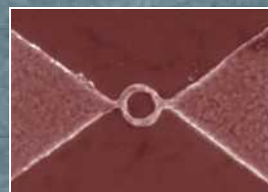
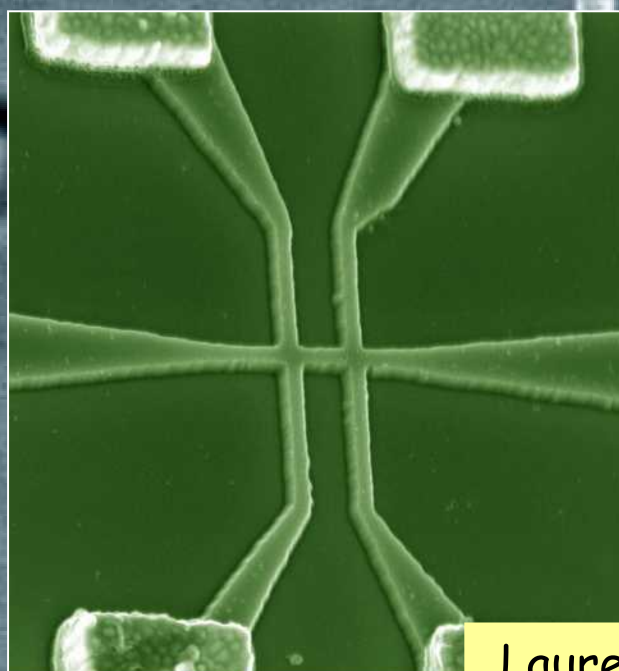
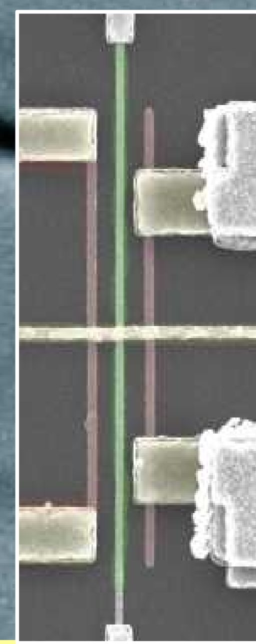
Material elaboration and nanofabrication techniques for spintronics

1 µm







Laurent VILA

Institute for Nanosciences and Cryogenic, CEA Grenoble, France

Material elaboration and nanofabrication techniques for spintronics

Why it is important ?

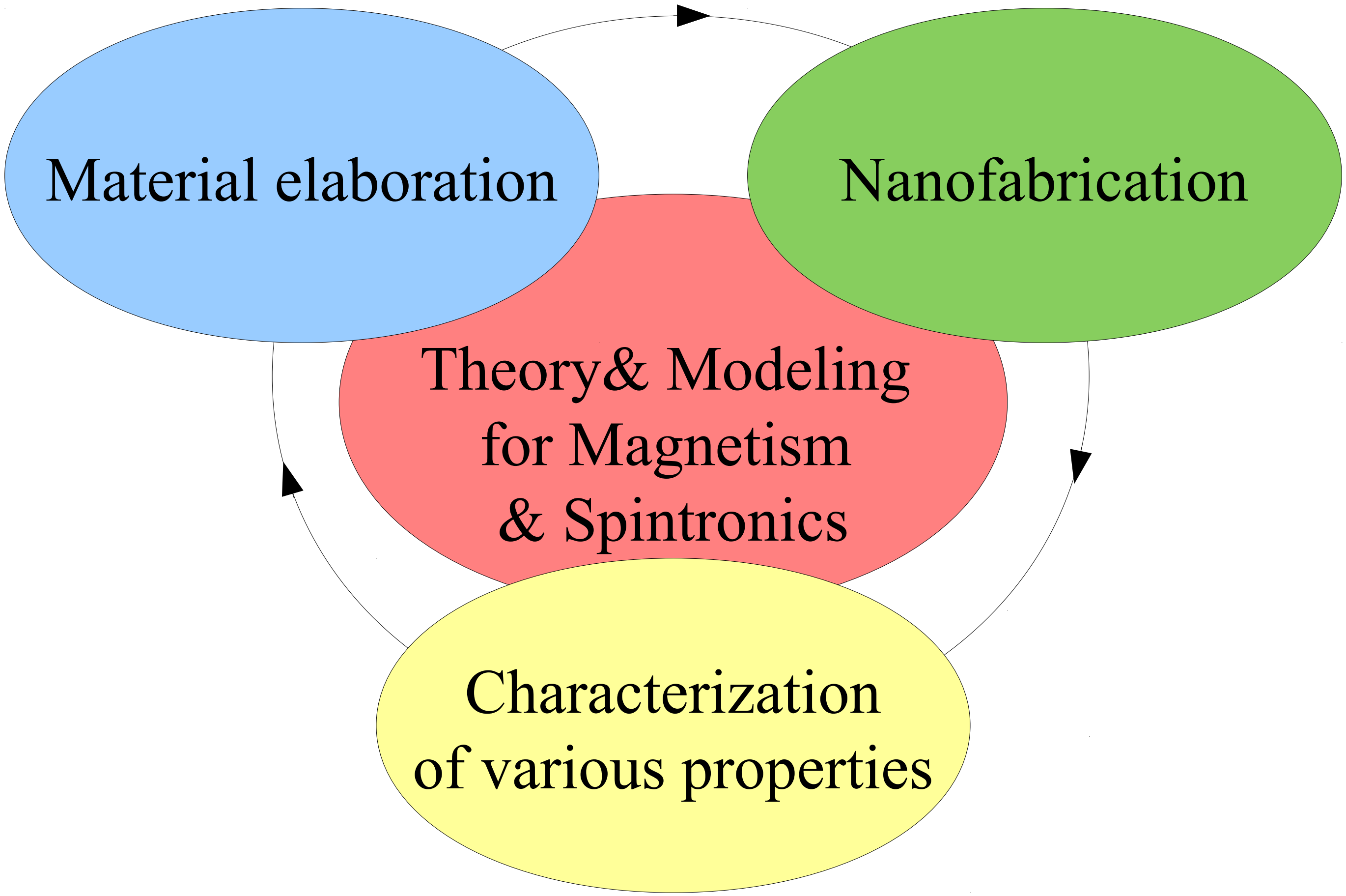
As a researcher, you might want to understand (and control) the properties of matter ; to develop new knowledge, materials and working principles

Theory & modeling
for Magnetism
& Spintronics

You need state of the art materials and devices !
And access to challenging characterization methods

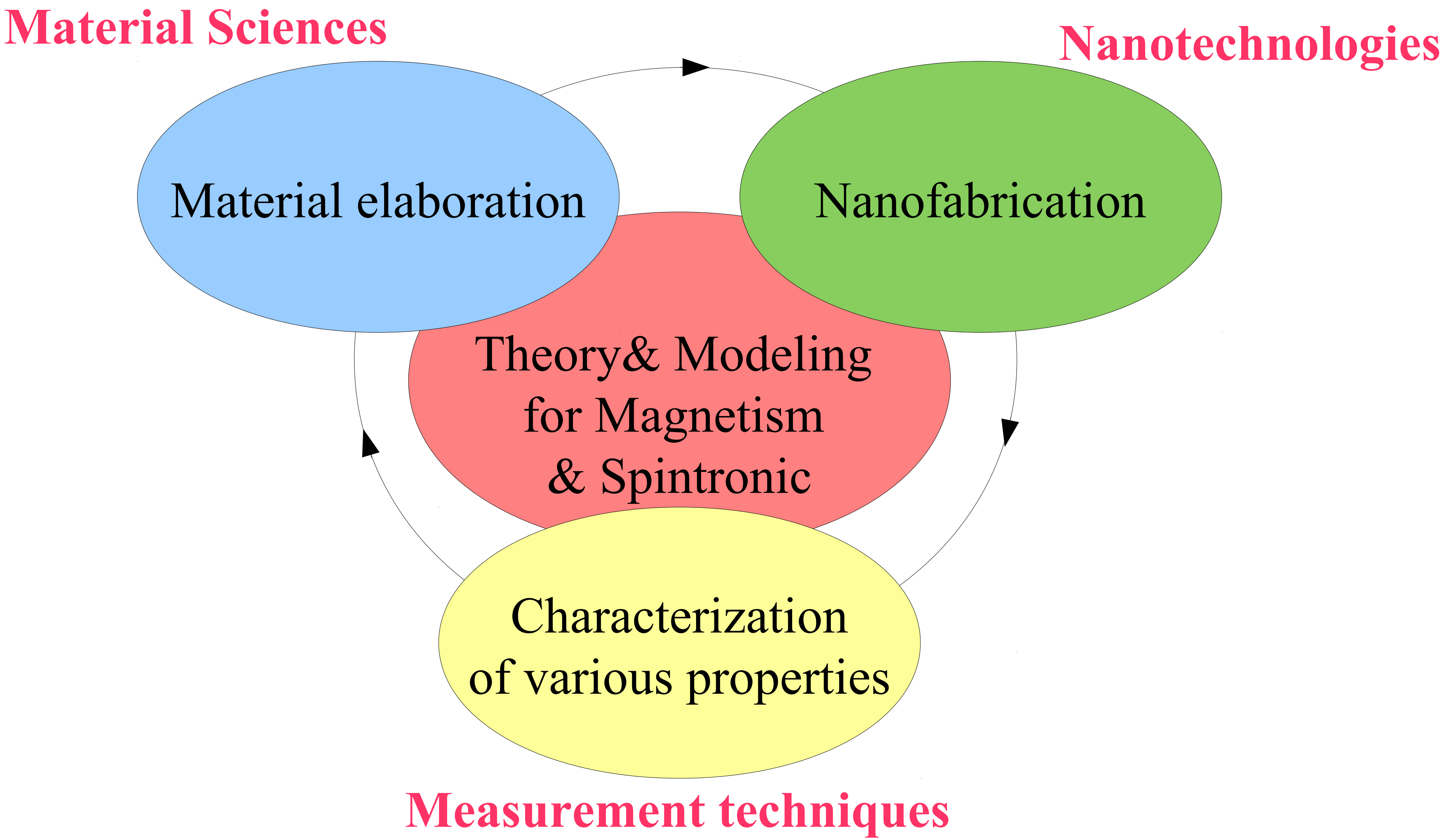
Material elaboration and nanofabrication techniques for spintronics *Why it is difficult ?*

You'll need to combine :



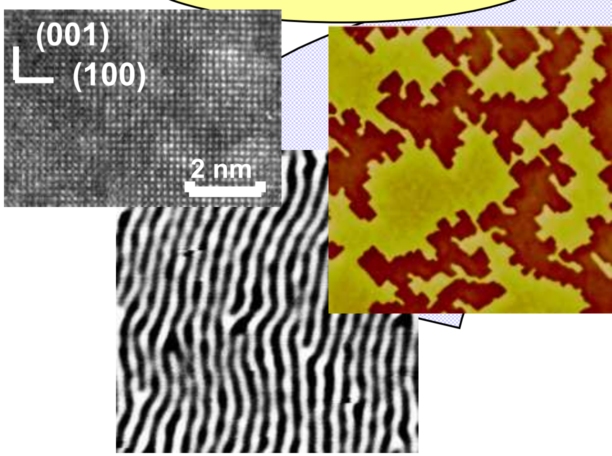
Material elaboration and nanofabrication techniques for spintronics *Why it is difficult ?*

and then to learn :

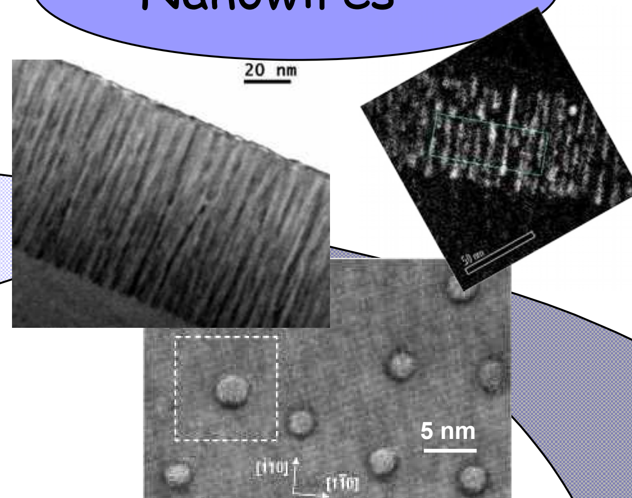


Ferromagnetic nanomaterials : metal & SC MBE, sputtering

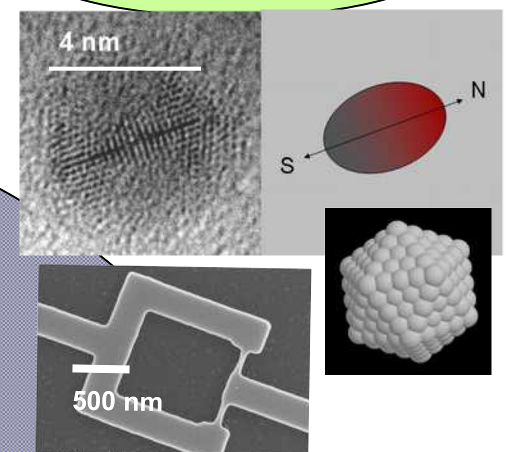
Thin films



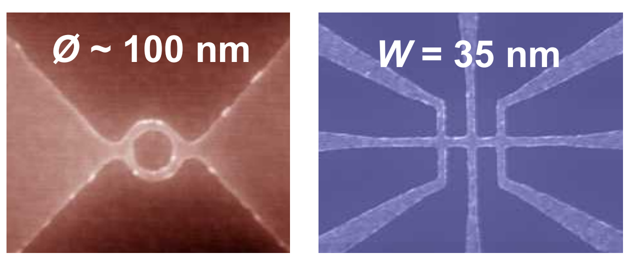
Nanowires



Nano-Clusters



Nanofabrication



Structural, magnetic, optical & electronic properties

Outline

I. material growth

II. nanofabrication

III. some metrology tools

IV. some examples of combination of top/down and bottom/up fabrication techniques

Part I - Material elaboration

Thin films and novel materials (alloys, heterostructures)

Deposited by physical or chemical means

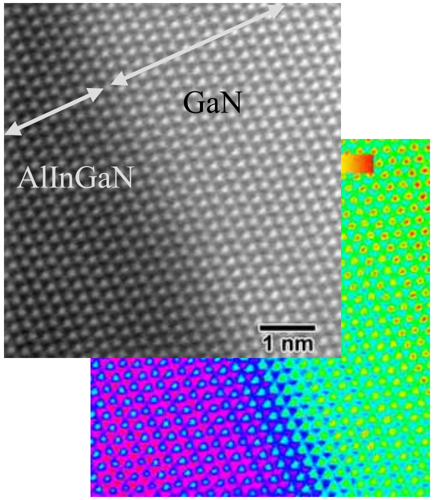
Material evaporation or sputtering

Chemical decomposition or electrolytic growth

Molecular beam epitaxy (MBE)
Sputtering deposition
UHV – evaporation chamber
Pulse Laser Deposition (PLD)
....

Chemical Vapor Deposition (CVD)
Atomic Layer Deposition (ALD)
Electron Beam Induced deposition (EBID)
Electro-plating
...

Material elaboration



Thin films on a flat substrate (few angstrom to 100 nm)

Amorphous, polycrystalline, epitaxial

Flat surface, very low roughness to do heterostructures

Control the thickness at the angstrom scale

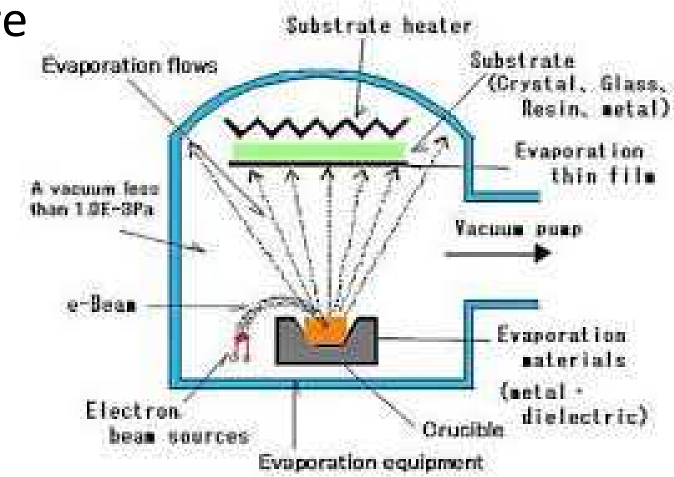
Avoid inter-diffusion (sharp interfaces) -> moderate temperature

Properties :

Perpendicular anisotropy, magnetic coupling, size effect (Tc, DW and domain structures
Electrical properties: from 2DEG, metals to insulating material or SC
In heterostructures GMR, TMR, SOT, DMI or alloys (DMI, Ms, Han)
Control of interfaces or surfaces properties
Various crystallographic phases and state of matter… 2D materials as graphene, TI
…

Physical Vapor Deposition

Principle : evaporation, sputtering or sublimation of a target under vacuum or partial pressure



E-gun evap.

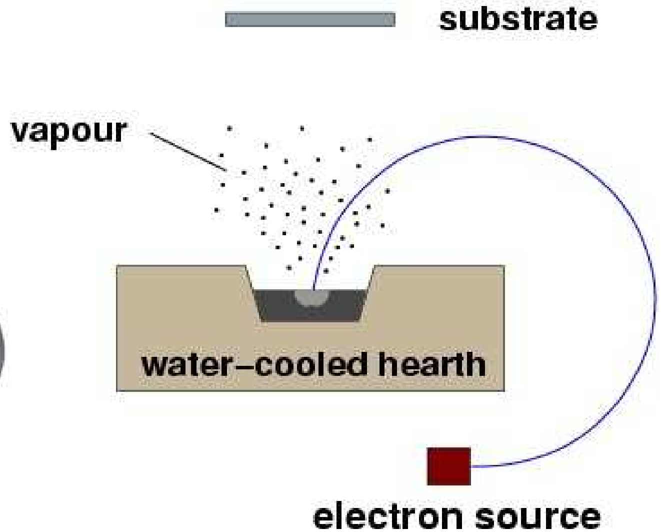
The vapor of atoms is transfer from the source to the substrate under vacuum or controlled atmosphere and will condensate on the substrate

There will be a combination of adsorption, diffusion, nucleation and desorption mechanisms

Your substrate or under-layer will be of great importance for the growth : wetting, adhesion, epitaxy, crystallographic phase

Evaporation techniques

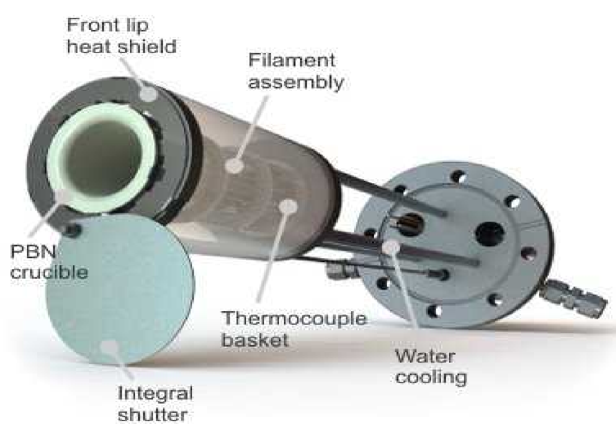
E-gun



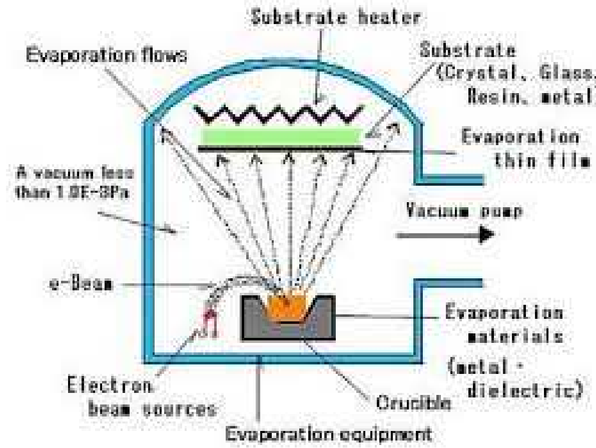
crusible

Joule heating

Knudsen cells



Material evaporation



Typical evaporation occurs above 1000 C for metals,
but for some species it starts from 200 C

Knudsen cells from 100 to 1200 C
E-gun up to 4000 C
Melt the raw material source and evaporate it

Evaporation under vacuum 10 -5 Pa at least and below 10-8 Pa in UHV systems
Avoid contamination, mean free path larger than the crusible/sample distance -> directional flux
Good for lift off !

It works for quite a lot of material from metal to SC, some organics (-refractive material as W).
Could be quite simple system to operate (clean rooms) or very complex clusters of various chambers (transfer tube of 20 m in Wursbrug, Nancy, Santa Barbara,...)

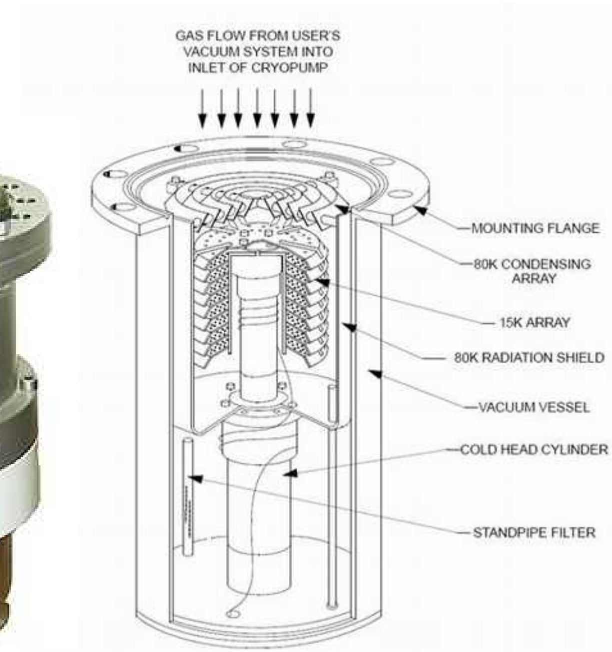
No control on grain size *a priori (except epitaxy), not for large surfaces, no conformal coating*

Heat to promote diffusion or ordering limited by inter-diffusion between layers (can be very important for metals, ex: Ni and Mn intermix at RT)

PVD, technologies based on vacuum techniques

✓ Some conversion units

SI: Pascal, 1 Pa = 1 N/m²
1 Pascal = 0,01 mbar
1 Torr = 1,33 mbar



✓ Pumping elements

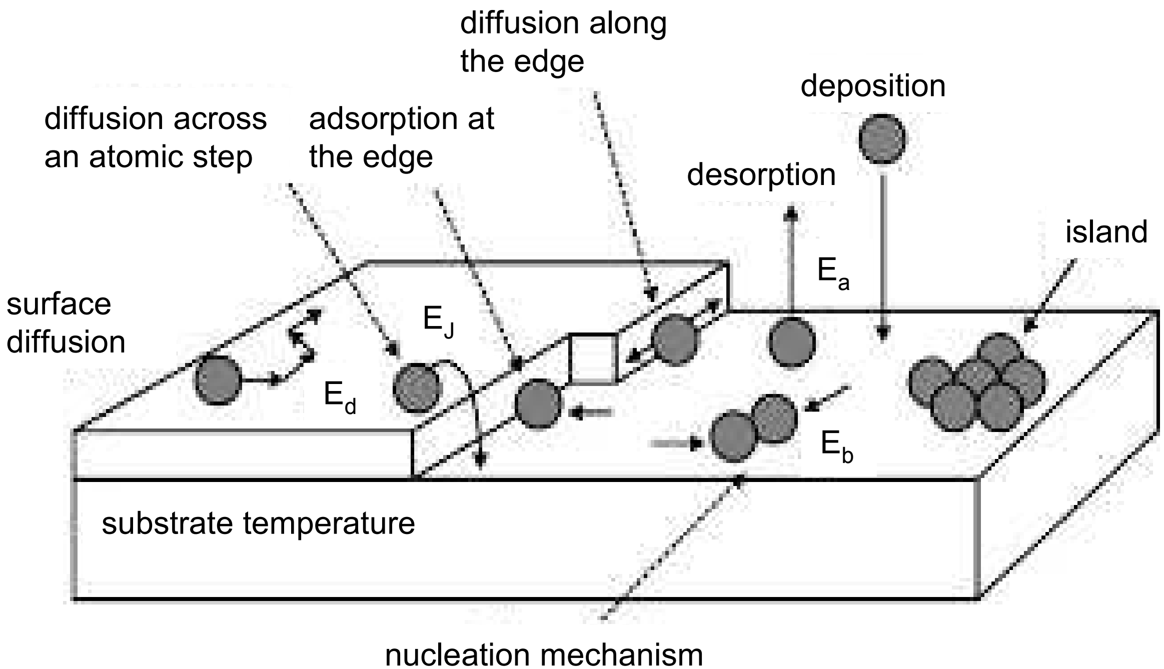
Rotary pumps, turbo molecular, cryogenics pumps, ion pumps

1 Pa — 10^{-5} Pa — 10^{-6} Pa — 10^{-8} Pa

+N2 cold panels, Ti sublimators, to degas chambers

Growth principles

Temperature of evaporation/sublimation is material dependent (1200°C for transition metals)



Energy of desorption 2 – 4 eV → desorption time at 800 K: 10^{12}s for 4 eV, 1s for 2 eV

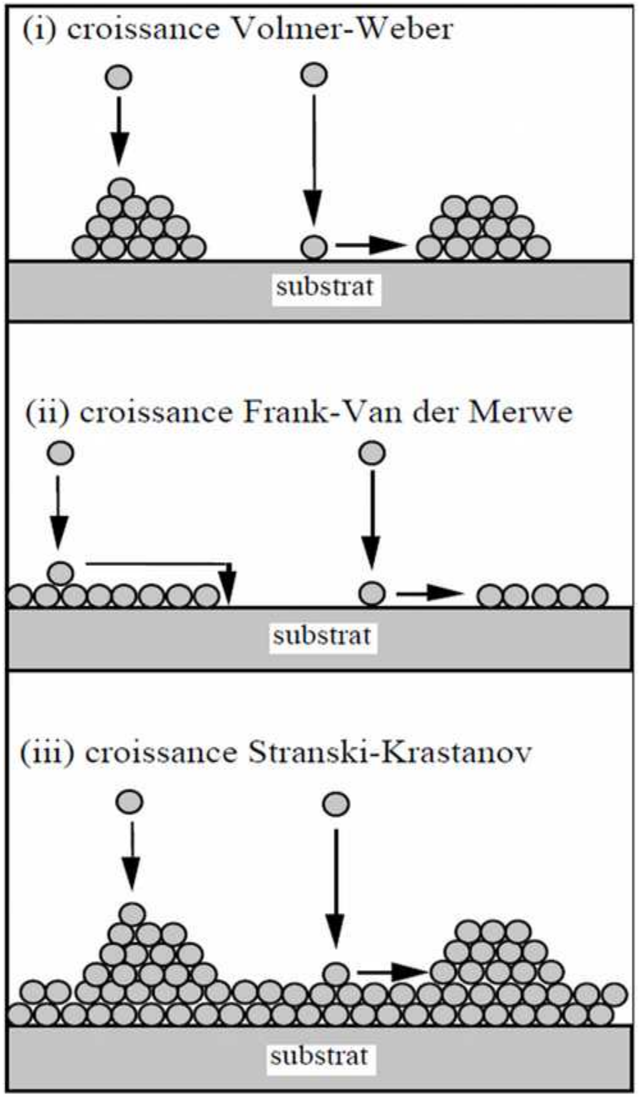
Metals

Energy of diffusion 0,1 to 1 eV (attempt frequency → $1/\omega = 10^{-11}$s for 0,1 eV, 10^{-4}s for 1 eV)

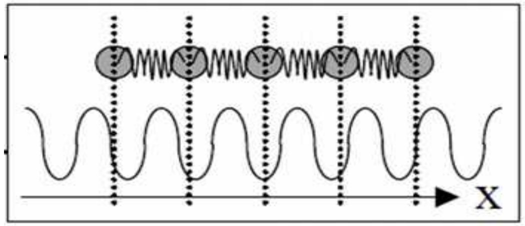
Metals to Semi-conductors (need to heat)

Growth principles

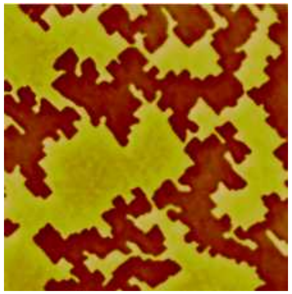
Cf S. Andrieu & O. Fruchart slides on ESM website



Depending on the competition between energy of surface, interface and misfit of crystal structures



S. Andrieu, Nancy



FePd, A. Marty, Grenoble

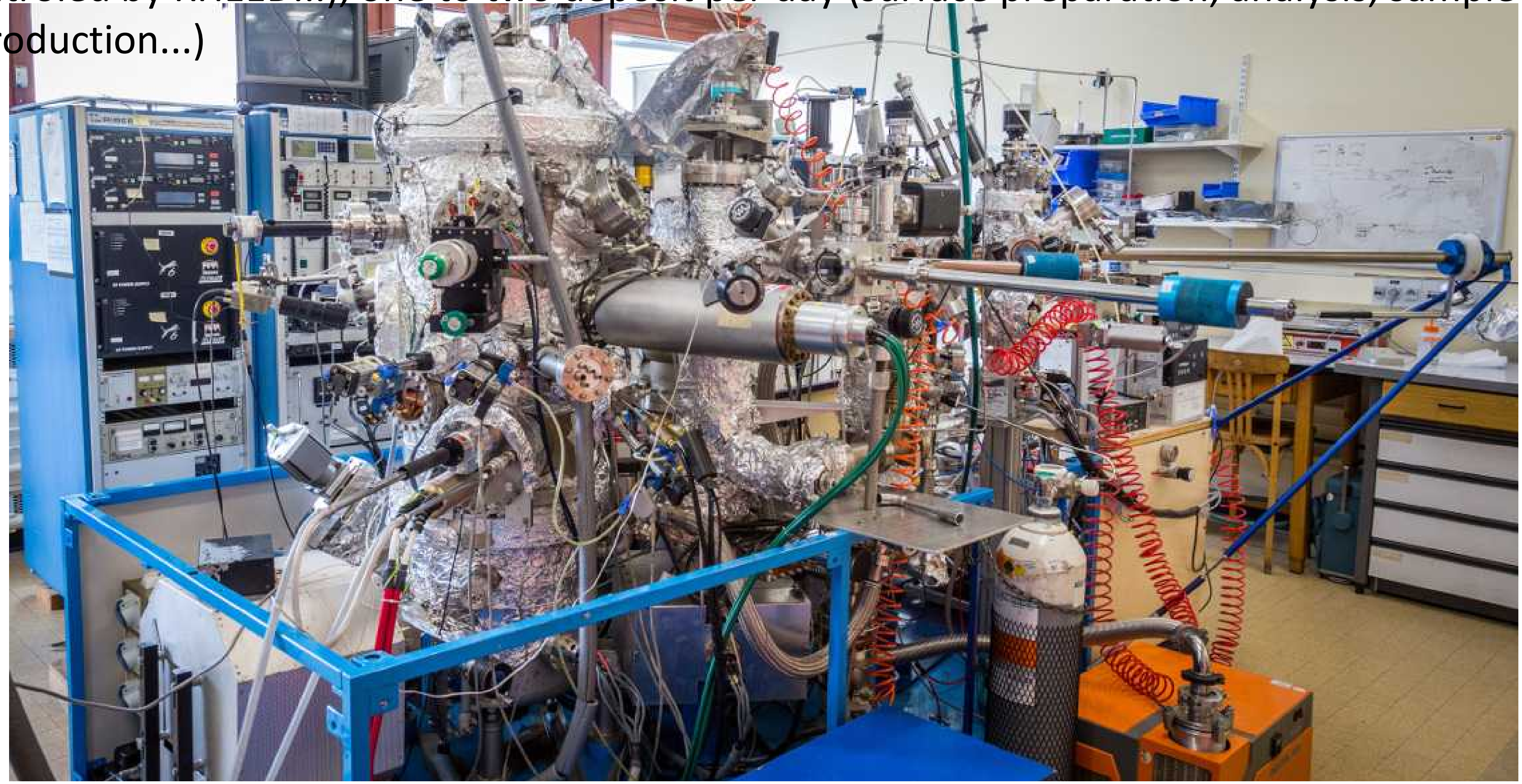
Misfit of crystal parameters leads to several relaxation mechanism: plastic deformation, dislocations, twins

Molecular beam epitaxy

Complex systems with usually in situ analysis : RHEED, STM, Auger, XPS...

Deposition rate ~0.1 A/s, vacuum < 10^{-9} Pa, ion pump + Nitrogen trap, owen ~1000 C

Basic research on materials because of multiple possibilities (co-deposition, in-situ annealing controled by RHEED...), one to two deposit per day (surface preparation, analysis, sample introduction...)



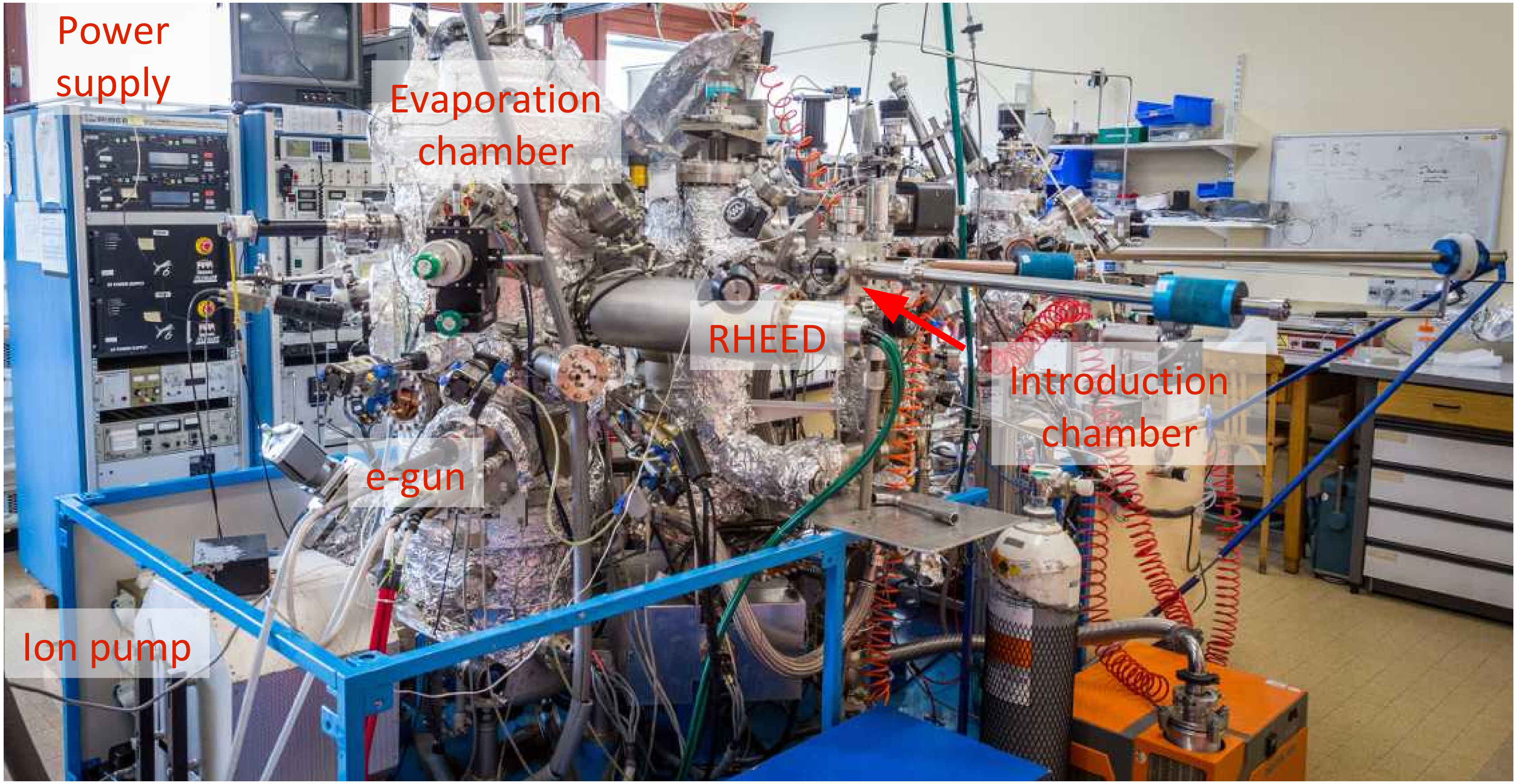
MBE system @ CEA, INAC:
introduction, preparation, evaporation, analysis, ion implantation, STM/AFM and sputtering chambers

Molecular beam epitaxy

Complex systems with usually in situ analysis : RHEED, STM, Auger, XPS...

Deposition rate ~0.1 A/s, vacuum < 10^{-9} Pa, ion pump + Nitrogen trap, owen ~1000 C

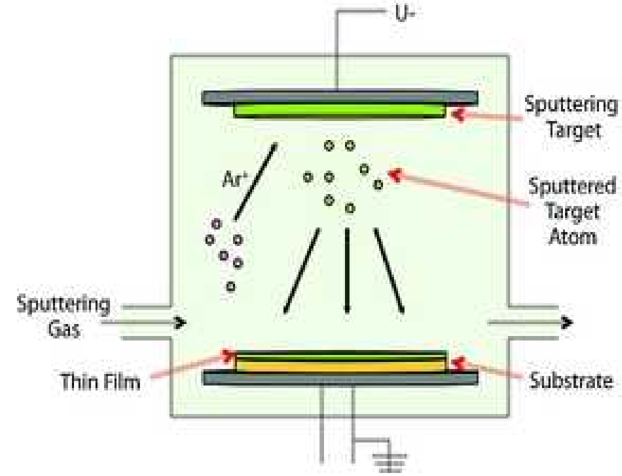
Basic research on materials because of multiple possibilities, one to two deposit per day (surface preparation, analysis,...)



MBE system @ CEA, INAC:
introduction, preparation, evaporation, analysis, ion implantation, STM/AFM and sputtering chambers

Sputtering deposition

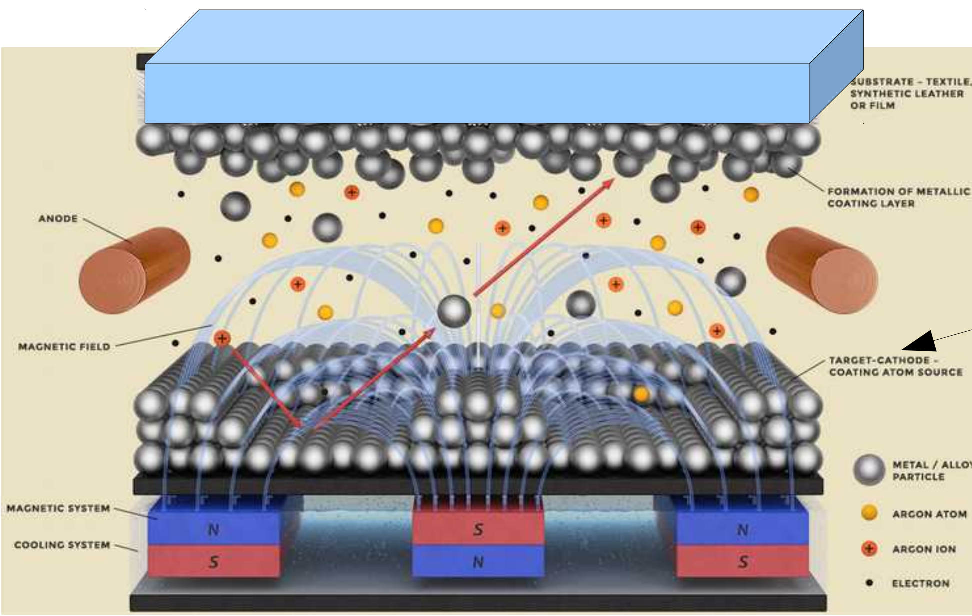
Principle: Ar atoms are used to sputter a target made of (almost) any material (DC for conductive, AC for isolating)

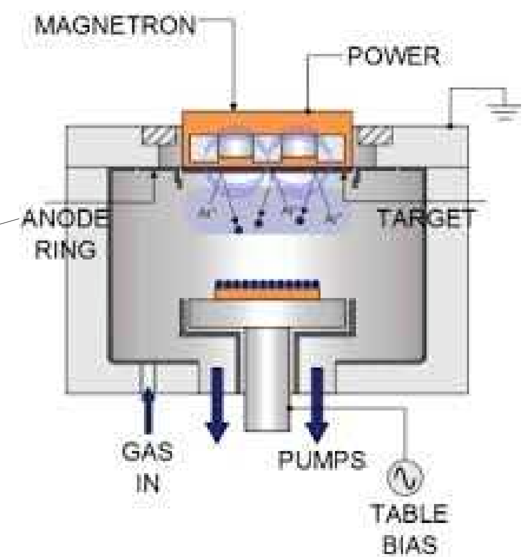


Plasma is created by an Rf electrical field, eventually enhanced by triode set-up (extra e^- source)

Operate generally at Ar pressure ~ 1 Pa and at RT
10 samples per day

Reactive Sputtering process: O2, N2





Magnetron sputtering: an magnetic field is used to confine the plasma

Sputtering rate of and Ion Beam etching systems (A/min)

Element	200 eV	500 eV	Element	200 eV	500 eV
Ag	1000	2200	Nb	180	440
Al	290	730	Ni	310	660
Au	710	1700	Os	200	510
Be	52	170	PbTe	1600	3800
C	13	44	Pd	600	1300
CdS (110)	1100	2300	Pt	390	880
Co	260	550	Re	230	520
Cr	330	580	Ru	240	610
Cu	530	1100	Si	160	380
Er		980	SiC (001)		350
Fe	260	530	SiO2		400
GaAs (110)		1500	Sm	510	1100
GaP (111)	690	1600	Sn	850	1800
GaSb (111)		1700	Ta	200	420
Gd	550	1100	TaC		100
Ge	490	1000	Ti	160	380
Hf	310	660	V	170	370
InSb		1300	W	180	380
LiNbO3		400	Y	450	960
Mo	240	540	Zr	270	620

Different yield of sputtering of material (as for Ion Beam Etching, IBE)

More conformal deposition (than evaporation), sputter material has any angle from +90 – 90 deg from the normal to the target

Deposition rate usually around 1 A/s

Oxydes by AC sputt. of the target, or from the metal and subsequent oxydation (repeated for MTJ)

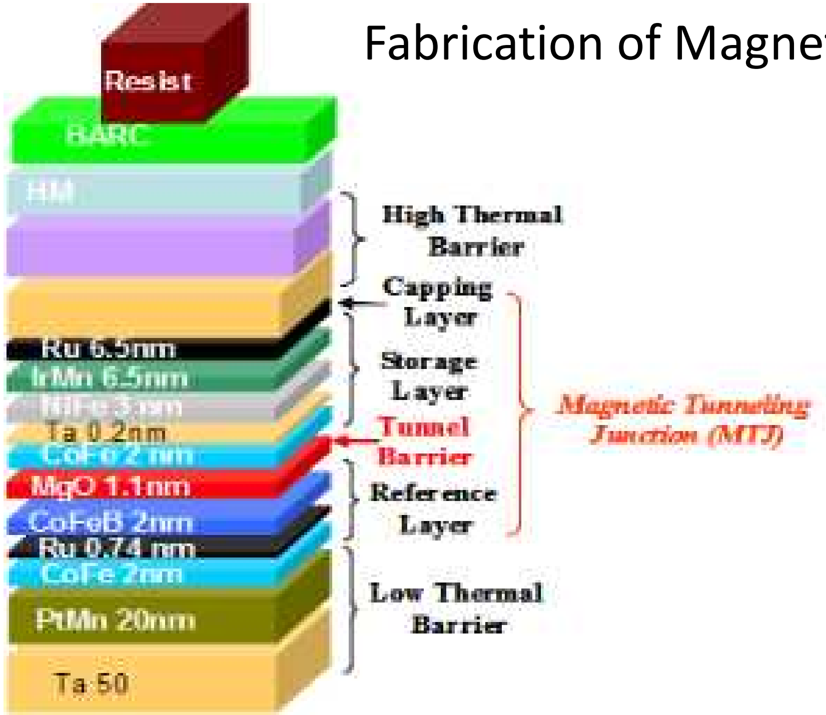
Grain size can be controlled to some extend by the gaze mixture and pressure

Large scale deposition (300 mm wafers)

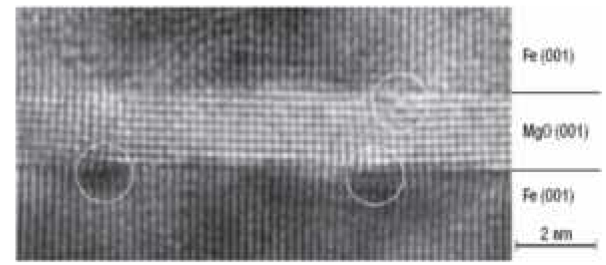
Control of layer thickness down to a few or even sub monolayer

Method of choice for MTJ preparation (MBE firstly used for Al2O3 and MgO, Nancy group)

Fabrication of Magnetic Tunnel Junctions and MRAMs by sputtering

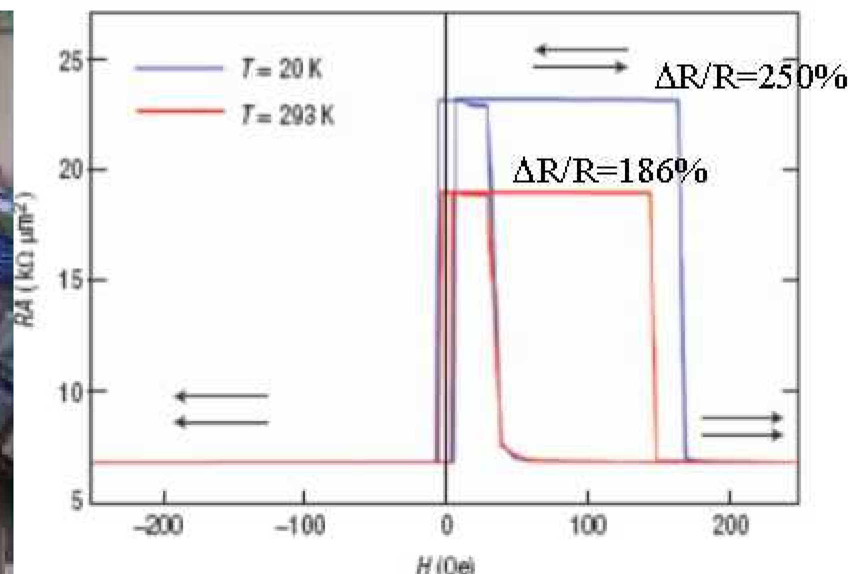


Magnetic tunnel junction with MgO



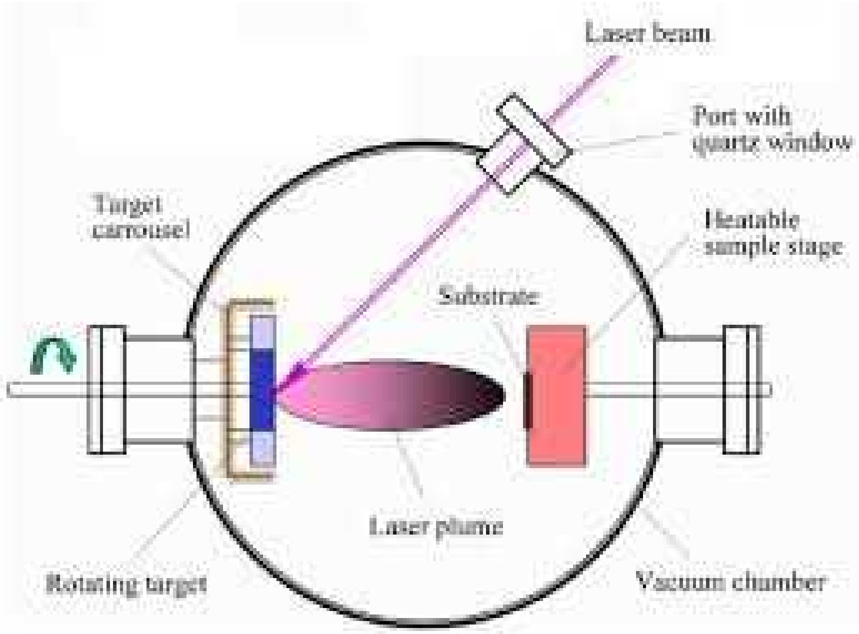
Yuasa et al, Nature Mat. 2004 (Canon Anelva)

Aist, Tsukuba, Japan

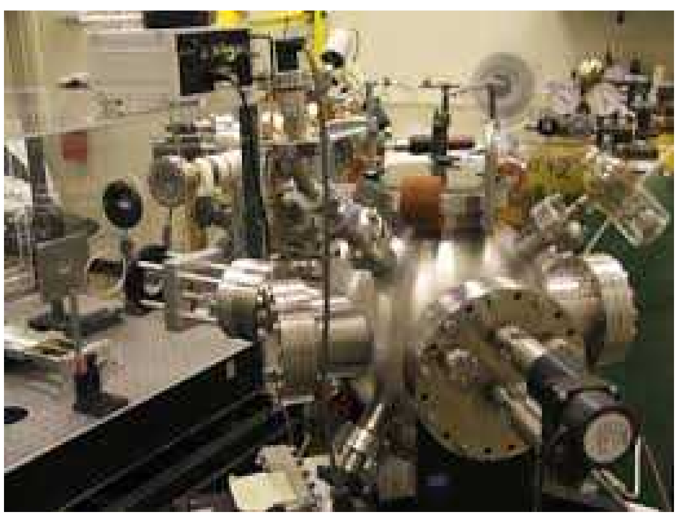


State of the art : 600 % at 300 K
Tohoko Univ. + Toshiba

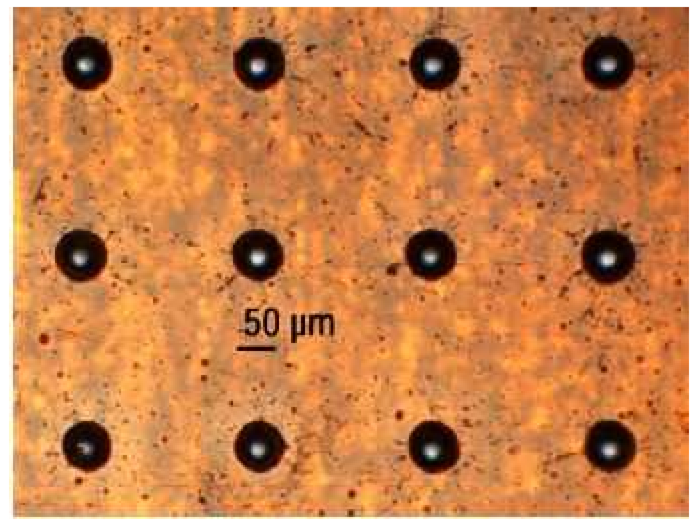
Pulse laser deposition (PLD)



Laser pulses sublimate the target
Formation of a plasma
Condensation on the substrate
Crystallization on appropriate substrates



mbelab.ucsb.edu



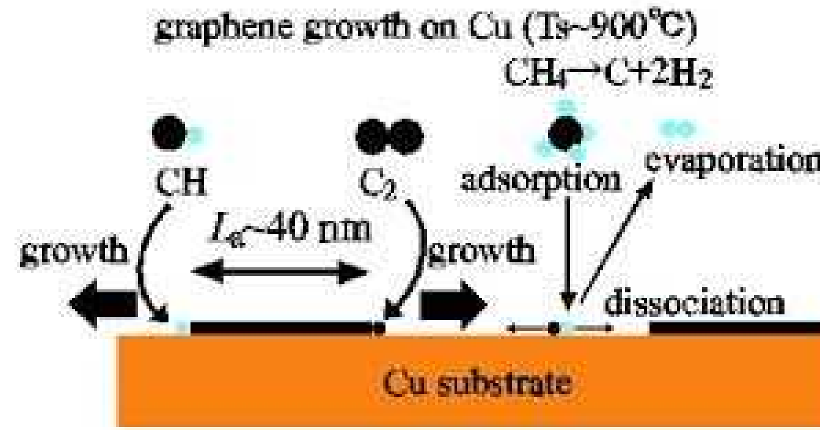
azom.com

Oxydes: STO, LAO, YIG: yttrium garnet
...

Chemical vapor deposition (CVD)

Many different types (Low Pressure, Metal-Oxyde, Plasma Enhanced,...) and often use in industry (Si, III-V), lower vaccum, higher deposition rates, very good quality

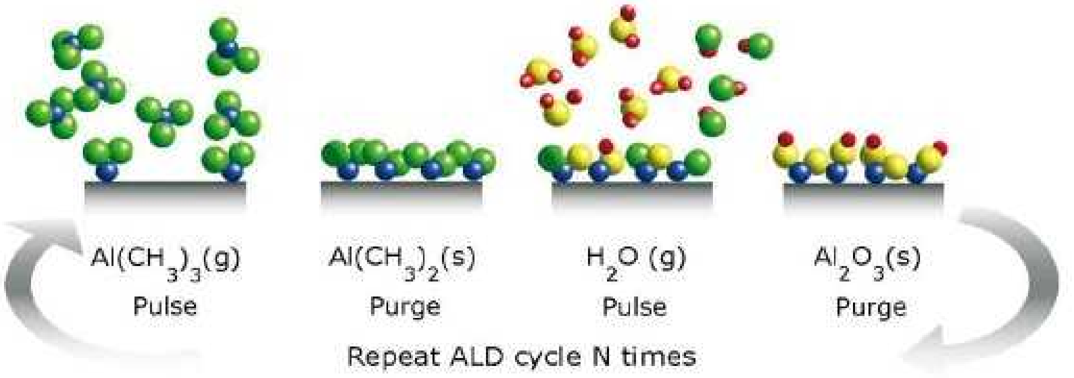
Species introduced in the chamber decompose or react on the substrate



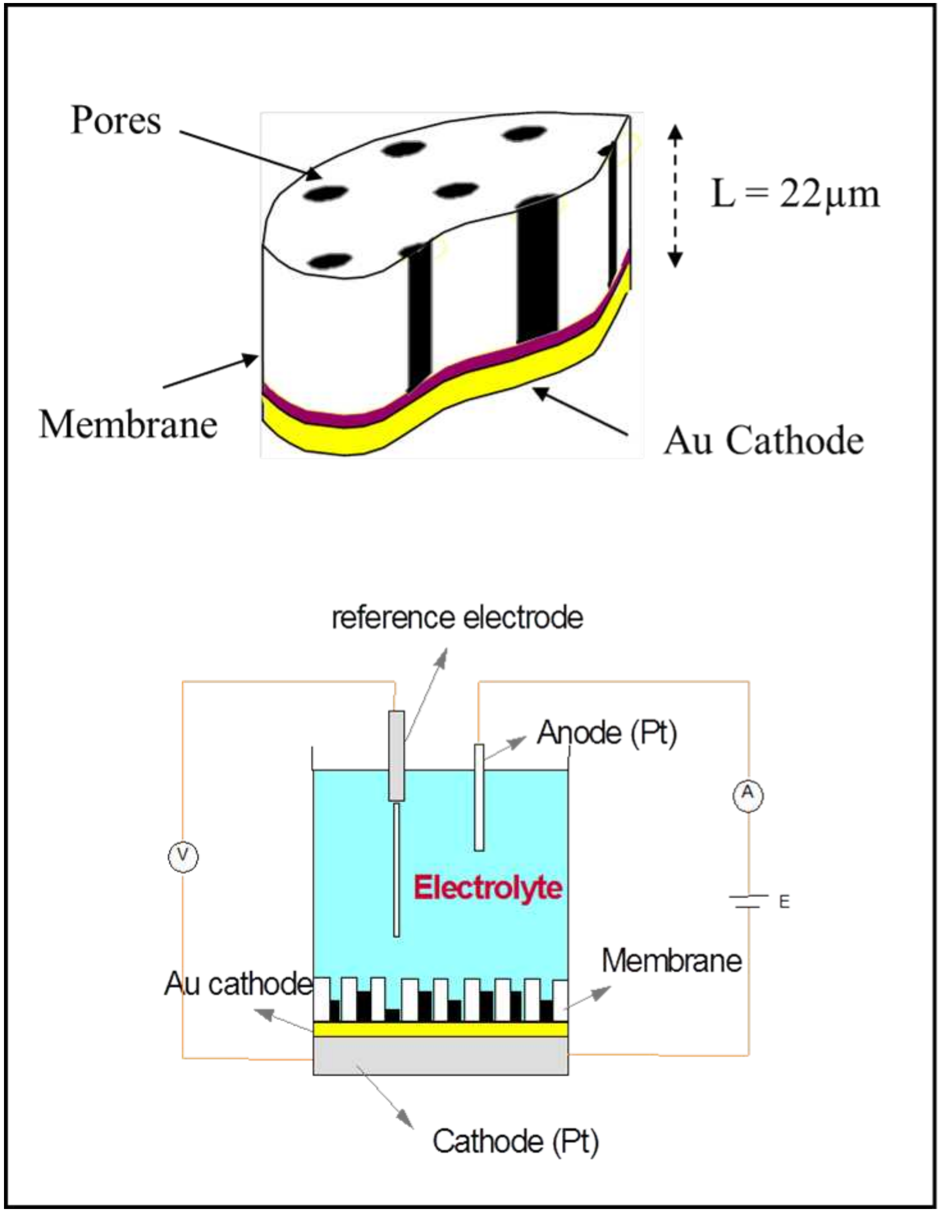
Amec MOCVD

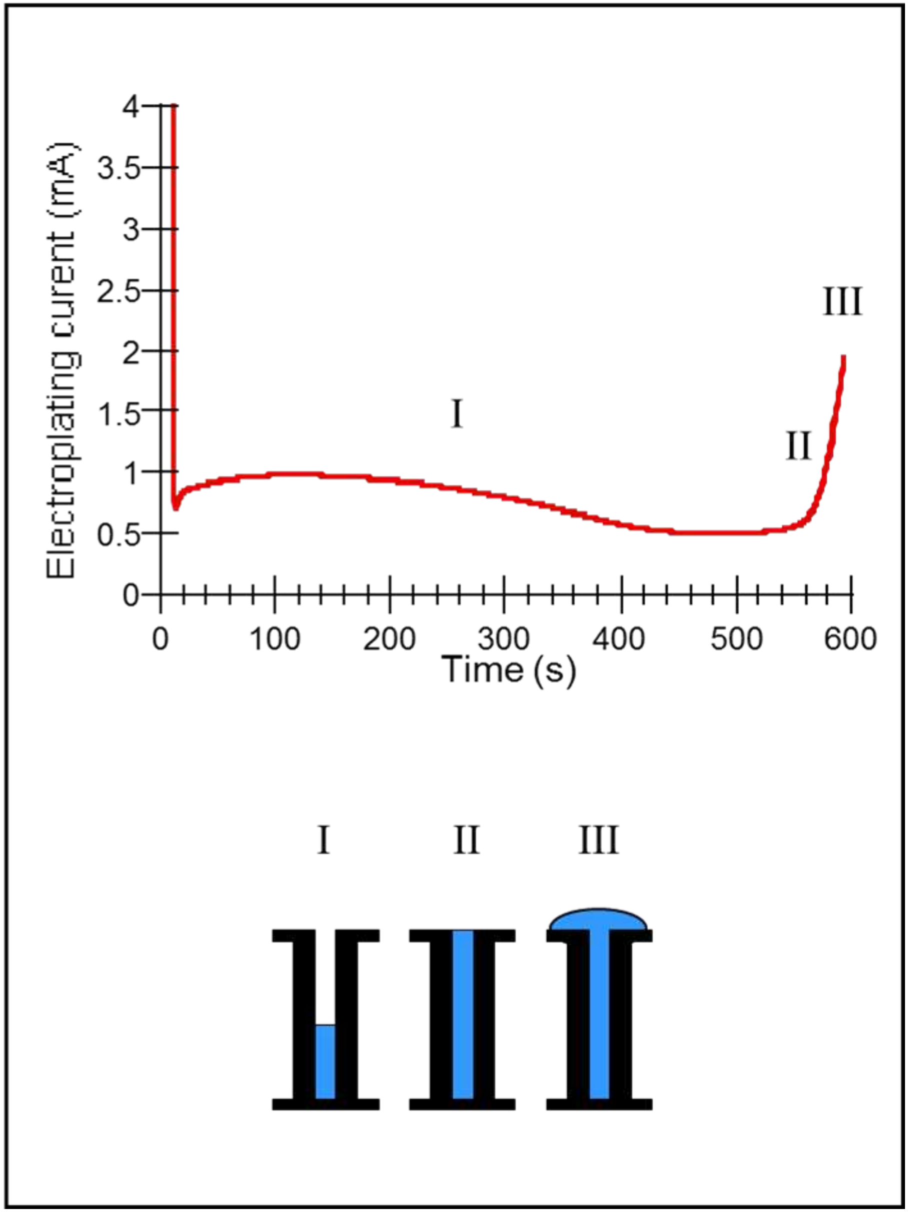
Atomic Layer deposition (ALD)

High K materials, but also metals, barriers ?



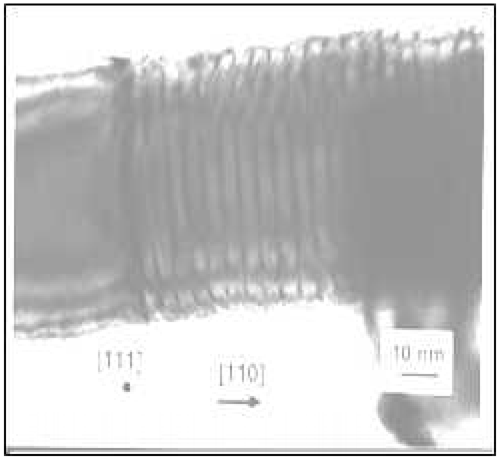
Electrodepostion into nanoporous media

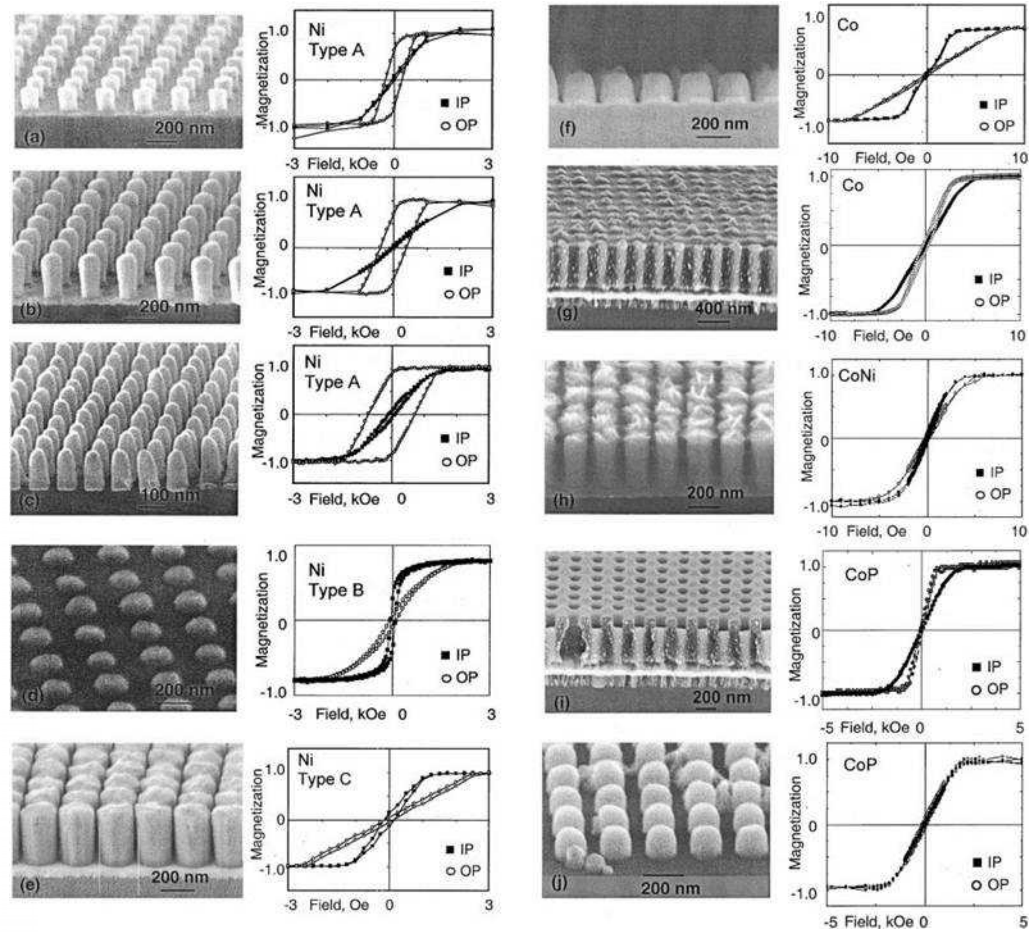




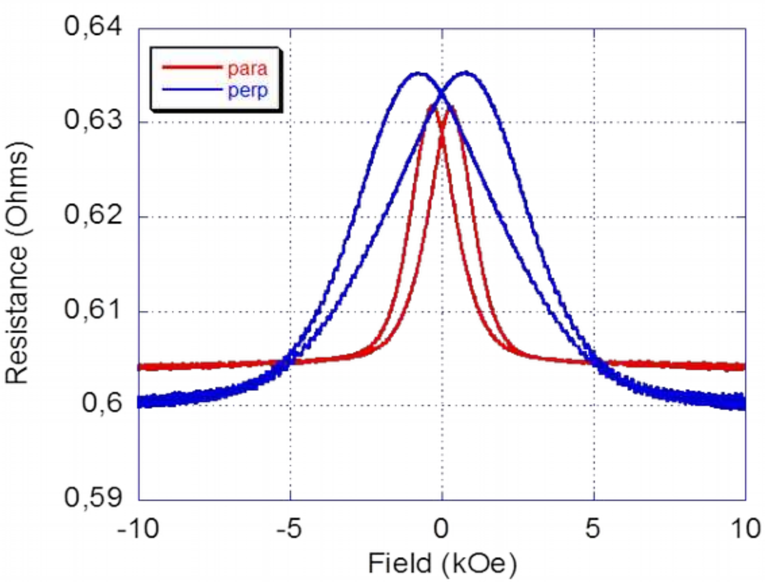
Nanowires of diameter smaller than 20 nm and 20 µm long

Electrodepostion into nanoporous media





C.A. Ross et al, PRB 65,144417 (2002)



Multi-layers: Co -0,95 V / Cu -0,5 V in low concentration, pure deposition of Cu and CoCu alloy

Part II - Nanofabrication

Engineering materials and devices at the (lateral) nanometer scale

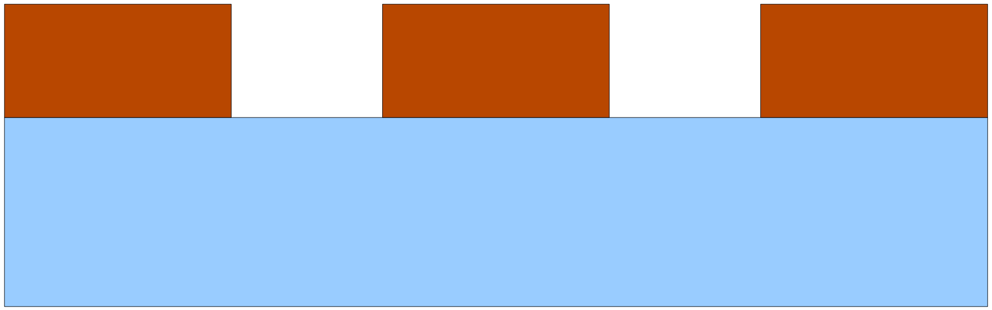
Usefull for physics, chemistry, bio

top/down	&	bottom/up
Deterministic organisation or shaping of materials		New approaches for the fabrication of **nanodevices**

They can be combined

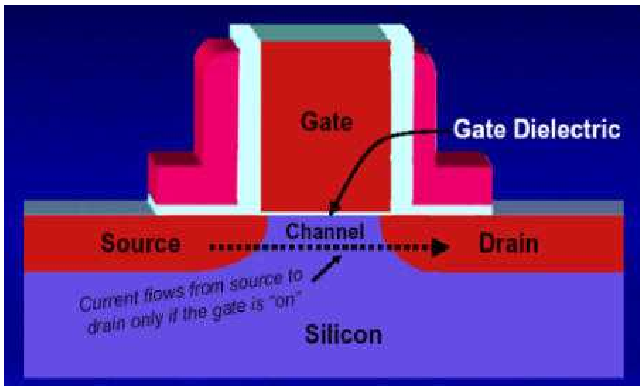
Top/down : consumer electronics

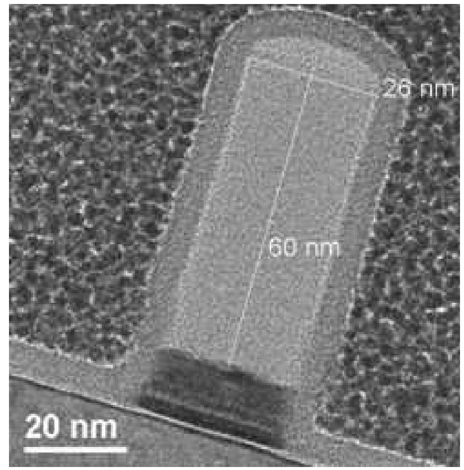
Top/down : consumer electronics

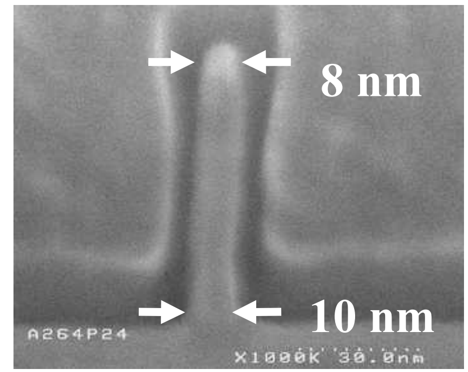


CMOS transistor downscaling

Front end of line: transistors



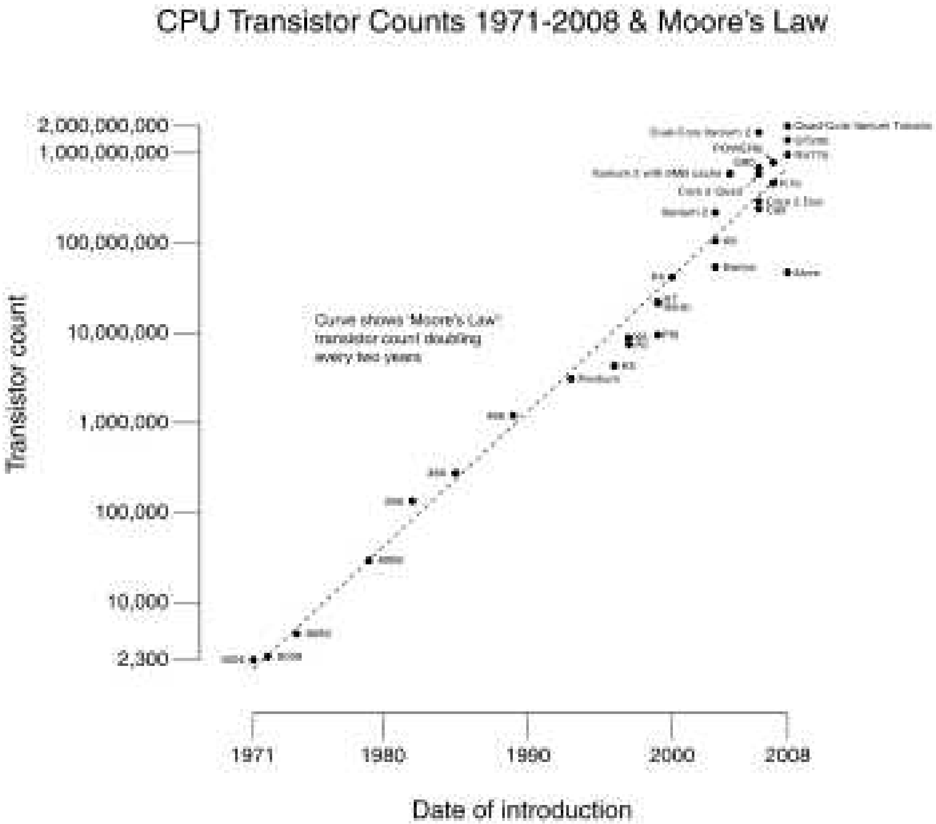




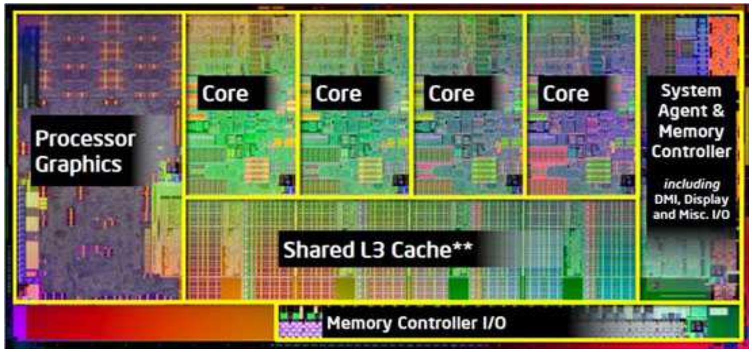
ITRS 2007 (International roadmap of Semiconductor)

Year of production	2007	2010	2013	2016	2019	2022
MPU Half pitch (nm)	65	45	32	22	16	11
MPU physical gate length (nm)	25	**18**	**13**	**9**	**6.3**	**4.5**
L gate 3σ variation (nm)	2.5	**2.16**	**1.56**	**1.08**	**0.76**	**0.54**

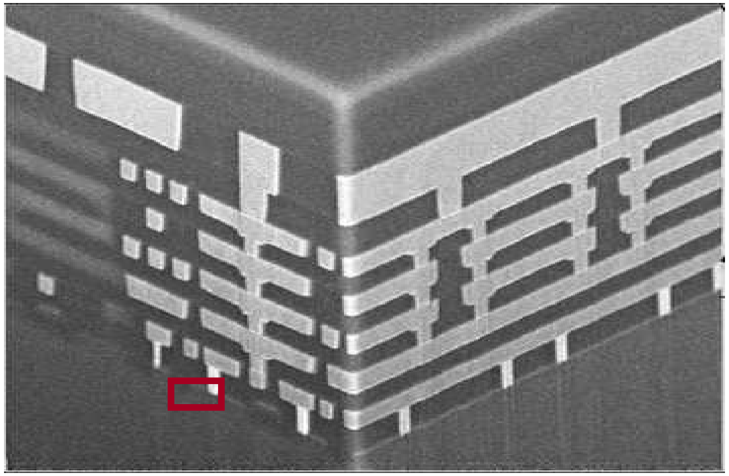
The miniaturization of CMOS devices increases the complexity of plasma etching processes and requires a control of the pattern dimensions at the nanometric scale



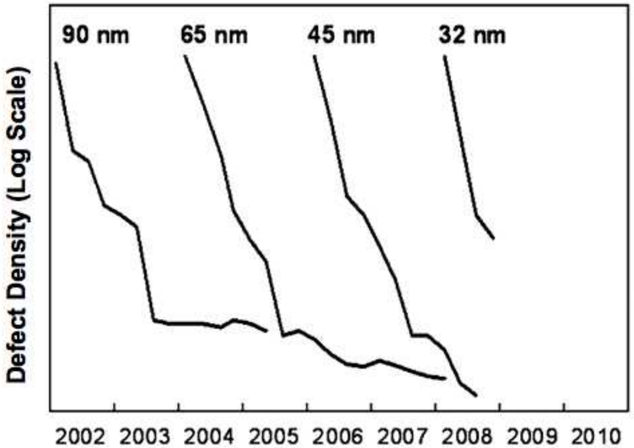
Few billions of transistors in nowadays CPU



Back end of line: interconnections

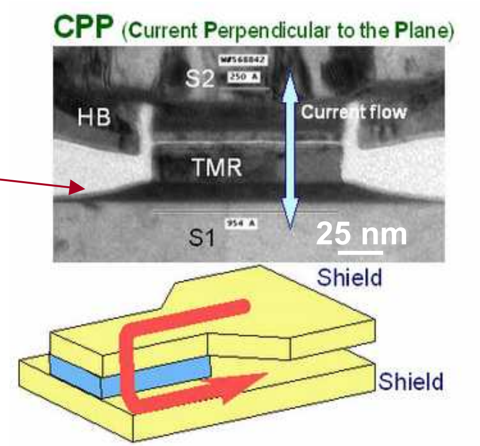


Defect tolerance (<1/10000)

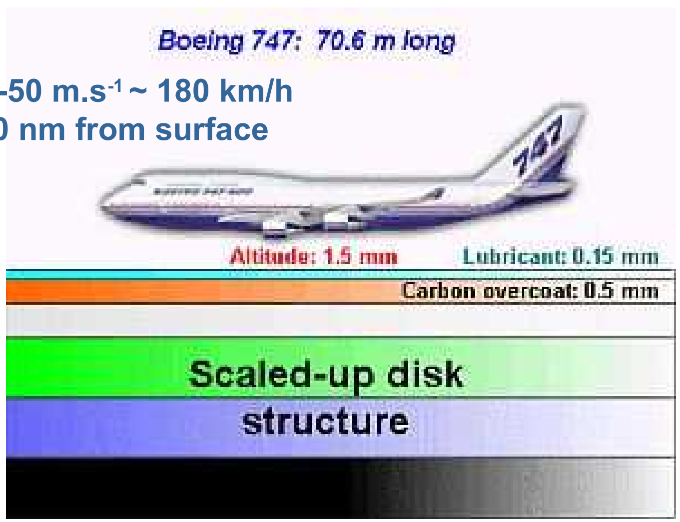


High yield, high output and low cost (Few billions dollars for a factory)

Nanomagnetism and Spintronic

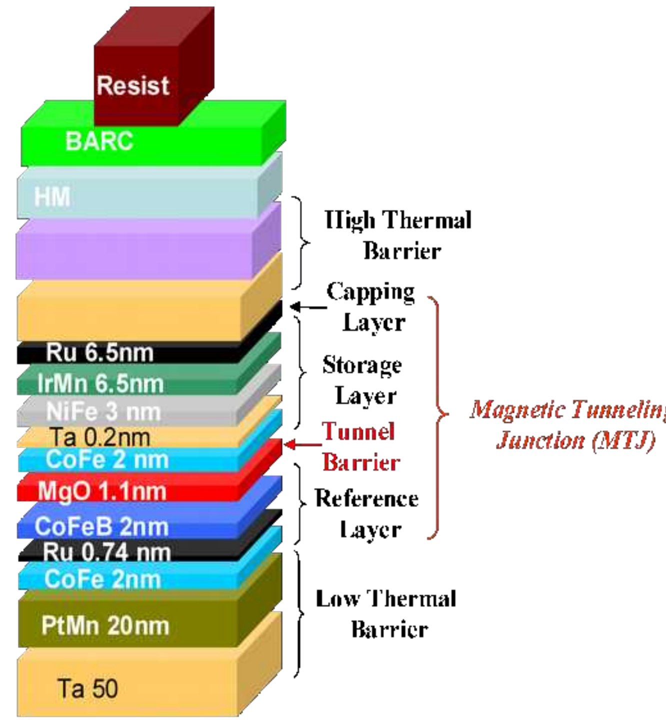


V ~ 40-50 m.s^{-1} ~ 180 km/h
at 10 nm from surface



1 non recoverable error per 10^{15} readed bits

Typical magnetic stack used for MRAM spintronics devices



- More than 15 active layers
- 18 elements of the Mendeleiev table
- Dimension << 50 nm
- CD control

Nanofabrication by lithography techniques

1. Mask fabrication

2. Transfer method

Clean room

Air is filtered and feed trough the clean room

Temperature and humidity is controlled

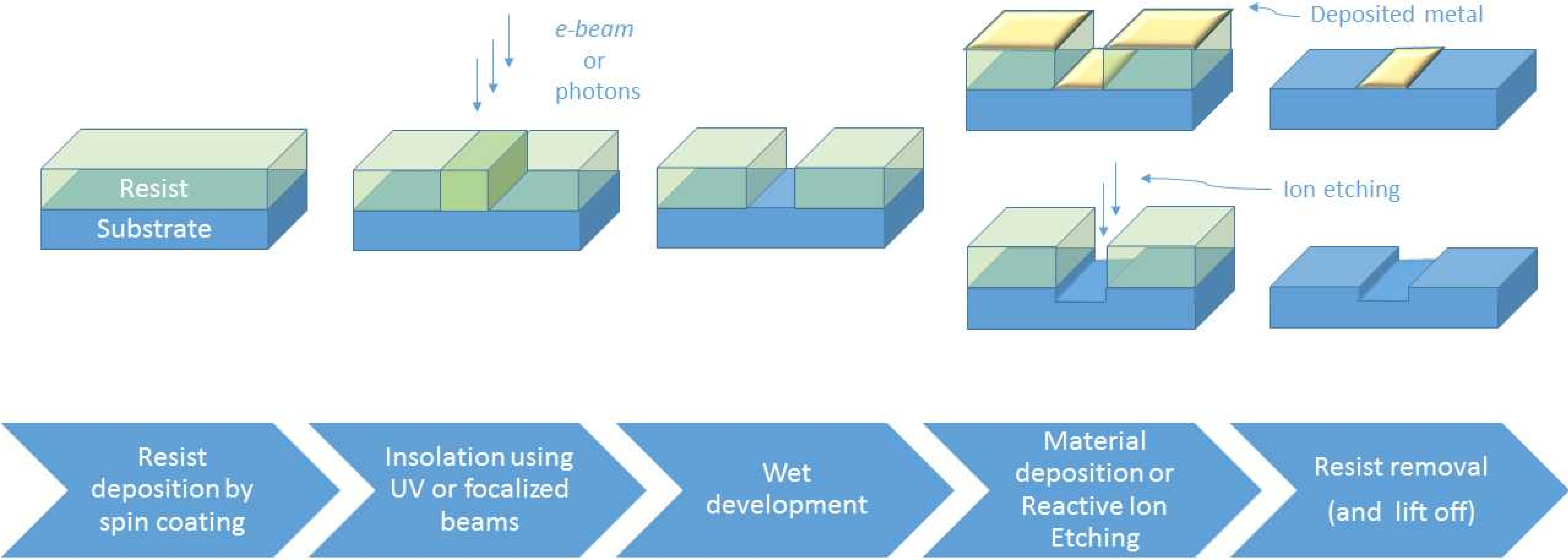
You'll find several equipments for:
-lithography : optical, ebeam, nano-imprint...

-deposition : evaporation, sputtering, cvd,
-etching : Reactive or Ion Beam Etching

-chemical benchs : s
etching

-metrology : Scannin
optical, AFM (Dekta

Typical flowchart



Basics steps for one lithography level.

Could be repeated several times. Difficulty of integrating several “simple” steps

Problem : the process is material dependent

Some examples :

-Ag reacts strongly with S

-metals don't like acids

-Al is etch by NaOH or some resist developpers

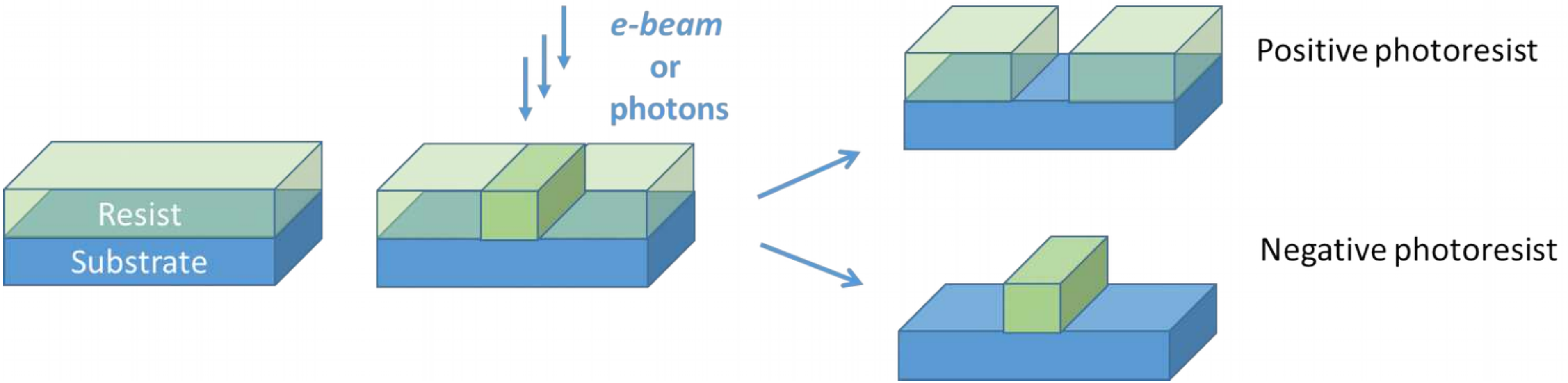
-Ti/Au doesn't stand HF, but Cr/Au does

-Al and Au dislike each other (react under heat treatment

-Oxydes are hard to be etched by physical means

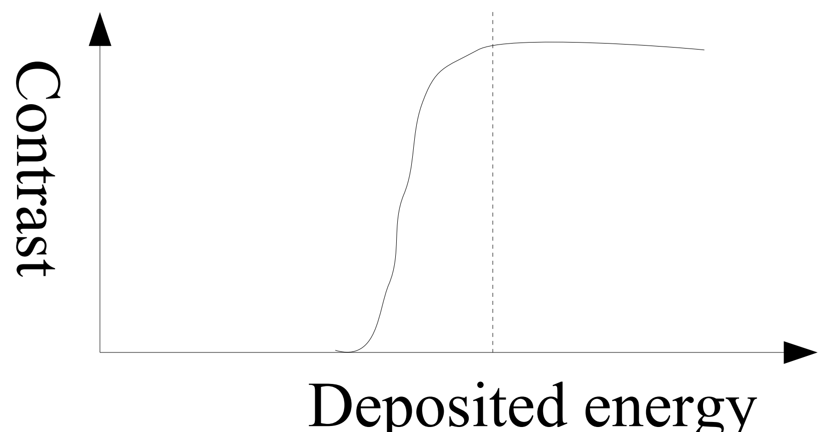
.....

Photoresists

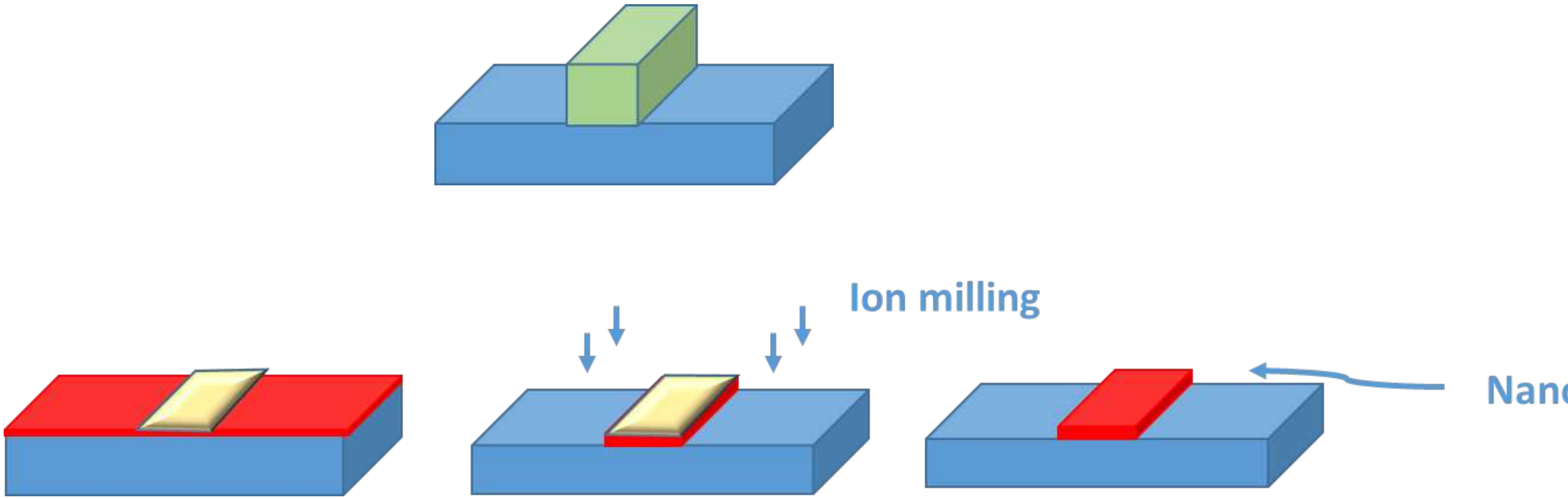


Polymers chains that are either break into small parts or crosslinked by the total energy deposited by electronic beam or photons.

Selective dissolution between exposed and non exposed area into appropriate solution

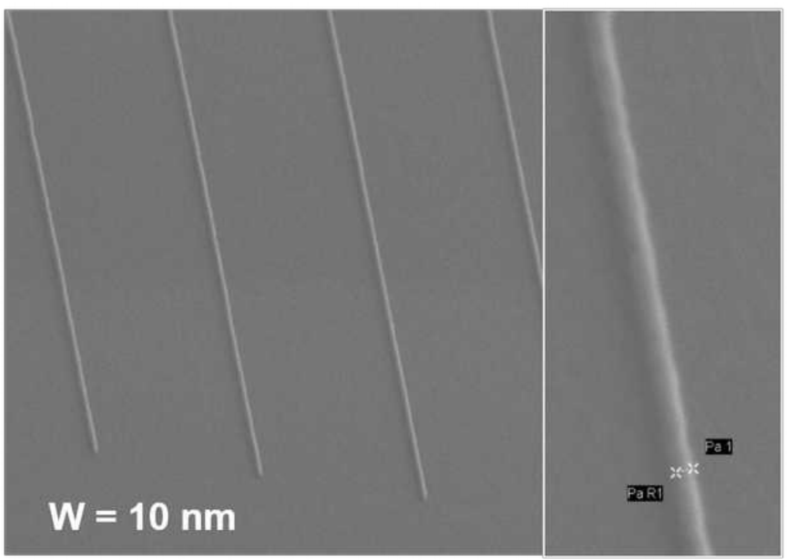


Some Hard Mask fabrication



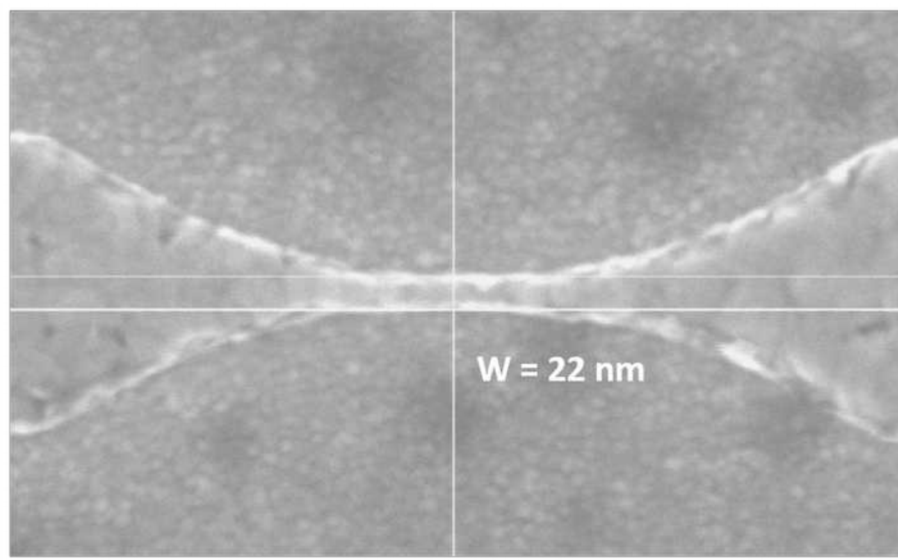
HSQ spin on glass

(a)

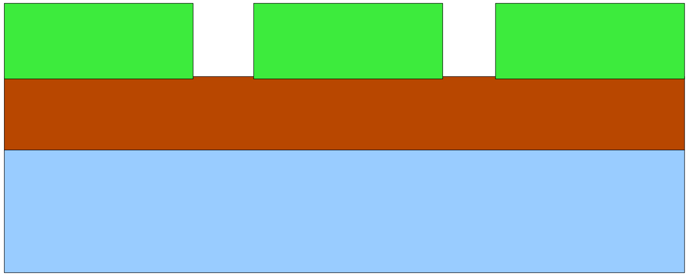


Metallic mask on top of Co/Ni stack

(b)



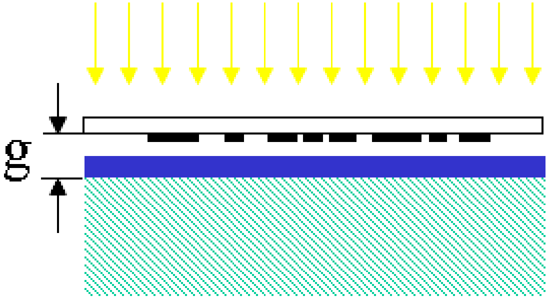
1. Mask fabrication



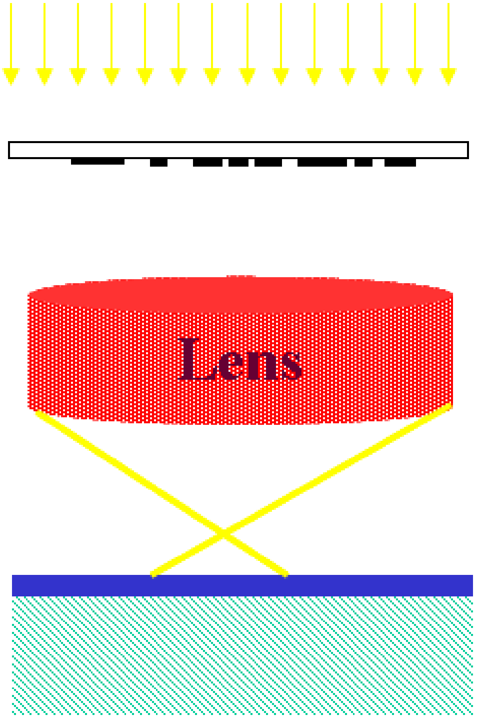
Lithography

Reproduction of a pattern ⇒ expose a resist to open windows in a controlled way

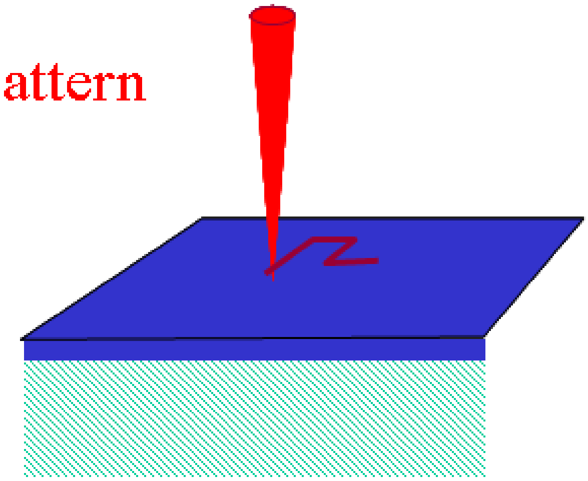
Crucial step which will fix the size of the pattern



contact
1:1



projection
1:5 à 1:20



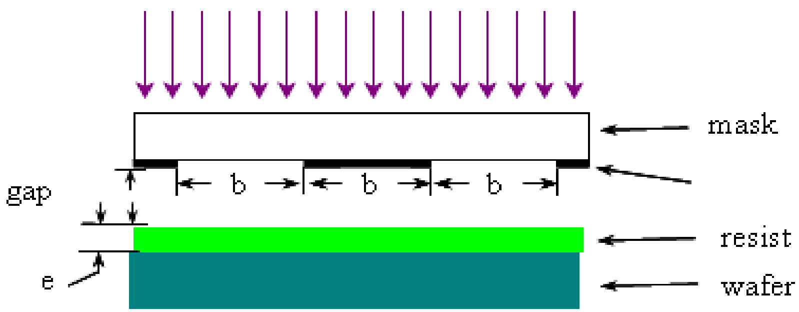
Direct writing by
Focused beams

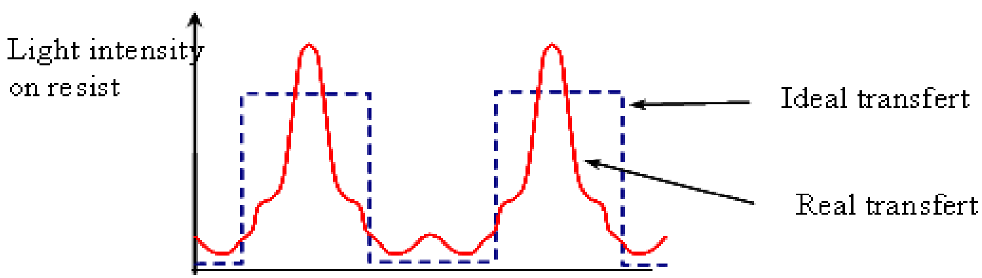
Nanoimprint
1:1

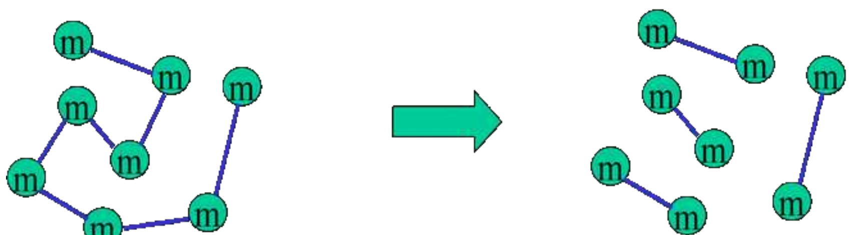
Optical lithography

Sensibility:

Dose = Incident Energy / Exposed Surface





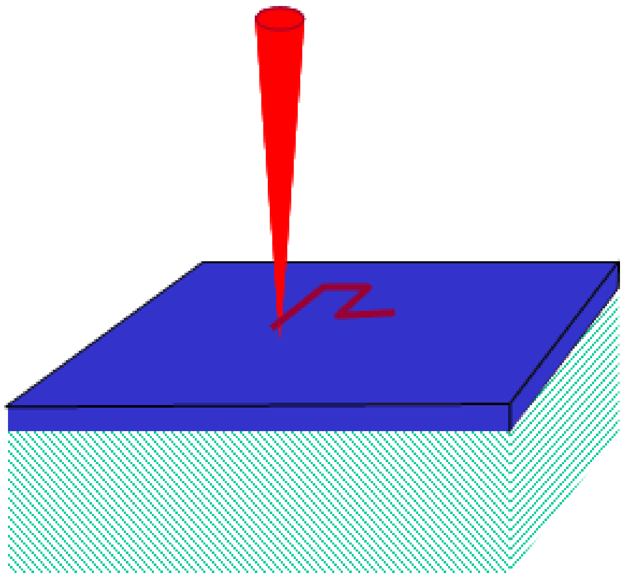


Typical recipes

Positive Photoresist	Spin Speed/Time	Thickness	Softbake Temp/Time	Exposure Time (assuming 10mW/cm^2)	Developer	Develop Time	Post-Exposure Bake Temp/Time	Minimum Feature Size
AZ 3312	4000rpm/60s	1um	90° C/60s	4-5s	AZ300MIF	30-40s	90° C/60s	0.5um
AZ 3330	5000-6000rpm/60s	2um	90° C/60s	8-12s	AZ300MIF	30-40s	90° C/60s	1um
Shipley 1.2L	4000rpm/70s	1um	90° C/60s	5-6s	Shipley MF-26A	30-40s	115° C/60s	0.5um
Shipley 1.8M	4000rpm/90s	2um	90° C/60s	10-11s	Shipley MF-26A	30-40s	115° C/60s	1um
AZ P4620	200rpm/30s, 6000/2s Clean off back of wafer	9um	70° C/60s, 100° C/4min	60s (soft contact else resist will crack)	AZ400K (diluted 1:4, agitate)	2min (repeat exposure/develop steps as many times as necessary)	70° C/5min, 90° C/5min, 110° C/10min	-

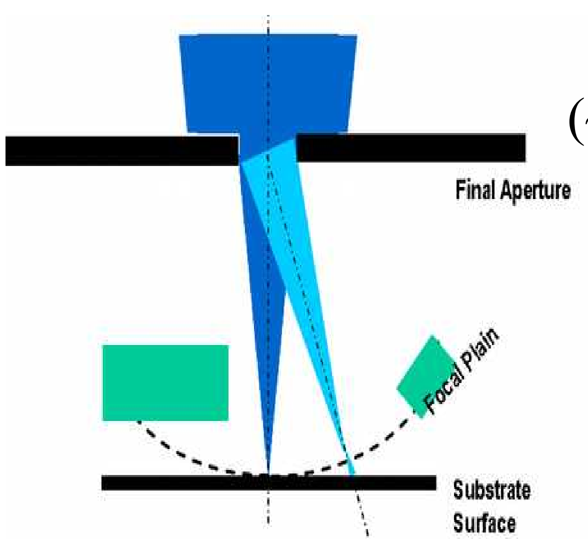
Resolution with contact lithography: 1-0.5 μm
(using UV or DUV light source)

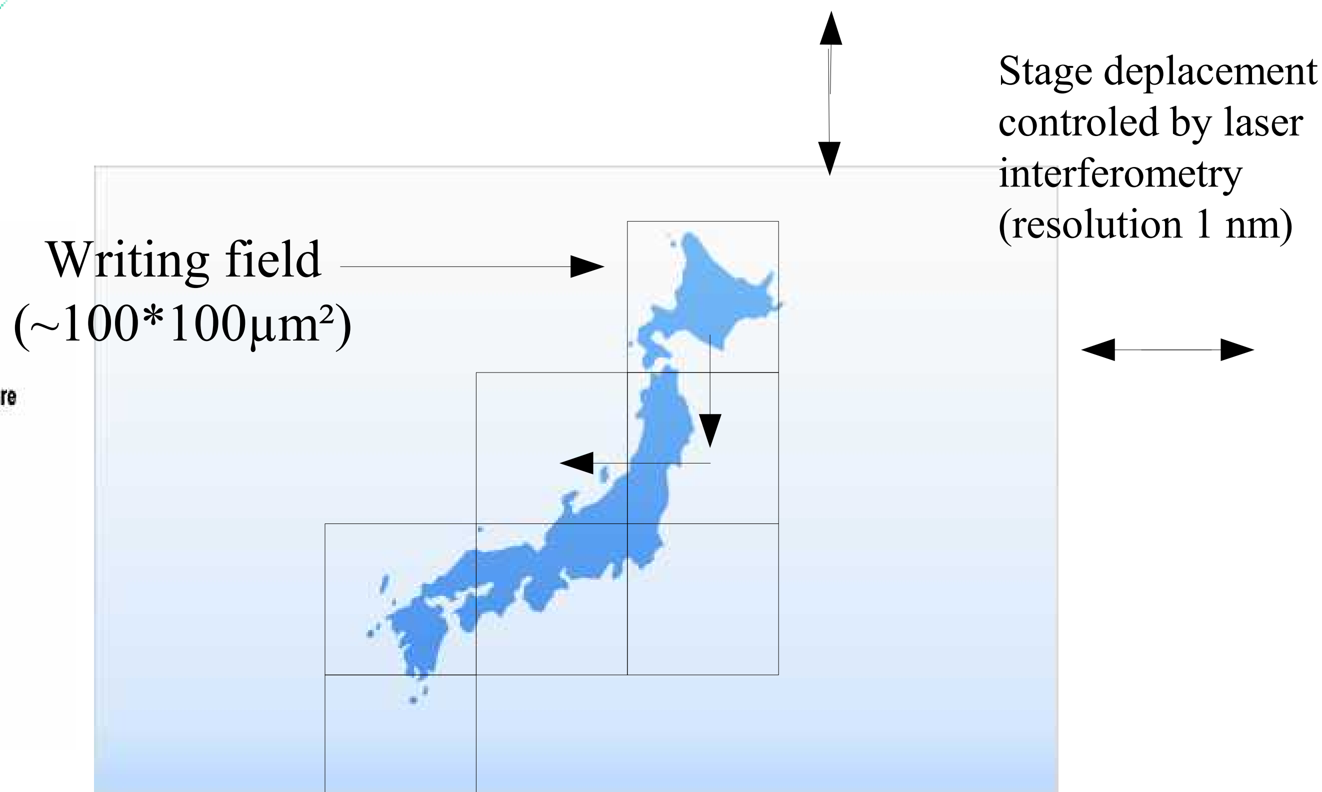
Electron beam lithography



Focused electron beam (down to 1 nm)
deflected over the surface

Resolution (limited by the resist) ~ 7 nm
Direct exposure (mask/pattern can be modified)
Sequential writing: small throughput





Ebeam nanowriter systems

3.2.2 Electron-Optical System

The figure below shows the structure of the electron-optical system of the lithography system. The explanation of each component follows on the next page.

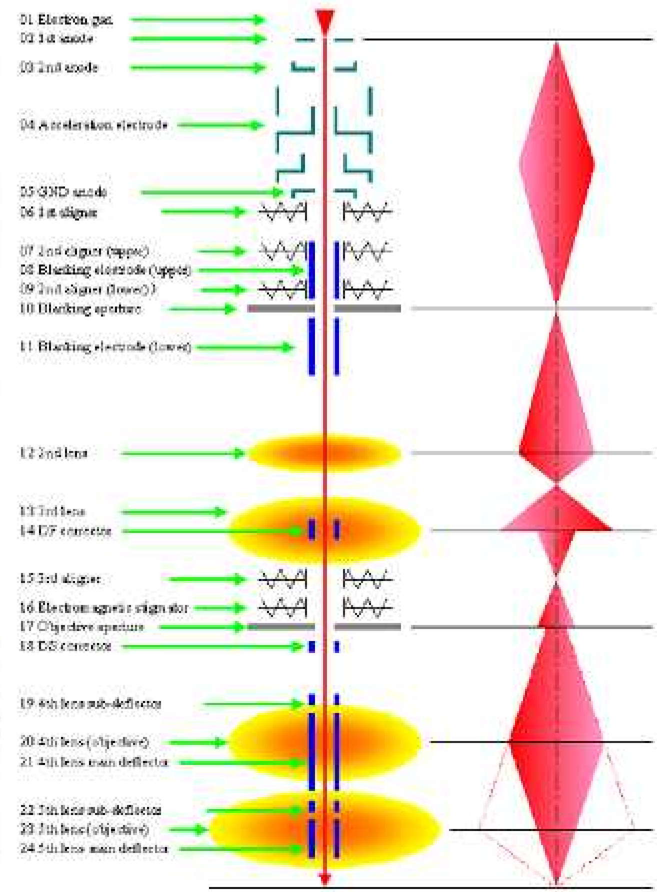
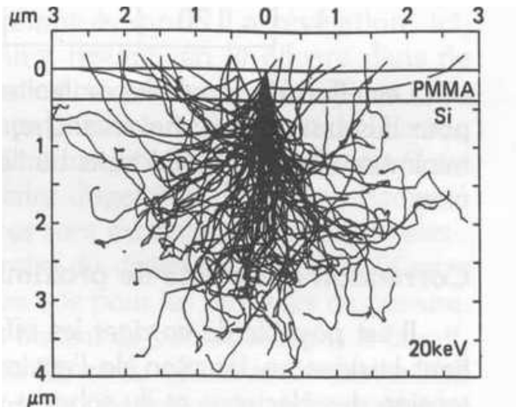


Fig. 3.3 Electron-optical system

Fig. 3.3 Electron-optical system

Working voltage 100 keV, cost >1 M€, room temperature stability of 0.1°C, batch operation mode, minimum line width of 7 nm

Proximity effects in ebeam lithography

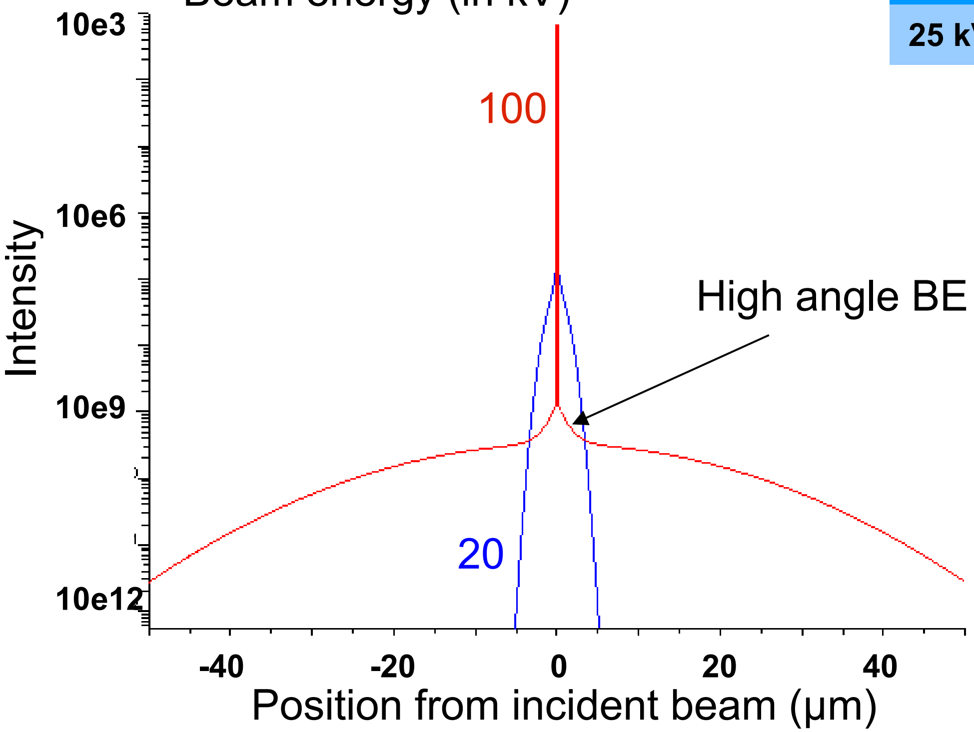


Sum of 2 gaussians and 1 decreasing exponential :
parameters : α forward scattering, β backward , γ high angle BE

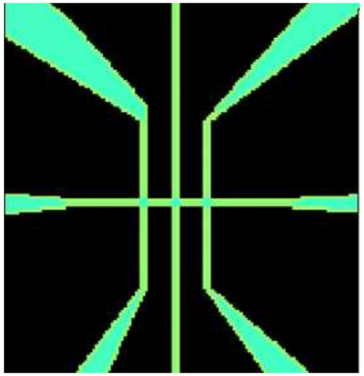
$$\frac{1}{\pi(1+\nu+\mu)}*[\frac{1}{\alpha^2}\exp(\frac{-r^2}{\alpha^2})+\frac{\nu}{\beta^2}\exp(\frac{-r^2}{\beta^2})+\frac{\mu}{2\gamma^2}\exp(\frac{-r}{\gamma})]$$

	α (nm)	β (nm)	γ (nm)	ν	µ	k
100 kV	13	22892	1193	1.16	0.02	11000
25 kV	14.7	1511	251	0.798	0.114	71486

From MC calculation for YBCO/MgO,
Y.M. Gueorguiev et al, Physica C 249, 187 (1995)

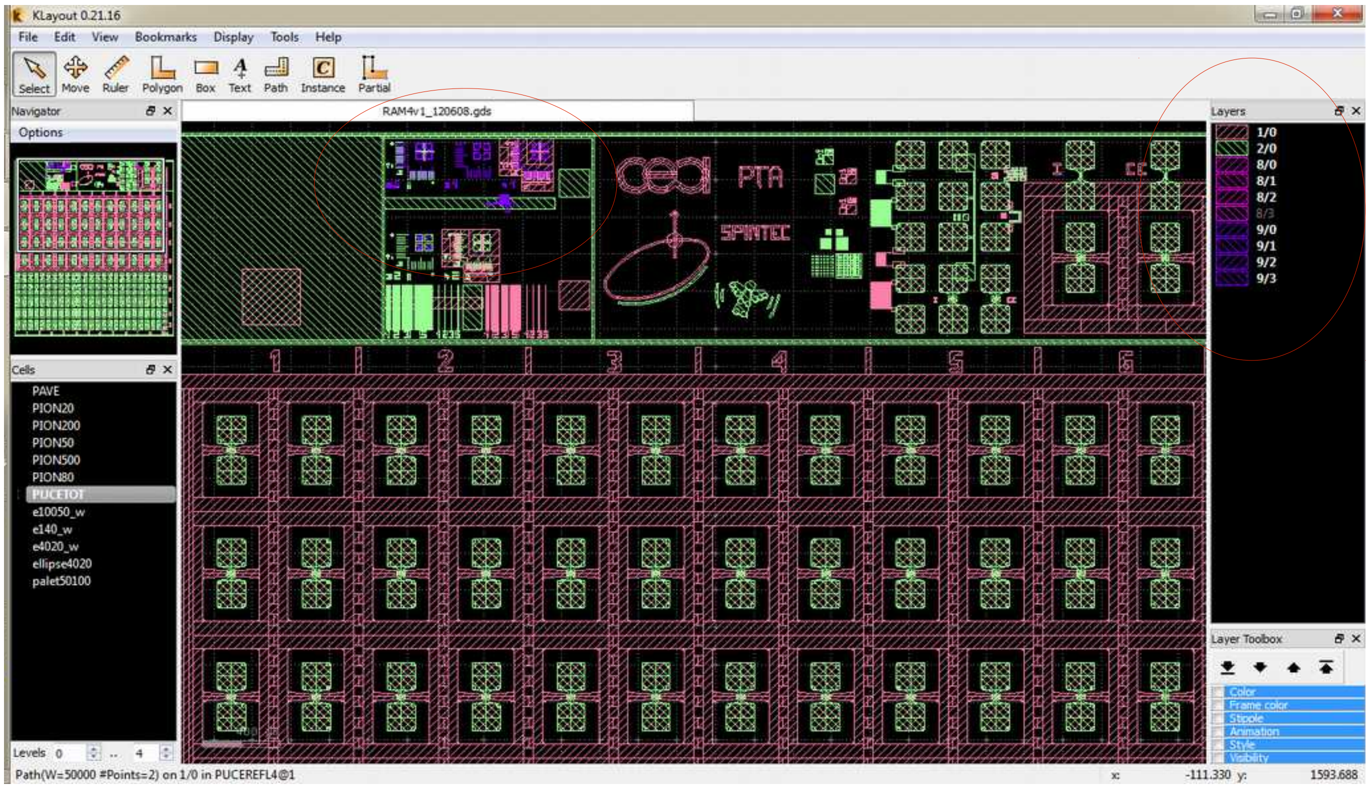


Convolution with a pattern

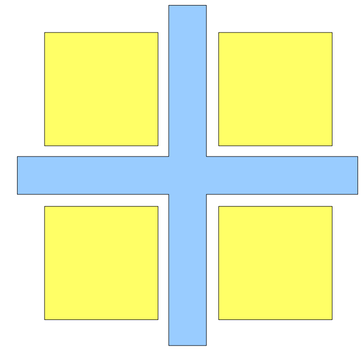


Multilevel lithography : repeating the whole process several time

Use of alignment marks for overlay alignment between levels

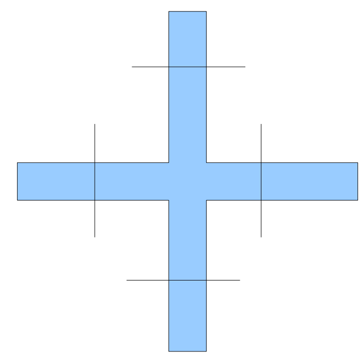


Optical marks



~ 1 µm

Ebeam marks

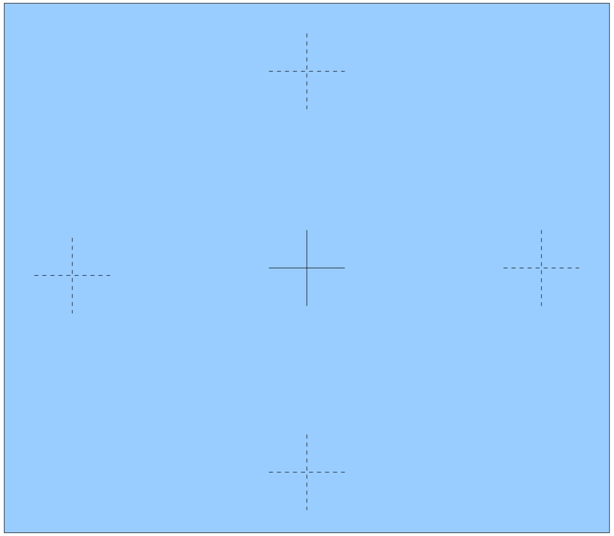


~ 20 nm

CAD software : for example Klayout (free software)

Draw the different levels with different layer numbers

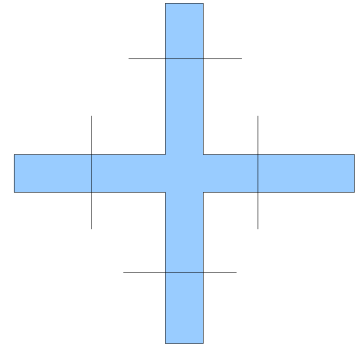
Deflection calibration



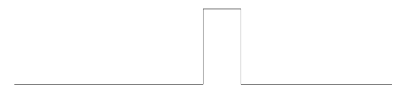
Find the cross at the center of the field, move the cross and control the distance by laser interferometer, deflect the beam to find the cross

Positioning error within the field (few 100 µm)
around 4-6 nm

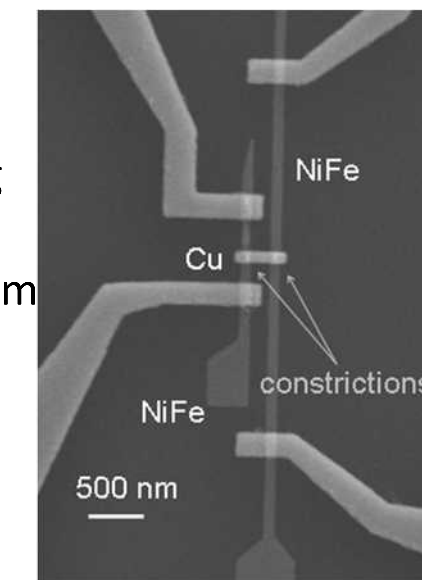
Overlay alignment

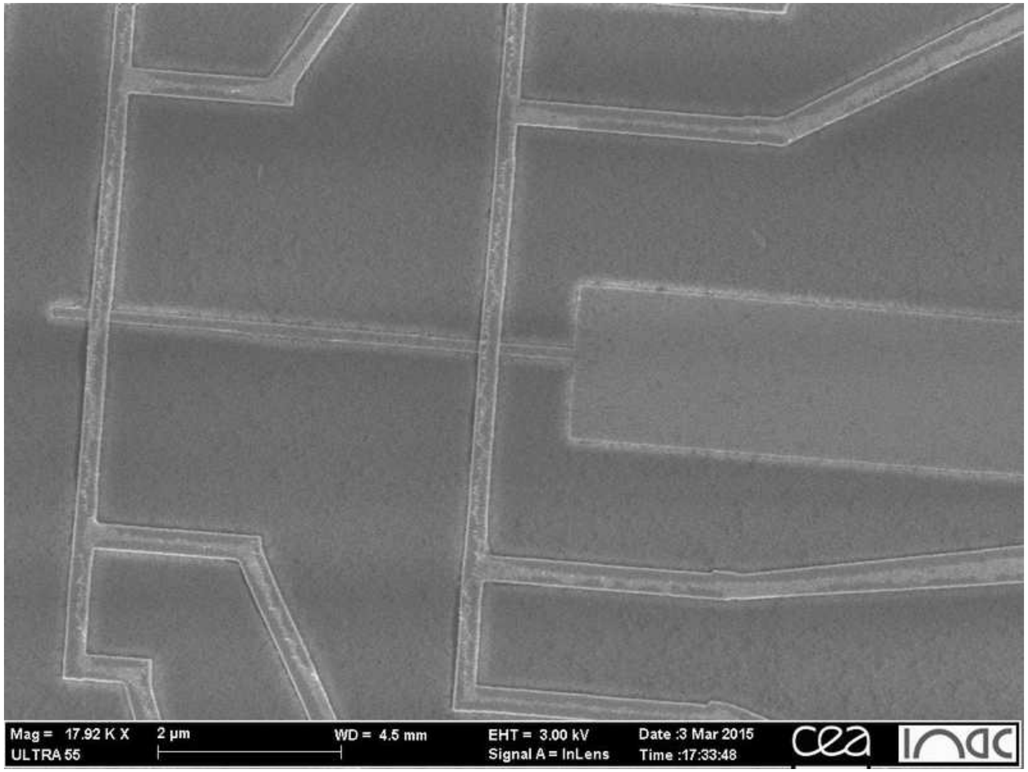


Scan a mark on the substrate



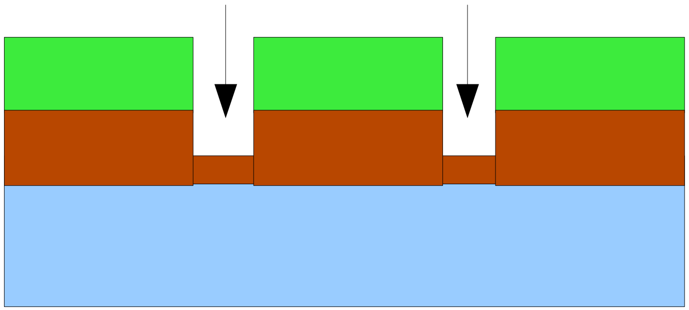
Find its exact position.
Travel to desire position away from the mark using laser interferometer.
Precision better than 10 nm





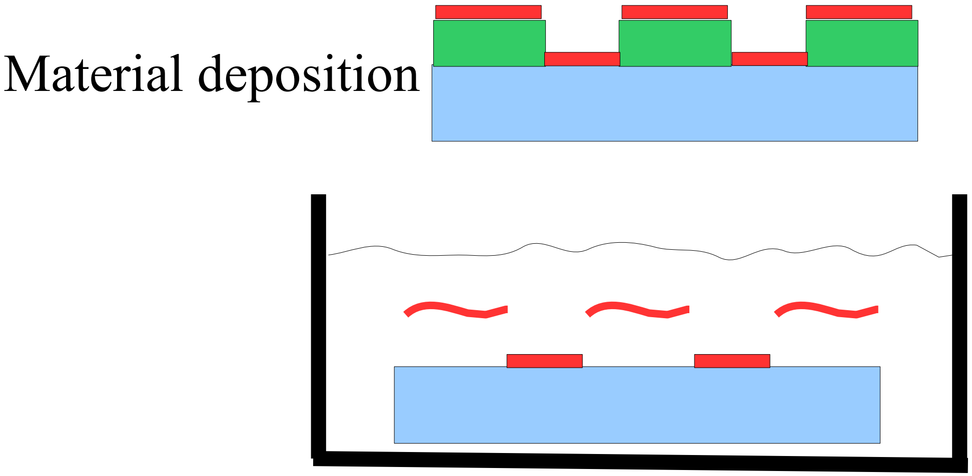
Patterning of FePt film grown on MgO substrate, deposition of various contact
Ebeam lithography on insulating substrate is possible !

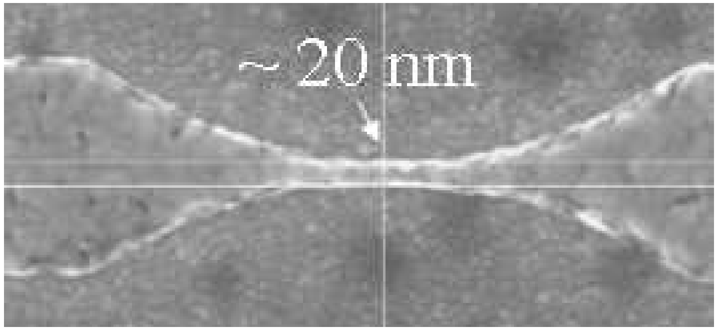
2. Transfer Methods



Transfer Methods (II)

1. Lift off



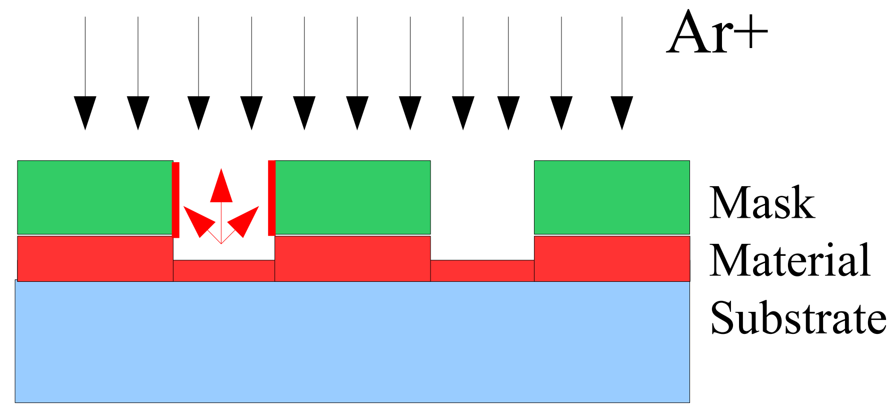


Dissolution of the resist in solvant (acetone)
From mirror like surface to rough surface
Release the metal from the surface using solvant flow, ultra sonic agitation
Avoid metal redepositon

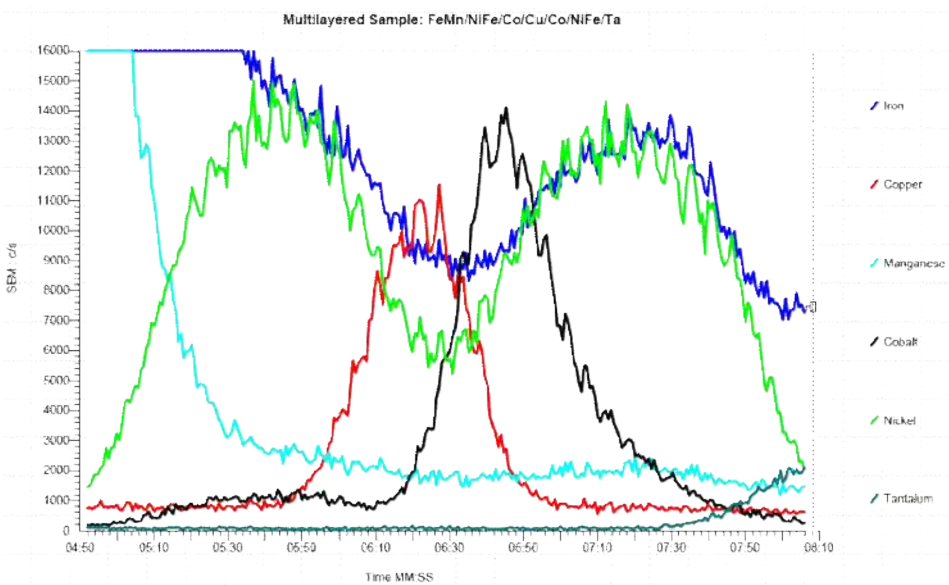
Transfer Methods (II)

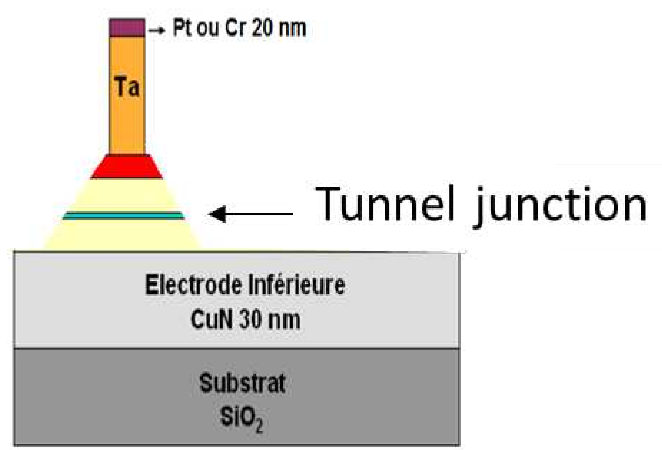
Ion Beam Etching

Sputtering of the surface atoms by Ar+ accelerated at 200-600 eV



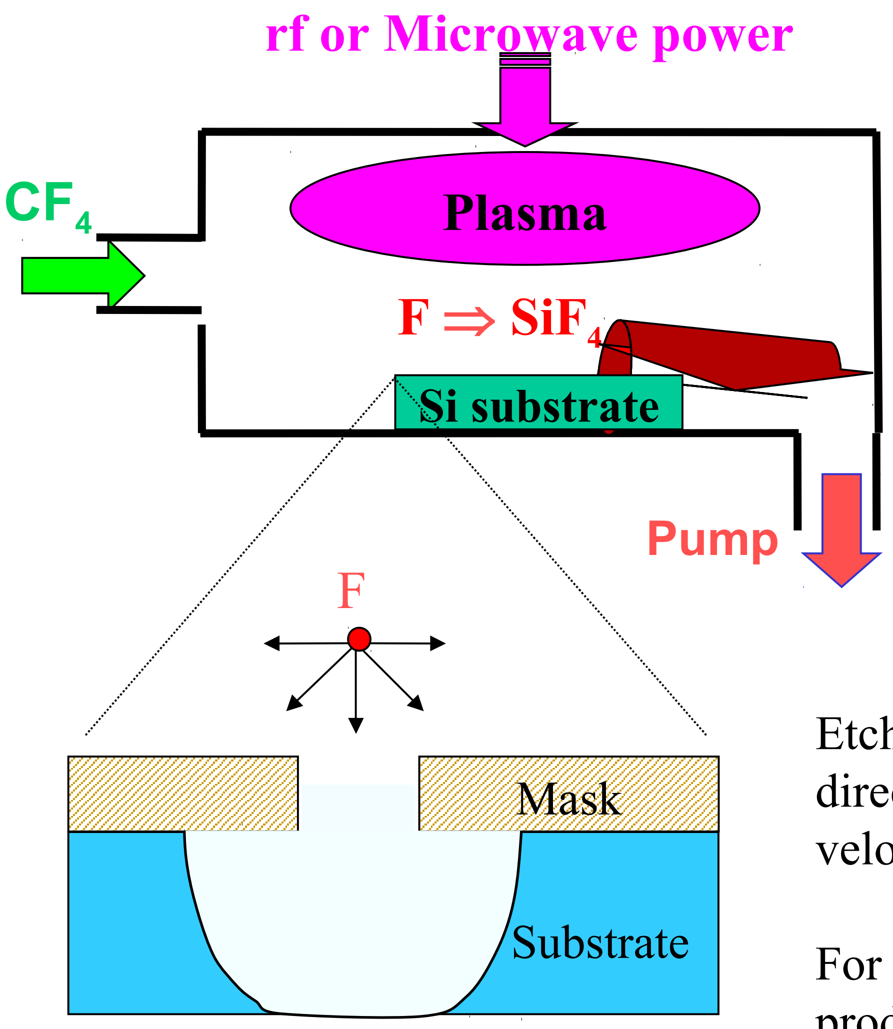
(not selective : mask and underlayer) + re-deposition





Transfer Methods (III): Reactive Ion Etching (RIE)

What is plasma etching ?



1) Flow <u>inert</u> CF_4 gas through the reactor.

2) Make discharge to create reactive species

$$CF_4 + e^- \rightarrow CF_3 + F + e^-$$

3) Choose chemistry so that the reactive species (F) react with the solid to form ***volatile*** etching products :

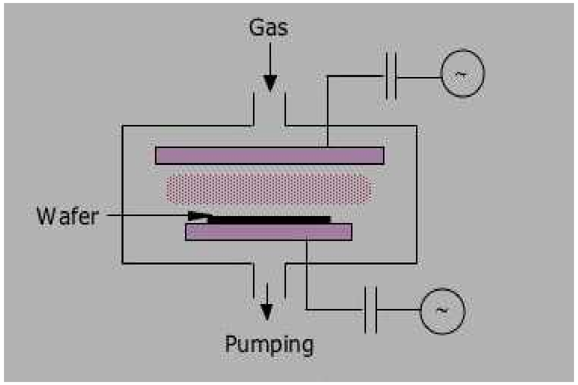
$$Si + 4\,F \rightarrow SiF_4 \uparrow$$

4) Pump away etching products = silicon removal from system

Etching is **isotropic** (etch rate is the same in all directions) because F atoms have an isotropic velocity distribution.

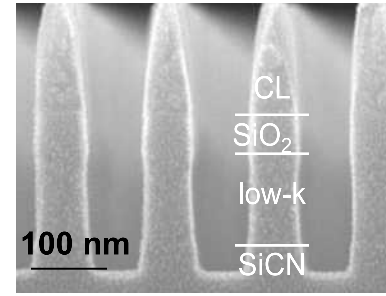
For some materials, the formation of volatile products requires a **high substrate temperature**

1-Reactive Ion Etching

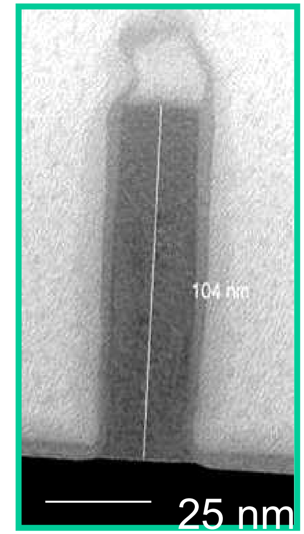


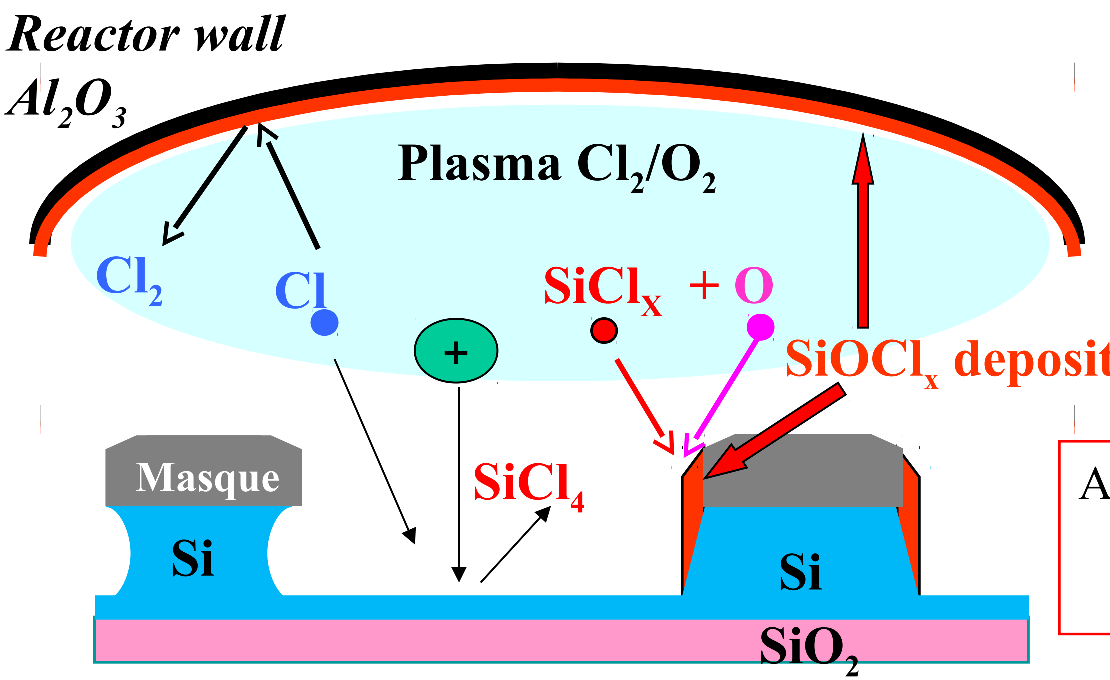
Ion density

Ion energy



CL
SiO_2
Low-k
SiCN





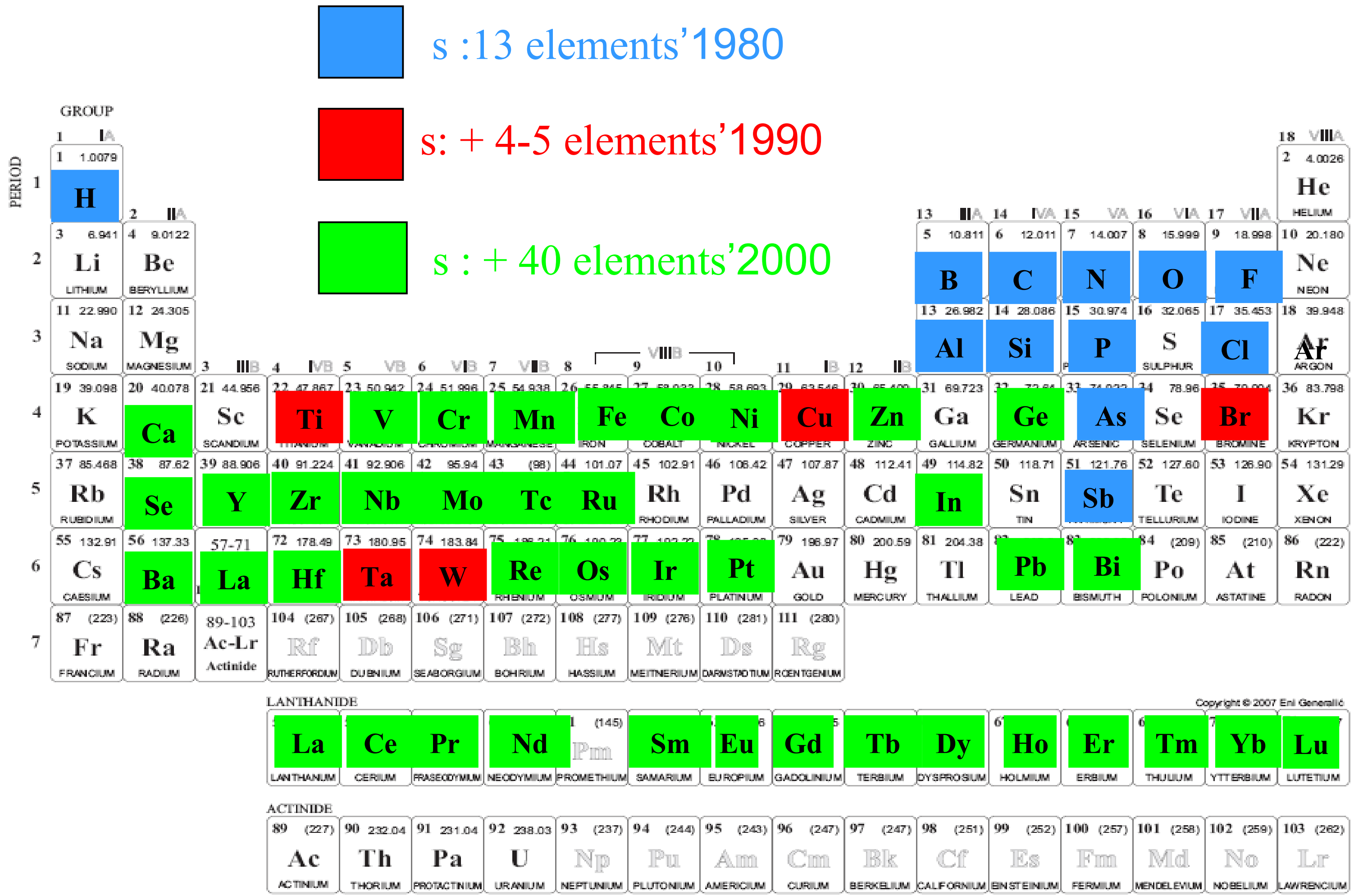
Anisotropic etching = formation of a passivating layer on the wall of the pattern

<u>**Note**</u>: passivating layer creates slope in etchning profile

Controling profile at the nm scale **= Controling thickness of passivating layer**

Understanding of depositing mecanisms are required to optimize the process

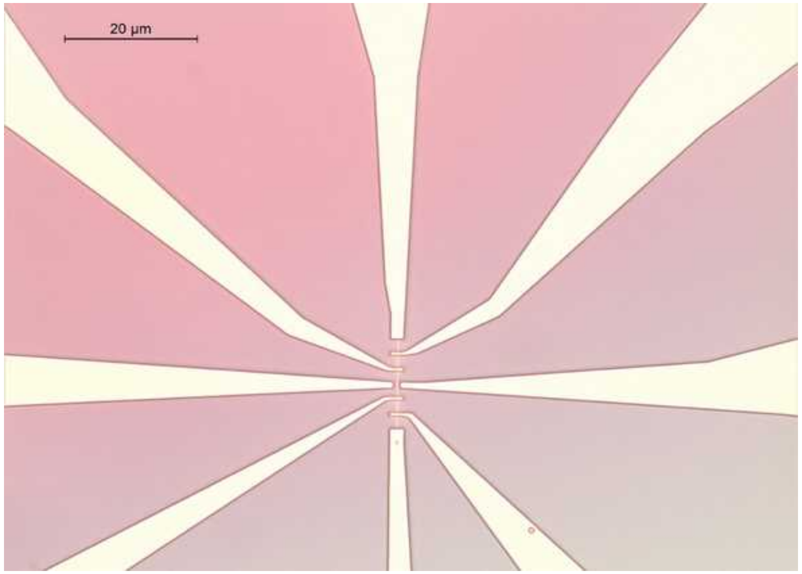
The march of materials for RIE

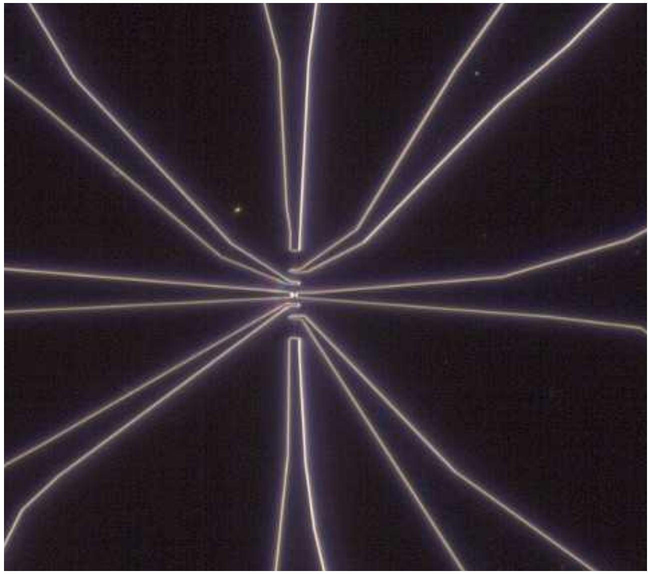


Source: Terrence J. McManus, Intel

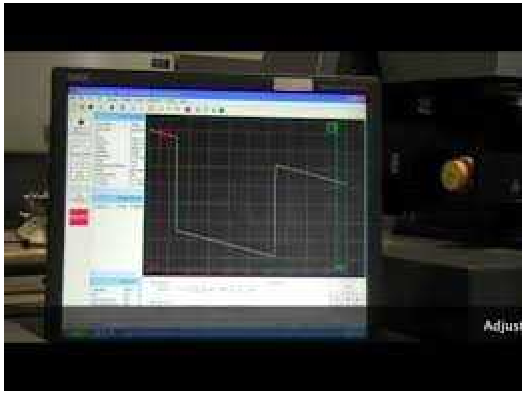
III. Some metrology tools

Optical microscopy





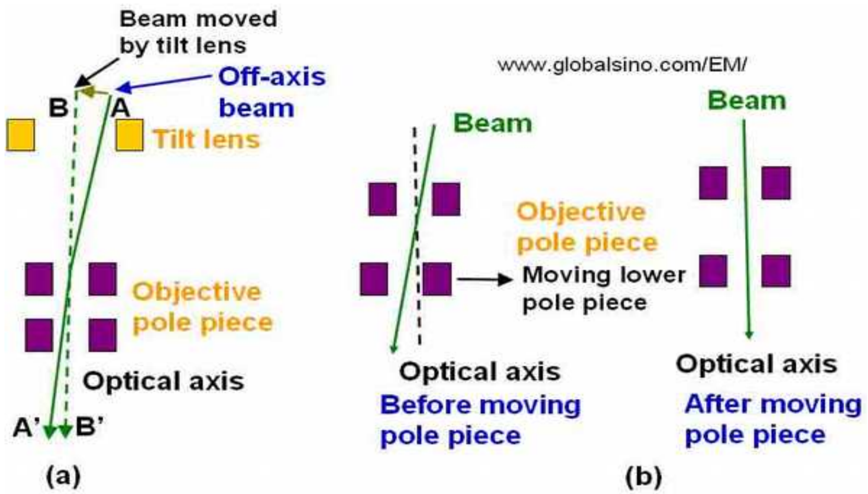
Allows fast control of the process at almost any step. Feature down to 50 nm, dark field, polarizer analyser (amorphous vs crystalin), focal depth

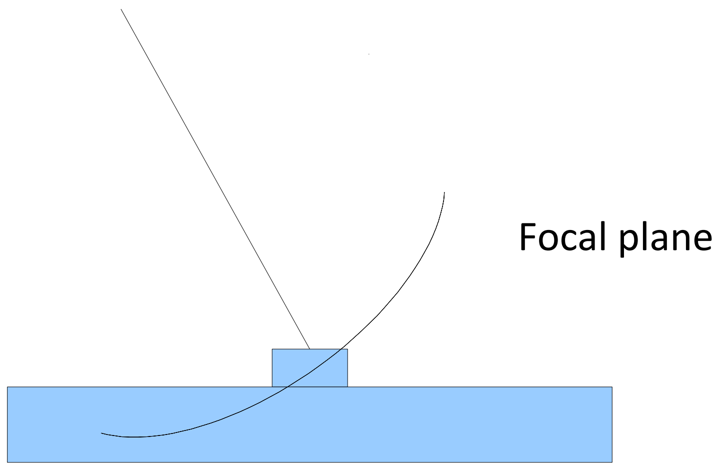


Profilometer to measure etching step, resolution 10 nm

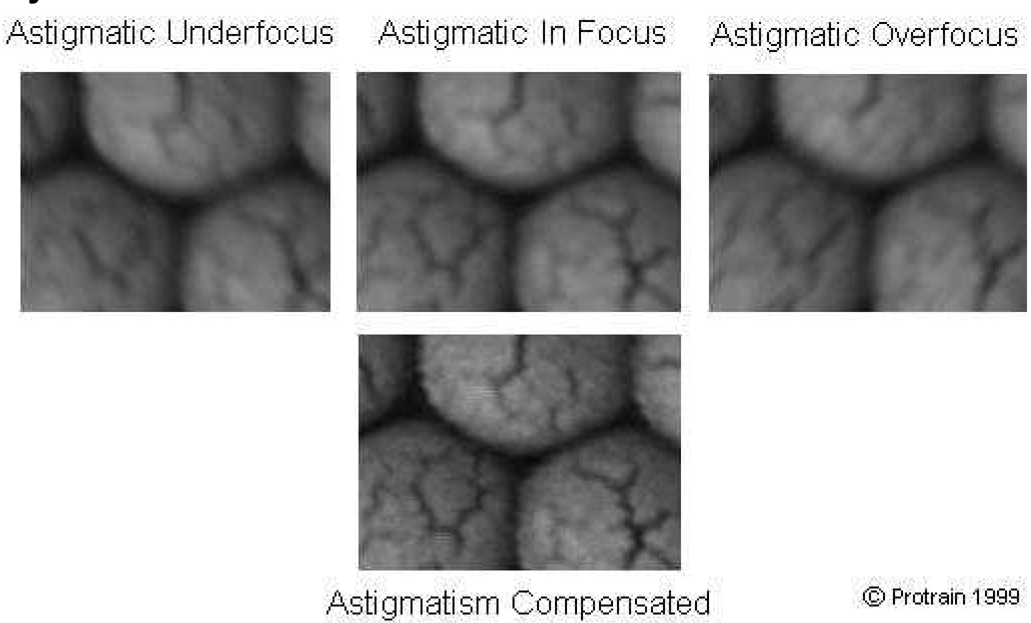
Scanning electron microscope (SEM)

Column alignment



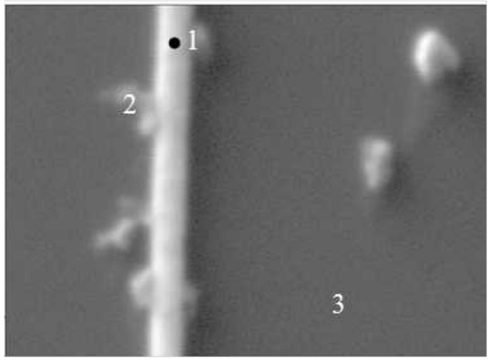


Astigmatism adjustement



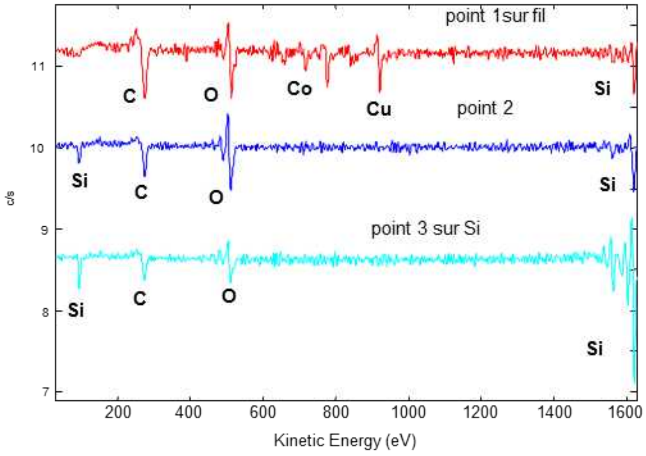
We can see but we need to have a "tongue"

Auger electron analysis in side SEM

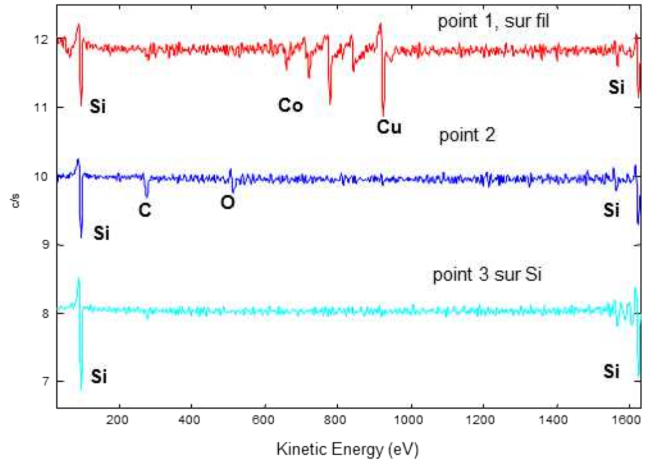


Auger probe size:
20 nm diameter
2-3 nm in thickness

Spectrum on 3 different points



After etching



in situ ion milling to remove comtaminant

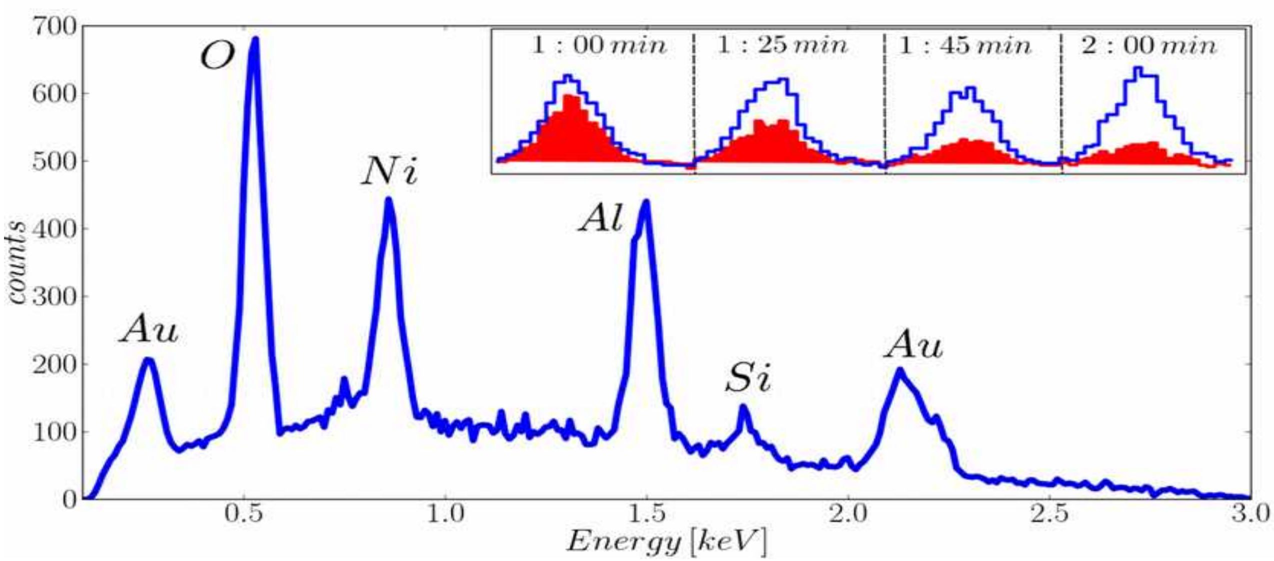
Ions Ar+, 500eV.

[1]Vila *et al*., Appl. Phys. Lett. **80**, 3805 (2002)

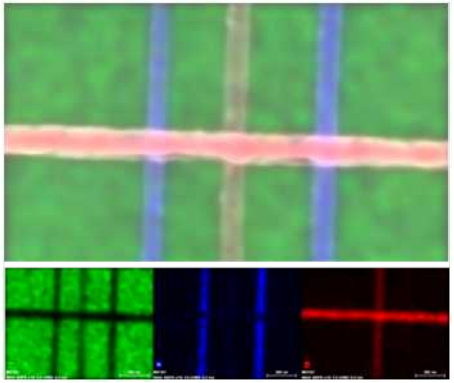
Important to clean the surface before depositing your contatcs

Energy Dispersive Xrays analysis (EDS or EDX)

Element analysis over a sample depth (dependent on incident beam energy)
Element identification, composition analysis, to follow an etching process



EDS mapping
50 nm wires



Can be combined with monte carlo simulation (Casino) for quantitative analysis or thick measurements

Patterning : conclusions

The choosen process is material dependent

either for mask fabrication or transfer technique

Tricks need to be used

according to process/approach
material selectivity/compatibility

Mask fabrication (lateral)

e-beam lithography (conventional basic research tool)
Altogether with emerged nanofabrication technologies

nanoimprint, near field...

Transfer (vertical)

pattern etching
eventually not critical for bottom/up

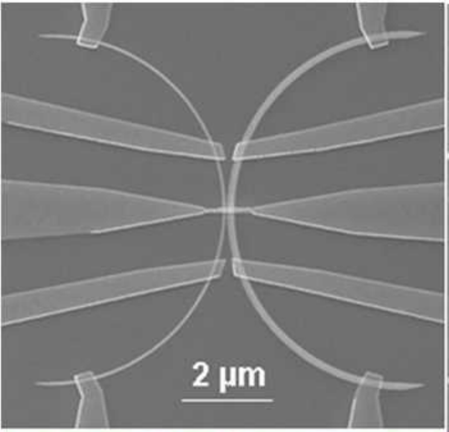
Combining bottom/up with top/down :

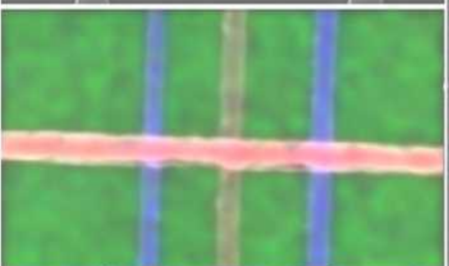
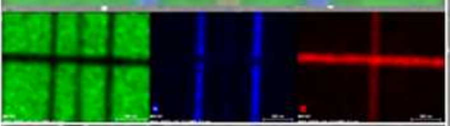
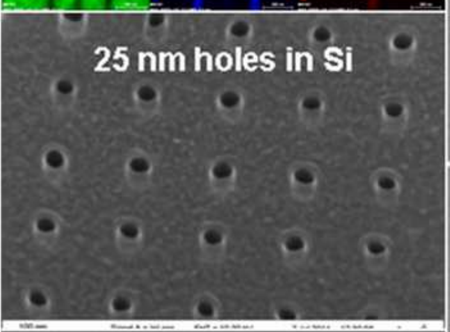
→ New materials/devices or technologies for novel or improved properties/functionalities

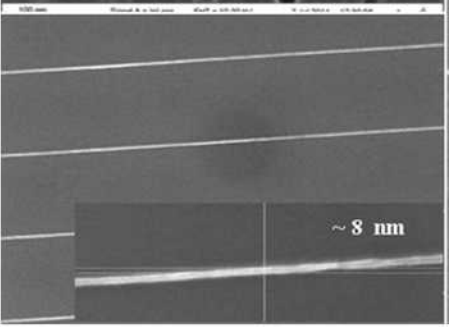
-To Control growth/organisation of the nano-objects

-To Measure/Probe the properties at the single object level

-To Insert nano-objects in devices or characterisation tools





Thank you !