Nanowires and Nanorods
One-dimensional structures have been called in different ways: nanowires, nanorod, fibers of fibrils, whiskers, etc. The common characteristic of these structures is that all they have a nanometer size in one of the dimensions, which produces quantum confinement in the material and changes its properties. Figure 1 shows different examples of nanorods and nanowires made in different materials.
Many techniques have been developed to synthesize these structures and can be grouped into four categories:
1- Spontaneous growth
2- Template synthesis
3- Electrospinning
4- Lithography
The first three categories are considered a bottom-up approach while lithography is a top-down approach.
Spontaneous growth results in the formation of nanowires or nanorods due to a preferential crystal growth direction depending on the crystal structure and surface properties of the nanowire materials. His method commonly conducts to single crystal nanowires. On the other hand template synthesis produces polycrystalline structures or even amorphous nanowires.

1. Spontaneous Growth
The spontaneous growth is driven by the reduction of the Gibbs free energy of the system. This reduction commonly means a phase transformation, a chemical reaction or a release of stress. Also it is needed an anisotropic growth: this is a preferential growth of
the crystalline structure in one determined direction. In the case of uniformly sized nanowires can be produced when the crystal grows in one direction whereas no growth is experimented in the other direction. Also in spontaneous growth, impurities on the growth surface can determine the morphology of the nanowire.

Evaporation-condensation growth
Nanowires and nanorods grown by evaporation-condensation are generally single crystals with very few imperfections. Several mechanisms results in anisotropic growth. For example
a) Different facets in the crystal have different growth rate
b) Presence of imperfections in specific crystal directions
c) Preferential accumulation of impurities ion specific facets.

Crystal growth can be considered as a heterogeneous reaction. A typical growth process is sketched in figure 2
The different steps can be summarized as follows:
1- Diffusion of the growth species from the bulk (vapor or liquid phase) to the growing surface. This is considered to occur rapidly enough so usually it is not a limiting factor.
2- Adsorption and desorption of the growth species onto and from the growing surface. This is a process that can be rate limited in the concentration of the growth species is low.
3- Surface diffusion of the adsorbed growth species. During this diffusion stage the growth species can be incorporated into a growth site and contribute to the crystal growth or escape from the surface.
4- Surface growth by irreversible incorporation the absorbed growth species in the crystal.
5- If a byproduct of a chemical reaction is produced, desorbs from the surface. Then the growth species can adsorb again and the growth process continues.
6- Byproduct chemical diffuses away from the surface.
For most crystal growth, the rate limiting step is either step 2 or step 4. When step 2 is the rate limiting process, the growth rate is determined by condensation rate given by the factor $J$ (atoms cm$^{-2}$ s$^{-1}$)

$$J = \frac{\alpha \sigma P_0}{\sqrt{2\pi m kT}}$$

where $\alpha$ is the accommodation coefficient, $\sigma = \frac{(P - P_0)}{P_0}$ is the supersaturation of the growth species, $P_0$ is the equilibrium vapor at temperature $T$, $m$ is the mass of the growth species and $k$ is the Boltzmann constant.

The growth rate increases linearly with the growth species concentration. Further increase in this concentration would result in a change from an adsorption limited to a surface limited process. When the surface becomes the limiting factor the growth rate becomes independent of the concentration.

An impinging growth species onto the growth surface can be described in terms of the residence time and/or the diffusion distance before scaping back to the vapor phase. The residence time on the surface is described by

$$\tau_s = \frac{1}{\nu} \exp \left(\frac{E_{des}}{kT}\right)$$

where $\nu$ is the vibrational frequency of the adatom, (typically $10^{12}$ s$^{-1}$) and $E_{des}$ is the desorption energy required for the growth species escaping back to the vapor. While residing in the surface, the growth species will diffuse in the surface with coefficient $D_s$ given by

$$D_s = \frac{1}{2} a_0 \nu \exp \left(-\frac{E_s}{kT}\right)$$

$E_s$ is the activation energy for surface diffusion and $a_0$ is the size of the growth species. So the mean diffusion distance $X$ for a growth species from the site of incidence is

$$X = \sqrt{2} D_s \tau_s = a_0 \exp \left(\frac{E_{des} - E_s}{kT}\right)$$

In a crystal surface, if the mean diffusion distance is much larger than the distance between growth centers, all adsorbed growth species will be incorporated in the crystal structure. In this case the accommodation coefficient will be $1$. On the other hand, if the diffusion distance $X$ is much smaller than the distance between growth sites, the growth species will return to the vapor and the accommodation coefficient will be zero. The accommodation coefficient is dependent on the desorption energy, the activation energy of surface diffusion and on the density of growth sites.

The growth sites can be understood as the number of broken or dangling bonds of the atoms in the surface. The broken bonds will be the sites where the growing species will be incorporated to the surface for a crystal growth.

All crystal facets can be characterized in three categories depending on the number of dangling periodic bond chains in a facet. These categories are flat surface, stepped surface and kinked surface. The number of periodic broken bonds chains can be understood as the number of broken bonds per atom on a given facet.

To exemplify the process let us imagine that we have a simple cubic crystal. Each atom will have a coordination number of 6 (this is 6 chemical bonds). If an atom is adsorbed...
in the surface it will diffuse randomly with a characteristic diffusion distance \( X \) defined above. If it is adsorbed in a flat (terrace) surface, it would form one chemical bond. Such atom is called an “adatom”. This atom will form one bond with the surface and it is considered an unfavorable energy state. Under this condition it will diffuse in the surface. If the adatom does not find a growth site (this is a more energetically favorable location in the surface) it will return to the bulk solution/vapor phase (figure 3a). If in its diffusion path the adatom finds a ledge or a ledge-kink in the surface it can form a double (ledge) or a triple (ledge-kink) chemical bond. In this situation the energy configuration is more favorable and the atom is incorporated to the crystal (figure 3b). The growth of a flat surface is due to the advancement of the steps (or ledges). For a given crystal facets and given growth condition, the growth rate will be dependent on the step density. A misorientation will result in an increased density of steps and consequently will lead to a high growth rate. An increased step density would favor the irreversible incorporation of adatoms by reducing the surface diffusion distance between the impinging site and the growth site, before adatoms escape back to the vapor phase.

Vapor-Liquid-Solid and Solution-Liquid-Solid growth (VLS and SLS)
In the VLS growth, a second phase material, commonly referred as either impurity or catalyst is purposely introduced to direct and confine the crystal growth. A catalyst forms a liquid droplet by itself or by alloying with growth material during the growth, which acts as a trap of growth species. Enriched growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in one-directional growth. The requirements for VLS growth are:

- The catalyst or impurity must form a liquid solution with the crystalline material to be grown at the deposition temperature.
- The distribution coefficient of the catalyst or impurity must be less than unity at the deposition temperature.
- The equilibrium vapor pressure of the catalyst or impurity over the liquid droplet must be very small to avoid (or minimize) evaporation of the catalyst in the droplet.
- The catalyst or impurity must be chemically inert.
- The interfacial energy plays an important role; the wetting characteristics influence the diameter of the nanowire. For a given volume of the droplet, a small wetting angle results in a large growth area and a large diameter nanowire.
For a compound nanowire growth, one of the constituents can serve as the catalyst.

For a controlled unidirectional growth the solid-liquid interface must be well defined crystallographically.

Figure 4 shows the principal steps in the VLS growth technique. In a first step, in a well defined oriented crystal surface the growth initiates with a liquid droplet nucleation that starts the unidirectional growth.

Let us take the growth of Si with gold as catalyst as an example to illustrate the VLS technique. A thin layer of Au is sputtered in the surface of Si and annealed at a temperature above the eutectic point of the Si-Au system. During the annealing Si and Au react to form a liquid mixture which forms a droplet on the Si surface. During the growth an equilibrium composition is achieved as determined by the phase diagram of the binary system. When the Si is evaporated from the source and preferentially condensed in the liquid droplet, it will become supersaturated with Si. The supersaturated Si will diffuse in the droplet to the liquid-solid interface resulting in a growth of the solid phase. The growth species (Si) is adsorbed in the vapor-liquid interface, incorporated in the liquid, diffuse to the liquid-solid surface and finally incorporated in the solid phase. The material transport is diffusion controlled and occurs essentially under isothermal conditions.

Solution-Liquid-Solid Growth (SLS)

In general it is necessary a high temperature to produce the VLS growth. An alternative is the SLS method developed by Buhro et al.
and used initially for the synthesis of InP, InAs and GaAs nanowires.
Let us take the growth of InP nanowires as an example. The precursor used is typically an organometallic compounds as \( \text{In(t-Bu)}_3 \) and \( \text{PH}_3 \) which are dissolved into a hydrocarbon solvent. In the solution the precursors reacts to form In and P compounds for the growth with the following reaction:

\[
\text{In(t-Bu)}_3 + \text{PH}_3 \rightarrow \text{InP} + 3(t-Bu)H
\]

Indium metal functions as the catalyst for the growth of InP nanowires. In melts and forms liquid droplets. Both P and In dissolve into the droplets and precipitate to form the InP nanowires. It was found that the nanowires are predominantly <111> similar to VLS method. Figure 5 (from Trentler et al, Science 270, 1791, 1995) shows the similarities and differences between the VLS and SLS methods.

2. Template based synthesis
This is a general method that can be used to grow nanorods and nanowires. Various templates with nanometer size channels have been explored for the template growth. The most commonly used are anodized alumina membranes, radiation track etched polymer membranes, nanochannel array glass, radiation track etched mica and mosoporous materials.

Alumina membranes with uniform parallel porous structure are made by anodic oxidation of Al in solutions of different acids. The pores are typically arranged in a hexagonal array and can achieve densities as high as \( 10^{11} \) pores per square centimeter. Polycarbonate membranes are made by bombardment a non-porous polycarbonate sheet with a thickness 6 to 20 microns with nuclear fission fragments to create damage tracks that are subsequently chemical etched. The pore distribution in this case is random with a typical density up to \( 10^9 \) pores per square centimeter.

Different materials have different synthesis or fabrication methods. In all cases the templates are intended to provide a regular array of sites with nanometer dimensions to guide the growth of nanowires or annorods in an organized fashion. Figure 6 shows several examples of such nanometer templates.

In addition to the pore size and distribution the template material must meet certain requirements. For example an electrical insulator is required for a template used in electrochemical deposition. Also, template materials should be chemically and thermally inert.

Figure 6: examples of nanometer size templates. Left cross section of anodized Al. Center, Al membrane. Right. 450 nm pores in glass
Electrochemical deposition
Also known as electrodeposition, this method involves an electrolysis process that results in the deposition of solid material in an electrode. The process involves:
- oriented diffusion of charged growth species through a solution with an external electric field.
- reduction of the charged growth species at the growth surface that also is one of the electrodes of the electrolysis process.

When electrodeposition (also known as electroplating) is confined inside the pores of template membranes, nanocomposites are produced. If the template is removed, nanorods or nanowires are prepared.

When a solid is immersed in a polar solvent or an electrolyte solution, surface charge will be developed. At an interface between an electrode and an electrolyte solution, an oxidation or reduction reaction occurs accompanied by a charge transfer through the interface until the equilibrium is achieved. For a given system, the electrode potential or surface charge density is described by the Nernst equation

\[ E = E_0 + \frac{R_g T}{n_i F} \ln(a_i) \]

\( E_0 \) is the electrode potential when the activity \( a_i \) of the ions is unity. \( R_g \) is the gas constant, \( F \) the Faraday’s constant and \( T \) the temperature.

When the electrode potential is more negative (higher) than the energy level of vacant molecular orbital in the electrolyte solution, electrons will transfer from the electrode to

![Figure 7](image-url)
the solution accompanied with dissolution or reduction of the electrode. The reaction stops when the equilibrium is achieved.

When two electrodes of different materials immerse into one electrolyte solution, each electrode will establish equilibrium with the solution. This equilibrium is broken when the electrodes are connected to an external circuit. Since different electrodes have different electrode potentials, this difference will drive electrons from the electrode with higher electrode potential to the lower one. To illustrate this effect let us consider Cu and Zn electrodes immersed in an aqueous solution. The Cu electrode has a more positive electrode potential (0.34 eV) than that of the Zn (-0.76 eV). In the external circuit electrons flow from the negative electrode (Zn) to the more positive (Cu). At the Zn/solution interface the following reaction takes place

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$$

These electrons flow through the external circuit to another electrode (Cu). At the same time Zn continues to dissolve from the electrode into the solution. At the Cu/solution interface a reduction reaction takes place resulting in the deposition of Cu

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$$

This process ends when an equilibrium is reached. The Cu electrode potential decreases due to a decrease in copper ion activity in the solution whereas the Zn electrode potential increases due to an increased activity of Zn ions in the solution as both electrochemical reactions takes place. This is a typical galvanic cell in which chemical potential is converted into electricity. This process can be altered or even reversed when an external electric field is introduced to the system.

When an electrical field is applied to two dissimilar electrodes, the electrode potentials can be changed so that electrochemical reactions at both electrode-solution interfaces are reversed and the electrons flow from a more positive to a more negative electrode. This process is called electrolysis and converts electrical energy to chemical potential. In the electrolytic deposition the electrode connected to the positive side of the power supply acts as the anode where the oxidation takes place. The electrode connected to the negative side of the power supply acts as the cathode where the reduction reaction takes place accompanied by deposition. Sometimes electrolytic deposition is also called cathode deposition.

A typical electrolytic process composes of a series of steps:

a- Mass transfer through the solution from one electrode to another
b- Chemical reactions at the interfaces between electrode-solution
c- Electrons transfer at the electrode surfaces and through the external circuit
d- Other surface reactions such as adsorption, desorption or recrystallization.

Templates with the desired channels are used to grow nanowires by electrochemical deposition. Figure 8 shows an experimental setup for this process. The template is attached to the cathode. The anode is placed parallel to the template. When the electric field is connected, nanowires grow in the pores of the template. The figure also schematically shows the current density at different deposition stages when a constant electric field is applied.