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ParisTech

SAINT-GOBAIN

Glass and Energy

Hervé Arribart

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Agenda :

Glass for energy saving in buildings

1. Glasswool
2. High performance thermal insulating glazing
3. Smart windows

Glass for the production of energy

4. Photovoltaics
5. Thermal solar
6. Windmills
7. Nuclear fission
8. Nuclear fusion

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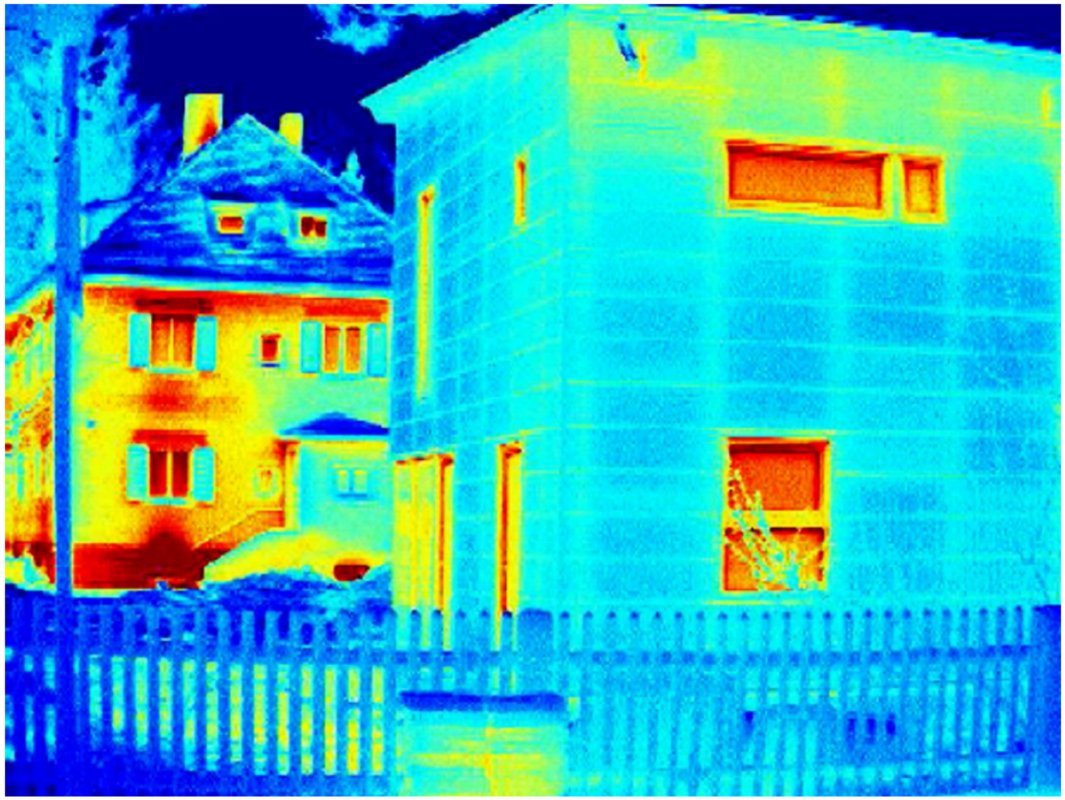
buildings

The problem to be solved



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buildings

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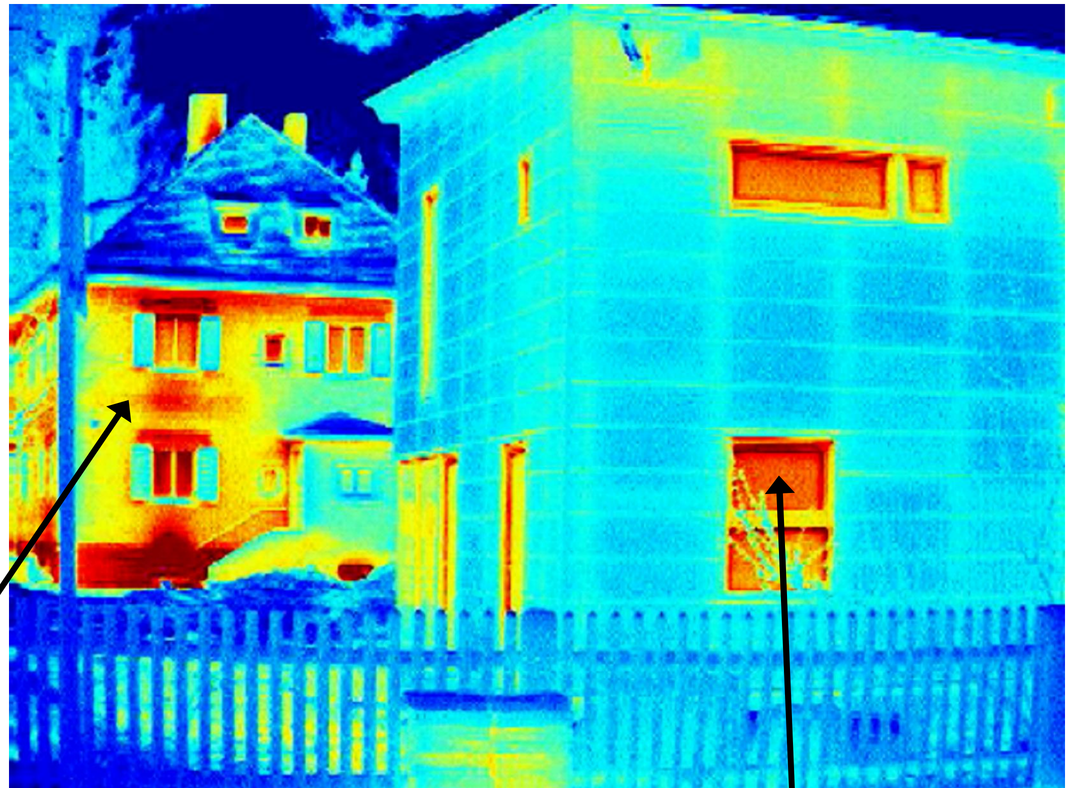

Non insulated wall

Non insulated window

Bad insulation means loss of energy and unuseful emission of CO_2

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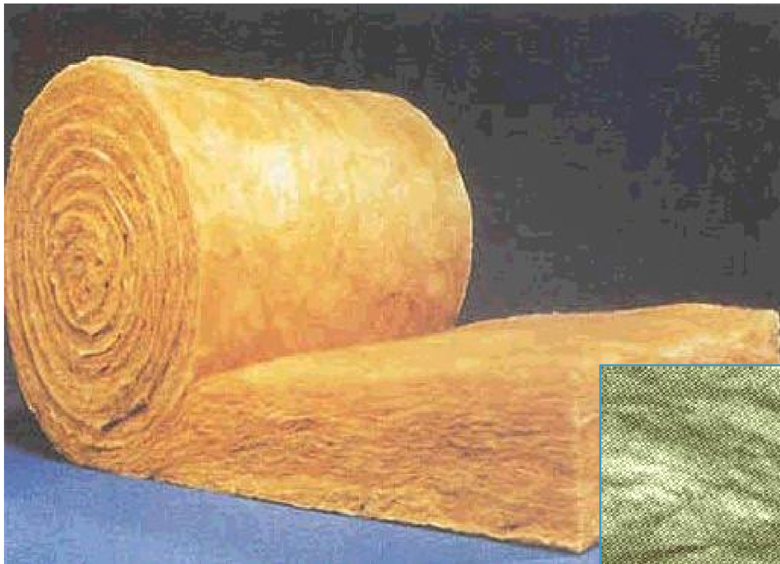
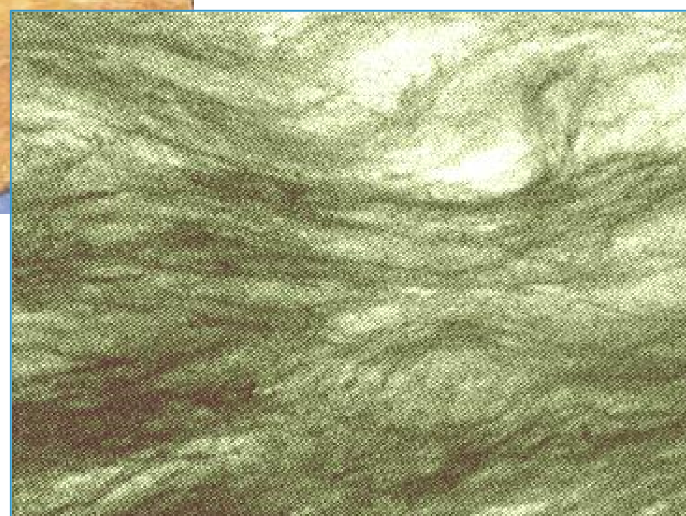
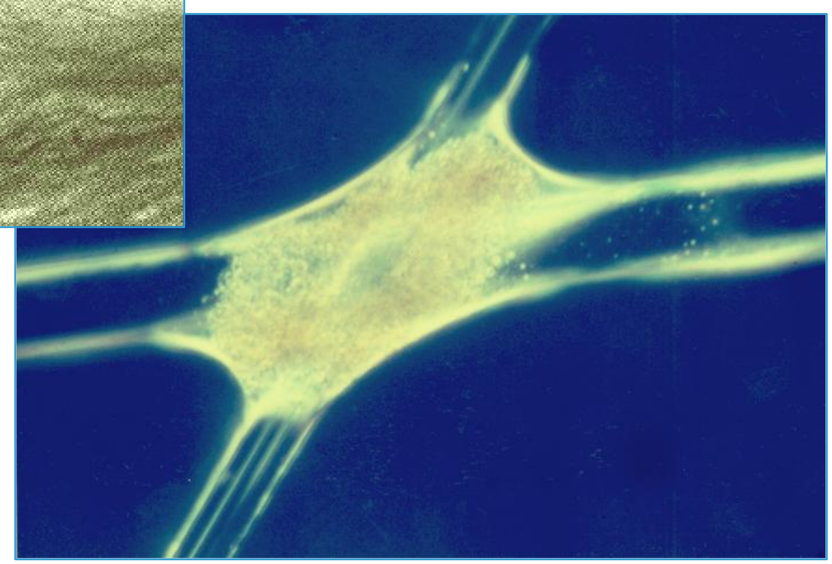
Principle of thermal insulation in glasswool(1/2)







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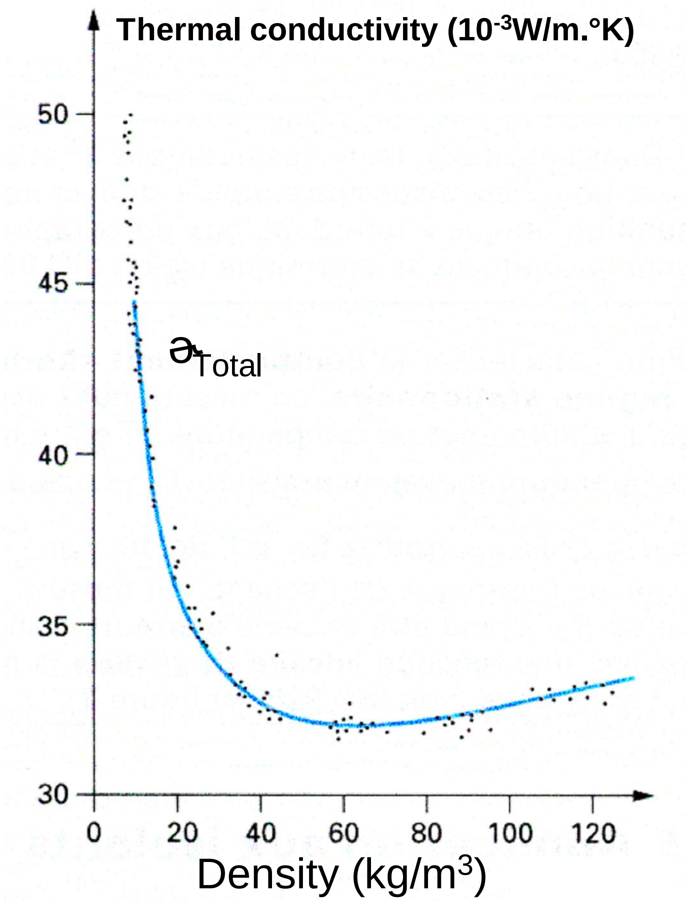
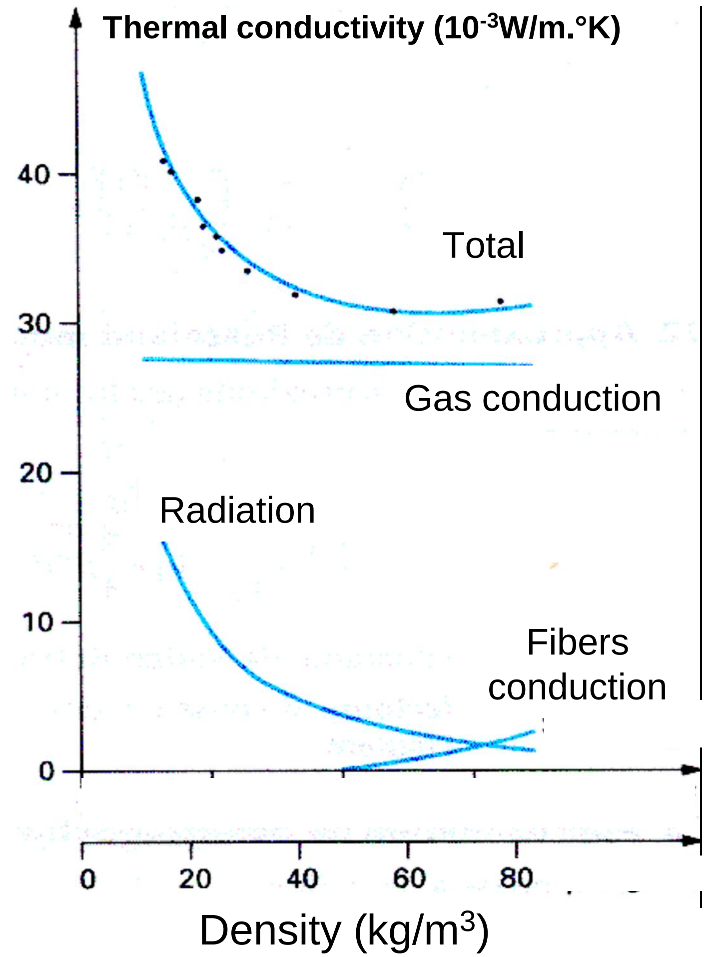
Principle of thermal insulation in glasswool(2/2)





$$\lambda_{convection} \approx 0$$

$$\lambda_{total} = \lambda_{air\ conduction} + \lambda_{solid\ conduction} + \lambda_{radiation}$$

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Fiberglass composition(1/3)

SiO_2	65
Al_2O_3	2
CaO	8
MgO	2.5
Na_2O	17
K_2O	1
B_2O_3	4.5

Typical composition (oxide weight %)

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Fiberglass composition(1/3)

SiO_2	65	
Al_2O_3	2	← Hydrolytic durability increases
CaO	8	
MgO	2.5	
Na_2O	17	← Hydrolytic durability increases
K_2O	1	
B_2O_3	4.5	← Radiative transfer increases

Typical composition (oxide weight %)

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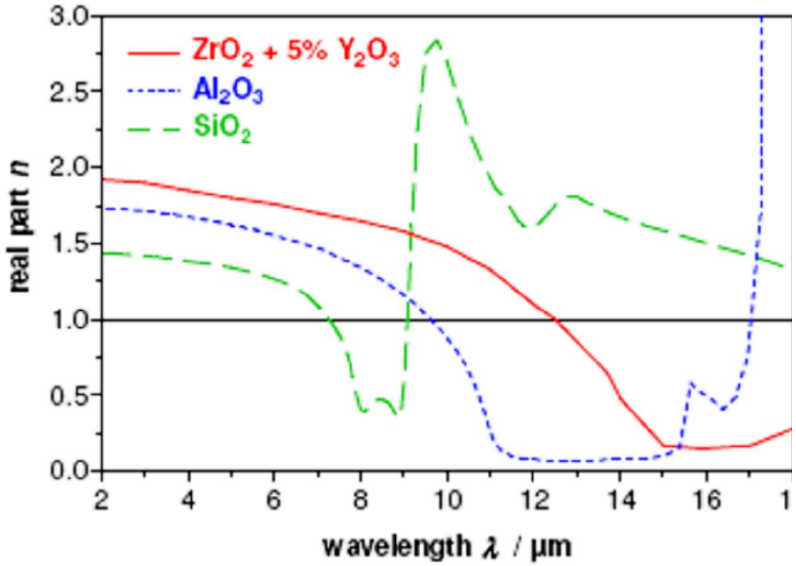
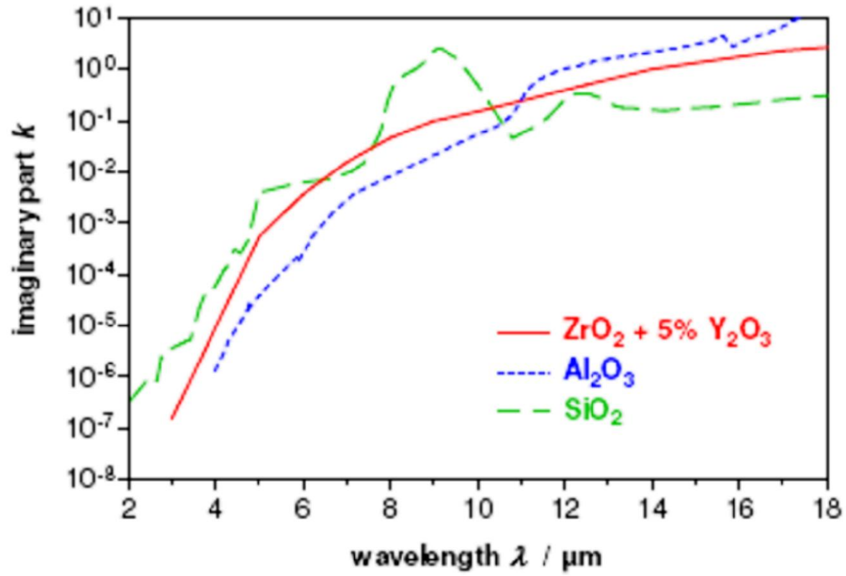
Fiberglass composition(2/3)

☞Role of boron oxide

- Near 7 and 9 μm, silicates are transparent (n=1 and k small)

→ glass fibers do not stop radiations at these wavelengths





- Boron oxide has strong optical absorption in this wavelength window

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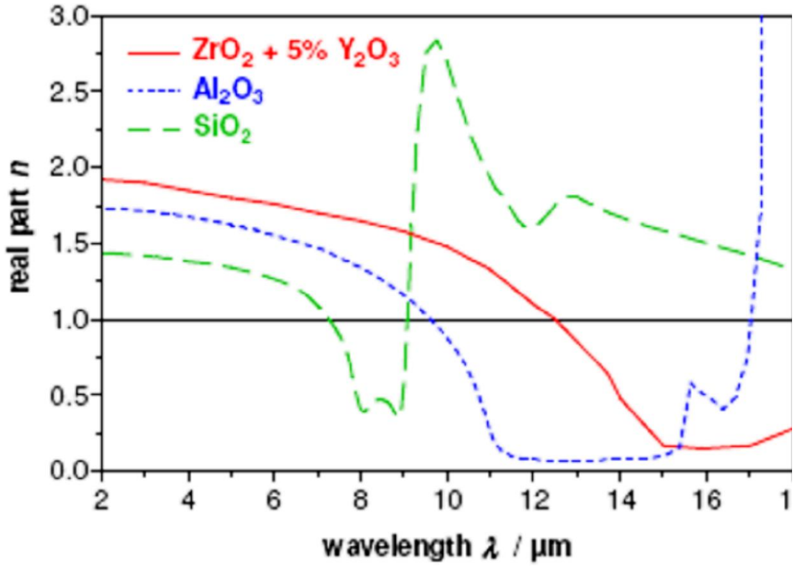

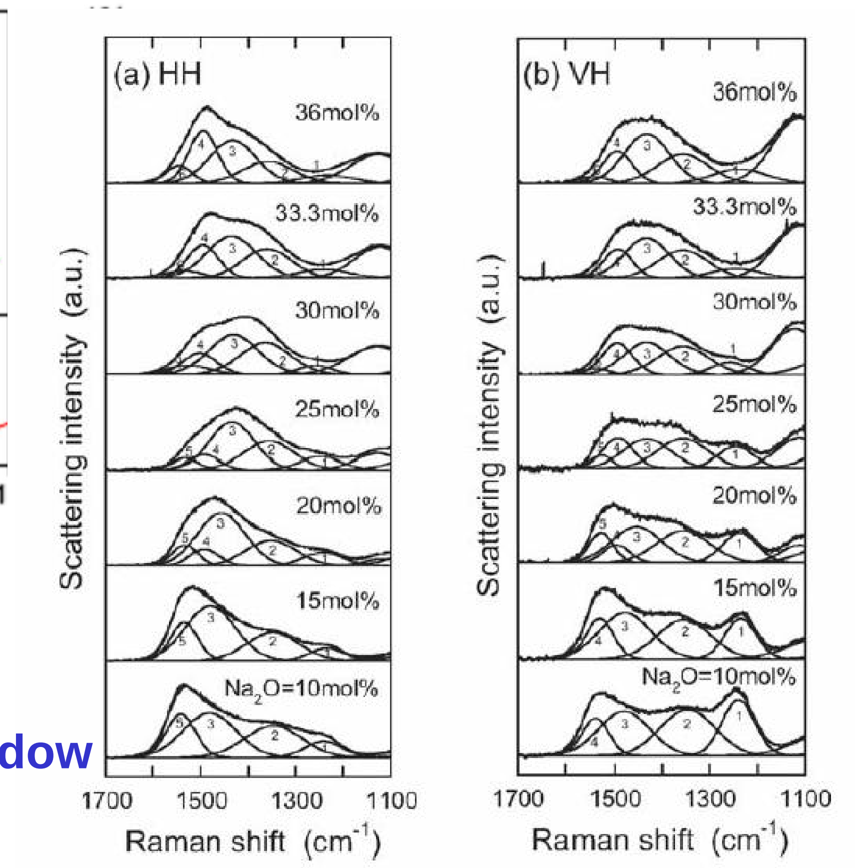

- Boron oxide has strong optical absorption in this wavelength window

T. Yano (2003)

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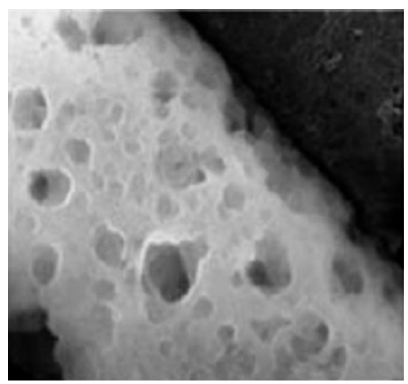
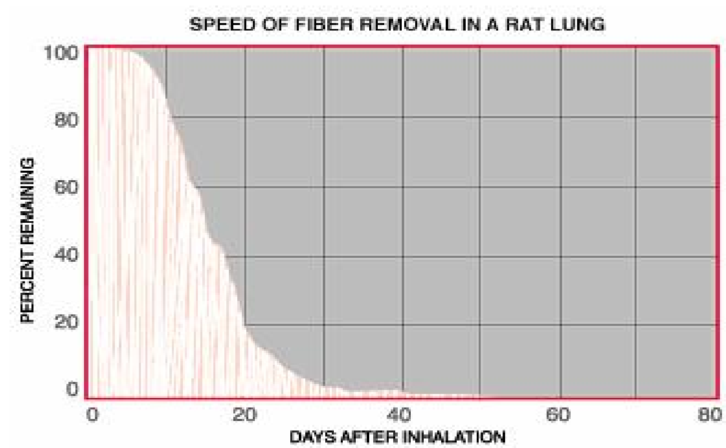
Fiberglass composition(3/3)

☞Hydrolitic resistance

- Insulation glass fibers have to be resistant at pH å 7 (normal condition in use) AND soluble at pH å 4, because this is the pH of macrophages present in lung alveoles. This solubility is called biosolubility. It garantees that inhaled fibers (with diameter below 1 µm) do not make any dammage of the kind that abestos fibers do.

Al_2O_3 and NaO contains result from these considerations.





crédit : Owens Corning Fiberglass

- Biosolubility at work

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...: thermal transfer(1/6)

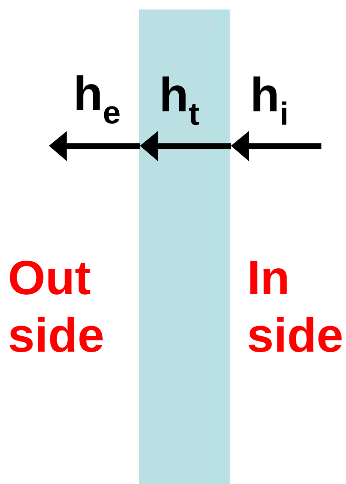
There are three modes of thermal transfer:

- **Conduction**
- **Convection**
- **Radiation**

Coefficient of thermal transfer across a glazing (in winter):

Thermal flux : $\Phi = K.(T_{inside} - T_{outside})$

$$\frac{1}{K} = \frac{1}{h_o} + \frac{1}{h_t} + \frac{1}{h_i}$$



Using double-glazing decreases h_o and h_t. We are left with h_i to decrease. h_i is mainly a radiation term. It accounts for the radiative energy exchange between the inside glass surface and the rest of the room.

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: thermal transfer(2/6)

☞Radiative transfer

It works with emission and reception of electromagnetic waves between bodies

When a body is submitted to an electromagnetic radiation of wavelength ə, it transmits a part of it, reflects a part of it, and absorbs a part of it. One has :

$$T(\lambda) + R(\lambda) + A(\lambda) = 1$$

☞Black body

The black body is an ideal model body which completely absorbs the radiative energy that it receives : A(ə)=1, ∀ə.

In other words, the only radiation coming from a B.B. is the radiation that it emits, and it depends only on its temperature ɗ.

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Reminder : thermal transfer(3/6)

☞ Planck's law

At temperature θ, and in the wavelength interval [λ, λ+dλ], the energy flux emitted per unit area by a B.B. is given by

$$\varphi(\lambda, \theta) = \frac{2\pi hc^2}{\lambda^5[\exp(hc/k\theta\lambda) - 1]}$$

h : Planck's constant
k : Boltzmann's constant
c : light velocity

☞ Wien's law

For every temperature θ, there is a wavelength λ_m for which the radiated energy flux is maximum :

$\lambda_m \cdot \theta = b$ **with b = 2,9 · 10^{-3} m.K**

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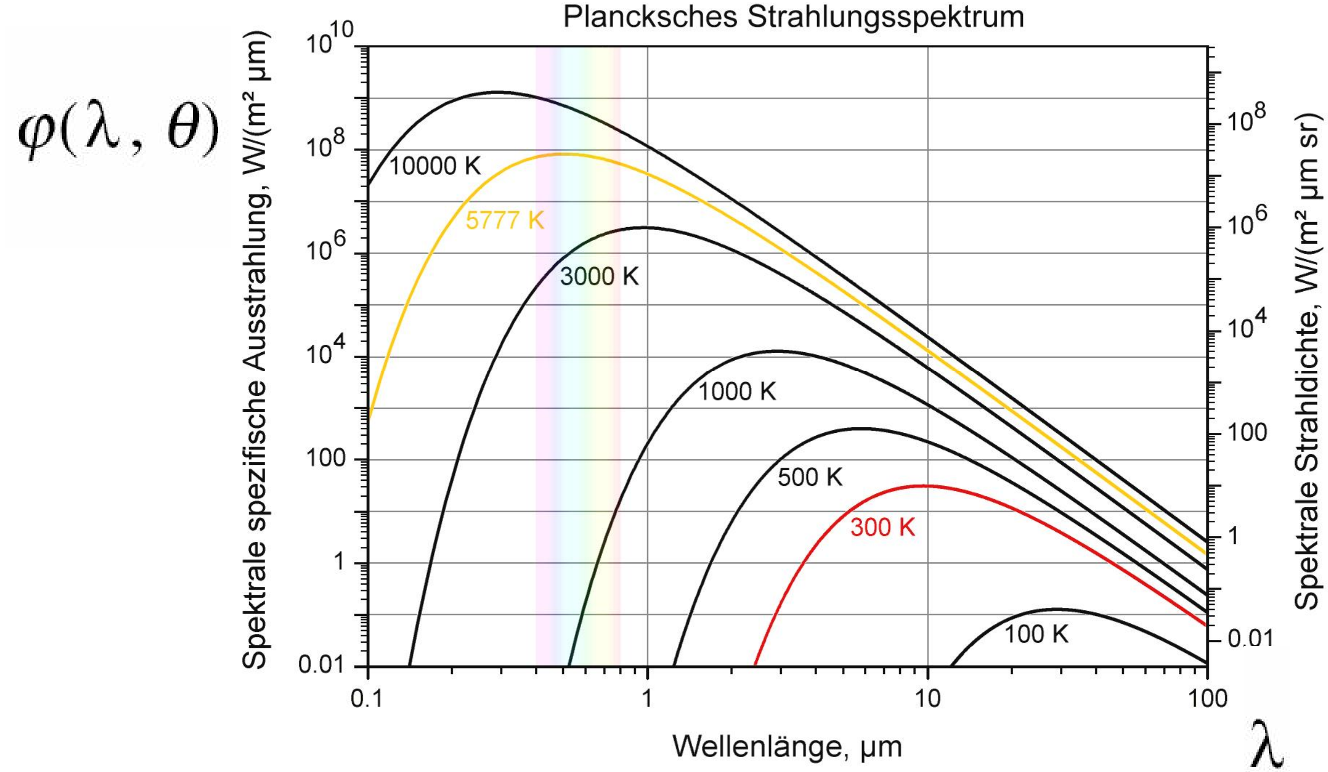
: thermal transfer(4/6)



☞Stephan-Boltzmannôs law

The total energy flux emitted per unit area by a B.B. at temperature ɗ is given by ū = ů ɗ^4, with :

$$\sigma = \frac{2\pi^5 k^4}{15 c^2 h^3} = 5{,}7 \cdot 10^{8}\ W \cdot m^{-2} \cdot K^{-4}$$

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Reminder : thermal transfer(5/6)

☞Definition of emissivity :

- At a given temperature θ, a given body emits its own radiation $E^*(\lambda)$, and it absorbs a part $A(\lambda)$ of the radiation $E(\lambda)$ that it receives. At thermal equilibrium :

$$E^*(\lambda) = A(\lambda)\, E(\lambda)$$; it is Kirchhoff's law

- For a B.B. : $A(\lambda) = 1$, and $E^*_{BB}(\lambda) = E(\lambda)$.

- The emissivity $\varepsilon(\lambda)$ of a given body is defined by :

$$\varepsilon(\lambda) = E^*(\lambda) / E^*_{BB}(\lambda)$$

- Thus, at thermal equilibrium $\varepsilon(\lambda) = A(\lambda)$

- In particular, for a transparent body, $\varepsilon(\lambda) = 0$
  for a non-transparent body, $\varepsilon(\lambda) = 1 - R(\lambda)$
  for a black body, $\varepsilon(\lambda) = 1$

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Reminder : thermal transfer(6/6)

☞ **emissivity of selected materials at T=300K and λ=10 µm:**

	ε(300K, 10µm)
Aluminum, polished	0.04
Aluminum, anodized	0.77
Asphalt	0.93
Brick	0.9
Concrete	0.85
Copper, polished	0.023 - 0.052
Glass	0.92
Iron, polished	0.14 - 0.38
Natural rubber	0.86
Silver, polished	0.02 - 0.03

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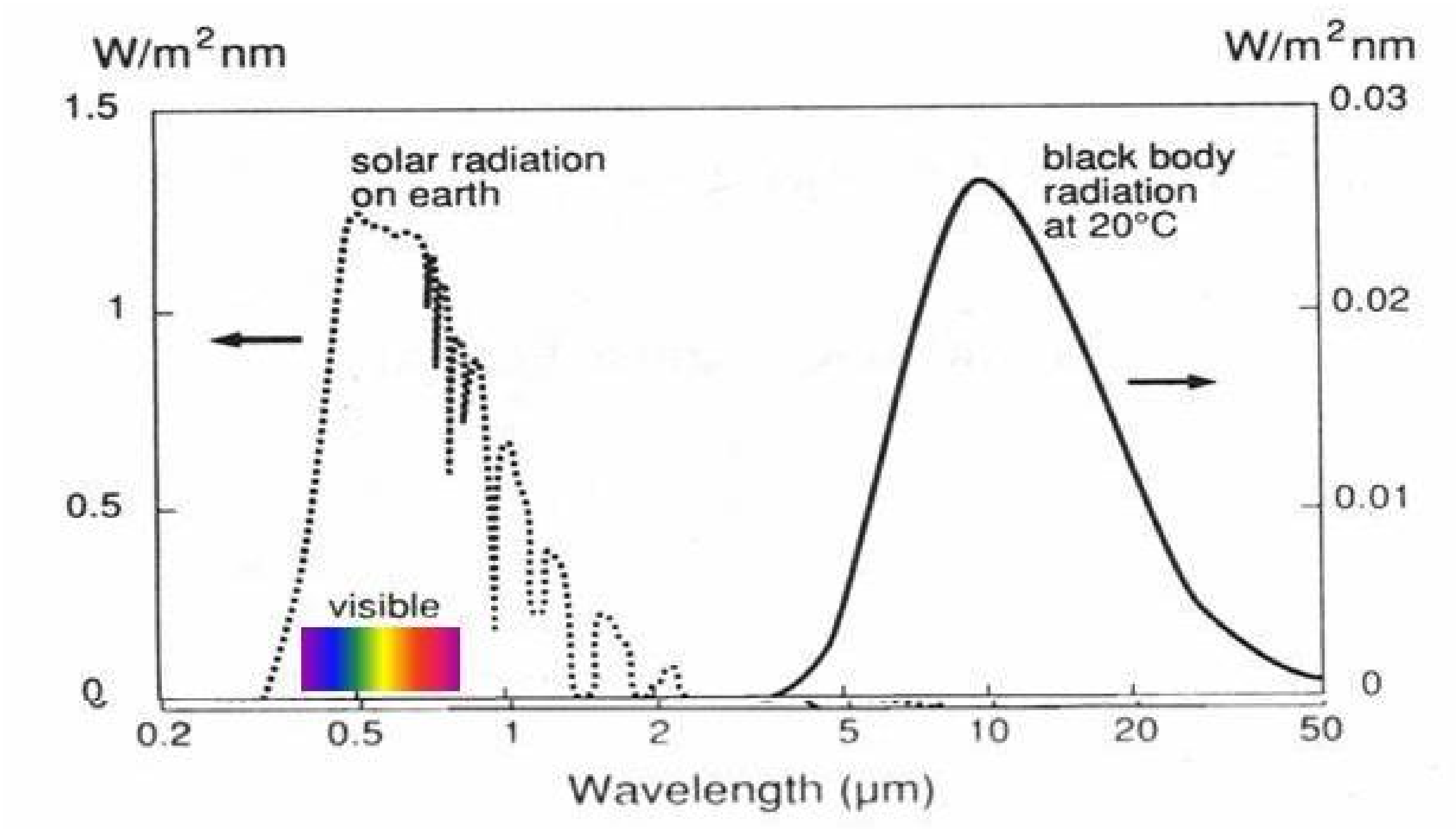
Principle of low-emissive glazing(1/3)

☞ambiant radiation

Ambiant radiation on earth has two major contributions :

-Solar radiation, around 0,6 µm

-Ambient thermic radiation, emitted by our environment, around 10µm



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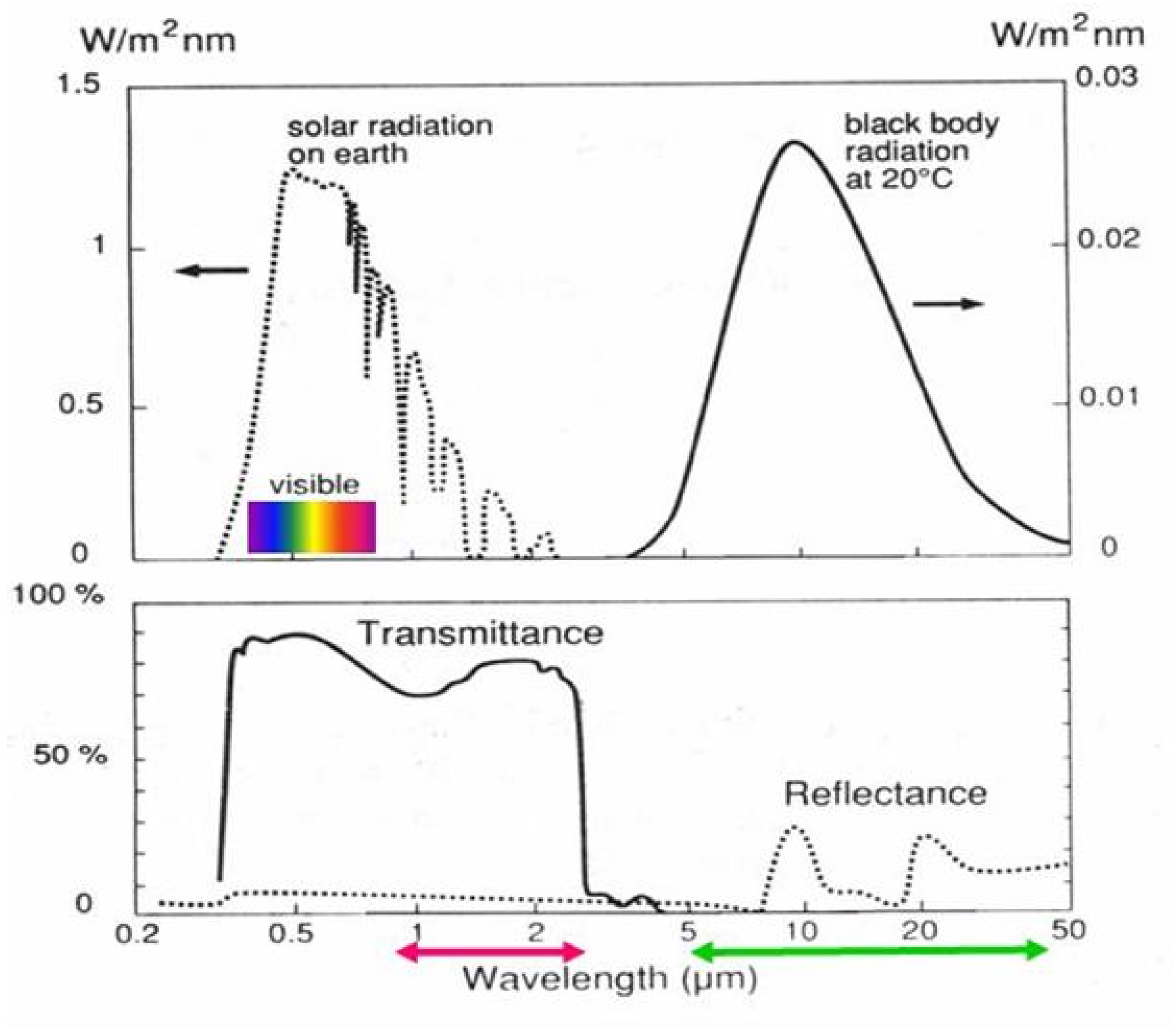
Principle of low-emissive glazing(2/3)

☞spectral properties of silicate glass

Åglass is transparent in the visible and in the near-infrared. There, Ůå 0

Åglass is principally absorbing in the thermal infrared. There, Ůå 1 - R



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…of low-emissive glazing(3/3)

☞**what we want to do in order to decrease h_i**

Transform the inside glass surface, in order that

. it becomes less emissive (more reflective) in the thermal infrared

. it remains transparent in the visible

☞**the way to achieve it**

Deposit on the inside surface of glass a coating made of a material which is

. low-emissive (highly reflecting) in the thermal infrared

. transparent in the visible

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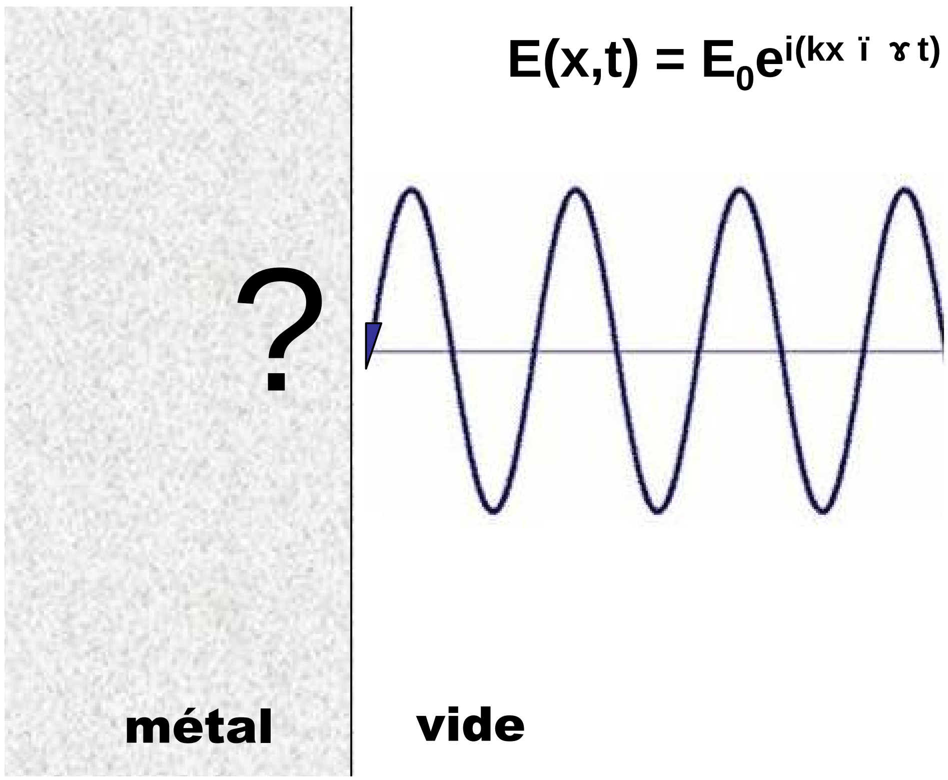
: optical properties of metals(1/8)

☞Electromagnetic wave at the air-metal interface

$$E(x,t) = E_0 e^{i(kx - \omega t)}$$

In air : $k = \omega / c$



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… : optical properties of metals(2/8)

Maxwell's equation in a metal

$$\begin{cases} \nabla\cdot\vec{E} = 0 & (1) \\ \nabla\times\vec{E} = -\dfrac{\partial\vec{B}}{\partial t} & (2) \\ \nabla\cdot\vec{B} = 0 & (3) \\ \nabla\times\vec{B} = \mu_0\vec{j} + \epsilon_0\mu_0\dfrac{\partial\vec{E}}{\partial t} & (4) \end{cases}$$

Using Ohm's law, (4) becomes :

$$\nabla \times \mathbf{B} = \mu_0\sigma\mathbf{E} + \mu_0\epsilon_0\frac{\partial\mathbf{E}}{\partial t}$$

σ = conductivity

Eliminating B, we get a differential equation for E :

$$\nabla^2\mathbf{E} = \mu_0\sigma\frac{\partial\mathbf{E}}{\partial t} + \frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}$$

One looks for solutions to this equation on the form $E(x,t) = E_0 e^{ikx - i\omega t}$:

$$\rightarrow \quad \boxed{k = \frac{\omega}{c}\left(1 + \frac{i\sigma}{\omega\epsilon_0}\right)^{1/2}}$$

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Reminder : optical properties of metals(2/8)

$$\begin{cases} \nabla \cdot \vec{E} = 0 & (1) \\ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} & (2) \\ \nabla \cdot \vec{B} = 0 & (3) \\ \nabla \times \vec{B} = \mu_0 \vec{j} + \epsilon_0 \mu_0 \frac{\partial \vec{E}}{\partial t} & (4) \end{cases}$$

Maxwellôs equation in a metal

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One looks for solutions to this equation on the form $E(x,t) = E_0 e^{ikx - i\omega t}$:

$$\rightarrow \quad \boxed{k = \frac{\omega}{c} \left(1 + \frac{i\sigma}{\omega \epsilon_0}\right)^{1/2}}$$

One concludes that a metal behaves as a medium of complex refractive index :

$$\tilde{N}(\omega) = (1 + \frac{i\sigma}{\omega \varepsilon_0})^{1/2}$$

Note : σ is a function of ω and can itself be complex

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...: optical properties of metals(3/8)

☞Drudeôs model

Classical equation of motion for free electrons (masse m, charge ï e) under an external electric field E and submitted to a friction force characterized by a time ***Ű(time ôbetween two collisionsöor örelaxation timeö)***

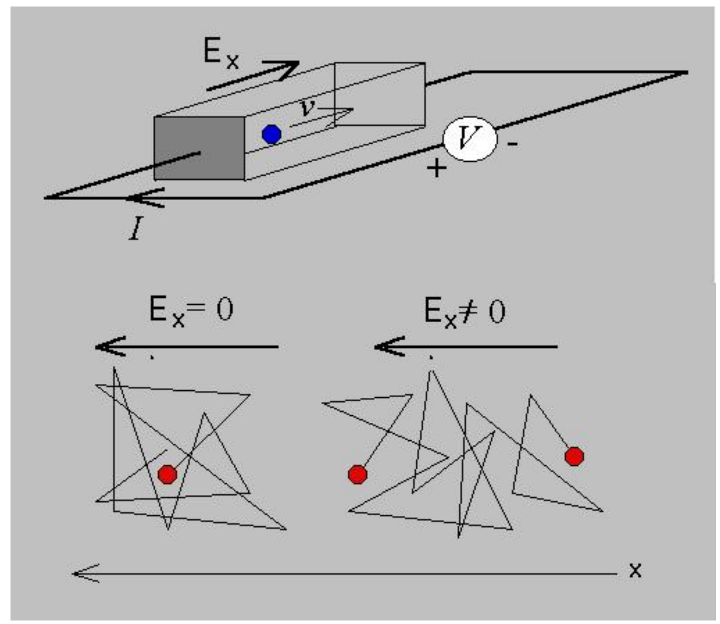
$$m\frac{d^2\vec{r}(t)}{dt^2}+\frac{m}{\tau}\frac{d\vec{r}(t)}{dt}=-e\vec{E}(t)$$

$$m\frac{d\vec{v}}{dt}+\frac{m}{\tau}\vec{v}(t)=-e\vec{E}(t)$$

$$\vec{v}(\omega)=\frac{-e\tau}{m}\frac{1}{1-i\omega\tau}\vec{E}(\omega)$$

$$\vec{j}(\omega)=-Ne\vec{v}(\omega)=\frac{Ne^2\tau}{m}\frac{1}{1-i\omega\tau}\vec{E}(\omega)$$

$$=\sigma(\omega)\vec{E}(\omega)$$



N : electron concentration

$$\sigma(\omega)=\frac{Ne^2\tau}{m}\frac{1}{1-i\omega\tau}=\sigma_0\frac{1}{1-i\omega\tau}$$ with $$\sigma_0=\frac{Ne^2\tau}{m}$$

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: optical properties of metals(4/8)

$$k^2 = \frac{\omega^2}{c^2}\left(1 + \frac{Ne^2\tau}{\varepsilon_0 m\omega}\ \frac{i}{1 - i\omega\tau}\right)$$

Optical frequencies are very large, therefore ɤ τ >> 1

$$k^2 = \frac{\omega^2}{c^2}\left(1 - \frac{Ne^2}{\varepsilon_0 m\omega^2}\right)$$

$$k^2 = \frac{\omega^2}{c^2}\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

which defines the plasmon frequency

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}}$$

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$$k^2 = \frac{\omega^2}{c^2}\left(1 + \frac{Ne^2\tau}{\varepsilon_0 m\omega}\ \frac{i}{1 - i\omega\tau}\right)$$

Optical frequencies are very large, therefore $\omega\tau >> 1$

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$$k^2 = \frac{\omega^2}{c^2}\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

which defines the plasmon frequency $\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}}$

i). At very high frequencies, $\omega >> \omega_p$

$k \approx \frac{\omega}{c}$ → Refractive index : $\tilde{N}(\omega) \approx 1$ → **Metal is transparent**

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: optical properties of metals(4/8)

$$k^2 = \frac{\omega^2}{c^2}\left(1 + \frac{Ne^2\tau}{\varepsilon_0 m\omega}\,\frac{i}{1 - i\omega\tau}\right)$$

Optical frequencies are very large, therefore $\omega\tau >> 1$

$$k^2 = \frac{\omega^2}{c^2}\left(1 - \frac{Ne^2}{\varepsilon_0 m\omega^2}\right)$$

$$k^2 = \frac{\omega^2}{c^2}\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

which defines the plasmon frequency $\omega_p = \sqrt{\dfrac{Ne^2}{\varepsilon_0 m}}$

i). At very high frequencies, $\omega >> \omega_p$

$$k \approx \frac{\omega}{c}$$

→ Refractive index : $\tilde{N}(\omega) \approx 1$ → **Metal is transparent**

ii). At intermediate frequencies, $1/\tau << \omega << \omega_p$

$$k \approx i\frac{\omega_p}{c}$$

$$E(x,t) = E_0 e^{-\frac{\omega_p}{c}x} e^{-i\omega t}$$

$1/e_p$

Evanescent wave of penetration depth e_p
Total reflection

→ Refractive index almost purely imaginary $\tilde{N}(\omega) \approx i\dfrac{\omega_p}{\omega}$

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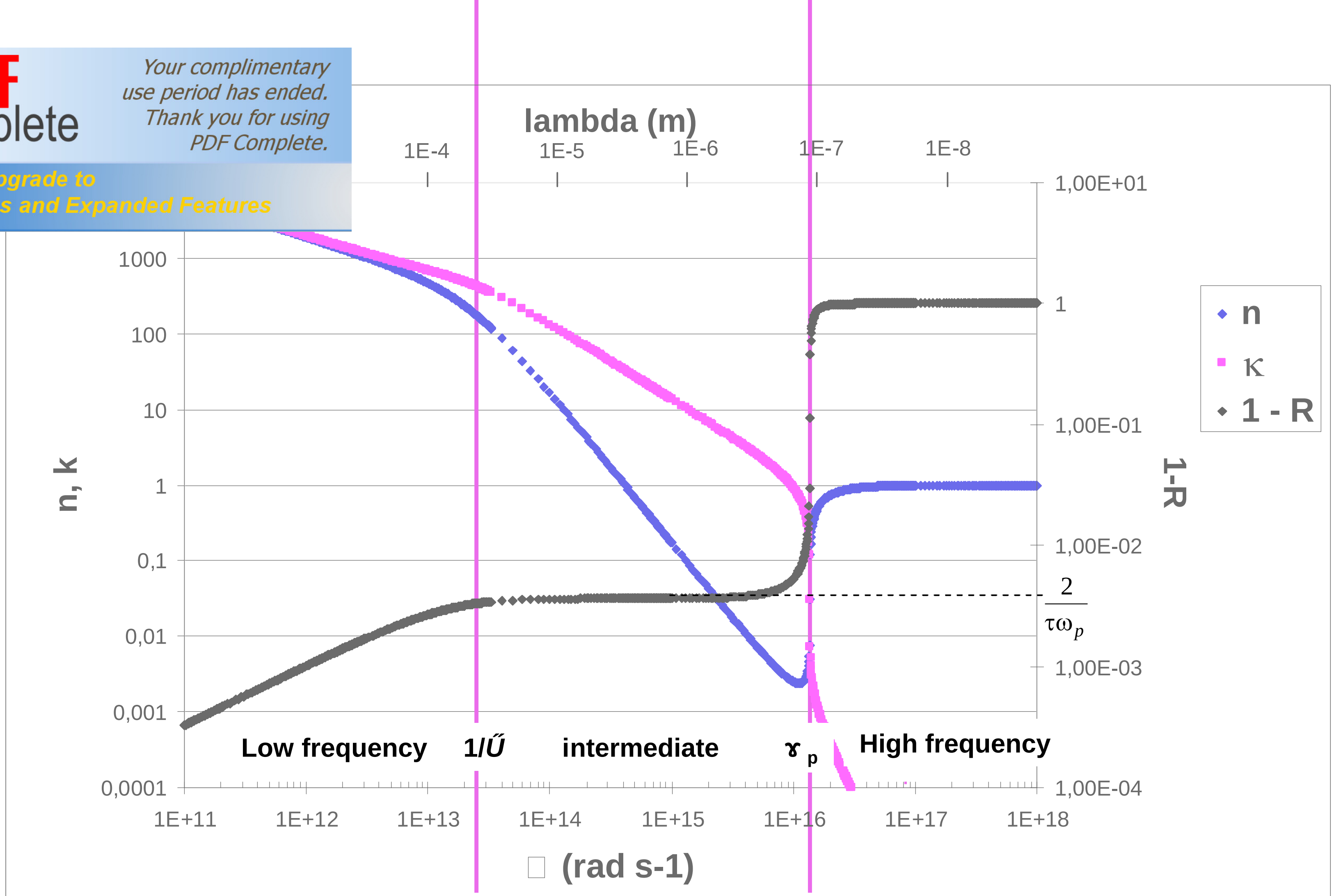

Drude model without approximation

Refractive index $\tilde{N}(\omega) = n(\omega) + i\kappa(\omega)$ **Reflection coefficient** $R = \left|\frac{1-\tilde{N}}{1+\tilde{N}}\right|^2 = \left|\frac{1-n-i\kappa}{1+n+i\kappa}\right|^2$

In the intermediate regime :

$$n(\omega) \approx \frac{\omega_p}{2\tau\omega^2} \quad \textit{and} \quad \kappa(\omega) \approx \frac{\omega_p}{\omega} \quad \Rightarrow \quad R = \frac{(1-n)^2+\kappa^2}{(1+n)^2+\kappa^2} \approx 1 - \frac{2}{\tau\omega_p}$$

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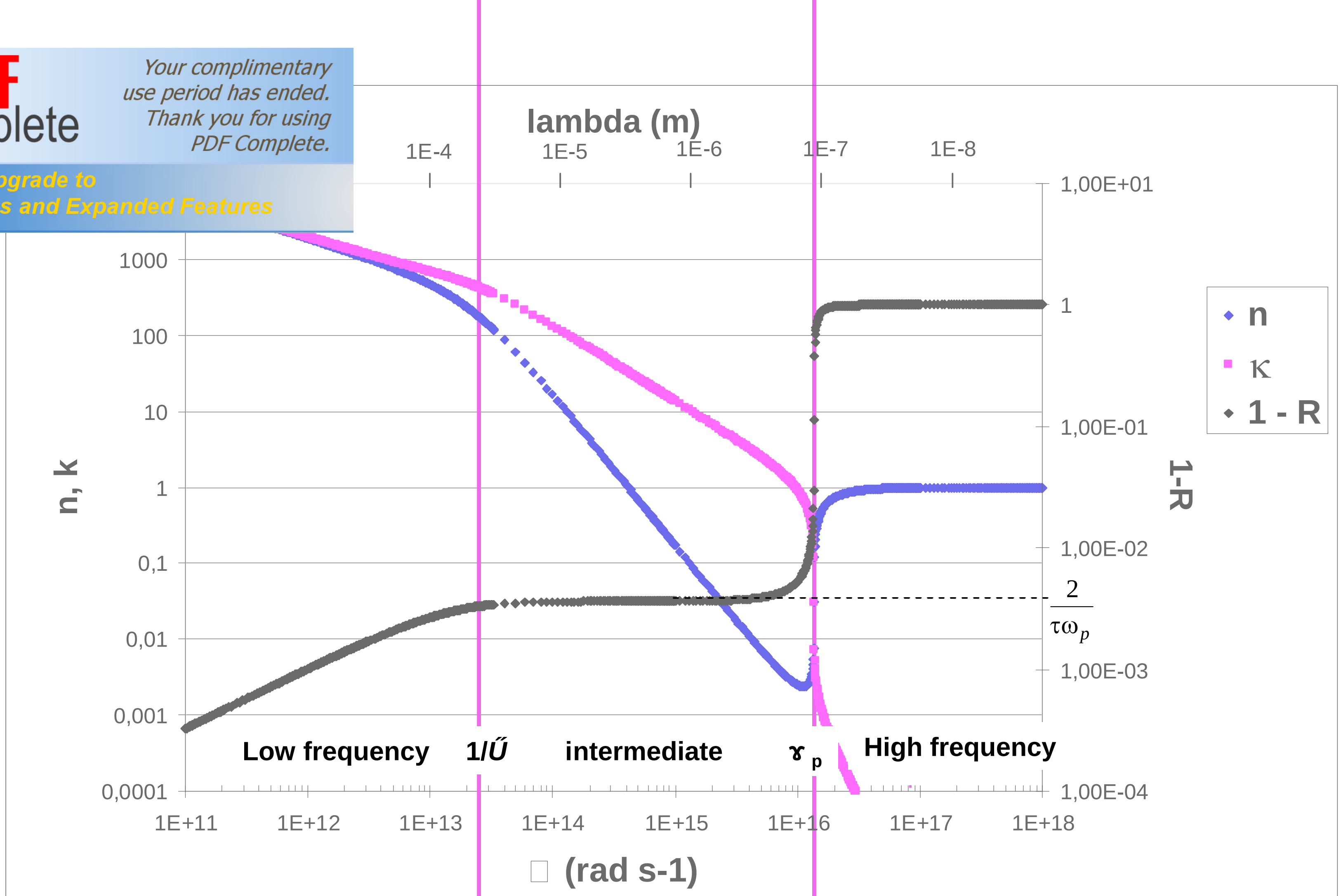

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In the intermediate regime :

$$n(\omega) \approx \frac{\omega_p}{2\tau\omega^2} \quad and \quad \kappa(\omega) \approx \frac{\omega_p}{\omega} \quad \Rightarrow \quad R = \frac{(1-n)^2+\kappa^2}{(1+n)^2+\kappa^2} \approx 1 - \frac{2}{\tau\omega_p}$$

absorption

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… : optical properties of metals(6/8)

☞ Exercise

For silver : **τ = 4.10^{-14} sec (at 300 K)**
N = 6.10^{22} cm^{-3}

1. Verify that the « intermediate regime » includes visible and thermal infrared ranges

2. Calculate the penetration depth of the evanescent wave

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: optical properties of metals(6/8)

For silver : τ **= 4.10^{-14} sec (at 300 K)**
N = 6.10^{22} cm^{-3}

Visible light : ɤ $_{vis}$ å 5.10^{15} sec^{-1}
Thermal infrared : ɤ $_{IR}$ = 1.10^{14} sec^{-1}

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}}$$ → **ɤ $_p$ = 1,3 10^{16} sec^{-1}, corresponding to ә$_p$=145 nm, in the UV**

It verifies 1/τ << ɤ $_{IR}$ < ɤ $_{vis.}$ < ɤ $_p$

Penetration depth of the evanescent wave : e$_p$ = c/ɤ $_p$ = 23 nm

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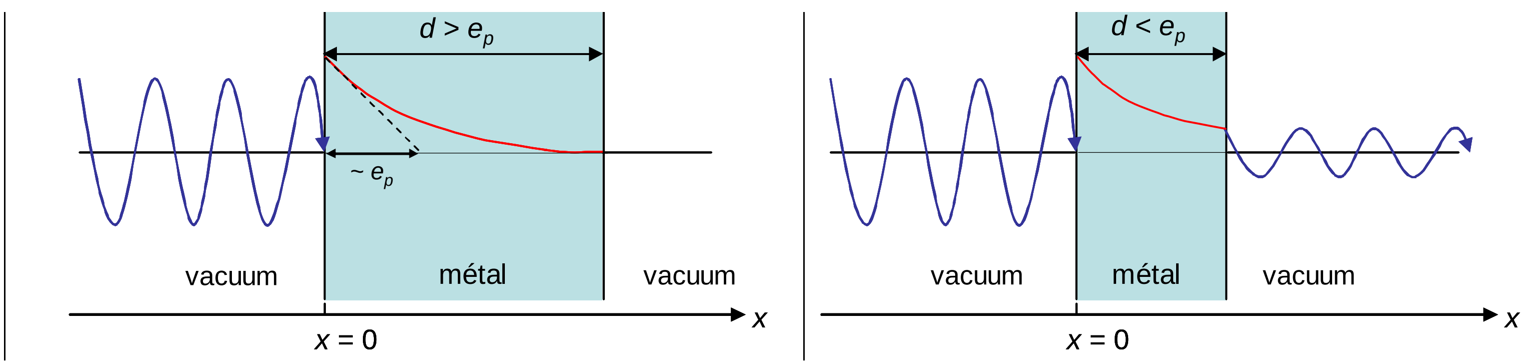
... : optical properties of metals(7/8)

- **If the metal thickness becomes as small as e_p,**
  a part T of the light intensity is transmitted, the rest of it being reflected.

$$T \approx e^{-2\frac{d}{e_p}} \approx e^{-2\frac{\omega_p}{c}d}$$



T = 0
R = 1

T Í 0
R=1-T

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: optical properties of metals(8/8)

☞ Sommerfeldôs and Drudeôs models

- Sommerfeldôs model is partly quantum mechanical
- Sommerfeldôs model uses Fermi-Dirac energy distribution instead of Boltzmannôs distribution
- In Sommerfeldôs model dc and ac conductivity and optical properties writes in the same way than in Drudeôs model, e.g. $\sigma_0 = \frac{Ne^2\tau}{m}$, but the meaning is different.

- In particular, Ű is that Ű of electrons located at the Fermi level.

☞ Matthiessenôs rule

- If there are several collision processes, characterized by scattering times Ű$_1$, Ű$_2$, Ű$_3$, é , the the effective Ű is given by : $\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \ldots$

- the same holds for the electron mean free path ş defined by ş=v$_F$Ű(v$_F$ is the Fermi velocity): $\frac{1}{\Lambda} = \frac{1}{\Lambda_1} + \frac{1}{\Lambda_2} + \frac{1}{\Lambda_3} + \ldots$

and for the electron mobility ε: $\frac{1}{\mu} = \frac{1}{\mu_1} + \frac{1}{\mu_2} + \frac{1}{\mu_3} + \ldots$

- resistivity : $\rho = \rho_1 + \rho_2 + \rho_3 + \ldots$

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…etal films(1/5)

☞ **For metals, $1/\tau \ll \omega_{IR} < \omega_{vis.} < \omega_p$**

We are in the intermediate regime

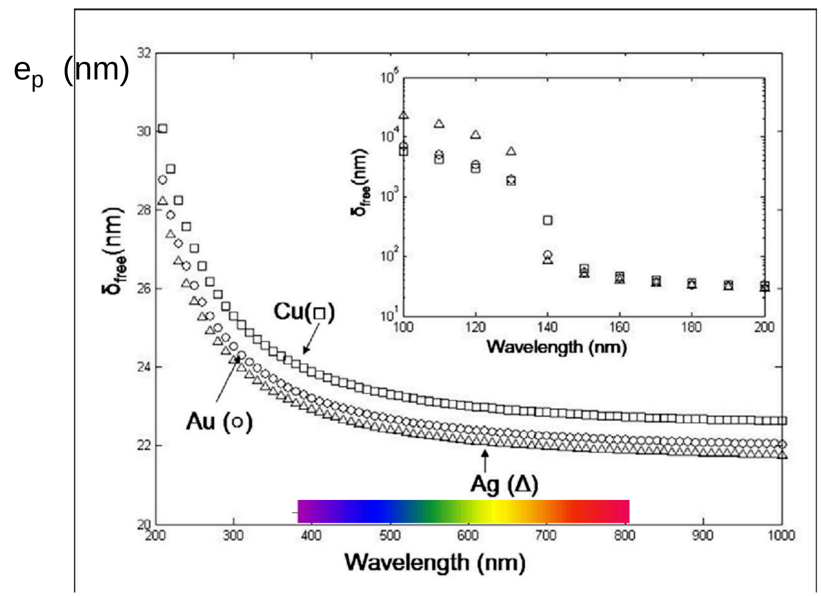
☞ **What can we expect from metal films ?**

If thin enough (thickness d not very large compared with e_p), a metal film is partly transparent.

By chance, would we get $T_{vis} \gg T_{IR}$ and $R_{IR} \ll R_{vis}$?

☞ **Would such a frequency dependence of T come from e_p ?**

No, because $e_p = c/\omega_p$ is almost independant of ω .



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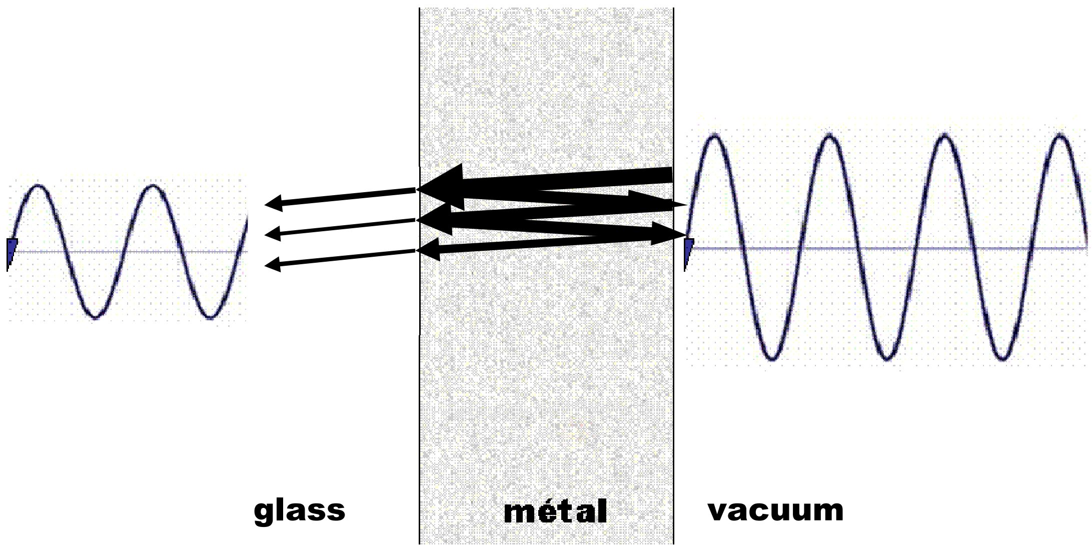
... metal films(2/5)

- **We have to go more deeply in the optics of the thin film and consider the situation below, with multiple reflections at both interfaces**



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metal films(3/5)

- **The result is**

$$T = \frac{(1-R)^2 + 4R\sin^2\delta}{\left(e^{\frac{\omega}{c}\kappa d} - e^{-\frac{\omega}{c}\kappa d}\right)^2 + 4R\sin^2\left(\delta + \frac{\omega}{c} n d\right)}$$

with $R = \frac{(1-n)^2 + \kappa^2}{(1+n)^2 + \kappa^2}$ **, reflection coefficient of the bulk metal,**

and

$$\tan\delta = \frac{2\kappa}{n^2 + \kappa^2 - 1}$$

n and κ are the real and imaginary part of the refractive index

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Ultrathin metal films(3/5)

☞ **The result is**

$$T=\frac{(1-R)^2+4R\sin^2\delta}{\left(e^{\frac{\omega}{c}\kappa d}-e^{-\frac{\omega}{c}\kappa d}\right)^2+4R\sin^2\left(\delta+\frac{\omega}{c}nd\right)}$$

For d large enough → $e^{2\frac{\omega}{c}\kappa d}$

with $R=\frac{(1-n)^2+\kappa^2}{(1+n)^2+\kappa^2}$ **, reflection coefficient of the bulk metal,** → **1**

and

$$\tan\delta=\frac{2\kappa}{n^2+\kappa^2-1}$$

→ **2/κ, and hence sinŭ å 2/κ**

n and κ are the real and imaginary part of the refractive index

Remind : in the intermediate frequency regime, n << κ and κ å ɤ$_p$/ɤ >> 1

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metal films(4/5)

☞ **Thus, in the intermediate frequency regime, and for d > e_p, one gets :**

$$T \approx 16 \frac{\omega^2}{\omega_p^2} e^{-2\frac{\omega_p}{c}d}$$

→ **$T_{vis} >> T_{IR}$**

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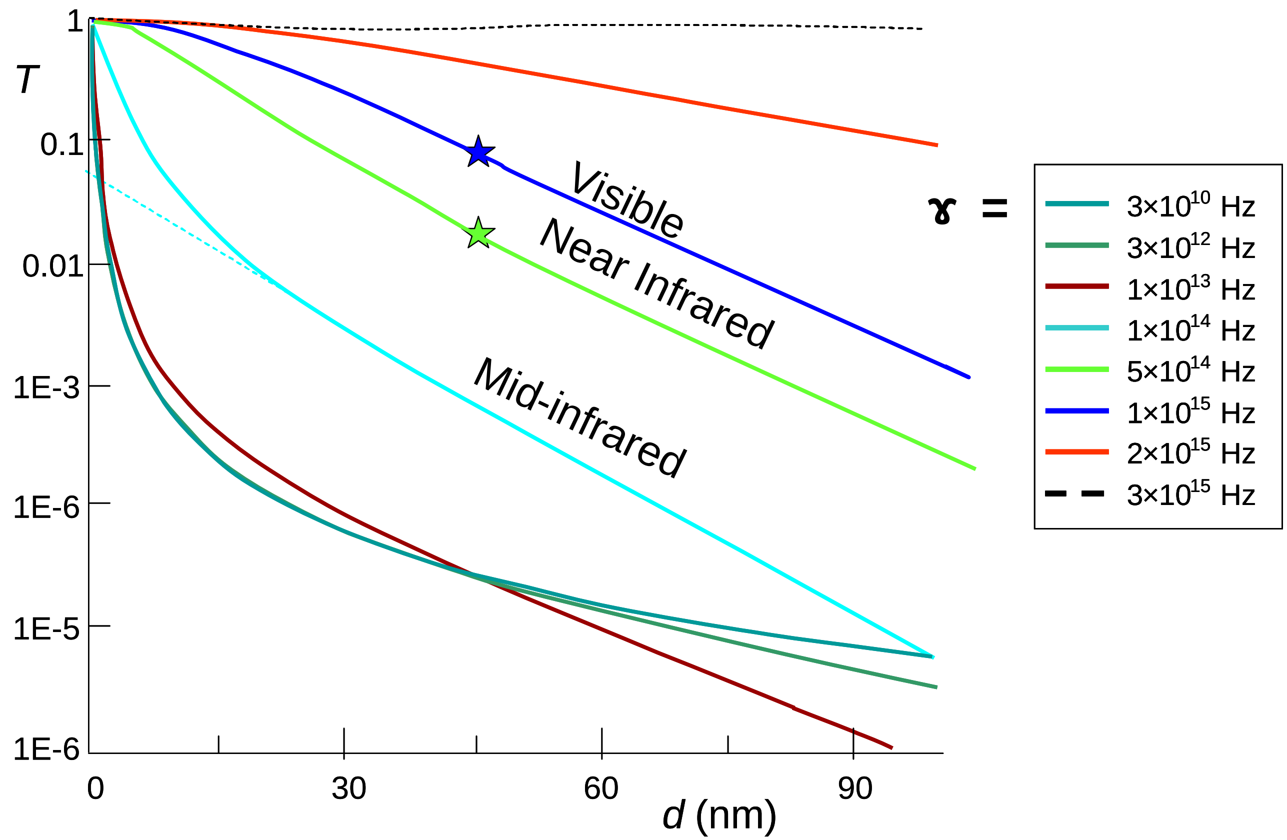
…metal films(4/5)

☞**Thus, in the intermediate frequency regime, and for d > e_p, one gets :**

$$T \approx 16 \frac{\omega^2}{\omega_p^2} e^{-2\frac{\omega_p}{c}d} \quad \rightarrow \quad T_{vis} >> T_{IR}$$

☞**Complete calculation (case of silver)**



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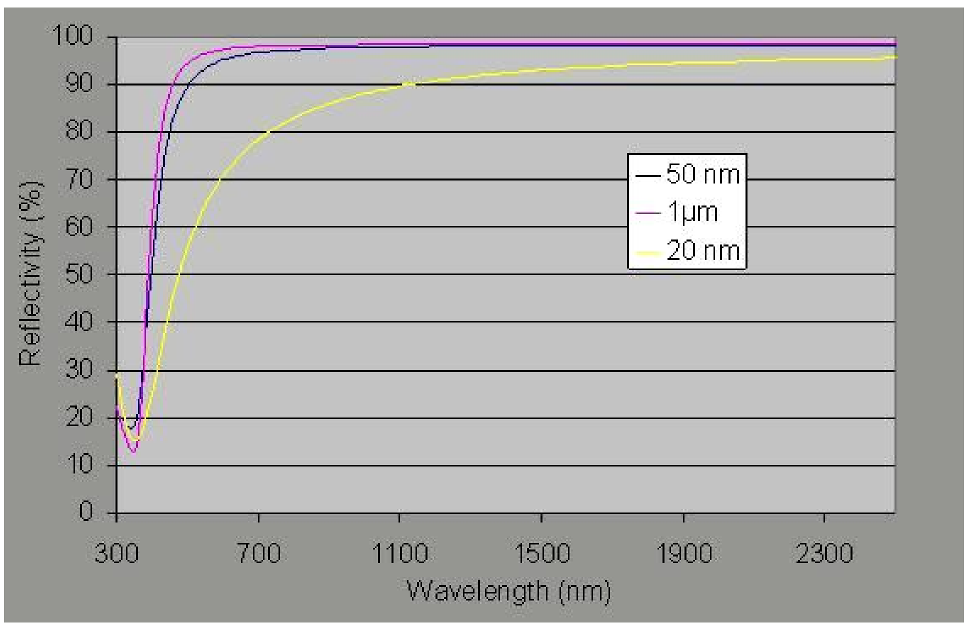
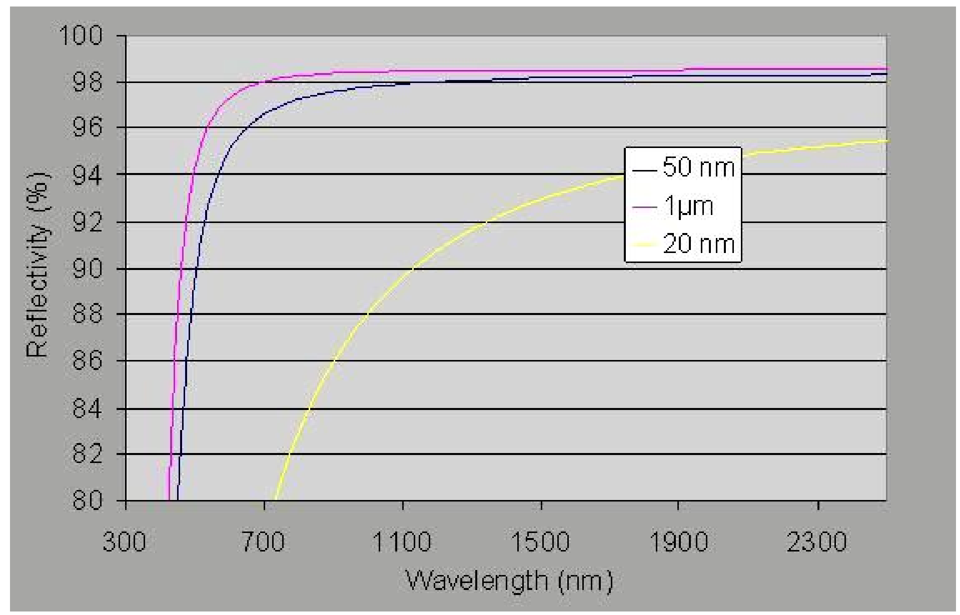
metal films(5/5)

☞Experimental results

Reflectivity R (=1-T) for three silver films of thickness 1 μm, 50 nm and 20 nm





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sing silver ?(1/7)

☞ In the visible, we want T large

$$T \approx 16 \frac{\omega^2}{\omega_p^2} e^{-2\frac{\omega_p}{c}d}$$

→ γ_p small → N small

Metal	Electron density (10^{28} m^{-3})
Cu	8.47
Ag	5.86
Au	5.90
Be	24.7
Mg	8.61
Ca	4.61
Sr	3.55
Ba	3.15
Nb	5.56
Fe	17.0
Zn	13.2
Cd	9.27
Al	18.1
Ga	15.4
In	11.5
Sn	14.8
Pb	13.2
Sm	8.8

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Sn	14.8
Pb	13.2
Sm	8.8

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…ing silver ?(2/7)

☞ For the thermal infrared, we need a highly reflecting metal

$$R \approx 1 - \frac{2}{\tau \omega_p}$$

→ Űarge

Metal	Relaxation time (10^{-14} sec)
Cu	2,7
Ag	4.0
Au	3.0
Be	0,51
Mg	1.1
Ca	2.2
Sr	0,44
Ba	0,19
Nb	0,42
Fe	0,24
Zn	0,49
Cd	0,56
Al	0,80
Ga	0,17
In	0,38
Sn	0,23
Pb	0,14
Sm	?

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Why choosing silver ?(2/7)

☞ For the thermal infrared, we need a highly reflecting metal

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Metal	Relaxation time (10^{-14} sec)
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Au	3.0
Be	0,51
~~Mg~~	~~1.1~~
~~Ca~~	~~2.2~~
Sr	0,44
Ba	0,19
Nb	0,42
Fe	0,24
Zn	0,49
Cd	0,56
Al	0,80
Ga	0,17
In	0,38
Sn	0,23
Pb	0,14
Sm	?

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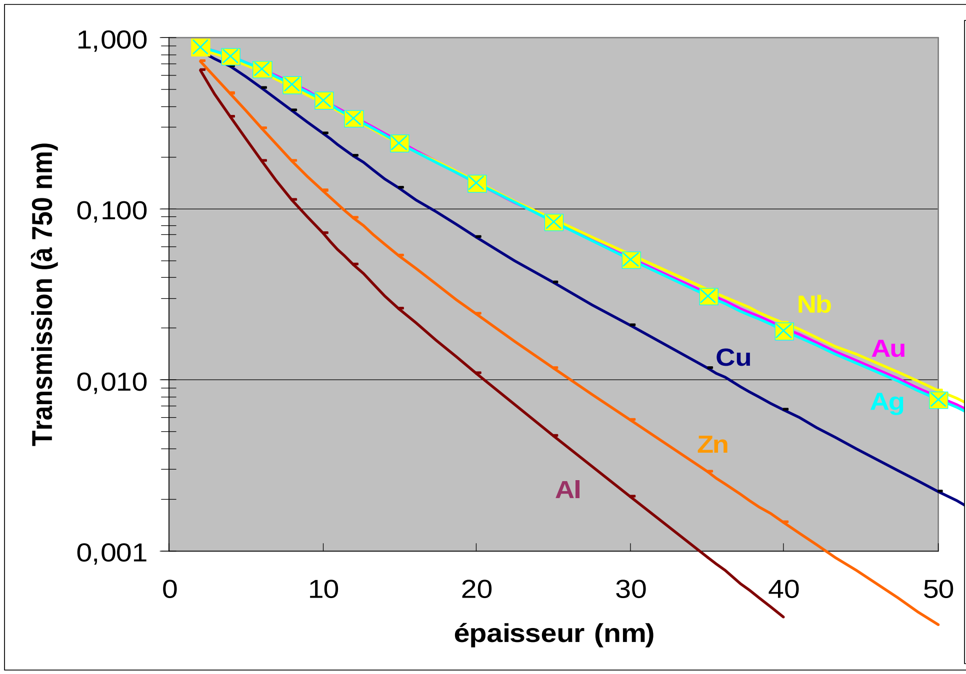
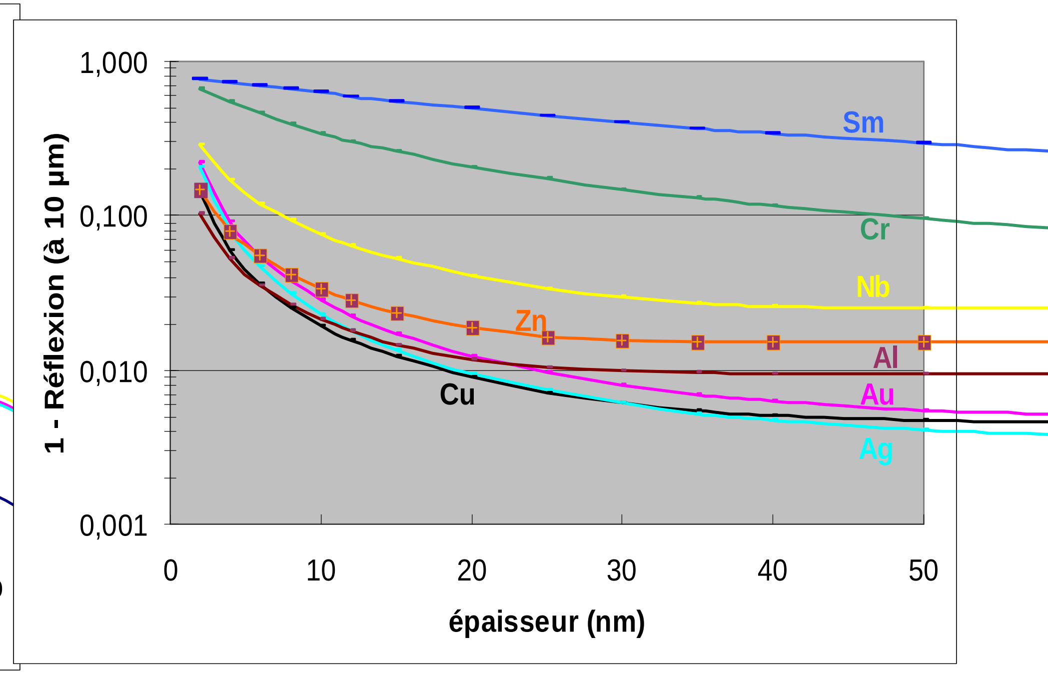
sing silver ?(3/7)



Transmission at 750 nm



1-Réflexion (at 10µm)

Calculation : Drudeȇs model, no approximation

☞ **Conclusion**

Silver, gold and copper look fine

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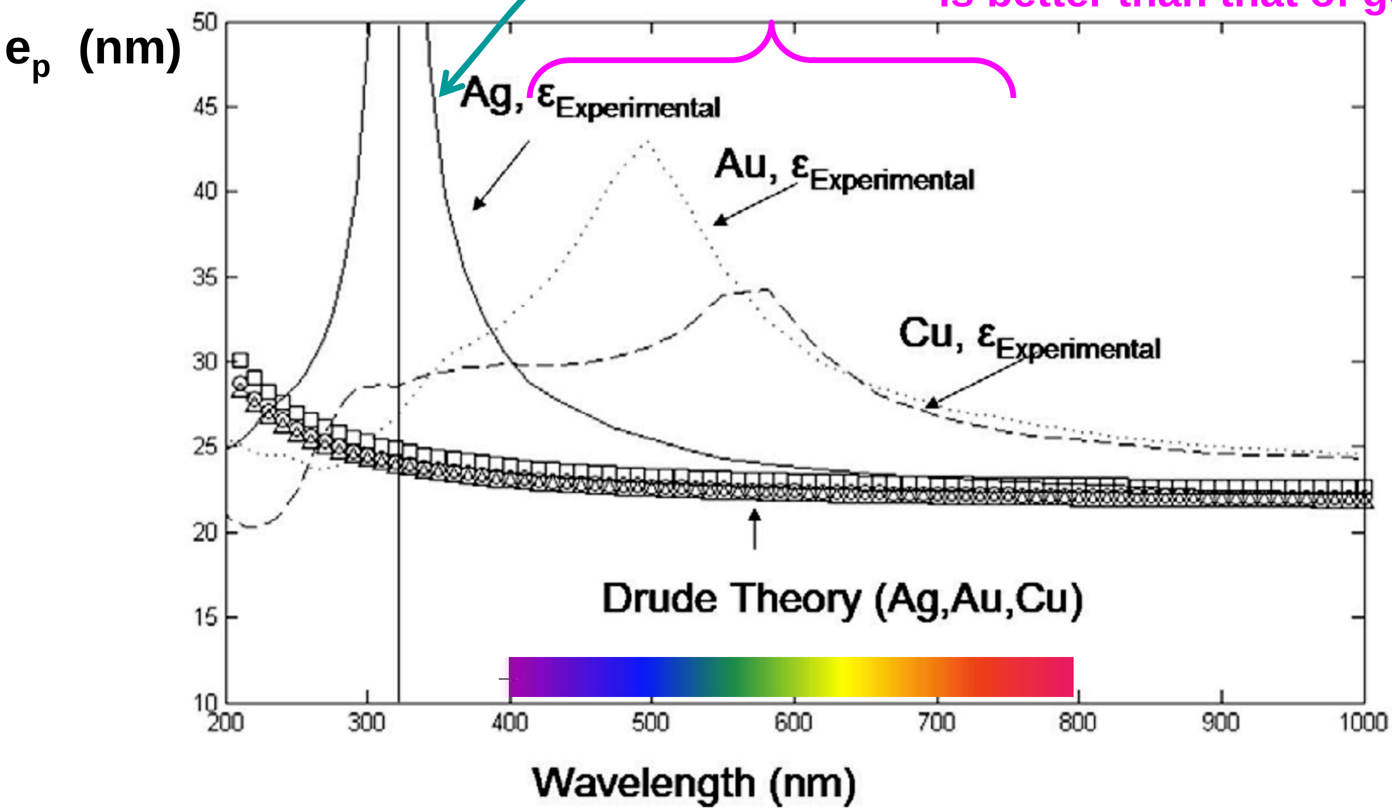
sing silver ?(4/7)

1. Of the three metals, silver is the most neutral : almost no frequency dependance in the visible
2. Transmission of silver in the visible is better than that of gold or copper



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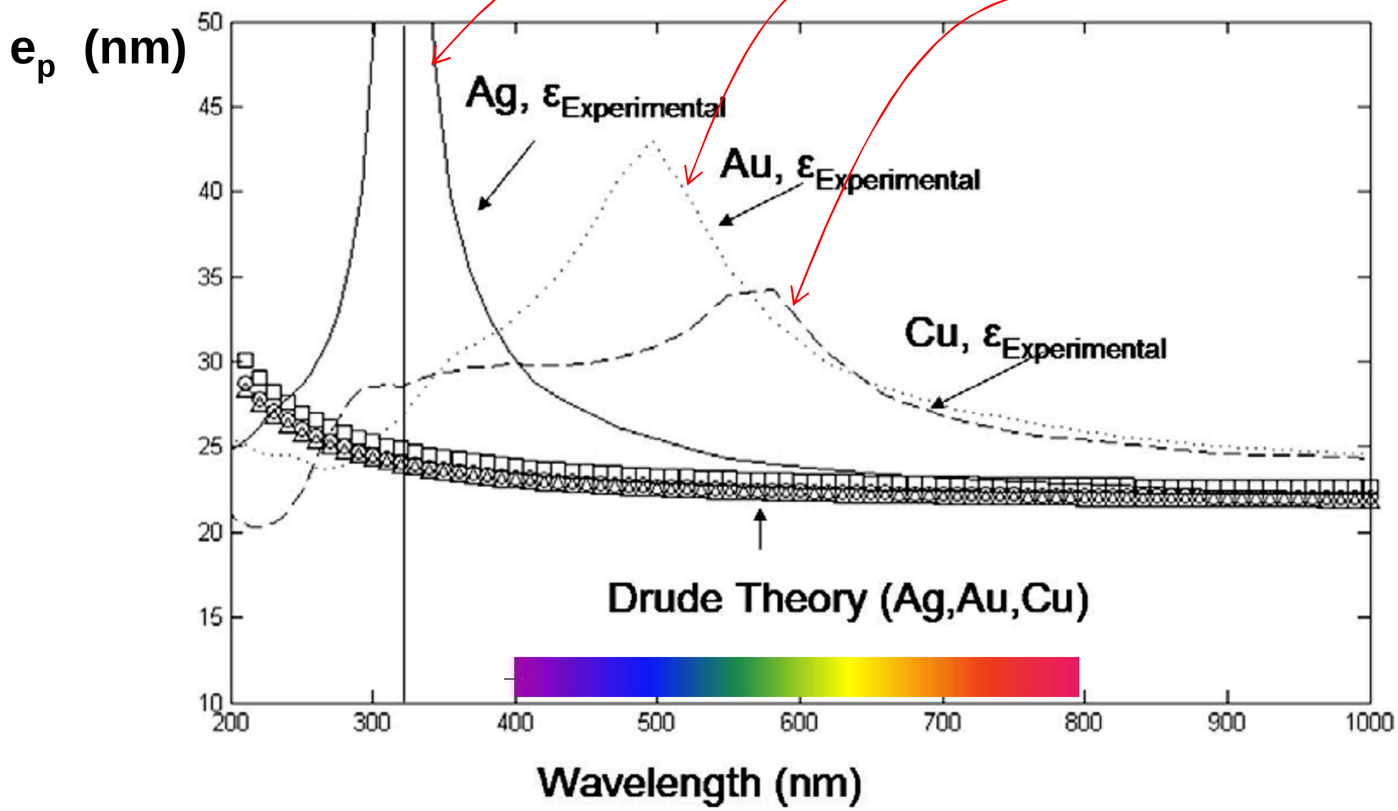
Why choosing silver ?(4/7)

What does that come from ?



☞**Drudeôs model is not adapted**

we need something else

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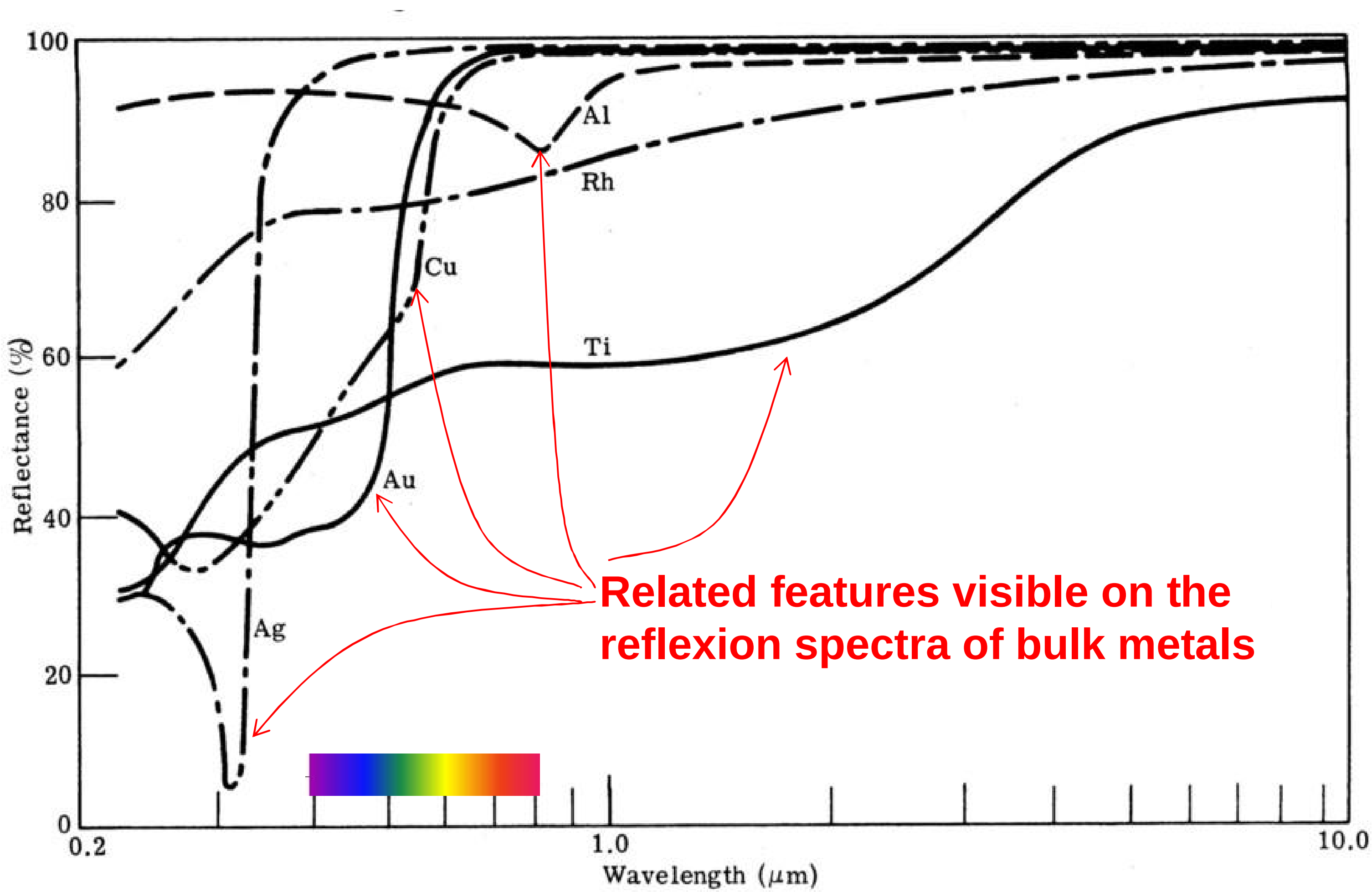
Why choosing silver ?(5/7)



☞ **Drudeôs model is not adapted**

we need something else

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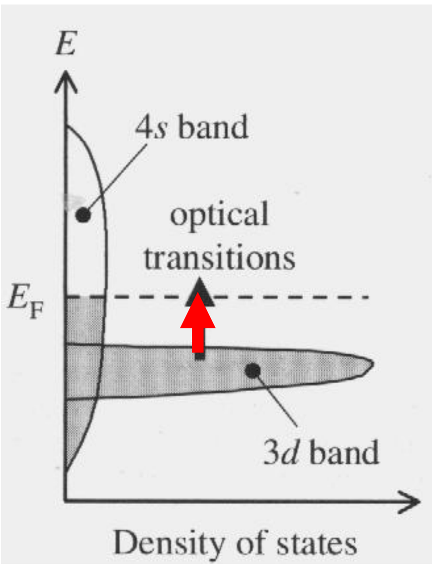
Why choosing silver ?(6/7)

☞Interband transitions



copper

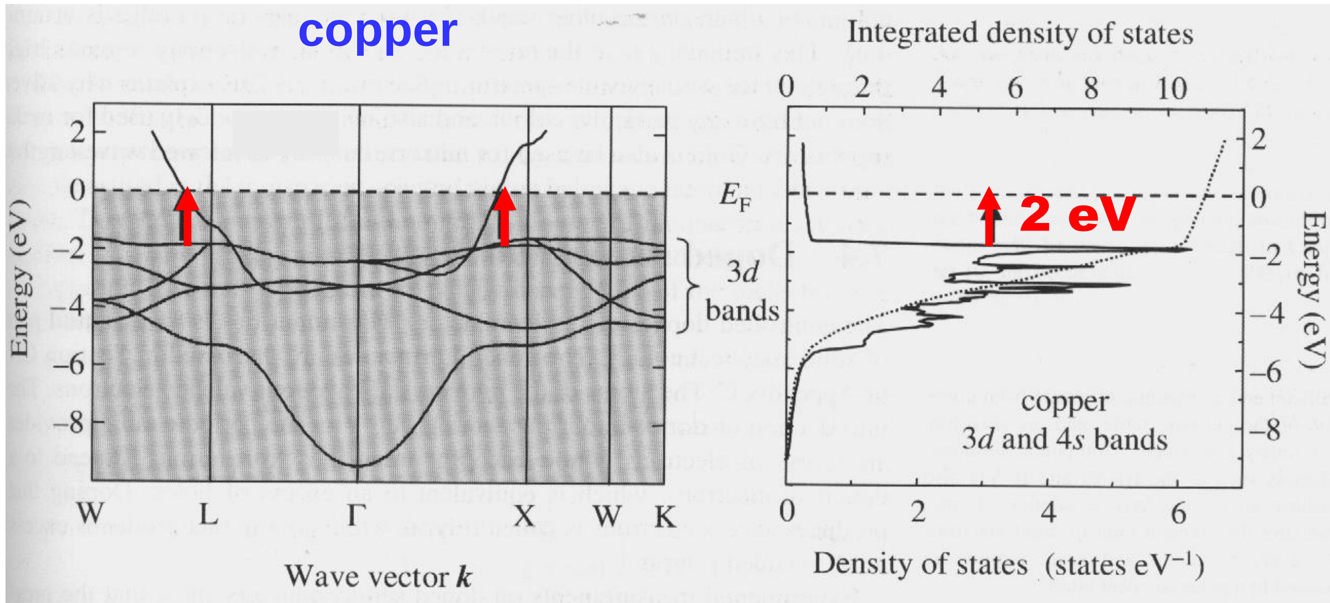


Fig. 7.5 Calculated band structure of copper. The transitions from the 3d bands responsible for the interband transitions around 2 eV are identified. The right hand side of the figure shows the density of states calculated from the band structure. The strongly peaked features between about −2 eV and −5 eV are due to the 3d bands. The dotted line is the integrated density of states. The Fermi level corresponds to the energy where the integrated density of states is equal to 11. After [5].

$$E(\vec{k}') = E(\vec{k}) + \hbar\omega$$

$$\vec{k}' = \vec{k} + \vec{q} \qquad |\vec{q}| = \frac{\omega}{c}$$

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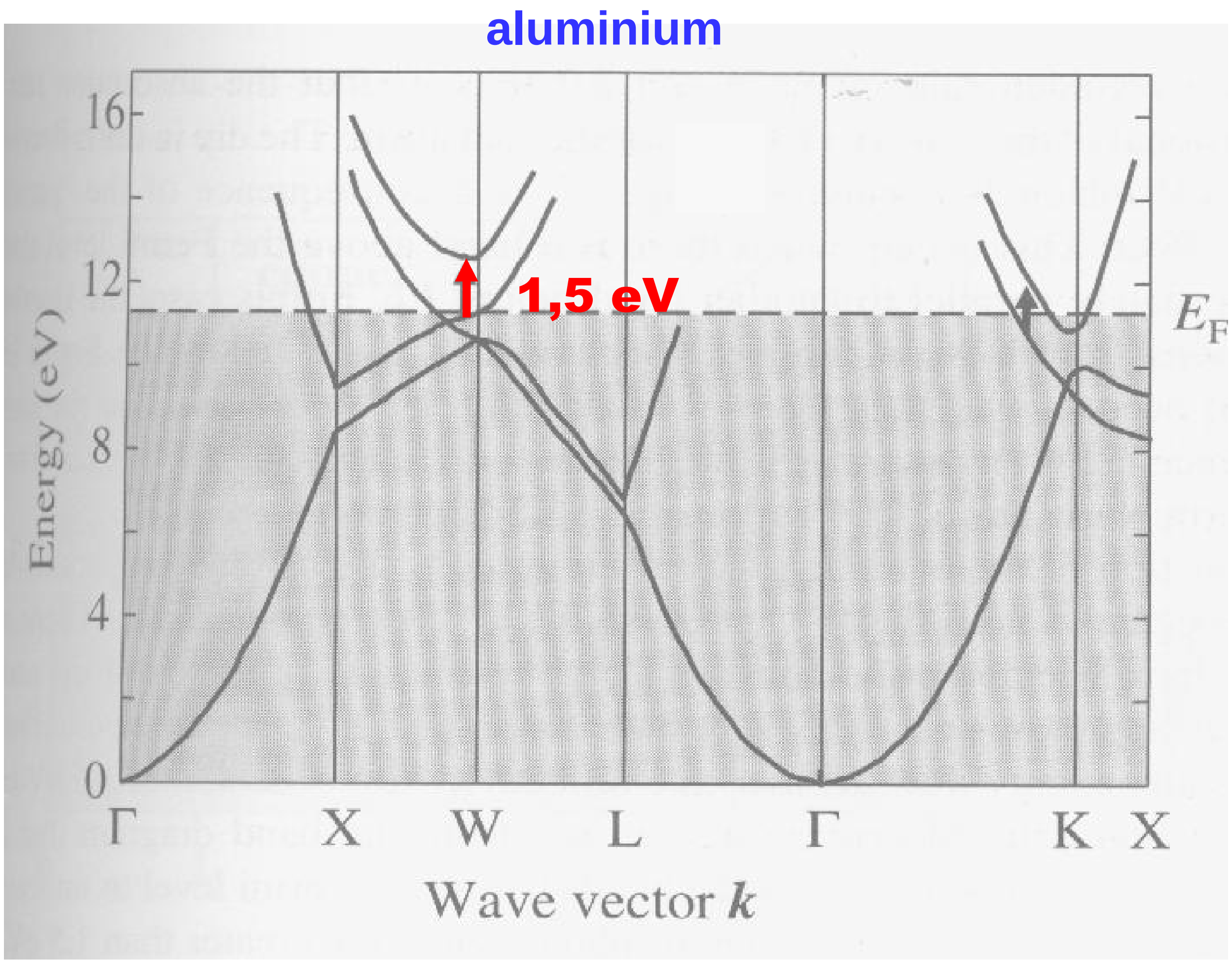
...Why choosing silver ?(7/7)

☞Interband transitions



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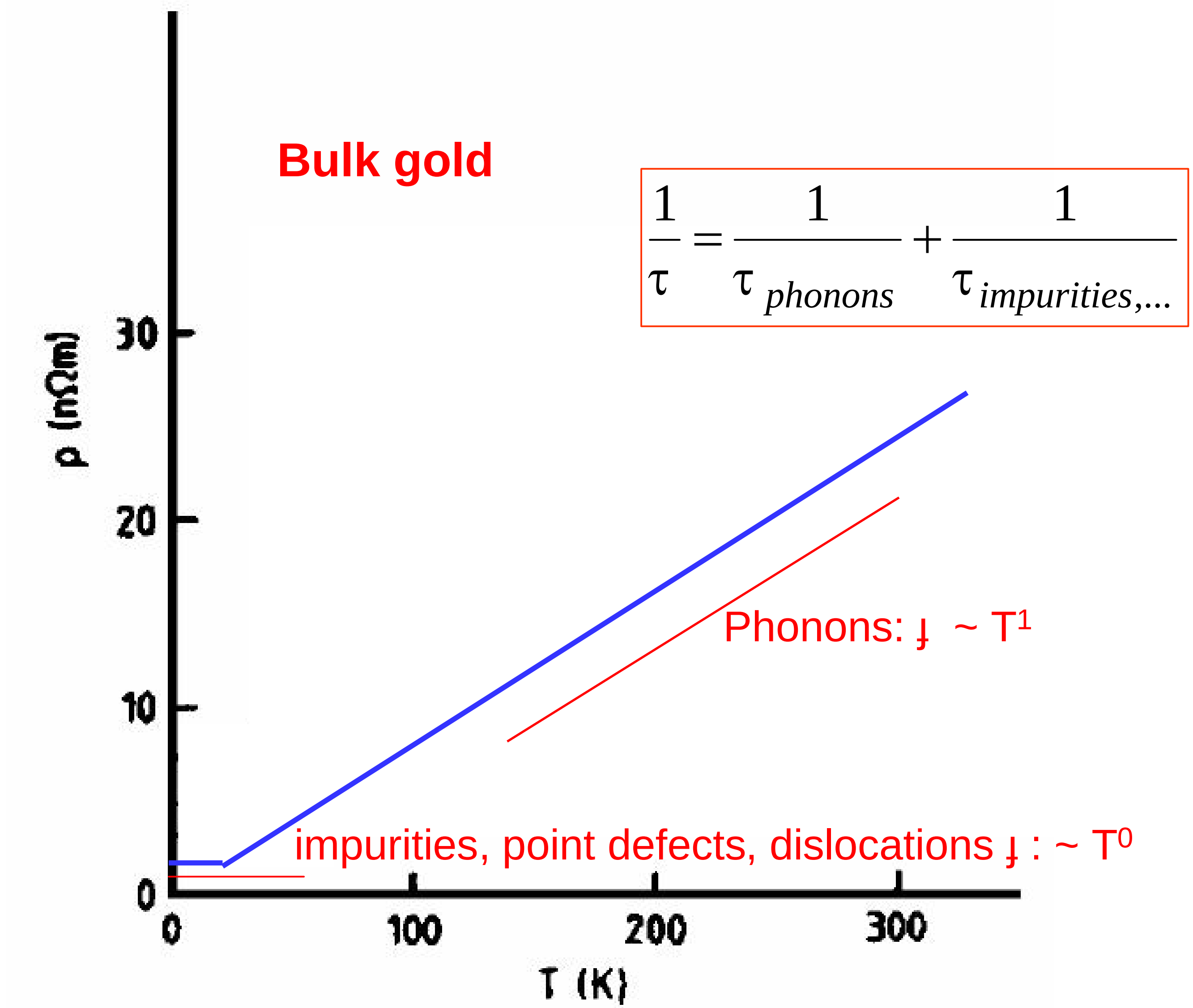
in ultrathin metal films (1/5)



$$\frac{1}{\tau} = \frac{1}{\tau_{phonons}} + \frac{1}{\tau_{impurities,...}}$$

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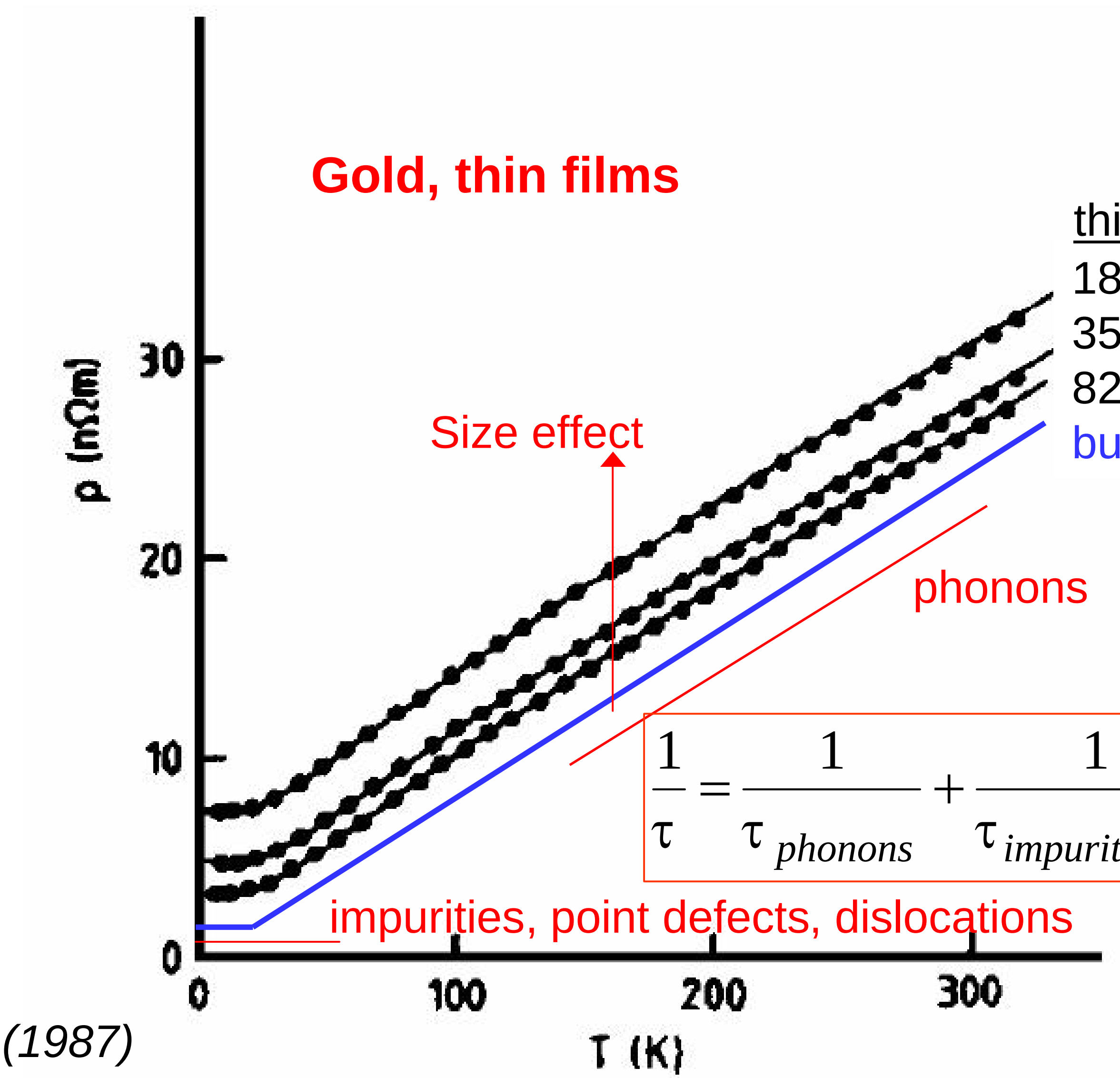
Size effect in ultrathin metal films (2/5)



$$\frac{1}{\tau} = \frac{1}{\tau_{phonons}} + \frac{1}{\tau_{impurities,...}} + \frac{1}{\tau_{"thickness"}}$$

de Vries (1987)

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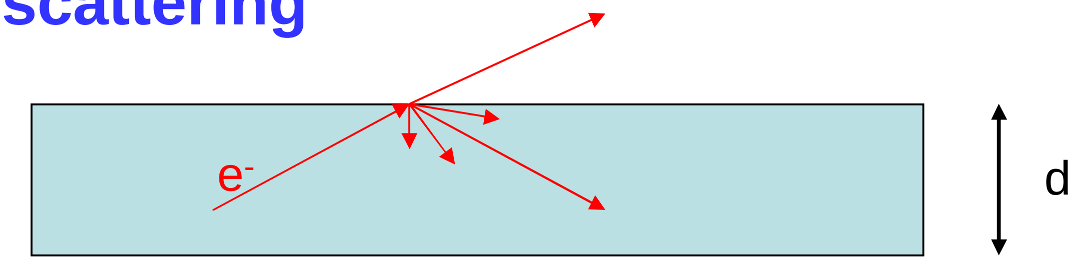
Size effect in ultrathin metal films (3/5)

- **Electron mean free path in <u>bulk</u> silver**

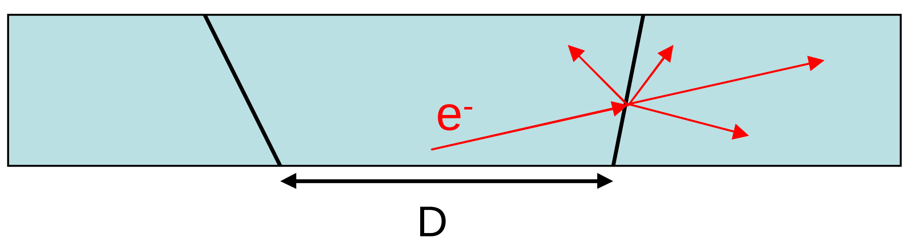
  $\ell = v_F \tau = 1,39\ 10^{8} .\ 4\ 10^{-14} = 5,4\ 10^{-7}$ cm = 54 nm

  Film thickness and grain boundary are smaller than that. Then, they provide extra collision (scattering) mechanisms

- **Surface scattering**



- **Scattering by grain boundaries**



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t in ultrathin metal films (3/5)

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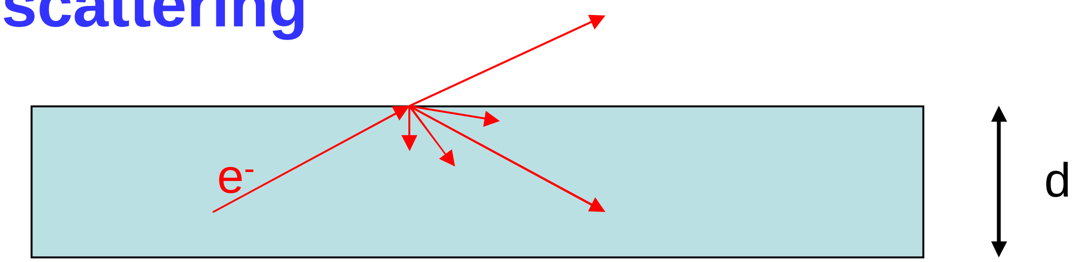
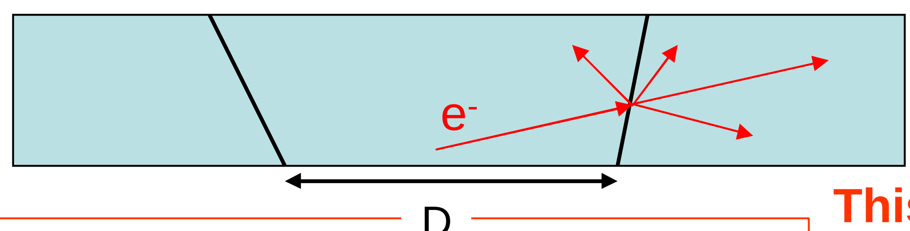


- **Scattering by grain boundaries**



$$\frac{1}{\tau} = \frac{1}{\tau_{phonons}} + \frac{1}{\tau_{impurities,...}} + \frac{1}{\tau_{surface}} + \frac{1}{\tau_{grain\ boundaries}}$$

This decrease of τ affects transport, but also reflectivity of thin films compared with bulk

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Size effect in ultrathin metal films (4/5)

☞ Scattering models

- Fuchs-Sondheimer (surface) $$\frac{1}{\tau_S} = \frac{3}{8}(1-p)\frac{\lambda}{d}\frac{1}{\tau_{bulk}}$$

p : probability for interaction with external surfaces being specular reflection

- Mayadas-Schatzkes (grain boundaries) $$\frac{1}{\tau_{GB}} = \frac{3}{2}\left(\frac{\eta}{1-\eta}\right)\frac{\lambda}{D}\frac{1}{\tau_{bulk}}$$

ɖ : probability for direct no-loss transmission at grain boundary

☞ Limiting the size effect means

- keeping p close to 1 and ɖ close to 0
- which means
  - surfaces as mirors for electrons
  - large grains,
  - grain boundaries transparent to electrons

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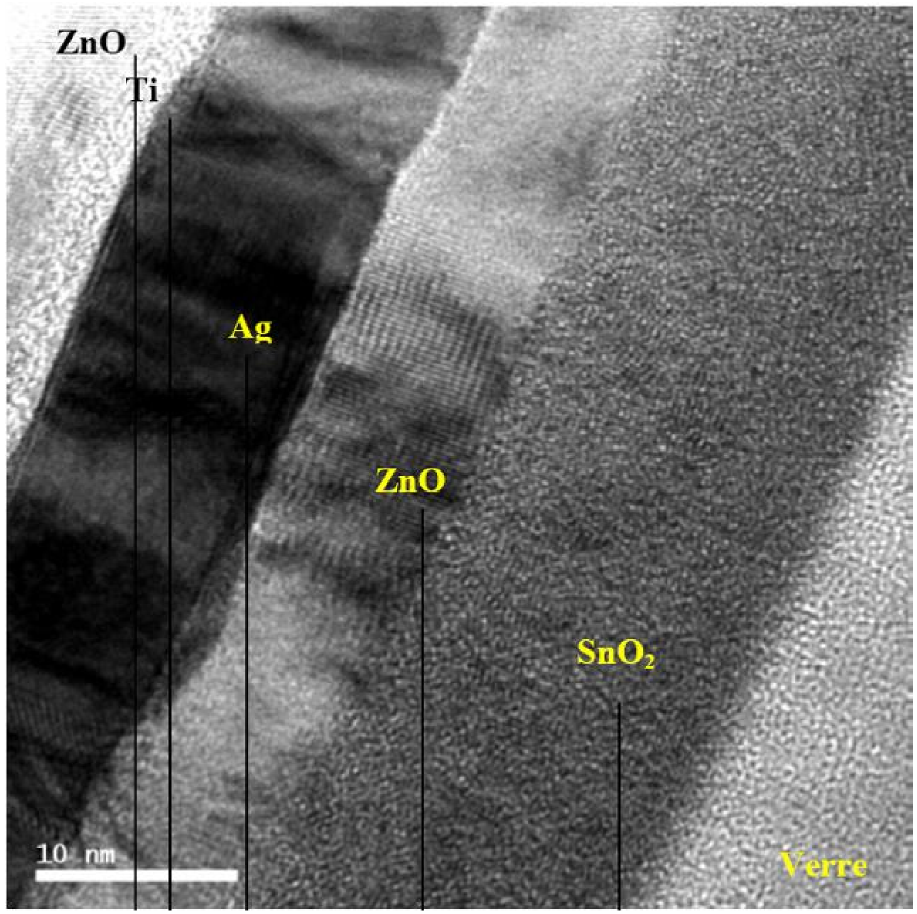
Size effect in ultrathin metal films (5/5)

☞The reality



é not so bad, but there is still place for improvement

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Silver based low-emissivity coatings(1/5)

Si_3N_4 - 40 nm

ZnO - 54 nm

Ag - 10 nm

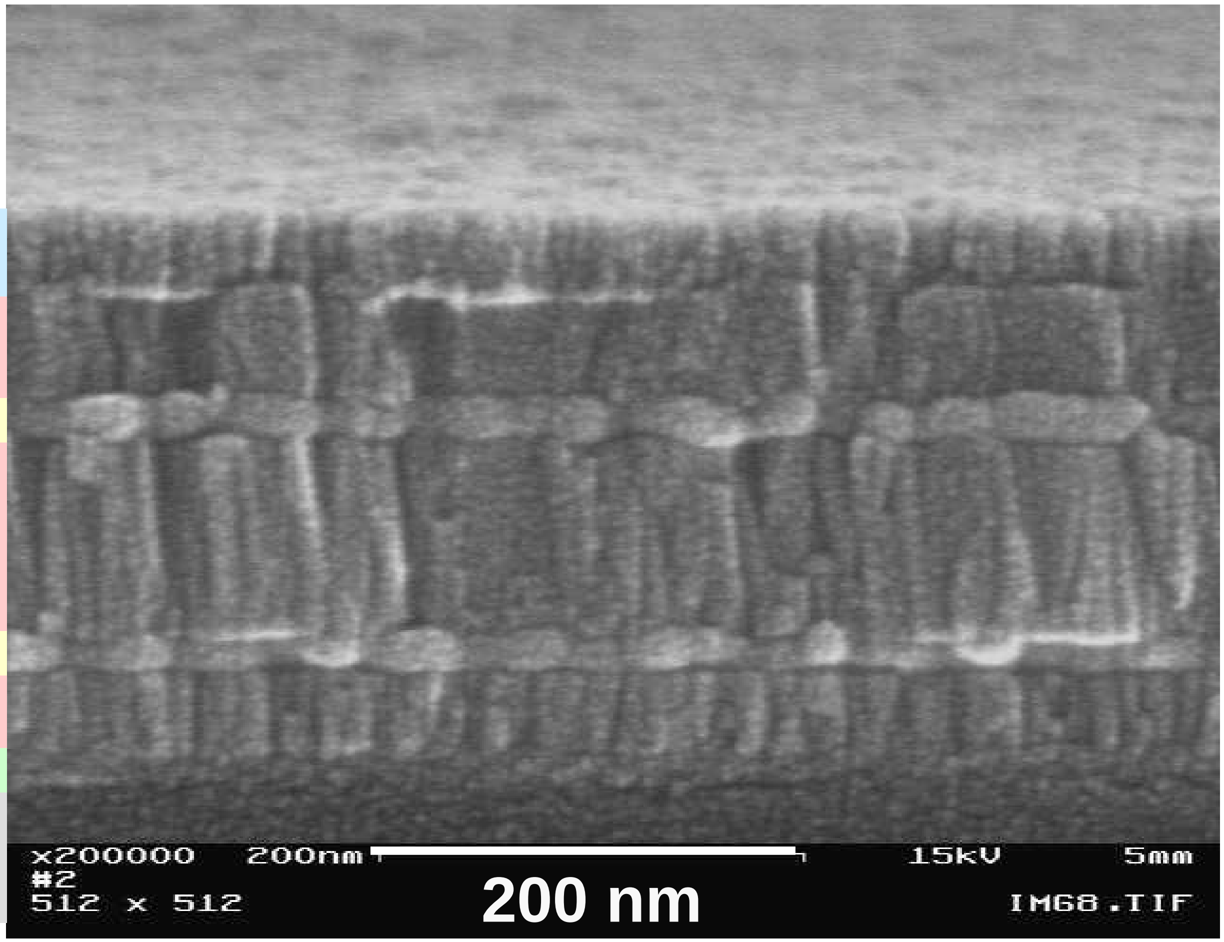
ZnO - 100 nm

Ag - 11 nm

ZnO - 54 nm

SnO_2 - 16 nm

Glass substrate



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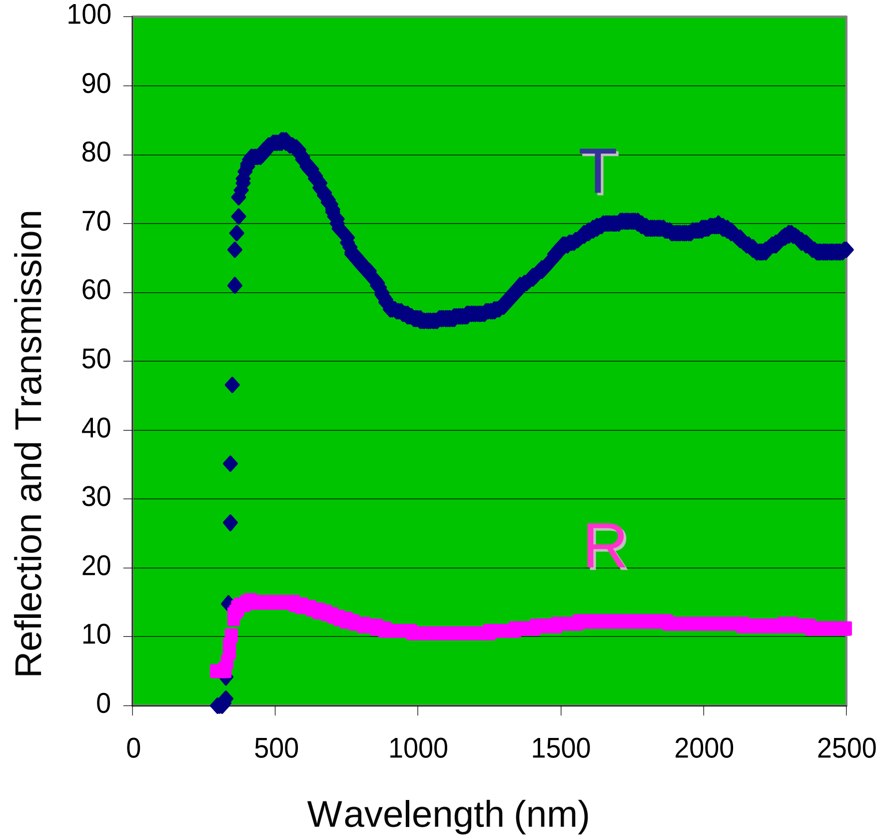
ed low-emissivity coatings(2/5)

☞Optimization of transmission in the visible

Double glazing unit



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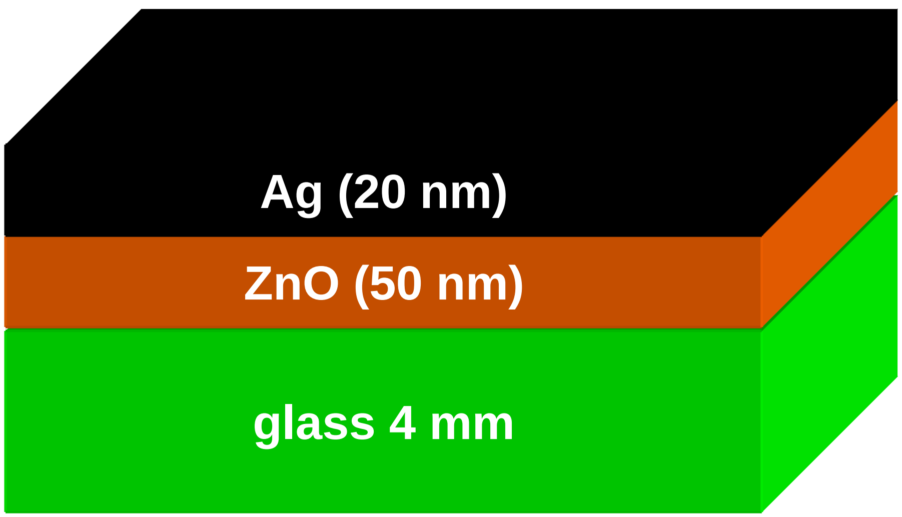
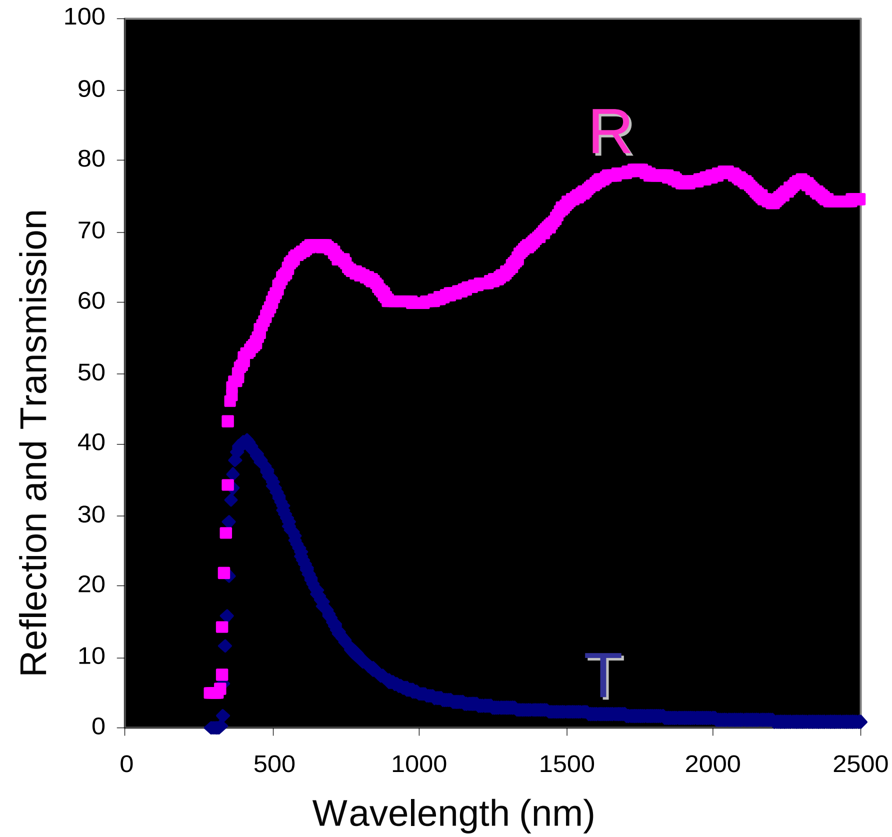
ed low-emissivity coatings(2/5)

☞Optimization of transmission in the visible





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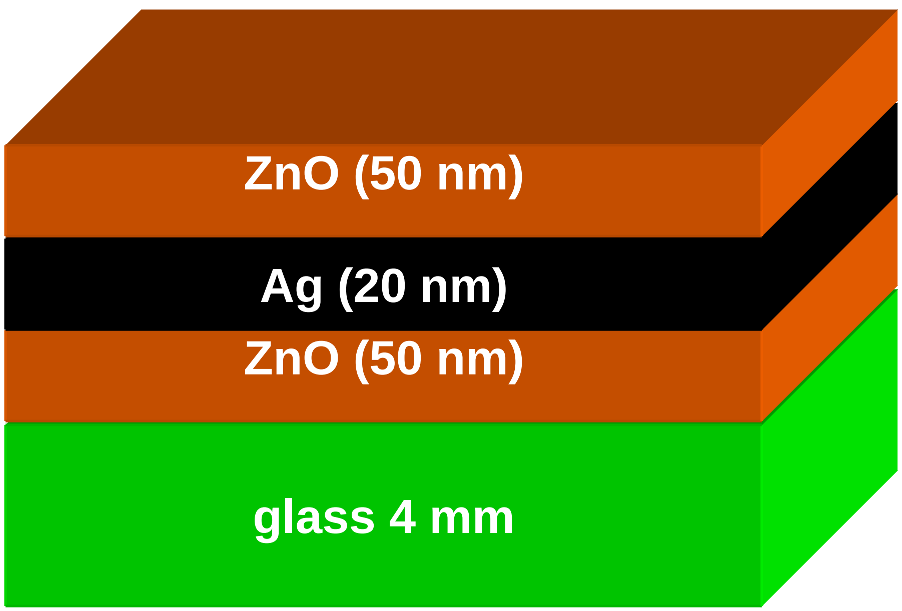
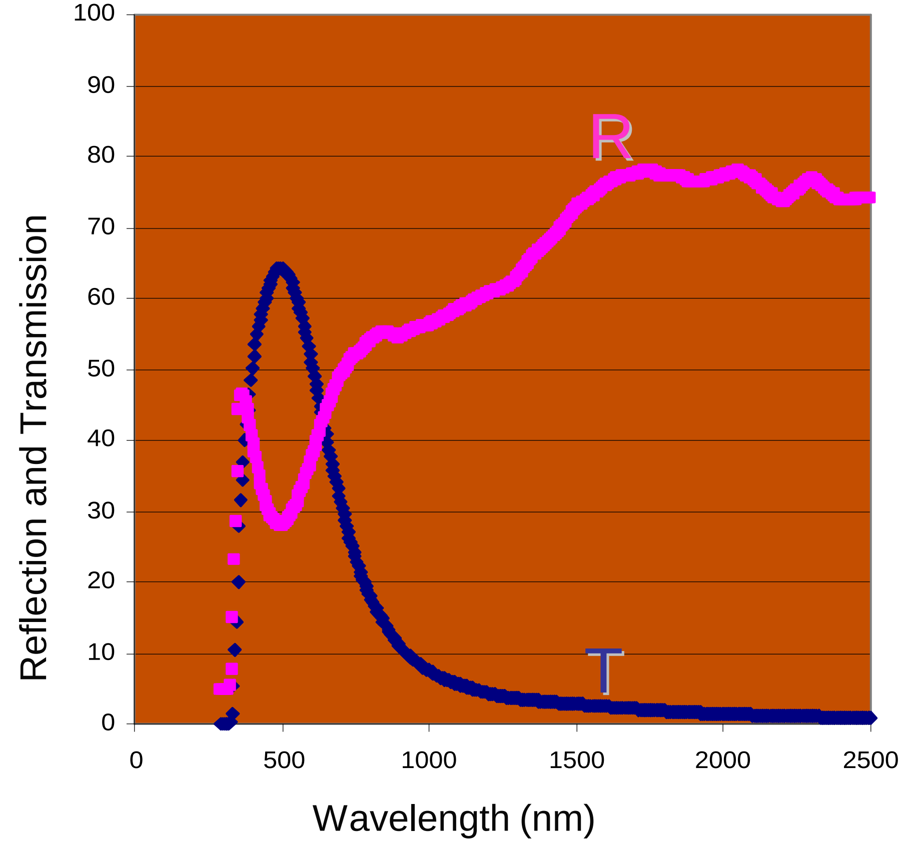
Silver based low-emissivity coatings(2/5)

☞Optimization of transmission in the visible





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ed low-emissivity coatings(2/5)

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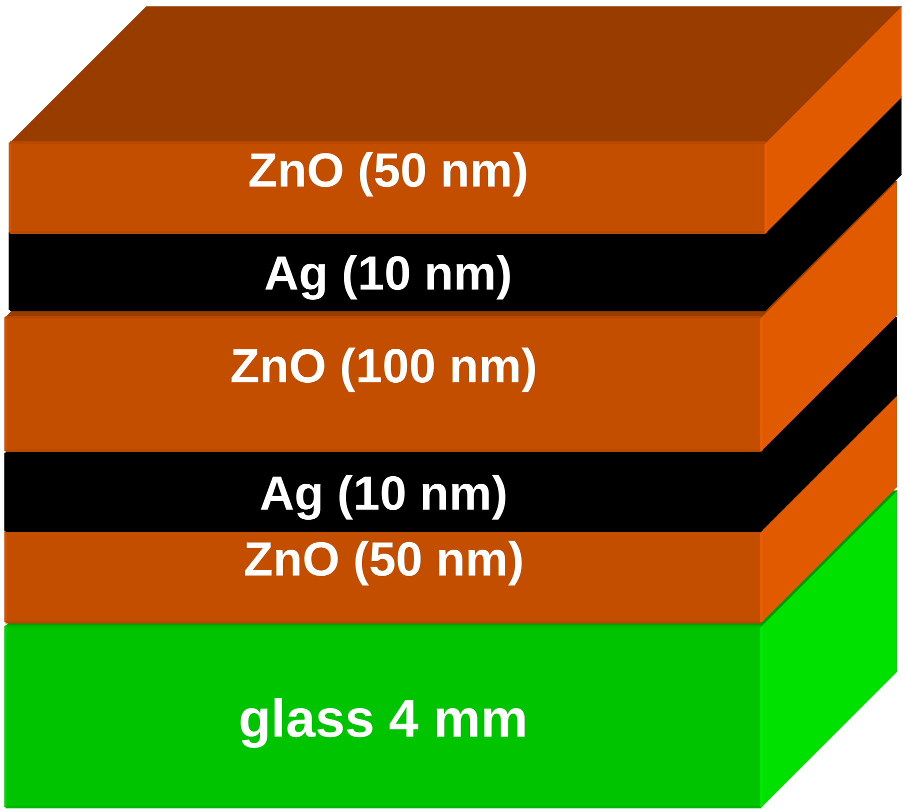

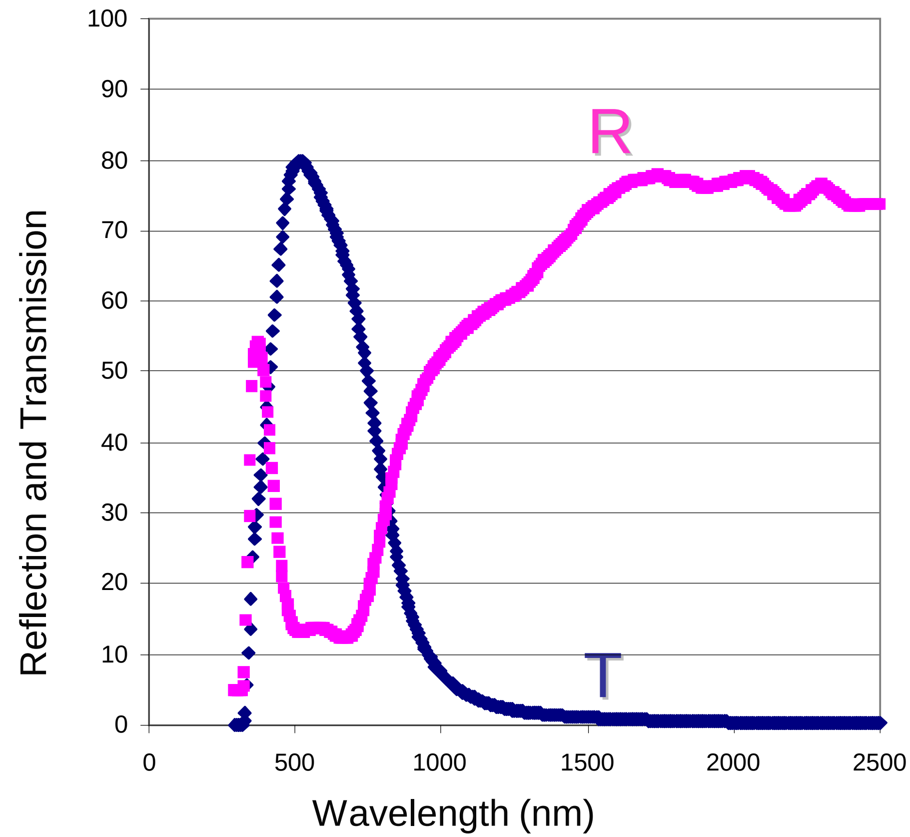

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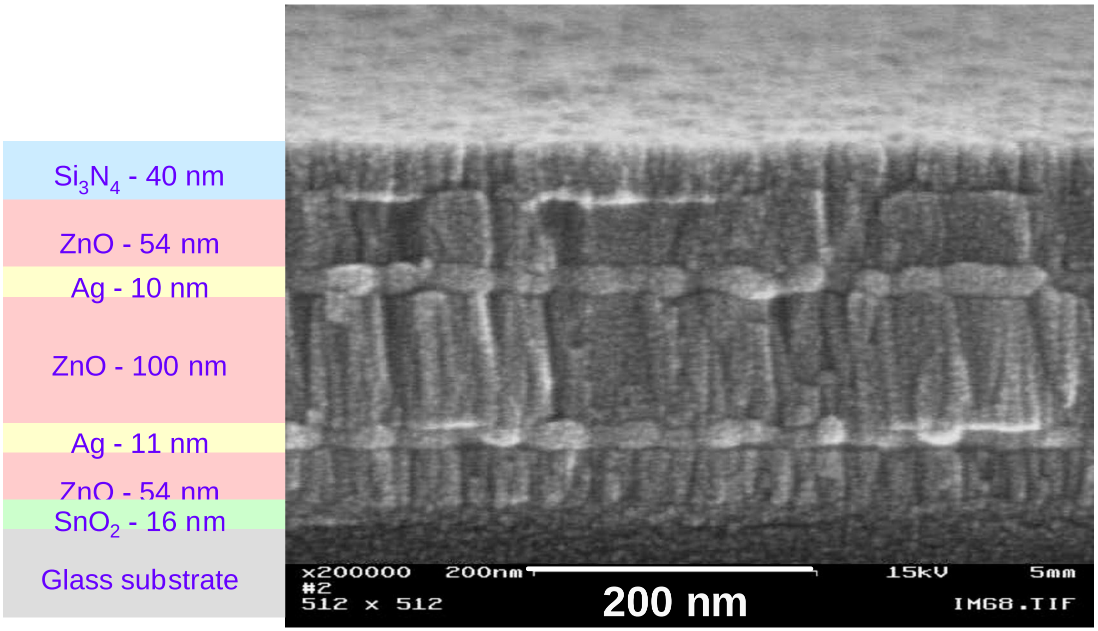
ed low-emissivity coatings(3/5)



☞Role of the SnO_2 underlayer

Improve adhesion on glass

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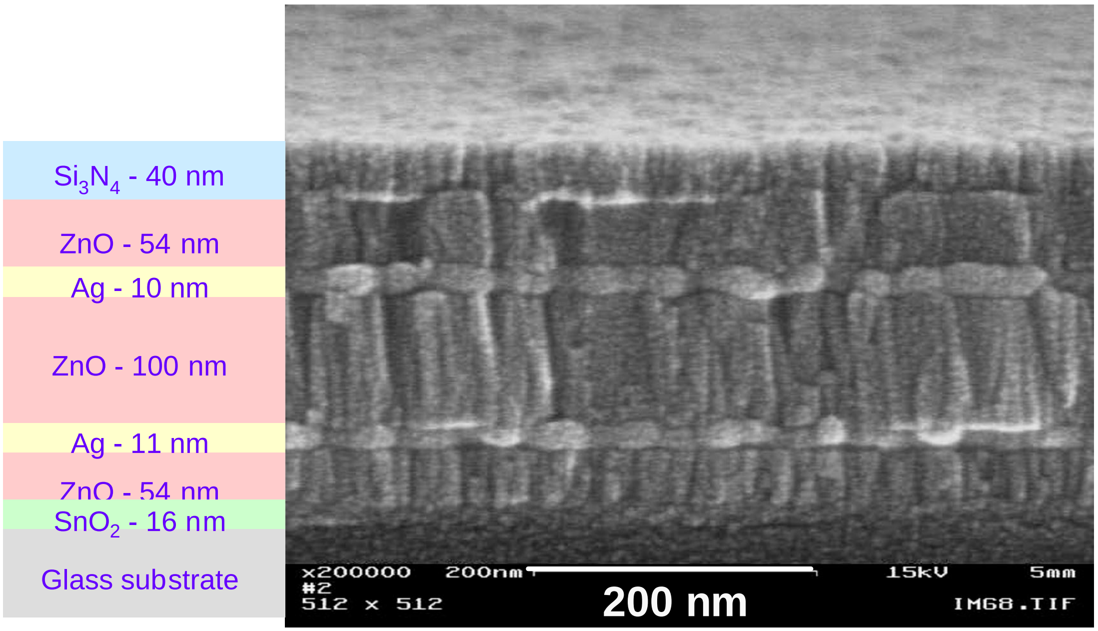
Silver based low-emissivity coatings(4/5)



☞Role of the ZnO layers

- **Improve crystallinity of the silver films**
- **Optical interferences for improving transparency in the visible**

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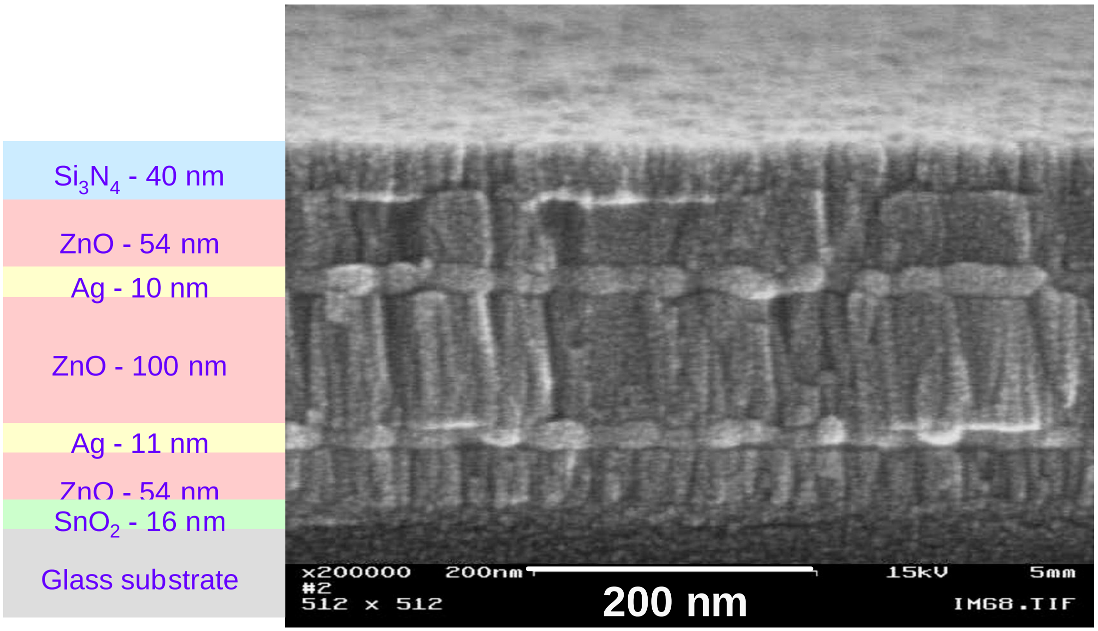
ed low-emissivity coatings(5/5)



☞Role of the Si_3N_4 overlayer

- **Chemical barrier (H_2O)**
- **Mechanical protection of Ag layers**

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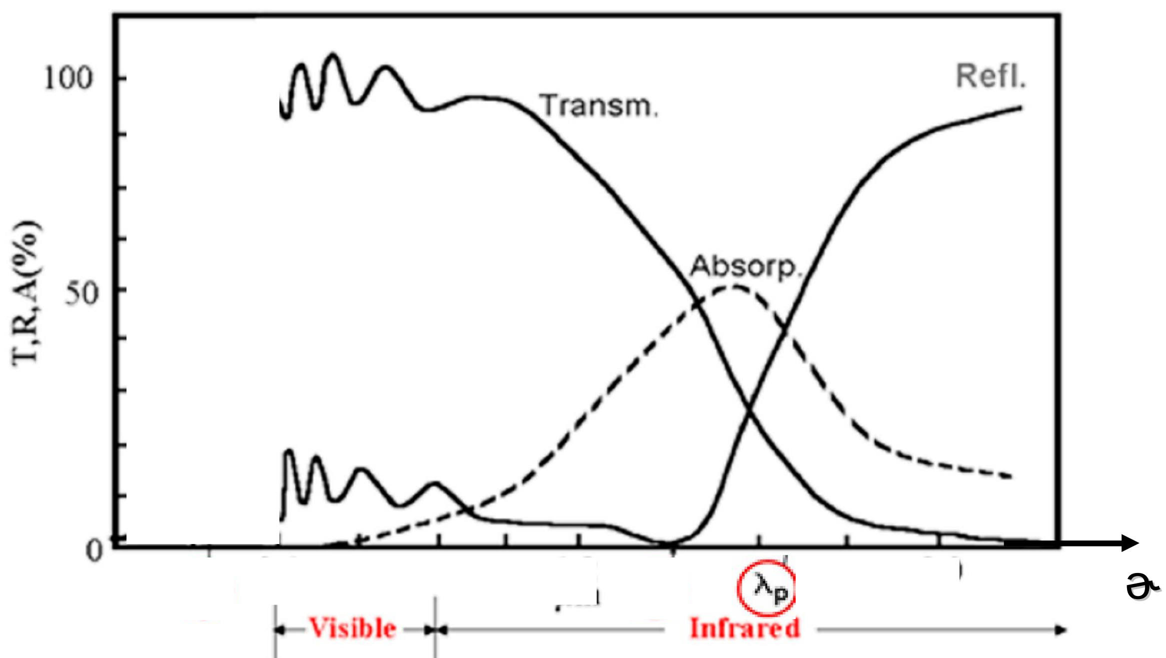
issive semiconducting oxide coating(1/6)

☞ **Find a metal such that ɤ$_p$ is between the visible and the thermal infrared**



→ $$\lambda_p = \frac{2\pi c}{\omega_p} = \frac{2\pi c}{e}\sqrt{\frac{\varepsilon_0 m}{N}} \approx 2\ \mu m$$

→ **N å 3. 10^{20} cm^{-3}. It can not be a normal metal : N_{metal} > 1. 10^{22} cm^{-3}**

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…issive semiconducting oxide coating(2/6)

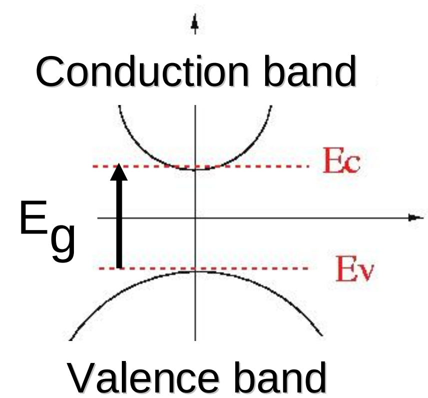
☞**This semiconductor should be very heavily doped**

remind : in semiconductor chips, N < 1. $10^{18}cm^{-3}$

☞**This semiconductor should transmit visible light**

→ **Energy band gap E_g such that**

$$\lambda_g = \frac{2\pi\hbar c}{E_g} < 400\ nm$$



→ **Eg Ó3 ev**

☞**But the bandgap should not be too large,**

because large bandgap semiconductors are not easy to dope

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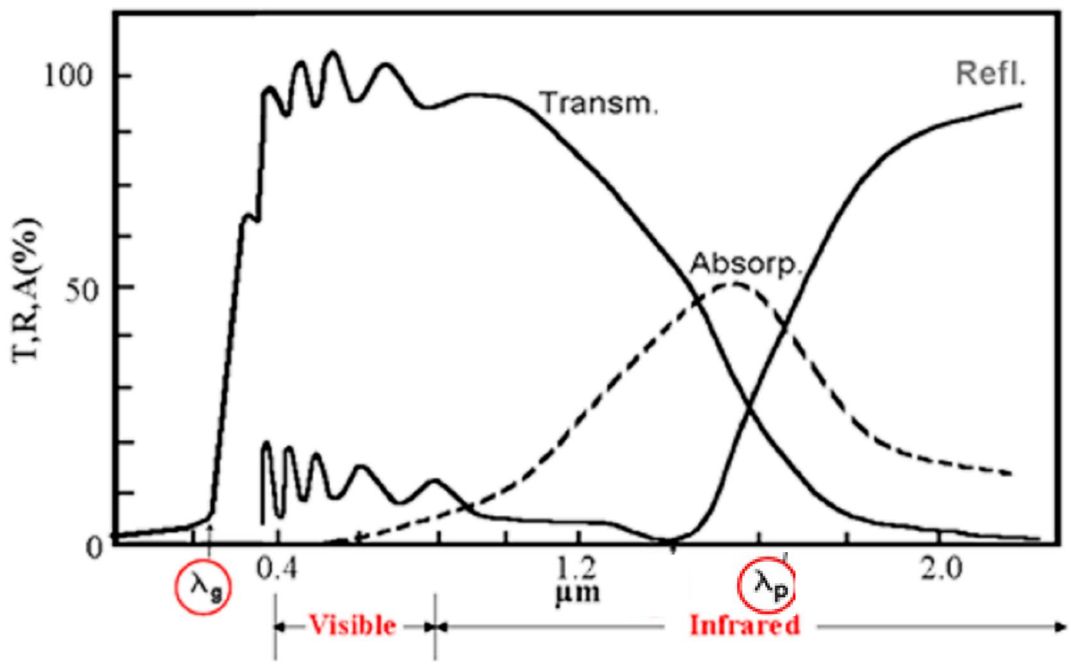
issive semiconducting oxide coating(3/6)

☞At last, this is what we need :



☞Small-gap oxides represent a natural choice

Material	Symbol	Band Gap (eV)
Cadmium telluride	CdTe	1.49
Diamond	C	5.5
Gallium antimonide	GaSb	0.7
Gallium arsenide	GaAs	1.43
Gallium nitride	GaN	3.1
Germanium	Ge	0.67
Indium arsenide	InAs	0.36
Indium oxide	In_2O_3	3.75
Lead telluride	PbTe	0.29
Silicon	Si	1.11
Silicon carbide	SiC	2.86
Zinc oxide	ZnO	3.37
Aluminum oxide	Al2O3	7

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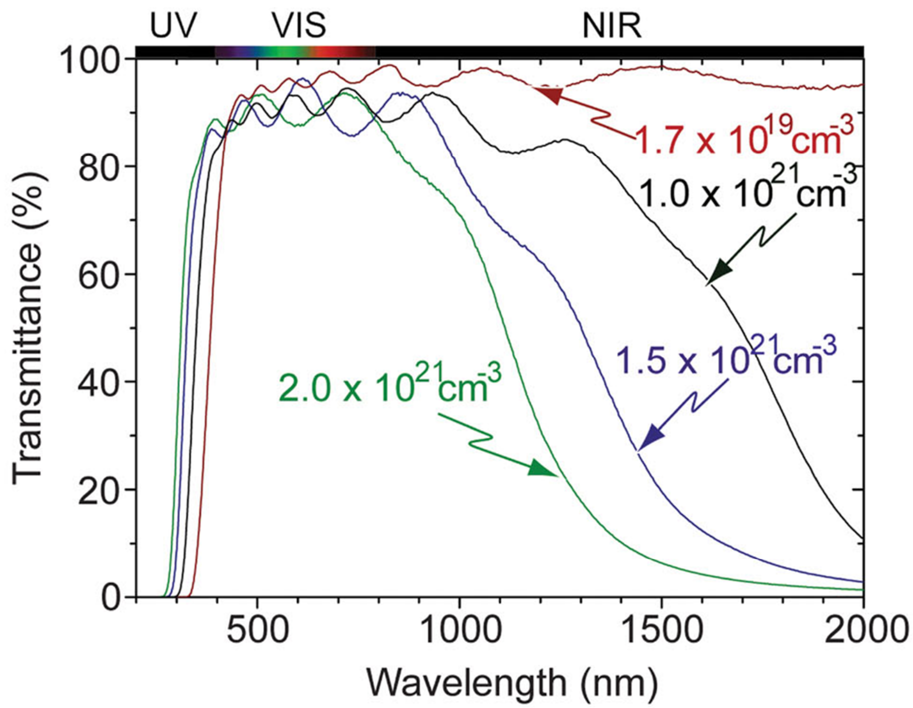
…issive semiconducting oxide coating(4/6)

☞**It works well**



Tin doped indium oxide (ITO)

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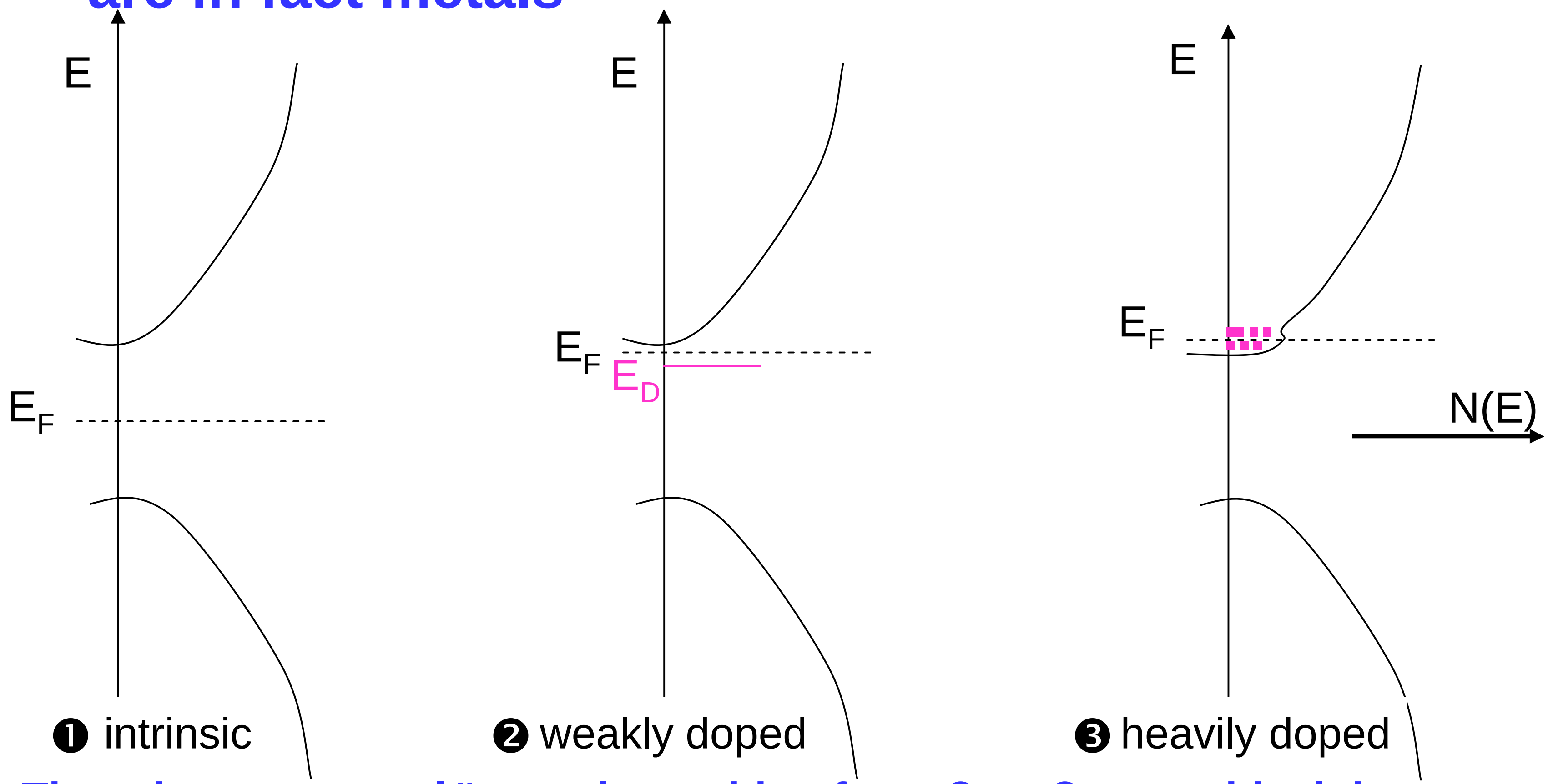
Principle of low-emissive semiconducting oxide coating(5/6)

☞ **It works well because heavily-doped semiconductors are in fact metals**



There is a non-metal ï metal transition from ❷ to ❸ at a critical donor concentration $N_{D,c}$ defined by $a_H^* . N_{D,c}^{1/3} = 0.25$ (Mott criterion).

a_H^* is the effective Bohr radius of the hydrogen-like donor center.

For most semiconductors, $N_{D,c}$ is between 10^{17} and 10^{19} cm^{-3}

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Oxides as highly-doped semiconductors(6/6)

☞Doping mechanism : case of tin-doped indium oxide

. Two doping mechanisms

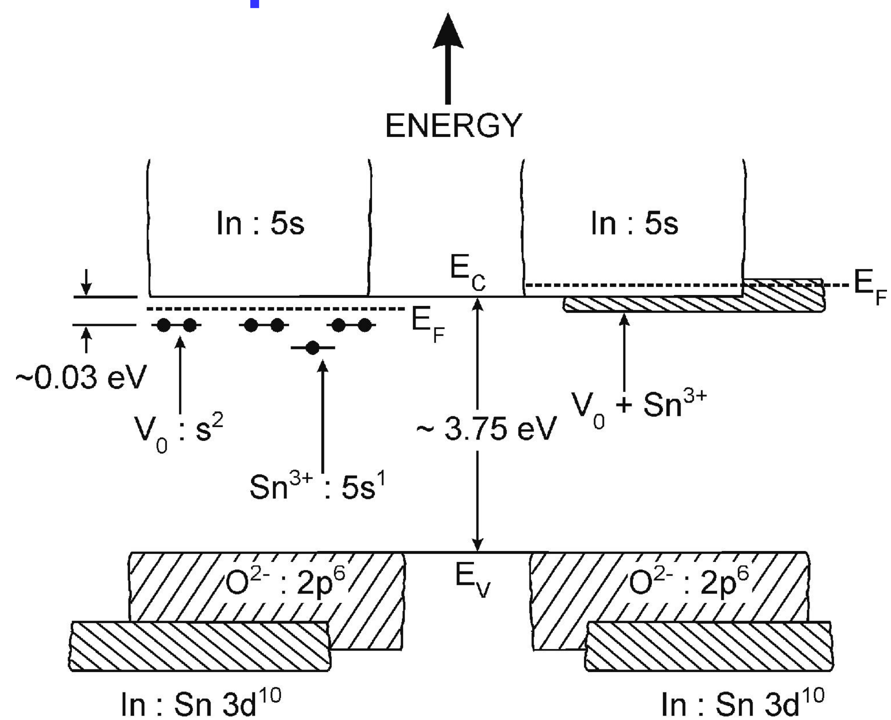
1. Oxygen vacancies

In_2O_{3-x}

Difficile à contrôler

2. Substitution of indium by tin $In^{3+}_{2-x}Sn^{4+}_{x}O^{2-}_{3}\left[xe^{-}_{C.B.}\right]$

. Both are n-type, with low activation energy



$N < 10^{18}$ cm^{-3}
Non-degenerate semiconductor

$N > 10^{18}$ cm^{-3}
Degenerate semiconductor

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Electrochromics(1/2)

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Electrochromics(1/2)

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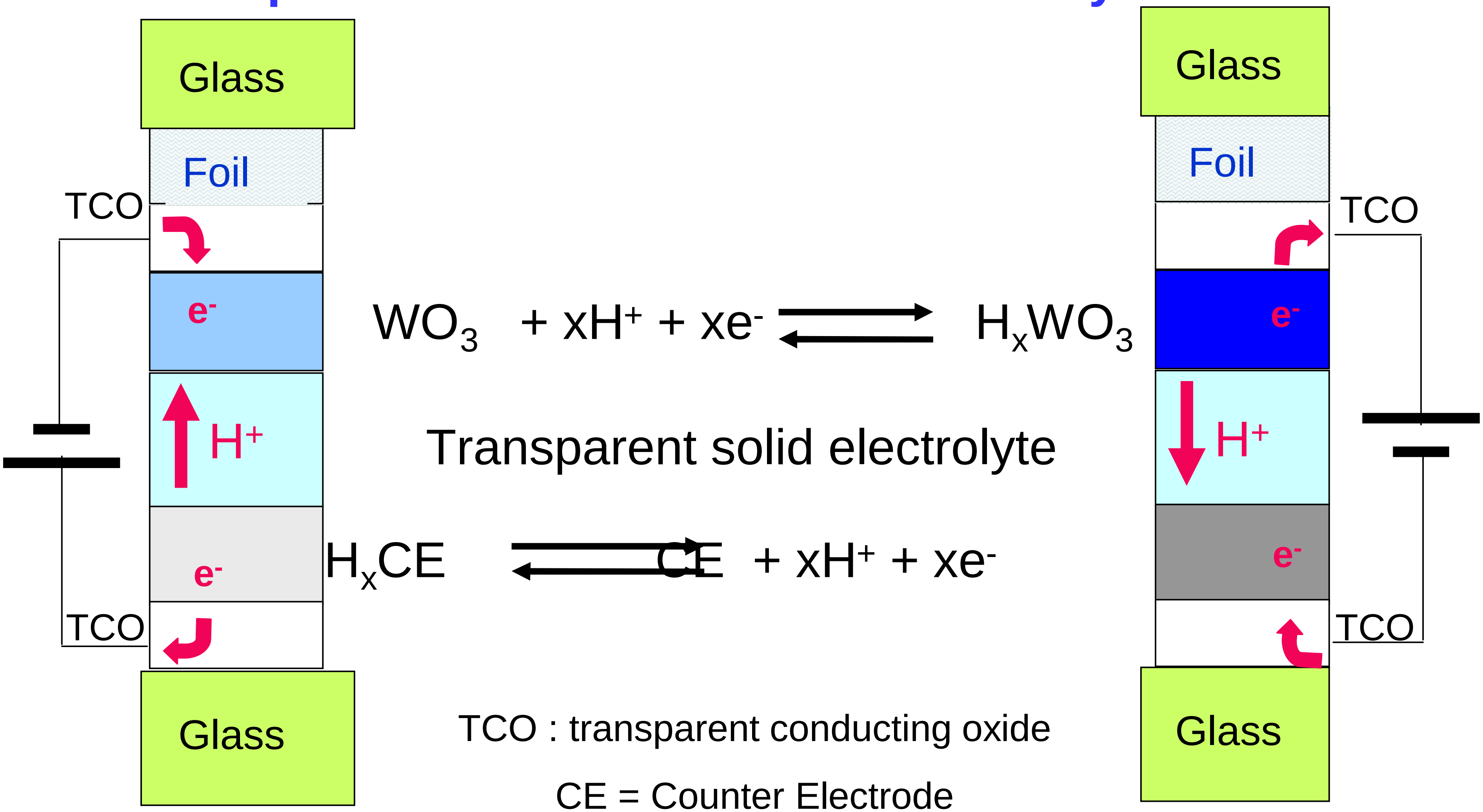
Electrochromics(2/2)

☞Principle : all solid state electrochemistry



$$WO_3 + xH^+ + xe^- \rightleftharpoons H_xWO_3$$

Transparent solid electrolyte

$$H_xCE \rightleftharpoons CE + xH^+ + xe^-$$

TCO : transparent conducting oxide

CE = Counter Electrode

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Already three generations of photovoltaic cells

First generation

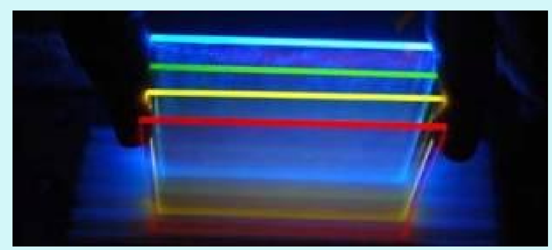
Silicon wafers

Second generation

- **Amorphous silicon thin films**
- **CIGS thin films**

Third generation

- **Dye-sensitized cells**
- **Electronductive polymers**



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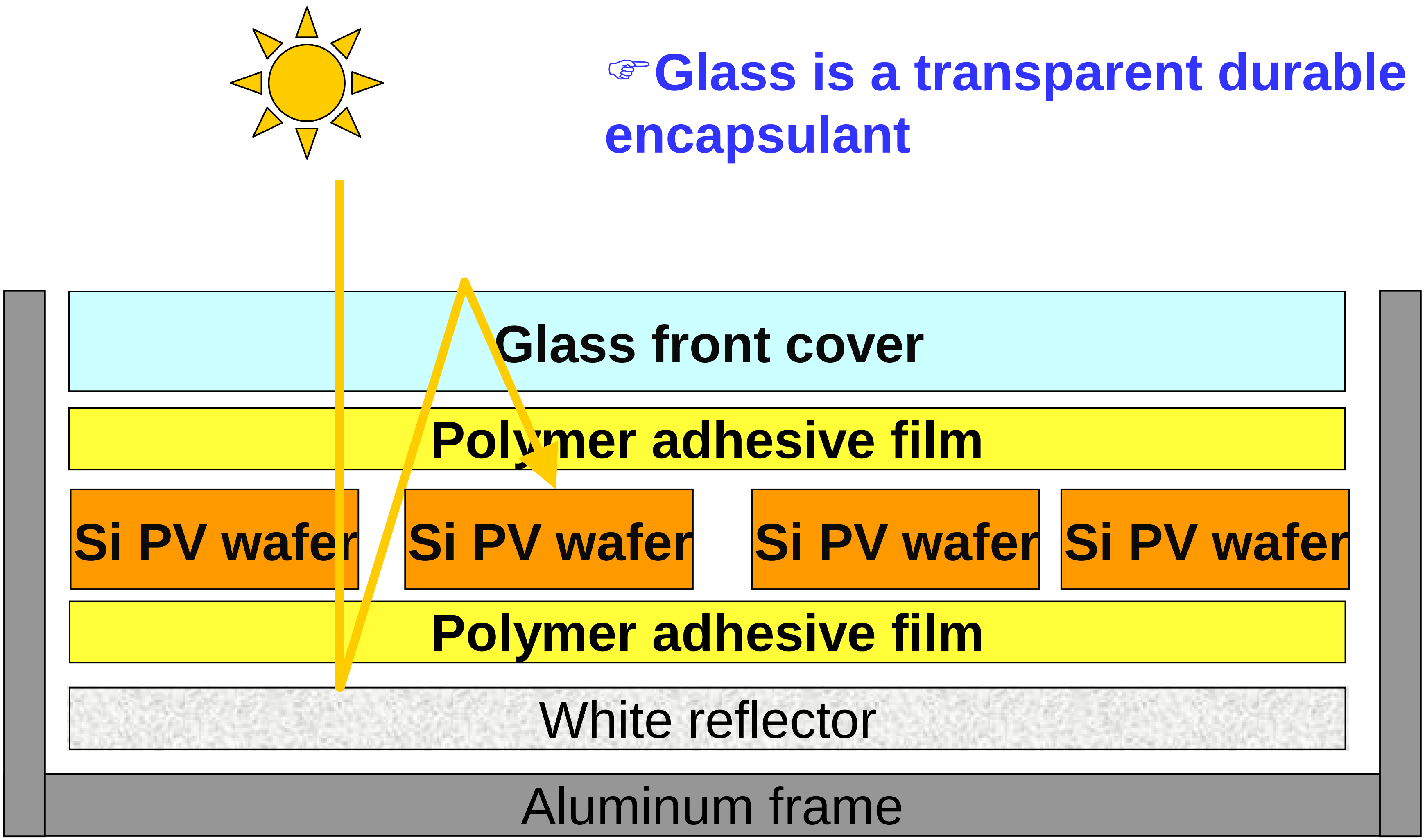
Glass for generation 1 photovoltaics(1/8)

☞Glass is a transparent durable encapsulant



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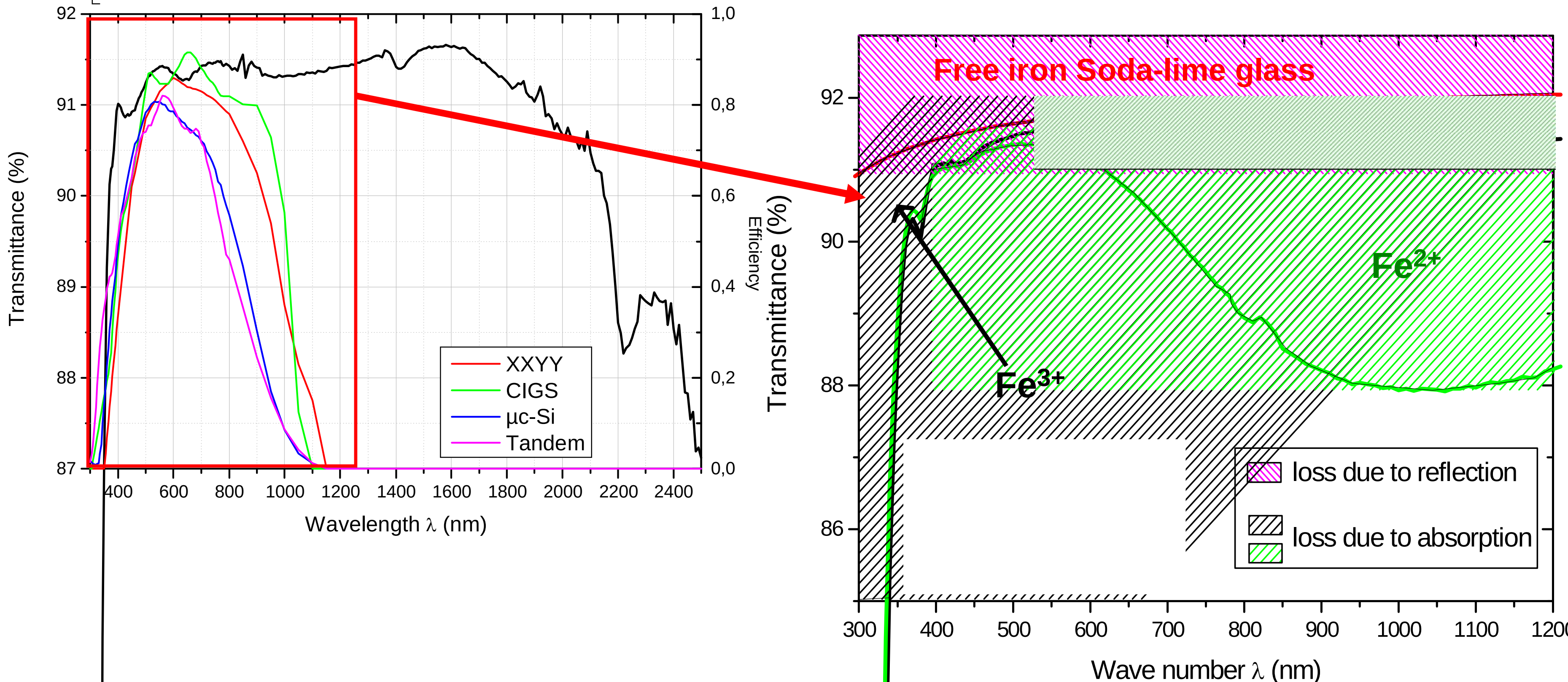
Glass for generation 1 photovoltaics(2/8)

PV solar cells efficient between 300 and 1200nm

Loss of energetic transmission due to reflection and/or absorption



☞**We need pure (low Fe contain), oxydized and low refractive index glass**

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Glass for generation 1 photovoltaics(3/8)

☞Purity is money

	Fe_2O_3	Raw Material price
Standard glass	700 ppm	63 ú/ton
PV glass	100 ppm	100 ú/ton

☞Oxidation is chemistry

$$Fe^{2+} + M^{X+} \leftrightarrow Fe^{3+} + M^{(X-1)}$$

M : Sb, Mn, Ce, é .

☞Low refractive index is composition

	n
SiO2	1.471
Al2O3	1.520
K2O	1.575
Na2O	1.590
MgO	1.610
CaO	1.730

Increasing n

Increase SiO_2 and Al_2O_3
Decrease CaO and MgO

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Glass for generation 1 photovoltaics(4/8)

☞Hydrolytic resistance

Mixing sodium and potassium and calcium and magnesium, to get a mixed alkali effect and a mixed alkaline-earth effect. This effects are known to decrease mobility of cations and hence slow down the hydrolytic attack.

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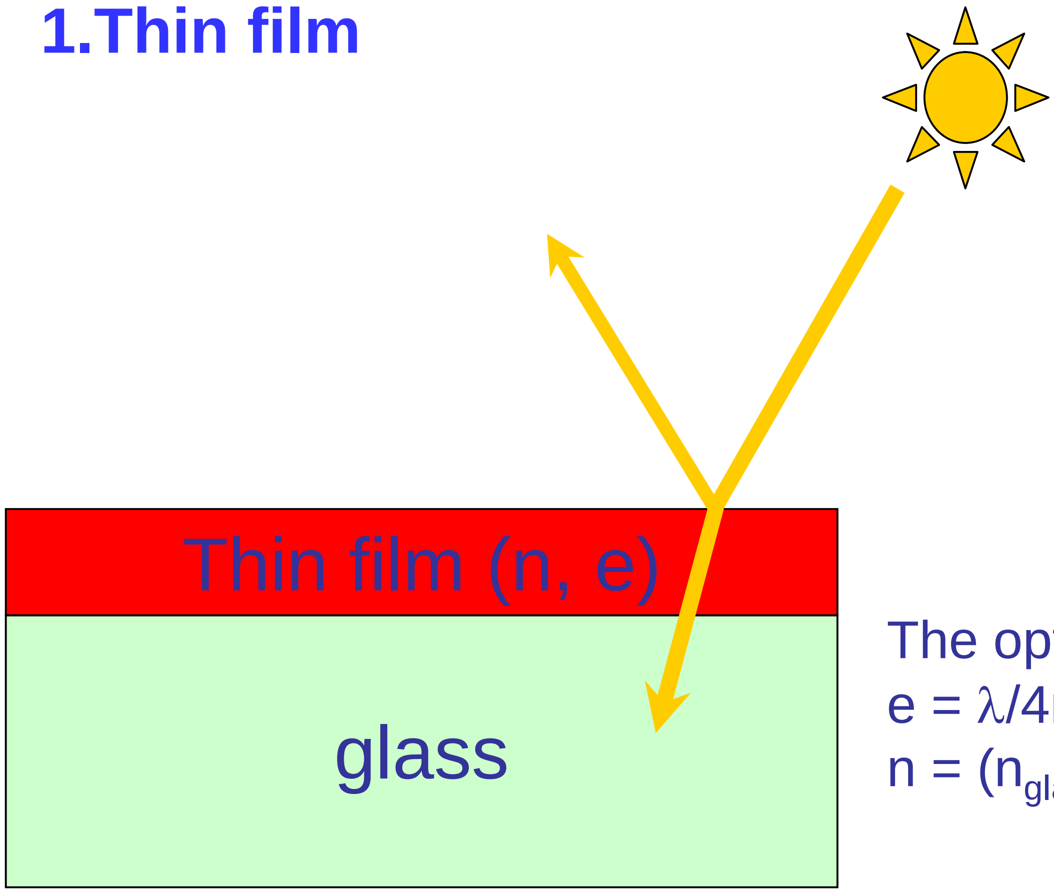
Glass for generation 1 photovoltaics(5/8)

☞**Surface treatments for anti-reflection and light-trapping :**

1.Thin film



The optimum AR efficiency would be for
$e = \lambda/4n \sim 100$ nm
$n = (n_{glass})^{1/2} \sim 1.21$

No known material display as low a refractive index !
→ We have to design it !

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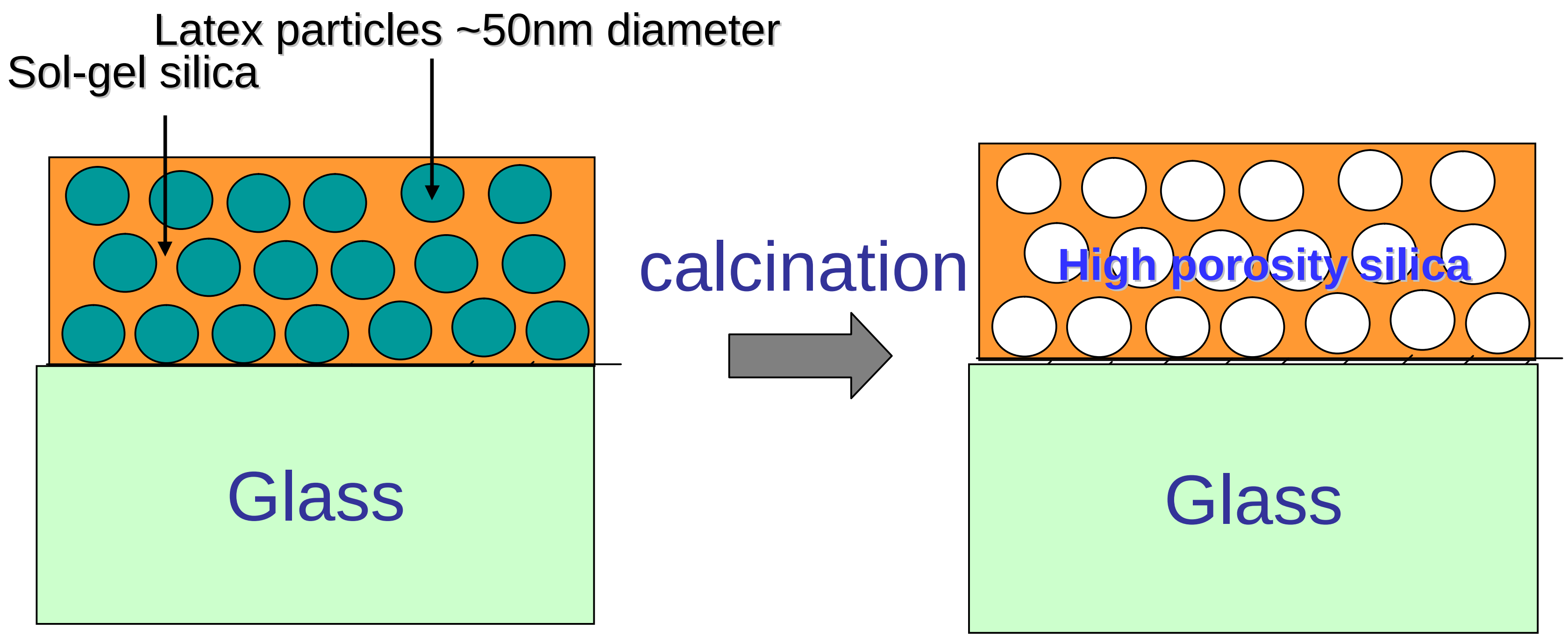
Glass for generation 1 photovoltaics(6/8)

☞low refractive index thin film



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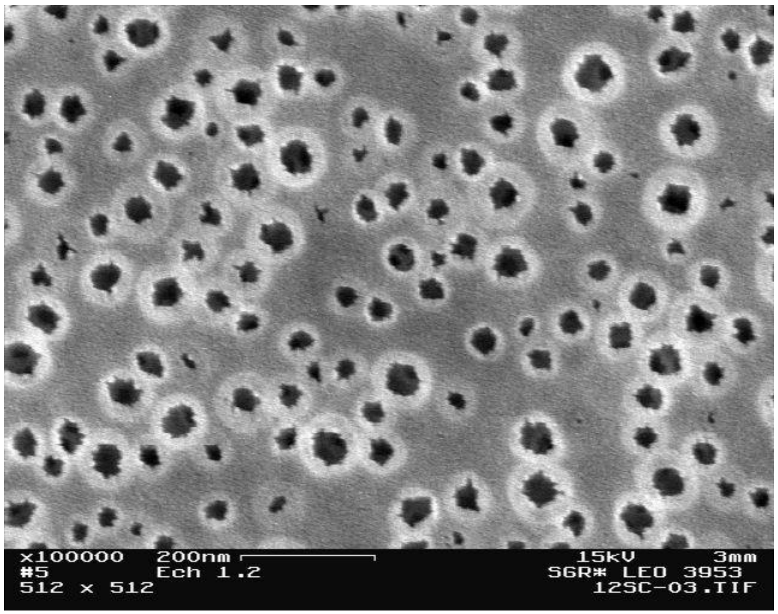
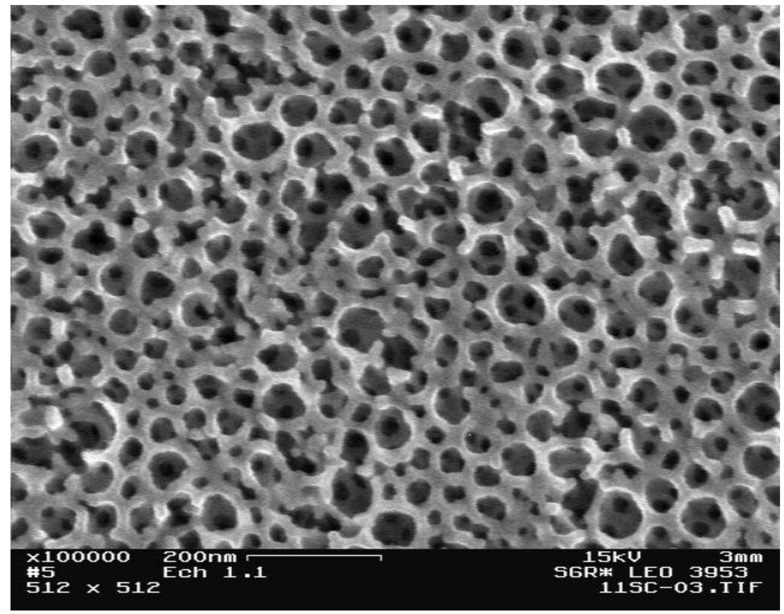
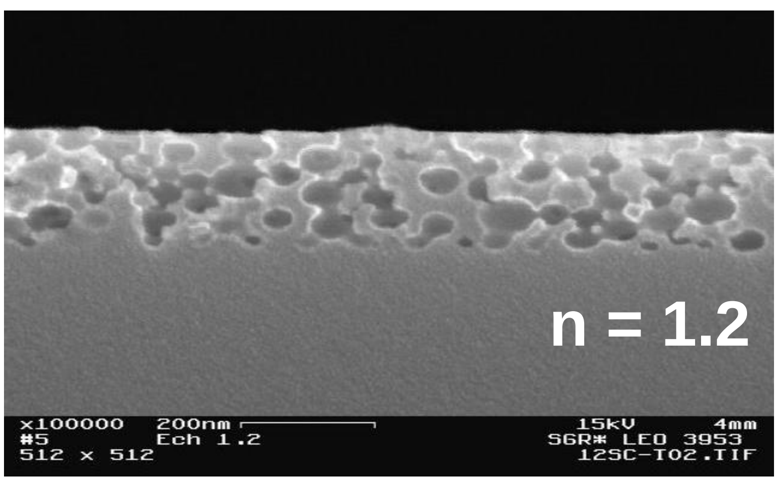
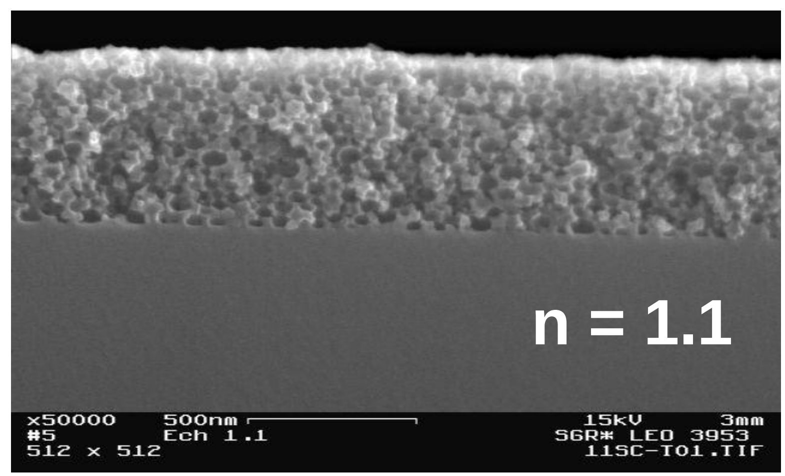
Glass for generation 1 photovoltaics(7/8)

☞low refractive index mesoporous silica thin films









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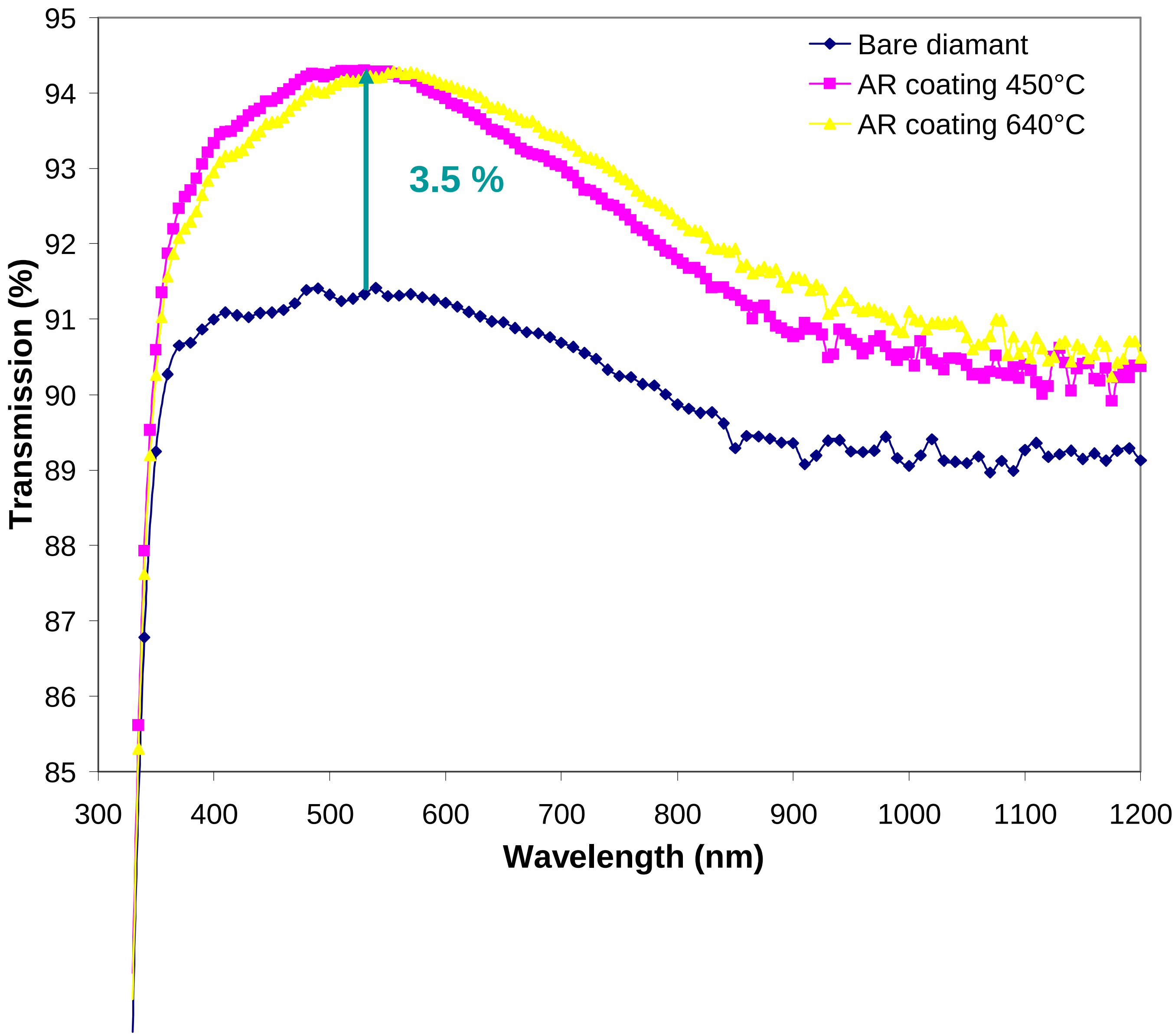
Glass for generation 1 photovoltaics(8/8)

☞Transmission gain with AR mesoporous coating



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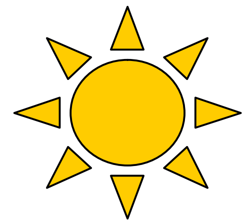
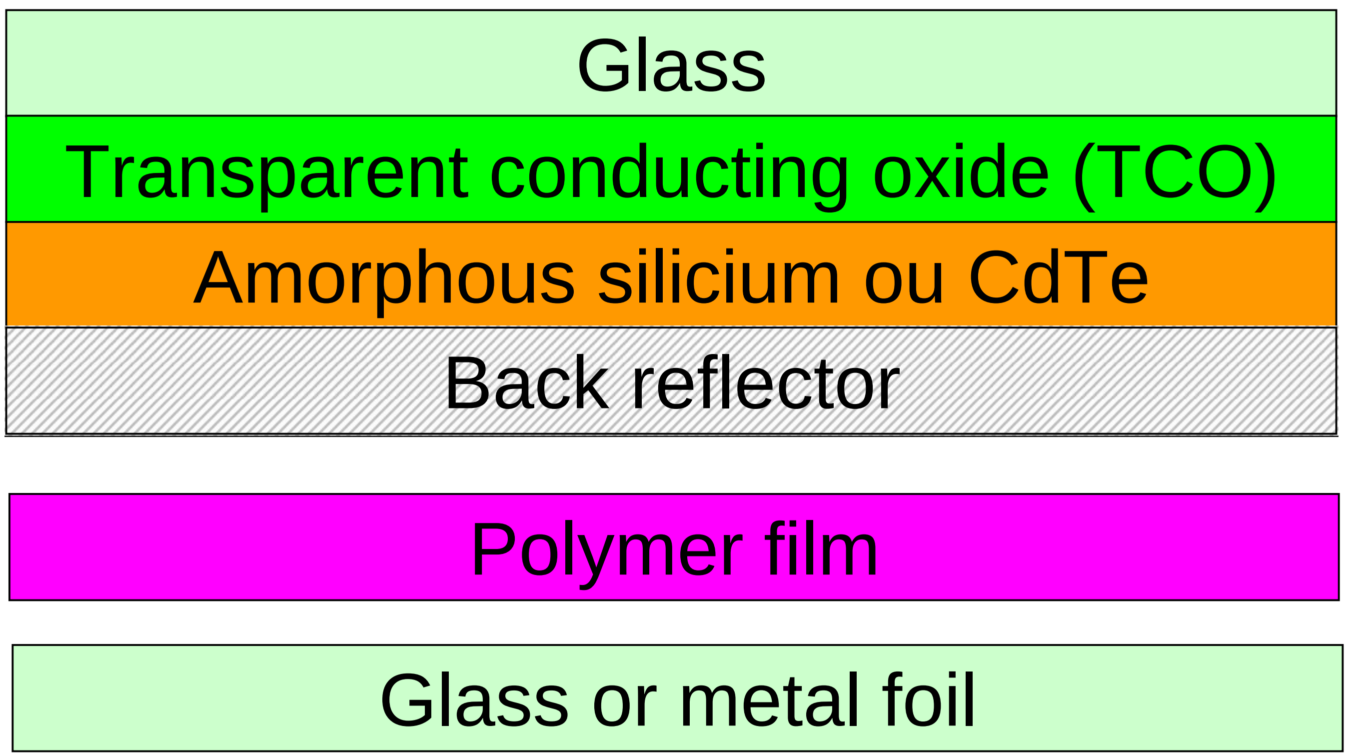
Glass for generation 2 photovoltaics(1/10)

☞ **Glass is a transparent durable encapsulant and a substrate for thin film**





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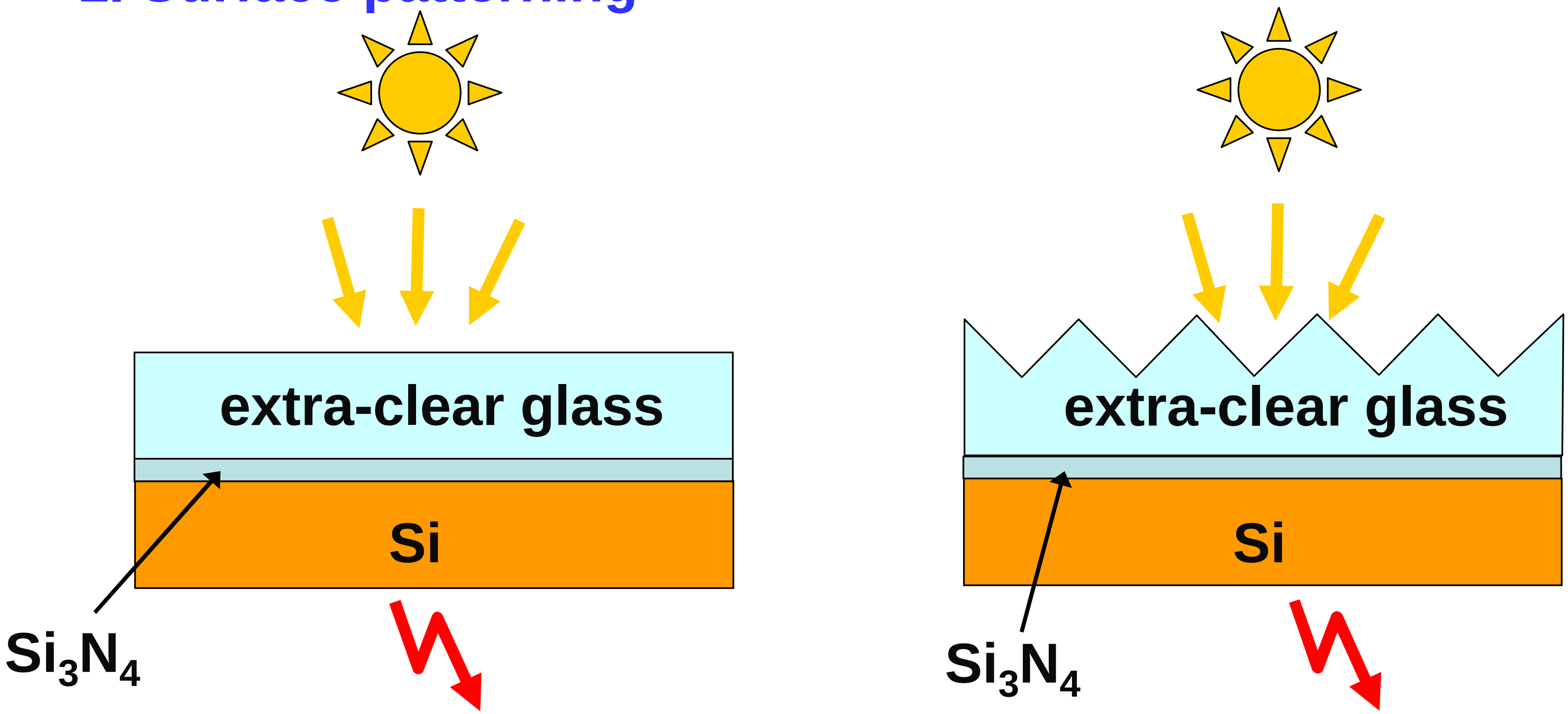
Glass for generation 2 photovoltaics(2/10)

☞Surface treatments for anti-reflection and light-trapping :

1. Surface patterning



2 effects: anti-reflection and light trapping

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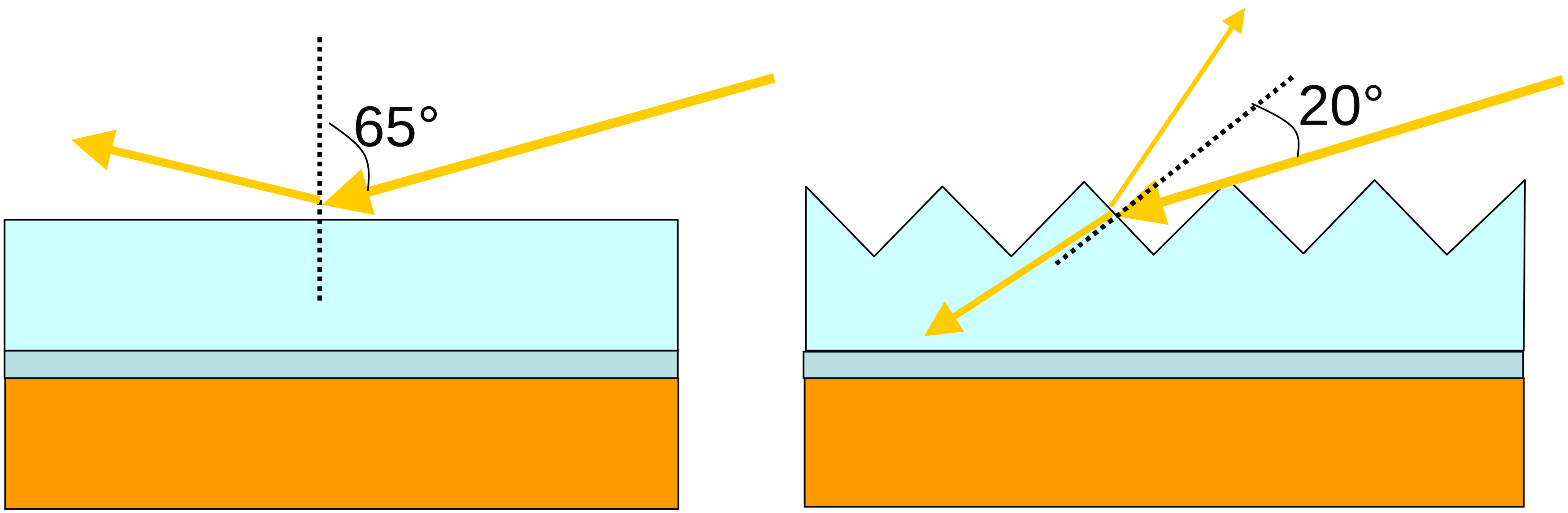
Glass for generation 2 photovoltaics(3/10)

☞ Antireflection



Reduction of the angle of incidence

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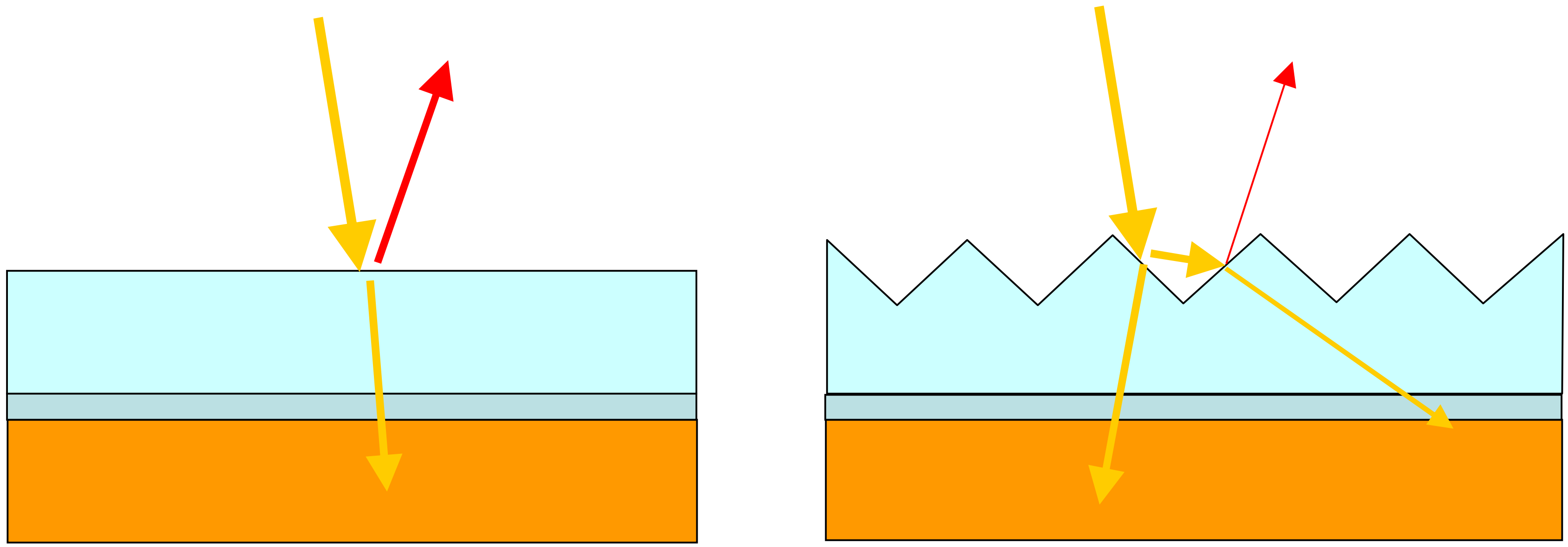
Glass for generation 2 photovoltaics(4/10)

☞Light trapping



Several reflections are needed to definitively « loose » a light ray

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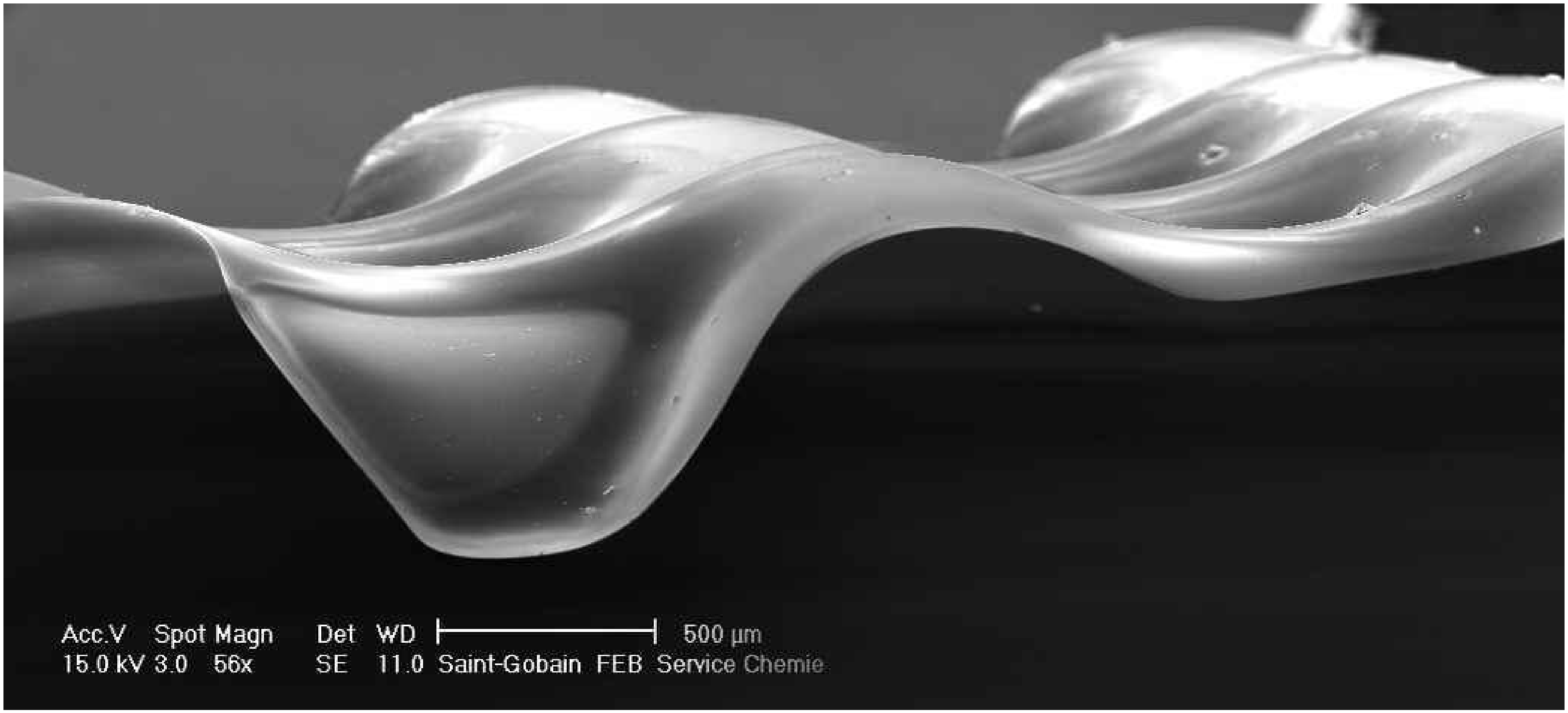
Glass for generation 2 photovoltaics(5/10)

☞Patterned glass



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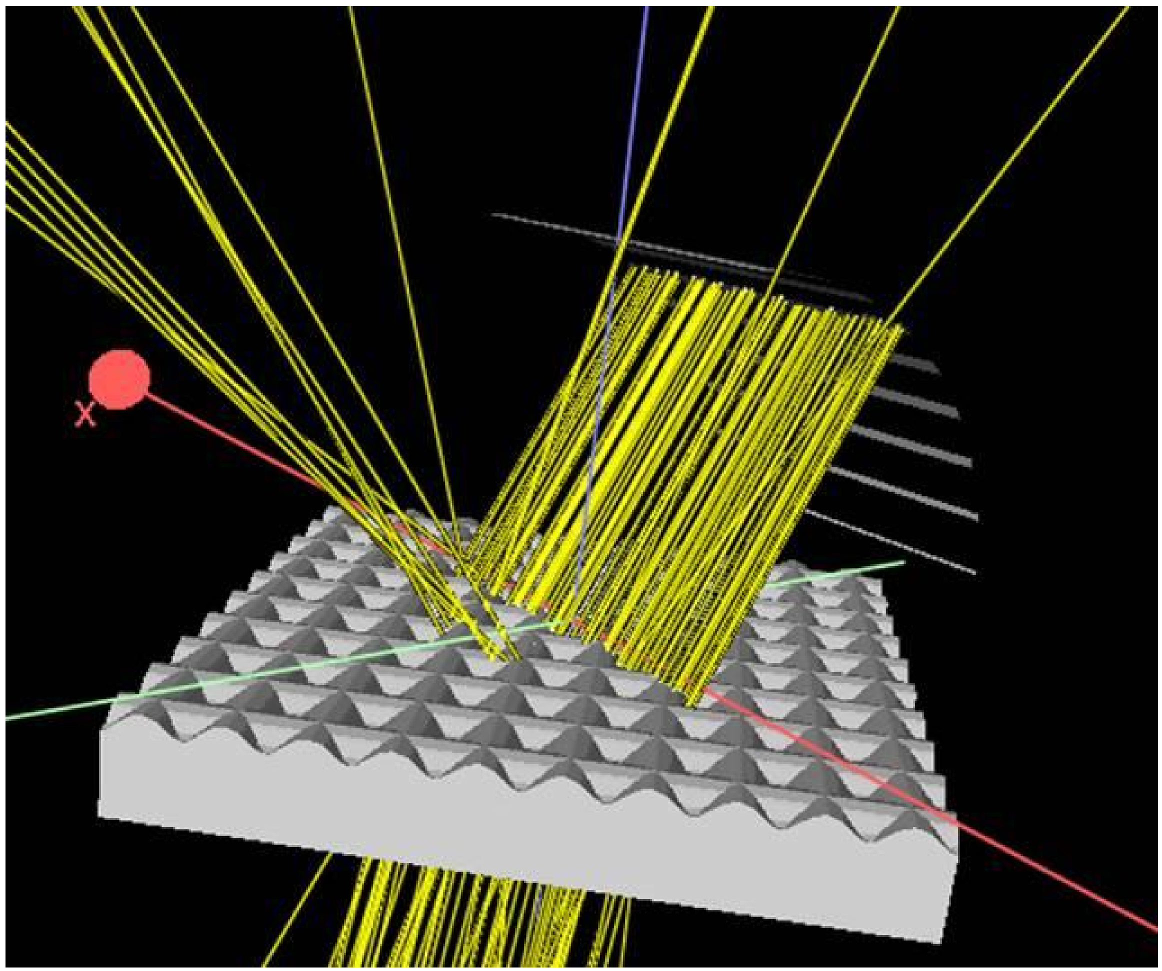
Glass for generation 2 photovoltaics(6/10)

☞Optical simulations of patterned glass (Monte-Carlo ray tracing)



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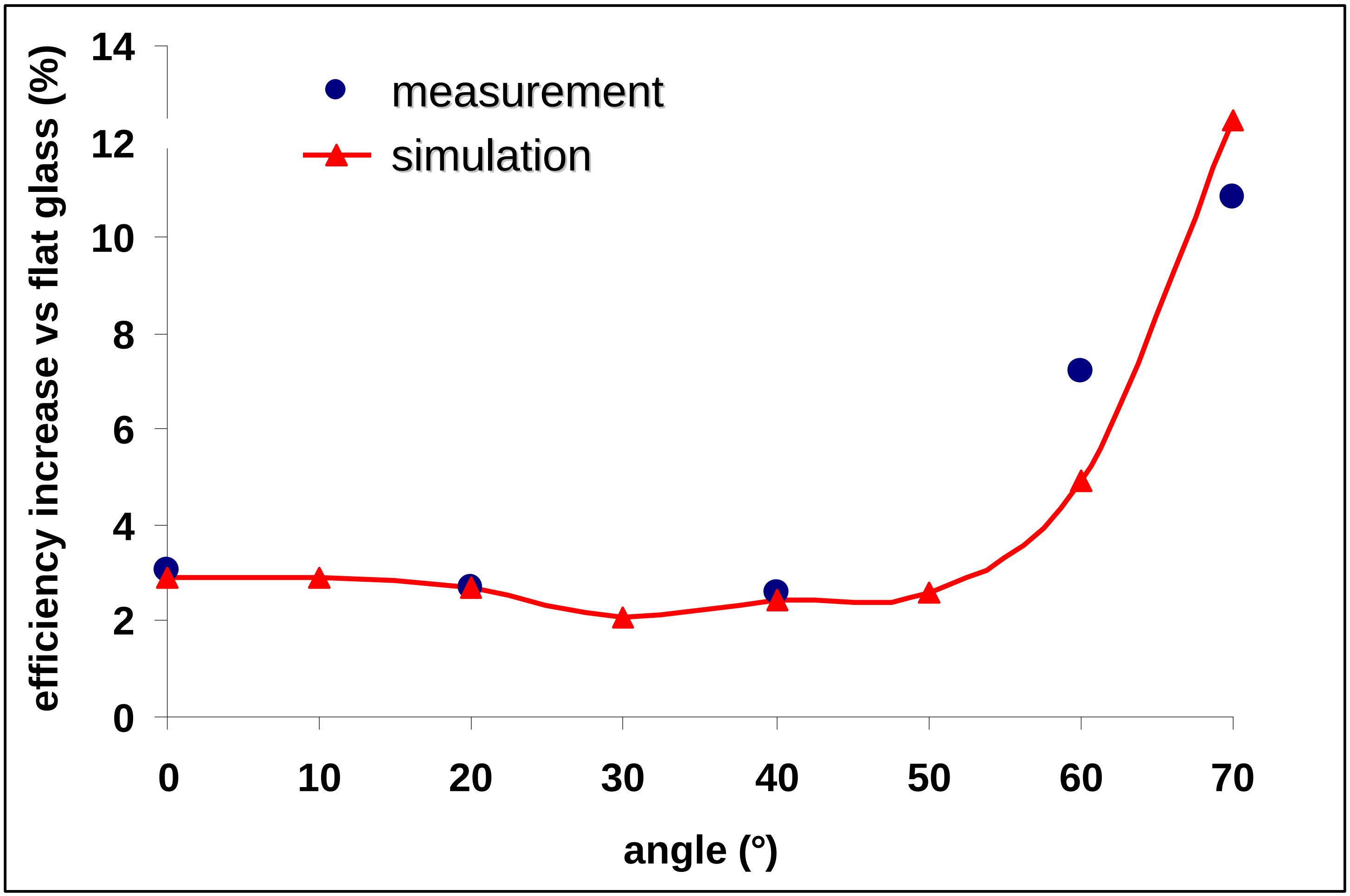
Glass for generation 2 photovoltaics(7/10)

☞ Increase of energy conversion efficiency



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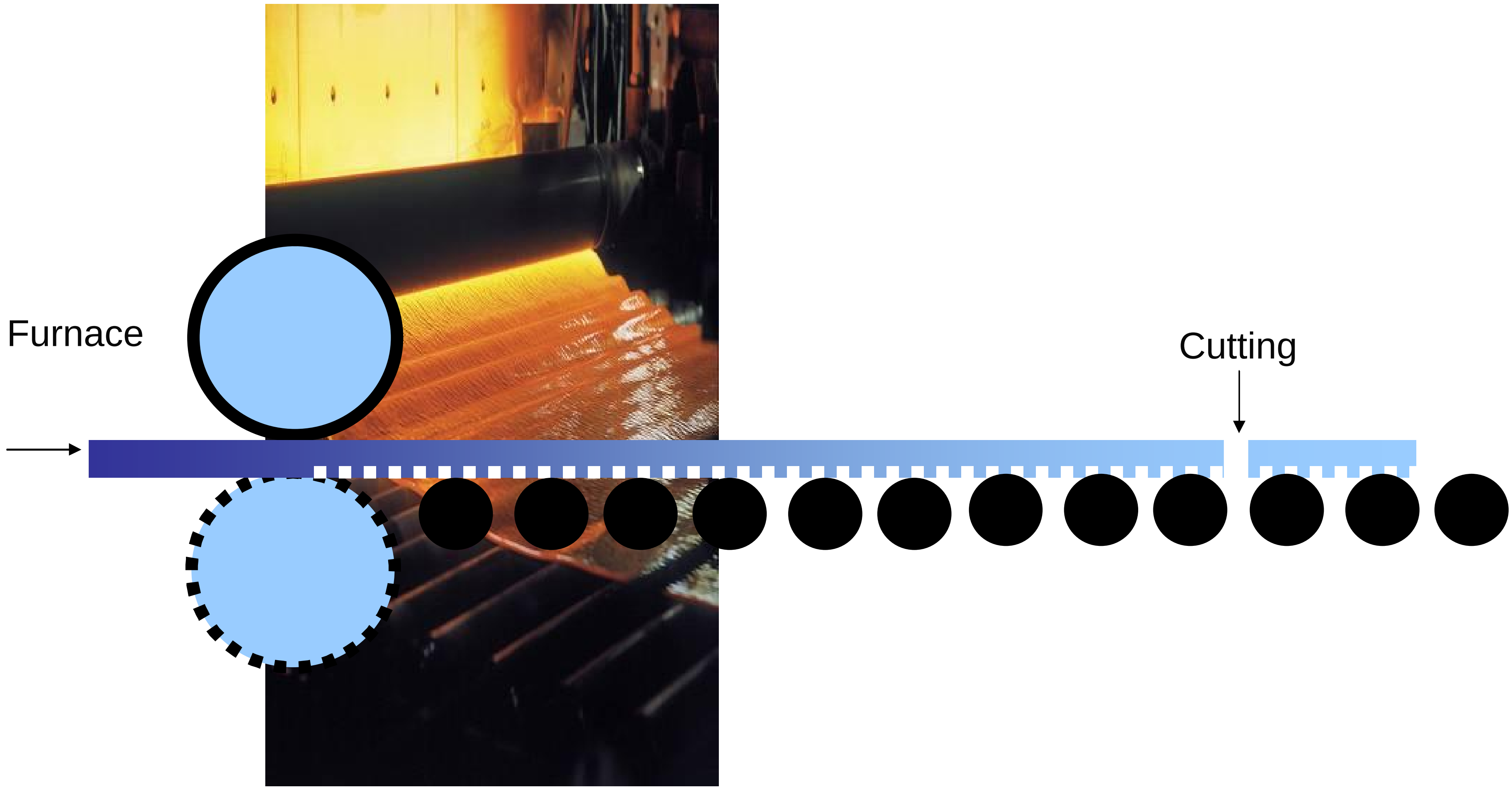
Glass for generation 2 photovoltaics(8/10)

☞Texturation process : lamination between master rolls



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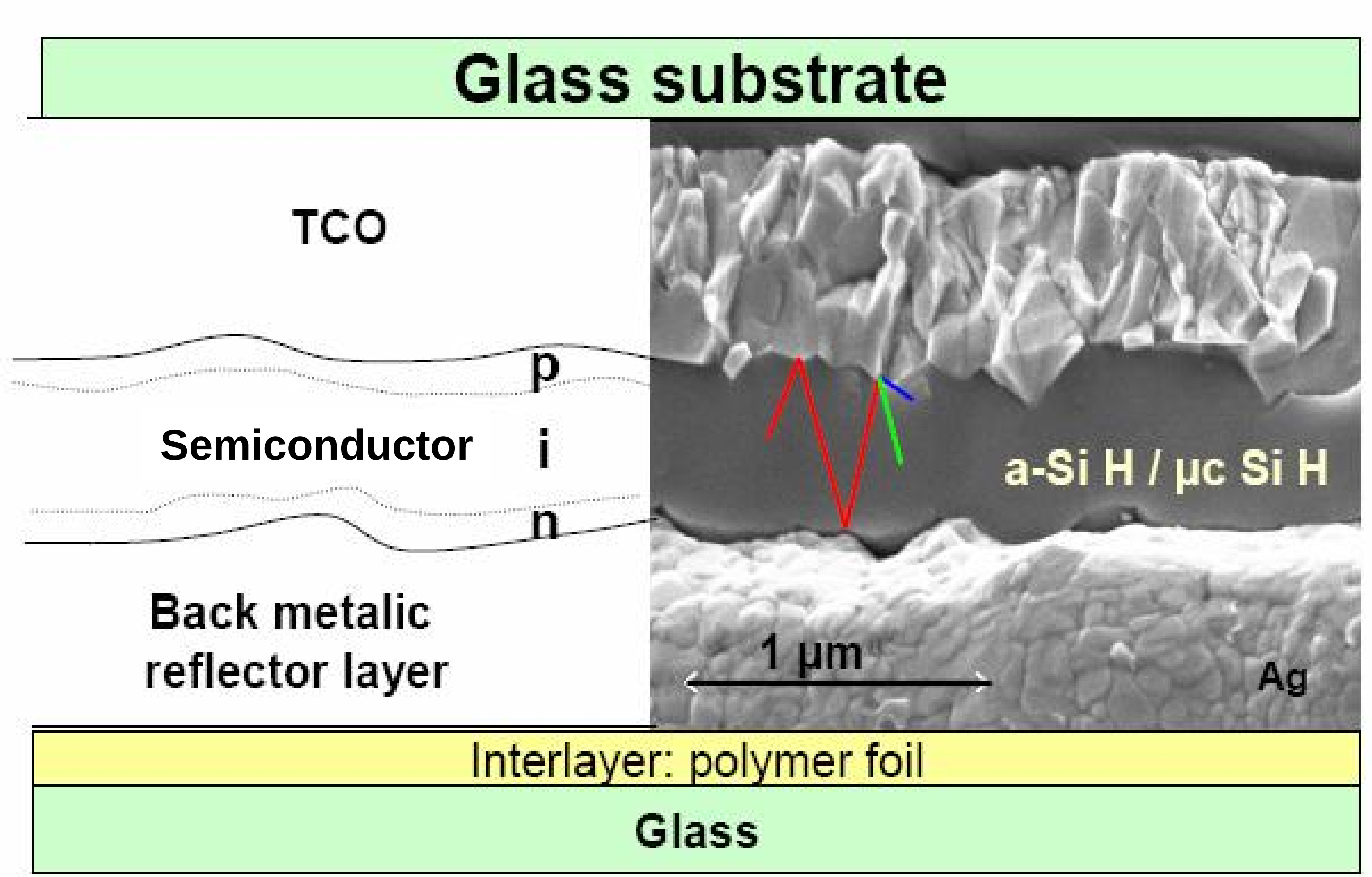
Glass for generation 2 photovoltaics(9/10)

☞Glass makers master all the technologies needed for the production of Gen 2 solar cells



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Glass for generation 2 photovoltaics(10/10)

☞Glass makers master all the technologies needed for the production of Gen 2 solar cells

→ Some of them become industrial players in solar cells : ex. Avancis, a subsidiary of Saint-Gobain

Extra-clear Glass

Polymer foil

Transparent conducting oxide (TCO)

Copper-Indium-Selenium

Molybdenum

Standard glass

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8. Nuclear fusion

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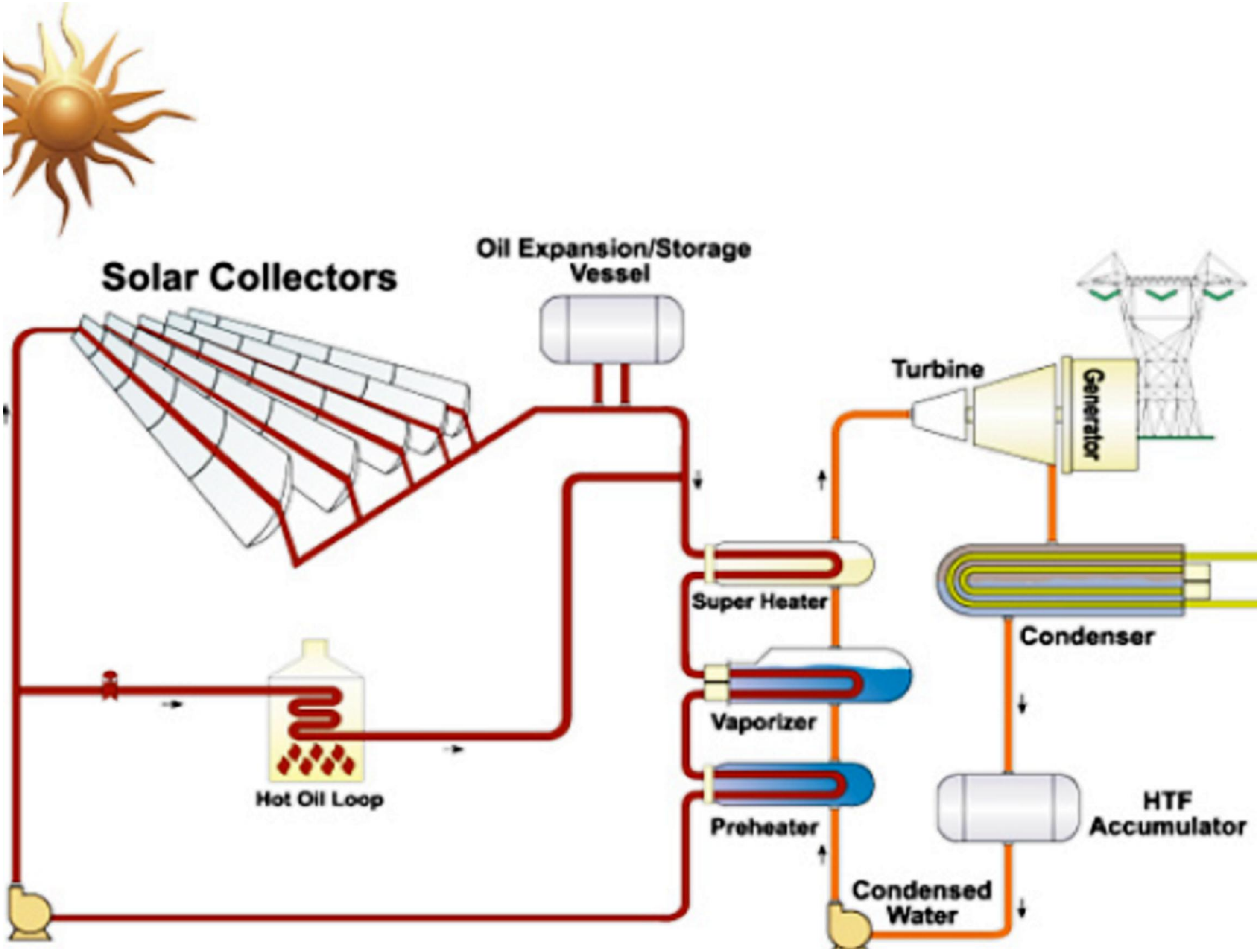
Concentrated solar power(1/2)



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Concentrated solar power(2/2)

☞**sunlight concentrating cylindrico-parabolic glass mirors**

ÅAntireflection coating on external glass surface
ÅGeometrical tolerance
ÅDurability of the reflective metal coating

☞**absorber tube**

In steel, with envelope tube consisting of coated, highly-transparent and robust borosilicate glass

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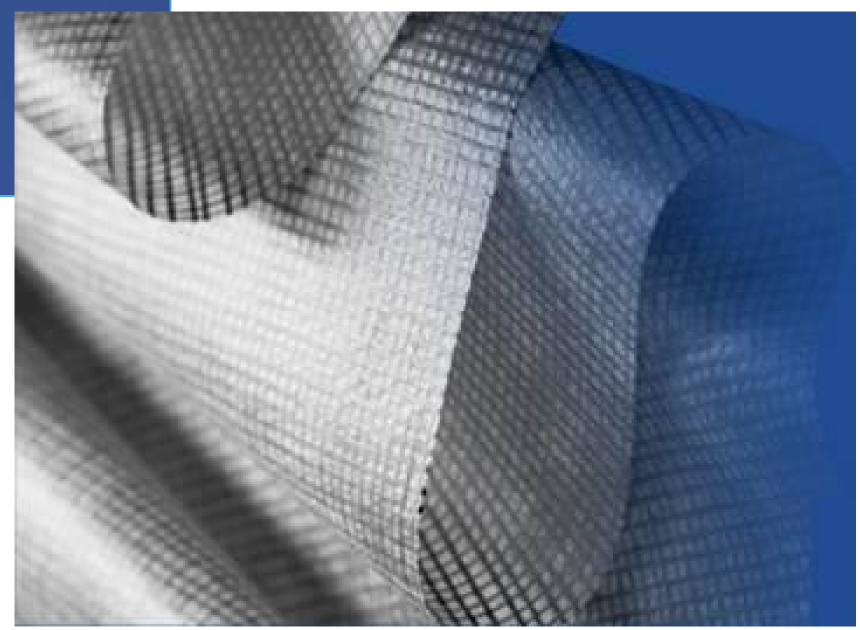
Reinforcing glass fabrics(1/2)



☞**High modulus glass**

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Reinforcing glass fabrics(2/2)

	E glass	Typical high modulus glass
SiO_2	55.7	59.5
Al_2O_3	13.2	15.9
CaO	23.1	14.8
MgO	0.2	8.8
B_2O_3	6.2	---
TLiquidus (°C)	1120	1230

☞**High modulus glass**

Young modulus å 94 GPa compared with 85 GPa for E glass.

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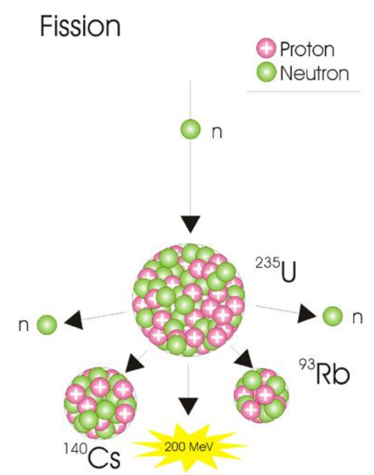
Glass for inerting nuclear waste(3/3)

☞òsimplifiedò composition of the CEA glass for nuclear waste confinement

Component (weight %)	SON68
Al_2O_3	4.9
B_2O_3	14.0
CaO	4.0
Fe_2O_3	2.9
Li_2O	2.0
MgO	~ 0
MoO_2	1.7
Na_2O	9.9
SiO_2	45.5
ZnO	2.5
Other components*	12.6
Total	100.0



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Glass for inerting nuclear waste(1/3)

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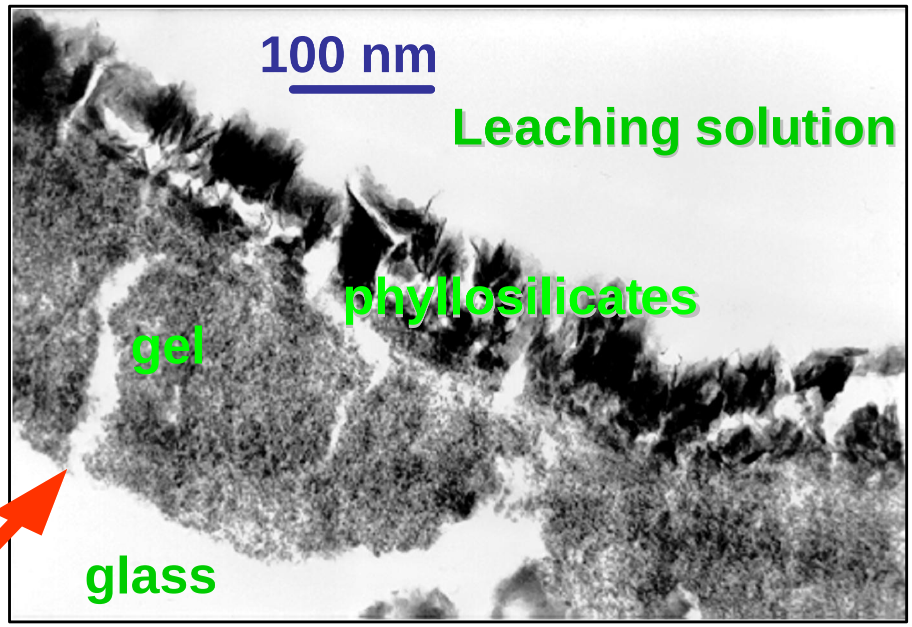

Glass-gel

☞**Need for very-long term hydrolytic resistance**

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Glass for inerting nuclear waste(2/3)

Elaborate a glass from waste is a compromise

Ability to accomodate the waste
Solubility (Cr, Ru, Rh, Pd, Ce, Pu, SO_4, Cl)
Phase separation (Mo, SO4, Cl, P)
Devitrification (Mo, P, F, Mg, …)
Maximize the waste loading

Formulation

Process / Technology

Ease of processing
Melting temperature
Viscosity, reactivity, residence time,
Electrical cond., thermal cond.
Additives needed

Glass performance

Properties for storage/disposal
Thermal stability
Chemical durability
Resistance to self irradiation
Mechanical properties

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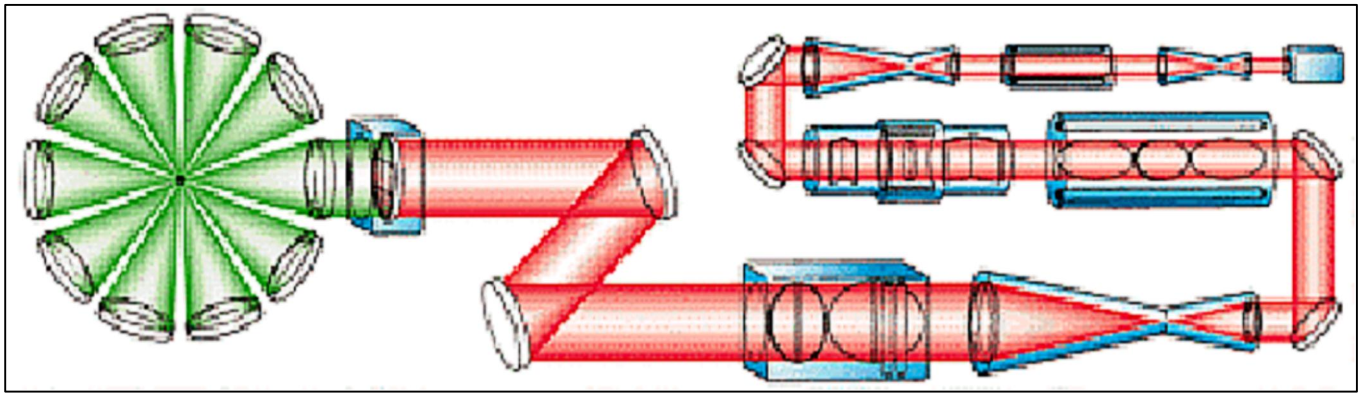
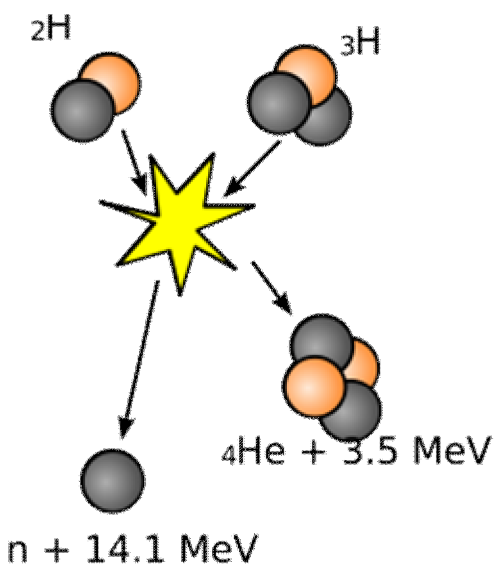
The energy of the future?(1/3)





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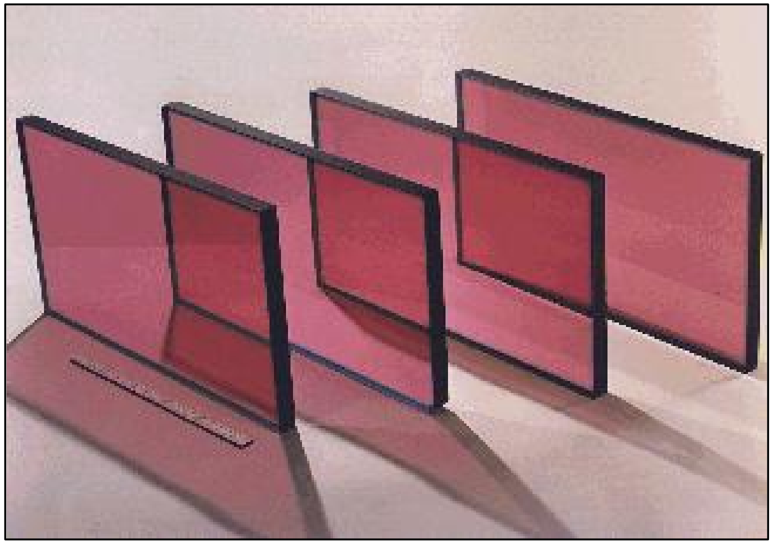
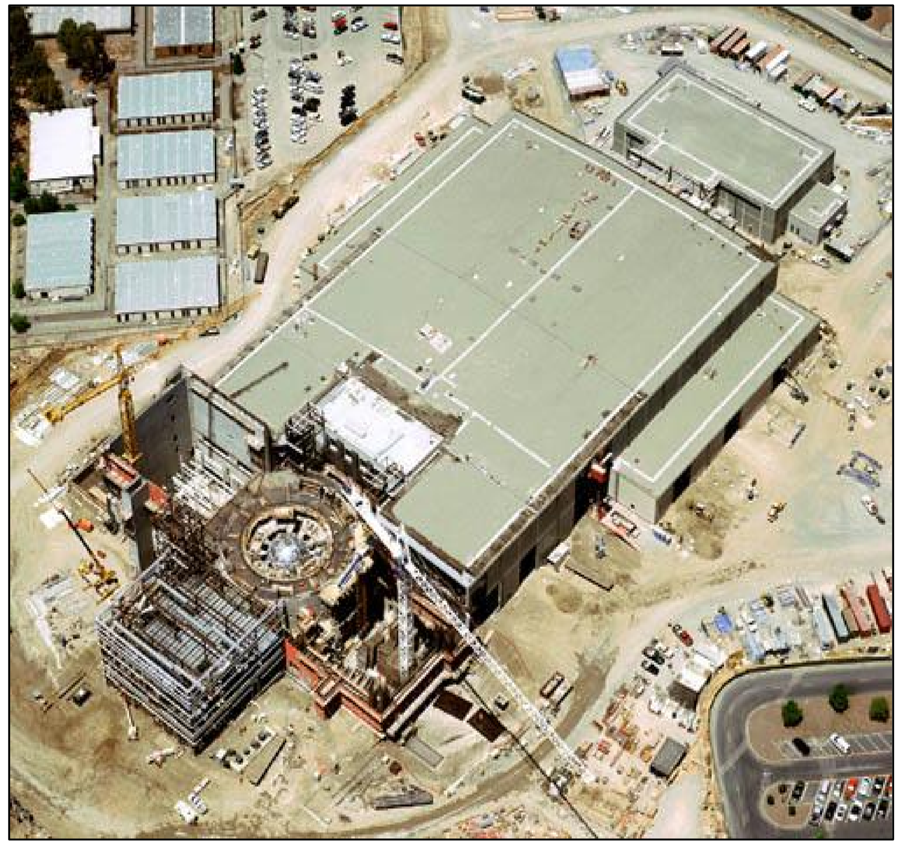
The energy of the future?(2/3)



☞**Each reactor would require hundreds of tons of optically amplifier glass**



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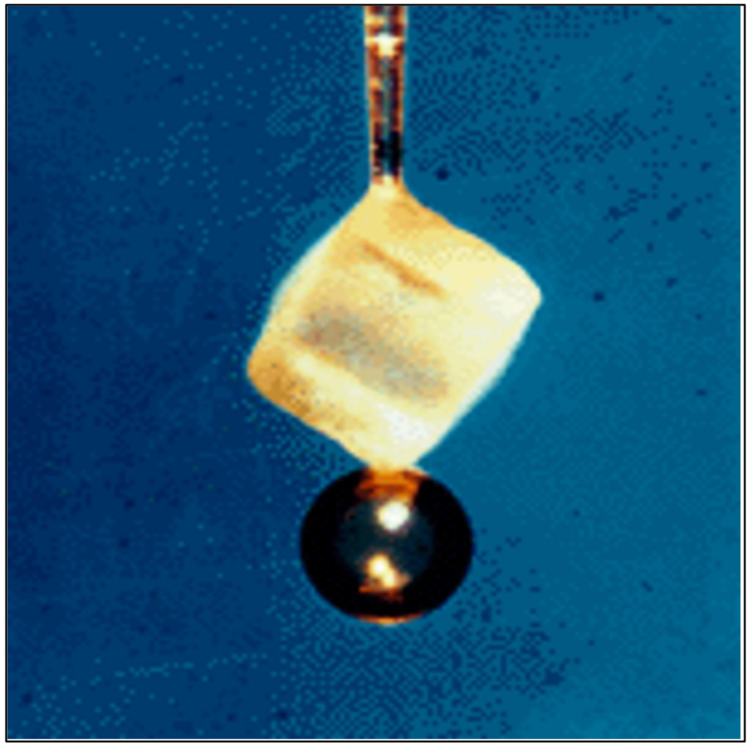
The energy of the future?(3/3)



☞The deuterium and tritium mixing is encapsulated in this 5 millimeters diameter capsule

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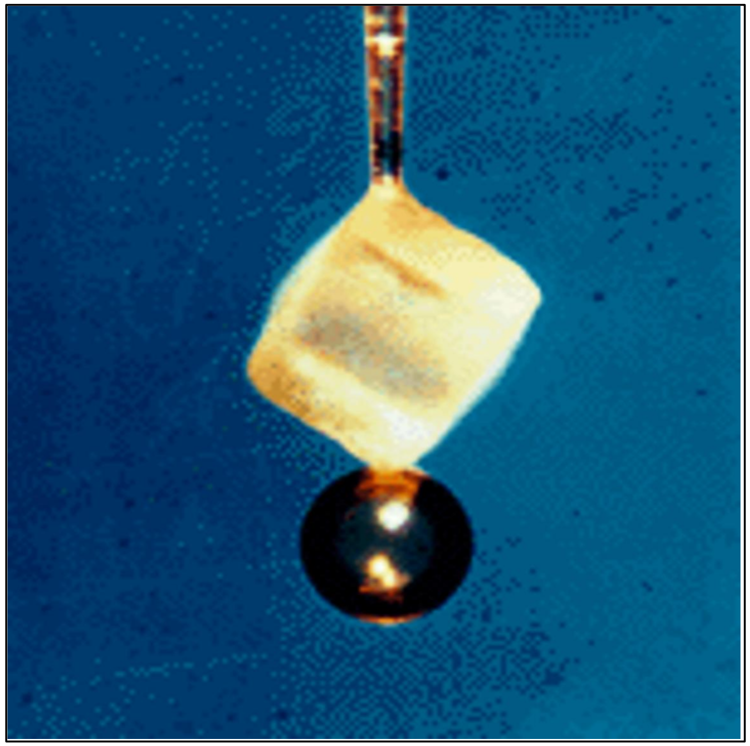
The energy of the future?(3/3)



☞**The deuterium and tritium mixing is encapsulated in this 5 millimeters diameter capsule, made of glass of course.**

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Conclusions

- **Energy represents a very promising future for glass**

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Conclusions

- **Energy represents a very promising future for glass**
- **Thin film science and technology is part of glass science and technology**
- **There is another important aspect of relation between energy and glass : energy used for making lass. Melting and fining of glass require a lot of energy. This has to be improved rapidly.**

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