

Università degli Studi di Trieste
Dipartimento di Ingegneria e Architettura
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Scienza e Tecnologia dei Materiali Ceramici

Modulo 2: Materiali Nanostrutturati

- Lezione 6 -


Vanni Lughi

vlughi@units.it

040 558 3769

Dipartimento di Ingegneria e Architettura
Università degli Studi di Trieste

5 μm

The background of the slide is a grayscale scanning electron microscope (SEM) image of a nanostructured ceramic material. The image shows a dense array of small, rounded particles or grains, with a scale bar in the bottom right corner indicating a length of 5 micrometers.

Nanowires

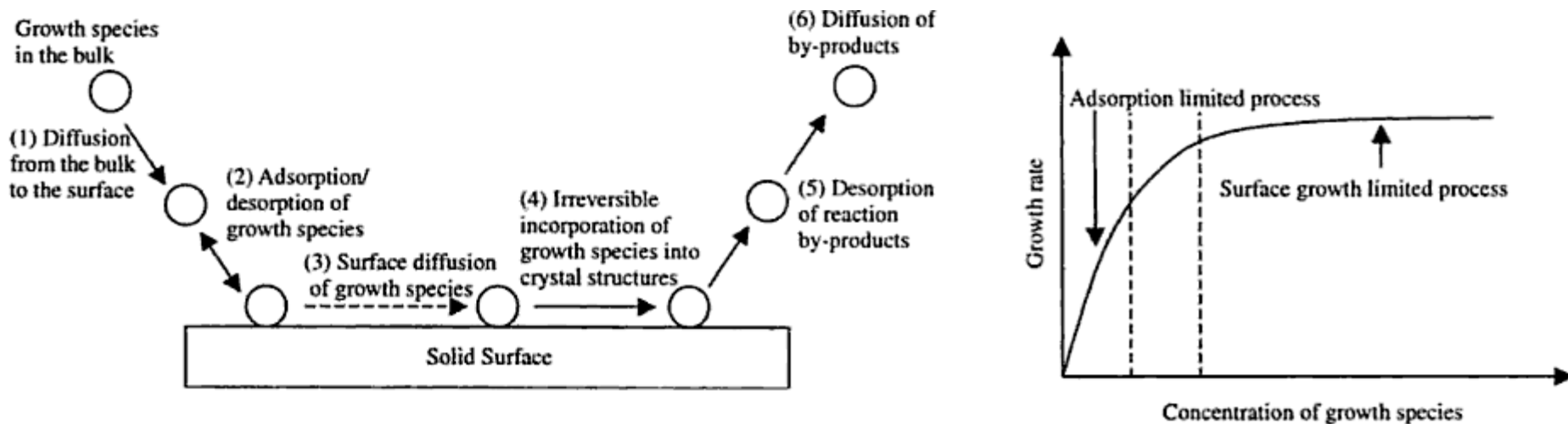
- Synthesis methods:
 1. **Spontaneous growth (bottom-up)**
 2. Template-based growth (bottom-up)
 - Electroplating and electrophoretic deposition
 - Colloid dispersion, melt, solution filling
 3. Electrospinning (bottom-up)
 4. Lithography (top-down)
- Properties

1. Spontaneous growth

- Main kinds of spontaneous growth:
 - Evaporation (or dissolution) – condensation
 - Vapor (or solution)-liquid-solid growth (VLS or SLS)
- Leads to preferentially aligned single crystals
- Driving force: reduction of chemical potential (from chemical reactions or phase changes)
- Important role of defects and impurities on the surface

Evaporation (or dissolution) – condensation growth

- Driving force: reduction of supersaturation and/or recrystallization
- It is a crystal growth process, and typically results in high quality single crystals; often faceted morphology and low aspect ratios

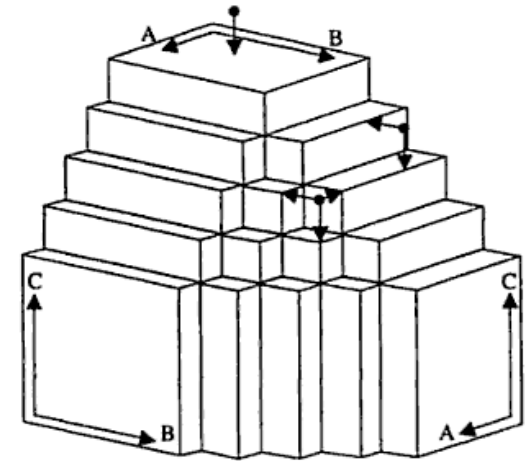
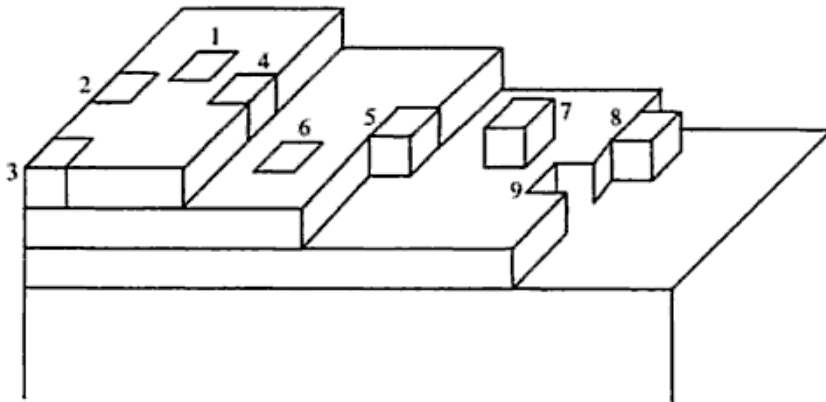


- Anisotropy derives from:
 - Different growth rates on different crystal facets
 - Imperfections (dislocations)
 - Preferential impurity accumulation on certain facets
 - Low supersaturation is required (concentration between the equilibrium concentration of the growing surface and that of the non-growing surface)

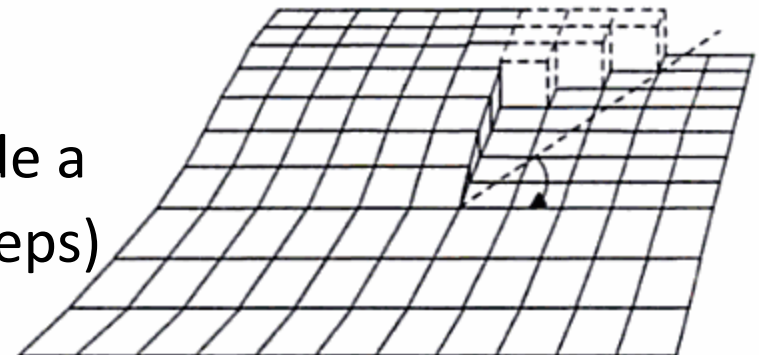
Evaporation (or dissolution) – condensation growth

Origin of anisotropy in crystal growth processes:

- **Surface energy**, i.e. Periodic Broken Bond Chains (PBS)



- **Screw dislocations**
(BCF theory: dislocations provide a continuous supply of surface steps)



Evaporation – condensation growth (Vapor-Solid, VS)

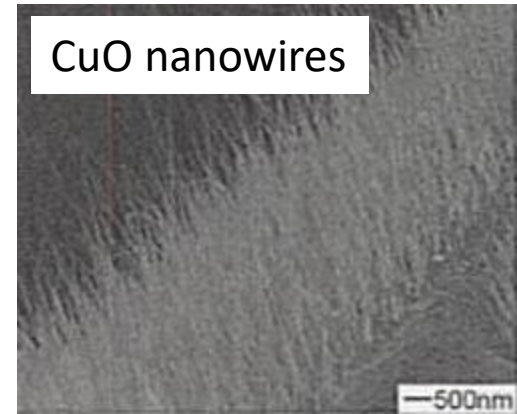
Nanowires of a number of materials have been grown by this method (metals like Hg, Cd, Ag, CdS, CdO, ZnO, CuO, In_2O_3 , Ga_2O_3 , SnO_2 , PbO_2 , etc.) by simply controlling temperature and supersaturation (ratio pressure/equilibrium pressure)

Simple growth mechanisms (PBS, dislocation-driven) rarely account for the observed structures and growth rates (oftentimes no dislocations are observed, and growth rates are faster than expected)

ZnO nanobelts



CuO nanowires



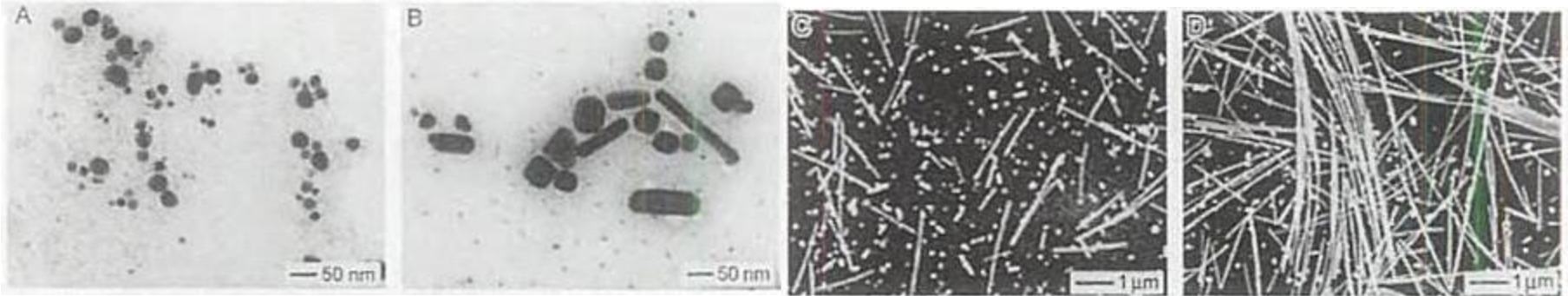
Dissolution – condensation growth

Growth steps (same as nanoparticles):

1. Dissolution of precursors in solution
2. Diffusion of the species
3. Deposition on the seed's surface

Various metals, II-VI and oxide semiconductors have been grown by this approach

Example of growth sequence (Ag nanowires from Pt seeds):

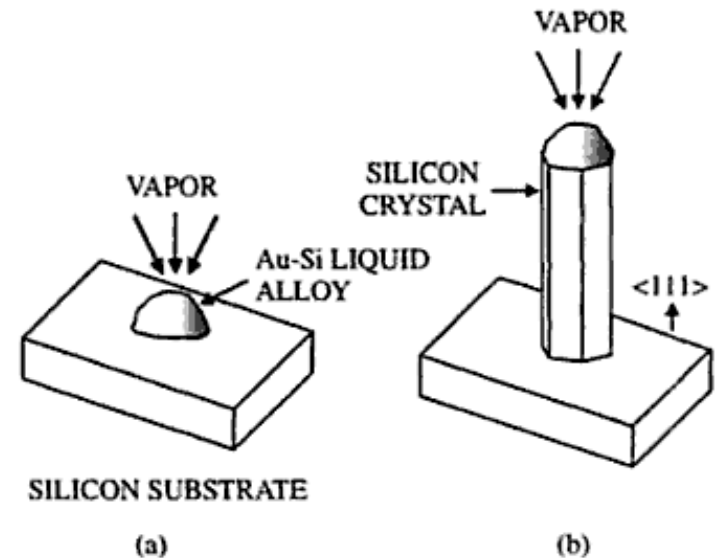


Vapor (Solution) – Liquid – Solid Growth: VLS (SLS)

- Addition of a third phase (“impurity or catalyst”) to confine growth to a specific direction
- Growth species are “trapped” in the catalyst, then precipitating on the growth surface
- Differs from VS (LS) because:
 - Growth is not mediated by dislocations
 - Growth can be fast even on low energy facets

- Growth steps:

1. Formation of the droplet
2. Vaporization of the growth species
3. Diffusion of the growth species from vapor to the droplet surface (preferential absorption occurs here, accommodation coefficient is unity)
4. Diffusion of the growth species from the LV interface to the interior of the droplet
5. Precipitation of the excess at the surface droplet-substrate



Vapor (Solution) – Liquid – Solid Growth: VLS (SLS)

Silicon Nanowires: A Review on Aspects of their Growth and their Electrical Properties

By Volker Schmidt,* Joerg V. Wittemann, Stephan Senz, and Ulrich Gösele

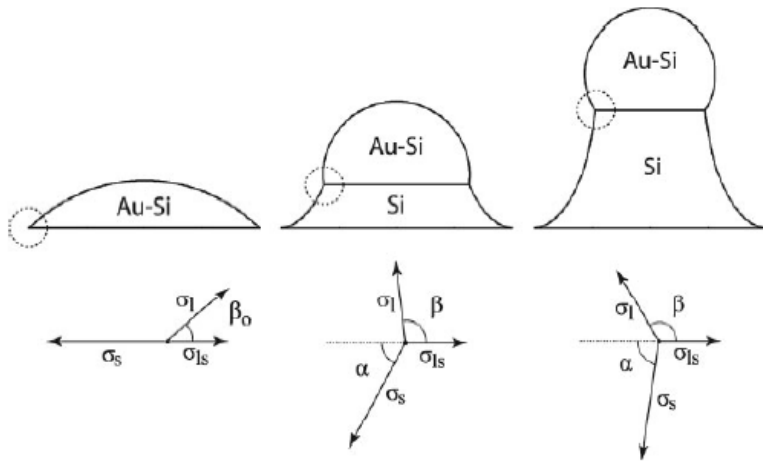


Figure 7. Schematic development of the droplet and wire shape in the initial phase of VLS wire growth. The shape corresponds to the calculated shape assuming $\sigma_s = 1.24 \text{ J m}^{-2}$, $\sigma_s = 0.85 \text{ J m}^{-2}$, and $\sigma_{ls} = 0.62 \text{ J m}^{-2}$. Below, the corresponding equilibrium balance of surface forces (at the left edge of the droplet) is indicated. Note that the horizontal force components add up to zero.

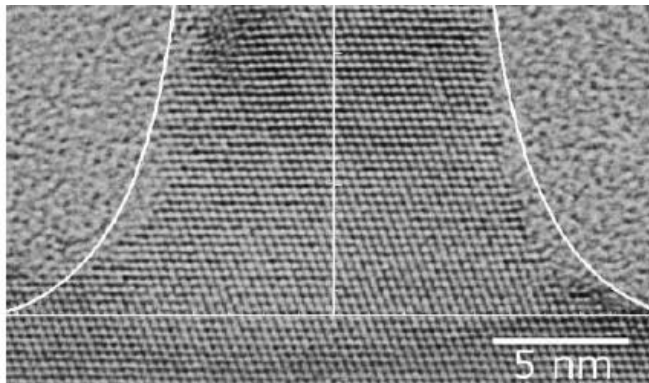


Figure 8. Transmission electron microscopy image of an epitaxially grown Si nanowire. The white line corresponds to the calculated shape assuming $\sigma_s = 1.24 \text{ J m}^{-2}$, $\sigma_s = 0.85 \text{ J m}^{-2}$, and $\sigma_{ls} = 0.62 \text{ J m}^{-2}$.

with respect to the supersaturation. To conclude, one can expect the growth velocity to generally depend on the interplay between the incorporation and the crystallization processes. On the one hand, this solves the dilemma concerning the discussion on the rate determining step, but on the other hand it renders the process more complicated.

Transforming the rates [atoms s^{-1}] into velocities [m s^{-1}] by multiplying them with $\Omega/(\pi r^2)$, we obtain the incorporation and crystallization velocities. At steady state, the incorporation and crystallization velocities have to be equal, which corresponds to a crossing of the two velocity curves in a velocity versus supersaturation space. The position of this crossing point then defines the steady-state growth velocity v and the steady-state supersaturation $\Delta\mu$. We can then define α , the derivative of the incorporation velocity with respect to the supersaturation at $\Delta\mu$, and ω , the derivative of the crystallization velocity with respect to the supersaturation at $\Delta\mu$. Using these derivatives and performing a Taylor expansion to first order around the crossing point, one can obtain a general expression for the steady-state supersaturation

$$\Delta\mu = \Delta\mu_\infty + \frac{\alpha_1}{\omega_1 - \alpha_1} \frac{2\Omega\sigma}{r}, \quad (10)$$

and the steady-state growth velocity

$$v = v_\infty + \frac{\omega_1\alpha_1}{\omega_1 - \alpha_1} \frac{2\Omega\sigma}{r}, \quad (11)$$

where $\Delta\mu_\infty$ and v_∞ are the steady state supersaturation and the steady state growth velocity at infinite radius, that is, for macroscopic wires. Ω and σ are the volume per atom and the

Vapor (Solution) – Liquid – Solid Growth: VLS (SLS)



VLS GaAs in gold.mp4

Vapor (Solution) – Liquid – Solid Growth: VLS (SLS)

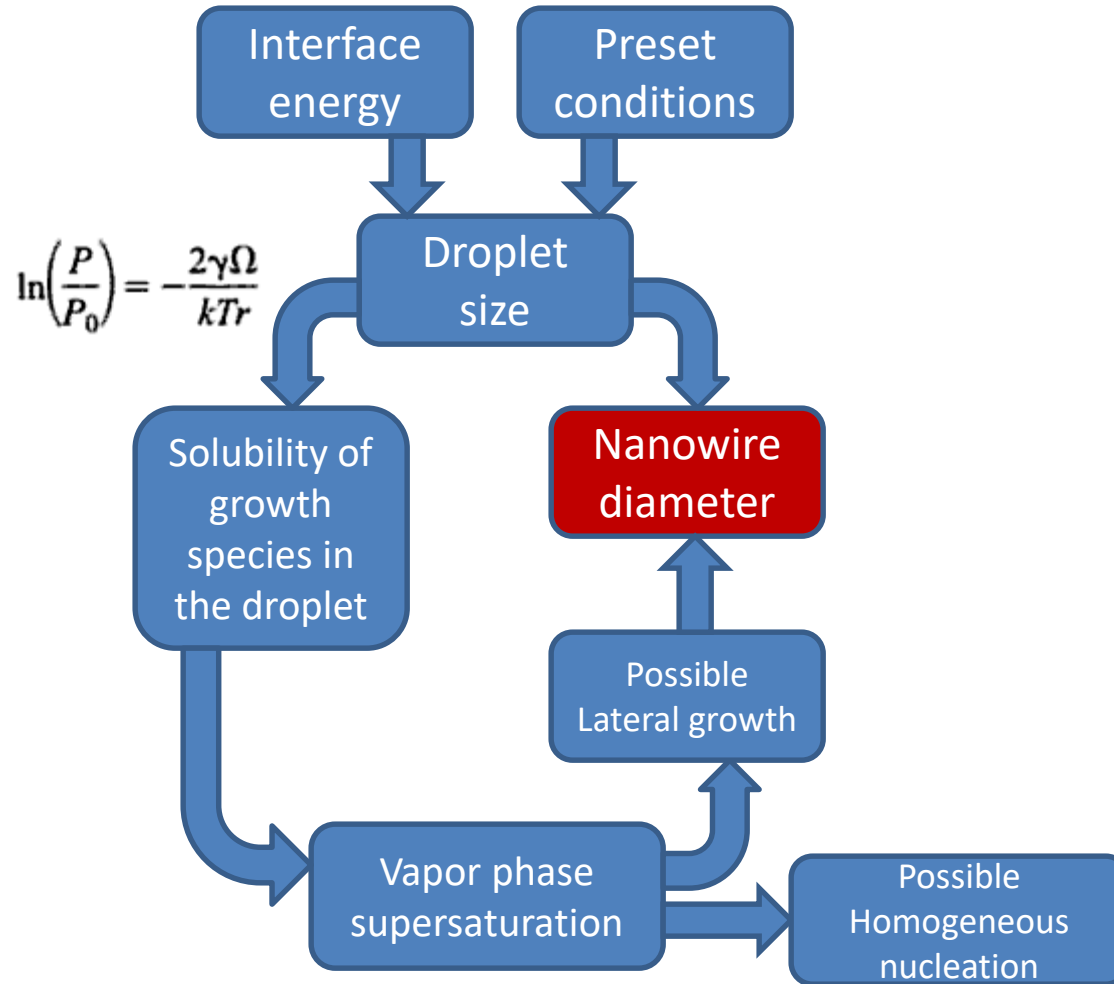
- Main characteristics:

- Very fast growth
- A number of materials can be grown by VLS: Si, Ge, III-V and II-VI compounds
- Growth is stoichiometric
- [111] direction is oftentimes preferred
- Substrate and growth conditions determine the microstructure (single crystal, polycrystal, amorphous)
- Surface is rarely faceted
- **Size is determined by the size of the droplet**

- Main requirements

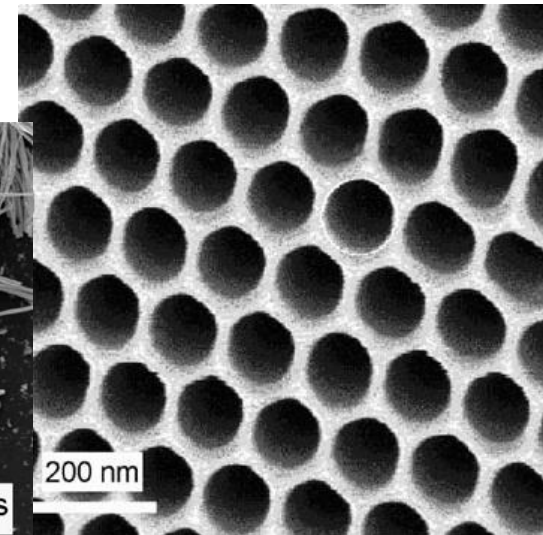
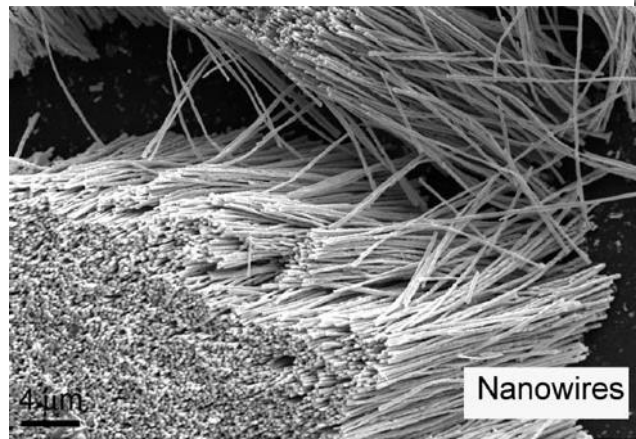
- Catalyst must form a liquid phase with the growth material
- Low vapor pressure of the catalyst (stable liquid droplet)
- Catalyst must be inert
- Interface energy control (determines diameter of the droplet, and therefore both the geometry of the nanowire, and **the solubility**)
- In growth of compounds, the catalyst can be one of the constituents
- S-L interface must be well defined crystallographically (starting substrates are usually single crystals)

Vapor (Solution) – Liquid – Solid Growth: VLS (SLS)

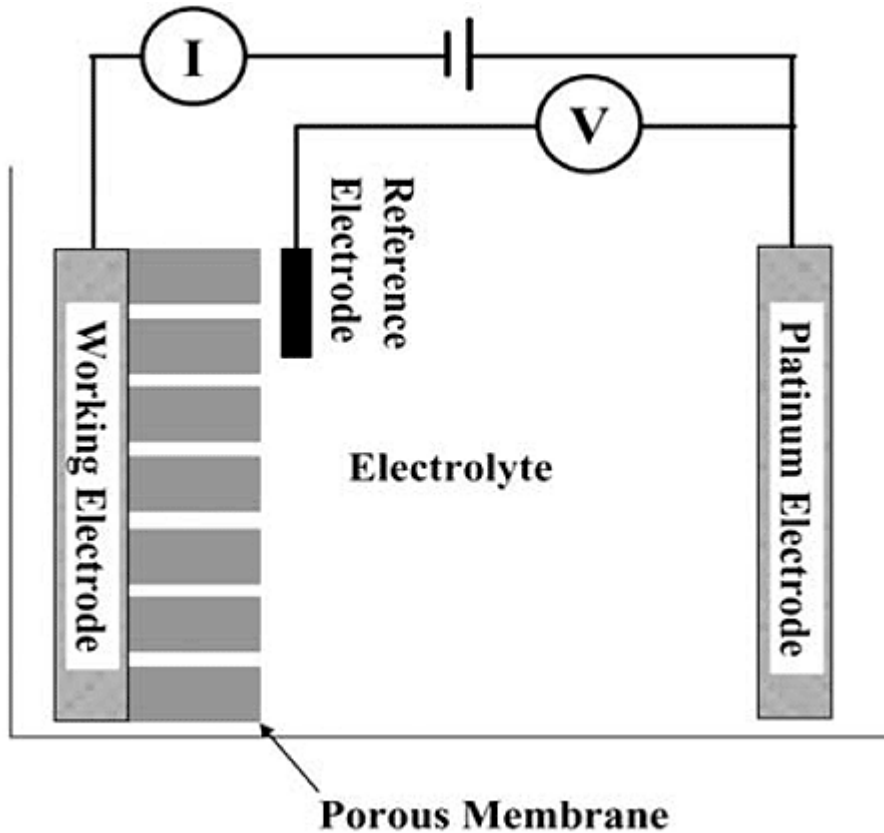


2. Template-based growth

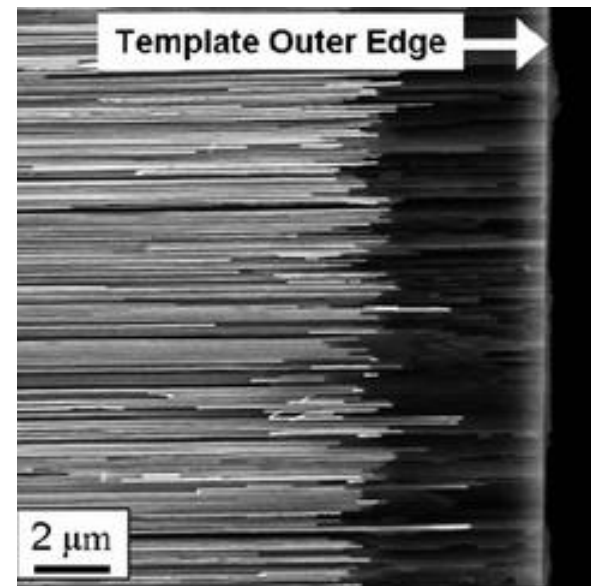
- Filling a template with the growth material
- Templates (even commercially available): anodized alumina membranes, etched polymer membranes, porous silicon, zeolites, carbon nanotubes. Channel density up to 10^{11} pores/cm², pore size down to 10 nm
- Requirements:
 - Compatible with the filling method (electrical insulator, etc.)
 - Chemically inert
 - Easy to remove



Electrochemical deposition

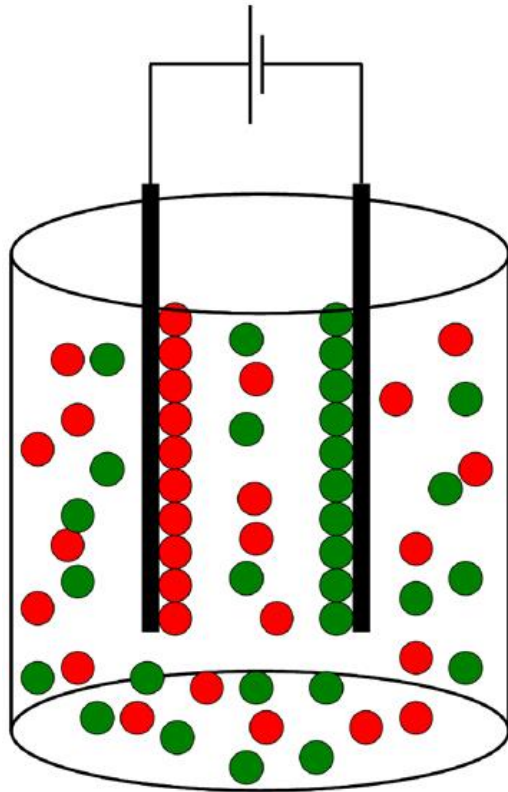


- Only for electrically conductive materials



Other methods of template-based growth

Electrophoresis



● Negatively charged particle

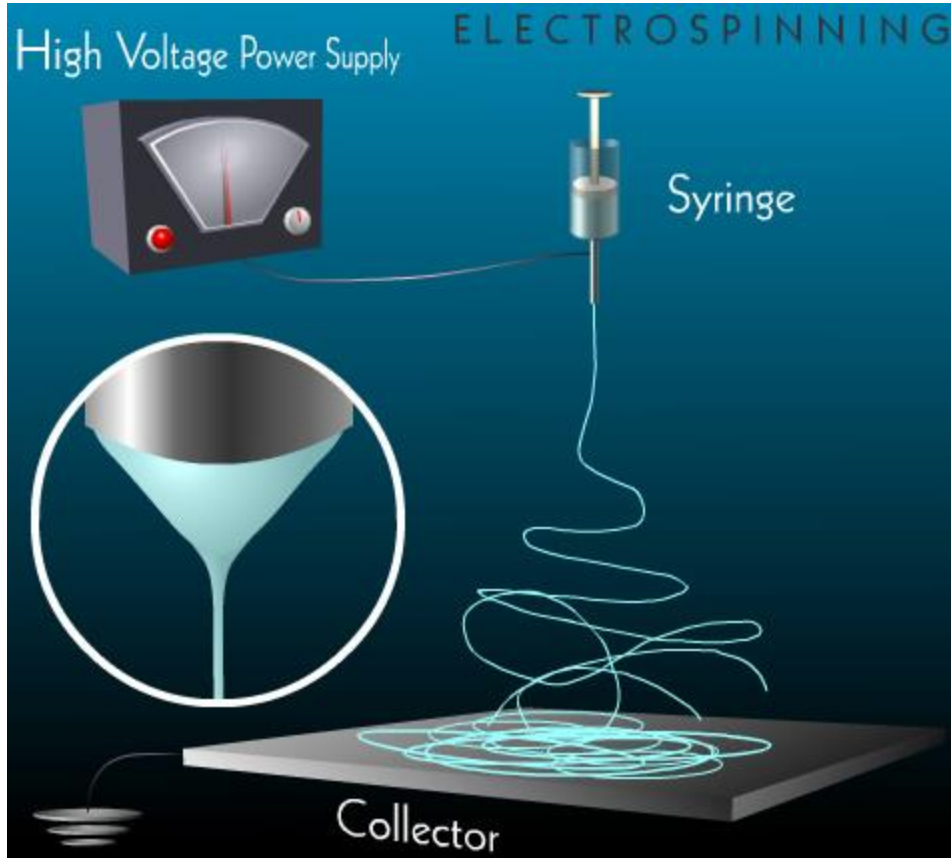
● Positively charged particle

Template filling by

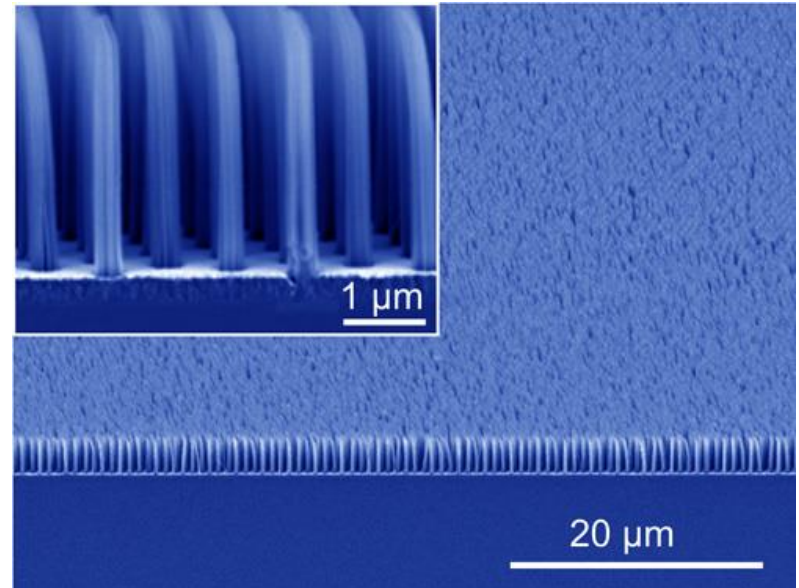
- Colloidal dispersion: sol is attracted within the channels by capillary forces, template is removed and gel is fired
- Molten metals, semiconductors, polymers
- Chemical vapor deposition
- Centrifugation of suspensions

Other methods of growth of nanowires

Electrospinning (polymers or hybrids)

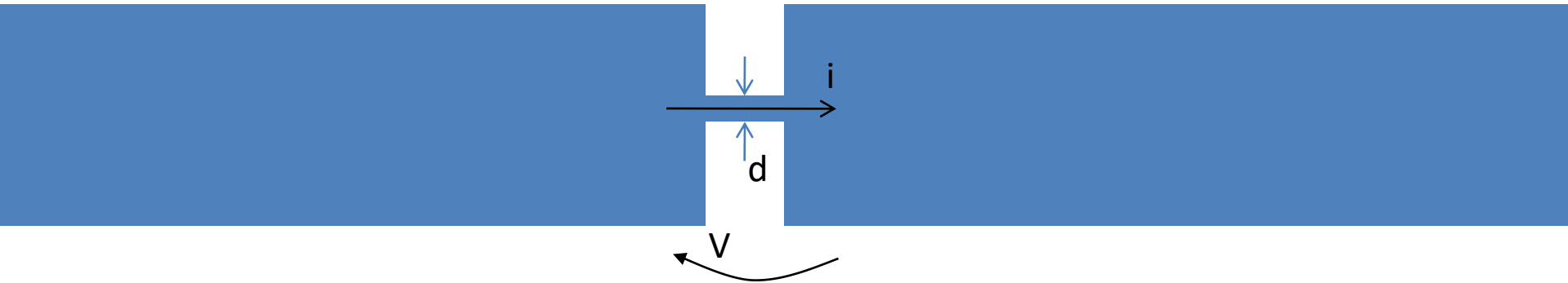


Lithography



Quantum conductance – Landauer Resistance

- Resistance (conductance) at a quantum point contact

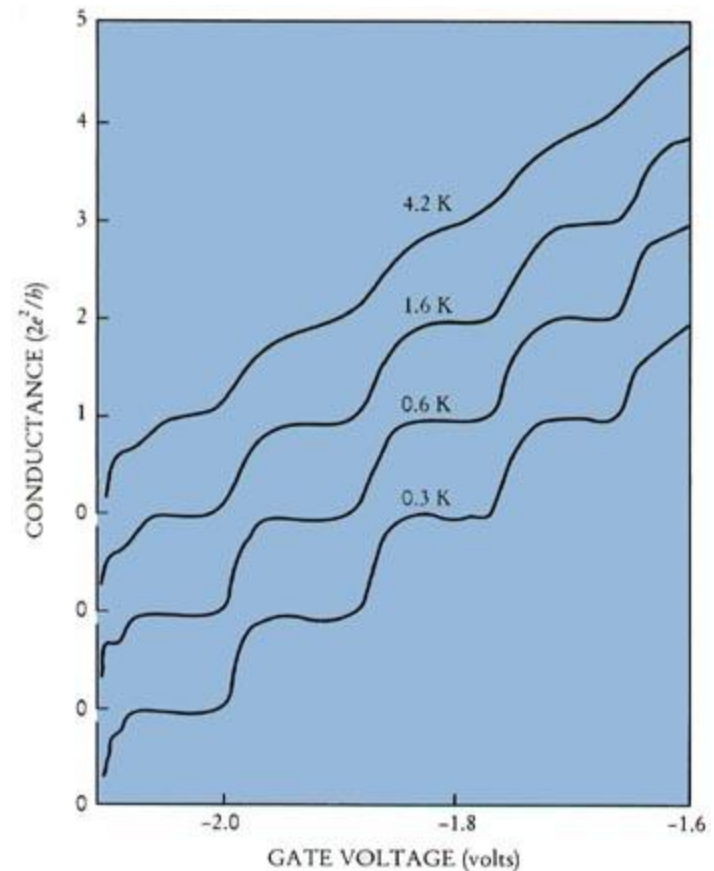
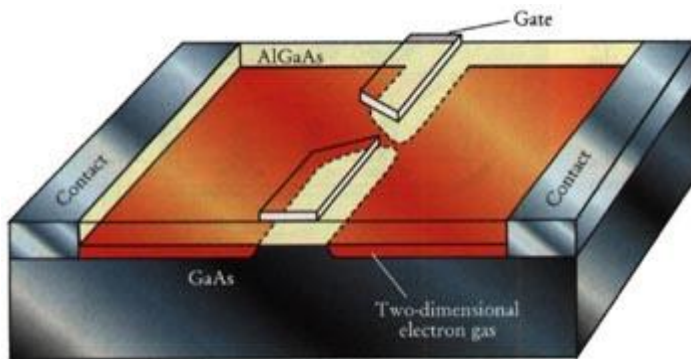


$$R_L = \frac{h}{2e^2}$$

h: Plank's constant
e: electron charge

Quantum conductance – Landauer Resistance

- As the quantum point contact widens continuously, the conductance increases stepwise ($2e^2/h$ steps)



Quantum conductance – Landauer Resistance

- Independent of material properties
- No dissipation occurs (no scattering)
- Reflects the probability of transmission of electrons as a function of the bias
- Upper size limit: mean free path for scattering
- Lower size limit: Fermi wavelength ($2\pi/k_F$), i.e. only one mode available
- Applications: fundamental studies, charge detectors, single electron detectors, quantum computers, STM