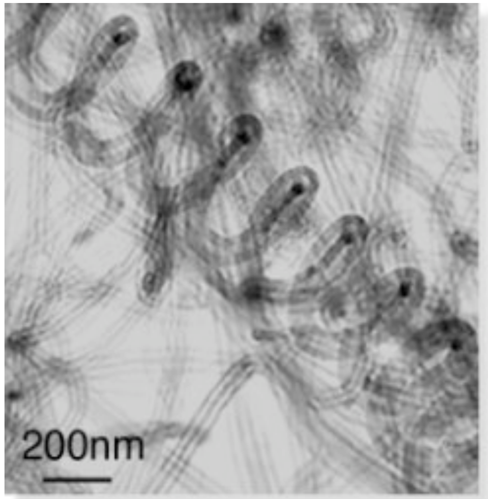
Nanotechnology

6th lecture



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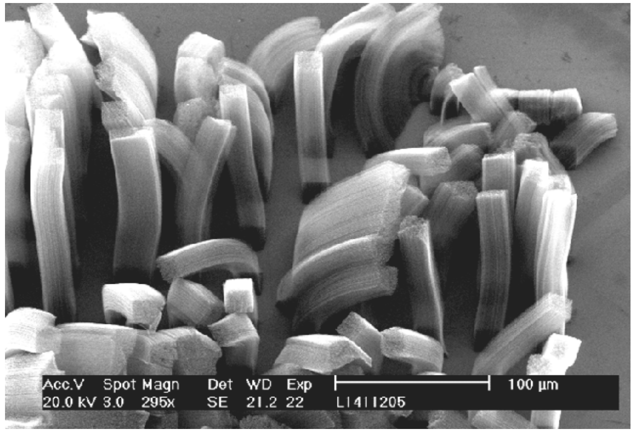

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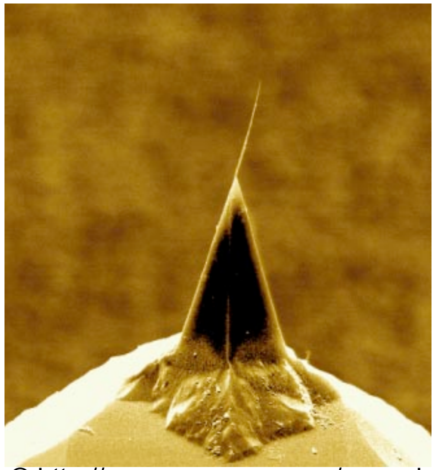
Plan for today:

4. Nanowires

4.1 Synthesis

4.2 Characterization and physical properties of nanowires

4.3 Applications



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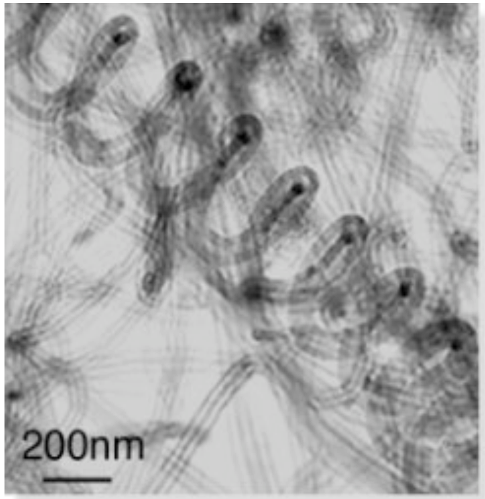

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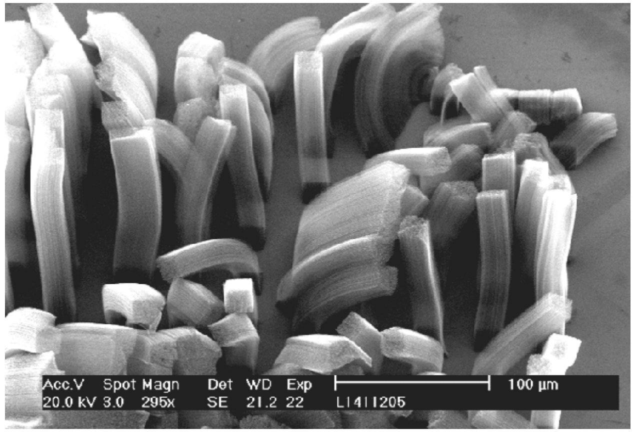

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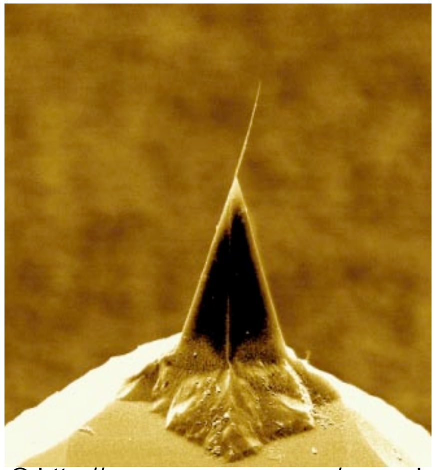

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Last time we had:

3. Introduction to Carbon Nanotubes

- ***3.4 Properties of Carbon Nanotubes***
- ***3.5 Carbon Nanotube based nano-objects***
- ***3.6 Applications of Carbon Nanotubes***

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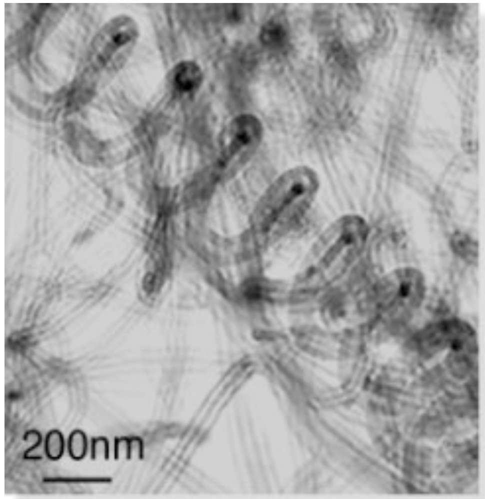

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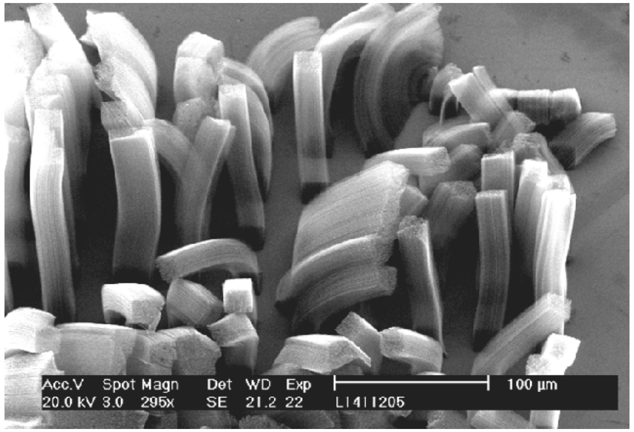

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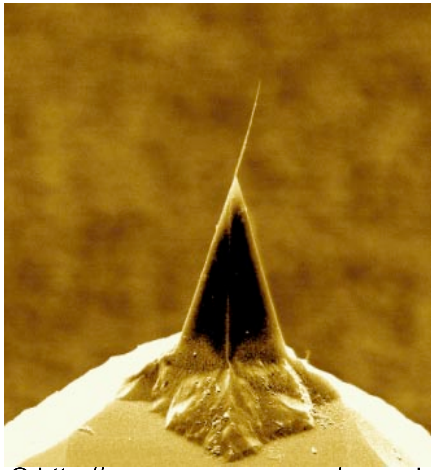

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4. Nanowires

- **Nanowires**, have **two quantum confined directions**, leaving one unconfined direction for electrical conduction.
- The nanowire research field has developed with exceptional speed in the last few years.

Properties of nanowires

- increased surface area
- very high density of electronic states
- joint density of states near the energies of their van Hove singularities (van Hove singularities are kinks in the density of states of a solid)
- enhanced exciton binding energy
- diameter-dependent bandgap
- increased surface scattering for electrons and phonons
- In all these ways (and some more) **nanowires differ from their corresponding bulk materials**.

Types of nanowires currently available

- Ag, Au Bi, Bi_2Te_3 , CdS, CdSe, Cu, Fe, GaN, GaAs, Ge, InAs, InP, Ni, PbSe, Pd, Se, Si, Zn and ZnO nanowires.
- Most of them are synthesized with template assistance.
- Synthesis methods:
  - electrochemical deposition
  - vapor-liquid-solid growth
  - chemical vapor deposition
  - and organometallic chemical vapor deposition.

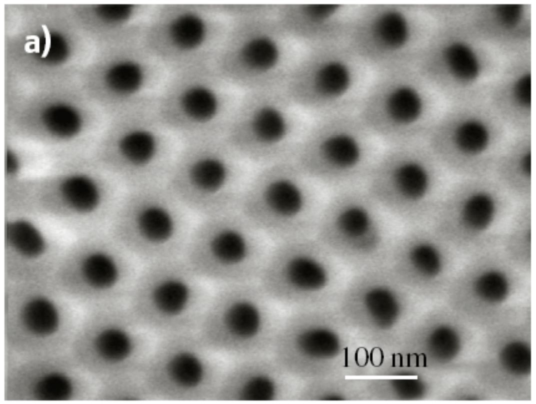
4.1. Nanowire synthesis

4.1.1. Template-assisted synthesis

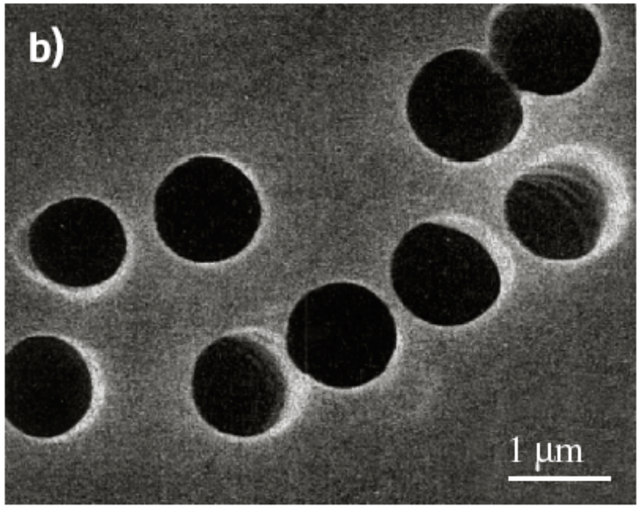
- The **templates contain** very small cylindrical **pores** or voids within the host material, and the empty spaces are filled with the chosen material.

Template synthesis

- Porous anodic alumina templates (see Figure) are produced by anodizing pure Al films in various acids.
- **Self-organization of the pore structure**
- The pore diameter can be systematically varied from <10nm up to 200nm with a pore density in the range of 10^9–10^{11} pores/cm^2.



- Another type of porous template commonly used for nanowire synthesis is the template type fabricated by **chemically etching particle tracks** originating from ion bombardment and high pressures (see Figure).



- **Nanochannel glass** contains a regular hexagonal array of capillaries, with a packing density as high as 3×10^{10} pores/cm^2.
- **Diblock copolymers**, polymers that consist of two chain segments with different properties, have also been utilized as templates for nanowire growth. 14nm diameter ordered pore arrays with a packing density of 1.9×10^{11} cm^{-3}.

Nanowire Template Assisted Growth by Pressure Injection

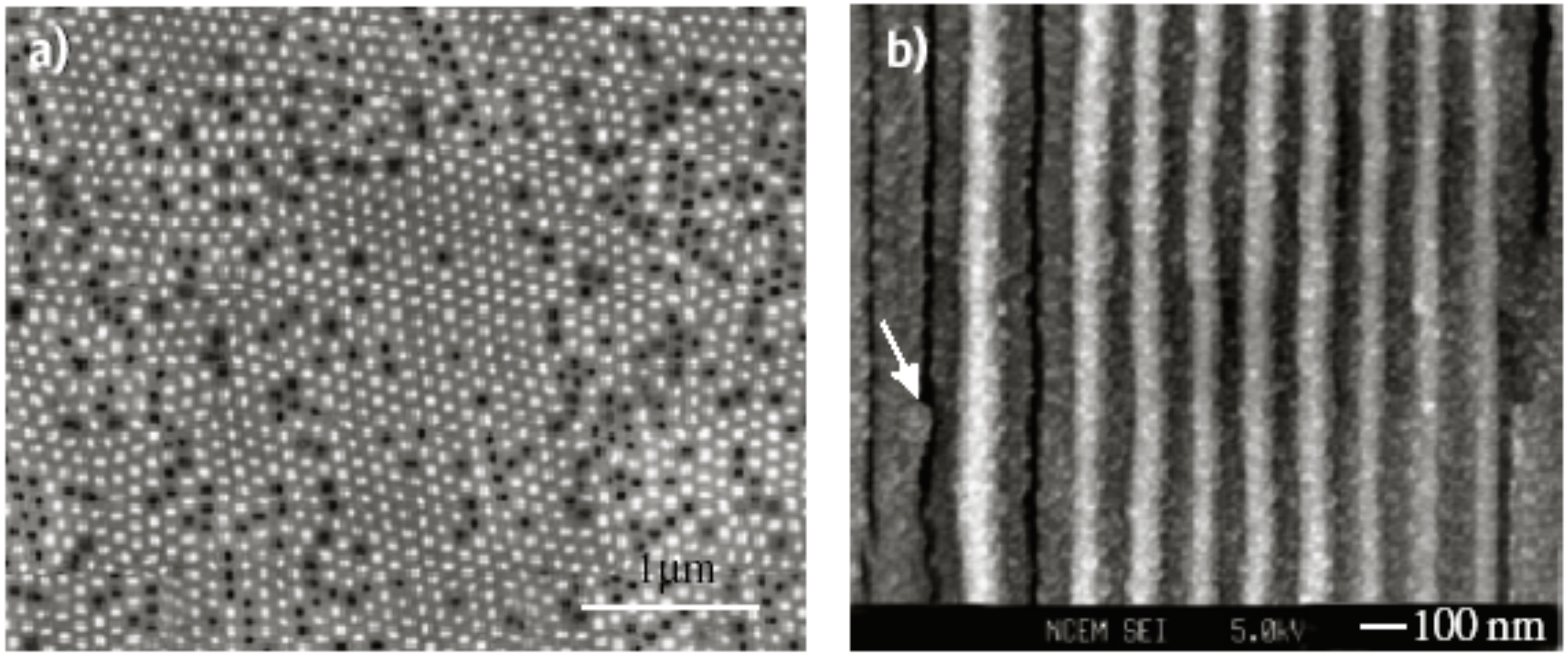
- In the **high-pressure injection method**, the nanowires are formed by pressure injecting the desired material in liquid form into the evacuated pores of the template.
- Anodic aluminum oxide films and nano-channel glass are two typical materials used as templates in conjunction with the pressure injection filling technique.
- Metal nanowires (Bi, In, Sn, and Al) and semiconductor nanowires (Se, Te, GaSb, and Bi_2Te_3) have been fabricated in anodic aluminum oxide templates using this method.

Nanowire Template Assisted Growth by Pressure Injection

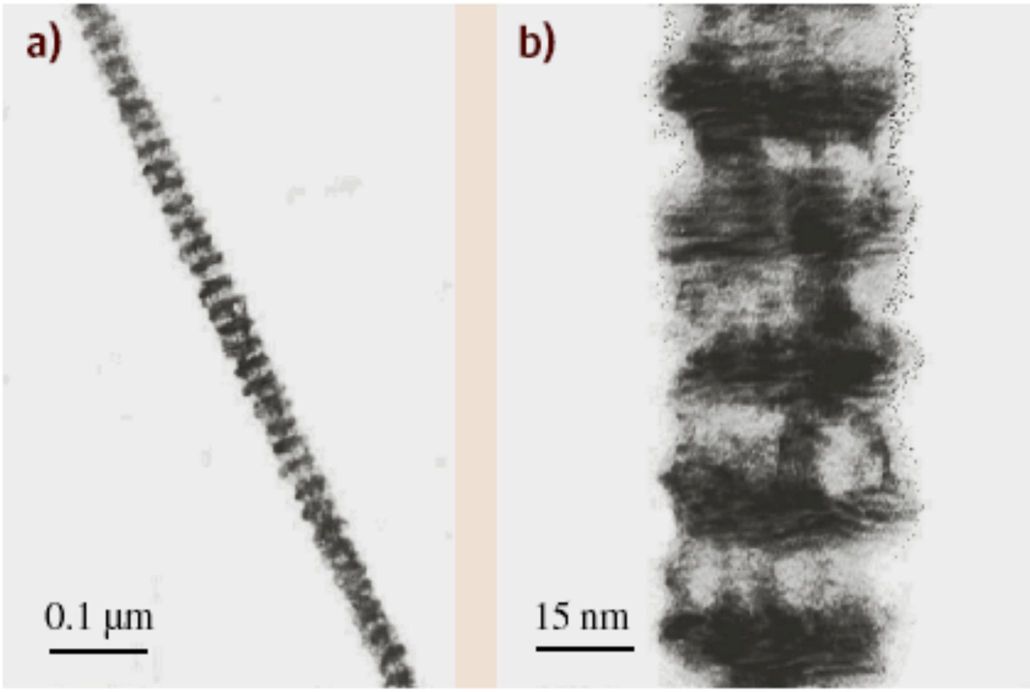
- The **pressure** *P* required **to overcome the surface tension** for the liquid material to fill the pores with a diameter d_W is determined by the Washburn equation:
  $d_W = -4\gamma(\cos\alpha)/P$,
  where γ is the surface tension of the liquid, and α is the contact angle between the liquid and the template.
- To reduce the required pressure and to maximize the filling factor, some **surfactants** are used to decrease the surface tension and the contact angle.
- Nanowires produced by the pressure injection technique usually possess **high crystallinity** and a preferred crystal orientation along the wire axis.

Electrochemical Deposition

- Traditionally, electrochemistry has been used to grow thin films on conducting surfaces.
- Templates are for example particle track-etched mica films or polymer membranes.
- Nanowires fabricated by the electrochemical process are usually **polycrystalline**.



- The figure shows **Bi_2Te_3 nanowires** which have been fabricated in alumina templates with a high filling factor using the dc electrochemical deposition.
- Figure: Black unfilled template, white filled template, grey matrix.



- One advantage of the electrochemical deposition technique is the **possibility of fabricating multilayered structures** within nanowires.
- By varying the cathodic potentials in the electrolyte that contains two different kinds of ions, different metal layers can be controllably deposited.
- The figure shows a Co(10nm)/Cu(10nm) multilayered nanowire.

Vapour deposition

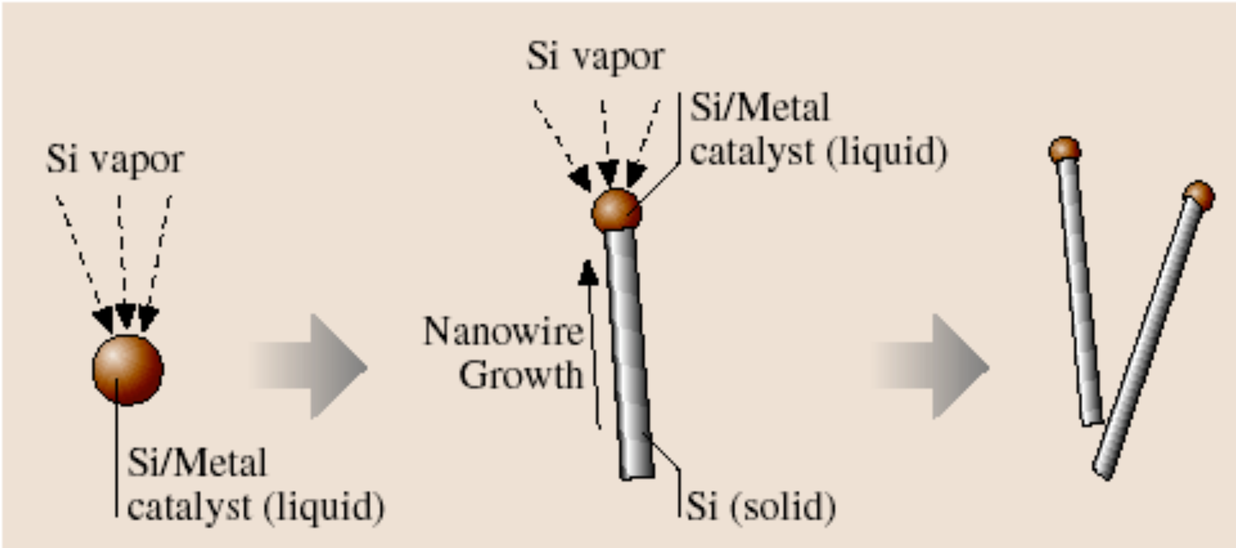
- Vapor deposition of nanowires includes physical vapor deposition (PVD), chemical vapor deposition (CVD) and metallorganic chemical vapor deposition (MOCVD).
- In physical vapor deposition the material is heated, becomes a vapor, is introduced through the pores of the template, and is cooled to solidify.
- E.g. Bi nanowires with diameters of 7 nm can be constructed in this way.
- Compound materials can be prepared by the chemical vapor deposition (CVD) technique.

Nanotube Synthesis with Templates and as Templates

- **Carbon nanotubes**, fabricated within the pores of anodic **alumina templates**
- metal catalyst deposited on the bottom of the pores
- furnace
- heated to 700–800 °C
- Obtain well-aligned nanotube arrays.
- Applications: cold-cathode flat panel displays.
- **Zeolite templates** are also used and can yield **carbon nanotubes** with diameters of 0.42 nm, having only 10 carbon atoms around the circumference.
- The hollow **cores of carbon nanotubes** have also been **used as templates** to synthesize a variety of nanowires of very small diameter have not yet been characterized regarding their physical properties.

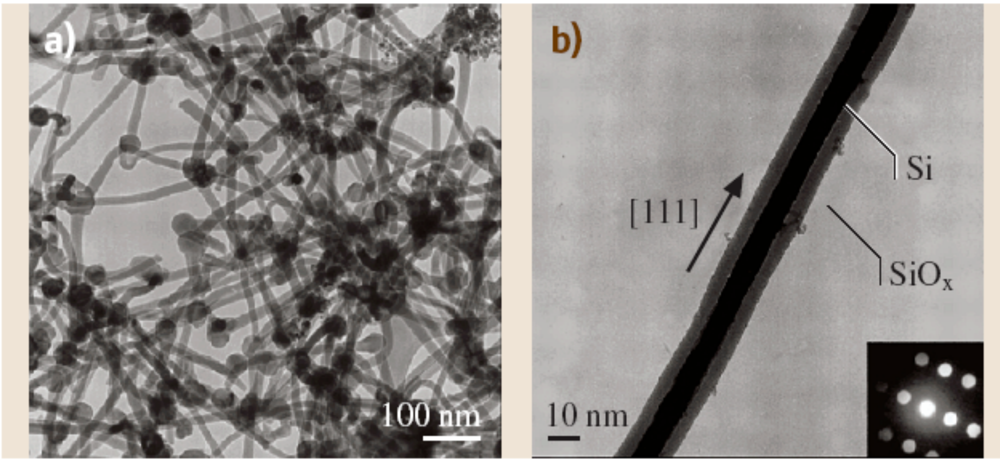
4.1.2 VLS Method for Nanowire Synthesis

- VLS: **v**apor-**l**iquid-**s**olid mechanism of anisotropic crystal growth.
- This growth mechanism involves the absorption of source material from the gas phase into a liquid droplet of catalyst.
- Upon supersaturation of the liquid alloy, a nucleation event generates a solid precipitate of the source material.
- The seed elongates into a nanowire or a whisker, whose diameter is dictated by the diameter of the liquid alloy droplet.
- Real-time observations of this process is possible by in situ TEM.



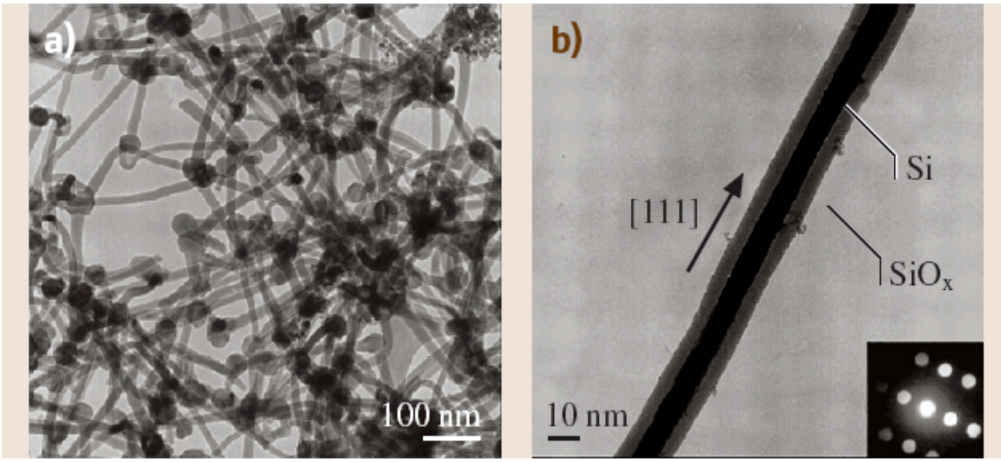
Schematic illustrating the growth of silicon nanowires by the VLS mechanism.

- With the **VLS** method, **elemental, binary, and compound semiconductor nanowires** can be fabricated.
- One has relatively good control over the nanowire diameter and diameter distribution.
- It is also possible to **fabricate compositionally modulated nanowires**, like GaAs/GaP nanowires, p-Si/n-Si nanowires, Si/$Si_{1-x}Ge_x$ nanowires or InAs/InP nanowires with atomically sharp interfaces.
- Compositionally modulated nanowires are of specific interest, since they are expected to exhibit exciting electronic, photonic, and thermoelectric properties.

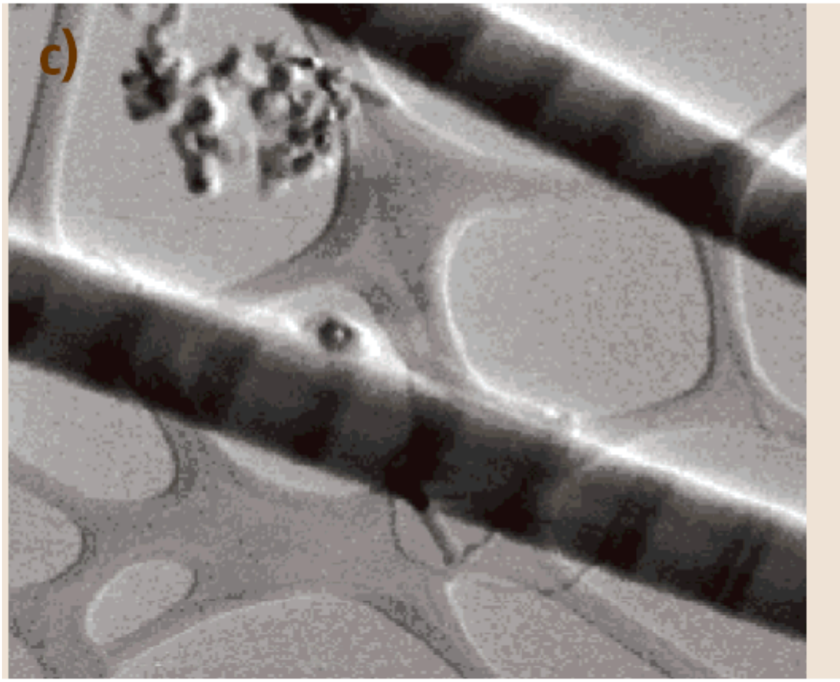


(**a**) TEM images of **Si nanowires** produced after laser ablating a $Si_{0.9}Fe_{0.1}$ target. The dark spheres with a slightly larger diameter than the wires are solidified **catalyst clusters**.

(**b**) Diffraction contrast TEM image of a Si nanowire. The crystalline Si core appears darker than the amorphous oxide surface layer. The inset shows the convergent beam electron diffraction pattern recorded perpendicular to the wire axis, confirming the nanowire crystallinity.



- Silicon and germanium nanowires produced by the VLS technique have a crystalline core coated by a relatively thick amorphous oxide layer (2–3 nm).
- During growth, the oxides serve as catalyst.



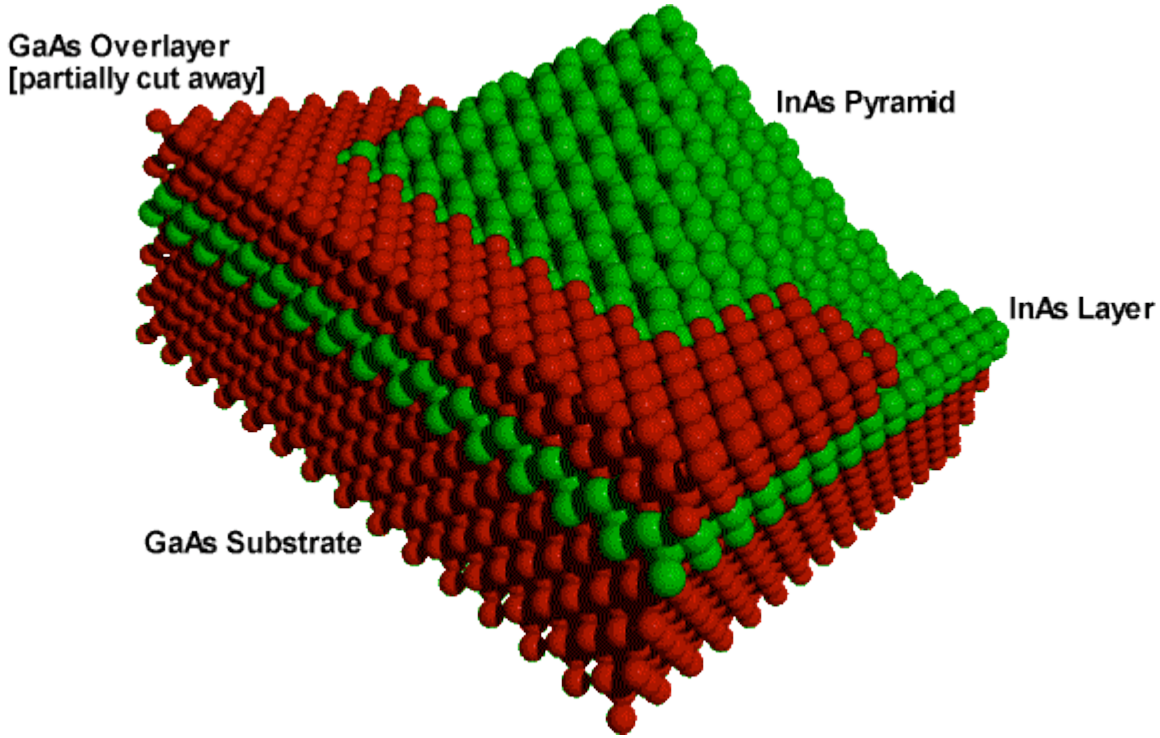
Compositionally modulated nanowire: STEM image of $Si/Si_{1-x}Ge_x$ superlattice nanowires in the bright field mode.

- A similar oxide induced yield enhancement was found in catalyst free Ge nanowires grown from ablation of Ge powder mixed with GeO_2.
- The initial nucleation events generate oxide coated spherical nanocrystals. The [112] crystal faces have the fastest growth rate, and therefore the nanocrystals soon begin elongating along this direction to form one-dimensional structures.

4.1.3 Other Synthesis Methods

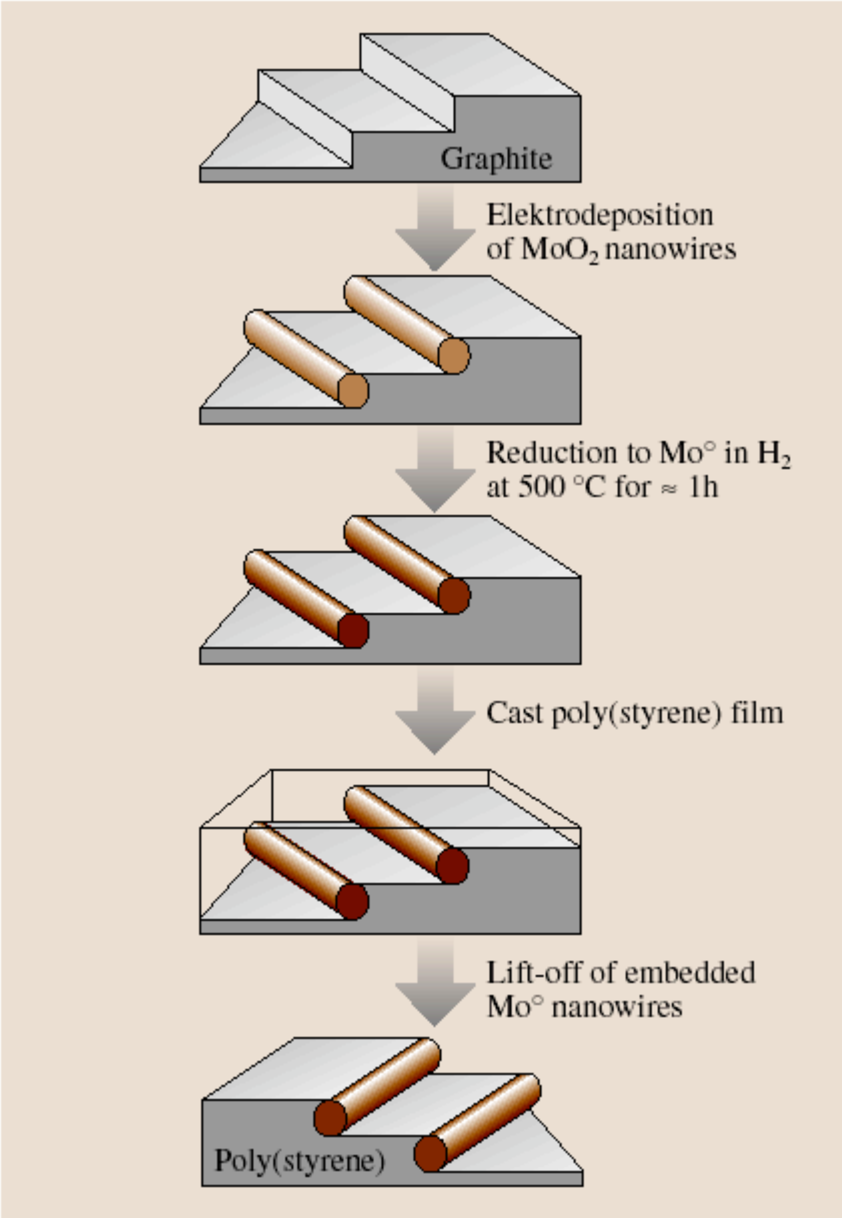
- We focus on “bottom-up” approaches that do not require highly sophisticated equipment (such as scanning microscopy or lithography based methods).
- Without the use of templates, catalysts, or surfactants, e.g. 1-D helical atomic chains are fabricated, which grows preferentially along one crystallographic axis.
- More often **surfactants are necessary**, e.g. **in quantum dot production:** To produce monodispersed quantum dots, i. e., zero-dimensional isotropic nanocrystals, surfactants are necessary **to stabilize the interfaces.**

Quantum dot


GaAs Overlayer
[partially cut away]
InAs Pyramid
InAs Layer
GaAs Substrate

CdSe and Bi Nanorods

- Different surfactants have different affinities and different absorption rates for the different crystal faces of CdSe.
- In the production of CdSe nanorods, this fact is exploited, regulating the growth rate of these faces.
- Stress-induced crystalline bismuth nanowires have been grown from sputtered films of layers of Bi and CrN.
- The nanowires presumably grow from defects and cleavage fractures in the film and are up to several millimeter in lengths with diameters ranging from 30 to 200nm.



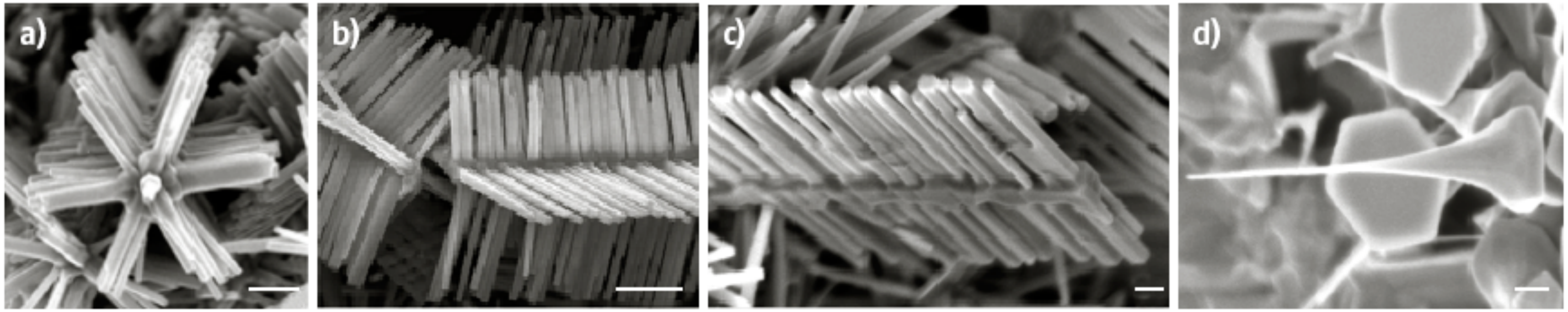
- Selective electrodeposition along the step edges in highly oriented pyrolytic graphite (HOPG) was used to obtain MoO_2 nanowires as shown in the Figure.
- These nanowires cannot be removed from the substrate, but they can be reduced to metallic molybdenum nanowires, which can then be released as free-standing nanowires.
- The substrate defines only the position and orientation of the nanowire, not its diameter.

Self-assembled grooves in etched crystal planes can also be used to generate nanowire arrays via gas-phase shadow deposition.

4.1.4. Hierarchical Arrangement and Superstructures of Nanowires

- **Ordering nanowires is a challenge**.
- The preparation of nanowires with a **graded composition** or with a **superlattice structure** along their main axis was demonstrated by controlling the gas-phase chemistry as a function of time.
- Control of the composition **along the axial dimension** was also demonstrated by a template-assisted method.
- E.g., the composition can be varied **along the radial dimension** of the nanowire by first using a VLS method and then CVD.
- There are Si/Ge and Ge/Si coaxial (or core-shell) nanowires.
- Quantum-dots can also induce a one-dimensional growth of a nanowire from each one of the facets.

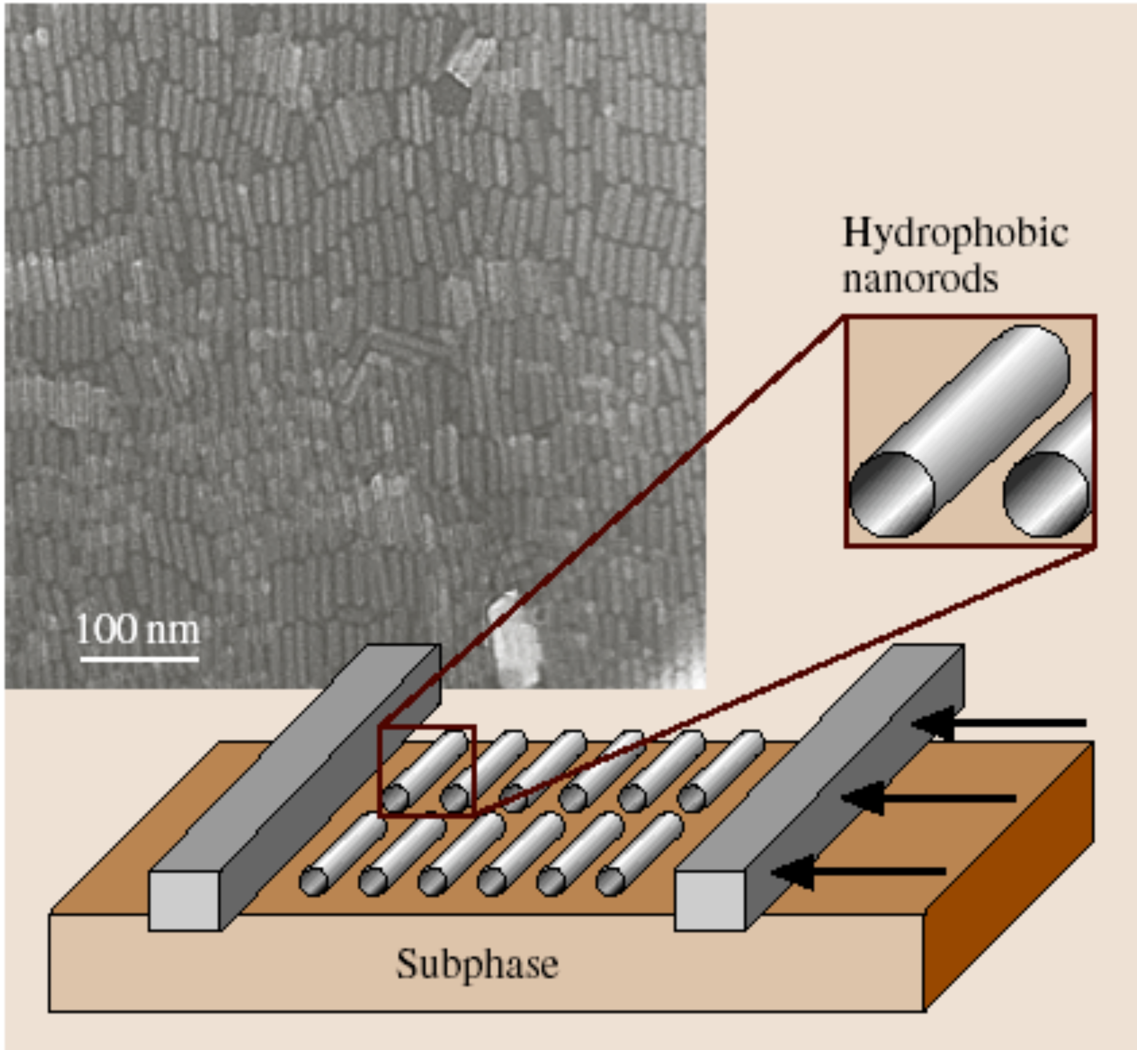
In_2O_3/ZnO hierarchical nanostructures



- **Two, four, or six rows of ZnO nanorods** could be found **on** different In_2O_3 **core nanowires**, depending on the crystallographic orientation of the main axis of the core nanowire, as shown in the Figure.
- **Comb-like structures and nano-nails** entirely made of ZnO were also reported.

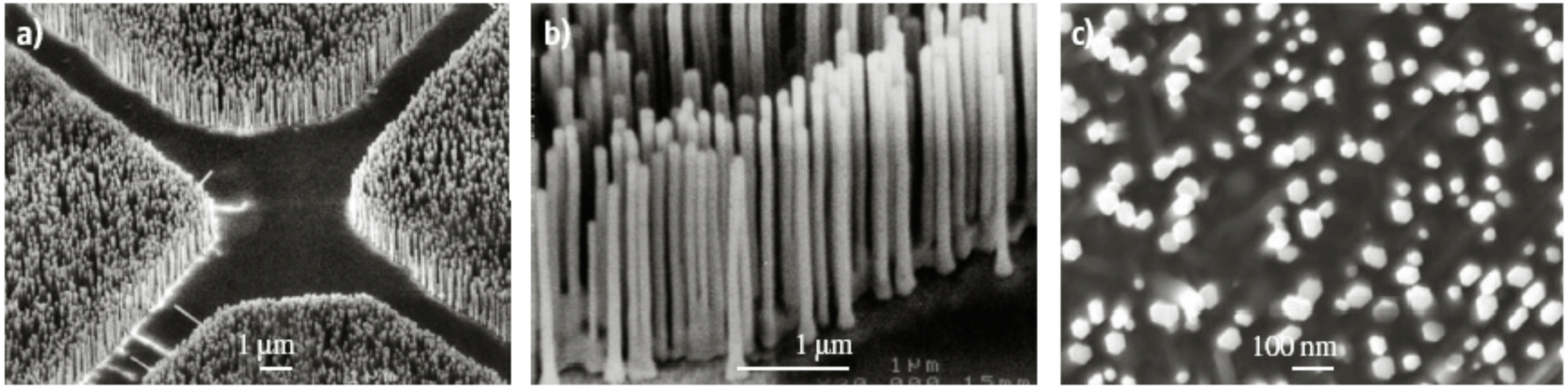
Aligning and positioning

- **Post-synthesis methods to align and position** nanowires include **microfluidic channels** (orientation of the nanowires by the liquid flow direction), **Langmuir–Blodgett** assemblies (see Figure) and **electric-field assisted assembly** (dielectrophoretic forces that pull polarizable nanowires toward regions of high field strength).
- These techniques have been successfully used to prepare electronic circuitry and optical devices out of nanowires.



A TEM image of a $BaCrO_4$ nanorod film (*left inset*) achieved by the Langmuir–Blodgett technique.

Aligning and positioning



Alternatively, **alignment and positioning** can be done **by patterning a film which serves as a catalyst**.

The figure shows an array of ZnO nanowire posts at predetermined positions, all vertically aligned with the same crystal growth orientation. The well-faceted nature of these nanowires has important implications for their lasing action.

Substrate: sapphire.

4.2. Characterization and Physical Properties of Nanowires

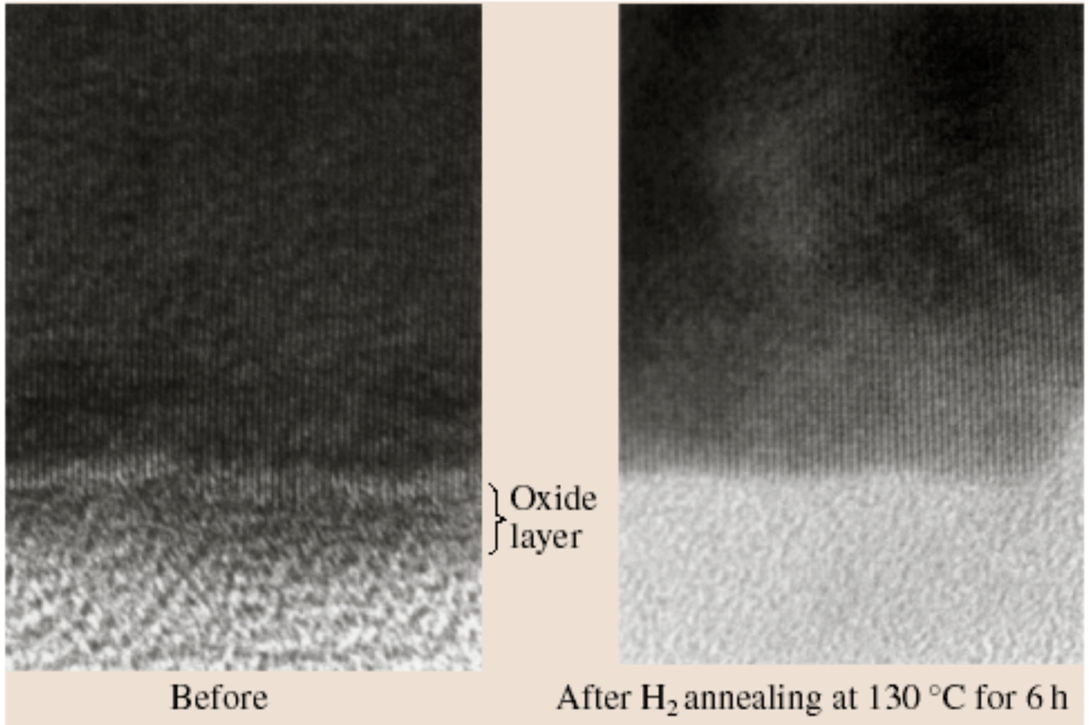
- The discovery and investigation of nanostructures were pushed by advances in various **characterization and microscopy techniques** that enable materials characterization to take place at smaller and smaller length scales, reaching down to individual atoms.
- Due to the enhanced surface-to-volume ratio in **nanowires**, their **properties may depend sensitively on their surface condition and geometrical configuration**.

4.2.1 Structural Characterization

- at the micron scale: **optical** techniques
- at smaller scales: **electron microscopy** techniques, **scanning probe microscopy** techniques, **diffraction** techniques
- For information on all types of microscopy, with great interactive features and animations, go to http://microscopy.fsu.edu/
- Scanning Electron Microscopy (**SEM**): structural features at the **10nm to 10μm** length scales can be probed.

Transmission Electron Microscopy (TEM)

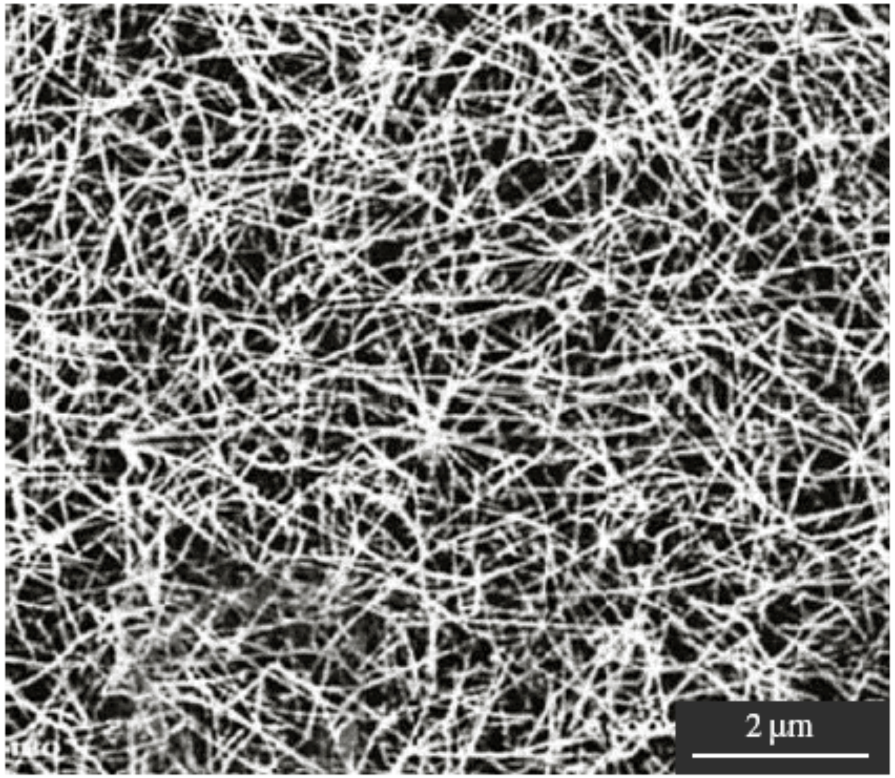
- TEM studies yield information regarding the crystal **structure**, crystal **quality**, grain size, and **crystal orientation** of the nanowire axis **at the atomic scale**.
- **Environmental TEM** allows for **in situ** observation when gases are introduced or the sample is heat treated.
- For example, it is possible to watch the dynamic oxide removal process in Bi nanowires (see Figure next slide).



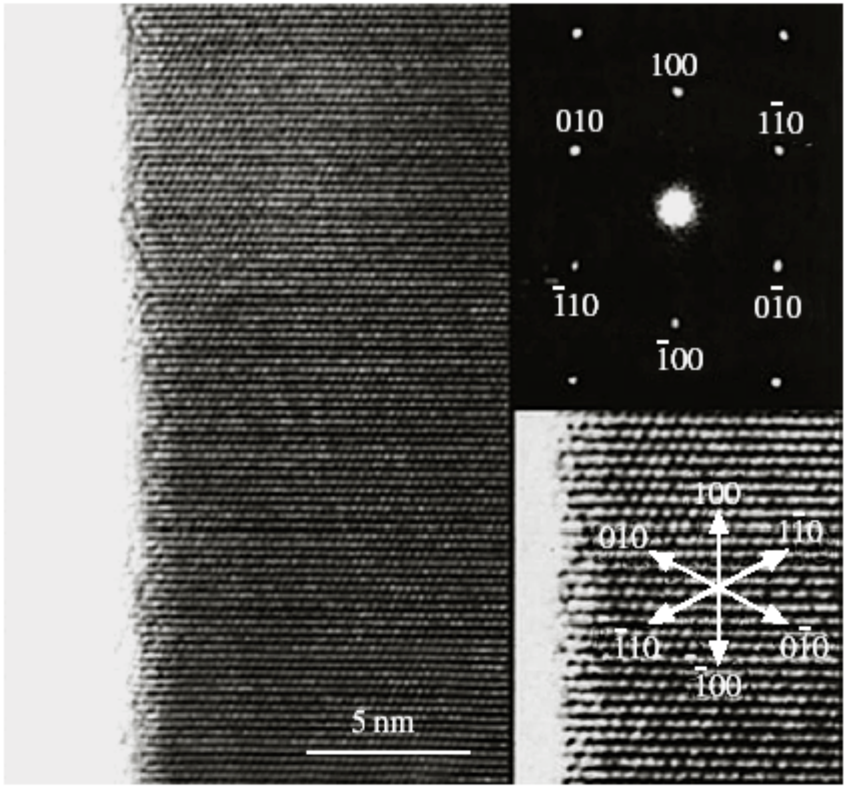
High resolution transmission electron microscope (HRTEM) image of a Bi nanowire (*left*) before and (*right*) after annealing in hydrogen gas at 130 $^{\circ}$C for 6 hours within the environmental chamber of the HRTEM instrument to remove the oxide surface layer.

Transmission Electron Microscopy (TEM)

Coupling the powerful imaging capabilities of TEM with other characterization tools, such as an electron energy loss spectrometer (EELS) or an energy dispersive X-ray spectrometer (EDS) within the TEM instrument, additional properties of the nanowires, like the chemical composition, can be probed.

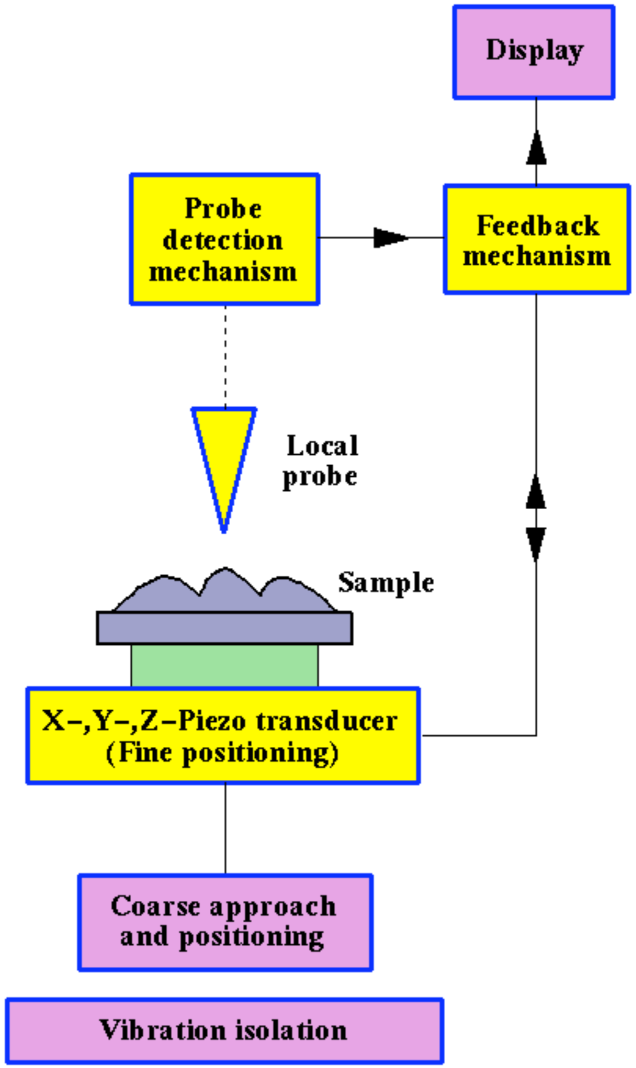


SEM



TEM with selected area electron diffraction patterns (SAED)

Scanning Probe Microscopy

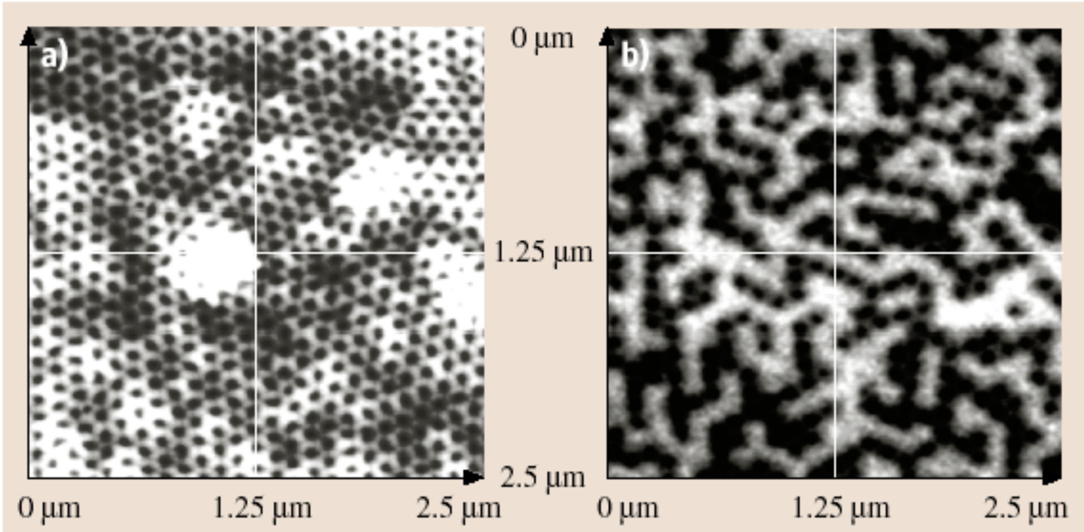


- A scanning probe microscope (SPM) **raster scans** a sharp probe over a surface.
- The mechanical, electrical, magnetic, optical and chemical interaction between the **sharp probe** and the **surface** provides a 3D representation of surface parameters at or near the atomic scale. The samples can be in **air**, **vacuum**, or immersed in some **liquid**.

Scanning Probe Techniques

- SPM allows for study of e.g. the structural, electronic, magnetic, and thermal properties of nanowires.
- E.g., STM/STS studies on specific Si nanowires, which show alternating segments identified with growth along [110] and [112] directions, reveal different I–V characteristics for the [110] segments as compared with the [112] segments.
- Scanning magnetic field microscopy (MFM) allows for measurement of the magnetic polarization of the sample.

Topography vs. MFM



(**a**) Topographic image of a highly ordered **porous alumina** template with a period of 100 nm **filled with** 35 nm diameter **nickel** nanowires. (**b**) The corresponding **MFM** (magnetic force microscope) image of the nano-magnet array, showing that the **pillars are magnetized alternately** "**up**" (*white*) **and** "**down**" (*black*).

That´s it for today.