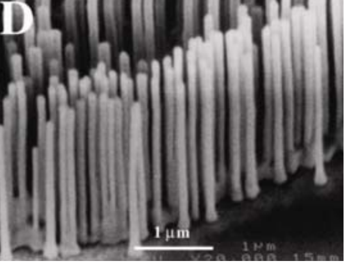
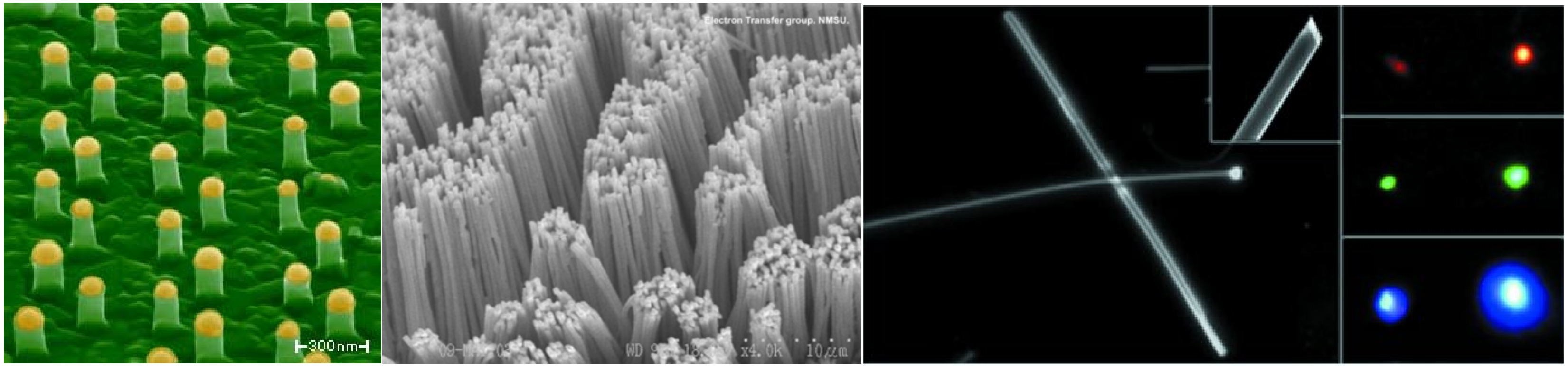
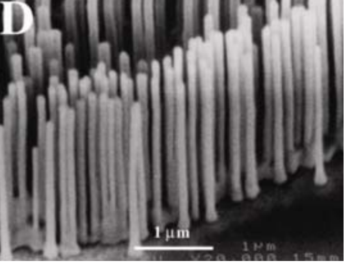




# Growth and Properties of Inorganic Nanowires

Moritz Hauf

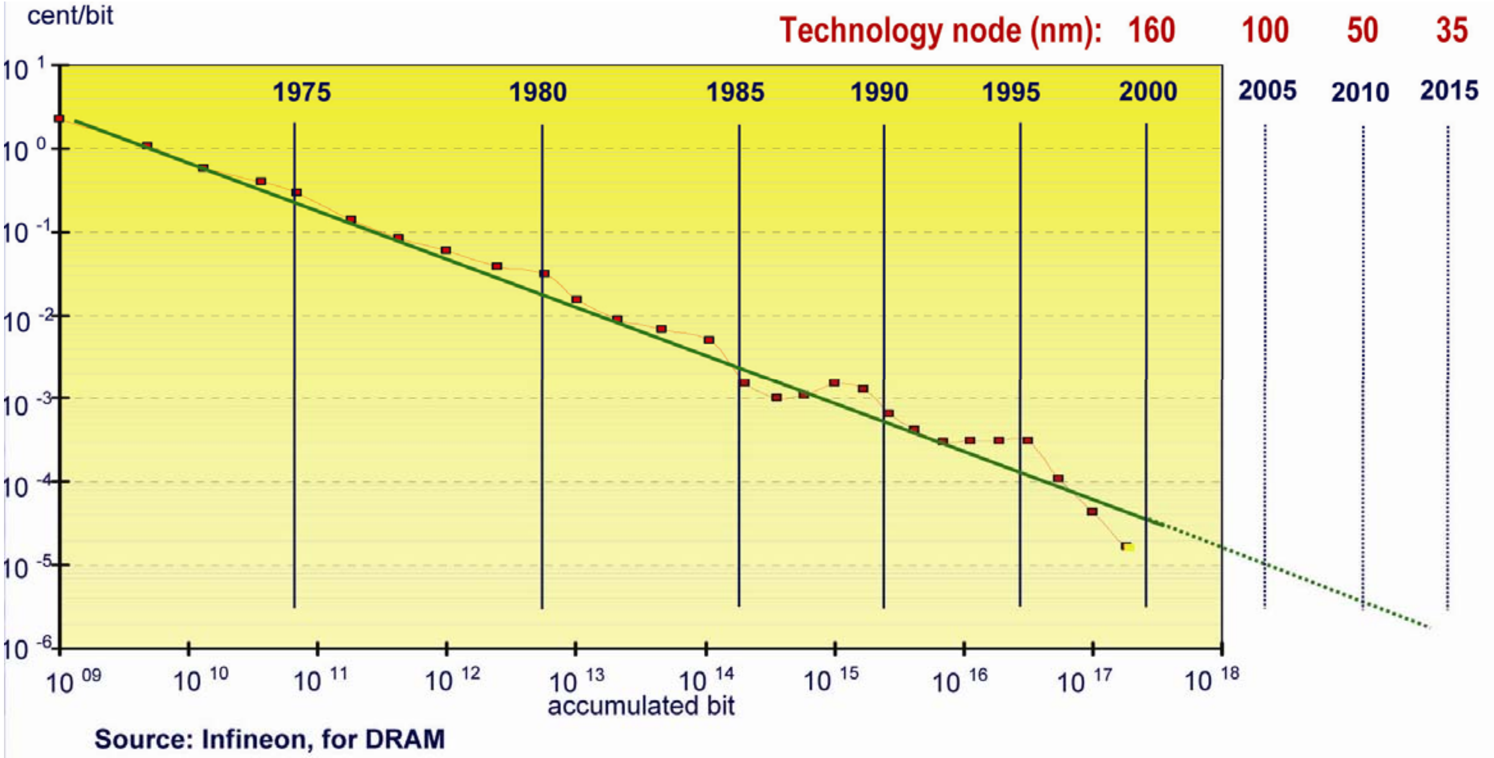
MB-JASS 2006 Moscow



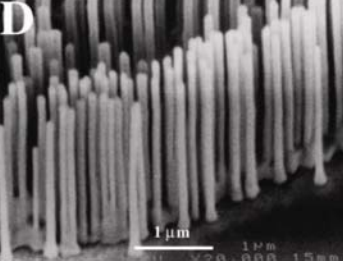
# Why do we need nanowires?

Moore's Law (1965):

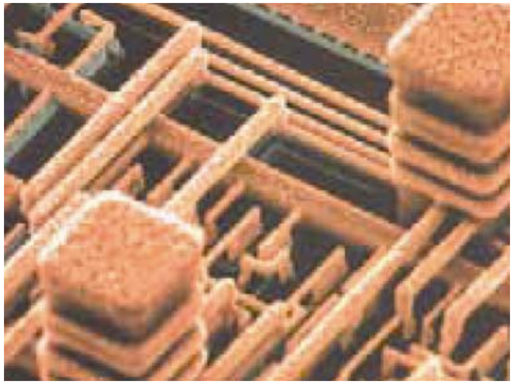
*“With unit cost falling as the number of components per circuit rises, by 1975 economics may dictate squeezing as many as 65.000 components on a single silicon chip”*



Source: Infineon, for DRAM



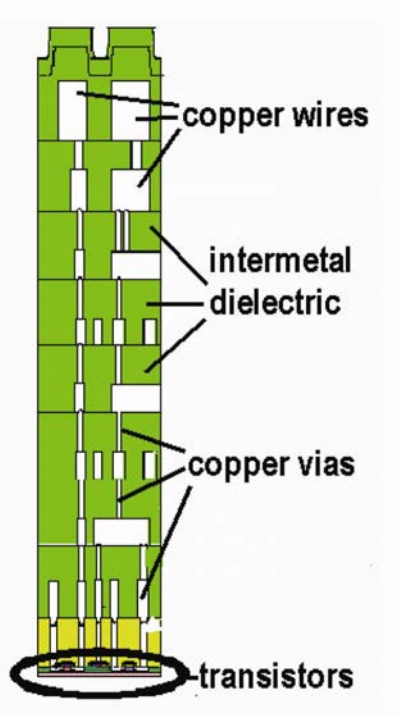
# Growing nanowires “bottom-up”



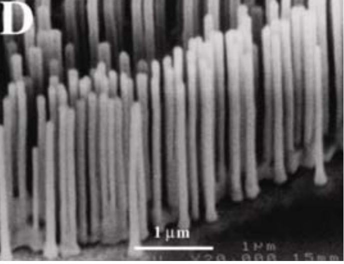
- Downsizing of chips / transistors

=> **Nanowires**

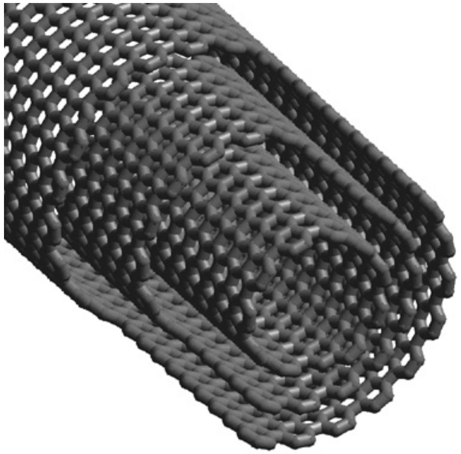
- Diameter: 10 – 100 nm
- Length: some microns



cross-section thru chip



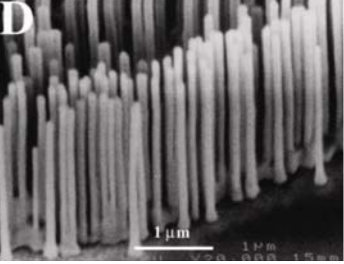
# Materials for Inorganic Nanowires



- **Carbon Nanotubes (CNT)**
- **Metal nanowires**

  e.g. Gold (Au)

- **Semiconductor nanowires:**
  - Zinc Oxide
  - Indium Phosphate
  - Gallium Arsenide
  - Gallium Nitride
  - Germanium
  - Silicon



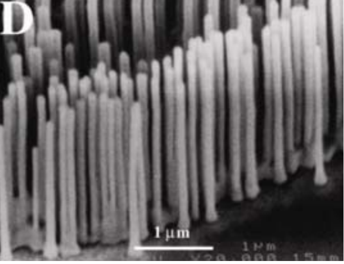
# Growing Nanowires “Bottom-Up”

- Limit (physical / financial) of Lithographie (Top-Down)
- Need for new techniques

=> **“Bottom-Up” - Technique**

Controlled Self-Organization

- Direct growth of smallest structures



# Overview: From single nanowires to systems

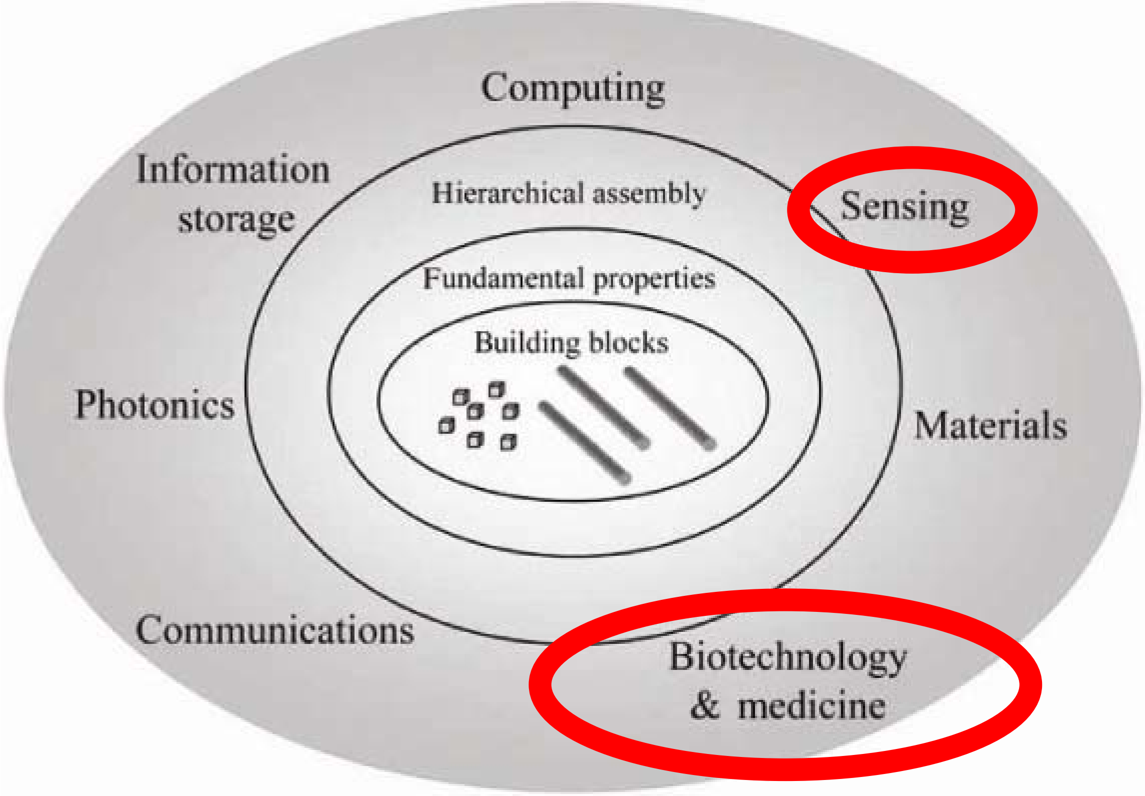
Nano building blocks like Lego

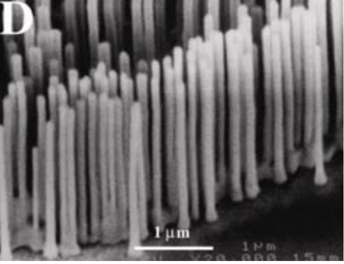
↓

Functional assembly

↓

System



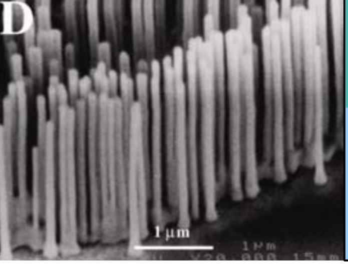


# Growing Nanowires “Bottom-Up”

Starting with building blocks

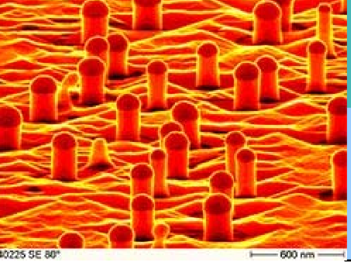
Parameters to control:

- Location
- Density
- Length
- Diameter
- Crystal orientation



# Different Methods for Bottom-Up

- Vapor-Liquid-Solid (VLS) Epitaxy
  - liquid alloy drop lets NW grow
- Vapor-Solid Epitaxy
  - like VLS
  - no catalytic alloy, growth on structural defects
- Template-Directed Synthesis
  - template as scaffold
  - often polycrystallline
  - limited quantities
- Self-Assembly of Nanoparticles
- Size Reduction of Micrometer Scale Strutures



## Main Idea

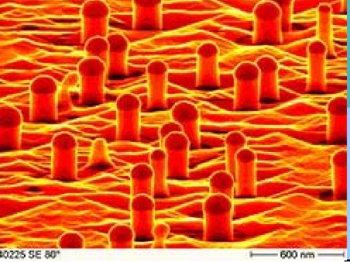
- First proposed by Wagner and Ellis in 1964
- Described in Detail by E. I. Givargizov 1975
- Need for systematic nanostructure syntheses -> renewed interest

- Crystal growth mechanism catalyzed by metal eutectic nanodroplet

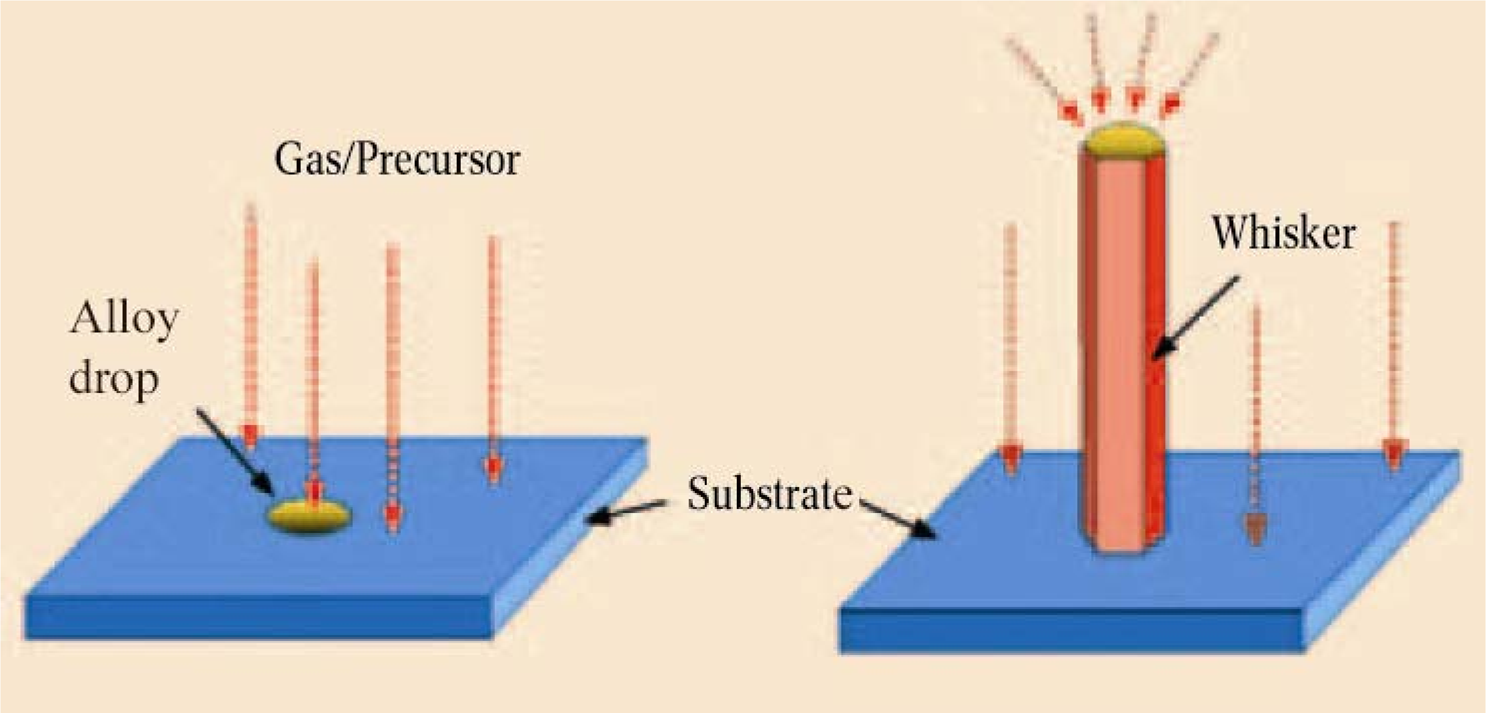
Crystallization:

  - Nucleation
  - Growth

=> not easy to control

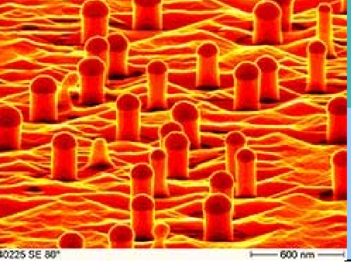


# Principal



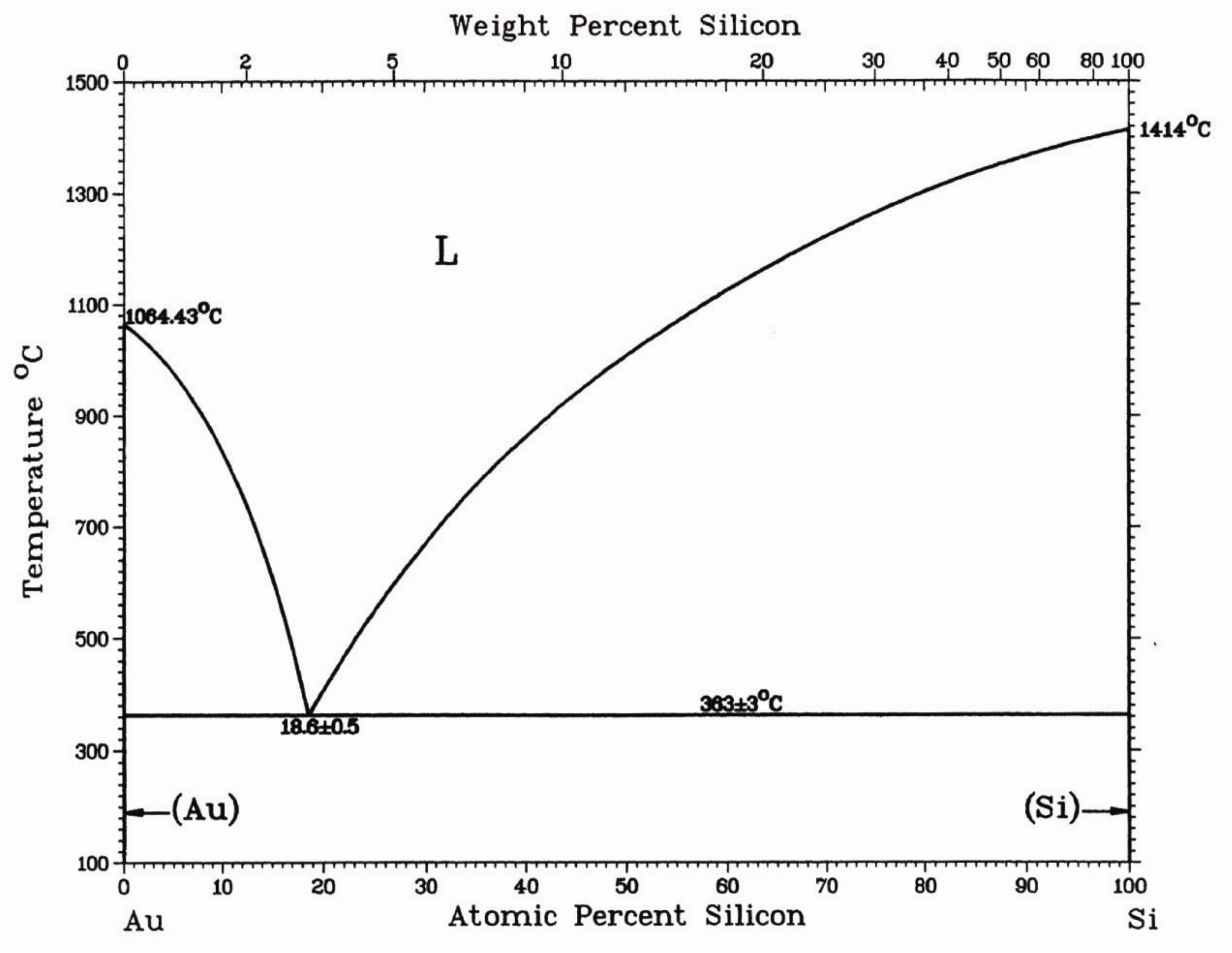
**Three main stages**

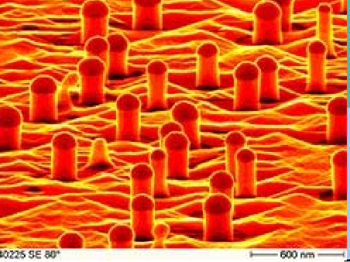
- Alloying
- Nucleation
- Growth



# Catalyst

- Catalyst cluster defines diameter and location of nanowire
- Equilibrium phase diagram to chose catalyst
- We need liquid alloy of metal with growing material (Silicon)



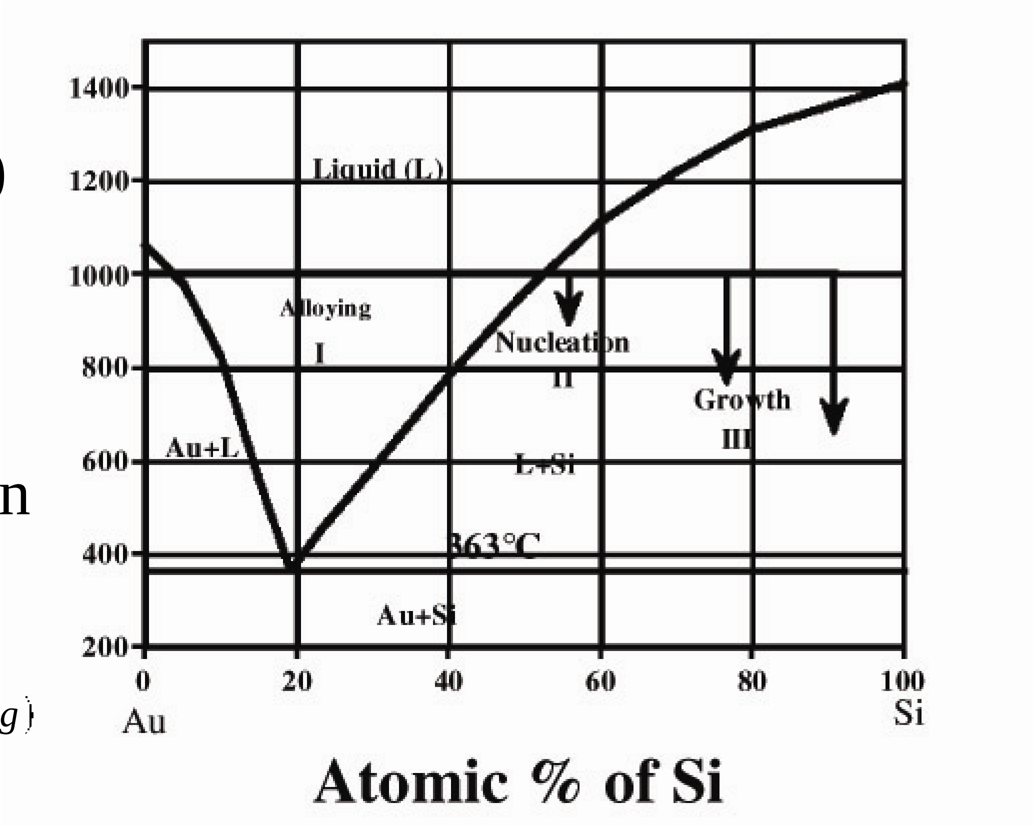


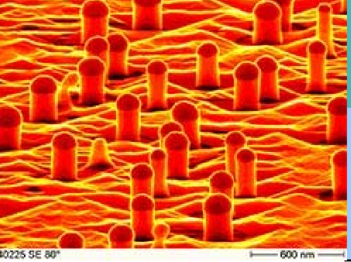
## Catalyst

- Temperature (1000°C) so that there is coexistence of liquid alloy and solid nanowire material
- Source material carrier gas (vapor)
  $SiH_4$
  $SiCl_4$
- More and more vapor condenses on alloy cluster

$$SiH_4 \rightarrow metal\ catalyst - Si_{\{l\}} + 2H_{2\{g\}}$$

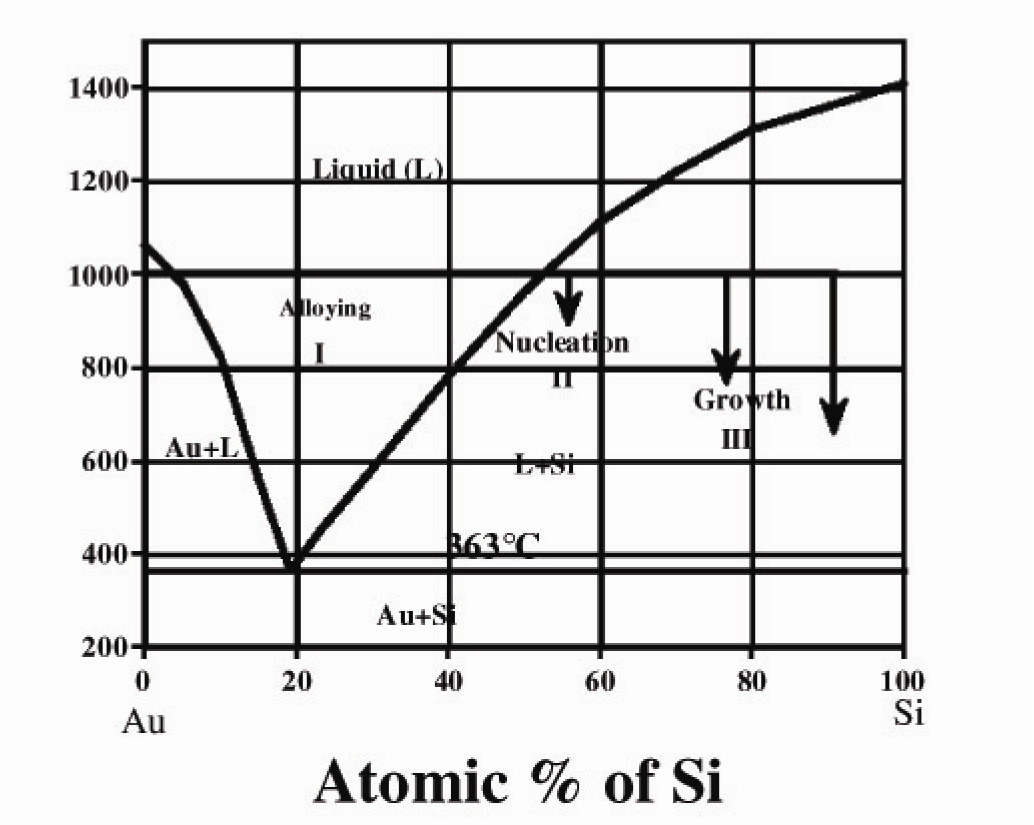
- Percentage of Si increase
- Supersaturation

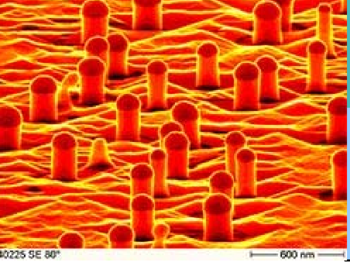




# Catalyst

- Liquid catalyst alloy cluster is a preferential site for absorption of reactant
- Higher sticking probability to liquid than to solid surface
- Solubility of Au in Si:
  $2 \cdot 10^{-4}$ Atomic %





# Catalyst

- Thicker NW grow faster

=> “Gibbs-Thomson-Effect”

- Driving force is difference of chemical potentials

$$\Delta\mu_{nanowire} = \Delta\mu_{bulk} - 4\frac{\Omega\alpha}{d}$$

$$\Delta\mu_{bulk} = \mu_{bulk} - \mu_{vapor}$$

$$\Delta\mu_{nanowire} = \mu_{nanowire} - \mu_{vapor}$$

- Effective chemical potentials $\mu$
- Atomic volume of Si $\Omega$
- Specific surface free energy $\alpha$
- Critical diameter $d_c$

$$\Delta\mu_{nanowire} = 0$$

$$\frac{\Delta\mu_{bulk}}{kT} = \frac{4\Omega\alpha}{kT}\frac{1}{d_c}$$

# Vapor-Liquid-Solid Epitaxy

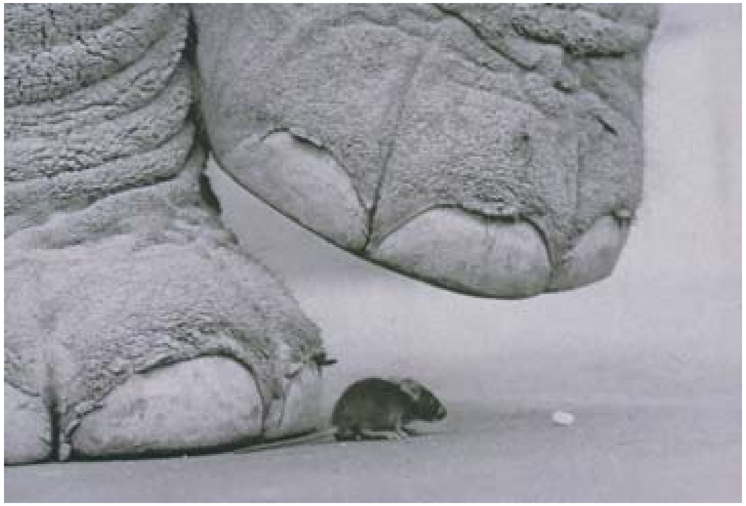
Equilibrium thermodynamics:
Minimum radius $r_{min}$

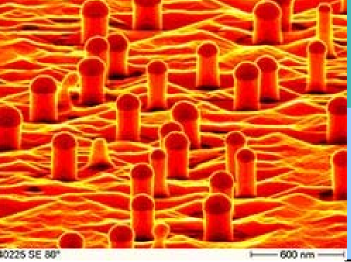
$$r_{min} = 2\sigma_{LV} V_L / RT \ln \sigma$$

Liquid-vapor surface free energy $\sigma_{LV}$
molar Volume $V_L$
as usual $R, T$
vapor phase supersaturation $\sigma$

-> minimum radius $r_{min} \approx 0{,}2\,\mu m$

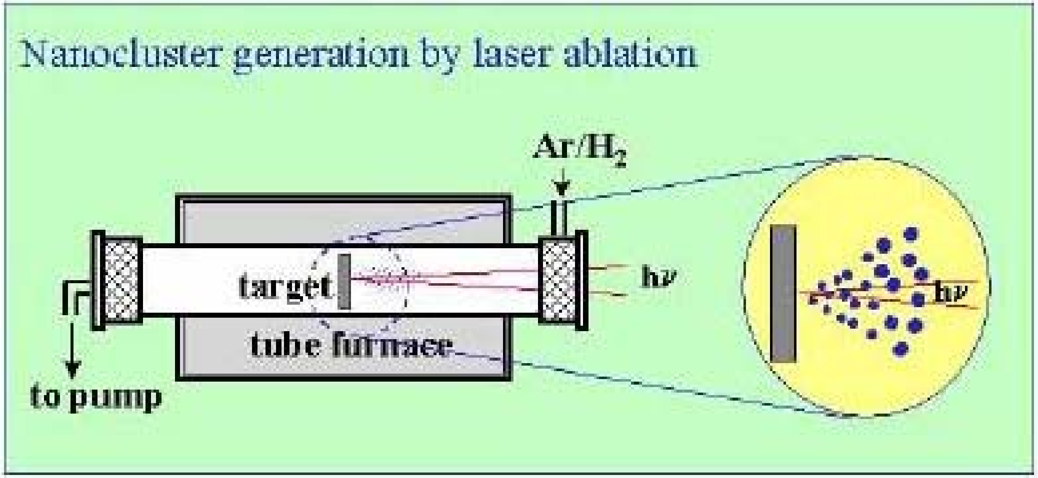
But we want SMALLER diameters!

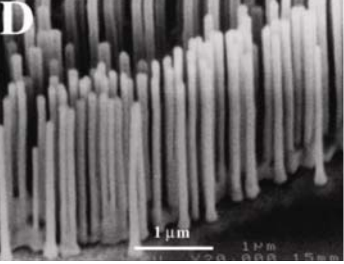




# Vapor-Liquid-Solid Epitaxy

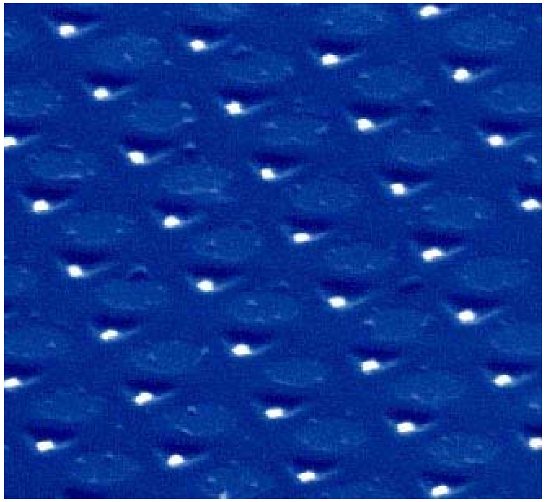
- Laser ablation and condensation
- Laser ablation of Si/catalyst target produces vapor
- Vapor rapidly condenses into liquid nanoclusters





# Controlling the Localization - Nanopatterning

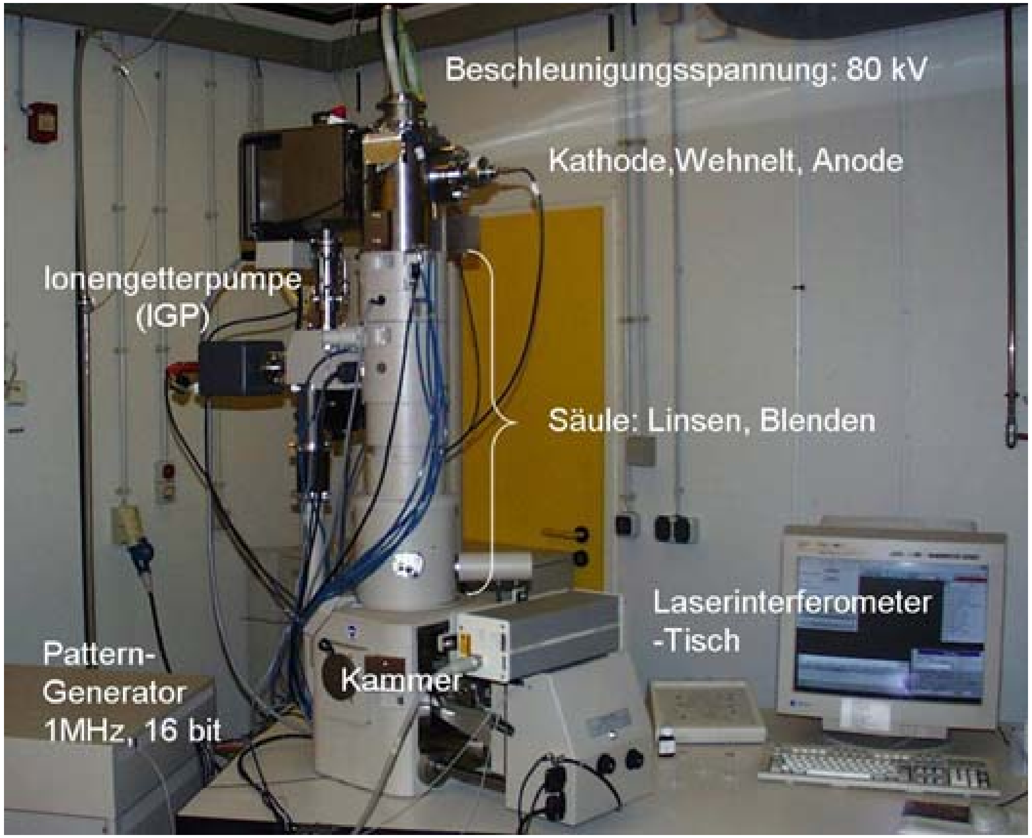
- Pattern on substrate
- Fast and cheap method

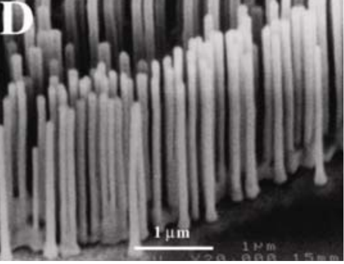


- Positioning of metal catalyst crystals
- Problem: high temperature leads to diffusion

# E – Beam Lithographie

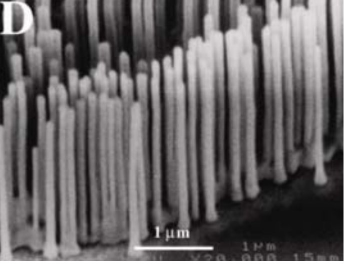
- Adjustable wavelength down to nanometer scale
- Not cheap enough for big areas
- Long time for exposure
- Difficult to keep parameters of E-Beam constant and stable





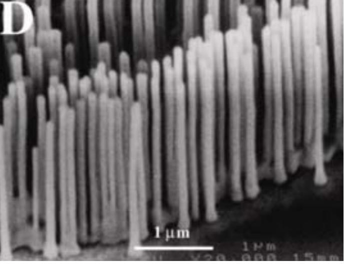
# Manipulation of Single Goldpoints

- Nice for demonstration
- Not usable for mass production
- Very clean conditions => ultra high vacuum



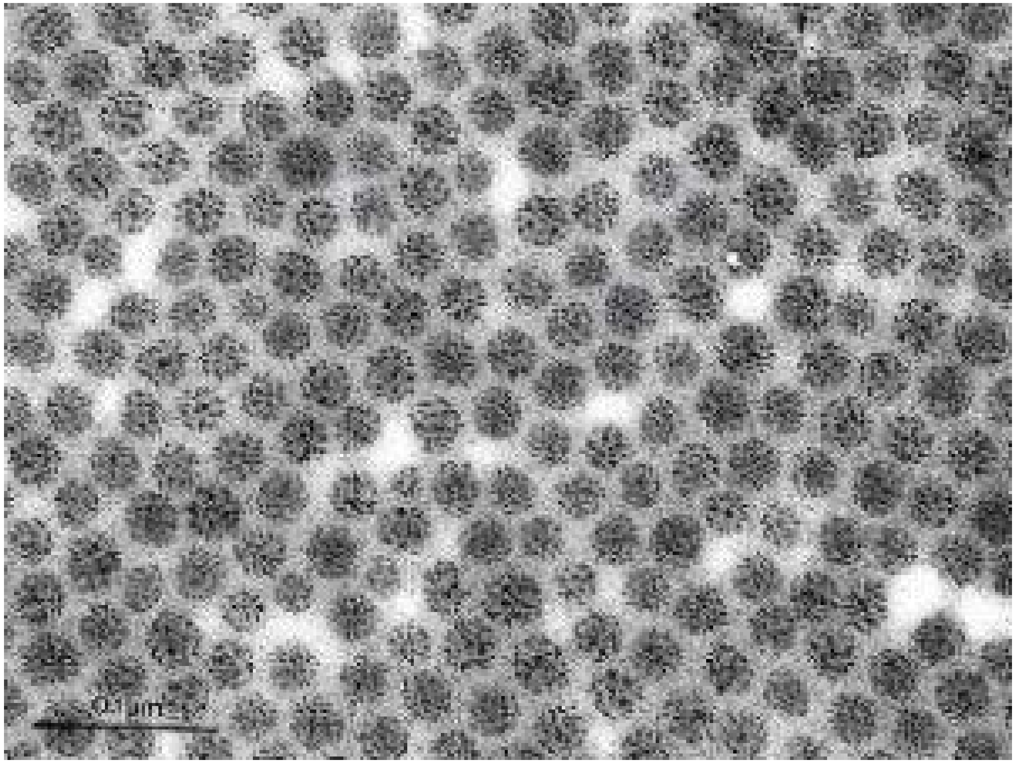
# Suspension of Gold Crystals

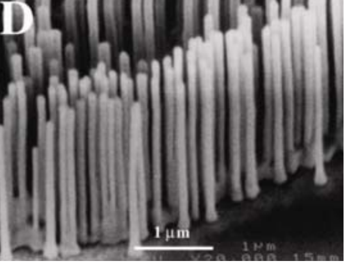
- Homogeneous size distribution
- Down to 2 nm without lithographic methods
- Adjustable density ($10^6 – 10^{12}$ $cm^{-2}$)
- Difficult to get regular pattern
- Important role of solvent and surface of substrate
- Let solvent dry => clusters of gold crystals



# Block Copolymers

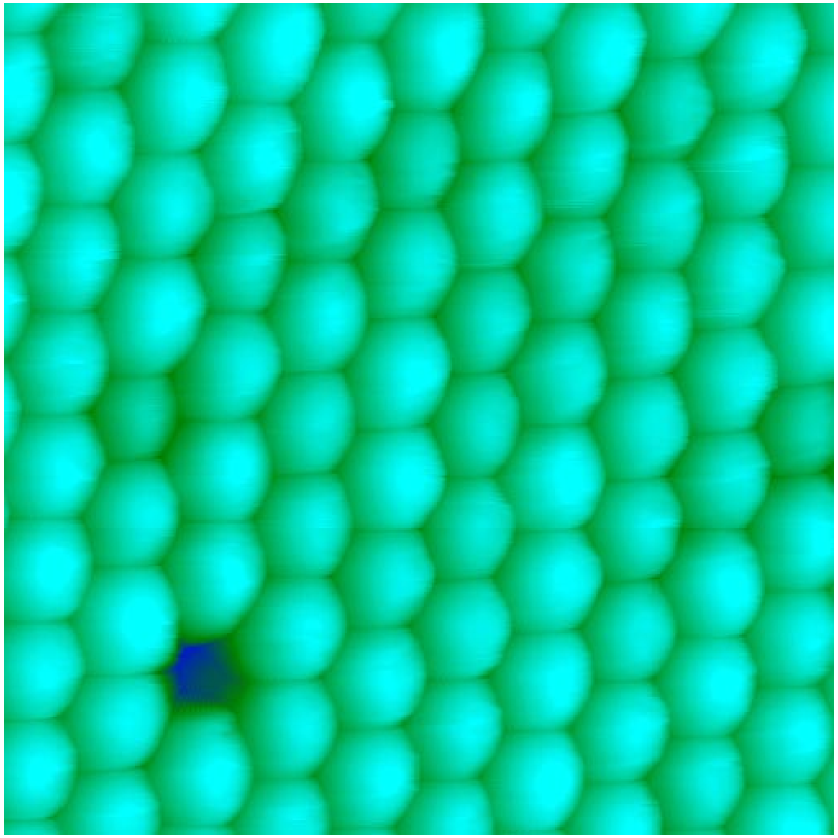
- Pattern with nanometer periodicity
- Two components determine structure
- Preparation on siliconnitride surface => etching copies structure to surface
- Filling holes with metal

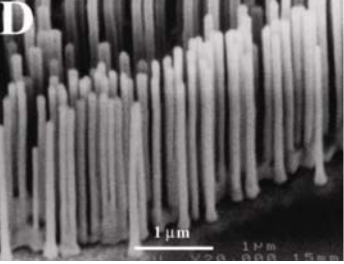




# Nanosphere Lithographie

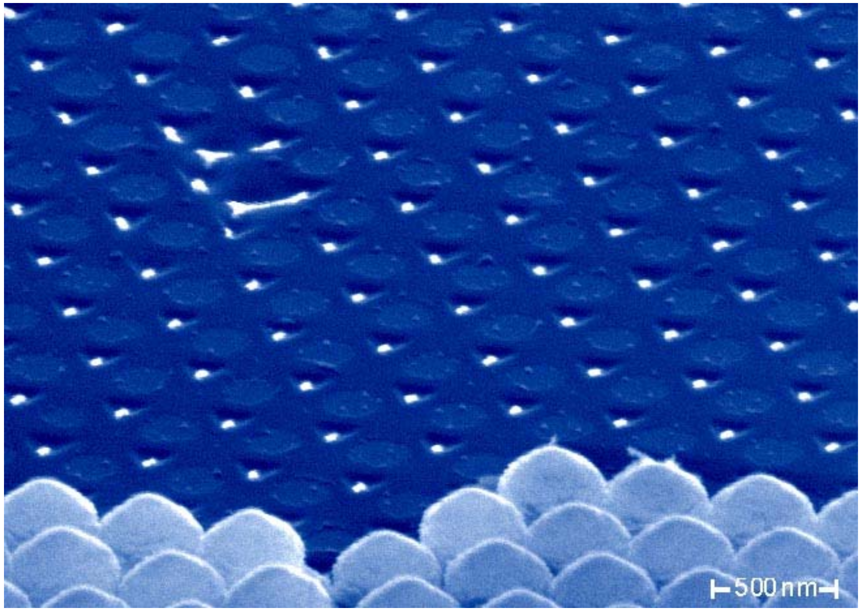
- Small spheres form hexagonal monolayer
- Definite sphere sizes
- Use of monolayer as template

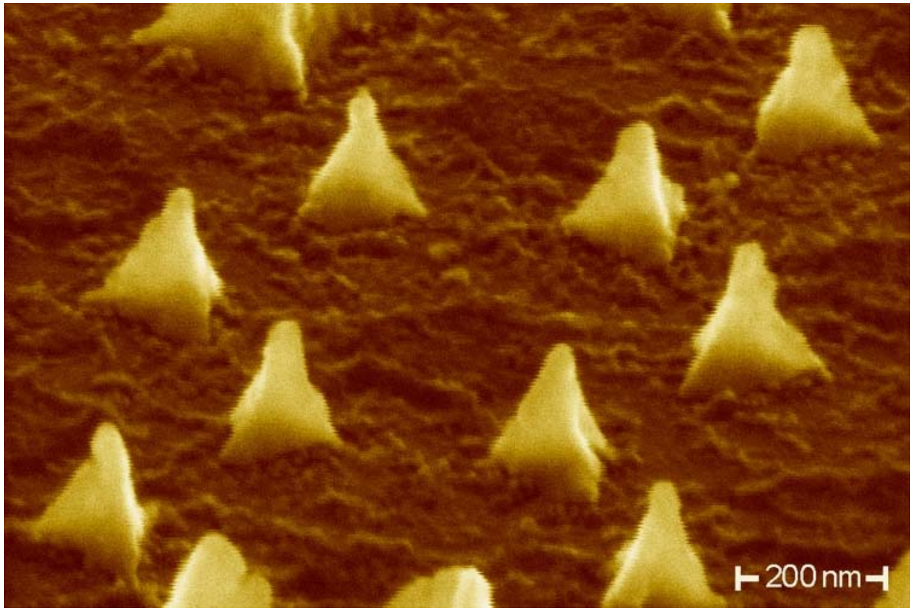




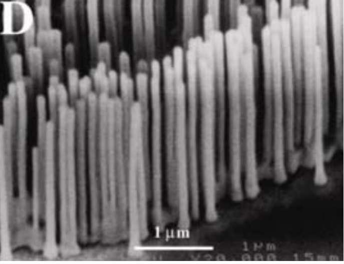
# Nanosphere Lithographie

- Sputtering metal against nanosphere monolayer



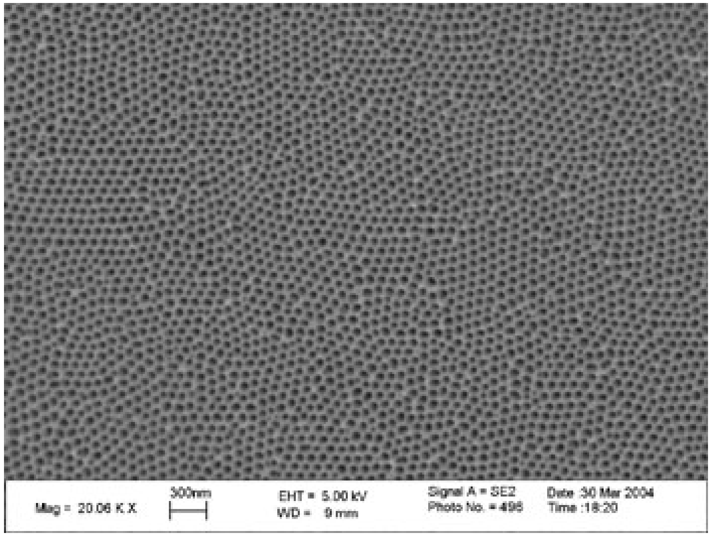


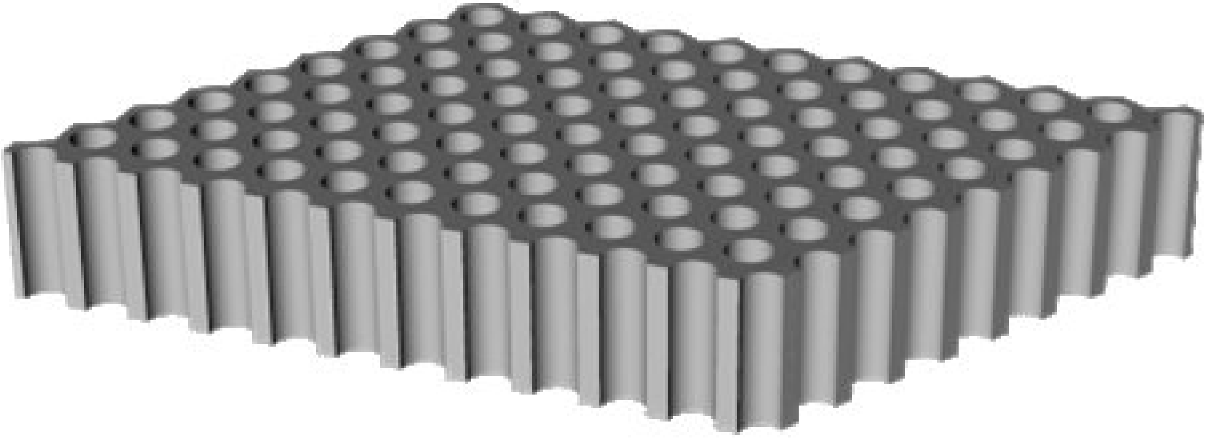
- no independent control of size and distance
- Large arrays ( > 1 cm²)
- Very few defects

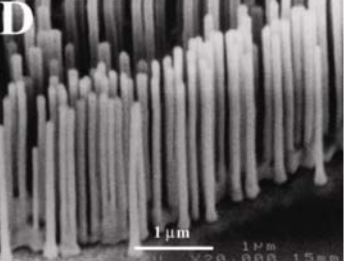


# Aluminum Oxide Template

- Electro chemical Oxidation of Aluminum
- Normally no specific distribution of pores
- Masuda & Fukuda (1995): Hexagonally distributed pores
- 100 microns deep

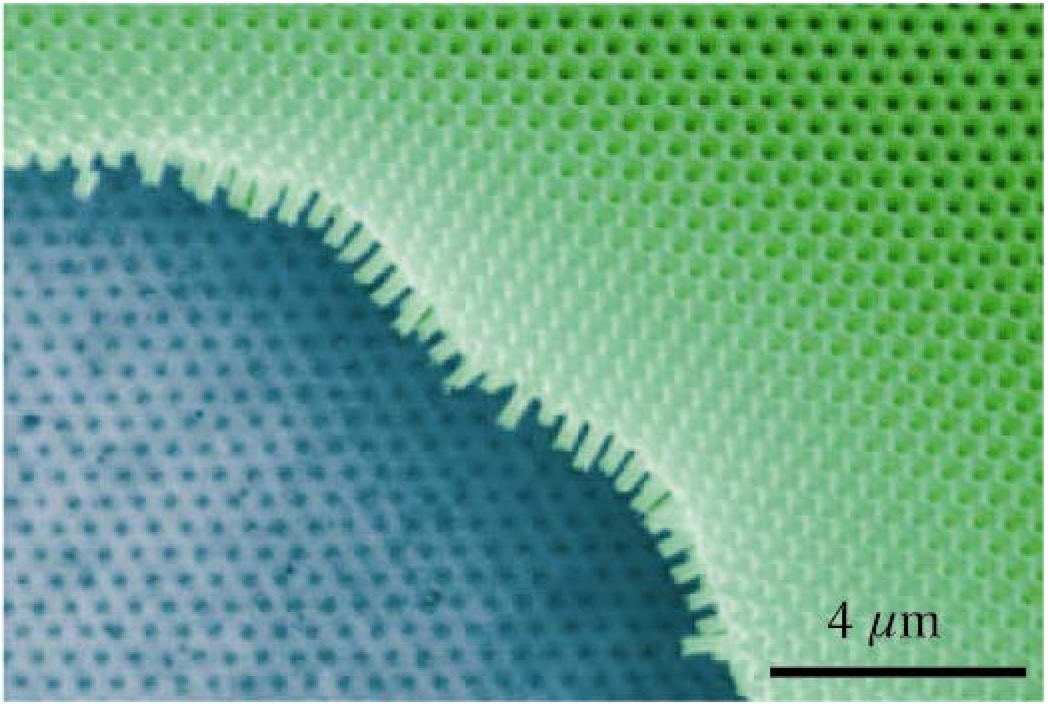


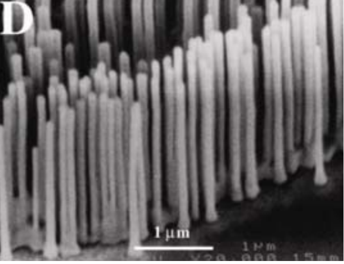




# Aluminum Oxide Template

- Aluminum Oxide as template for metal membrane
- Electrochemical deposition of metal on porous $Al_2O_3$
- Stable metal membrane
- Large areas can be created

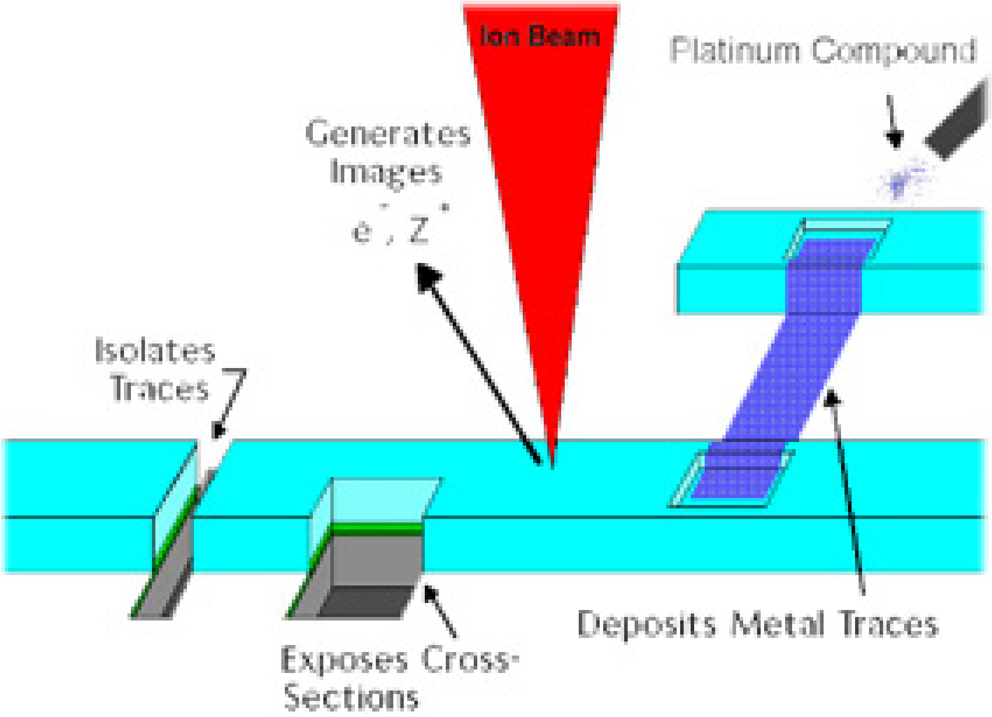


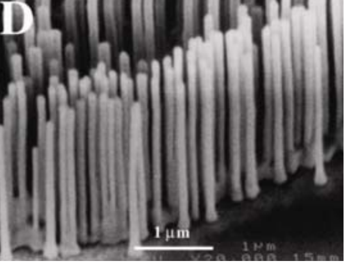


# Focused Ion Beam

- Getting images (like Scanning Electron Microscope)
- Also manipulating!

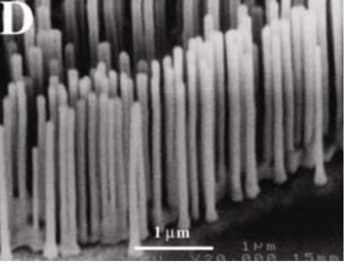
Deposition of metal





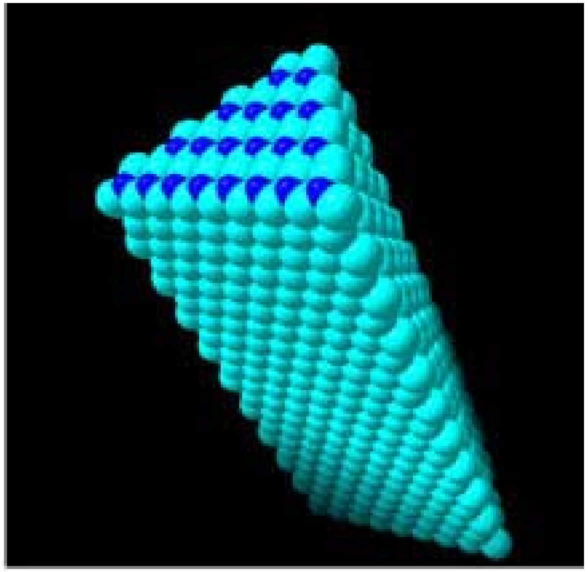
# Controlling the Localization - Nanopatterning

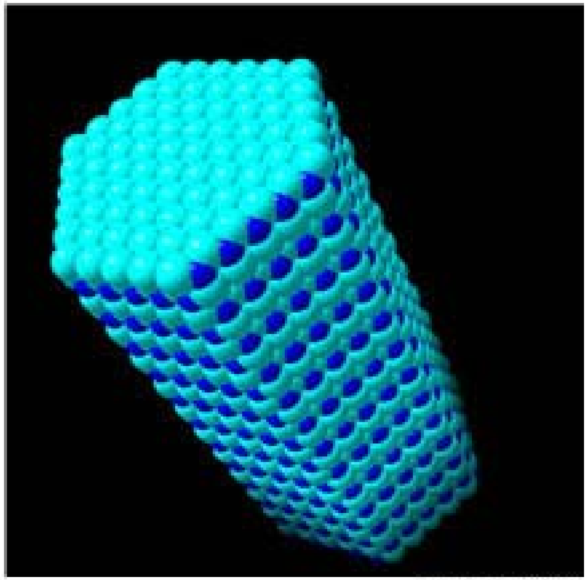
- E-Beam Lithographie
- Manipulating of single Drops
- Suspension of Gold-Crystals
- Di-Block Copolymers
- Nanosphere – Lithographie
- Alumina as a Mask
- Focused Ion Beam



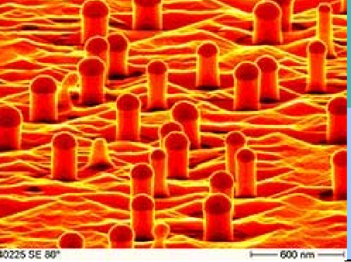
# Controlling the Crystal Orientation

- Important for applications
- Appropriate substrate (single-crystalline) selection
- ZnO grows along [001] direction on (110) substrate
- GaN on MgO(111) grows in [001] with hexagonal cross section



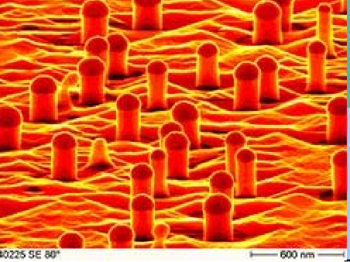


Source: UC Berkeley



# Template-Directed Synthesis

- Template as scaffold
- Nanostructure has complementary morphology to template
- Post-synthesis treatment removing template
  - => harvest of nanostructures
- Simple
- High through-put
- Limitation: polycrystalline NW



# Templating Against Features on Solid Substrates

- Templates by lithography or etching

(A) 15 nm metal NW against Si(100) wafer

(B) long, parallel NW arrays (e.g. by MBE)

(C) very precise size control due to MBE

(D) electrodeposition against steps of pyrolytic graphite

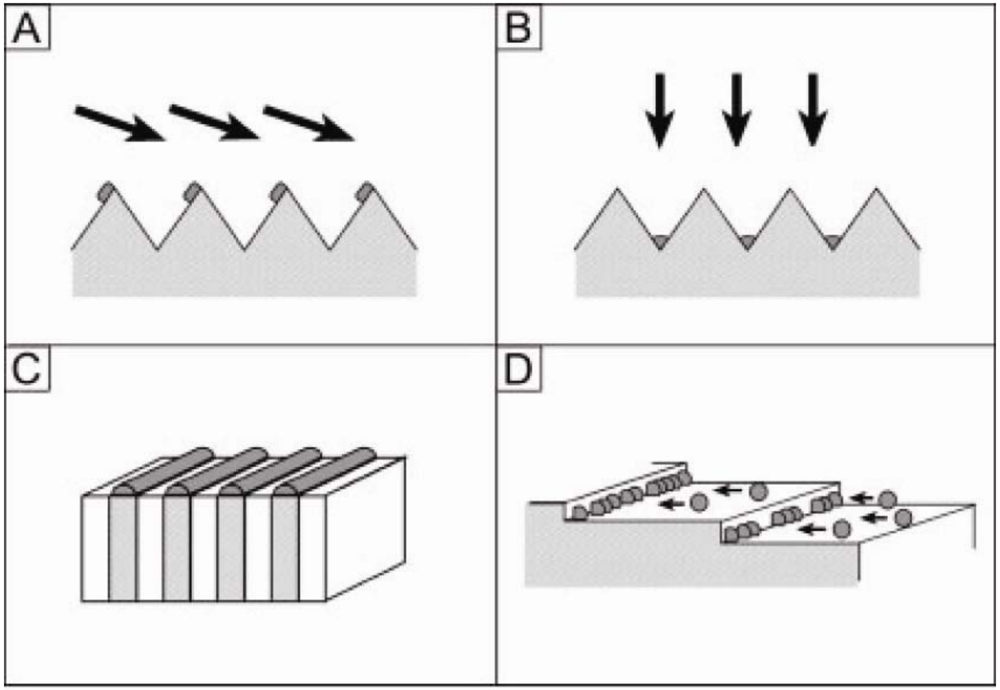
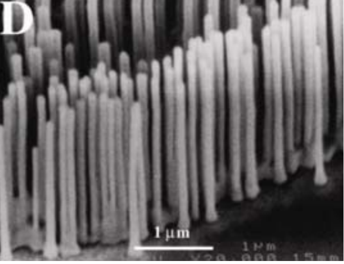
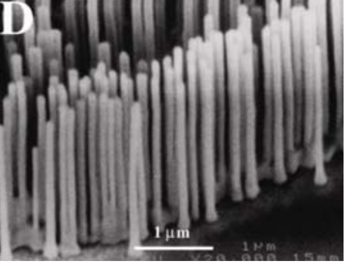


Fig. 6. Schematic illustrations of procedures that generated 1D nanostructures by A) shadow evaporation [58]; B) reconstruction at the bottom of V-grooves [60]; C) cleaved-edge overgrowth on the cross-section of a multilayer film [64]; and D) templating against step edges on the surface of a solid substrate [68].



# Properties of semiconductor nanowires

- Thermal stability
- Mechanical properties
- Thermal conductance
- Electrical conductance
- Photoluminescence



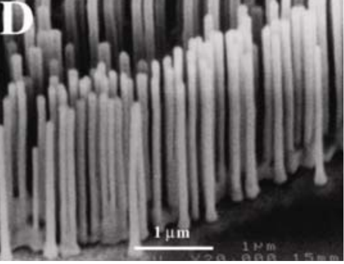
# Thermal Stability

- Melting point greatly reduced in nanostructures

- Ge nanowire 55 nm coated with thin carbon sheath
  - Starts to melt at 650°C (bulk: 930°C)
  - Hysteresis: recrystallization at 558°C

- Photothermal melting (Gold nanorods)
  - moderate energy: one spherical particle
  - high energy: fragmented and transformed into small spherical particles

- Low melting point -> zone refining at modest temperatures
- Cutting, welding and interconnecting at mild temperatures
- Reduced thickness -> more sensitive to environmental changes
  => spheriodization at room temperature



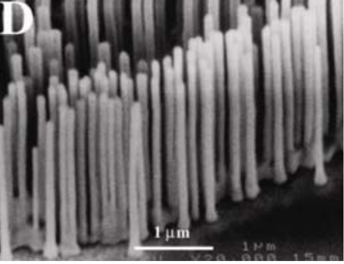
# Mechanical Properties

- Micrometer scale:
  smaller grain size -> increase of hardness and yield stress (Hall-Petch effect)

- Nanometer scale:
  softer with decreasing grain size
  -> characteristic length for toughest strength

- Very strong 1D single-crystalline nanostructures
  -> very low number of defects per length

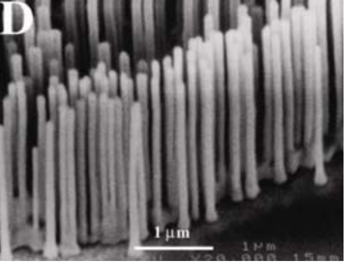
- Wang-group: resonance vibration of CNT



# Mechanical Properties

- AFM elongation-compression cycles (Fernandez)
  nanowires between two gold structures
  - Elongation in steps of multiples of 0,176 nm
  - Shorten in steps of 0,152 nm

-> sliding crystal planes -> stacking faults -> from ccp to hcp

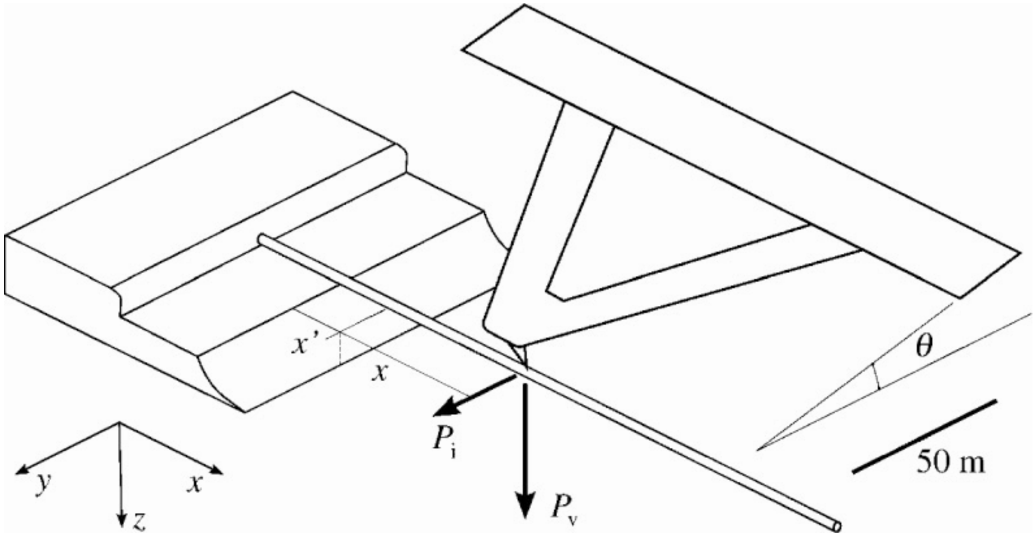


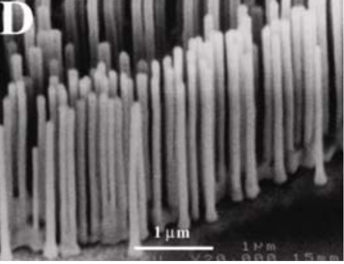
# Stiffness of Silica NW

- No dependence on physical dimensions for diameter > 5 µm
- What about smaller diameters?

Setup:

- Amorphous silica wire with uniform diameter (variation <1%)
- SPM
- Position by camera
- $x'$ not visible





# Stiffness of Silica NW

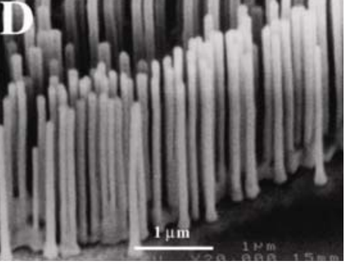
- Continuum beam theory:

$$F=\frac{3El}{x^3}d$$

$$\frac{F}{d}=\frac{3El}{(x+x')^3}$$

- Vertical deflection $F_v$

- Horizontal deflection $F_h=\frac{F_v}{\tan\Theta}$



# Stiffness of Silica NW

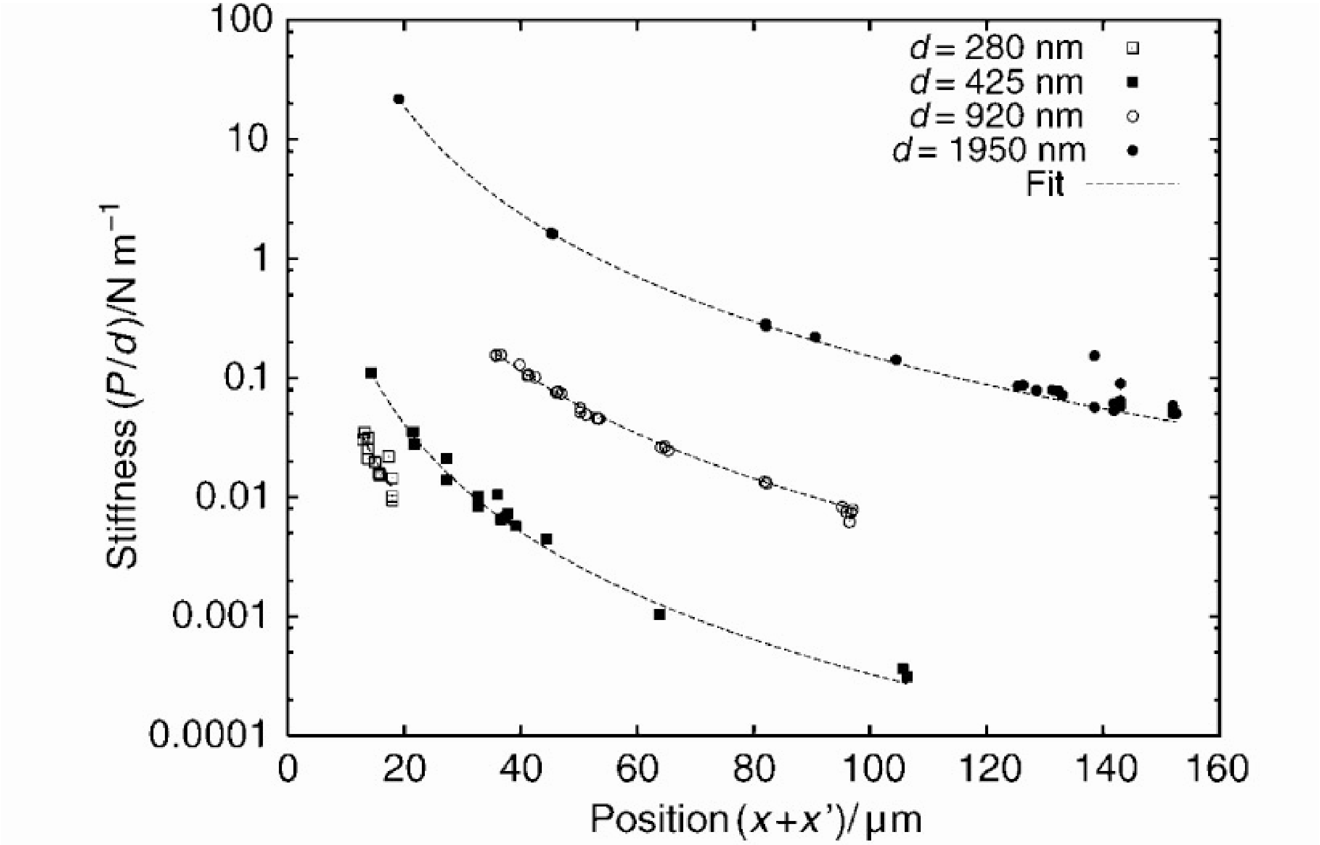
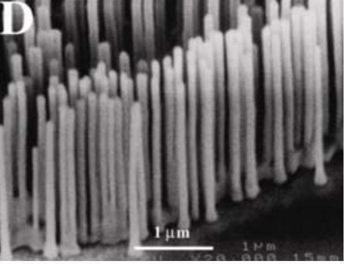


**Figure 1.** Bending stiffness versus force application point for vertical loading. Dashed curves are best fits using Eq. (2).

$$\frac{F}{d}=\frac{3EI}{(x+x')^3}$$



# Stiffness of Silica NW

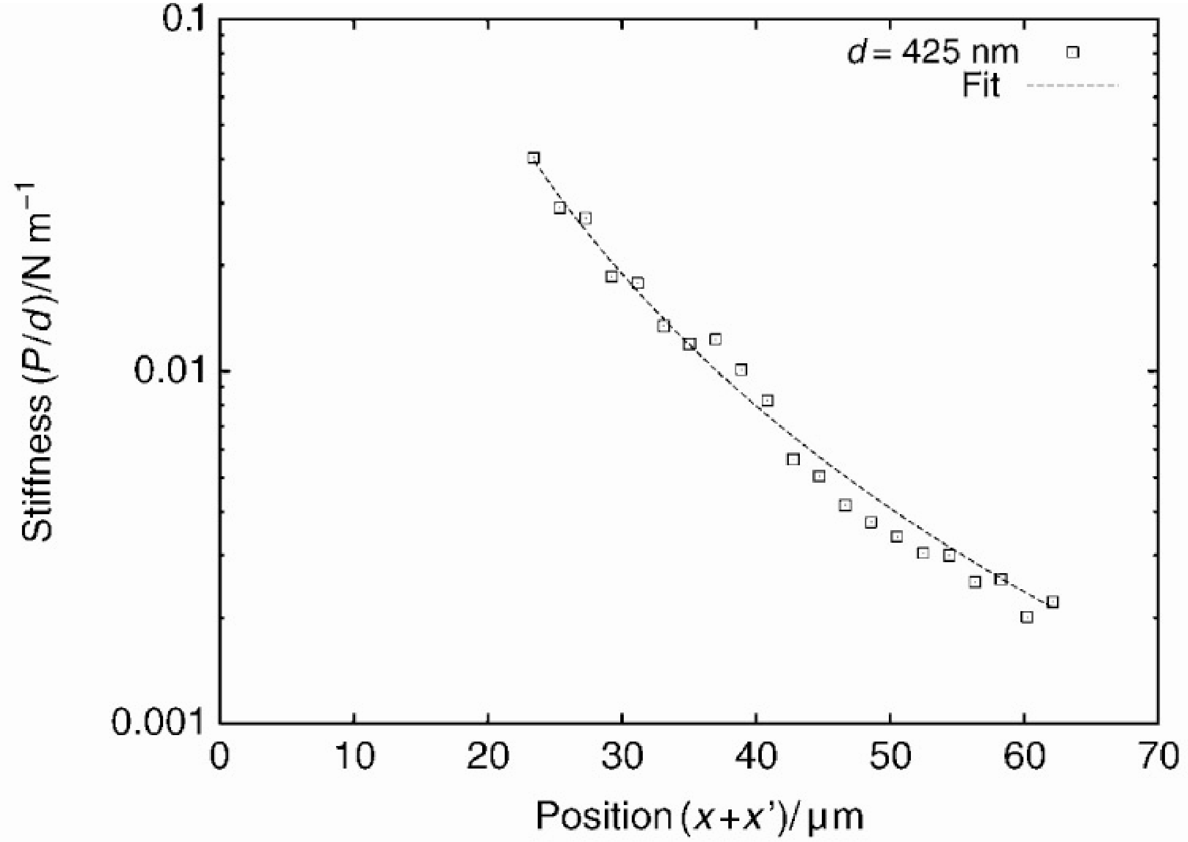
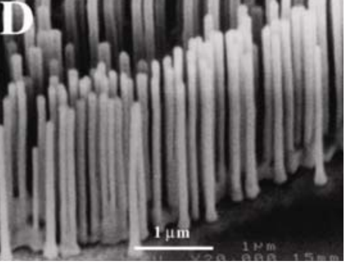


**Figure 2.** Bending stiffness versus force application point for in-plane loading. The dashed curve is a best fit using Eq. (2).

$$\frac{F}{d}=\frac{3El}{(x+x')^3}$$



# Stiffness of Silica NW

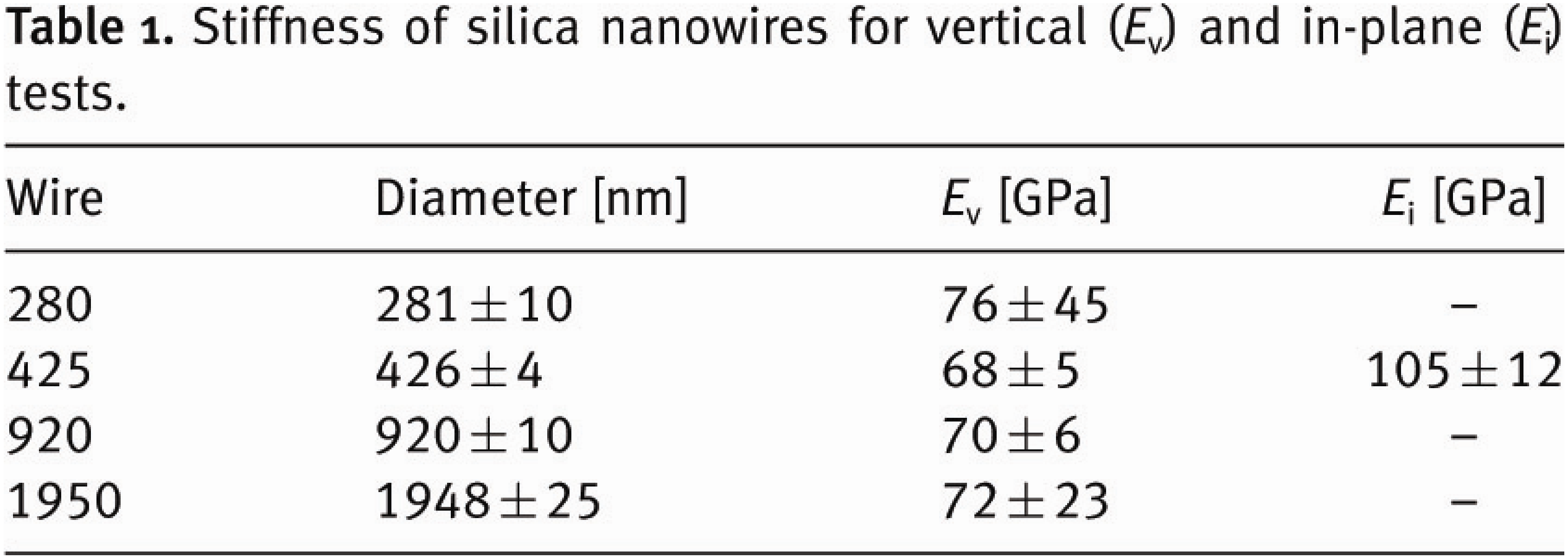


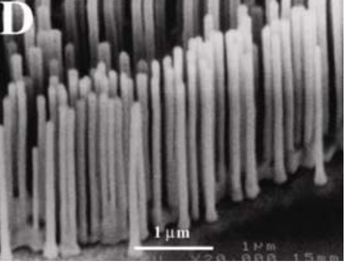
**Table 1.** Stiffness of silica nanowires for vertical ($E_v$) and in-plane ($E_i$) tests.

| Wire | Diameter [nm] | $E_v$ [GPa] | $E_i$ [GPa] |
|---|---|---|---|
| 280 | 281 ± 10 | 76 ± 45 | – |
| 425 | 426 ± 4 | 68 ± 5 | 105 ± 12 |
| 920 | 920 ± 10 | 70 ± 6 | – |
| 1950 | 1948 ± 25 | 72 ± 23 | – |

- No general trend observed
- Bulk amorphous silica E = 72 GPa
- Smaller diameters (43 nm to 95 nm) by Wang et al.: E = 27 GPa

=> not yet fully understood

- Comparison: 610 – 660 GPa for SiC !!

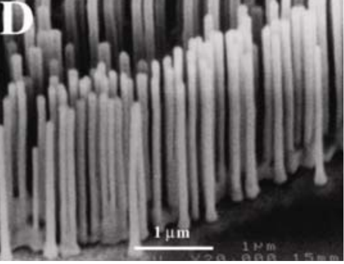


# Phonon-Transport Properties

- Dimension is about the phonon mean free path
- Reduced thermal conductivity due to scattering by boundaries
- Desirable for thermoelectric cooling and power generation

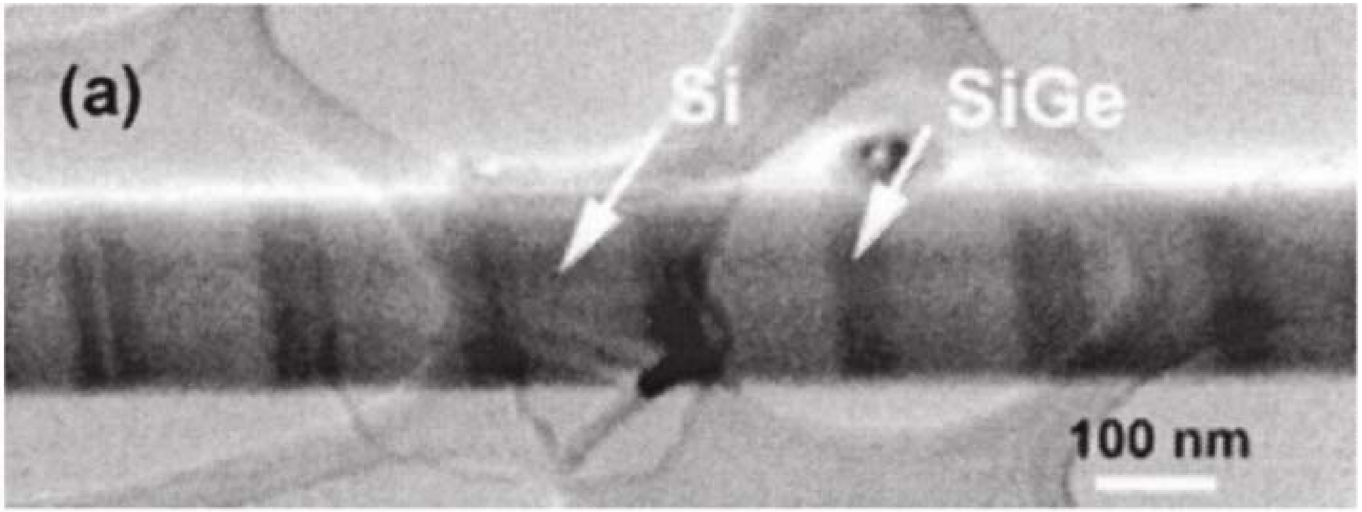
  => Increase of figure of merit

- Not preferable for electronics and photonics

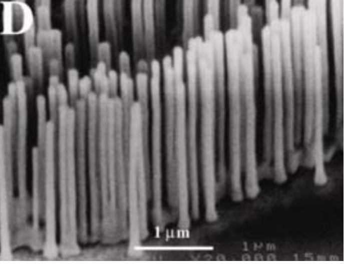


# Thermal Conductivity of Si/SiGe

- Nearly dislocation-free single crystalline Si/SiGe superlattice NW

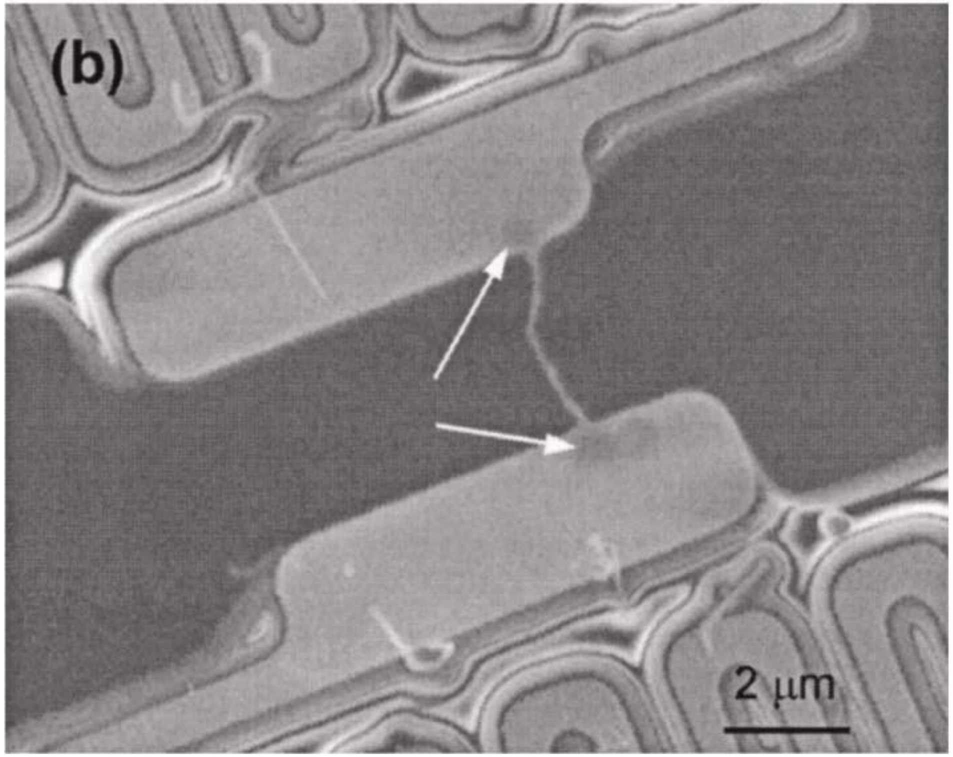


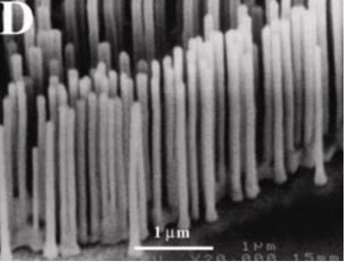
- Microdevice with one NW between pads
- Cryostat at vacuum level (2x10$^{-6}$ Torr)



# Thermal Conductivity of Si/SiGe

- 2 silicon nitride membranes
- Pt resistance coils as heater and resistance thermometer
- 83 nm superlattice NW
- Amorphous carbon films for contact (error < 4% )



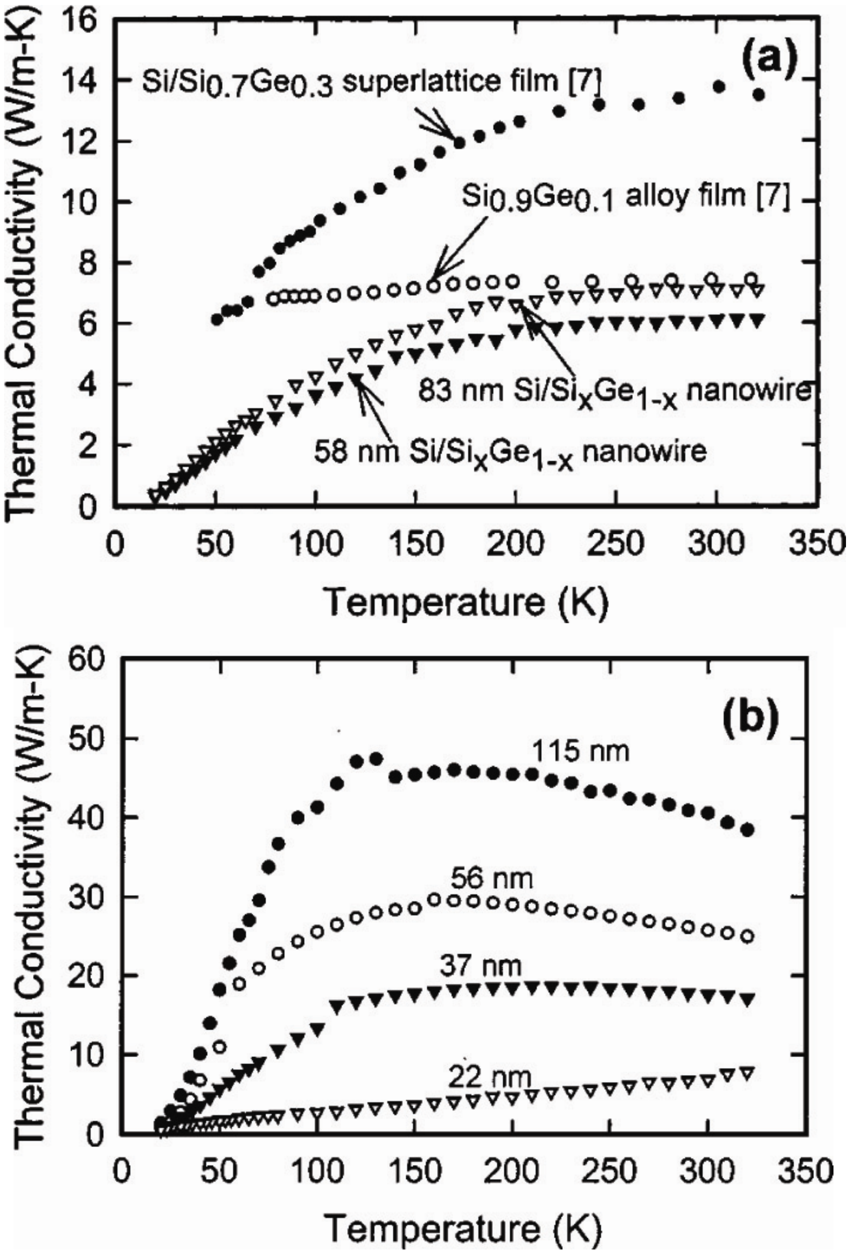


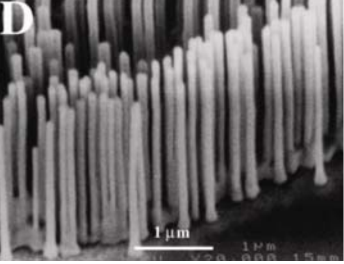
# Thermal Conductivity of Si/SiGe

Superlattice film

- 3 µm thick, 30 nm period
- 3,5 µm thick alloy film

Single crystalline Si Nanowires





# Thermal Conductivity of Si/SiGe

Phonon scattering mechanisms:

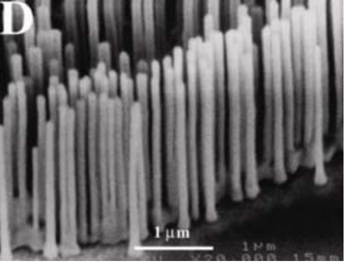
- Alloy (impurity) scattering
- Interface scattering due to mismatch in acoustic impedance
- Scattering by defects and dislocation at interfaces

$Si_xGe_{1-x}/Si_yGe_{1-y}$ 2D superlattice:

$|x-y| \leq 0.1$ Alloy scattering dominant

$|x-y| \approx 0.3$ Lattice mismatch is low enough
but acoustic impedance mismatch reflects phonons
at interfaces

$|x-y| \geq 0.6$ Crystal imperfections dominate scattering



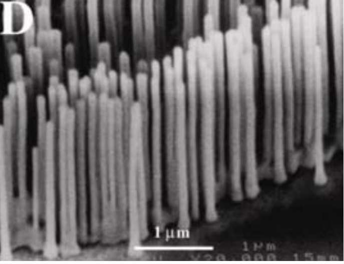
# Thermal Conductivity of Si/SiGe

Nanowires:

- Length: 2.08 and 2.86 µm
- Diameter: 58 and 83 nm
- Periods: 100 and 150 nm
- Small number of interfaces (< 28)

We expect: dominant alloy scattering

Additionally: much lower conductivity than film
=> **nanowire boundary scattering**



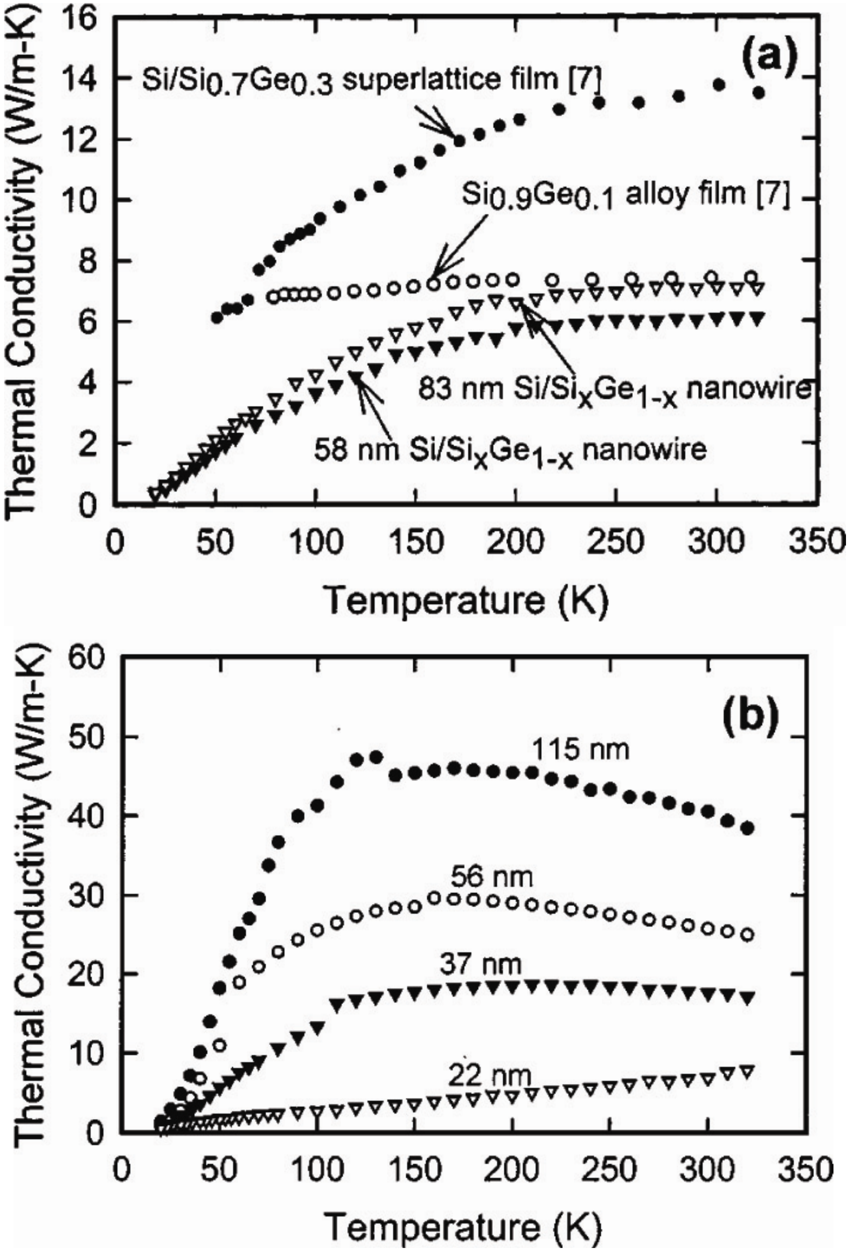
# Thermal Conductivity of Si/SiGe

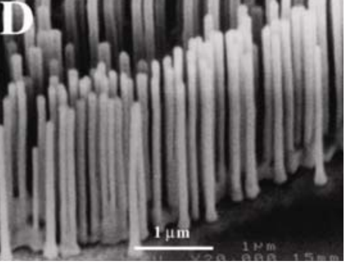
- Conductivity of superlattice NW much lower than single crystalline NW
  => Alloy scattering in SiGe

- The diameter is important
  => boundary scattering

- Si wires more dependent on diameter

- no decrease of conductivity for superlattice NW





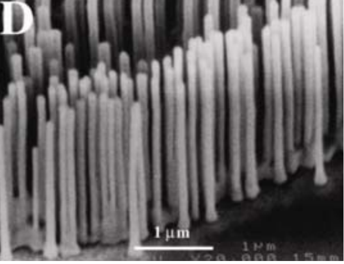
# Electron Transport Properties

- Interesting due to different effects compared to micrometer scale
- Some metal nanowires become semiconducting

  Dresselhaus: Bi single-crystalline nanowires transition at 52 nm.

  (increasing resistance with decreasing temperature)

- Quantum confinement: external conduction sub-band and valence sub-band open up band gap.
- Carrier mobility suppressed by carrier confinement along the long axis of wire by surface imperfection
- GaN with 17.6 nm still semiconductors
- Si nanowires with 15 nm are insulators

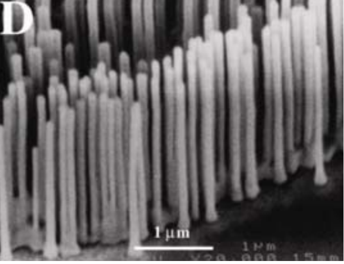


# Optical Properties

- Absorption edge blue-shifted (Si NW compared to Si bulk)
- Photoluminescence
- Crystal orientation important
- Polarized light (along longitudinal axis)

  -> polarization-sensitive nanoscale photodetectors

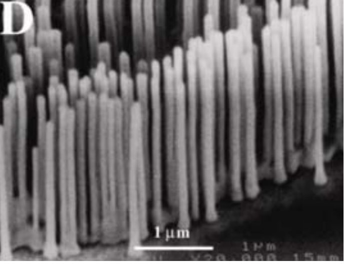
- Nanowires as optical resonance cavities -> Lasing
- Yang: ZnO nanorods UV-lasing at room temperature
- Semiconductor NW as frequency converters
- Photoconductance extremely sensitive to UV exposure (6x reduced)
- Very sensitive UV-detectors



# Heterostructures

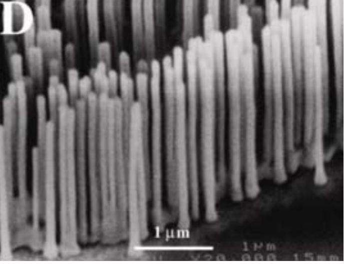
Semiconductor integrated circuits need heterostructures:

- Controlled doping and interfacing to manipulate properties
- COHN
- LOHN



# Coaxial Heterostructured Nanowires

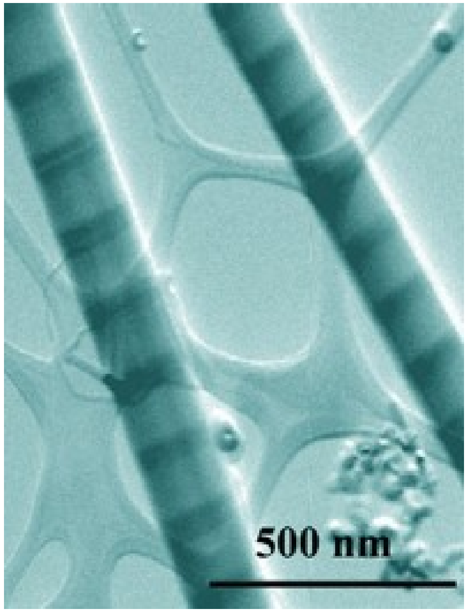
- Coating with second material
  - Excellent control of uniformity and sheath thickness is needed
  - e.g. Coating with amorphous layer of $SiO_2$
- Single-crystalline coating
  - Materials with similar crystallographic symmetries and lattice constants
- Anisotropic coating by shadow effect
- Single-crystalline Nanotubes by dissolving the inner core
  - Different chemical stabilities



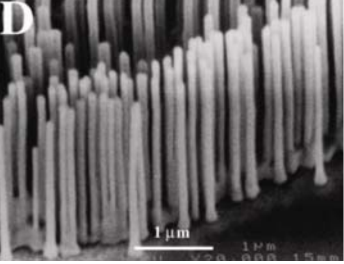
# Longitudinal Heterostructured Nanowires

- VLS with alternately Si & Ge vapor

  => superlattice NW



- Creating NWs in custom-designed fashion
- Building blocks for nanoscale electronic ciruits
  - p-n junction
  - Transistors

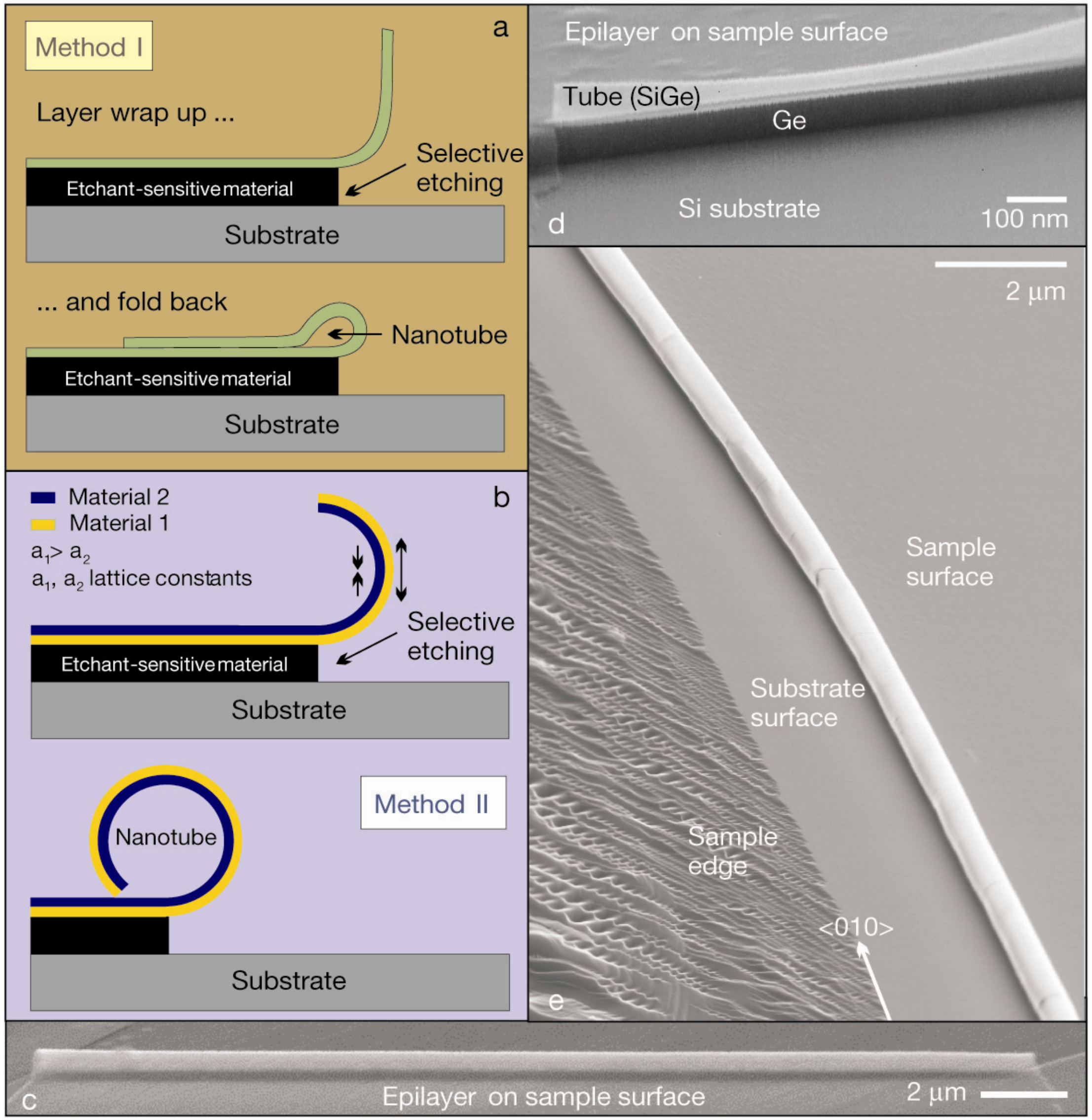


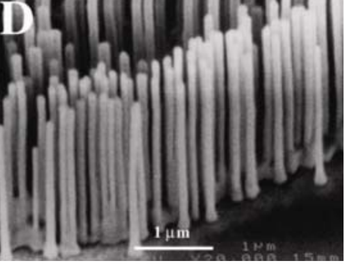
# Roll-Up Nanotubes

- Thin solid film
- Selective etching
- Position by etching time
- Precise thickness control

Method

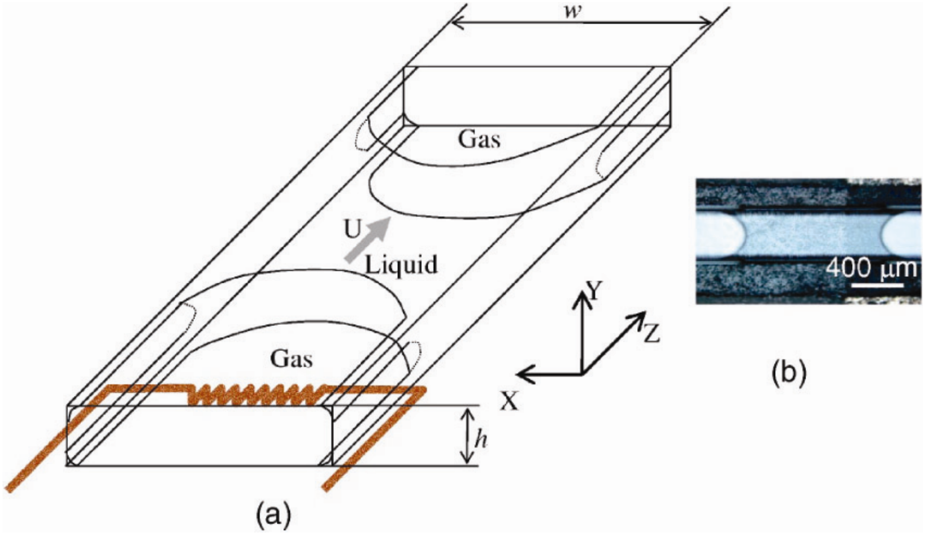
- Bilayer with different lattice constants
- (e.g. InAs/GaAs)





# Fluidic Assembly

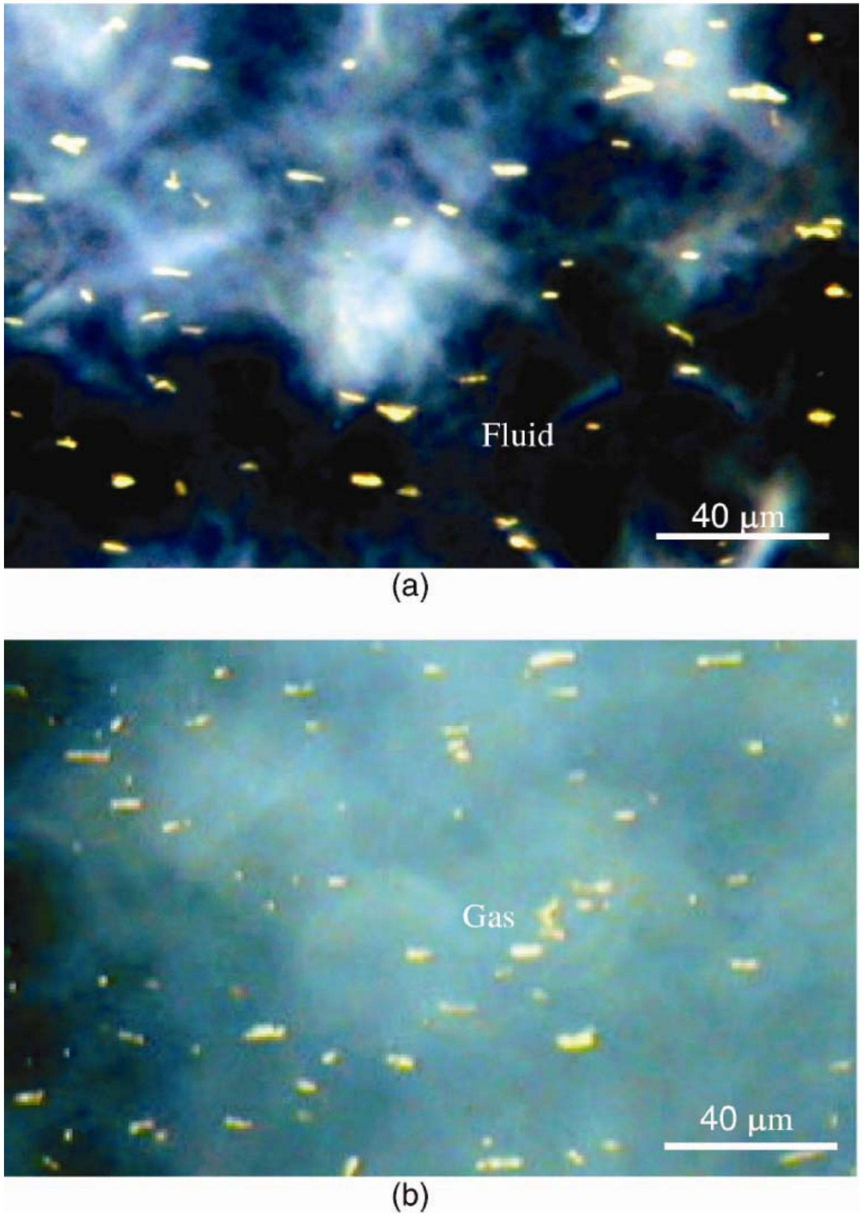
- Control of NW alignment
- Solution of Gold NW
- Thermocapillary motion due to temperature gradient and surface tension difference
- Alignment with flow direction ( > 85%), sometimes flip-over
- Adsorbance on microchannel surface with good alignment

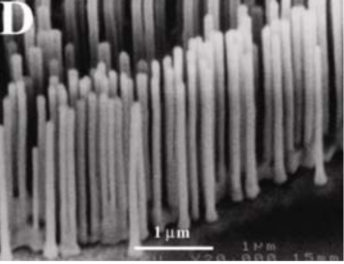


# Fluidic Assembly

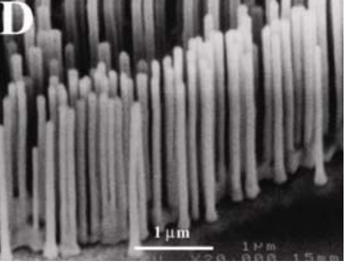
(a) Poiseullie flow region with orientated NW

(b) Aligned NWs on microchannel's surface



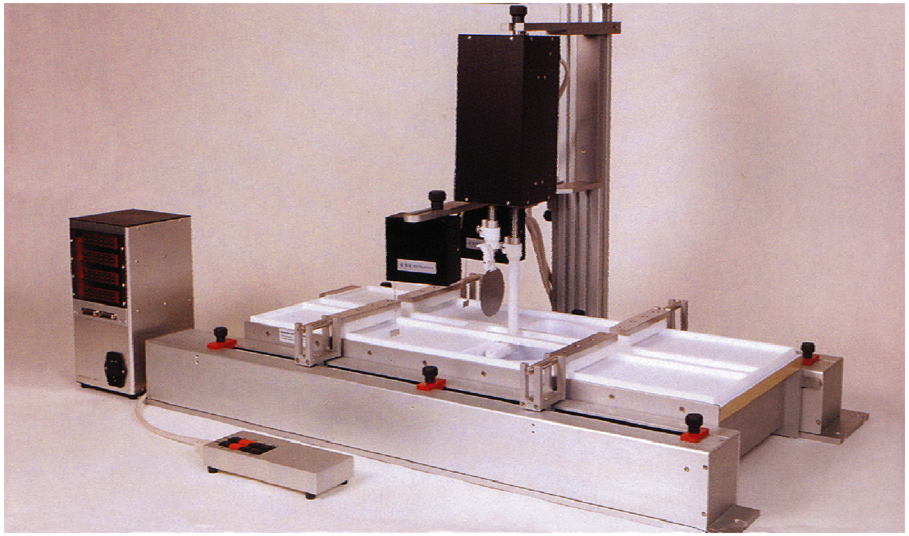


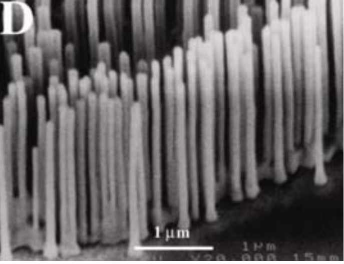
# Fluidic Assembly



# Langmuir - Blodgett

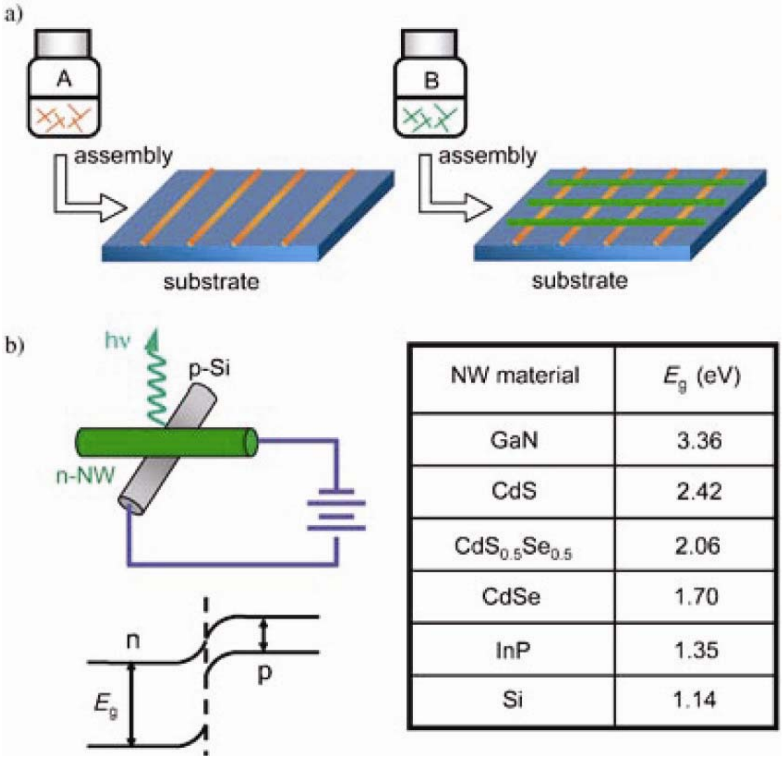
- “logs-on-a-river” approach
- NW suspension dispersed on water surface => floating NWs
- Compression
- Alignment parallel to trough barrier
- Transfered on substrate
- Assembly of large areas
- No direct addressing of single NW



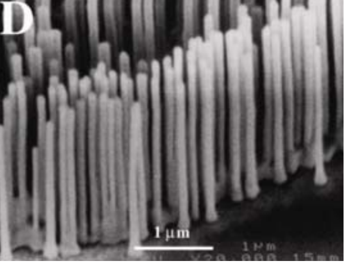


# Nanowires for Nanophotonics

- Crossed NW p-n structure
- Active device area is of nanometer dimension
- Single- and mulitcolor arrays
- On rigid and flexible substrates
- Quantum efficiency 0.1%
- CdS-Si NW with 510 nm visible by naked eye in dark room

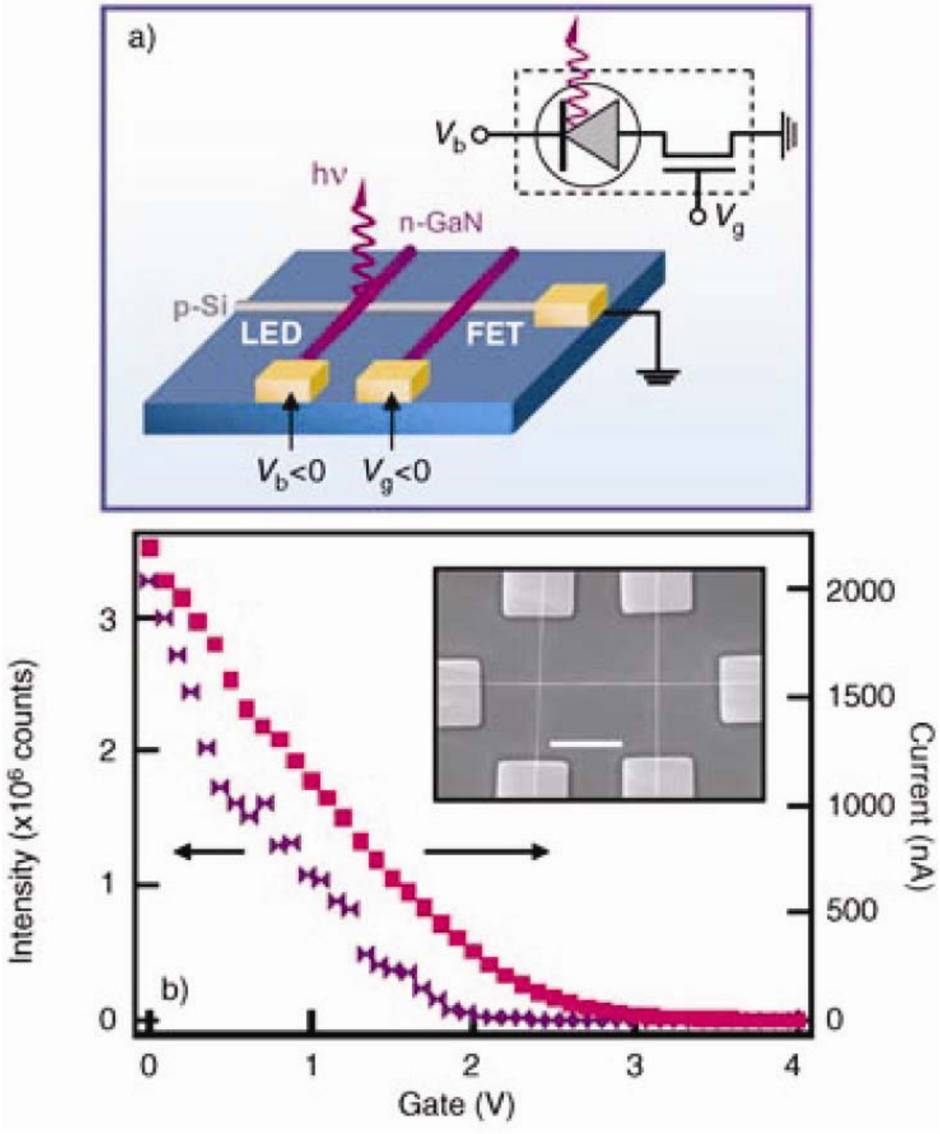


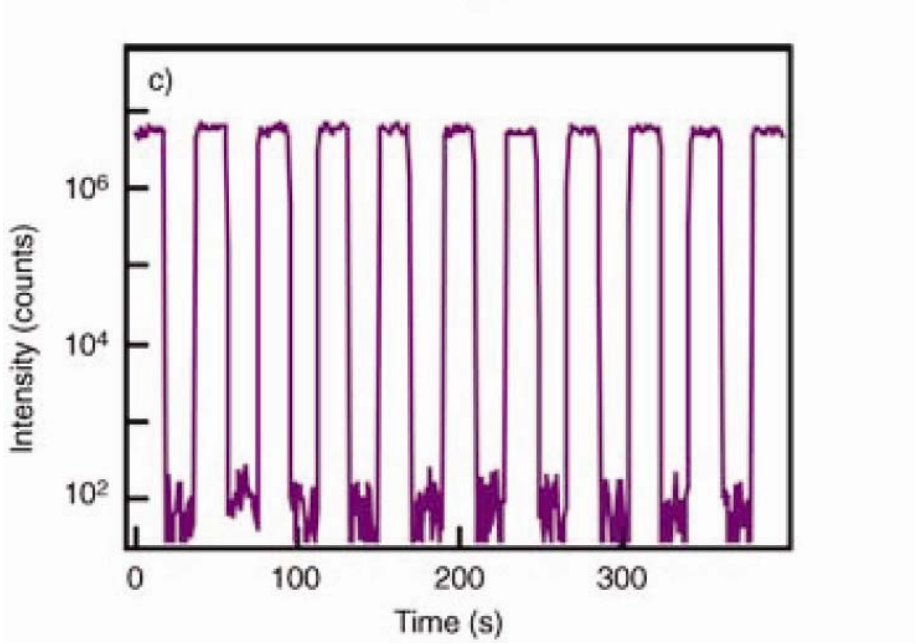
| NW material | $E_g$ (eV) |
|---|---|
| GaN | 3.36 |
| CdS | 2.42 |
| $CdS_{0.5}Se_{0.5}$ | 2.06 |
| CdSe | 1.70 |
| InP | 1.35 |
| Si | 1.14 |

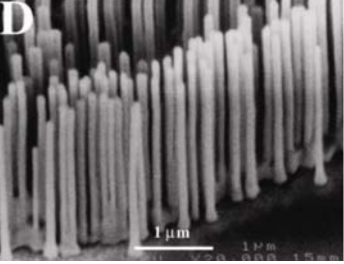


# Nanowires for Nanophotonics

- Two-by-one array, GaN on Si
- One GaN NW is p-n diode (positivly biased)
- The other GaN NW can emit light (negativly biased at -6V)



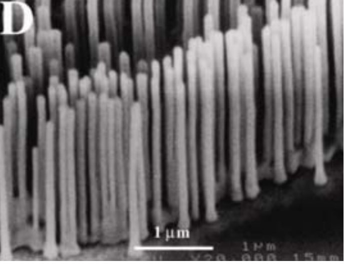




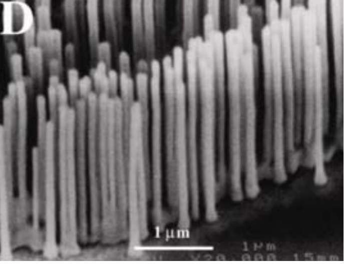
# Sensing Applications

- Sensing of important molecules for medical, environmental or security-checking purposes
- High surface-to-volume ratio -> extremely sensitive
- Cu NW with gaps to adsorb organic molecules

  => reduced quantized conductance (electron scattering)
- Pd NW with thin polymeric film: hydrogen detection
- Semiconductor NW for detection of pH and biological species
- Room-temperature photochemical $NO_2$

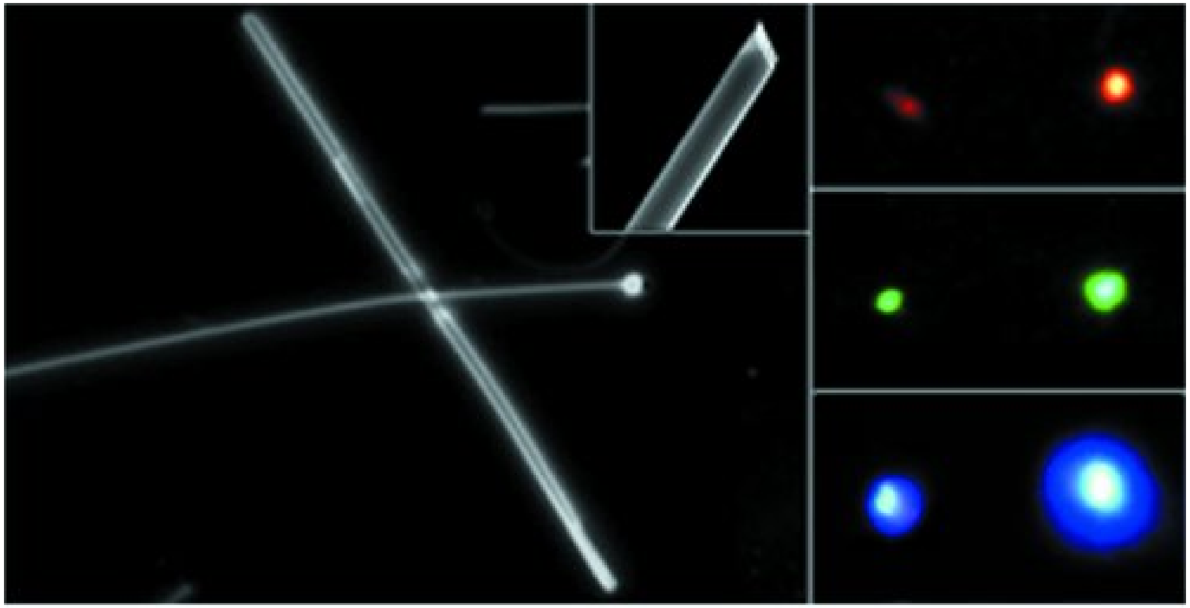


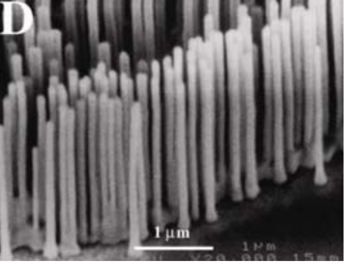
# Sensing Applications



# Waveguiding

- Link for various elements in photonic nano circuits
- NW can be bent and shaped by commercial micro/nanomanipulator
- Curved into loops with radii ~5 microns



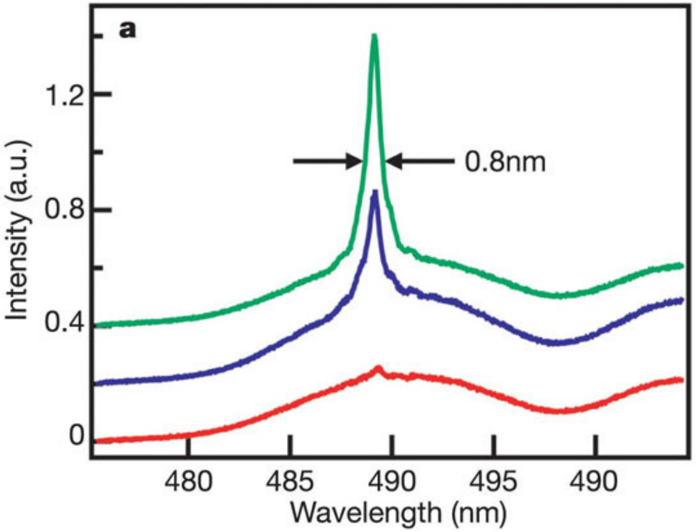


# Nanowire Lasing

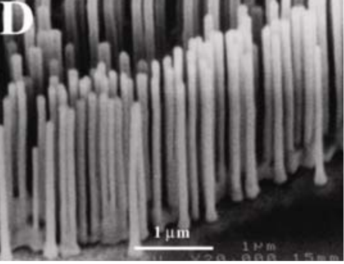
NW with flat end facets
=> resonance cavities

- Diffraction losses
- Low reflectivities of end facets

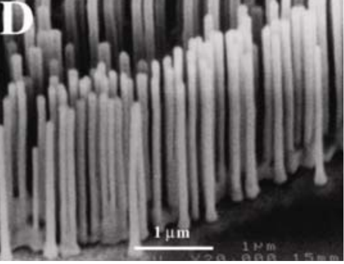
room-temperature UV lasing of ZnO and GaN
- Optically pumped
- GaN/Al$_x$Ga$_{1-x}$N core-shell NW
- Smaller refractive index decreases losses



Emission spectra from a CdS nanowire end with a pump power of 190, 197 and 200 mW (red, blue, green) recorded at 8 K. The spectra are offset by 0.2 intensity units for clarity.



# - The End -



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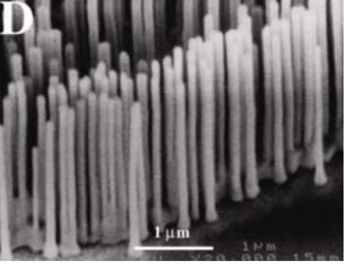

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