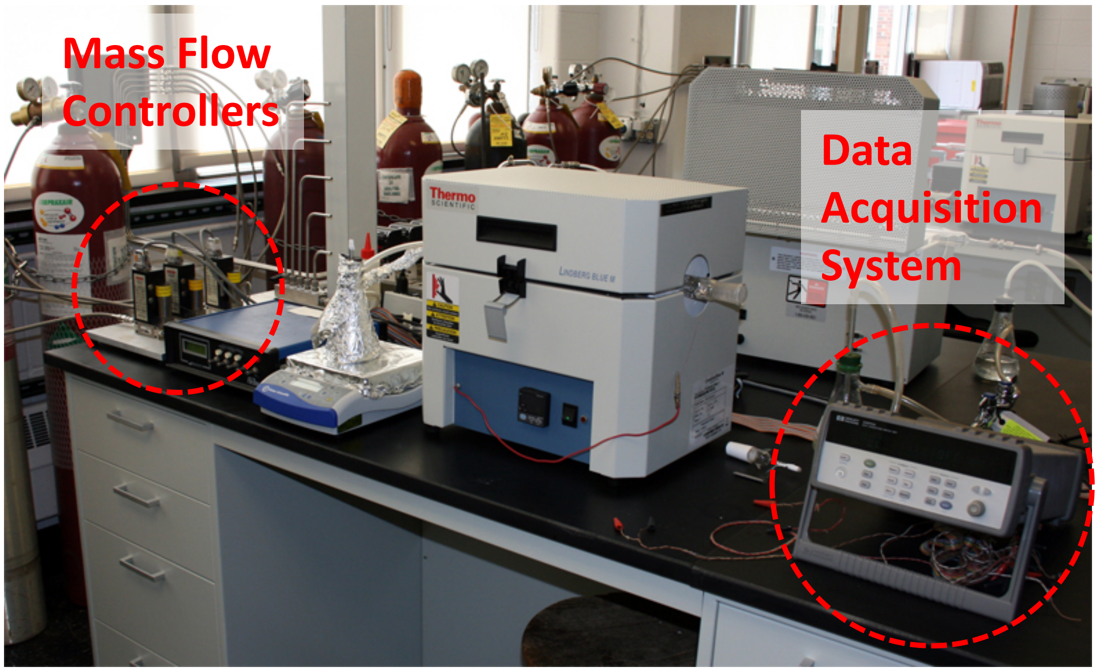
$$E = -\frac{1}{F}\left[\left(\bar{\mu}^{B}_{[M]} - \bar{\mu}^{A}_{[M]}\right)\right] = -\frac{RT}{z_M F}\ln\frac{a^{B}_{M}}{a^{A}_{M}}$$

C.O. Park, S.A. Akbar and W. Weppner,
J. Matls. Sci., 38, 4639 (2003).

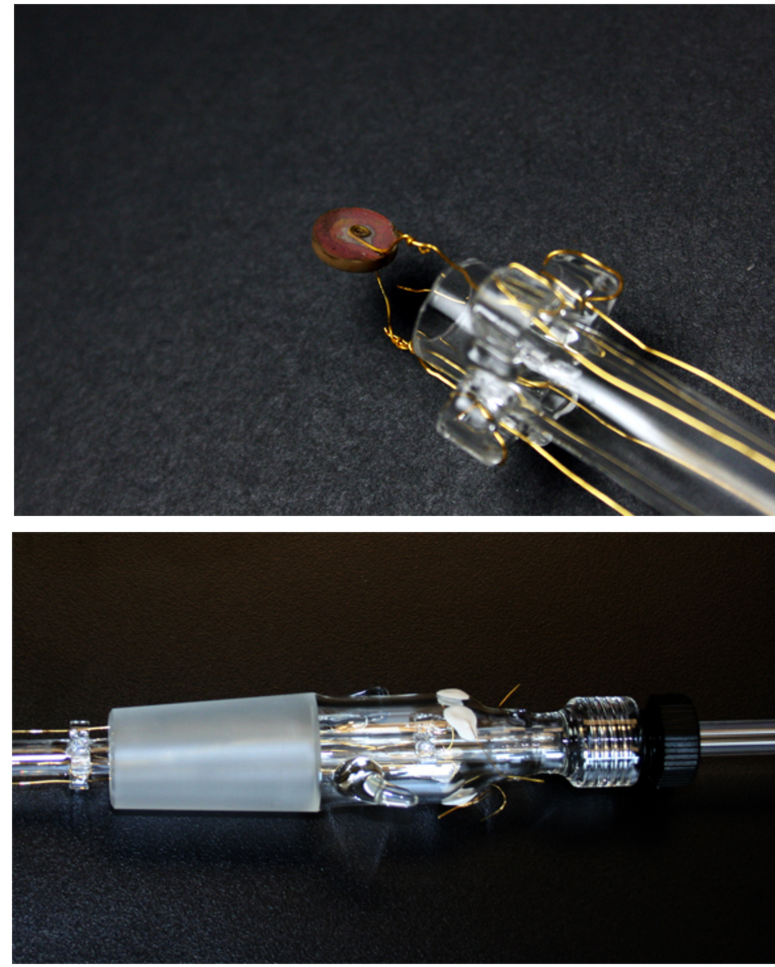
The underlying theme in our sensor development has been the use of materials science and chemistry to promote high-temperature performance with selectivity.

Sensor fabrication and testing

We fabricate **bulk, thick-film** ***(screen- and inkjet-printing)*** **and thin-film** sensors

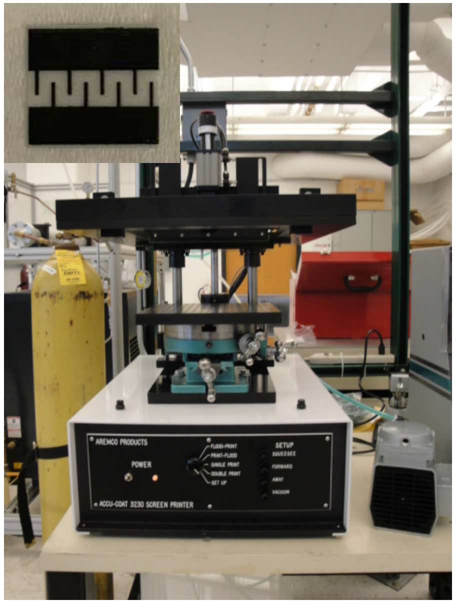


A sensor test set-up in CISM

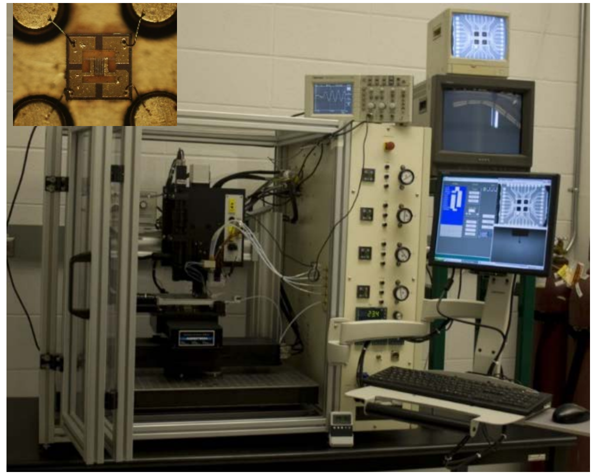


A Sensor holder

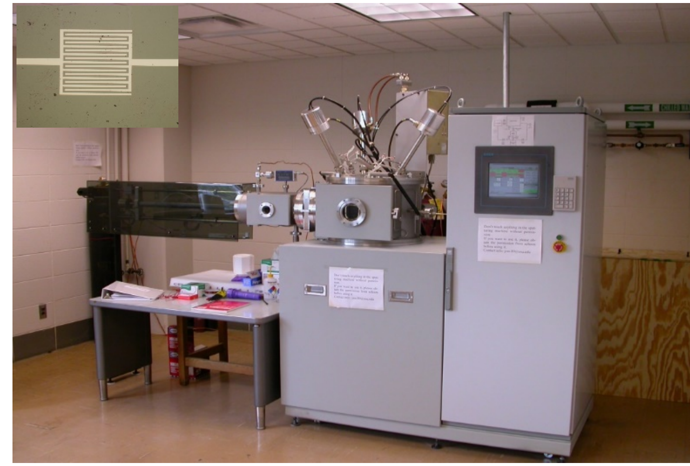
Sensor Fabrication and Lab-designed Testing Facility



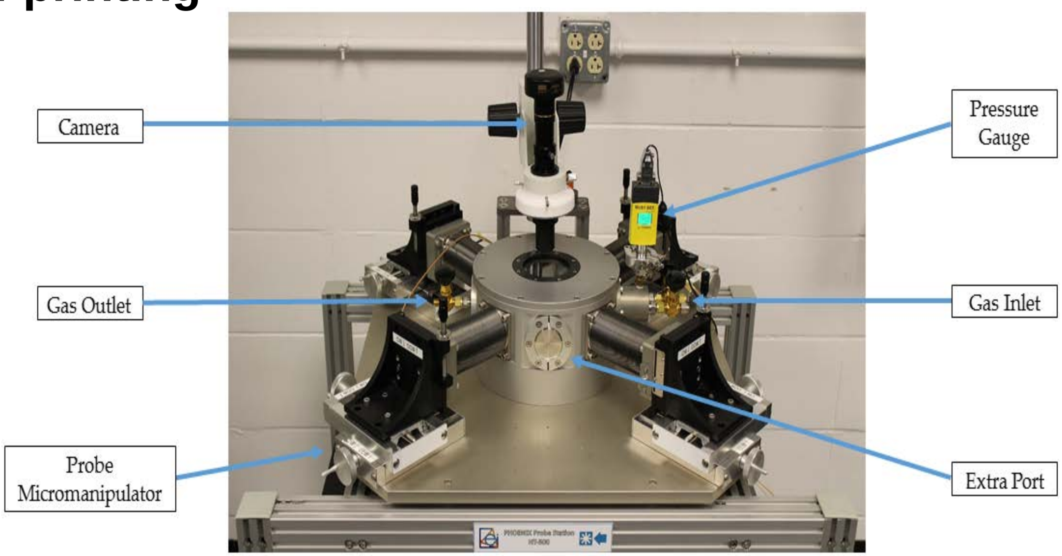
Screen-printing



Ink-jet printing



Thin-film by sputtering



Probe station for high throughput sensor test

- Our lab-designed and assembled by Kreus Design Inc.
- Enables fast throughput testing/quick turnaround
- 4 probes allow for 2-point (2 sensors) and 4-point (1 sensor) measurements
- Gas input/output ports and extra ports allow for additional customization

Nano-structures by surface modification

Nanotechnology by materials design!

Inexpensive; non-lithographic route

- No need for e-beam/x-ray lithography
- No need for highly trained technician
- Simple setup (furnaces and gas cylinders)

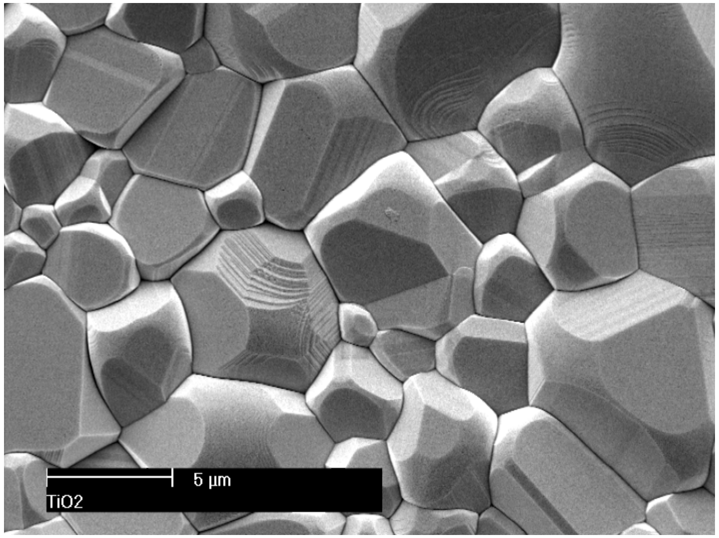
Highly scalable

- Large area coverage in a single step

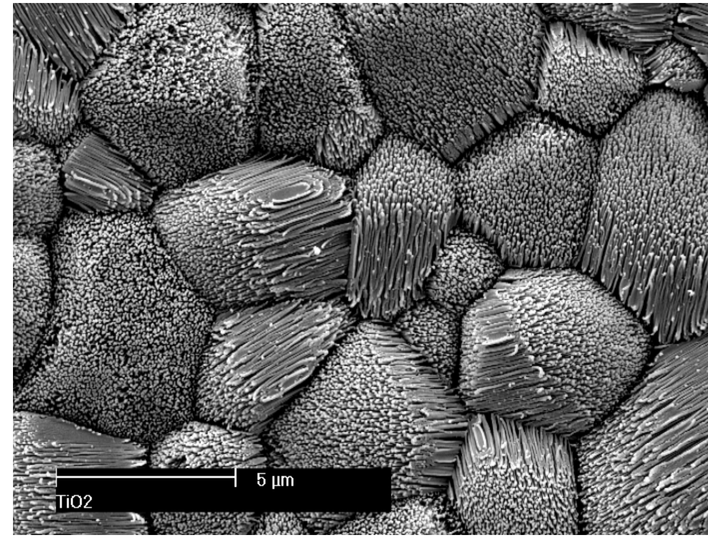
Platform for

- Sensing, catalysis and bio-applications

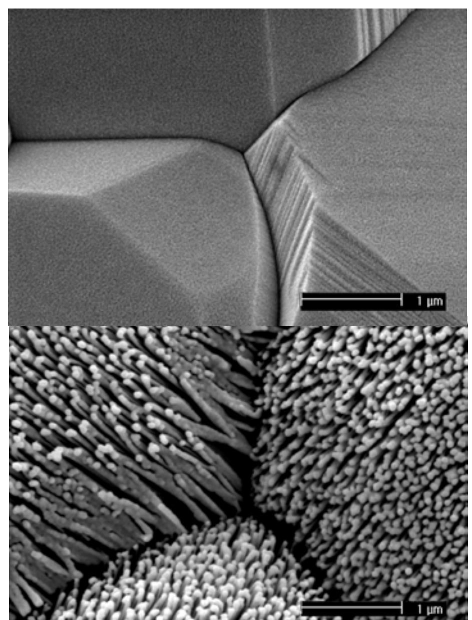
Invention of titania nano-fibers



Sintered TiO_2



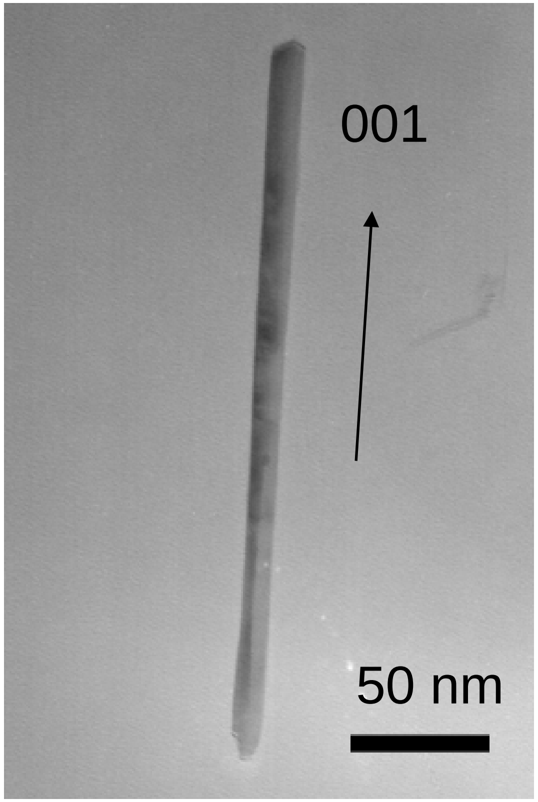
H_2 heat-treated TiO_2

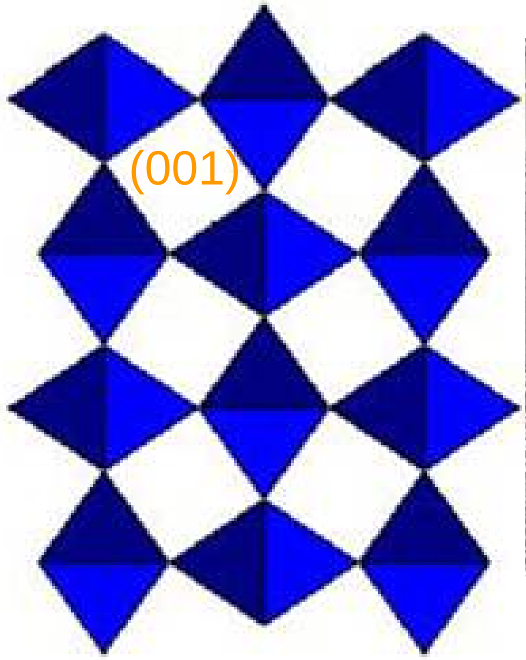


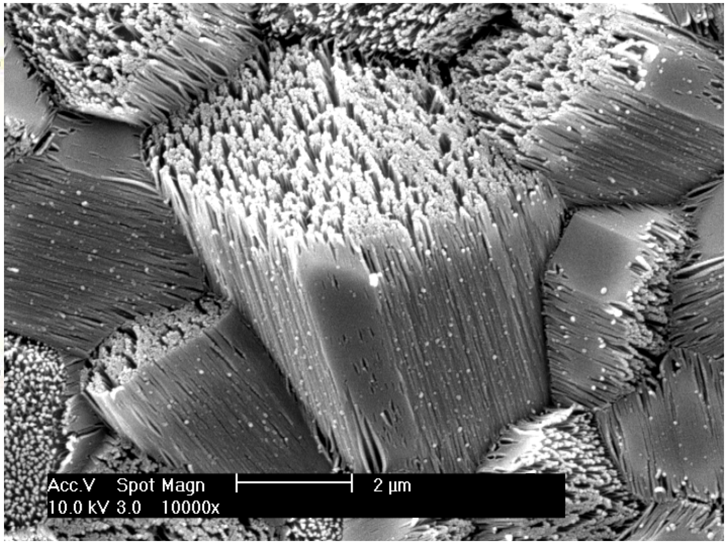
Adv. Matls., 16[3], 260 (2004)
US patent # 7,303,723

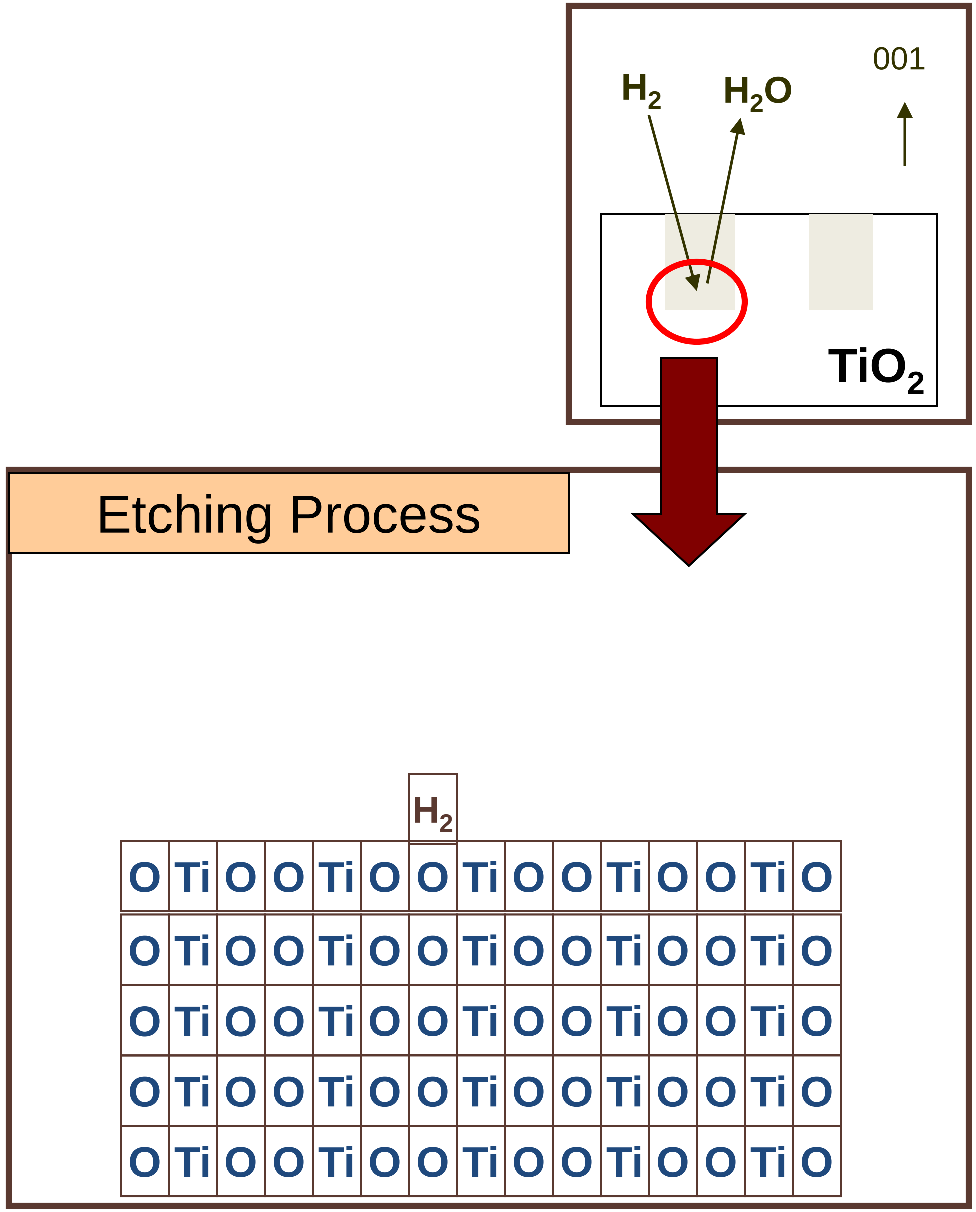
Phase and fiber direction by TEM

- XRD and XPS confirms rutile TiO_{2-x}
- SAED confirms nano-fiber to be rutile TiO_{2-x}
- Fiber direction is (001) and it is single crystal



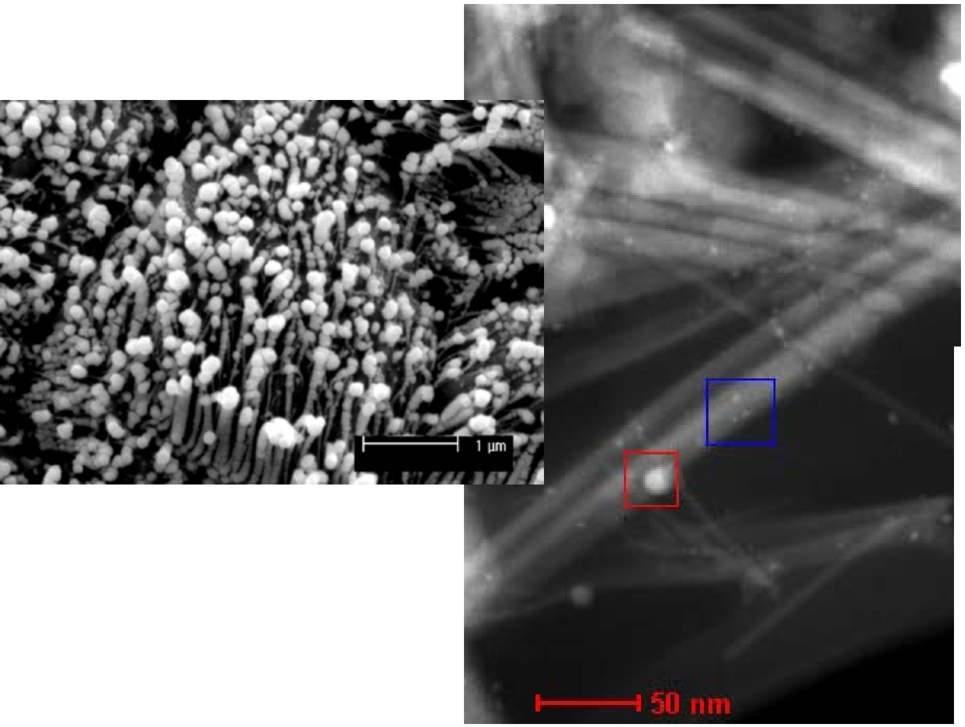


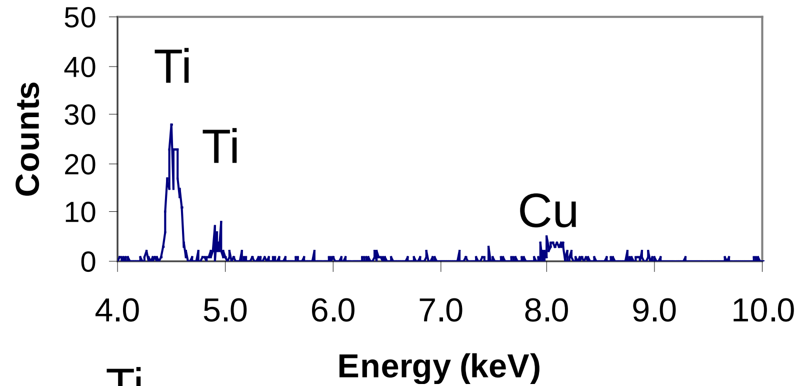


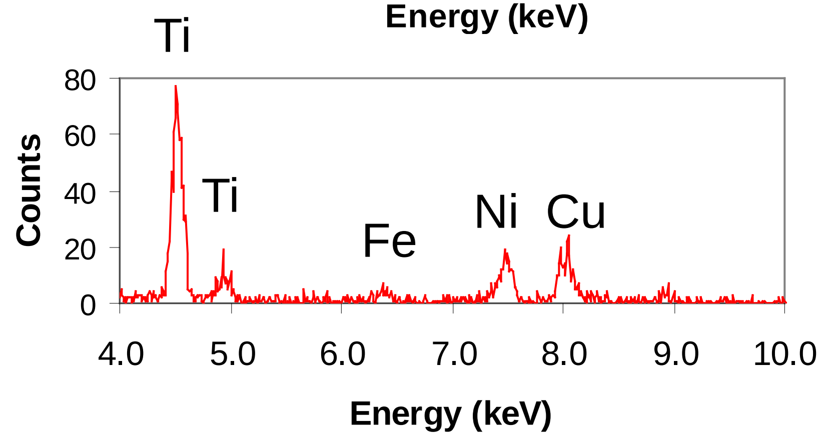


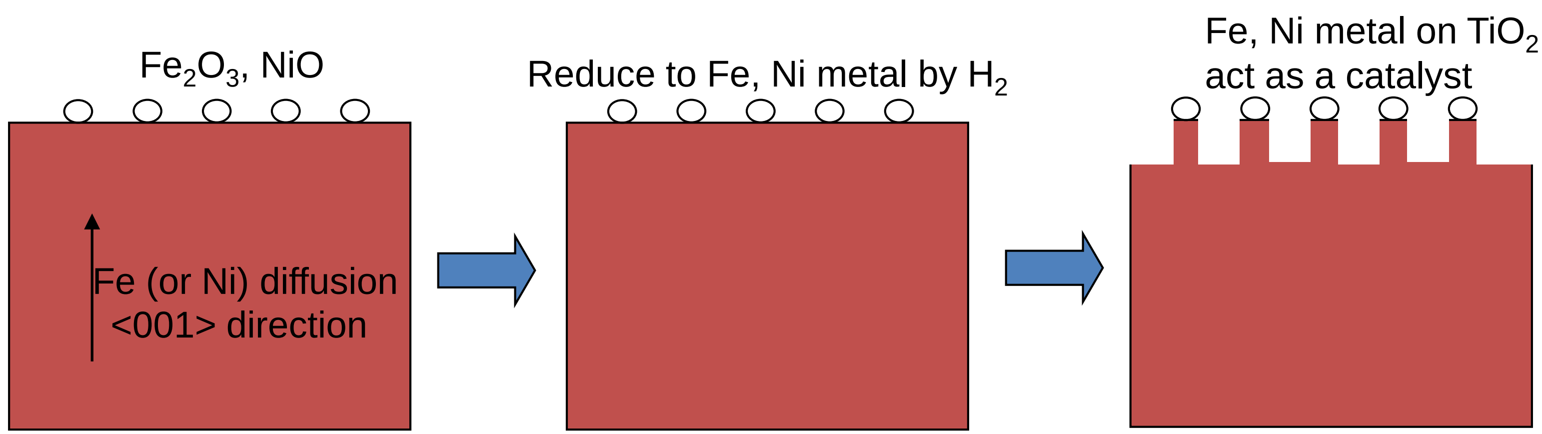
H2
H2O
001
TiO2
Etching Process
H2
O Ti O O Ti O O Ti O O Ti O O Ti O
O Ti O O Ti O O Ti O O Ti O O Ti O
O Ti O O Ti O O Ti O O Ti O O Ti O
O Ti O O Ti O O Ti O O Ti O O Ti O
O Ti O O Ti O O Ti O O Ti O O Ti O

TEM-EDS confirms the fiber tip to contain Fe and Ni

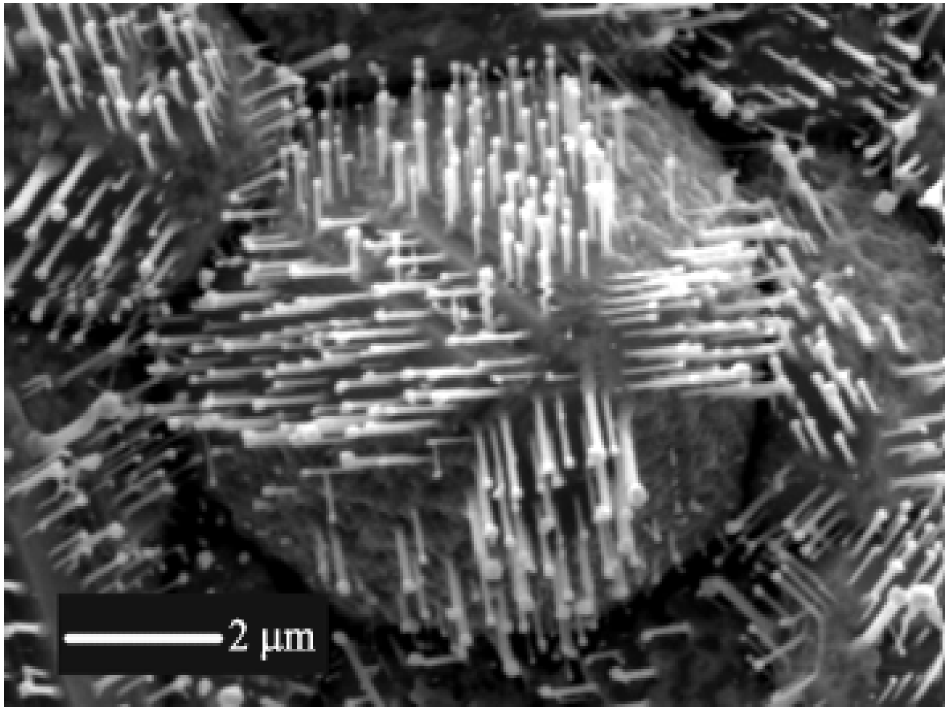


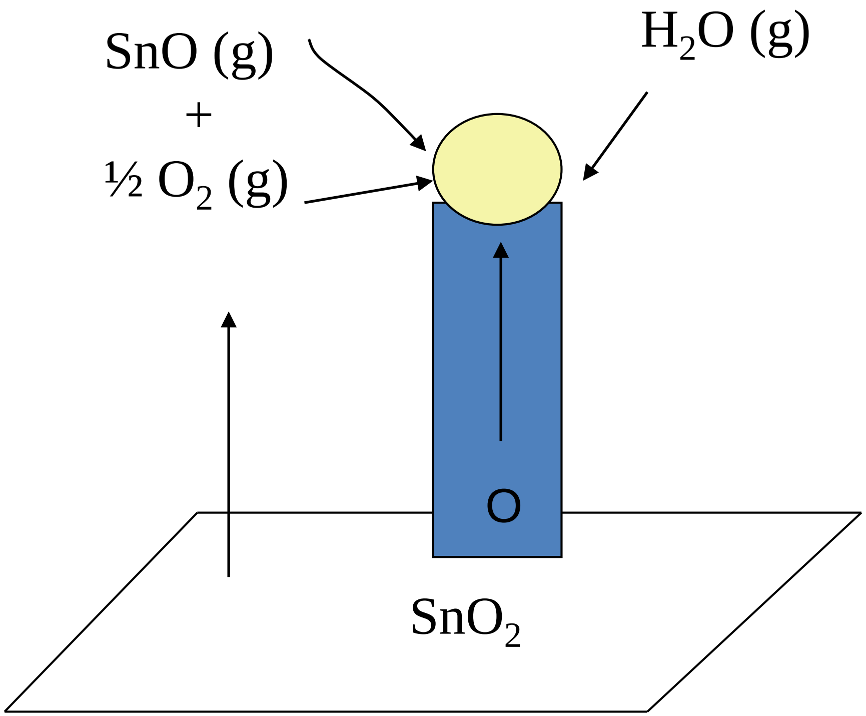






Au-catalyzed Growth

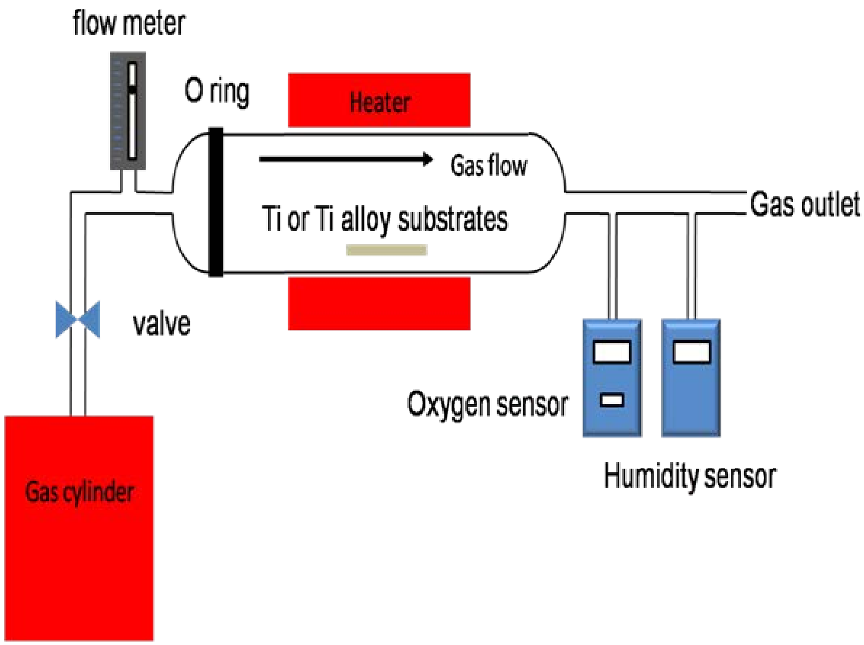




SnO_2 doped with 5 wt% CoO (as a sintering aid) and reacted with 5% H_2-N_2 gas at 720 °C for 2 hours. Fibers grow perpendicular to crystal facets in Au-coated regions.

J. Matls. Res., 23, 2639(2008).

Oxide fiber growth by thermal oxidation

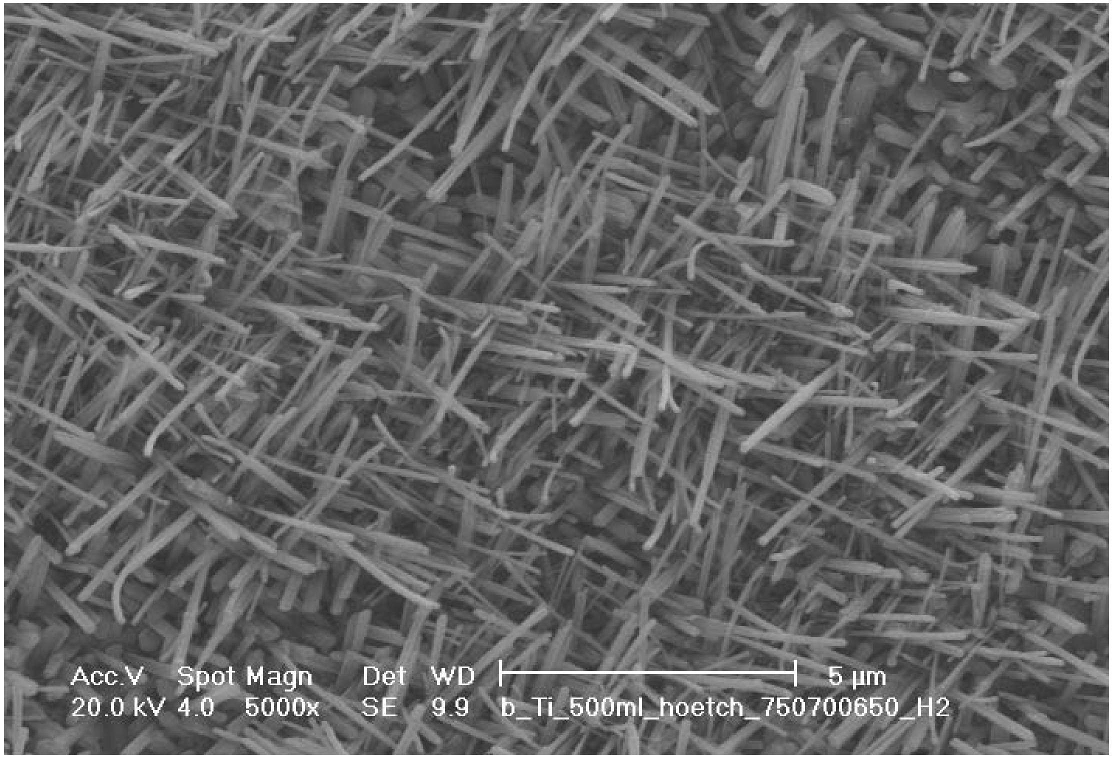


- A metal sample (*Ti and Ti alloys*) is placed in a 1 inch diameter quartz tube.
- Samples are heat treated at a target temperature (600-900 C)
  - ✓ Ar gas (99.998%, 10s of ppm oxygen)
  - ✓ mixture of Ar gas with water vapor
  - ✓ mixture of Ar gas with pure oxygen
- The gas flow is controlled by a flow meter
- Oxygen sensor and humidity sensor to monitor oxygen and humidity content
- Growth on *bulk, foil, thin-film and particles*

Functional Nanomaterials Letters, 2[3], 87-94 (2009)

Journal of Nanomaterials, vol. 2010, Article ID 503186, 7 pages (2010)

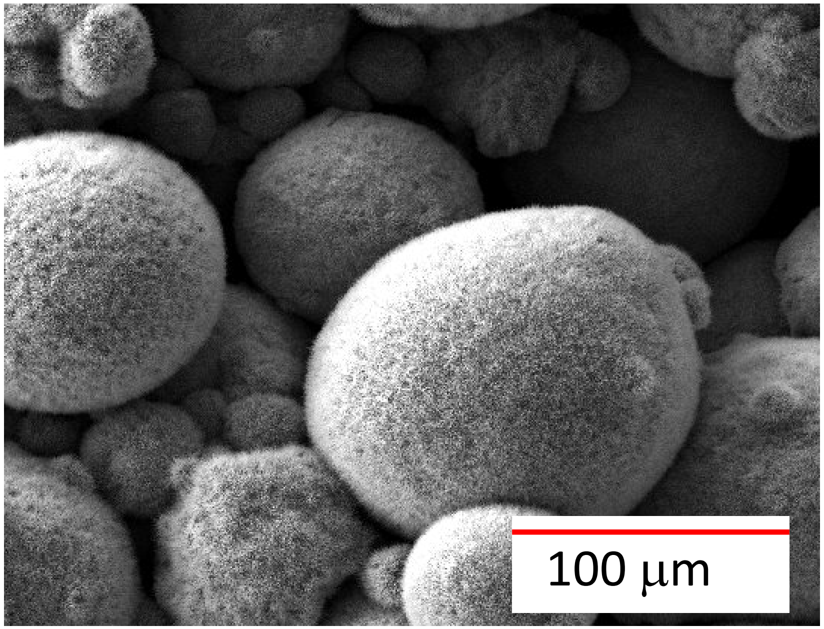
Oriented nanowires via thermal oxidation

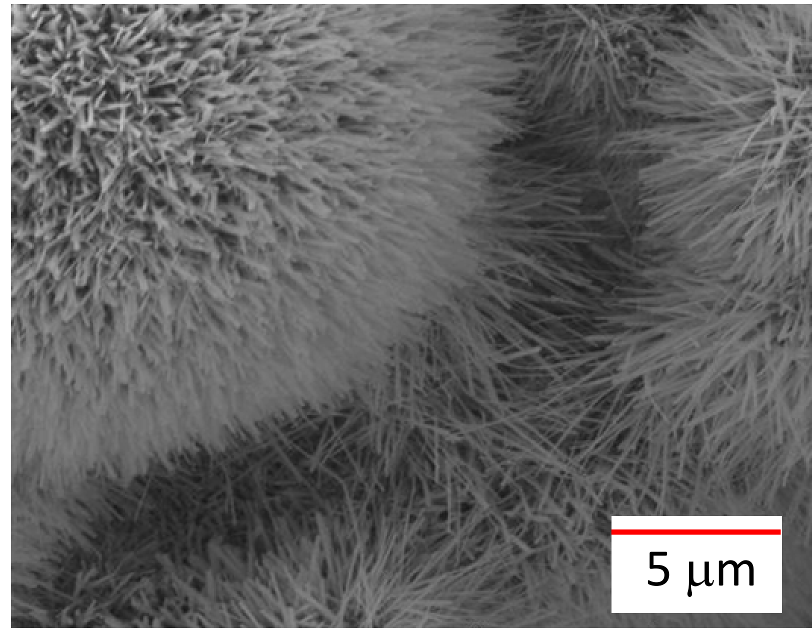


TiO_2 nano-fibers grown on β-Ti (5-5-5) alloy in Ar atmosphere (containing 10s of ppm of O_2) at 700°C for 8 hr. The growth of nanowires on (110) grain showing that the directions of nanowires are perpendicular to each other.

Extension to Ti alloy powder

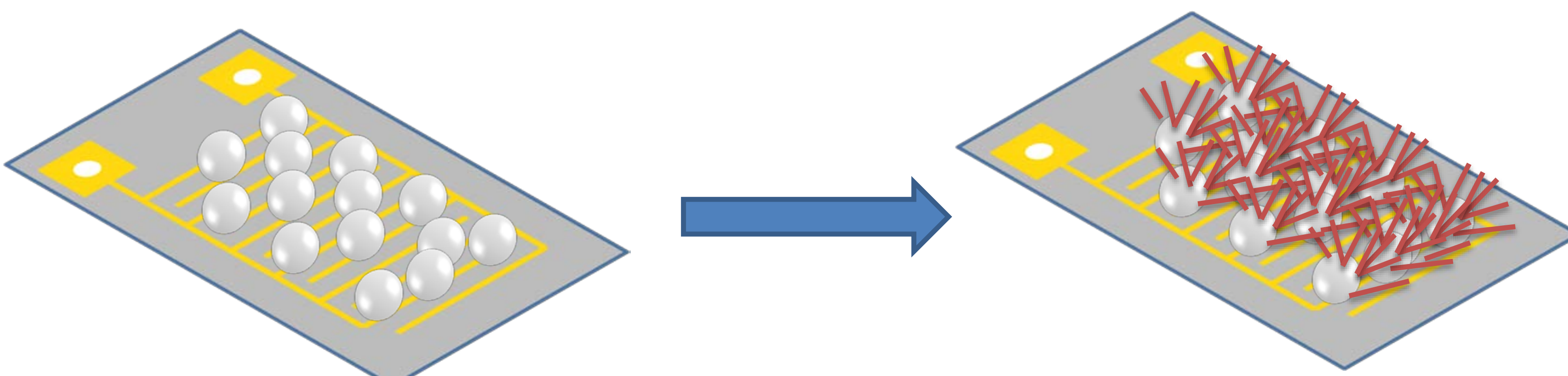
Annealing at 700C for 8 hr in 500 L/min flowing Ar gas



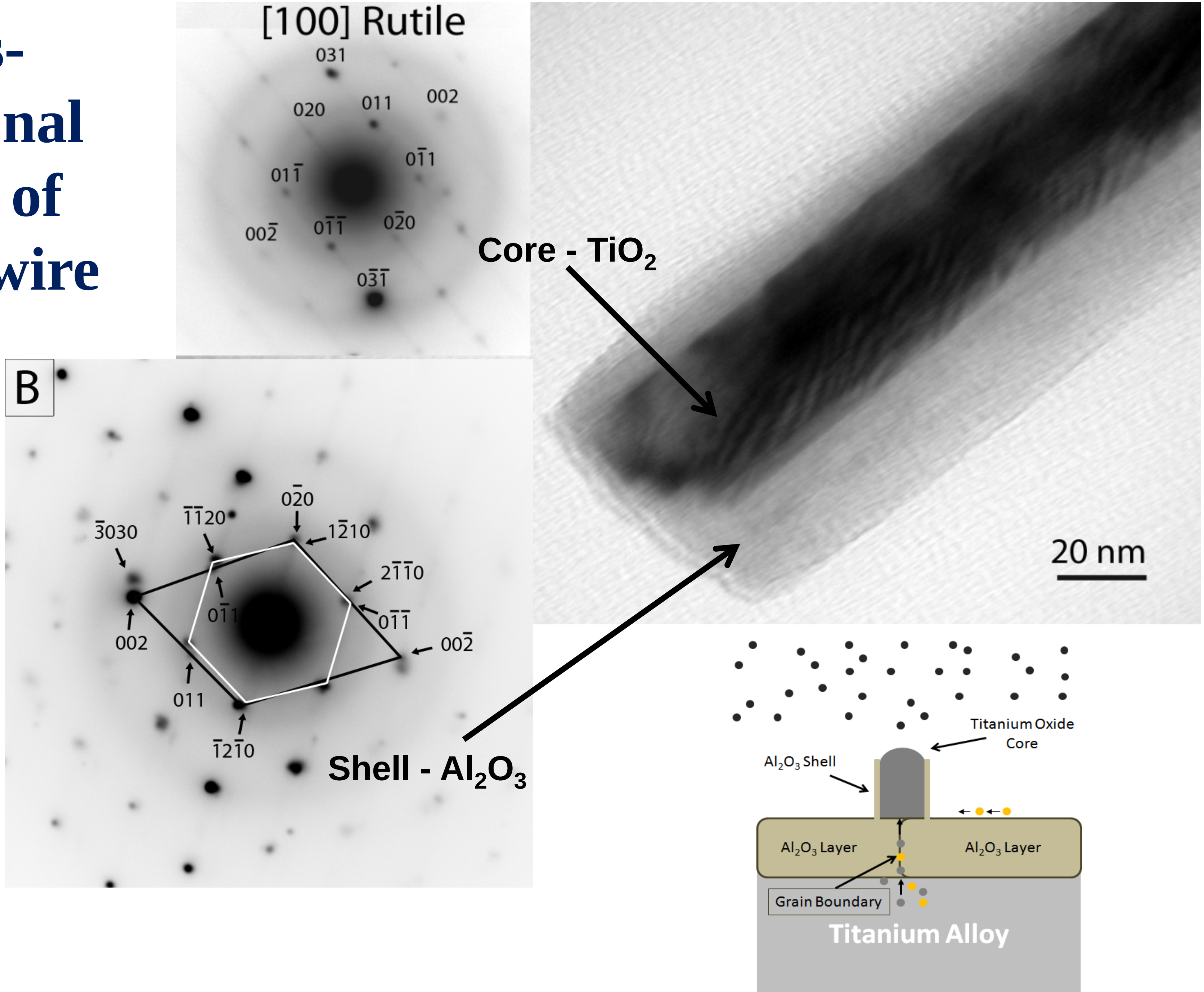


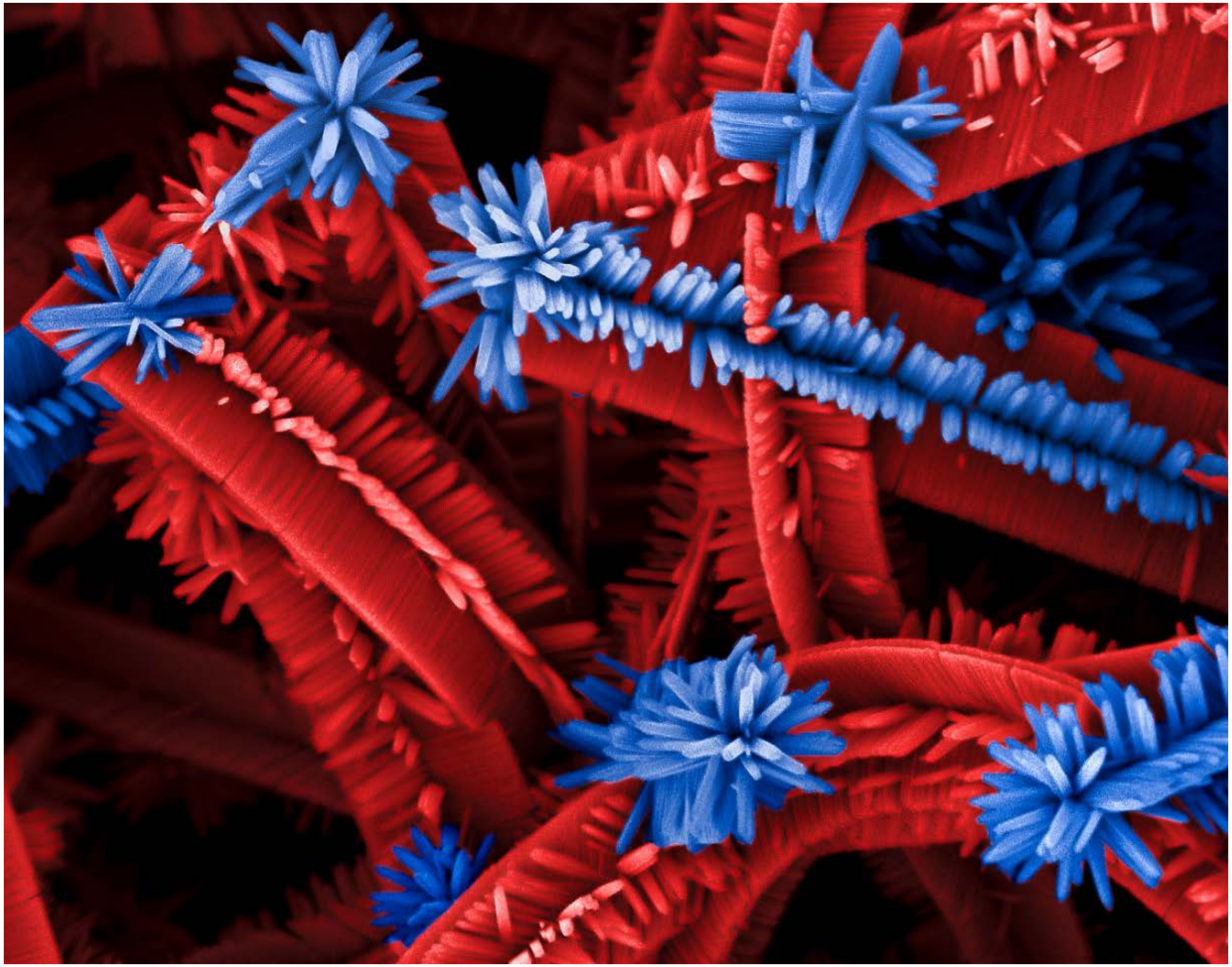
Particle surface

Interparticle contact via NW



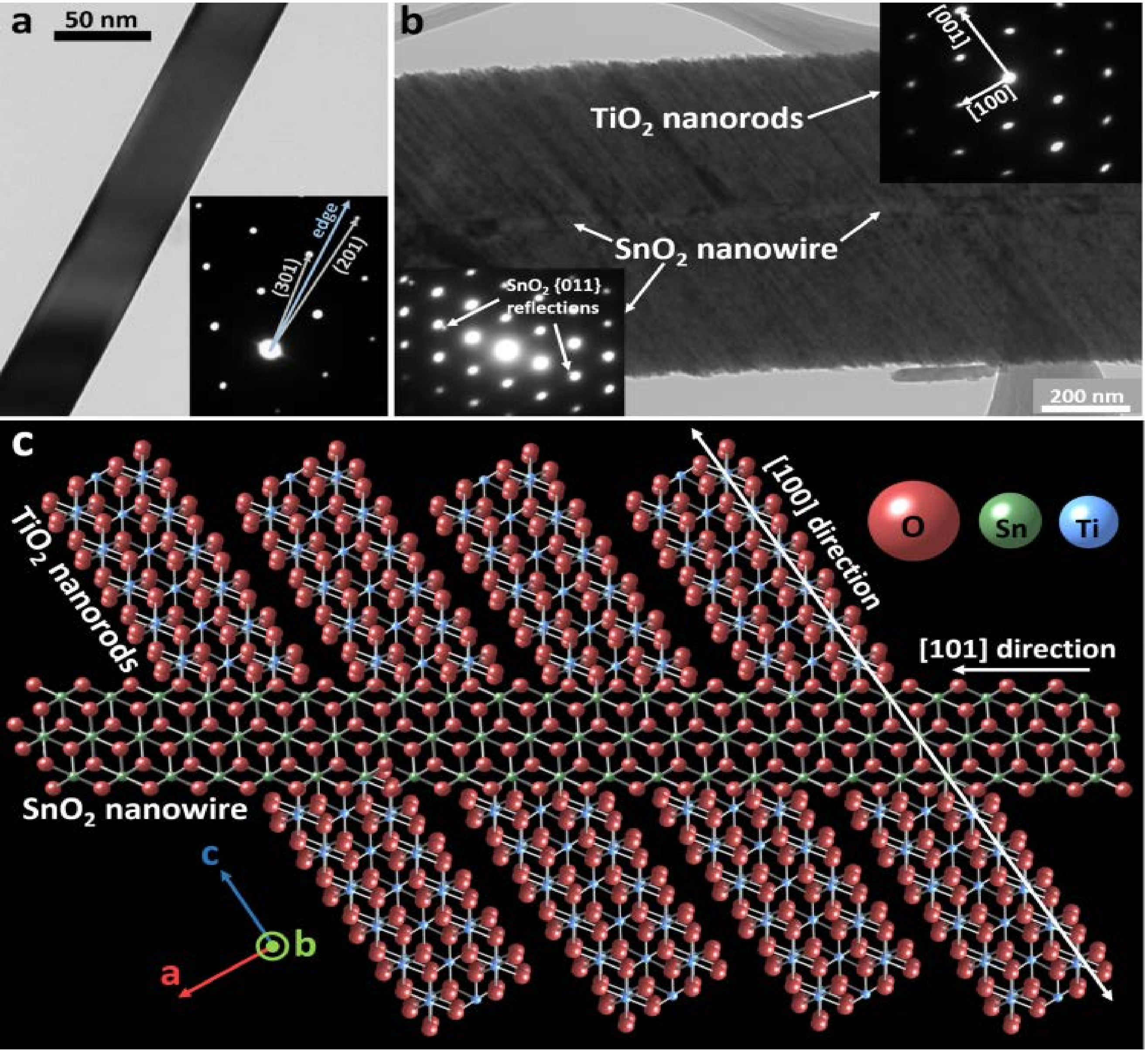
Cross-sectional TEM of nanowire





SnO_2 nanowires grown from commercial FTO slides using the vapor-liquid-solid (VLS) method forming the backbone of these long strands. These were placed in a microwave-assisted hydrothermal chamber where TiO_2 nanorods nucleated radially from the SnO_2 nanowire cores. This "nano-tinsel" structure is being investigated for its gas-sensing and photovoltaic properties.

Micro-Nano Letters (2017) doi:10.1007/s40820-017-0136-6

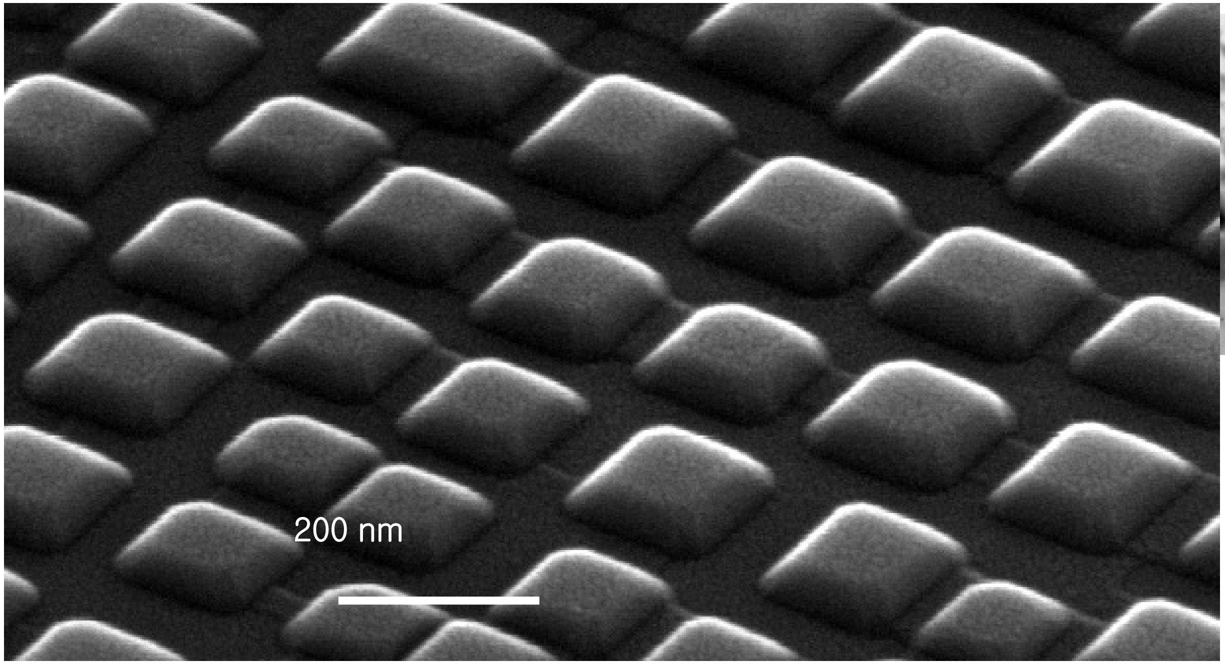


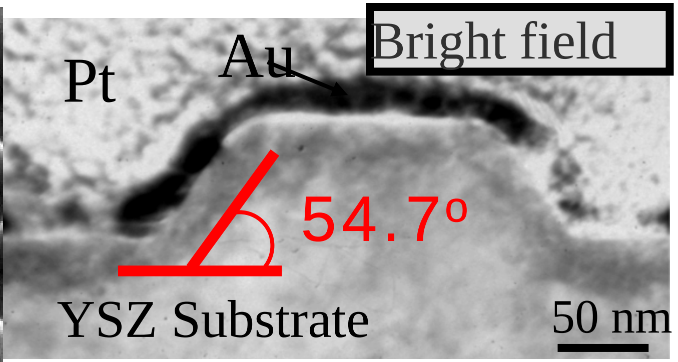
a: TEM image of pristine SnO_2 nanowire with inset SAED pattern showing a growth direction of [101].

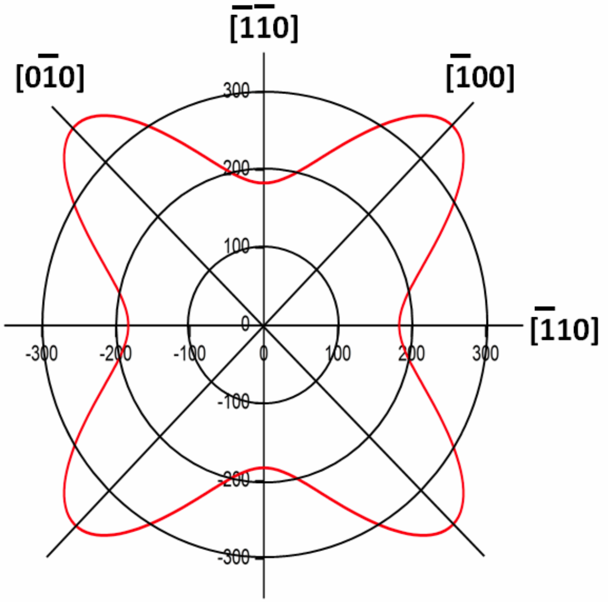
b: TEM image of SnO_2-TiO_2 brush with one plane of TiO_2 nanorods growing at 33 degrees from perpendicular to the nanowire axis. Inset top right shows the [001] growth direction of the TiO_2 nanorods.

c: An atomic model showing the epitaxial relationship of the angled nanorods growing from the SnO_2 nanowire looking down the [010] zone axis.

Self-assembled nano-islands via a strain-driven process







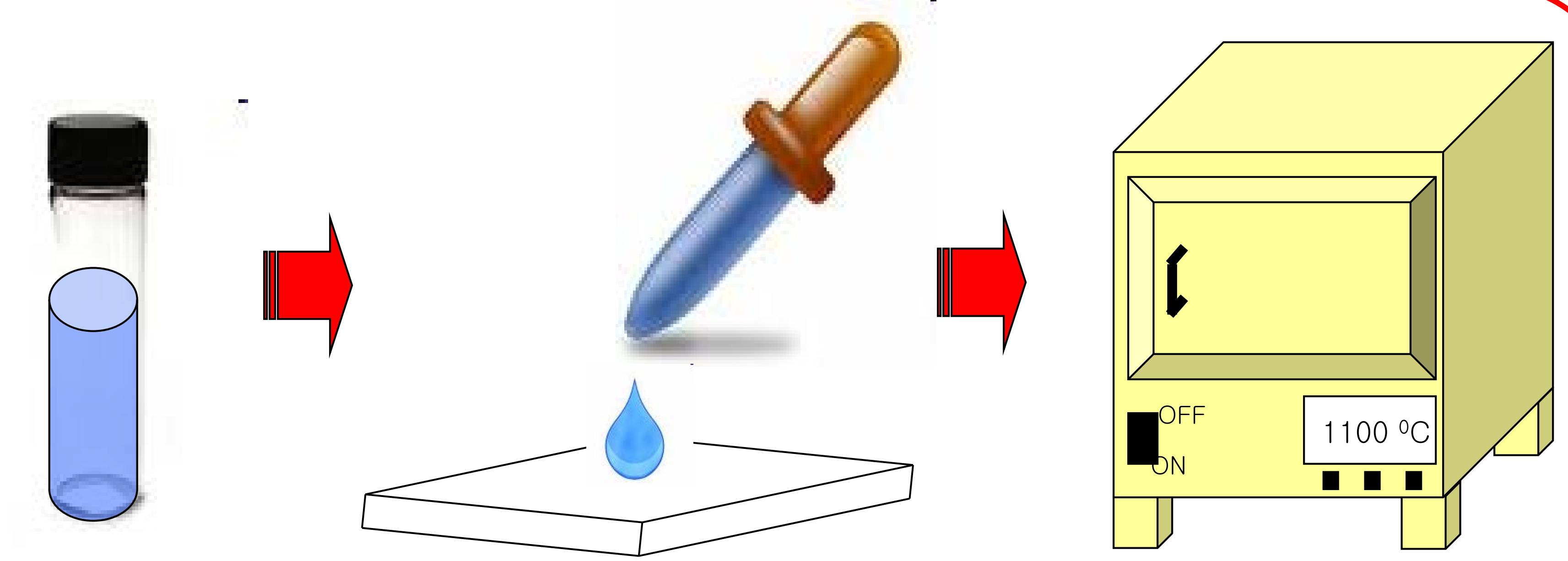
$(Gd,Ce)O_2$ thin film on (001) YSZ substrate breaks up into a psuedo-periodic array of single crystal islands with average size of 200 nm upon annealing at 1150°C.

Advanced Materials, 20, 1699 (2008).

Size similarity and ordering are remarkably different than dewetting and ATG-SK

Powder-based method of nano-islands *(Ansari)*

- Advantages of the powder-based process
  - Bypasses the expensive lithography (followed by sputtering) process
  - Flexible and easy to apply
  - Suspension can be made of any powder of any composition



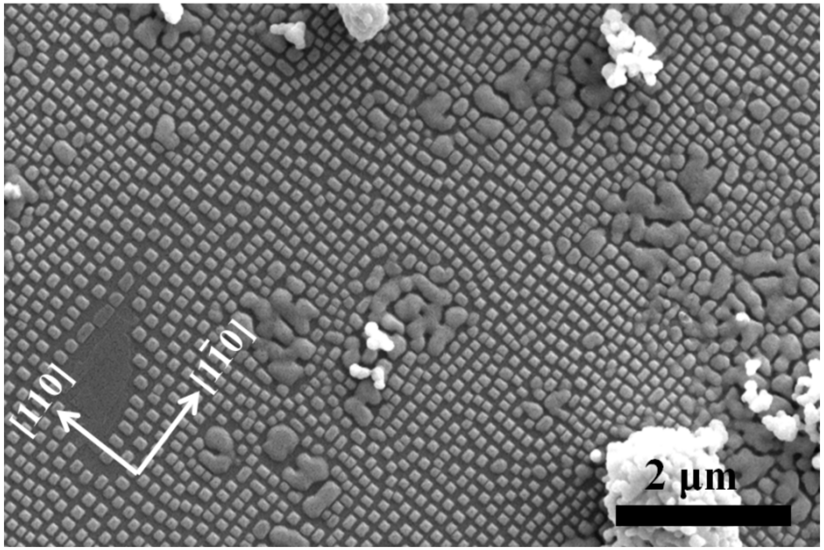
GDC Suspension in water

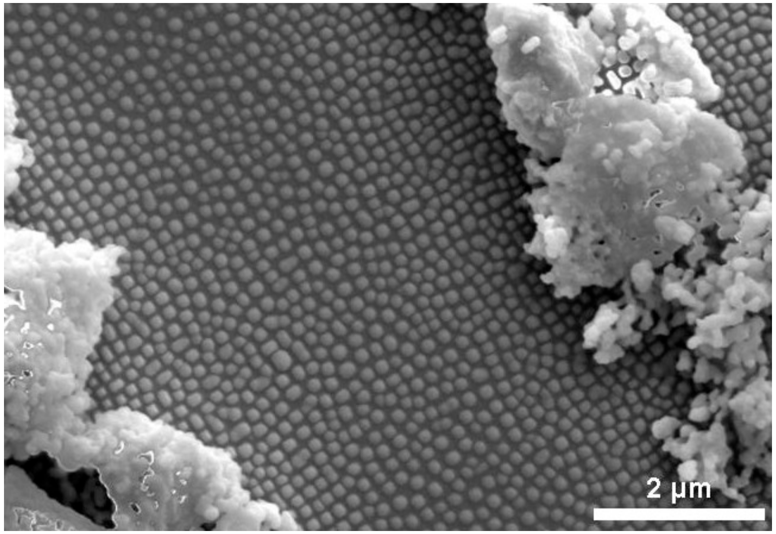
A drop applied to YSZ (001) substrate

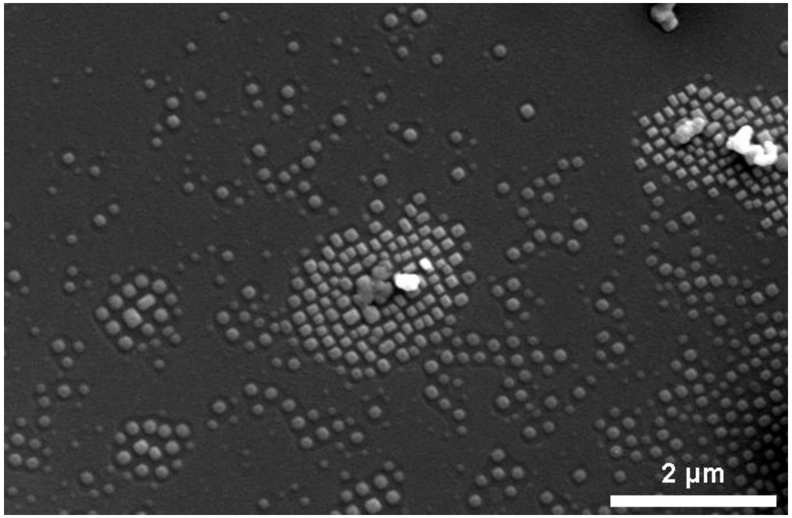
Annealing in a box furnace at 1100 ⁰C for 5 – 25 hours

Nanoislands via powder-based method

- Islands are correlated with GDC sources. YSZ-(001) surface contains only <100> and <110> principal directions, the nanoisland arrays align along the more compliant <110> directions.
- Where bigger GDC particles fed the area between them, wall to wall coverage was observed between particles

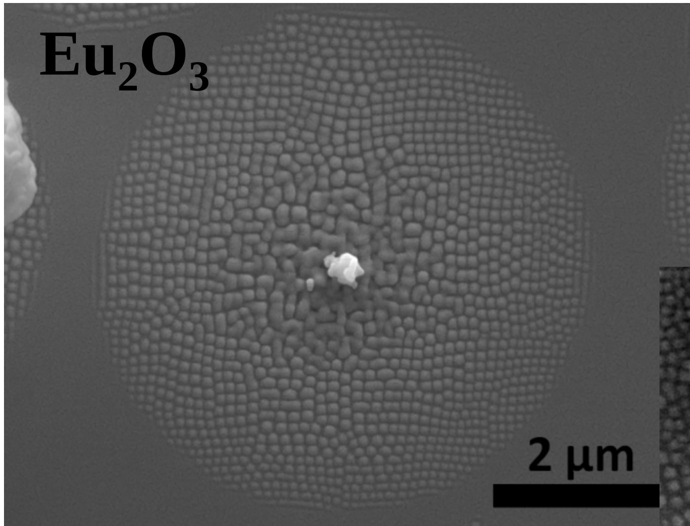


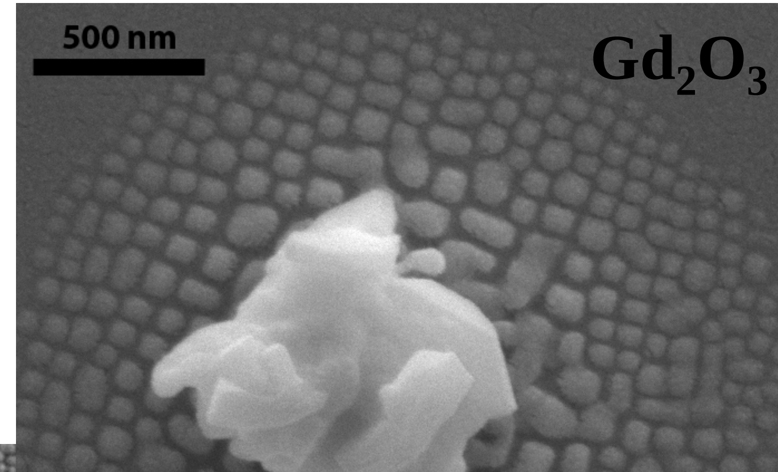


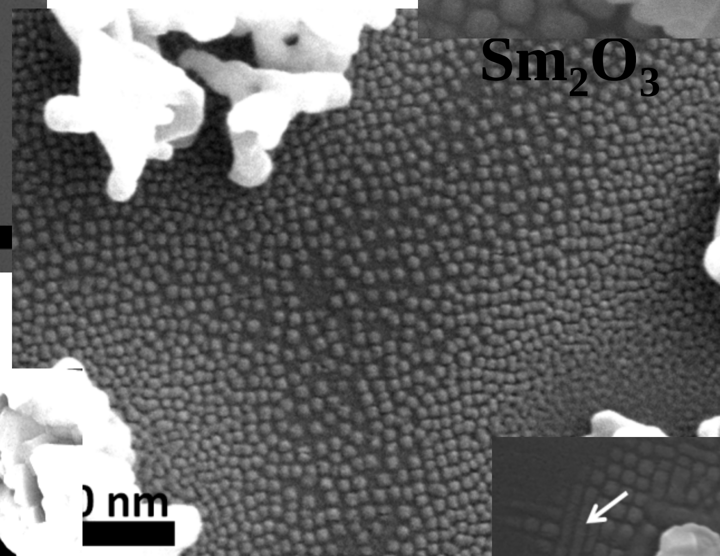


Sci. Adv. Mater., 3, 821-844 (2011).

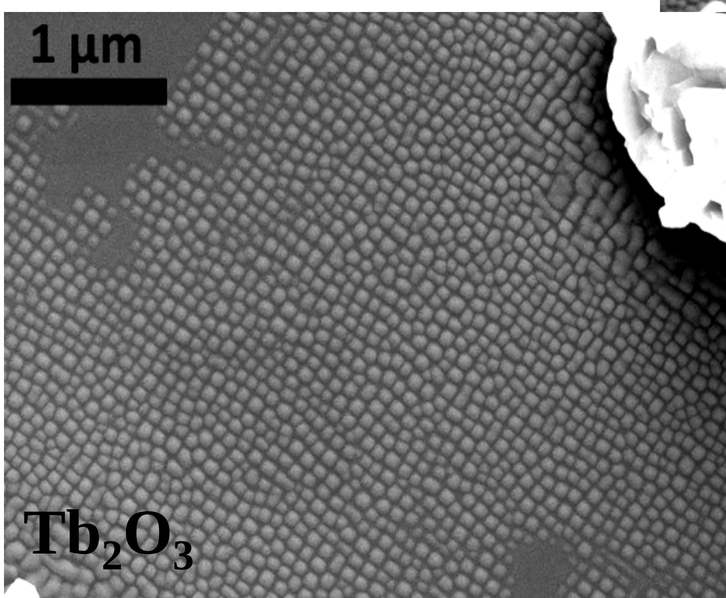
Forms in other oxides

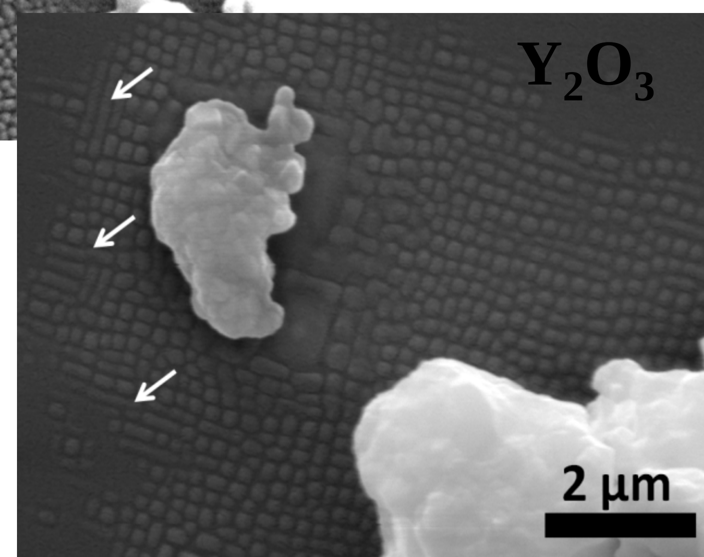






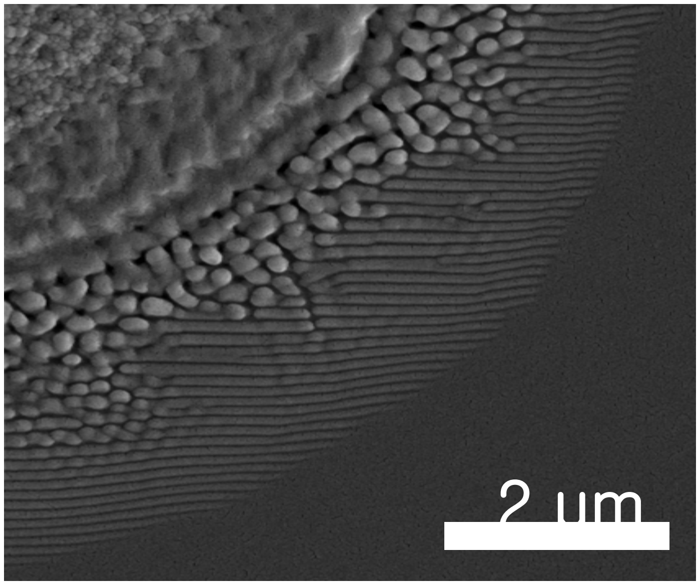
1. Substrate with strong elastic anisotropy
2. Source material with some solid solubility

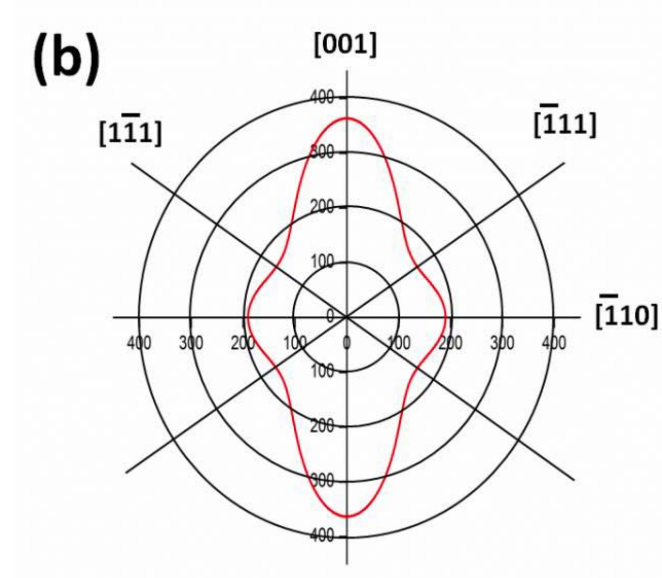


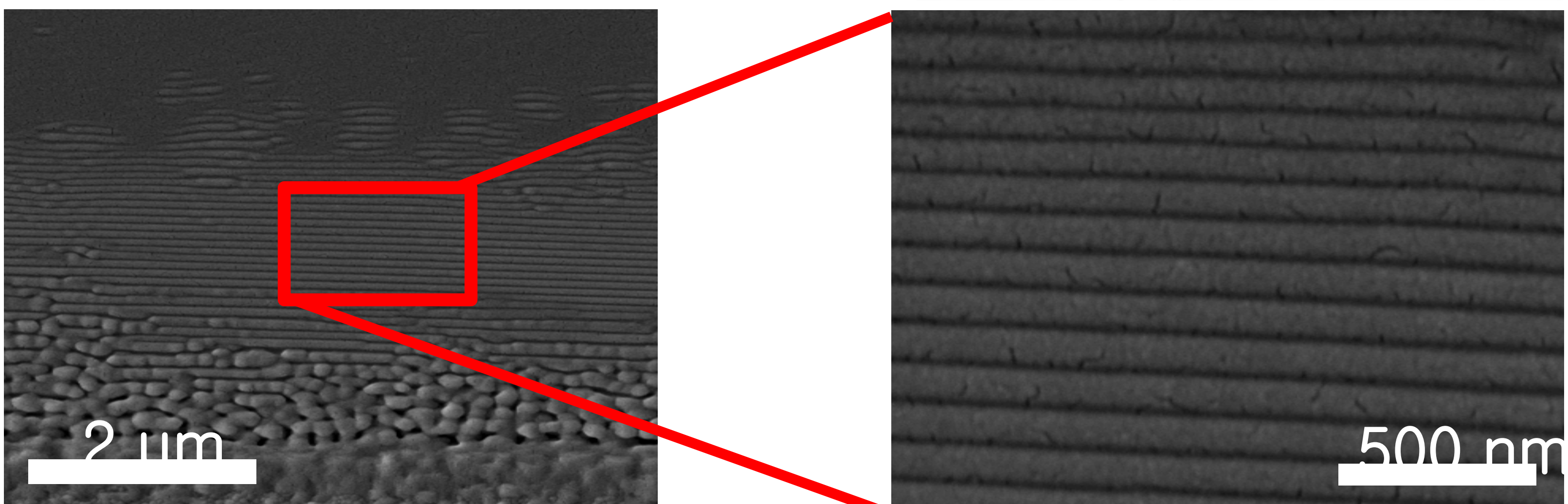


Does island morphology change with substrate orientation?

Aligned nano-bars on (110) YSZ





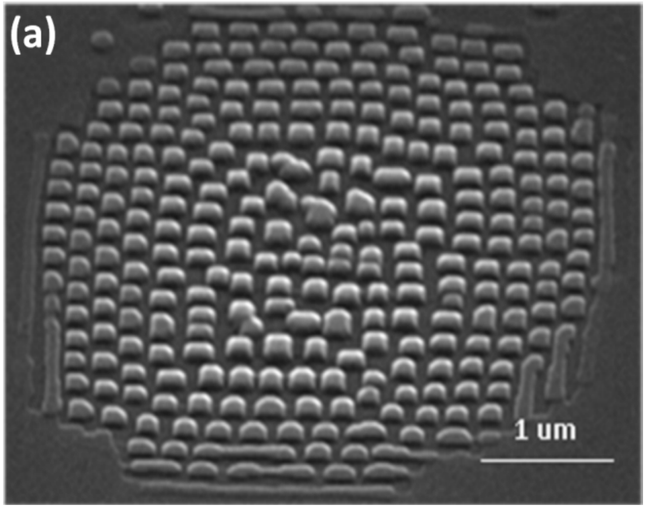


1200 °C for 5 hrs @ 10 °C/min cooling rate in box furnace

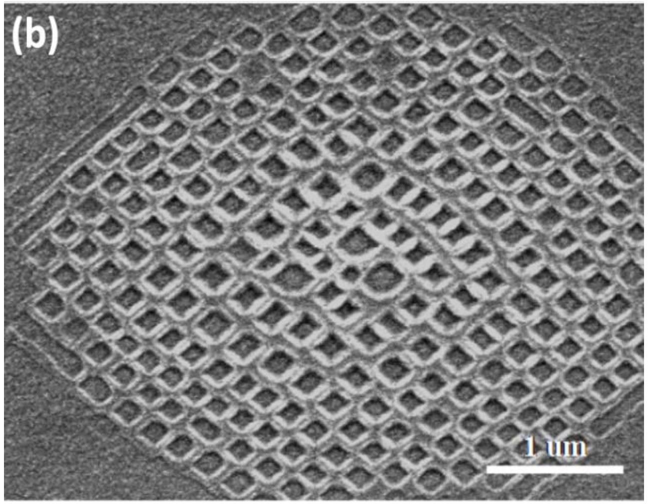
ACS Nano (2017), doi.org/10.1021/acsnano.7b00081

Pattern Transfer by Replica Molding

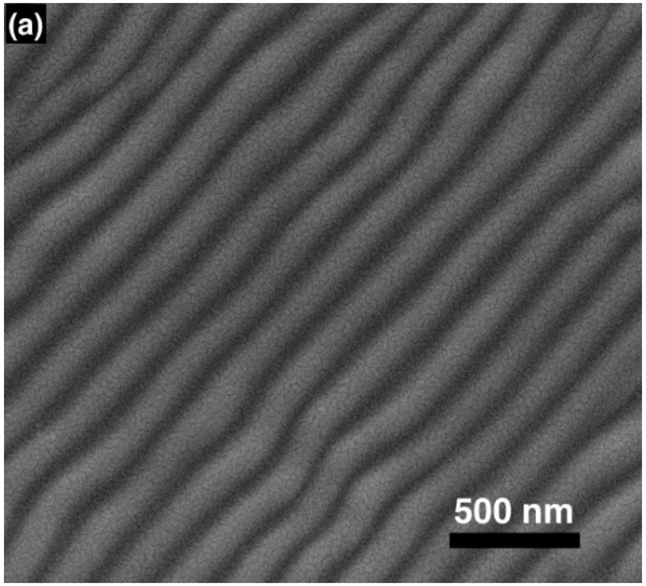
PDMS Soft Imprint Pattern Transfer of nanoisland and nanobars

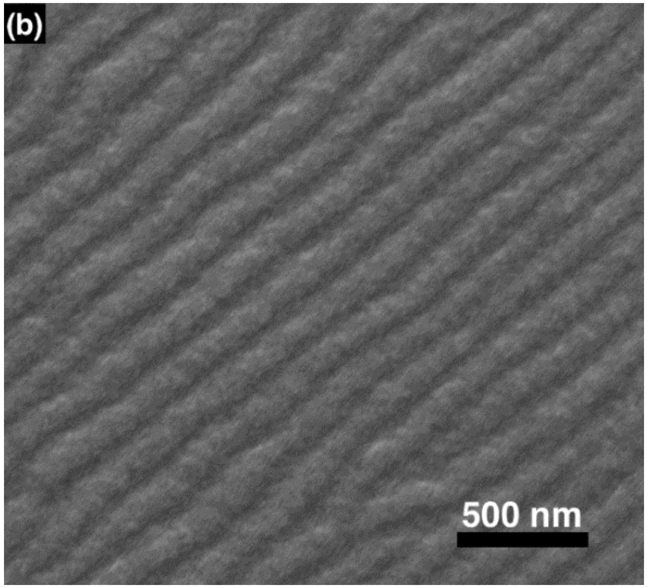


(a) YSZ (100) and (110) master mold



(b) PDMS replica





Sensors

1. Ceramics International, **30**[7], 1121-26 (2004)
2. Sensors and Actuators B, **108**, 29-33 (2005)
3. Sensors and Actuators B. 136, 138, (2009)
4. Encyclopedia of Semiconductor Nanotechnology, American Scientific Publishers, vol. 7, Chapter 5, pp. 1-23 (2011)
5. Sensors and Actuators B, **165**, 13-18 (2012)
6. *Sensors*, ***12***, 7207-7258 (2012)
7. Ceramics International, **38**, 6341-6347 (2012)
8. Sensors and Actuators B, **204**, 250-272 (2014)
9. Sensors, **14(8)**, 13613-13627 (2014)
10. J. Alloys and Compounds, **618**, 455-462 (2015)
11. Sensors and Actuators B, doi:10.1016/j.snb.2016.07.135
12. Reviews in Advanced Sciences and Engineering, ASP, vol. 5, pp. 88-105 (2016).
13. Sensors and Actuators B, **238**, 972-984 (2017).
14. Sensors Actuators B Chem. **240**, 193-203 (2017).
15. Sensors Actuators B Chem. 241, 99-108 (2017).
16. Reference Module in Materials Science and Materials Engineering, Oxford, Elsevier, pp. 1-5 (2017).
17. Chapter 3 in Nanomaterial-based Flexible and Multifunctional Sensors, Eds., Eric Singh and Hari Singh Nalwa, pp. 113-160, American Scientific Publishers (2018).
18. Sensors and Actuators B, 286, 624-640 (2019).
19. Sensors and Actuators B, 295, 127-143 (2019).
20. Front. Mater., 07 June (2019)
21. Sensors and Actuators B, 301 (2019)

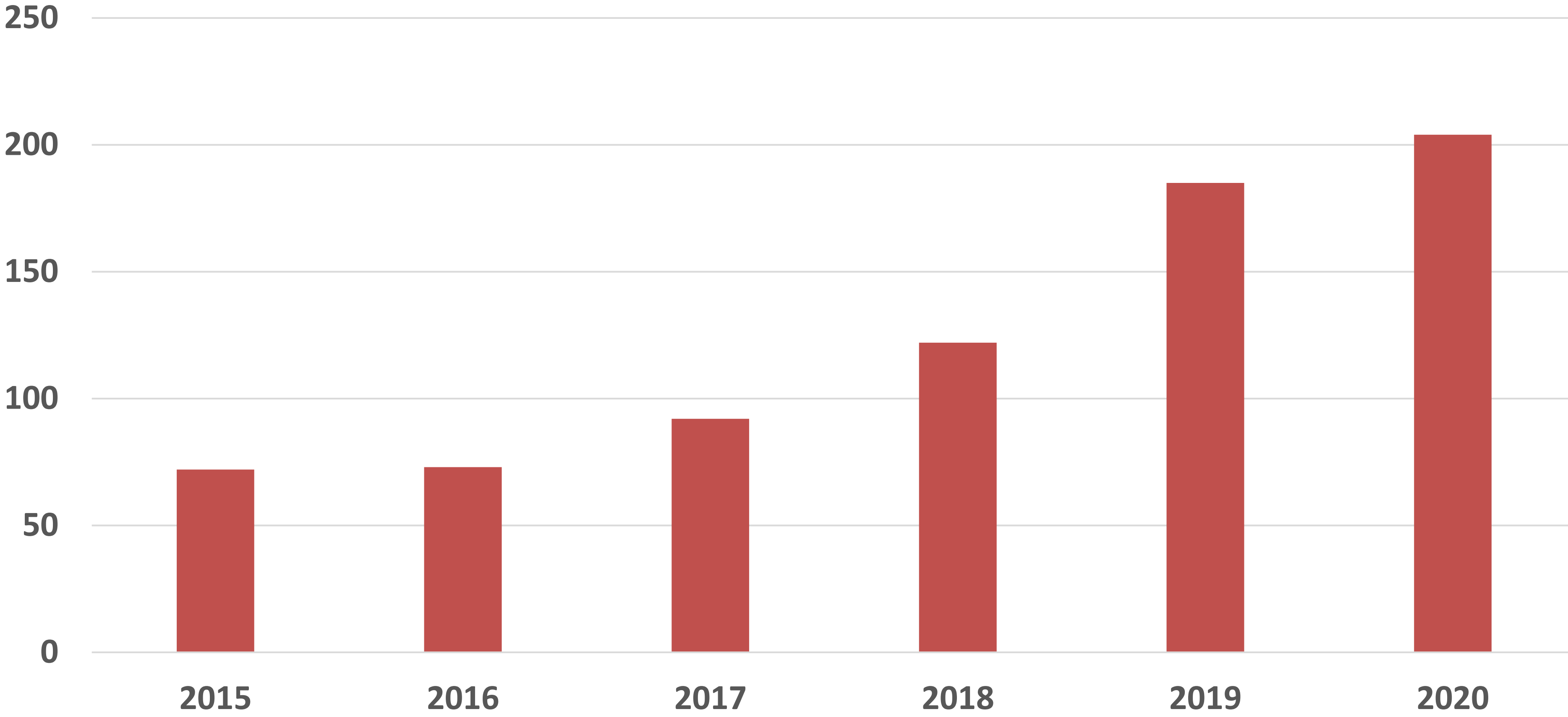
Biomedical

1. Materials Science and Engineering **C. 32**: 2469–2475 (2012)
2. Ceramics International, **39**, 5949-5954 (2013)
3. Journal of Materials Science 48 (24), 8337-8353 (2013)
4. Ceramics International, **40 (6)**, 8301-8304 (2014)
5. Applied Surface Science, **320**, 161-170 (2014)
6. International Journal of Nanomedicine, **9**, 5389-5401 (2014)

9. Applied Mechanics and Materials, vol. 575, pp. 219-222 (2014)
10. Materials Research Innovations, Volume 18, Issue S6, pp. S6-220-S6-223 (December 8, 2014)
11. Materials Design, S0264-1275(15)31031-5, doi: 10.1016/j.matdes.2015.12.173
12. Key Engineering Materials, Vols. 656-657, pp. 63-67, June (2015).
13. Journal of the Mechanical Behavior of Biomedical Materials, DOI: 10.1016/j.jmbbm.2017.01.028.

Today – sensor future direction

Publication trends in nano-hetero-structure gas sensors



Opportunities

- Optimizing heterostructure thickness, spatial distribution, and morphology
- Observing how crystallographic facets direct surface reactions
- Optimization of sensor properties by synergistic effects at the interface
- Understanding conduction mechanisms for different nanostructures
- Relating gas response to morphology of heterostructures
- Use of IS to gain fundamental knowledge; single nanowires are ideal structures for fundamental studies
- Advanced techniques such as STEM-CL; also other in-situ methods such as APXPS (atmospheric pressure x-ray photoelectron spectroscopy) offer obvious advantages
- A well-designed testing setup can increase throughput; community adopting standard methods/techniques can improve development of theory
- Miniaturizing sensor circuit for decreased energy consumption
- Utilization of light for wearable room-temperature gas sensors
- Collaboration with catalysis, LED, solar cell research, bio-medical

Challenges

- Determining robust synthesis methods for controlling low-dimensional building blocks to desired architecture
- Deposition of sensing material on electrodes that produces consistent material coverage and junctions for conductivity
- Elucidating the carrier transport behavior at the heterojunctions
- Linking defect structure/material properties to gas sensing behavior; Use impedance spectroscopy (IS) to separate contributions to response; IS measurements on nanomaterials difficult; IS data analysis/modeling not straightforward
- Proper defect characterization; different techniques illustrating variability (e.g. STEM-CL vs PL)
- Accuracy of gas sensing measurements with well designed and standardized testing setup
- Linking defect structure/material properties to gas sensing behavior; electrical measurements can be difficult and time consuming

Sensing based on nano-heterostructures
Need for fundamental studies

- **Recent studies combine oxides on a nano-scale to achieve unique electronic and sensing properties**
- **Studies have been largely <u>trial-and-error</u> and <u>not systematic</u>**
- **More <u>fundamental</u> and <u>systematic</u> studies are needed to understand the behavior of these materials as gas sensors**

  Characterize electronic properties of hierarchical structures on a nano-scale and compare to expected bulk properties

  Develop methods by which nano-heterostructures can be <u>designed</u> in a bottom-up fashion for specific applications

- **Bulk and surface defect states and band edge positions in nano-heterostructures affect sensing properties**

  Defect level analysis via STEM-Cathodoluminescence

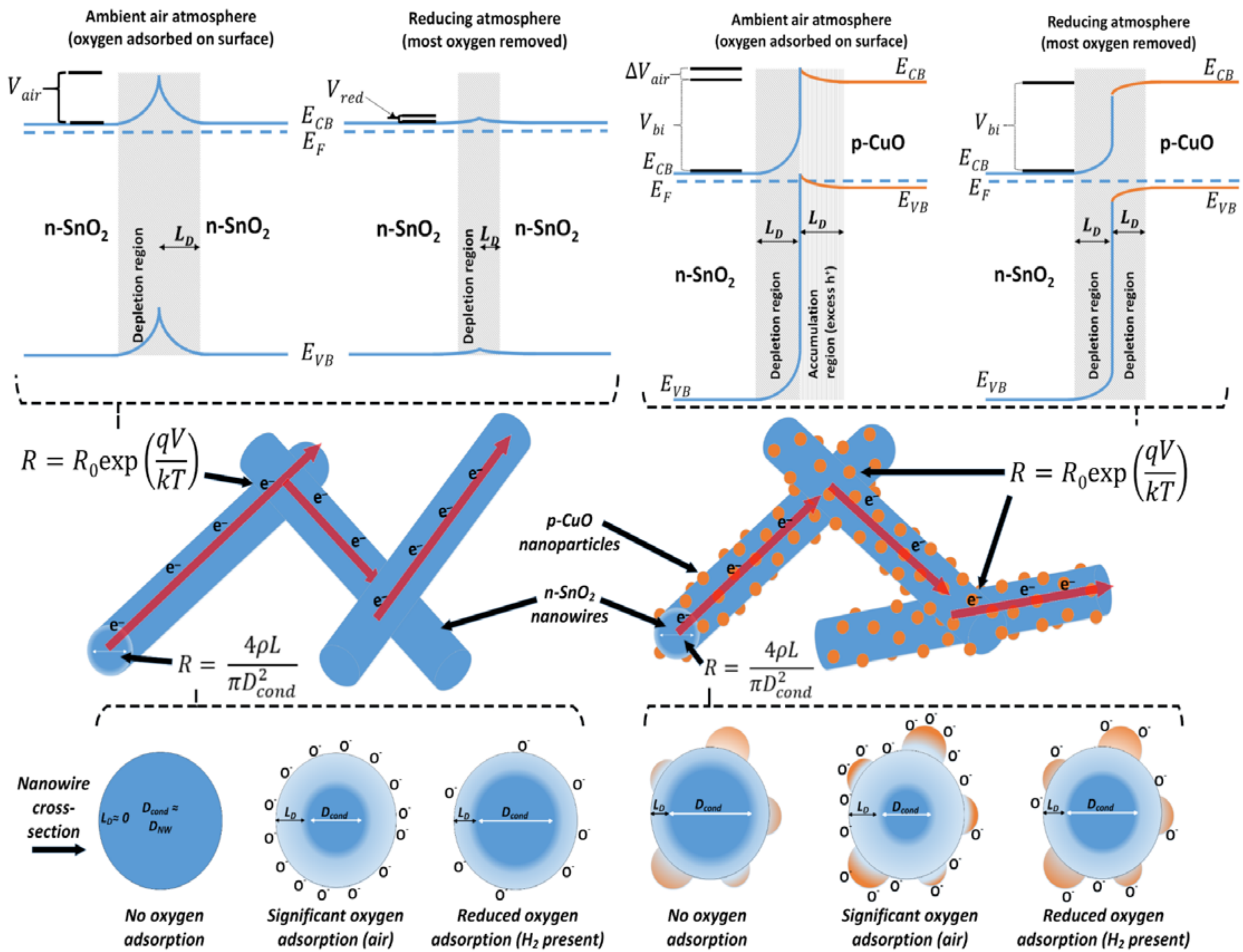
  Band gap measurement via valence-loss EELS

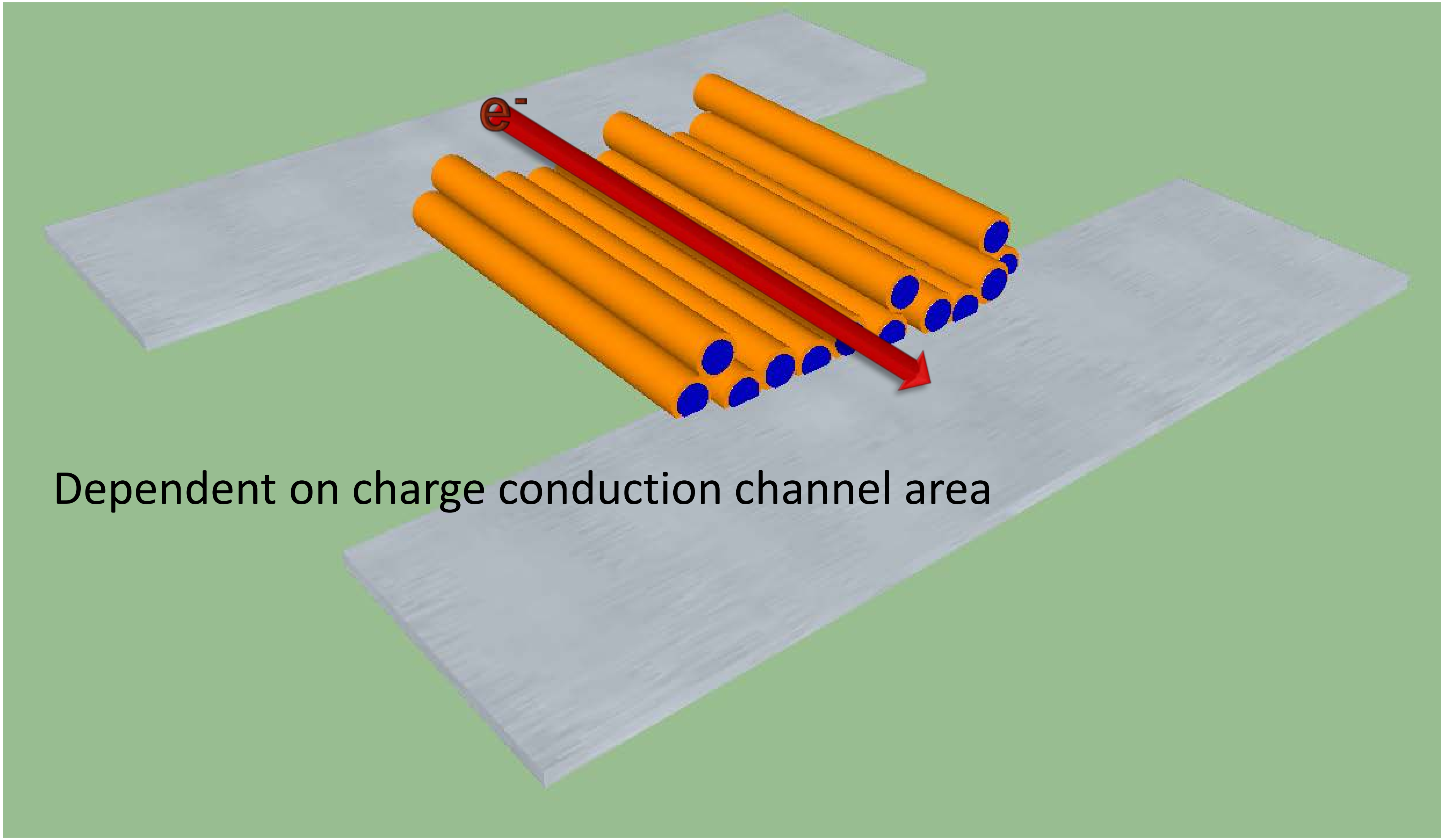
Importance of interfaces and hetero-structures in sensing

Interfacial mechanism

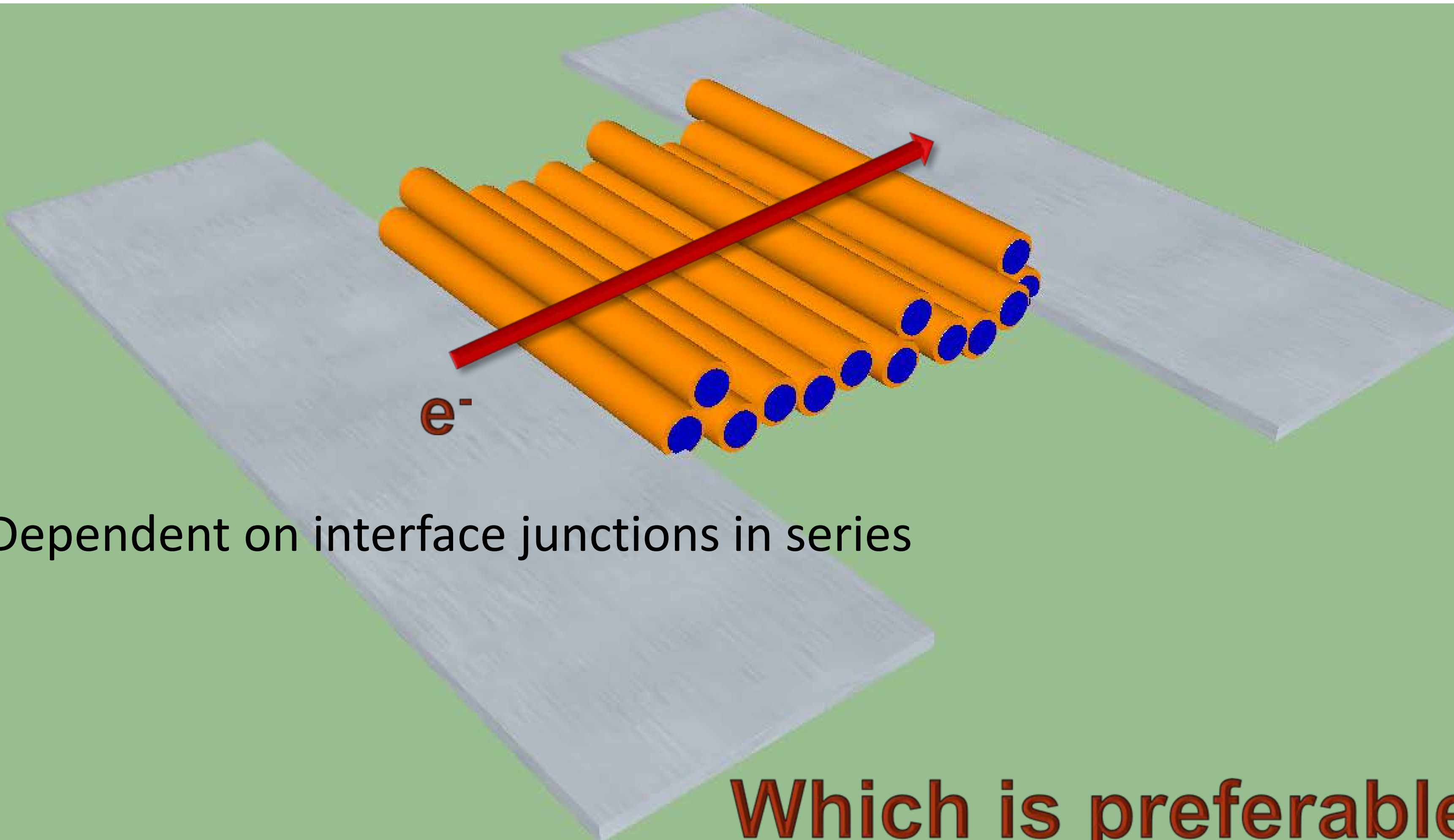
Conduction channel mechanism

D.R. Miller, et al., *"Nanoscale Metal Oxide-Based Heterojunctions for Gas Sensing: A Review,"* Sensors Actuators B Chem. 204 (2014) 250–272.





Dependent on charge conduction channel area

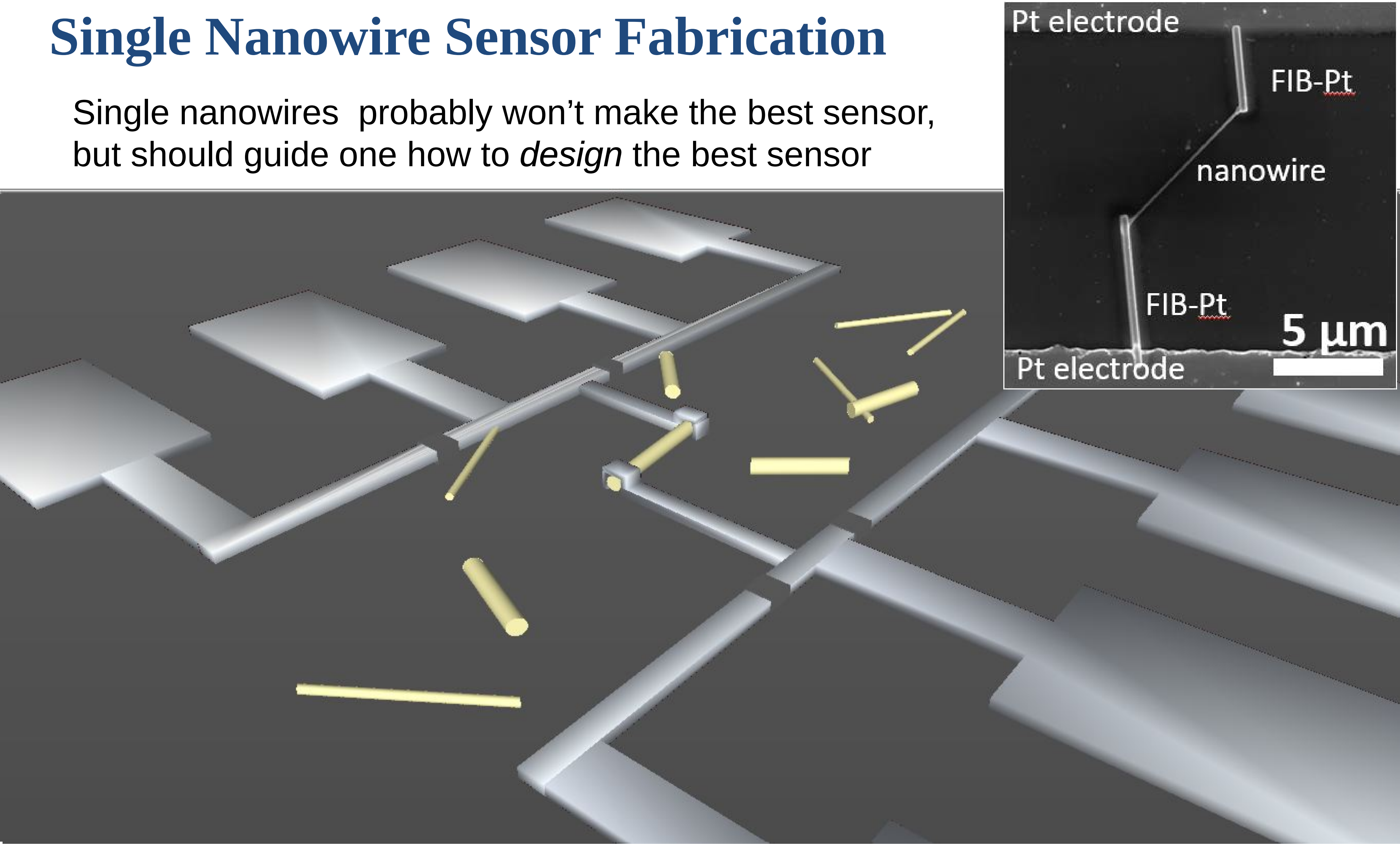


Dependent on interface junctions in series

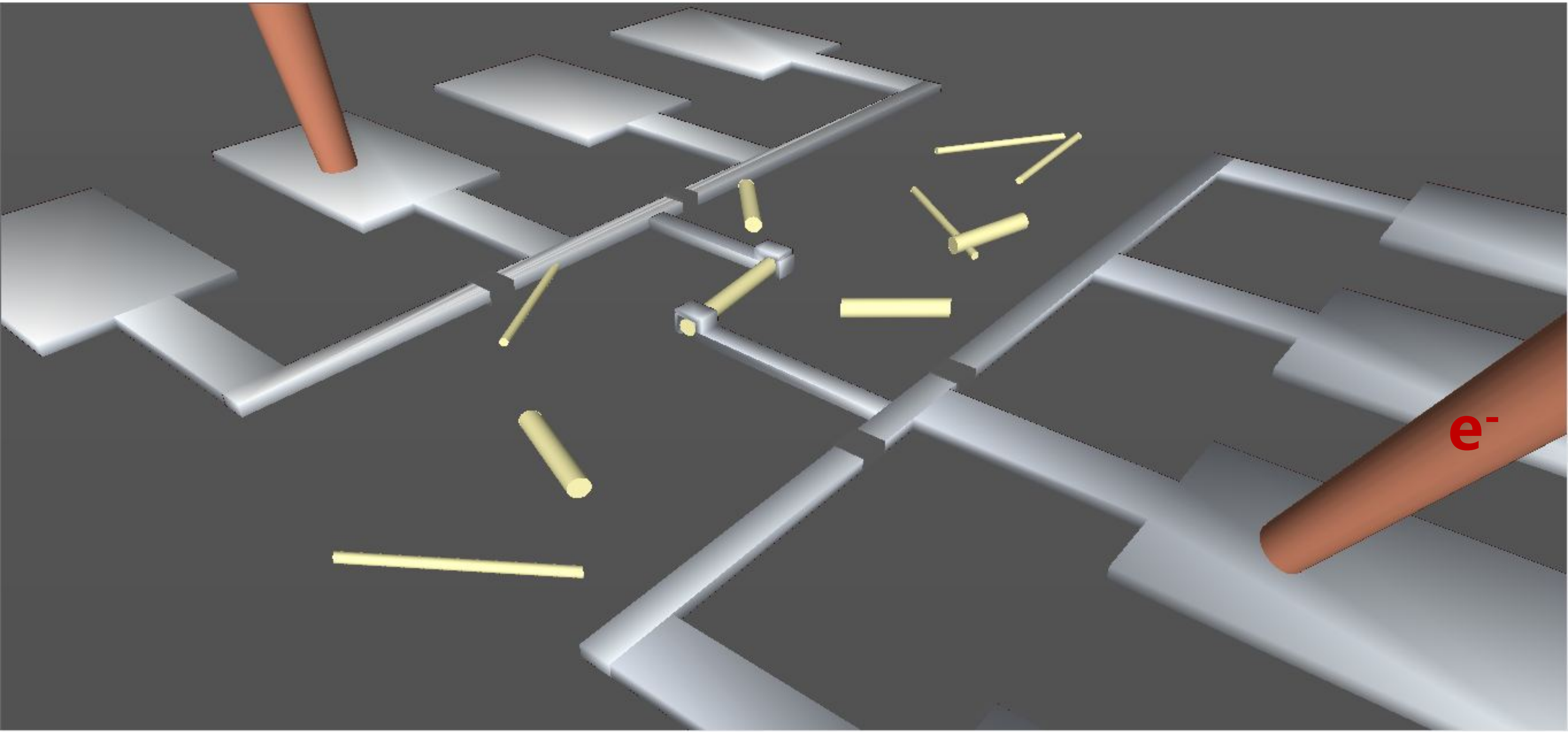
Which is preferable?

Single Nanowire Sensor Fabrication

Single nanowires probably won't make the best sensor, but should guide one how to *design* the best sensor

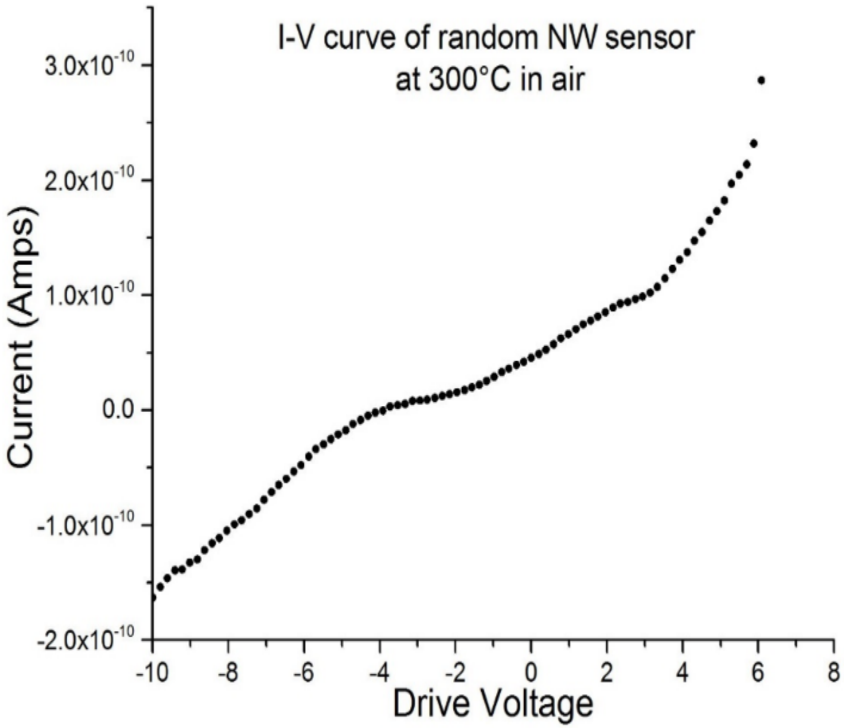


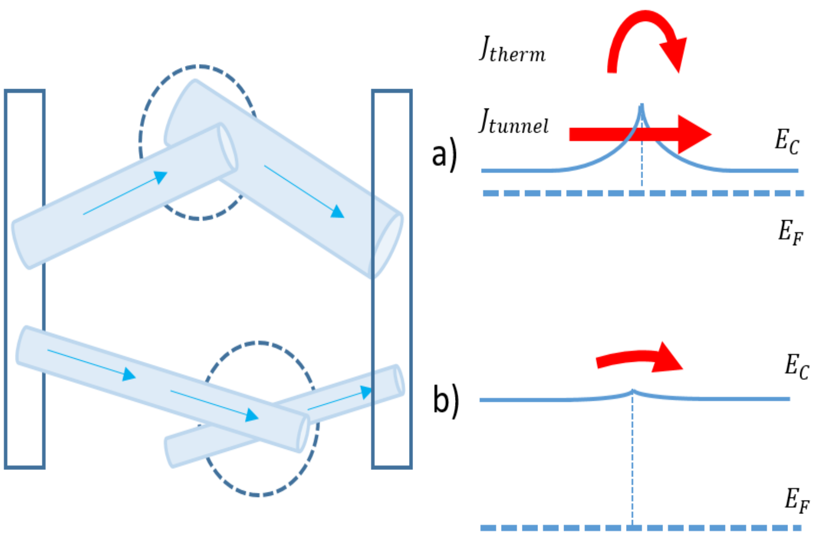
Single Nanowire Sensor Fabrication



Random multi-NW I-V behavior is a mixture of Ohmic and Schottky junctions due to NW size dispersion

- Wide NWs do not get fully depleted
  - stay Schottky
- Thin NWs become fully depleted
  - Ohmic





Schipani, Federico, et al. "Conduction mechanisms in SnO_2 single-nanowire gas sensors: an impedance spectroscopy study." *Sensors and Actuators B: Chemical* 241 (2017): 99-108.

Role of Defects – oxygen vacancy

Sensors Actuators B Chem., Aug. 2019, doi: https://doi.org/10.1016/j.snb.2019.126845

Receptor/Surface properties

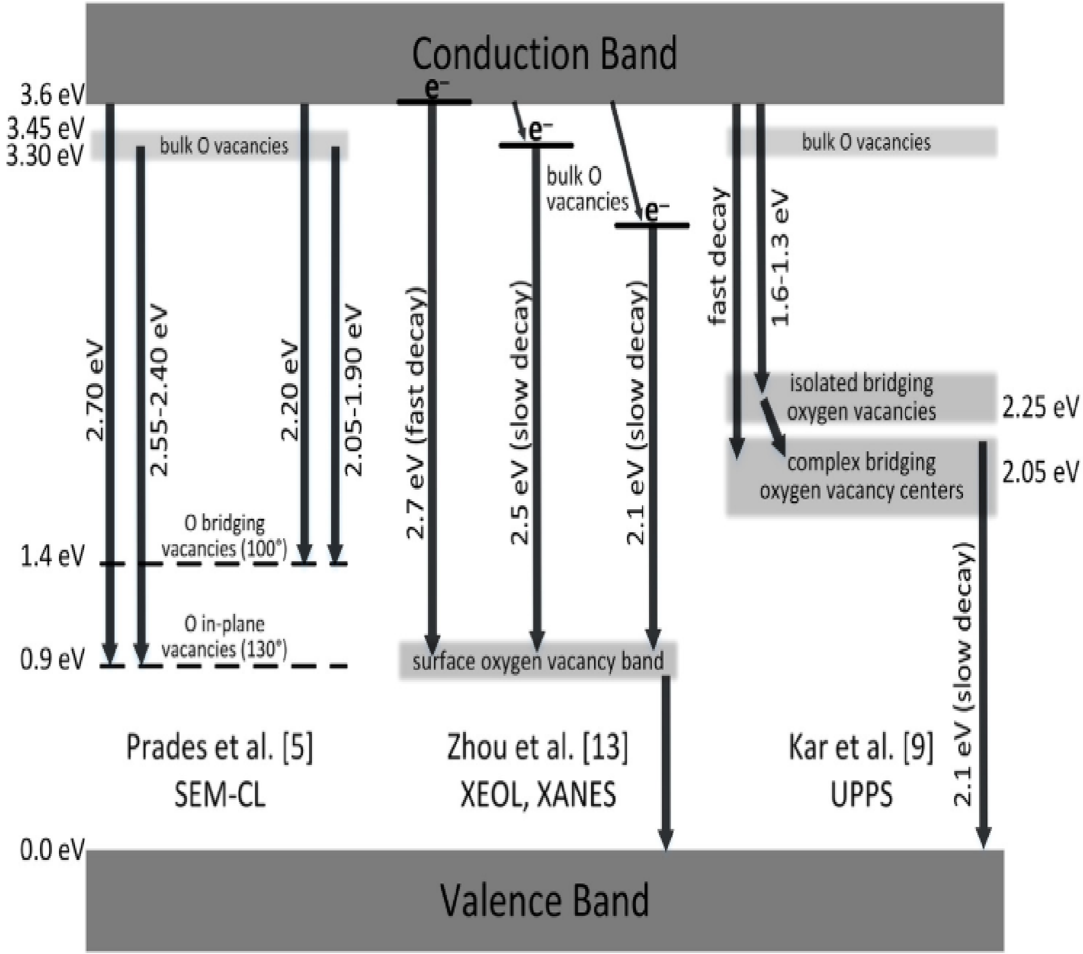
- Do certain defects promote preferential adsorption?
- Are there different considerations for high vs. low temperature sensing?
- What are the implications on understanding/limiting/controlling humidity interference?

Transduction/Conduction mechanisms

- How does oxygen in/out diffusion impact sensing mechanisms?
- How do defects impact conduction mechanisms?

What are the possible implications/considerations for heterostructures?

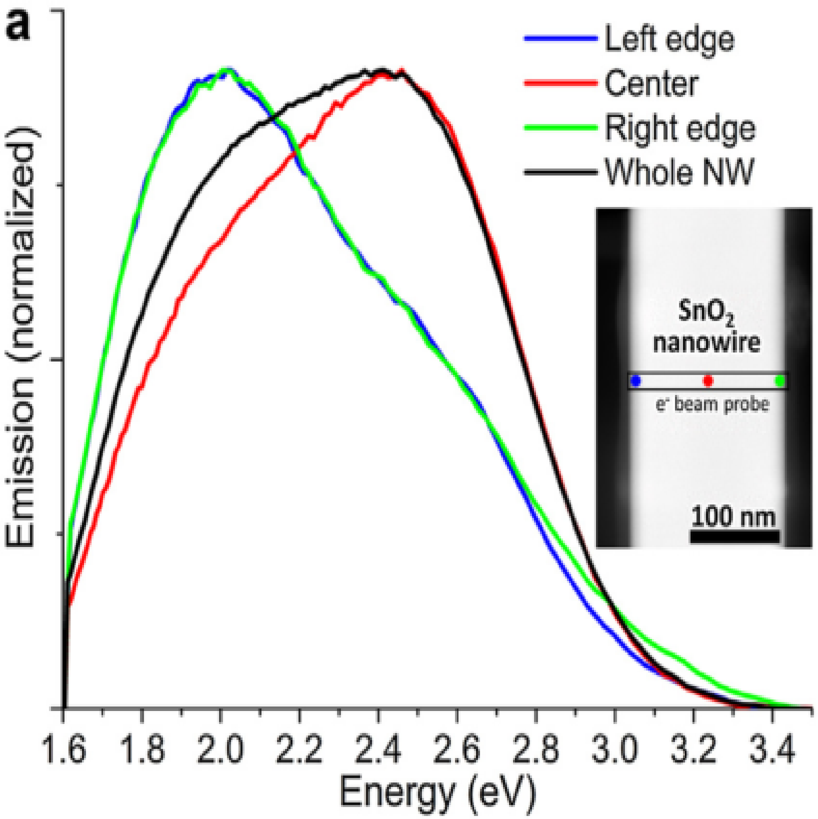
Defect Characterization Techniques



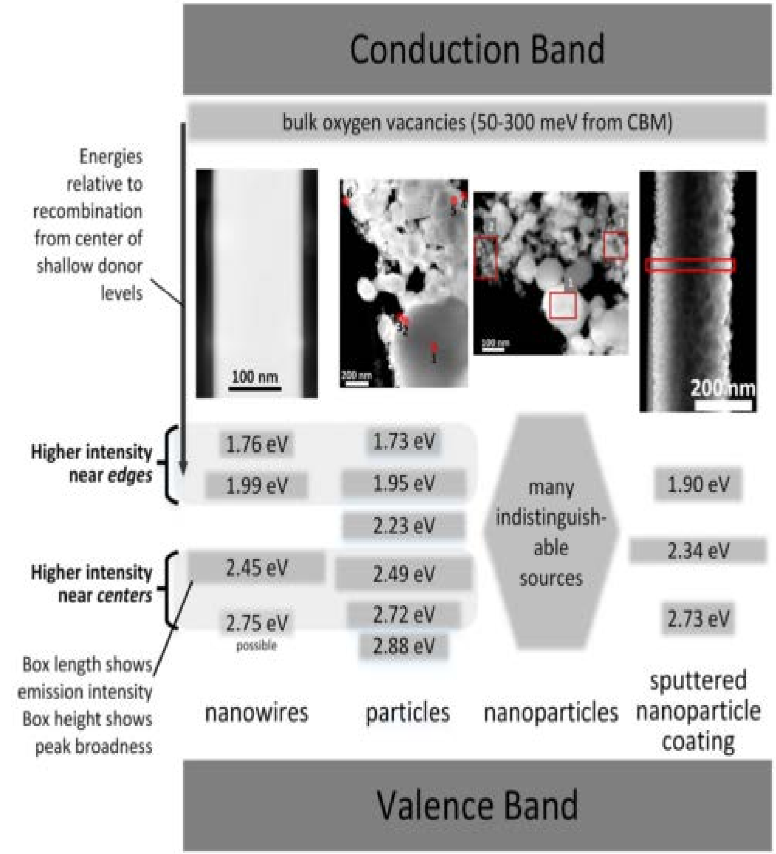
Proposed band structures/recombination pathways in SnO_2 nanowires from studies that use different techniques illustrating variability

Miller, Derek R., et al. "STEM-cathodoluminescence of SnO2 nanowires and powders." *Sensors and Actuators B: Chemical* 240 (2017): 193-203.

Advanced Defect Characterization Techniques



STEM-CL spectroscopy showing how defect structure can vary across a single SnO_2 nanowire

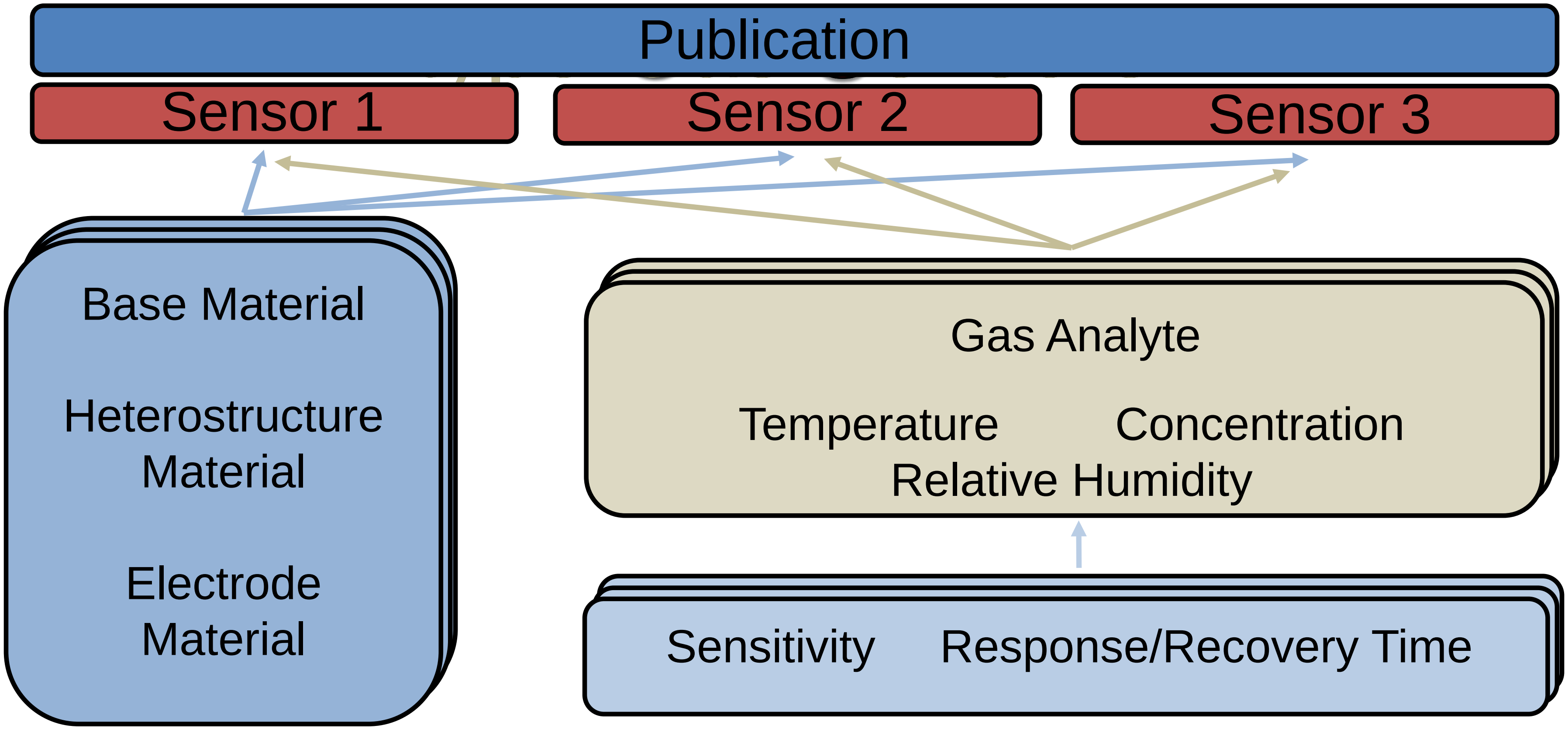


Proposed band structure with various defect levels deduced from STEM-CL showing how defect structure varies for different forms of SnO_2

Miller, Derek R., et al. "STEM-cathodoluminescence of SnO2 nanowires and powders." *Sensors and Actuators B: Chemical* 240 (2017): 193-203.

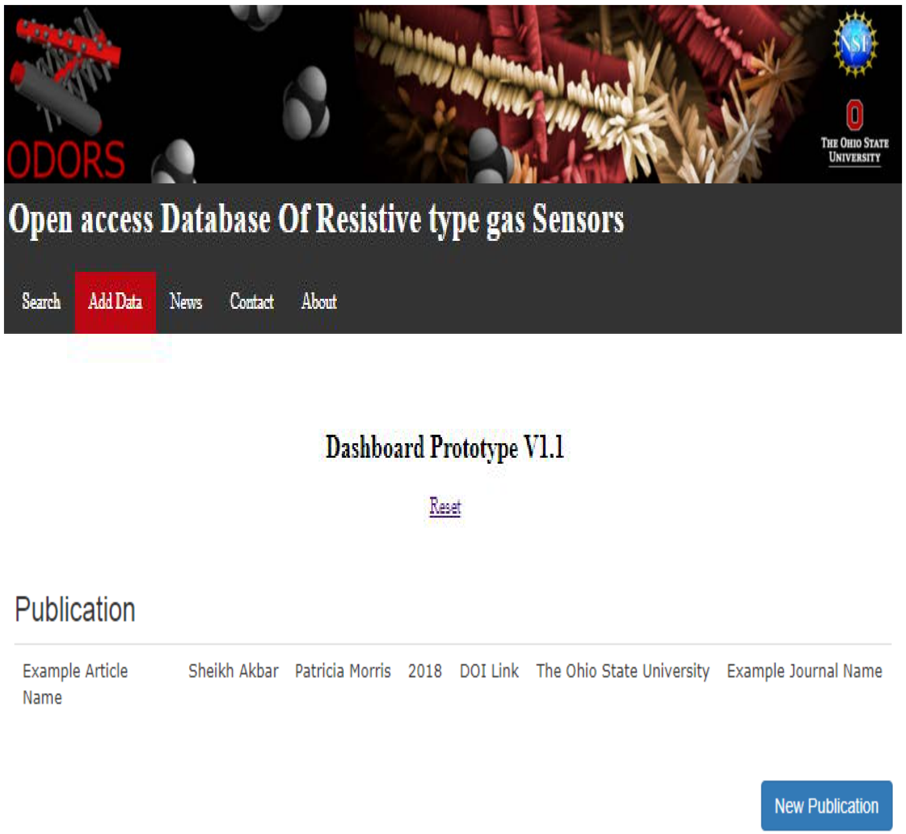
Open-access Database Of Resistive-

ODORS



Open-access Database Of Resistive-type Gas Sensors (ODORS)

- Prototype data input form



Open-access Database Of Resistive-type Gas Sensors

Programming Database → Testing Database → Data Search finding trends

- Thus far, data from ~150 publications
- Eventually self-sustained by the community
- **Paper link:** https://doi.org/10.1016/j.snb.2020.128591
- **ODORS web-page:** www.odorsdatabase.com

Contact Prof. Sheikh Akbar (akbar.1@osu.edu)
to stay up to date on the progress of ODORS

CISM
Center for Industrial Sensors and Measurements
A National Science Foundation Center

BPS – Feb 7, 2021

The Ohio State University