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Nanowires: synthesis & applications

Outline

- Introduction to Nanowires
- Nanowires: Synthesis
  - Spontaneous growth
  - Template assisted
- Nanowires: Applications
  - Piezoelectric Nanogenerators
  - Thermoelectric Nanowires
  - Dye-Sensitized Solar Cells
  - Metamaterials
  - FETs, Sensors

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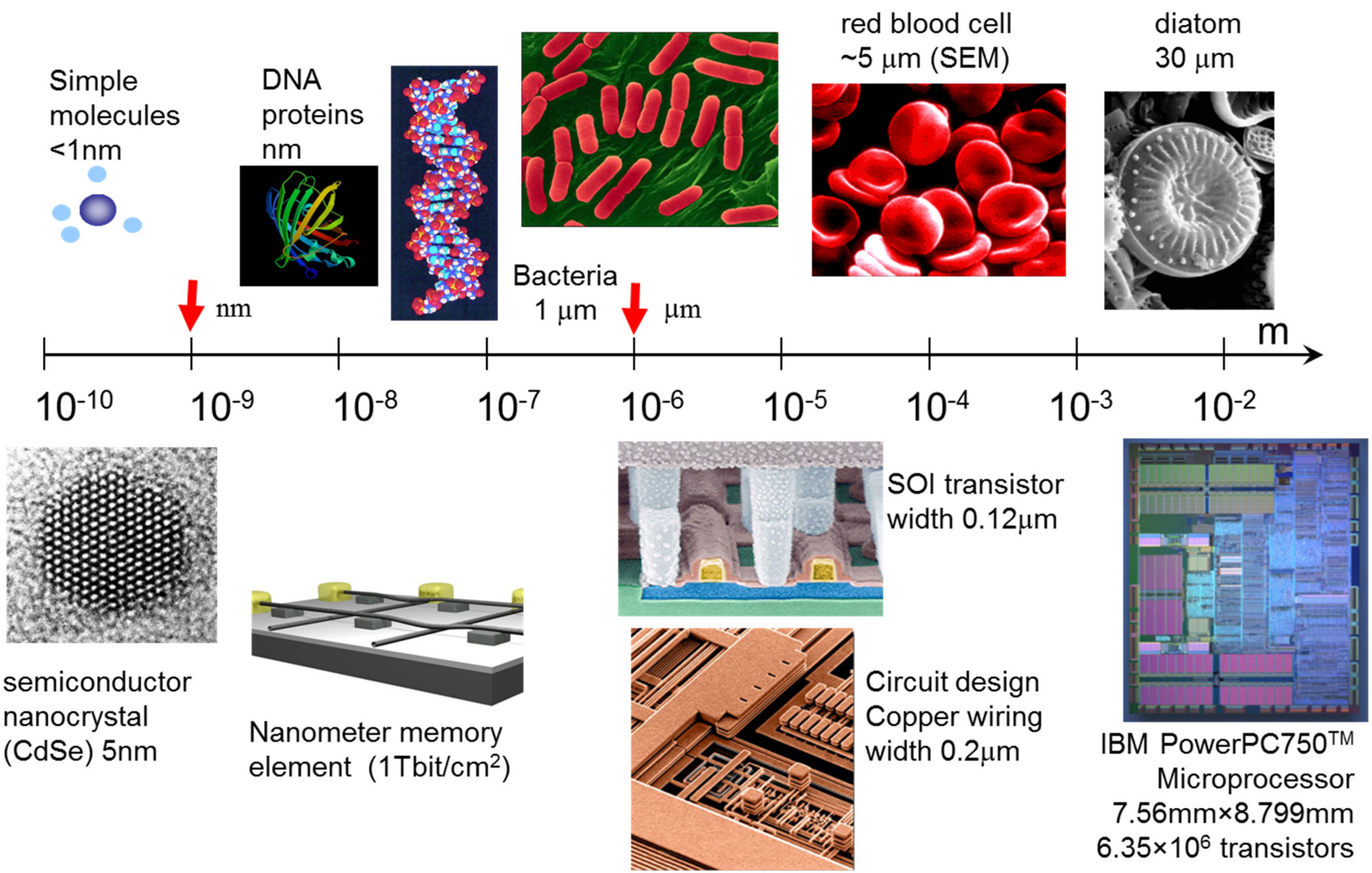
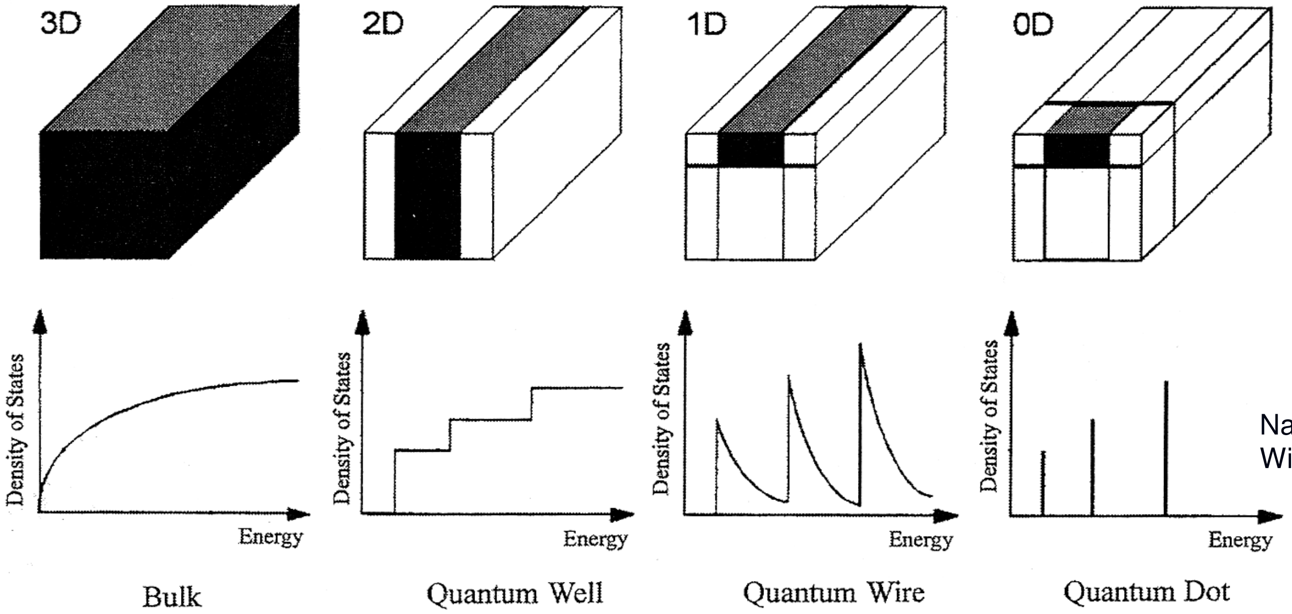
Nanowires:

synthesis & applications

Small worlds



From 3D to 0D

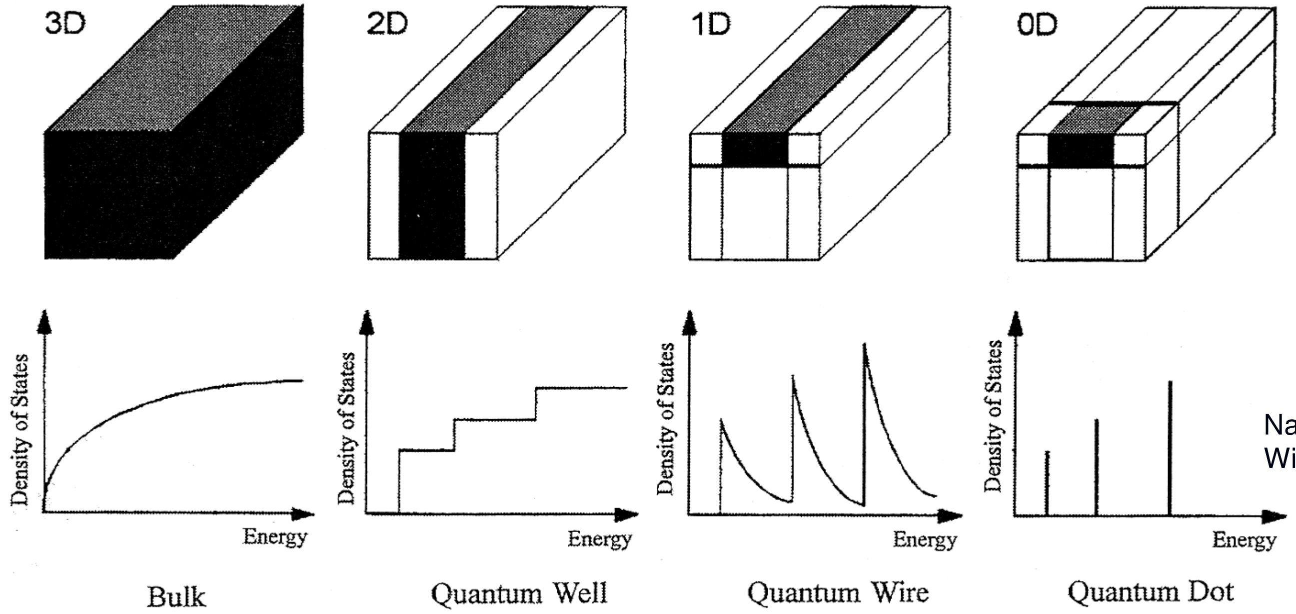


- **0D: quantum dots**
- **1D: Nanowires**
- **2D: superlattices, heterostructures**

Nanoscale Materials in Chemistry, Wiley, 2001

- Classification according to the number of reduced dimensions (usually refers to the number of degrees of freedom in the momentum).
- 3 D or bulk system: no wuantization of the particle motion.
- 2D system: quantization of the particle motion in one direction.
- 1D system: quantization of the particle motion in two directions.
- 0D system: quantization of the particle motion in all directions.

From 3D to 0D



- **0D: quantum dots**
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Nanoscale Materials in Chemistry, Wiley, 2001

$$\frac{dn}{dE} \propto E^{\frac{1}{2}}$$

$$\frac{dn}{dE} = \frac{Am}{2\pi\hbar^2}$$

Constant for each electronic band

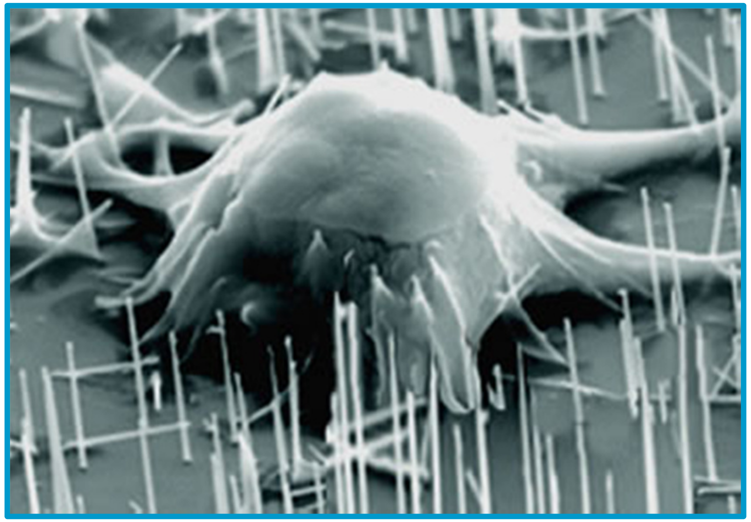
$$\frac{dn}{dE} \propto E^{-\frac{1}{2}}$$

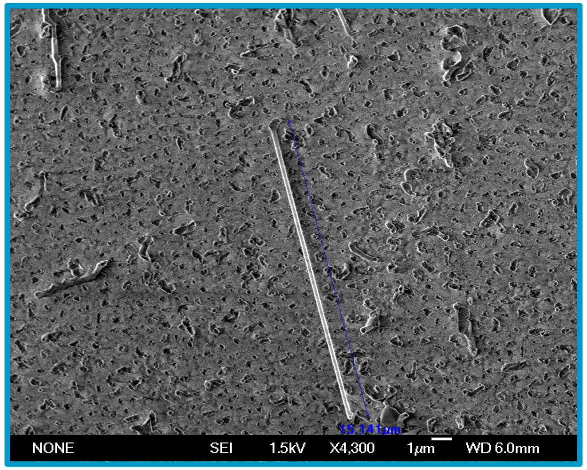
At each atomic level, the DOS decreases as the reciprocal of the square root of energy.

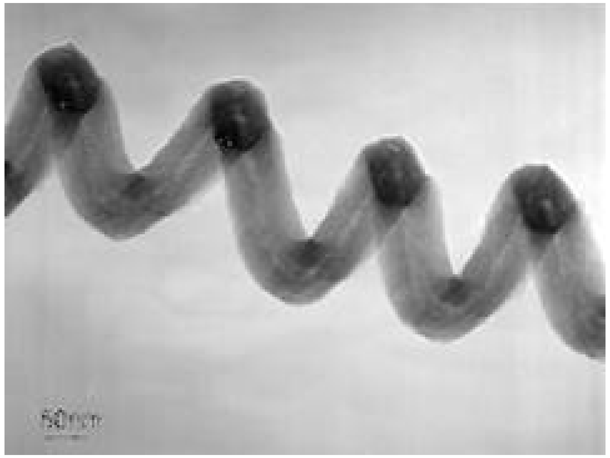
Sharp levels corresponding to the eigenstates of the system

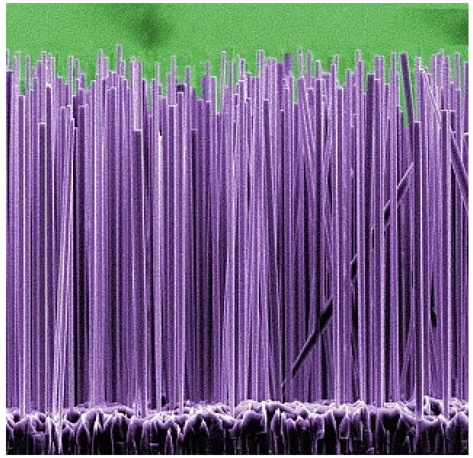
Nanowires

- 1D structures
  - Diameter: 1-100 nanometers (10^{-9} m)
  - Length: microns (10^{-6} m)
  - Typical aspect ratios of 1000 or more.
- Crystal structures close to that of the bulk material
- Promising framework for applying the "bottom-up" approach for the design of nanostructures

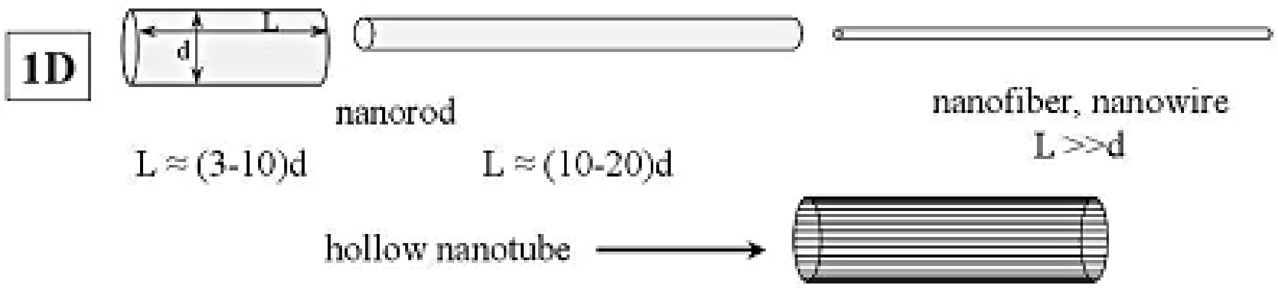




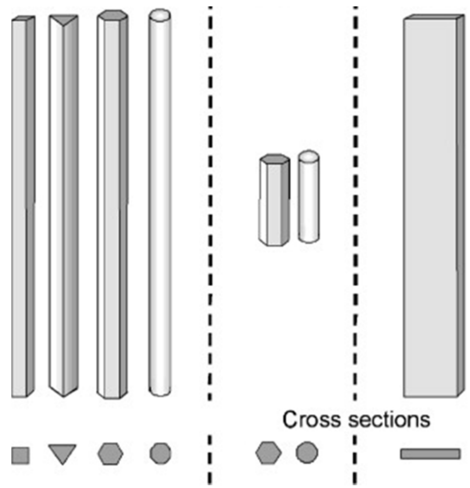




Nanowires



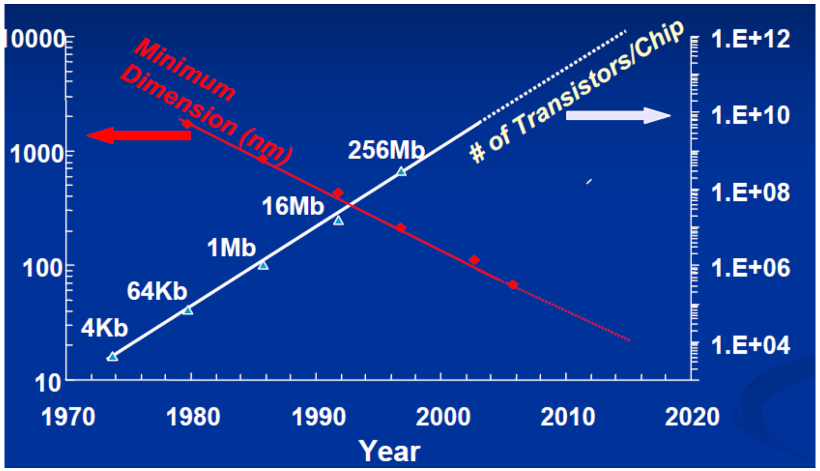
- Different *types*:
  - **Whiskers, fibers:** 1D structures up to several hundred microns
  - **Nanowires:** large aspect ratios
  - **Nanorods:** small aspect ratios.
- Different *materials*:
  - Metallic (Ni, Pt, Au, …)
  - Semiconducting (Si, InP, GaN, …)
  - Insulating (SiO2, TiO2, …)
  - Molecular (DNA, MoSI, …)



Nanowires

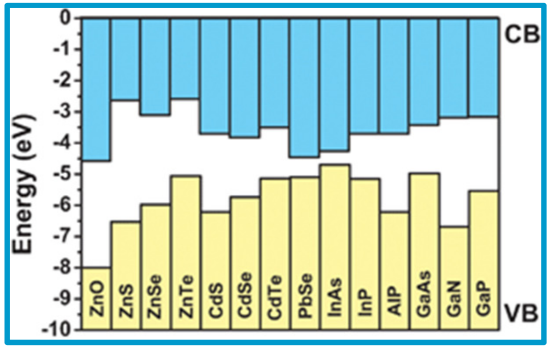
> "They represent the smallest dimension for efficient transport of electrons and excitons, and thus will be used as interconnects and critical devices in nanoelectronics and nano-optoelectronics."
>
> *(CM Lieber, Harvard)*

- 1D nanostructures represent the smallest dimension structure that can efficiently transport electrical carriers (e-, h+):
  - Can act as both nanoscale devices and wiring to link components into extremely small circuits.
- Unique density of electronic states:
  - significantly different optical, electrical, and magnetic properties from bulk counterparts.

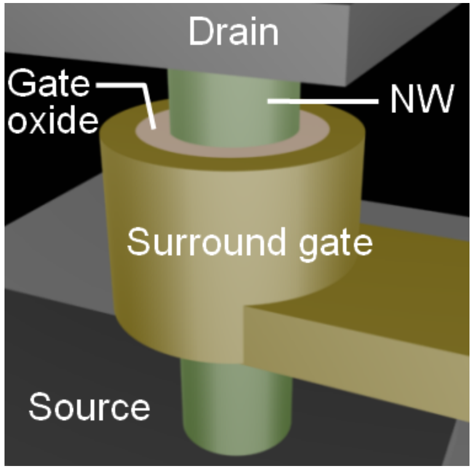


Nanowires

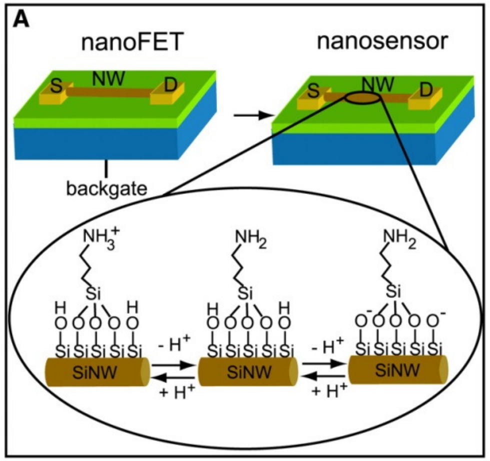
- Increased surface area
- Diameter-dependent bandgap
- Increased surface scattering for electrons and phonons
- Controlled synthesis
  - Diameter, length, composition
  - Electronic structure
- Quantum confinement
  - Present in some, absent in others
  - Unique magnetic & electronic properties
- Millions more transistors per microprocessor



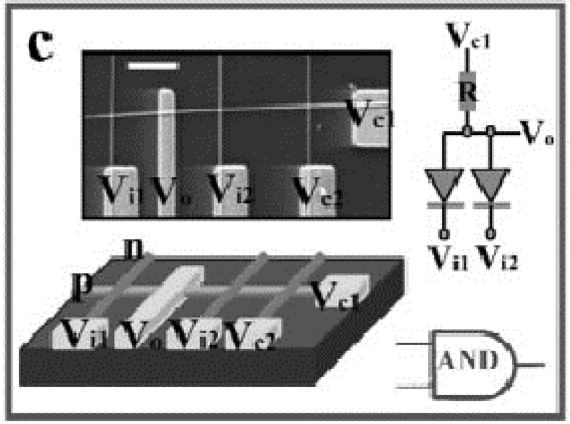
Nanowires: Applications



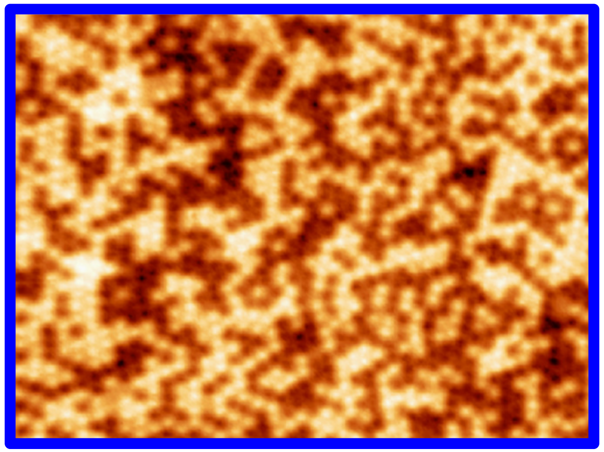
Field Effect Transistors



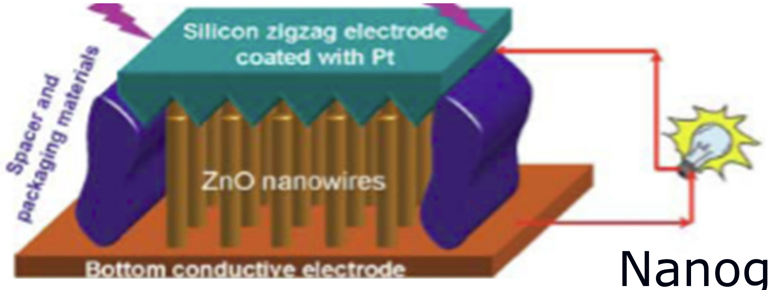
Chemical, biological sensors



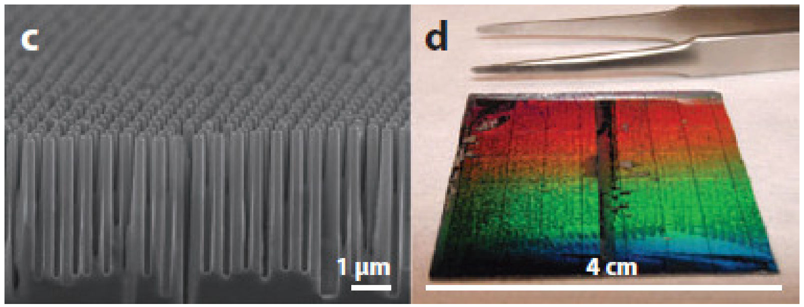
Logic gates



Magnetic devices



Nanogenerators



Solar Cells

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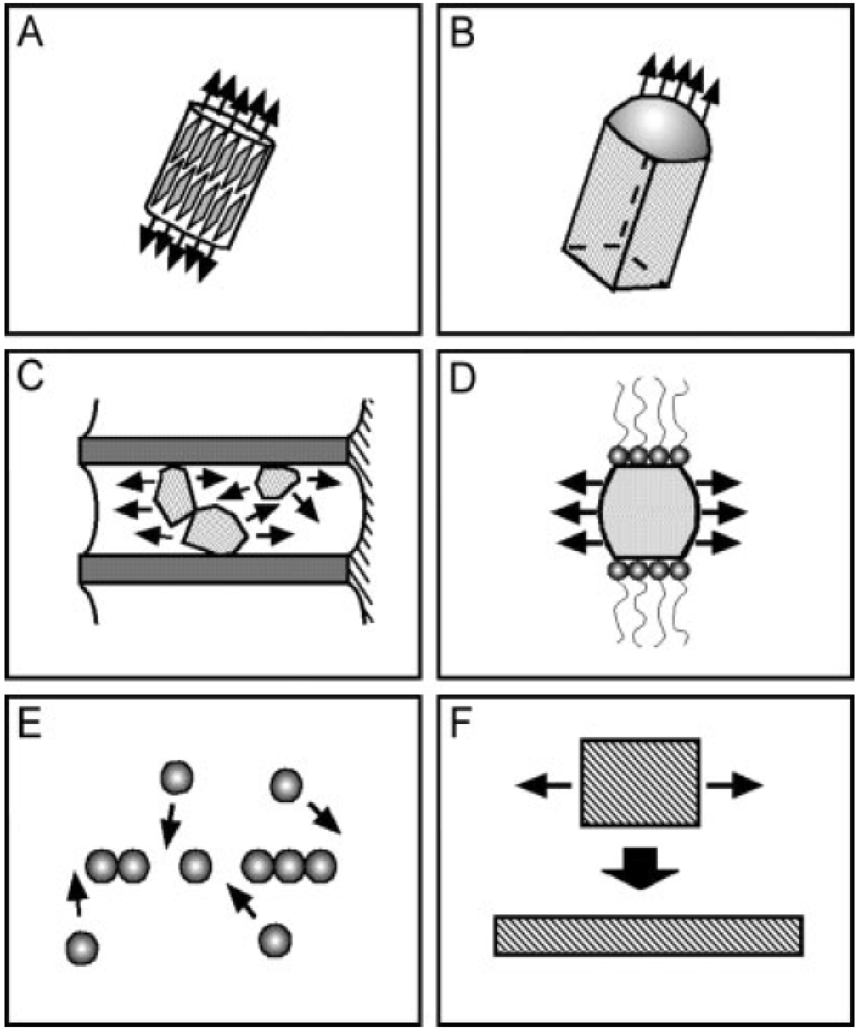
Nanowires:
synthesis & applications

Nanowires: synthesis

- Development of 1D structures for long hindered by difficulties associated with its syntesis and fabrication (dimension control, morphology, chemical composition).
- Can be fabricated using a number of advanced nanolithography techniques:
  - e-beam lithography
  - Focused Ion Beam
  - X-ray, extreme-UV lithography
- Unconventional methods might provide alternative approach in terms of cost, throughput and high volume production
- Different stratagies use individual building blocks to fabricate increasingly complex structures
  - Challenging processing
  - Low device-to-device reproducibility
  - Alignment is the critical first step for developing devices

Nanowires: synthesis

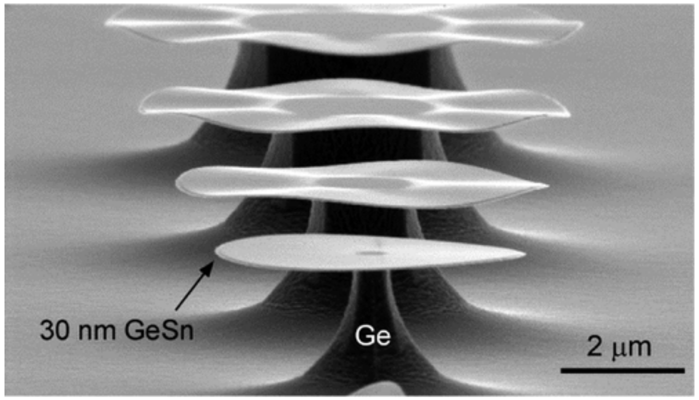
- **Lithography**
- **Spontaneous growth:**
  - Evaporation condensation
  - Dissolution condensation
  - Vapor-Liquid-Solid growth (VLS)
- **Template-based synthesis:**
  - Electrochemical deposition
  - Electrophoretic deposition
  - Colloid dispersion, melt, or solution filling
  - Conversion with chemical reaction

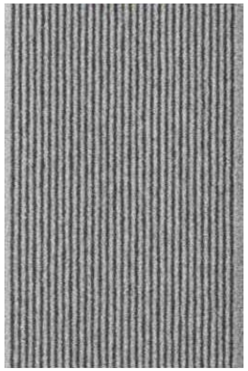


Adv. Mater. 15, 353 (2003)

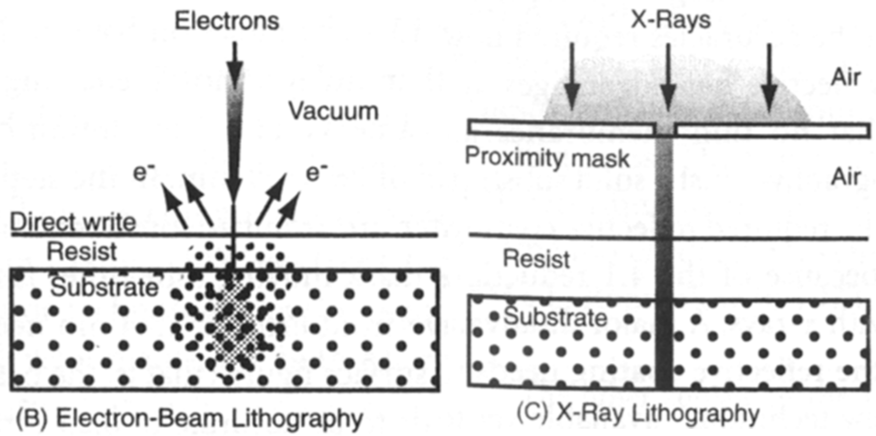
Lithography

- Top-down approaches used to reduce the size of a thin film into a 1D structure
  - e-beam lithography
    - vacuum environment
    - direct write systems (software masks)
    - slow writting over large areas
    - very high system cost
  - Focused ion beam
    - Resists are more sensitive than electron beam resists
    - Site-specific analysis
    - Deposition
    - Ablation of materials
    - Expensive, slow
  - X-ray lithography
    - Air environment
    - Very small wavelength (< 14Å)
    - Complex mask fabrication
    - No optics involved – limited to 1:1 shadow printing
    - Resists have low sensivity
    - High cost X-ray sources (e.g. Synchrotron)



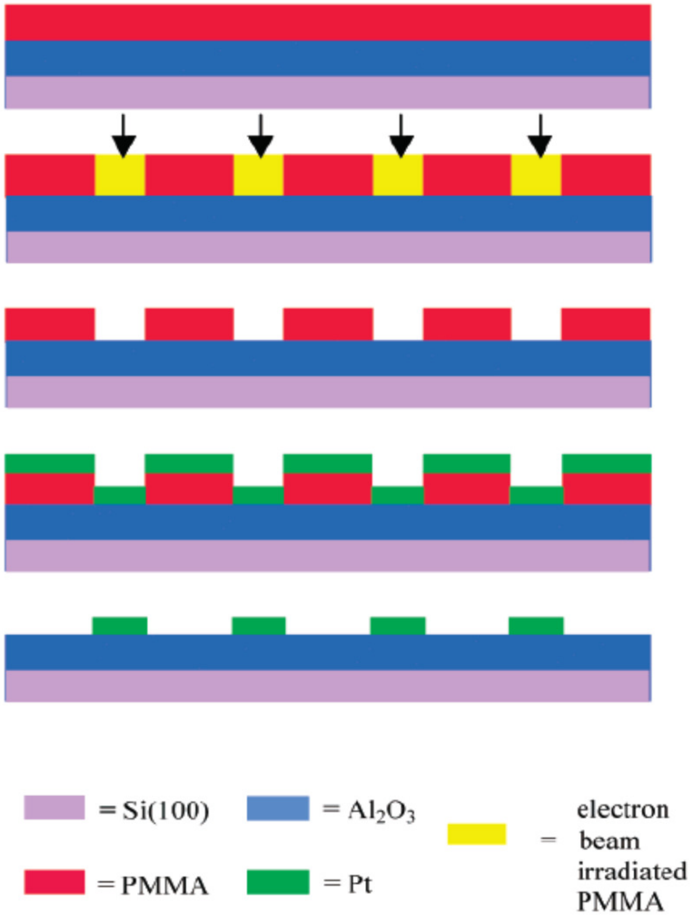


25 nm



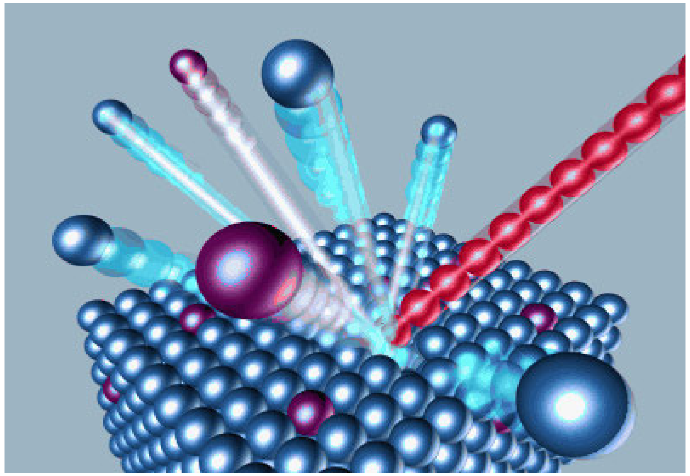
Lithography

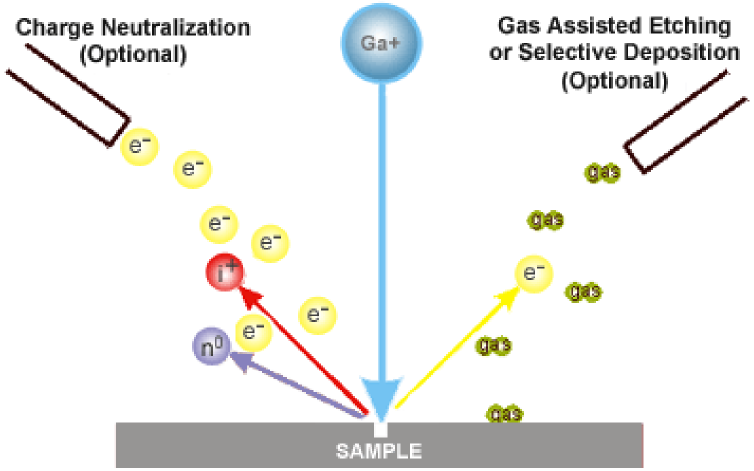
e-beam lithography



Focused ion beam

Highly focused ion beam sputters material from a selected domain on a sample surface.



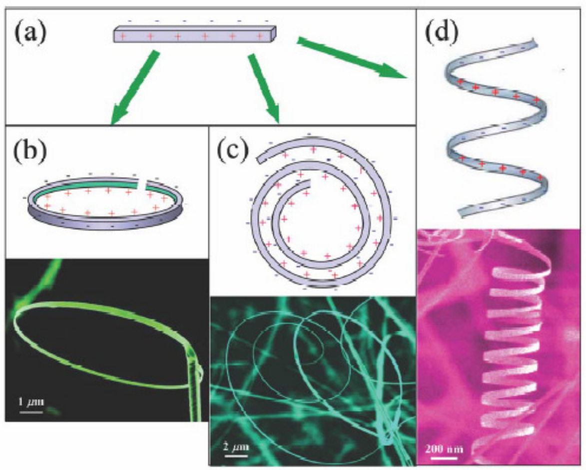


Spontaneous growth

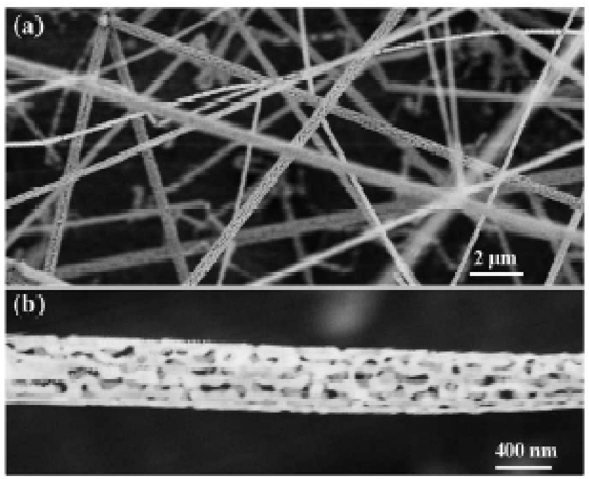
- A growth driven by the reduction of Gibbs free energy or chemical potential.
- This can be from either recrystallization or a decrease in supersaturation.
- Anisotropic growth is required
- Crystal growth proceeds along one direction, where as there is no growth along other direction.
- Uniformly sized nanowires (i.e. the same diameter along the longitudinal direction of a given nanowire)

Evaporation condensation

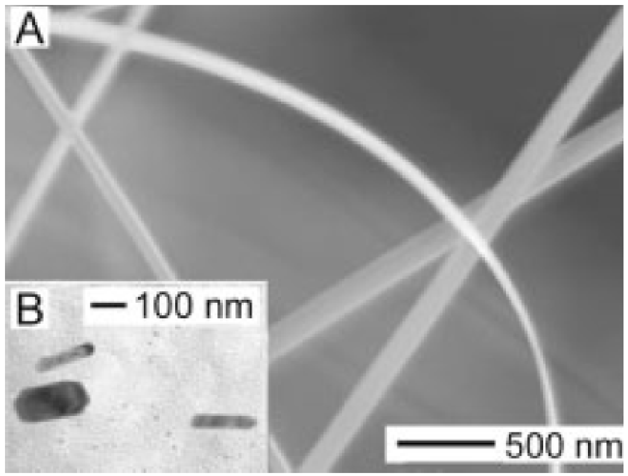
- Vapor-Solid (VS) technique
- Simple and accessible
- Vapor species are generated (e.g. by evaporation) and transported and condensated onto a substrate placed in a zone with temperature lower than that of the source material
- Nanowires grown by this method are commonly single crystals with few imperfections
- The formation of nanowires is due to anisotropic growth
- Different facets in a crystal have different growth rates
- No control on the direction of growth of nanowire using this method



"Nanostructures of zinc oxide," Z. Wang

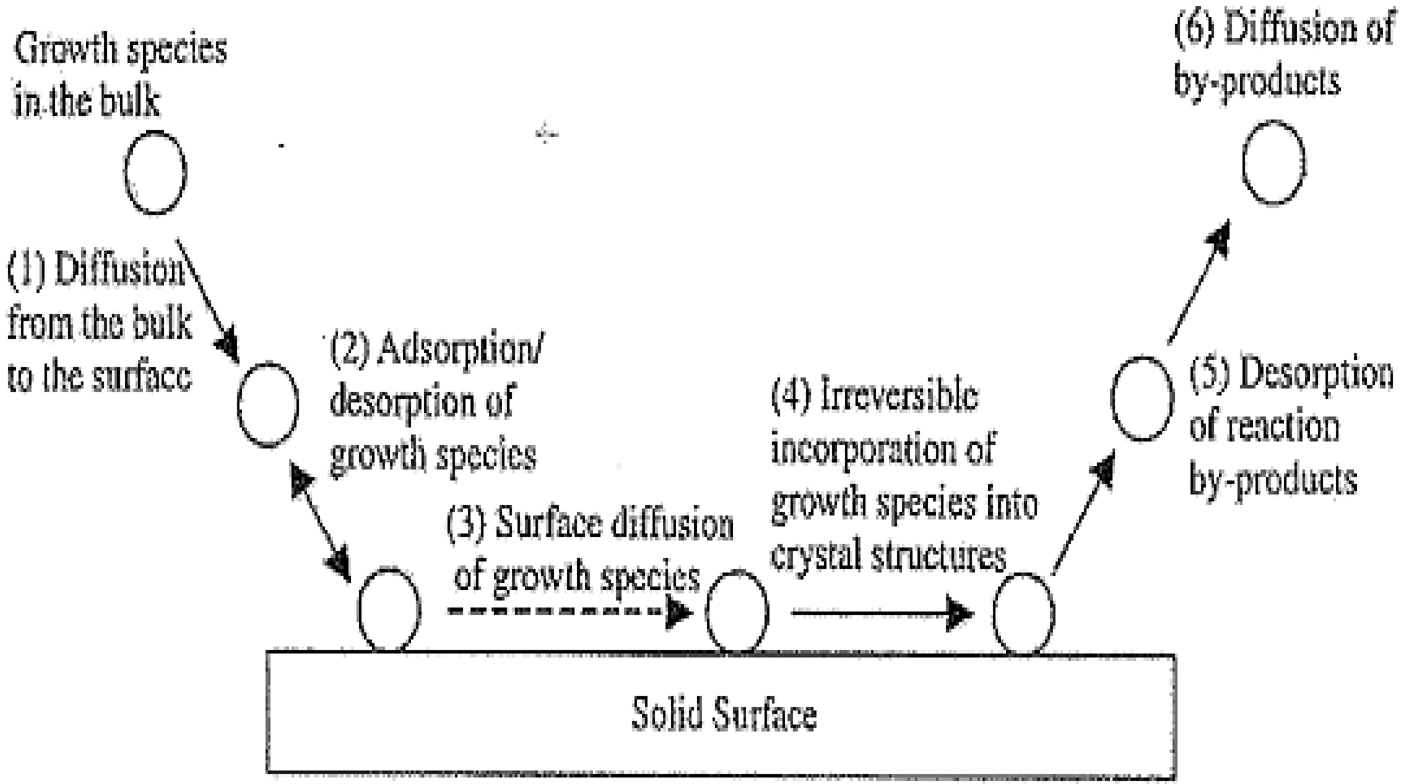


Mesoporous ZnO nanowires



Ultra-narrow ZnO nanobelts

Evaporation condensation



(1) Diffusion of growth species from the bulk (such as vapor or liquid phase) to the growing surface

(2) Adsorption and desorption of growth species onto and from the growing surface.

(3) Surface diffusion of adsorbed growth species. During surface diffusion, an adsorbed species may either be incorporated into a growth site, which contributes to crystal growth, or escape from the surface.

(4) Surface growth by irreversibly incorporating the adsorbed growth species into the crystal structure.

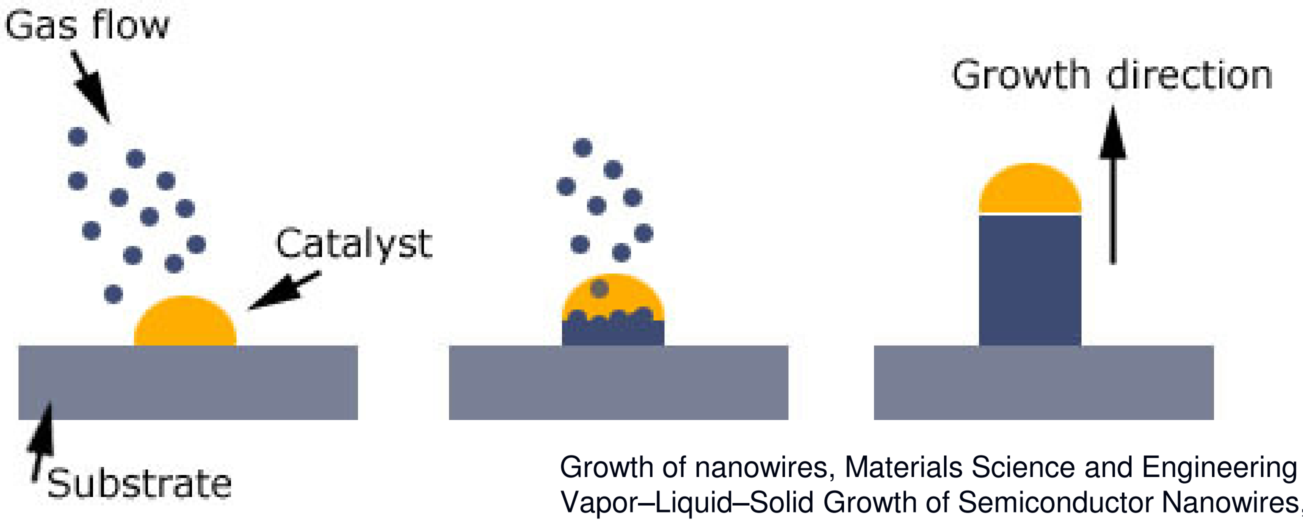
(5) If by-product chemicals were generated on the surface during the growth, by-products would desorb from the growth surface, so that growth species can adsorb onto the surface and the process can continue.

(6) By-product chemicals diffuse away from the surface so as to vacate the growth sites for continuing growth.

Vapor-Liquid-Solid growth (VLS)

A second phase material, commonly referred to as ***catalyst***, is introduces to direct and confine the crystal growth on a specific orientation and within a confined area.

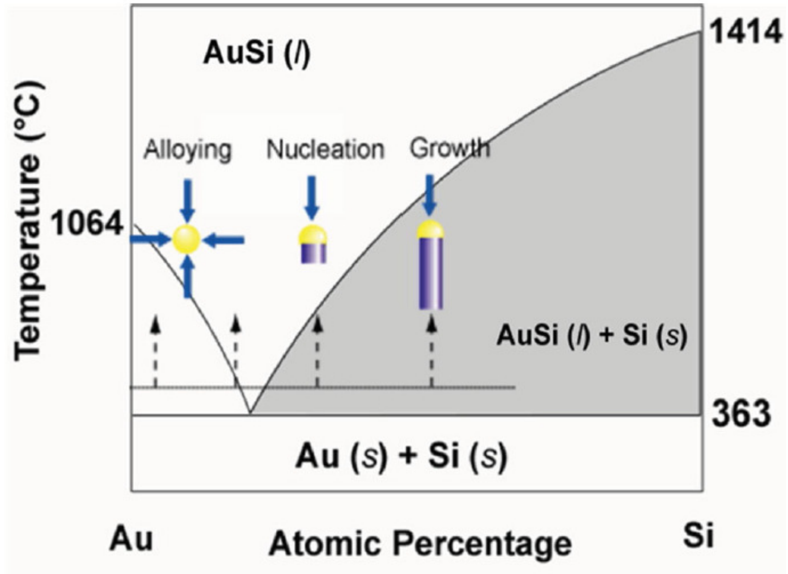
- The most successful method to generate single crystal nanowires in relatively large quantities
- Catalyst forms a **liquid droplet** by itself or by alloying with the growth material, which then acts as a trap of the growth species
- The growth species is evaporated first and then diffuses and dissolves into a liquid droplet
- Enriched growth species in the catalyst droplets subsequently precipitate at the substrate/liquid interface, resulting in the one-directional growth.
- The diameter of each nanowire is largely determined by the size of the catalyst droplet



Growth of nanowires, Materials Science and Engineering R 60 (2008) 1–51
Vapor–Liquid–Solid Growth of Semiconductor Nanowires, Heon-Jin Choi

Vapor-Liquid-Solid growth (VLS)

- Coexistence of **three** phases
- Lowest temperature where system is still totally liquid



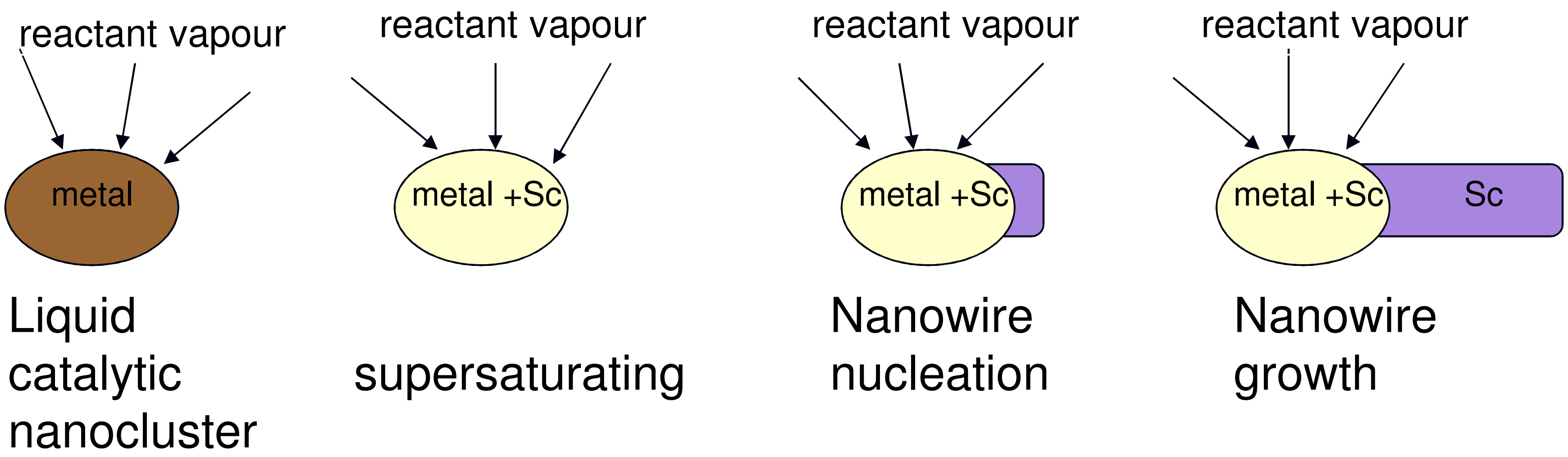
Synthesis of semiconductors

binary III-V materials (GaAs, GaP, InAs, InP)

ternary III-V materials (GaAs/P, InAs/P)

binary II-VI materials (ZnS, ZnSe, CdS, CdSe)

binary Si Ge alloys



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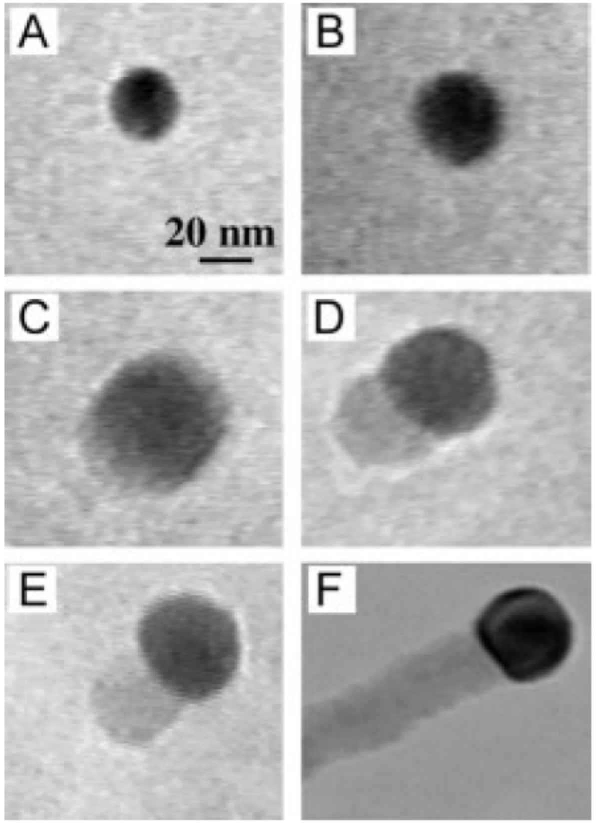
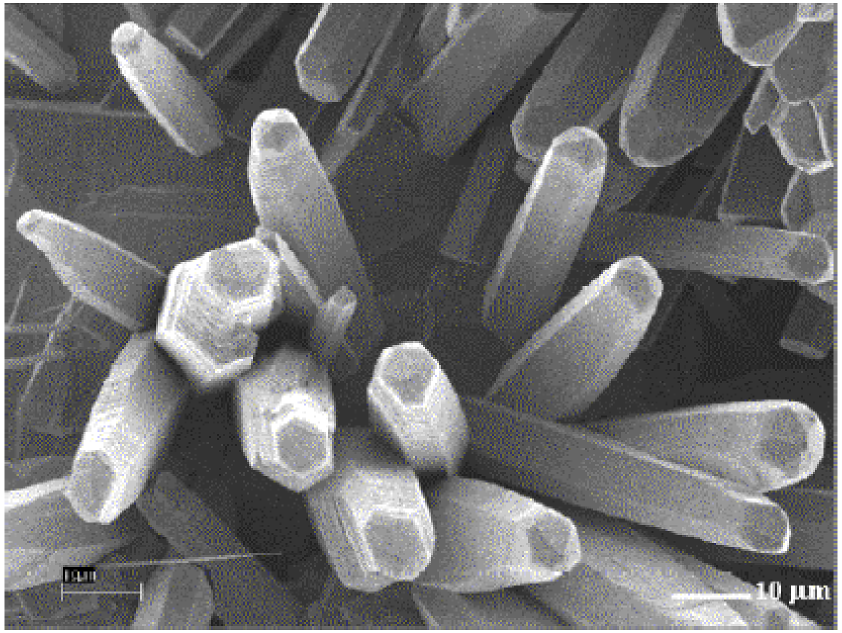
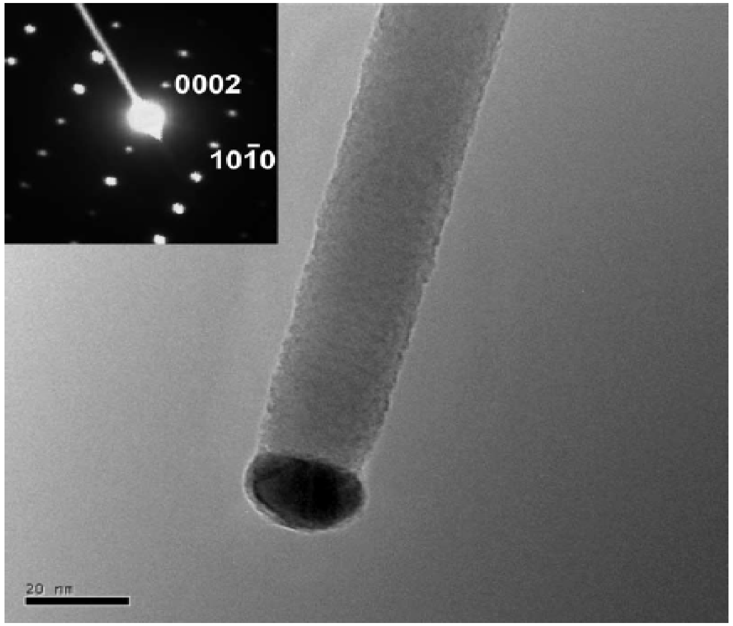


Fig. 16. The birth of a Ge nanowire on a Au nanocluster, as observed using in-situ TEM. It is clearly seen that the Au nanocluster started to melt after the formation of Ge–Au alloy, and this was followed by an increase in the liquid droplet size during the Ge vapor condensation process. When the droplet was supersaturated with the Ge component, a Ge nanowire grew out of this droplet of Au–Ge alloy and became longer as time elapsed [135].

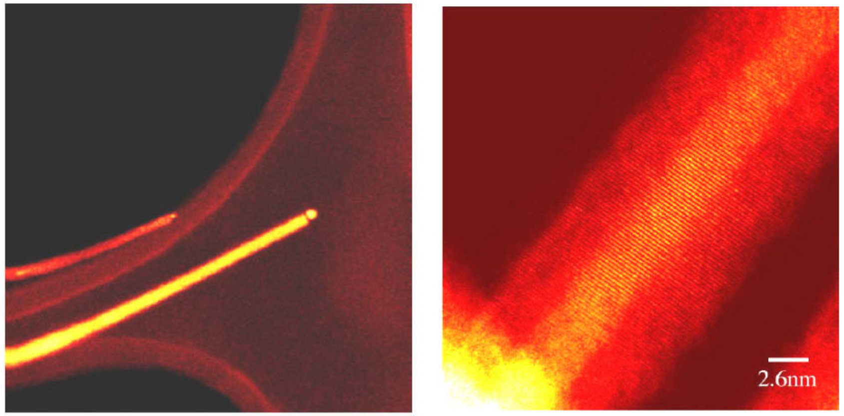
Vapor-Liquid-Solid growth (VLS)



A Non-Traditional Vapor-Liquid-Solid Method for Bulk Synthesis of Semiconductor Nanowires," S. Sharma and M. K. Sunkara,



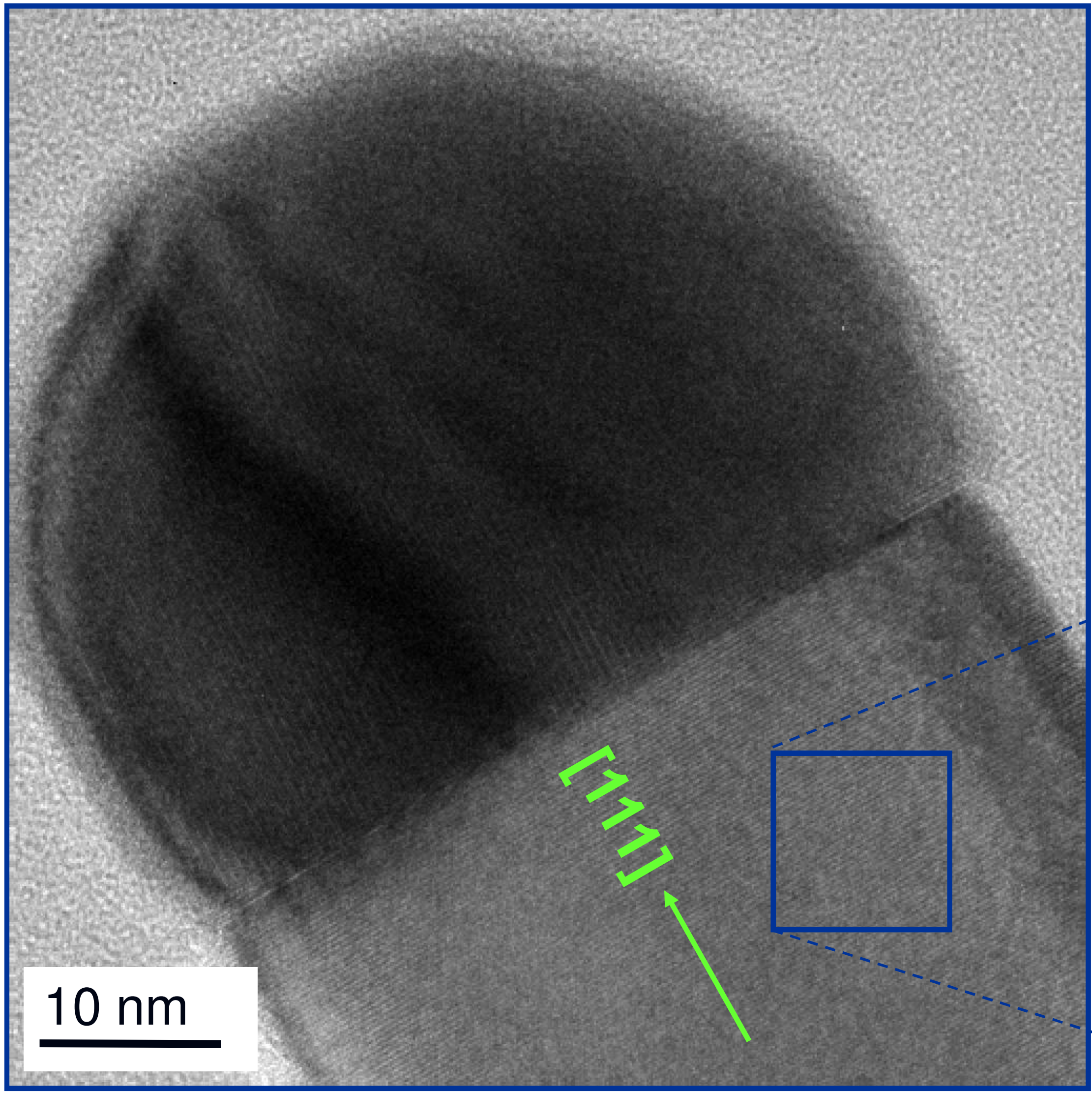
TEM of a single crystal ZnO nanorod



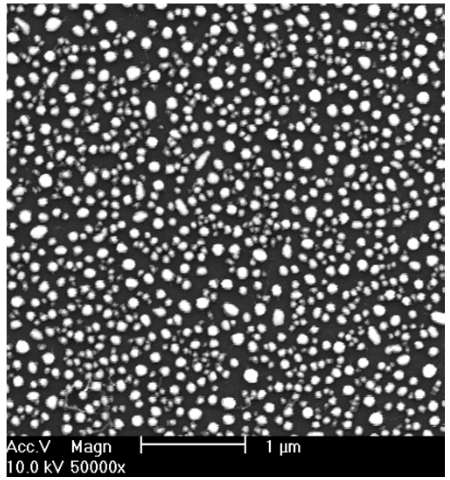
ZnO nanowire growth and devices, Materials Science and Engineering R47) 1–47 (2004

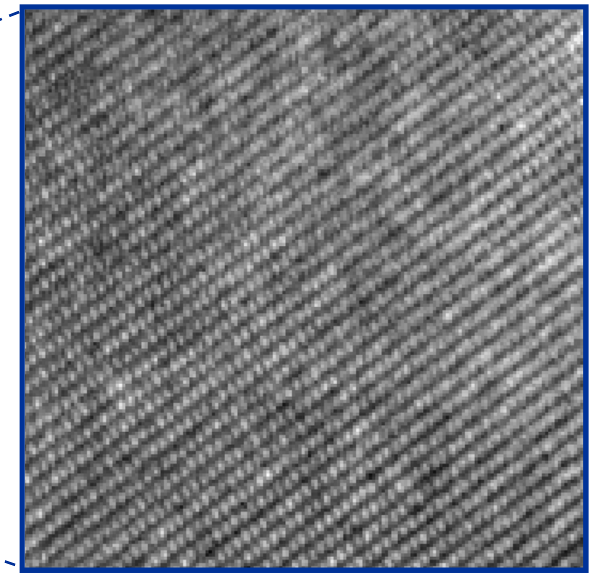
Z-contrast scanning transmission electron microscopy image of a (Zn,Mg)O nanorod with a Ag catalyst particle at the rod tip.

VLS Nanowires: InP on SiO2

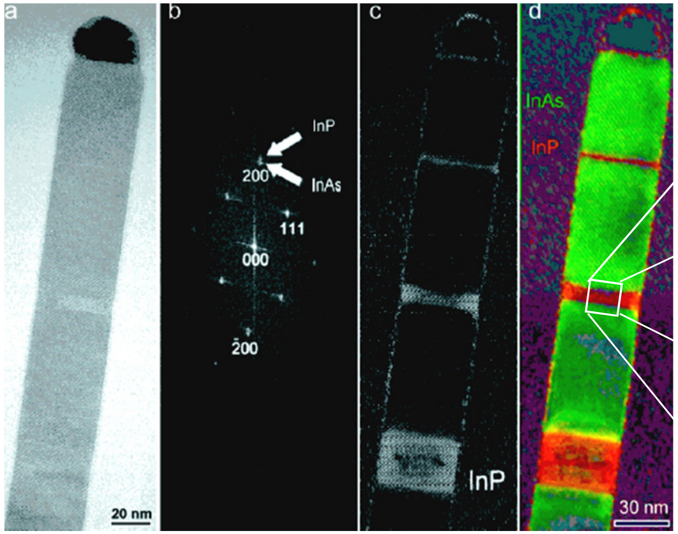


Before growth

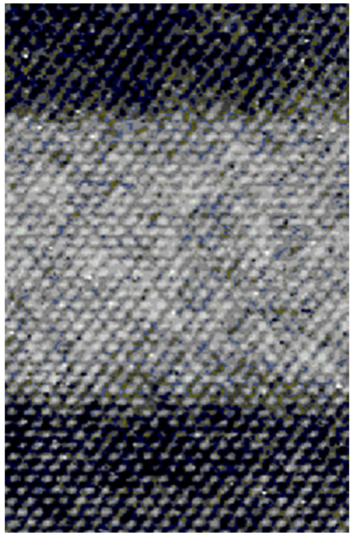




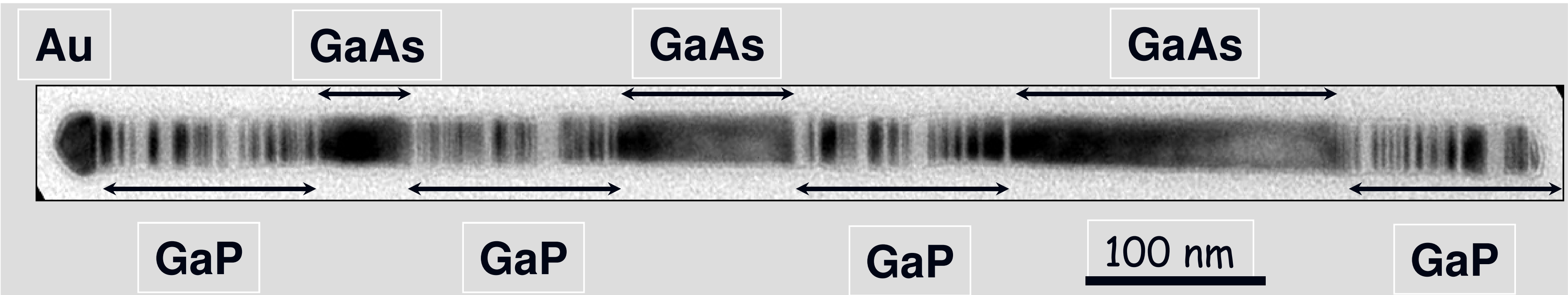
VLS Nanowires: Heterostructures



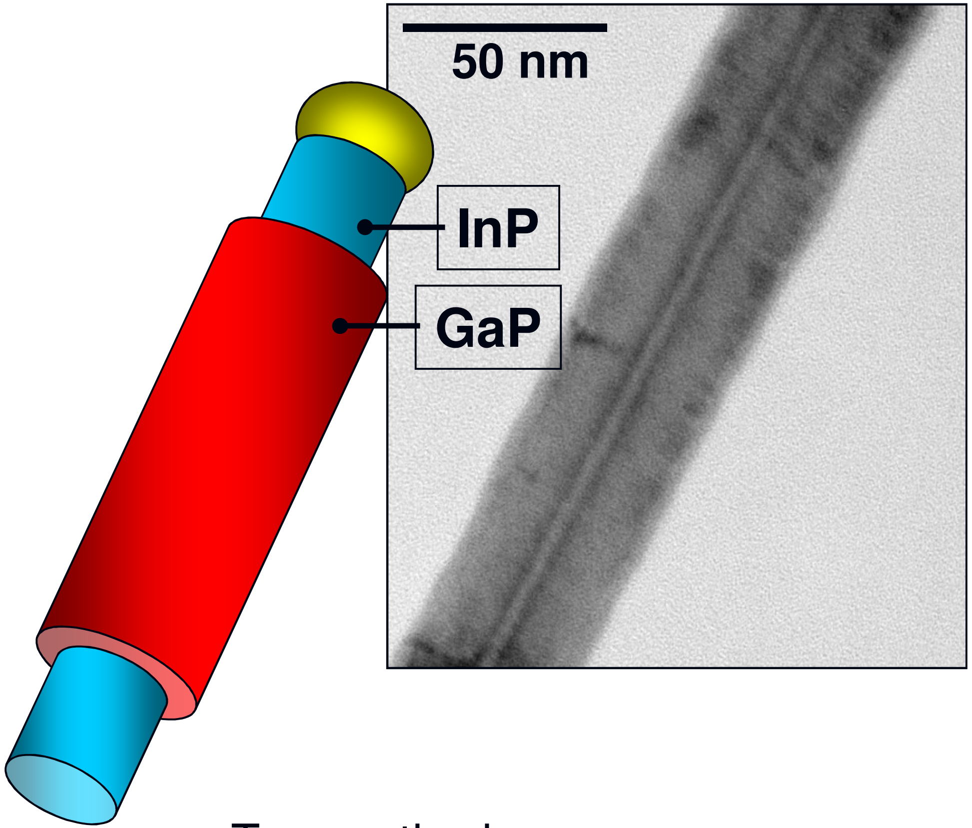
Björk et al., NanoLetters **2**, 87 (2002)

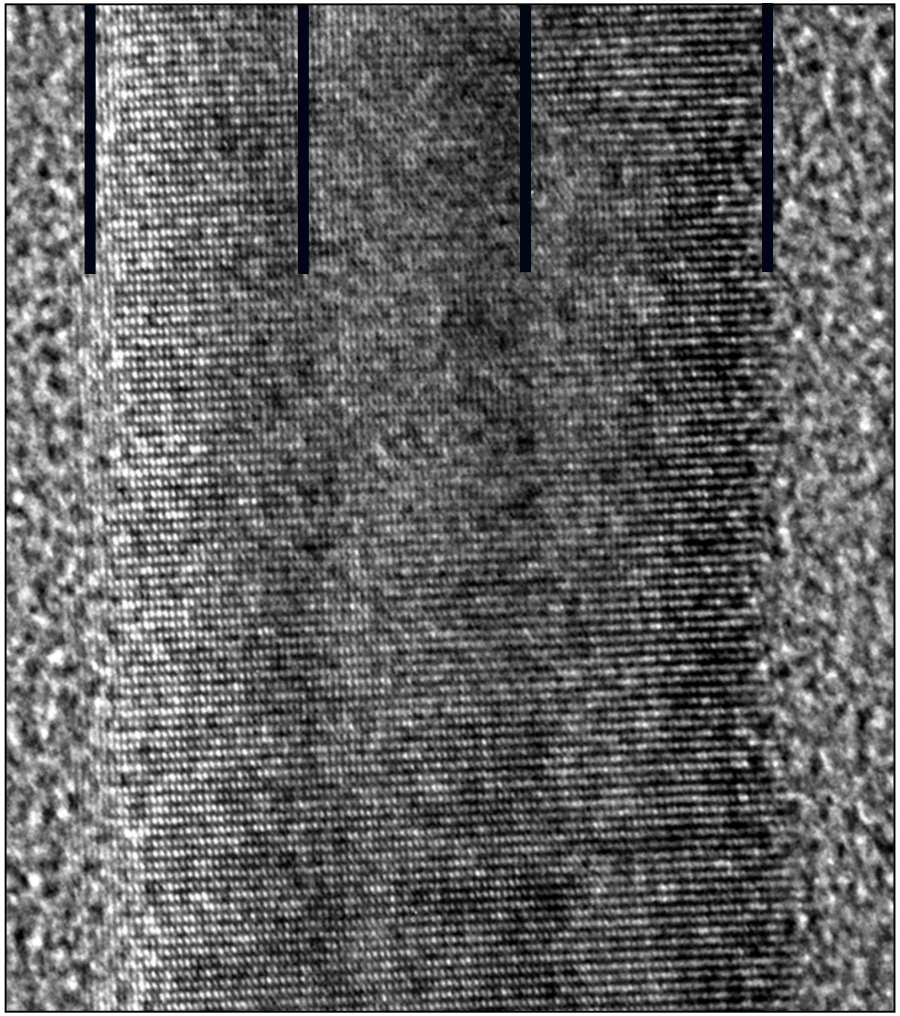


- Almost atomically sharp interfaces
- No strain-induced dislocations (stress can relax at the surface)



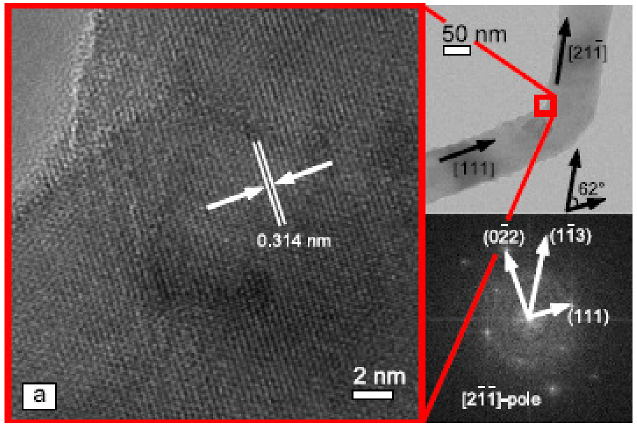
VLS Coaxial Nanowires: InP/GaP

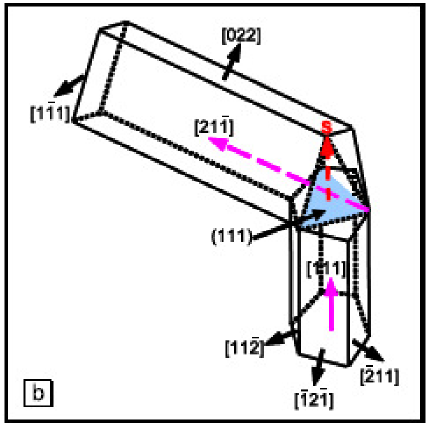


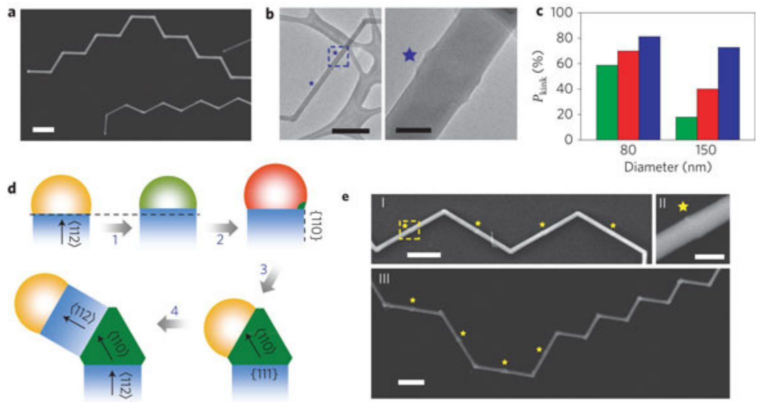


Two methods:
-VLS followed by VS mechanisms
-Spontaneous phase separation

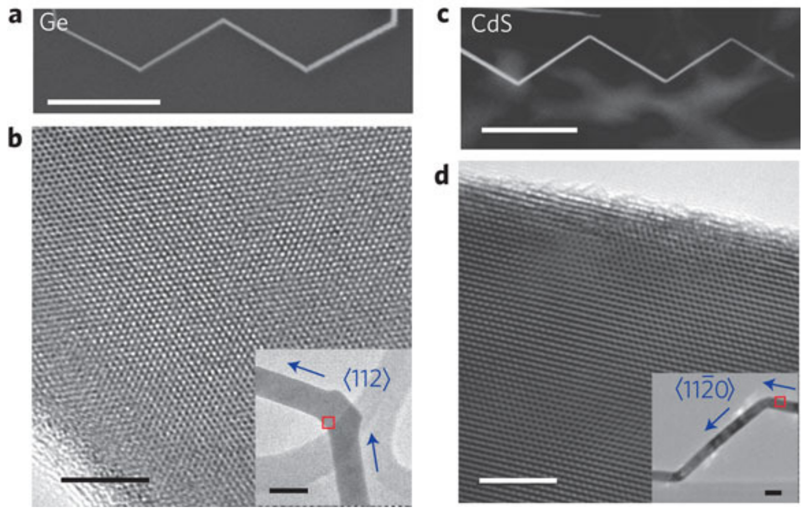
VLS kinked nanowires







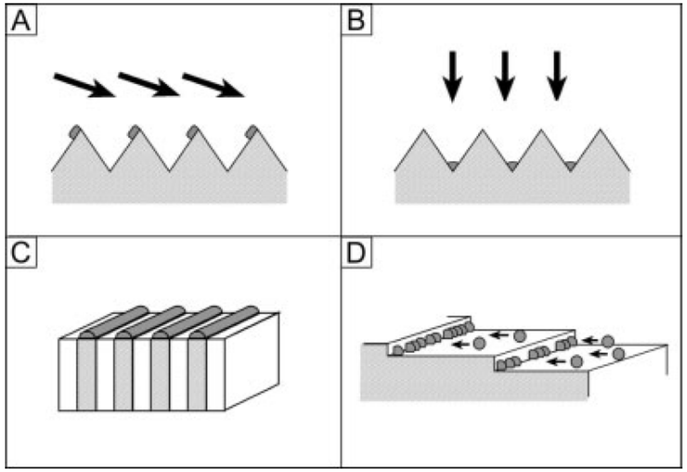
-Change in the growth direction induced by a sudden change of the pressure
-Pressure of 3 mbar lead to 111 Si NWs, while 15 mbar favours the 112 direction.

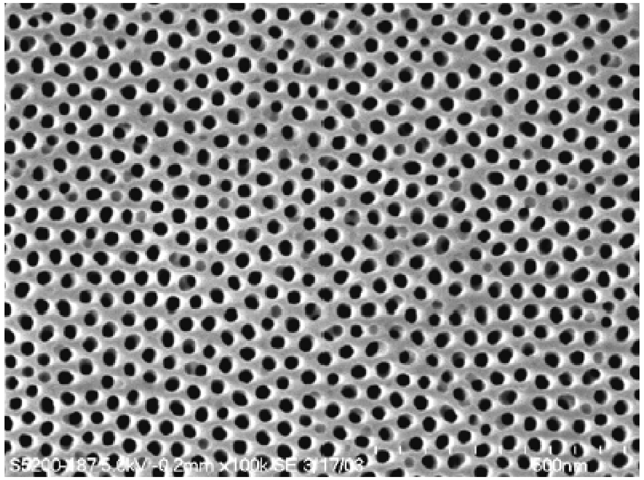


Orientation specific synthesis of kinked silicon nanowires grown by the vapour–liquid–solid mechanism, Nanotechnology 20 125606 (2009).

Template based

- Straightforward route to 1D nanostructures (simple, high-throughput, cost effective, but leads to polycrystals and limited number of structures can be fabricated by run)
- The template serves as a scaffold within (or around) which a different material is grown
- Example of templates include steo edges at the surface of a solid substrate, channels within porous materials, biological macromolecules
- Use in fabrication of nanowires, and nanotubes of polymers, metals, semiconductors, and oxides



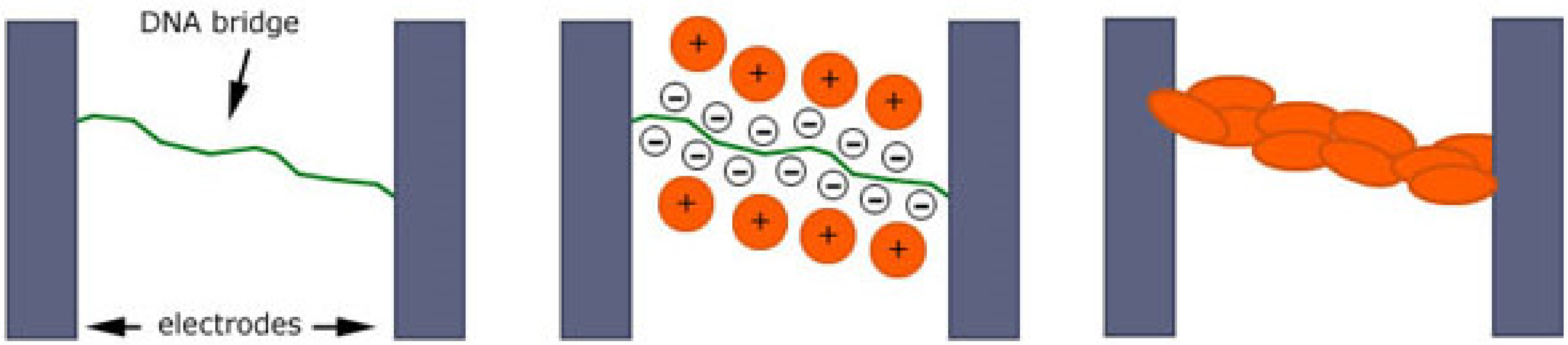


DNA based templates

- Nanowires are formed on the outer surface of the templates
- Diameter of the nanowires is not restricted by the template sizes and can be controlled by adjusting the amount of materials deposited on the templates

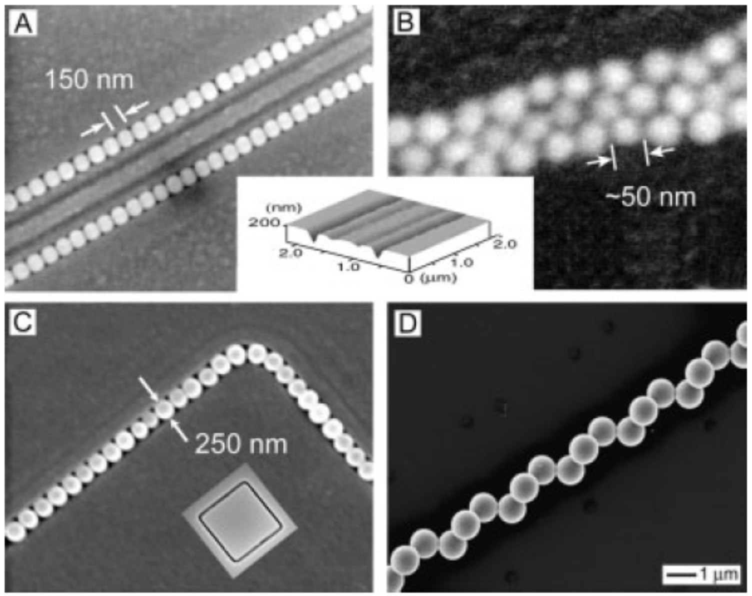
DNA is an excellent choice as a template to fabricate nanowires because its diameter is ~2 nm and its length and sequence can be precisely controlled

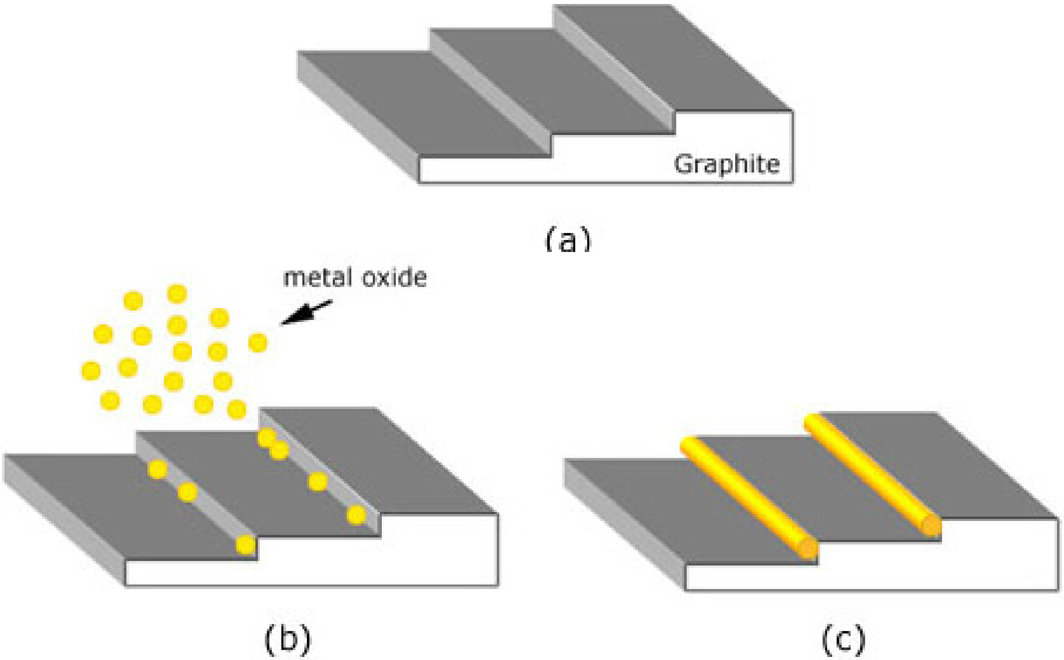
- Fix a DNA strand between two electrical contacts
- Exposed to a solution containing some ions
- Ions bind to DNA and are then form some nanoparticles decorating along the DNA chain



Surface step-edge templates

- Relief structures (natural or patterned) on the surface of a substrate can be used as templates to grow nanowires.
- The method takes the advantage of the fact that deposition of many materials on the surface often starts preferentially at defect sites, such as surface step-edges.
- The problem is that these nanowires can not be easily removed from the surface on which they are deposited

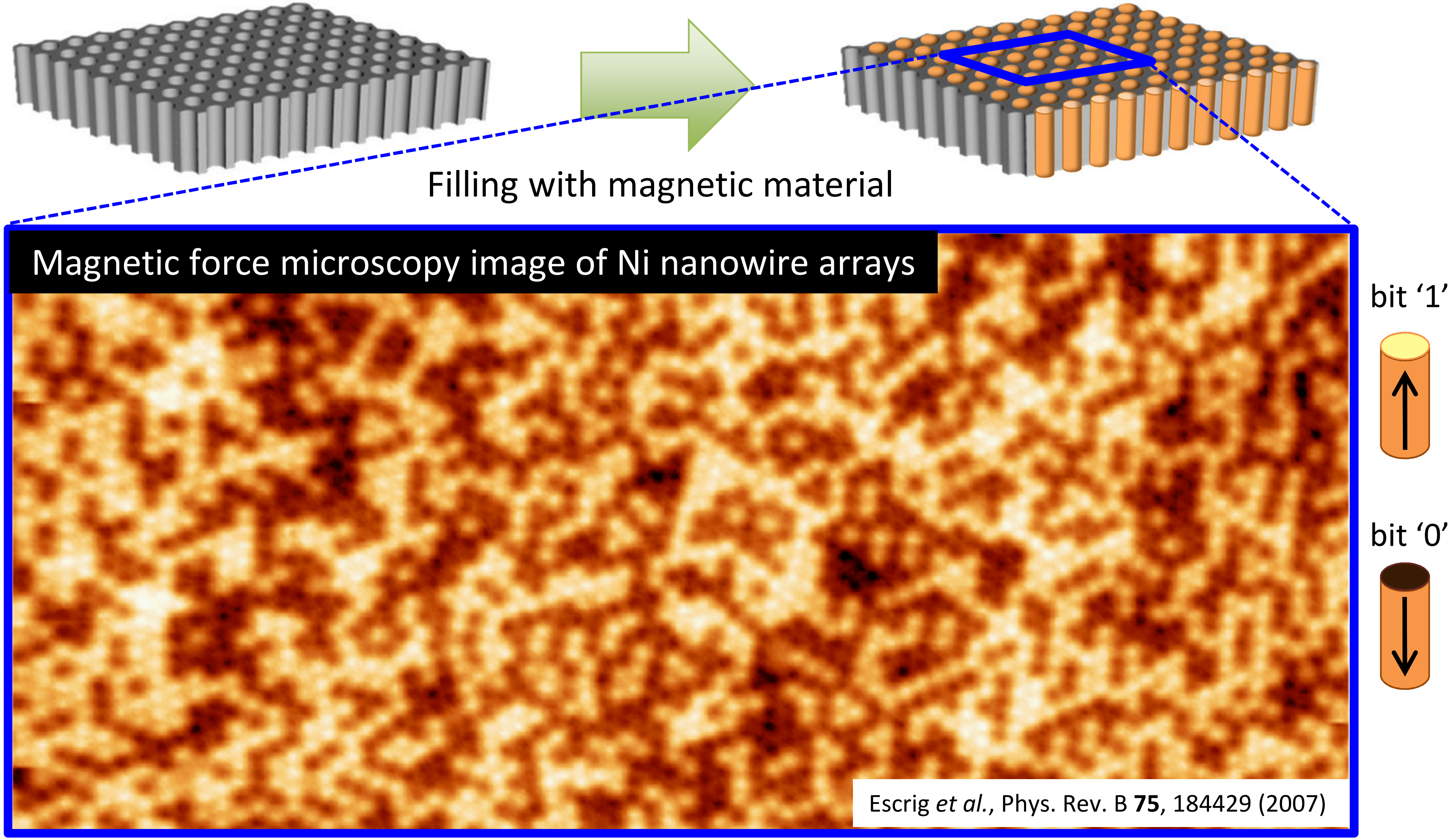




MAGNETISM IN ONE-DIMENSIONAL METAL SYSTEMS, PIETRO GAMBARDELLA

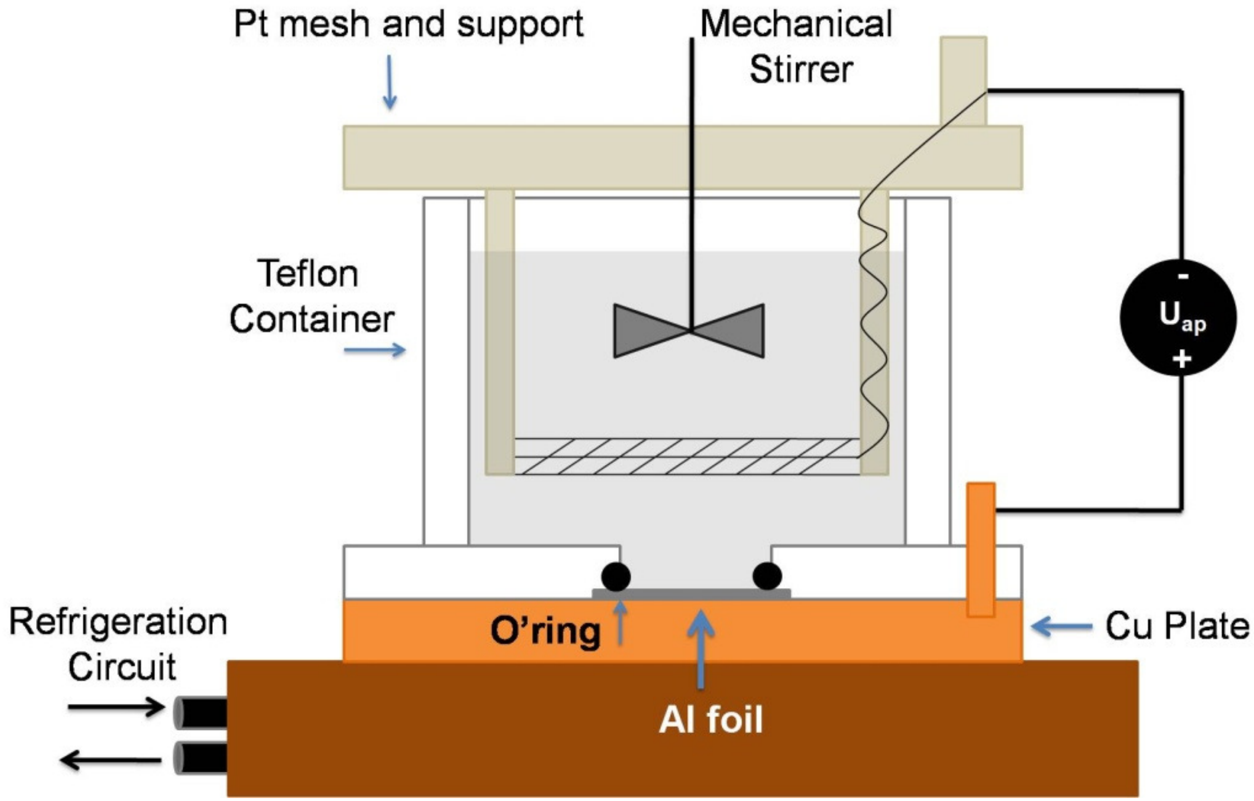
Nanoporous Alumina Templates

Use of **Nanoporous Alumina** as Templates

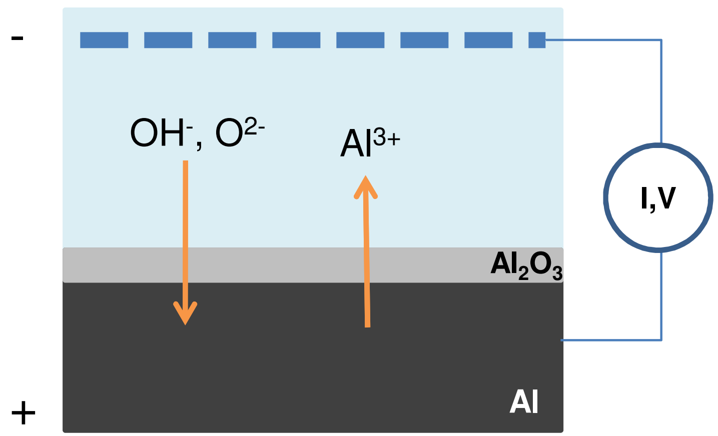


Anodization process

Experimental set up



Anodization process



Electrochemical Processes

- To form a porous-type layer an electrolyte where the oxide is soluble is required.
- A window of anodization potentials exists for porous films;

At the Anode:

- Electrical field driven oxidation of Al;
- Thermal assisted oxide dissolution;
- Incorporation of other electrolyte species and voids into the oxide.

$$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$$

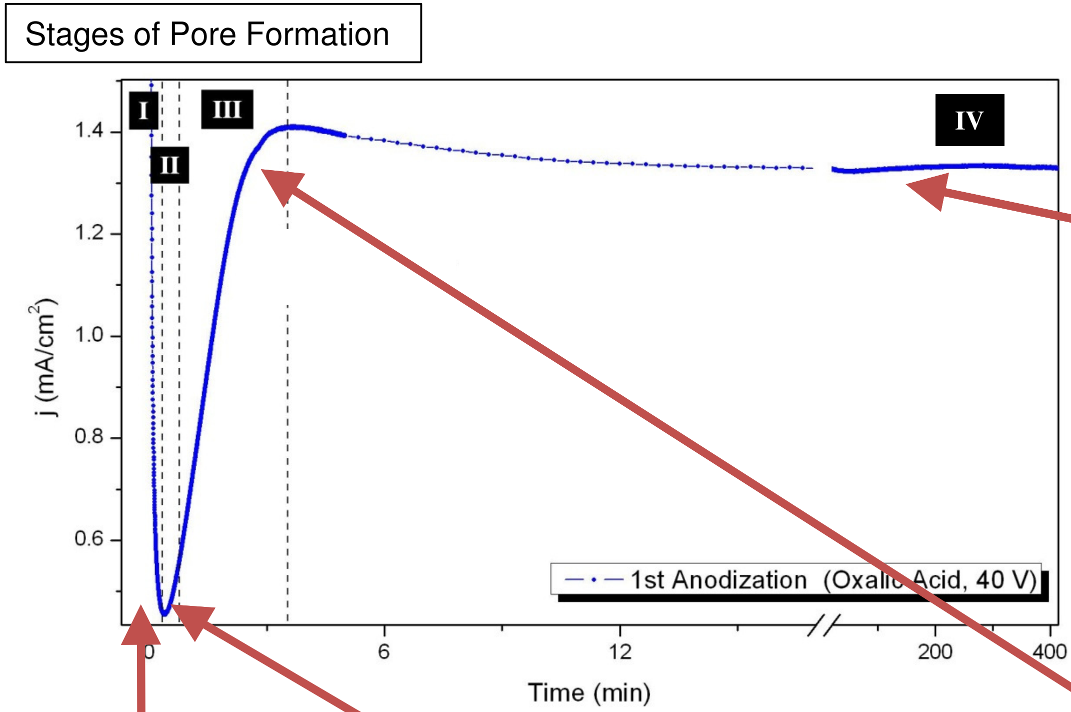
$$Al_2O_3(s) + nH_2O(l) \rightarrow Al^{3+}(aq) + O^{2-}(aq) + OH^-(aq) + H^+(aq)$$

At the Cathode:

- Inert cathode;
- Neutralization of H^+ ions resulting in hydrogen bubbles.

$$6H^+(aq) + 6e^- \rightarrow 2H_2(g)$$

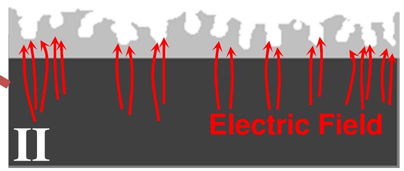
Anodization process



Stage IV: equilibrium between oxide growth and oxide dissolution.

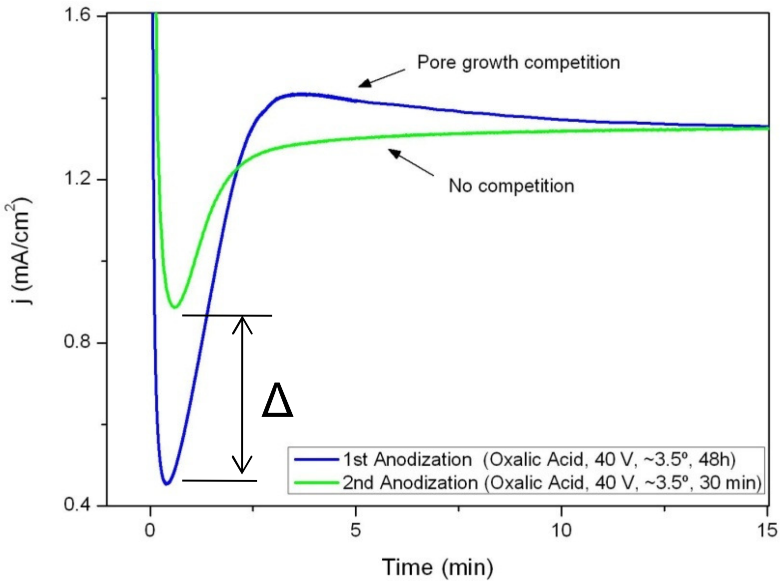
Stage III: further growth and formation of current paths.

Stage I: initial voltage drop, due to oxide layer formation.



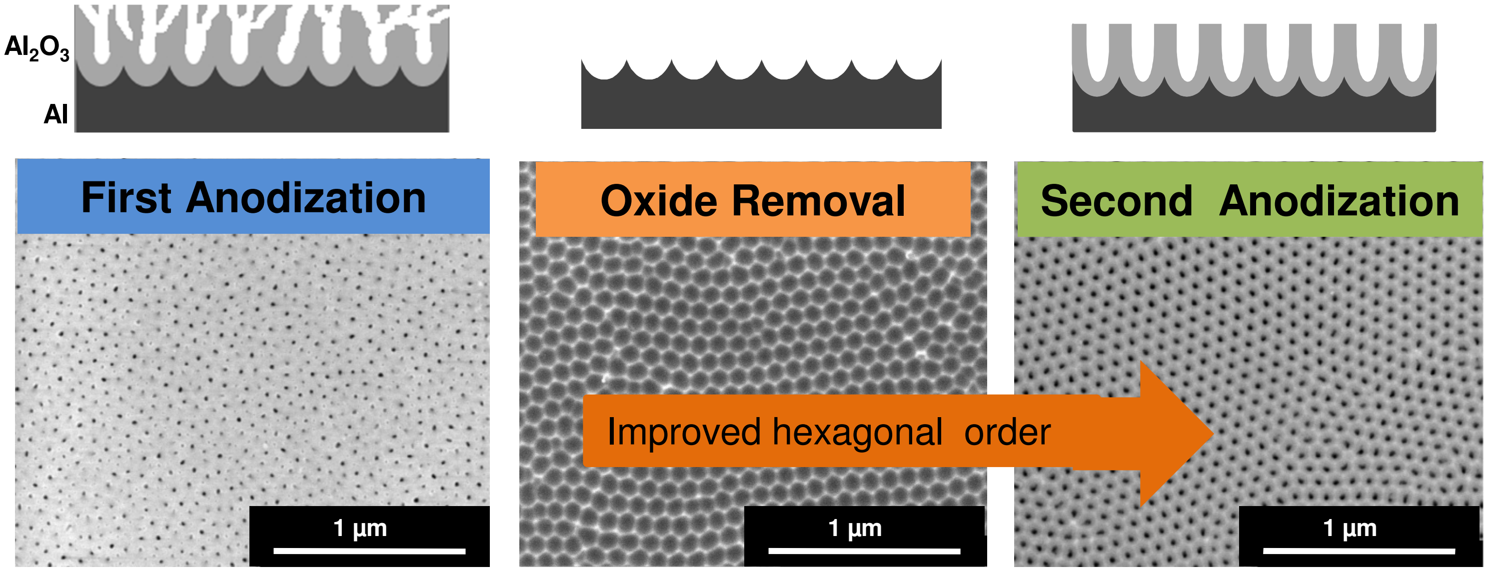
Stage II: nucleation of current paths by assisted oxide dissolution.

Two-step Anodization

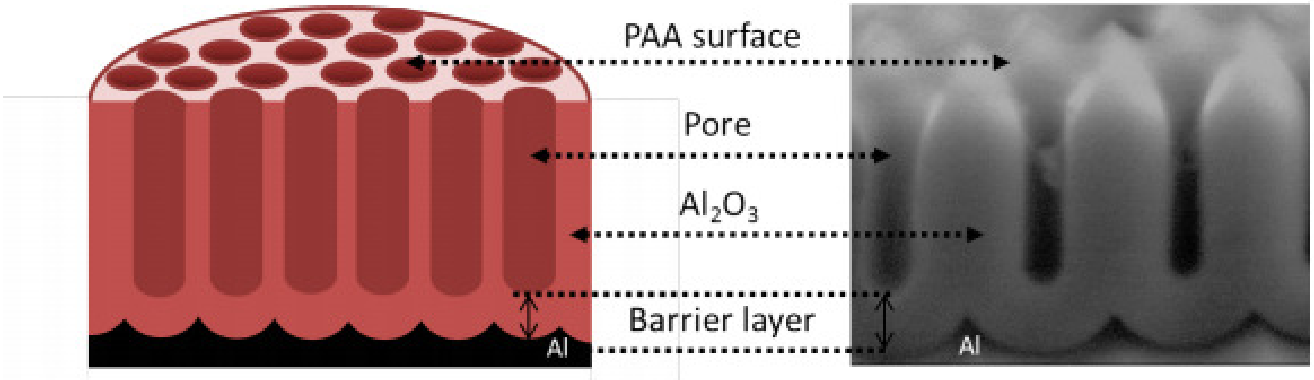


First Anodization: competition among the nucleated current paths (pores).

The difference Δ emphasizes the distinct number of current paths grown.



Nanoporous Alumina Templates



Pore: D_{int}= k V , K = 2.5 nm/V

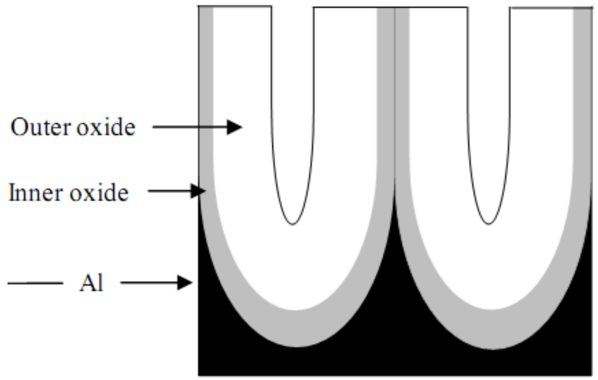
D_p= k V , K = 0.7 nm/V

$$P = \frac{2\pi}{\sqrt{3}}\left(\frac{r}{D_{\text{int}}}\right)^2$$

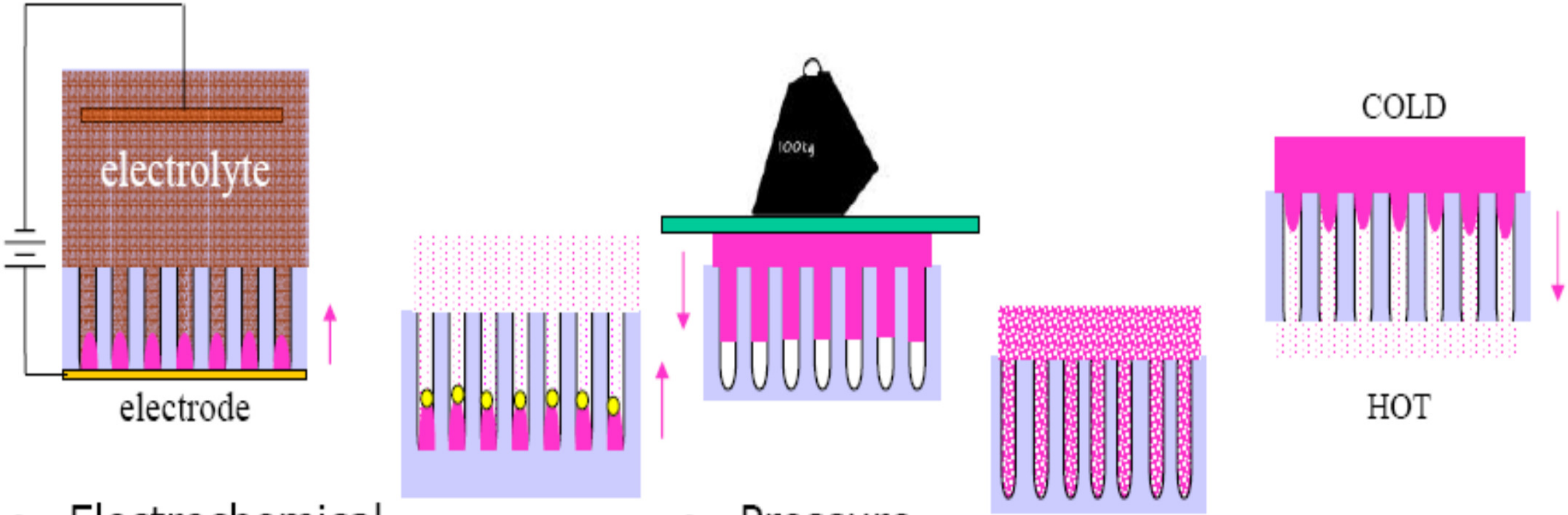
Self-organized regime:
P = 10 %

Barrier layer:

δ_b=kV , K = 1.3 nm/V



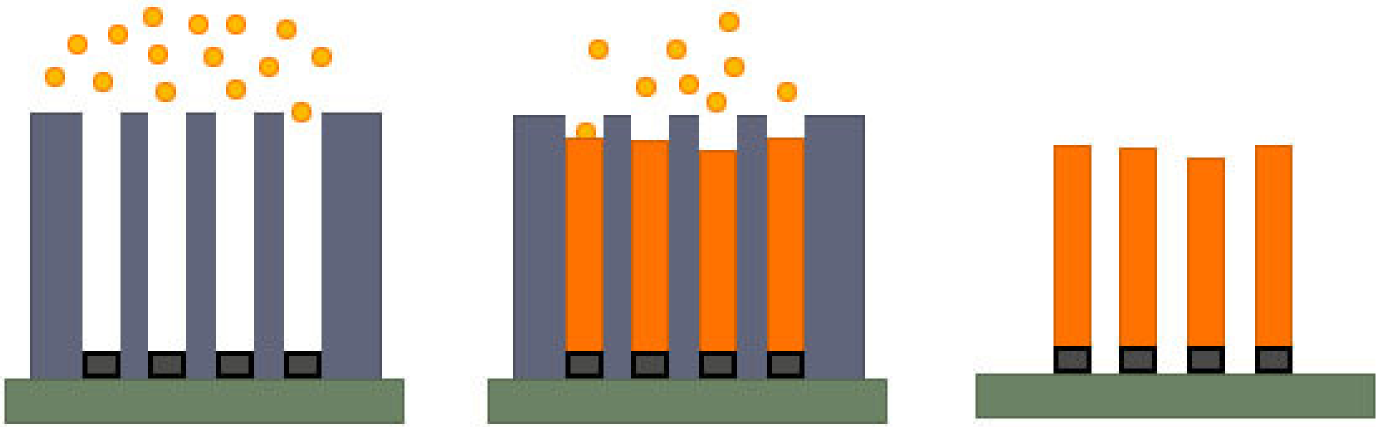
Filling methods

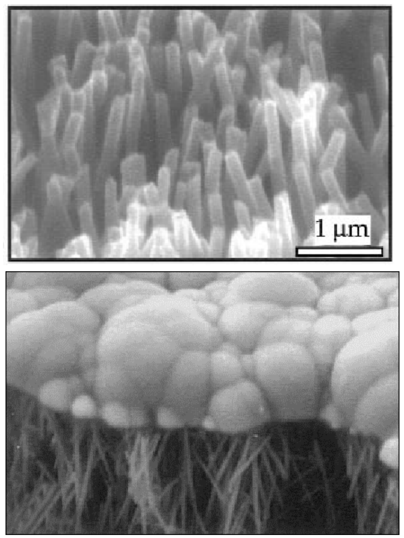


- Electrochemical deposition
- Chemical vapor deposition
- Pressure injection of melt
- Vapor condensation
- Sol-Gel

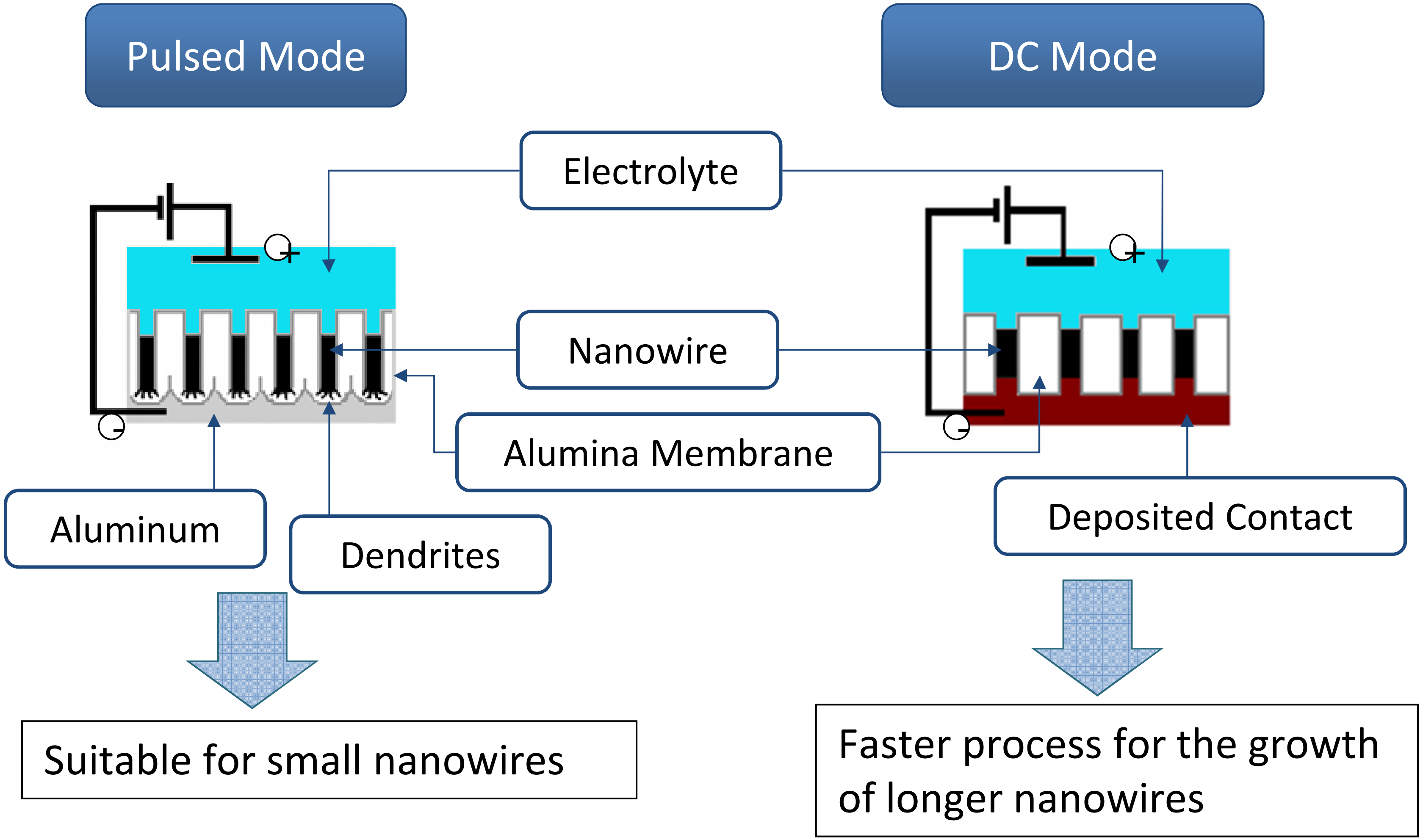
Electrodeposition

- This method can be understood as a special ***electrolysis*** resulting in the deposition of solid material on an electrode
- Only applicable to electrically conductive materials: metals, alloys, semiconductors, and electrical conductive polymers.
- Electrodeposition often requires a ***metal film*** on one side of the freestanding membrane to serve as a working electrode on which electrodeposition takes place
- If dissolve away the host solid material, free-standing nanowires are obtained.
- The diameter of the nanowires is determined by the geometrical constraint of the pores
- electrodeposited nanowires tend to be dense, continuous, and highly crystalline in contrast to other deposition methods.
- the ability to control the aspect ratio of the metal nanowires by monitoring the total amount of passed charge.

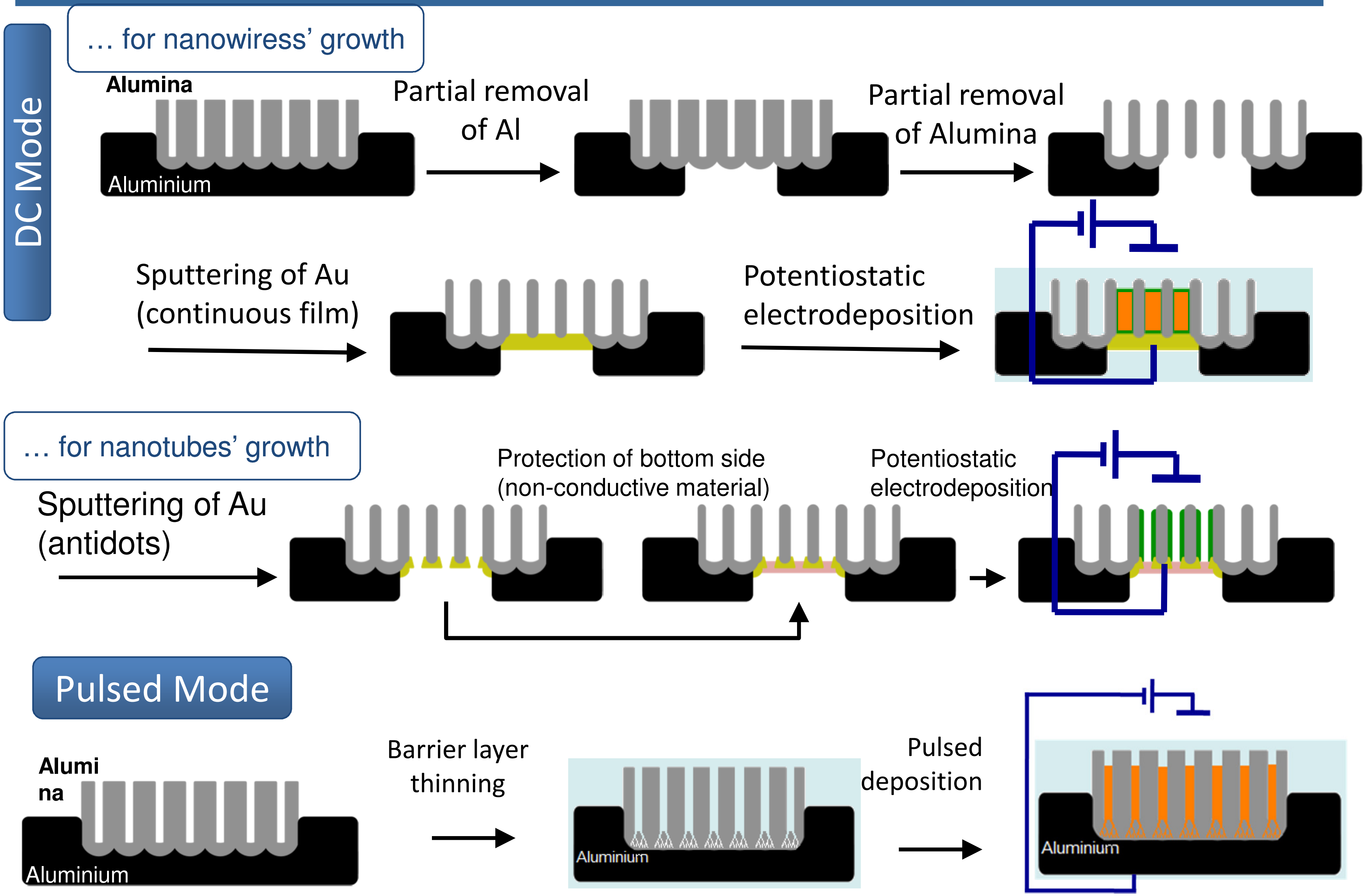




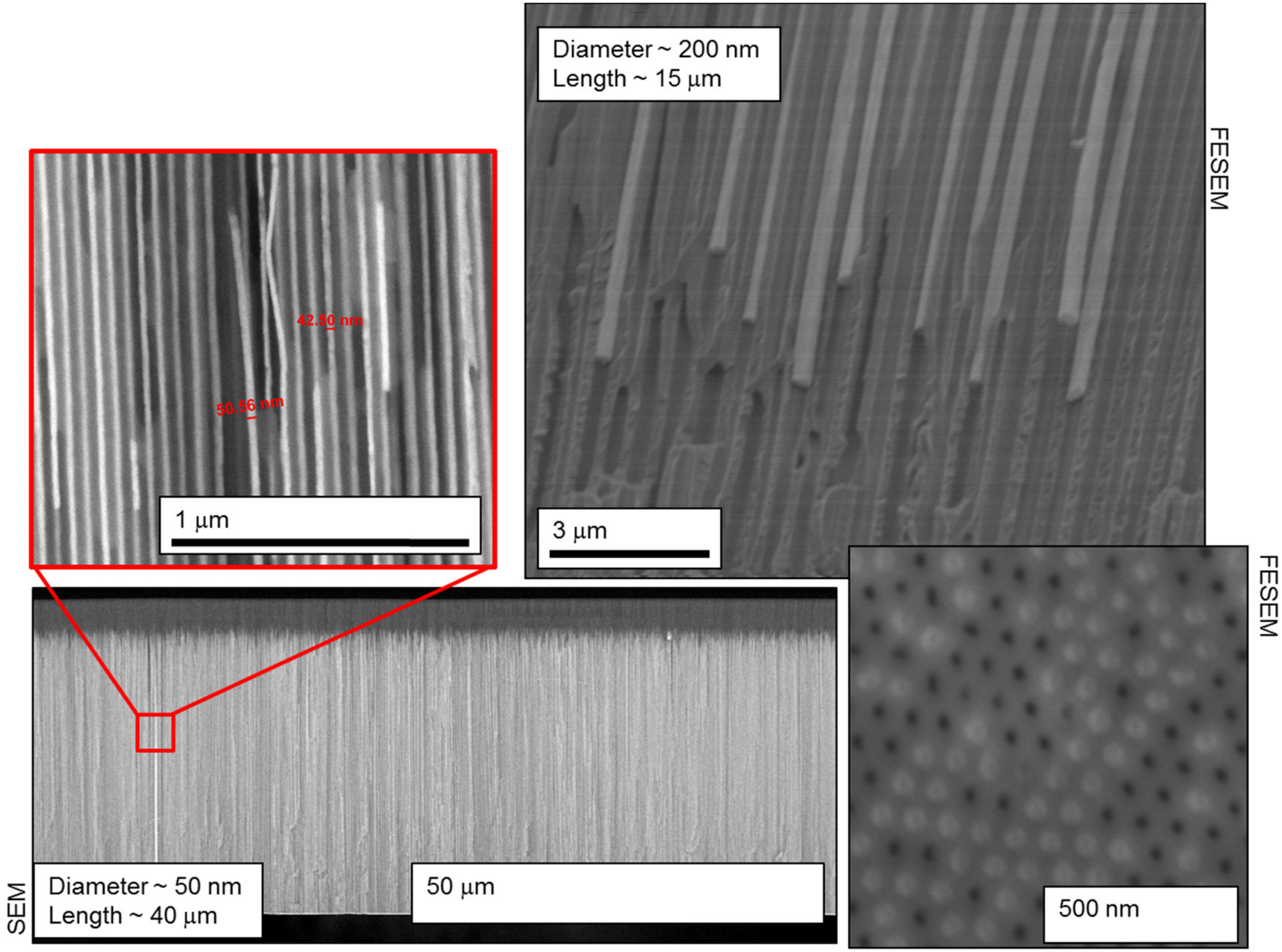
Electrodeposition



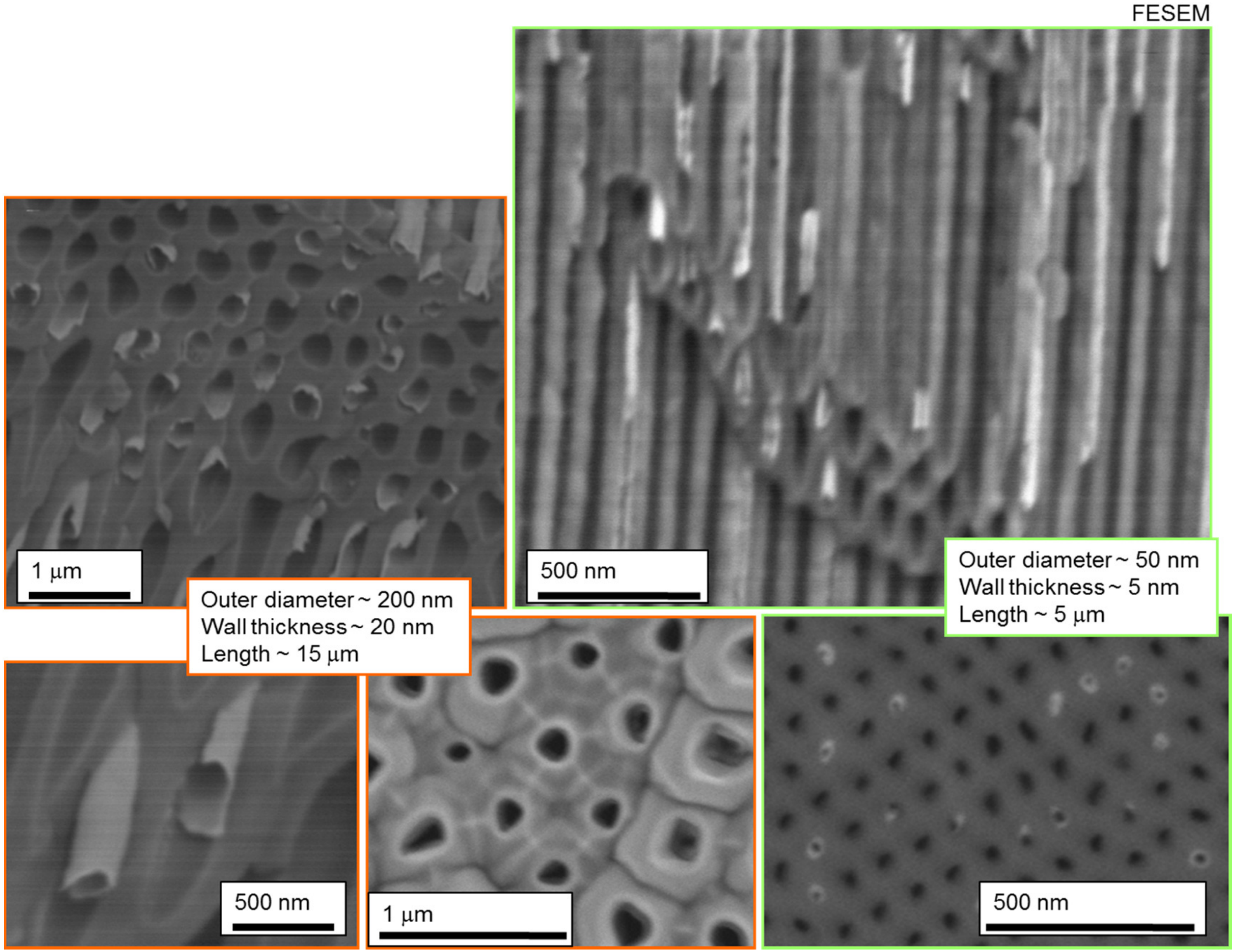
Alumina templates preparation



Ni nanowires



Ni Nanotubes



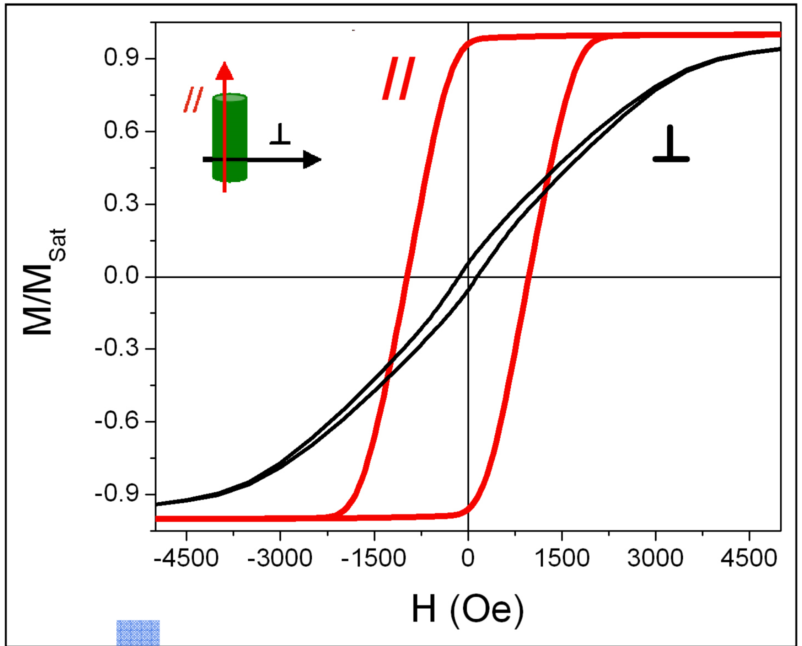
Magnetic properties

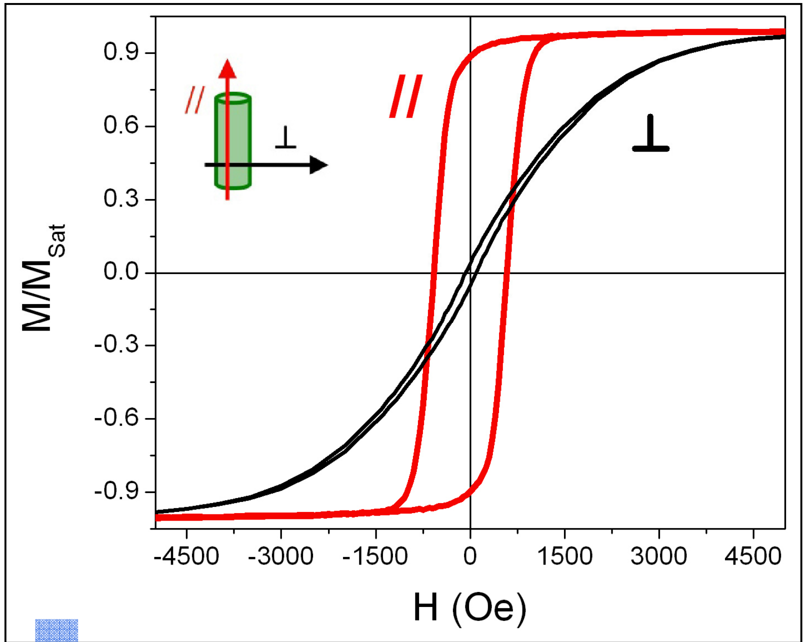
Ni Nanowires

50 nm diameter
50 μm length

Ni Nanotubes

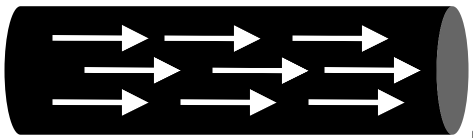
50 nm diameter
10 nm wall thickness
50 μm length

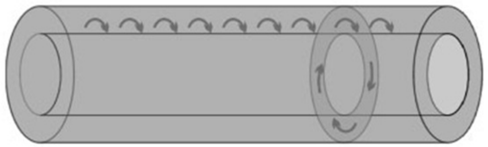




Sharp magnetization reversal, high $H_C^{//}$ and **large squareness** along // direction.

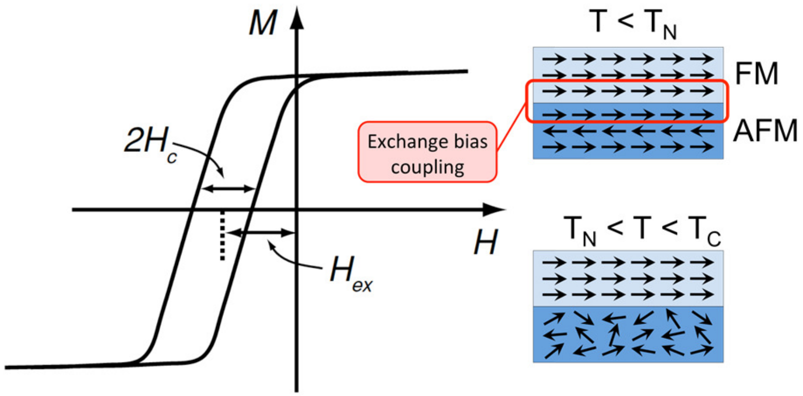
Small H_C and **squareness** along both directions. **Smooth reversal process** along //-direction.



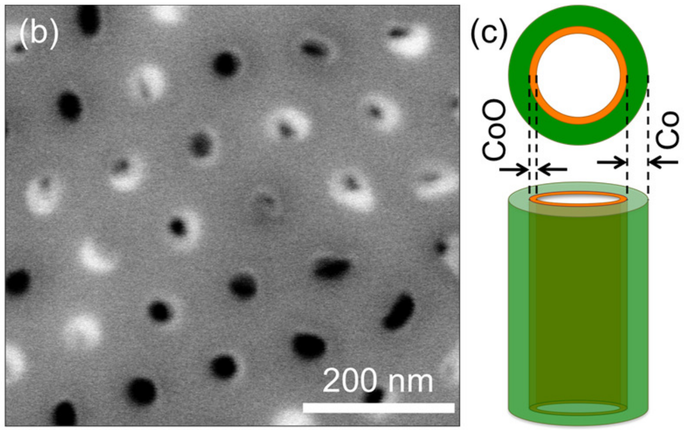


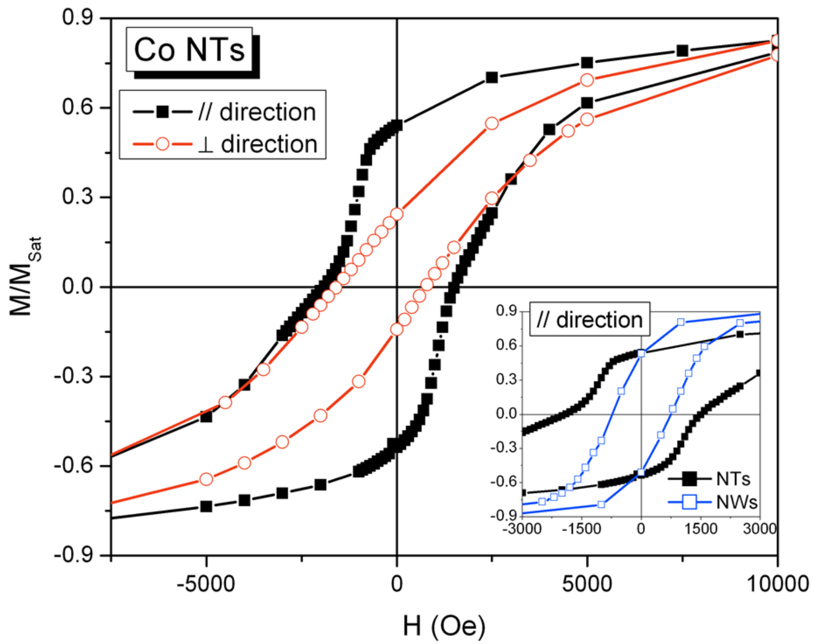
M. P. Proenca *et al.*, Nanoscale Res. Lett. **7** 280 (2012)

Exchange Bias in Co/CoO NTs



J.M.D. Coey, *Magnetism and magnetic materials*, 2009 (adapted)





M(H) measured at 6 K, after field-cooling in 50 kOe from 320 K (above T_N^{CoO} ~ 290 K)

Exchange bias effect is observed along both directions

No exchange bias effect is observed in the Co nanowires

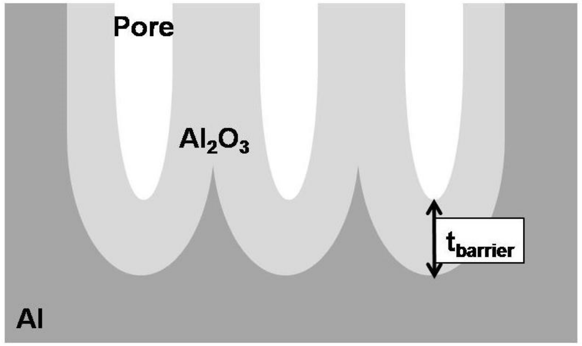
M. P. Proenca *et al.*, Phys. Rev. B 87, 1300-7 (2013)

Alumina barrier layer

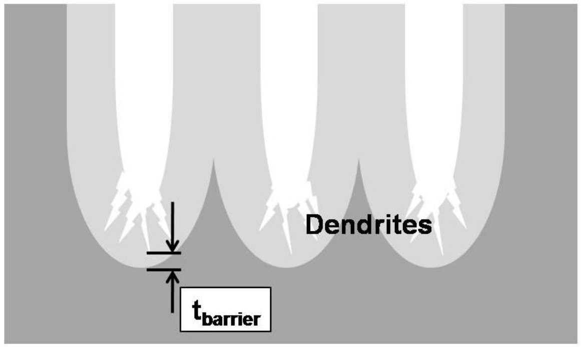
A non-conductive barrier-layer exists at the pores bottom:

$$\delta_b \approx \alpha V$$

α between 1.2 and 1.4 nm/V.

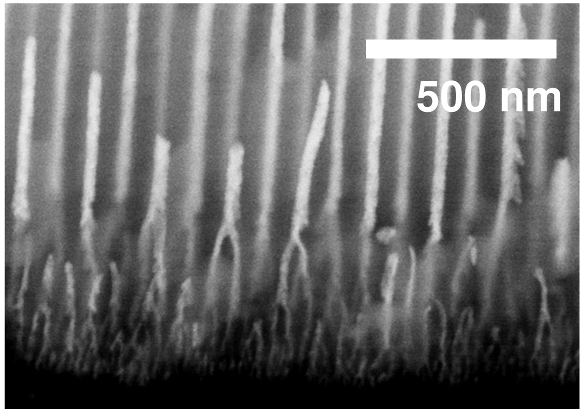


$t_{barrier} \sim 50nm$



$t_{barrier} \sim ?nm$

To electrodeposit metallic nanowires, the electrical current has to flow, thus $t_{barrier}$ must be thinned down.



The reduction procedure gives origin to dendrites (small channels in the alumina) enabling the current to tunnel through the barrier layer.

Barrier layer reduction

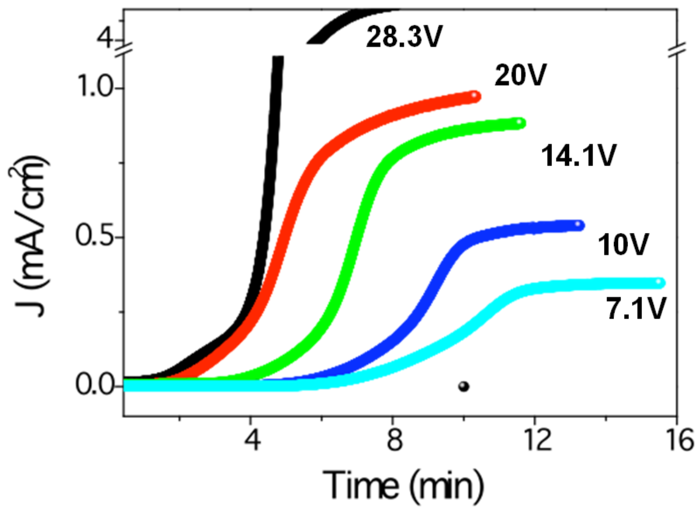
Dendrites

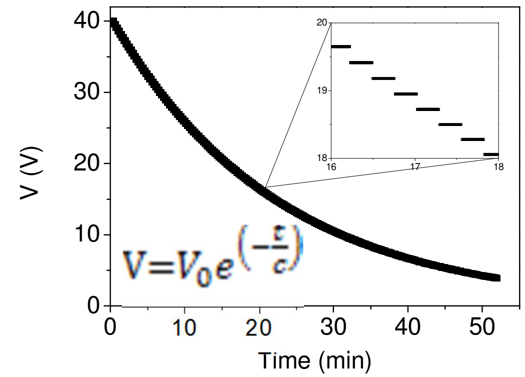
Branched alumina (Steady-state anodization)	**Tree-like alumina (Non steady-state anodization)**

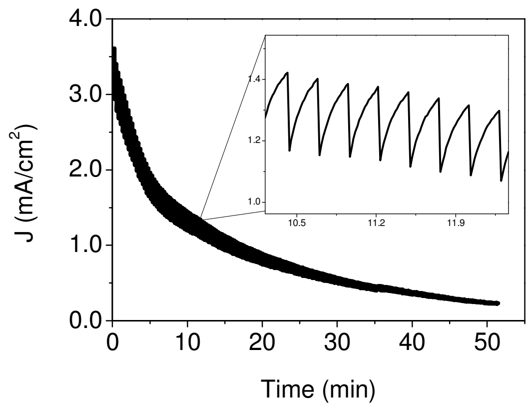
→ $D_{pore} \propto V_{anod}$

→ Constant area

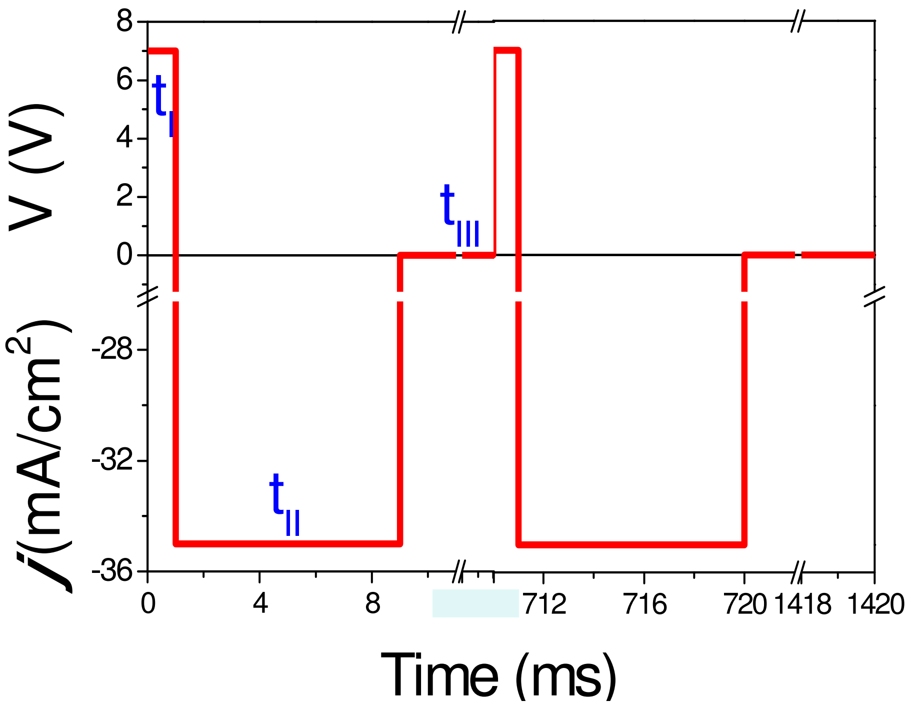
$$V_f = \frac{1}{\sqrt{n}} V_s$$

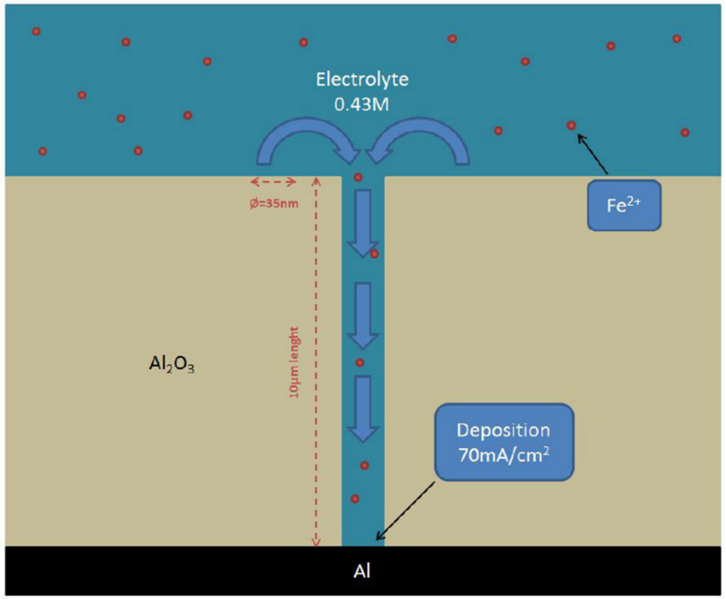


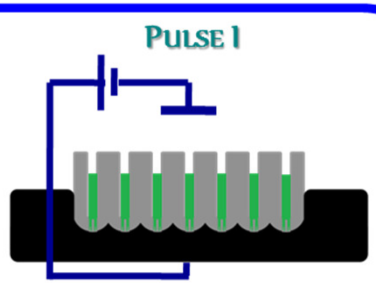




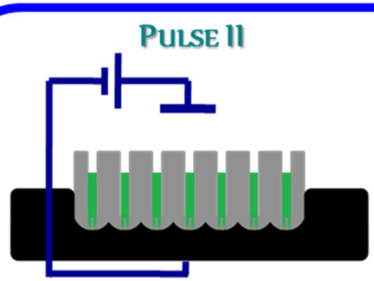
Pulsed electrodeposition



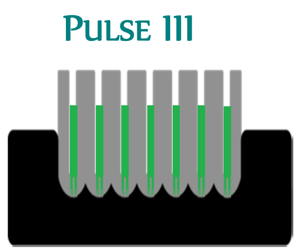




t_I – Discharge the capacitance of the alumina barrier layer



t_{II} – Deposition of the material

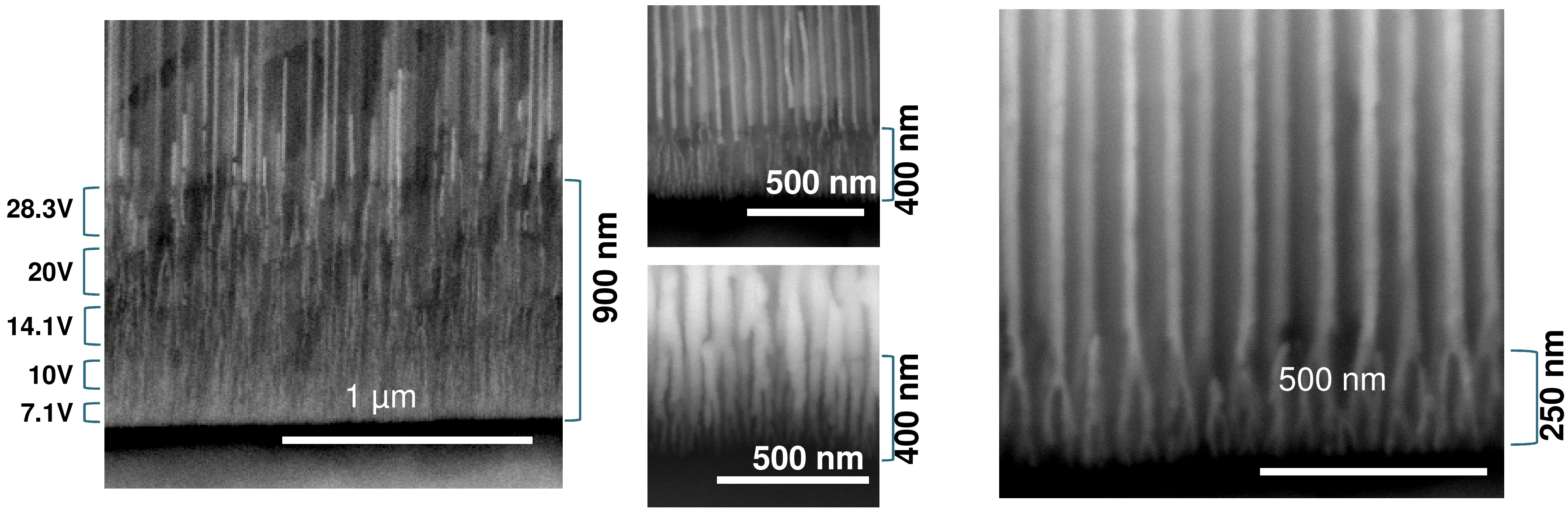


t_{III} - Reposition of the metal ions in the deposition interface

Ni nanowires

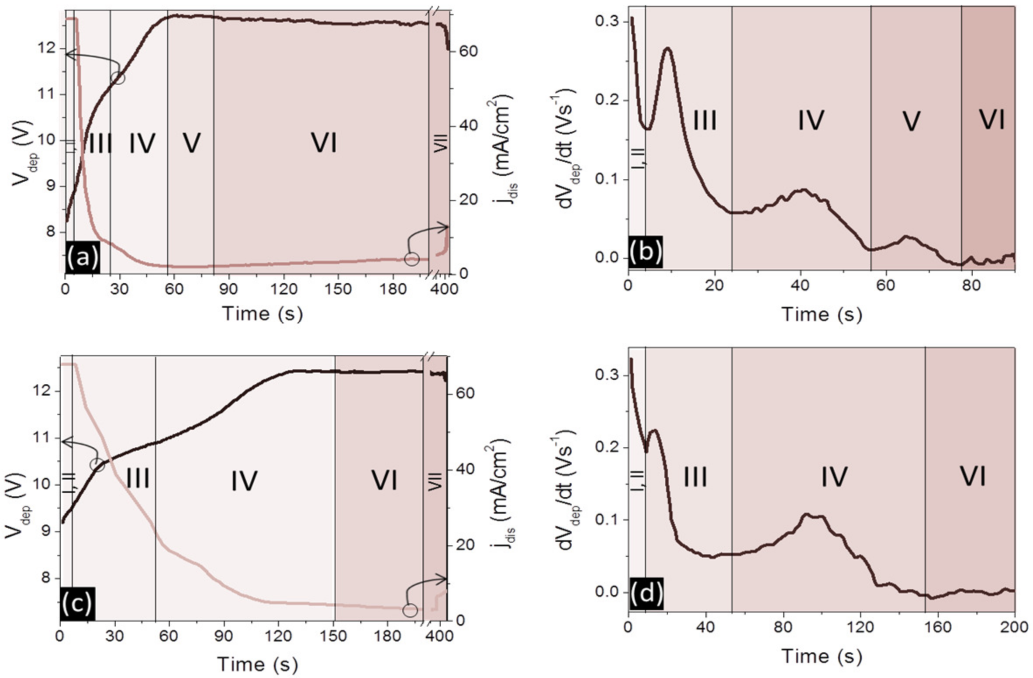
Dendrites

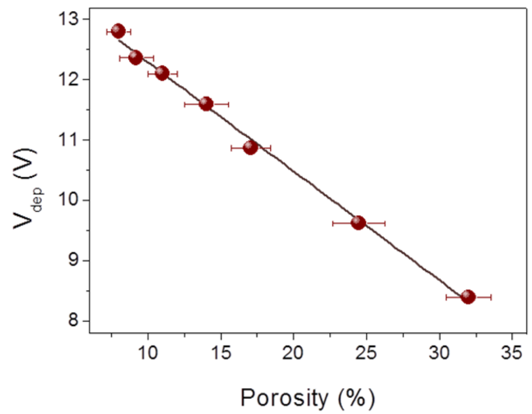
- **Branched alumina (Steady-state anodization)**
- **Tree-like alumina (Non steady-state anodization)**

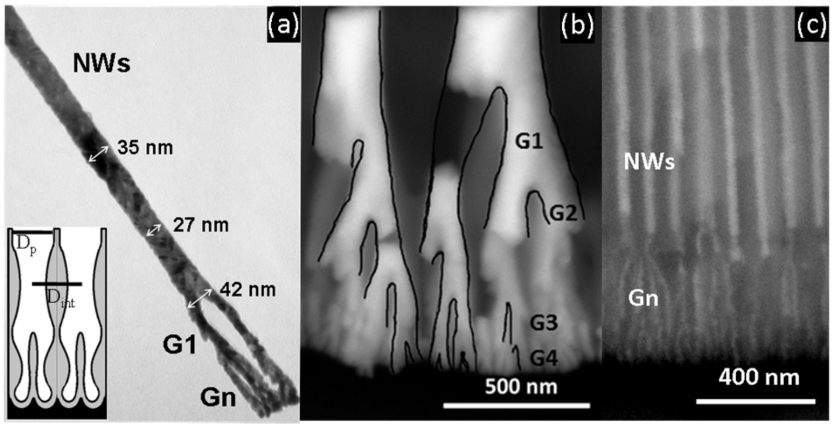


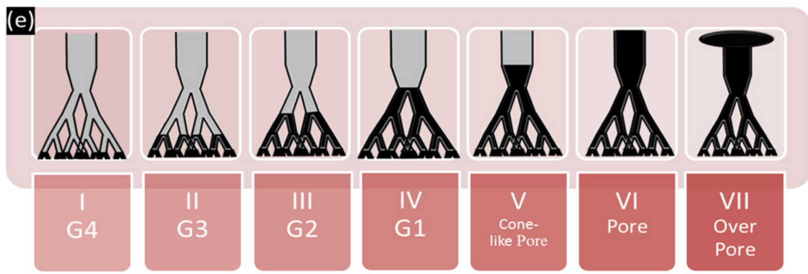
SEM images in tree-like alumina and branched alumina.

Branched pore filling



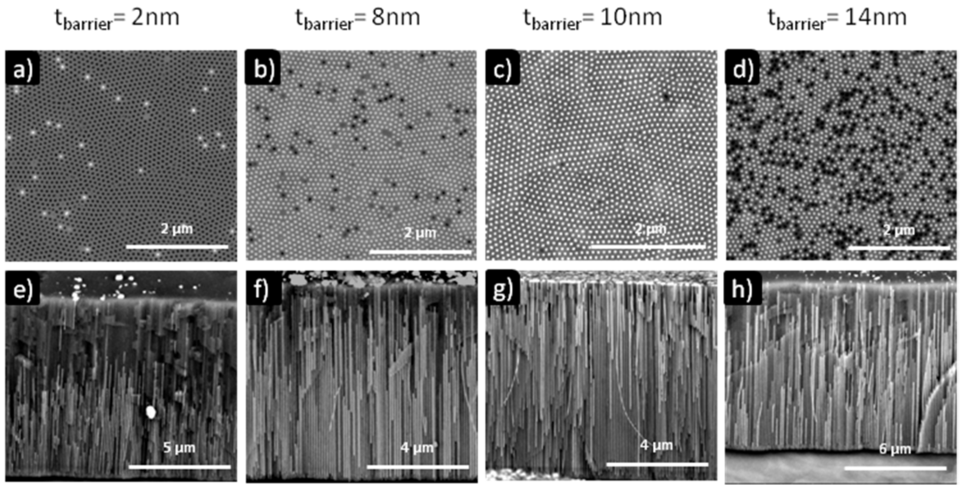


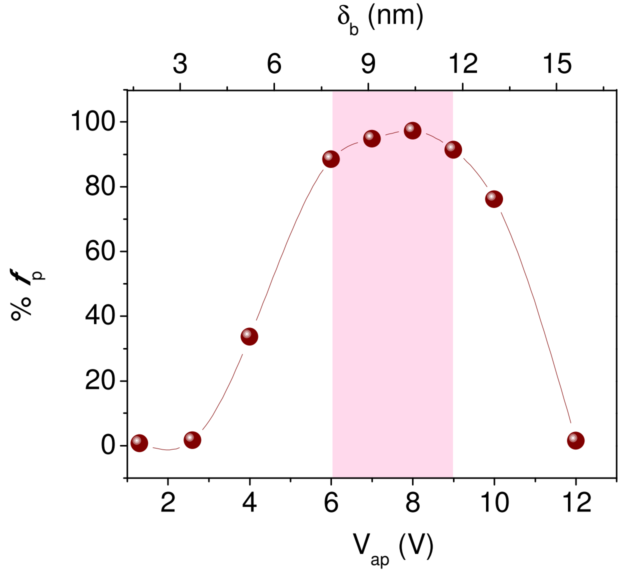


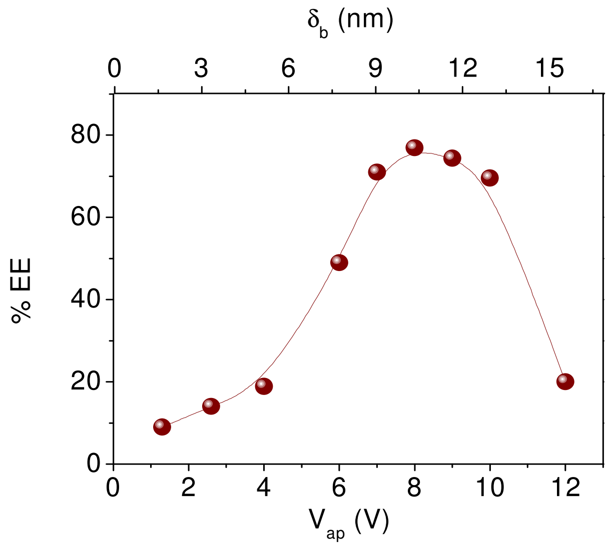


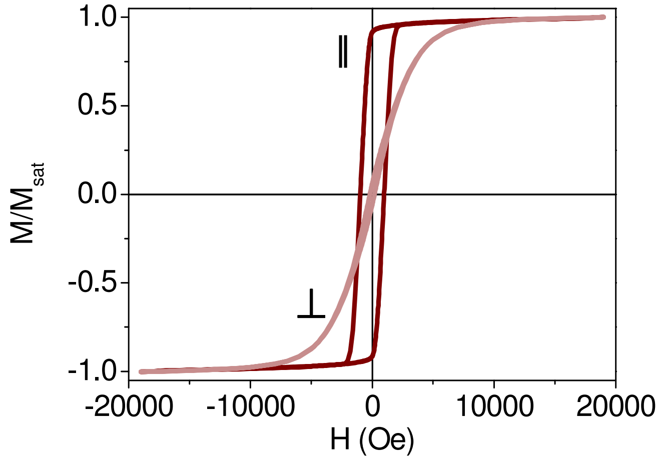
Precise control of the filling stages in branched nanopores, J. Mater. Chem. 22, 3110 (2012).

Tuning pore filling controlling δ_b







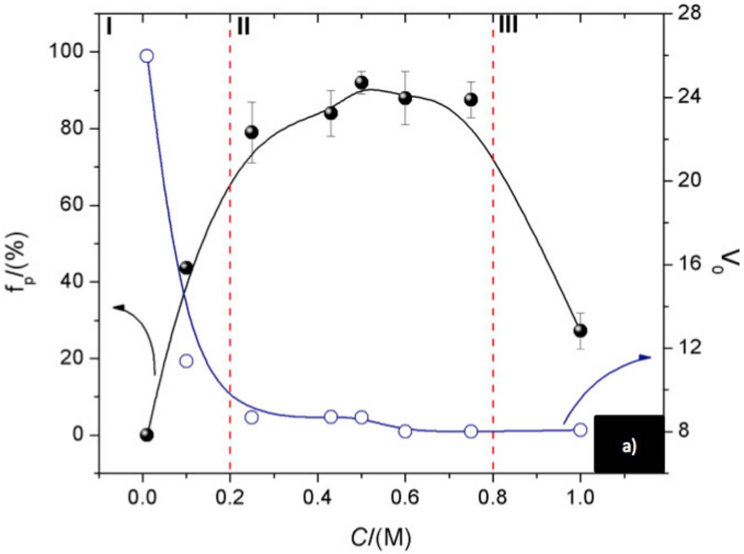


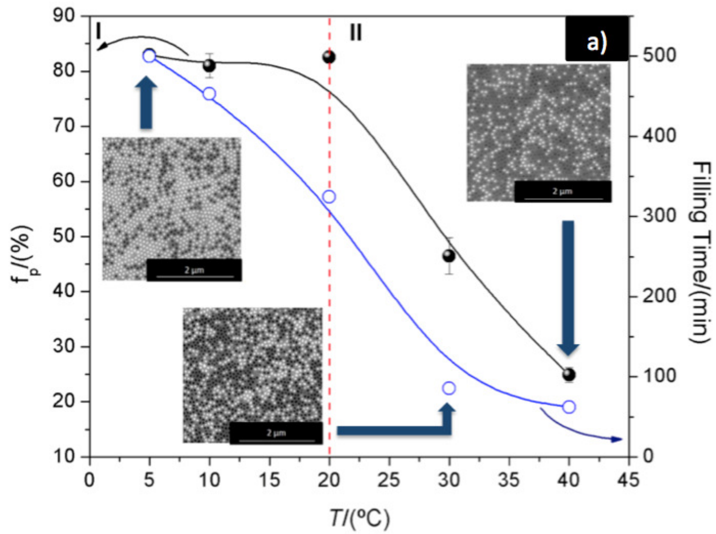
$$\mathrm{EE} = \frac{m_a}{m_t}.$$

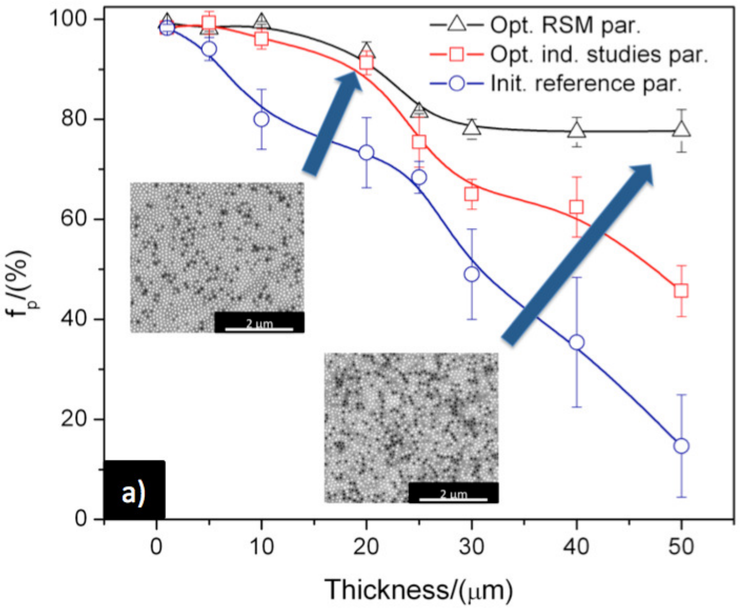
$$\int_0^t I\,dt = neN_A\frac{m_t}{M},$$

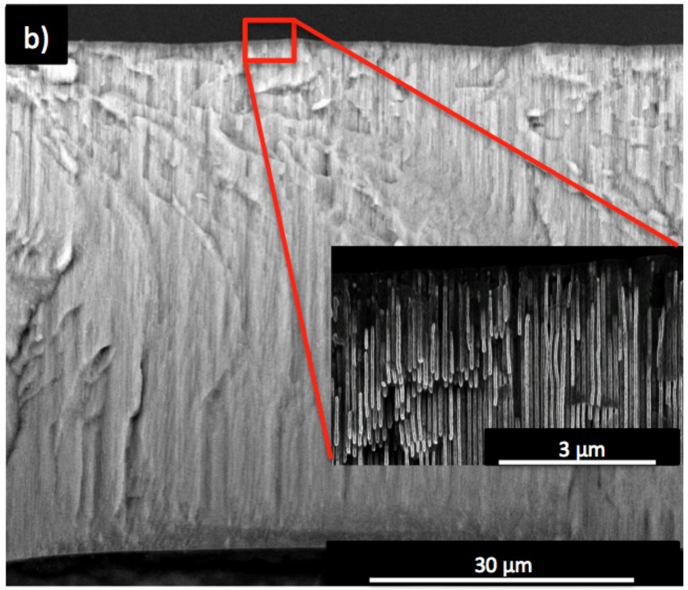
C.T. Sousa et al, Nanotechnology 22 (2011) 315602

Electrodeposition parameters optimization

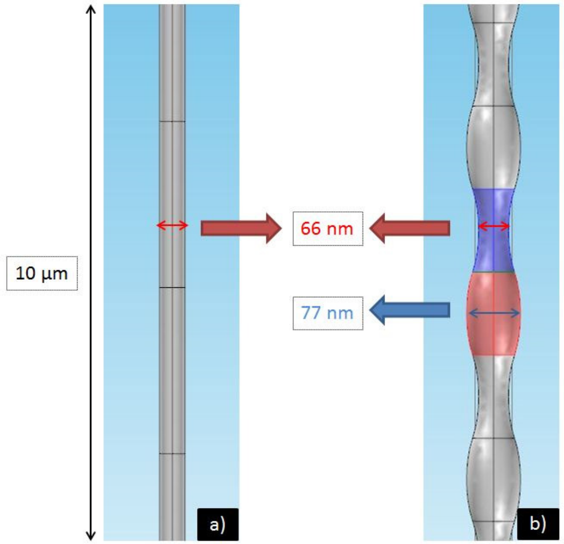


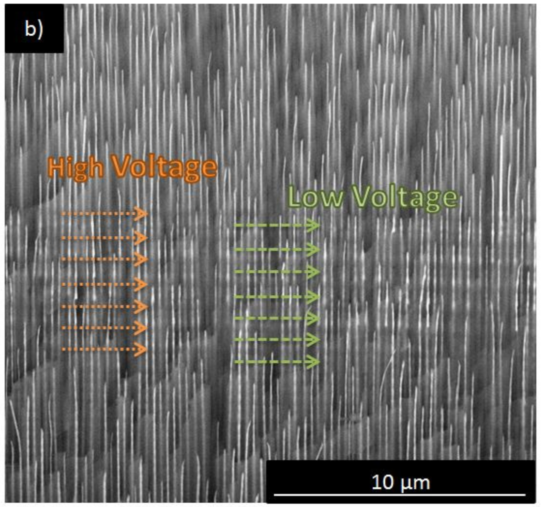


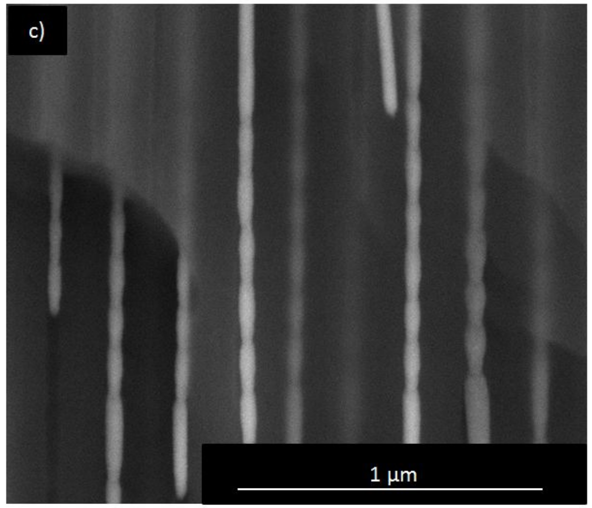


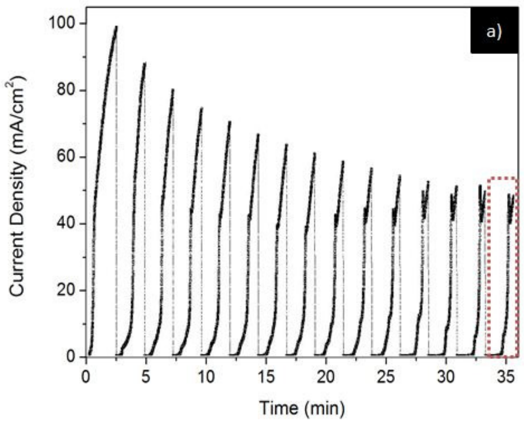


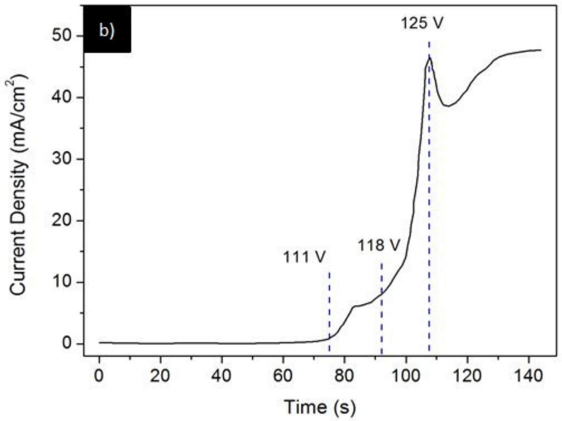
Modulated nanowires

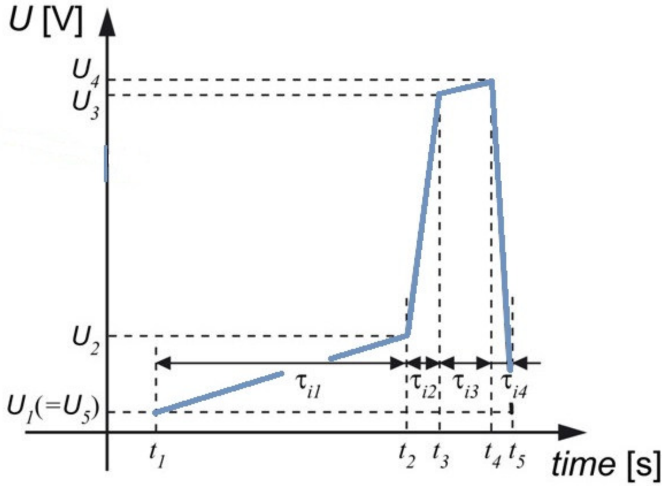






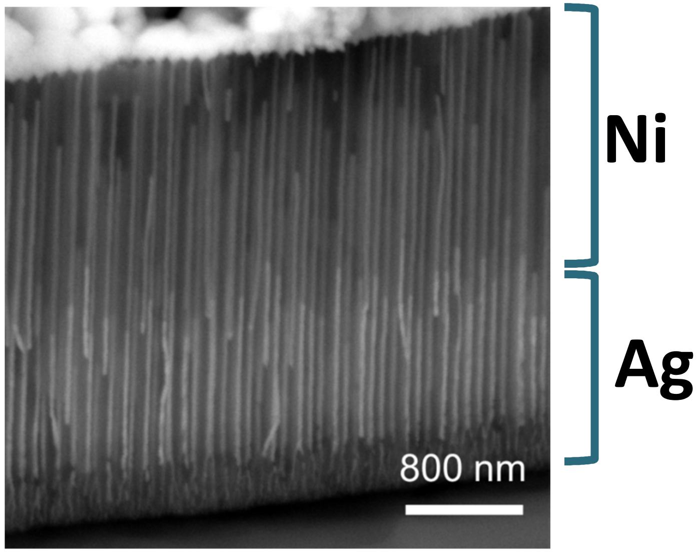


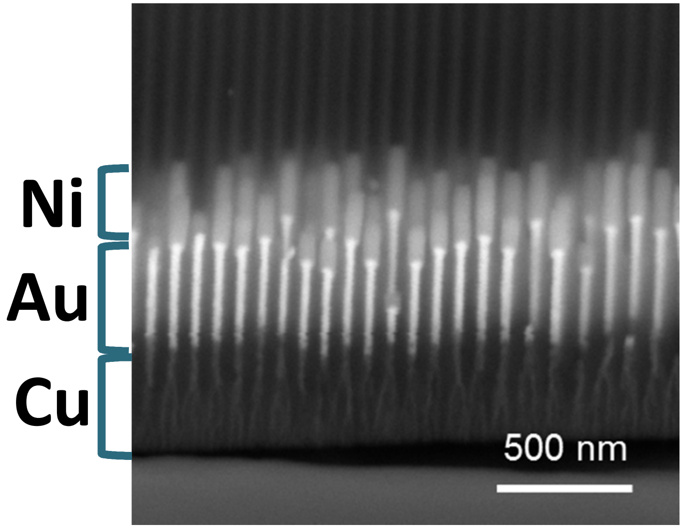




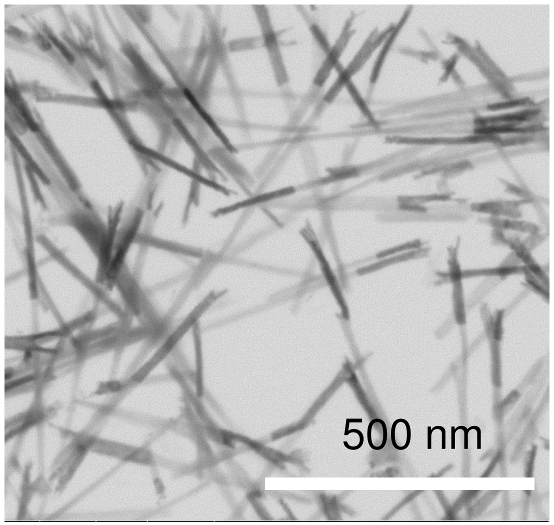
Segmented nanowires

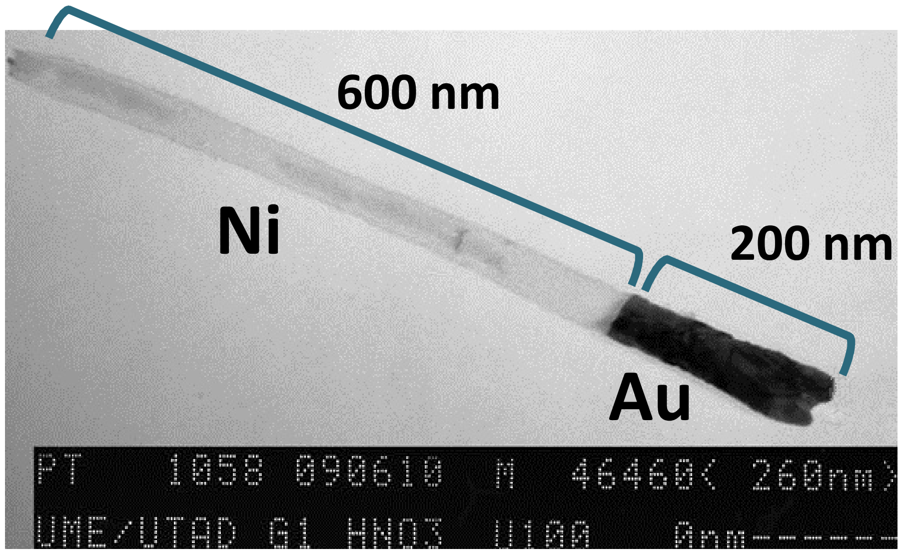
2 Layers





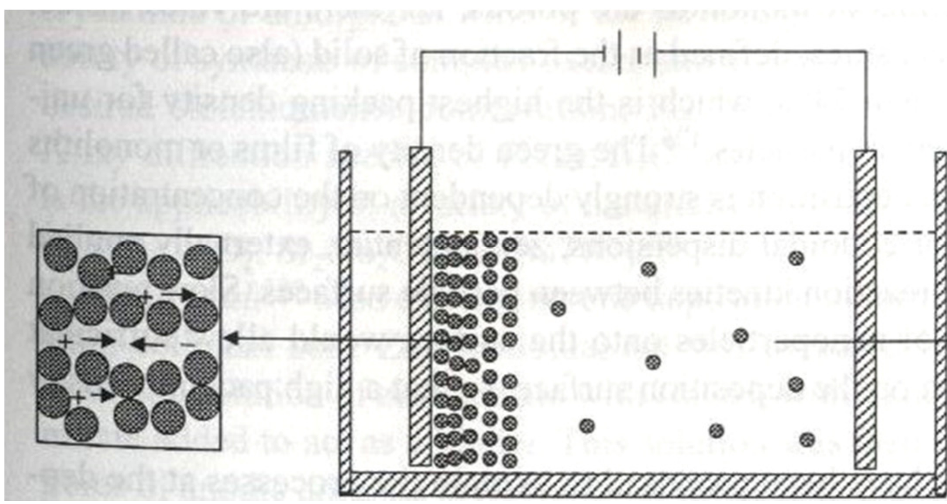
3 Layers

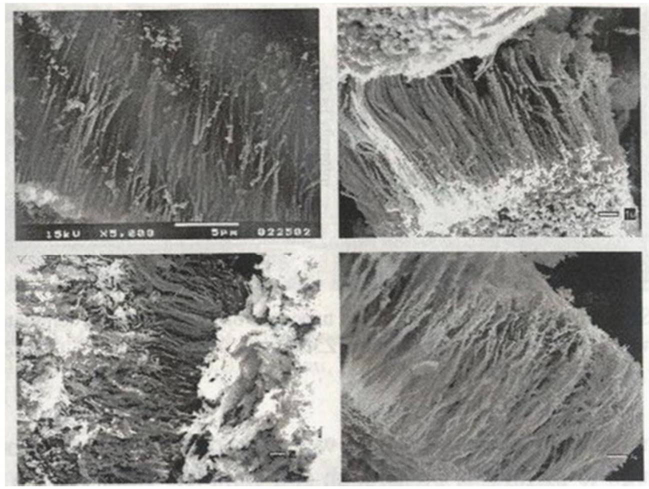




Electrophoresis

- The deposit need not be electrically conductive
- Particularly suitable for oxide nanowires: SiO2, TiO2, Bi2O3, etc.
- Over the surface of nanoparticles develops an electrical charge via some chemical techniques. This combination is typically called counter-ion
- Upon application of an external electric filed to a system of charged nanosize particle system, the particles are set in motion in response to the electric filed
- This type of motion is referred to as electrophoresis.





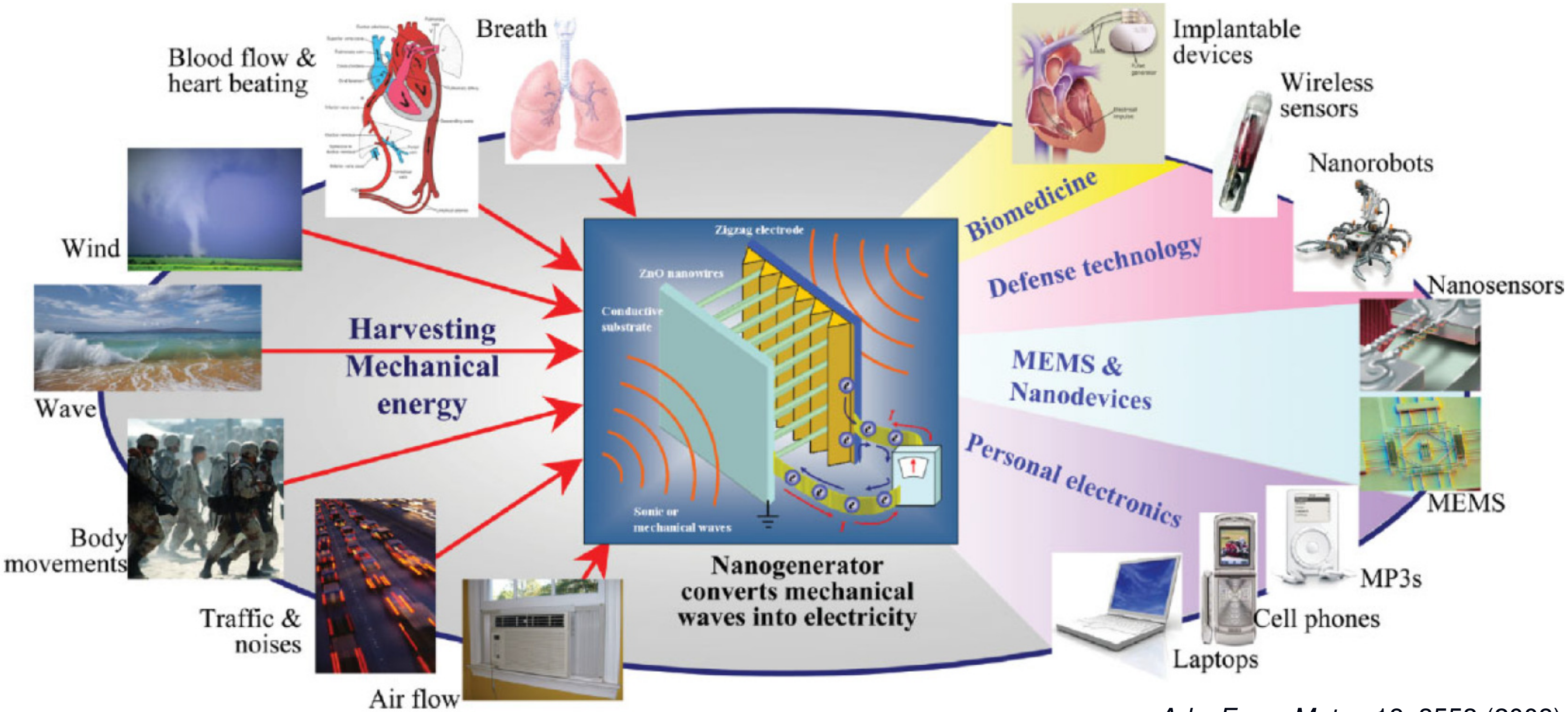
João Ventura

IFIMUP and IN – Institute of Nanoscience and Nanotechnology

Nanowires:
synthesis & applications

Nanogenerators

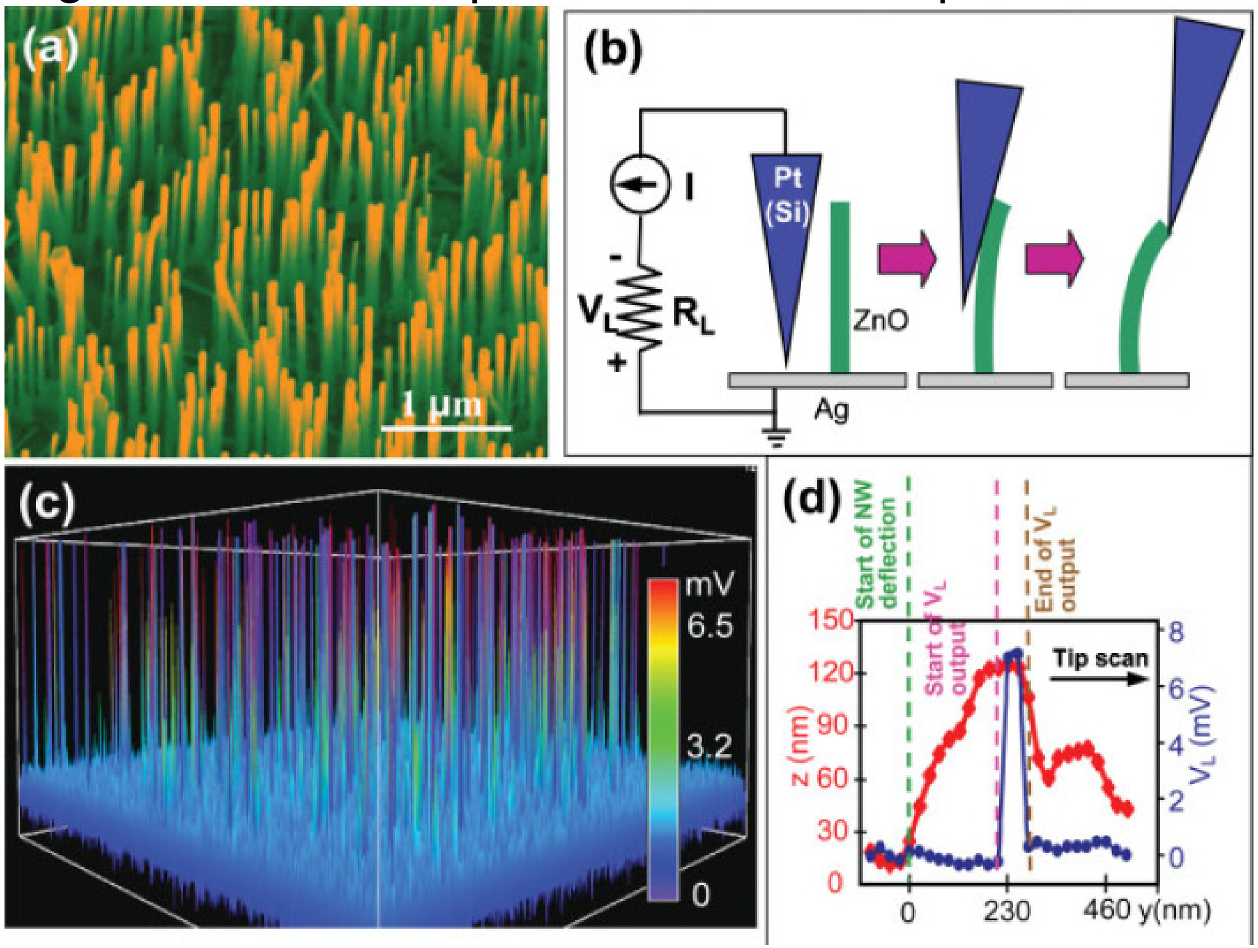
- Self-powered devices can greatly reduce the size of integrated nanosystems for optoelectronics, biosensors and more.
- Scavenging energy produced by acoustic waves, ultrasonic waves, hydraulic pressure/force or environment
- Powered by body movements
- Small
- No batteries or electrical outlets



Adv. Func. Mater. 18, 3553 (2008).

ZnO Piezoelectric nanogenerators

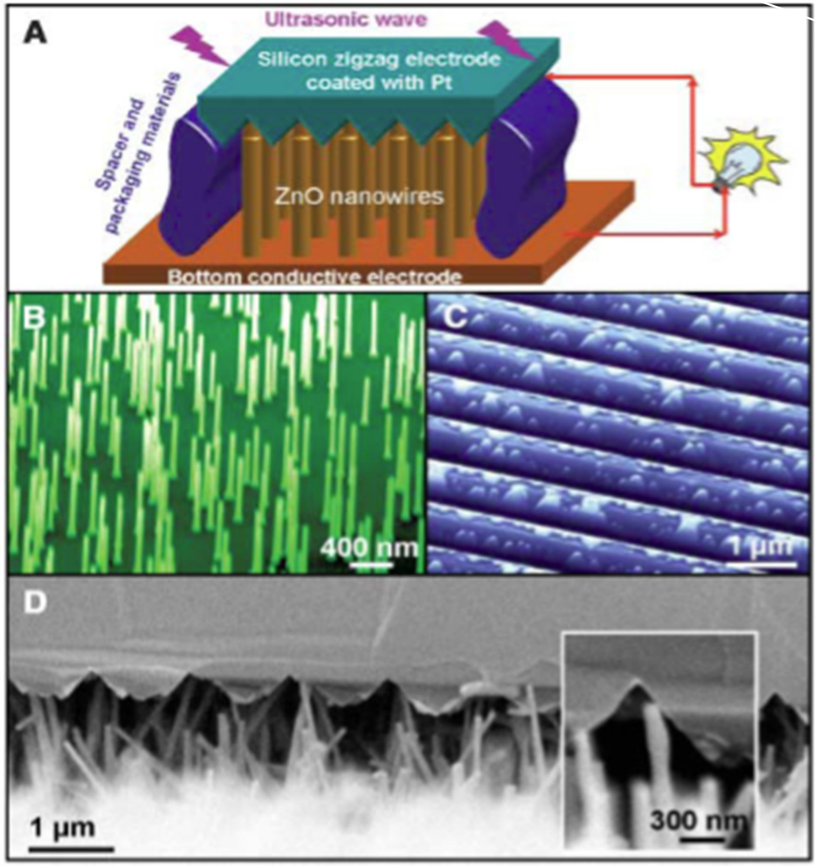
- Sharp output voltage, V_{peak}~6-9mV
- Peak corresponds to maximum deflection of NW
- Discharge occurs when tip contacts with compressed side

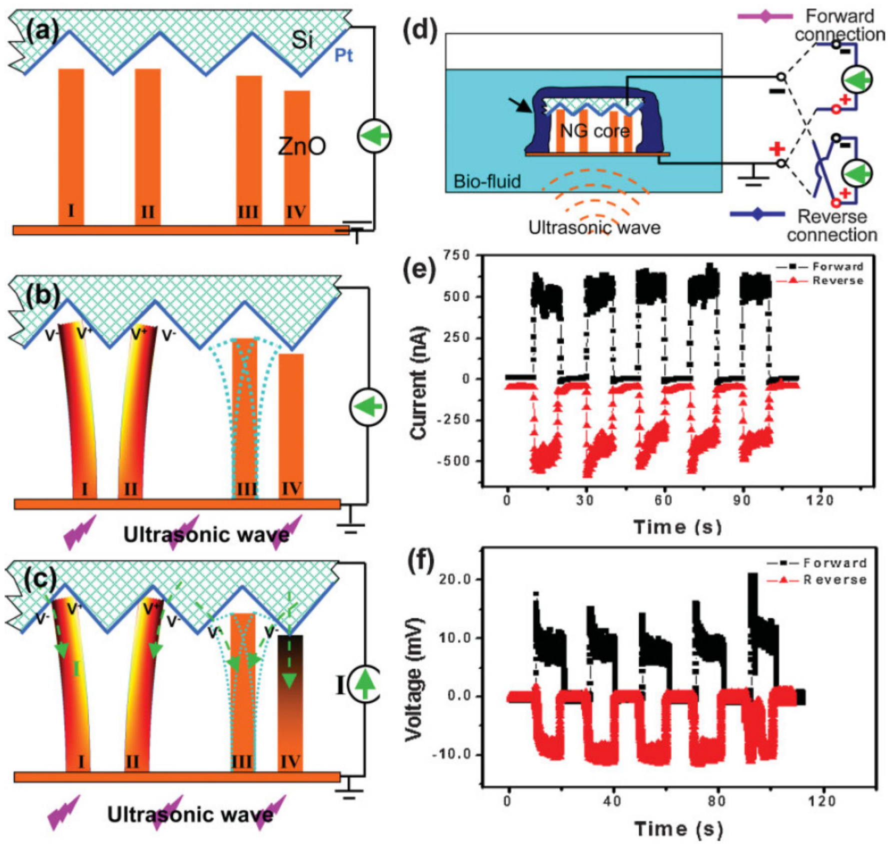


Science, 312 (2006) 242-246.

ZnO Piezoelectric nanogenerators

-Nanogenerator driven by ultrasonic waves
-Zig-Zag Pt coated Si electrode plays the role of an array of AFM tips

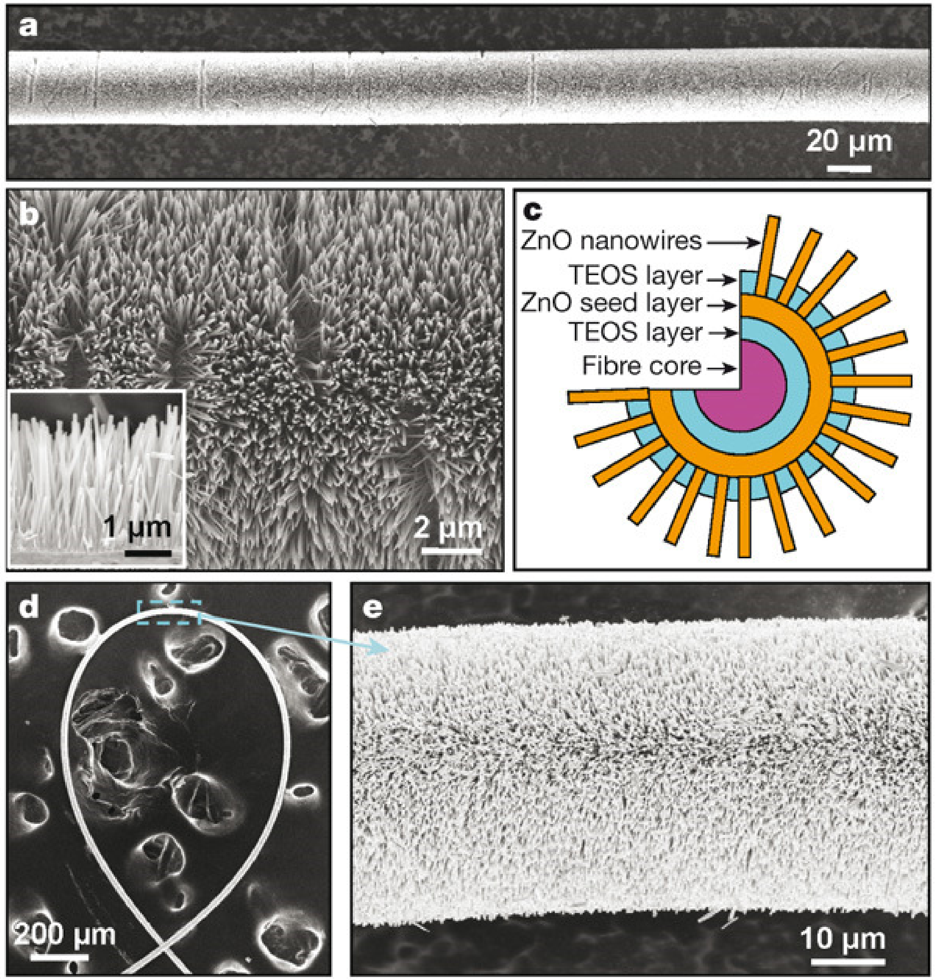




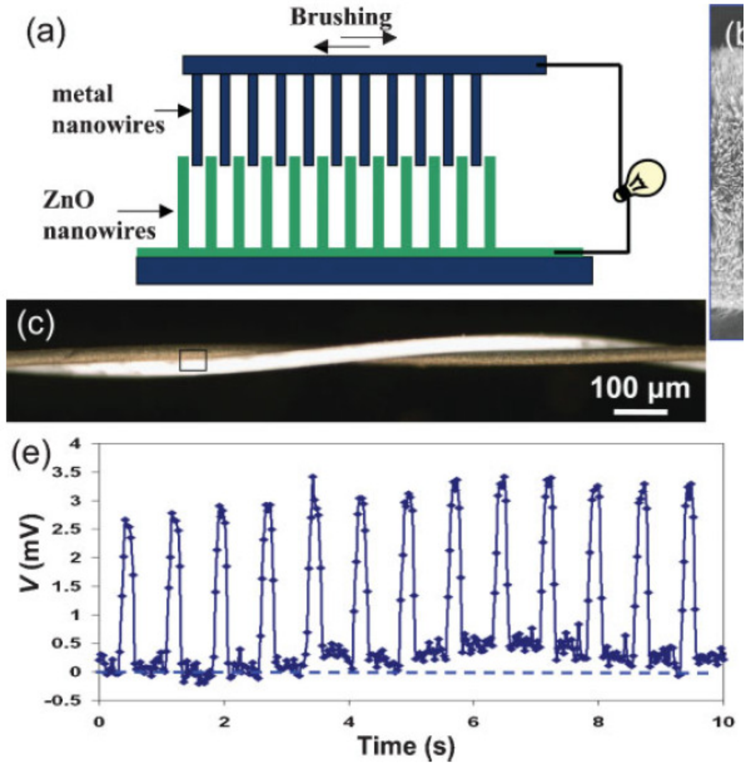
Science 2007, 316, 102

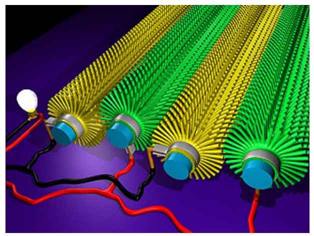
ZnO Piezoelectric nanogenerators

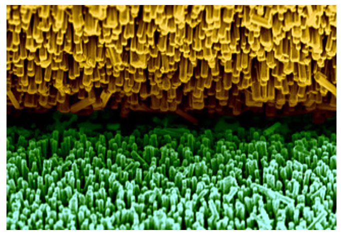
-Piezoelectric zinc oxide nanowires grown radially around Kevlar textile fibres
-Hybrid ZnO/metalic nanowire generators



Nature 451, 809-813 (14 February 2008)

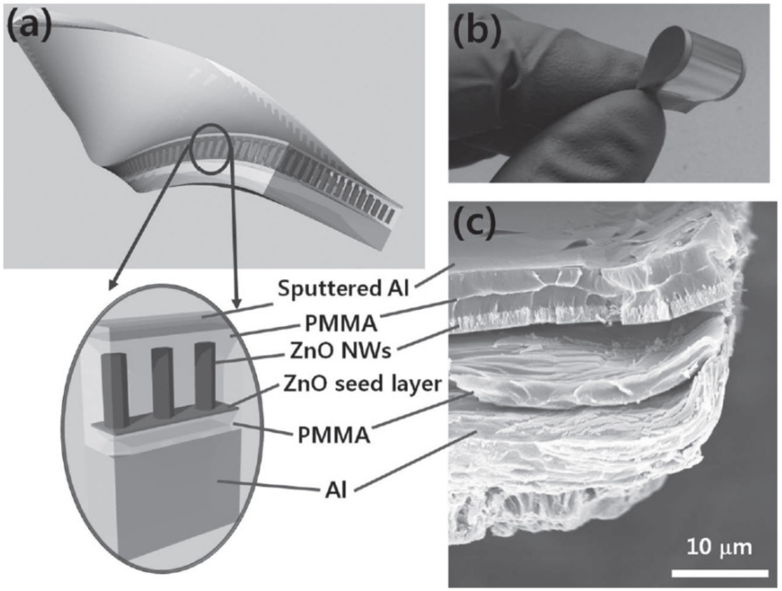


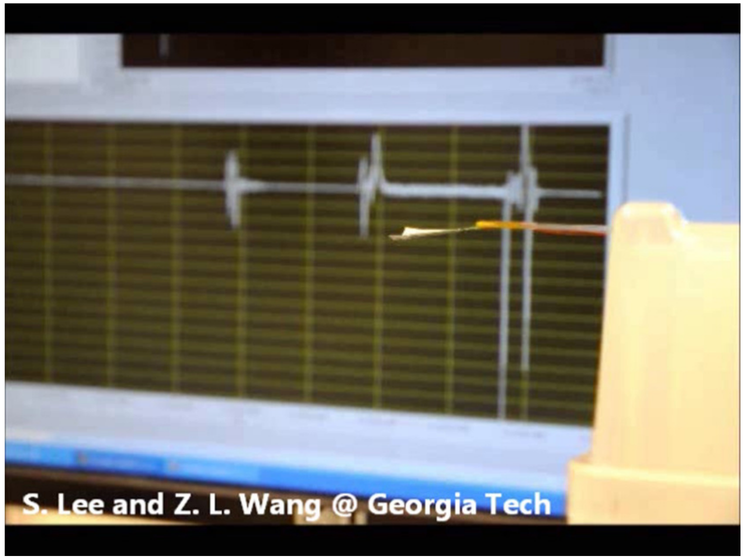




ZnO Piezoelectric nanogenerators

-Flexible Nanogenerator for Energy Harvesting from Wind



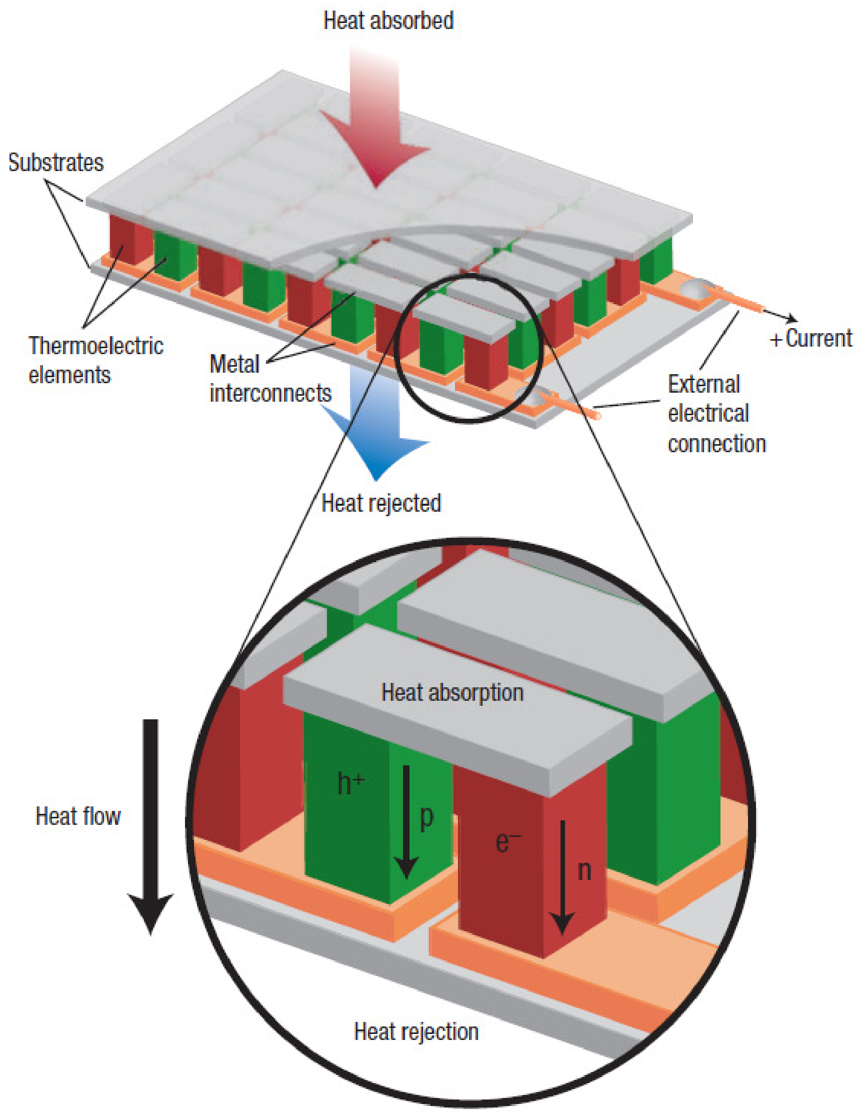


Advanced Functional Materials 23, 2445–2449 (2013).

Thermoelectric nanogenerators

- Over 60% of consumed energy is dissipated as waste heat
- The world's data centers are projected to surpass the airline industry as a greenhouse gas polluter by 2020
- About 40 percent of the energy content of gasoline burned in automobile IC engines is lost as exhaust heat and another 30 percent is lost through engine cooling
- Generation of voltage along a conductor subjected to a temperature difference
- Initially, carriers (electrons or holes) move from hot to cold; Resulting potential difference opposes further current flow

  - Seebeck effect $S = \frac{\Delta V}{\Delta T}$
  - Figure of Merit $ZT \equiv \frac{S^2 \sigma}{\kappa} T$

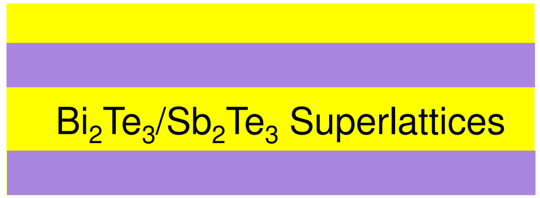


Thermoelectric nanogenerators

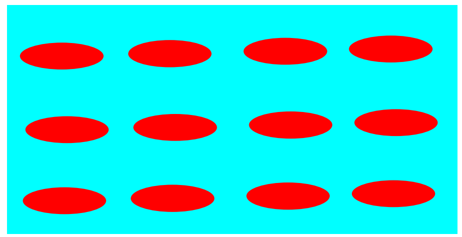
Nanostructured thermoelectric materials
- Improvement of ZT
- Improvement of Electrical Conductivity
- Improvement in Thermal Resistance
- Increased Density of States near the Fermi Level, high $S^2\sigma$
- High-ZT nanowire materials

Venkatasubramanian et al. *Nature* 413, 597

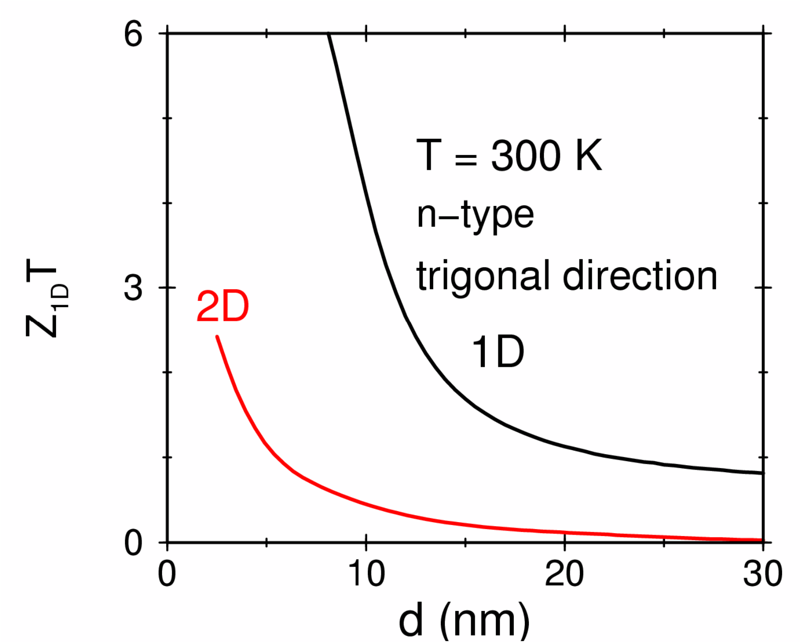
2.5-25nm

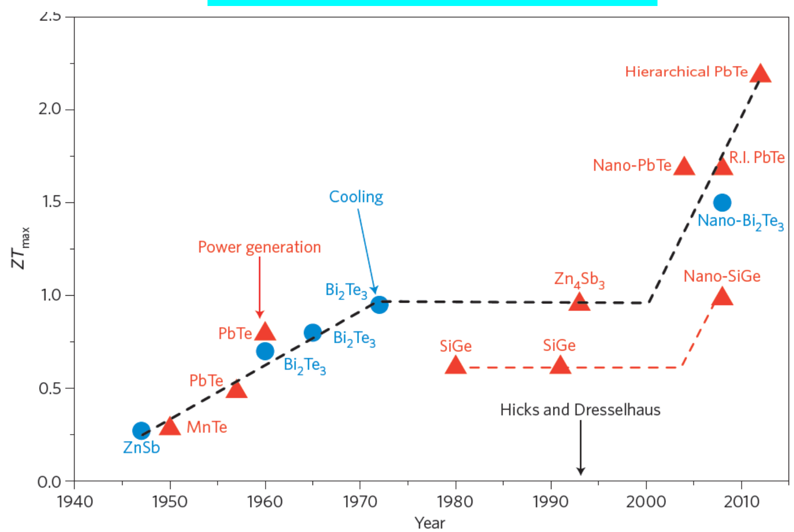


Harman et al., *Science* 297, 2229



Quantum dot superlattices

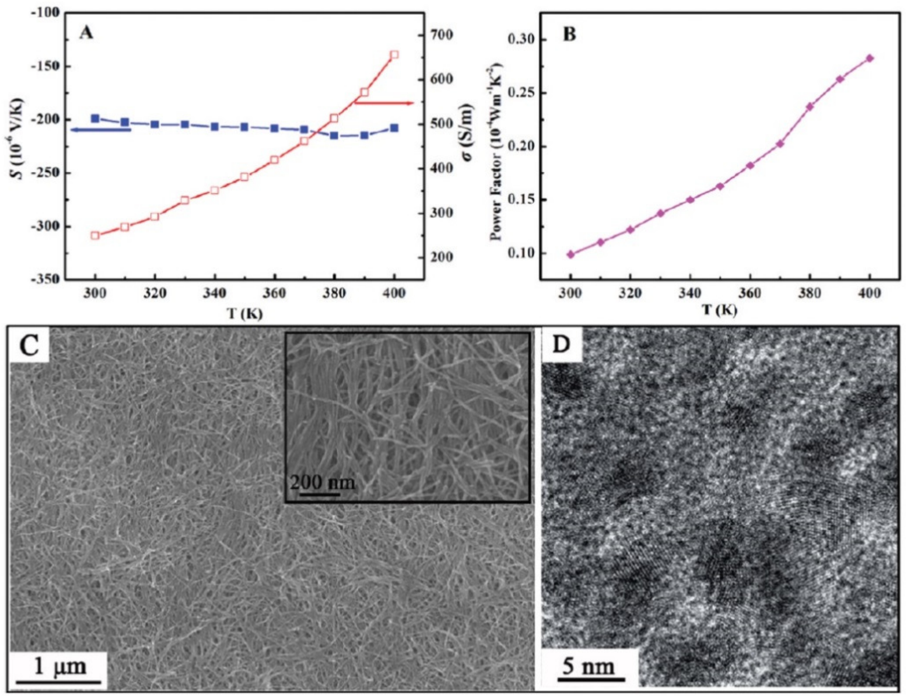


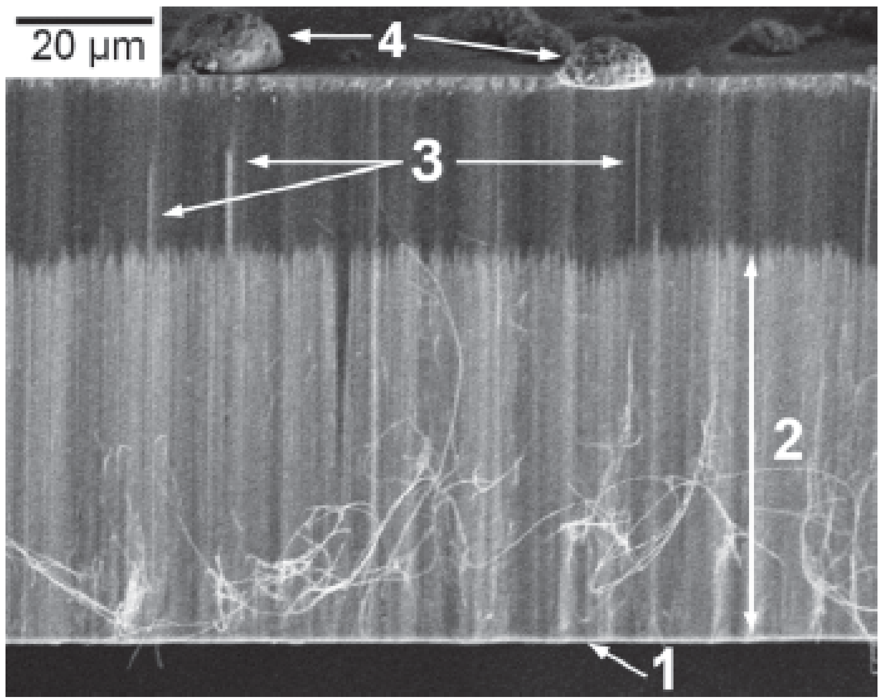


Complex thermoelectric materials, Nature Materials 7, 105 (2008)

Bi_2Te_3 Thermoelectric nanogenerators

- Different approaches can be used to grow Bi2Te3 nanowires
- Enhancement of the ZT value by 13%.

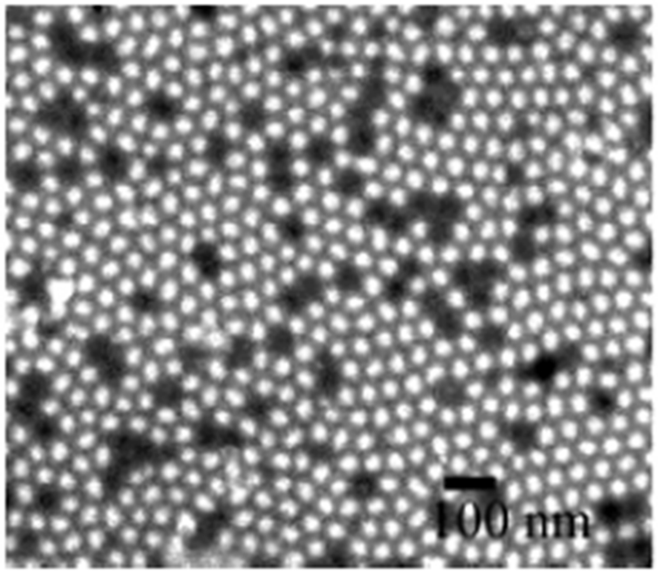




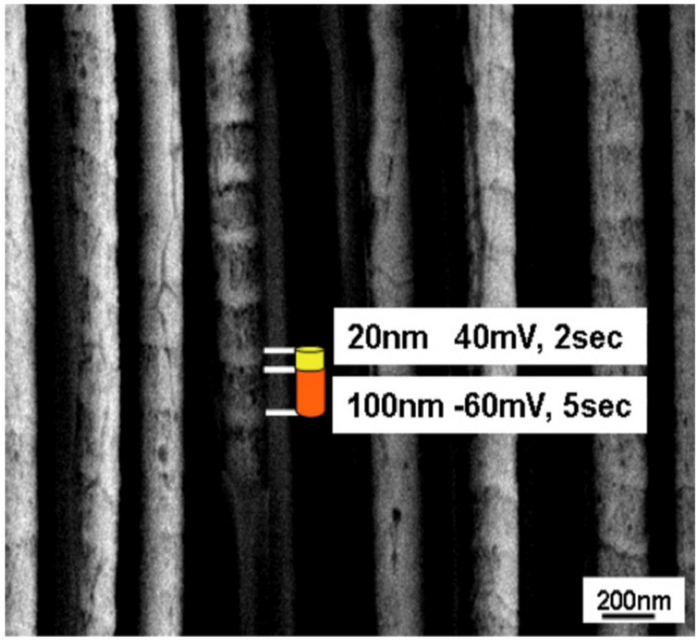
Bi_2Te_3 Thermoelectric nanogenerators

- Nanoscale control of grain size and composition modulation (lateral and radial) with a scalable synthesis technique
- First electrodeposited Bi_2Te_3 nanowire (280 nm) arrays into porous anodic alumina (Sapp et al., 1999)

40 nm diameter Bi_2Te_3 nanowires electrodeposited into porous anodic alumina (Prieto et al., 2001)



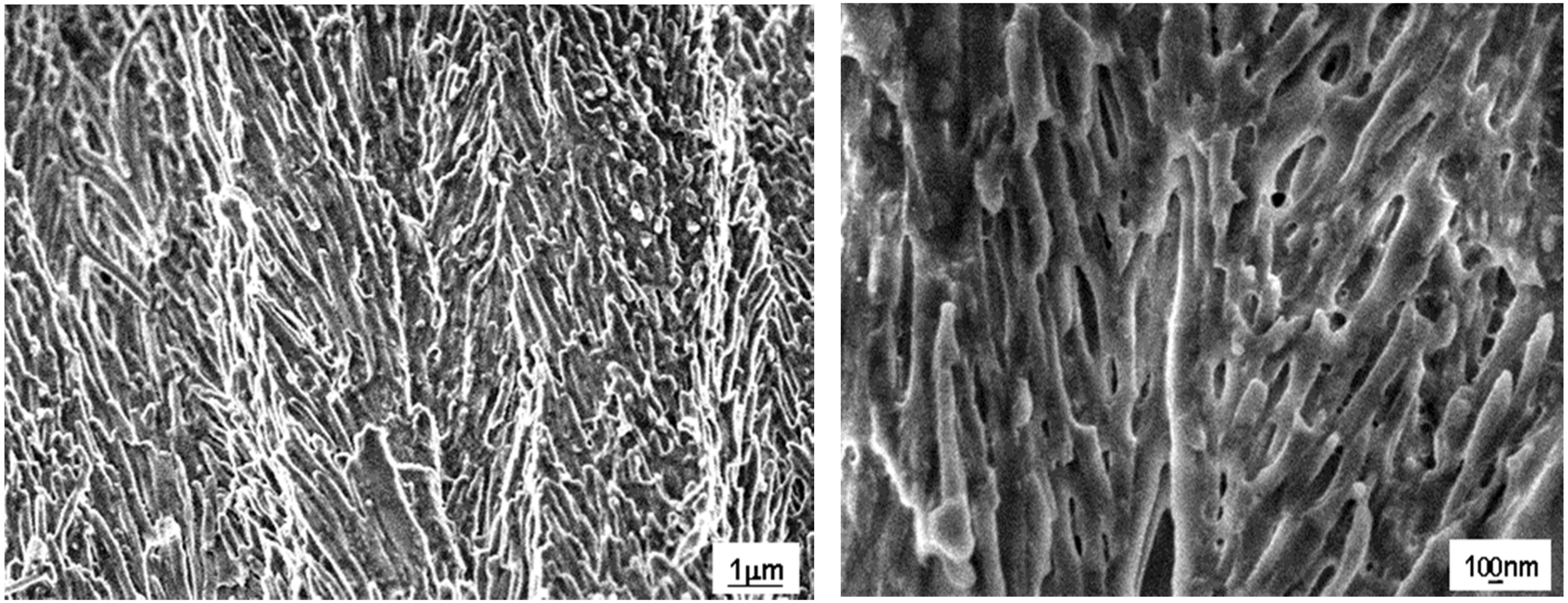
Composition-modulated $Bi_2(Te,Se)_3$ nanowires.



-By varying the electrodeposition potential, the composition of the NWs can be varied.
-Substantial suppression of apparent thermal conductivity

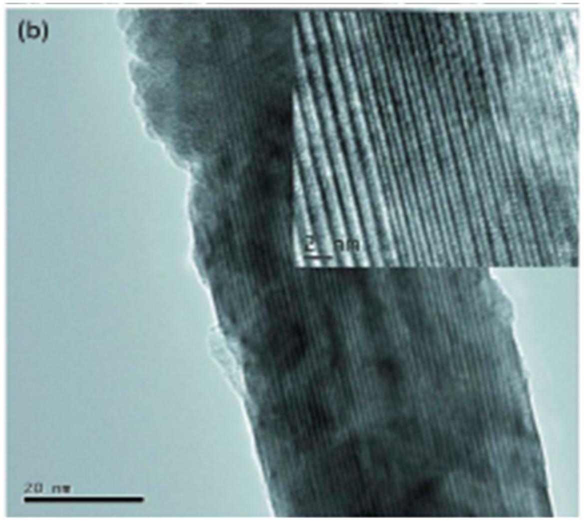
Bi_2Te_3 Thermoelectric nanogenerators

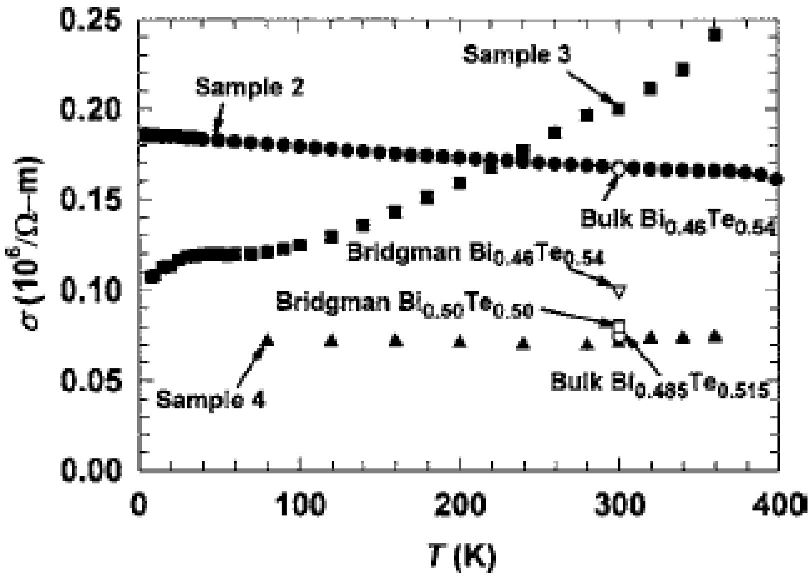
- Elimination of the alumina matrix: Self-supporting nanowire arrays
- Branched Porous Anodic Alumina

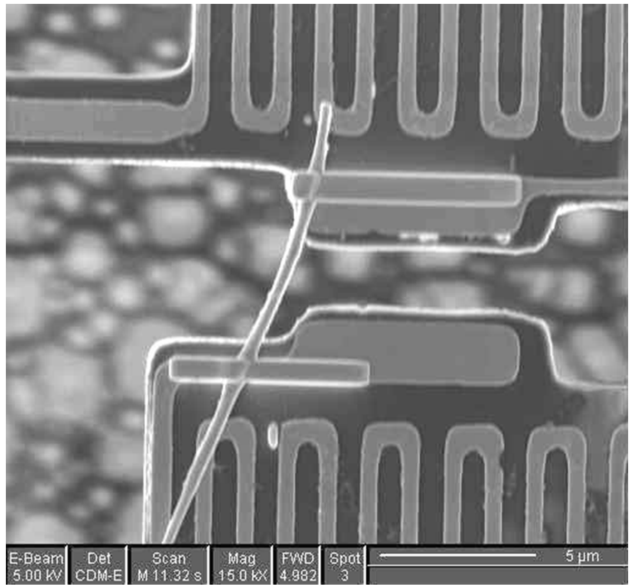


Bi_2Te_3 Thermoelectric nanogenerators

- Measurements on single nanowires
- Highly variable S and s; k lower than bulk by 28-57% (APL 87 2005)
- zT estimated to be 0.1 at 400K; Doping level too high; minimal reduction (~20%) in k due to surfaces and grain boundaries (JAP 105 2009)

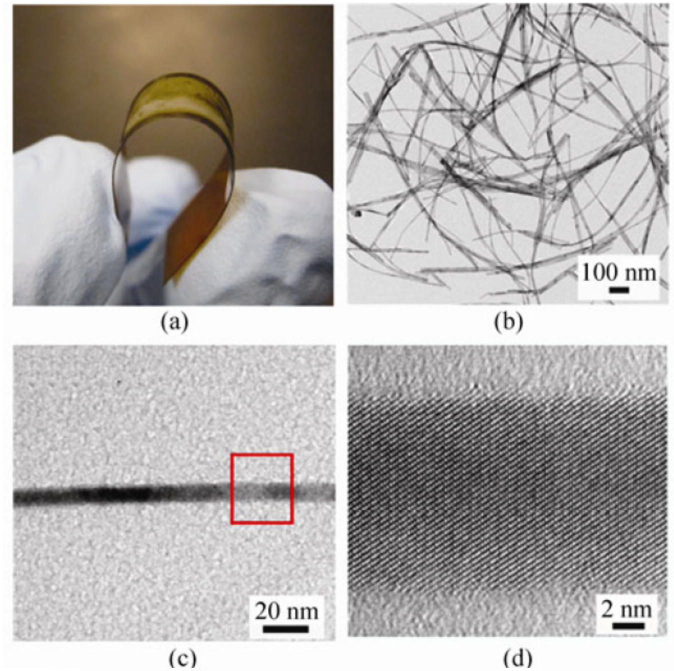


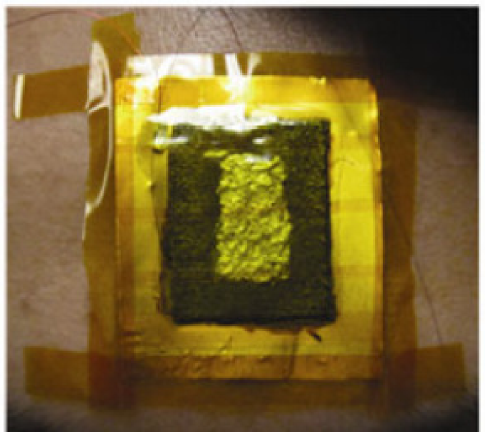


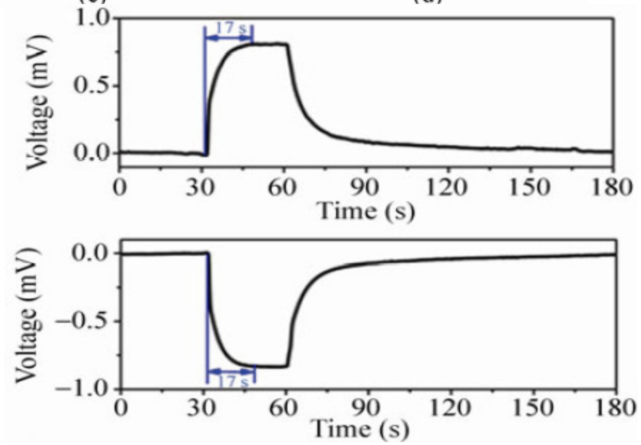


Bi_2Te_3 Thermoelectric nanogenerators

- Flexible
- Integratable into fabric
- Self-powered

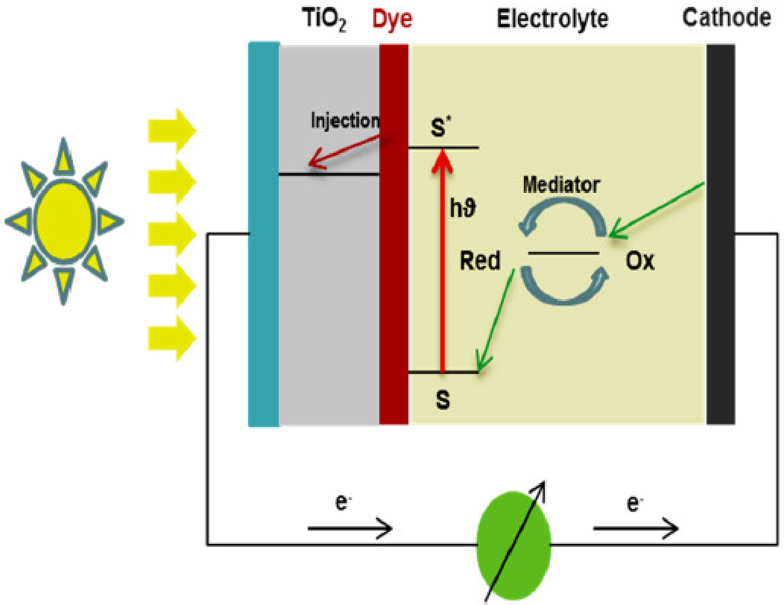






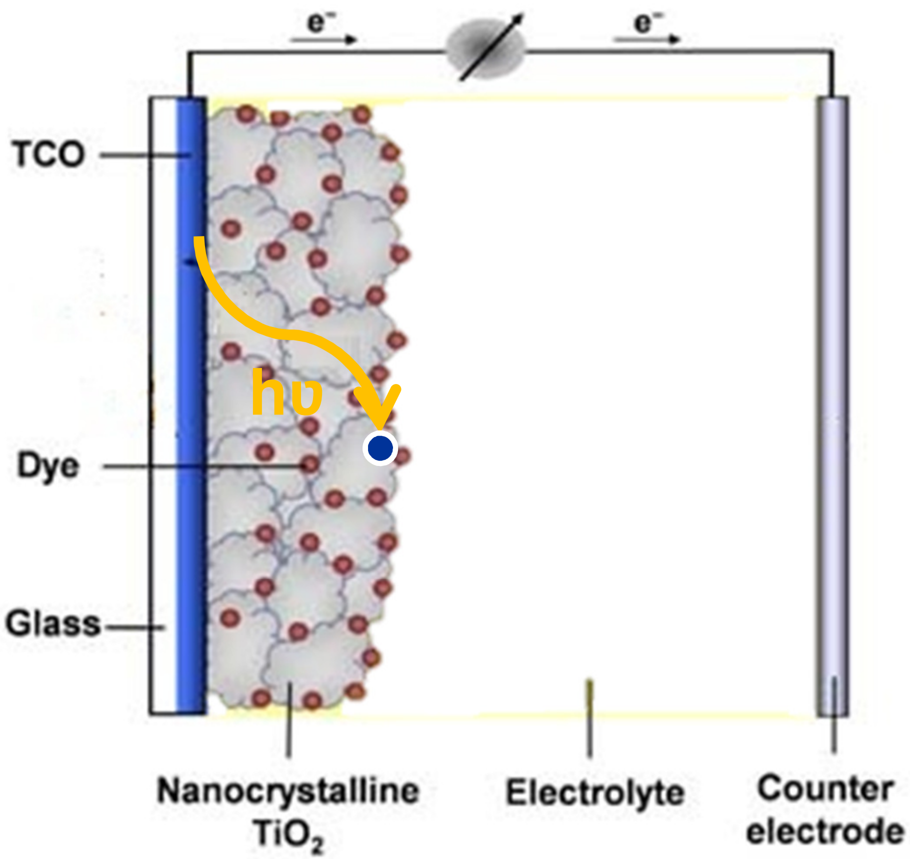
Nanowire-Composite based Flexible Thermoelectric Nanogenerators and Self-Powered Temperature Sensors, Nano Research 5, 888 (2012)

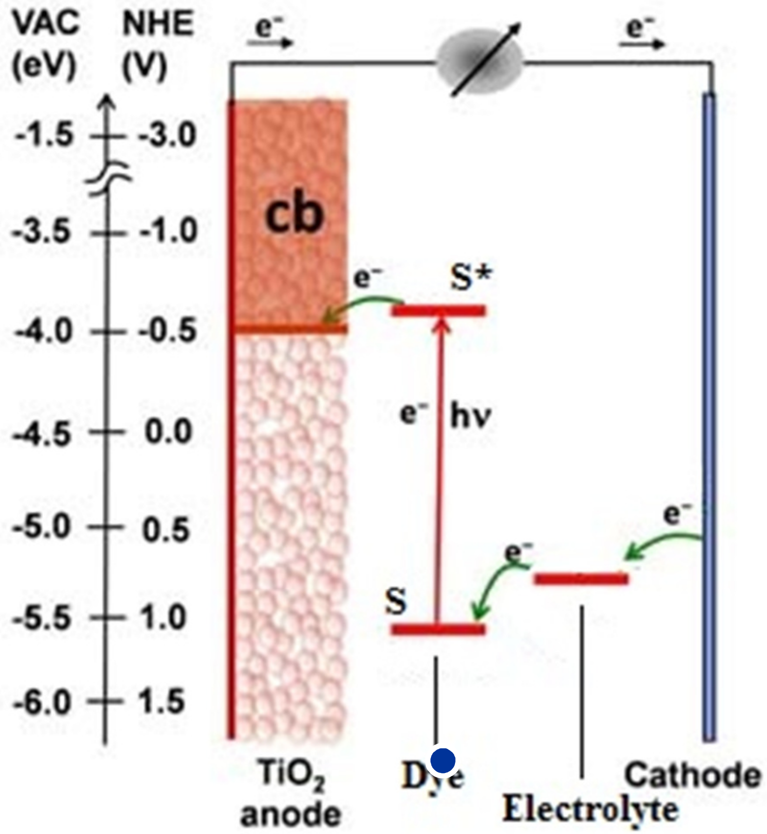
Dye-Sensitized Solar Cells



- Dye-sensitized solar cell - could offer a cheaper alternative to silicon-based photovoltaics
- A dye produces excited electrons after absorbing photons from the sunlight and injects them in the conduction band of a TiO2 thin film
- Electrons flow through the external load and return to the electrolyte through the counter-electrode
- Dye molecule is regenerated by the redox system

Dye-Sensitized Solar Cells





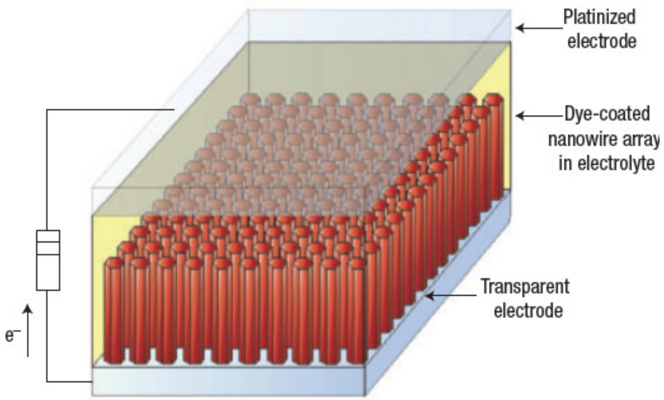
Dye-Sensitized Solar Cells

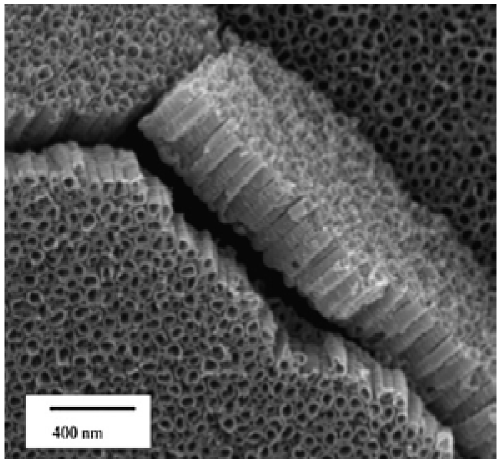
- Current approaches use mesoporous thin films, random nanoparticle network
- Problems: slow electron transport, difficult to fill with electrolyte.
- The use of aligned nanotube arrays allows the enhancement of the absorption coeficient (larger surface area), a direct pathway for electron transport, reducing probablility of electron-hole recombination (holes can reach at the surface faster than other architectures) and facilitates the filling of the pores with the electrolyte

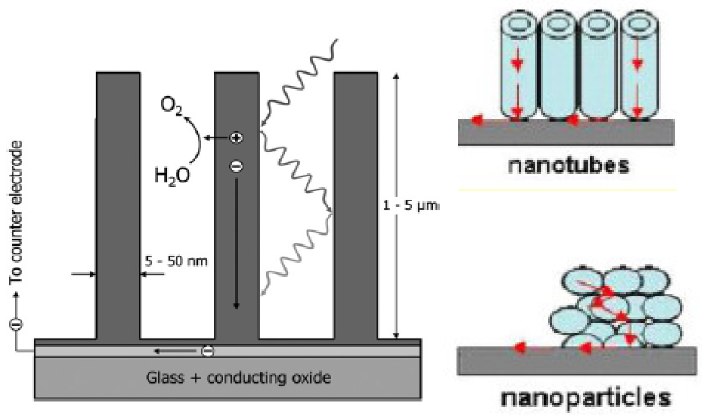
Nanoparticles – higher surface area (efficiency 10-11%)

Nanowires and **Nanorods** – reduce the electron recombination but have a smaller surface area

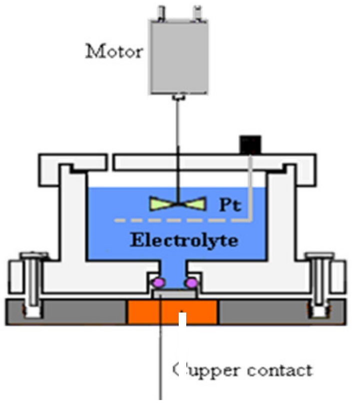
Nanotubes – have a bigger surface area than nanorods and nanowires (efficiency 7%)







TiO_2 nanotubes



Titanium foil

Anodizing conditions:

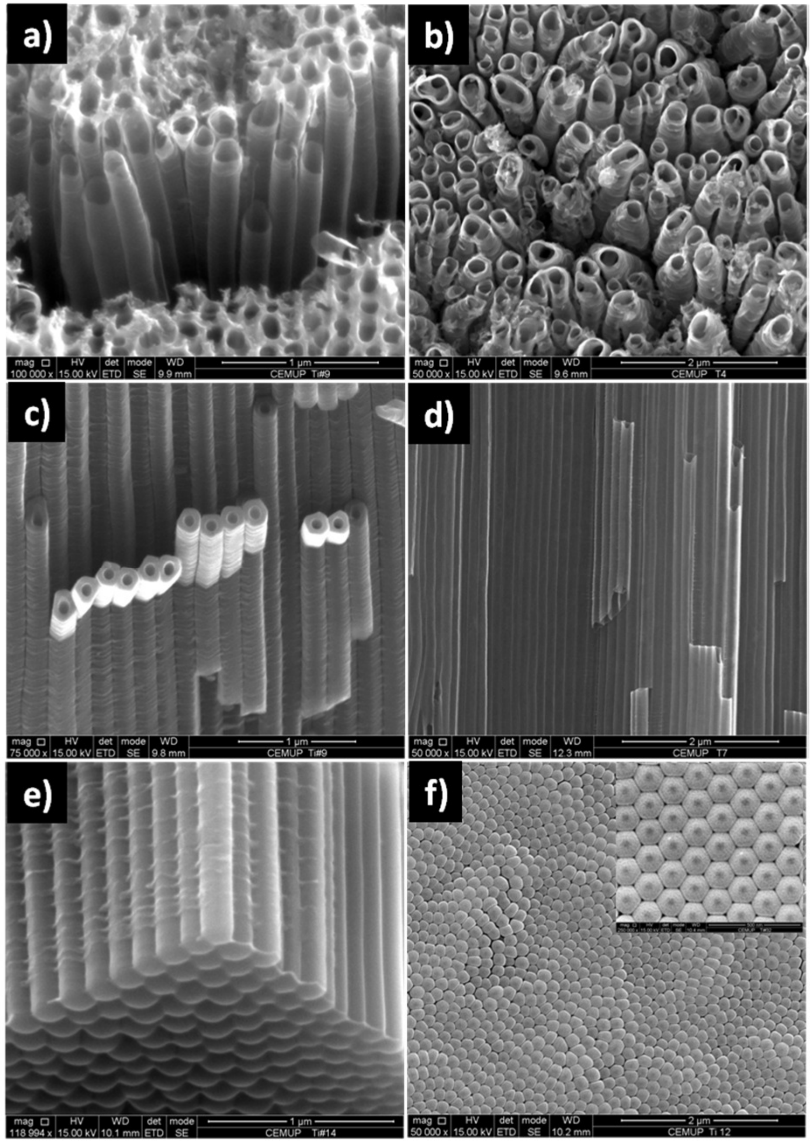
ELECTROLYTE:
Ethyleneglycol
(2 % water+0.3 wt% NH_4F)
VOLTAGE;TIME

Several parameters to control

Electrolyte type and concentration, pH and applied potential.

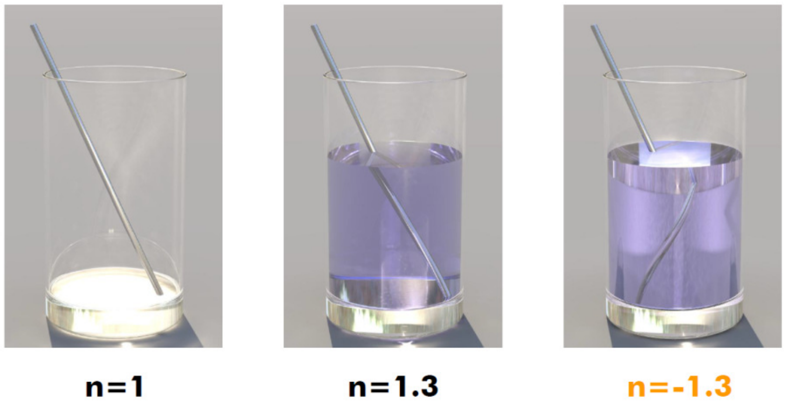
Nanotubes structure :

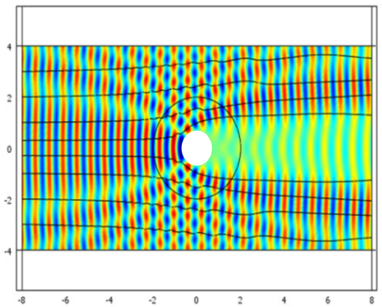
-NTs diameter and wall thickness
-NTs length
-NTs Organization

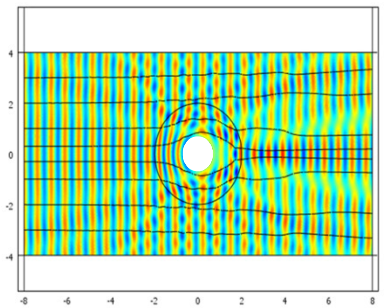


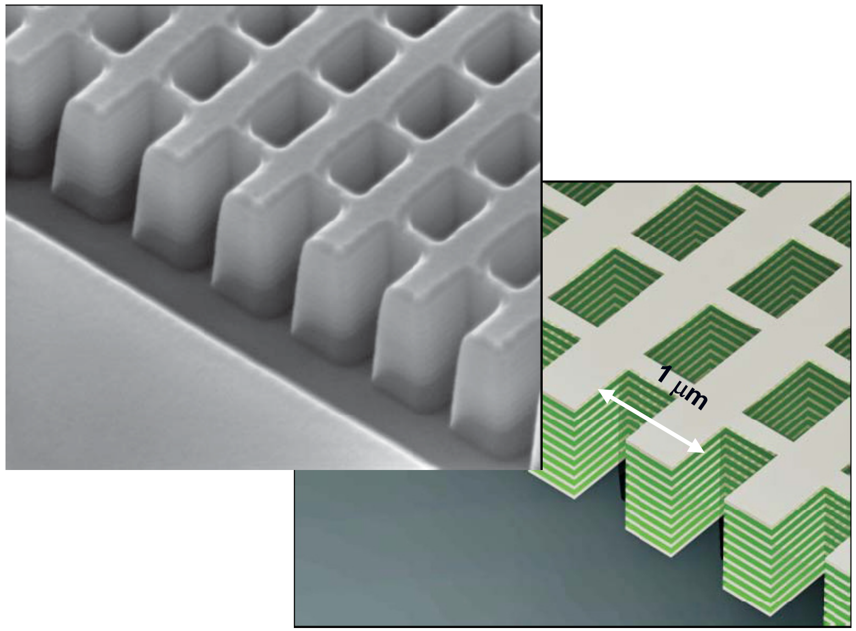
Metamaterials

- Engineered composites in which the dielectric permittivity and magnetic permeability are artificially manipulated
- Periodical structures that in some range of frequencies react to the electric and magnetic fields as medium with negative ε or μ.
- Negative refractive index materials can make an object invisible (cloaking applications; most have been made for microwaves). For visible light requires structures small compared with the corresponding wavelength.





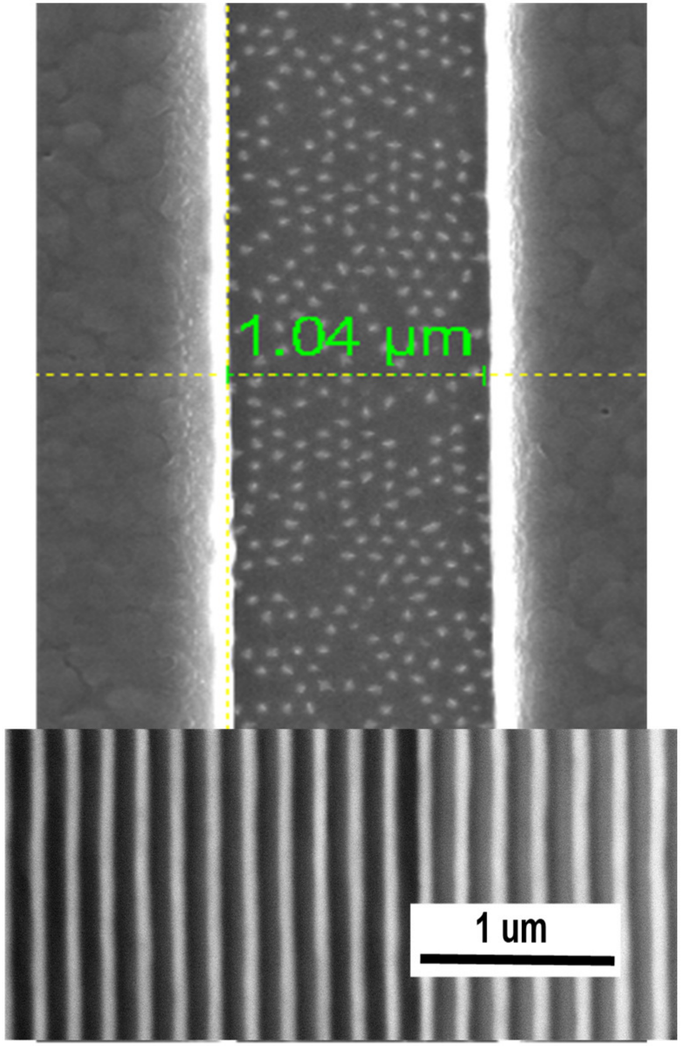


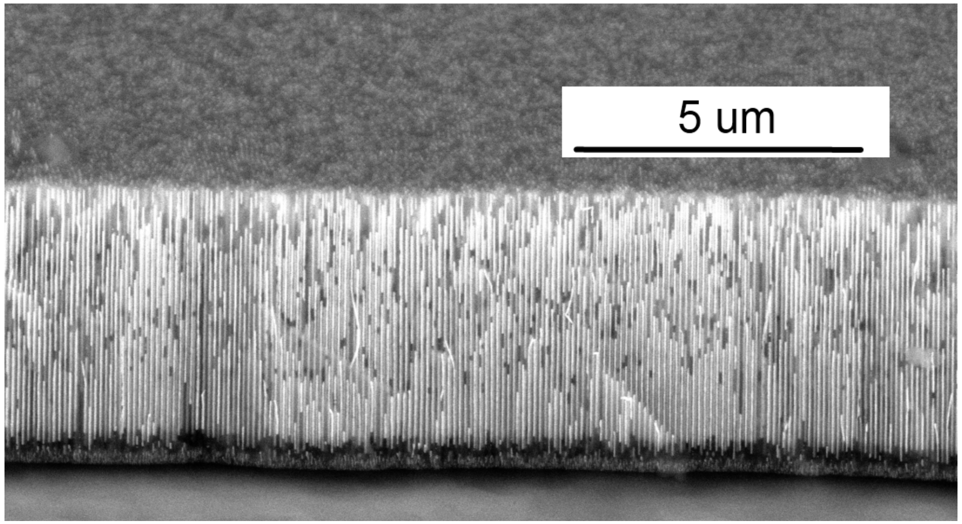


Nanowire-based Metamaterials

Optical properties and applications:

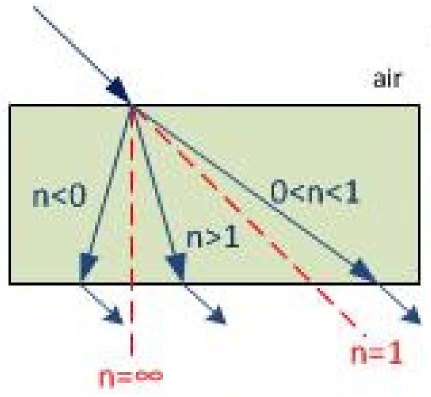
- *Subdifraction imaging (hyperlens)*
- *Freedom of refraction up to 180º*
- *Superfine spatial polarizer*
- *Ultra sensitive Raman sensors*
- *Nanoplasmonics devices*

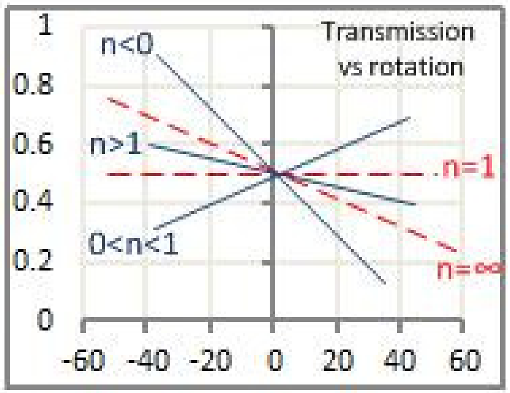


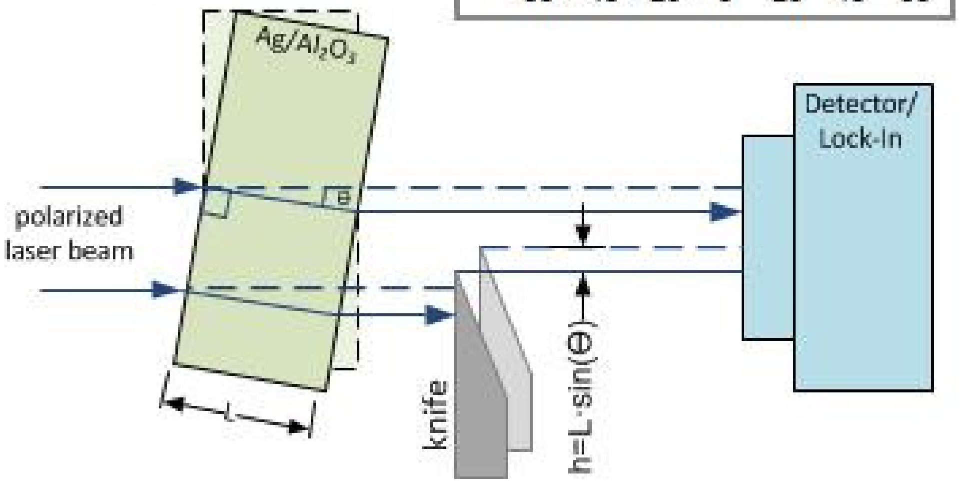


Nanowire-based Metamaterials

Refraction as with a refractive index of n>1 is Regular Refraction; 0<n<1 is Anomalous Refraction; n<0 is Negative Refraction

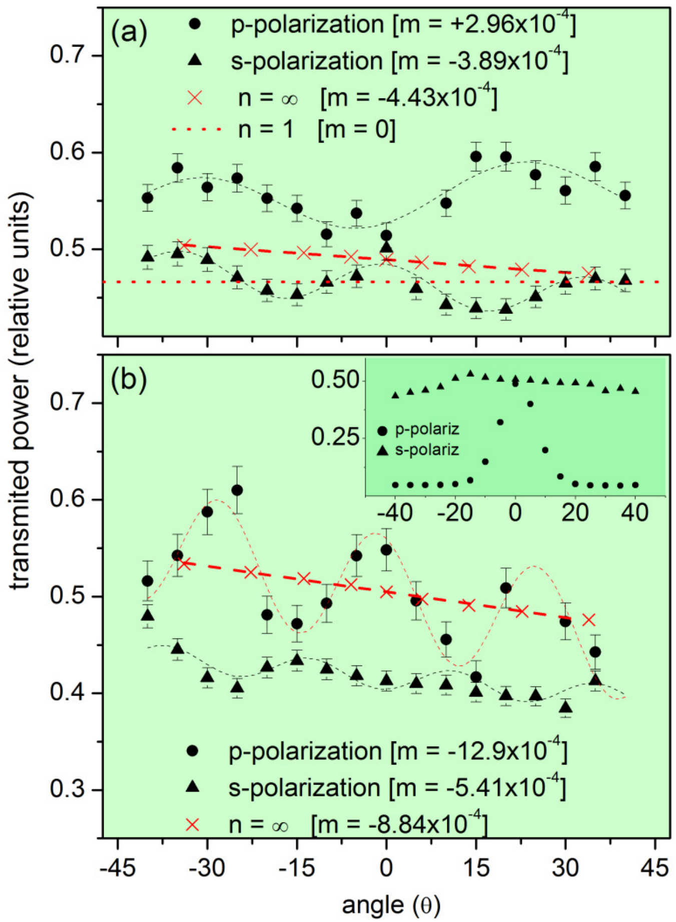






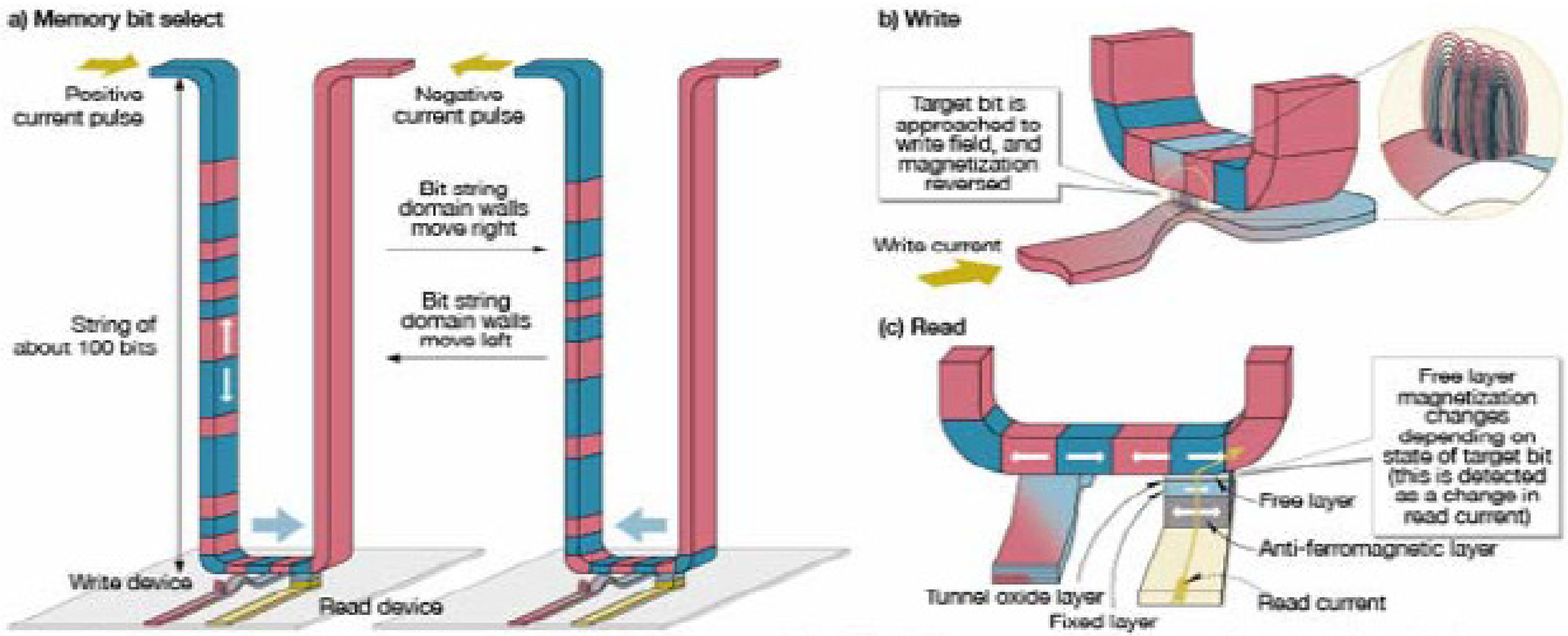
Experim. Results

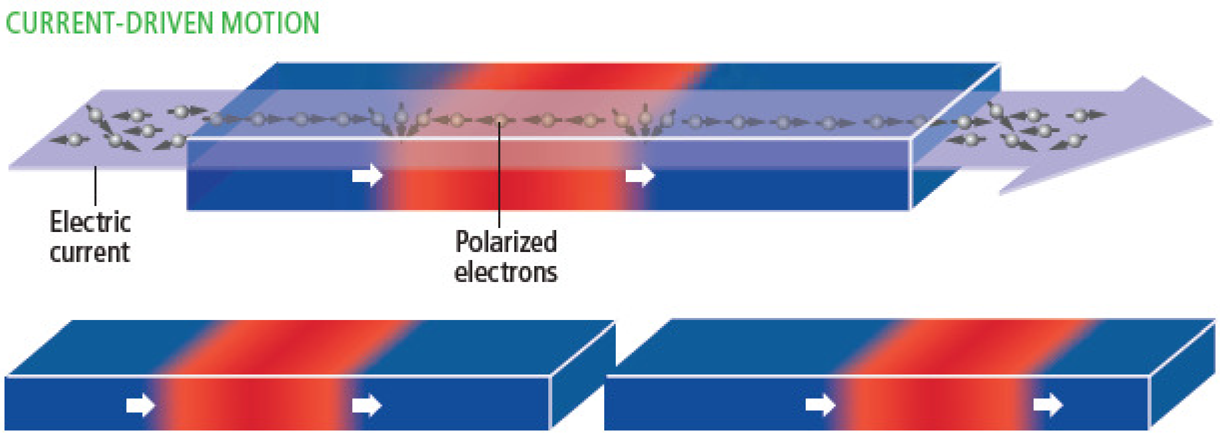
[fitted linear contribution slopes]



Birefringence swap at the transition to hyperbolic dispersion in metamaterials, Physical Review B 85, 165408 (2012)

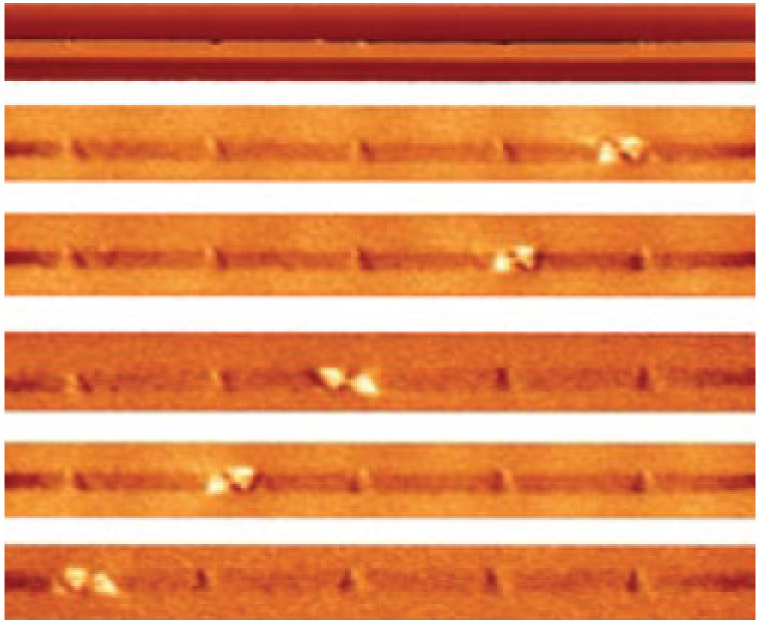
Racetrack memory

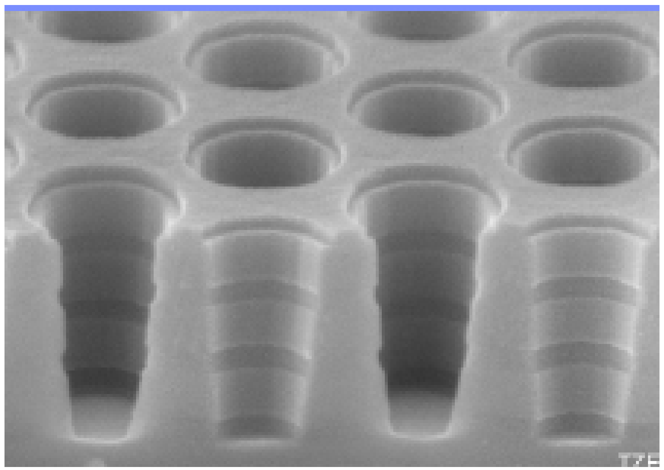


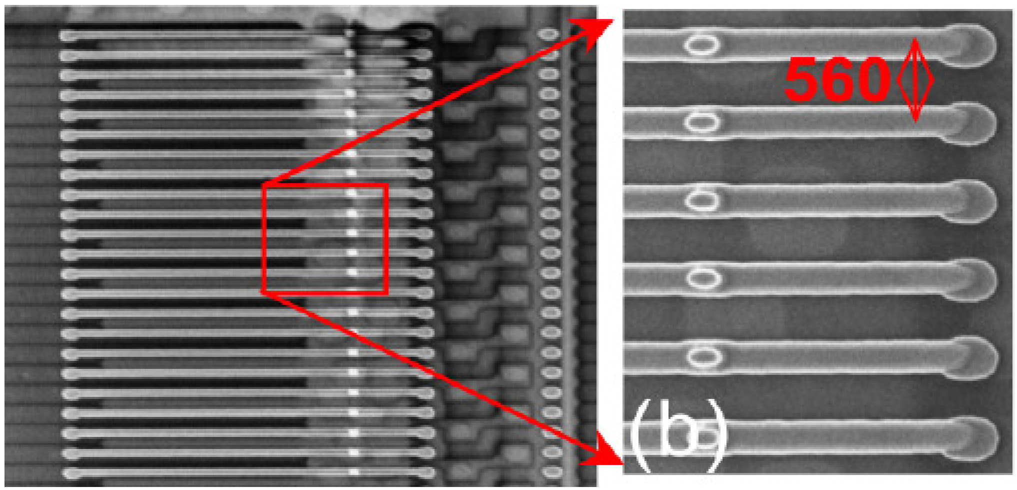


Racetrack memory

• Need deep trench with notches to “pin” domains
• Need sensitive sensors to “read” presence of domains
• Must insure a moderate current pulse moves every domain one and only one notch
Promise (10-100 bits/F^2) is enormous…

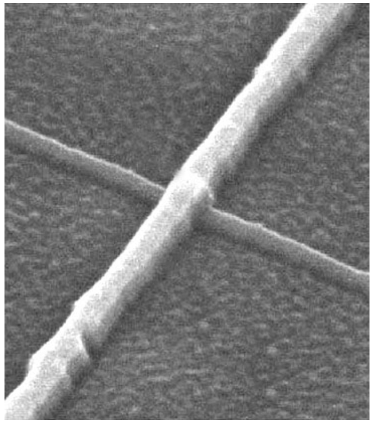


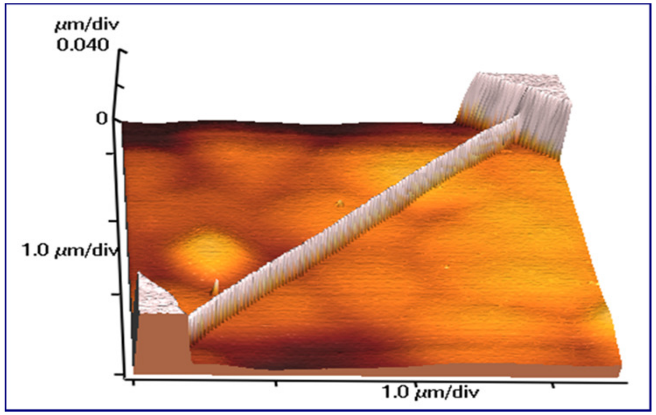


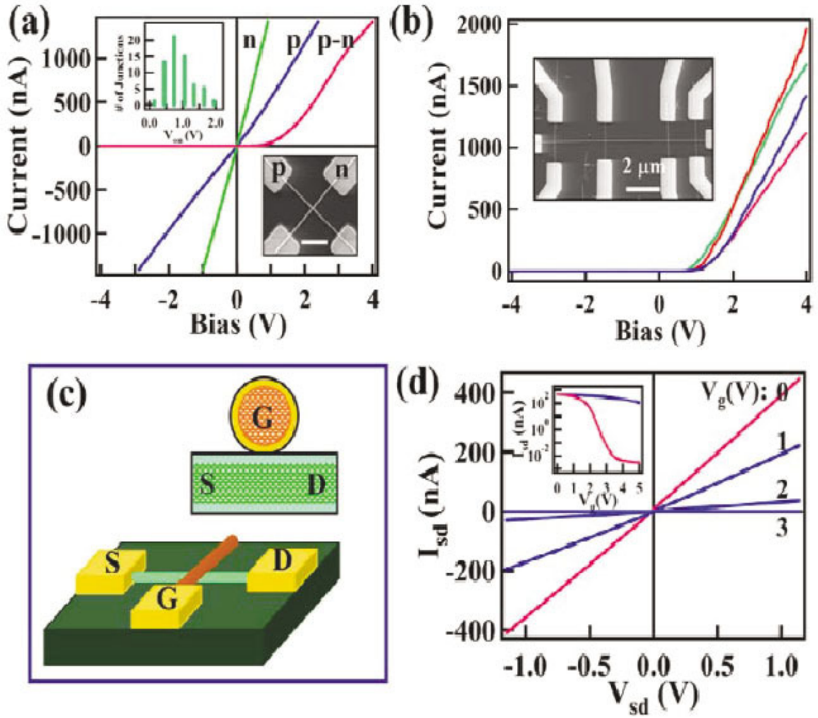


Nanowire based Field Effect Transitors

- The crossed NW structure can be configured into a variety of devices, such as diodes and transistors
- A p-n diode can be obtained by simply crossing p- and n-type NW
- Crossed NW p-n diodes and NW-FETs enable more complex circuits, such as logic gates to be produced
- Nano-logic gates







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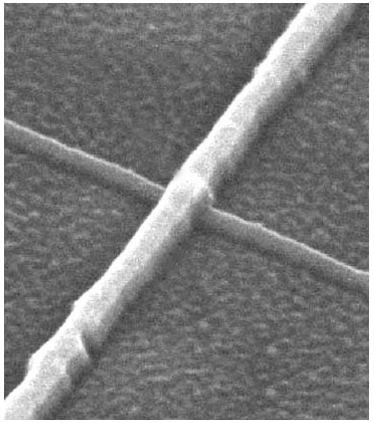
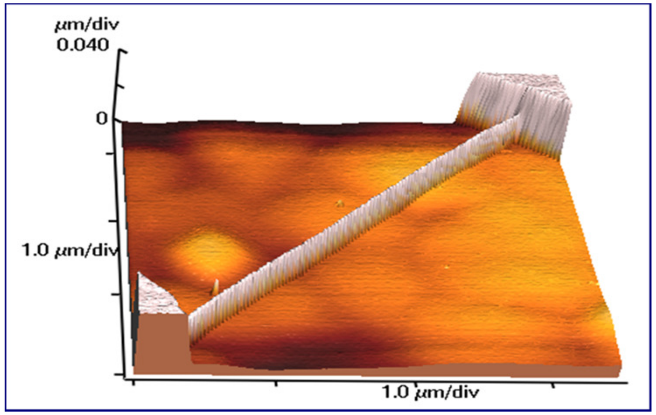
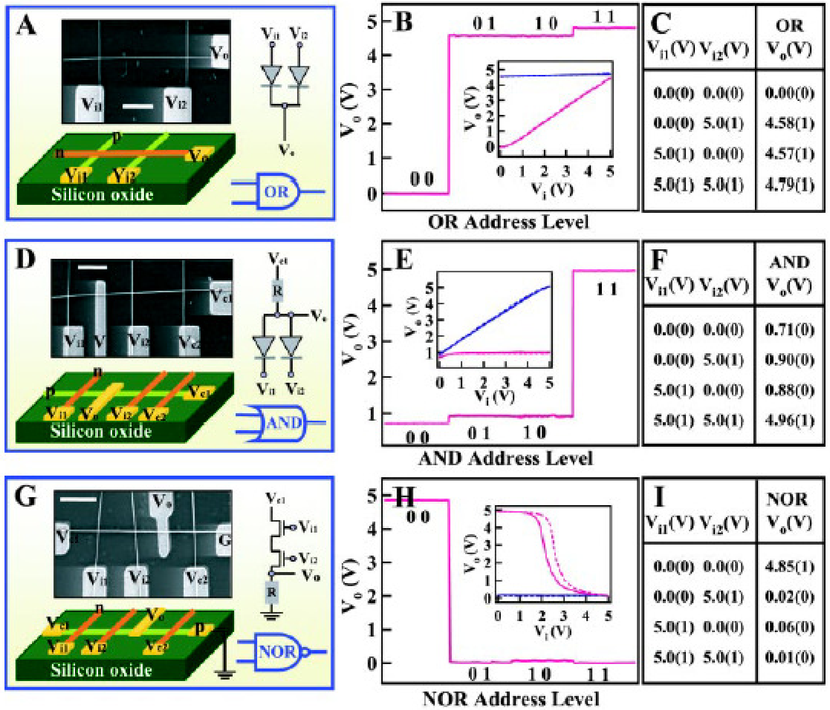
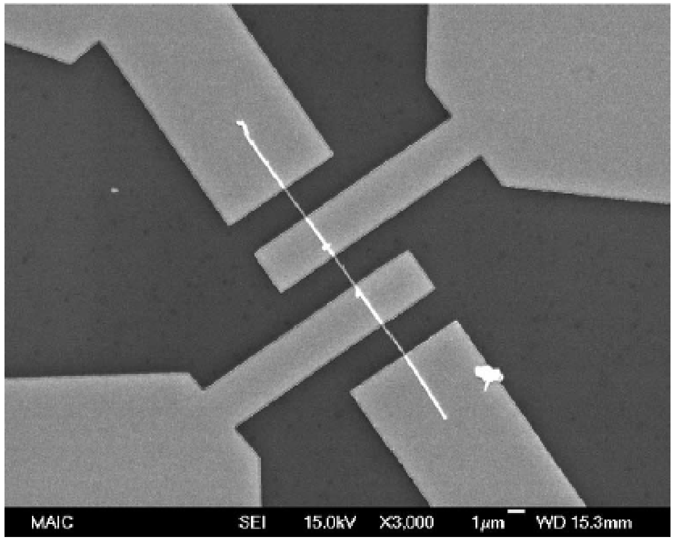


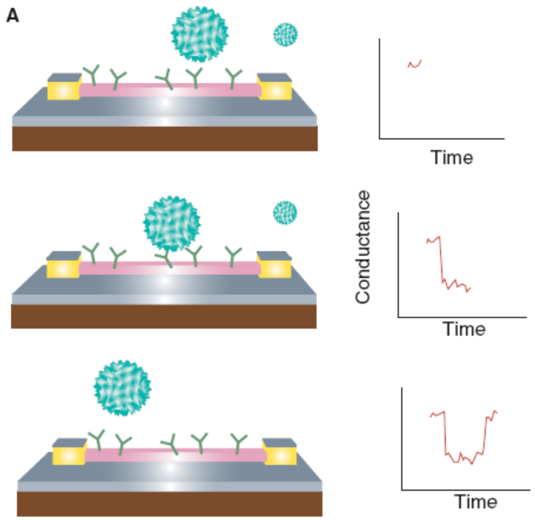


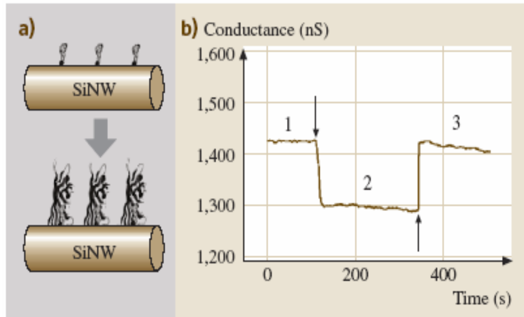


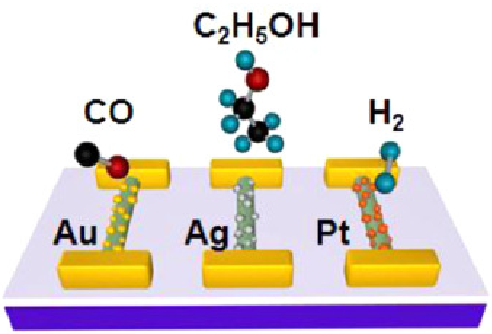
Sensing Devices

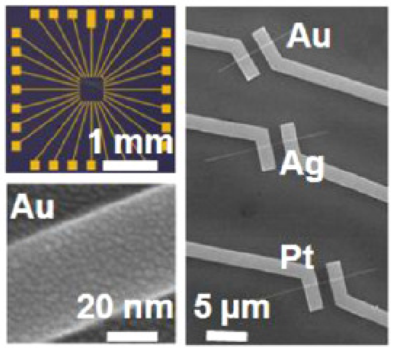
- Nanowire sensors will potentially be smaller, more sensitive, demand less power, and react faster
- pH sensors, single virus detection, protein binding, gas sensors

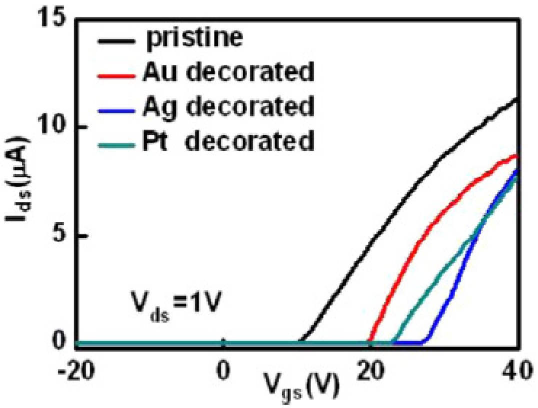












Rational Design of Sub-Parts per Million Specific Gas Sensors Array Based on Metal Nanoparticles Decorated Nanowire Enhancement-Mode Transistors, Nano Letters 13, 3287 (2013)

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Nanowires: synthesis & applications