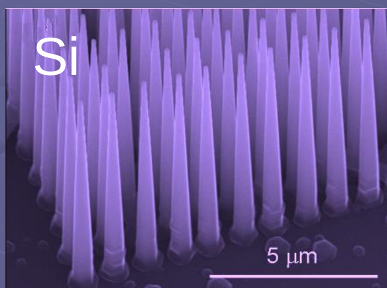
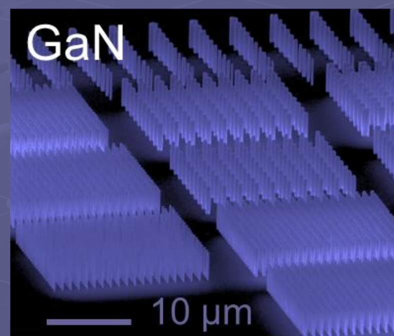
Low-dimensional semiconductors for sensors, electronics, energy

Albert Davydov, Materials Science & Engineering Division, NIST

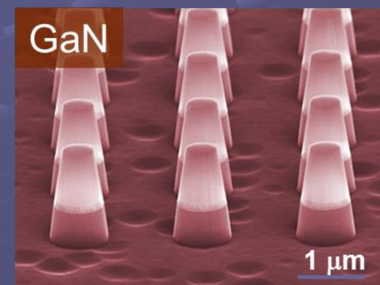
- About NIST : National Measurement Laboratory
- What we do: nanowires and 2D-layers - from fabrication to measurements
- Fabrication:



Si NWs by CVD

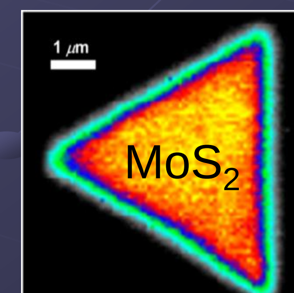


GaN NWs by MBE



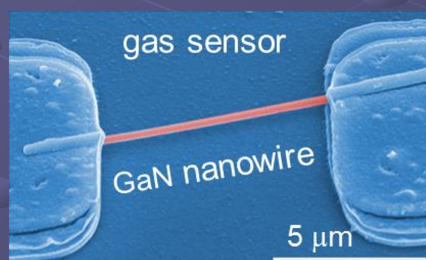
Dry etch

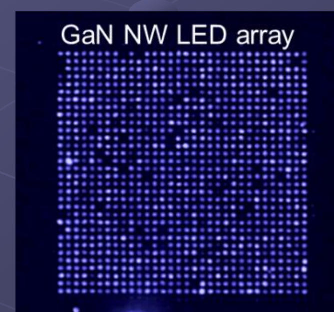
HVPE

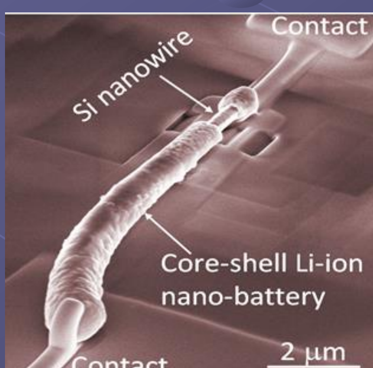


CVD

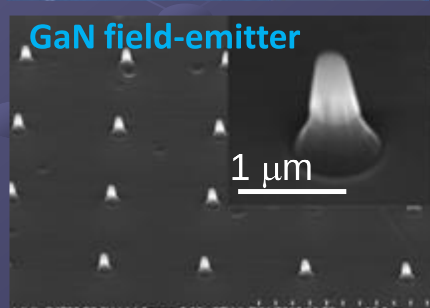
- Devices:

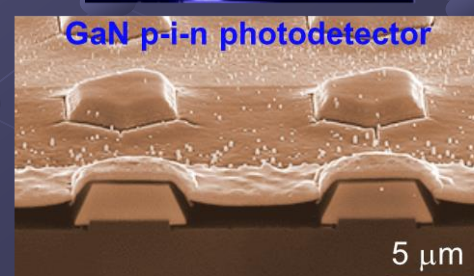






Li-ion battery





Acknowledgements

- Abhishek Motayed – project design
- Matt King – MOCVD growth of GaN films on 4” Si
- Sergiy Krylyuk – HVPE growth of GaN and Si NWs
- Kris Bertnes, Norm Sanford – MBE growth and spectroscopy of GaN NWs
- John Bonevich, Vladimir Oleshko – in-situ TEM
- Jong-Yoon Ha, Deepak Sharma, Baomei Wen, Ratan Debnath – device fabrication/electrical & optical measurements
- Geetha Aluri, Ritu Bajpai, Elissa Williams – sensing measurements
- Tony Ivanov’s group – MoS_2 materials and FETs
- Jim Maslar – CVD growth of MoS_2
- Sergey Baryshev – GaN field emitters
- Brian Bryce – SiNW integrated devices on a chip
- Sam Berweger, Pavel Kabos – Microwave near-field Imaging of WSe_2

Customers & Sponsors:

National Institute of Standards & Technology

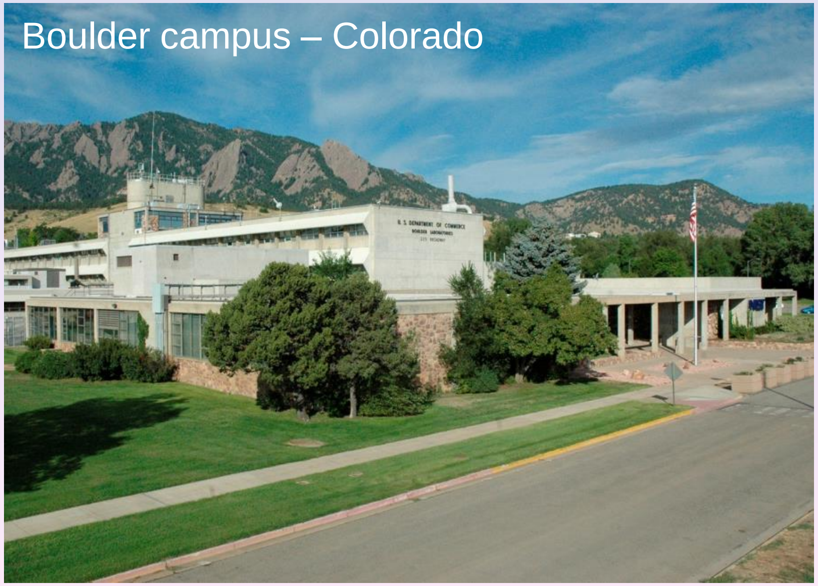
- National Measurement Laboratory: oldest physical science lab in US (1901)
- **Central Mission**: Support industrial innovation with Measurements, Standards, and Data
- World class facilities, national networks, international reach
- 3000 Employees

➢ Measurement Research
  2,200 publications/year

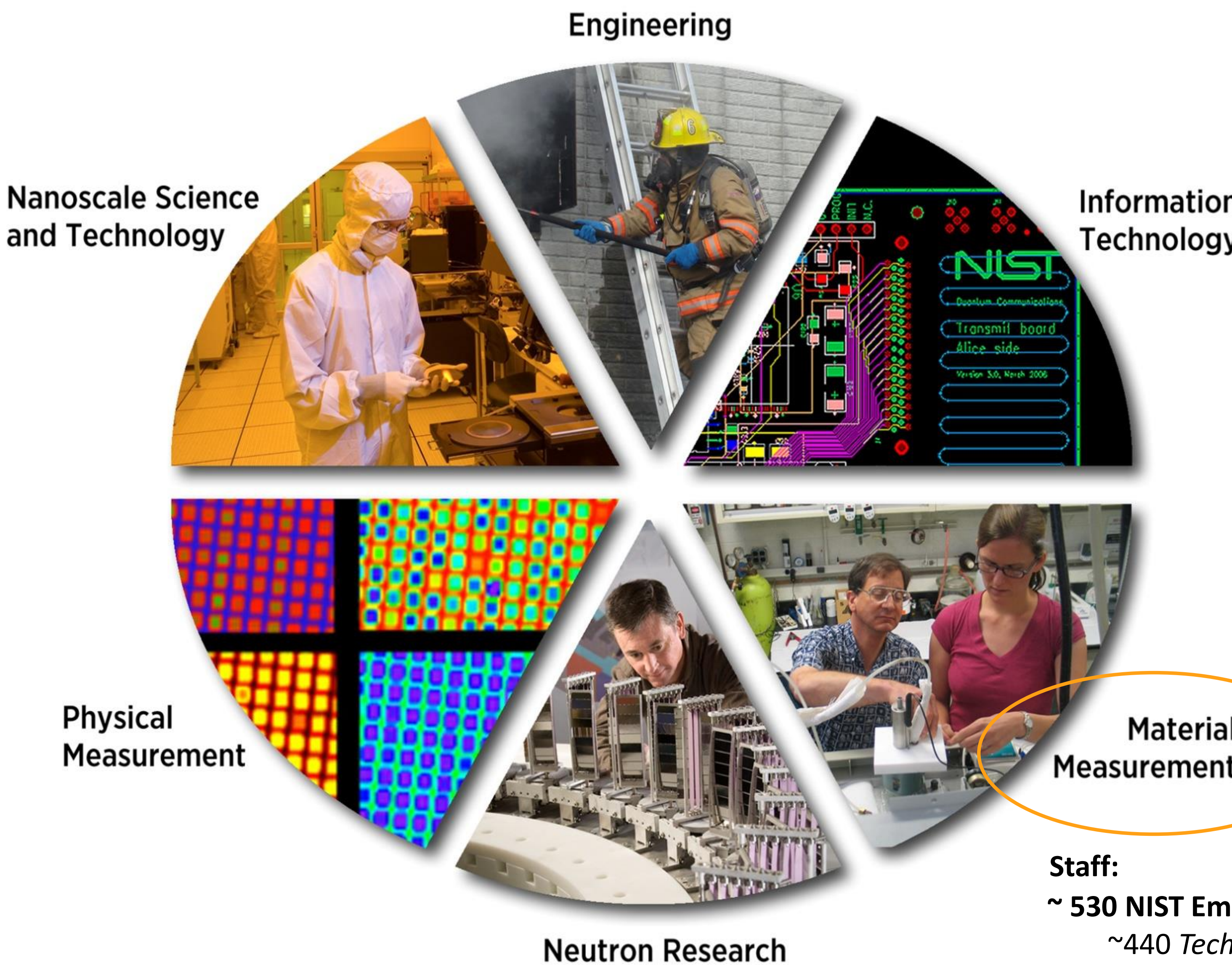
➢ Standard Reference Data
  100 types available
  130 million datasets downloaded/year

➢ Standard Reference Materials
  1,300 products available
  33,000 units sold/year


Main campus – Gaithersburg, Maryland


Boulder campus – Colorado

6 Laboratories and User Facilities at NIST



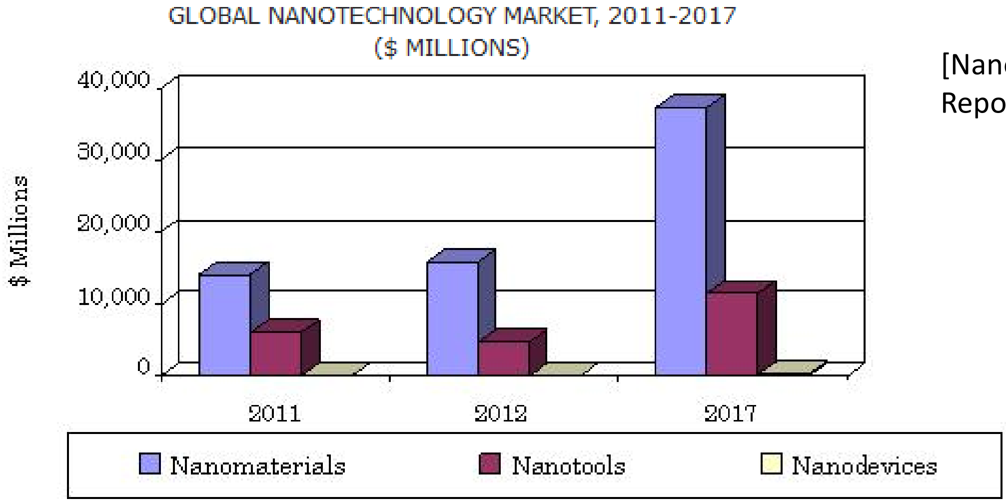
Staff:

~ 530 NIST Employees

~440 *Technical Staff*

~ 350 NIST Associates

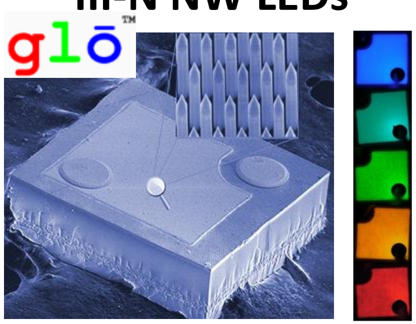
Nanowire devices: Hype or a New Horizons?

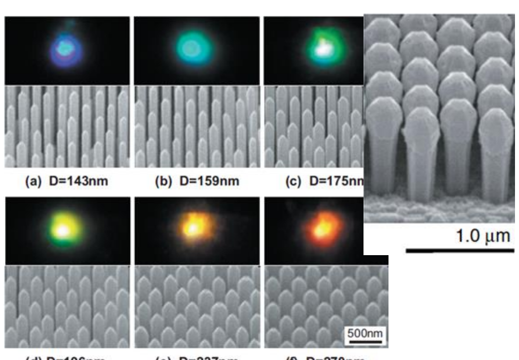


[Nanotechnology: A Realistic Market Assessment; Report Code: NAN031D, Published: September 2012]

Semiconductor nanowire front-runners:

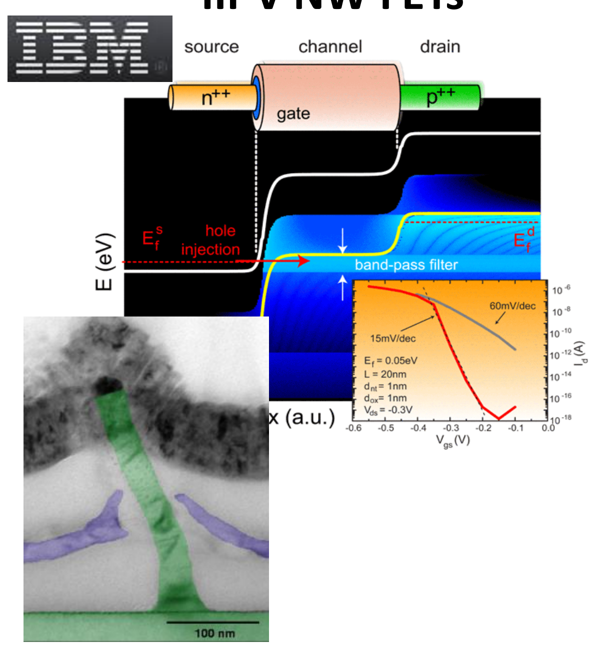
III-N NW LEDs



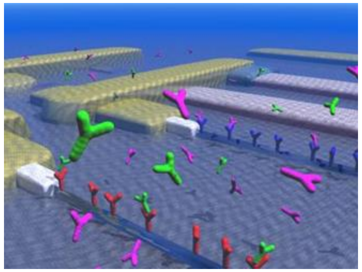


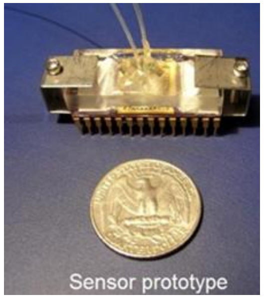
Sophia University (Japan)

III-V NW FETs



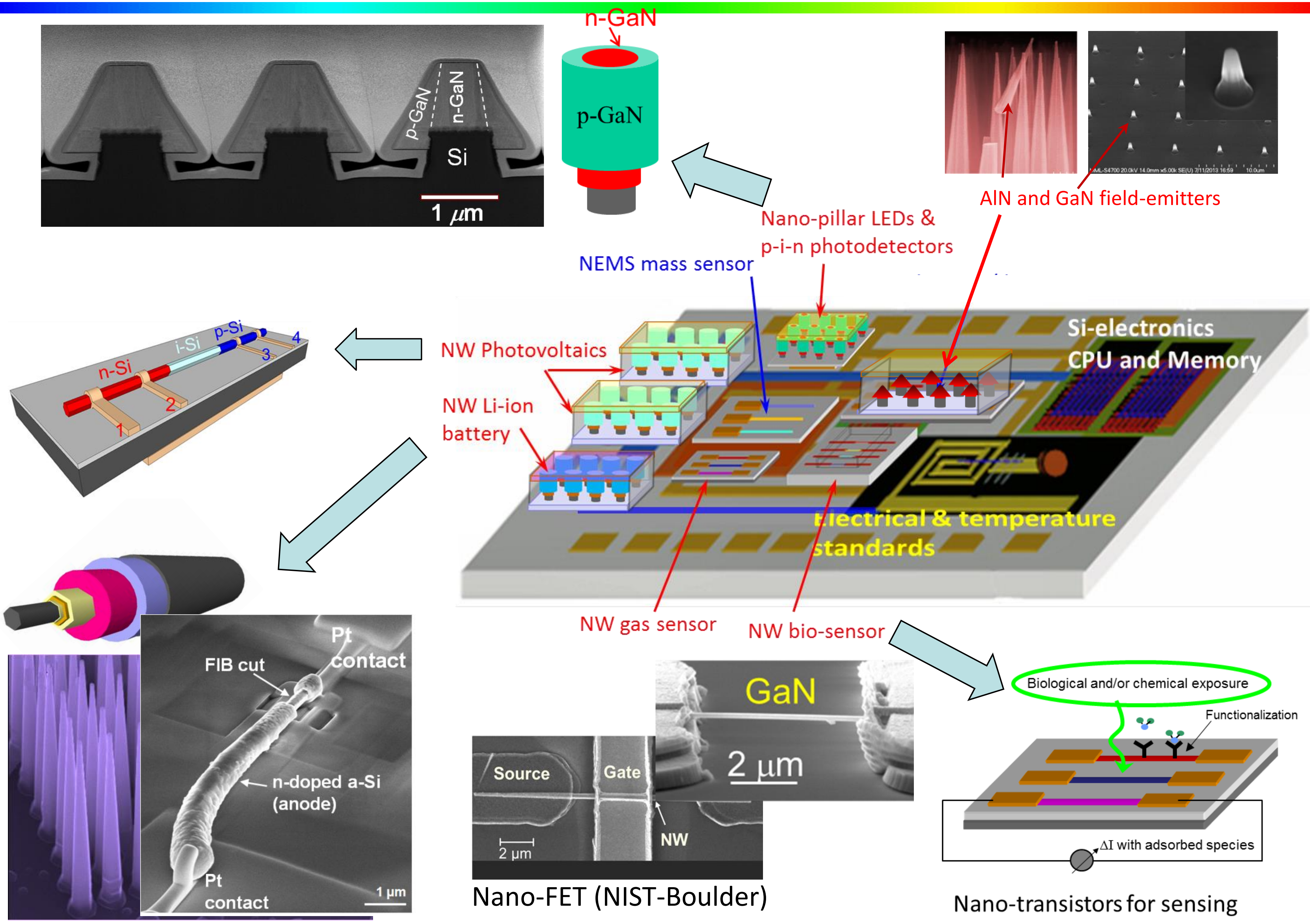
NW gas- and bio- sensors





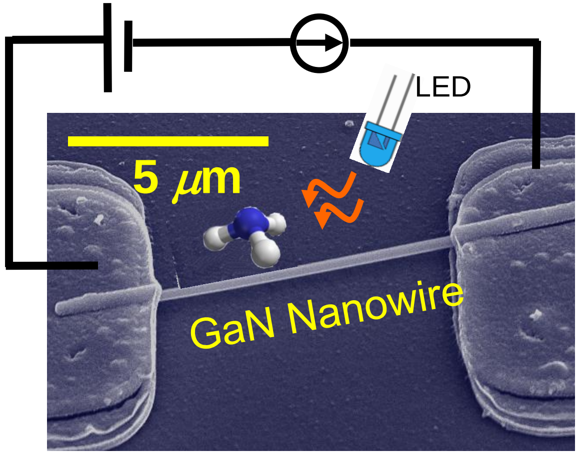
Harvard, Technion, NIST, etc.

Integrated nanowire devices on a chip

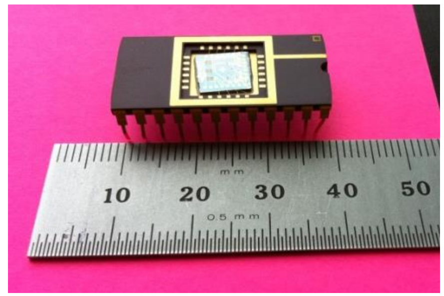


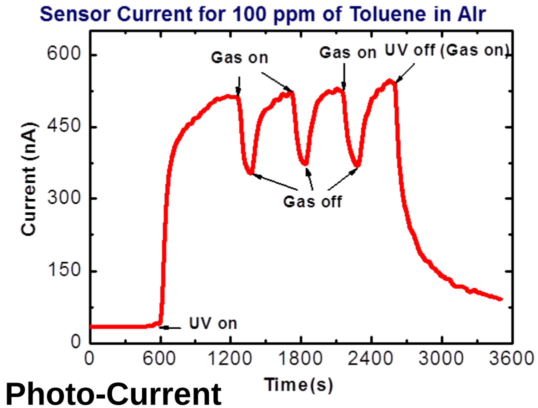
GaN nanowire chip-scale gas sensors

Nanowire Photoconductive Chemiresistor

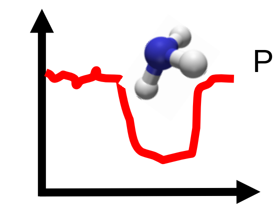


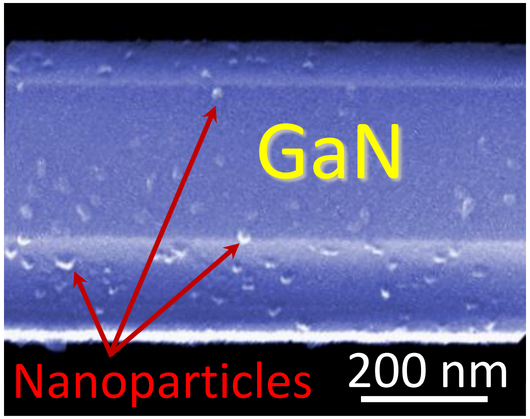
Actual Sensor Chip

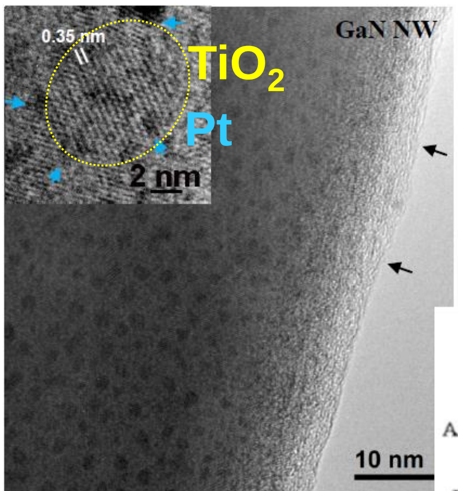




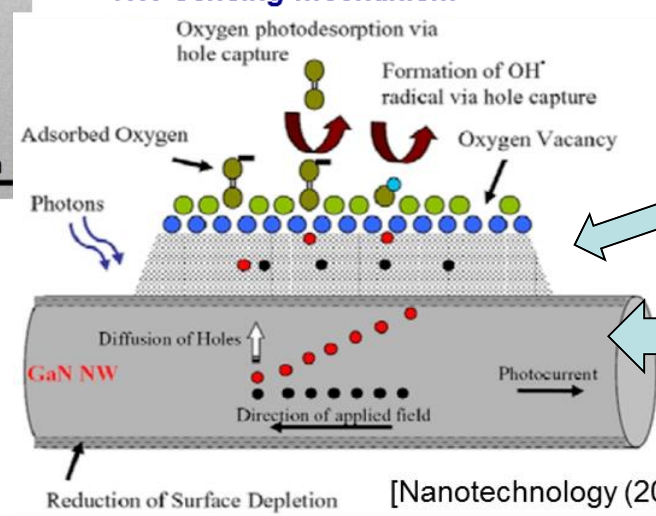
Sensor Photo-Current







NW sensing mechanism



Catalytic nanoparticle

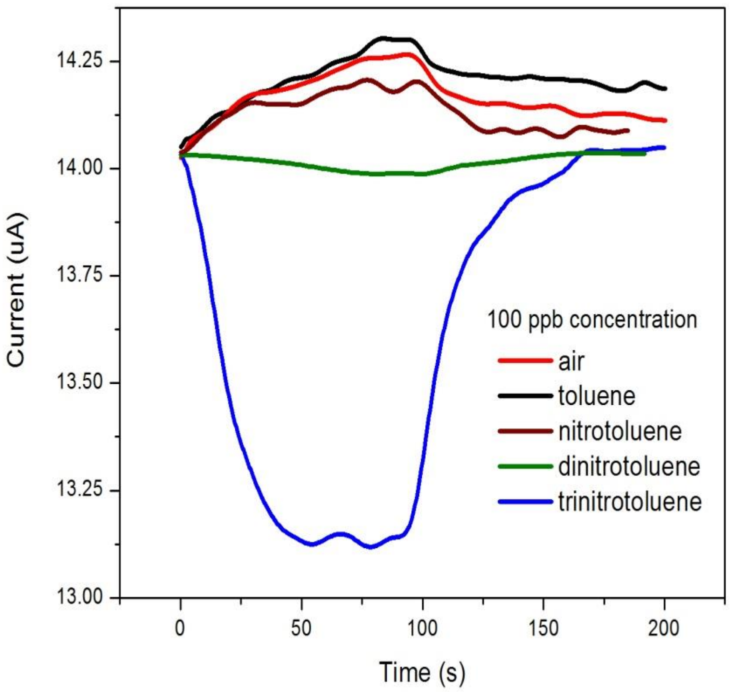
nanowire

[Nanotechnology (2011) 22 295503]

Sensing Using GaN NW-TiO_2 Nanocluster Hybrids

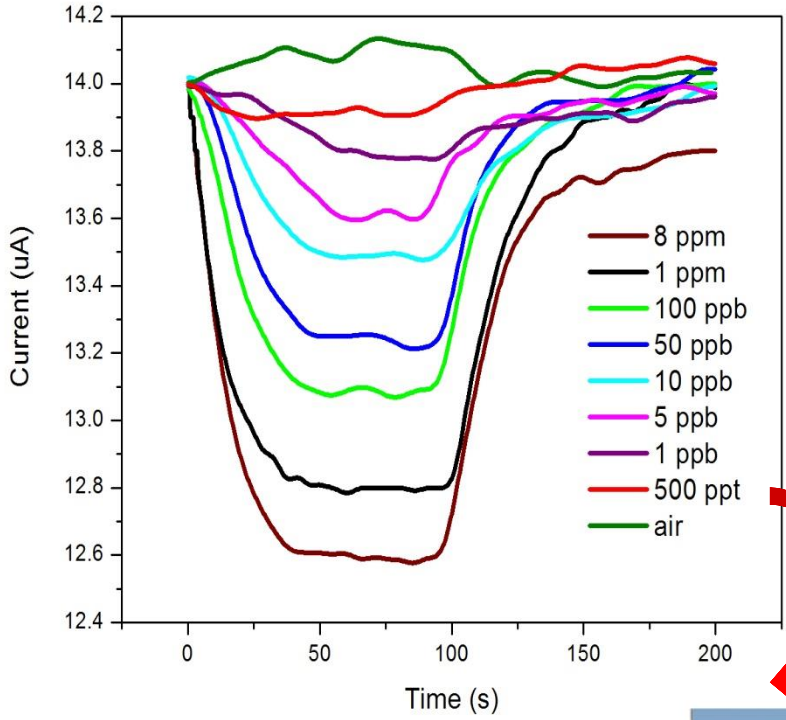
IEEE Sensors Journal (2013) 13, 1883

100 ppb of chemicals

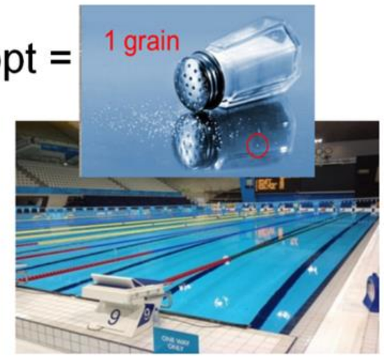


Response to TNT

Sensitivity: < 1 ppb



1 ppt =



- ❑ The response and recovery times for TNT are ~ 45s and ~30s
- ❑ The response and recovery times for other nitro-aromatics are ~ 60s and ~80s respectively

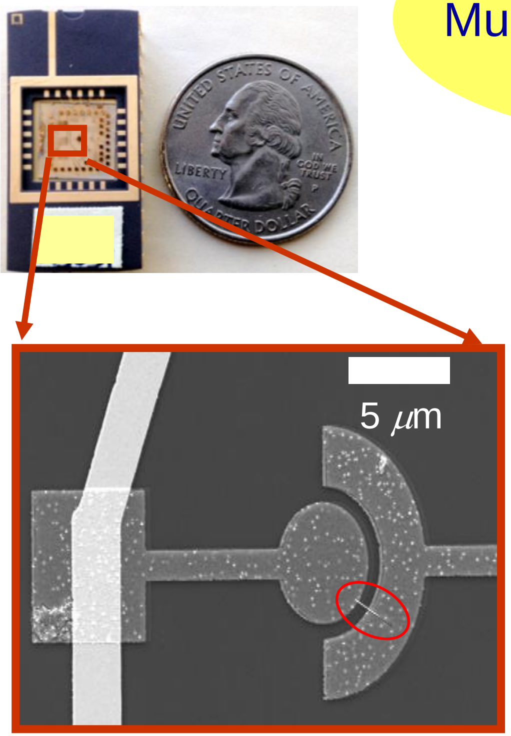
Advantages of Hybrid NW Sensor Technology

Ultra-sensitive
ppb/ppt concentration levels

Wide Sensing Range (ppb to %)
With one single sensor
Dynamic range modulation

Highly Selective

Multianalyte Capability

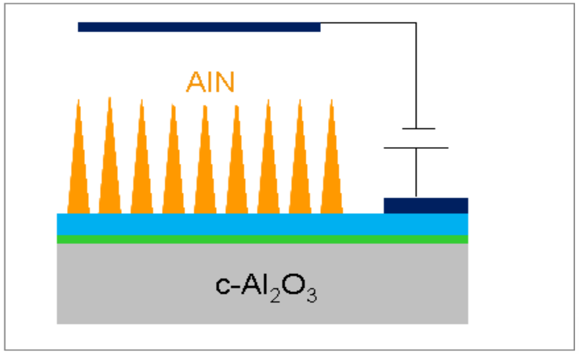


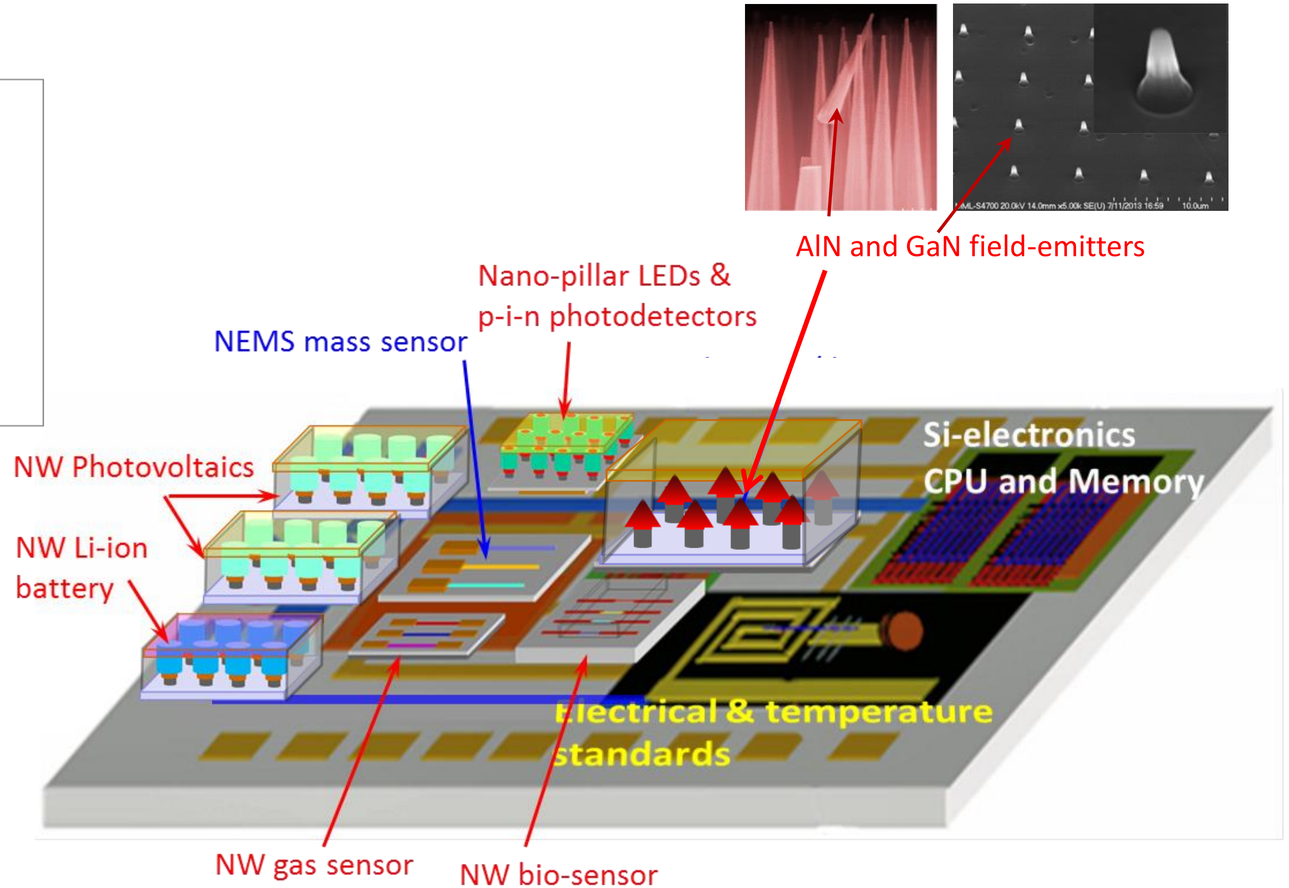
Small, Low-power
(use UV-light, no heater)

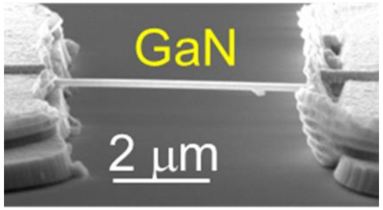
Long Operational Life, Reliable

Nanowire devices for "NIST-on-a-chip" program

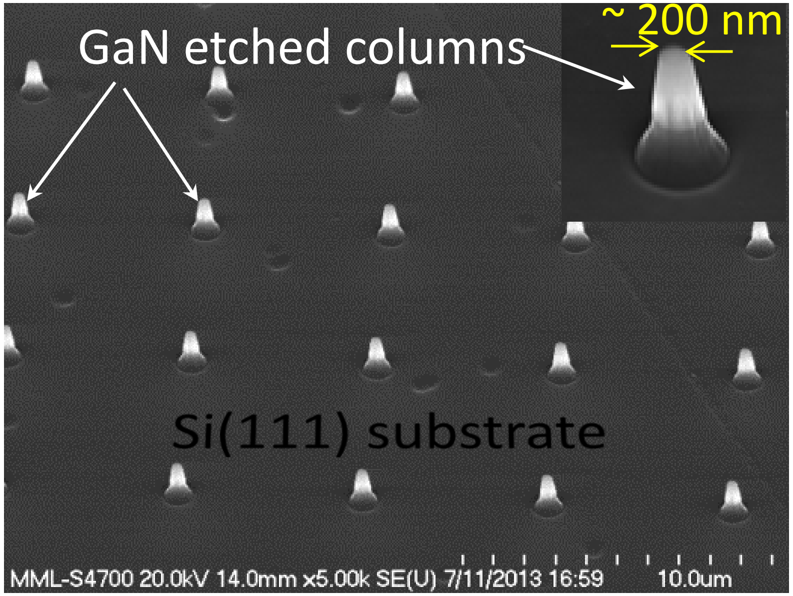
AlN NW Field-Emitter



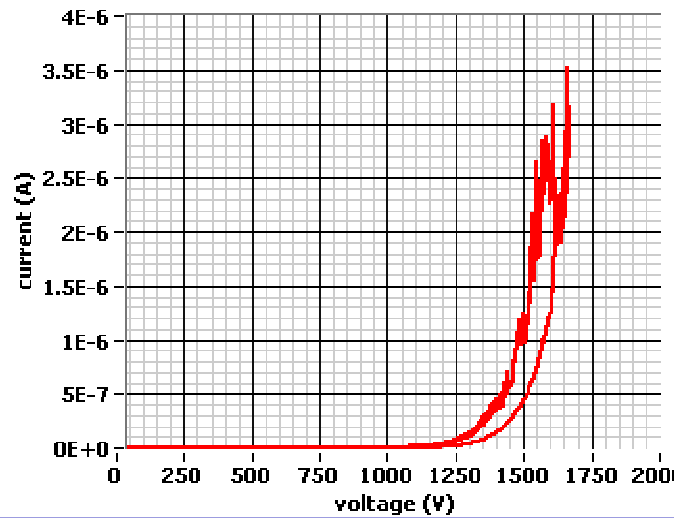




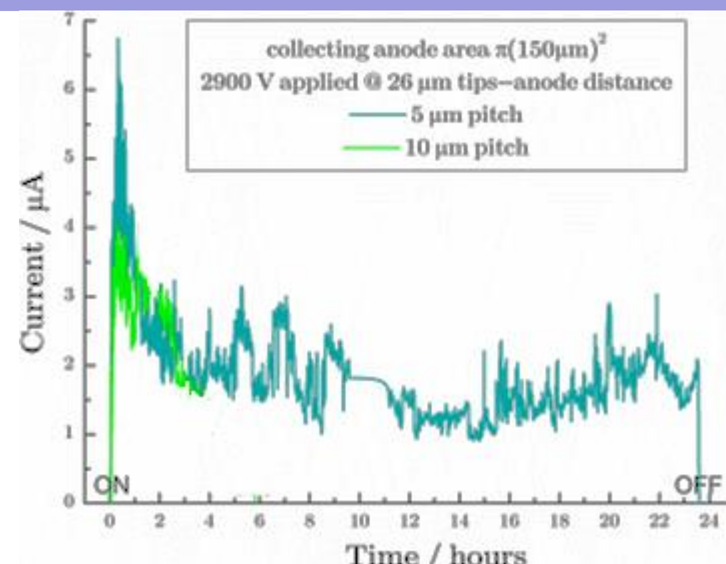
GaN top-down dry-etch: field-emission pillars



Field-Emission from Single GaN Nanocone



Emission Stability



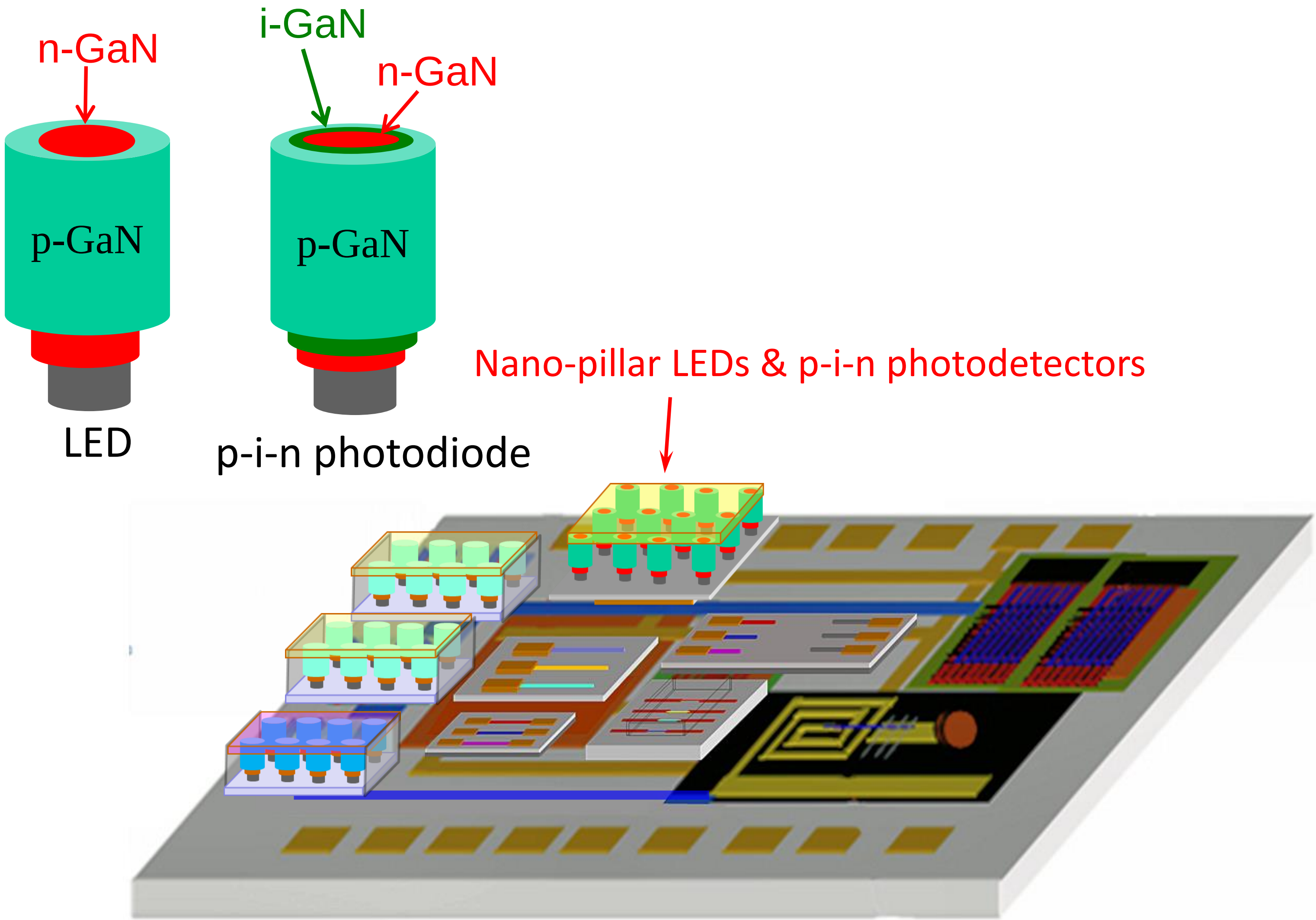
Compact, low-temperature field-emitters for electron source in accelerators

Argonne NATIONAL LABORATORY

Fermilab

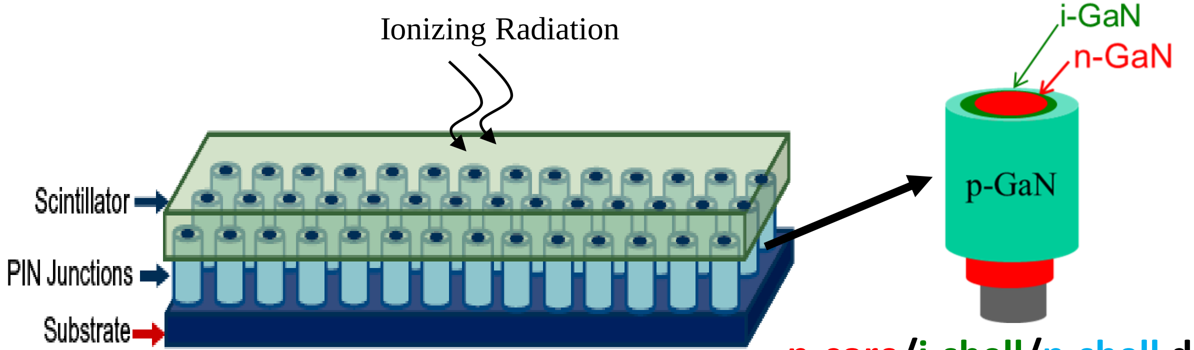
euclid TECHLABS

Nanowire devices: LEDs and Photodetectors



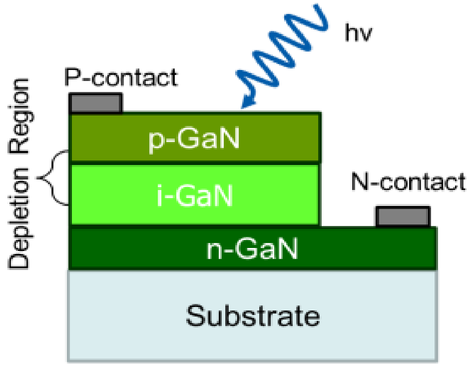
Array of Vertical p-i-n GaN Photodetectors

Goal: Realization of light-weight, low noise, high efficiency nanowire based detectors for wavelengths <425nm coupled to scintillators, suitable for replacing PMT



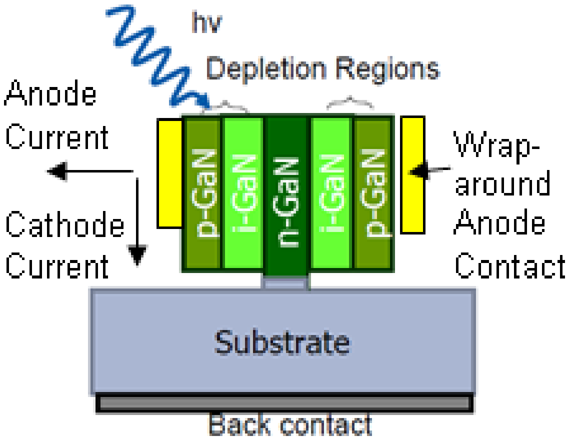
n-core/i-shell/p-shell detector

Conventional thin-film p-i-n device



Conventional GaN PIN Photodetector

Proposed Vertical Architecture

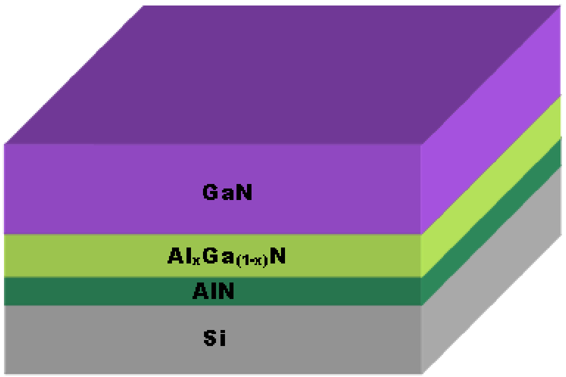


- Efficient photo-generation of carriers due to direct light access and trapping
- High active surface area
- Utilization of non- and semi-polar GaN surfaces
- Unique nanoscale characterization capabilities

Fabrication: top-down (etch) + bottom-up (growth)

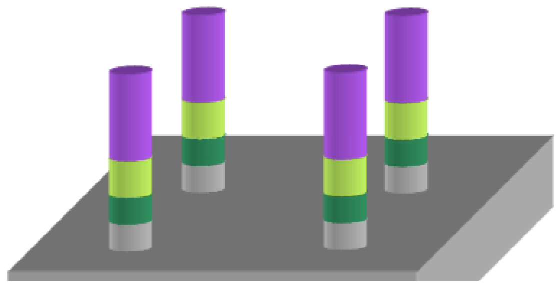
STEP 0

GaN Thin-Film Epitaxial Growth on 4 inch Si Substrates



STEP 1

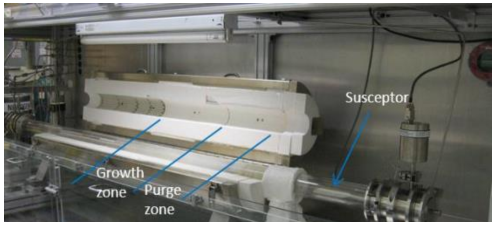
Large-area GaN Cores using Lithography and Etching

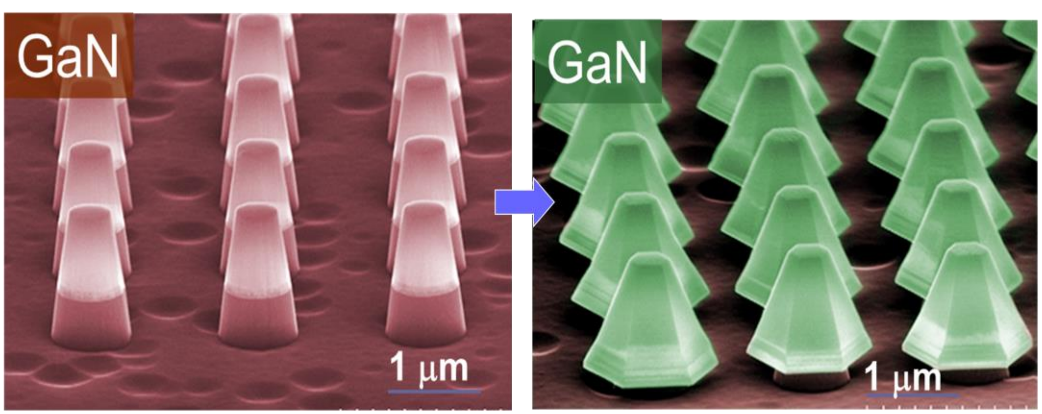


STEP 2

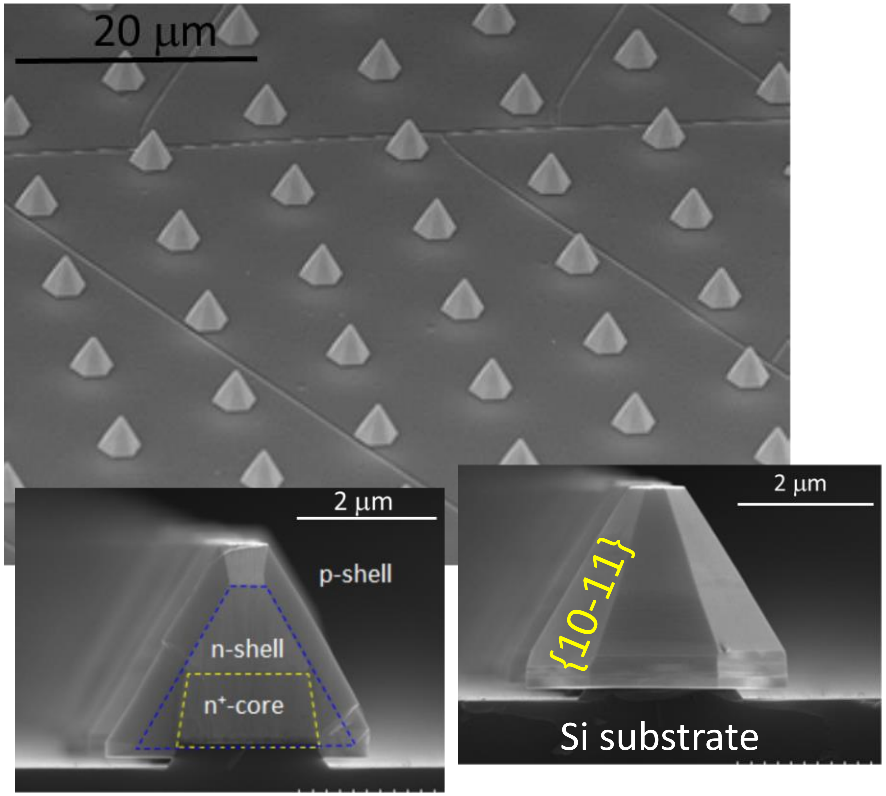
Core-Shell p-i-n Structures by Selective Area Epitaxy

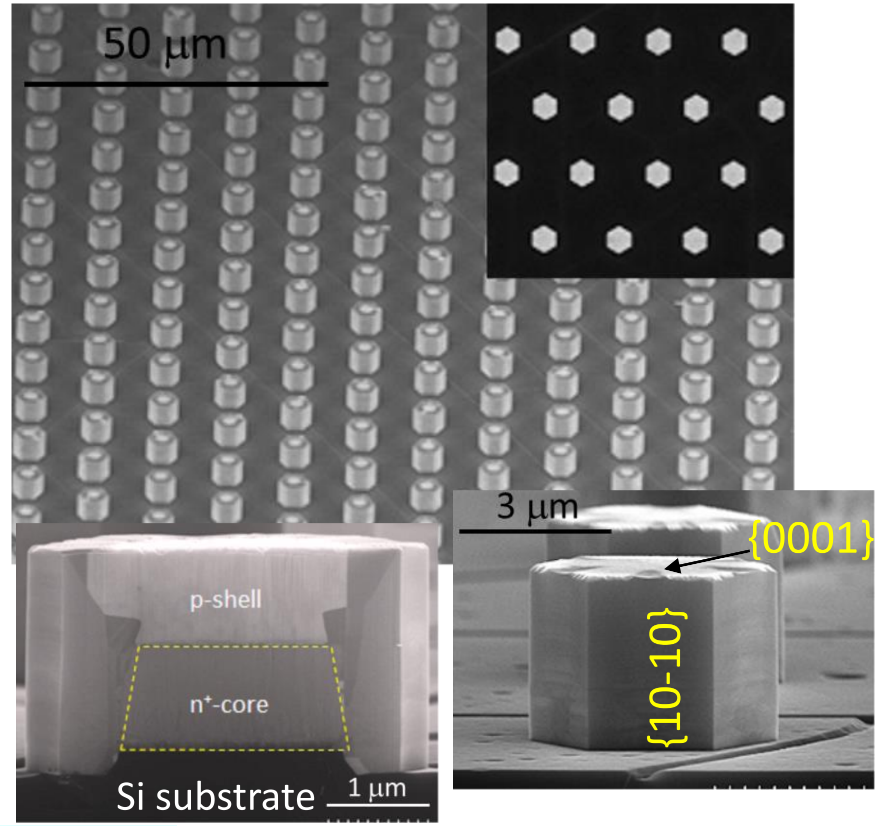
Halide Vapor Phase Epitaxy (HVPE)



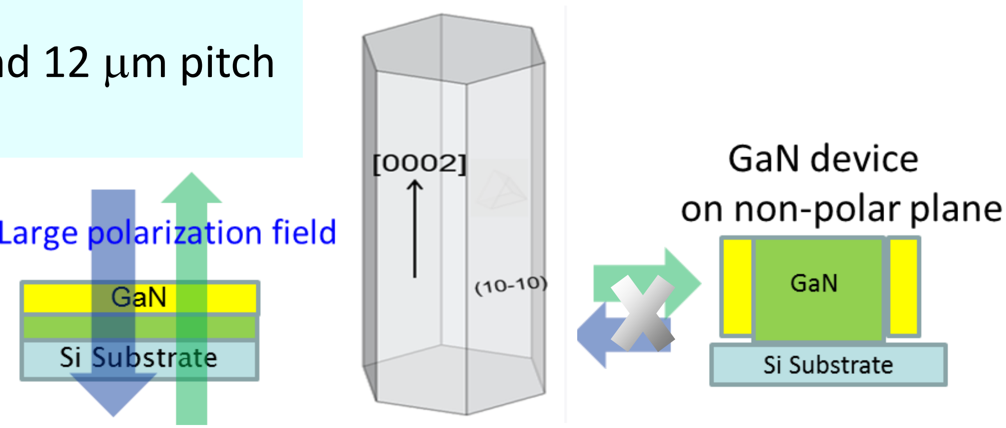


Step 2: Array of Core/Shell Pillars by HVPE growth



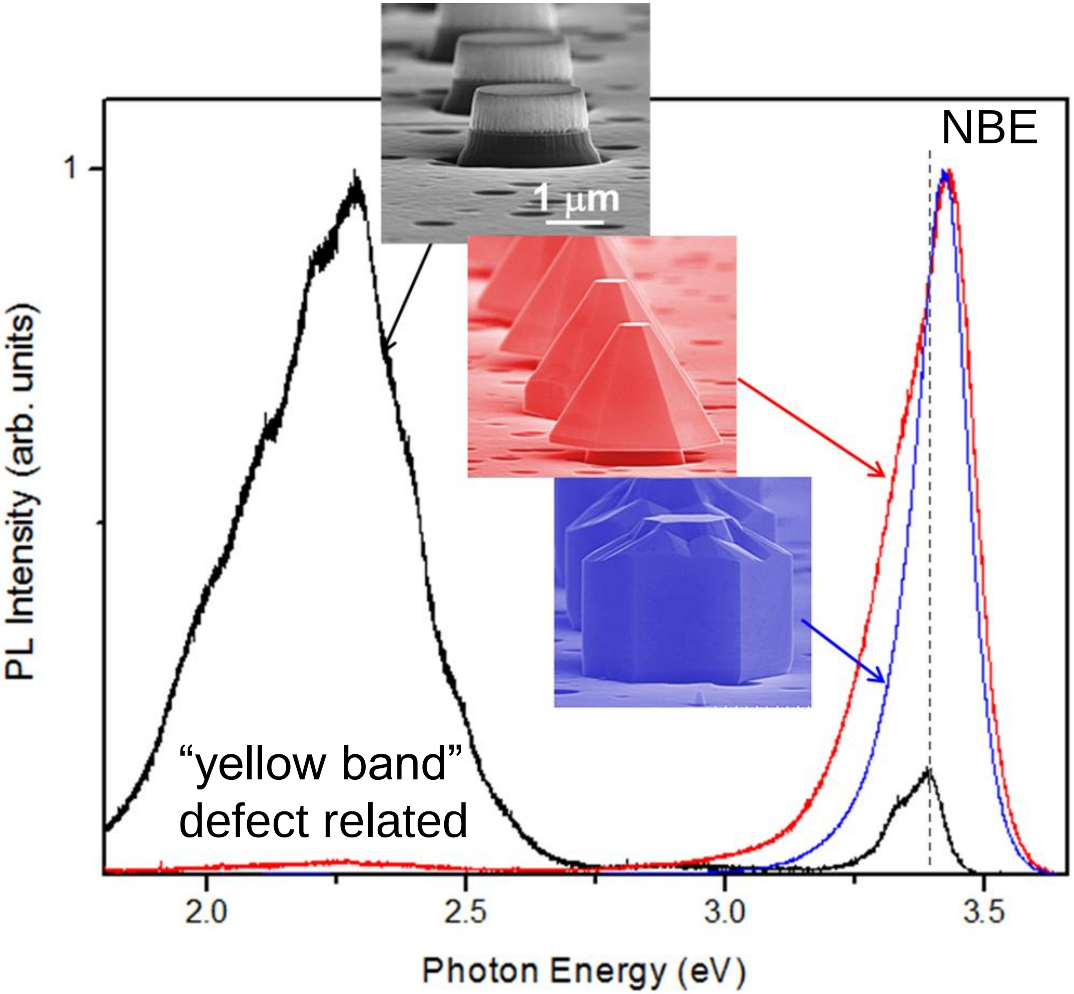


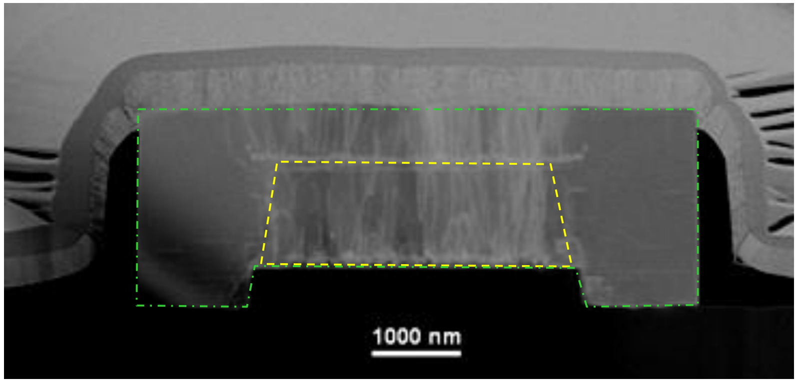
- ❑ 5 mm x 5 mm arrays
- ❑ ICP-etched pillars with 2 µm diameter and 12 µm pitch
- ❑ controlled GaN shell shape and doping

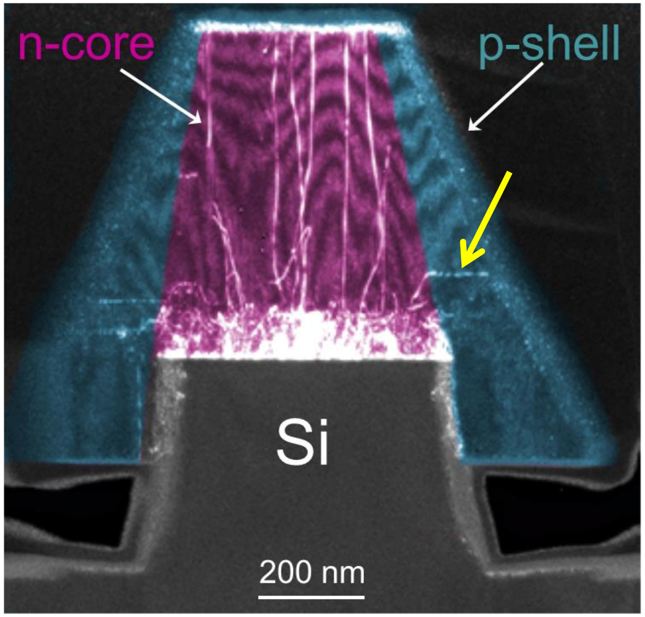


- ❑ Absence of polarization on m-plane => better control of device performance

PL on n-Core and n- and p- Shells



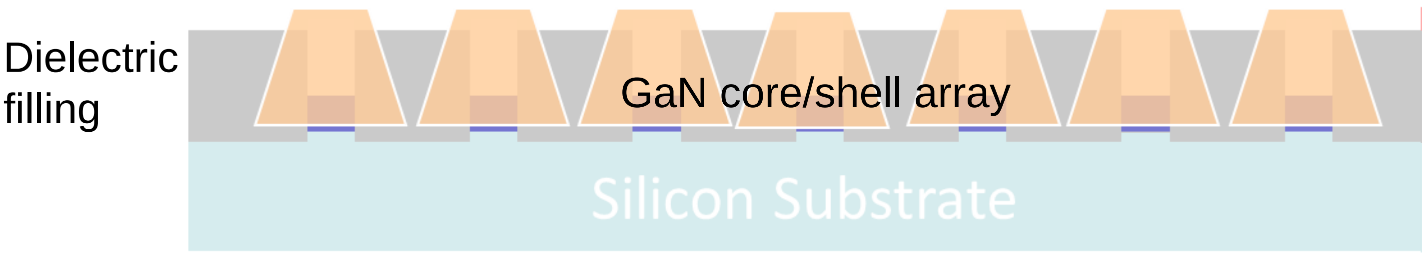


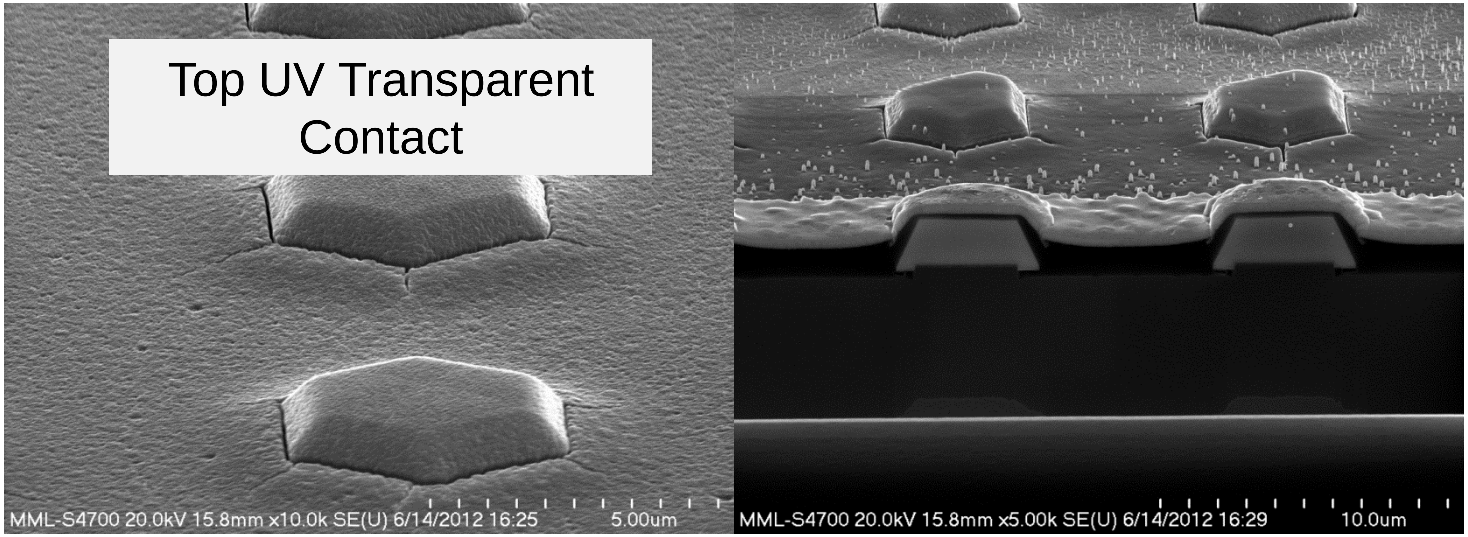


- ❑ High structural quality material in the shell:
  - ✓ Almost dislocation-free

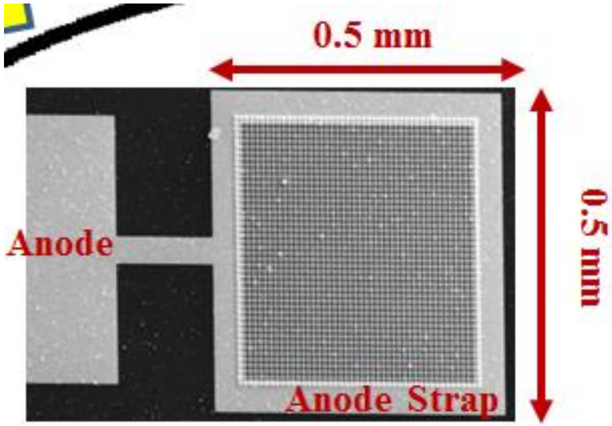
- ❑ Lower strain as Raman & PL data suggest

Developing UV Transparent Conducting Top Contact

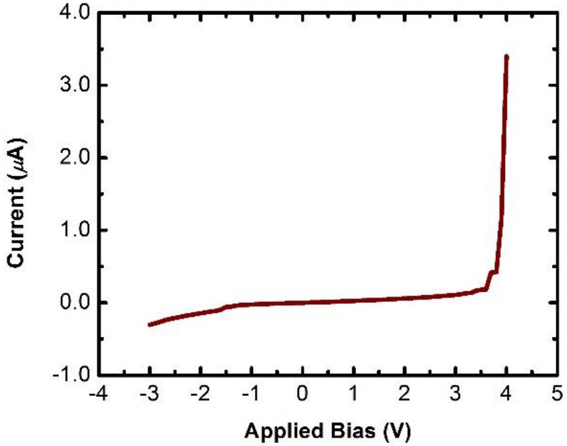




Photodetection Using p-i-n Core/Shell Diodes

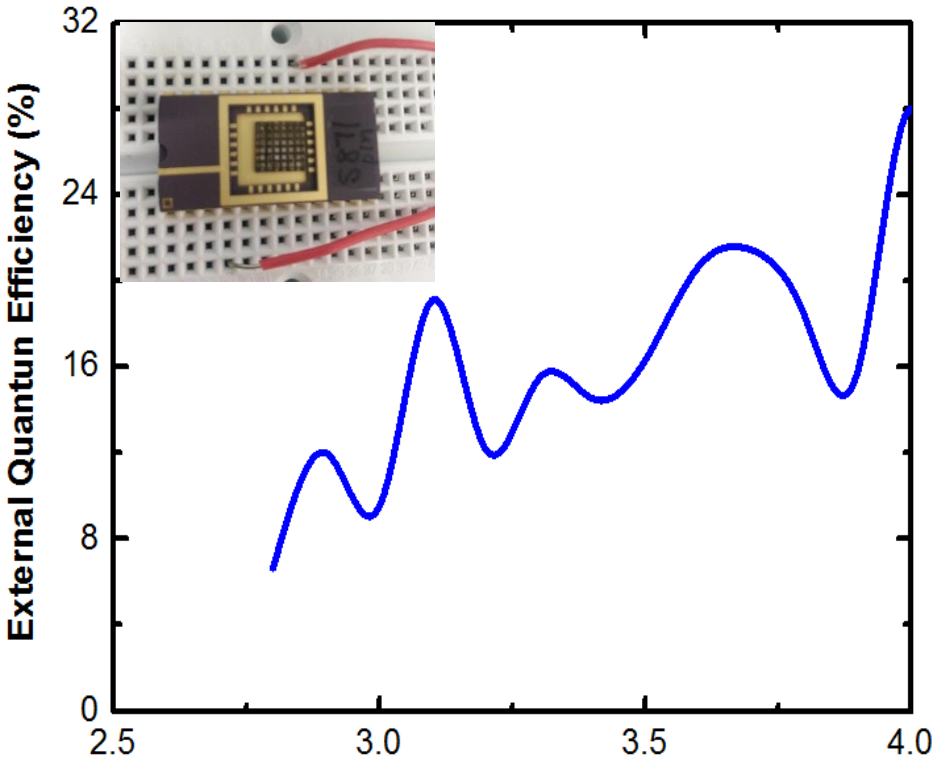


~ up to 2500 individual detectors connected in parallel



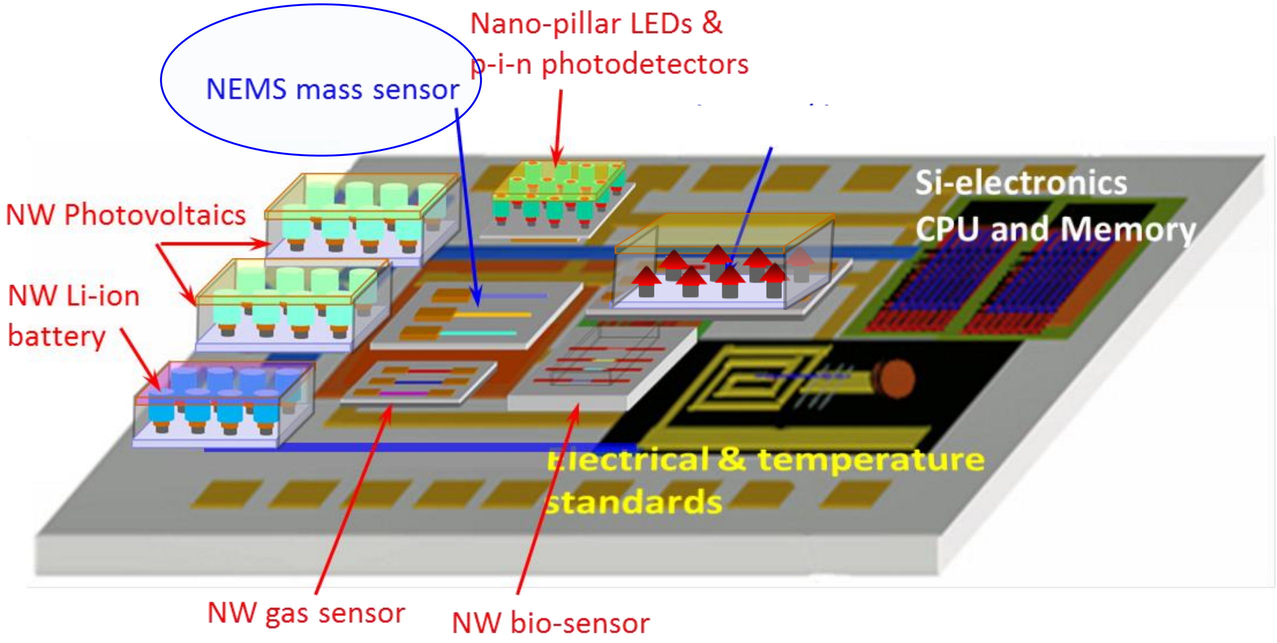
I-V from p-i-n Diode Array

Room-Temperature External Quantum Efficiency

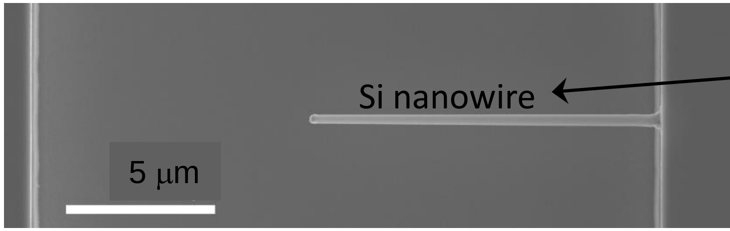


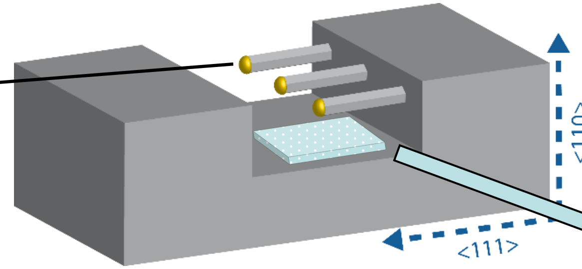
Best EQE ~ 25% at 3.5 V Reverse Bias

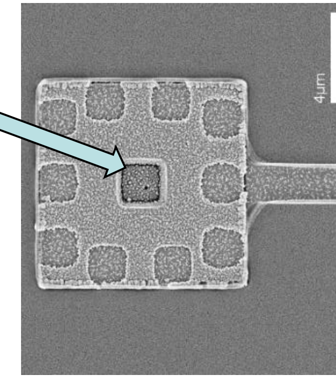
Nanowire Devices for “lab-on-a-chip”



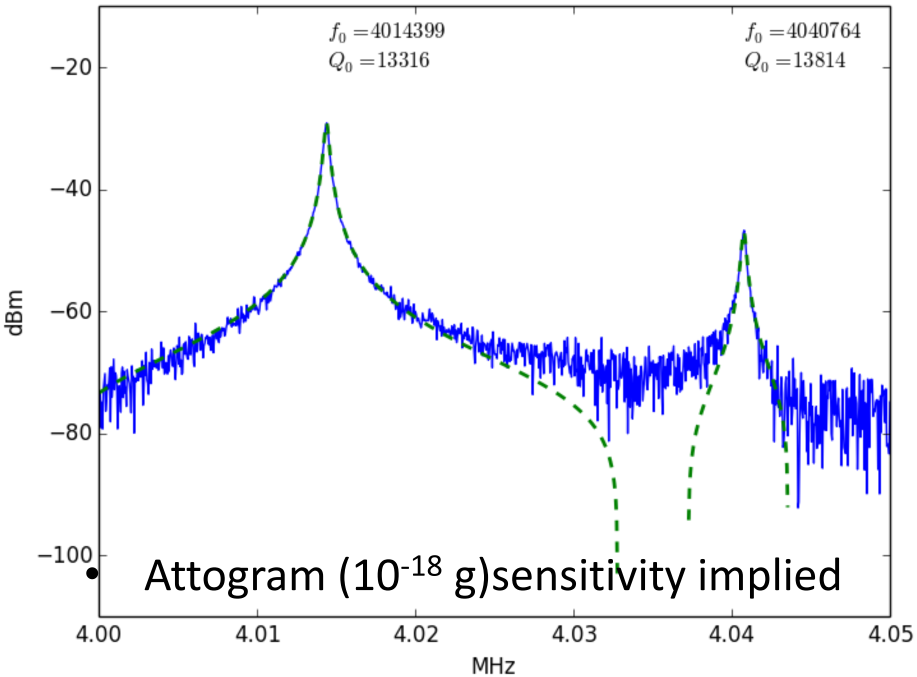
SiNW cantilevers for mass sensing (Brian Bryce)





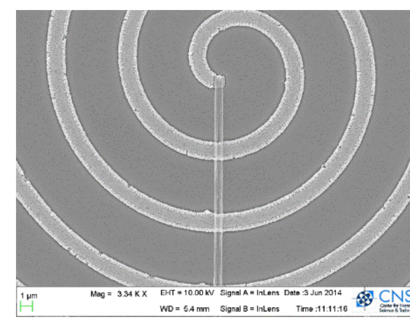


Integrated near-field photodiode



- Attogram (10^{-18} g)sensitivity implied

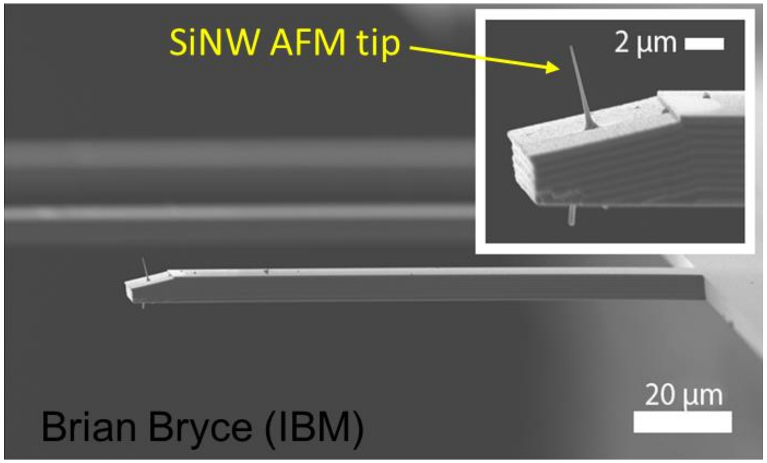
Electromagnetic coil actuator

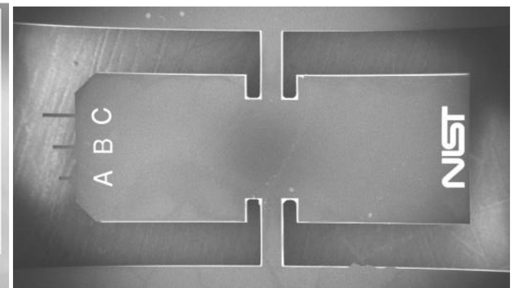


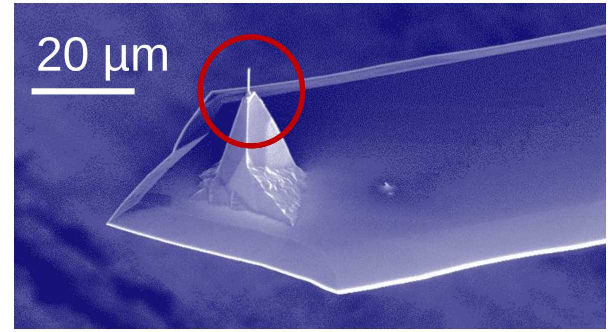
Next steps:

- Integrated optical detection with *near-field* diode (local Fabry-Perot cavity)
- Magnetic actuation? (Est. forces ~ 1 fN -> displacement ~ 10*Q*F)
- CCD integration for stroboscopic mass readout
- Light source integration

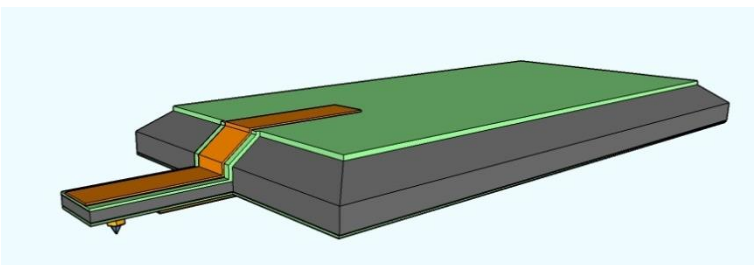
NW tips for multi-functional scanning probe



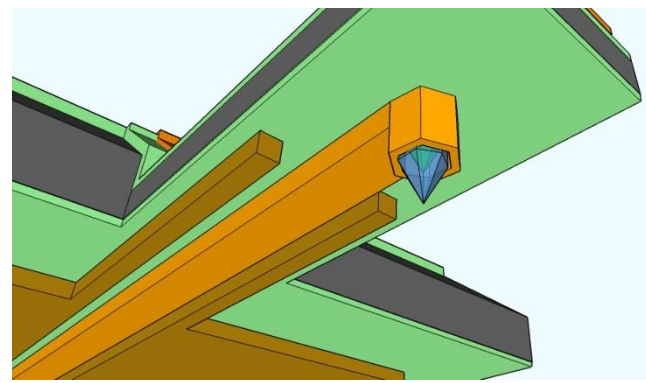




GaN NW AFM tip:
Kris Bertness, Norm Sanford
(NIST-Boulder)



NIST-Boulder

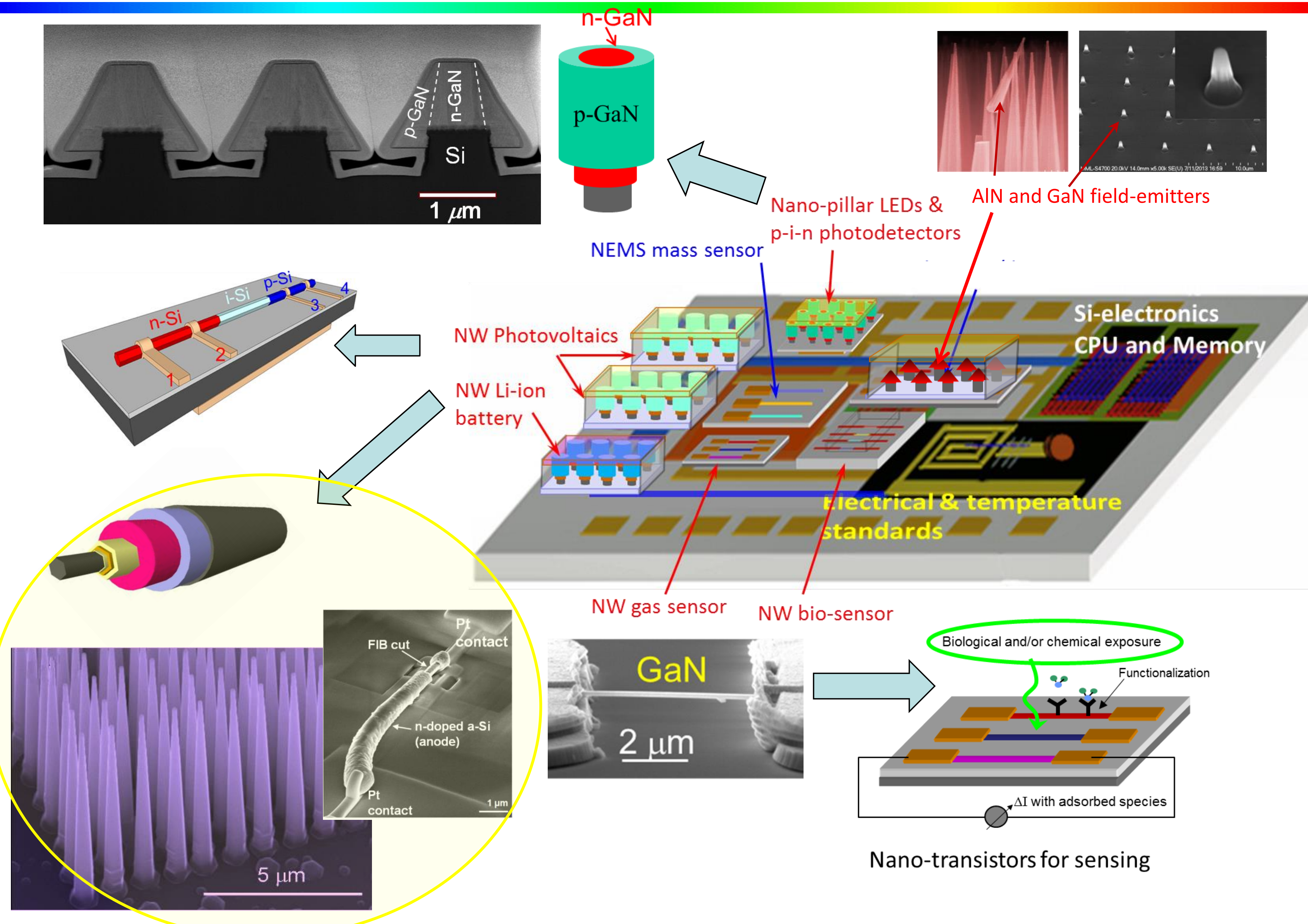


Combine near-field scanning microwave microscopy with near-field scanning optical microscopy using GaN nanowire LED as light source

- Stable tip shape = stable probe capacitance and greater sensitivity to device under test
- Robust tips for hundreds of scans
- 2x higher index of refraction for better light confinement

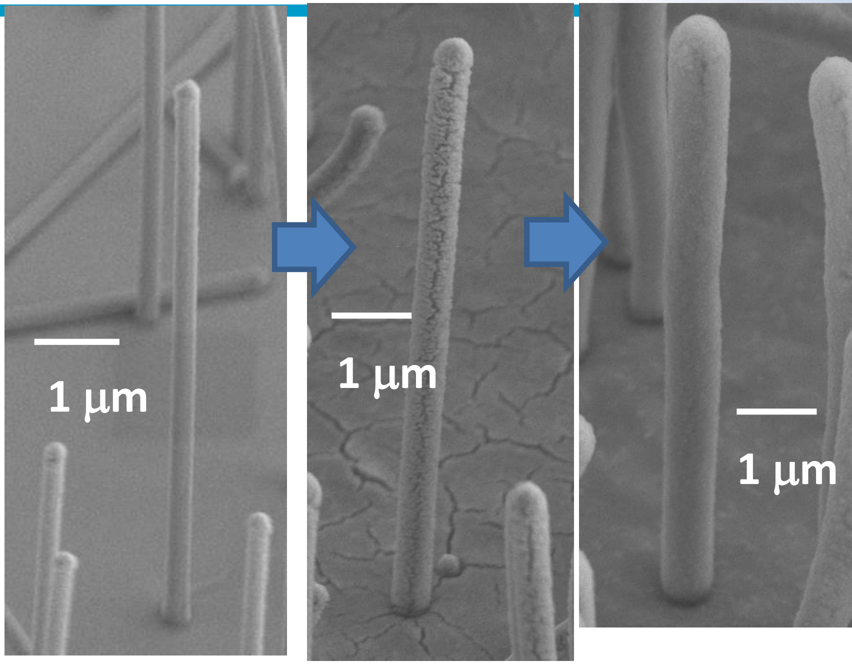
Kris Bertness, Norm Sanford (NIST-Boulder)

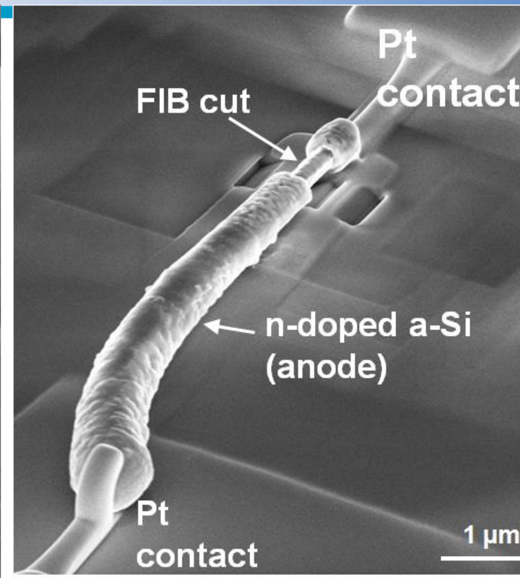
All solid state Li-ion nanowire battery

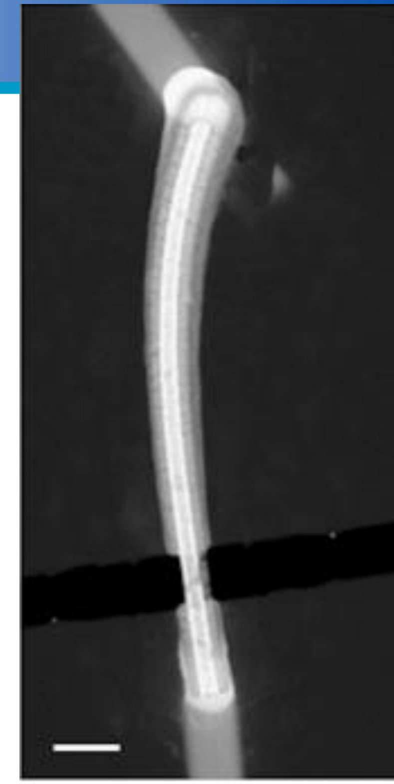


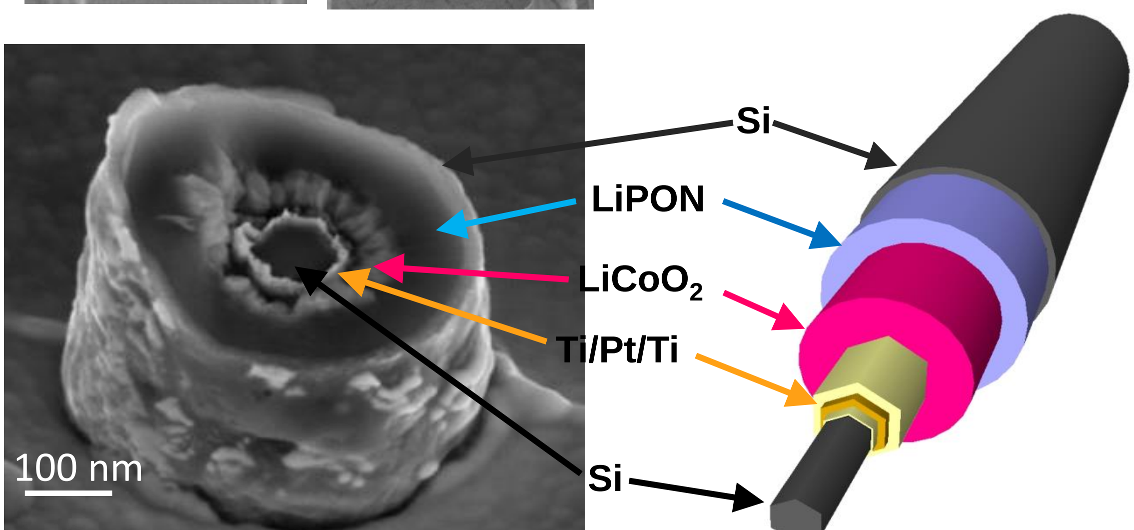
Fabrication of single nanowire Li-ion battery

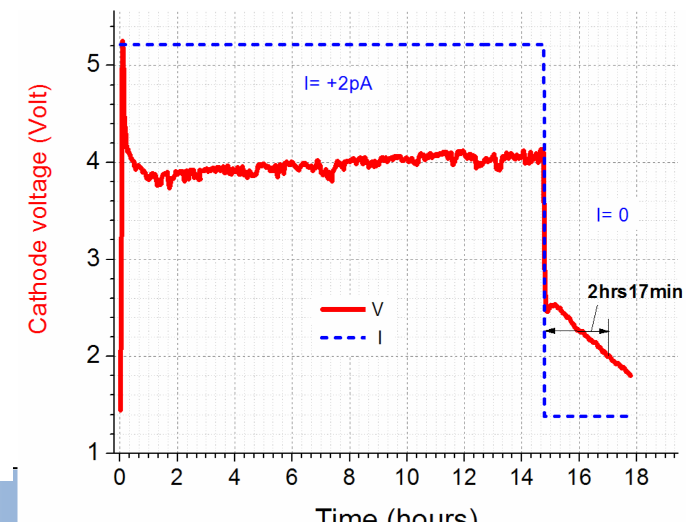
Nanoletters, 12 (2012) 505





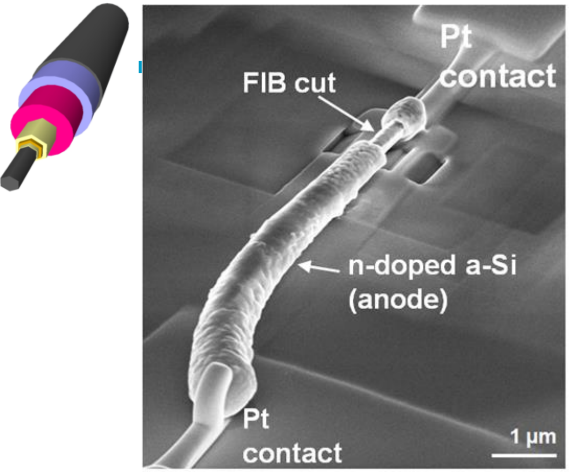


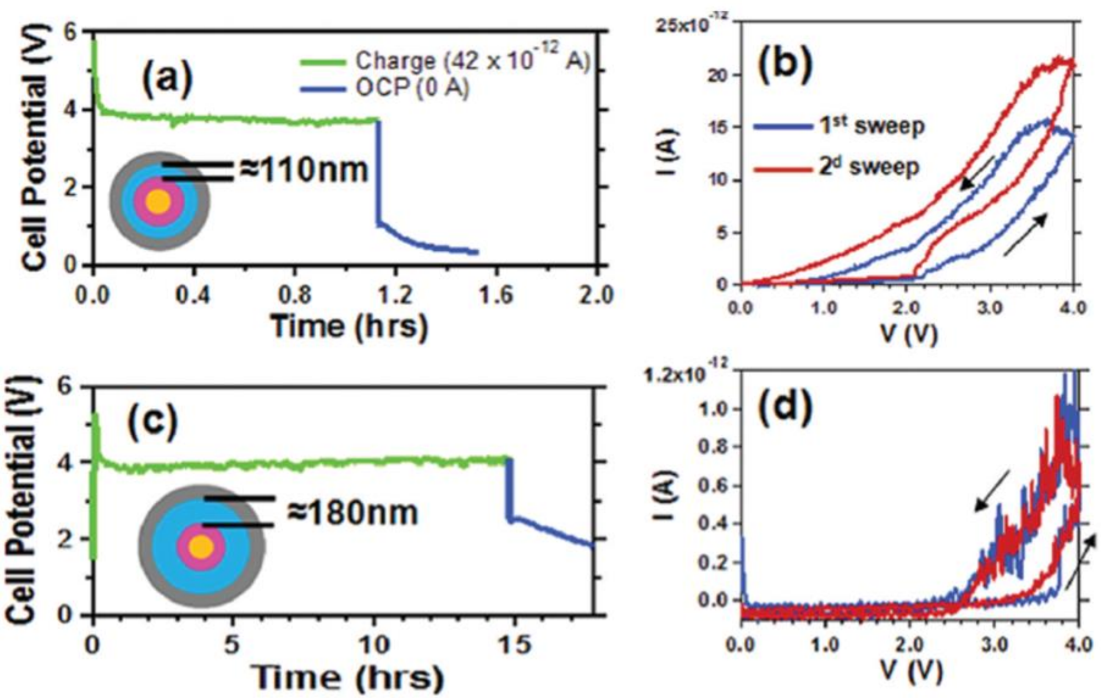


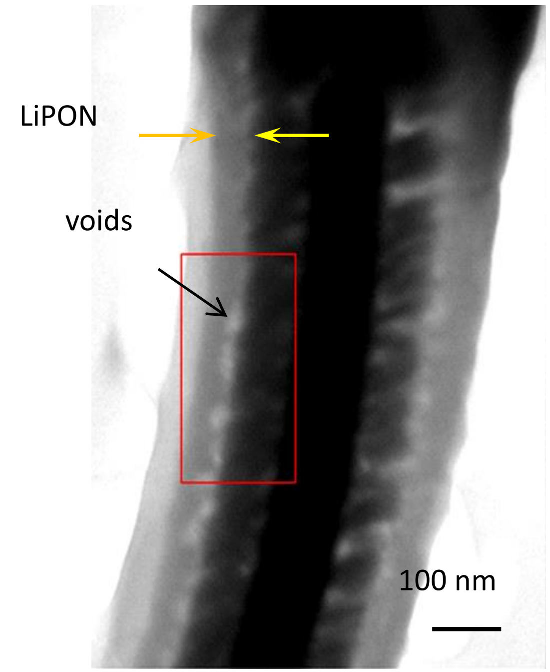


Single Si NW solid-state battery

Nanoletters, 12 (2012) 505

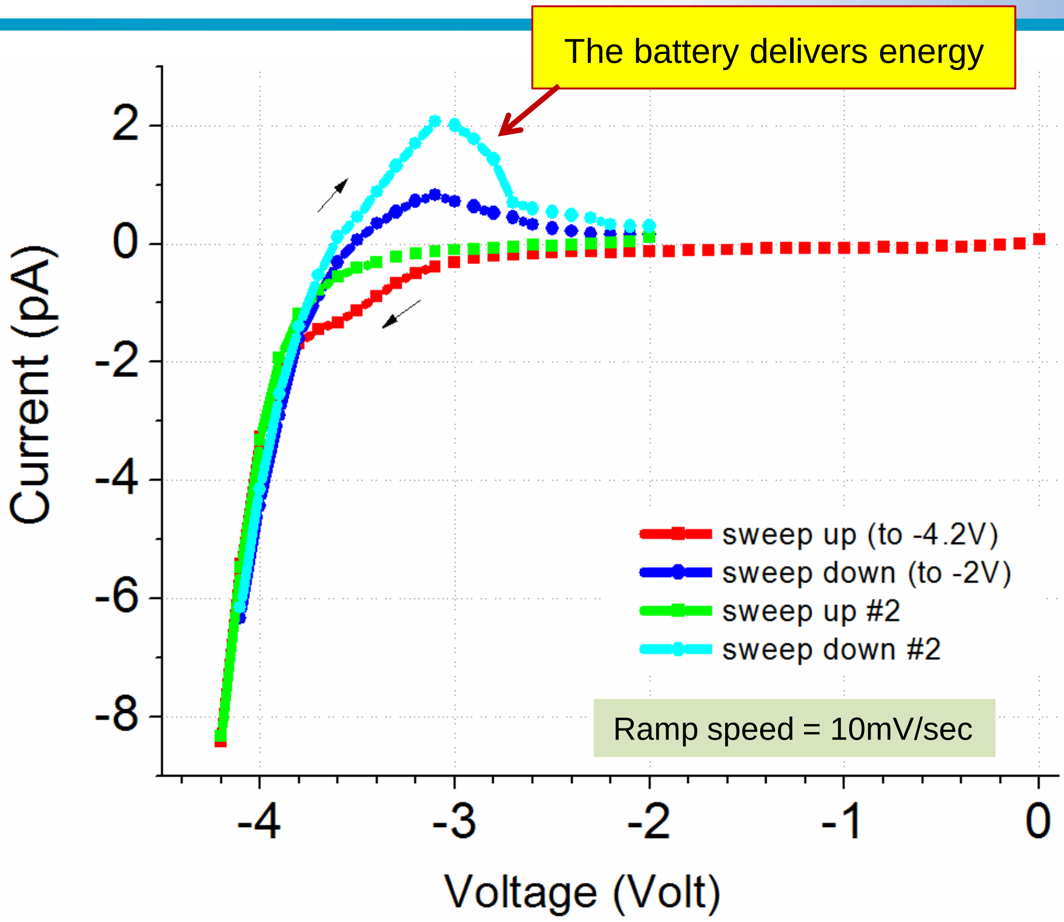




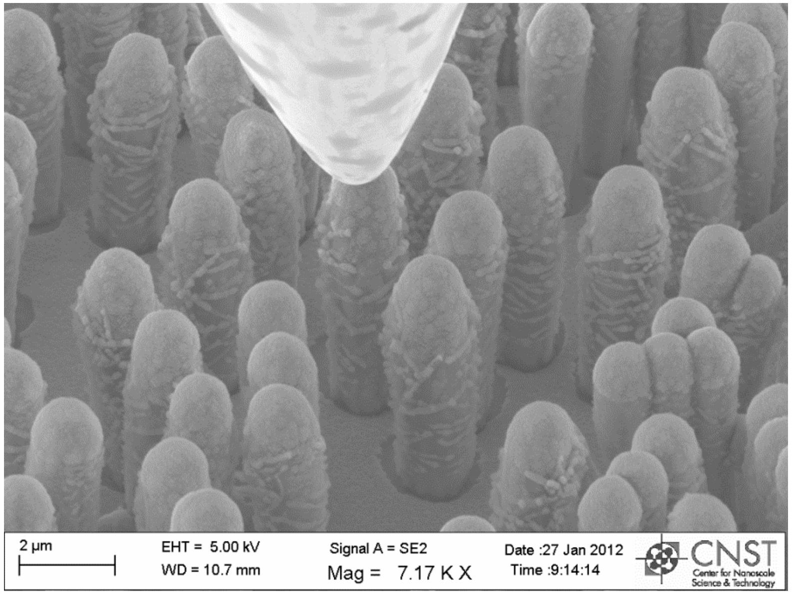


Electrolyte breakdown

Working single nanowire battery



During contact

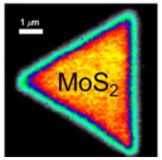


Measured NWB discharge capacity ≈ 0.03 pA h (discharge in 1min) ~ 3% of theoretical capacity.

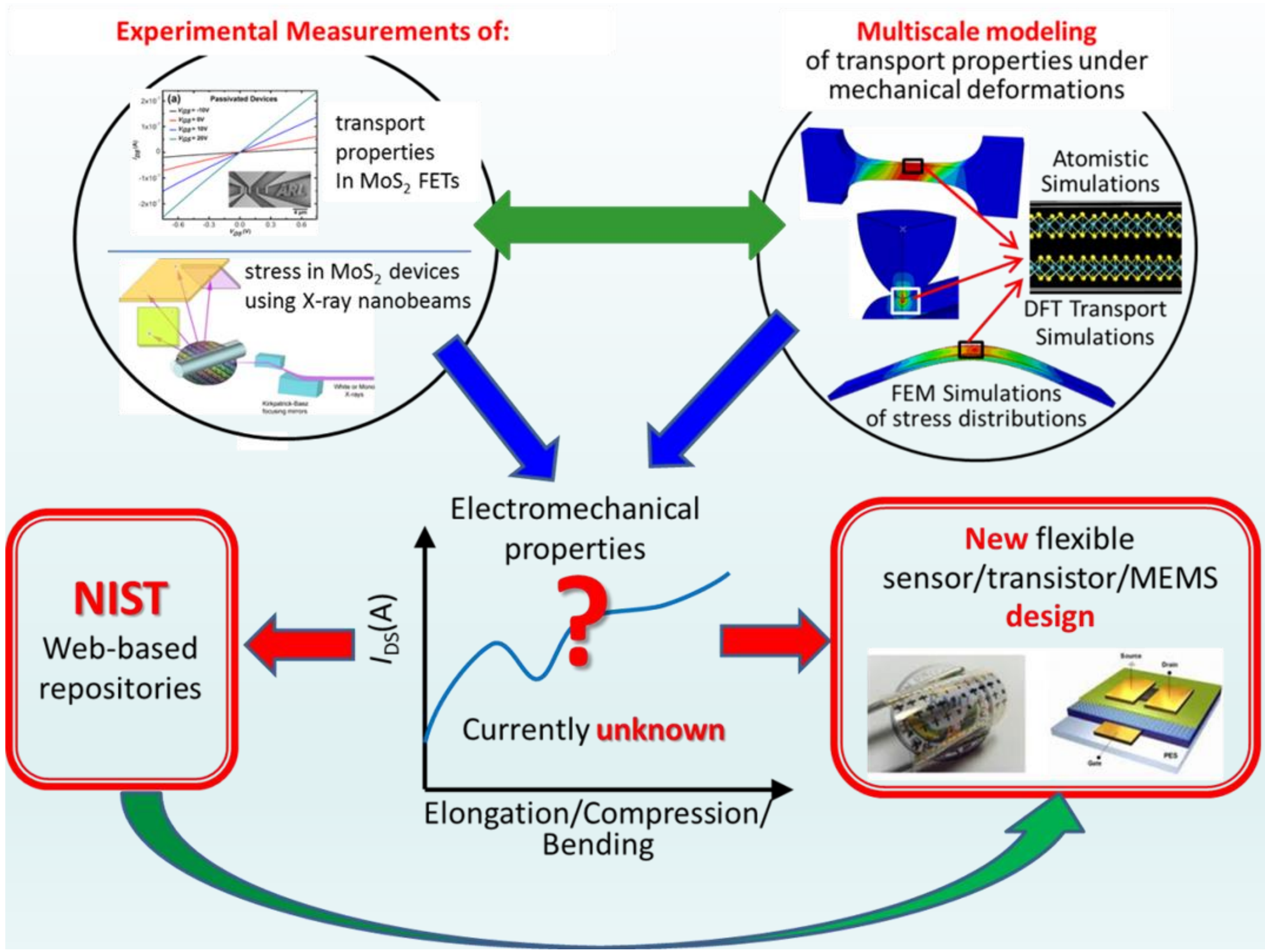
Peak discharge current = +2pA – single NWB
= +4pA – doublet NWB

Theoretical NWB capacity ≈1pA h (by $LiCoO_2$ volume).

2D layers: correlating materials modeling with expts.



CHiMaD: Center for Hierarchical Materials Design
(Mark Hersam, Lincoln Lahoun, Northwestern Univ.)



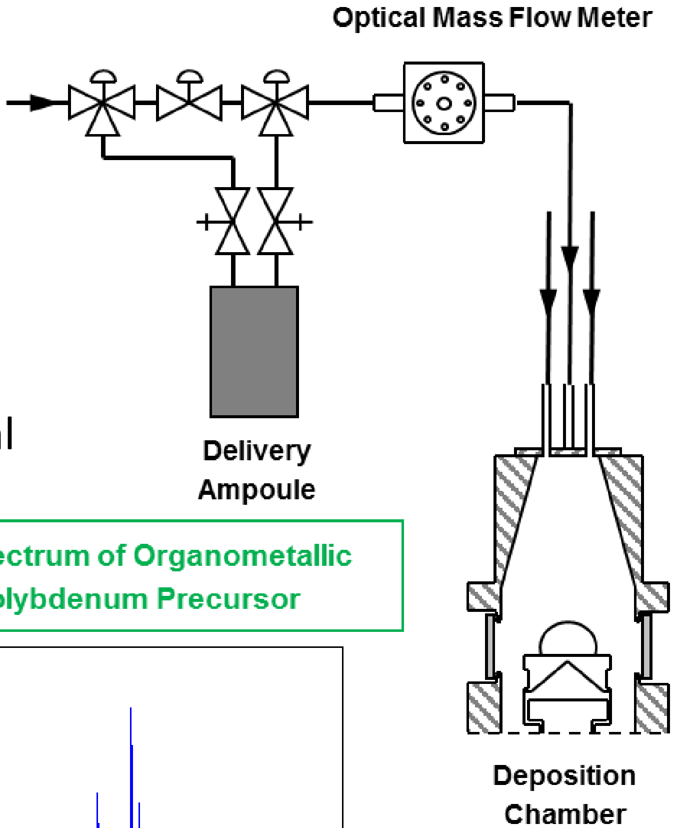
Characterizing Precursor Chemistry for MoS_2 CVD

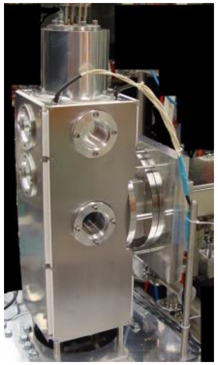
Project Team: J.E. Maslar, W.A. Kimes, B.A. Sperling (MML)

Goal: Identify CVD chemistries for large-area TMDC high-volume manufacturing

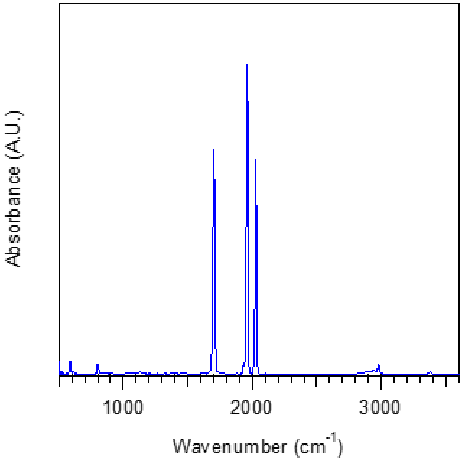
- *In situ* and *ex situ* study of decomposition and deposition chemistry during CVD
  - FTIR, Raman, Reflection-Absorption IR Spectroscopies
  - Range of precursors: organometallics; metal halides, carbonyls, and thiols

Schematic of Deposition System





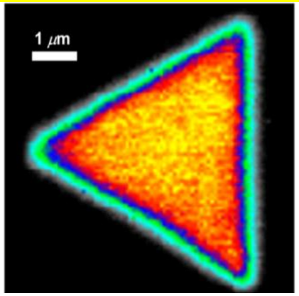
IR Spectrum of Organometallic Molybdenum Precursor



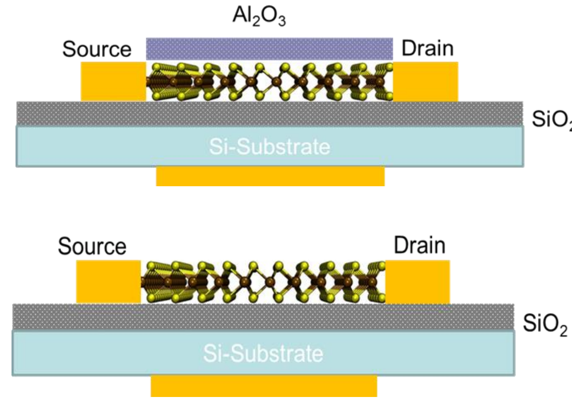
Spectrum recorded under delivery temperature of 100 °C and shows no evidence of decomposition

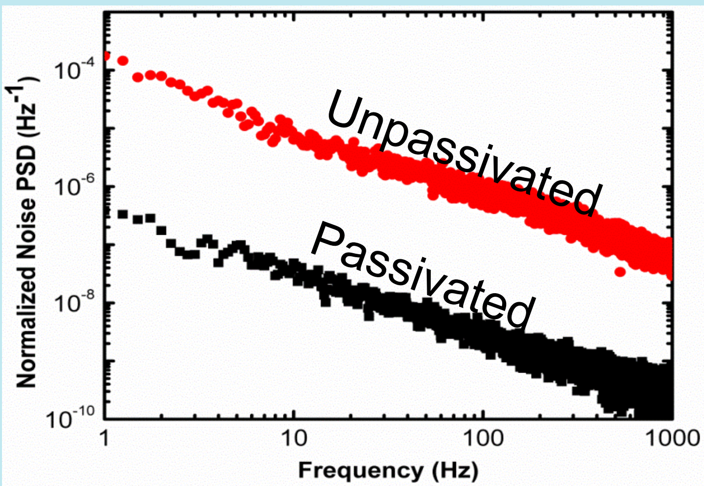
Transport measurements: low-frequency noise in MoS_2 FETs

CVD grown MoS_2 monolayer

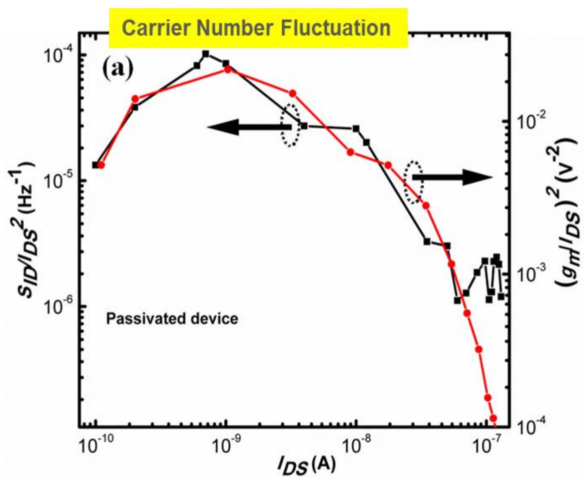


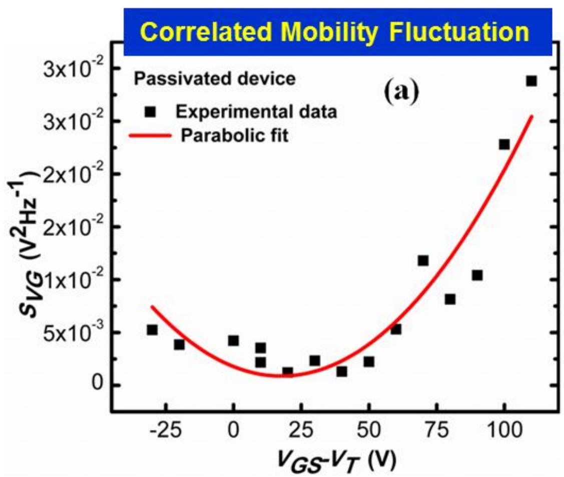
MoS_2 Monolayer FET





Surface passivation removal increases channel current noise



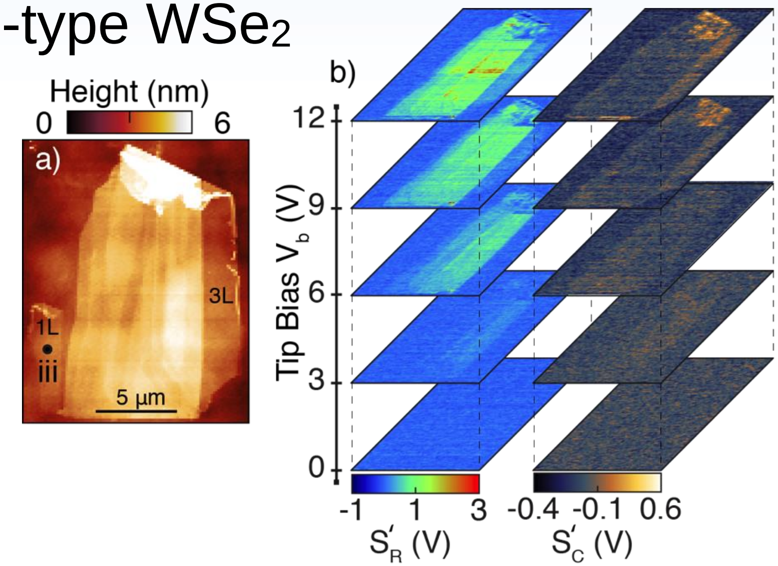


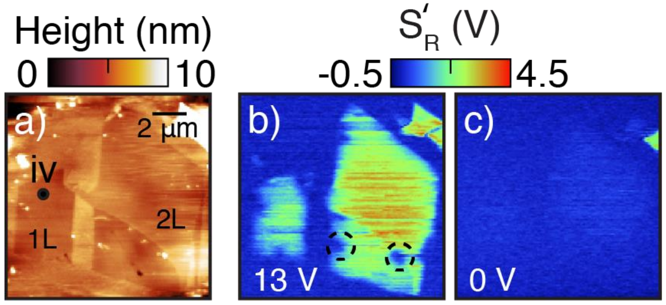
"Unified" 1/f noise model (typical for MOSFETs)

Ref: Electrical transport and low-frequency noise in chemical vapor deposited single-layer MoS2 devices, Nanotechnology (2014) 25, 155702

Microwave near-field Imaging:
Sam Berweger, Pavel Kabos (NIST-Boulder)

n-type WSe_2





p-type WSe_2

Bias-dependent conductivity: Local doping and dominant carrier type

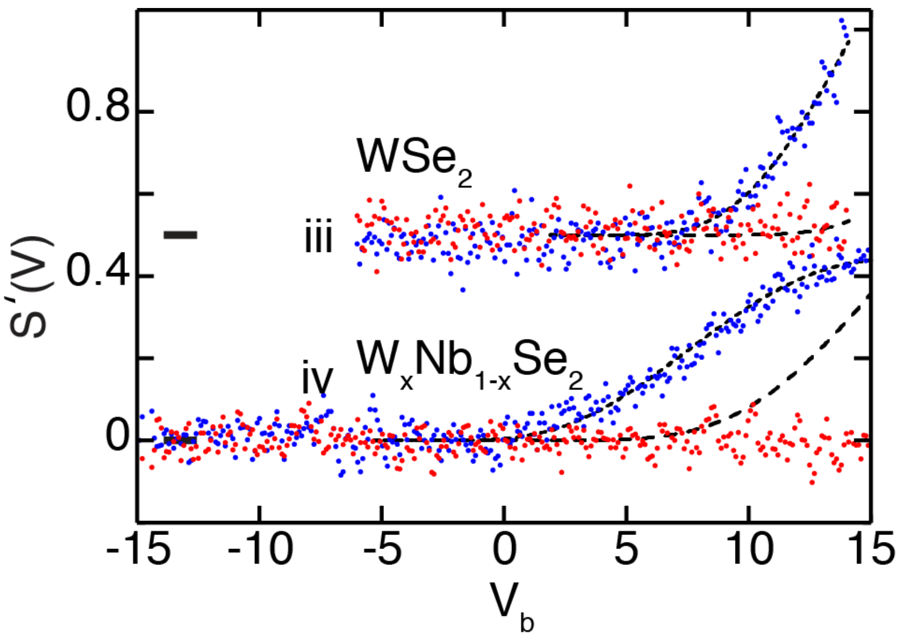
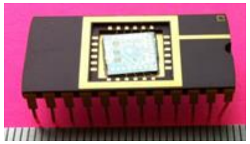
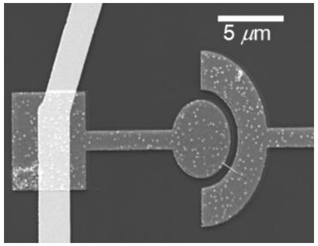


Image and identify defects and electronic inhomogeneities

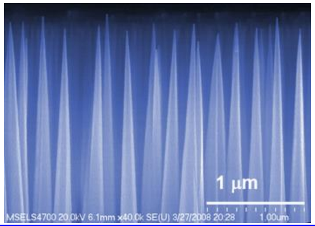
Samples from Nate Lewis Group, Caltech

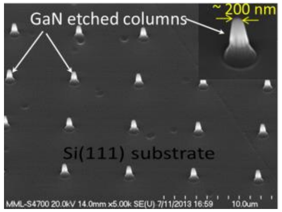
Summary: Nanowire devices for on-chip integration

- **GaN NW sensors:**
  - multiplexed selectivity tuning by nano-catalysts
  - ppb/ppt sensitivity and large operational range
  - RT operation (UV-triggered); low power; low degradation

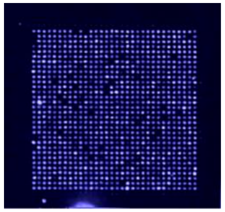
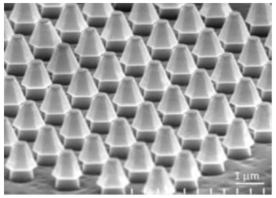



- **AlN needles and GaN top-down etched pillars for field-emitters**
  - Sharp tips (easy escape for electrons)
  - Stable cathode material as compared to CNT and Si
  - AlN to GaN alloy tunability

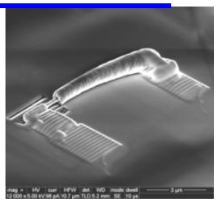
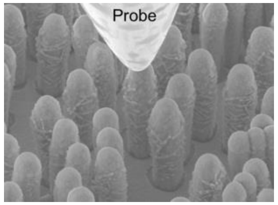




- **GaN p-n and p-i-n core/shell arrays for LED & PD:**
  - access to non-polar surfaces
  - scalability (due to top-down patterning)
  - Potential high-efficiency in photo-detectors (direct light access)

- **Li-ion all-solid-state SiNW batteries:**
  - miniaturization
  - high surface area, cathode thinning=>power density increase

- **2D materials and devices:**
  - Computational materials design (collaboration with CHiMaD)
  - Correlating electronic structure to transport properties