

# Nanotechnology

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# 1 Introduction

## 1.1 Definitions

We should start our study of nanotechnology by defining the concepts of nanoscience and nanotechnology:

**Nanoscience:** Nanoscience studies the phenomena occurring in systems in which at least one of the dimensions is nanometric, from 1 to 100 nm

**Nanotechnology:** Design, fabrication, and use of nanometric structures, by controlling its form and crystalline structure, in order to obtain designed materials with the desired properties

## 1.2 Historical introduction

In 1968, Alfred Cho and John Arthur from Bell Labs pioneered a groundbreaking technique known as Molecular Beam Epitaxy. This method allowed for the precise deposition of individual atomic layers on surfaces, revolutionizing material science and semiconductor technology. Over a decade later, in 1981, Gerd Binnig and Heinrich Rohrer made another monumental contribution by developing the Scanning Tunneling Microscope (STM). This remarkable invention could display images of individual atoms and earned them the Nobel Prize for their achievements.

The year 1985 marked a significant discovery by Robert Curl, Harold Kroto, and Richard Smalley, who identified buckyballs—spherical molecules with a diameter of approximately one nanometer. These molecules opened new frontiers in nanotechnology. Just a year later, in 1986, K. Eric Drexler published *\*Engines of Creation\**, a visionary book that introduced the world to the potential of nanotechnology and inspired future innovations in the field.

In 1989, Donald Eigler of IBM demonstrated unprecedented precision by spelling the letters "IBM" using individual atoms, showcasing the potential for manipulation at the atomic scale. Shortly thereafter, in 1991, Sumio Iijima from NEC Japan discovered carbon nanotubes, which have since become a cornerstone of nanotechnology due to their remarkable strength and electrical properties.

Progress continued in 1998, when researchers at Delft University of Technology in the Netherlands created a transistor using a single carbon nanotube, illustrating the potential for miniaturized electronics. A year later, in 1999, James Tour and Mark Reed demonstrated that individual molecules could function as switches, paving the way for molecular-scale devices.

Finally, in 2000, Donald Eigler and his team achieved another milestone by creating a quantum mirage. By placing a magnetic atom at the focal point of an elliptical arrangement of atoms, they induced the appearance of a mirage atom at the opposing focus, enabling wireless transmission of information. These breakthroughs collectively represent pivotal moments in the development of nanotechnology, highlighting the extraordinary progress made over just a few decades.

## 1.3 Nanotechnology today

In this day and age, nanotechnology is actually all around, for instance, the face masks FFP2 have a nanofiber coating, or tennis rackets are made of carbon nanotubes in order to increase its resistance.



## 1.4 Semiconductor nanostructures

We should also discuss the concept of heterojunctions, junctions made of 2 dissimilar semiconductors; that way we will have new degrees of freedom. There will be differences in the band energy, and the alignment of the valence and conduction bands.

We will have different kinds of alignments given by Anderson's law.

The conduction band offset  $\Delta E_c$  is given by the difference in electron affinities of the two materials  $\chi$

$$\Delta E_c = \chi_2 - \chi_1 \quad (1)$$

The valence band offset  $\Delta E_v$  is determined using the bandgap energies  $E_g$  and the conduction band offset

$$\Delta E_v = E_g^1 - \Delta E_c - E_g^2 \quad (2)$$

We will need the heterojunctions to be monocrystalline, the reticle of the different materials has to approximately coincide, if not, impurities such as dislocations or cracks will prevail.

## 1.5 Phenomena in the nanoscale

Under a certain characteristic length, quantum effects rule the behaviour of a material.

Furthermore, materials interacting strongly with their environment show macroscopical quantum effects if they are little enough. For instance, the quantum hall effect or the fact that conductivity takes quantized values  $\sigma = \nu \frac{e^2}{h}$

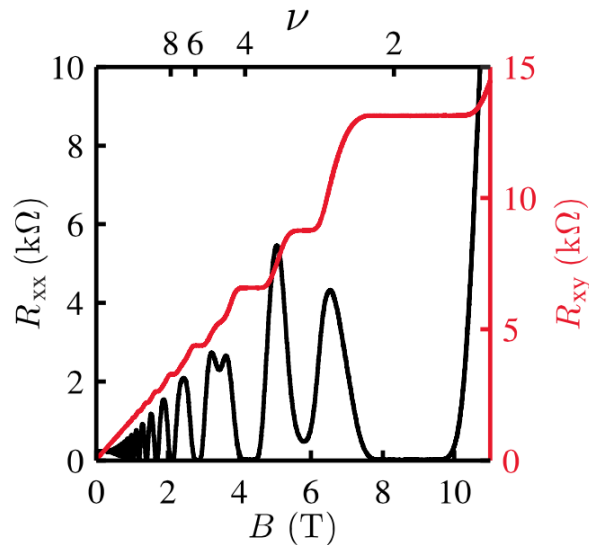


Figure 1: Quantum hall effect

## 2 Quantum confinement

Confinement refers to reducing dimensions in our system. To obtain a 2D system we have to reduce one of the dimensions to nanoscale, that's a 1D confinement, which leads to, for instance, quantum wells. If we confine the 3 dimensions, we obtain a 0D system, with extremely restricted movement for the electrons, those are the so called quantum dots.

### 2.1 Quantum dots

Quantum dots are semiconductor particles whose band gaps grow as they decrease in size.

$E_g = k \frac{1}{\lambda}$ , if the gap grows the wavelength decreases. The electronic transitions vary with the size of the quantum dot because of the discretization of the energy states.

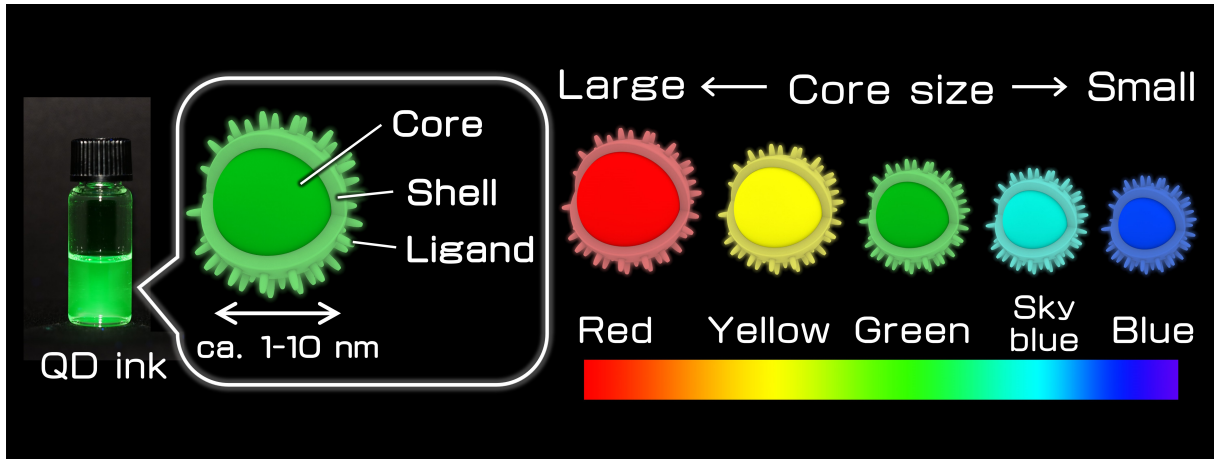


Figure 2: Figure showing the relation between size and wavelenght

### 2.2 Not confined electrons vs confined electrons

Let's consider an electron in a 1D box of length  $L$ .

Let's also consider that the potential  $V(x)$  of the time independent Schrödinger equation is 0 in the box and infinite outside of the box.

In this particular case the probability of finding the wave function in the box is 1.

Our wave function will have the form

$$\Psi(x) = A \sin(kx) \quad (3)$$

and since the function has to go to 0 at the walls of the box

$$k = \frac{n\pi}{L} \quad (4)$$

Now let's consider the effects of confinement, we can see them studying the case of the finite potential well.

In this case the potential outside of the box is  $V(x) = V_0$  and our wave function will have to satisfy the following equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = (E - V_0) \Psi \quad (5)$$

and making the substitution  $\alpha = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$  we find a solution of the following kind

$$\Psi = C e^{\alpha x} + D e^{-\alpha x} \quad (6)$$

and the energy eigenvalues associated to those functions are

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \quad (7)$$

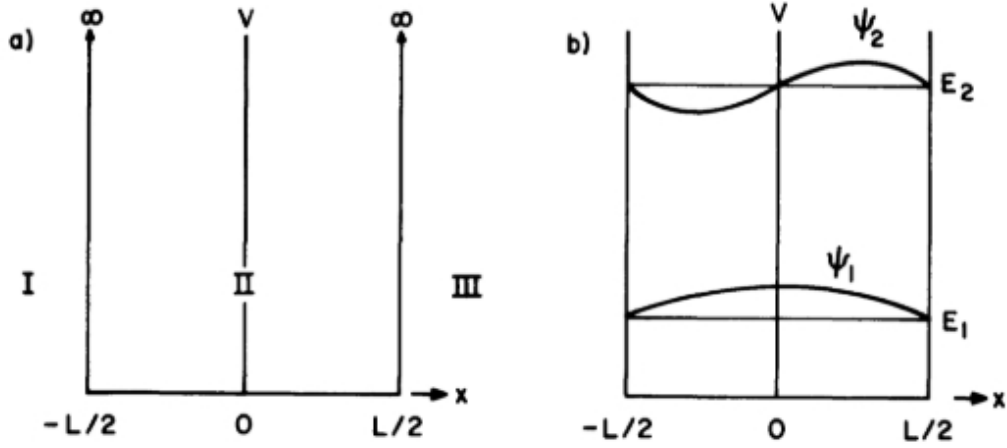


Figure 3: Potential diagram for the infinite and finite potential well

In the case of the finite potential well we can see how our wave function goes beyond the box, the energy levels of the confined electron are therefore lower than those of the infinite potential well.

### 2.3 Fermi Gas

A fermi gas is a state of matter, an ensemble of many non interacting fermions. As a result of Pauli's exclusion principle fermions tend to avoid occupying the same quantum states and are distributed uniformly in a given region.

We find fermi gases in regions of very low temperatures and high densities.

The delocalized valence electrons moving freely around positive ions are an example of a fermi gas. Let's consider the sample is inserted in a cube of side  $L$ , so that the cube's volume is  $V = L^3$ , the distance  $d$  between two adjacent electrons is  $2\pi/L$ .

For a free particle

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \quad (8)$$

with  $K_i = \frac{2n_i\pi}{L}$  At  $T = 0K$  the fermi gas electrons occupy all the reticular points of the momentum space at a distance  $k_F$  (fermi's wave vector) from the origin  $k = 0$ , which corresponds to Fermi's energy

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad (9)$$

Fermi's level can therefore be understood as the surface of Fermi gas at  $T = 0K$ .

The three dimensional isotropic and non relativistic fermi gas is known as the Fermi sphere. In a Fermi sphere the energy goes from  $E = 0$  to  $E = E_F$  at Fermi's surface, the same will happen for the Fermi gas in 1 dimension and 2 dimensions.

When we have a confinement in 1 or 2 dimensions the conduction electrons are distributed at the corresponding wells of potential under the Fermi level in the directions of confinement, according to their respective degenerations.

The nature of the dimensionality and confinement associated to a structure has an important effect on its properties.

$$n = \frac{V}{d} = \int_{E_1}^{E_2} g(E) dE \quad (10)$$

At  $T = 0K$ , all the electrons are dispersed isotropically.

The number of conduction electrons with a certain energy depend on the value of that energy and the dimensionality of the space.

In a sphere of radius  $k_F$  and volume  $V = \frac{4}{3}k_F^3$  and the distance between two adjacent electrons is  $d = (\frac{2\pi}{L})^3$ , then

$$n = \left(\frac{L}{2\pi}\right)^3 \frac{4}{3}\pi K_f^3 \quad (11)$$

and the number of states between  $k$  and  $k+dk$  is

$$\frac{dn}{dk} = \left(\frac{L}{2\pi}\right)^3 4\pi k_F^2 \quad (12)$$

finally we can define the density of states as

$$\rho(E) = \frac{dn}{dE} \quad (13)$$

## 2.4 Density of states

Let's study the density of states for the different dimensionalities in semiconductor devices

### 2.4.1 Density of states in 3D

In 3 dimensions we don't have any confinement and the particles are free. We take a generic wave vector  $k$

$$|\vec{k}| = k = \sqrt{k_x^2 + k_y^2 + k_z^2} \quad (14)$$

then we can write

$$n = 2 \frac{4}{3} \pi k^3 \frac{1}{\left(\frac{2\pi}{L}\right)^3} \frac{1}{L^3} = 2 \frac{4\pi k^3}{3(2\pi)^3} \quad (15)$$

and the density of states can be written as

$$\rho(E) = \frac{dn}{dk} \frac{dk}{dE} = 2 \frac{4\pi k^2}{(2\pi)^3} \frac{dk}{dE} \quad (16)$$

the energy levels are given by

$$E = E_c + \frac{\hbar^2 k^2}{2m^*} \quad (17)$$

from which we can find  $k$  as a function of  $E$

$$k = \sqrt{\frac{2m^*(E - E_c)}{\hbar^2}} \quad (18)$$

so now we can write

$$\frac{dk}{dE} = \sqrt{\frac{2m^*}{\hbar^2}} \frac{1}{2} \frac{1}{(E - E_c)^{1/2}} \quad (19)$$

and finally we can write the density of states

$$\rho(E) = 2 \frac{4\pi 2m^*(E - E_c)}{(2\pi)^3 \hbar^2} \sqrt{\frac{2m^*}{\hbar^2}} \frac{1}{2} (E - E_c)^{-1/2} \quad (20)$$

which can be rewritten as

$$\rho(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \sqrt{E - E_c} \quad (21)$$

this is the density of states for a three dimensional semiconductor with no confinement

### 2.4.2 Density of states in 2D: Quantum Well

Proceeding in an analogous way we can determine the density of states for a two dimensional system under a 1 dimensional confinement, a quantum well.

In this case since there is confinement in the  $z$  direction  $k = \sqrt{k_x^2 + k_y^2}$

$$n = 2\pi k^2 \frac{1}{\left(\frac{2\pi}{L}\right)^2} \frac{1}{L^2} = \frac{2k^2}{4\pi} \quad (22)$$

and using equations (13) and (17) we end up finding

$$\rho(E) = \frac{m}{\pi \hbar^2} \quad (23)$$

A quantum well confines particles in one dimension, forcing them to occupy a planar region. In semiconductor nanostructures, the energy bands are divided in subbands with energy separations of from tens to hundreds of meV. Those energy separations depend almost exclusively of the sequence of quantum wells and barriers separating them.

This means that within the limits of the fabrication of the nanostructures we can design materials with whichever properties we desire. We can substitute the search for a natural material with the properties we want by designing the adequate sequence of quantum wells and barriers for a material.

#### 2.4.3 Density of states in 1D:Quantum Wire

For a one dimensional system under two dimensional confinement, a quantum wire, we find that the density of states is

$$\rho(E) = \frac{dn}{dE} = \sqrt{\frac{2m^*}{\hbar^2}}(E - E_c)^{-1/2} \quad (24)$$

In a quantum wire the the electron's movement is allowed only along the length of the wire (one-dimensional), while it is confined in the other two dimensions by a potential barrier.

This strong confinement results in discrete energy levels for the electrons in the transverse directions, akin to the quantization in atoms or quantum dots.

#### 2.4.4 Density of states in 0D:Quantum dot

Quantum dots are the most extreme case of dimensionality reduction, all three dimensions are nanometric, resulting in what is known as three-dimensional quantization, or 3D quantization. This reduction leads to discrete energy levels, as the electrons and holes are confined in all three dimensions. The confinement occurs because the quantum dot is surrounded by materials that have very large energy gaps, which prevent the free movement of charge carriers.

As the size of the quantum dot decreases, the energy gap increases. This phenomenon, often referred to as the "quantum confinement effect," is a direct consequence of the reduced size of the structure. Typical quantum dots range in size from 1 to 10 nanometers, with the reduction in size leading to increased energy separation between quantized states.

In a zero-dimensional structure such as a quantum dot, there is no possible free movement in any of the dimensions. Since there is no longer a continuous wave vector (k-space) to fill with electrons, the available states for charge carriers exist only at discrete energy levels. As a result, the density of states for such a structure is described using a delta function, which mathematically represents the discrete nature of the available energy states.

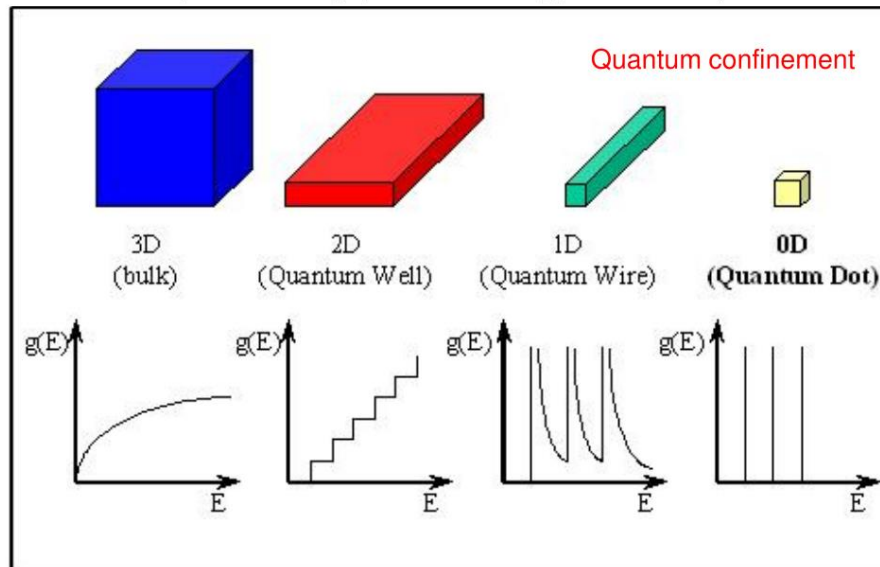
$$\rho(E) = 2\delta(E - E_c) \quad (25)$$

This concept of quantized energy levels and confined charge carriers is at the heart of many applications of quantum dots, including in optoelectronics and nanotechnology, where their unique properties are harnessed for innovative devices such as lasers, solar cells, and quantum computers. The behavior of electrons in quantum dots, confined in all three dimensions, is significantly different from that of bulk materials, and this leads to novel optical and electronic characteristics that can be tailored by simply changing the size of the quantum dot.

## 2.4.5 Graphical summary

# Density of States

(how closely packed energy levels are)





### 3 Growth techniques

Now let's study the different techniques to fabricate our semiconductor nanostructures

#### 3.1 Bottom-up approach

The bottom up approach consists of assembling nanostructures from smaller starting materials, atoms, molecules or clusters.

Forces like van der Waals's, electrostatic forces and different interatomic or intermolecular forces cause this atoms to coalesce into nanometer-sized particles.

This technique is used in the chemical synthesis of nanoparticles.

It has the following advantages:

- 1.The generation of a wide range of nanoparticles with small to large scale sizes.
- 2.An homogeneous particle size distribution.

Generally, bottom-up methods are most attractive for both laboratory and industrial-scale nanomaterial synthesis due to the controllability in size and properties of materials via proper control of the reaction conditions.

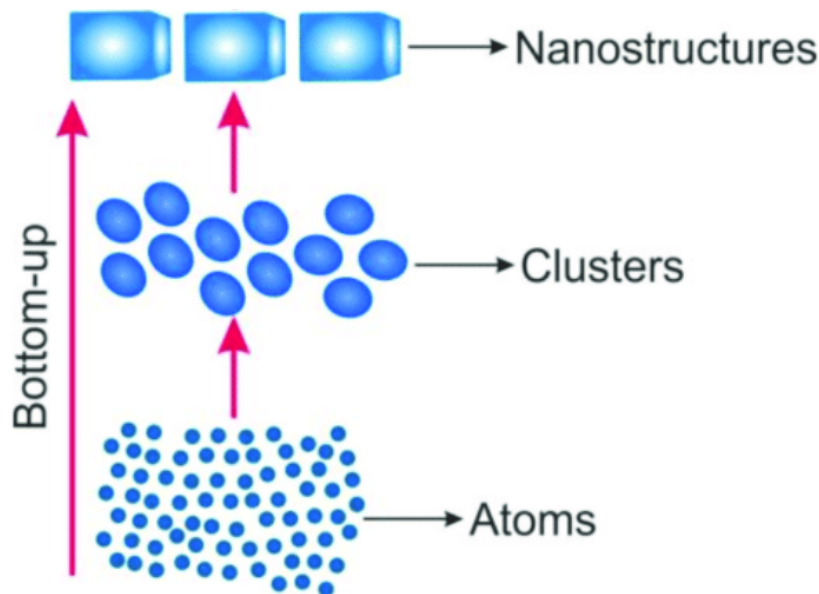


Figure 4: Schematic view of the bottom up approach

#### 3.2 Self Assembly

Self-assembly relies on natural forces and carefully designed environments to guide components into forming desired structures. Among its core principles, the role of template-guided growth and the strategic use of gold nanoparticles are noteworthy.

Template-guided growth using holes involves the use of structured templates, such as holes or patterned surfaces, to influence the arrangement and growth of materials.

These templates act as physical constraints or energy wells, effectively directing the self-assembly process by ensuring that components align in a specific geometry.

The dimensions, spacing, and arrangement of these holes can be carefully adjusted to control the deposition of materials, leading to the formation of structures such as nanowires, thin films, or crystalline networks.

This approach is widely applied in the fabrication of nanostructures for fields like electronics, photonics,

and biosensing.

Gold nanoparticles (AuNPs) play a crucial role as catalysts and directional guides in self-assembly processes. They possess catalytic properties that facilitate chemical reactions or the assembly of materials on their surfaces.

When strategically placed within holes or templates, AuNPs promote directional growth, often inducing anisotropic development in specific crystallographic directions to create structures like nanowires or rods. Additionally, gold's unique optical and electronic properties, including surface plasmon resonance (SPR), can influence the assembly of surrounding components, offering further control over the growth process and enhancing the functionality of the resulting materials.

### 3.3 Epitaxy

Epitaxy refers to a type of crystal growth or material deposition in which new crystalline layers are formed with one or more well defined orientations with respect to the crystalline seed layer. The deposited crystalline film is called epitaxial layer.

One of the main applications of epitaxial growth is in the semiconductor industry, semiconductors can be grown epitaxially on semiconductor substrate wafers.

We will focus on heteroepitaxy, an epitaxy performed with materials that are different from each other. Heteroepitaxial growth can be classified in three different kinds of growth modes: Volmer-Weber, Frank-Van der Merwe, Stranski-Krastanov.

#### 3.3.1 Volmer-Weber

In Volmer-Weber's mode, the interaction of the adsorbed atoms is much stronger among them than with the substrate surface, which leads to the formation of clusters or three dimensional islands. As growth proceeds, these islands expand, widening their volumes, whose height greatly exceeds the thickness of a monolayer, leading to the simultaneous growth of atomic layers with rough surface, this growth is shown in figure (5a)

#### 3.3.2 Frank-Van der Merwe

In Frank-van der Merwe's mode, the atoms adsorbed on the surface have a stronger interaction with the surface, leading to the formation of a complete monolayer before another starts to grow. This layer-by-layer growth mode is often referred as a bi-dimensional growth. This mode of growth is shown in figure (5b)

#### 3.3.3 Stranski-Krastanov

The last mode of growth, called Stranski-Krastanov, is characterized by mixing both previously mentioned. In this mode, the adsorbed atoms begin to grow layer-by-layer. When the critical layer thickness is reached, which value depends on the specific physical properties of each compound, the elastic energy accumulated in the growth relaxes, resulting in the formation of clusters or islands. This mode of growth is shown in figure (5c).

All of these growth modes have their particular applications, and therefore have certain importance, however, when it comes to the fabrication of low dimensional structures, for instance, quantum dots, the growth parameters of the Volmer-Weber mode are determined to control the density, size, and distribution of the islands.

### 3.4 Liquid phase epitaxy

Liquid phase epitaxy is a method to grow semiconductor crystal layers from the melt on solid substrates. A semiconductor is dissolved in the melt of another material.

This method takes place at temperatures below the melting point of the semiconductor we are depositing. When we reach conditions near the equilibrium between the dissolution and the deposition, the deposition of the semiconductor crystal is fast and uniform.

Some of the substrates that are usually used are indium phosphide or other substrates like glass or ceramic.

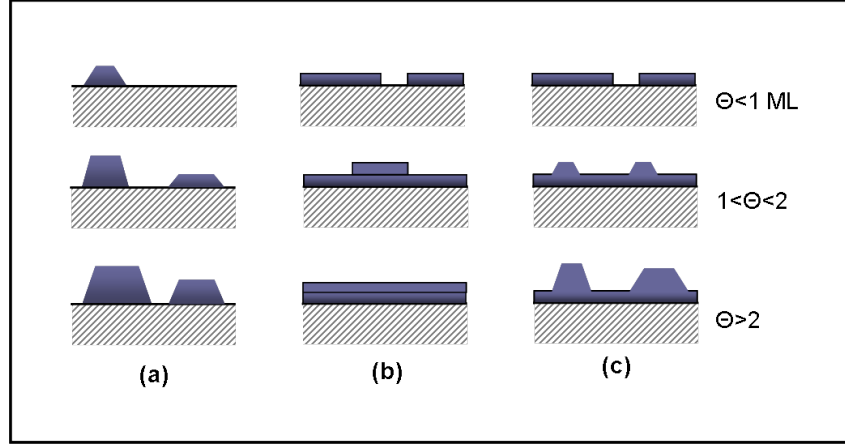


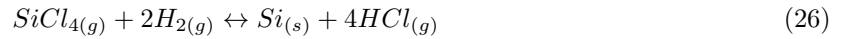
Figure 5: Figure showing the three primary modes of thin-film growing

### 3.5 Vapor phase epitaxy

It is also important to consider homoepitaxy, as in the kind of epitaxy performed with only one material, in this case, a crystalline film is grown on a substrate of the same material.

Homoepitaxial growth of semiconductor thin films are generally done by chemical or vapor phase deposition methods.

For example, silicon is commonly deposited from silicon tetrachloride



This reaction is reversible, and the growth rate depends strongly upon the proportion of the two source gases. Growth rates above 2 micrometres per minute produce polycrystalline silicon.

Another possible reaction used in vapor phase epitaxy is using silane as a base gas:



This reaction occurs at 650 °C

Vapor phase epitaxy (VPE) is often categorized based on the chemistry of the source gases, with notable types including hydride vapor phase epitaxy (HVPE) and metalorganic vapor phase epitaxy (MOVPE or MOCVD).

The reaction chamber used for vapor phase epitaxy may be heated externally by lamps to facilitate the process.

A commonly employed technique for growing compound semiconductors is molecular beam epitaxy (MBE). In this method:

- The source material is heated to produce an evaporated beam of particles.
- These particles travel through an extremely high vacuum to reach the substrate, initiating epitaxial growth.

In contrast, chemical beam epitaxy is another ultra-high vacuum process, but it utilizes gas-phase precursors to create the molecular beam.

### 3.6 Droplet epitaxy

As a final note, a brief comment on an innovative epitaxial growth technique called droplet epitaxy.

Droplet Epitaxy is an epitaxial technique, mostly used for III-V semiconductors, for the fabrication of a variety of nanostructures, such as Quantum Dots. It relies on the spontaneous formation of group III metallic droplets, which are subsequently crystallized into quantum dots by the supply of a group V source material. DE was initially discovered and developed in Molecular Beam Epitaxy in 1991.

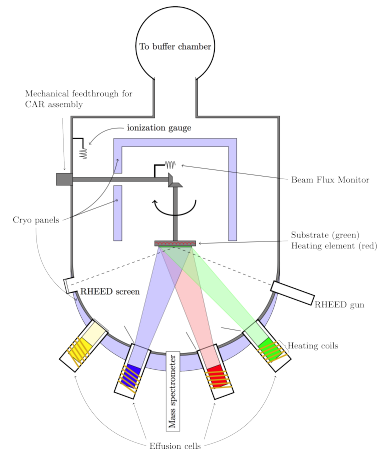


Figure 6: Growth chamber of a molecular beam epitaxy

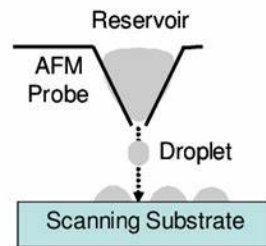


Figure 7: Figure showing droplet epitaxy schematically