One-dimensional structures have been called in different ways: nanowires, nanorod, fibers of fibrils, whiskers, etc. These structures have a nanometer size in one of the dimensions, which produces quantum confinement in the material and changes its properties. Many techniques have been developed to synthesize these structures and can be grouped into four categories: Spontaneous growth, Template synthesis, Electrospinning, Lithography.
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:

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.

Impurities on the growth surface can determine the morphology of the nanowire.

**Evaporation-condensation growth**

Typical growth process

![Diagram of growth process](image-url)
Nanowires and nanorods: Spontaneous Growth

For most crystal growth, the rate limiting step is either adsorption/desorption or surface growth. When step adsorption/desorption is the rate limiting process, the growth rate is determined by condensation rate given by the factor $J$ (atoms cm$^{-2}$ s$^{-1}$)

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

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

$$\tau_s = \frac{1}{\nu} \exp\left(\frac{E_{\text{des}}}{kT}\right)$$
While residing in the surface, the growth species will diffuse in the surface with coefficient \( D_s \) given by

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

So the mean diffusion distance \( X \) for a growth species from the site of incidence is

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

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: the accommodation coefficient will be 1.

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.

\[
J = \frac{\alpha \tau P_0}{\sqrt{2\pi mkT}}
\]
Crystal facets can be characterized in three categories depending on the number of dangling periodic bond chains in a facet: 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.

Example: cubic crystal. Each atom have a coordination number of 6

If it is adsorbed in a flat surface, it would form one chemical bond. This atom is considered a unfavorable energy state. It will diffuse in the surface. If the adatom does not find a growth site it will return to the bulk solution/vapor phase
Nanowires and nanorods: Spontaneous Growth

If in its diffusion the adatom finds a ledge or a ledge-kink in the surface it can form a double (ledge) of a triple (ledge-kink) chemical bond. In this situation the energy configuration is more favorable and the atom is incorporated to the crystal.

The surface grows by the continuous advancement of the edge due to the incorporation of the atoms in the ledge.
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 must form a liquid solution with the crystalline material to be grown at the deposition temperature.
* The distribution coefficient of the catalyst must be less than unity at the deposition temperature
* The equilibrium vapor pressure of the catalyst over the liquid droplet must be very small
* The catalyst must be chemically inert
* 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.
Nanowires and nanorods: Spontaneous Growth

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.

Growth occurs in a preferential crystal orientation.
Solution-Liquid-Solid Growth (SLS)

It is necessary a high temperature to produce the VLS growth. An alternative is the SLS method. Example: growth of InP nanowires. The precursor is an organometallic compounds as \( \text{In} (t\text{-Bu})_3 \) and \( \text{PH}_3 \) dissolved into a hydrocarbon solvent. In the solution the precursors reacts to form \( \text{In} \) and \( \text{P} \) compounds for the growth with the following reaction:

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

Indium metal functions as the catalyst for the growth of InP nanowires. It was found that the nanowires are predominantly <111> similar to VLS method.
Nanowires and nanorods: Template based synthesis

This method 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.
Electrochemical deposition, electrodeposition or electroplating

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

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

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 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.
Nanowires and nanorods

Example 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.

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.
Nanowires and nanorods

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.