Chapter 3:
Fabricating nanostructures

3.1 Crystal Growth

3.2 MOS transistors

3.3 Lithography

Crystal Growth

SiO_2

NaCl

Crystal Growth

- Crystal Growth of Bulk Materials:
  - Single Crystal Growth at Low Temperature
  - Single Crystal Growth from Vapor Phase
  - Single Crystal Growth from Liquid Phase
- Crystal Growth of Thin Films:
  - Evaporation under Vacuum
  - Chemical Methods from Vapor Phase
- Crystal Growth of QDs
  - Colloidal QDs in solution
  - Direct Growth of QDs on a substrate

Single Crystal Growth at Low Temperature

Hidrothermal :
A solution (generally aqueous) in saturated conditions goes to supersatutation conditions (and solid deposition) by the control of temperature or the control of concentration.

Temperature Control

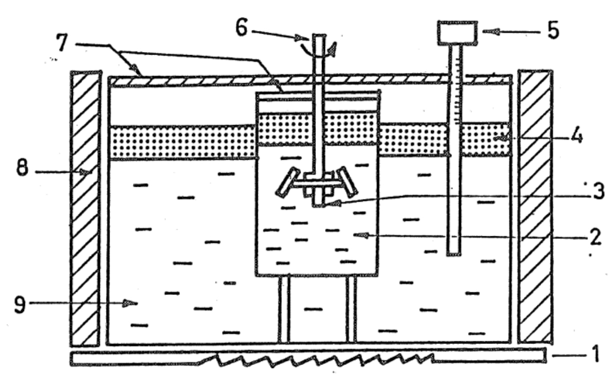
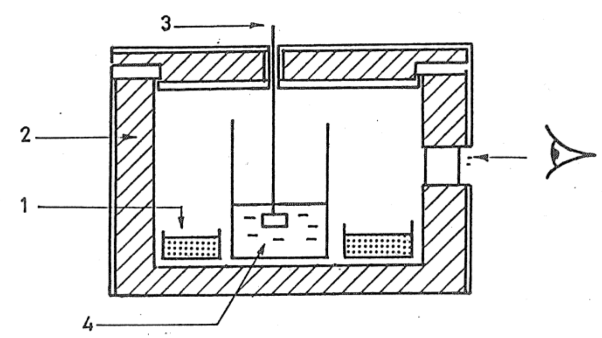


Figura 12.1. *Técnica de crecimiento por descenso de la temperatura: (1) elemento calefactor, (2) cubeta de crecimiento, (3) germen, (4) capa aislante de parafina, (5) termómetro de contacto, (6) agitador, (7) tapas de metacrilato, (8) aislante lateral de fieltro, (9) cubeta de baño.*

Concentration Control



12.2 *Modificación de la técnica de crecimiento mediante evaporación a temperatura constante: (1) desecante, (2) aislante, (3) germen, (4) cubeta de crecimiento.*

Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

Single Crystal Growth at Low Temperature

Sol-Gel :

Gel acts as a viscous (porous) media enabling the control mix of two components A and B. When the solubility point is attained there is a precipitation of the AB compound. The growth rate depends on the material diffusion in the gel media

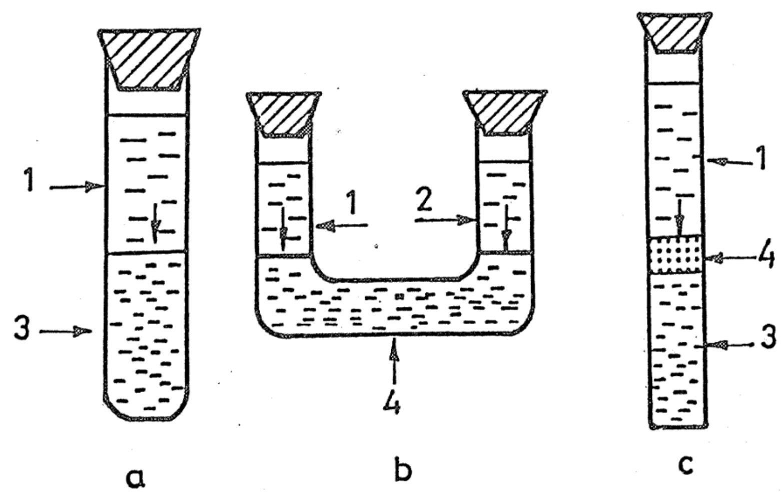


Figura 12.4 *Dispositivo de crecimiento en gel: a) tubo de ensayo, b) tubo en «U», c) modelo de tres capas. (1) componente A, (2) componente B, (3) componente B+gel, (4) gel.*

Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

Single Crystal Growth from Vapor Phase

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Chemical Vapor Transport (CVT):
In a sealed ampoule the source material (and seed) are subject to temperature gradient. In addition there is a gas that is working as a transporting media. At high temperature the gas reacts with the source material producing a compound that It is transported in vapor phase. In the deposition region, at lower temperature, the reverse reaction is produced.

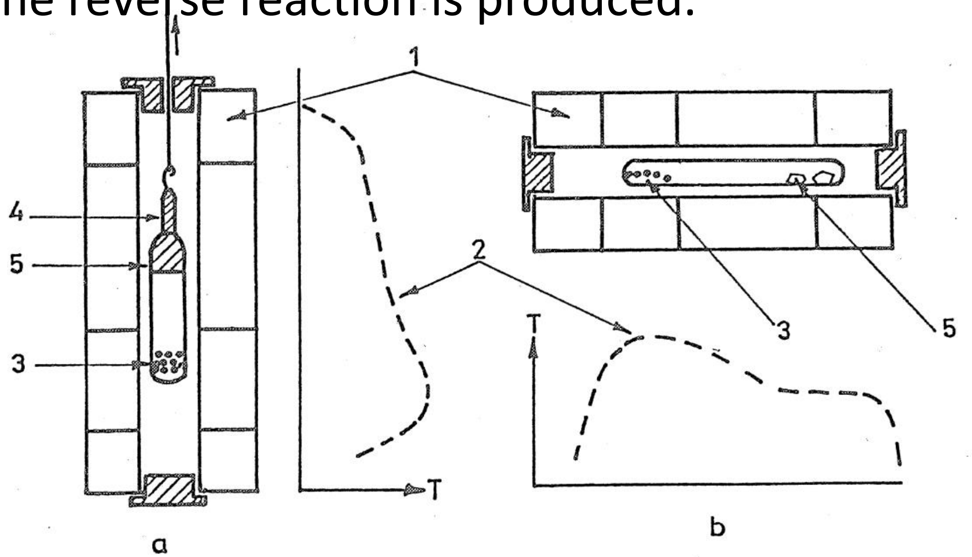


Figura 12.5. *Técnica de crecimiento CVD en un sistema: a) con germen, y b) sin germen. (1) varios elementos calefactores, (2) perfil de temperatura utilizado, (3) nutriente, (4) germen, (5) cristal.*

Example ZnO growth:

ZnO (g)+CO (g)→ Zn (g)+ CO_2 (g)

C (s)+ CO2 (g)→ 2CO (g)

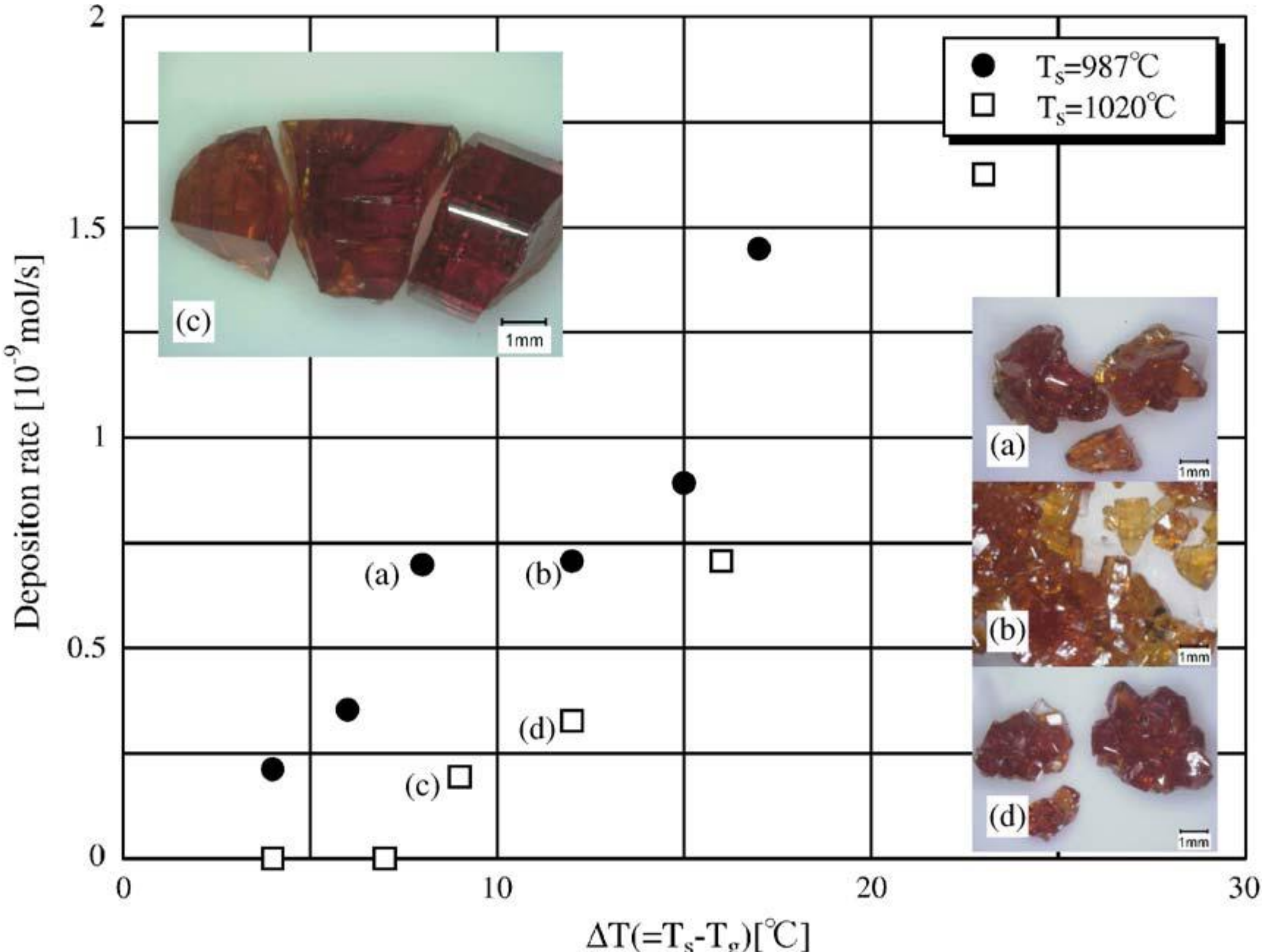
Mikami et al., J. Crystal Growth 276 (2005) 389–392

Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

Single Crystal Growth from Vapor Phase

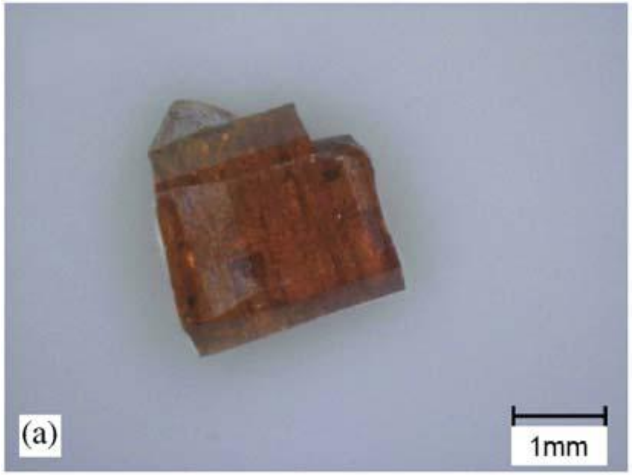
Mikami et al., J. Crystal Growth 276 (2005) 389–392

Chemical Vapor Transport ZnO:



Single Crystal Growth from Vapor Phase

Chemical Vapor Transport ZnO:



As grown

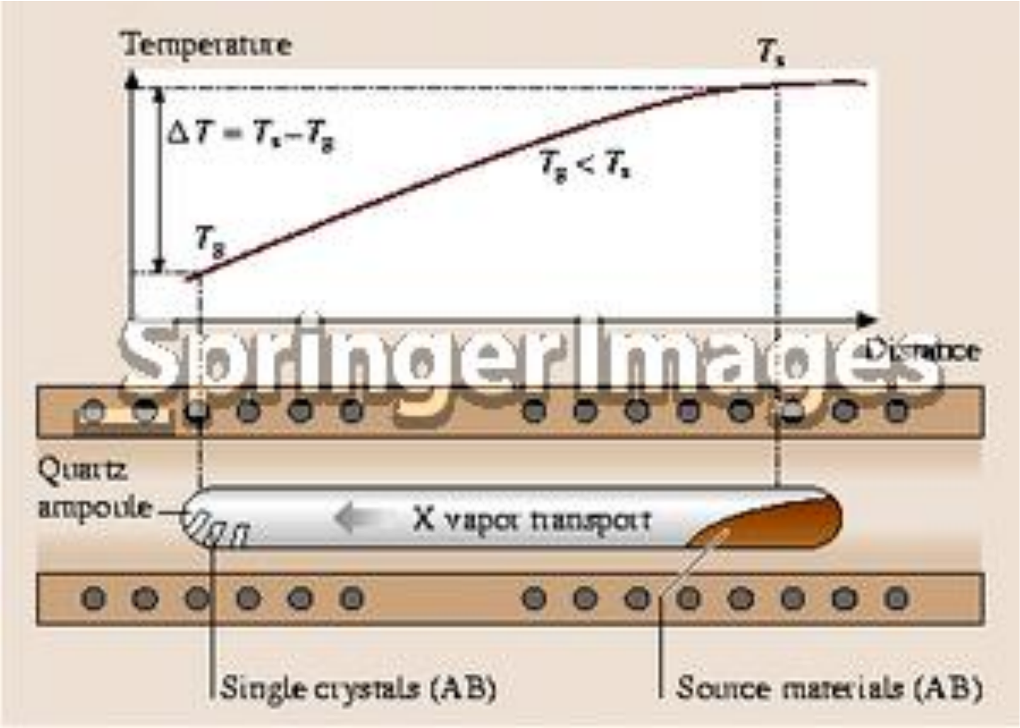
O_2 annealing

Zn annealing

Mikami et al., J. Crystal Growth 276 (2005) 389–392

Single Crystal Growth from Vapor Phase

Physical Vapor Transport (PVT):
It is similar to CVD but no chemical reaction (no transporting agent) is required. Source material sublimates and it is deposited in the coldest part of the sealed ampoule.



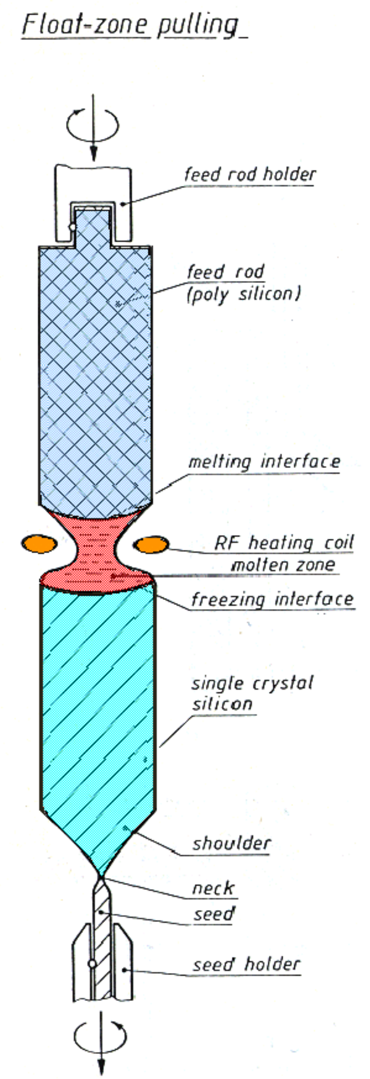
Single Crystal Growth from Liquid Phase

Float-zone (no crucible):
The basic idea in float zone (**FZ**) crystal growth is to move a liquid zone through the material. If properly seeded, a single crystal may result.

This technique is also use for purification as certain impurities can be segregated in the melted region.

Since the melt never comes into contact with anything but vacuum (or inert gases), there is no incorporation of impurities.

If it would only be held in place by *surface tension*, the maximum diameter of crystals possible in this way would be about 20 mm. A hole of wider ingots could be used but the Diameter is limited to 150 mm.

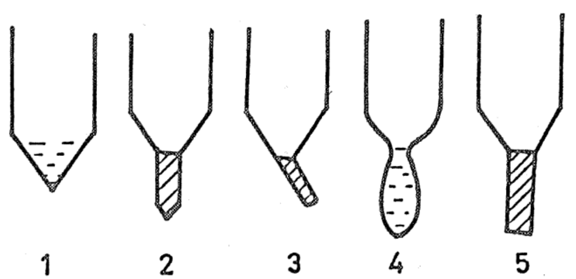


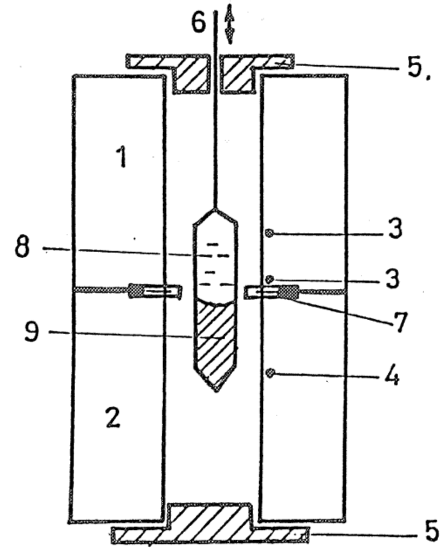
http://www.tf.uni-kiel.de/matwis/amat/elmat_en/kap_6/advanced/t6_1_3.html

Single Crystal Growth from Liquid Phase

Bridgman Method (with relative crucible movement):
A sealed ampoule or crucible is moved relatively along a temperature profile with an initial nucleation at one end of the ampoule. From this initial nucleation a monocrystal is formed from the solidification of the liquid phase as the temperature decreases.

	P. Fusión (C)	Velocidad (mm/h)	Crisol
Al_2O_3	2.037	2- 8	Molibdeno
$FeAl_2O_3$	1.790	5-10	Iridio
Cu	1.083	6-60	Grafito
$NaNO_2$	271	3- 6	Teflón



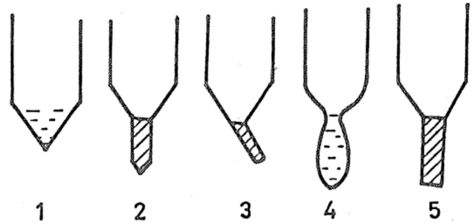


Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

Figura 12.10. *Diseño de un equipo Bridgman: (1, 2) elementos calefactores, (3, 4) termopares de medida y control, (5) cierre de cerámica, (6) sistema de desplazamiento de crisol, (7) separador cerámico para obtener perfil de temperatura, (8) fundido, (9) cristal.*

Single Crystal Growth from Liquid Phase

Bridgman Method (some examples):



LiNbO3:Cu:Ce

Xu et al., J. of Crystal Growth 275 (2005) e791–e797

Aluminum Crucible

http://www.tradekorea.com/product-detail/P00095055/Bridgman_Method_Single_Crystal_Crucible.html

Single Crystal Growth from Liquid Phase

Bridgman Method (Horizontal Method):

This method is used for a large amount of material

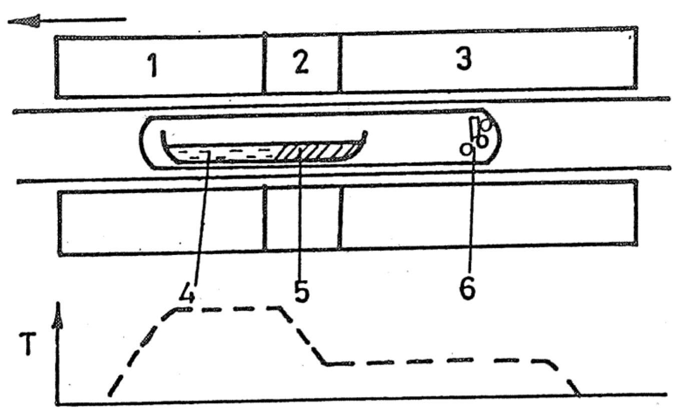
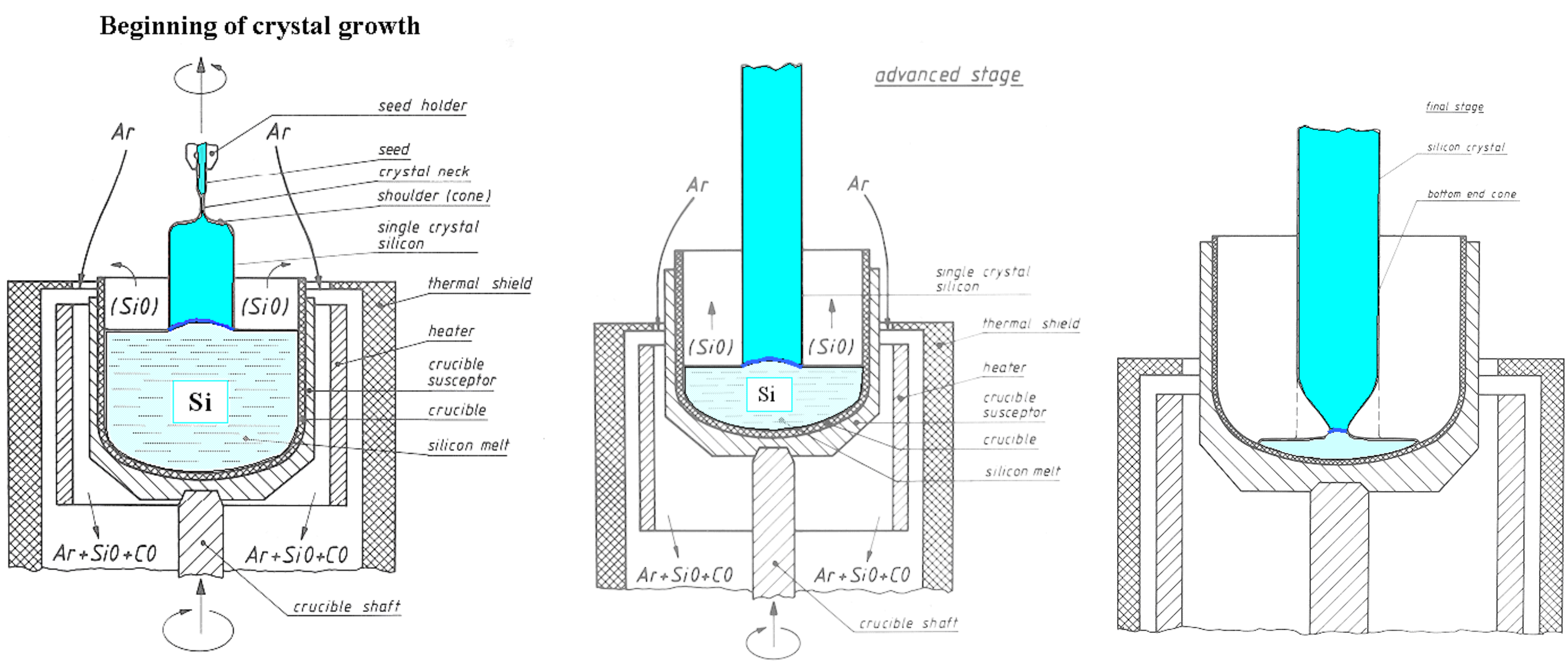


Figura 12.12. *Sistema de crecimiento para el AsGa en barquilla horizontal, mostrando el perfil de temperatura: (1, 2, 3) elementos calefactores, (4) fundido, (5) cristal, (6) exceso de As.*

Single Crystal Growth from Liquid Phase

Czochralski Method (no crucible movement):

Is the most employed technique in the industry, especially for Si growth. Materials need to melt in congruent way (melt composition similar to solid). It is need an appropriated atmosphere and crucible for high T.



http://www.tf.uni-kiel.de/matwis/amat/elmat_en/index.html

Single Crystal Growth from Liquid Phase

Czochralski Method (no crucible movement):

Is the most employed technique in the industry, especially for Si growth. Materials need to melt in congruent way (melt composition similar to solid). It is need an appropriated atmosphere and crucible for high T.

Condiciones de crecimiento de monocristales para algunos materiales por el método CZ

	P. Fusión (C) (°C)	Rotación (rpm)	Tiro (mm/h)	Crisol	Atmósfera
Al_2O_3	2.037	30-50	1-3	Iridio	Ar
Si	1.420	10-20	100-200	Cuarzo	Ar
$LiNbO_3$	1.250	20-30	3-6	Platino	O_2
GaAs	1.237	20-30	20-30	Cuarzo	As
Ge	937	20-50	5-20	Grafito	H_2/O_2
$Bi_4Ge_3O_{12}$	930	10-40	2-10	Platino	O_2

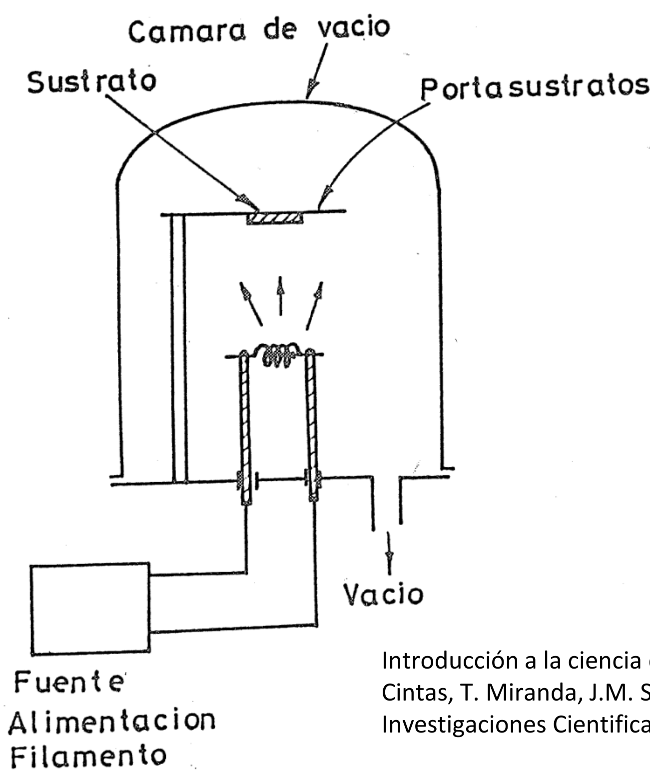
Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

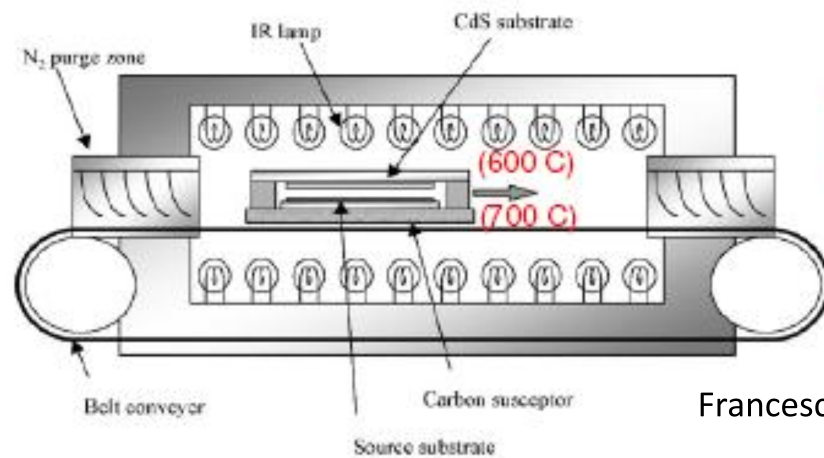
http://www.huali-europe.com/en/solarenergy/siliconingots.htm

Thin Films
Evaporation Under Vacuum

Sublimation:

The material source is heated sublimating and depositing in a substrate (with or without temperature control). A particular case is the Close Space Vapor Transport (CSVT) where the source and substrate are positioned very close. It is specially interesting for CdTe solar cells:





Deposition rate: 1 μm/min !

Francesco Biccari

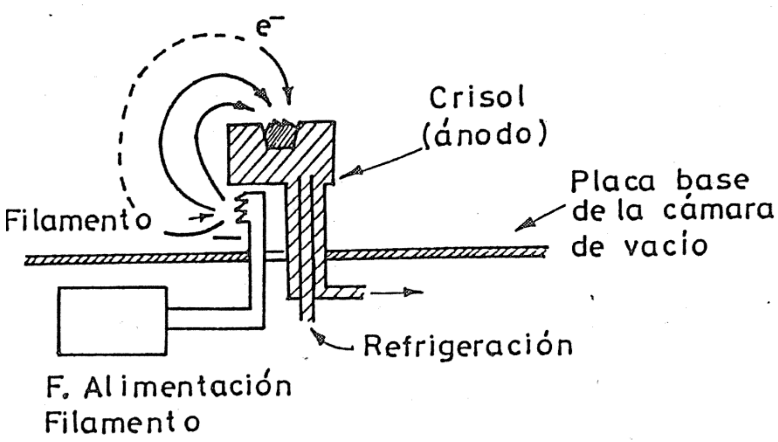
Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

Thin Films
Evaporation Under Vacuum

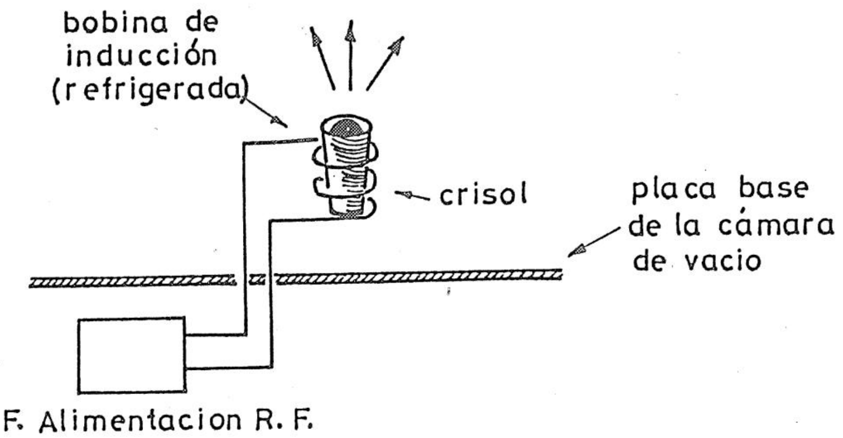
Sublimation:

There are different systems to heat the source:

Electron Beam



Inductance

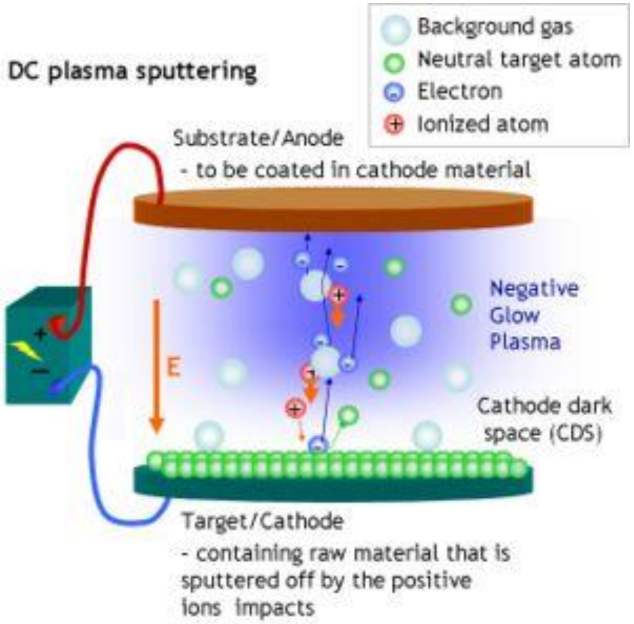


Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

Thin Films
Evaporation Under Vacuum

Sputtering:

Plasma ions of an inert gas are accelerated towards the cathode bombing the material source. The source emit particles, due to the ion bombing, that are deposited on the substrate. It is not needed to heat the source. It is valid even for materials with high melting point. The atoms have higher energy than in sublimation and are better glued on the substrate. It can be used for metallic alloys



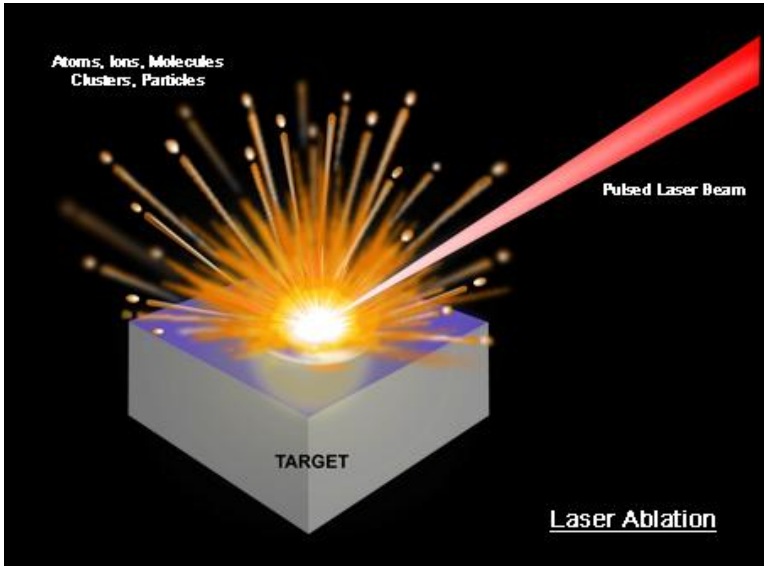
http://www.etafilm.com.tw/PVD_Sputtering_Deposition.html

Cornell University NanoScale Science and Technology Facility

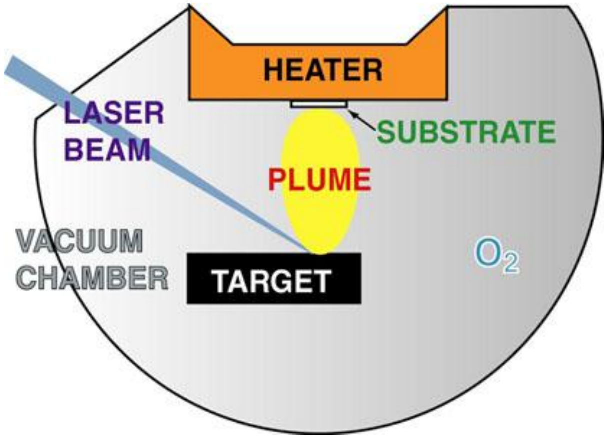
Thin Films
Evaporation Under Vacuum

Laser Ablation:

In laser ablation, high-power laser pulses are used to evaporate matter from a target surface such that the stoichiometry of the material is preserved in the interaction. As a result, a supersonic jet of particles (plume) is ejected normal to the target surface. The ablation process takes place in a vacuum chamber - either in vacuum or in the presence of some background gas. In the case of oxide films, oxygen is the most common background gas. Idem for nitrogen and nitrides.



http://www.astrobio.net/pressrelease/4605/green-laser-spectroscopy

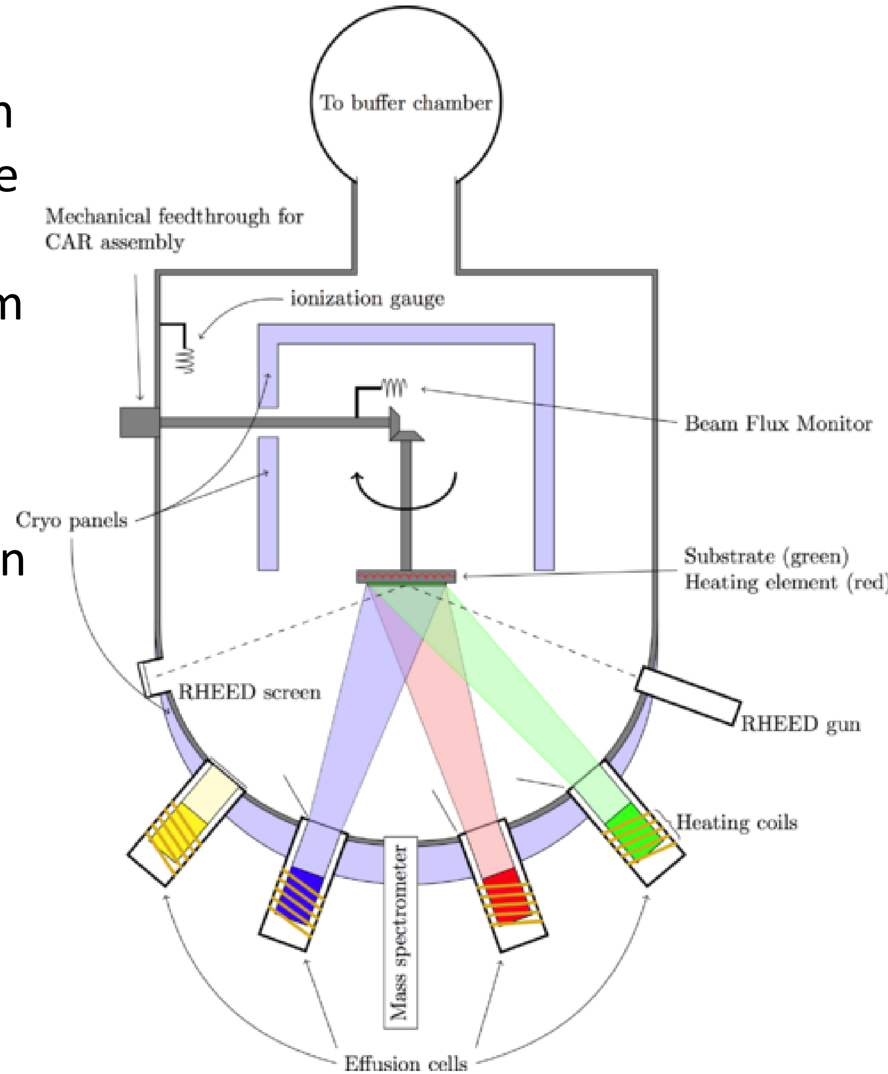


http://tfy.tkk.fi/aes/AES/projects/prlaser/ablation.htm

Thin Films
Evaporation Under Vacuum

Molecular Beam Epitaxy (MBE):

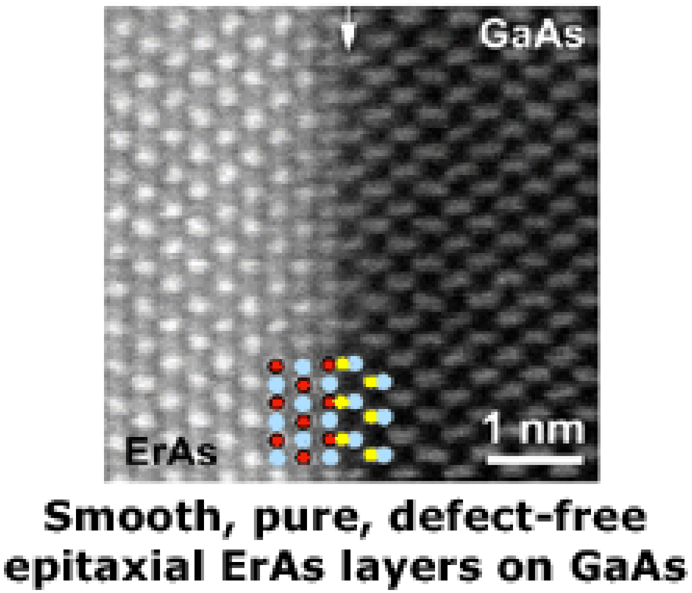
Molecular beam epitaxy takes place in high vacuum or ultra-high vacuum (10^{-8} Pa). The most important aspect of MBE is the deposition rate (typically less than 3000 nm per hour) allows the films to grow **epitaxially**. In solid-source MBE, elements (such as gallium and arsenic), in ultra-pure form, are heated in separate quasi-Knudsen effusion cells until they begin to slowly sublime. The gaseous elements then condense on the wafer, where they may react with each other.



http://en.wikipedia.org/wiki/Molecular_beam_epitaxy

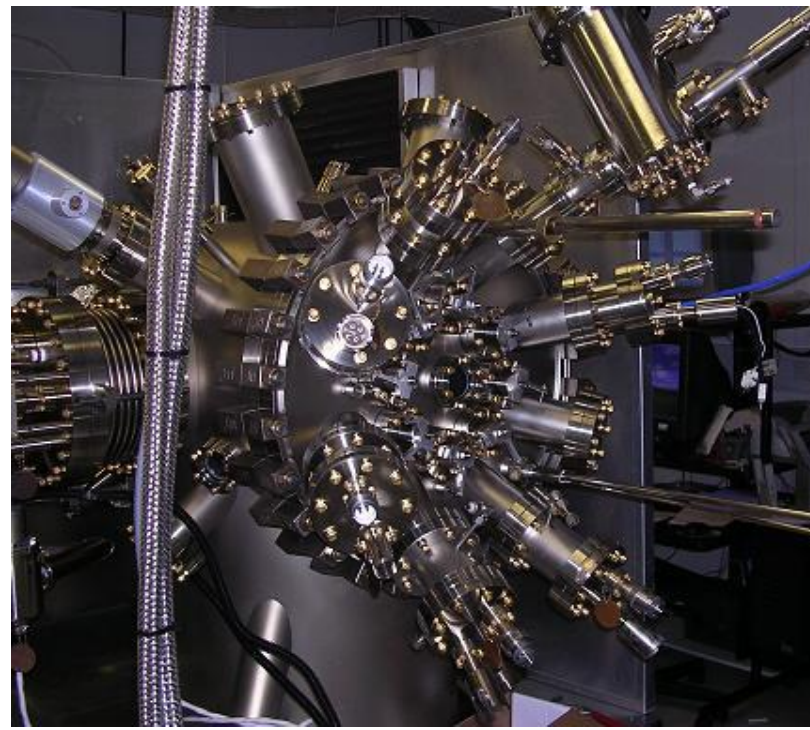
Molecular Beam Epitaxy (MBE):

High Growth Control



http://www.mrsec.org/research/nanostructured-materials-molecular-beam-epitaxy

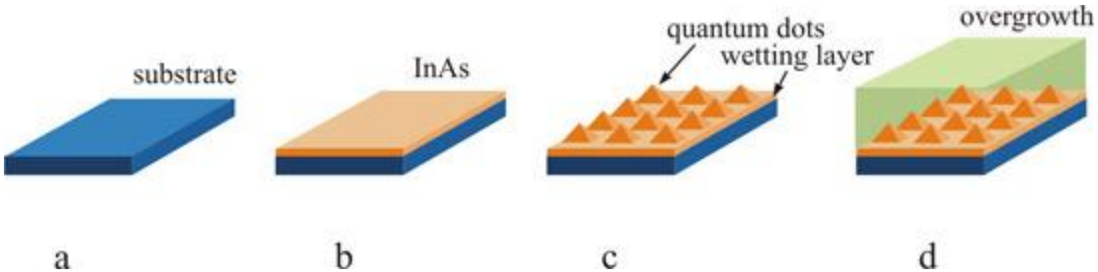
High Hardware Complexity



http://www.phy.cam.ac.uk/research/sp/mbe.php

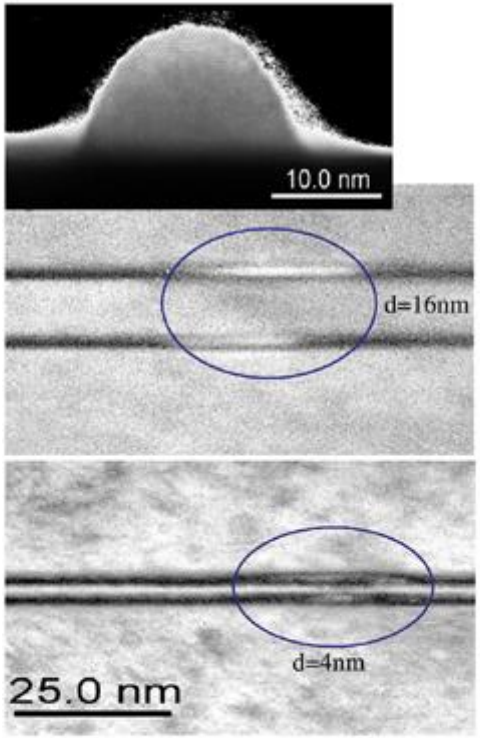
Molecular Beam Epitaxy (MBE):

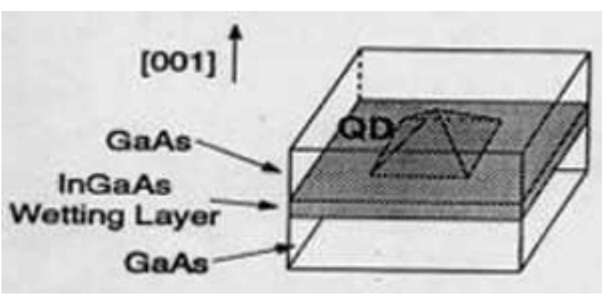
Quantum Dot Growth by MBE:

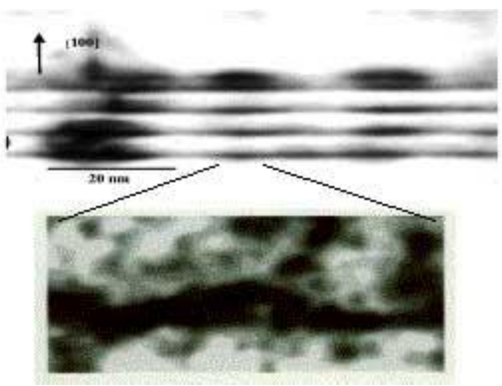


http://www.fotonik.dtu.dk/English/Research/ResearchActivities/NanoDevices_research/Quantum%20dots.aspx

http://www.nrl.navy.mil/research/nrl-review/2004/electronics-and-electromagnetics/reinecke/







http://www.engin.umich.edu/research/cuos/ResearchGroups/US/Research/Quantum_Dots.html

Thin Films
Chemical Methods from Vapor Phase

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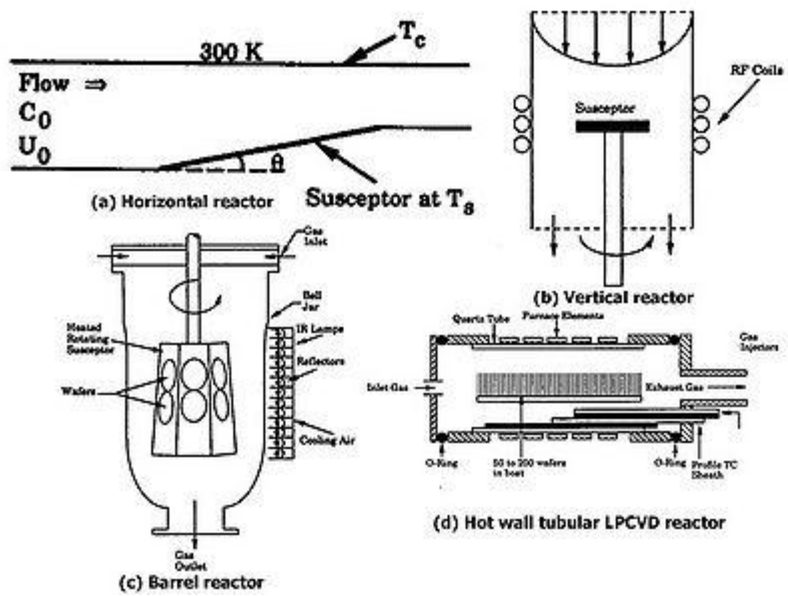
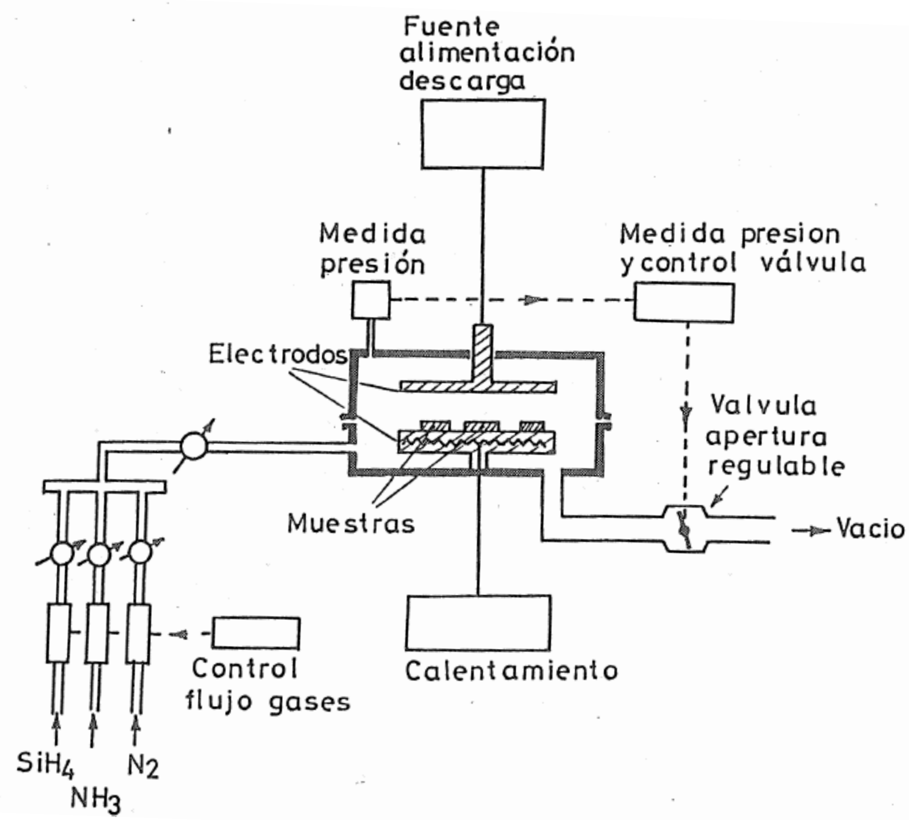
Chemical Vapor Deposition (CVD):
In this technique one or various gases reacts in a reaction chamber to give a product, generally a thin film on a substrate.





https://www.thermalfluidscentral.org/encyclopedia/index.php/Basics_of_Chemical_Vapor_Deposition

Introducción a la ciencia de materiales. J.M. Albella, A.M. Cintas, T. Miranda, J.M. Serratosa. Consejo Suoerior de Investigaciones Cientificas, Madrid, 1993

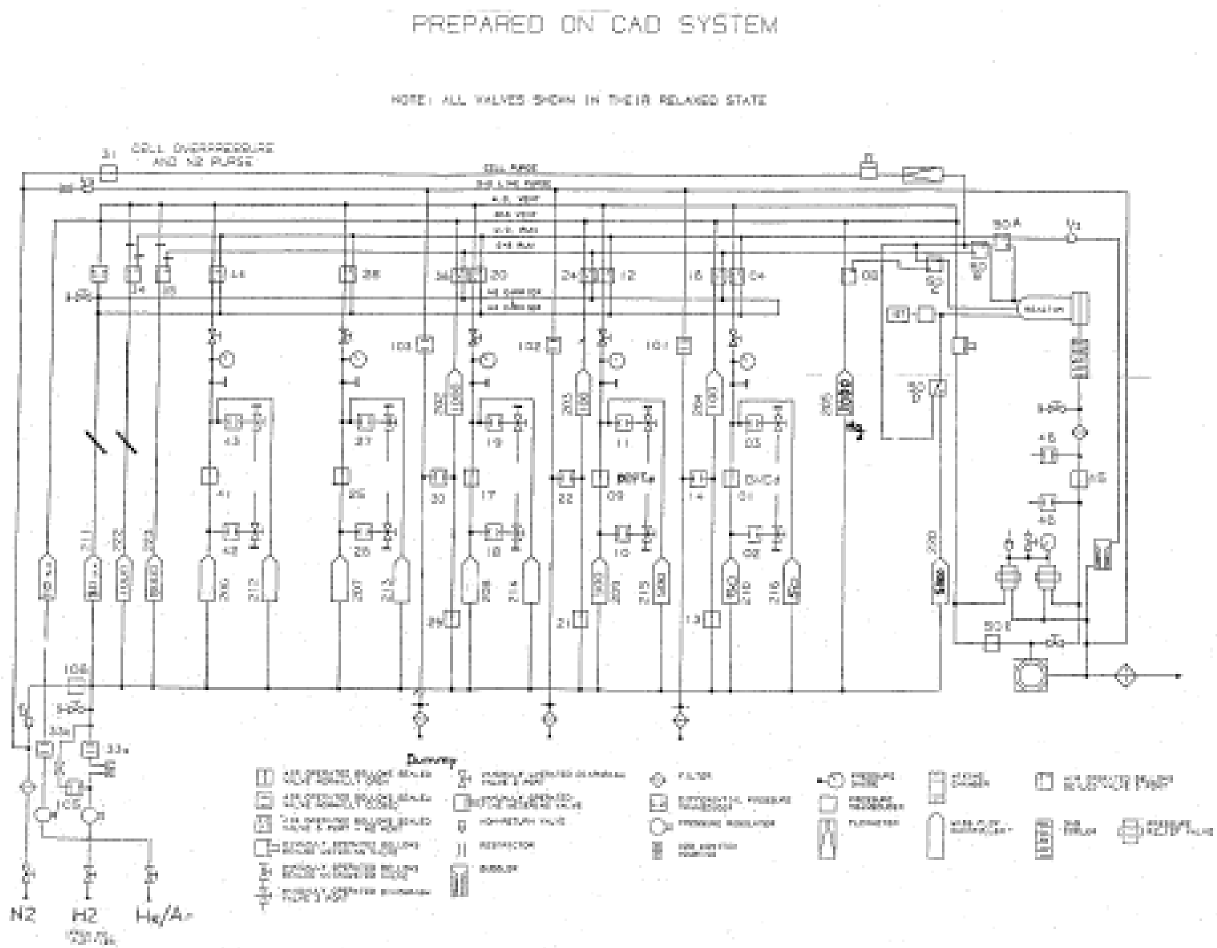
Chemical Methods from Vapor Phase

Metal Organic Chemical Vapor Deposition (MOCVD):

The precursors used in the film deposition are metal organic and are transported by a inert carrier gas. In the reaction chamber the metal organic compounds pyrolice on the hot substrate depositing the metallic atoms. The amount of precursor is controlled by the flux of carrier gas and the temperature of the precursors bath.

http://www.hlphys.jku.at/fkphys/epitaxy/mocvd.html

Metal Organic Chemical Vapor Deposition (MOCVD):

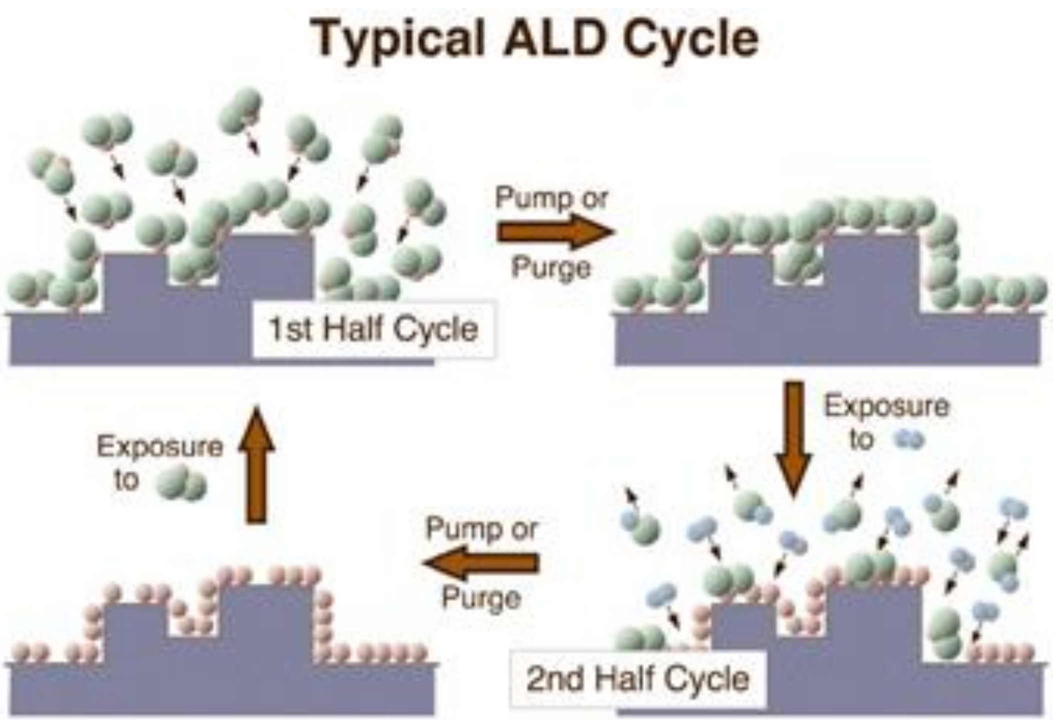


MOCVD system could present a complicated gas flux control.

I. Mora-Seró.Tesis "Crecimiento de compuestos II-VI mediante la técnica MOCVD: Aplicación al crecimiento de CdTe, HgTe y $Hg_{1-x}Cd_xTe$." Universidad de Valencia ISBN: 84-370-6078-8; (2005)

Thin Films
Chemical Methods from Vapor Phase

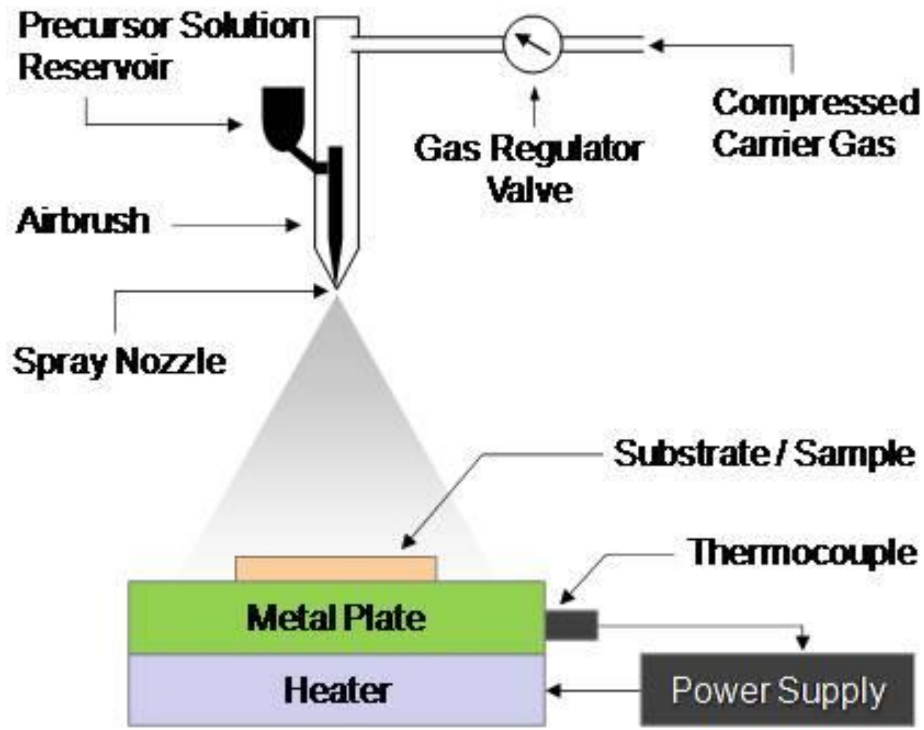
Atomic Layer Deposition (ALD):
ALD is, generally, a two self-limiting and complementary reactions. By alternating the two chemical steps, films can be grown conformally and with atomic thickness resolution even on rough surfaces. However, several fundamental issues such as the elimination of impurities and the control of film morphology need to be resolved before ALD can be widely used in microelectronics fabrication.



http://research.chem.ucr.edu/groups/zaera/ongoingproject4.html

Thin Films
Chemical Methods from Vapor Phase

Spray Pyrolisis (SP):
In this technique a solution is sprayed on a hot substrate. It is commonly used for oxide deposition.



http://research.chem.ucr.edu/groups/zaera/ongoingproject4.html

UNIVERSITAT JAUME I

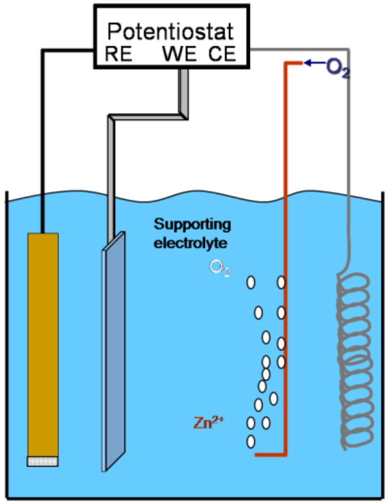
GRUP DE DISPOSITIUS FOTOVOLTAICS I OPTOELETRÒNICS

Thin Films
Electrochemical Methods

Electrodeposition:

Deposit of thin layer by the pass of current thought an electrolyte.

Example ZnO Nanowire deposition:



Increase of the local pH by the reduction of an oxygenated precursor:

O_2 *D. Lincot et al, C.Lévy-Clément et al.*

NO_3^{2-} *Izaki et al.*

H_2O_2 *D. Lincot et al*

1. Electrochemical O_2 reduction (OH^- production)

2. Chemical reaction

$$O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$$

$$Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

- O_2 diffusion to the cathode
- kinetics of "charge transfer"

- Zn^{2+} diffusion to the cathode
- kinetics of precipitation (fast!)

-R. Tena- Zaera, J. Elias, C. Lévy-Clément, Y. Luo, I. Mora-Seró and J. Bisquert, *phys. stat. sol. (a)* 250, (2008) 2345.

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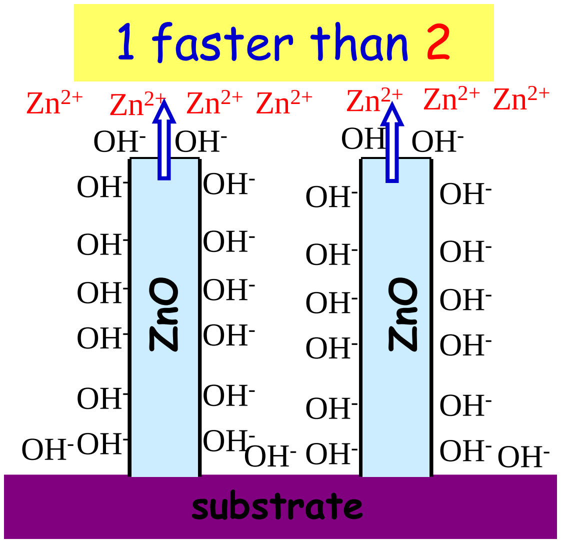
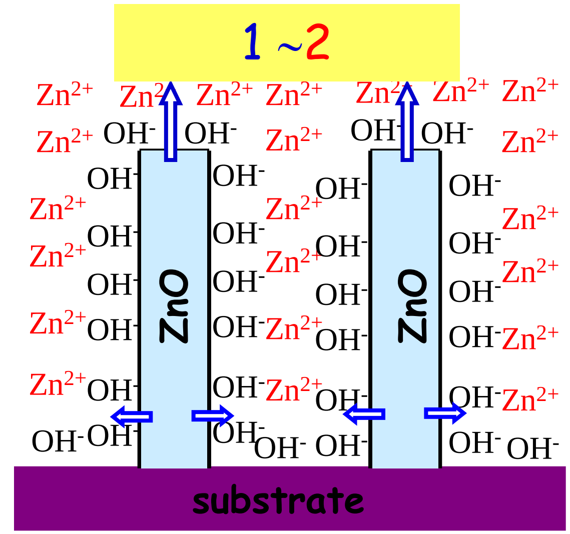
GRUP DE DISPOSITIUS FOTOVOLTAICS I OPTOELETRÒNICS

Thin Films
Electrochemical Methods

Electrodeposition:





Only longitudinal growth

Longitudinal + lateral growth

Tailoring of NW dimensions (diameter: 25- 500 nm, length: 0.1-10 μm) and donor density (n_D 10^{18} – 10^{20} cm^{-3}) depending on growth conditions, precursor & supporting salt concentration and reaction time.

R. Tena-Zaera et al. J. Phys. Chem. C (2007)
J. Elias et al. J. Electroanal. Chem. (2008)

I. Mora-Sero et al. Appl. Phys. Lett. (2006)
R. Tena-Zaera et al. J. Phys. Chem C (2008)

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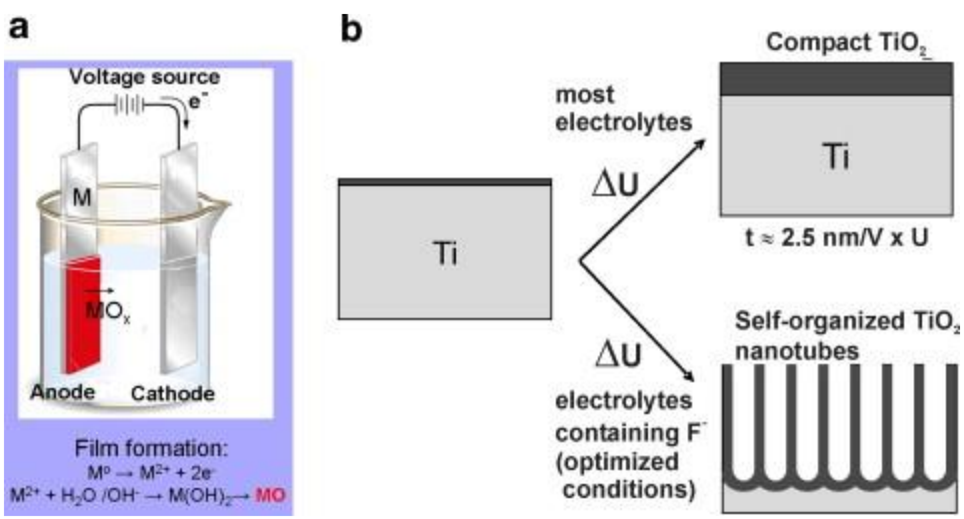
GRUP DE DISPOSITIUS FOTOVOLTAICS I OPTOELETRÒNICS

Thin Films
Electrochemical Methods

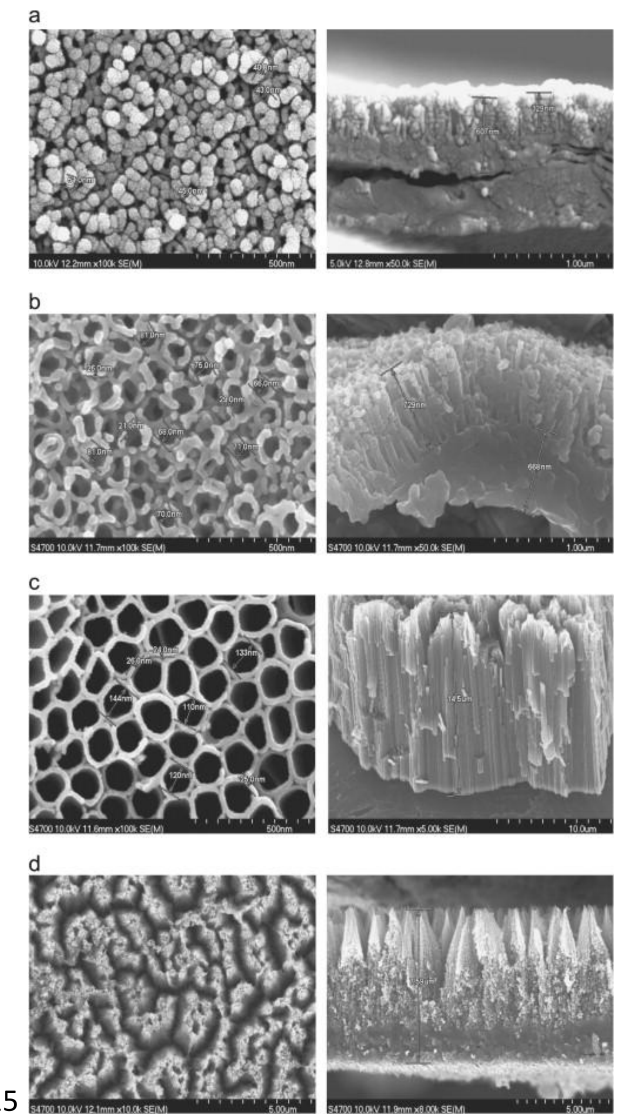
Anodization:

It is a particular case of electrodeposition. When an acid is used instead of a salt there is a Hydrogen formation in the cathode, while in the anode reactions with production of oxigen (or oxides) occurs.

Example TiO2 Nanotubes:



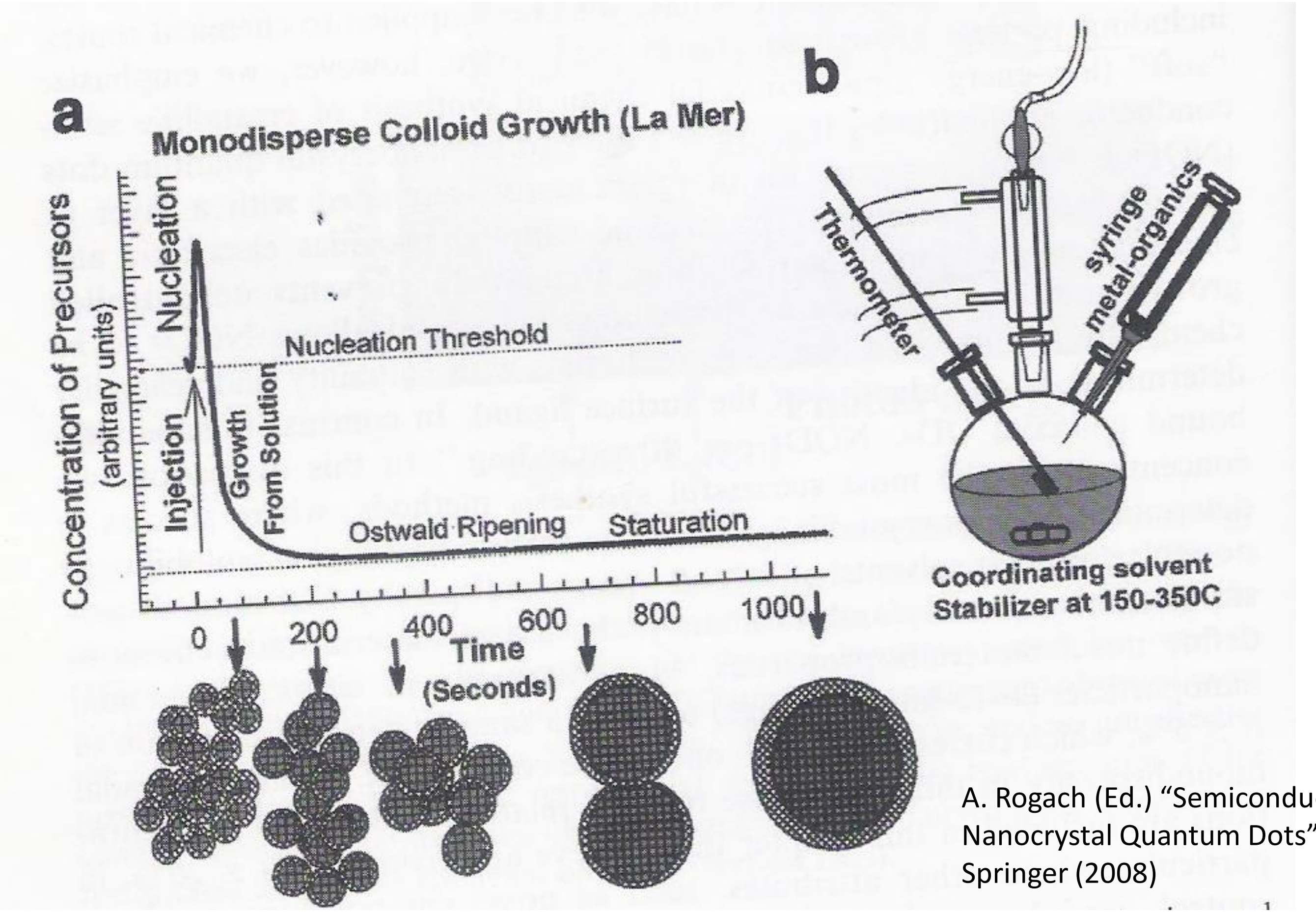
Macak et al., Current Opinion in Solid State and Materials Science 11 (2007) 3–18



Nam et al. Solar Energy Materials & Solar Cells 94 (2010) 1809–1815

Colloidal QDs in solution

Hot Injection:
One metallic precursors is heated with organic molecules than control the growth (capping). The growth starts when the second precursor is injected.



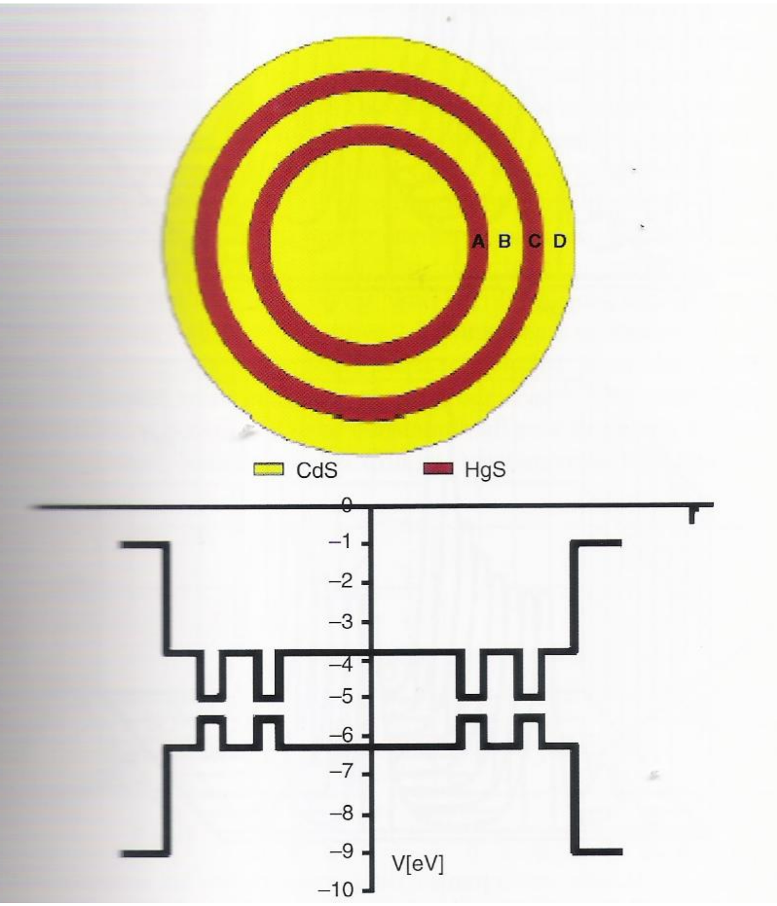
A. Rogach (Ed.) "Semiconductor Nanocrystal Quantum Dots"; Springer (2008)

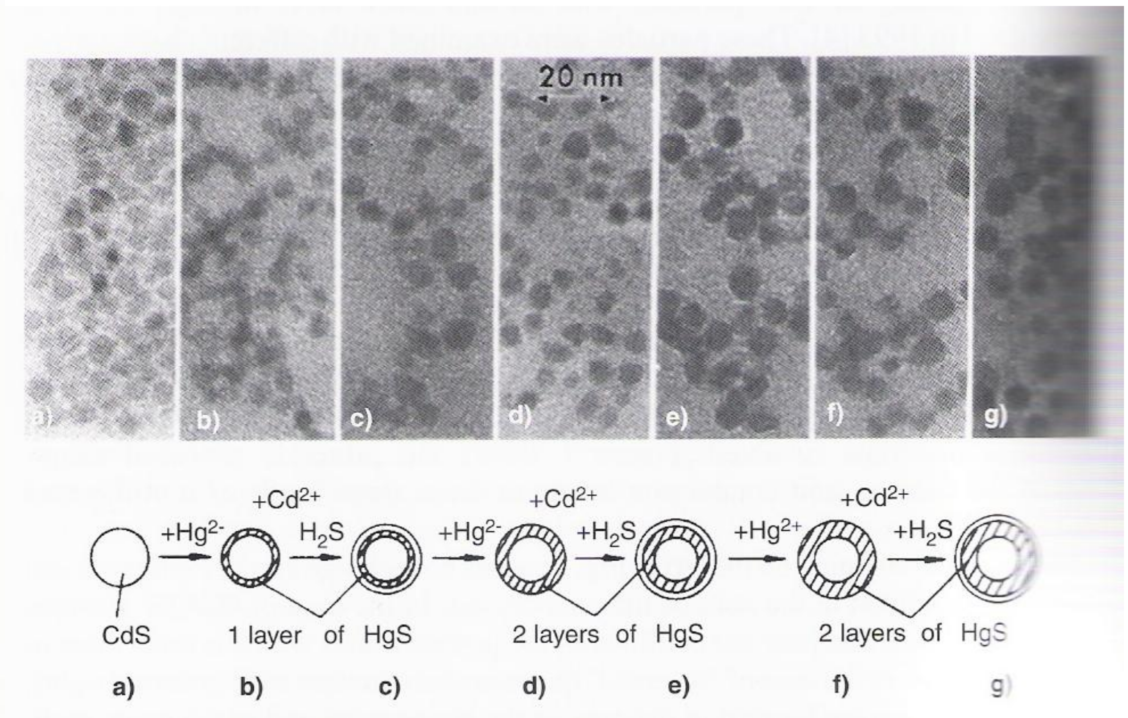
http://education.mrsec.wisc.edu/Edetc/nanolab/CdSe/index.html

Colloidal QDs in solution

Core/Shell QDs:

Sophisticated structures can be produced.

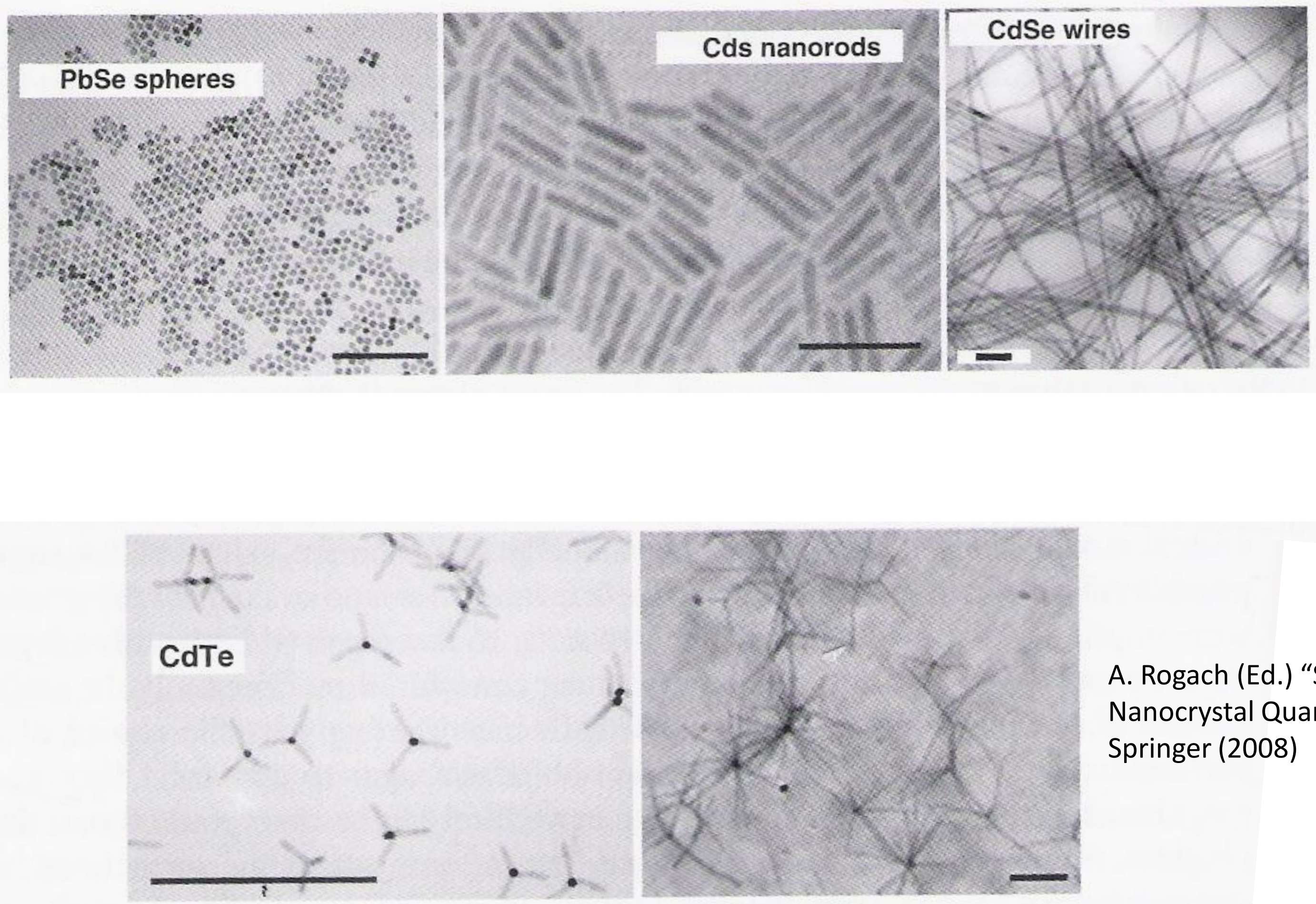




A. Rogach (Ed.) "Semiconductor Nanocrystal Quantum Dots"; Springer (2008)

Colloidal QDs in solution

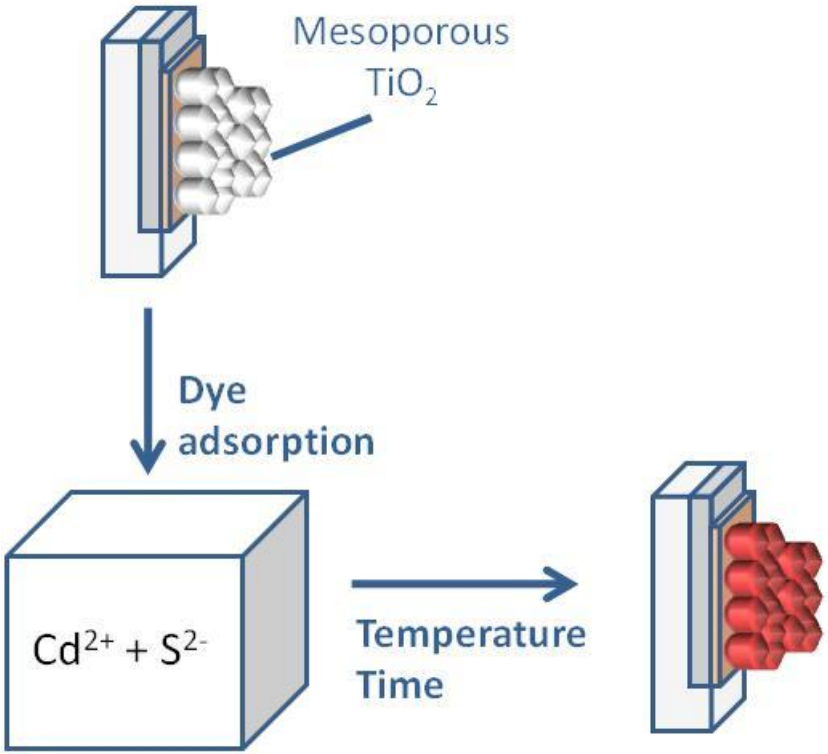
Shape Control:



A. Rogach (Ed.) “Semiconductor Nanocrystal Quantum Dots”; Springer (2008)

Direct Growth of QDs on a substrate

Chemical Bath Deposition (CBD):

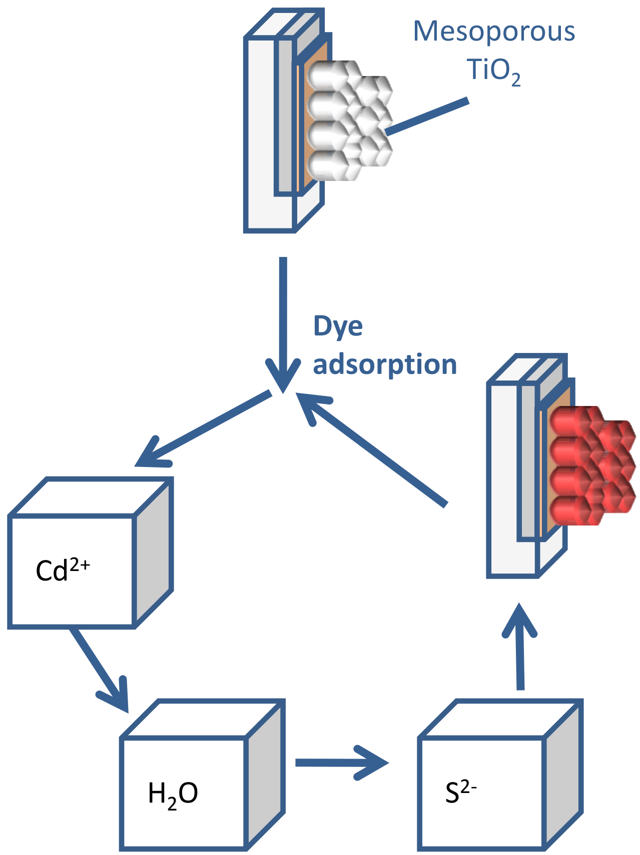


Parameters to control:
•Solution concentration
•Reaction time
• Solution Temperature.

Niitsoo et al., Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 306–313

Direct Growth of QDs on a substrate

Successive Ionic Layer Adsorption And Reaction (SILAR):



Parameters to control:
•Solution concentration
•Immersion time
•Number of cycles

H.Lee et al. ***Nano Lett., Vol. 9, No. 12, 2009,* 4221-4227**.