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Gallium Nitride Nanowires for Biomedical Applications

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Sandia National Laboratories

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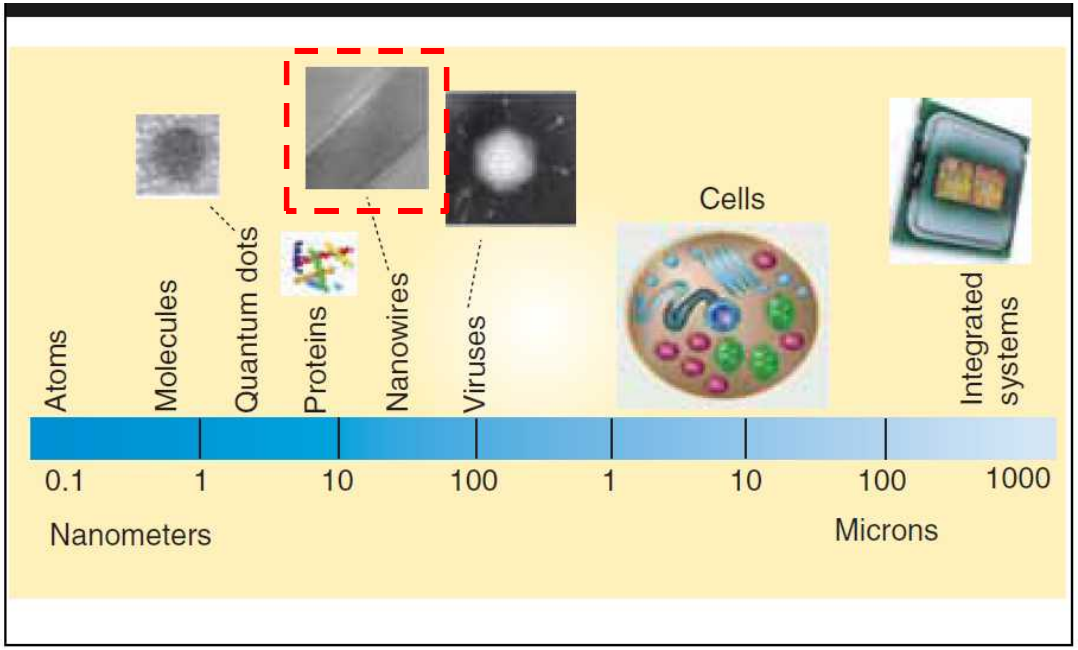
Outline

- Motivation
- Lateral Gallium Nitride (GaN) Nanowire Synthesis
- Nanomechanical Properties
- Biomedical Applications

What is a nanowire?

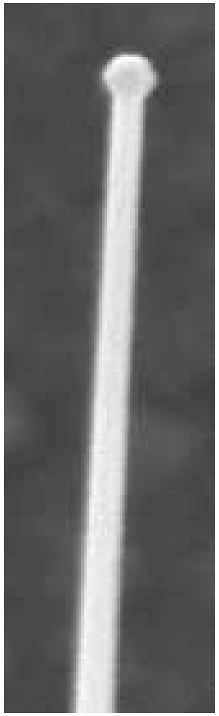
1 nanometer = one billionth of a meter (10^{-9} m) (about 1/100 000 the diameter of a human hair)

Comparison of the sizes of biological, chemical and nanoscale structures, assemblies and systems



F. Patolsky, G. Zheng, C.M. Lieber, Nanomedicine, (2006), 1, 51, (2006)

Nanowire

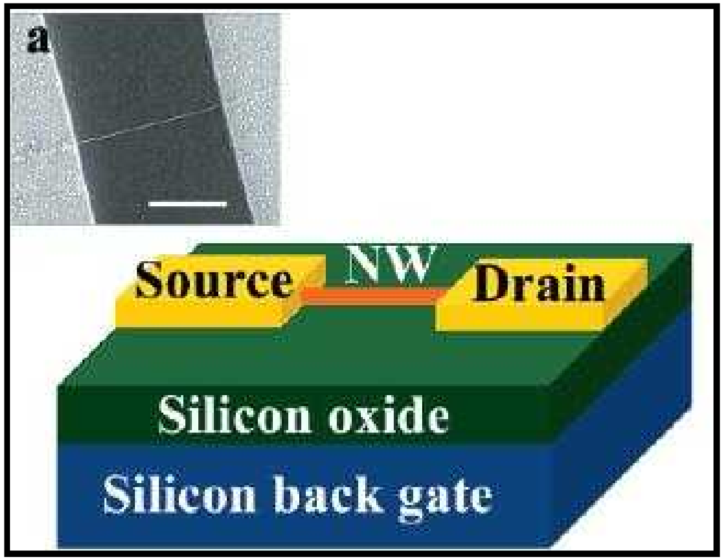


- ❖Device miniaturization (nanoelectronic circuits)
- ❖High surface-to-volume ratio (nanowire sensors)

Functional nano-electronic devices

Invention of nanoscale electronic device that switches current on and off (transistor)

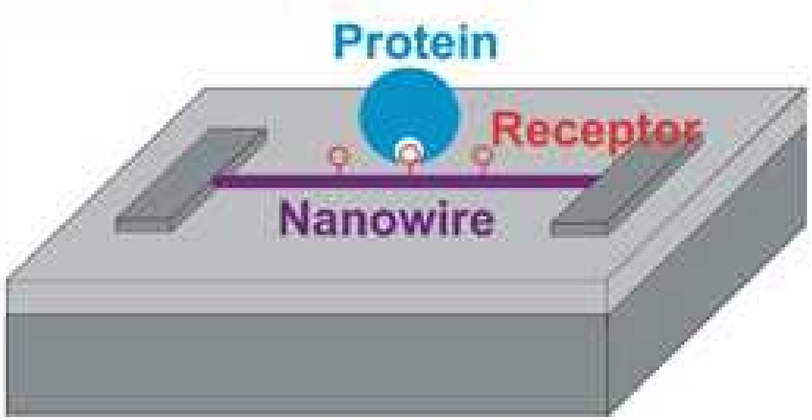
Nanowire Field Effect Transistor



Y. Huang, et. al. Nanolettt. 2, 101 (2002).

Why nanowires for biological sensors?

Nano-Chem/Bio Sensors



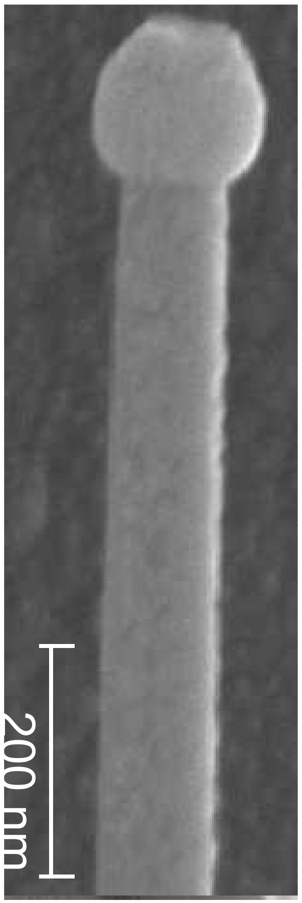
Patolsky et. al., Natl. Acad. Sci. USA 101, 14017 (2004)

- High surface-to-volume ratio
  - -High sensitivity
  - -Highly selective
  - -Takes advantage of conductance property of nanowire
  - -Molecules can bind to the nanowire surface

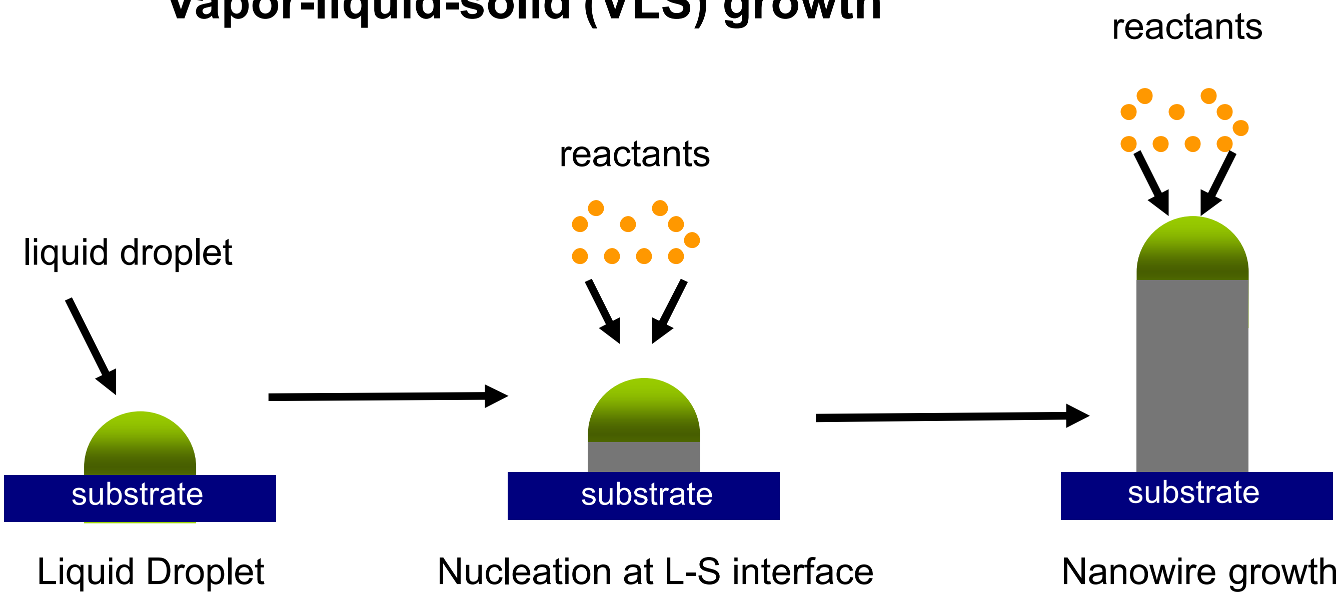
Characterization

- <u>Structure/Orientation</u>
- **Secondary Electron Microscopy (SEM)**
  - Produces images using an electron beam
  - E-beam knocks out electrons from the surface of sample
  - The electrons are detected and amplified.
- **Transmission Electron Microscopy (TEM)**
  - Uses electron diffraction to determine crystal structure and orientation
  - Monochromatic electron beam passes through a crystal volume

Bottom-up nanowire growth



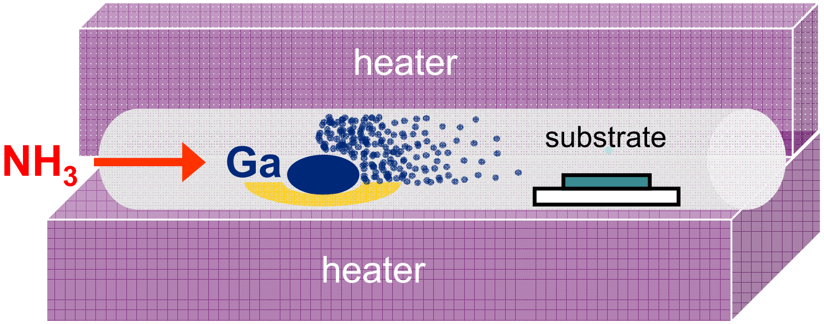
Vapor-liquid-solid (VLS) growth



- ❑ Catalyst preparation
- ❑ Eutectic alloying (phase diagram, catalyst support)
- ❑ Inception phase (supersaturation, interfacial energy)
- ❑ Nanowire Growth

GaN nanowires are grown in a tube furnace by the vapor-liquid-solid (VLS) mechanism

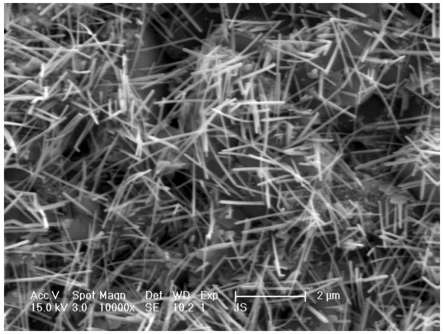
Hot wall tube furnace
Near equilibrium condition



✓ Built-in supersaturation gradient, easy to find the optimal growth condition
✓ Low cost and simple setup

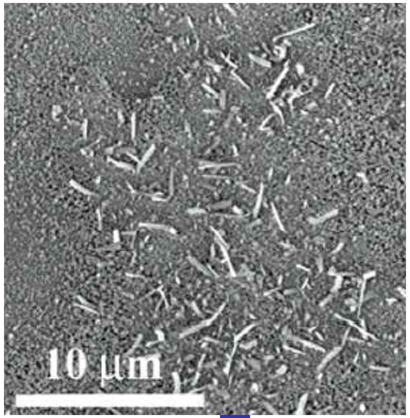
Approach to Alignment, Processing and Contacting Nanowires

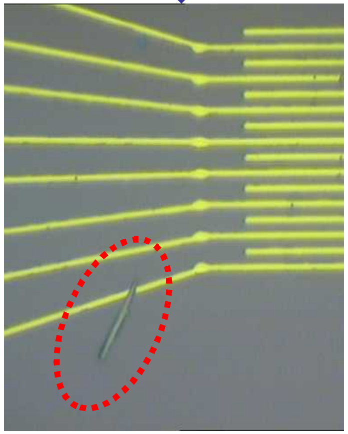
VLS synthesis

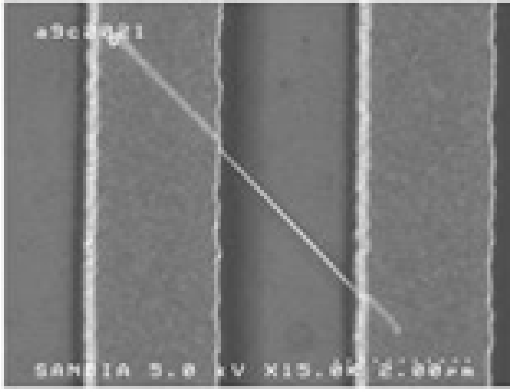


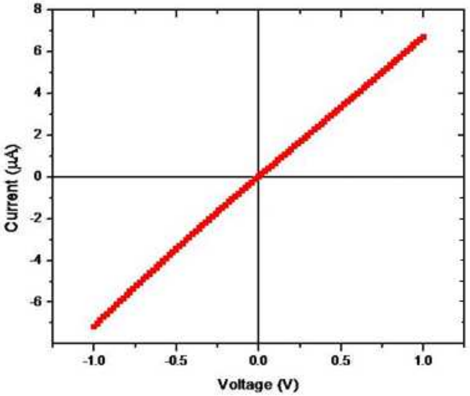
solution suspended after sonication

random disperson & contact



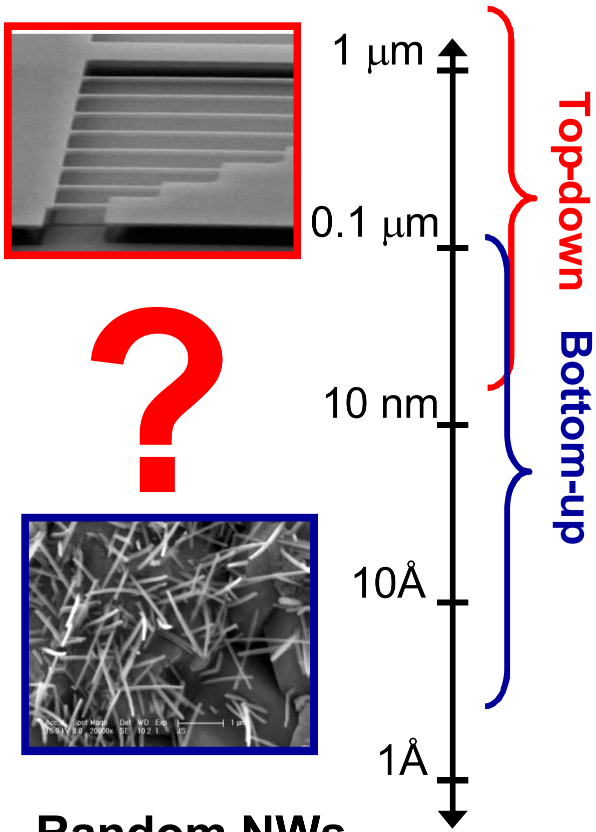






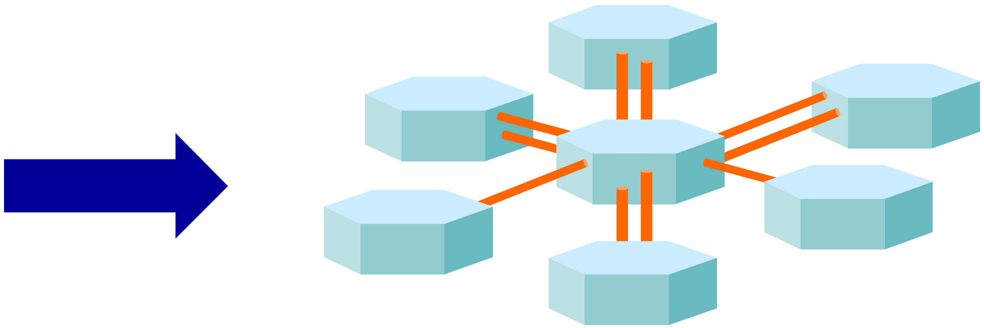
Controllable aligned nanostructures

E-beam patterning



Random NWs

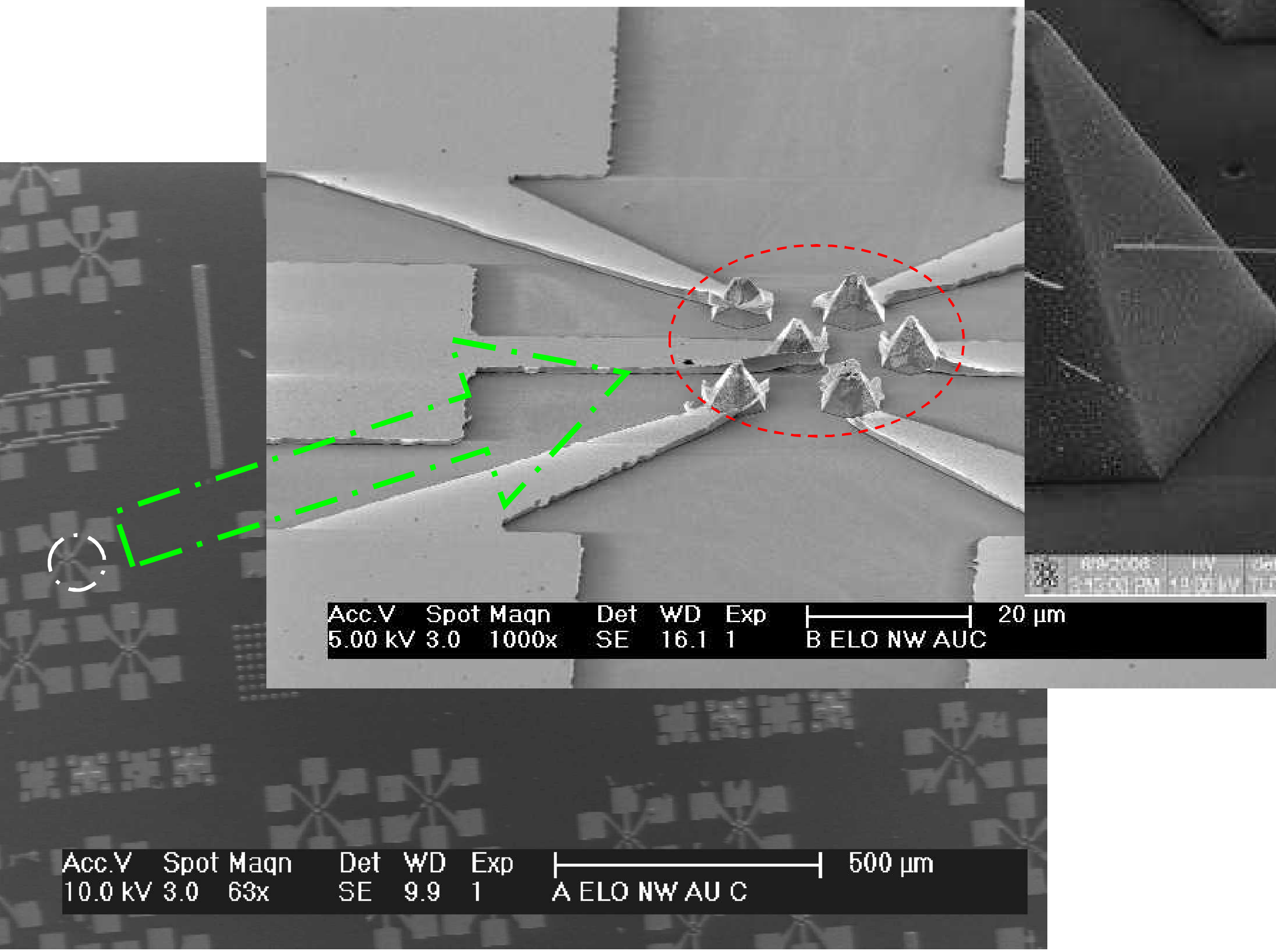
Alignment

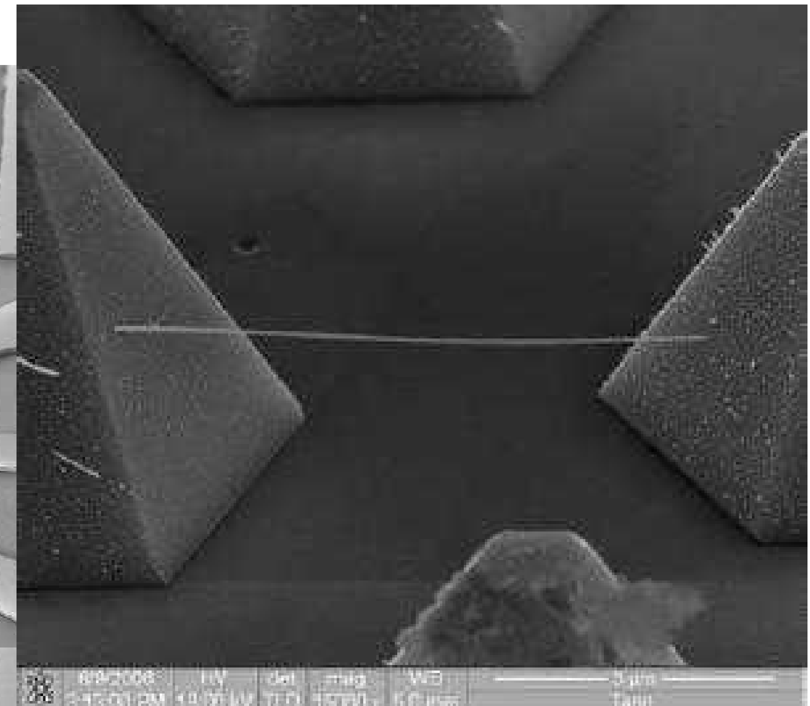


Directed Synthesis of GaN Nanowires for Biomedical Applications

Top-down photolithography

Bottom-up nanowire growth

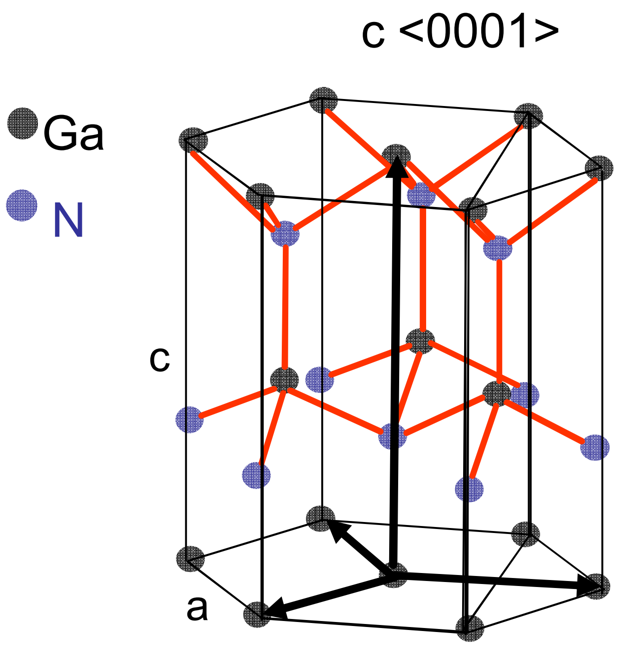




Outline

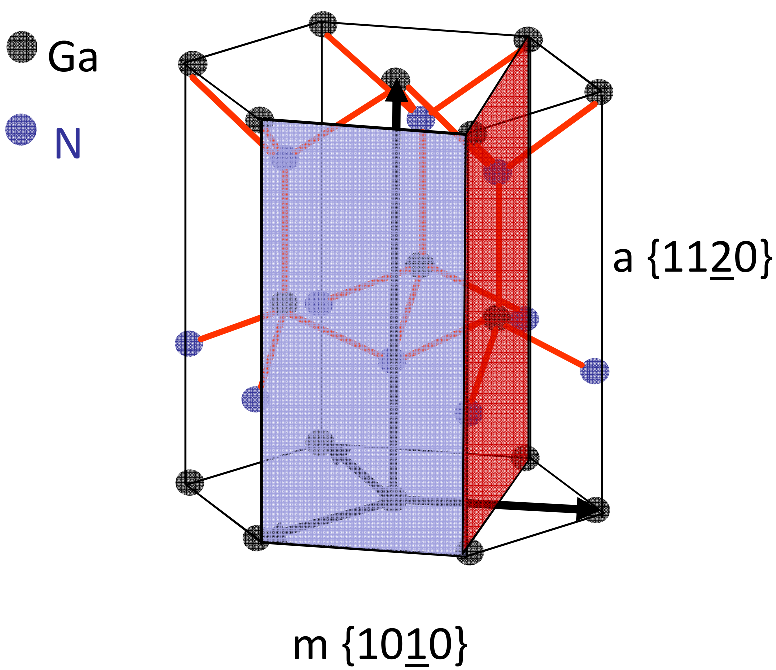
- Motivation
- **Lateral GaN Nanowire Synthesis**
  - Preferred M-axis Orientation
  - Control of Nanowire Orientation
  - Control of Nanowire Diameter
- **Nanomechanical Properties**
- **Biomedical Application**

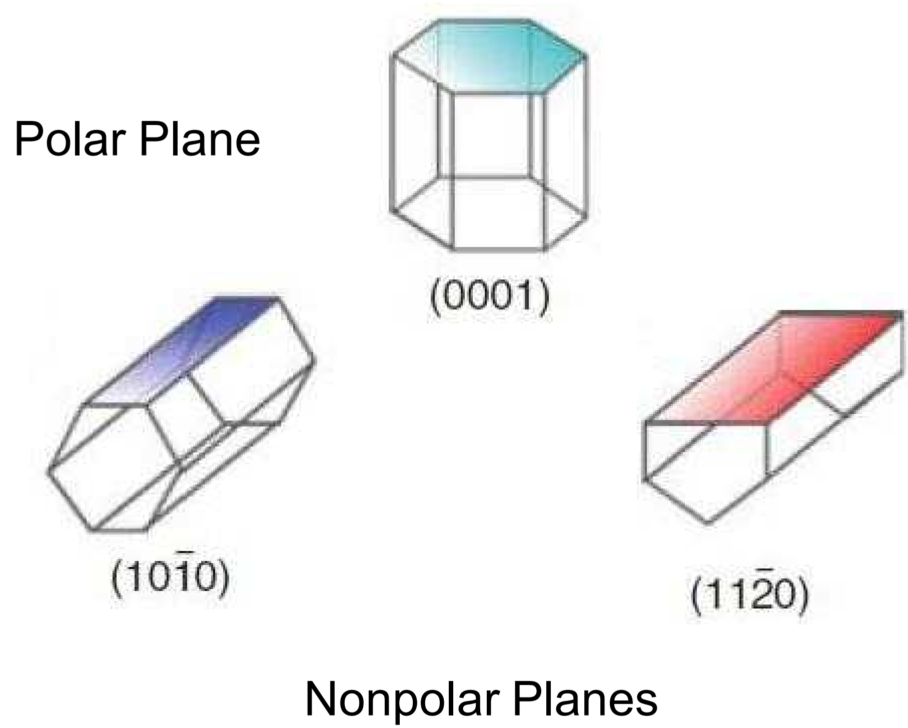
Gallium Nitride



- Ga-N covalent bond
- Wide direct bandgap = 3.42 eV

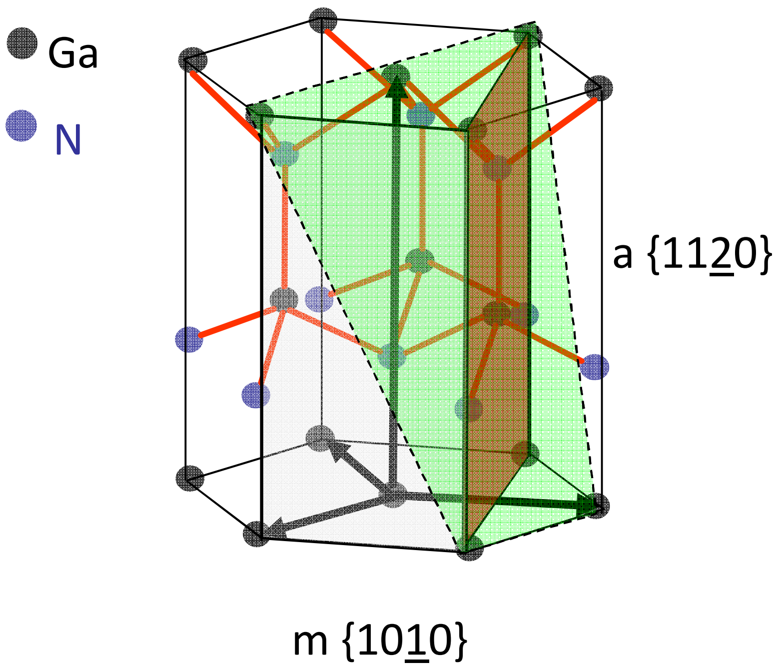
Gallium Nitride Crystal Structure, Polar and Nonpolar planes

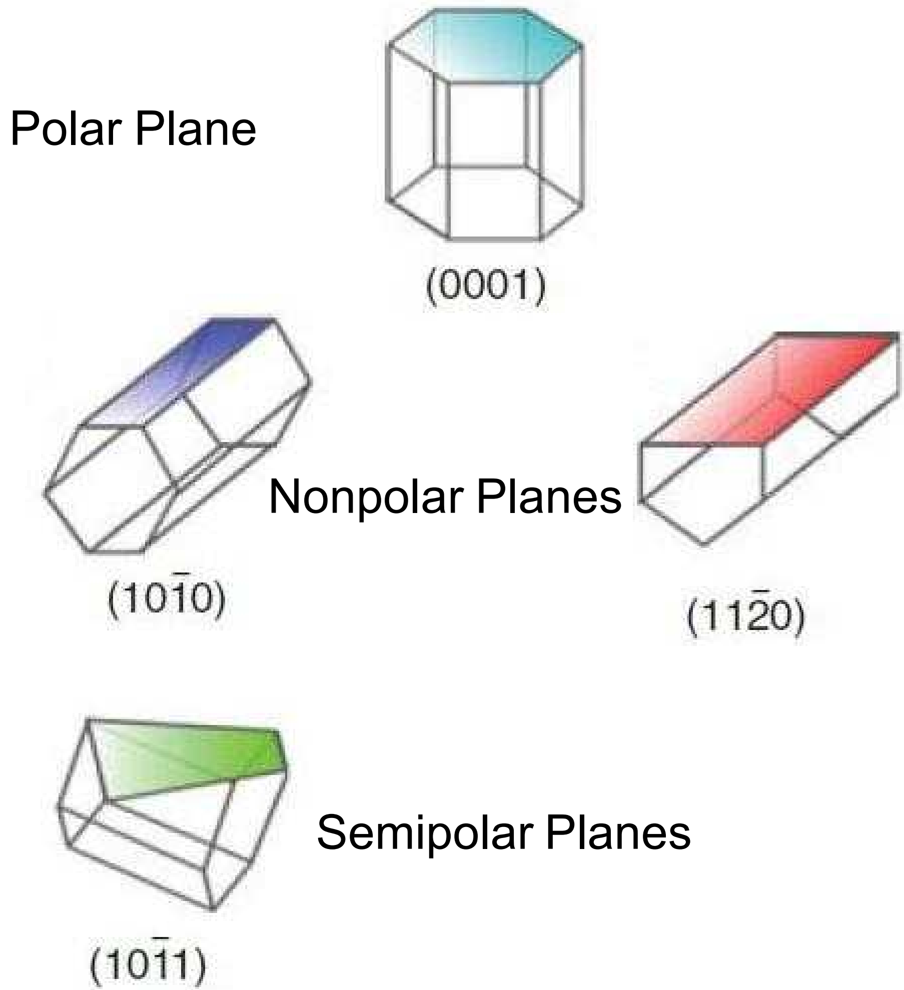




J.S. Speck et. al *MRS Bulletin, 34 (May 2009)*

Gallium Nitride Crystal Structure, Polar and Nonpolar planes





J.S. Speck et. al *MRS Bulletin, 34 (May 2009)*

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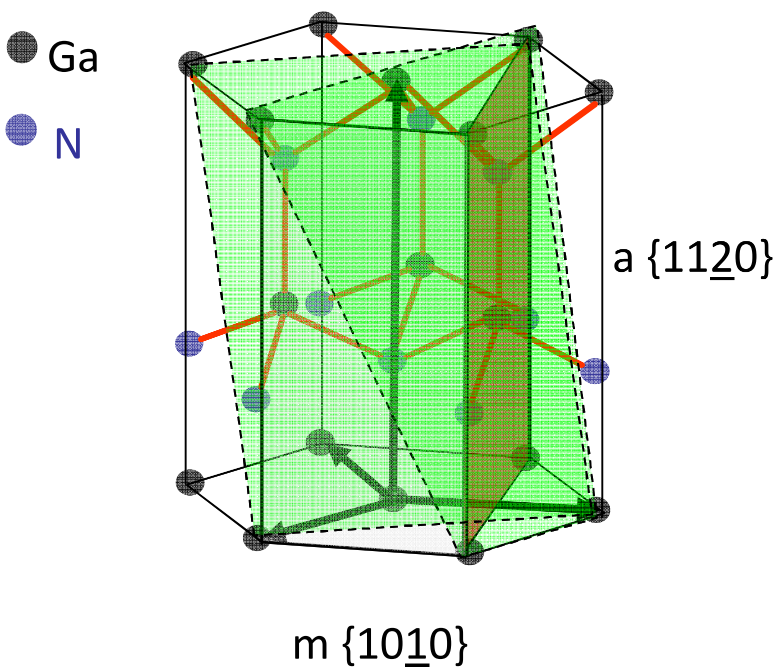
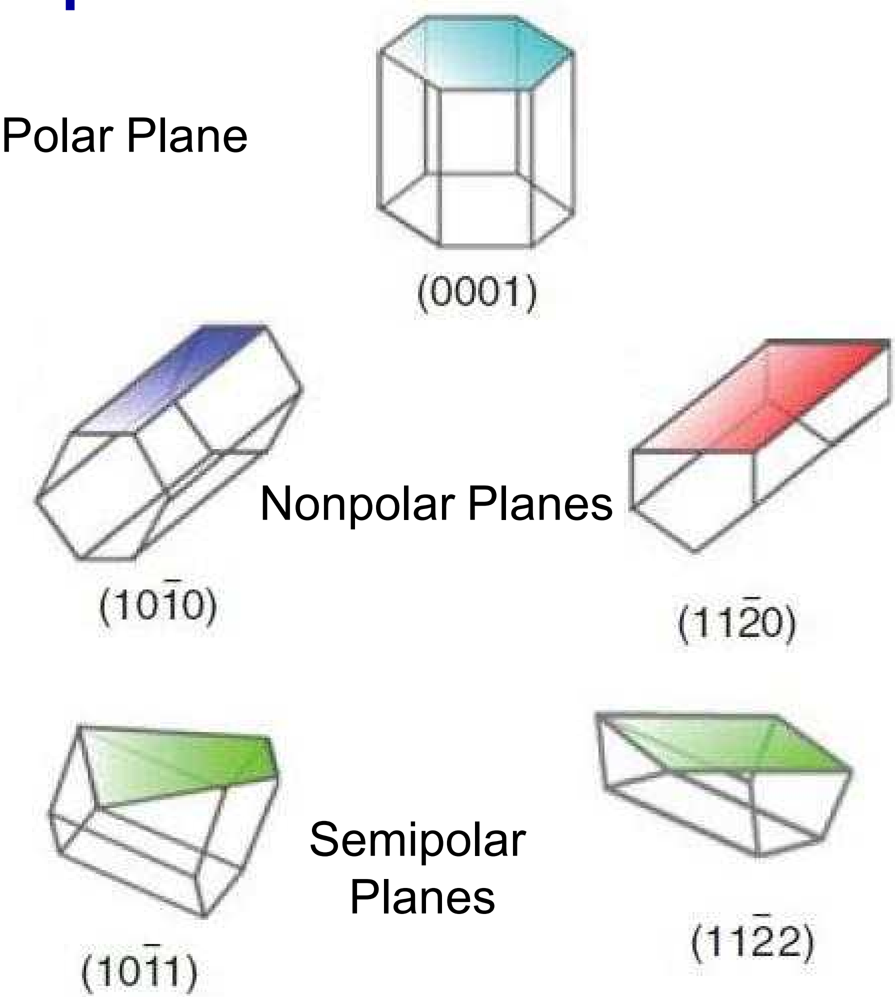
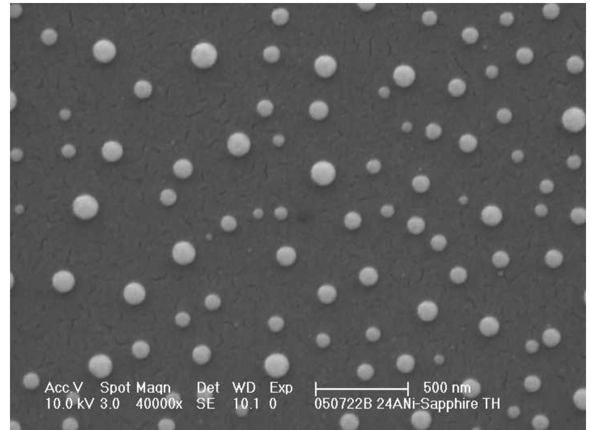
Gallium Nitride Crystal Structure, Polar, Nonpolar and Semipolar planes





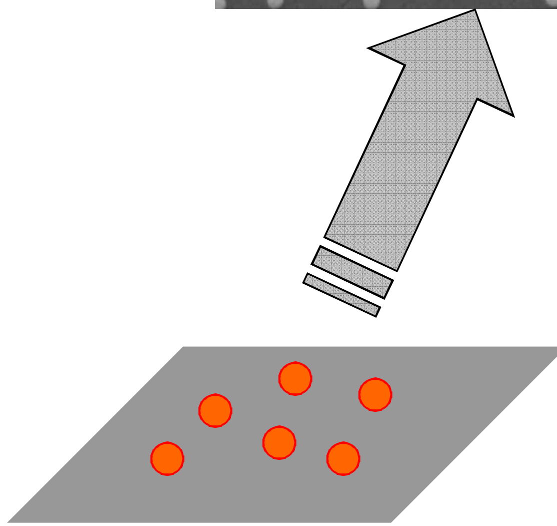
J.S. Speck et. al *MRS Bulletin, 34 (May 2009)*

Toward Nanowire Growth

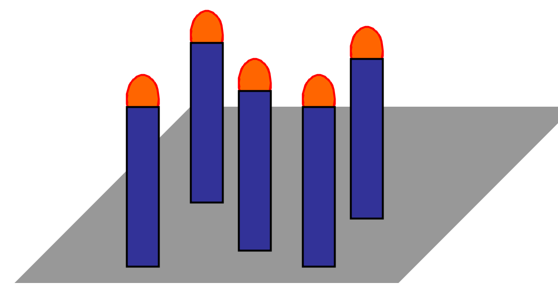


thin film deposition of nickel catalyst by electron beam evaporation

NW growth

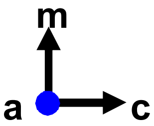


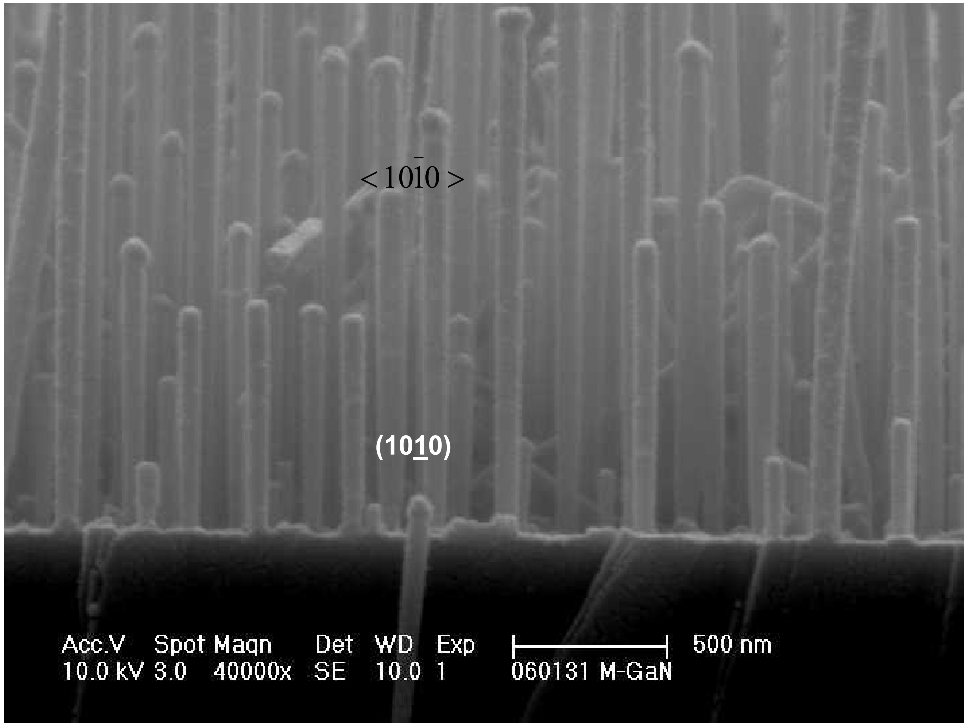
metallized substrate



Nanowire growth

Vertical GaN nanowires on *m*-plane substrate





Nonpolar Plane

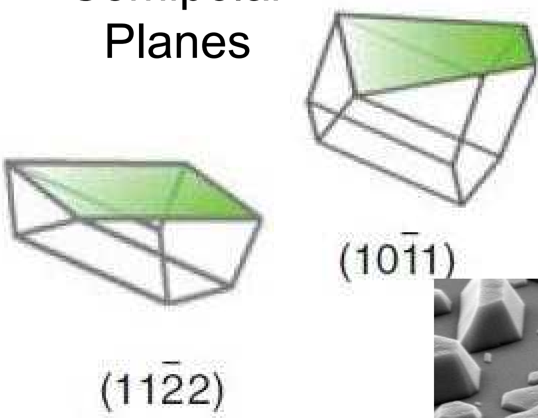
(10$\bar{1}$0)
m-plane

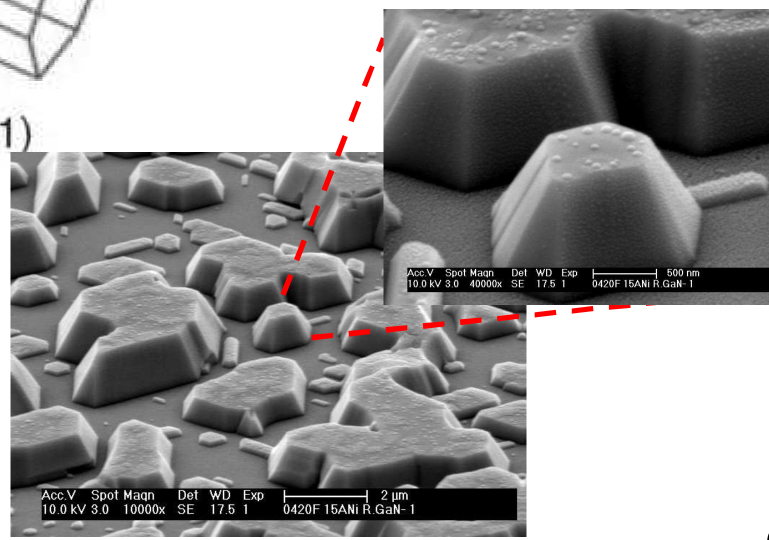
Growth Conditions

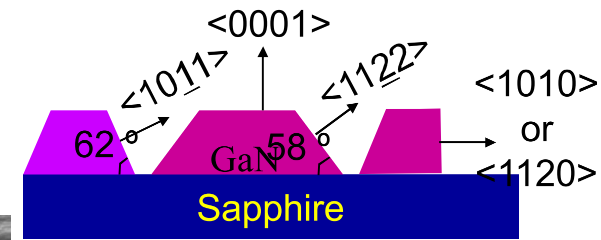
Temperature = 950 °C
NH_3 Flow Rate = 40-50 sccm
Mass of Ga ≈ 2.5 g
Growth Time = 30 minutes

Lateral GaN nanowire growth in the m-direction

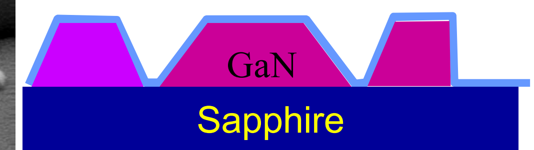
Semipolar Planes



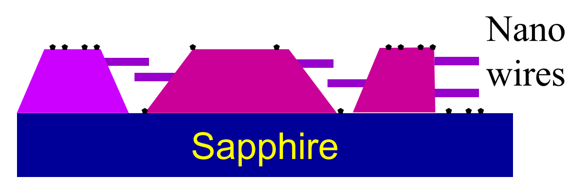




(a) One-step GaN growth



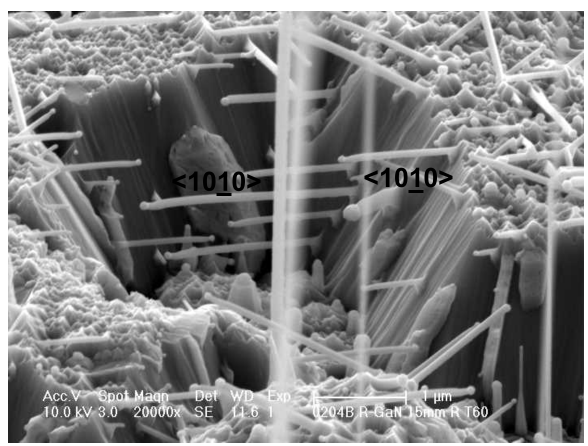
(b) E-beam evaporation of Ni

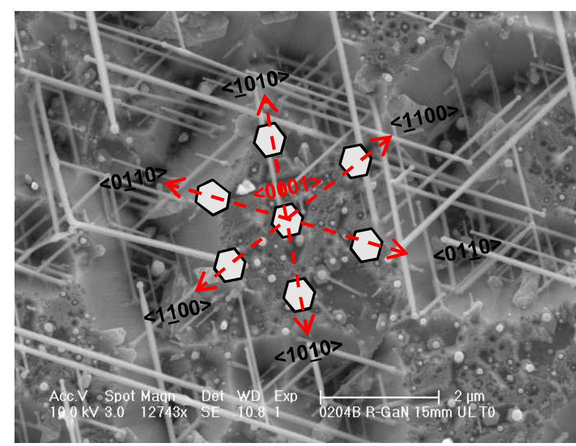


(c) CVD nanowire growth

Growth Conditions

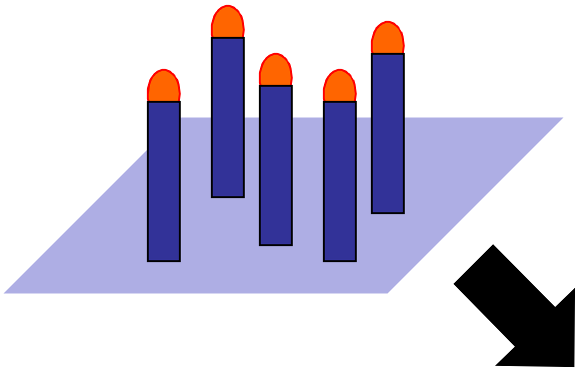
Temperature = 950°C
NH_3 Flow Rate = 50 sccm
Mass of Ga ≈ 2.5 g
Growth Time = 30 minutes





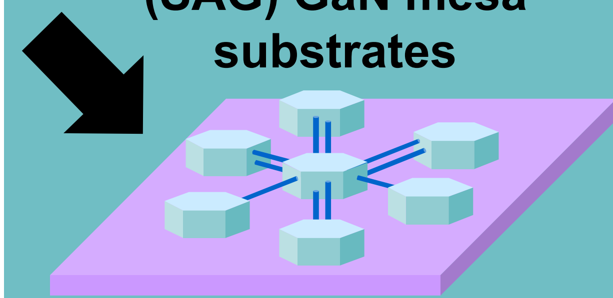
Selection of vertical non-polar and semipolar GaN planes for nanowire alignment

Planar GaN substrates



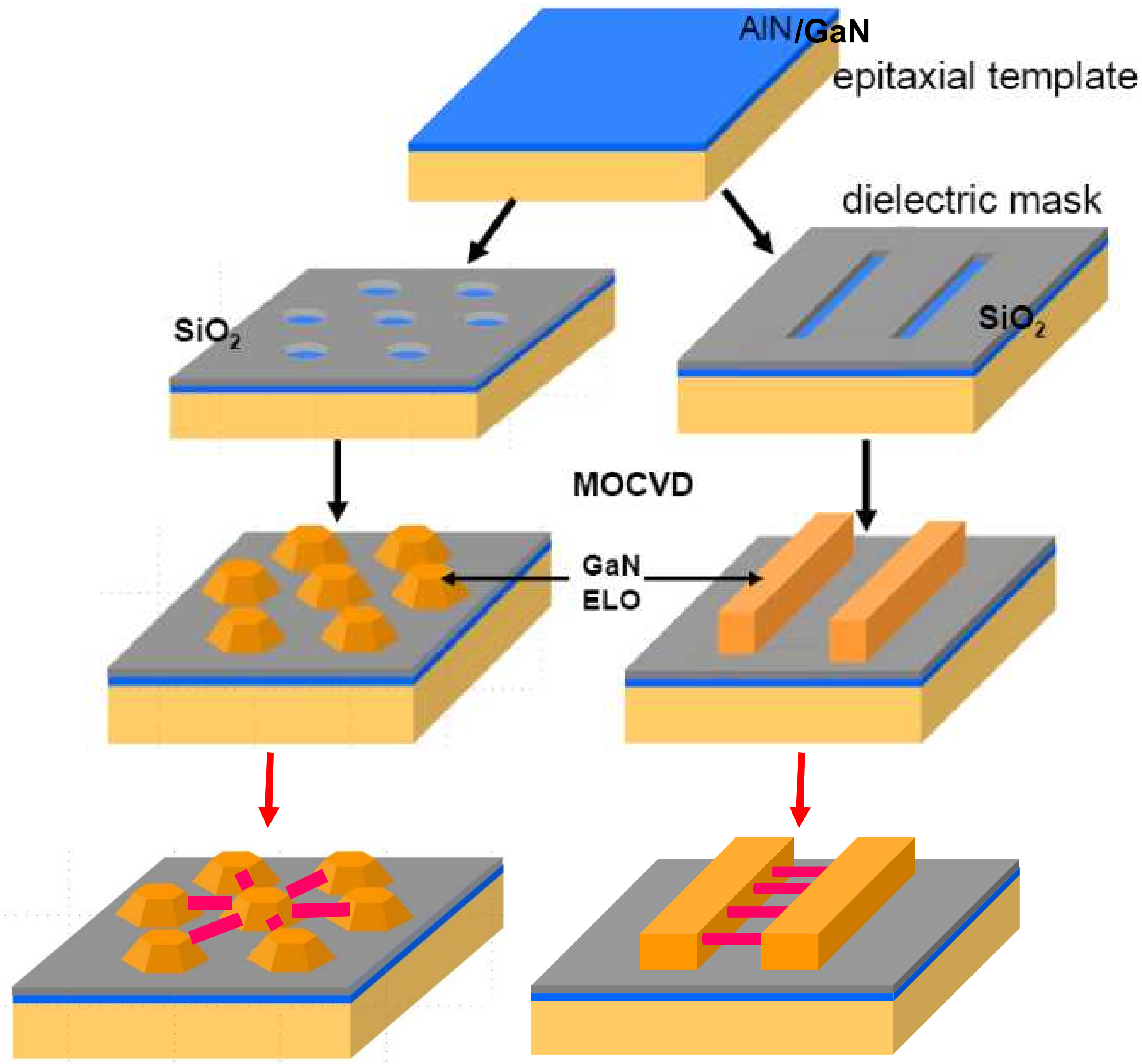
Rough GaN substrates

Selective Area Grown (SAG) GaN mesa substrates



GaN nanowire direction is primarily defined by the crystallographic orientation of the substrate

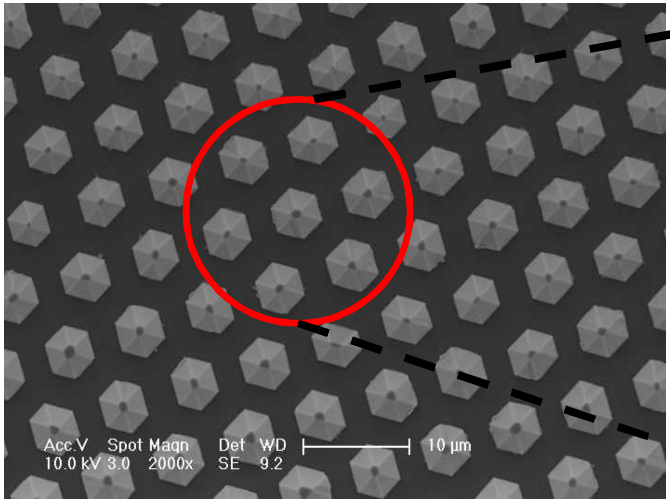
Integration of Selective Area Growth (SAG) of GaN with catalytic nano-epitaxy

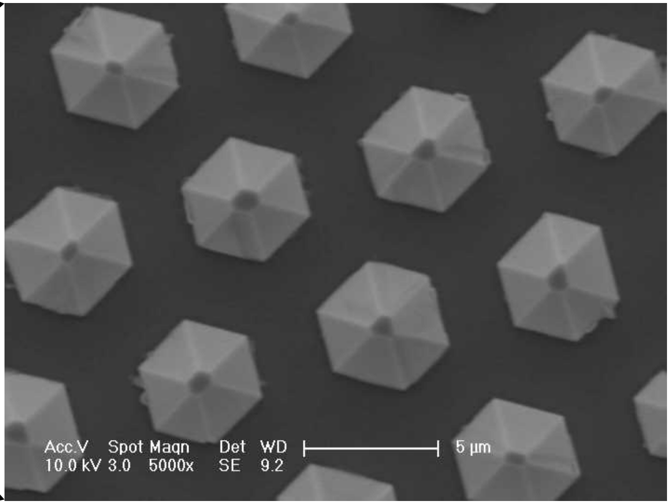


GaN nanowire arrays form hexagonal networks in the m-direction

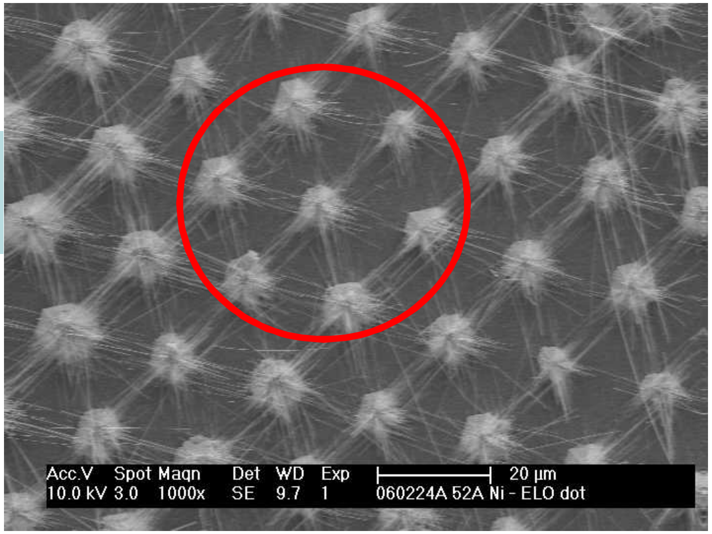
6 semipolar {10$\bar{1}$1} facets

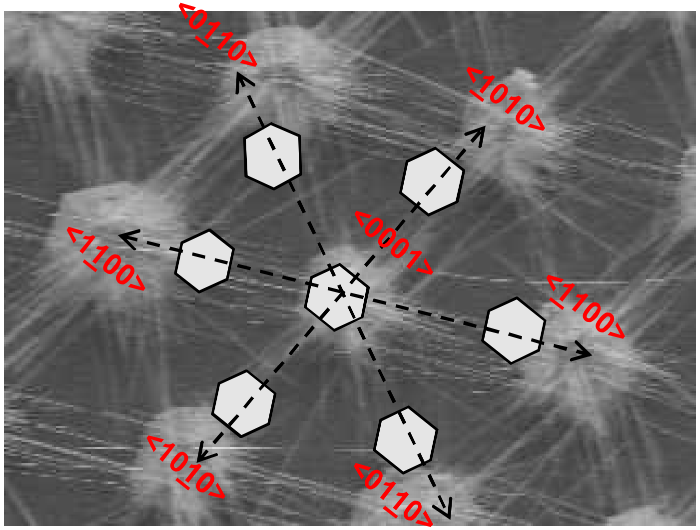
Before Growth





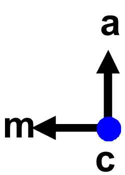
After Growth

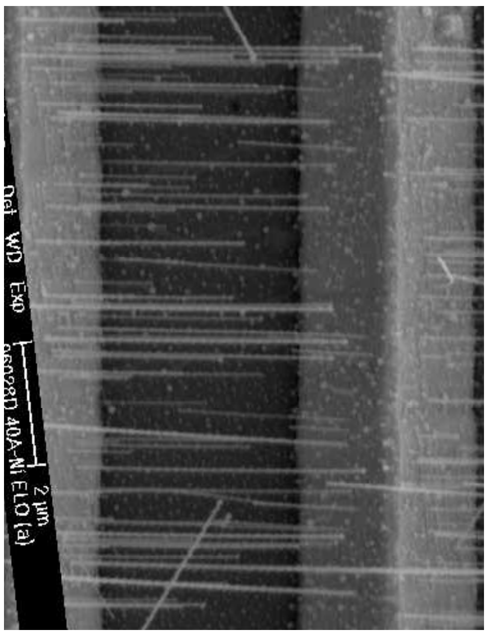


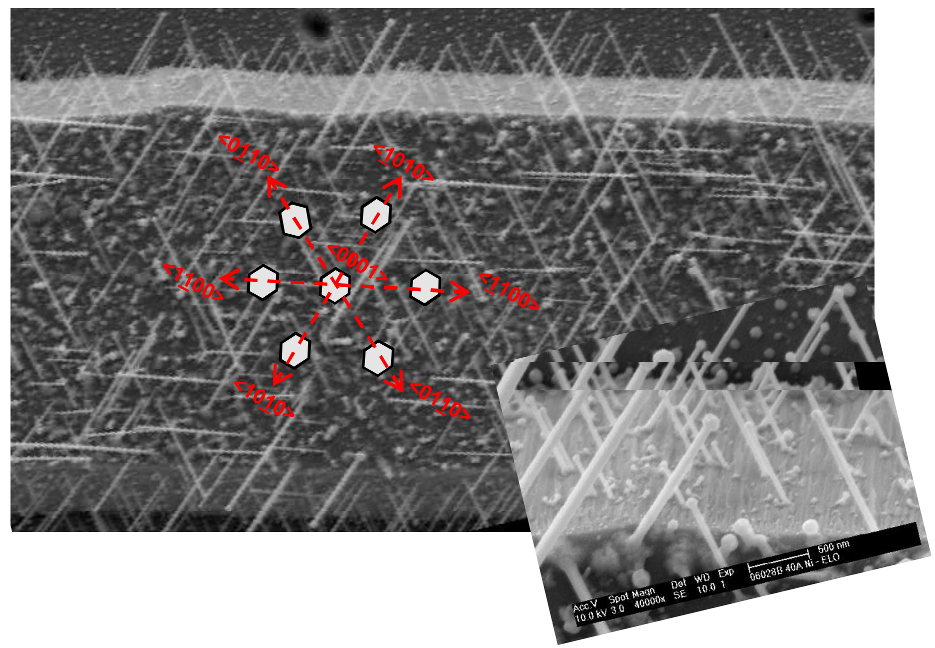


M-direction preferred on the sidewalls of SAG stripes

Nanowires on a-axis stripe Nanowires on m-axis stripe







Preferential growth along m-axis!

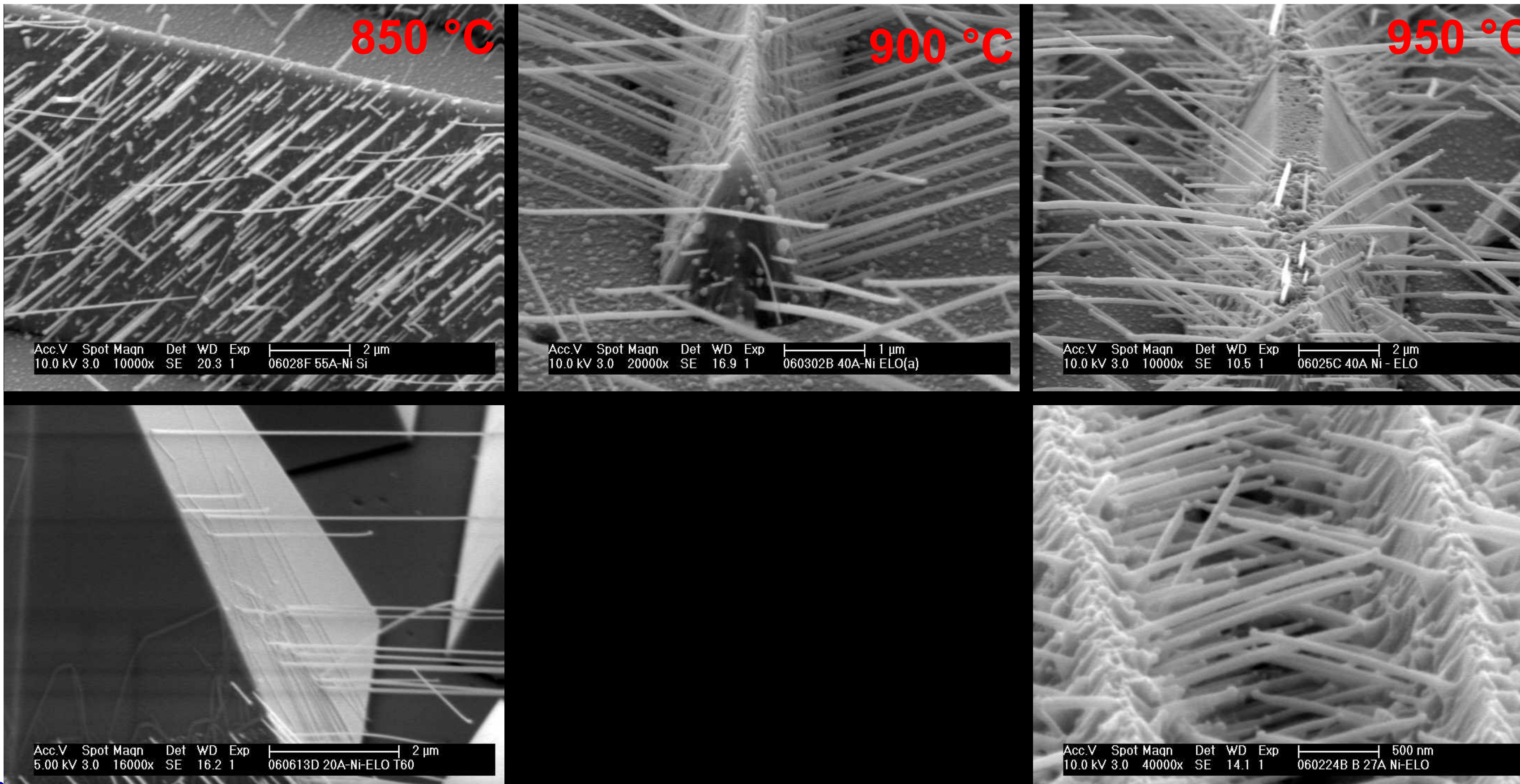
Controlling the Growth Direction

Temperature

4.0-5.5nm

Catalyst Thickness

2.0-2.7 nm

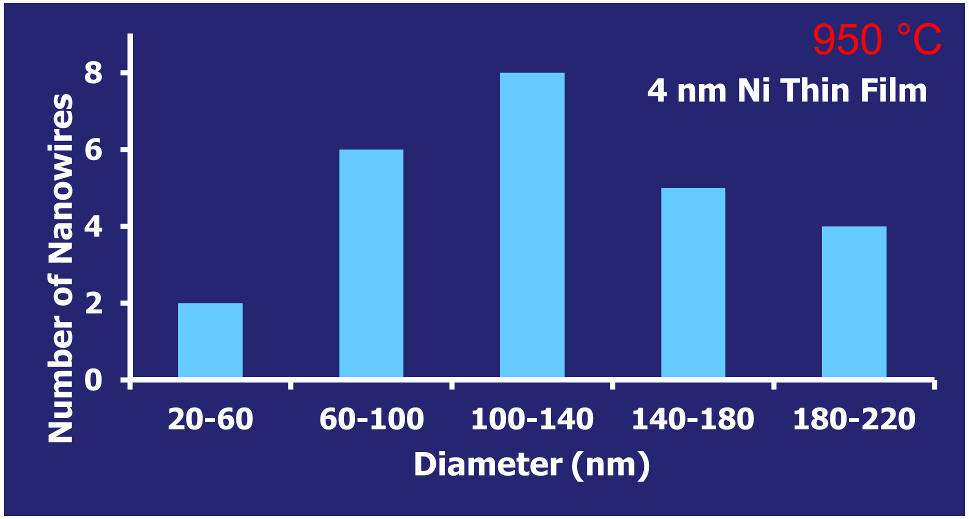


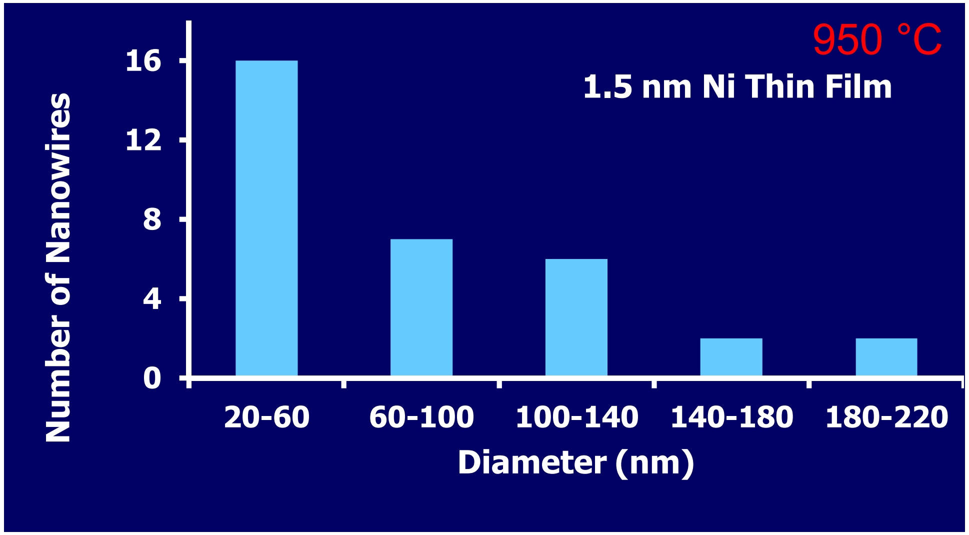
$\langle 10\bar{1}0 \rangle$ horizontal

NW Direction

$\langle 10\bar{1}n \rangle$ inclined

Controlling Nanowire Diameter

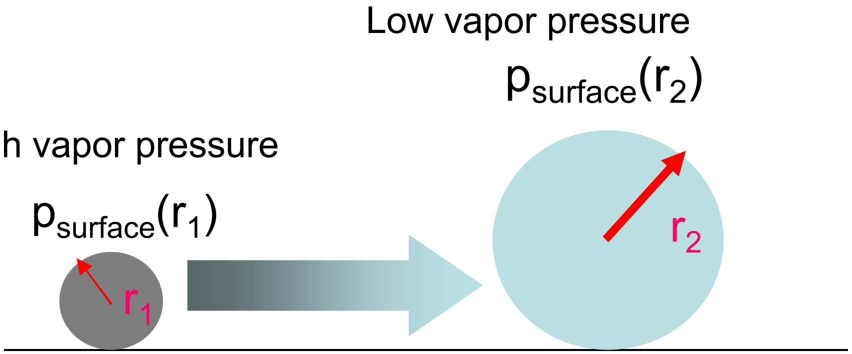




Dr. Christine Broadbridge, A.Lehman,T. Herbert, L. Sze, A. Anthony (<u>Southern Connecticut State University, Physics Department)</u>

Thicker nanowires tend to grow longer

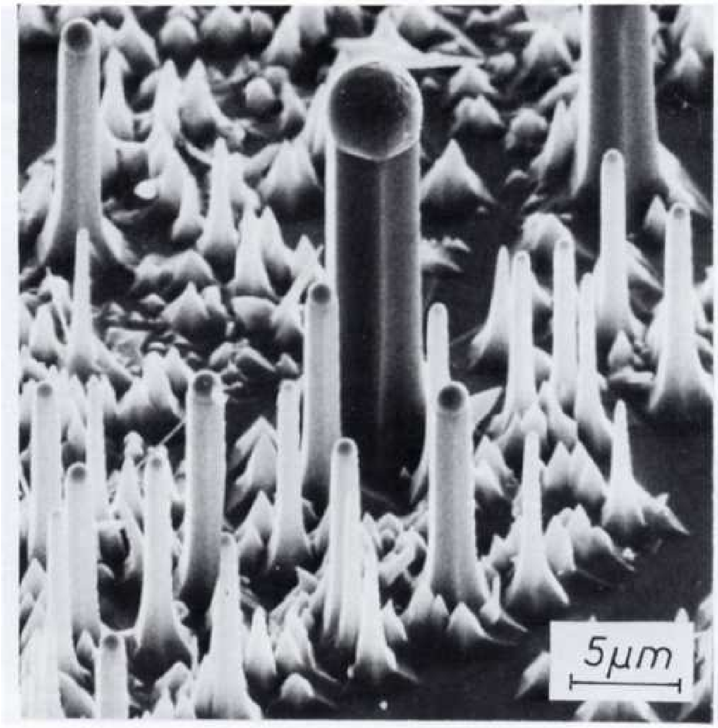
Thomson-Gibbs effect



$$\boxed{p_{surface}(r) = p_0 \exp(\frac{2\gamma\Omega}{r\,k\,T})}$$

$\boxed{\text{Supersaturation } \sigma = (p-p_0)/p_0}$

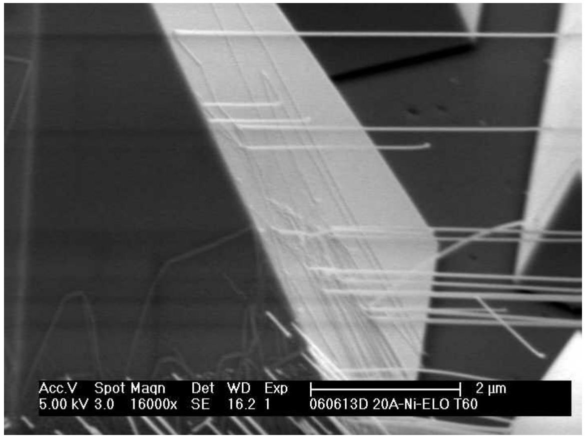
High surface pressure for the smaller droplet!



E. I. Givargizov (1978)

Synthesis Summary

- <u>Horizontal GaN nanowires achieved</u>
- Preferred orientation for GaN nanowires
  - Nonpolar <10$\bar{1}$0>/m-axis
- Control of nanowire diameter
  - 1.5 nm Ni film → 20-60 nm diameter nanowires
  - 4 nm Ni film → 100-140 nm diameter nanowires
- Control of nanowire direction
  - 850°C→ horizontal nanowires
  - 900-950°C→ inclined nanowires



Outline

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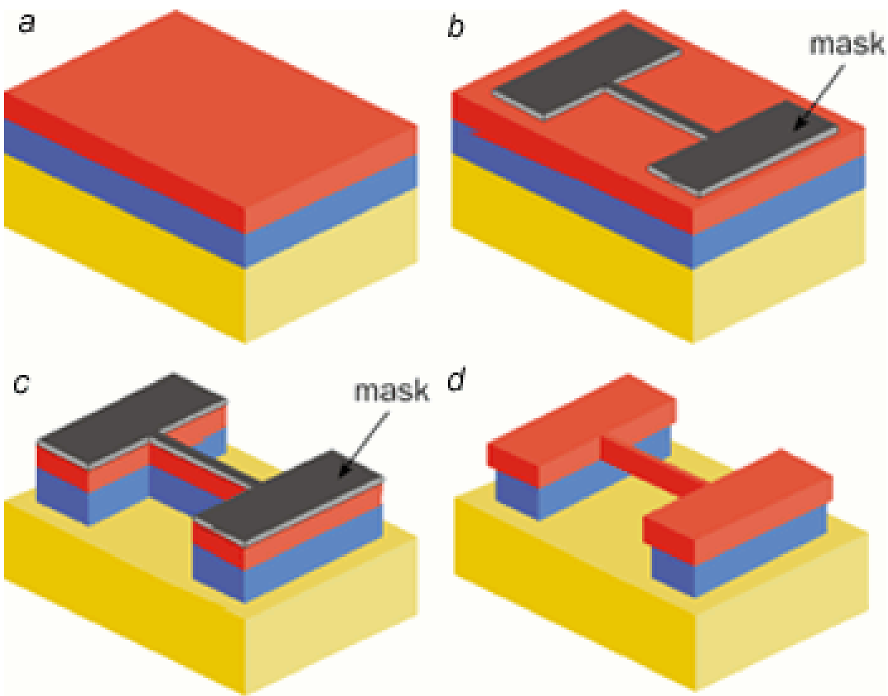
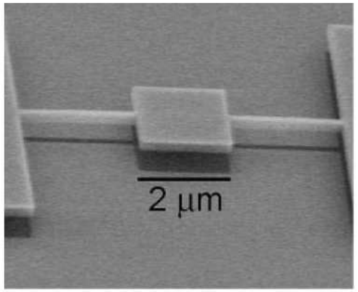
- Biomedical Applications

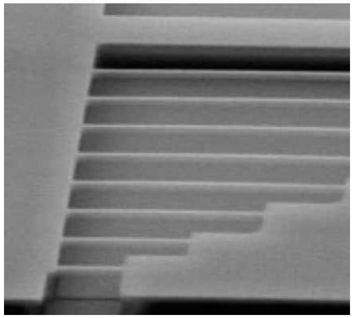
NEMS Resonators thru e-beam lithography: gravimetry-based chem/bio sensing



Physics Web (Roukes, Caltech)



H. G. Craighead, Science, 290, 1532 (2000)



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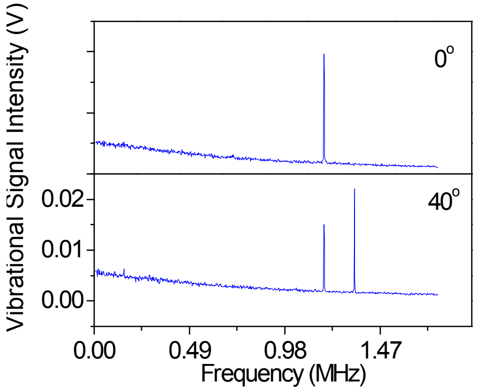
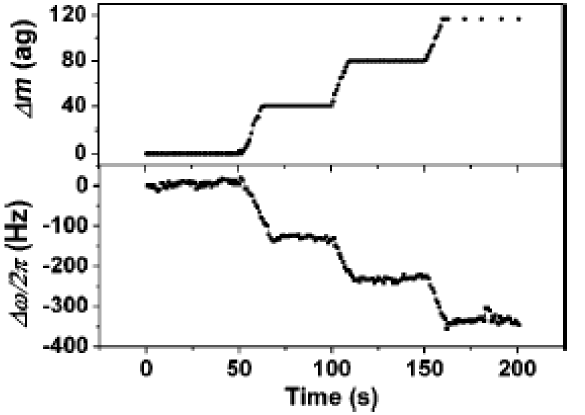


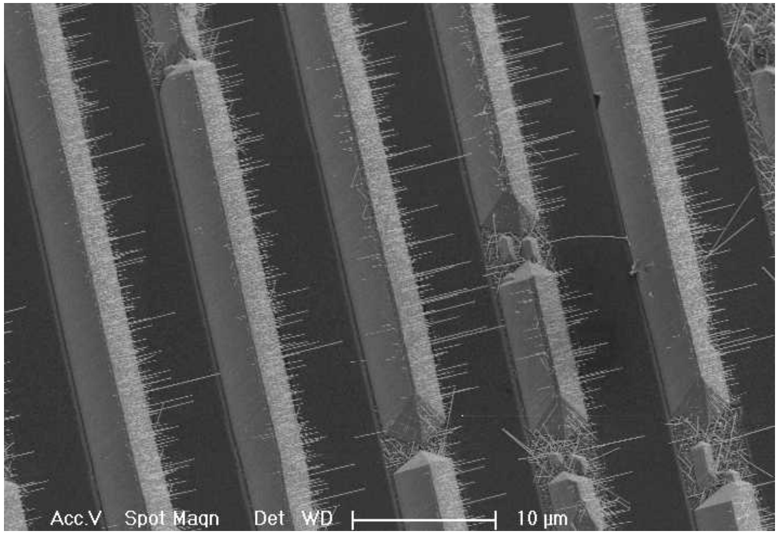


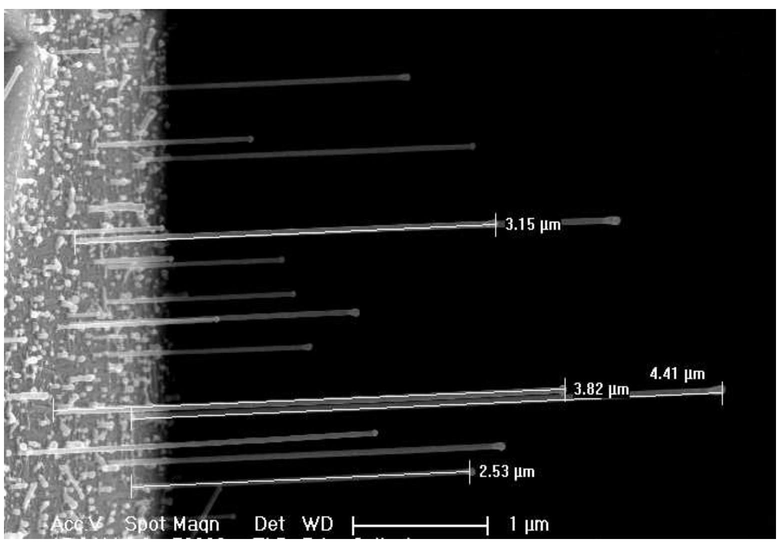
Ekinci, K.L., Appl. Phys Lett 84, 4469 (2004)

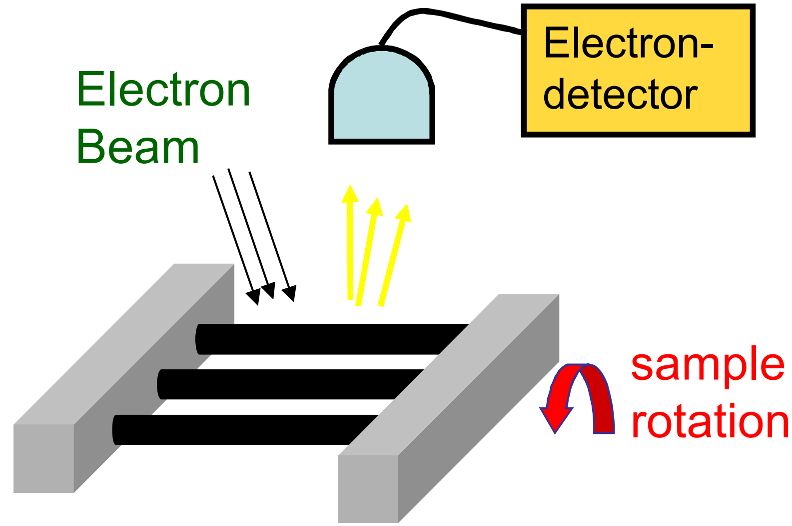
$$\boxed{\frac{\Delta M}{M_{Eff}} \approx \frac{\Delta f}{f_0}}$$

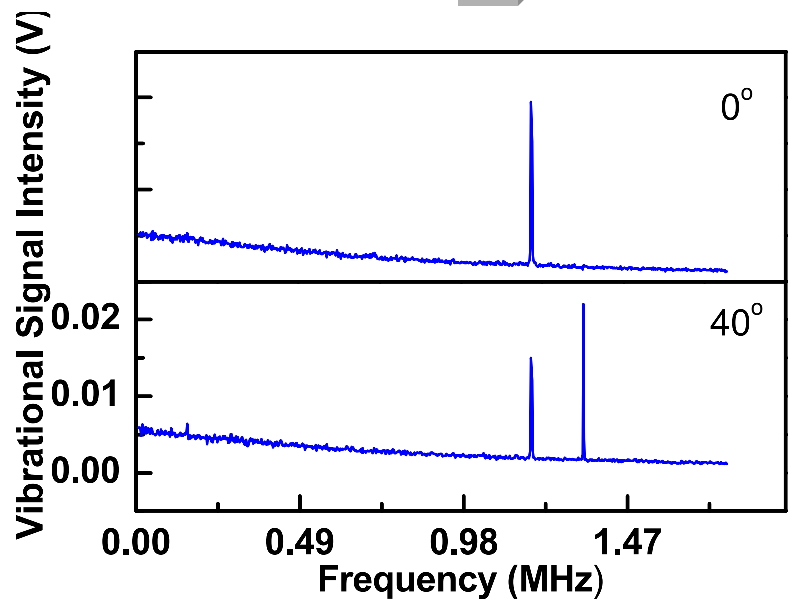
$$\boxed{f_0 \propto \sqrt{\frac{E}{\rho}}}$$

NEMS measurement on horizontal GaN NWs

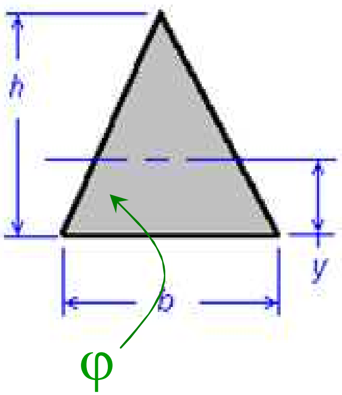


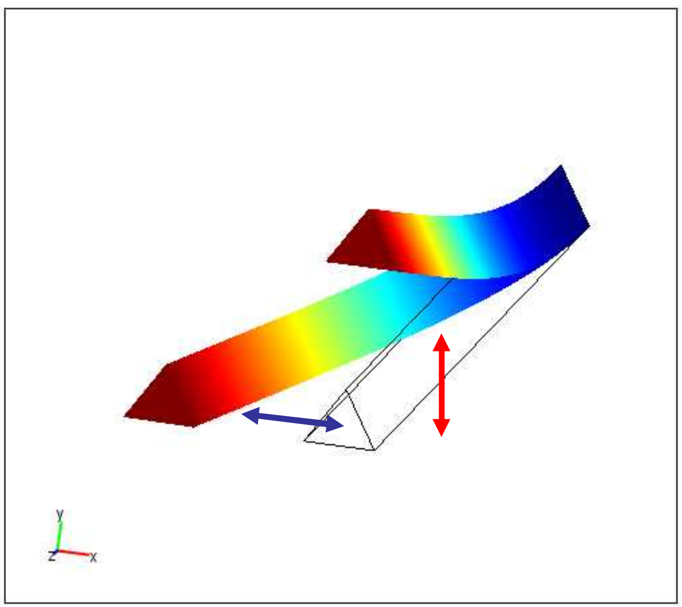


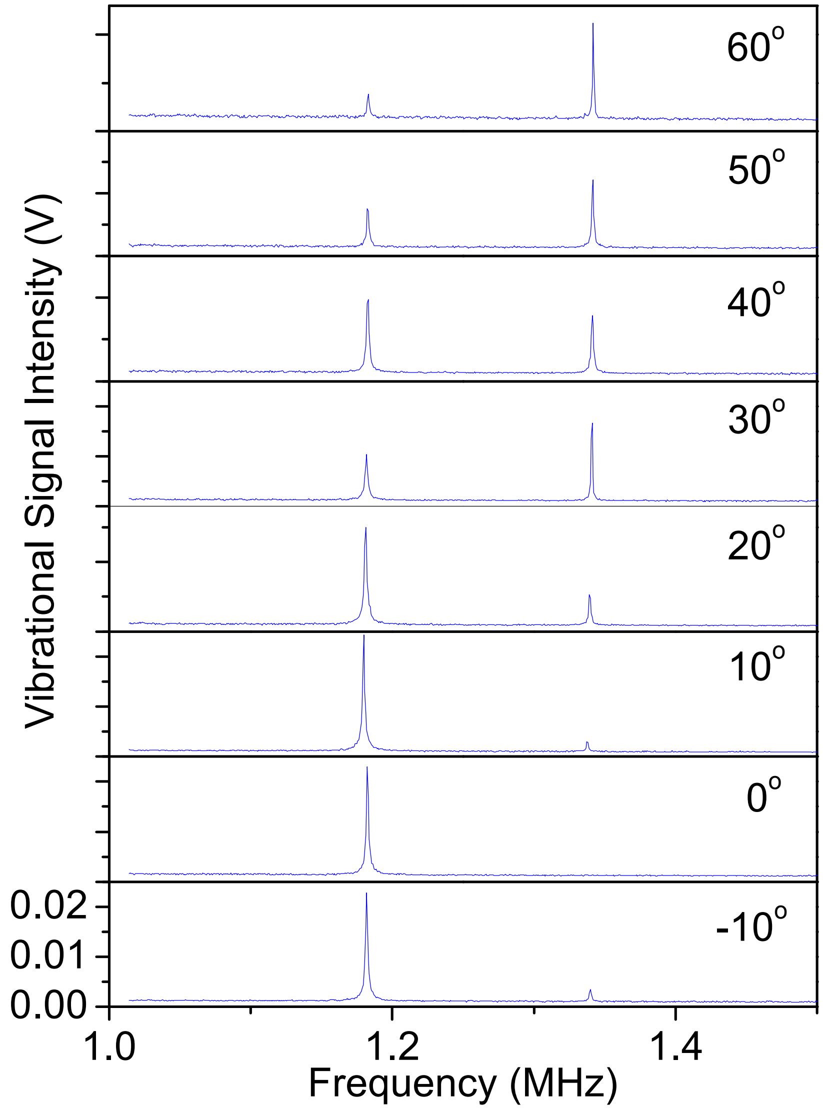




Resonance as a function of detection angle



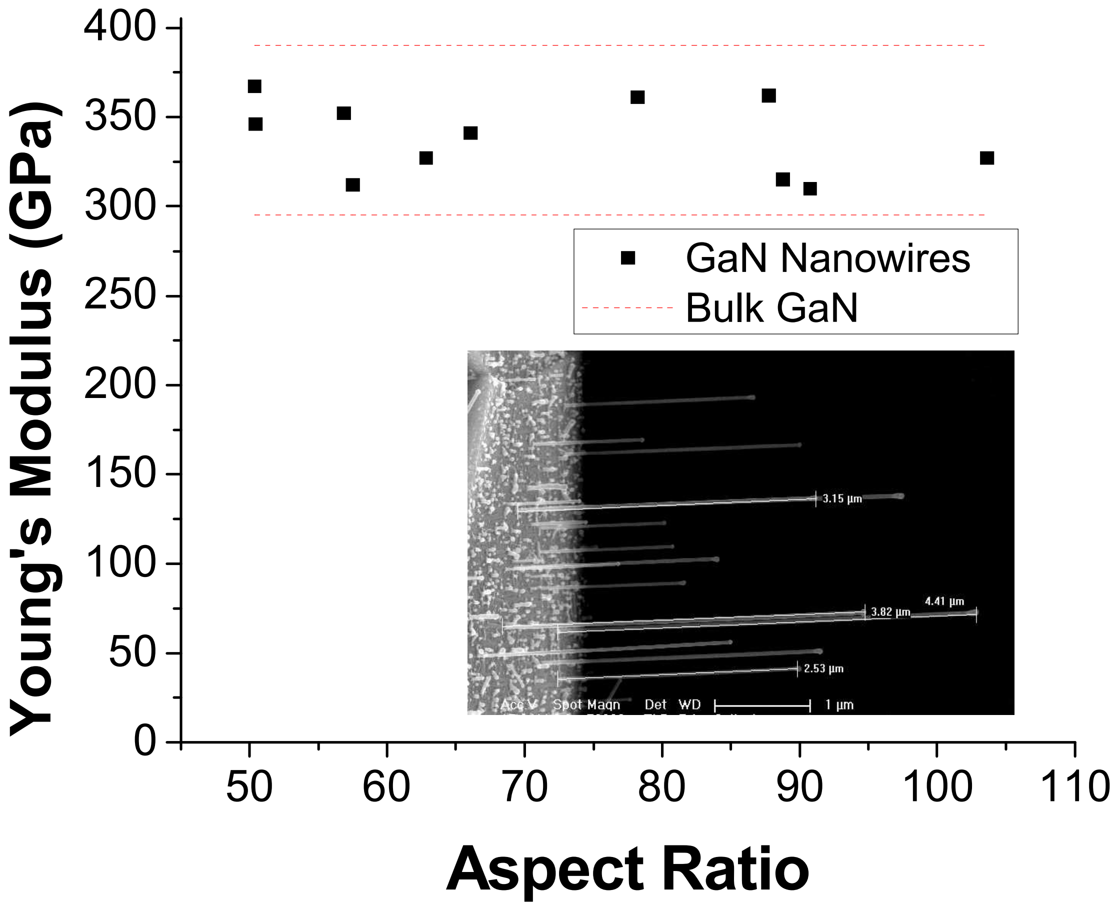




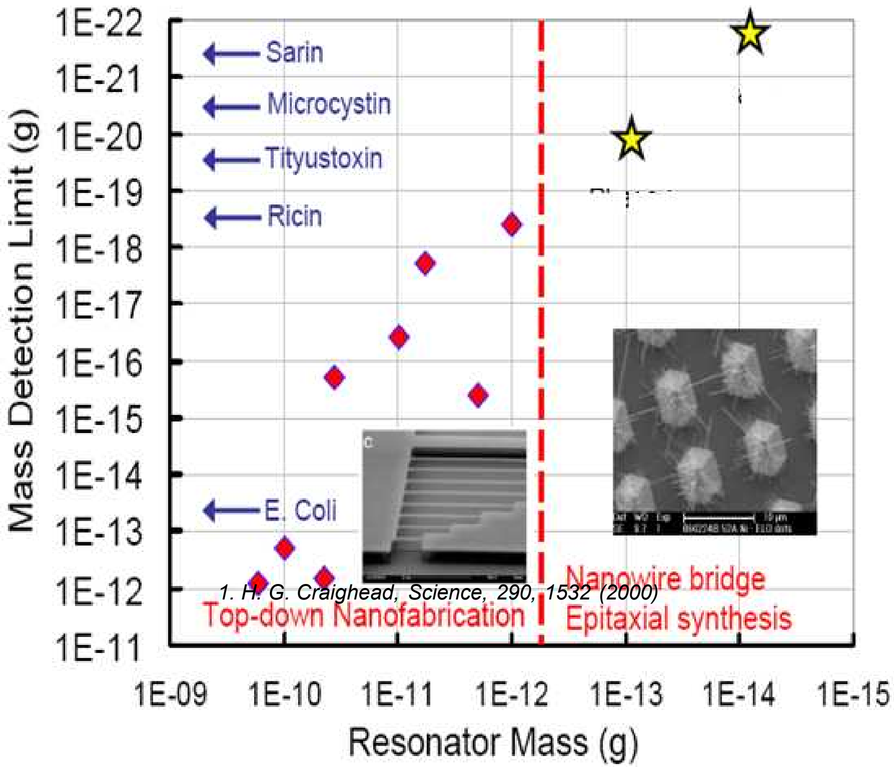
Summary of nanowire resonance analysis

Wire No.	L (um)	b (nm)	f_x (MHz)	f_y (MHz)	Q	E (GPa)	φ
0826_1	4.3	49	2.062	2.323	591	362	62.87°
0826_2	2.68	46.6	4.679	5.279	542	312	62.90°
0826_3	2.89	46	4.046	4.589	757	327	63.02°
0826_4	2.98	45.1	3.771	4.320	895	341	63.25°
0826_5	2.17	43	6.903	7.828	929	346	63.02°
0826_7	2.50	44	5.303	6.081	867	352	63.28°
0826_8	2.04	40.5	7.420	8.584	1008	367	63.48°
0826_9	4.81	53	1.645	1.859	717	310	62.94°
0826_10	4.66	52.5	1.756	1.975	693	315	62.83°
0826_11	3.52	45	2.805	3.179	905	361	63.00°
0826_12	6.0	57.9	1.182	1.340	400	327	63.01°

GaN Nanowire Young's Modulus



Summary

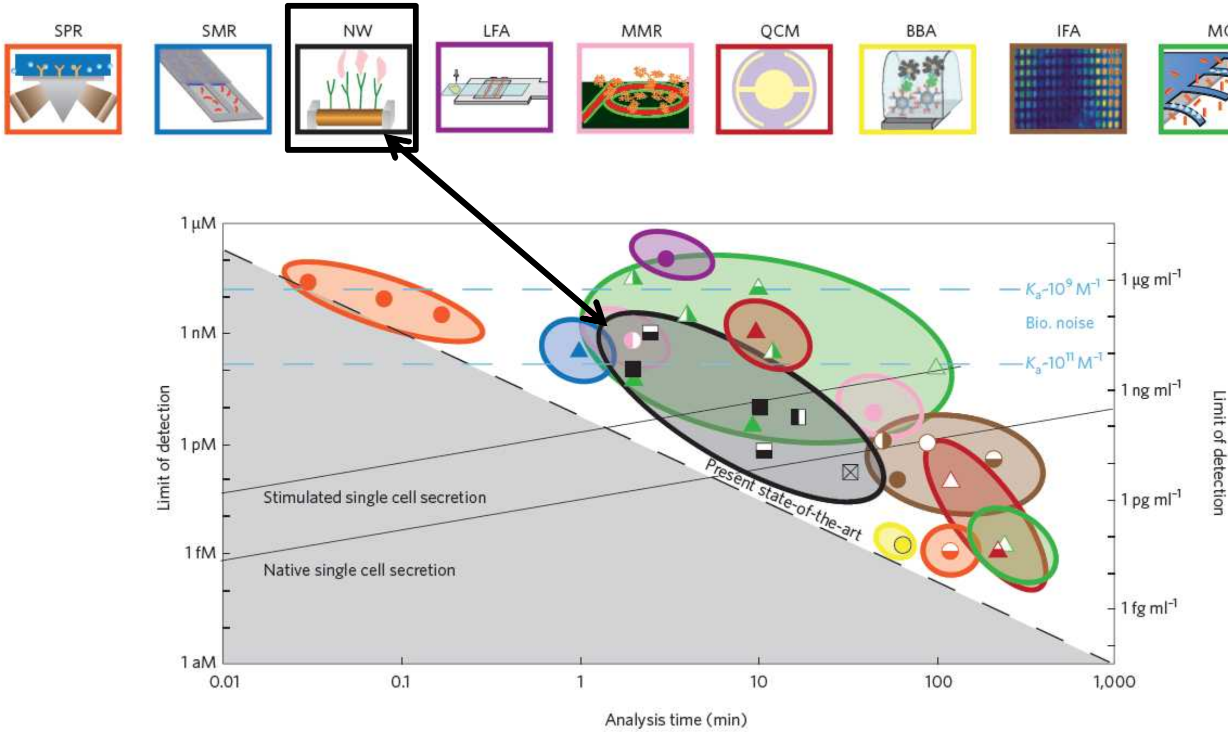


- Bottom-up synthesis of horizontally connected GaN nanowires, having a high Young's modulus and high PE coefficient, could offer a unique pathway to the fabrication of NEMS devices.

Outline

- Motivation
- Lateral Gallium Nitride (GaN) Nanowire Synthesis
- Nanomechanical Properties
- **Biomedical Applications**

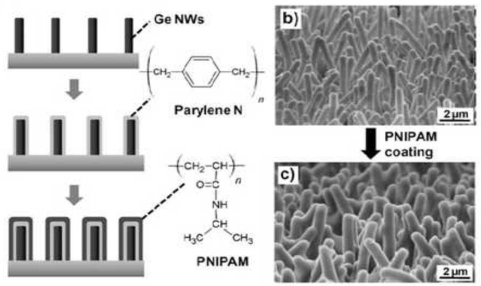
Current state of the art sensors



J.L.et. al., Nature Nanotechnology, ***6,*** *203, (2011)*

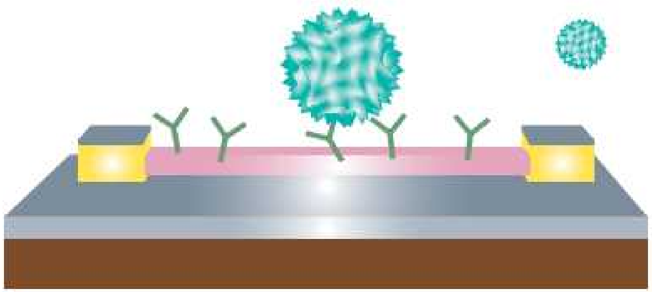
Nanowires; biomedical applications

Thermal Heating



H. Ko et. al., Angew. Chem. Int. Ed. 49, 616, (2010)

Nano-Chem/Bio Sensors



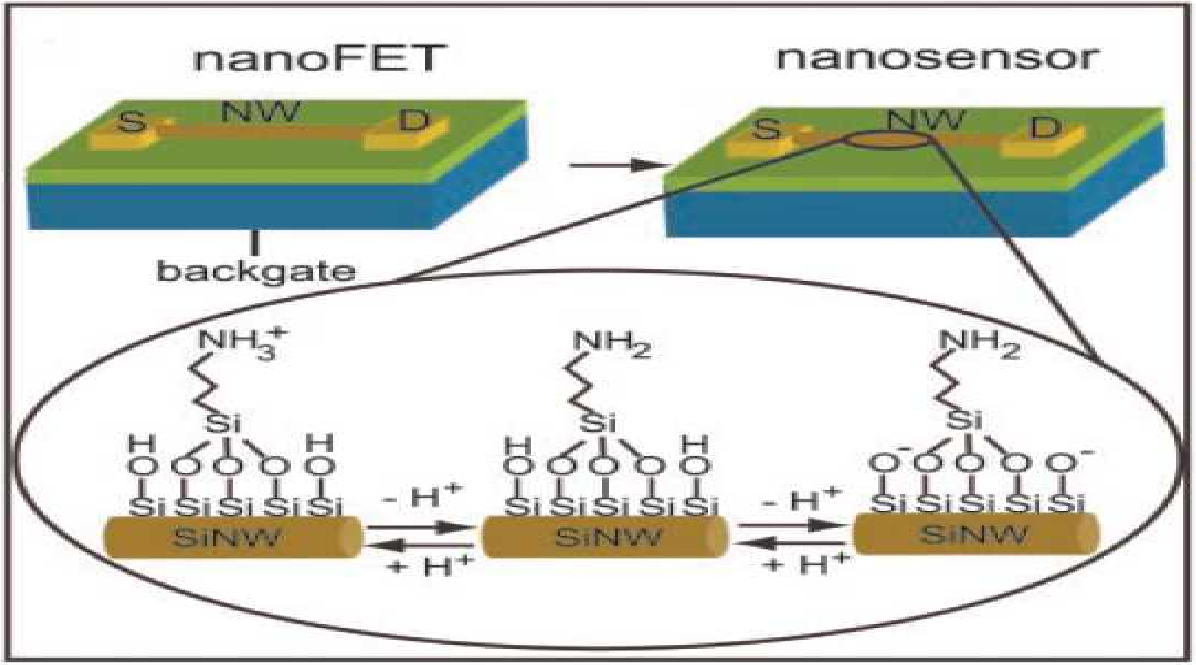
F. Patolsky, G. Zheng, C.M. Lieber, Nanomedicine, (2006), 1, 51, (2006)

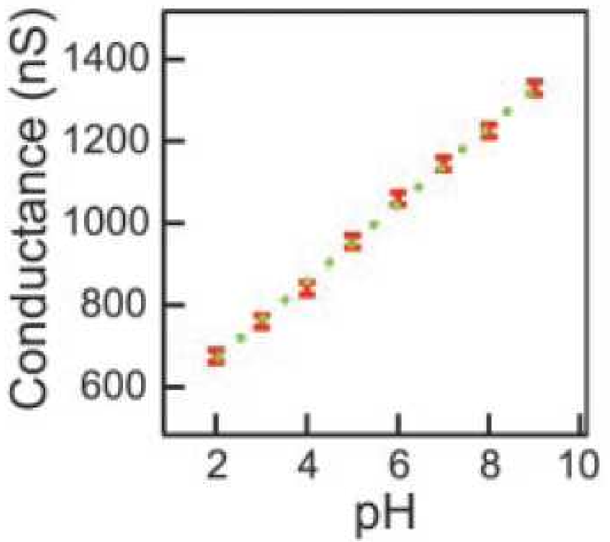
NEMs Sensors

N. Lavrick et.al SPIE's oemagazine [February 2005]

Bio-molecular sensing
Nanowire sensors

Nano-Chem/Bio Sensors

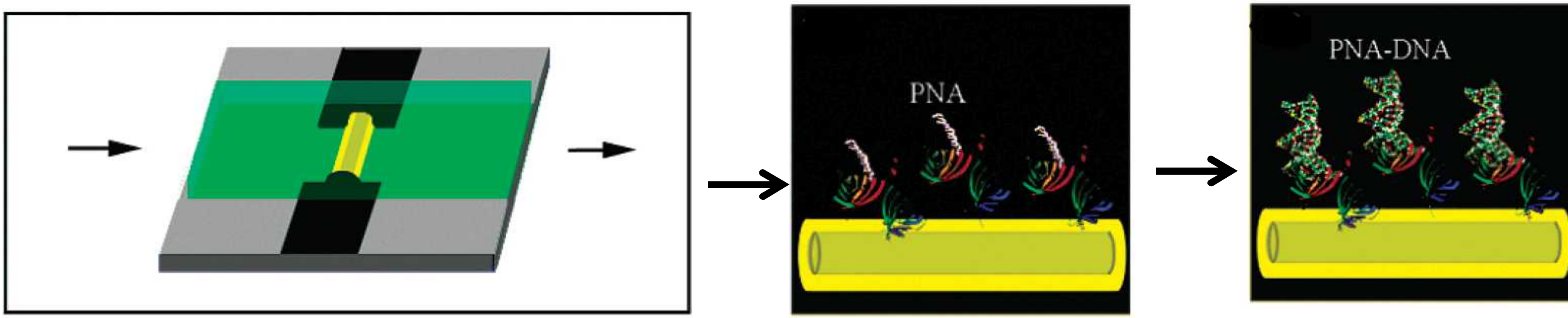




Y. Cui, et. al "293, 1289, (2001).

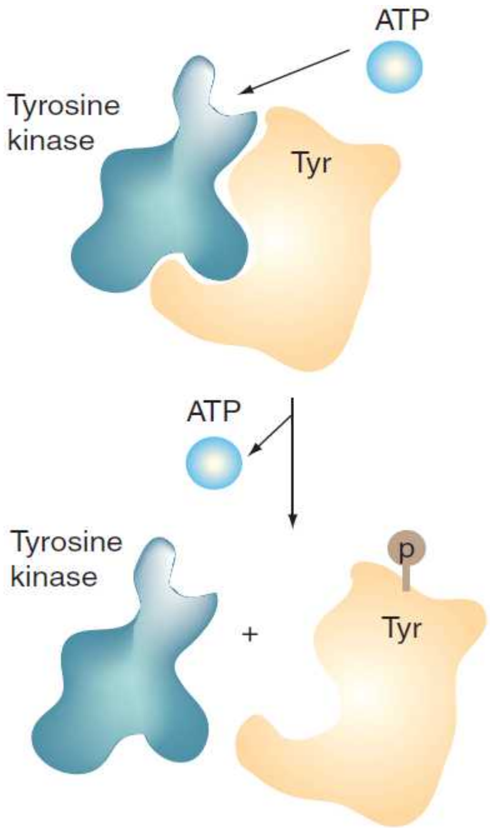
- High surface-to-volume ratio
  - -Highly sensitive and selective biological and chemical sensing purposes
  - -Takes advantage of conductance property of nanowire
  - -Molecules can bind to the nanowire surface

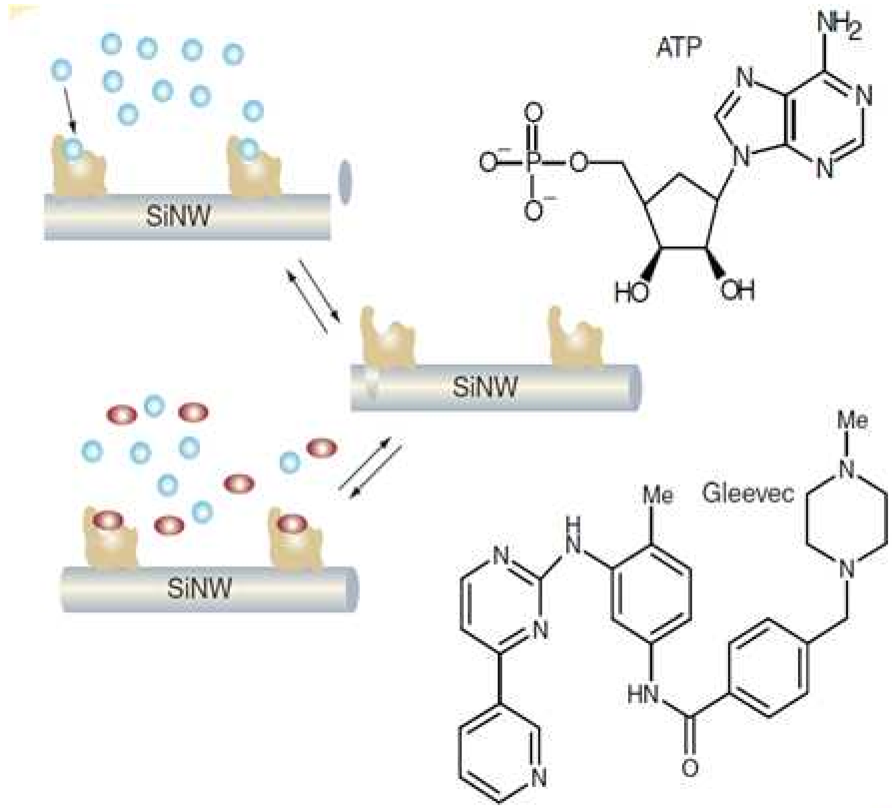
Bio-molecular sensing
Nanowire sensors



J. I. Hahm, Nanolett, 4, 51, (2004)

Drug Delivery





F. Patolsky, G. Zheng, C.M. Lieber, Nanomedicine, (2006), 1, 51, (2006) Sandia National Laboratories

Conclusions

LUX ET VERITAS

Achieved high density of aligned lateral GaN nanowire arrays

Nanoelectromechanical properties measured to obtain Young's modulus and quality factors of GaN nanowires

Nanowires have useful biomedical applications

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Jung Han's Lab
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Ainissa Ramirez's Lab
- Professor Ainissa Ramirez, Dr. Xu Huan, Dr. Brian Lewis

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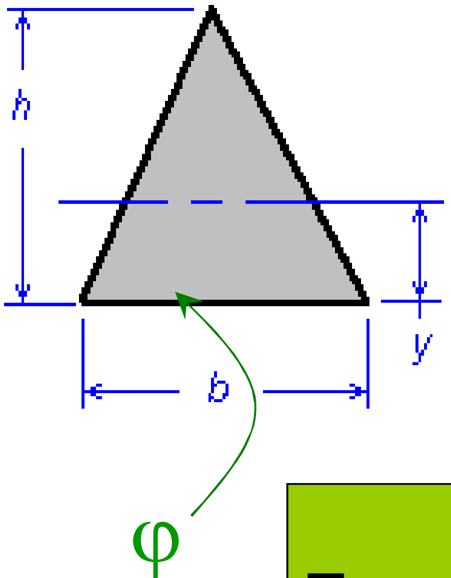
California Institute of Technology, CA
- Professor Hong Tang, (currently at Yale University)

BACKUP SLIDES

Modal Analysis



$$f_0 = B_i^2 \big/ 2\pi L^2 \sqrt{EI / \rho A}$$

$B_1 = 1.875$

$$I_x = \frac{bh^3}{36}, I_y = \frac{b^3 h}{48}, A = \frac{bh}{2}$$

Two orthogonal modes:

$$f_{0x} = B_i^2 \big/ 2\pi L^2 \sqrt{Eh^2 / 18\rho}$$

$$f_{0y} = B_i^2 \big/ 2\pi L^2 \sqrt{Eb^2 / 24\rho}$$

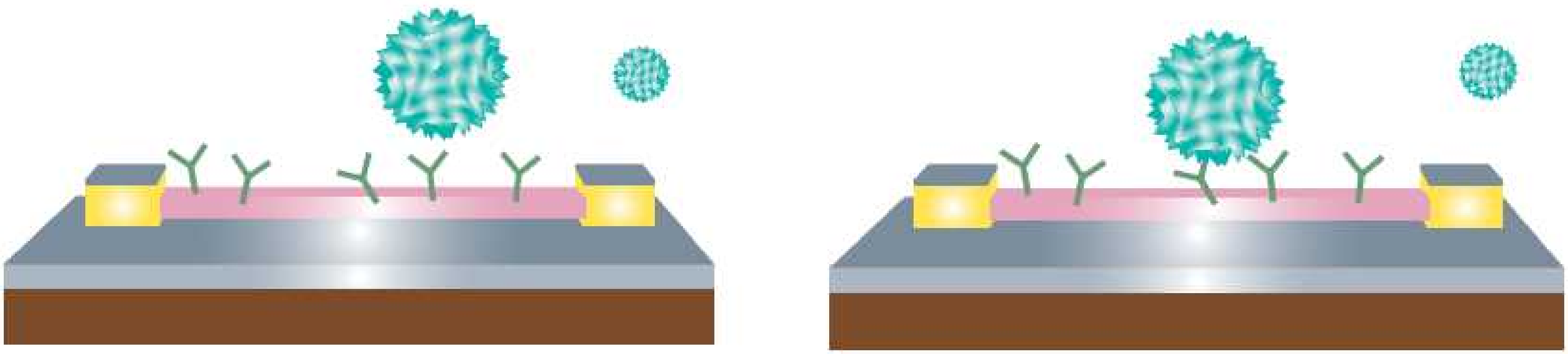
$$\frac{f_{0x}}{f_{0y}} = \frac{\sqrt{3}}{\tan\varphi}$$

For equilaterals: $\varphi = 60^\circ \quad \dfrac{f_{0x}}{f_{0y}} = 1$

Otherwise: $\varphi = \tan^{-1}\left(\sqrt{3} f_{0y} \big/ f_{0x}\right)$

Motivation
(bio-molecular sensing)

Nano-Chem/Bio Sensors

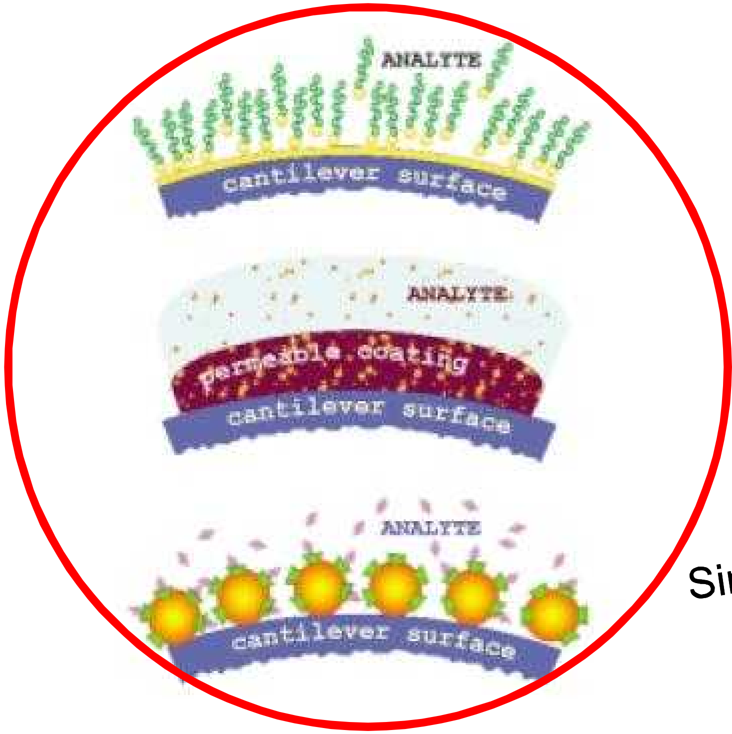


F. Patolsky, G. Zheng, C.M. Lieber, Nanomedicine, (2006), 1, 51, (2006)

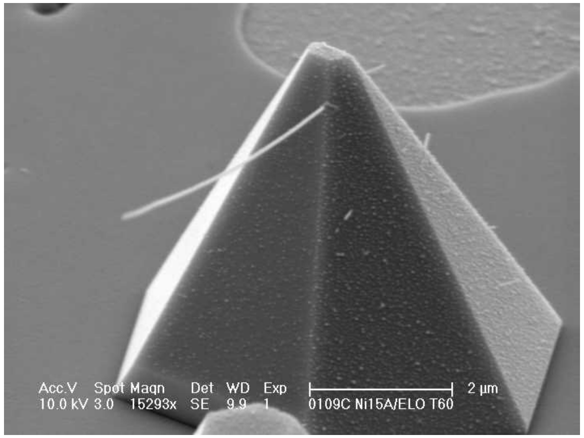
➢High surface-to-volume ratio

-Highly sensitive and selective biological and chemical sensing purposes

Nanowire Cantilever-sngle nanowire sensors

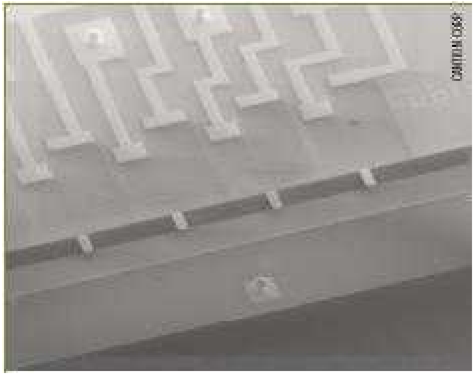


Single NW cantilever



N. Lavrick et.al SPIE's oemagazine [February 2005]

Multiple nanowire sensors



Stimulus affects mechanical state of cantilever

Multiple NW cantilevers