Deposition

Franssila: Chapters 5 & 6

Peter Hadley

Silicon wafers

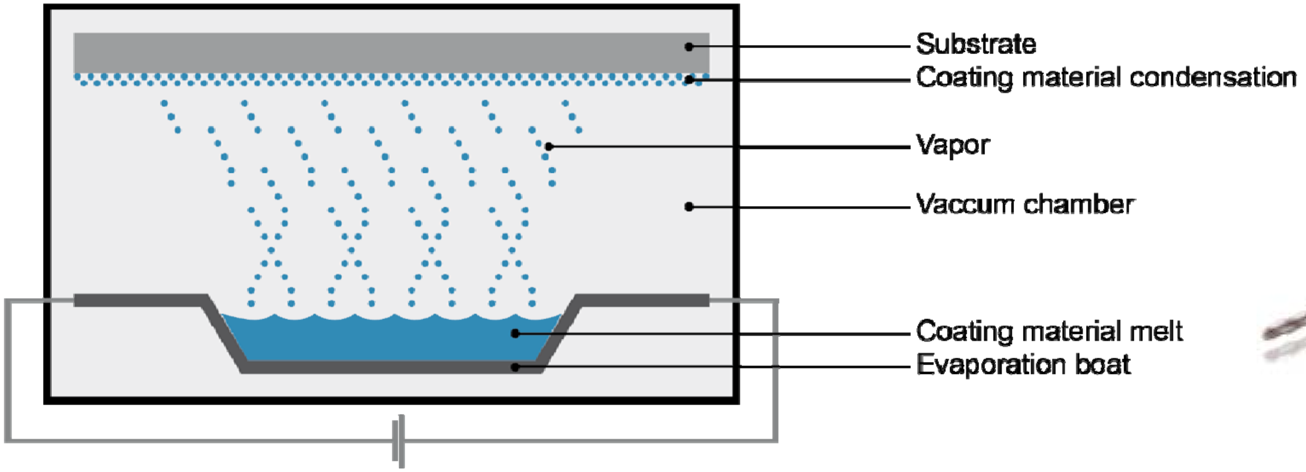
- Total Thickness Variation: a good 8" Prime wafer would be < 15 µm
- Site flatness measurement: < 0.3 µm flatness across each 20×20 mm site.
- Bow: < 30 µm concave or convex
- Warp: < 20 µm (like a potato chip)
- Resistivity variation: 2%-15%

http://www.processpecialties.com/siliconp.htm

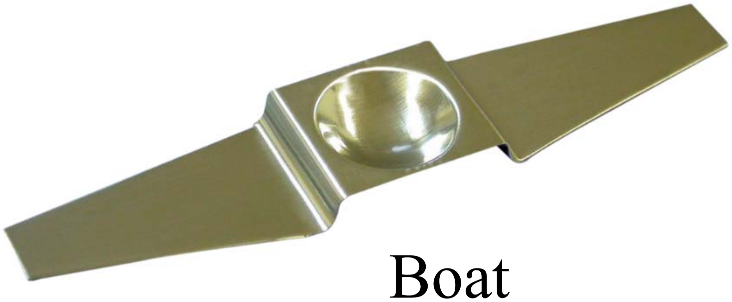
Physical Vapor Deposition (PVD)

Thermal evaporation
E-beam evaporation
Knudsen cell, Effusion cell
Molecular Beam Epitaxy (MBE)
Sputtering
Laser ablation

Thermal evaporation



Coil



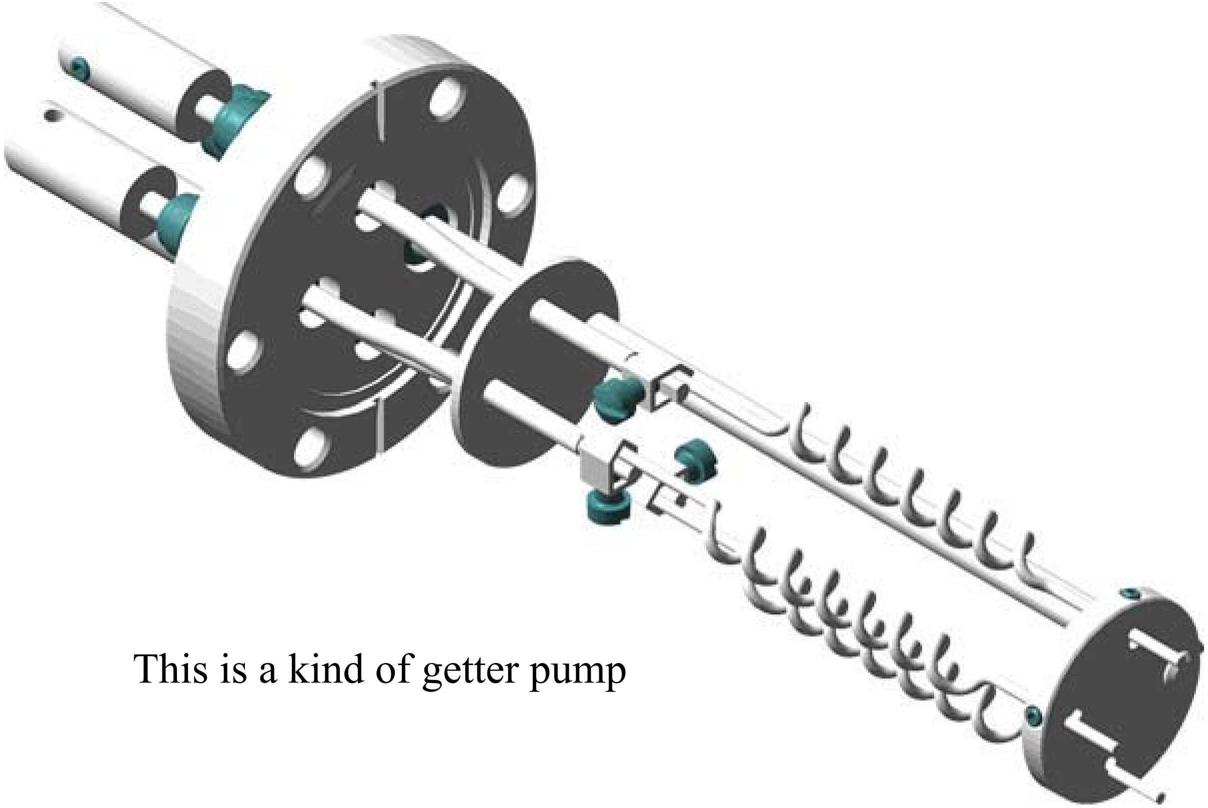
Boat

Knudsen cell

Covers substrate features like snow.
Polycrystalline films.

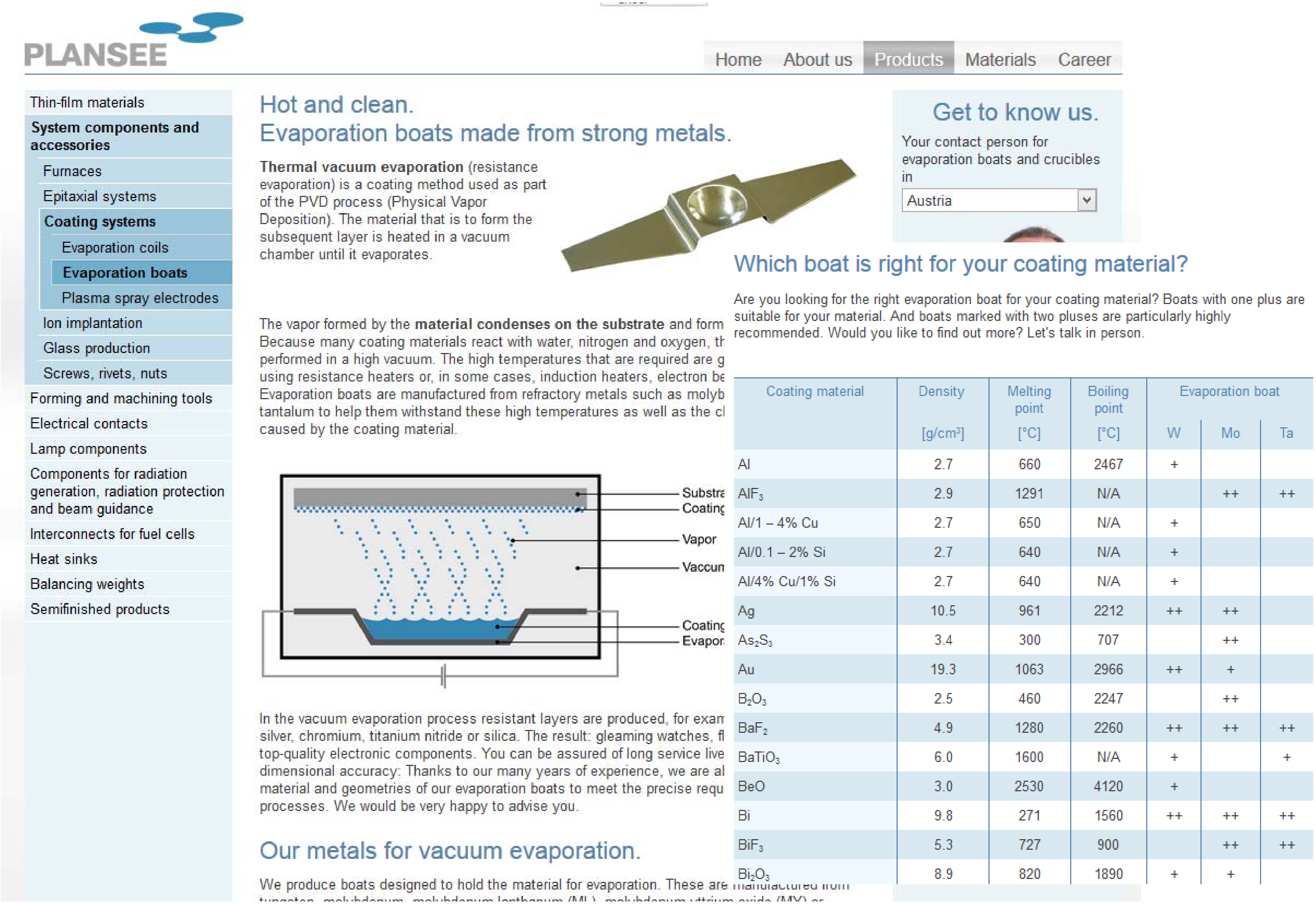
http://www.plansee.com/en/Products-System-components-and-accessories-Coating-systems-Evaporation-boats-100.htm

Titanium Sublimation Pump (TSP)



This is a kind of getter pump

http://www.lesker.com/newweb/vacuum_pumps/ionpump_gamma_ionpump_tisub.cfm



Hot and clean.
Evaporation boats made from strong metals.

Thermal vacuum evaporation (resistance evaporation) is a coating method used as part of the PVD process (Physical Vapor Deposition). The material that is to form the subsequent layer is heated in a vacuum chamber until it evaporates.

The vapor formed by the **material condenses on the substrate** and form
Because many coating materials react with water, nitrogen and oxygen, th
performed in a high vacuum. The high temperatures that are required are g
using resistance heaters or, in some cases, induction heaters, electron be
Evaporation boats are manufactured from refractory metals such as molyb
tantalum to help them withstand these high temperatures as well as the cl
caused by the coating material.

In the vacuum evaporation process resistant layers are produced, for exam
silver, chromium, titanium nitride or silica. The result: gleaming watches, fl
top-quality electronic components. You can be assured of long service live
dimensional accuracy: Thanks to our many years of experience, we are al
material and geometries of our evaporation boats to meet the precise requ
processes. We would be very happy to advise you.

Our metals for vacuum evaporation.

We produce boats designed to hold the material for evaporation. These are manufactured from
tungsten, molybdenum, molybdenum lanthanum (ML), molybdenum yttrium oxide (MY) or

Get to know us.

Your contact person for evaporation boats and crucibles in

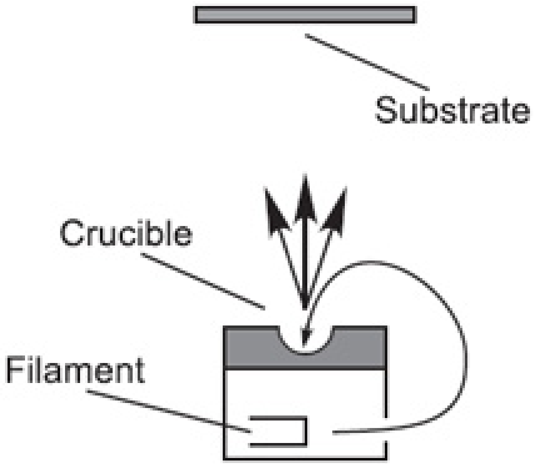
Which boat is right for your coating material?

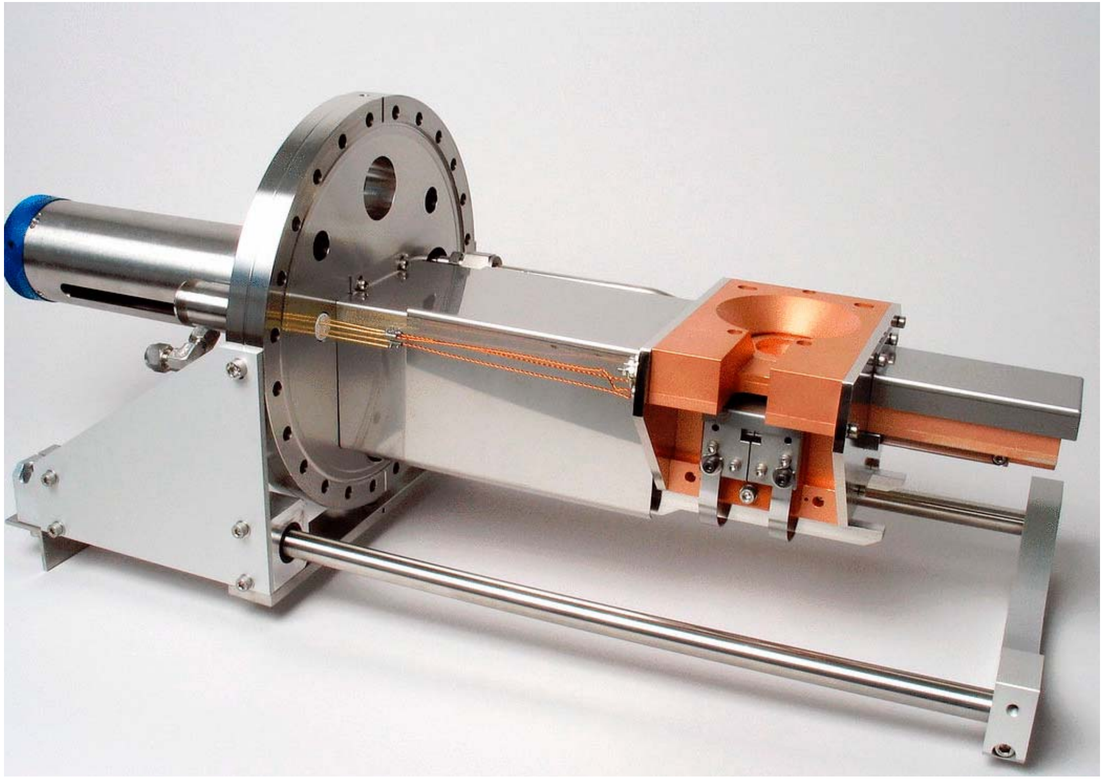
Are you looking for the right evaporation boat for your coating material? Boats with one plus are suitable for your material. And boats marked with two pluses are particularly highly recommended. Would you like to find out more? Let's talk in person.

Coating material	Density [g/cm³]	Melting point [°C]	Boiling point [°C]	Evaporation boat		
				W	Mo	Ta
Al	2.7	660	2467	+		
AlF_3	2.9	1291	N/A		++	++
Al/1 – 4% Cu	2.7	650	N/A	+		
Al/0.1 – 2% Si	2.7	640	N/A	+		
Al/4% Cu/1% Si	2.7	640	N/A	+		
Ag	10.5	961	2212	++	++	
As_2S_3	3.4	300	707		++	
Au	19.3	1063	2966	++	+	
B_2O_3	2.5	460	2247		++	
BaF_2	4.9	1280	2260	++	++	++
$BaTiO_3$	6.0	1600	N/A	+		+
BeO	3.0	2530	4120	+		
Bi	9.8	271	1560	++	++	++
BiF_3	5.3	727	900		++	++
Bi_2O_3	8.9	820	1890	+	+	

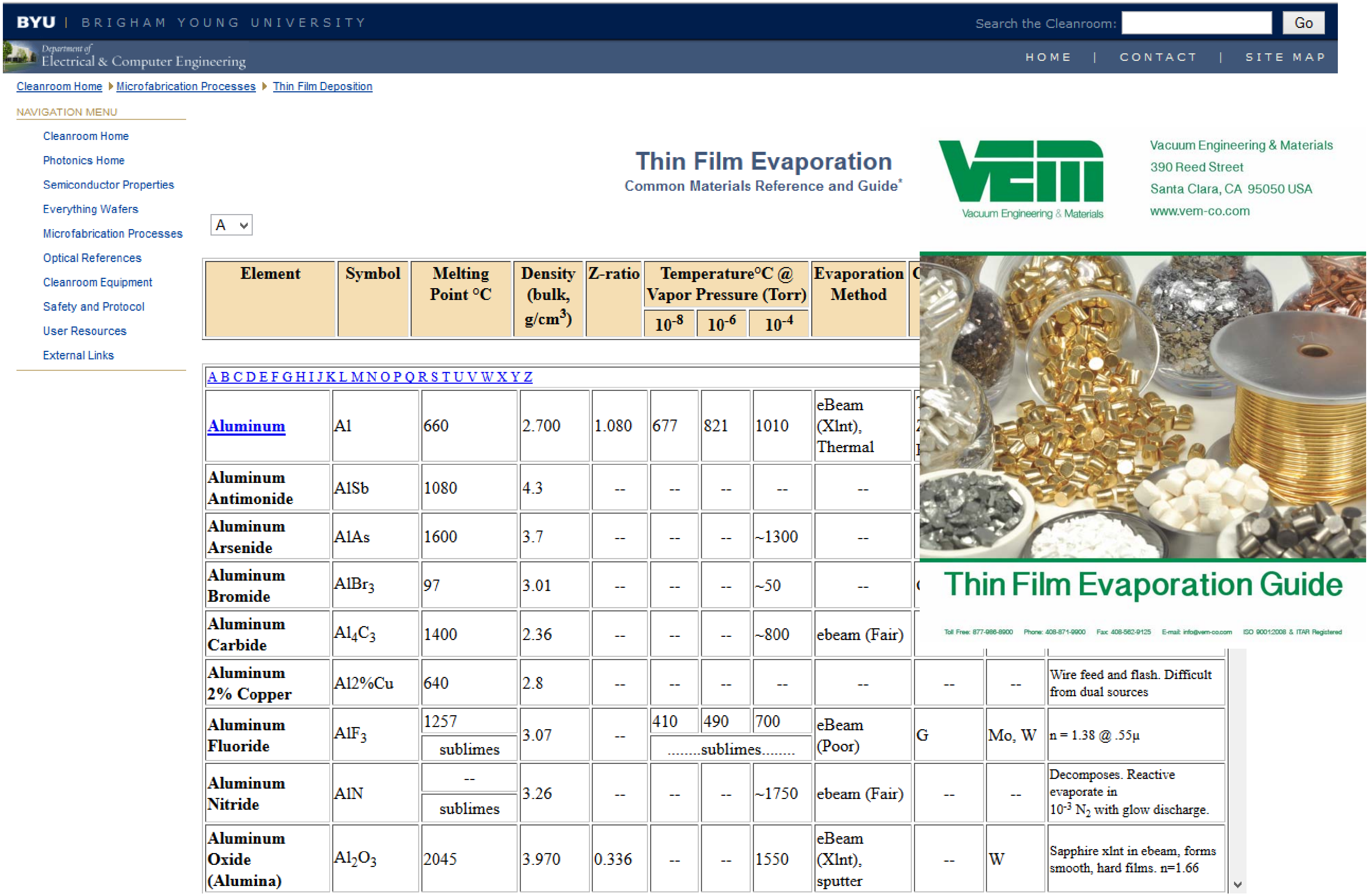
http://www.plansee.com/en/Products-System-components-and-accessories-Coating-systems-Evaporation-boats-100.htm

Electron-beam evaporation





http://www.polyteknik.com/E-Beam_Evaporation.html
http://www.directindustry.com/prod/omicron/evaporators-electron-beam-20757-1062065.html



Thin Film Evaporation

Common Materials Reference and Guide*

Vacuum Engineering & Materials
390 Reed Street
Santa Clara, CA 95050 USA
www.vem-co.com

Element	Symbol	Melting Point °C	Density (bulk, g/cm³)	Z-ratio	Temperature°C @ Vapor Pressure (Torr)			Evaporation Method			
					10^{-8}	10^{-6}	10^{-4}				
Aluminum	Al	660	2.700	1.080	677	821	1010	eBeam (Xlnt), Thermal			
Aluminum Antimonide	AlSb	1080	4.3	--	--	--	--	--			
Aluminum Arsenide	AlAs	1600	3.7	--	--	--	~1300	--			
Aluminum Bromide	$AlBr_3$	97	3.01	--	--	--	~50	--			
Aluminum Carbide	Al_4C_3	1400	2.36	--	--	--	~800	ebeam (Fair)			
Aluminum 2% Copper	Al2%Cu	640	2.8	--	--	--	--	--	--	--	Wire feed and flash. Difficult from dual sources
Aluminum Fluoride	AlF_3	1257 sublimes	3.07	--	410 ....sublimes........	490	700	eBeam (Poor)	G	Mo, W	n = 1.38 @ .55µ
Aluminum Nitride	AlN	-- sublimes	3.26	--	--	--	~1750	ebeam (Fair)	--	--	Decomposes. Reactive evaporate in 10^{-3} N_2 with glow discharge.
Aluminum Oxide (Alumina)	Al_2O_3	2045	3.970	0.336	--	--	1550	eBeam (Xlnt), sputter	--	W	Sapphire xlnt in ebeam, forms smooth, hard films. n=1.66

Thin Film Evaporation Guide

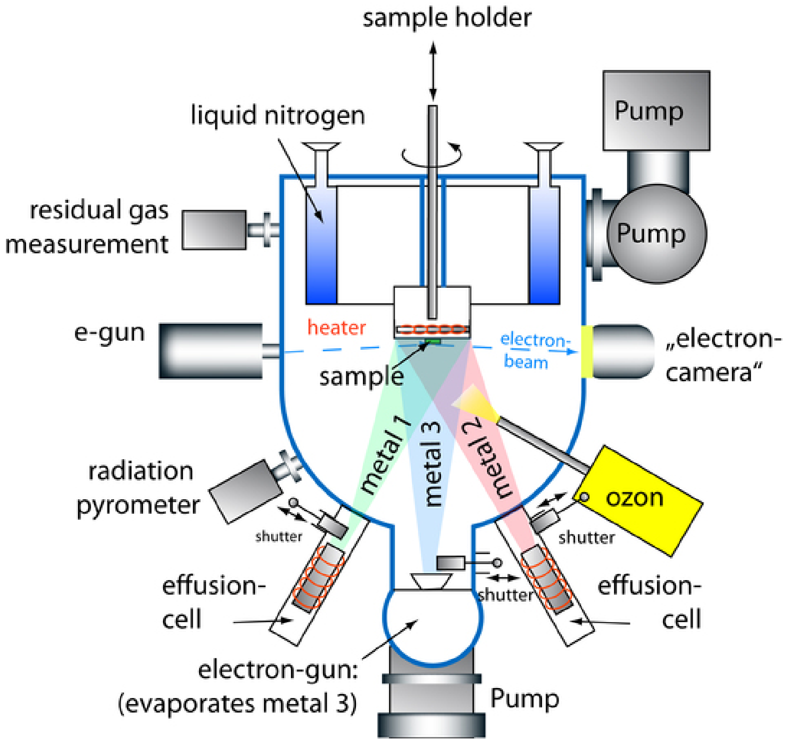
Toll Free: 877-986-8900 Phone: 408-871-9900 Fax: 408-562-9125 E-mail: info@vem-co.com ISO 9001:2008 & ITAR Registered

http://www.cleanroom.byu.edu/TFE_materials.phtml

Electron-beam evaporation

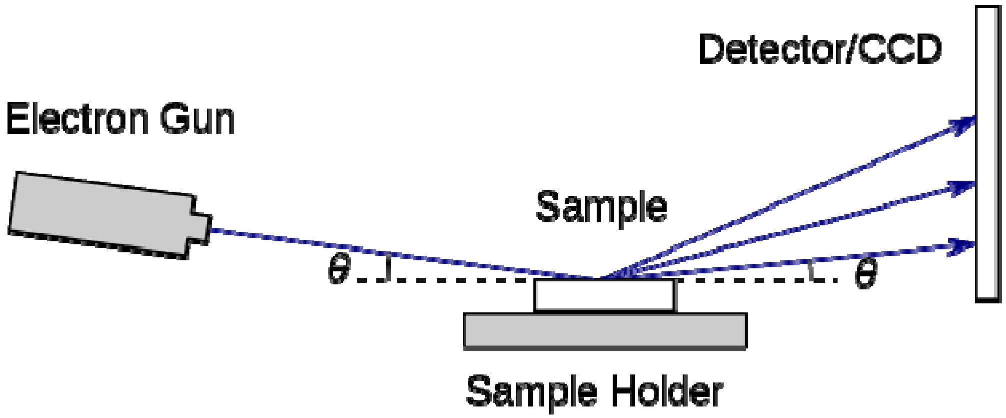
Electron accelerating voltages: 3 kV – 40 kV
10 - 100 kW power
High vacuum
x-rays and secondary electrons are emitted
deposition rate from 0.1 µm / min to 100 µm / min
Alloys can be difficult because the components evaporate at different rates
Co-evaporation is sometimes used for alloys
line-of-sight deposition process
Not suitable for large areas or coating complex shapes

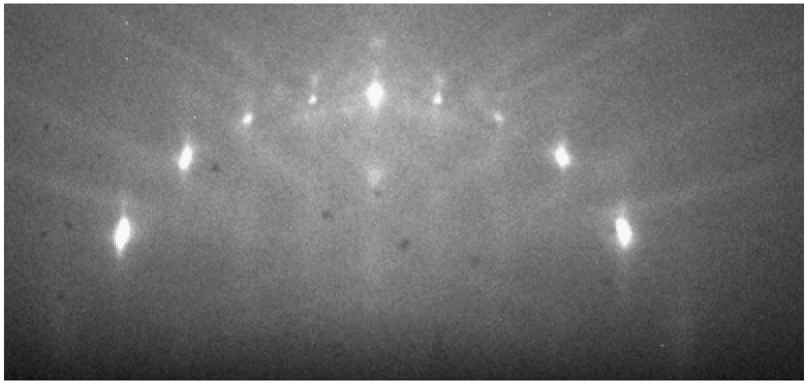
Molecular Beam Epitaxy (MBE)

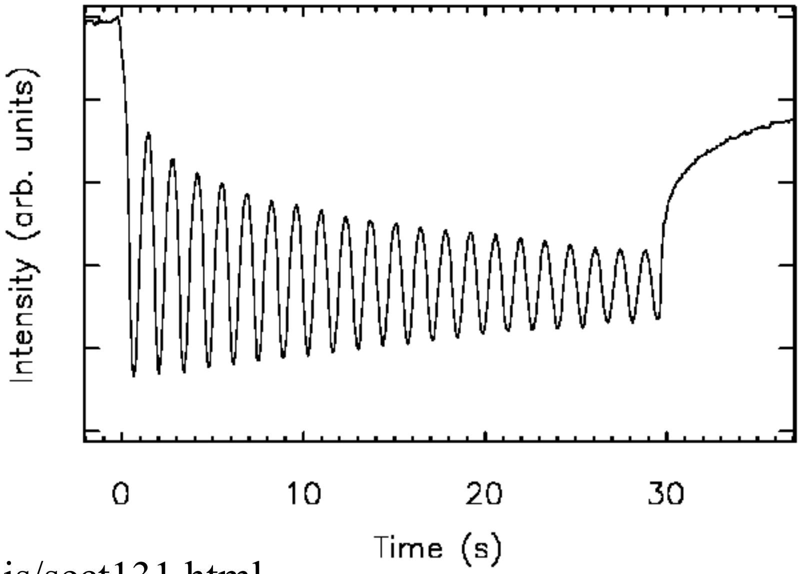


http://www.eps.hw.ac.uk/institutes/photonics-quantum-sciences/mbe.htm
http://www.fkf.mpg.de/273938/30_Oxide_MBE_Lab

RHEED
(Reflection high-energy electron diffraction)

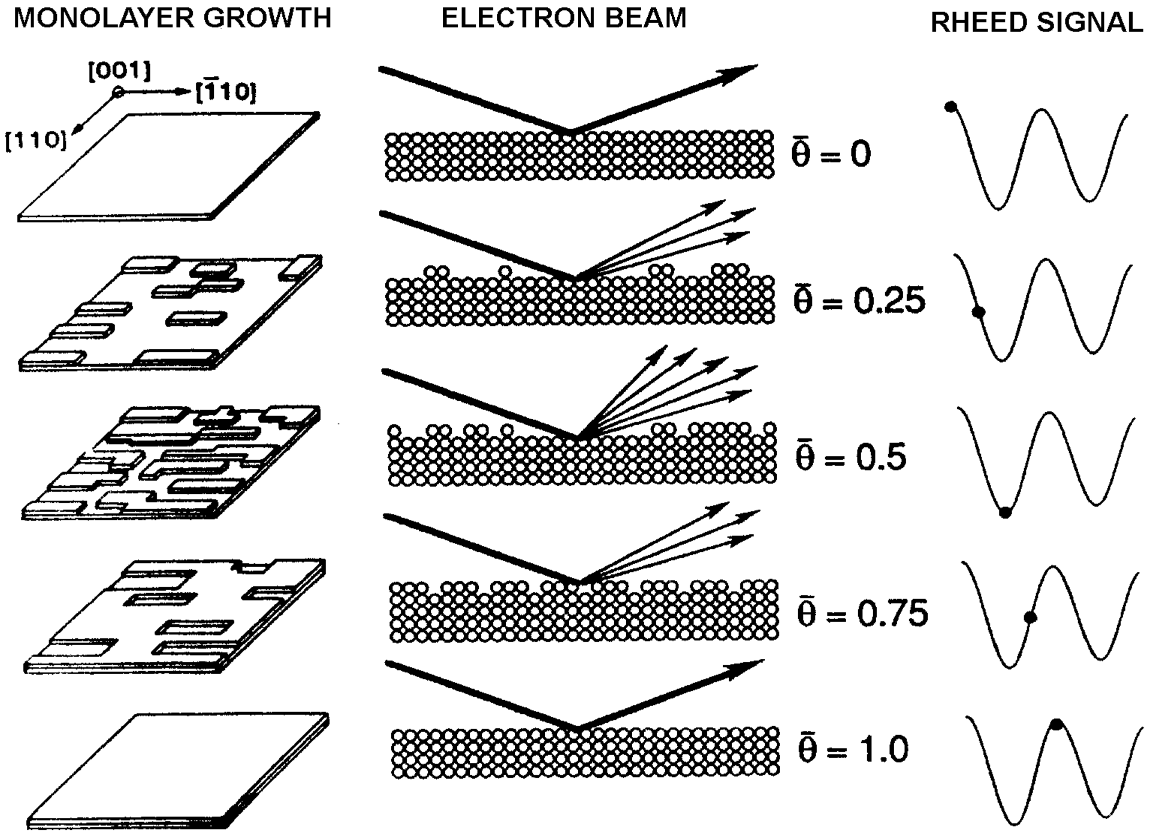






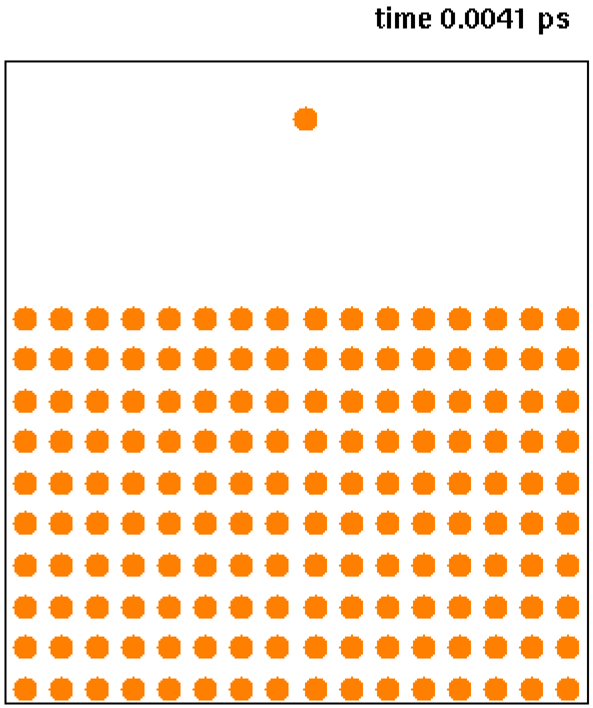
http://asumbe.eas.asu.edu/formermembers/wolfgang/thesis/sect131.html
http://en.wikipedia.org/wiki/Reflection_high-energy_electron_diffraction#mediaviewer/File:RHEED.svg

RHEED



M. Ohring, *The Material Science of Thin Films*, Academic Press, 1992.

Molecular dynamics



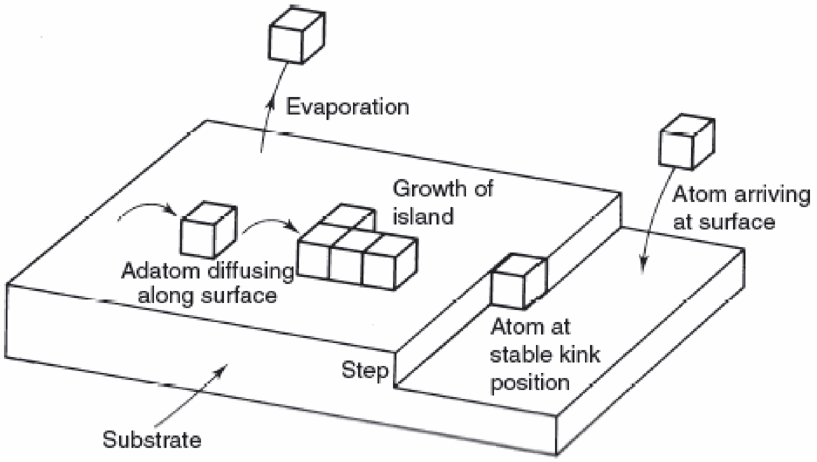


Figure 6.8 Terrace step kink (TSK) growth model of epitaxy: growth proceeds at kinks, and adatoms on flat surface diffuse to energetically favorable positions at kinks. Wafer miscut creates terraced structure. Reproduced from Jenkins (1995)

Calculate the motions of the atoms at the surface.

Growth modes

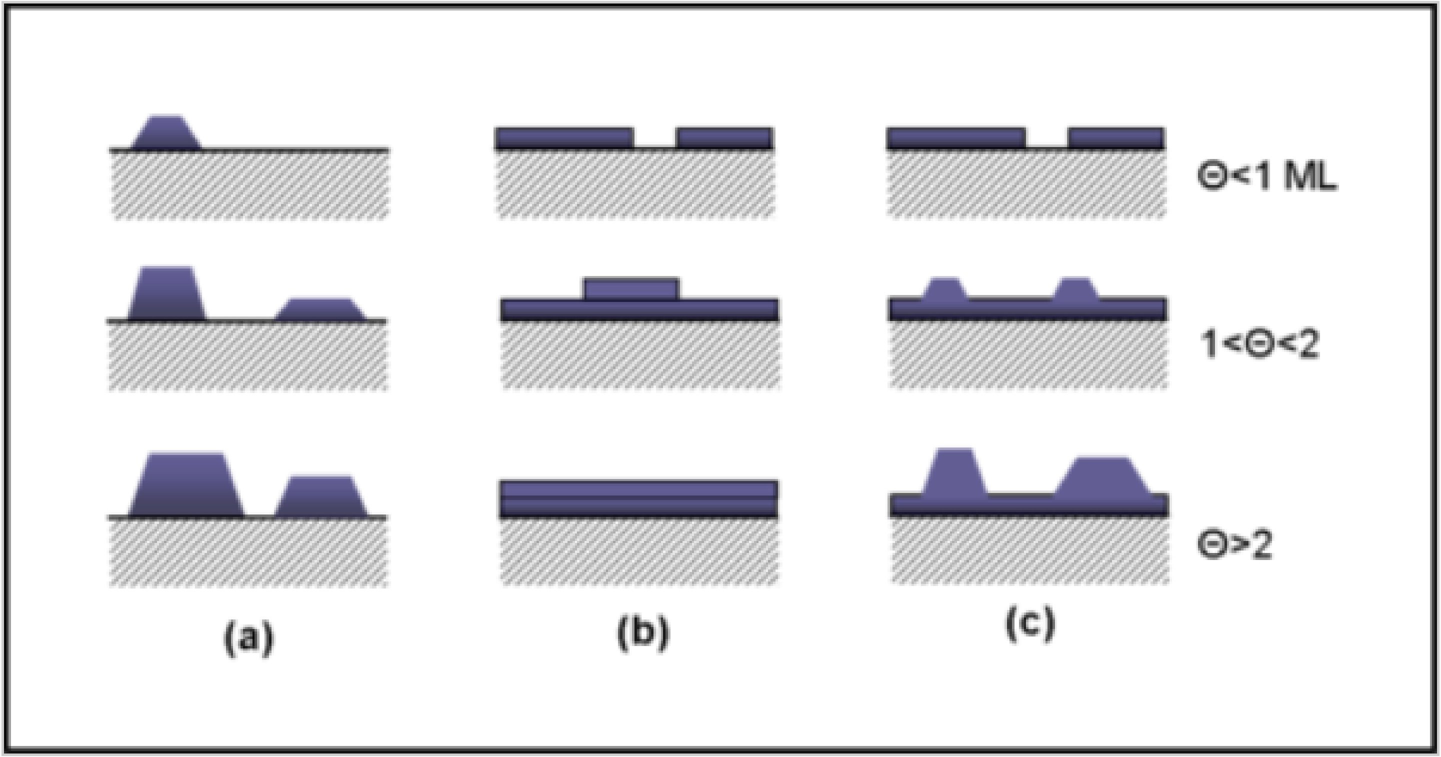
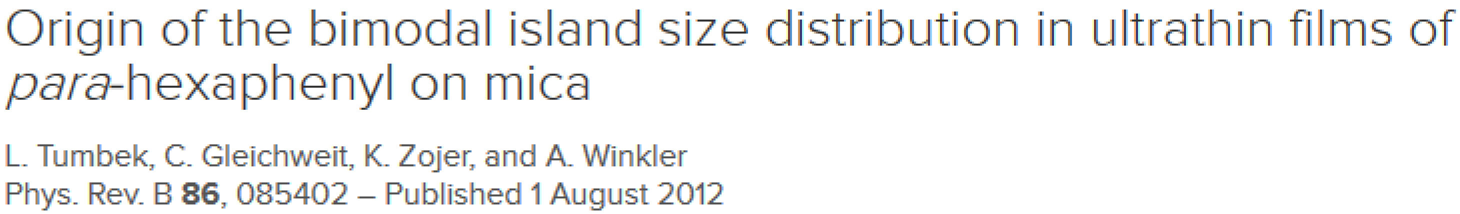


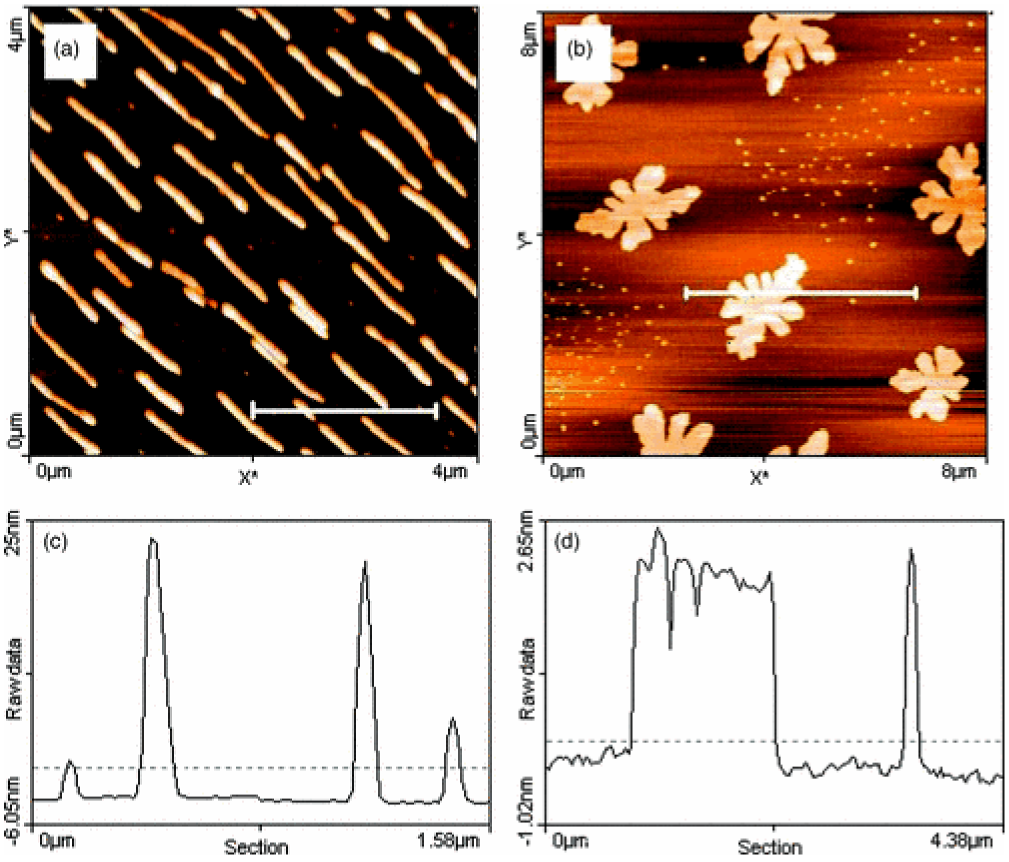
Figure 1. Cross-section views of the three primary modes of thin-film growth including (a) Volmer–Weber (VW: island formation), (b) Frank–van der Merwe (FM: layer-by-layer), and (c) Stranski–Krastanov (SK: layer-plus-island). Each mode is shown for several different amounts of surface coverage, Θ.

http://en.wikipedia.org/wiki/Stranski%E2%80%93Krastanov_growth



Origin of the bimodal island size distribution in ultrathin films of *para*-hexaphenyl on mica

L. Tumbek, C. Gleichweit, K. Zojer, and A. Winkler
Phys. Rev. B **86**, 085402 – Published 1 August 2012



Evaporated atoms or molecules may form layers, needles, or clusters.

Heteroepitaxy

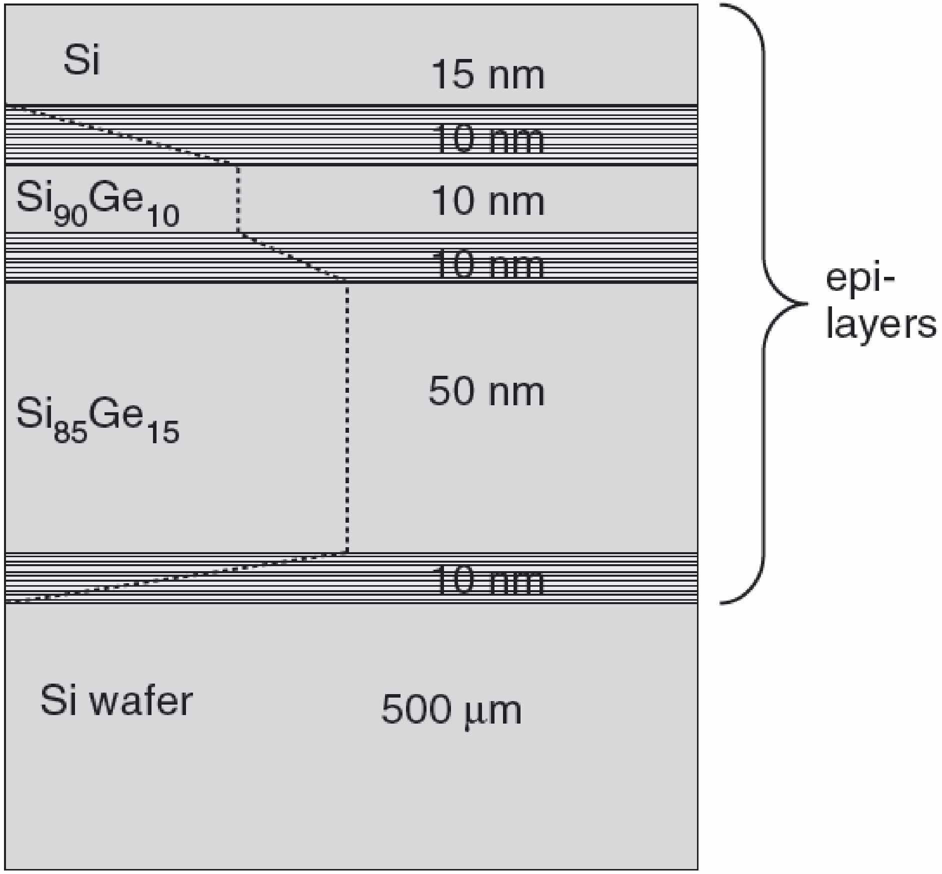
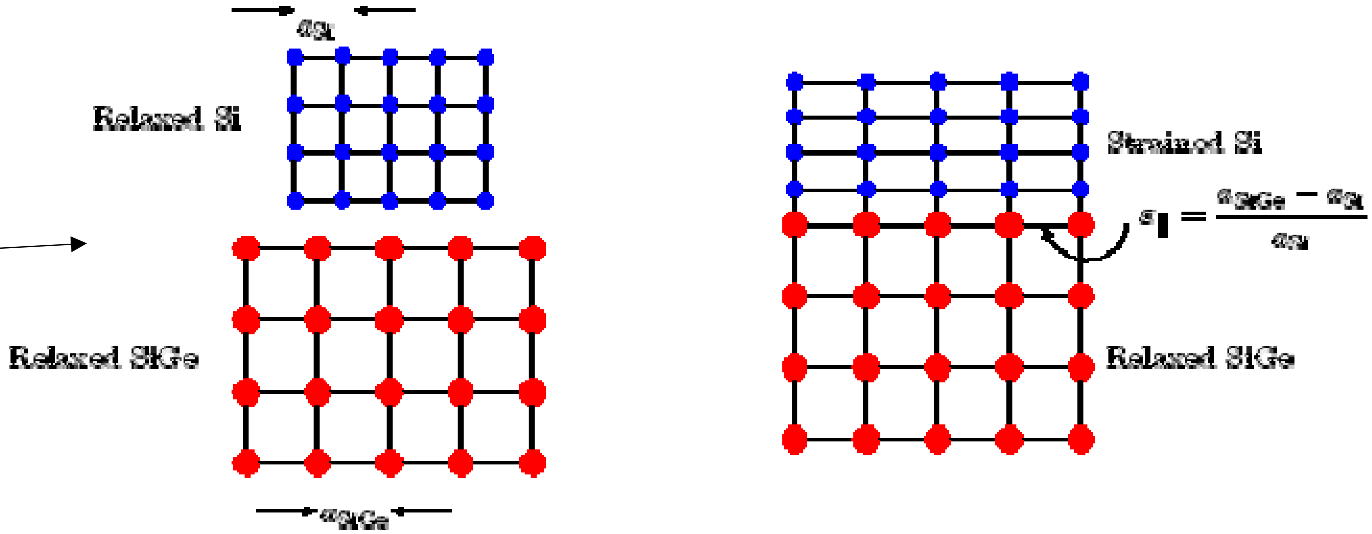


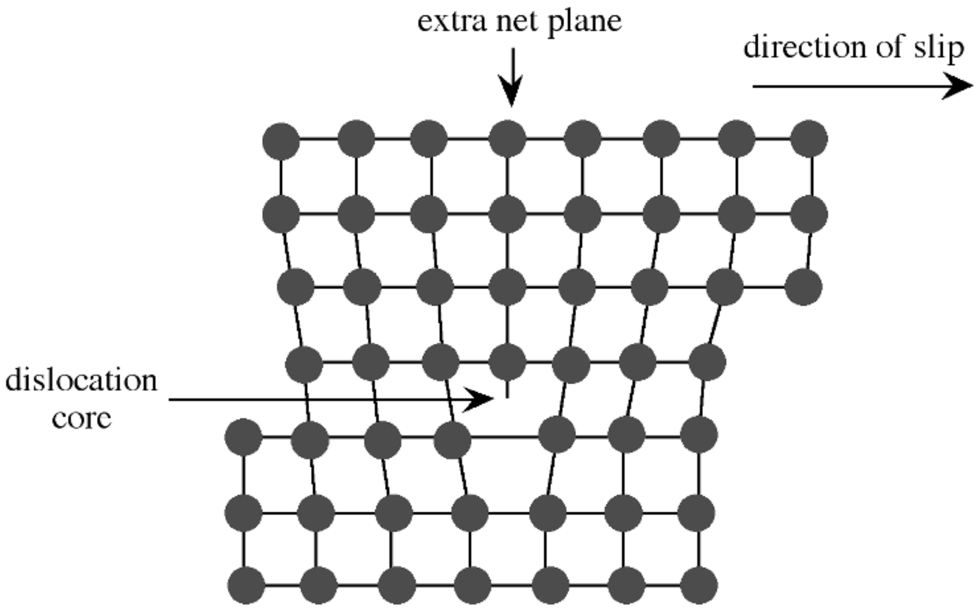
Figure 6.6 Thin heteroepitaxial $Si_{1-x}Ge_x$ layers for high-speed bipolar transistors. The hatched layers are graded epilayers with constantly changing germanium content

Fransila

Strain induced by lattice mismatch



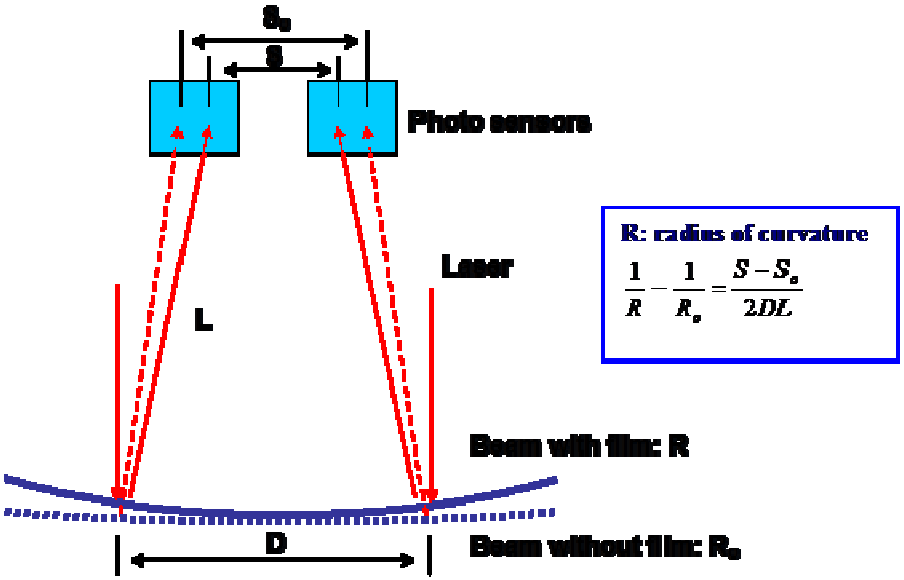
http://www.iue.tuwien.ac.at/phd/dhar/node12.html



http://cnx.org/contents/e90d5161-66b0-4214-bd6c-9f1d20a35bae@10/Crystal_Structure

Stoney's formula

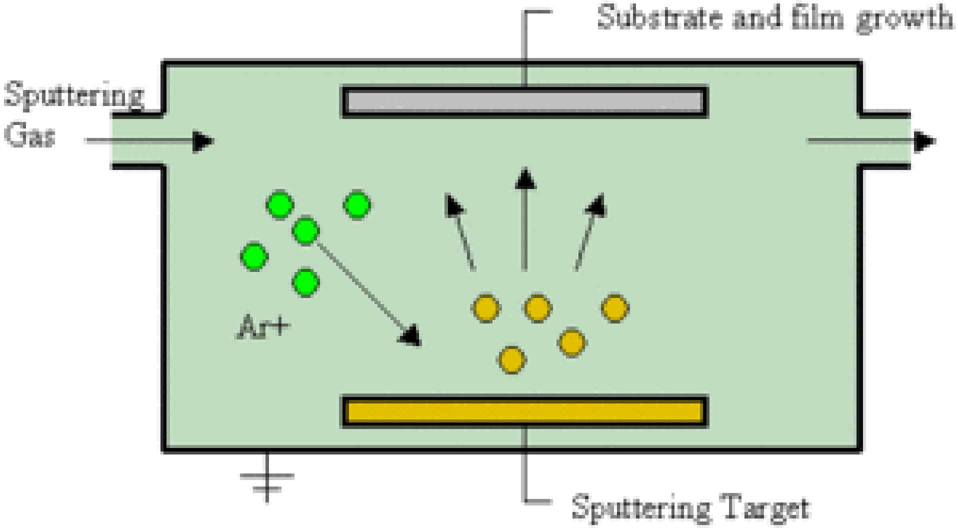
$$\sigma_f = \frac{E_s h_s^2 \kappa}{6h_f(1-\nu_s)}$$



The stress σ_f in the film depends on
E_s Young's modulus in the substrate
ν_s Poisson's ratio of the substrate
h_s thickness of the substrate
h_f thickness of the film
κ curvature

Only holds for uniform curvature

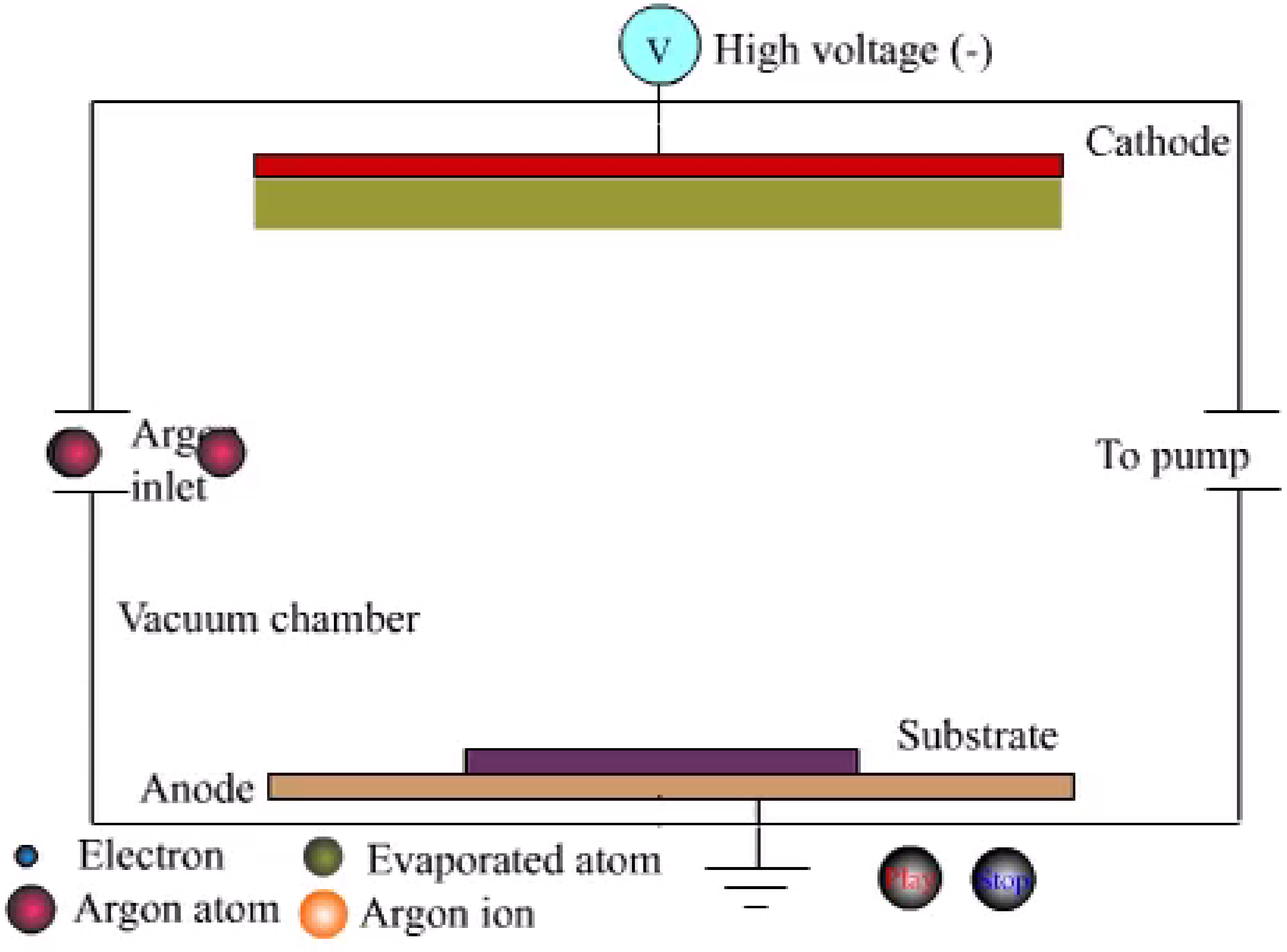
Sputtering



Sputtering can be used to clean a surface and to deposit material.
Low-emissivity coatings on double-pane window glass.

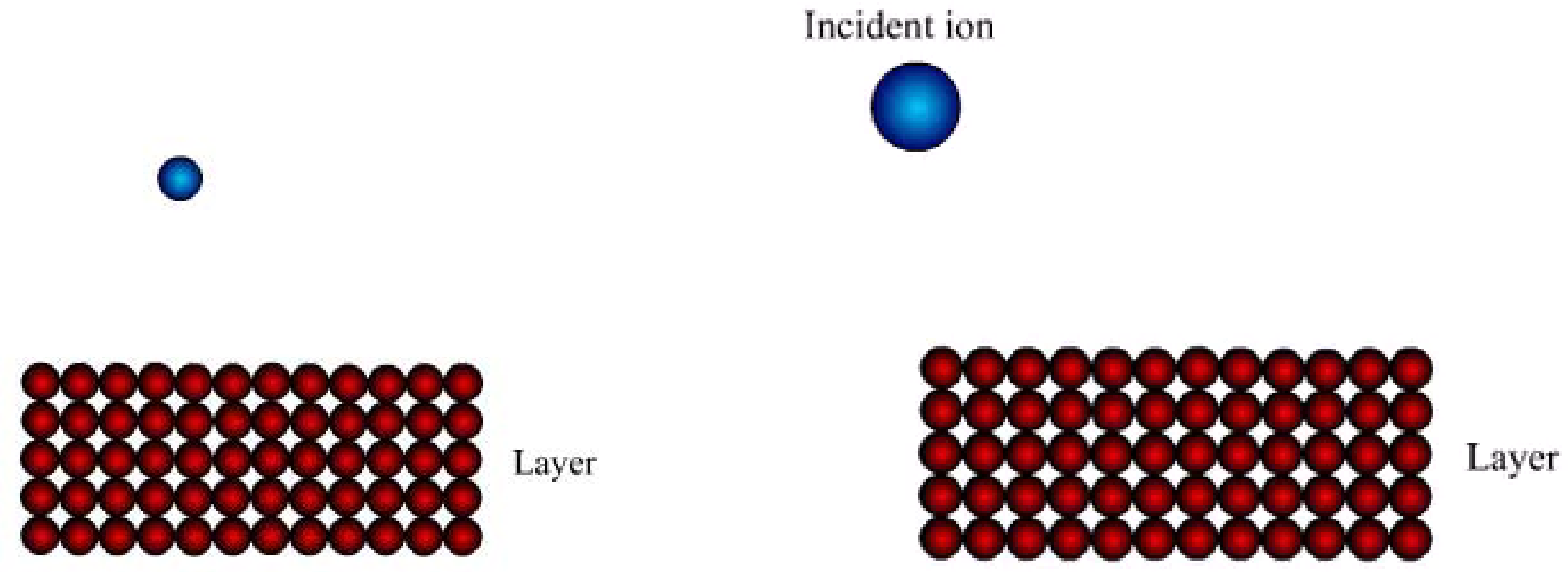
http://en.wikipedia.org/wiki/Sputtering
http://en.wikipedia.org/wiki/Sputter_deposition

Sputtering



http://81.161.252.57/ipci/courses/technology/inde_146.htm

Sputtering



Depending of the particle energy and angle, it may be implanted or bounce off. The sputter gas can bounce off the target and get implanted in the film.

http://81.161.252.57/ipci/courses/technology/inde 147.htm

Deposition Materials

MANUFACTURING DIVISION
- Manufacturing Overview
- Vacuum Chambers

PROCESS EQUIPMENT DIVISION
- Thin Film Deposition Systems
- Deposition Sources
- Process Equipment
- Thin Film Deposition System Components

MATERIALS DIVISION
- Deposition Materials
- Evaporation Sources

VACUUM MART DIVISION
- Feedthroughs & Viewports
- Flanges & Components
- Gas & Liquid Mgmt
- Manipulation & Motion
- Pressure Measurement
- Traps & Filters
- Vacuum Fluids
- Vacuum Pumps
- Vacuum Valves

Deposition Materials > Sputtering Targets > Material Names A -

Material Names A - C:

- Aluminum, Al
- Aluminum Copper, Al/Cu
- Aluminum Nitride, AlN
- Aluminum Oxide, Al_2O_3
- Aluminum Silicon Copper, Al/Si/Cu
- Aluminum Silicon, Al/Si
- Antimony, Sb
- Antimony Telluride, Sb_2Te_3
- Barium, Ba
- Barium Cerium Yttrium Zirconate, $BaCe_{(1-x-y)}Y_{(x)}Zr_{(y)}O_3$
- Barium Ferrite, $BaFe_{12}O_{19}$
- Barium Fluoride, BaF_2
- Barium Strontium Titanate, $Ba_{(1-x)}Sr_{(x)}TiO_3$
- Barium Strontium Titanate, $Ba_{0.5}Sr_{0.5}TiO_3$
- Barium Titanate, $BaTiO_3$
- Barium Zirconate, $BaZrO_3$
- Bismuth, Bi
- Bismuth Calcium Ferrite, $Bi_{0.9}Ca_{0.1}FeO_3$
- Bismuth Dysprosium Iron Gallate, $Bi_2DyFe_4GaO_{12}$
- Bismuth Ferrite (Garnet), $Bi_3Fe_5O_{12}$

- Bismuth Dysprosium Iron Gallate, $Bi_2DyFe_4GaO_{12}$
- Bismuth Ferrite (Garnet), $Bi_3Fe_5O_{12}$

- Bismuth Ferrite, $BiFeO_3$
- Bismuth Lanthanum Ferrite, $Bi_{(1-x)}La_xFeO_3$
- Bismuth Lutetium Iron Gallate, $Bi_{1.5}Lu_{1.5}Fe_4GaO_1$
- Bismuth Manganate, $Bi_{2.4}MnO_3$
- Bismuth Oxide, Bi_2O_3
- Bismuth Selenide, Bi_2Se_3
- Bismuth Telluride, Bi_2Te_3
- Bismuth Titanate, $Bi_4Ti_3O_{12}$
- Boron, B
- Boron Carbide, B_4C
- Boron Nitride, BN
- Cadmium, Cd
- Cadmium Selenide, CdSe
- Cadmium Sulfide, CdS
- Cadmium Telluride, CdTe
- Calcium, Ca
- Calcium Manganate, $CaMnO_3$
- Calcium Titanate, $CaTiO_3$
- Carbon, C (graphite)
- Carbon, C (pyrolytic graphite)
- Cerium, Ce
- Cerium Bismuth Ferrite, $Ce_{2.2}Bi_{0.8}Fe_5O_{12}$
- Cerium Fluoride, CeF_3
- Cerium Oxide, CeO_2
- Cerium Yttrium Ferrite, $Ce_{2.5}Y_{0.5}Fe_5O_{12}$
- Chromium, Cr
- Chromium Oxide, Cr_2O_3
- Chromium Silicide, $CrSi_2$
- Cobalt, Co
- Cobalt, Oxide, CoO
- Cobalt Ferrite, $CoFe_2O_4$
- Copper, Cu
- Copper Oxide, CuO

Heraeus

Sputtering Targets Applications & Markets

Our versatile product development specialists work with you to meet even the most demanding production parameters in the wide range of applications for sputtering targets.

Magnetic Data Storage
Hard Disk Drives are an important part of everyday life. We master the complex metallurgy behind this high density storage technology.
▸ **More**

Electronics / Semiconductor
From cars to refrigerators - electronics are literally everywhere. Miniaturization of circuits and structures makes sputtering targets indispensable.
▸ **More**

Display
Advancements in visual media fuel display technologies - and vice versa. Now sputtered displays are found in TVs, PCs, and Mobile Devices.
▸ **More**

Wear Resistance
The Wear Resistance market is characterized by the sputtered high performance thin film coatings which have to meet various wear, corrosion and scratch resistance requirements.
▸ **More**

Glass
Modern Glass coatings influenced and changed today's architecture. Why and how? Sputtering targets are the answer.
▸ **More**

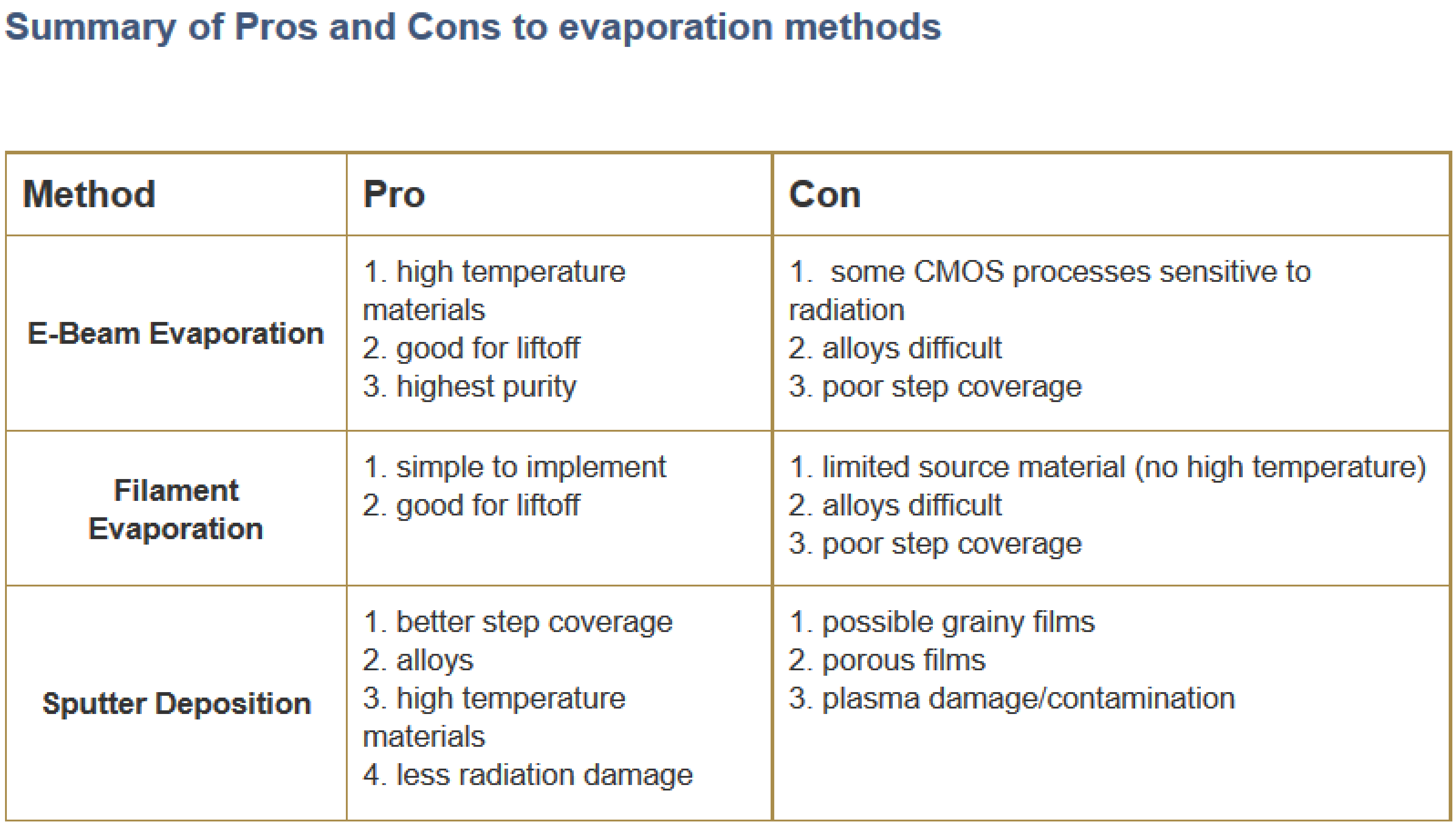
Photovoltaics
Providing a promising solution to upcoming energy scenarios, both thin film and crystalline PV are driven by sputtering processes.
▸ **More**

Solar Thermal
Solar thermal and CSP systems offer great prospects for the growing energy demand and gain momentum.
▸ **More**

http://heraeus-targets.com/en/products_1/_materials/sputtering_materials.aspx

Sputtering

You can almost sputter anything
Chemical composition of the film is the same as the target
High melting point materials can be deposited
Better step coverage than evaporation
Large areas (2x2 meters) are possible
Sputter gases are incorporated in the film

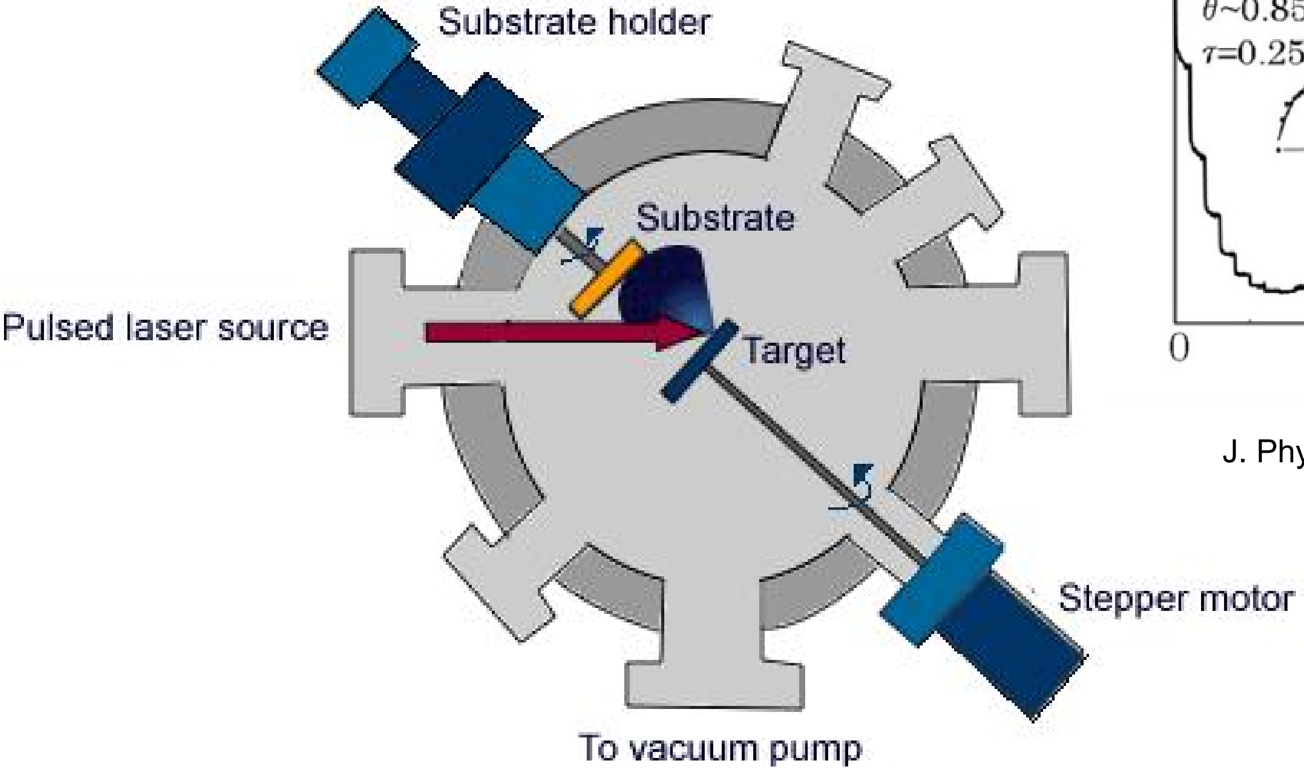


Summary of Pros and Cons to evaporation methods

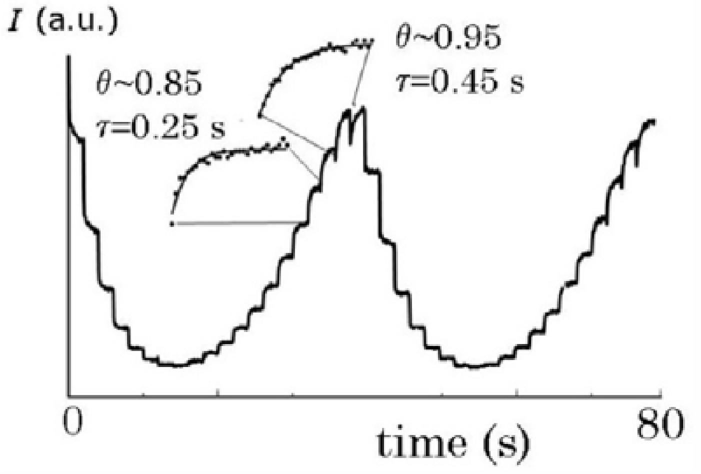
Method	Pro	Con
E-Beam Evaporation	1. high temperature materials 2. good for liftoff 3. highest purity	1. some CMOS processes sensitive to radiation 2. alloys difficult 3. poor step coverage
Filament Evaporation	1. simple to implement 2. good for liftoff	1. limited source material (no high temperature) 2. alloys difficult 3. poor step coverage
Sputter Deposition	1. better step coverage 2. alloys 3. high temperature materials 4. less radiation damage	1. possible grainy films 2. porous films 3. plasma damage/contamination

http://www.cleanroom.byu.edu/metal.phtml

Laser ablation



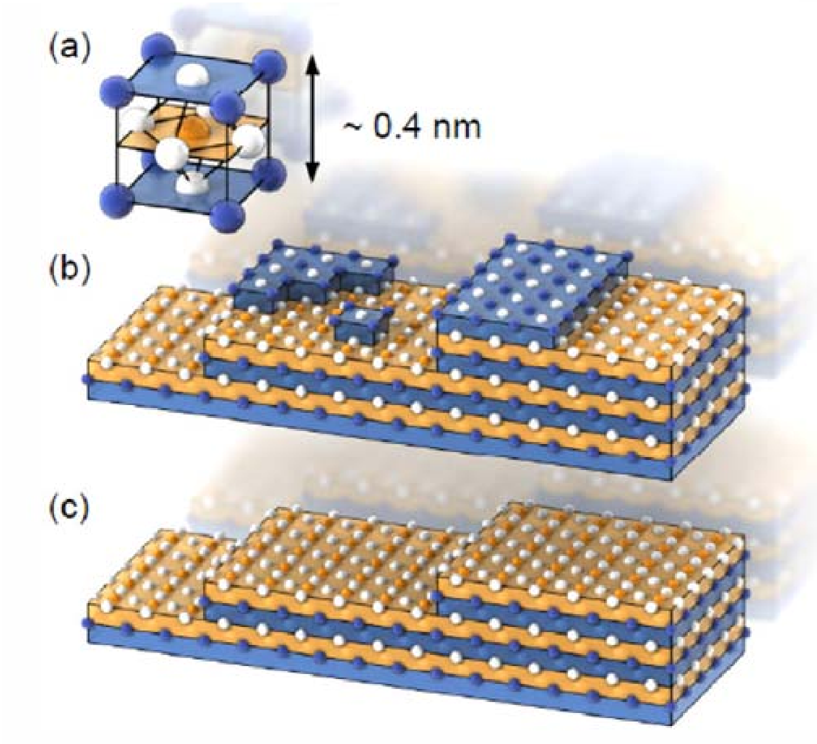
RHEED



J. Phys. D: Appl. Phys. **47** (2014) 034006

http://www.pvd-coatings.co.uk/theory/how-are-pvd-coatings-deposited/pulsed-laser-ablation/

Laser ablation



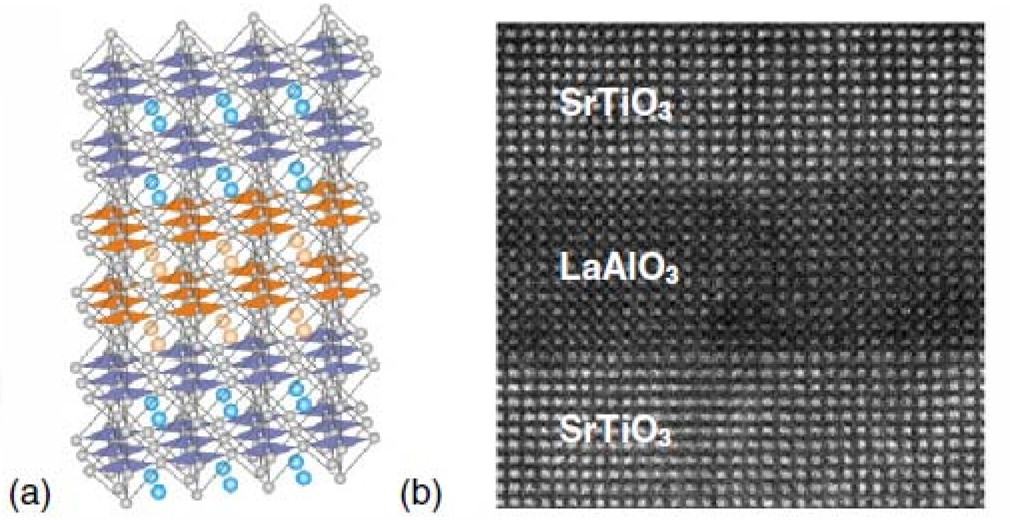


Figure 5. Schematic view of a $SrTiO_3/LaAlO_3/SrTiO_3$ heterostructure (*a*). Cross-section high-angle annular dark field (HAADF) TEM image of the $LaAlO_3/SrTiO_3$ superlattice along the [0 0 1] zone axis (*b*).

J. Phys. D: Appl. Phys. **47** (2014) 034006

Electrochemical Deposition (ECD)

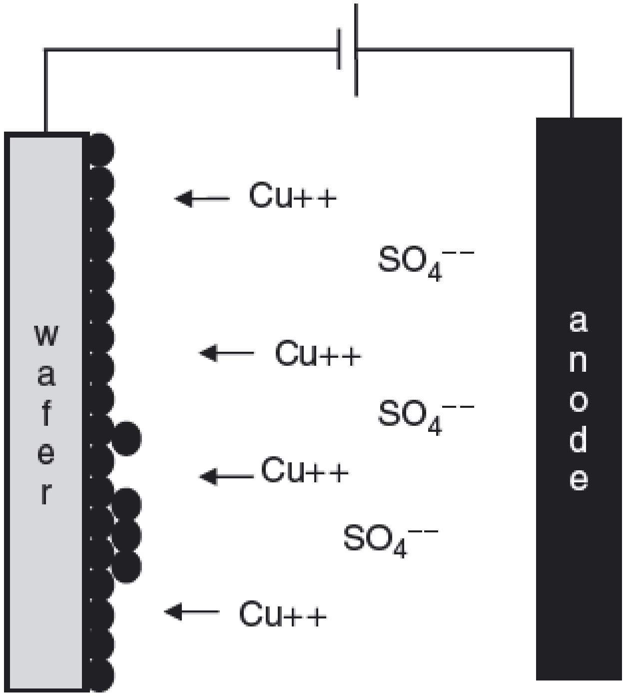


Figure 5.10 Electroplating: $CuSO_4$ electrolyte ionizes to produce Cu^{++} and $SO_4{}^{2+}$ ions, copper film deposits at the cathode

Copper

At cathode	$Cu^{2+} + 2\ e^- \longrightarrow Cu(s)$
	electrolyte solution: $CuSO_4$
At anode	$Cu \longrightarrow Cu^{2+} + 2\ e^-$

Lithography and Galvanic plating (LIGA)

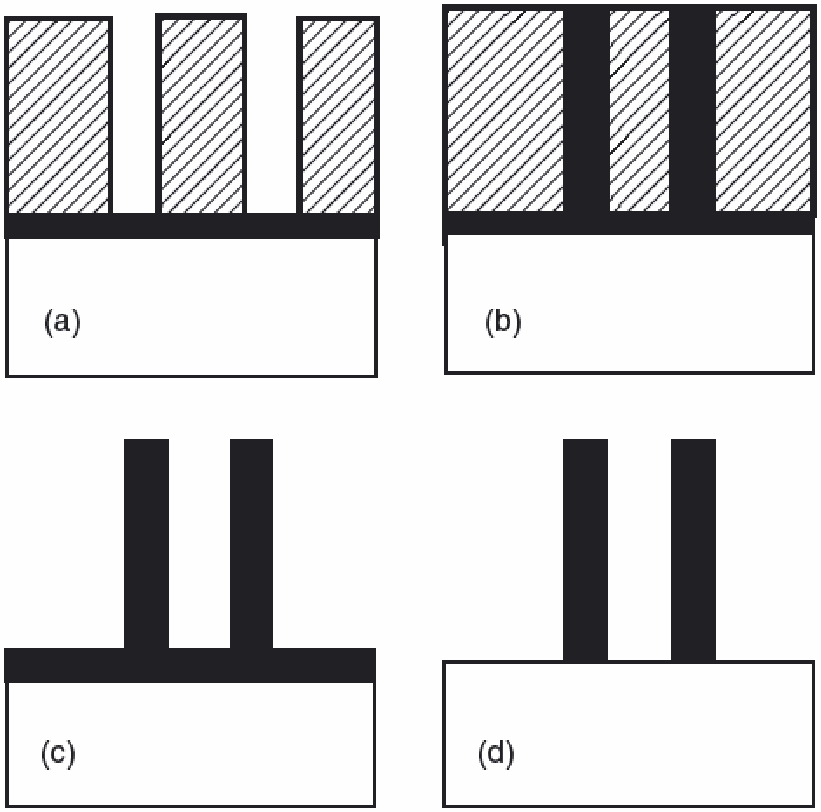


Figure 5.12 Resist masked plating (LIGA, for Lithography and Galvanic plating): (a) seed layer deposition and lithography; (b) plating; (c) resist stripping; (d) seed layer removal

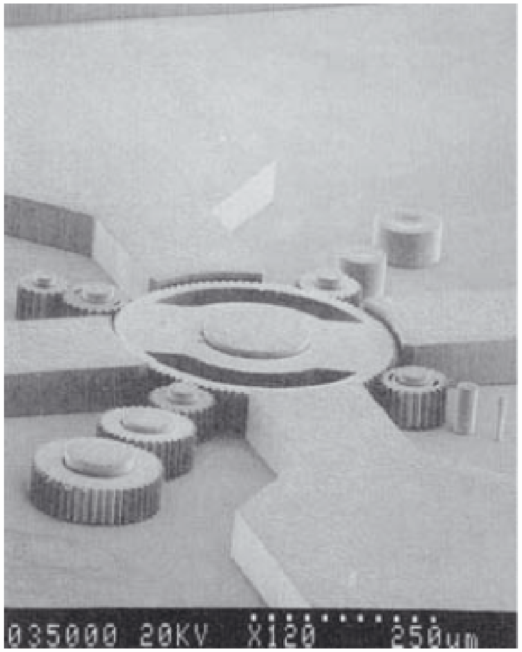
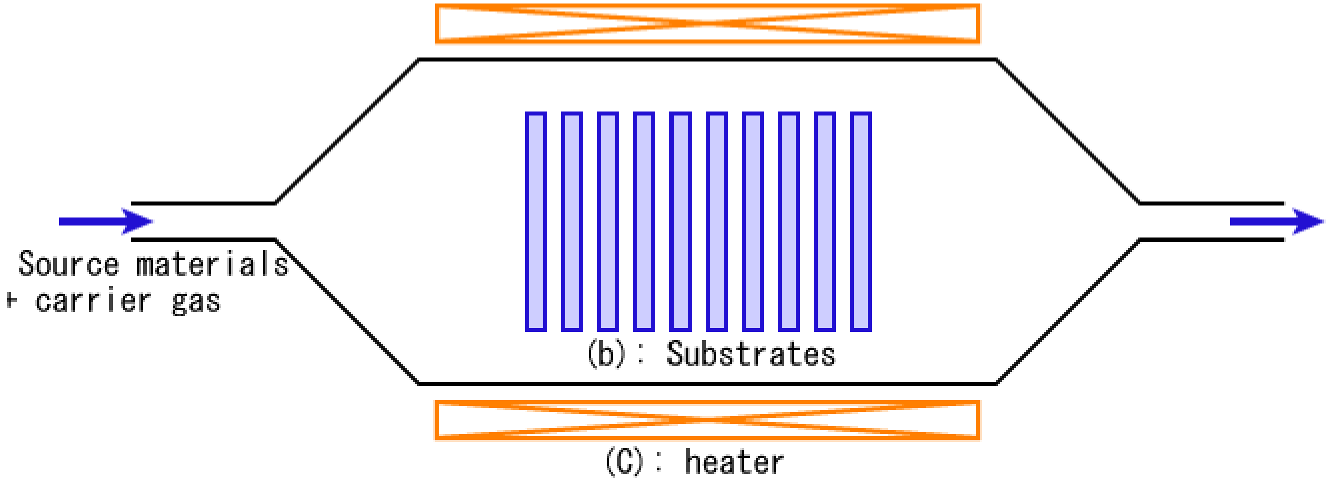


Figure 5.11 Nickel gear structures (50 µm high) made by electroplating. Reproduced from Guckel (1998) by permission of IEEE

Fransila

Chemical vapor deposition

image from wikipedia



Epitaxial silicon CVD SiH_4 (silane) or SiH_2Cl_2 (dichlorosilane)
PH_3 (phosphine) for n-doping or
B_2H_6 (diborane) for p-doping.

http://www.asm.com/solutions/products/epitaxy-products/epsilon-epitaxy

Si CVD

$$\mathrm{SiH_4\ (g) \Longrightarrow Si\ (s) + 2\ H_2\ (g)} \qquad \sim 600\,^{\circ}\mathrm{C}$$

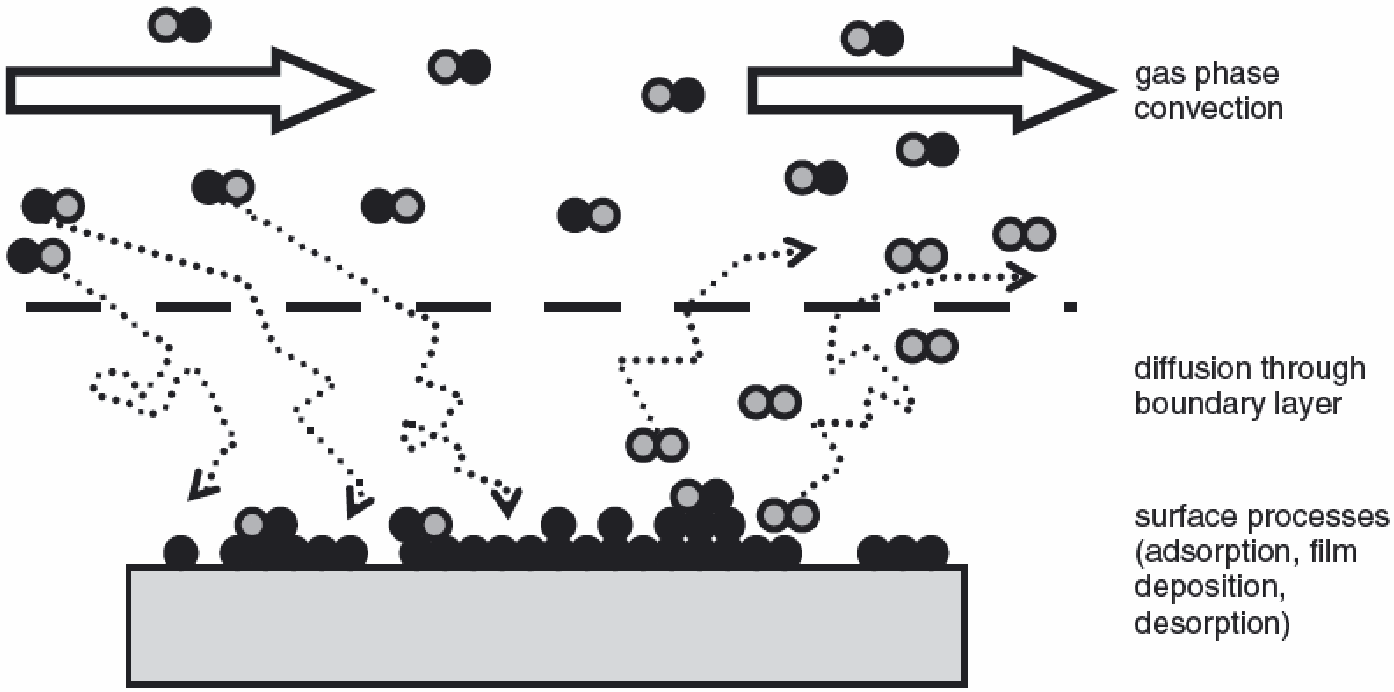


Figure 5.6 CVD: source gas molecules adsorb and react on surface to form a film, and the reaction products are desorbed, diffused and pumped away

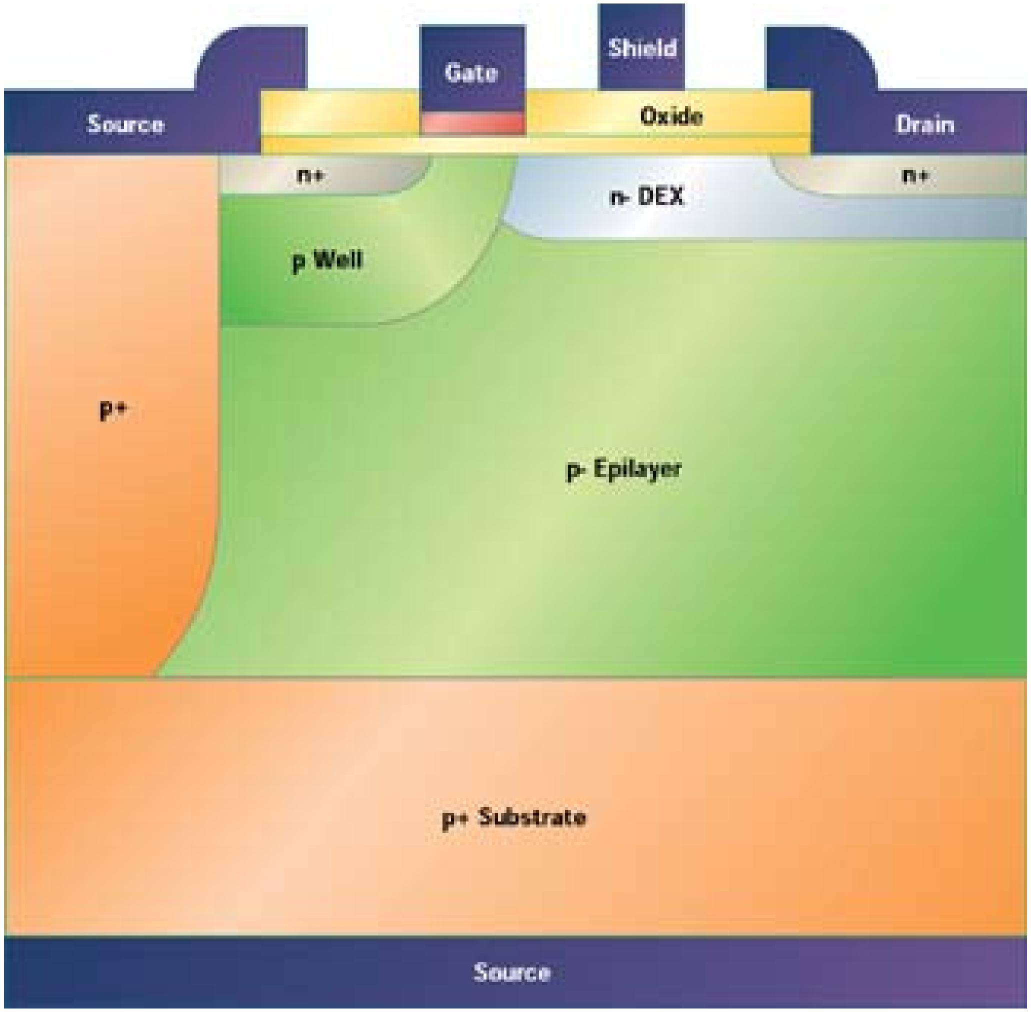
Fransila

Epi - layers

Chemically purer than substrate

Doping controlled independently

Commonly used in CMOS and bipolar device technology



Epi-wafers can be purchased

epitaxial lateral overgrowth (ELO)

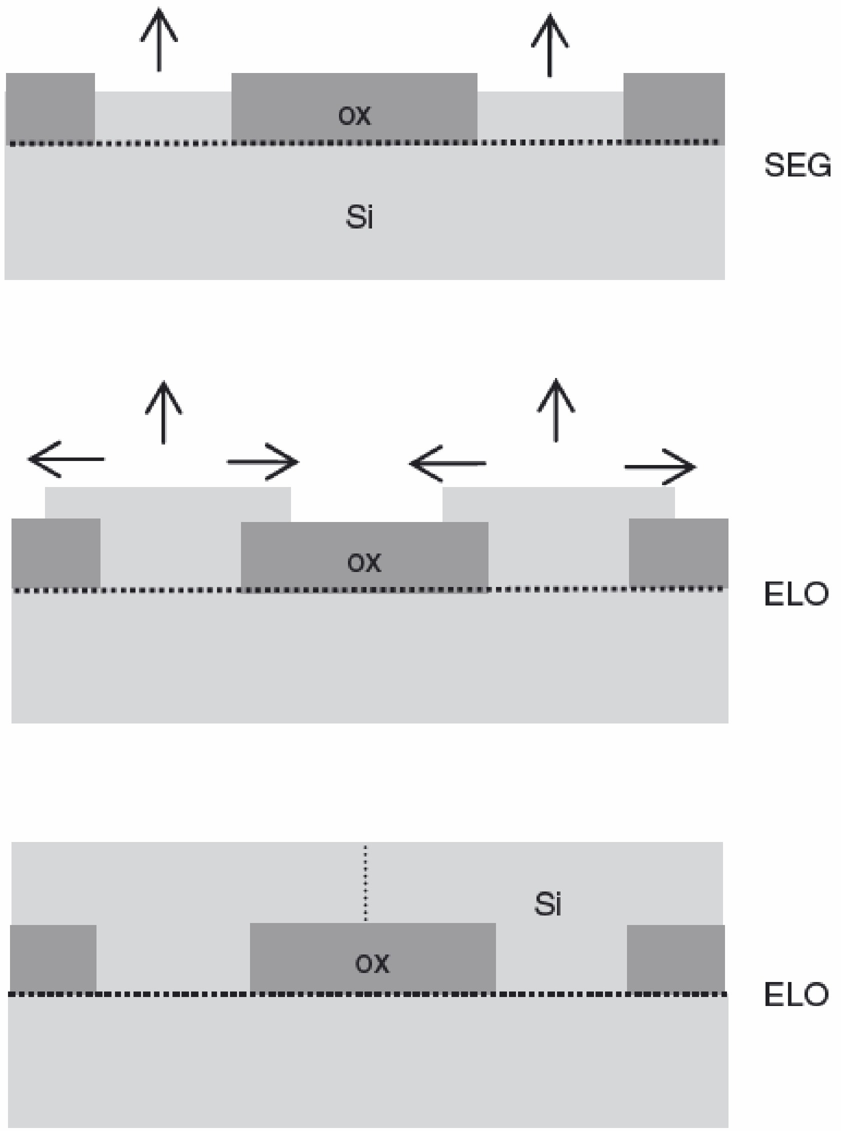
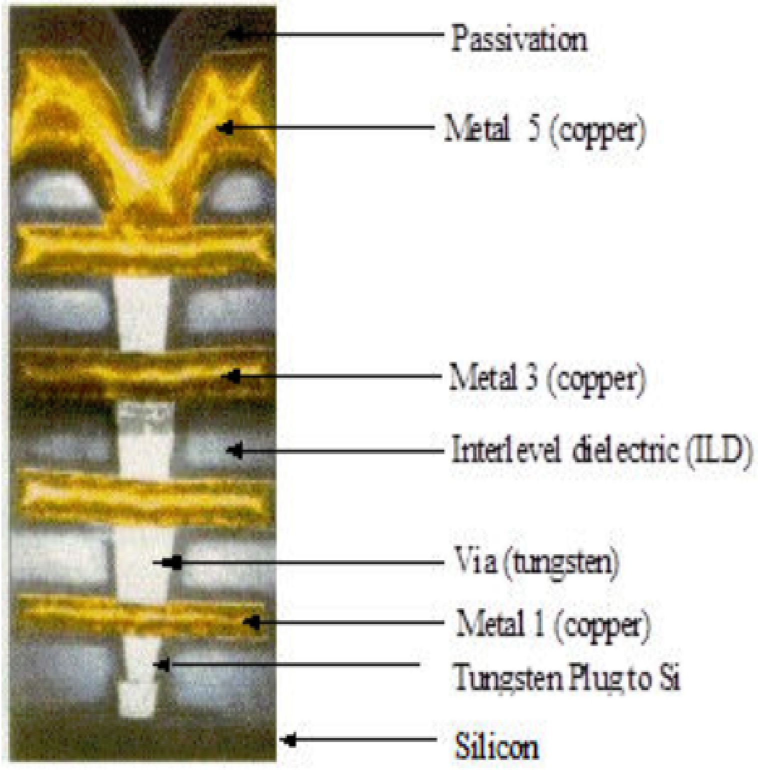


Figure 6.12 SEG, selective epitaxial growth, no deposition on oxide; ELO, epitaxial lateral overgrowth; merging of epitaxial film fronts over oxide

Defect density can be high where the films meet

Tungsten CVD



The tungsten precusor is tungsten hexafluoride, WF_6. WF_6 is a quite volatile liquid at room temperature, the vapor is delivered to the reaction chamber through a mass flow controller from the reservoir. WF_6 reacts readily with any moisture present to produce tungsten oxides and hydrofluoric acid, HF. It is imperative to avoid moisture in the plumbing: purged high quality stainless steel and metal seals are required.

In the semiconductor industry CVD tungsten has found a very particular niche because of its properties and its ability to deposit uniformly over patterned substrates. It's most common application has been and continues to be the filling of vias between metallisation levels and contacts windows to device silicon.

CVD Tungsten requires a an adhesion or nucleation layer to allow deposition on dielectrics, typically Ti or TiN.

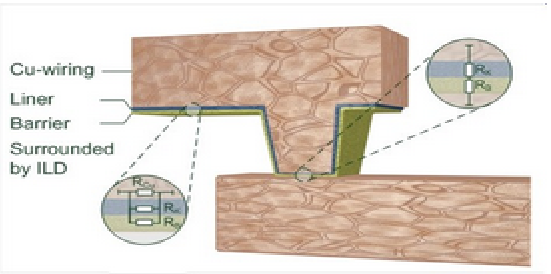
$$\mathrm{WF_6\ (g) + 3\ H_2\ (g) \Longrightarrow W\ (s) + 6\ HF\ (g)}$$

http://www.qub.ac.uk/research-centres/QAMEC/ResearchActivities/Metallisation/CVDTungsten/

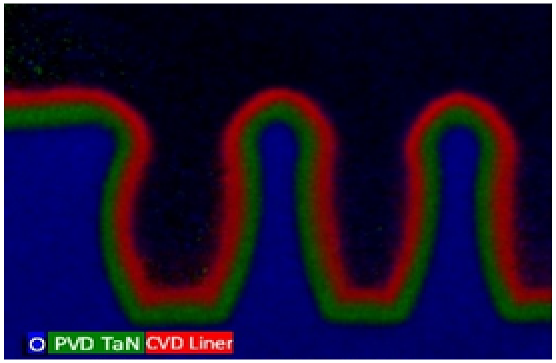
Interconnects: Copper Diffusion Barriers

Fraunhofer Institute for Photonic Microsystem

Advanced Copper Diffusion Barriers



Cross section of a via/trench structure with liner and barrier.

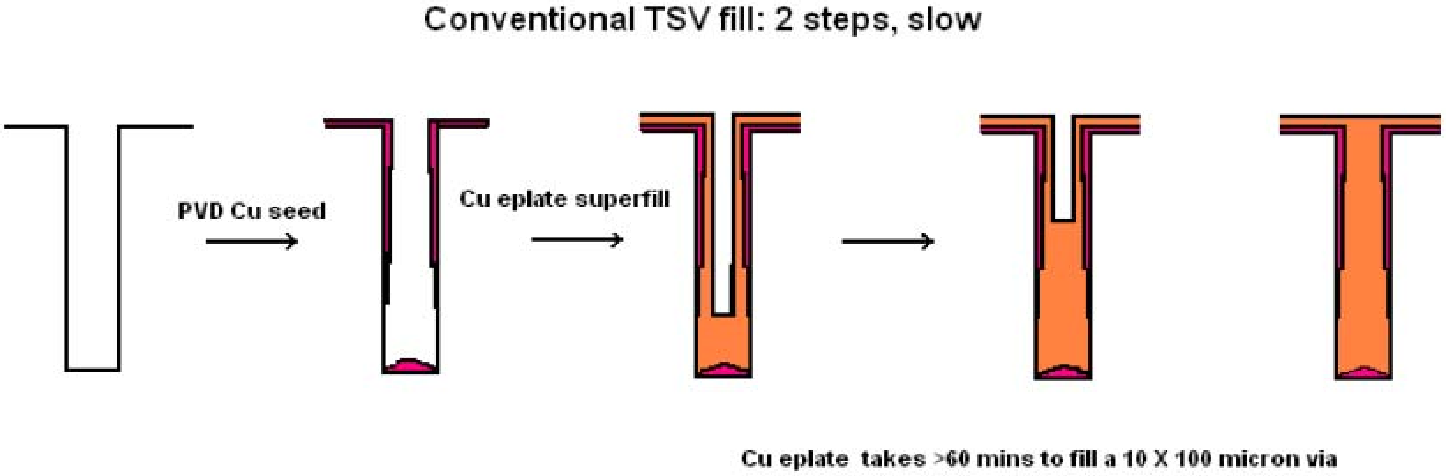


EDX-TEM map of a CVD liner in dense sub-50 nm structures.

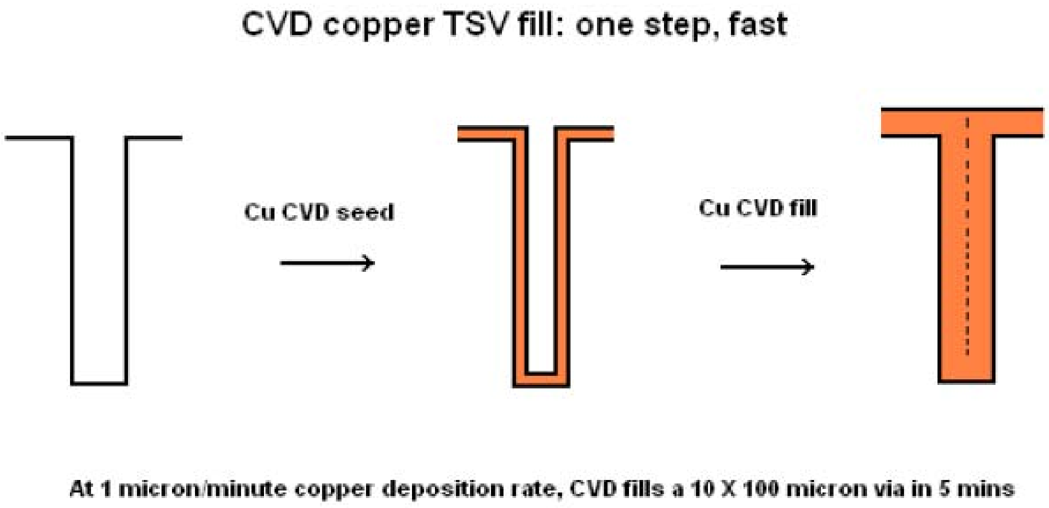
Today, a processor die contains more than 3.5 km of copper interconnects on 1 cm² with increasing tendency. Small changes in material properties are influencing the performance and power consumption of processor dies. There are two reasons, why copper and dielectric materials are not in direct contact but separated by a thin barrier/liner film (Figure 1). First, the barrier prevents copper and oxygen diffusion, and second, the liner works as an adhesion layer between these two parts.

As the barrier/liner does not improve the electrical performance of the wiring system, it should be as thin as possible. That means it should exhibit highest quality in terms of adhesion, resistance and conformity at lowest possible film thickness. In the future, those demands are neither achieved with PVD (physical vapor deposition) processes nor with the conventional materials. One possible solution is CVD (chemical vapor deposition), which provides high quality and very conformal films (Figure 2). The possibility of tuning the chemical structure allows a further variation of the liner properties and therefore optimization potential even for the narrowest structures.

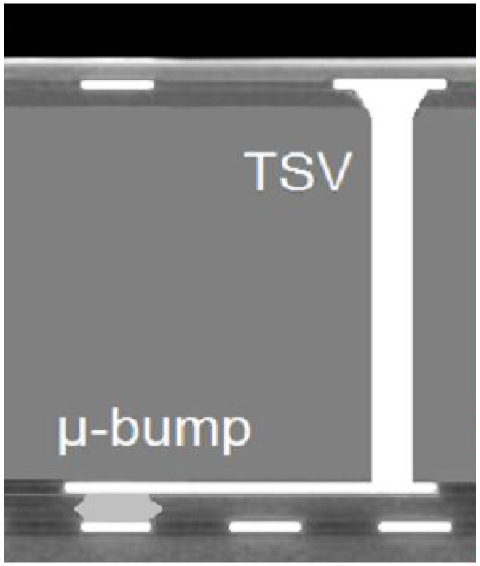
Through Silicon Vias (TSVs)


Conventional TSV fill: 2 steps, slow

Cu eplate takes >60 mins to fill a 10 X 100 micron via


CVD copper TSV fill: one step, fast

At 1 micron/minute copper deposition rate, CVD fills a 10 X 100 micron via in 5 mins

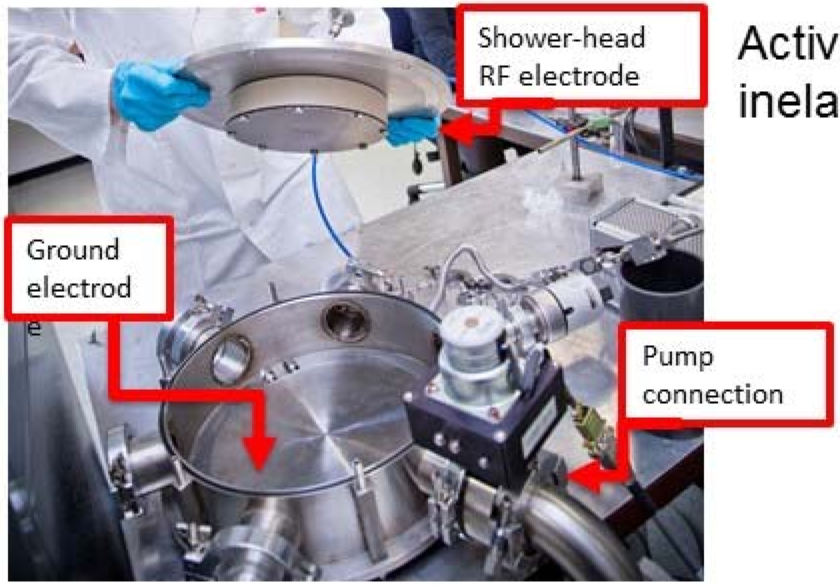


http://www.intechopen.com/books/finite-element-analysis-new-trends-and-developments/the-finite-element-analysis-of-weak-spots-in-interconnects-and-packages

www.sematech.org/meetings/archives/3d/8510/poster/Air_Products.pdf

Plasma enhanced CVD (PECVD)

Gas inlet to the shower-head electrode



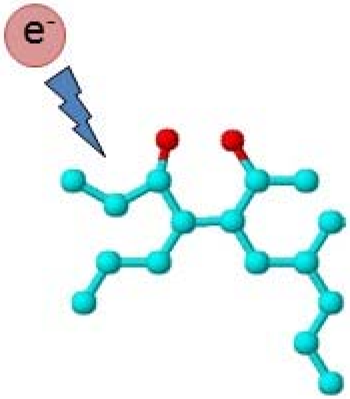
Shower-head RF electrode

Ground electrode

Pump connection

Active fragments are created through inelastic electronic collisions

Fragmentation depends on the kinetic energy of colliding electrons



- Every combination of gas is reactive e.g. CH_4, N_2, Ar
- Used to obtain cross-linked polymers or inorganic networks (e.g. SiO_x or SiN_x)

PECVD

SiO_2
Silicon nitride

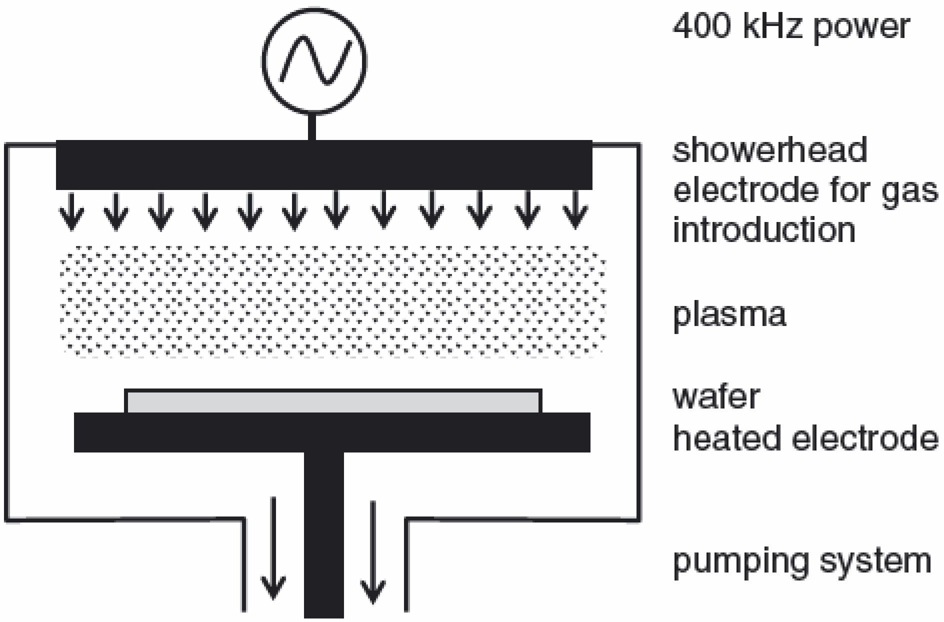
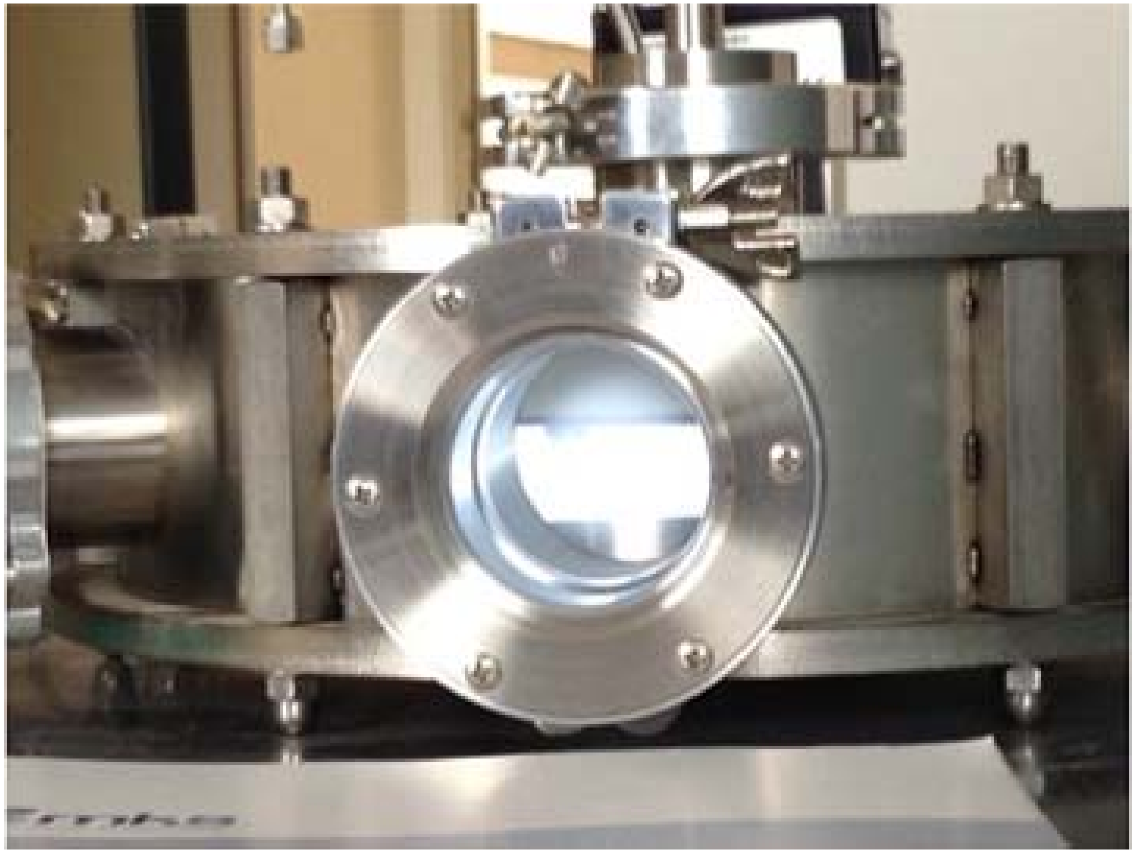


Figure 5.7 Schematic PECVD system

SiC: $SiH_4\ (g) + CH_4\ (g) \longrightarrow SiC\ (s) + 4\ H_2\ (g)$

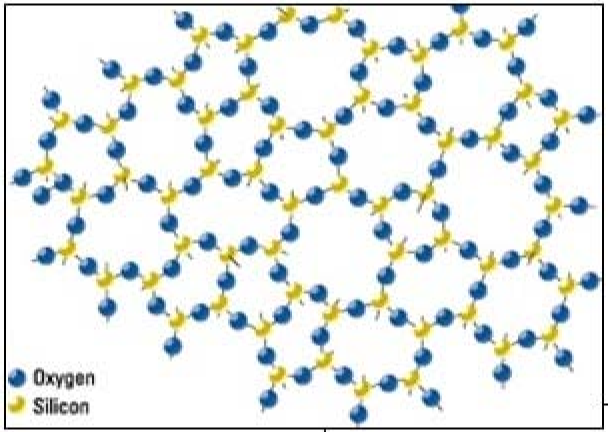
Carbon: $CH_4\ (g) \longrightarrow C\ (s) + 2\ H_2\ (g)$

PECVD



Bring substrate to the desired temperature
Establish correct gas flow conditions
Strike plasma for deposition
Turn off plasma, purge with cleaning gasses

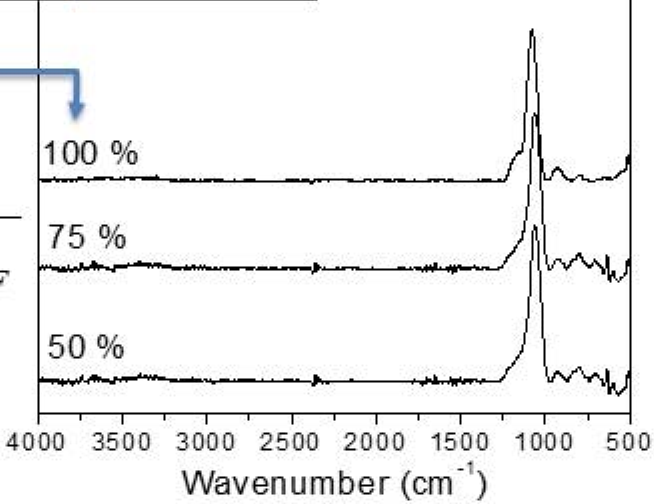
SiO_x layer deposition in pulsed plasmas



- CONDITIONs to obtain SiOx from organosilicon monomers: high power, high O_2 flow rate
- high density of Si-O network (no Si-OH or Si-H or Si-Si)
- hard material (E=89.9 Gpa, H=11.9 Gpa)

Duty cycle:

$$DC = \frac{t_{ON}}{t_{ON} + t_{OFF}}$$



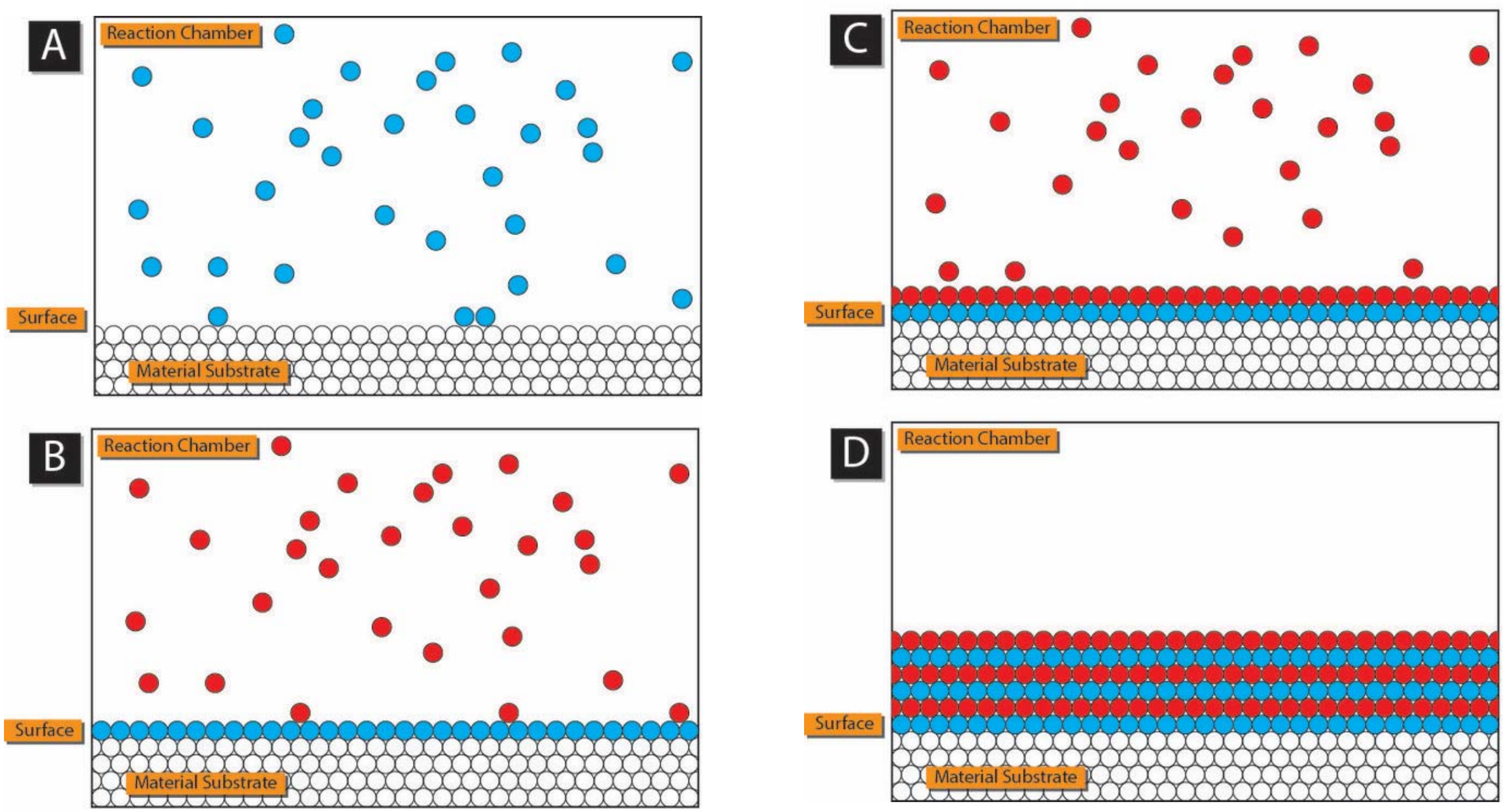
FT-IR spectra of the SiOx layer deposited by PECVD at different duty cycle

DC (%)	E (GPa)	H (GPa)
50	74.2	6.3
75	84.4	9.5
100	89.9	11.9
Thermal SiO_2*	80	12

Elastic constant, hardness, density, optical constant, etc. depend on deposition conditions

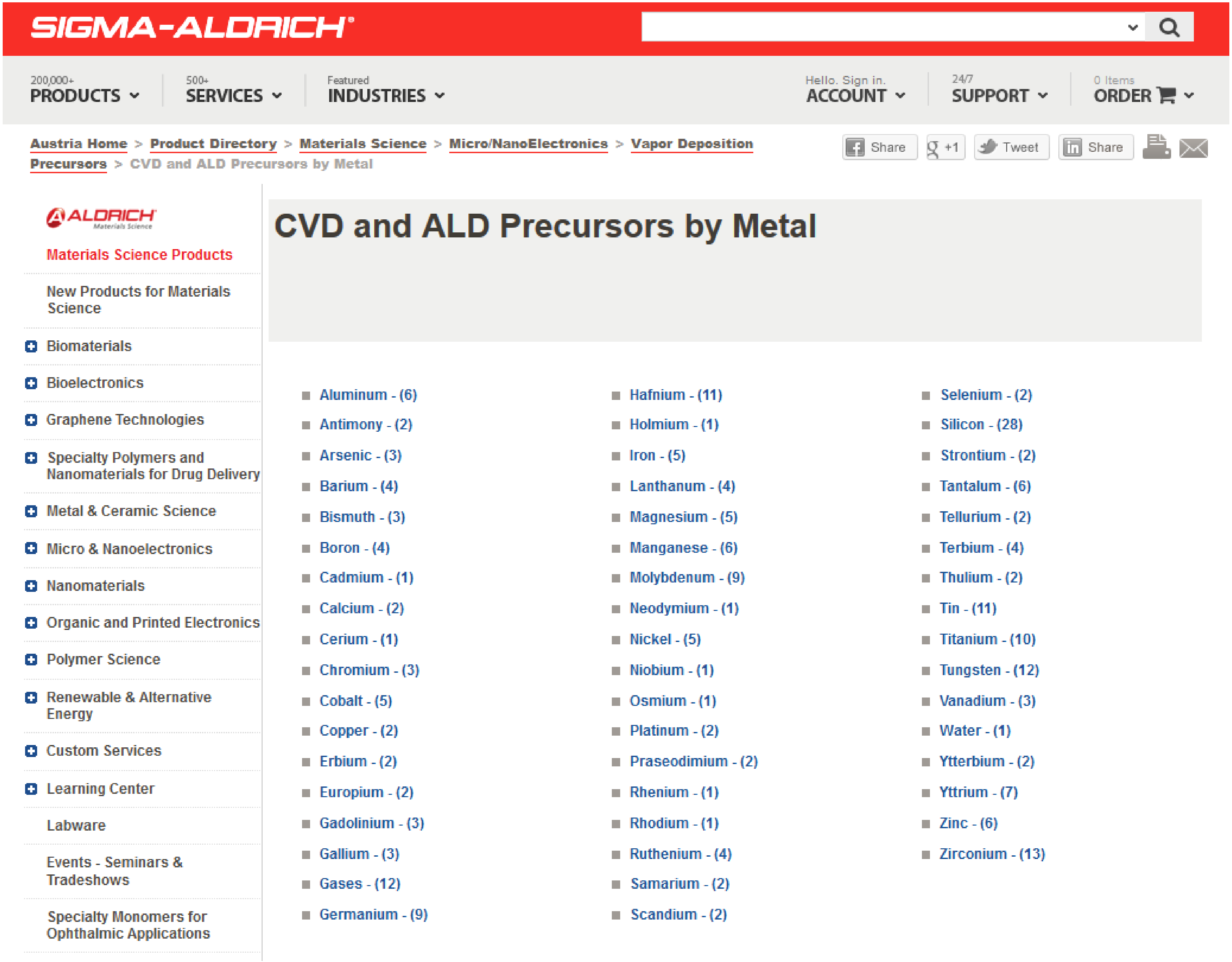
* Jung et al. J Mat Res 2004

Atomic Layer Deposition(ALD)



AlO_x for diffusion barriers OLED displays

http://en.wikipedia.org/wiki/Atomic_layer_deposition#/media/File:ALD_schematics.jpg



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CVD and ALD Precursors by Metal

- Aluminum - (6)
- Antimony - (2)
- Arsenic - (3)
- Barium - (4)
- Bismuth - (3)
- Boron - (4)
- Cadmium - (1)
- Calcium - (2)
- Cerium - (1)
- Chromium - (3)
- Cobalt - (5)
- Copper - (2)
- Erbium - (2)
- Europium - (2)
- Gadolinium - (3)
- Gallium - (3)
- Gases - (12)
- Germanium - (9)
- Hafnium - (11)
- Holmium - (1)
- Iron - (5)
- Lanthanum - (4)
- Magnesium - (5)
- Manganese - (6)
- Molybdenum - (9)
- Neodymium - (1)
- Nickel - (5)
- Niobium - (1)
- Osmium - (1)
- Platinum - (2)
- Praseodimium - (2)
- Rhenium - (1)
- Rhodium - (1)
- Ruthenium - (4)
- Samarium - (2)
- Scandium - (2)
- Selenium - (2)
- Silicon - (28)
- Strontium - (2)
- Tantalum - (6)
- Tellurium - (2)
- Terbium - (4)
- Thulium - (2)
- Tin - (11)
- Titanium - (10)
- Tungsten - (12)
- Vanadium - (3)
- Water - (1)
- Ytterbium - (2)
- Yttrium - (7)
- Zinc - (6)
- Zirconium - (13)