# Preparation of Nanostructures (Příprava Nanostruktur)

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# Outline

1. Content
2. Relation between symmetry of crystals and crystal properties
3. Introduction
4. Bulk crystal growth
5. Thin film preparation
6. Lateral structures
7. ATR / Surface plasma resonance

# Překrytí obsahu přednášky s jinými předměty:

- MBE, napařování (sputtering) → Hlubina (vakuová fyzika)
- absorbce, desorbce molekul na površích→ Hlubina (vakuová fyzika)
- tenké vrstvy (napařování, sputtering, CVD) → Postava
- techniky studia tenkých vrstev (XRD, SEM, AFM, RHEED, LEED) → jiné předměty

# Vyučující (2014-2015)

## Vyučující (2014-2015)

- Jaroslav Hamrle
- Rudolf Sýkora
- Illa Ramakanth
- Radek Ješko

# Nabízený obsah přednášky:

## Illa Ramakanth (3 lessons)

1. Chemical deposition methods for the formation of thin films
   - Chemical approach (preparation)
   - Chemical Vapor Deposition (CVD) process (chemical method)
   - Electrodeposition and solid phase method (chemical method)
   - Co-precipitation approach (chemical method)
   - Sol-gel (chemical method)
   - Hydrothermal synthesis / Solvothermal method (chemical method)
   - Ultrasonic assisted wet chemical route
   - Spin coating (chemical method)
   - Lithography
2. Fullerenes: Structure, Preparation, Properties & applications
3. Carbon Nanotubes: Structure, Preparation, Properties & applications

# Nabízený obsah přednášky:

**Rudolf Sýkora**

- krystalografie, 2D krystalografie, pocitani vzdalenosti rovin
- relaxace povrchu,
- elektronova struktura povrchu (kap 2 ze surface science)
- kap. 8. + 9.rekonstrukce povrchu; atomova struktura povrchu
- kap. 11. elektronova struktura povrchu

**Radek Ješko**

- fyzikální depozice: MBE, naprašování (sputtering) [bude upřesněno]

# Nabízený obsah přednášky:

**Jaroslav Hamrle**

- symetrie krystalů a jejich vliv na vlastnosti materiálů
- absorbce, desorpce, teorie růstů krystalů a tenkých vrstev (?)
- charakterizační techniky podle zájmu (např. NMR, surface plasmons a ATR, MOKE ?)

# Praktikum z pokročilých technologií

Dvě možnosti jak proběhne praktikum:

1. exkurze nebo
2. příprava a charakterizace feritů:
    - např. $CrFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, $NiFe_2O_4$, $BiFeO_3$
    - 8 vzorků (2 tlouš̌tky, 4 žíhací teploty), připraveno pomocí dipping
    - charakterizace: XRD, VSM, AFM (případně SEM), případně elipsometrie a magento-optická spectroskopie, případně XPS
    - reálná šance opublikovat výsledky (nyní studujeme podobnou sadu vzorků)

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# Type of structures

## Types of structures

- bulks (including bulk superstructures)
- layers
- 2D structures (lithography, self-organizing growth)
- 3D structures (special lithography, 3D printing)

# Basic material structures

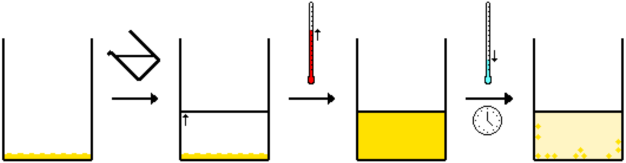
**Basic material structures from material point of view:**

- single crystal (also known as monocrystals or epitaxial)
- polycrystals (small single crystals randomly oriented)
- amorphous (e.g. glass)

# Outline

# Crystal growth techniques I: using one solvent

- slow cooling of the solvent (*rozpouštědlo*): substances that are much more soluble in a solvent at high temperature than at low temperature



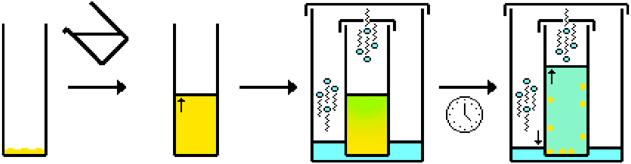
- slow evaporation of the solvent [solvent evaporates → crystal growth]
- solvent can be also liquid metal (e.g. Sn-tin)

`http://en.wikipedia.org/wiki/Recrystallization_(chemistry)`

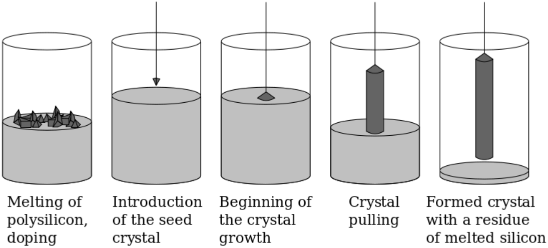
# Crystal growth techniques I: using two solvents

Two solvents (substances that are very soluble in one solvent and insoluble in a second solvent. The two solvents must be miscible, i.e. soluble in each other in all proportions):

- two solvent evaporation [dissolve substance in good solvent → add bad solvent → good solvent evaporates → crystal growth in bad solvent]
- two solvent liquid diffusion [dissolve substance in good solvent → add bad solvent → crystal growth in mixture of bad and good solvent].
- two solvent vapour diffusion [dissolve substance in good solvent → add bad solvent to surrounding → bad solvent mixes with good through diffusion of vapours → crystal growth in bad solvent]



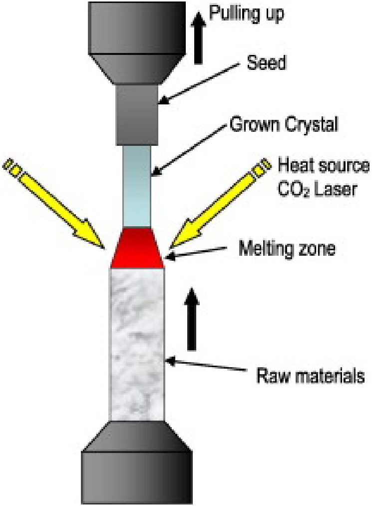
# Crystal growth techniques II: Czochralski process



- hight quality crystal growth of single crystals, to very large size (length 1-2 m, industrial diameter for wafers upto 450 mm)
- semiconductors (e.g. Si, Ge, GaAs), metals (e.g. Pd, Pt, Ag, Au), salts, etc.
- defects later removed by subsequent zone recrystallization.

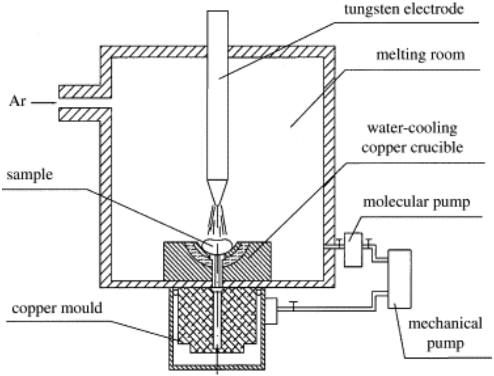
# Crystal growth techniques III: Laser Heated Pedestal Growth (LHPG)

- similar to Czochralski process, but no crucible needed
- heating by power laser
- high purity and low stress crystals
- allows to growth materials with very high melting points
- when heating starts with single crystal on top, can produce single crystal



# Polycrystal growth: arc melting/remelting

- melting or remelting in week vacuum (usually Ar residual atmosphere)
- creation of metal polycrystals, with defined composition
- allows to melt small amounts of materials
- vacuum remelting and slow cooling: removal of residual gas and high vapour pressure elements (C,S,O,Mg), larger crystal size, stable structure obtained.



Huag et al, Materials Science and Engineering: A 422, 309, (2006)

# Crystal growth: nucleation

## 1. Crystal nucleation:

- small particle of crystal is created (nucleated), with random crystallographic orientation.
- homogenous/heterogenous (without/with influence of the external particle).
- nucleus appears slowly (then crystal may growth quickly).
- external crystal can be used as a seed.

# Crystal growth: growth

## 2. Crystal growth:

- In ideal case, crystal grows layer by layer added to the nucleated seed. The interface between crystal and vapour/solvent is atomically sharp.
- Non-uniform lateral growth: The surface advances by the lateral motion of steps which are one interplanar spacing in height.
- Uniform lateral growth: The surface advances normal to itself without the necessity of a stepwise growth mechanism.

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# Thin film preparation

## Techniques of thin film preparation

- physical techniques (usually physical vapour deposition, differing by source of vapour (MBE, sputtering, ion plating))
- chemical techniques (spin coating, chemical solution deposition (sol-gel), chemical vapour deposition)

# Physical depostion techniques: physical vapour deposition (PVD)

PVD involes: **Vapour formation → vapour transformation → film formation**

Vapour phase creation:

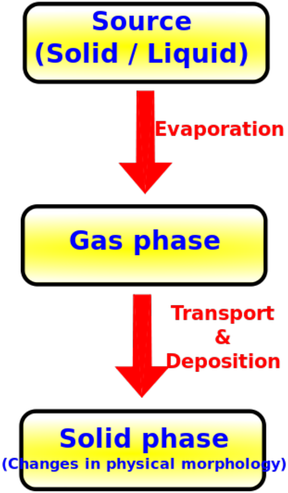
- evaporation
- sputtering
- ion plating

Vapour transportation:

- collisions (can be related with cluster formation)
- ionizations

Condensation on substrate:

- nucleation, growth, ion bombardment, redeposition etc.



**Source (Solid / Liquid)**

**Evaporation**

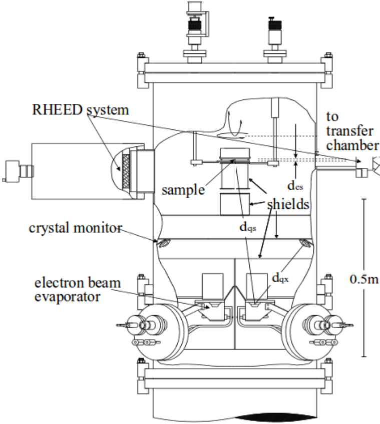
**Gas phase**

**Transport & Deposition**

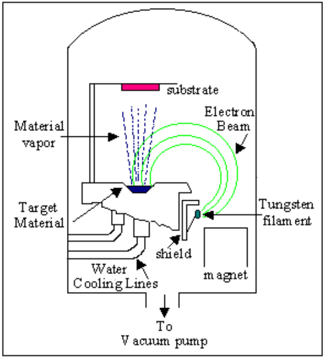
**Solid phase**

**(Changes in physical morphology)**

# Example of molecular beam epitaxy, (M.Jourdan, Mainz)

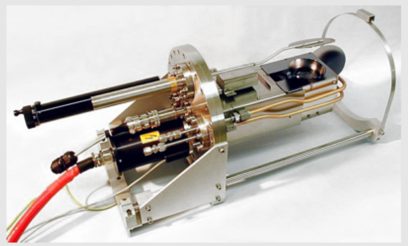


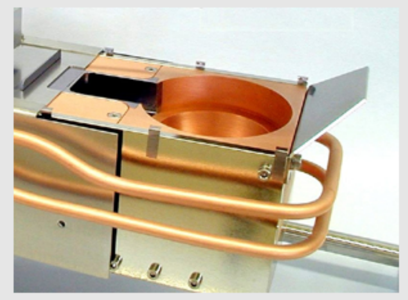
# Sources of vapours I: electron beam evaporators



Local heating by electron bombardment → evaporation of the target material → clean deposition of the target

www.mbe-components.com

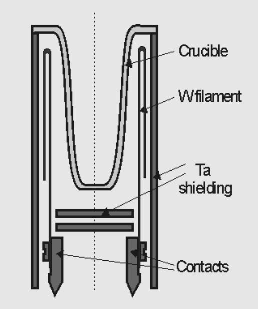


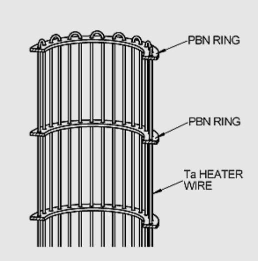


# Source of vapours II: Effusion cells (Knudsen Cell)

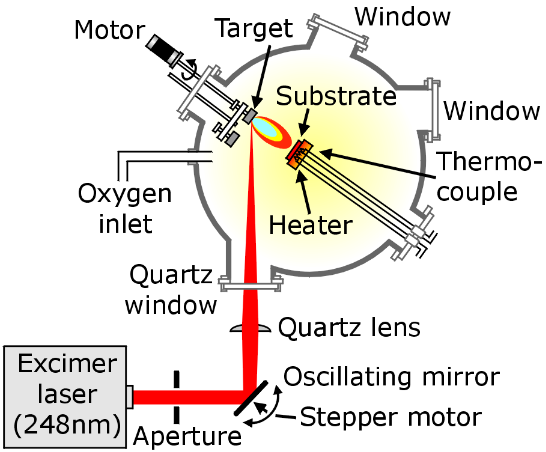
Thermal evaporation out of a heated crucible (Tmax ≈ 1800°C)

www.mbe-components.com





# Source of vapour III: Pulse laser deposition (PLD)



Problem of PLD: droplets ($\mu$m-sized balles deposited together with vapour).

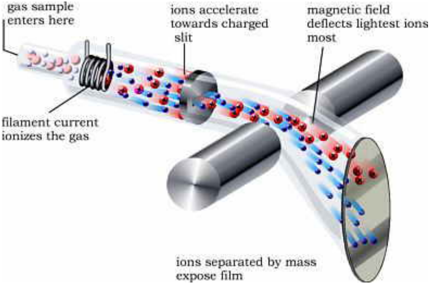
`http://www.egr.msu.edu/`

# Control of the deposition

**Deposited thickness gauge**

Oscillating Crystal Monitor [change of mass → change of resonance frequency]

**Mass Spectrometer**

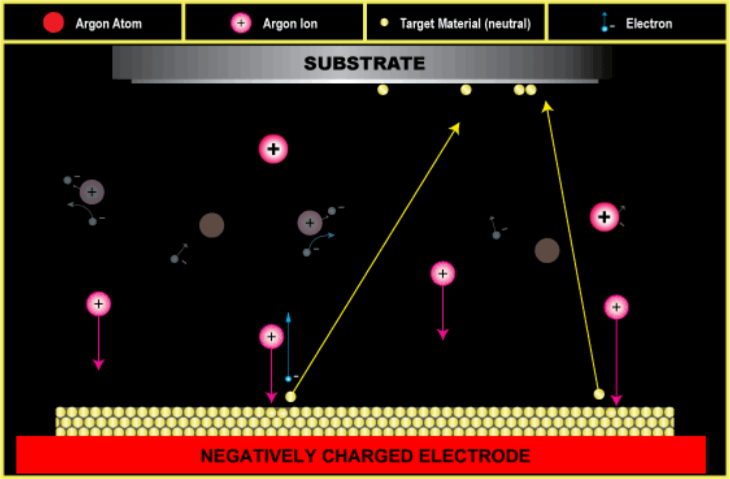


# Sputtering

## Sputtering:

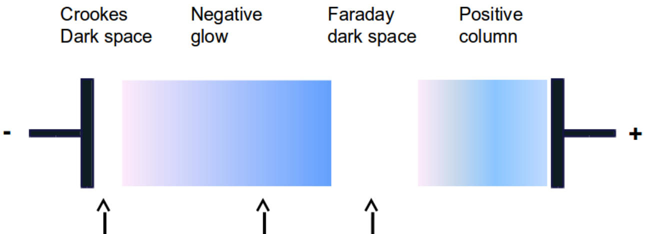
- ejection of atoms from target due to bombardment of energetic particles ($E \gg 1\,eV$).
- commonly use for thin-film deposition, etching or analytical material study.
    1. create plasma (dc, rf, mw)
    2. plasma looses energy to surroundings (bombardment)
    3. for plasma, atoms of noble gas of similar weight as target is used (e.g. Ar for 3d metals)

# dc-sputtering



http://www.ajaint.com/whatis.htm

# dc-sputtering: Glow Discharge


Crookes Dark space

Negative glow

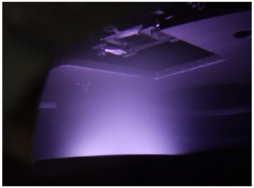
Faraday dark space

Positive column

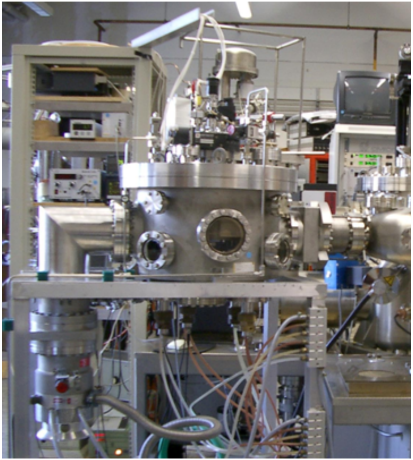
Accumulated ions -> electric field

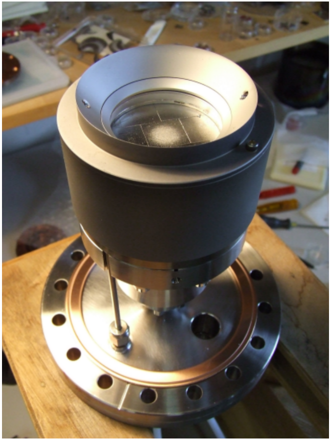
Screened ions -> almost field free

Low electron energy -> no ionization



# Sputtering: example

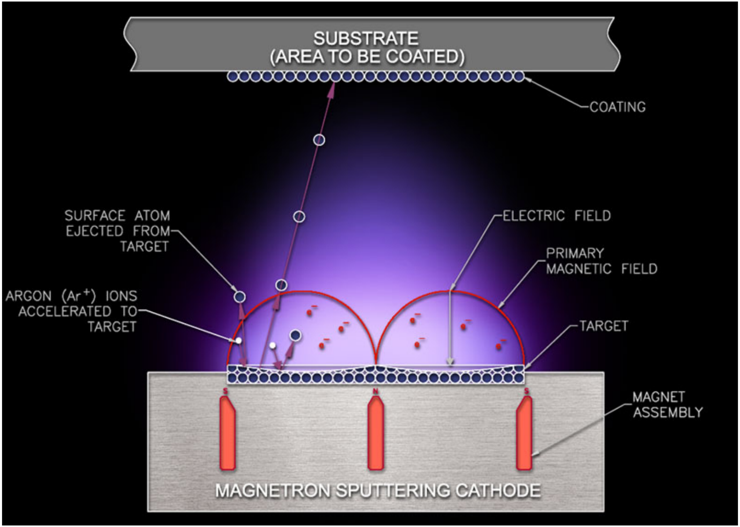




# Sputtering: industrial sputtering of glass

**Figure 1:** Horizontal inline sputter coater for architectural glass; annual throughput up to 8,000,000 $m^2$

# Sputtering: magnetron

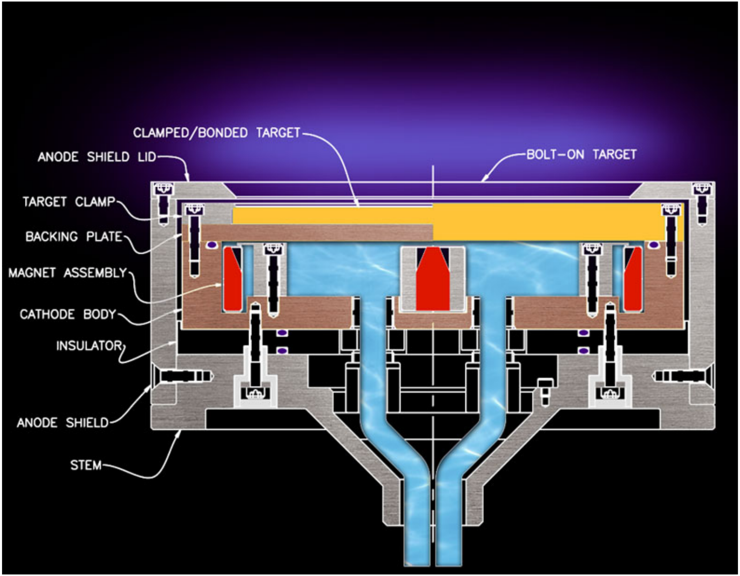


# Sputtering: magnetron

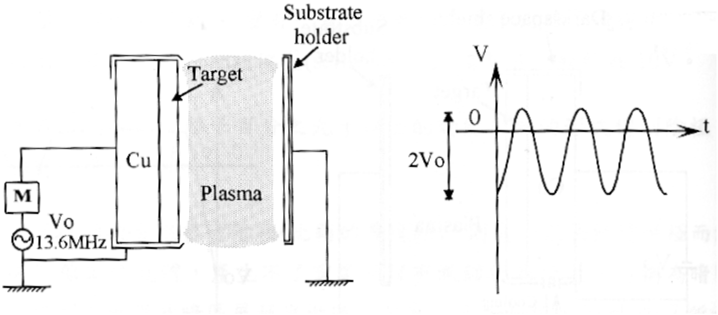
**Added magnetic field drives free electrons:**

- electrons do not touch the target, and hence do not heat it
- electrons are localized above the target, and hence enhancing probability of ionization of nobel gas ⇒ increases deposition rates
- reccombination of free electrons and ions ⇒ glowing plasma

# Sputtering: magnetron



# Sputtering: rf sputtering



- Plasma is generated by radio-frequency (rf) field (MHz).
- Rf-sputtering avoids charge build-up on insulating targets (e.g. allows to sputter oxides).

# Ion plating

Atoms of target are ionized, to increase their speed prior the deposition → atom can penetrate deeper into the substrate

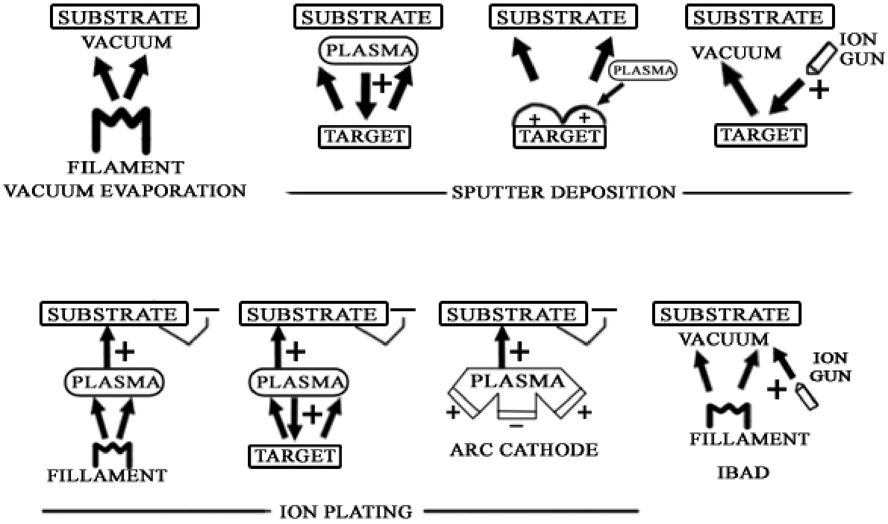
**Goal (1):** placement of atoms into substrate:

- gold plating
- steel hardening (e.g. layer of TiN)

**Goal (2):** crystal defects caused by atom irradiation:

- interface roughness control (magnetization anisotropy control)
- defects in AFM/FM interface ⇒ exchange bias control
- . . .

# PVD techniques - comparison



http://www.eclatcoating.com/learn/pvdcoating.php

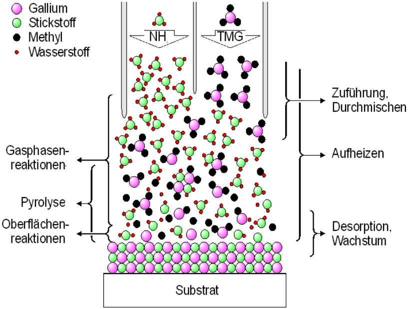
# Chemical deposition

- Involves chemical change at a solid surface
- Unidirectional deposition
  - electroplating (Although very cheap, very high quality Au/Co layers with atomically sharp interface has been demonstrated.)
  - chemical solution deposition (CSD), or sol-gel (transformation of colloidal solution (sol) into solid layer (gel))
  - spin-coating: liquid precursor is spread on a thin plate by spinning.
  - chemical vapour deposition (CVD): gas precursor.
  - dip coating
  - electrospray deposition

# Chemical vapour deposition (CVD)

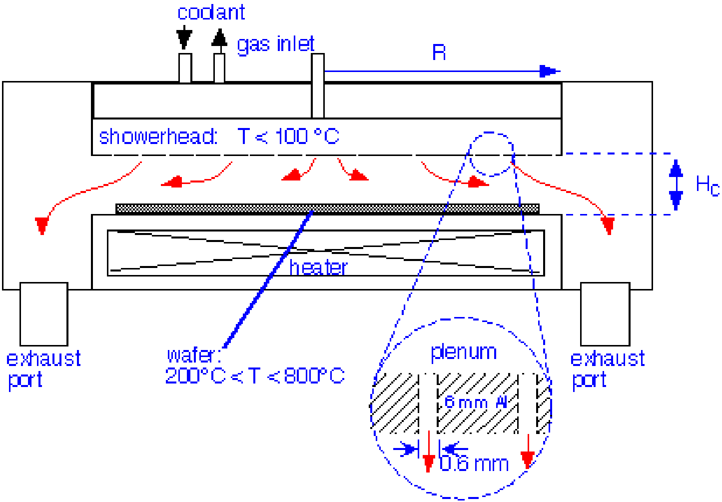
- Film components bound in gas molecules
- Gas molecules directed on heated substrate
- Chemical reaction creates film material
- Gaseous by-products

GaN deposition ($NH_3$+TriMetylGalium)



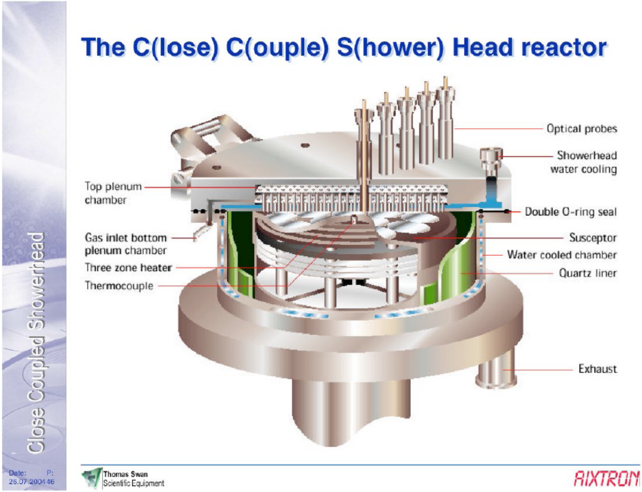
`http://thermodynamik.uni-duisburg.de/mitarbeiter/atakan/cvd_intro.htm`

# CVD - reactors



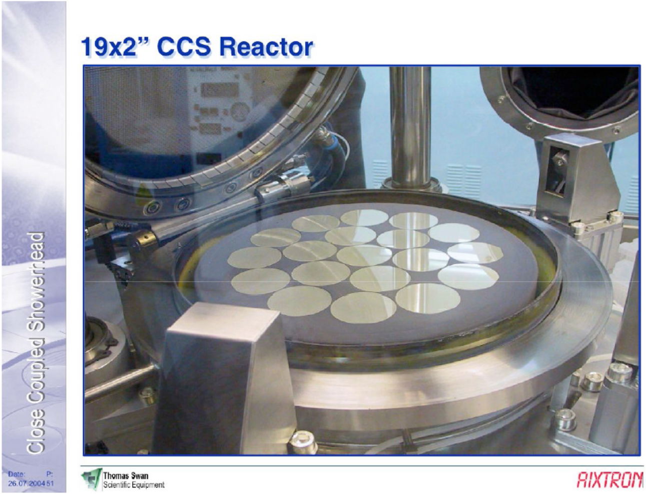
http://www.timedomaincvd.com

# gallium nitride – industrial CVD reactor



## The C(lose) C(ouple) S(hower) Head reactor

# gallium nitride – industrial CVD reactor



## 19x2” CCS Reactor

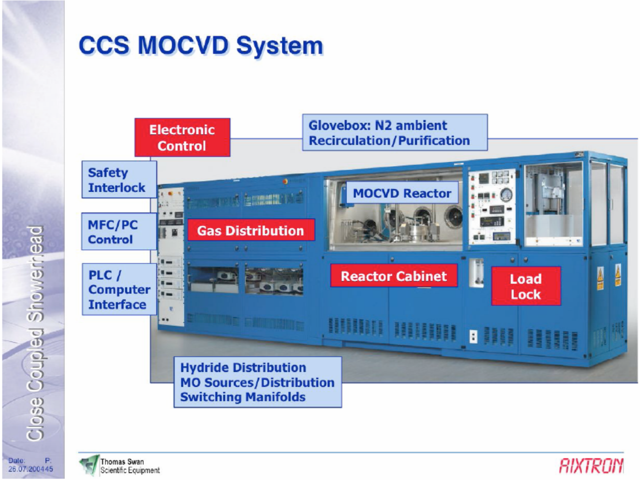
Close Coupled Showerhead

Date: 26.07.2004 P: 51

Thomas Swan
Scientific Equipment

AIXTRON

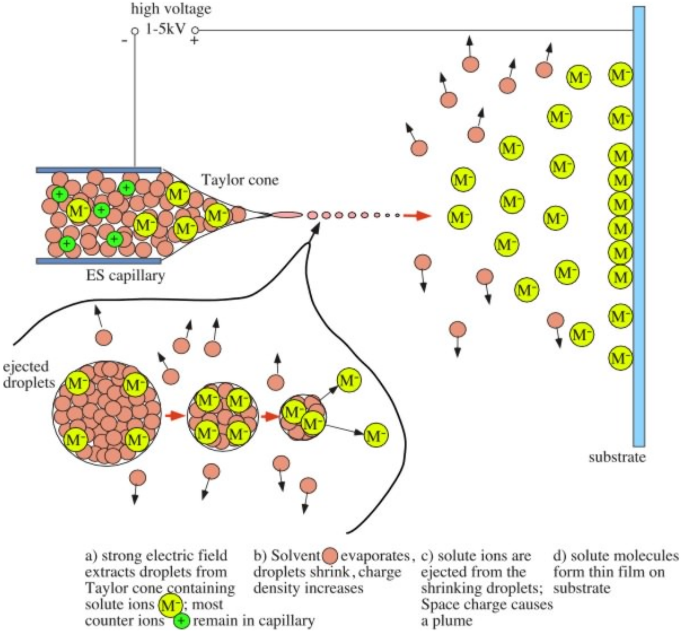
# gallium nitride – industrial CVD reactor



## CCS MOCVD System

Date: 26.07.2004 P: 45

# Electrospray deposition



a) strong electric field extracts droplets from Taylor cone containing solute ions (M⁻); most counter ions (+) remain in capillary

b) Solvent ● evaporates, droplets shrink, charge density increases

c) solute ions are ejected from the shrinking droplets; Space charge causes a plume

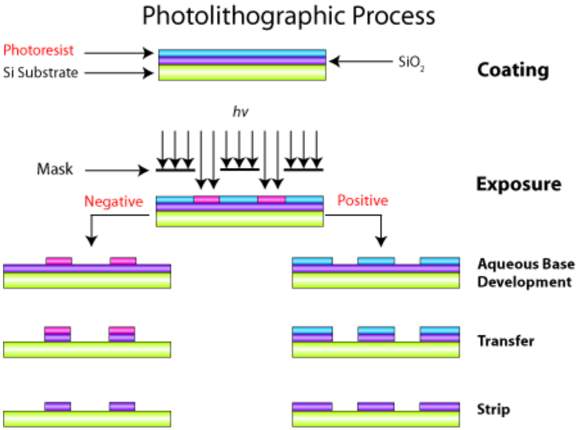
d) solute molecules form thin film on substrate

http://rsl.eng.usf.edu/Pages/ResearchElectrosprayAmbient.html

# Outline

# Photolithography: top-down approach

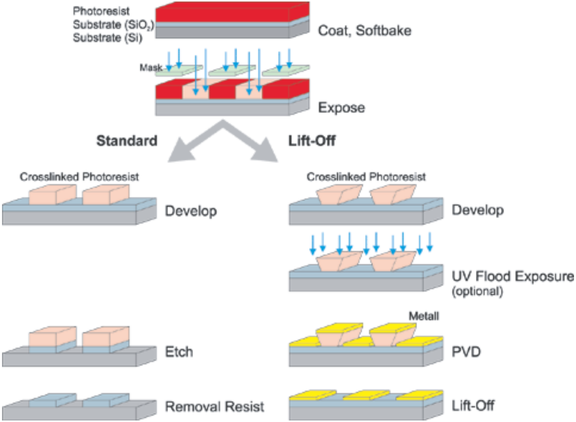
- First, entire layered structure is grown. Then part of it is etched.
- Lateral limit given by optical resolution (can be overcome UV light, extreme UV, X-ray etc, sub-wavelength diffraction masks, immersion photolithography)
- Instead of mask and subsequent optical illumination, exposure can be done by e-beam.
- current lateral resolution cca 16 nm.



http://withfriendship.com/user/levis/photolithography.php

# Lithography: standard and lift-off process

Lift-off: mainly to have good metal/metal interface.
Advantages:
•do not need etching.
Disadvantages
•Retention: not all (usually metallic) layer is washed out and stays on the wafer.
•Ears: When the metal is deposited, and it covers the sidewalls of the resist, "ears" can be formed.
•Redeposition: it is possible that particles of metal will become reattached to the surface, at a random location.

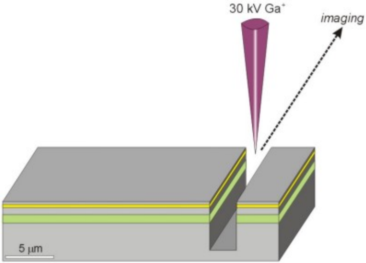


http://www.microresist.de

# Focused ion beam (FIB) nanofabrication

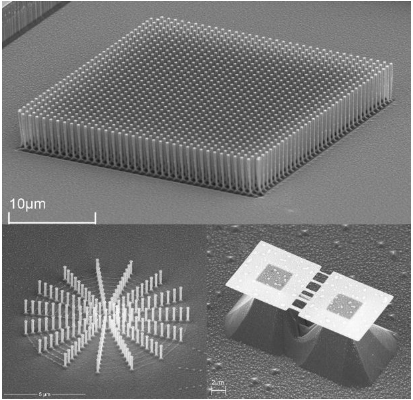
Focused ion beam (FIB):

1. source of ions (usually $Ga^+$ or $He^+$)
2. beam optics (similar to scanning electron microscopy)
3. ions ar focused to sample surface (focus diameter down to 1 nm)
4. local remove of atoms by ions (FIB-milling)

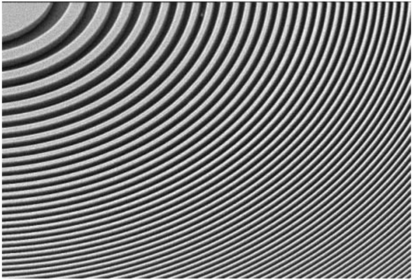


http://web2.ges.gla.ac.uk/~mlee/FIBtec.htm

# FIB nanostructures examples



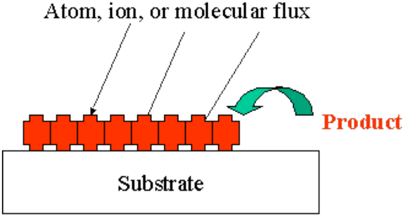
http://nano.aalto.fi/en/research/groups/mqs/research/micro_and_nanofabrication/



www.raith.com

# Bottom-up approach

- The opposite of the top-down approach.
- Instead of taking material away to make structures, the bottom-up approach selectively adds atoms to create structures.



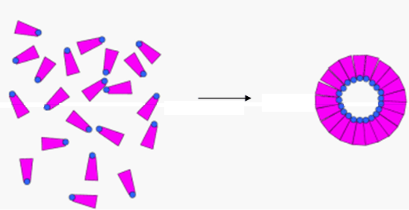
`http://idol.union.edu/~malekis/ESC24/KoskywebModules/sa_topd.htm`

# The Ideas Behind the Bottom-up Approach

Nature uses the bottom up approach.

- Cells
- Crystals
- Humans

Chemistry and biology can help to assemble and control growth.



http://www.csacs.mcgill.ca/selfassembly.htm

# Why is Bottom-Up Processing Needed?

- Allows smaller geometries than photolithography.
- Certain structures such as Carbon Nanotubes and Si nanowires are grown through a bottom-up process.
- New technologies such as organic semiconductors employ bottom-up processes to pattern them.
- Can make formation of films and structures much easier.
- Is more economical than top-down in that it does not waste material to etching.

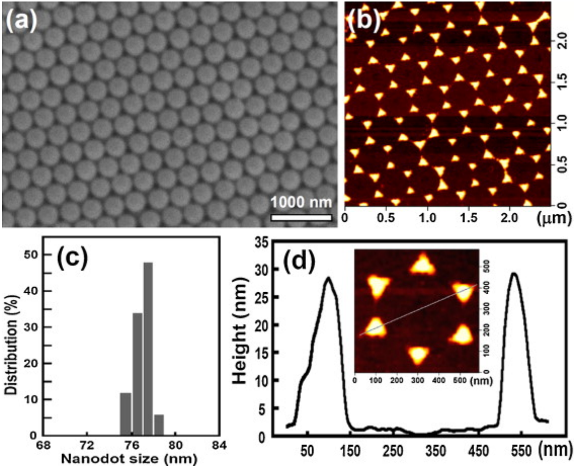
`http://courses.ee.psu.edu/ruzyllo/ee518/EE518_Top-down%20and%20Bottom-up1.ppt`

# Self Assembly

- The principle behind bottom-up processing.
- Self assembly is the coordinated action of independent entities to produce larger, ordered structures or achieve a desired shape.
- Found in nature.
- Start on the atomic scale.

# Example 1: self-assembled nanodots

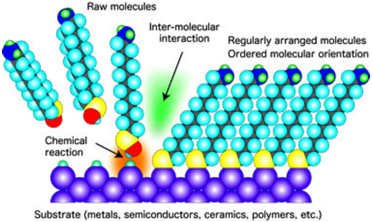
1) Self-assembled monolayer of 340 nm-diameter polystyrene spheres
2) Ni film deposited and balls removed



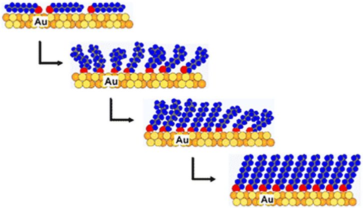
AppliedSurfaceScience257,8712,(2011)

# Example 2: Self-assembled Monolayers (SAMS)

- Molecules are deposited molecule-by-molecule to form a self-assembled monolayer.
- Creates a high quality layers.
- Layers are deposited one layer at a time.
- Organic molecules can't be deposited using extreme conditions because it would damage the organic molecules.
- SAMS technique does not damage organic molecules.
- SAMS films are nearly defect free.
- Used to deposit organic semiconductors.



`http://www.mtl.kyoto-u.ac.jp/english/laboratory/nanoscopic/nanoscopic.htm`



`http://www.seas.upenn.edu/`

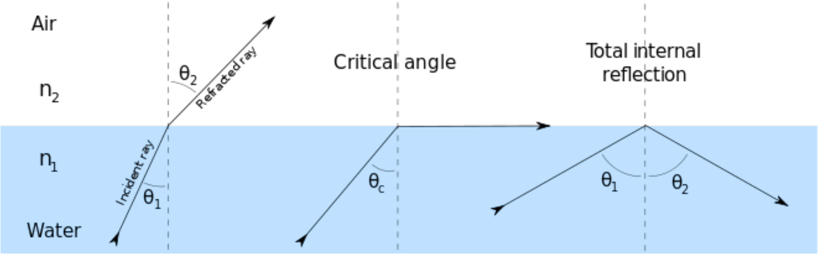
# Other examples of self assembly

- carbon nanotubes
- . . .

# Outline

1. Content
2. Relation between symmetry of crystals and crystal properties
3. Introduction
4. Bulk crystal growth
5. Thin film preparation
6. Lateral structures
7. ATR / Surface plasma resonance

# Reflection and total reflection



Snell law:

$$\sqrt{\varepsilon_1}\sin\varphi_1 = \sqrt{\varepsilon_2}\sin\varphi_2$$

Critical angle:

$$\sin\varphi_c = \sqrt{\frac{\varepsilon_2}{\varepsilon_1}}$$

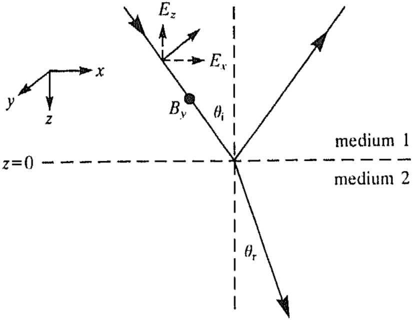
# Light reflection on the interface

① Maxwell equations

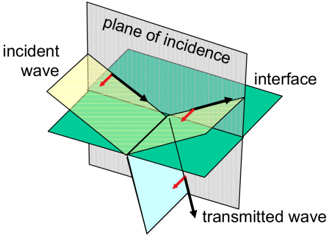
② solution as plane wave
$E = E_0 \exp(i(\vec{k} \cdot \vec{r} - \omega t))$

③ boundary conditions at the interface:
$\vec{E}, \vec{H}$ fields: continuous transverse ($x$, $y$) components
$\vec{D}, \vec{B}$ fields: continuous normal ($z$) components

④ for total reflection, solution of transverse wave is in form so called evanescent wave, non-propagating in $z$-direction
$E = E \exp(-k_z z)$



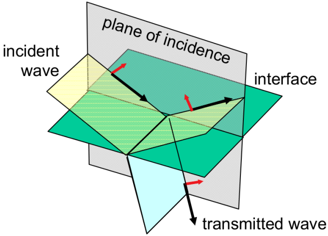
# Light reflection on the interface



## s-polarized light:

$$r_{\perp} = \frac{n_i \cos(\theta_i) - n_t \cos(\theta_t)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)}$$

$$t_{\perp} = \frac{2 n_i \cos(\theta_i)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)}$$



## p-polarized light:

$$r_{\parallel} = \frac{n_i \cos(\theta_t) - n_t \cos(\theta_i)}{n_i \cos(\theta_t) + n_t \cos(\theta_i)}$$

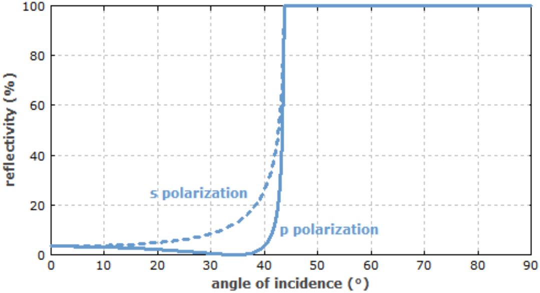
$$t_{\parallel} = \frac{2 n_i \cos(\theta_i)}{n_i \cos(\theta_t) + n_t \cos(\theta_i)}$$

And, for both polarizations: $n_i \sin(\theta_i) = n_t \sin(\theta_t)$

`http://www.ece.rice.edu/~daniel/262/pdf/lecture14.pdf`

# Light reflection on the interface

Reflection on glass/air



# Total reflection

Critical angle:

$$\sin\varphi_c = \sqrt{\frac{\varepsilon_2}{\varepsilon_1}} = \frac{n_2}{n_1}$$

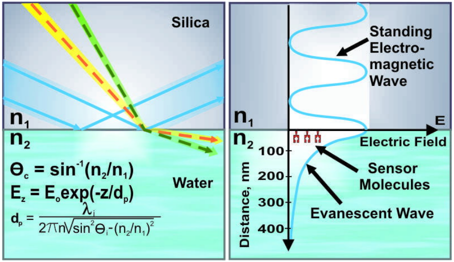
Evanescent wave:

$$E = E_t \exp(-z/\delta - i\omega t)$$

Penetration depth:

$$\delta = \frac{1}{k_0\sqrt{(n_1 \sin\varphi_1)^2 - (n_2^2)}}$$

Example: glass($n_1$)/water($n_2$) inteerface; $n_1 > n_2$



http://www.tirftechnologies.com/principles.php

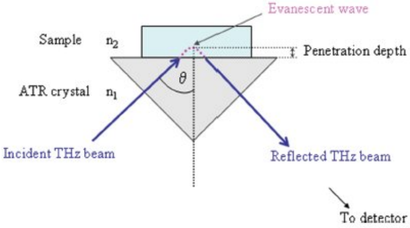
# Attenuated total reflectance (ATR)

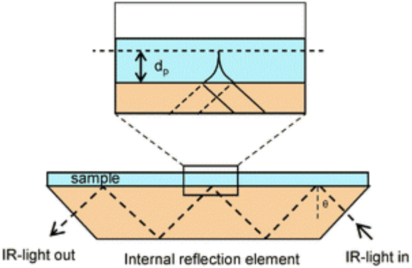
(Zeslabený úplný odraz)

- probes sample by evanescent wave

⇒ sensitive to surface of the sample

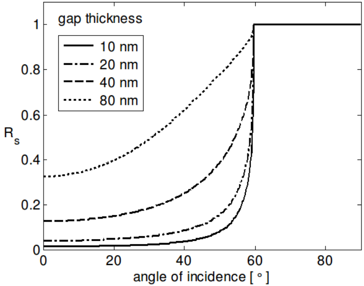
- sample modifies evanescent wave → partial absorption or transmission of light in sample → total reflection is decreased (attenuated).
- reflected beam does not follow exactly geometrical optics → The Goos-Hänchen shift



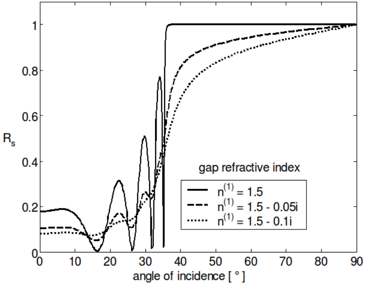


# Attenuated total reflectance (ATR): gap effect

Gap thickness (refractivity of gap=1):



Absorption in gap (gap thickness 960 nm):



# Surface plasmon I: derivation

Electric field in the vicinity of the interface:

$$E = E_O \exp[i(k_x x + k_z z - \omega t)]$$

where

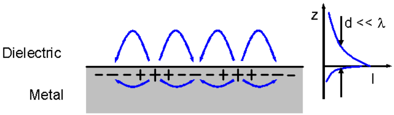
$$k^2 = k_x^2 + k_z^2 = \epsilon \left(\omega/c\right)^2 = \epsilon k_0^2 \qquad (1)$$

At the interface of two materials $\epsilon_1$ and $\epsilon_2$:
(a) $k_x$ continuous over the interface;

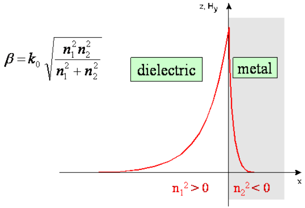
$$k_{x1} = k_{x2} \qquad (2)$$

(b) $D_z$ and $E_x$ continuous over the interface

$$k_{z1}/\epsilon_1 = k_{z2}/\epsilon_2 \qquad (3)$$



Surface Plasmon Resonance



Note! There is only a single p-polarized (TM) surface plasmon !

`http://www.physics.uwo.ca/~smittler/`

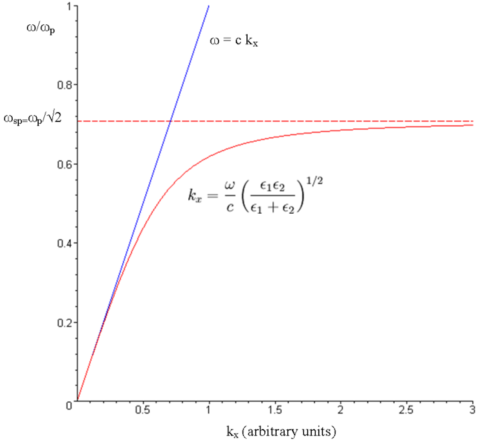
# Surface plasmon II: dispersion relation

- From Eqs.(1–3) follows dispersion relation for surface plasmon:

$$k_x = k_0 \sqrt{\left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}\right)}, \qquad (4)$$

where $k_0 = \omega / c$.

- Surface plasmon appears only for p-polarized (TM) wave, as this mode has normal (z) component of $D = \epsilon \epsilon_0 E$ field.

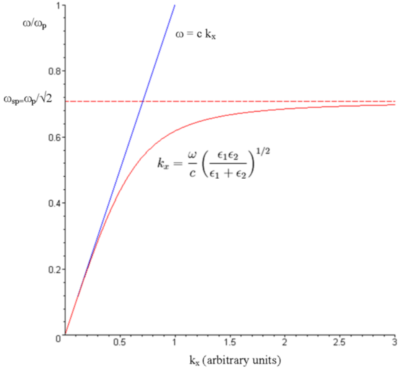


# Surface plasmon III: example

Example: assuming $\epsilon_1 = 1$ (air) and $\epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2}$ (metal as free electron model of an electron gas). Then

$$k_x = \frac{\omega}{c}\sqrt{\left(\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}\right)} \qquad (5)$$

Hybridization between photon ($\omega = ck_0$) and plasmon $\omega_{SP} = \omega_p/\sqrt{2}$.



# Surface plasma resonance (SPR) I

• Resonance between incident wave photon and surface plasmon. Resonance means that both (pseudo)-particles have equal $\omega$ and $k_x = k_{x,inc} = \Re(k_{x,sp})$.

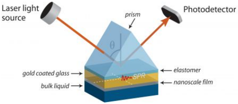
•Description of incident wave from material $\epsilon_1$ under angle $\varphi$:

$$k_{x,inc} = \frac{\omega}{c}\sqrt{\epsilon_1}\sin\varphi \qquad (6)$$

• Description of surface plasmon:

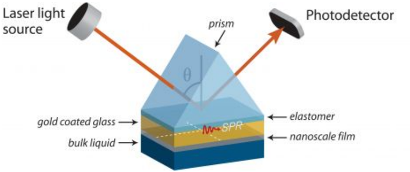
$$k_{x,sp} = \left(\frac{\omega}{c}\right)\sqrt{\left(\frac{\epsilon_1\epsilon_2}{\epsilon_1+\epsilon_2}\right)}, \qquad (7)$$

Condition for existence of the resonance: $\Re(\epsilon_2) < -\epsilon_1$ (i.e. $\Re(\epsilon_2)$ must be negative; fulfilled by coinage metals, Au, Ag, Cu). Here, $\epsilon_1$ is assumed to be non-absorbing material (i.e. $\Im(\epsilon_1) = 0$).



# Surface plasma resonance (SPR) II

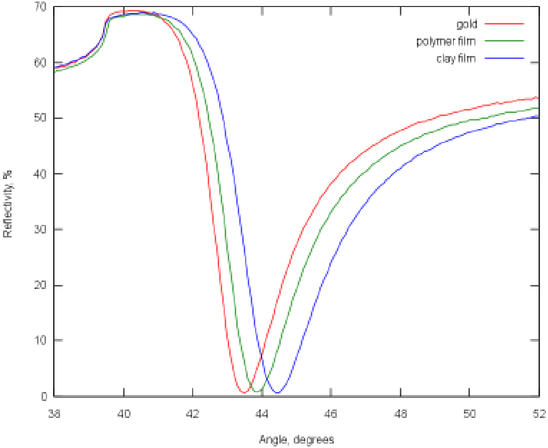
Surface plasmons are very sensitive to slight perturbations within the skin depth ⇒ surface plasmons are often used to probe tiny changes of refraction index near the interface (extreme sensitive detector of small changes of the refraction index).
⇒ Readout of many bio-sensors based on this detection technique.



http://www.bionavis.com/technology/spr/

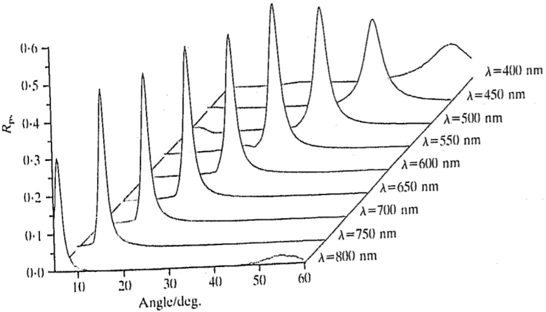
# SPR: detection I

- presence of resonance increases absorption and reduces reflectivity.
- position of reflection minima very sensitive to refractivity index in position of the evanescent wave.



# SPR: detection II

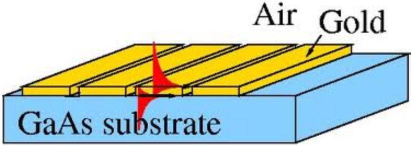
- presence of resonance increases absorption and reduces reflectivity.
- position of reflection minima very sensitive to refractivity index in position of the evanescent wave.



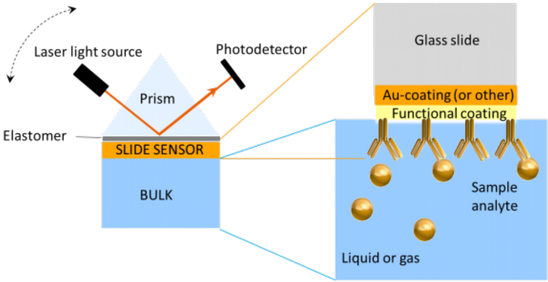
# SPR: how to couple surface plasmon and photon?

- couple light by high-refraction index prism
- lateral modulation of the interface (roughness or structuring)

$$\omega/c \sin\varphi + 2\pi/b = \omega/c\sqrt{\frac{\varepsilon_2}{\varepsilon_2+1}} \quad (8)$$



# SPR: bio sensors



http://www.bionavis.com/technology/spr/