



COLLÈGE
DE FRANCE
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Chaire Innovation technologique
Liliane Bettencourt 2021-2022

Énergie solaire photovoltaïque et transition énergétique



Reconnue d'utilité publique depuis 1987

Mercredi 9 février 2022

L'essor du photovoltaïque moderne : aspects
fondamentaux de la conversion photovoltaïque

Daniel LINCOT

À la recherche des performances ultimes pour la
conversion photovoltaïque

Jean François Guillemoles

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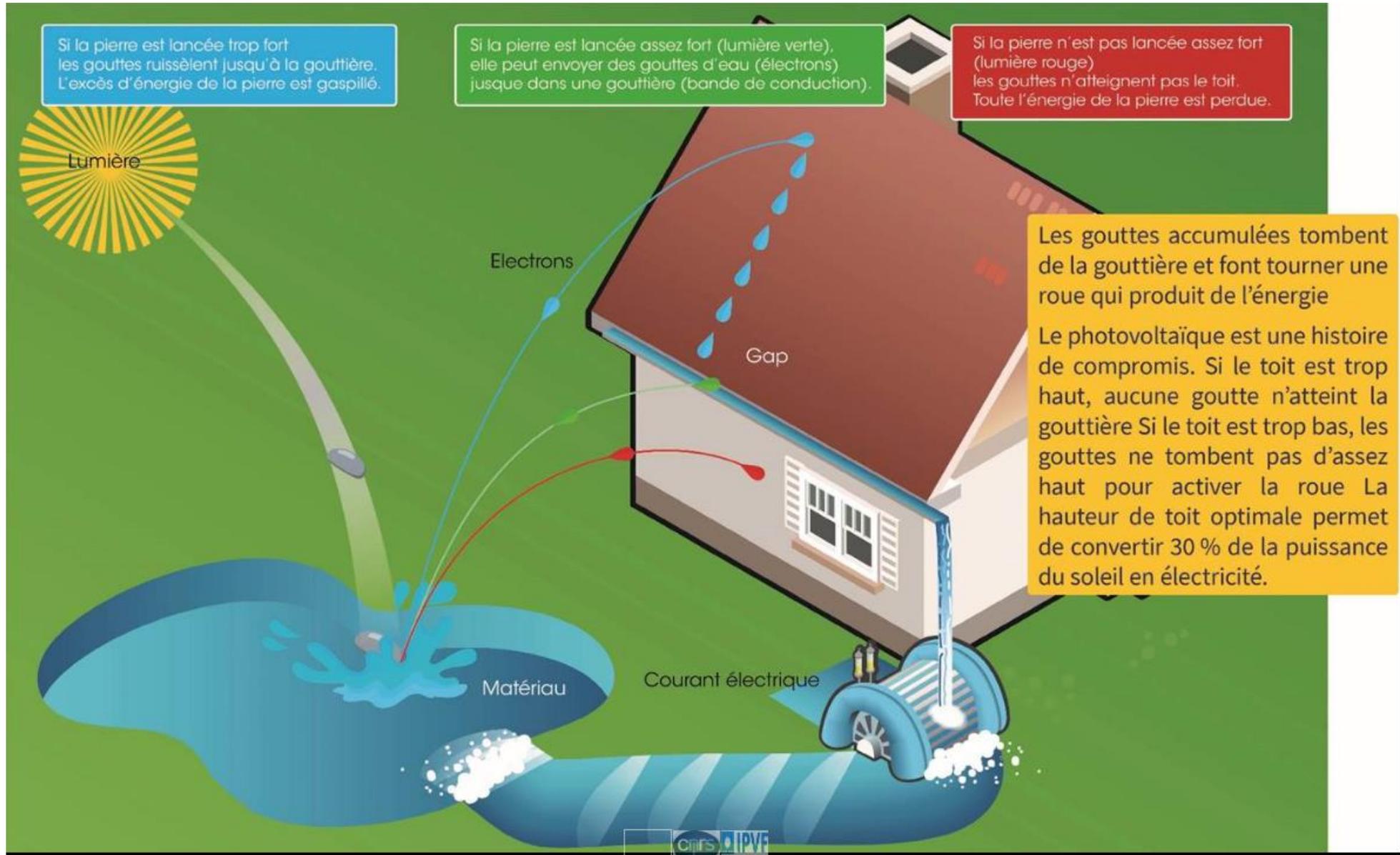
Mercredi 2 février 2022

L'essor du photovoltaïque moderne : aspects fondamentaux de la conversion photovoltaïque

Daniel LINCOT

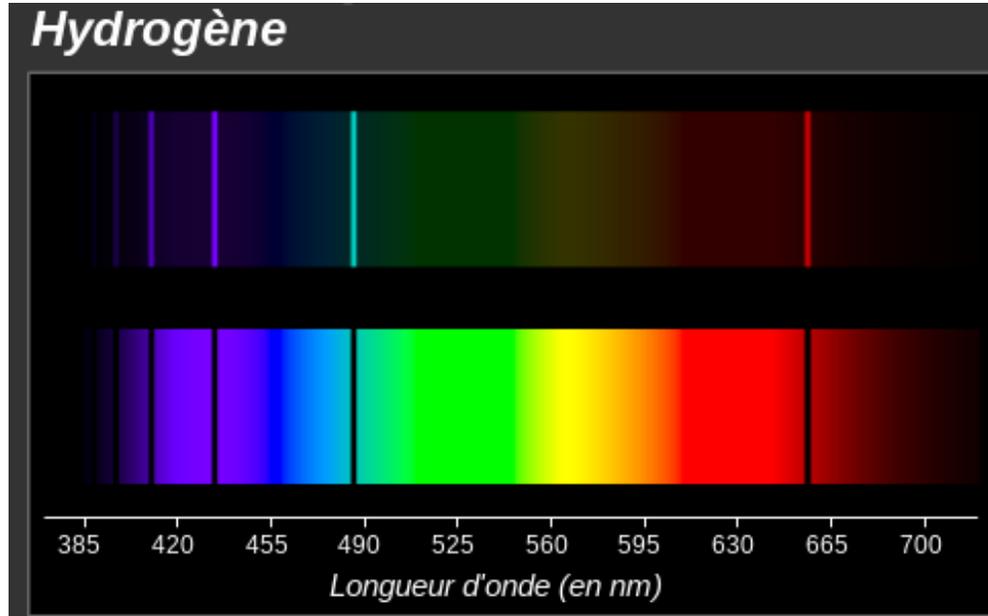
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Un clin d'œil au cycle de l'eau

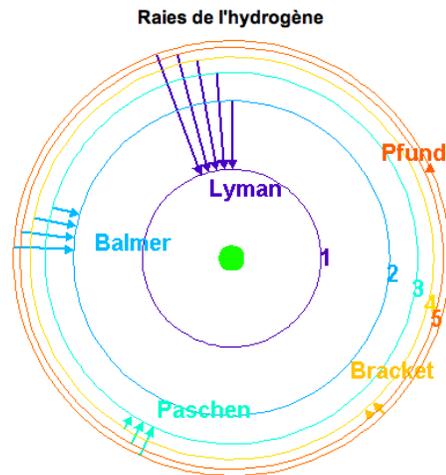
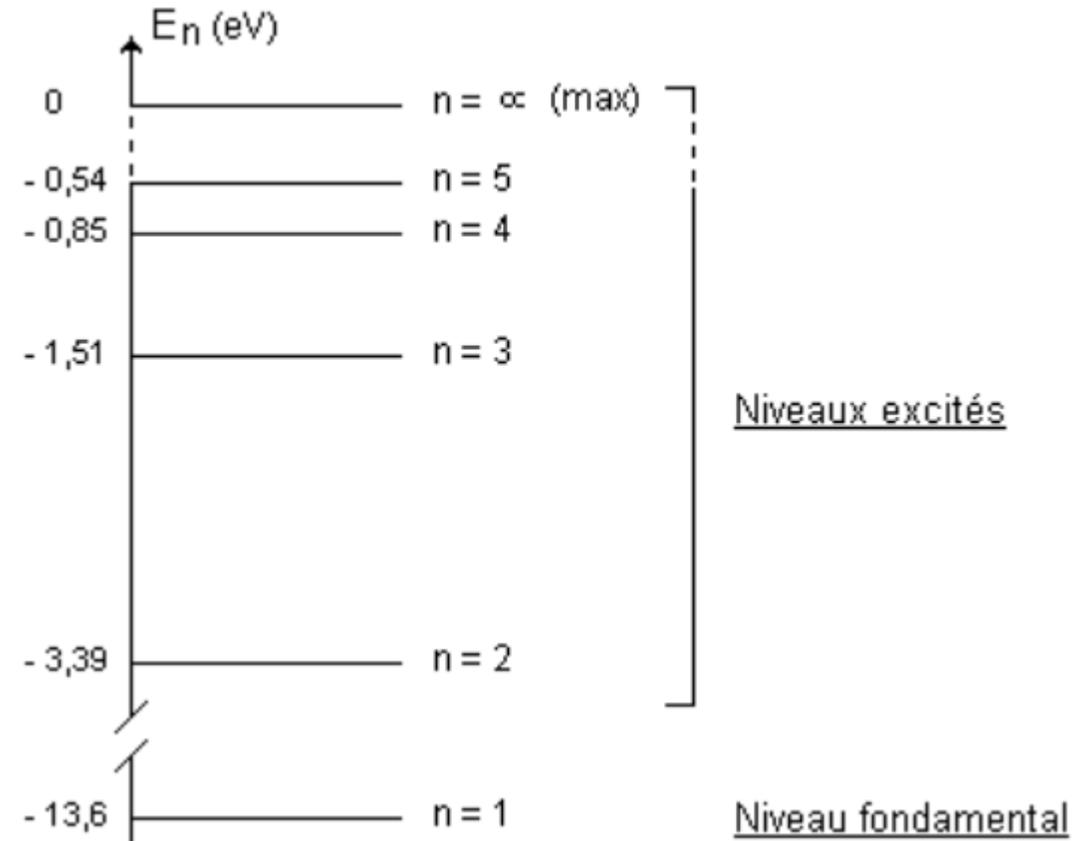


La renaissance des diagrammes de bandes

Des raies de Balmer à la physique quantique

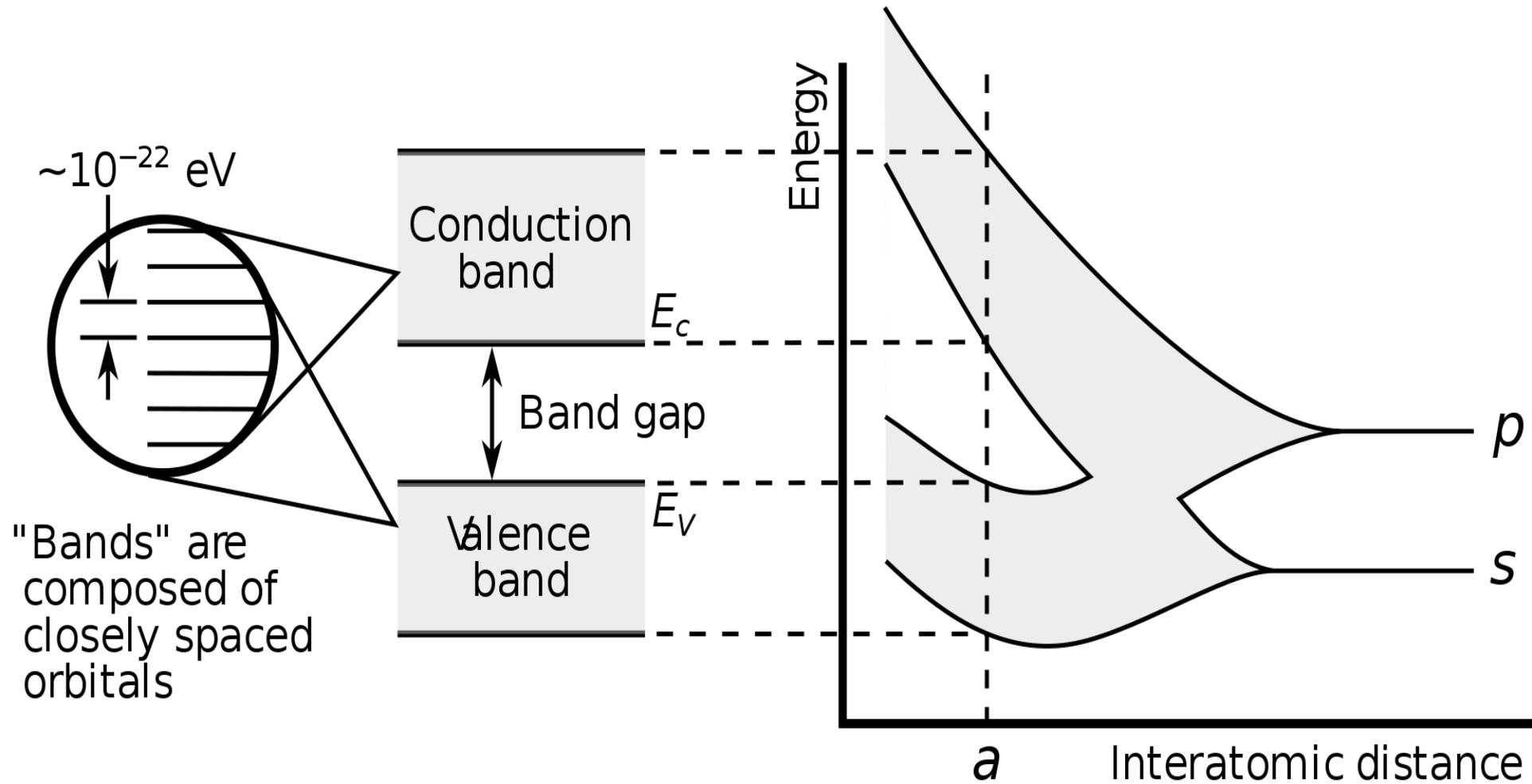


$$E_n = -\frac{13,6}{n^2}$$



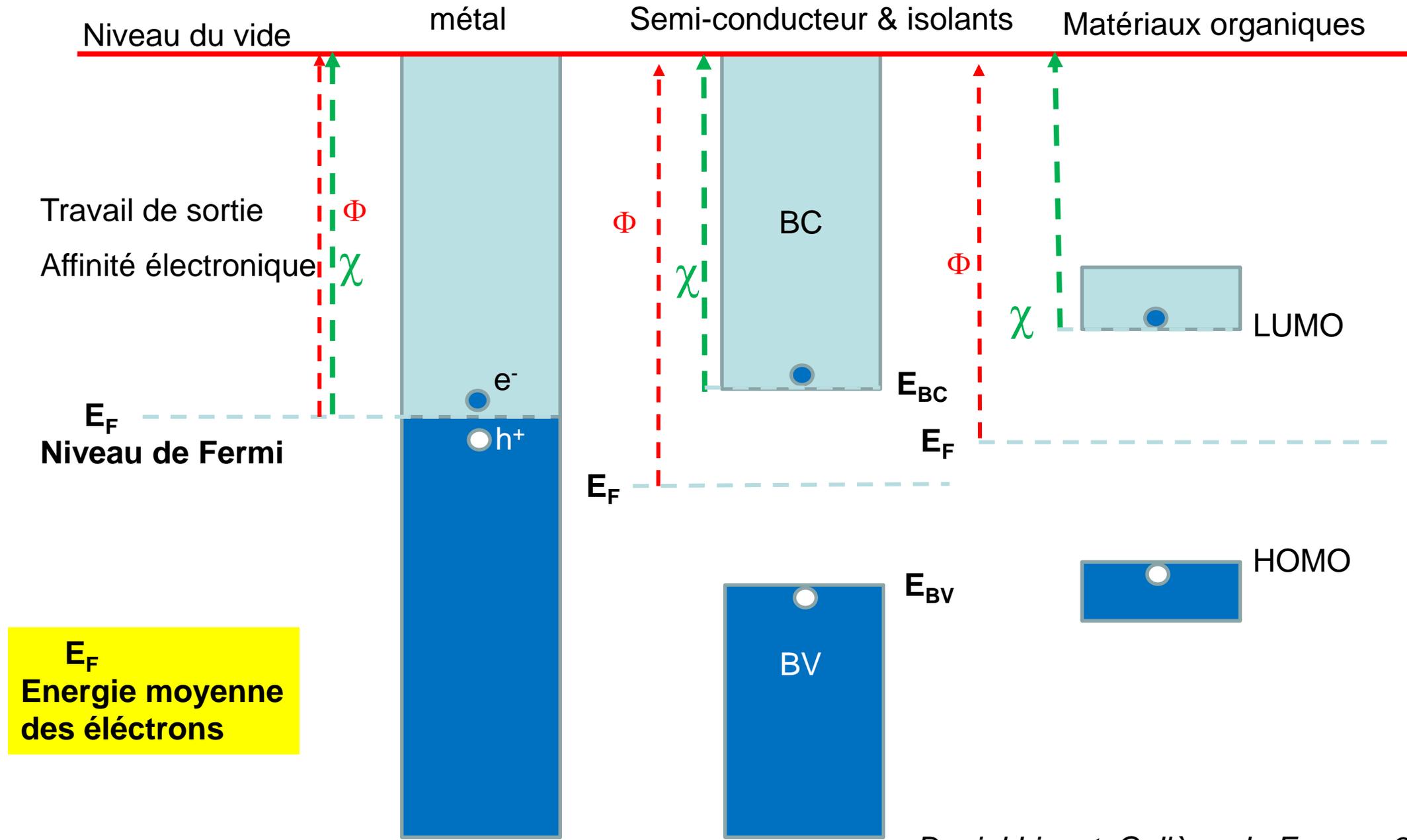
<https://laboiteaphysique.fr/site2/index.php/quotidien/la-lumiere/transferts-quantiques-denergie>

Des niveaux atomiques aux bandes d'énergie



Qui se déclinent suivant toutes les classes de matériaux...

Energie (eV)



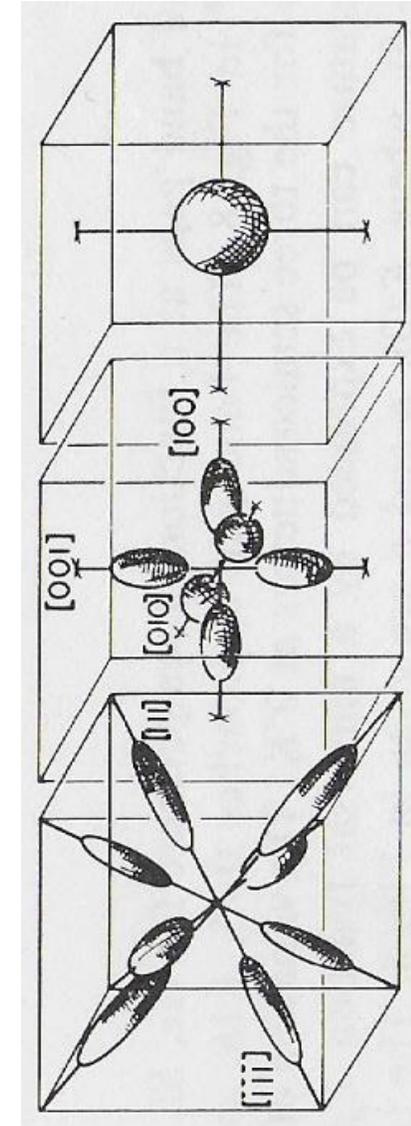
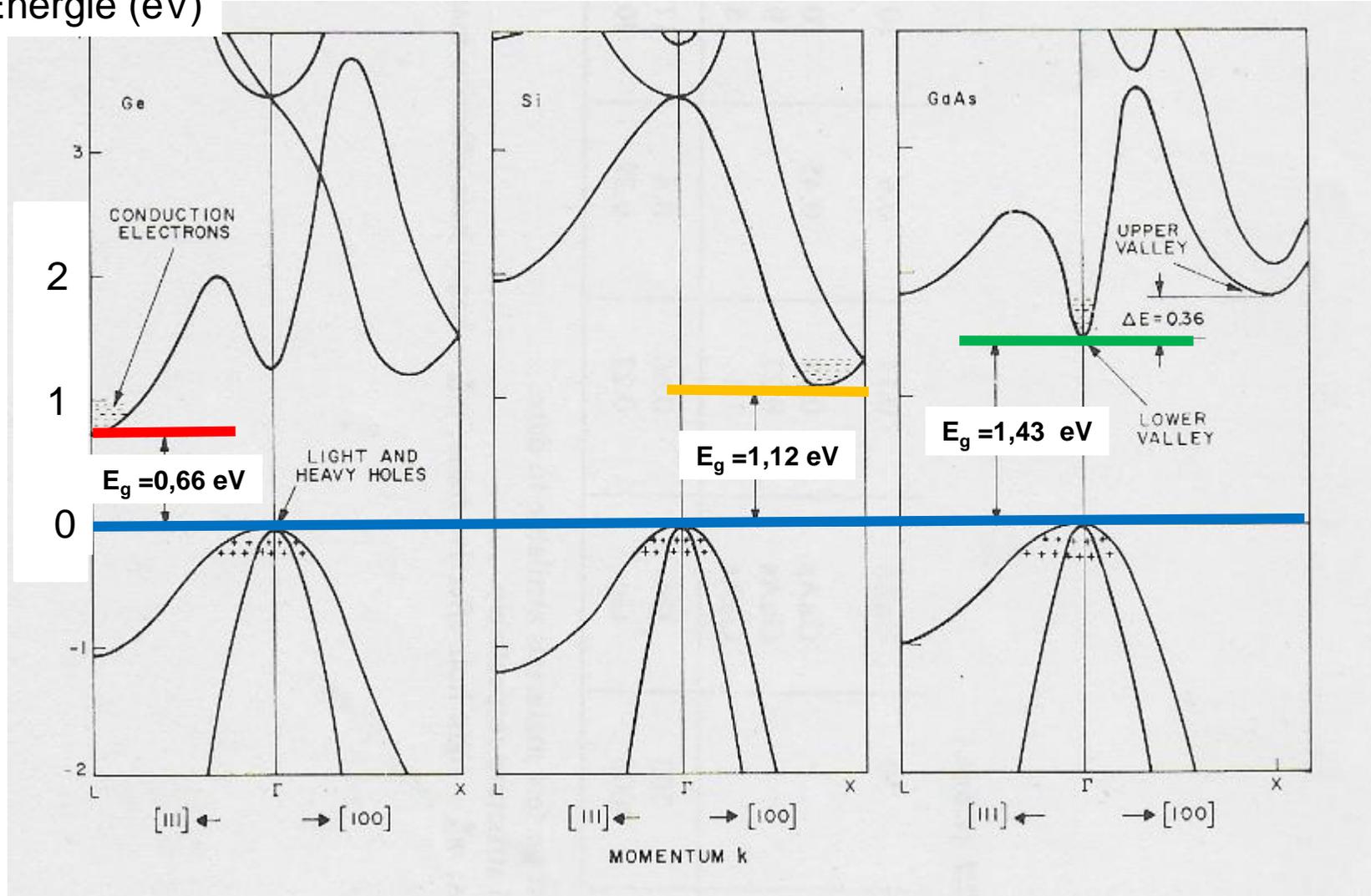
Structure de bandes des solides

Ge

Si

GaAs

Energie (eV)



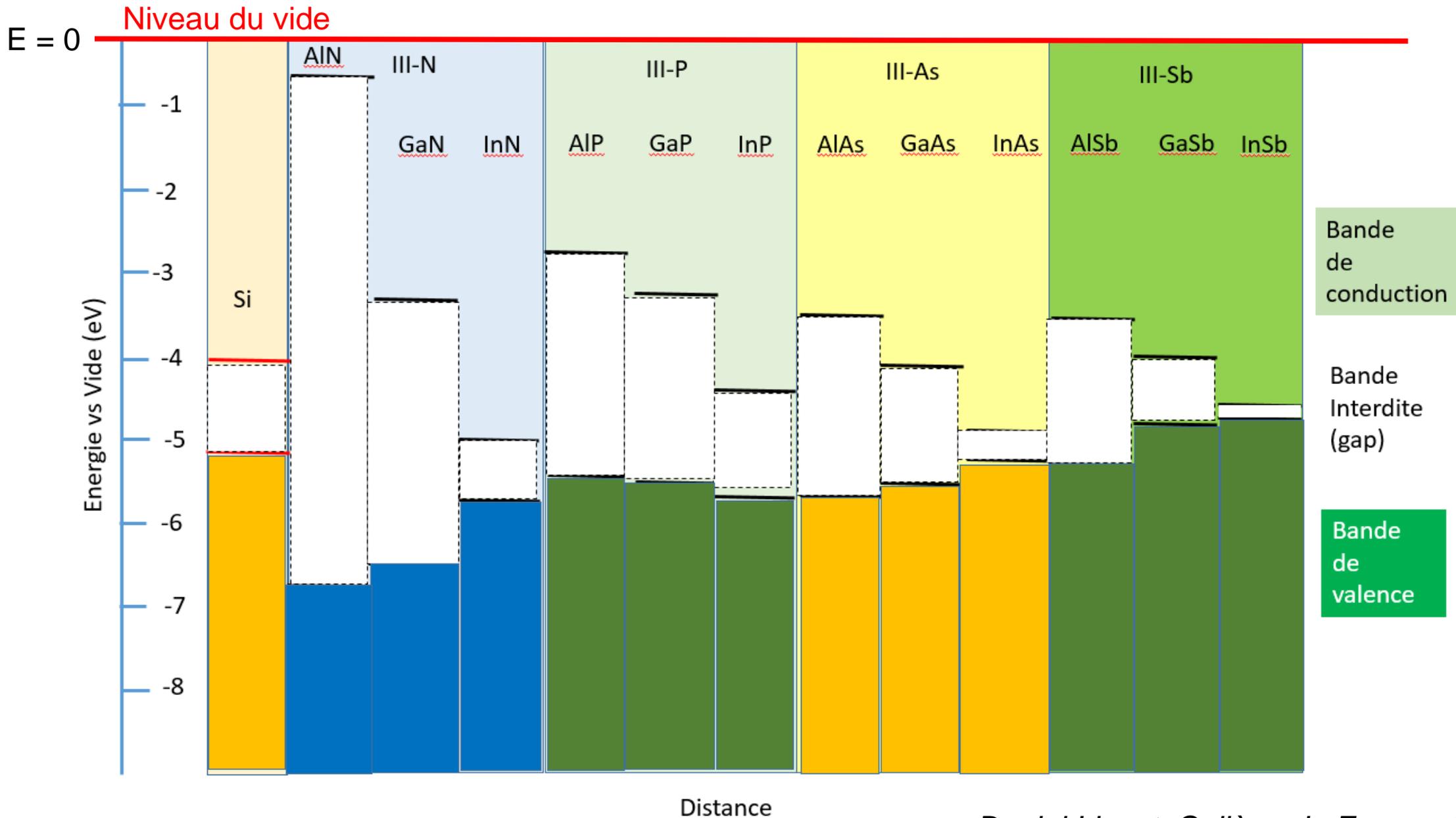
GaAs

Si

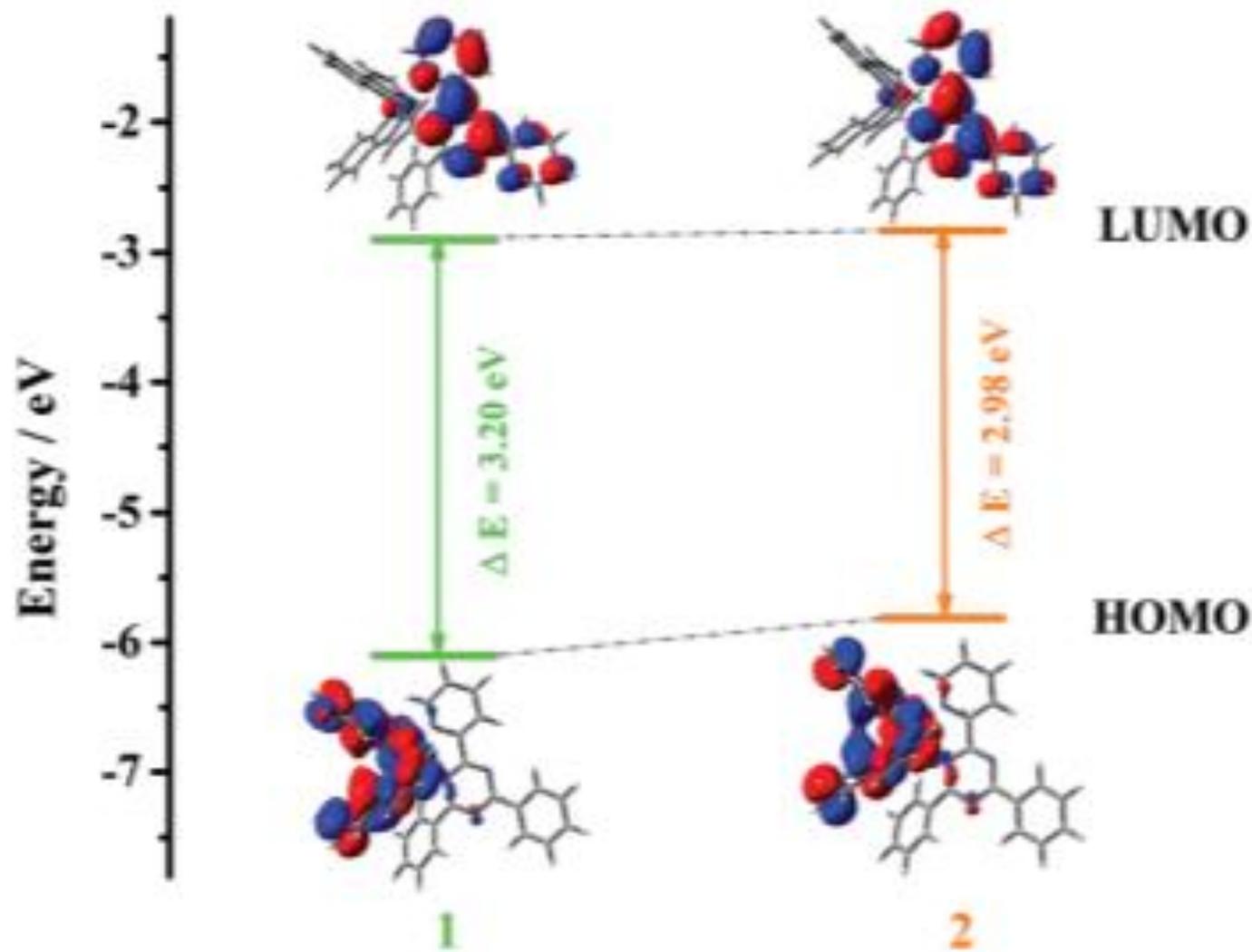
Ge

Surfaces d'énergie constante

Diagrammes énergétiques des semiconducteurs (V=0)

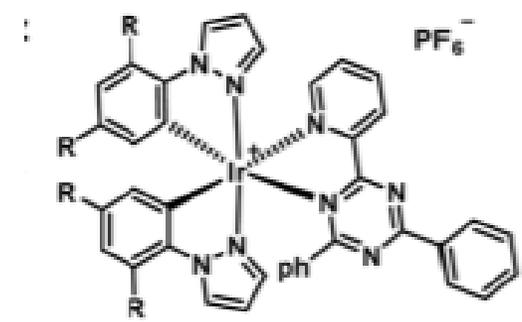


Matériaux organiques



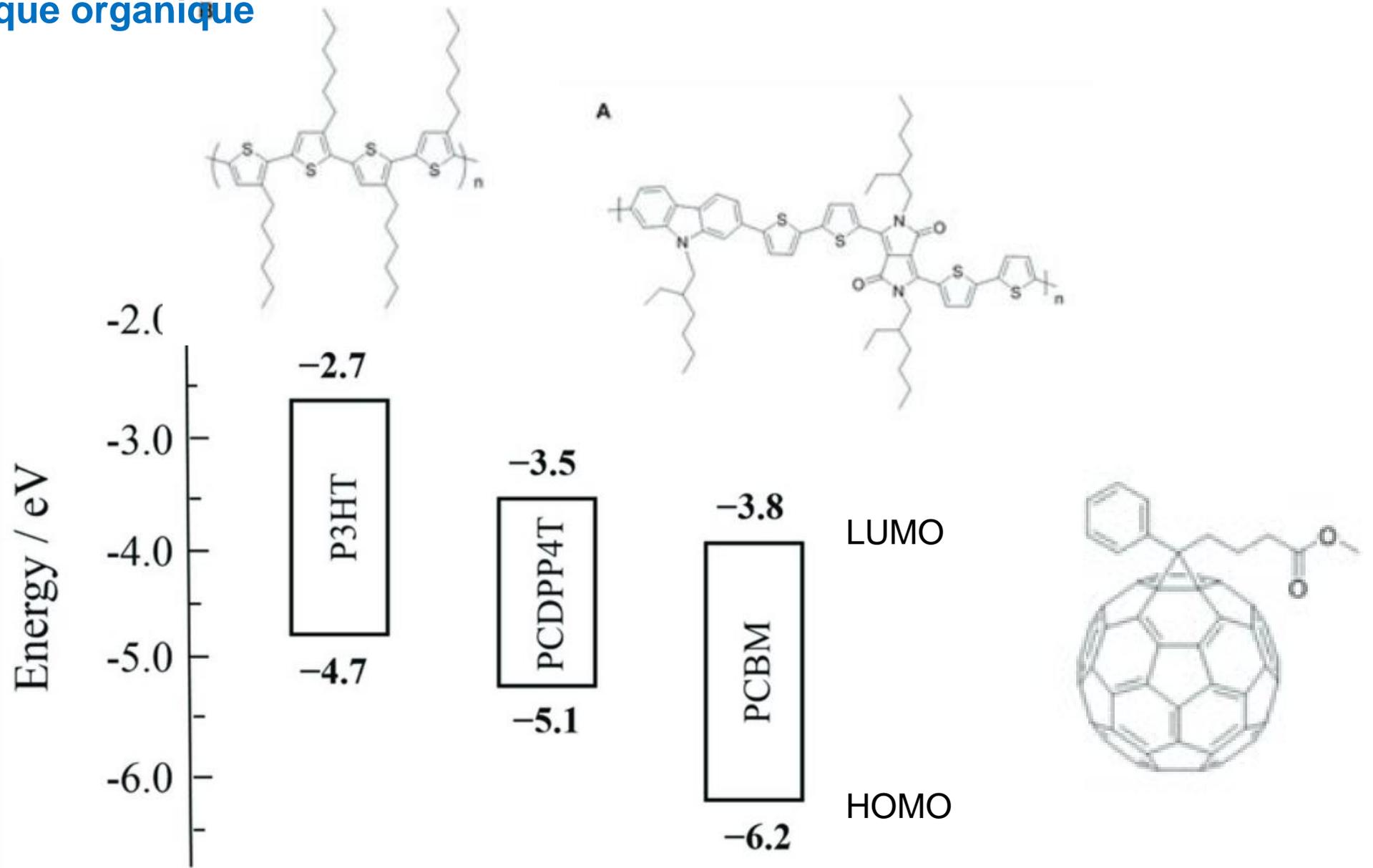
Molecular orbital diagrams and calculated HOMO–LUMO energy levels : Complexes for aggregation-induced emission and piezochromic luminescence

[(dfppz)₂Ir(DPhTz)][PF₆] (1) and [(ppz)₂Ir(DPhTz)][PF₆] (2), with the 2,4-diphenyl-6-(pyridine2-yl)-1,3,5-triazine ancillary ligand (DPhTz)



1: R = F
2: R = H

Pour le photovoltaïque organique

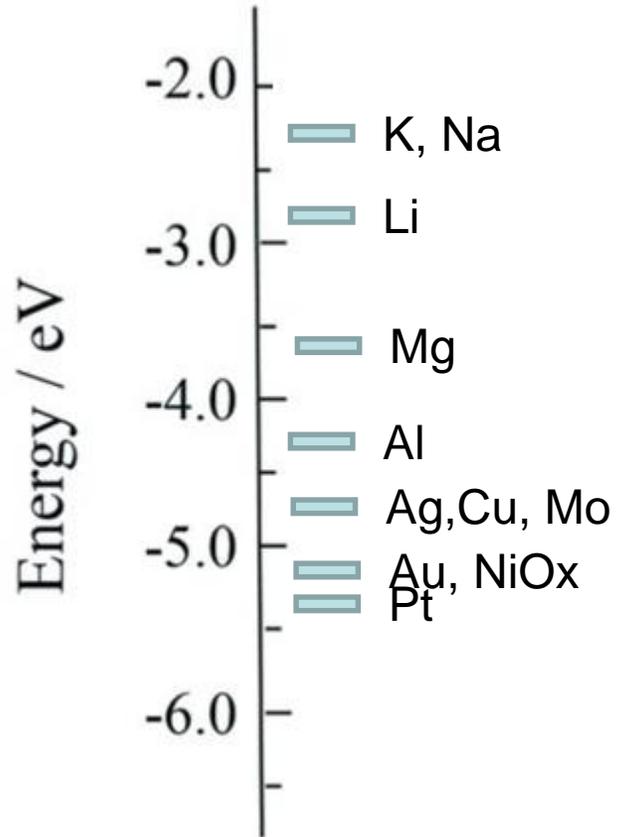


Wang et al., Frontiers in Energy Research 6 (2018)113

Métaux et couples rédox

Métaux

Travail de sortie

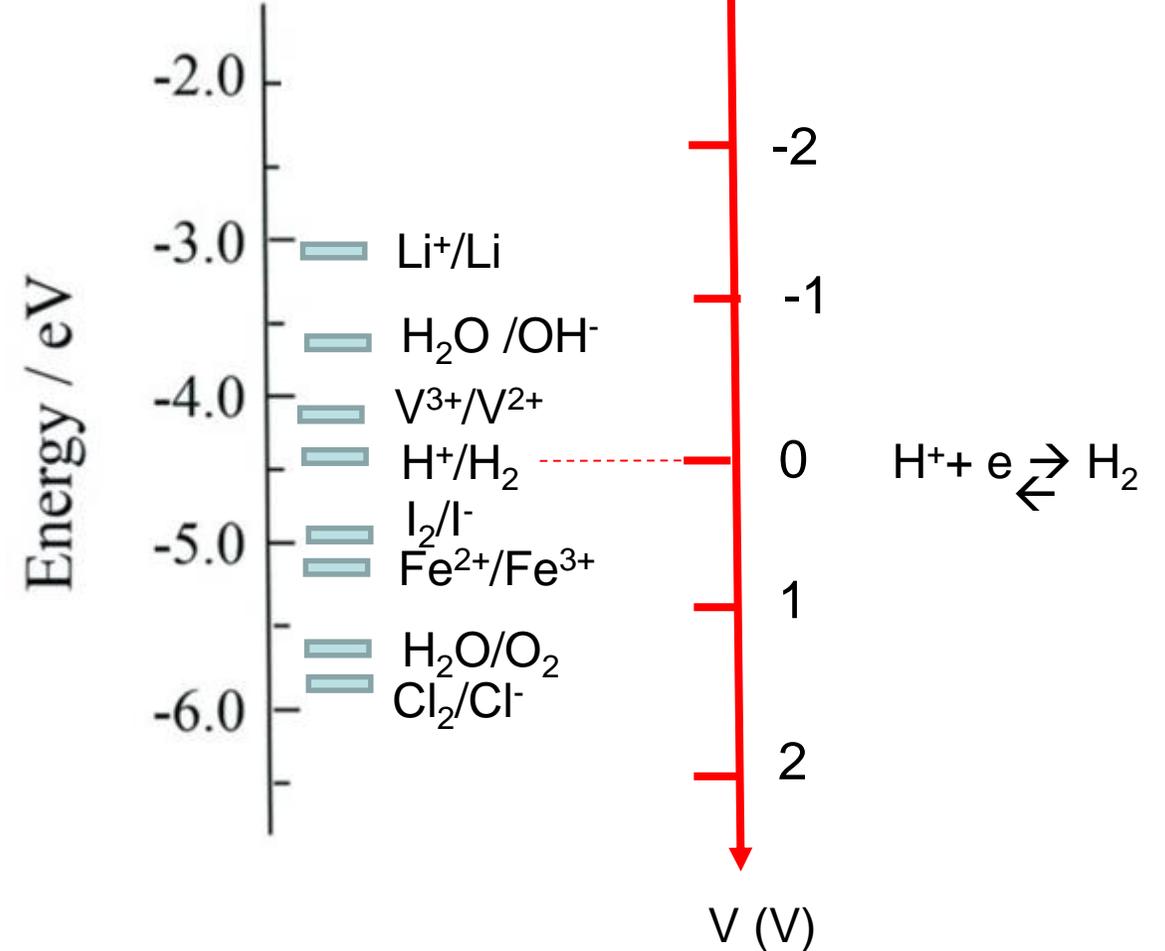


Couple oxydo-réducteurs en solution

$$E = E_0 + \frac{RT}{nF} \text{Log} \left(\frac{[\text{ox}]}{[\text{red}]} \right)$$

Echelle énergie / vide

Echelle électrochimique



Le niveau de remplissage des électrons : niveau de Fermi : E_F

Probabilité d'occupation d'un niveau d'énergie (Fermi-Dirac)

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Si $|E - E_F| \gg kT$

$$f(E) = \exp\left[-\frac{(E - E_F)}{kT}\right]$$

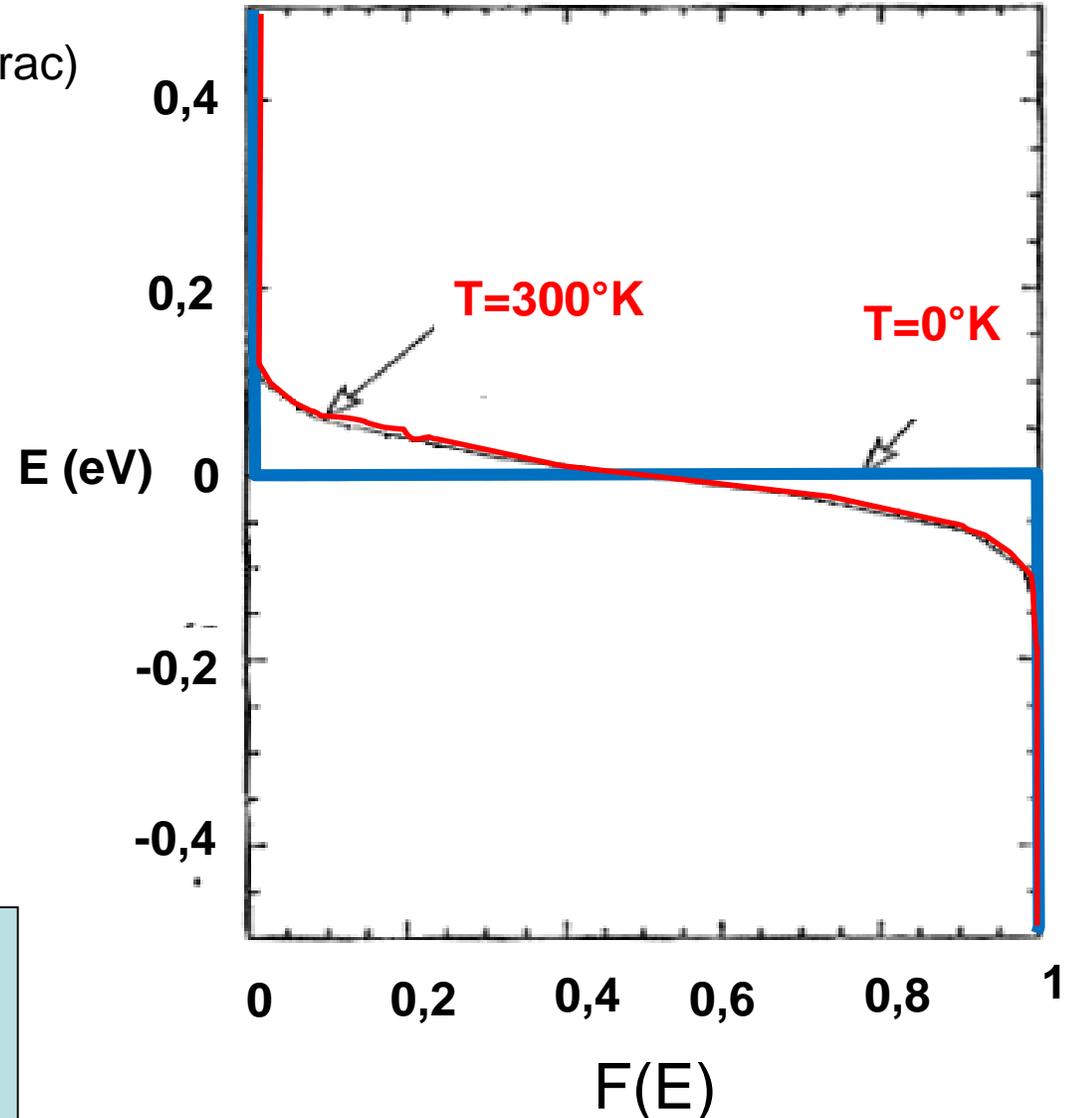
Influence du potentiel

$$E = E(0) - qV \quad q = 1,6 \cdot 10^{-19} \text{ C}$$

E_F Potentiel électrochimique moyen d'un électron

$$E_F = \frac{\tilde{\mu}_e}{N_{\text{Avogadro}}} \quad \tilde{\mu}_e = \mu_e - FV$$

F : Faraday (96500 C)



Silicium : $E_g = 1,12 \text{ eV}$, $n_i = 1,4 \cdot 10^{10}$, $N_{A,D} \rightarrow 10^{15}-10^{20} \text{ at/cm}^3$

Dopage



Intrinsèque

type N

Type P



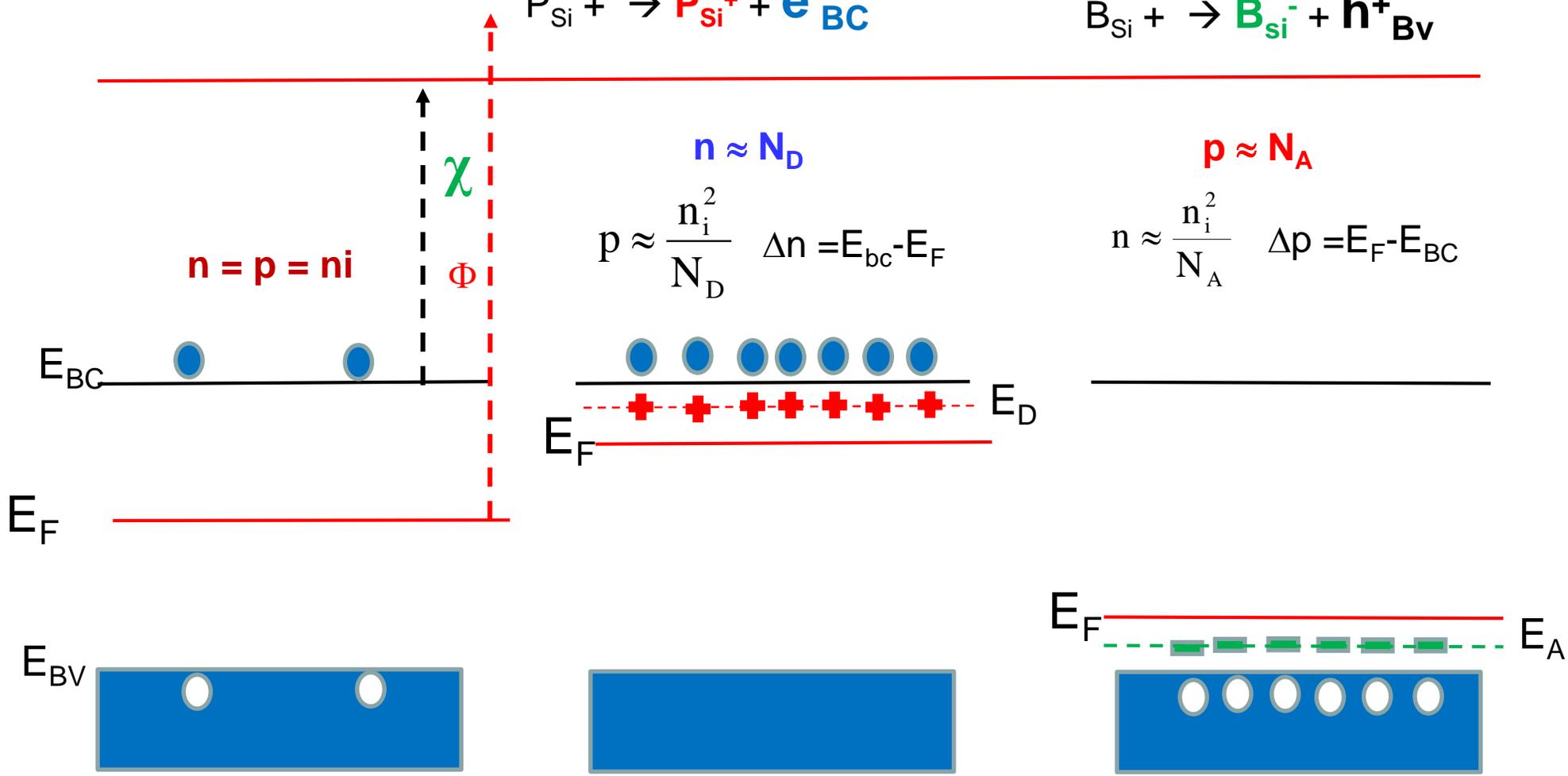
$$n \approx N_D$$

$$p \approx \frac{n_i^2}{N_D} \quad \Delta n = E_{bc} - E_F$$

$$p \approx N_A$$

$$n \approx \frac{n_i^2}{N_A} \quad \Delta p = E_F - E_{BC}$$

$$n = p = n_i$$



$$n = N_C \exp\left[-\frac{E_C - E_F}{kT}\right]$$

$$n_i = (N_C N_V)^{1/2} \exp\left[-\frac{E_g}{2kT}\right]$$

$$p = N_V \exp\left[-\frac{E_F - E_V}{kT}\right]$$

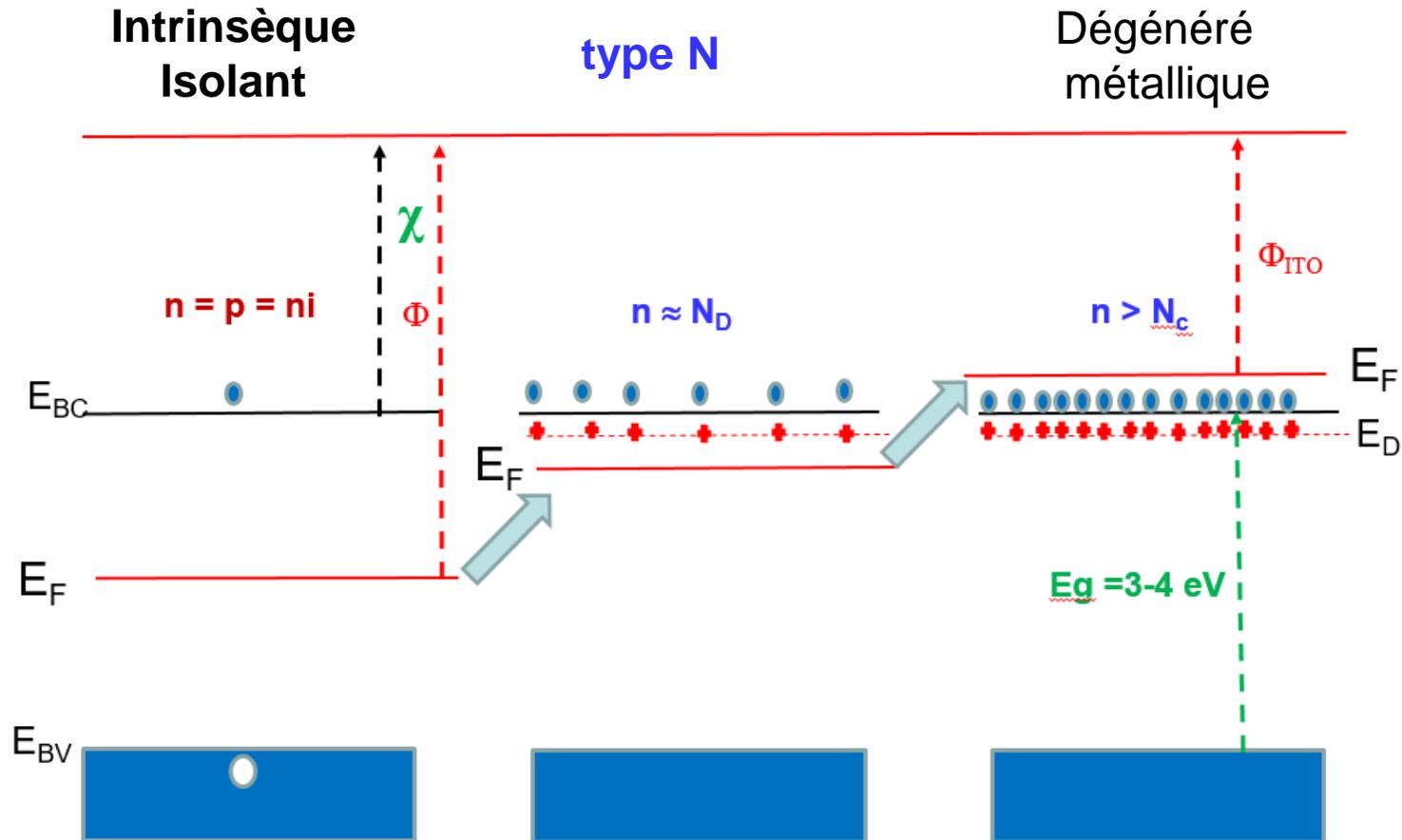
N_C : densité effective d'états dans la bande de conduction (Si: $2,8 \cdot 10^{19} \text{ cm}^{-3}$)

N_V : densité effective d'états dans la bande de valence (Si: 10^{19} cm^{-3})

Daniel Lincot, Collège de France, 9/02/2022

Effet du dopage : de l'isolant au métal

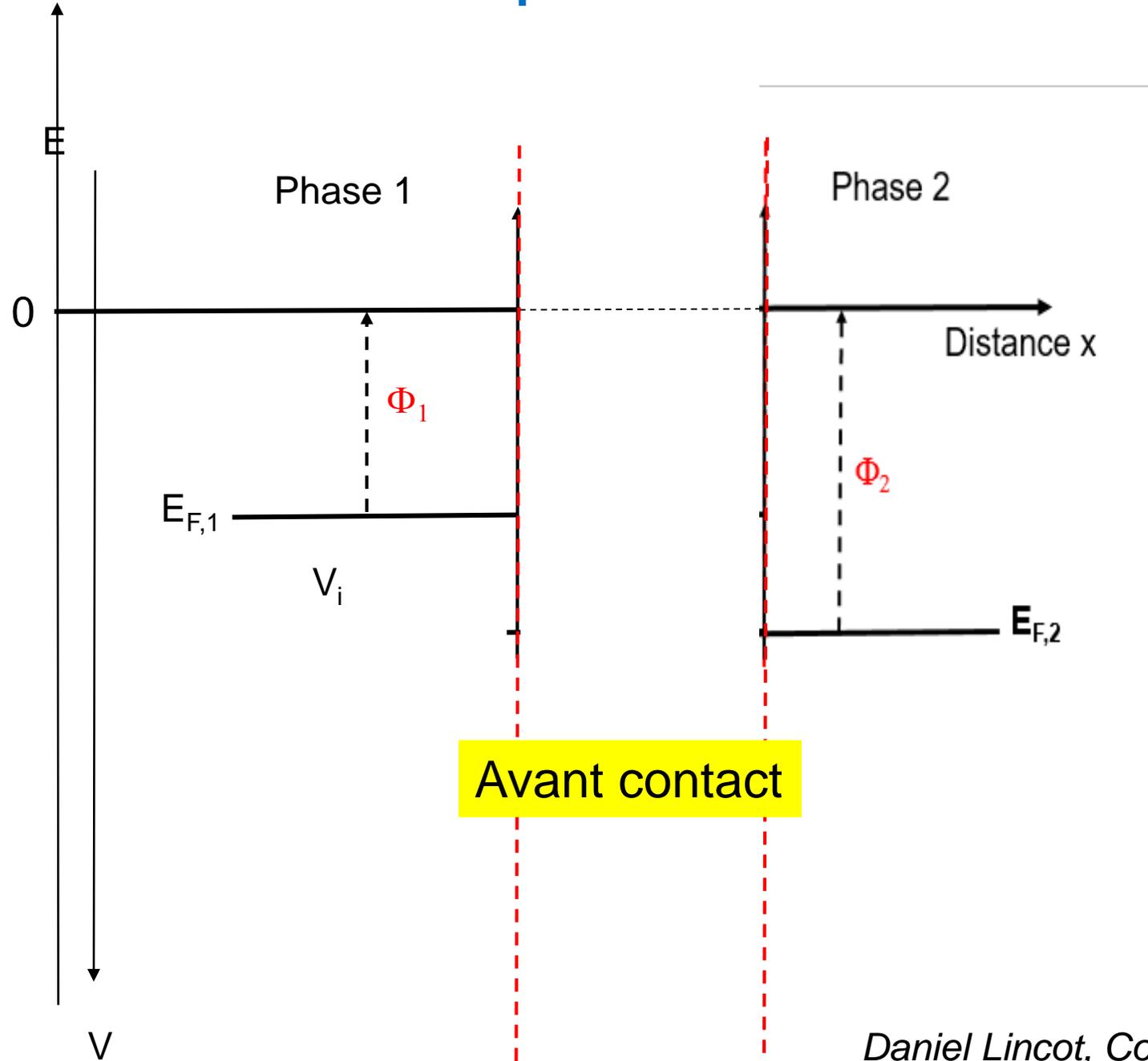
Oxydes transparents conducteurs (TCO) : $\text{In}_2(\text{Sn})\text{O}_3$ ITO



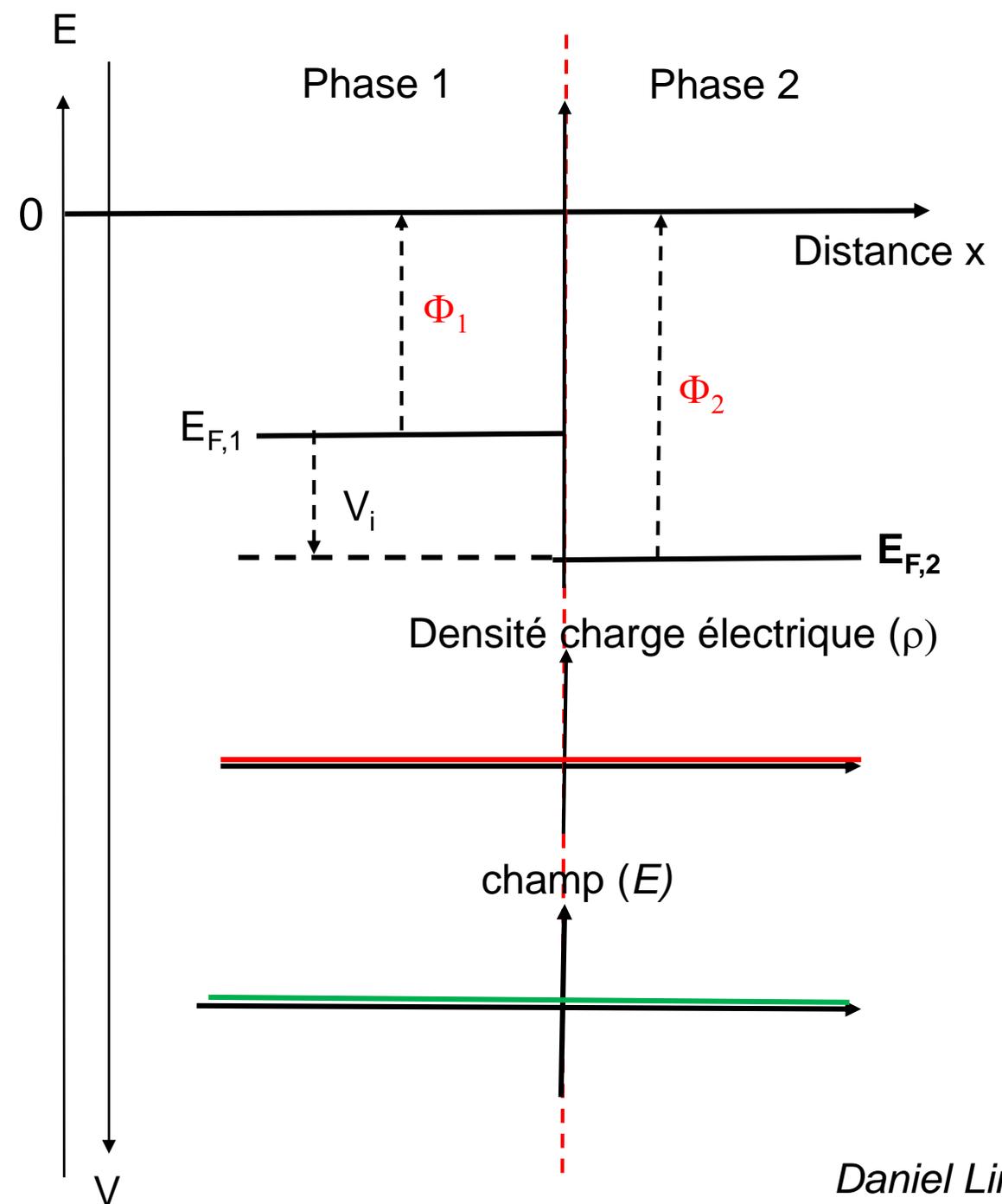
TCO de type n :
ITO, $\text{Sn}(\text{F})\text{O}_2$, $\text{Zn}(\text{Al})\text{O} \dots$

TCO de type p
 NiO , $\text{MoO}_3 \dots$

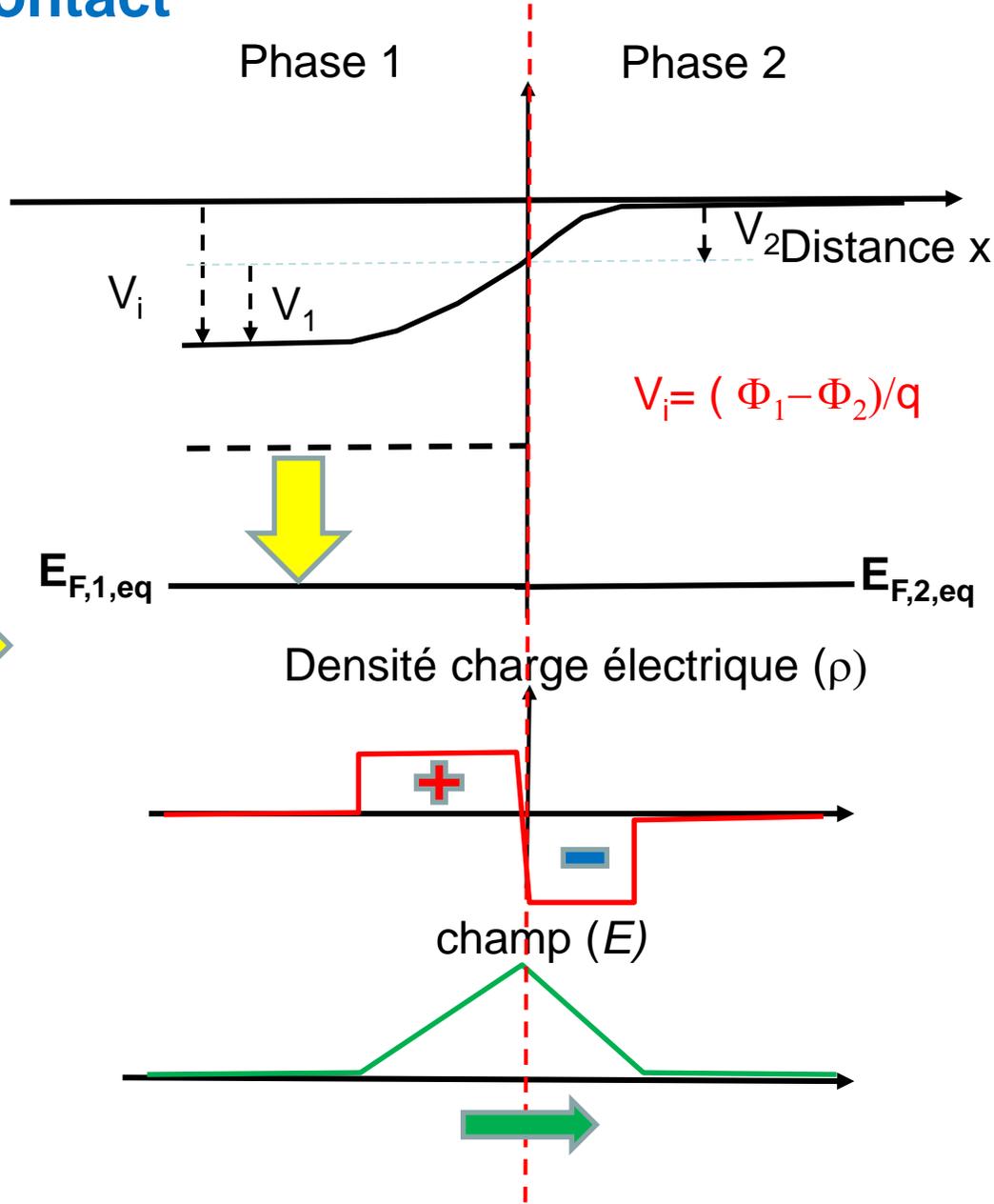
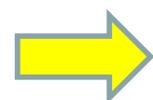
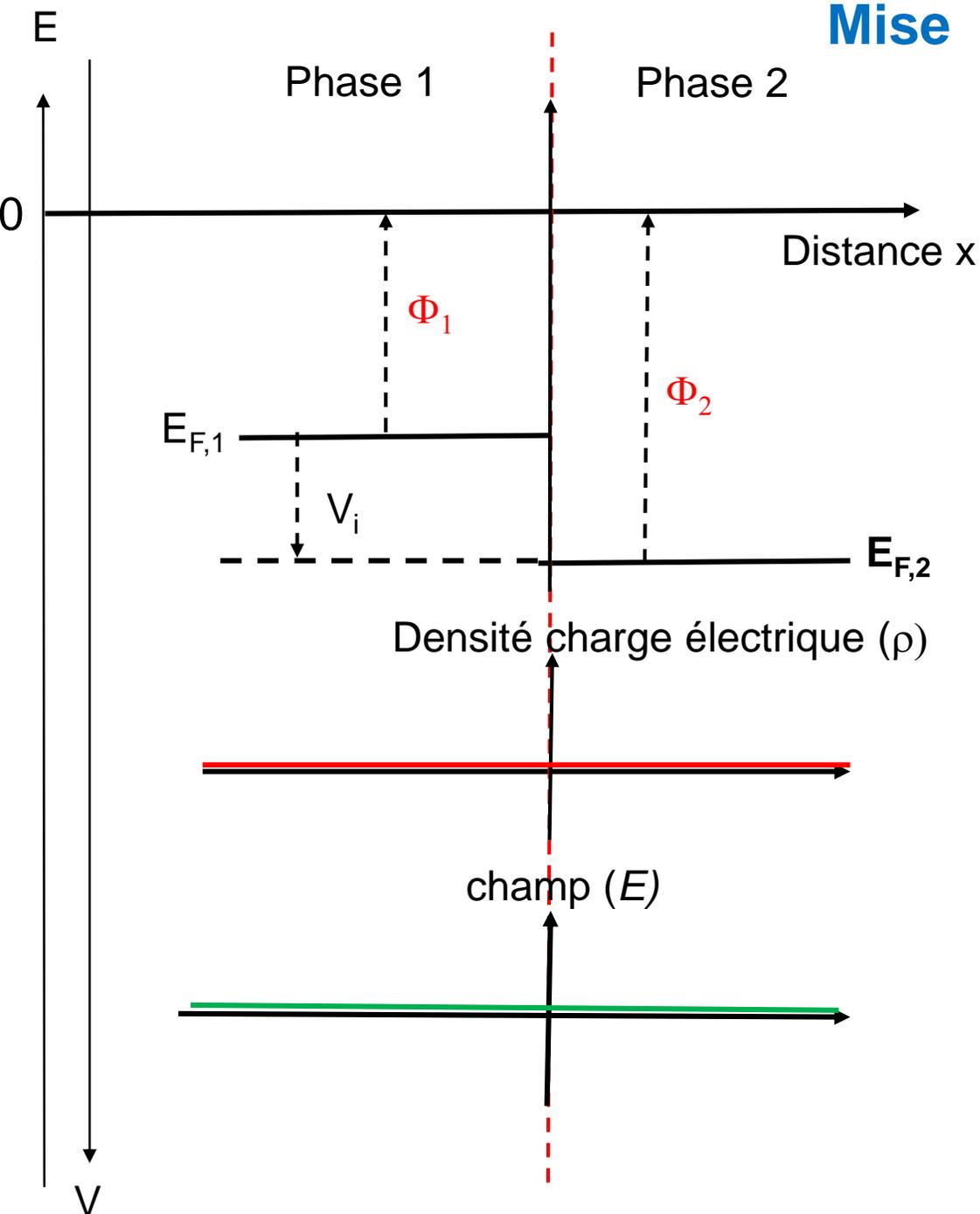
Contact entre deux phases

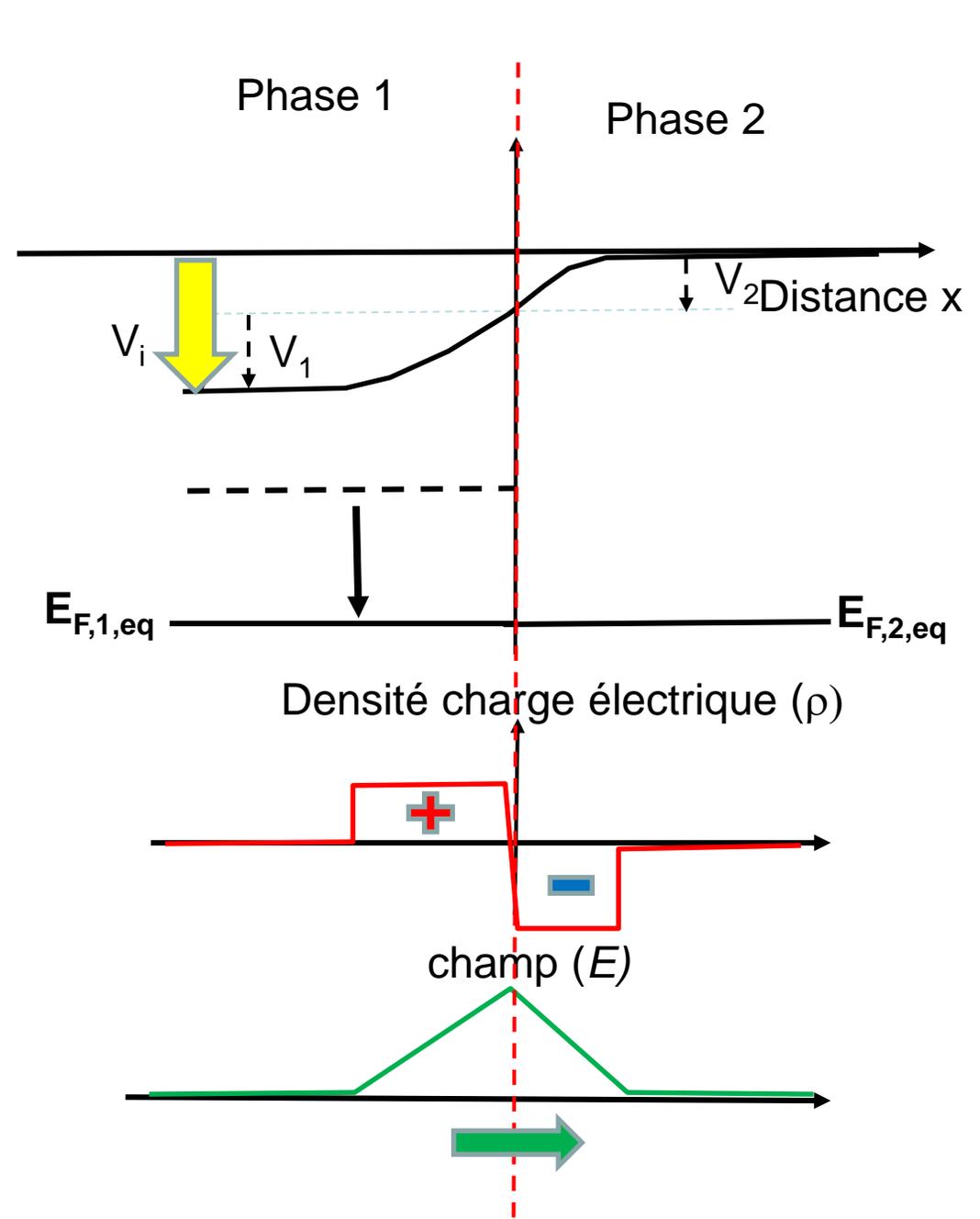
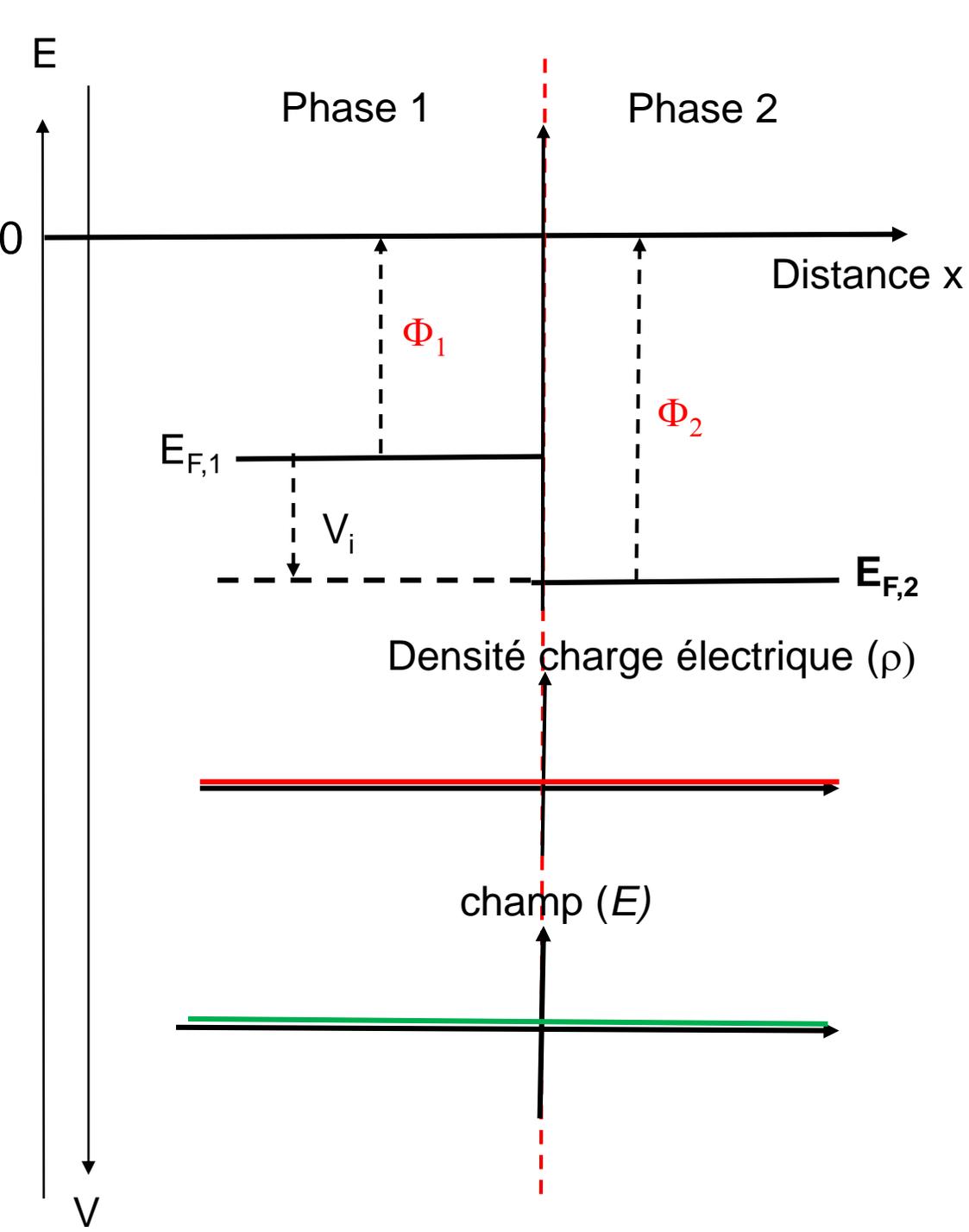


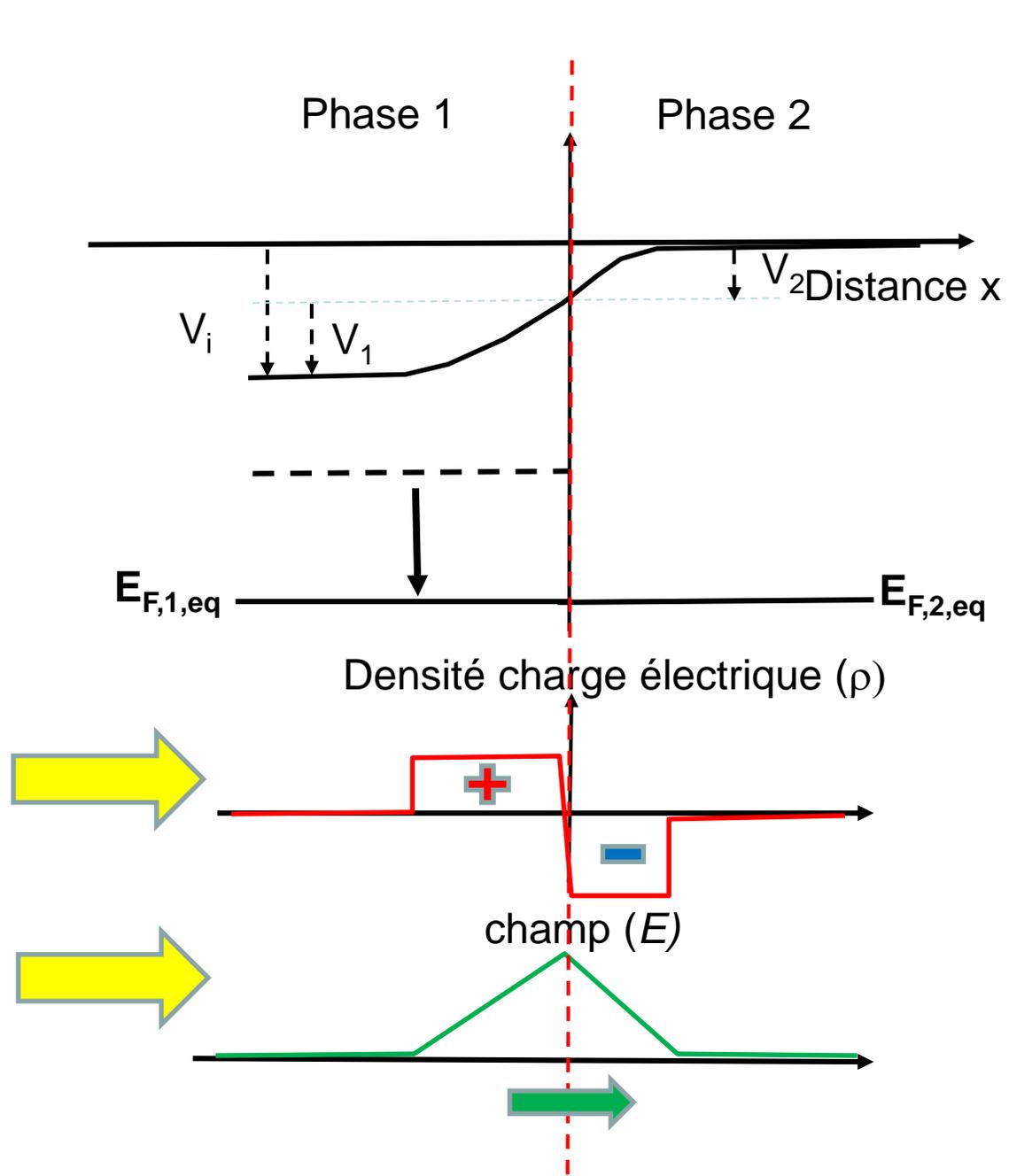
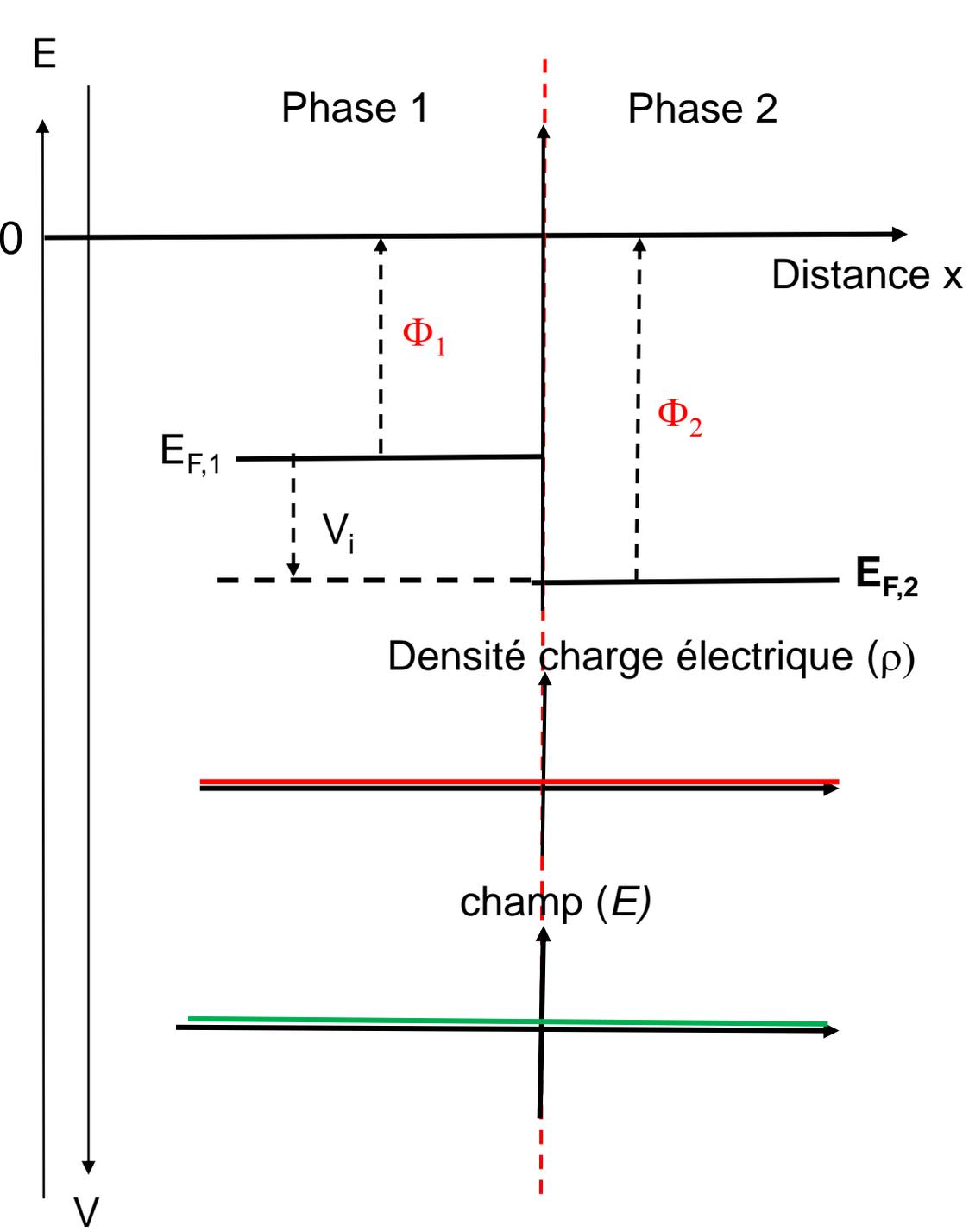
$$E = E(0) - qV$$



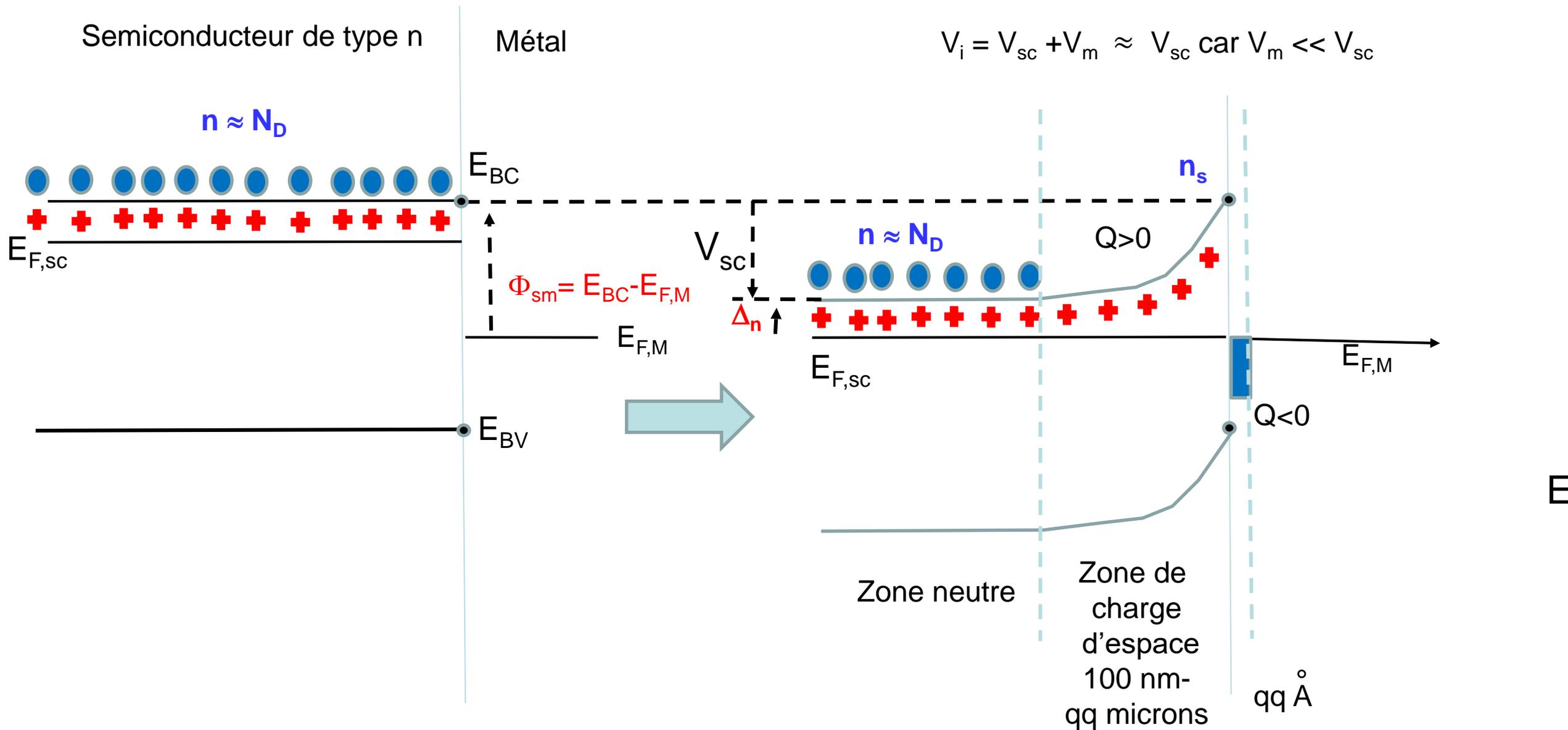
Mise en contact







Jonction métal- semiconducteur : barrière de Schottky



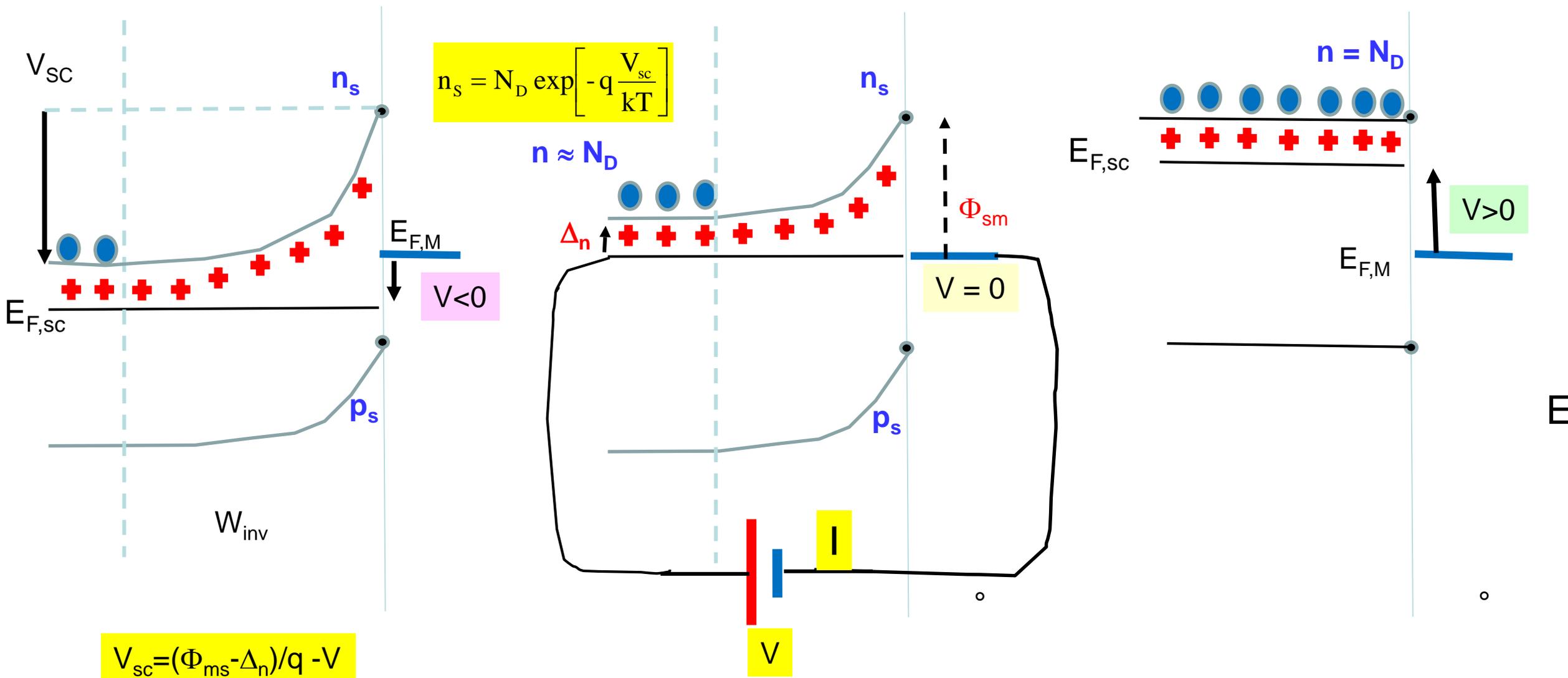
Influence de la polarisation

$$V = -(E_{FM} - E_{F,sc})/q$$

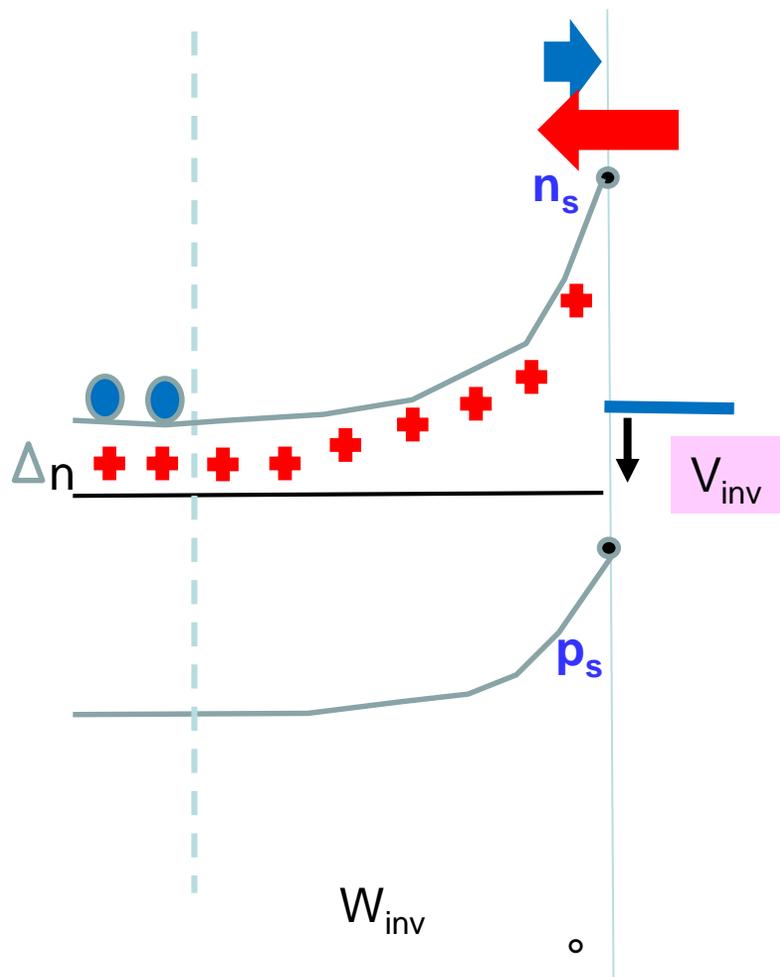
Polarisation directe, conditions de bandes plates

Polarisation inverse

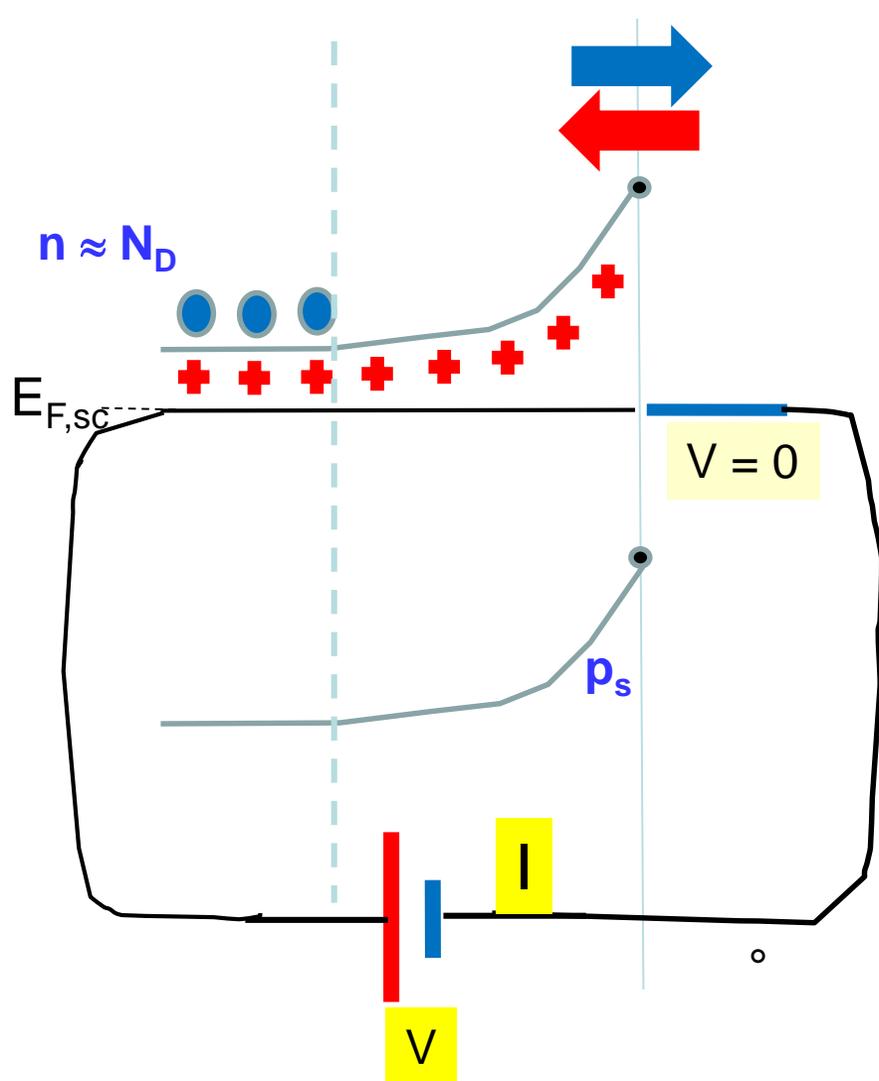
A l'équilibre



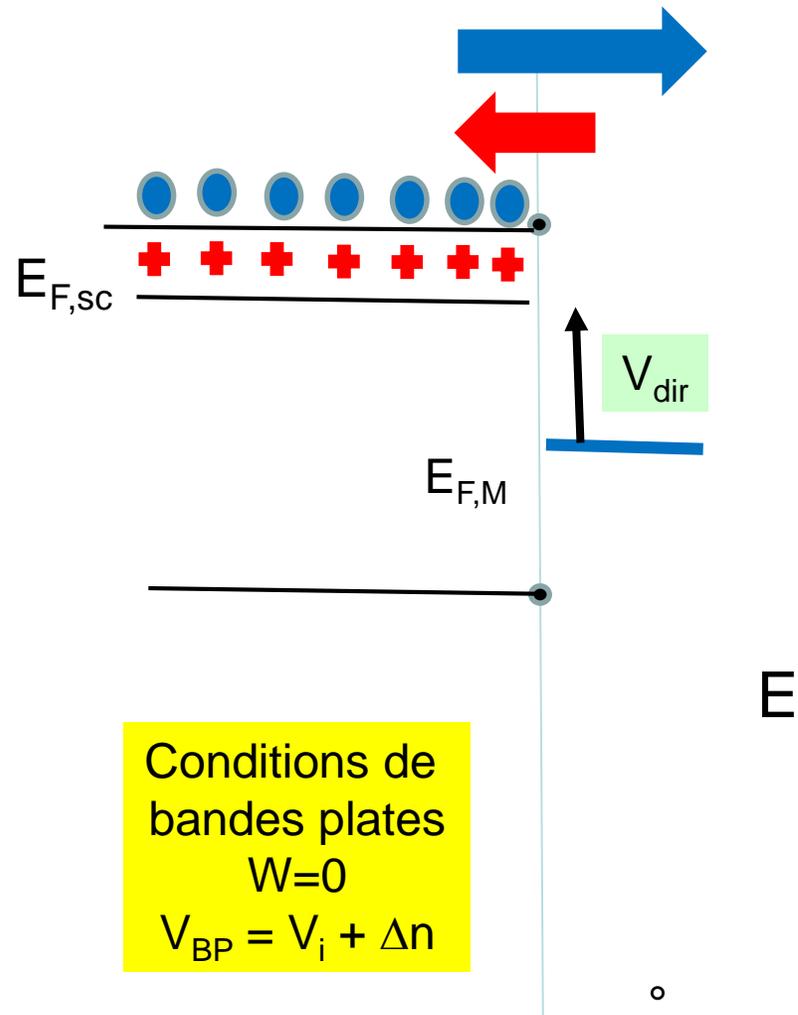
Polarisation inverse



A l'équilibre

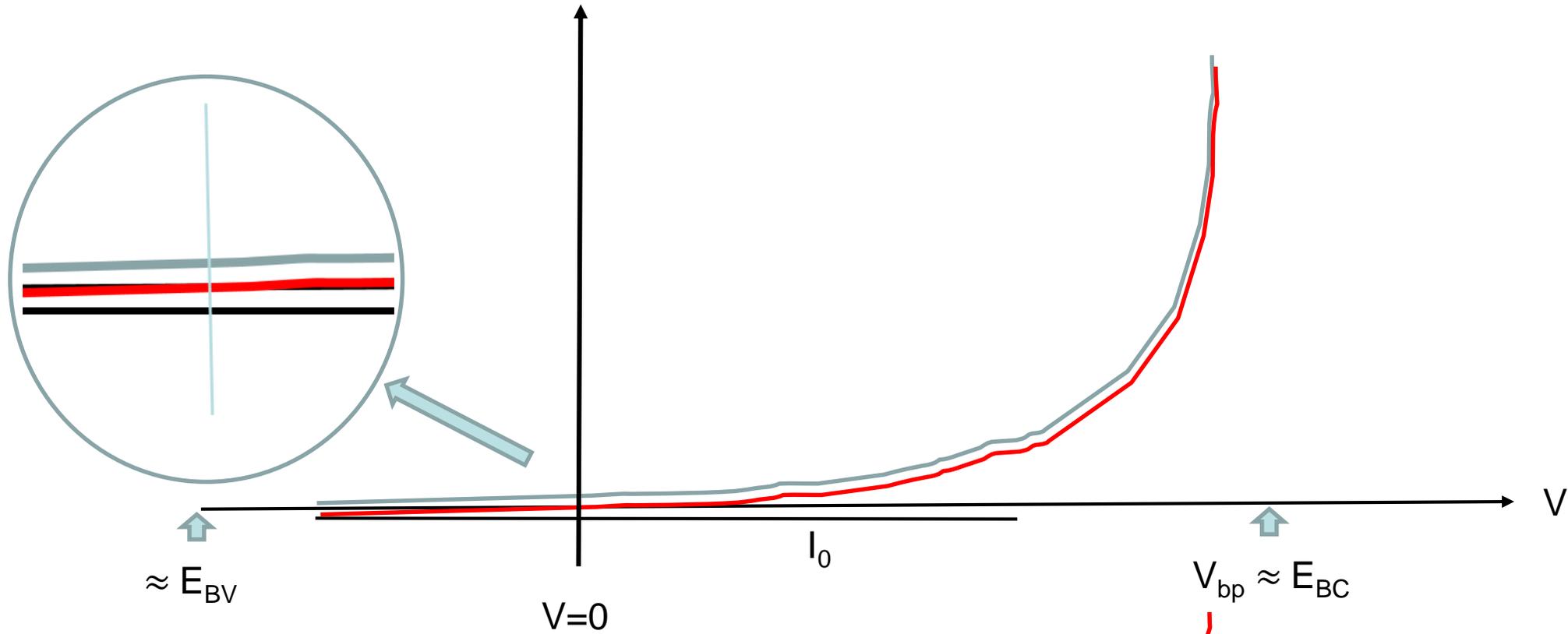


Polarisation directe



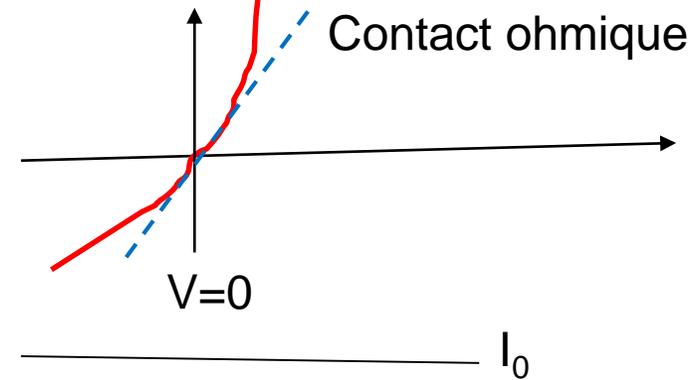
E_{BV}

$$I = I_0 (\exp (qV/kT) - 1)$$

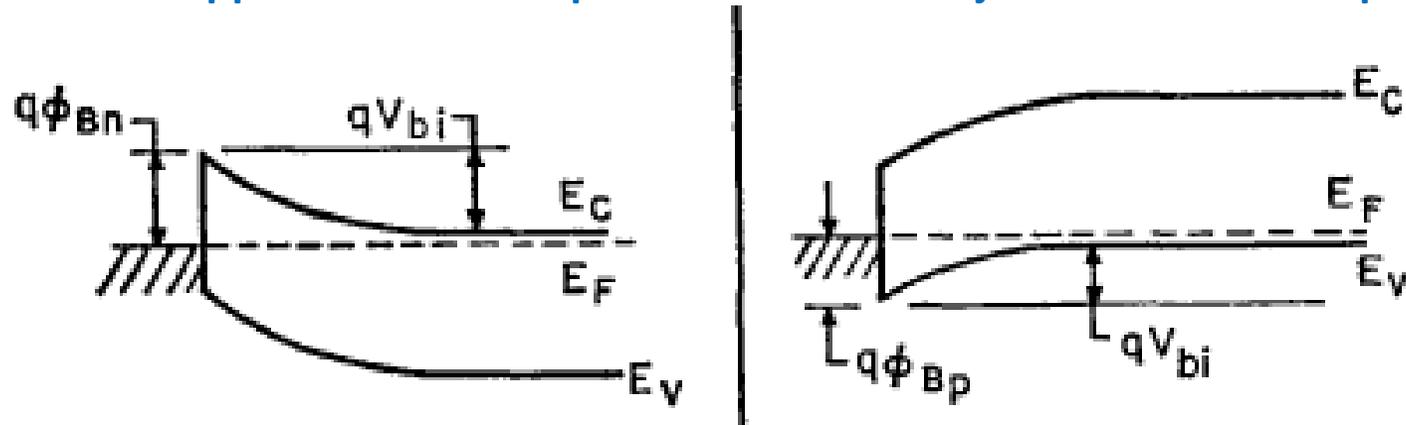


La position de $V=0$ dépend du métal

Φ



Application numérique : mécanisme d'injection thermoionique



$$J_n = \left\{ A^* T^2 \exp\left(-\frac{q\phi_{Bn}}{kT}\right) \right\} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]$$

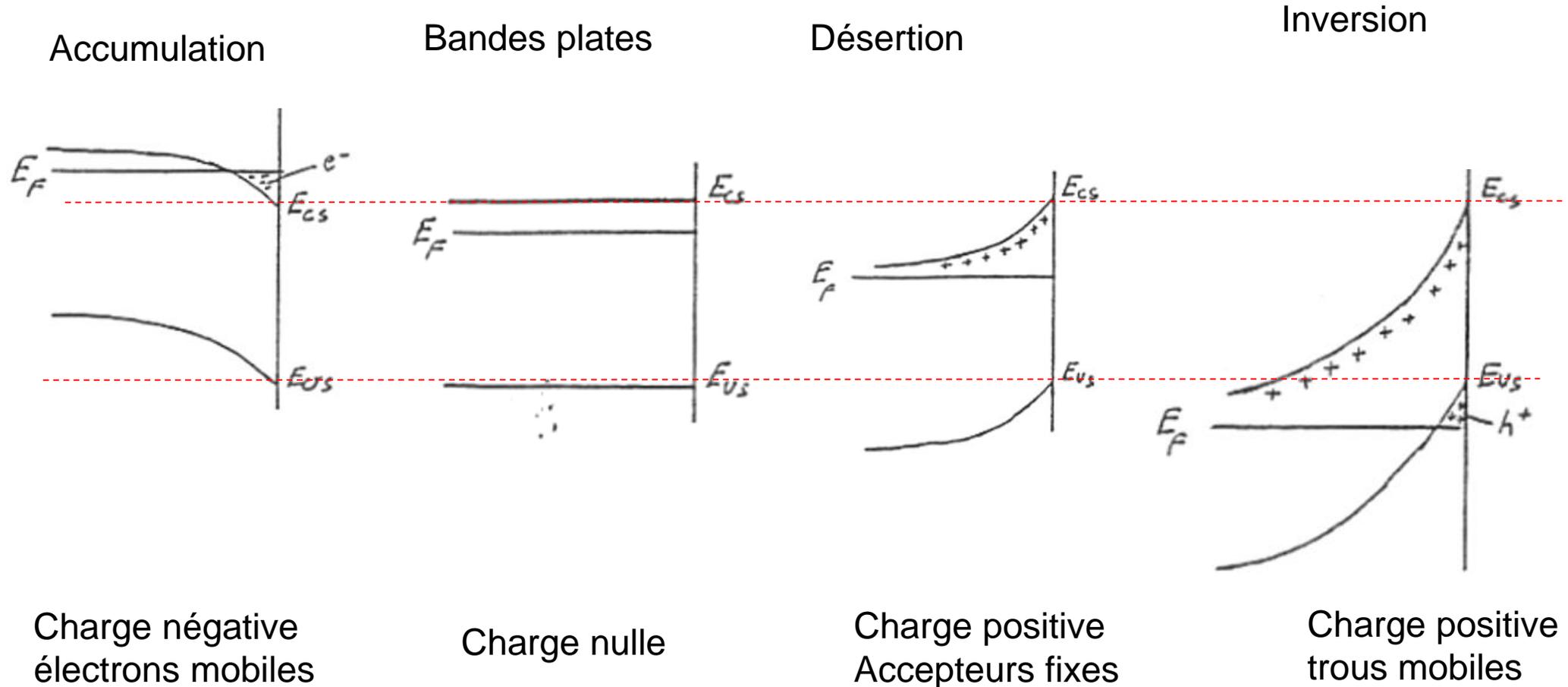
$$= J_{ST} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]$$

$$J_{ST} \equiv A^* T^2 \exp\left(-\frac{q\phi_{Bn}}{kT}\right).$$

For free electrons, $A^* = 120 \text{ amp/cm}^2/\text{K}^2 \equiv A$

$q/kT = 40 \text{ V}^{-1}$ à 25°C

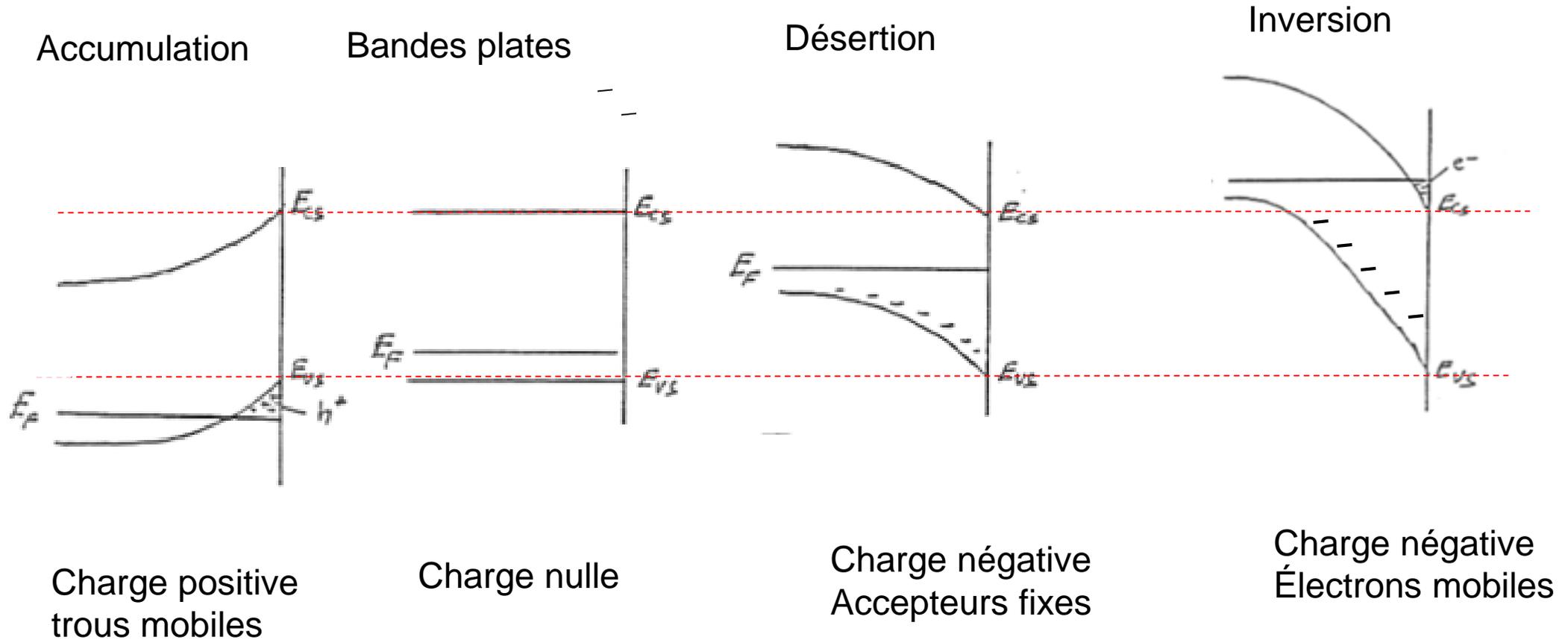
Les différents régimes de polarisation d'une barrière de Schottky : Type N



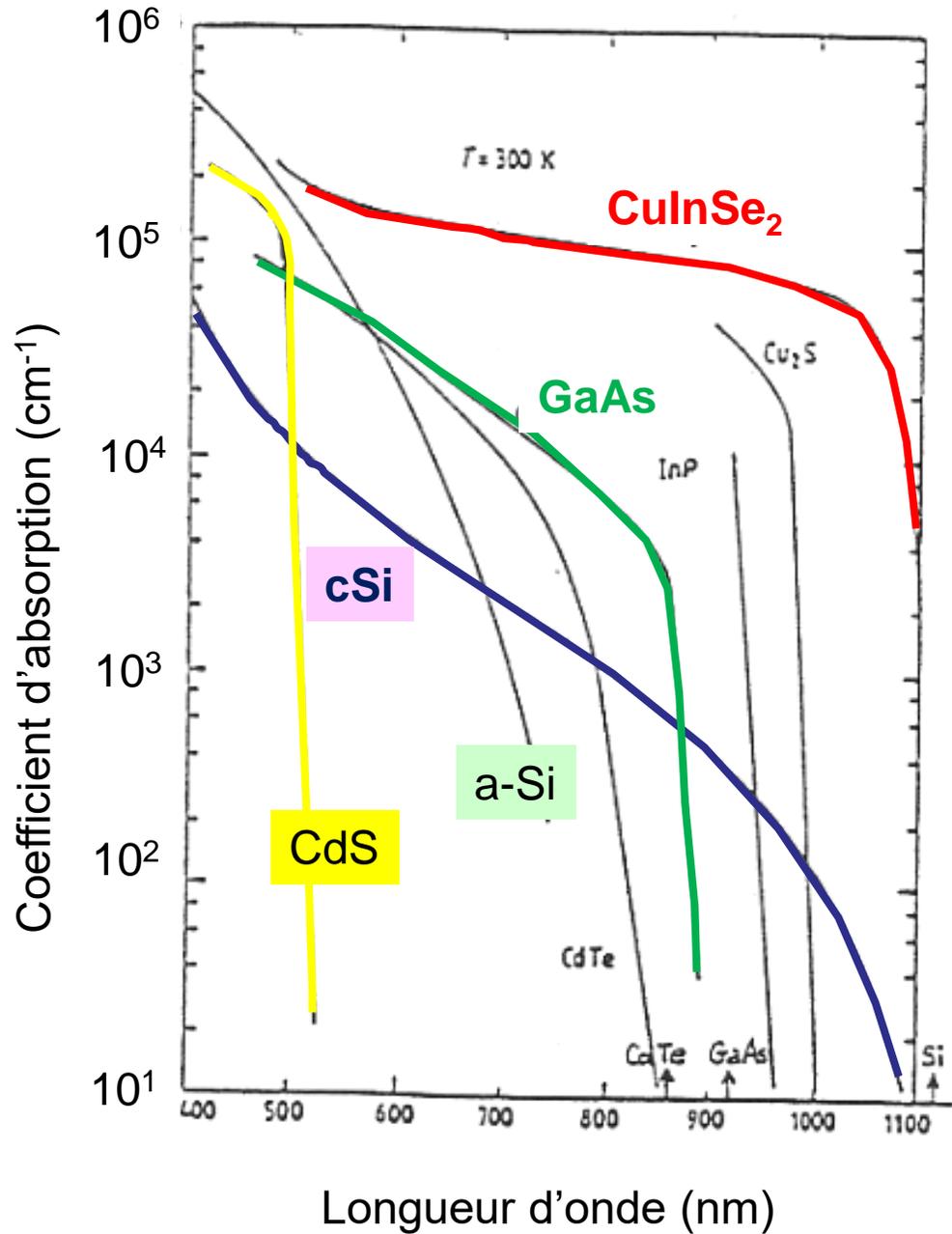
Ces régimes de polarisation peuvent être obtenus:

- En fonction du travail de sorties de la phase de contact
- En fonction de la polarisation pour une phase de contact donnée

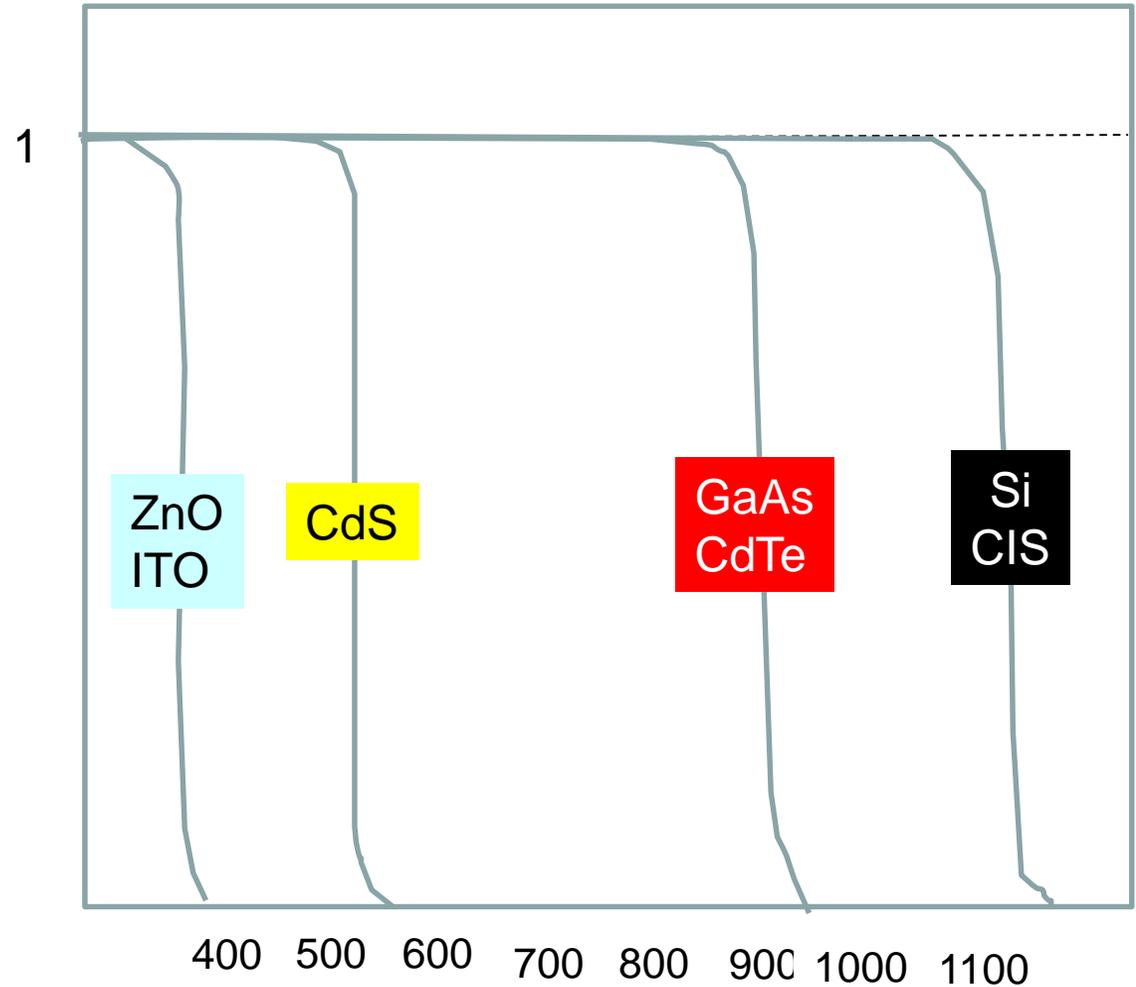
Les différents régimes de polarisation d'une barrière de Schottky : Type P



Génération du photocourant sous rayonnement monochromatique



Spectre d'absorption (épaisseur adaptée)

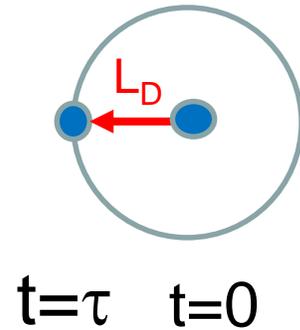


Génération du photocourant sous rayonnement monochromatique

L_D = Longueur de diffusion

$$L = \sqrt{D\tau}$$

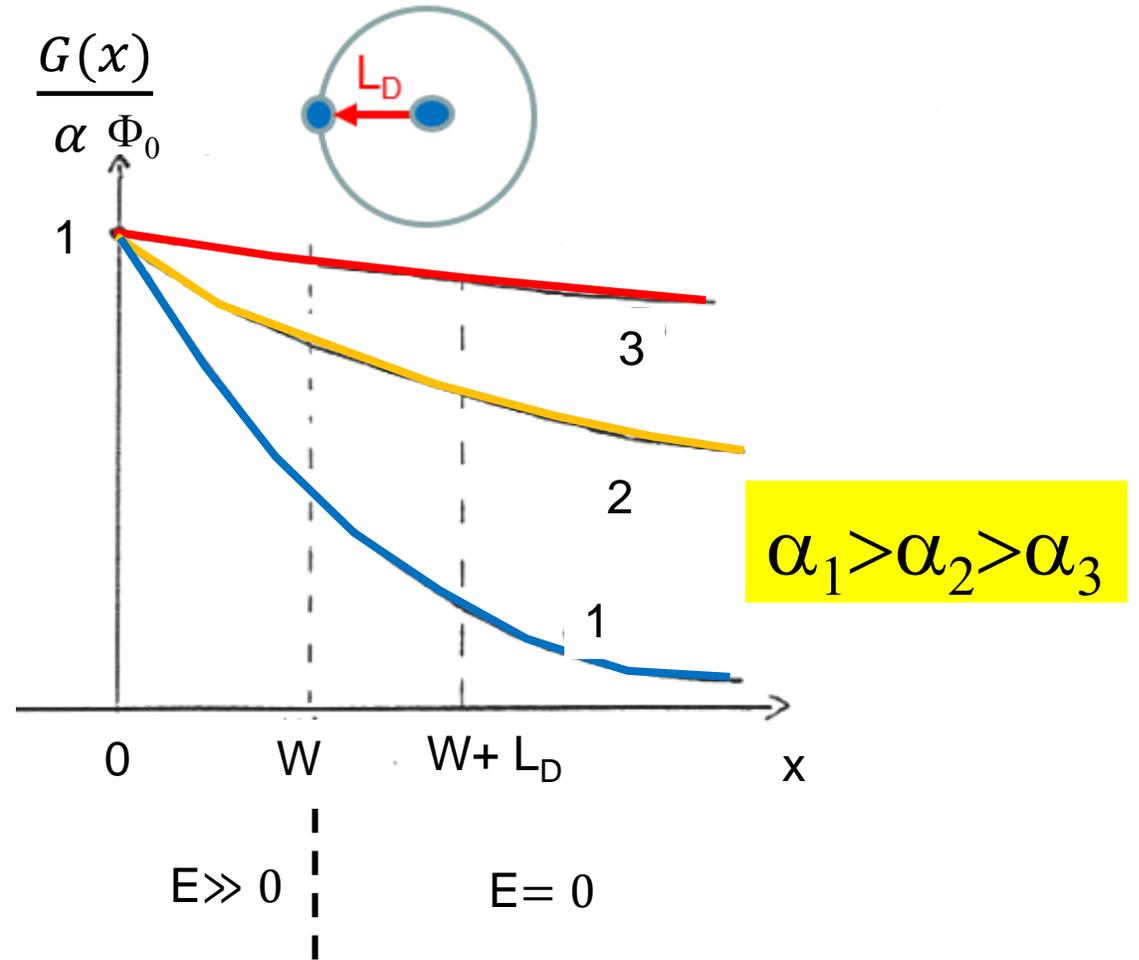
Relation d'Einstein



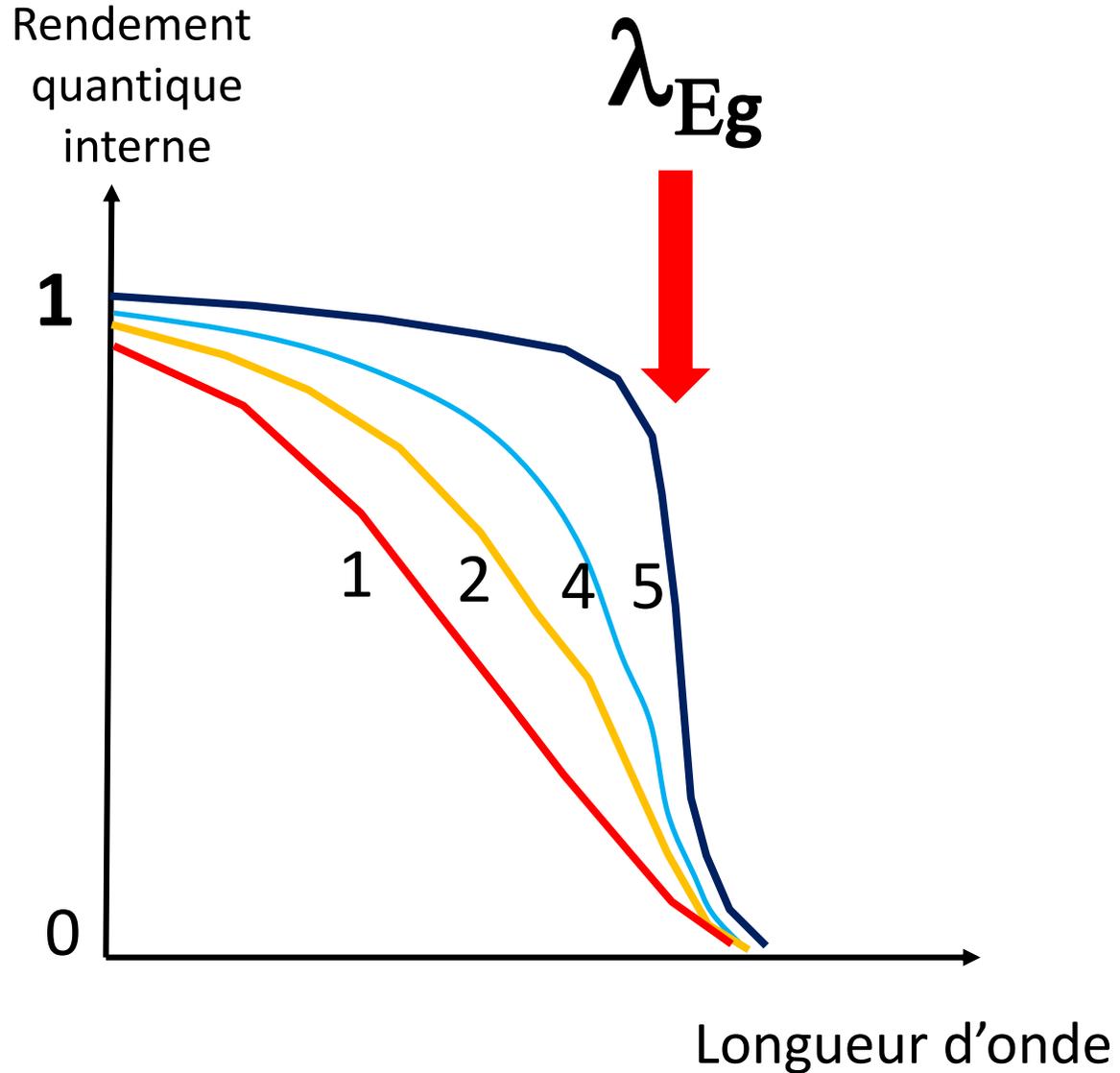
$$0-W \quad J_{ZCE} = q(1-R)\phi_o [1 - \exp(-\alpha W)]$$

$$W+L_D \quad J_{ZN} = q(1-R)\phi_o \left[\frac{\alpha L_D}{1 + \alpha L_D} \right] \exp(-\alpha W)$$

$$J_{ph} = J_{ZCE} + J_{ZN} = q(1-R)\phi_o \left[1 - \frac{\exp(-\alpha W)}{1 + \alpha L_D} \right]$$



Réponse spectrale



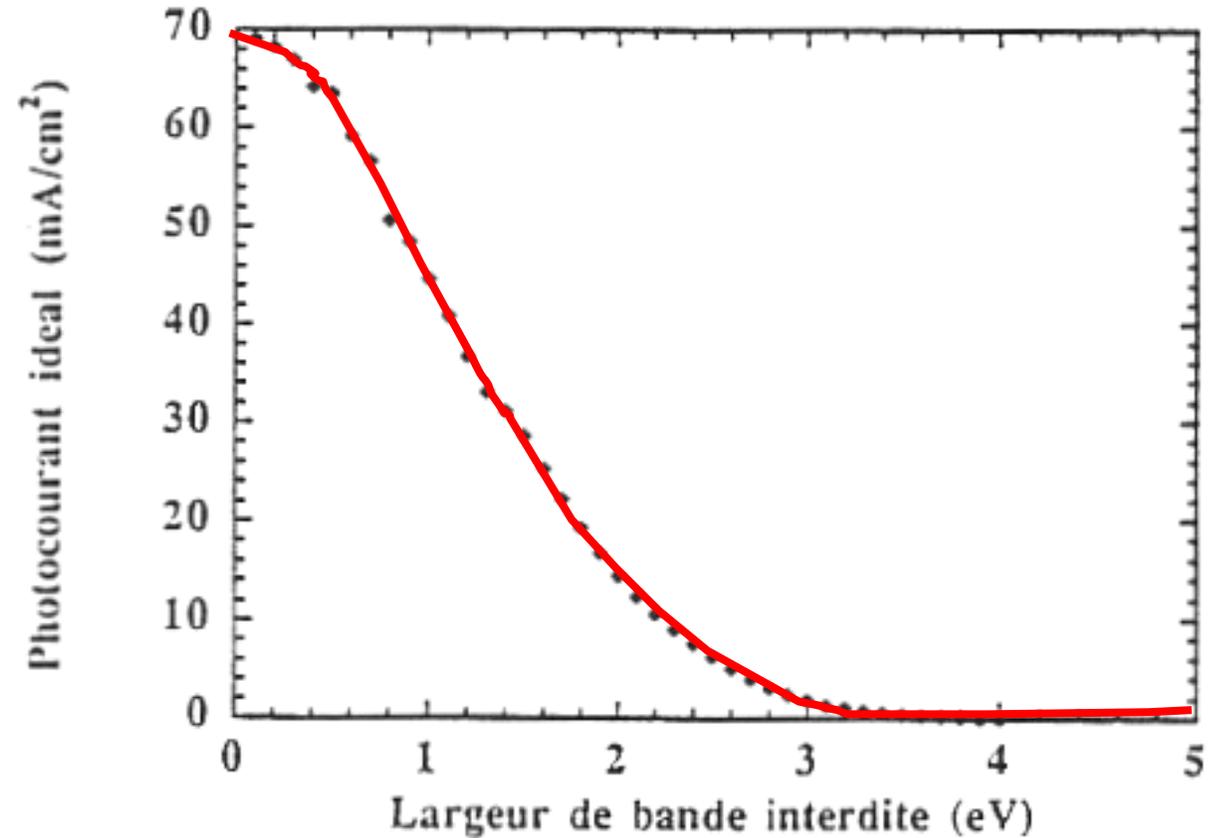
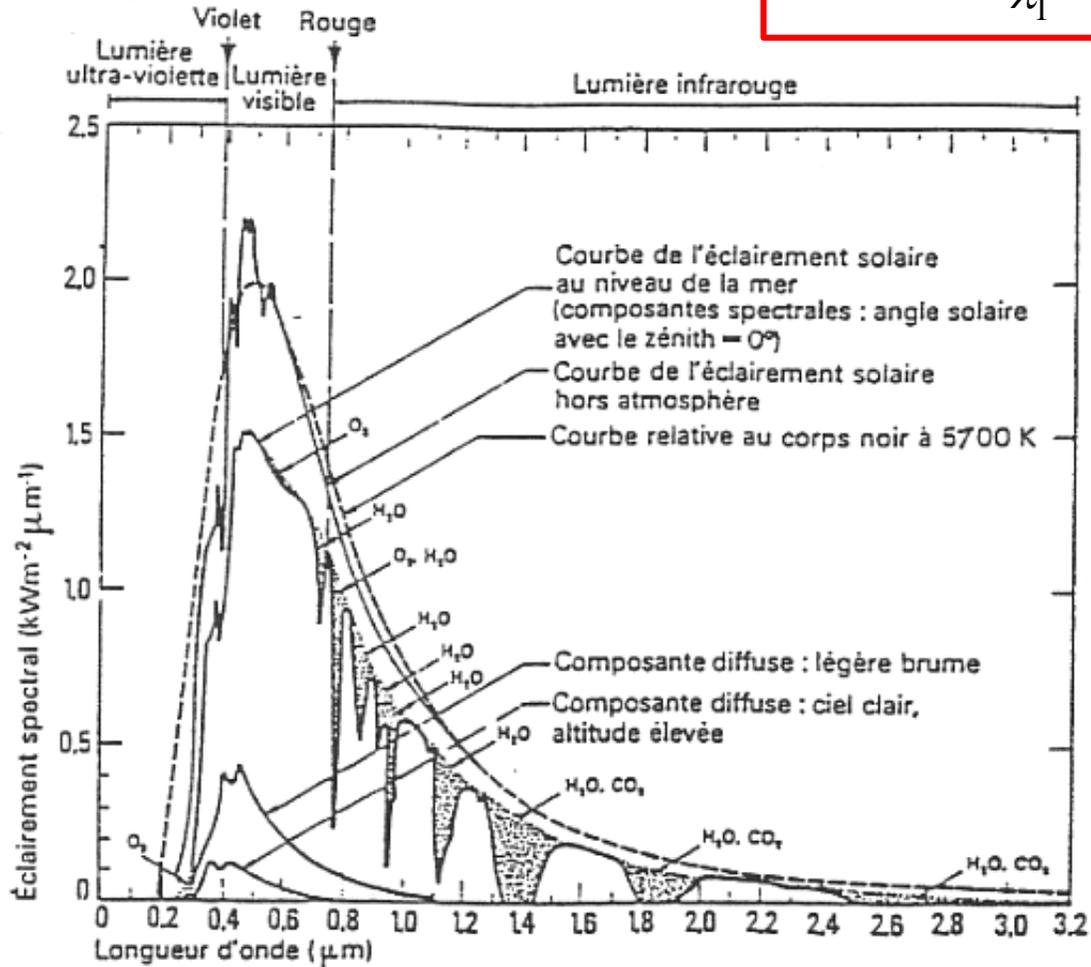
$$RQ_{ext}(\lambda) = \frac{J_{ph}(\lambda)}{q\phi_o(\lambda)} = (1-R) \left[1 - \frac{\exp(-\alpha W)}{1 + \alpha L_D} \right]$$

$$RQ_{int}(\lambda) = 1 - \frac{\exp(-\alpha W)}{1 + \alpha L_D}$$

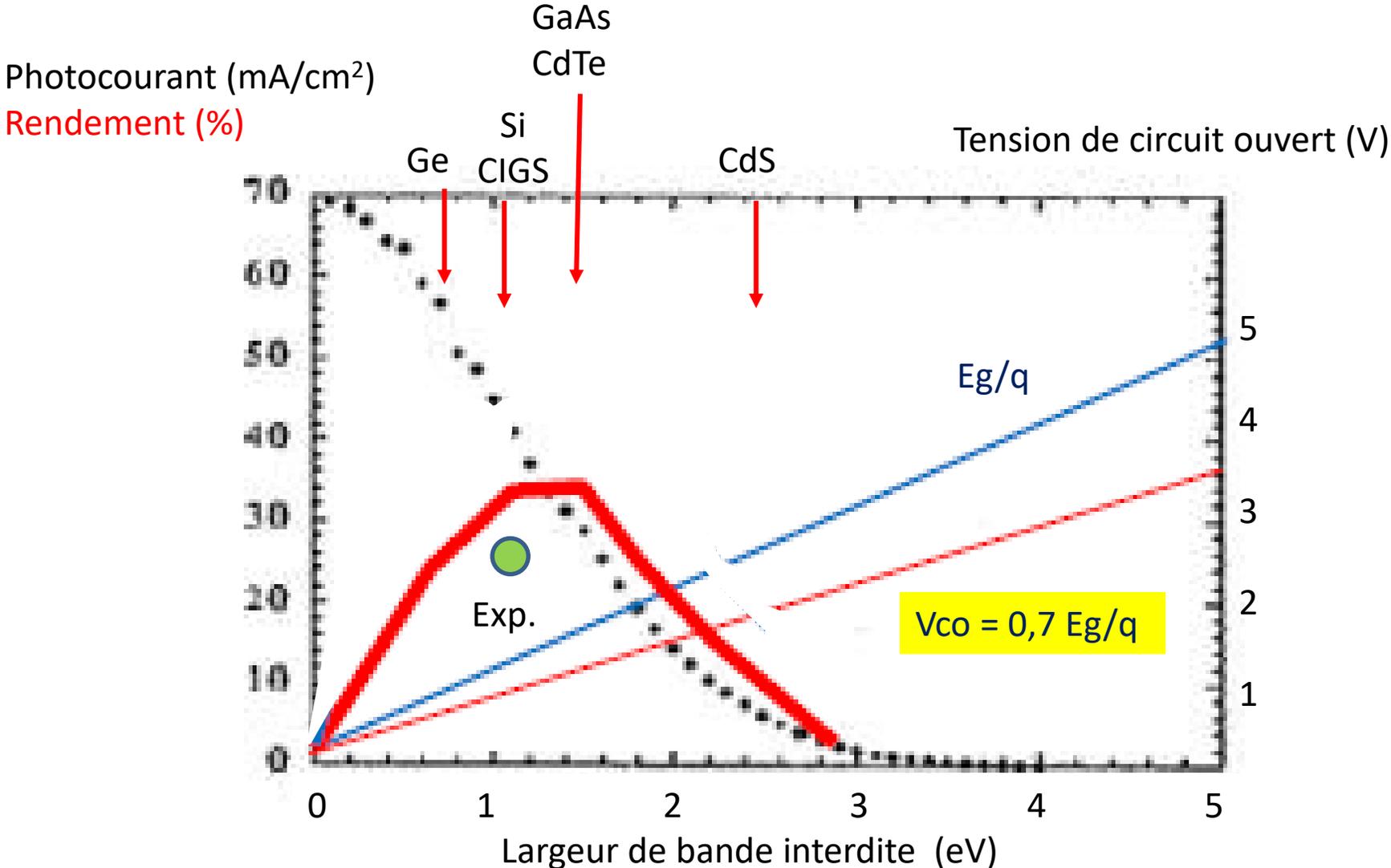
Qualité du matériau augmente
 $5 > 4 > 3 > 2 > 1$
 Longueur de diffusion croissante :

Génération du photocourant sous éclairage solaire

$$I_{\text{ph}} = q \int_{\lambda_1}^{\lambda_2} \phi_o(\lambda) RQ_{\text{ext}}(\lambda) d\lambda$$

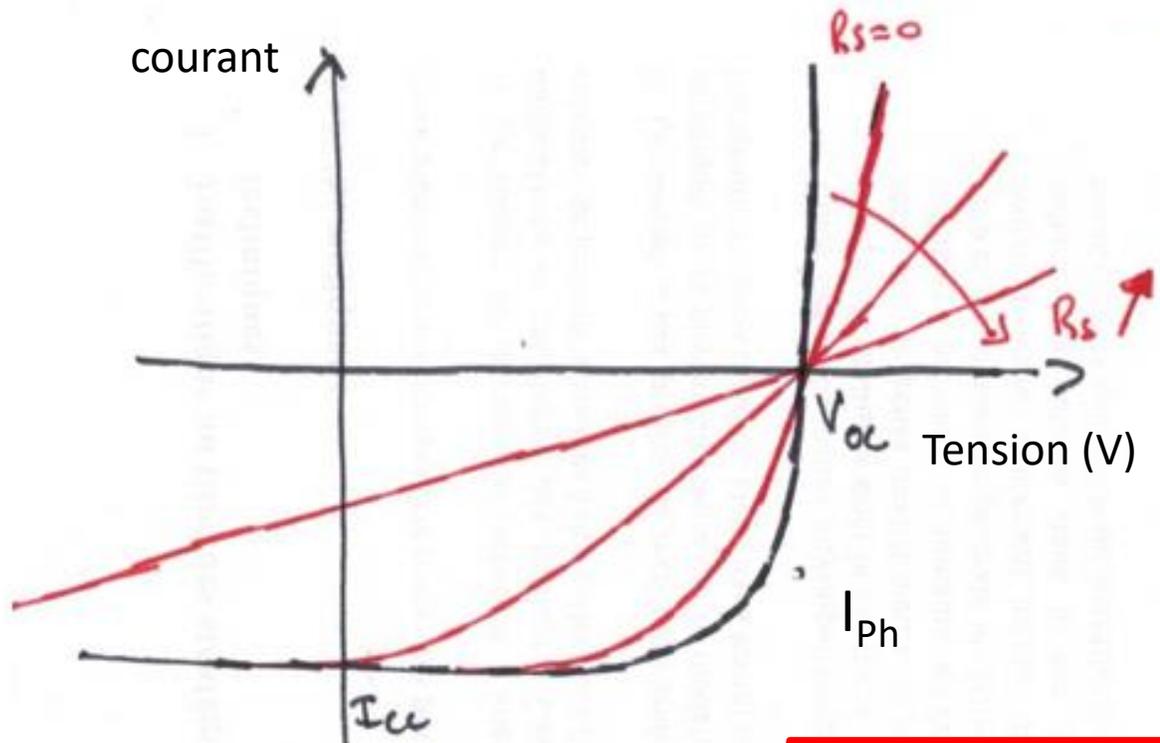


Rendement maximum « avec les mains » : où l'on retrouve la limite de Shockley-Queisser

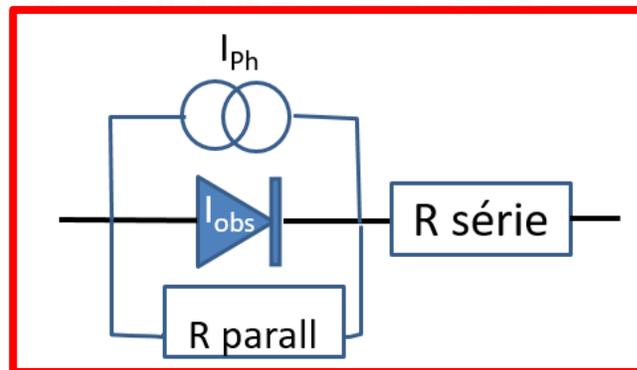
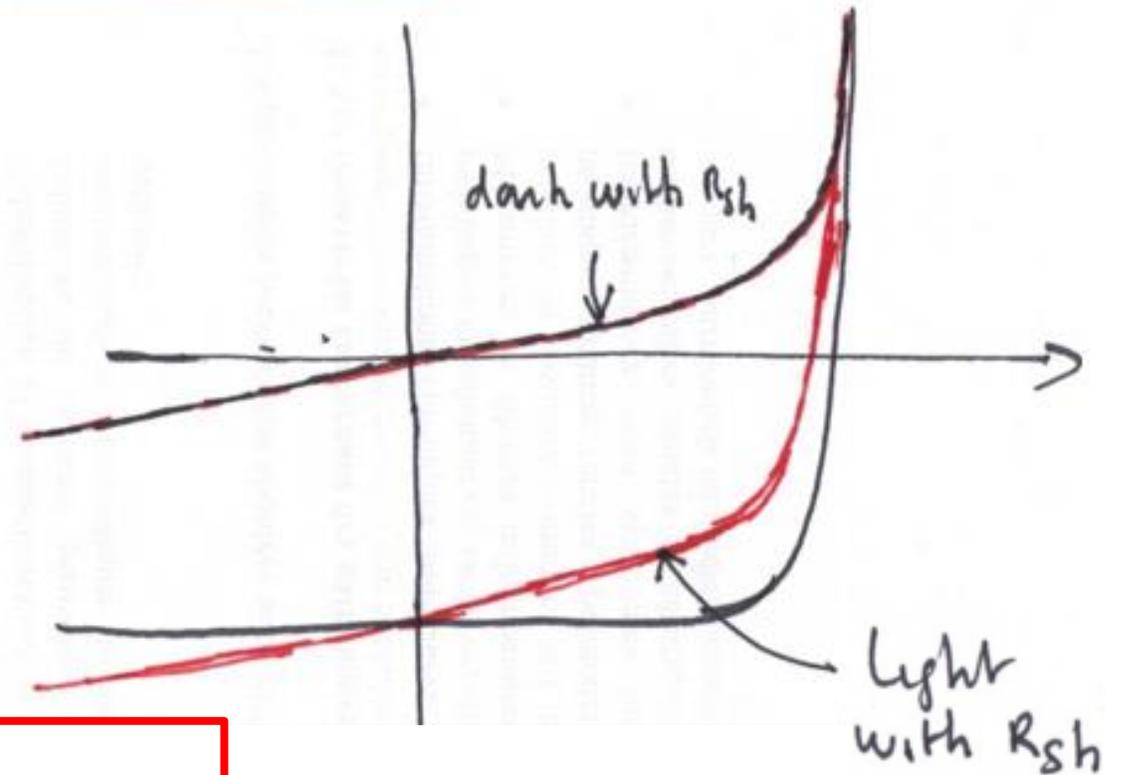


Pertes par résistance série et résistance shunt

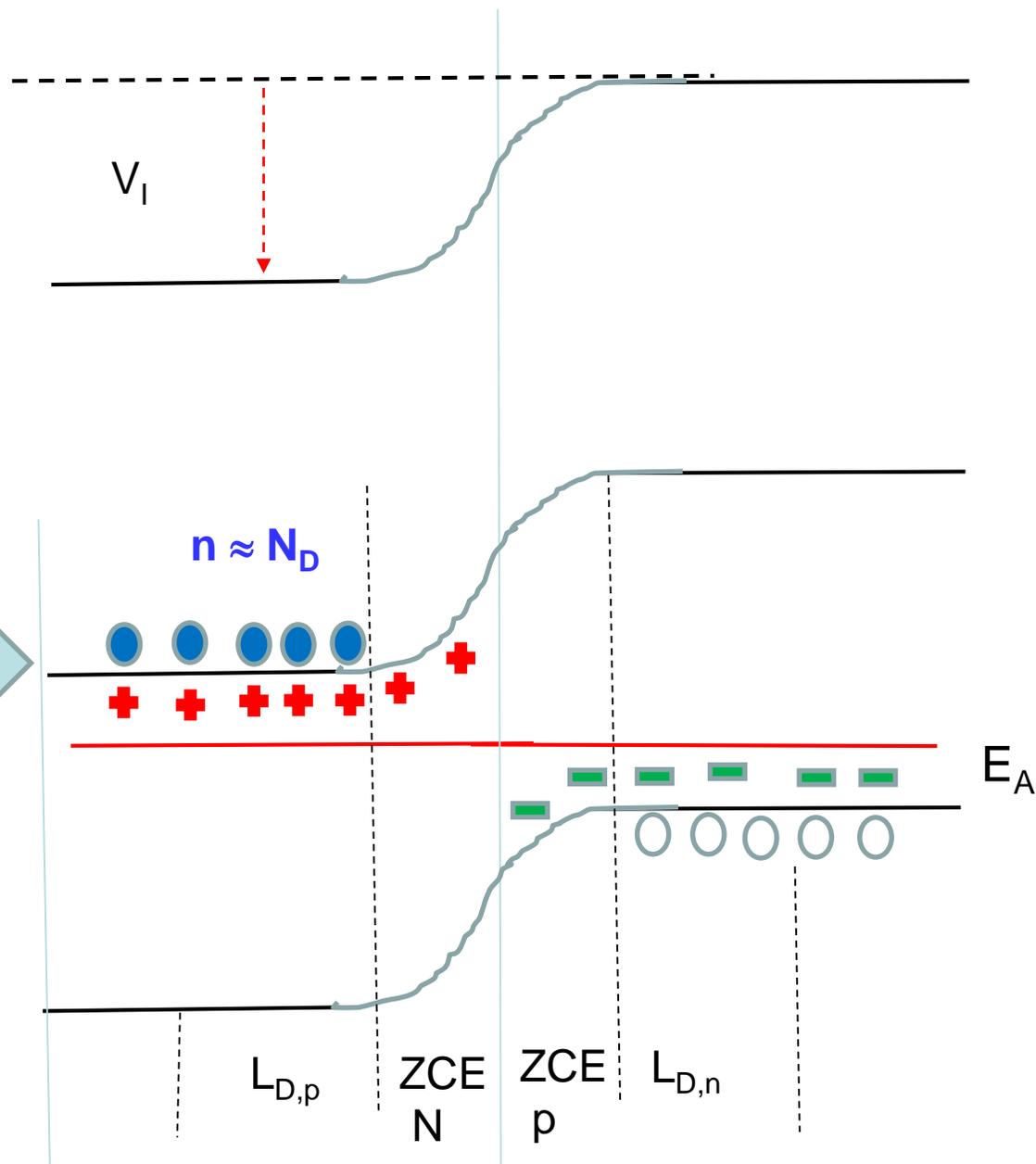
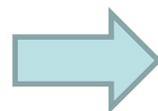
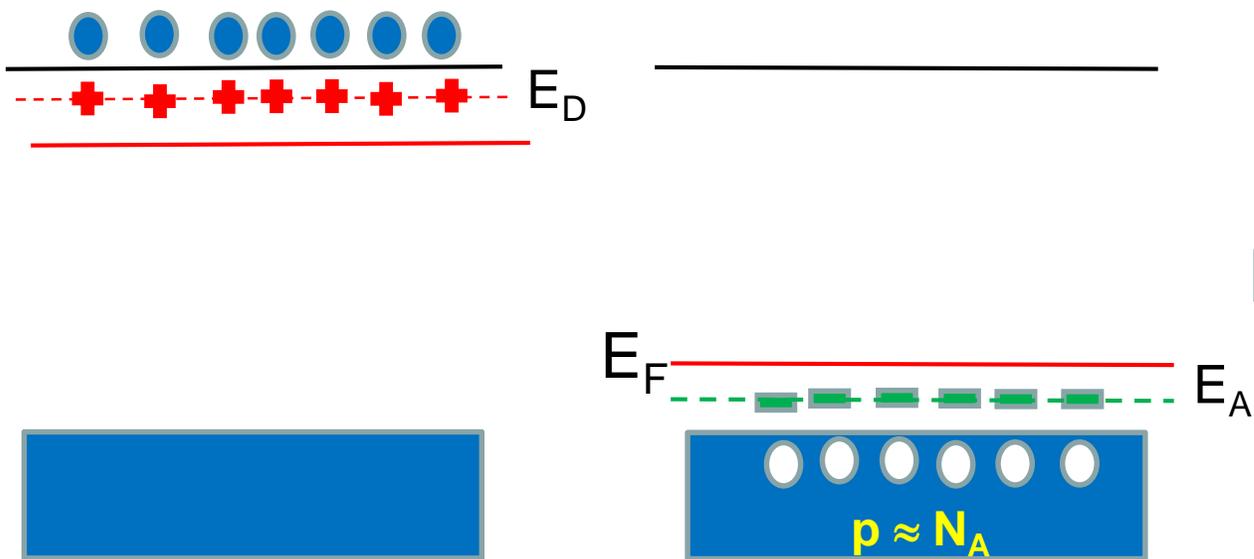
Résistance série sous lumière



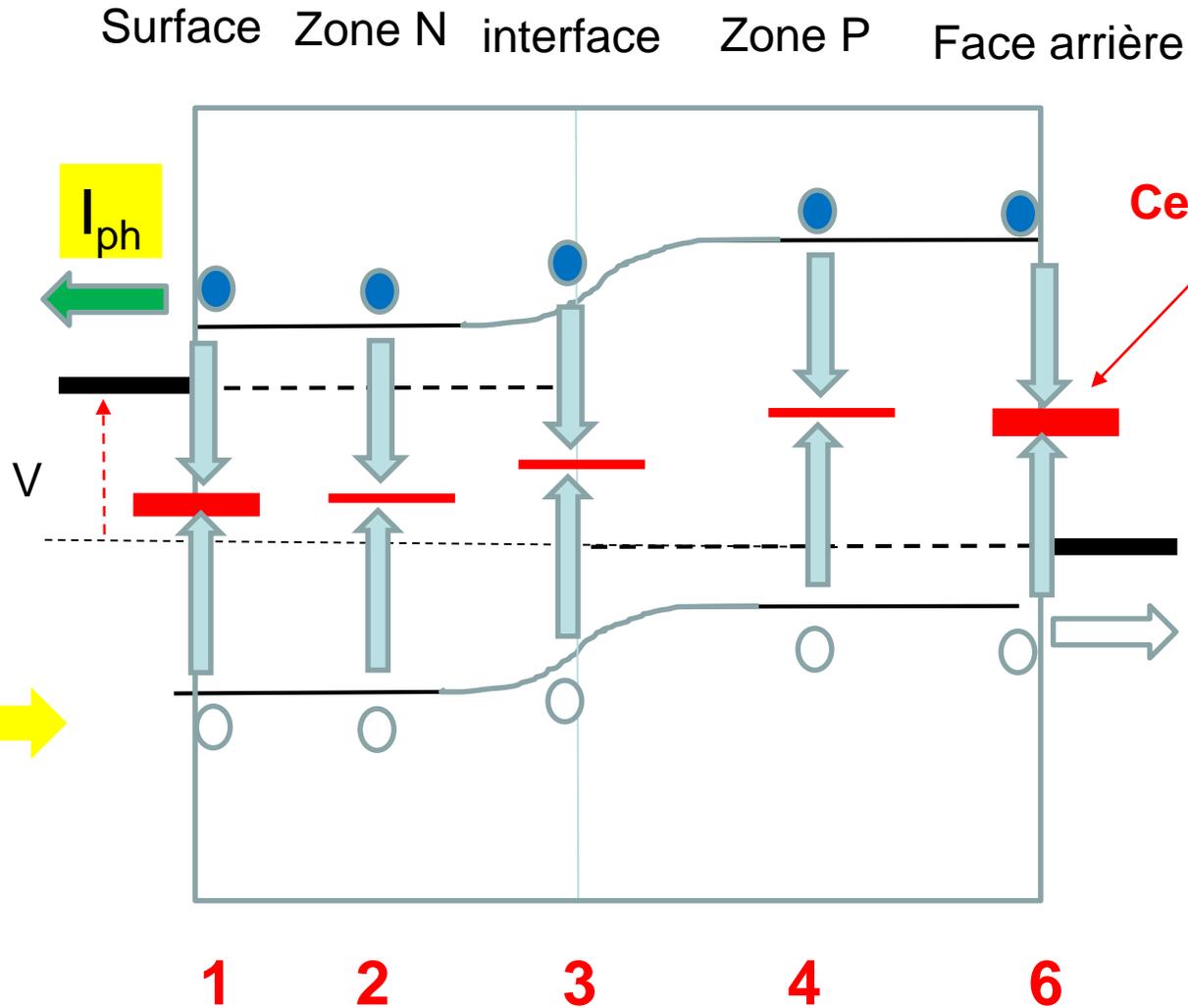
Résistance shunt



Cas de l'homojonction n-p



Pertes de photocourant par mécanismes de recombinaison



- 1 : recombinaison de surface
- 2: recombinaison zone N
- 3: recombinaison interface n-p
- 4: recombinaison zone p
- 5: recombinaison face arrière

défauts

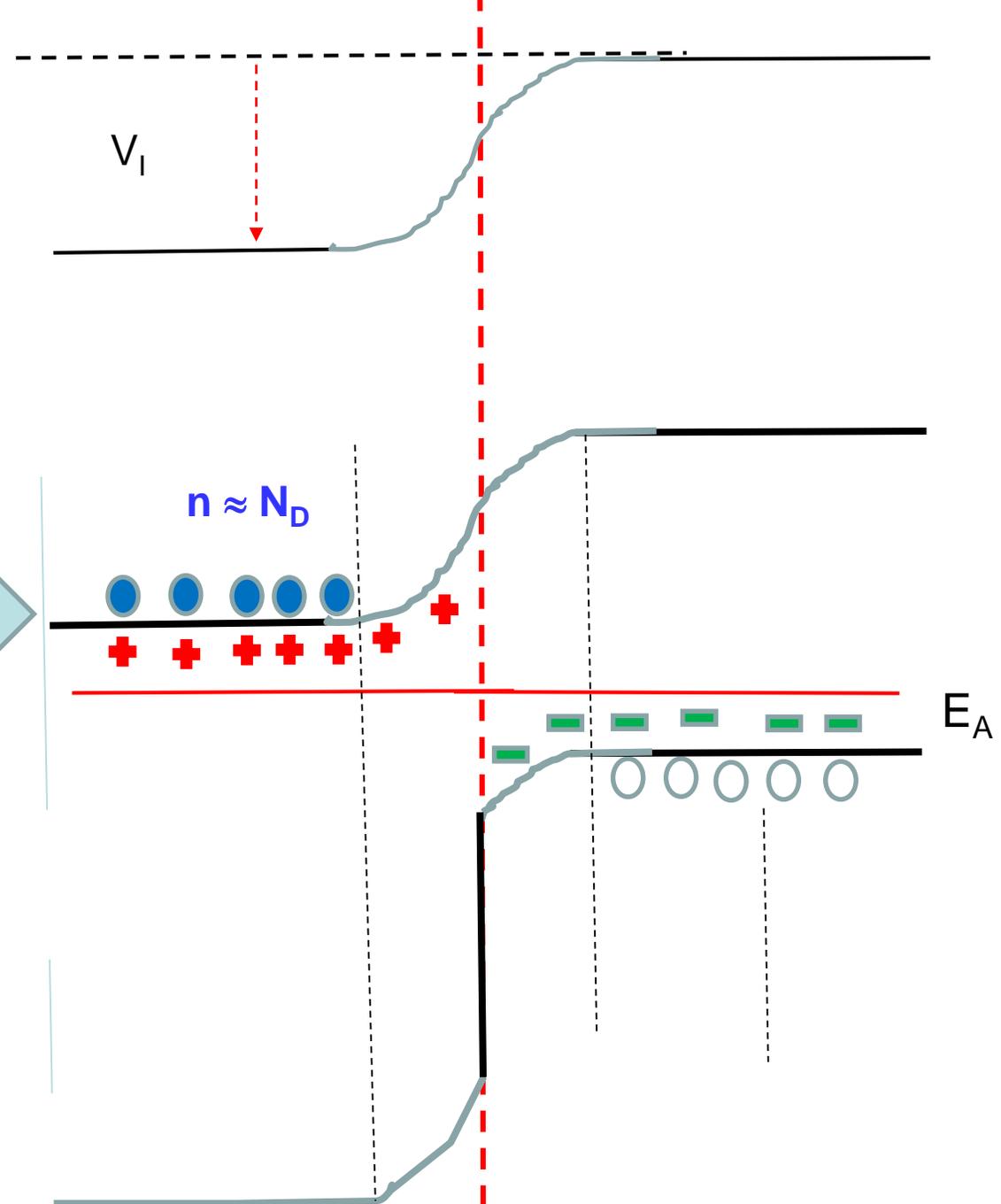
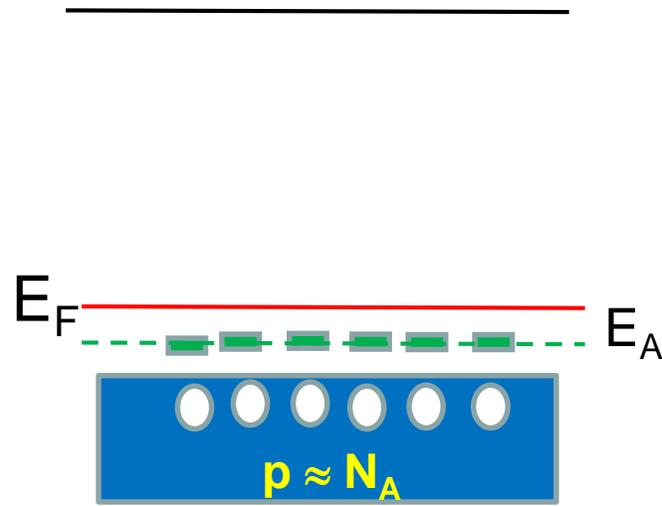
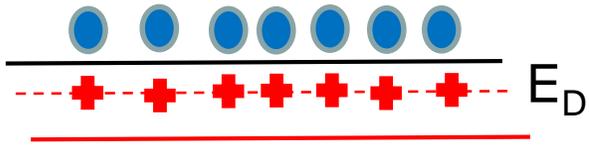


$$n^* p^* \gg n_i^2$$

Hétérojonction n-p

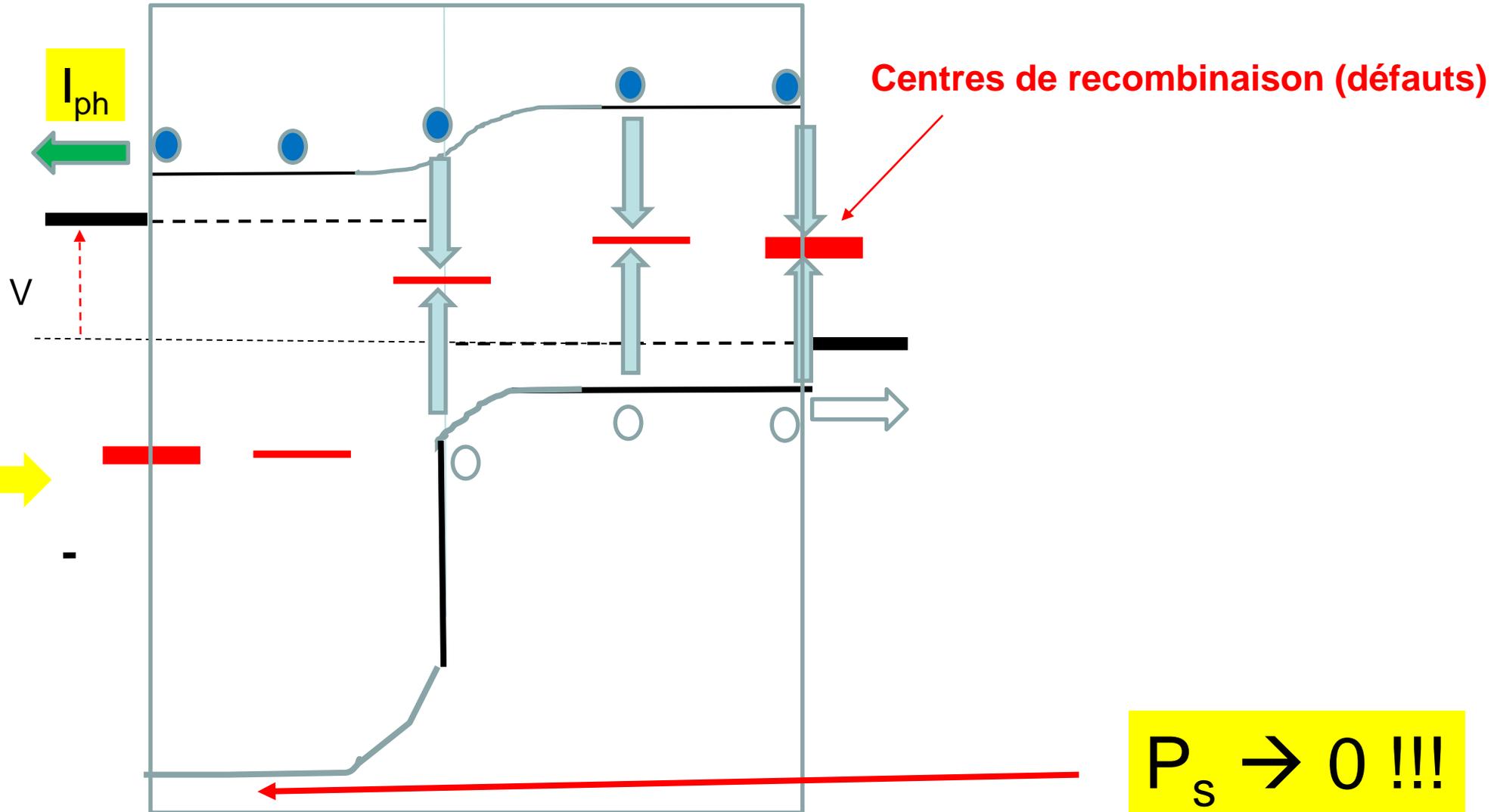
Exemple aSi
CdS, ZnO, GaAlAs

Exemple Si
GaAs, CdTe...



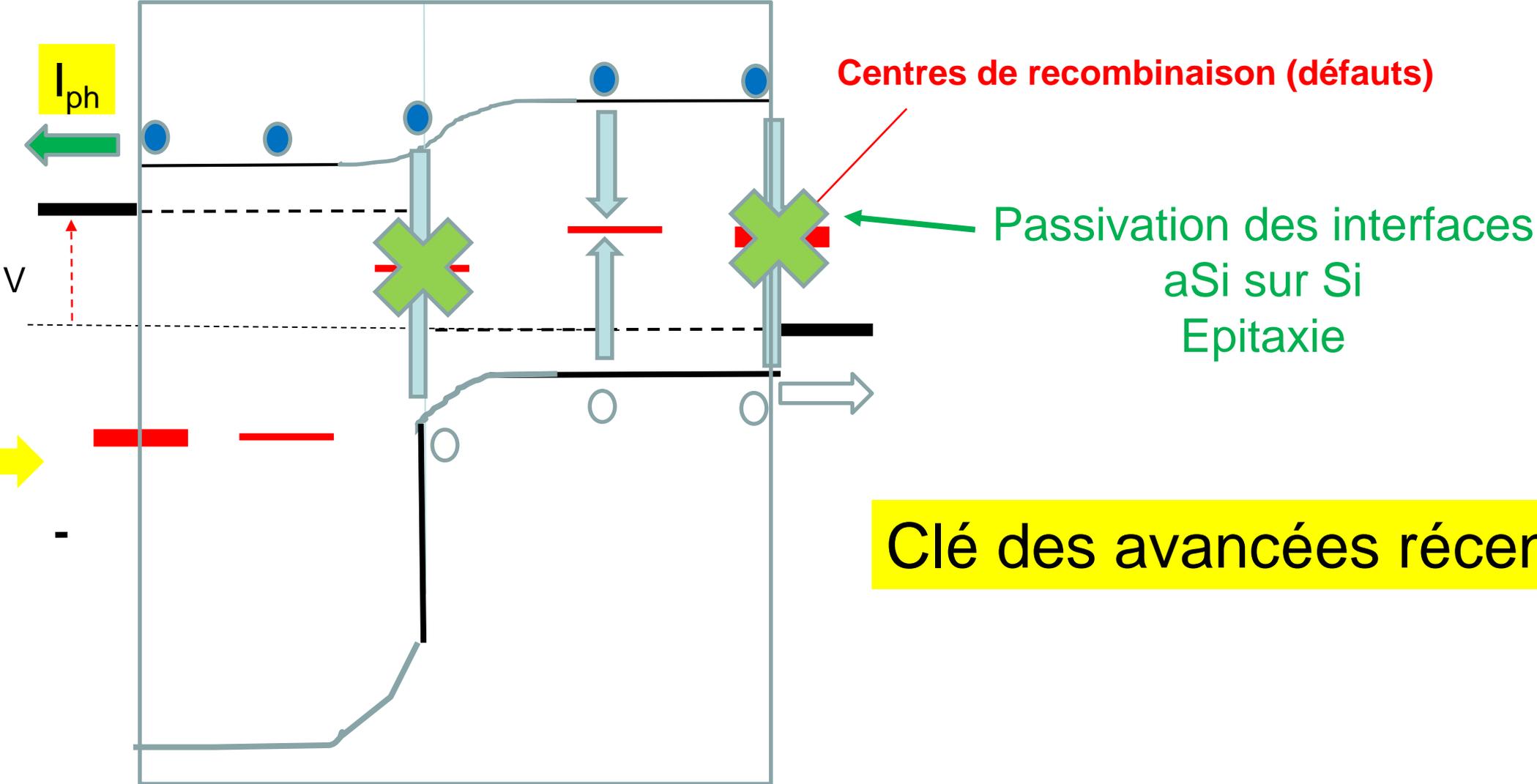
Pertes de photocourant par mécanismes de recombinaison : cas des hétérojonctions

Surface Zone N interface Zone P Face arrière



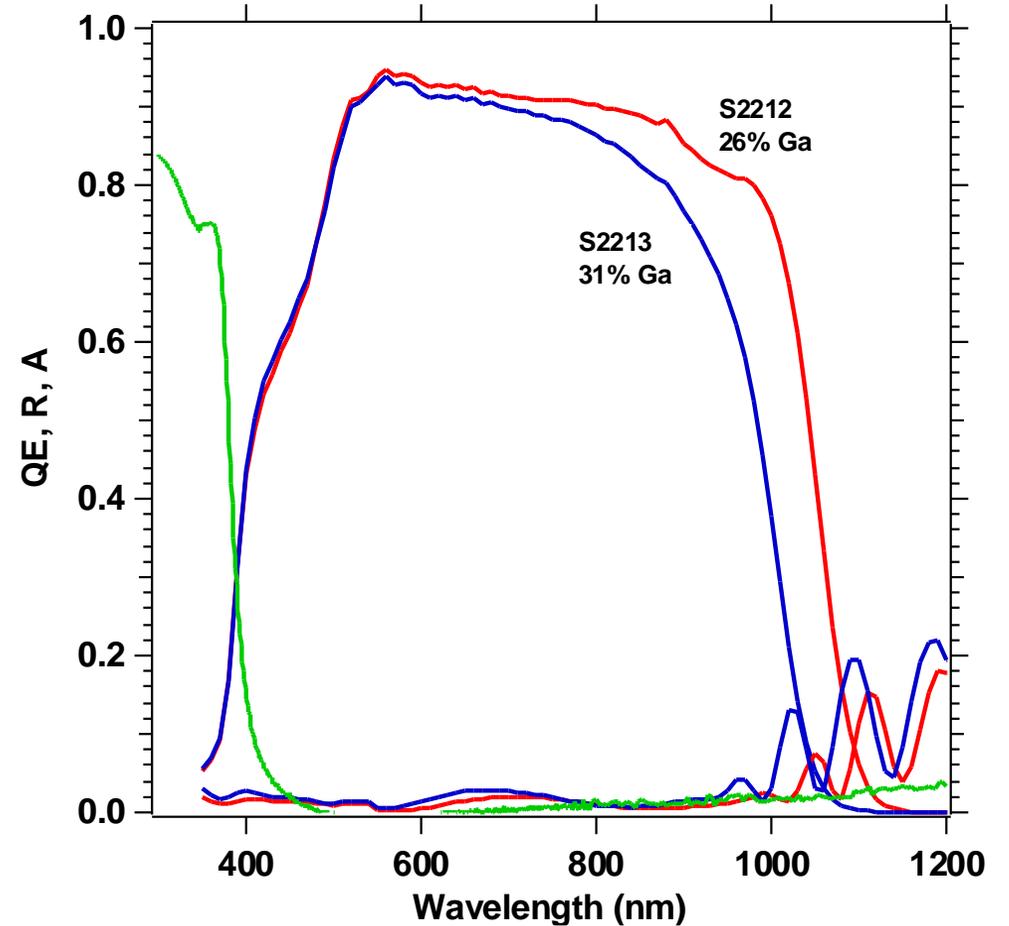
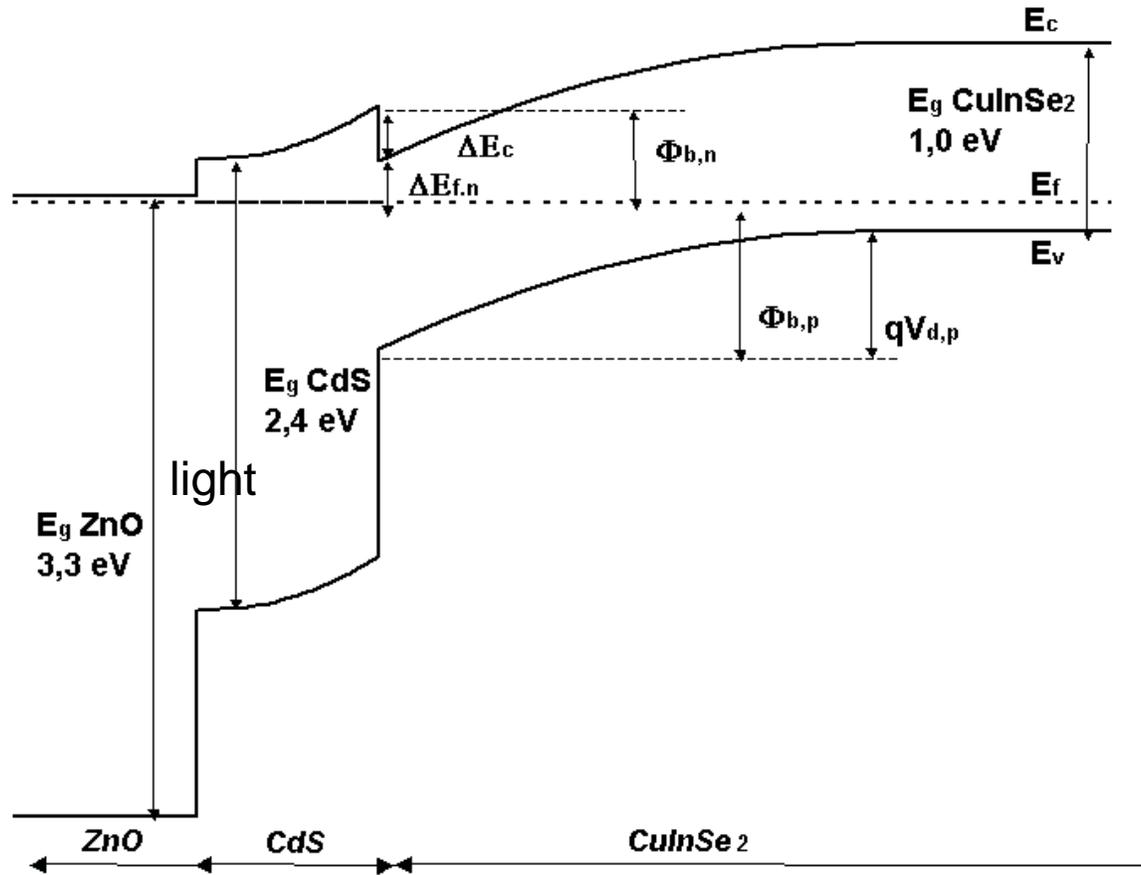
Pertes de photocourant par mécanismes de recombinaison: cas de hétérojonctions

Surface Zone N interface Zone P Face arrière



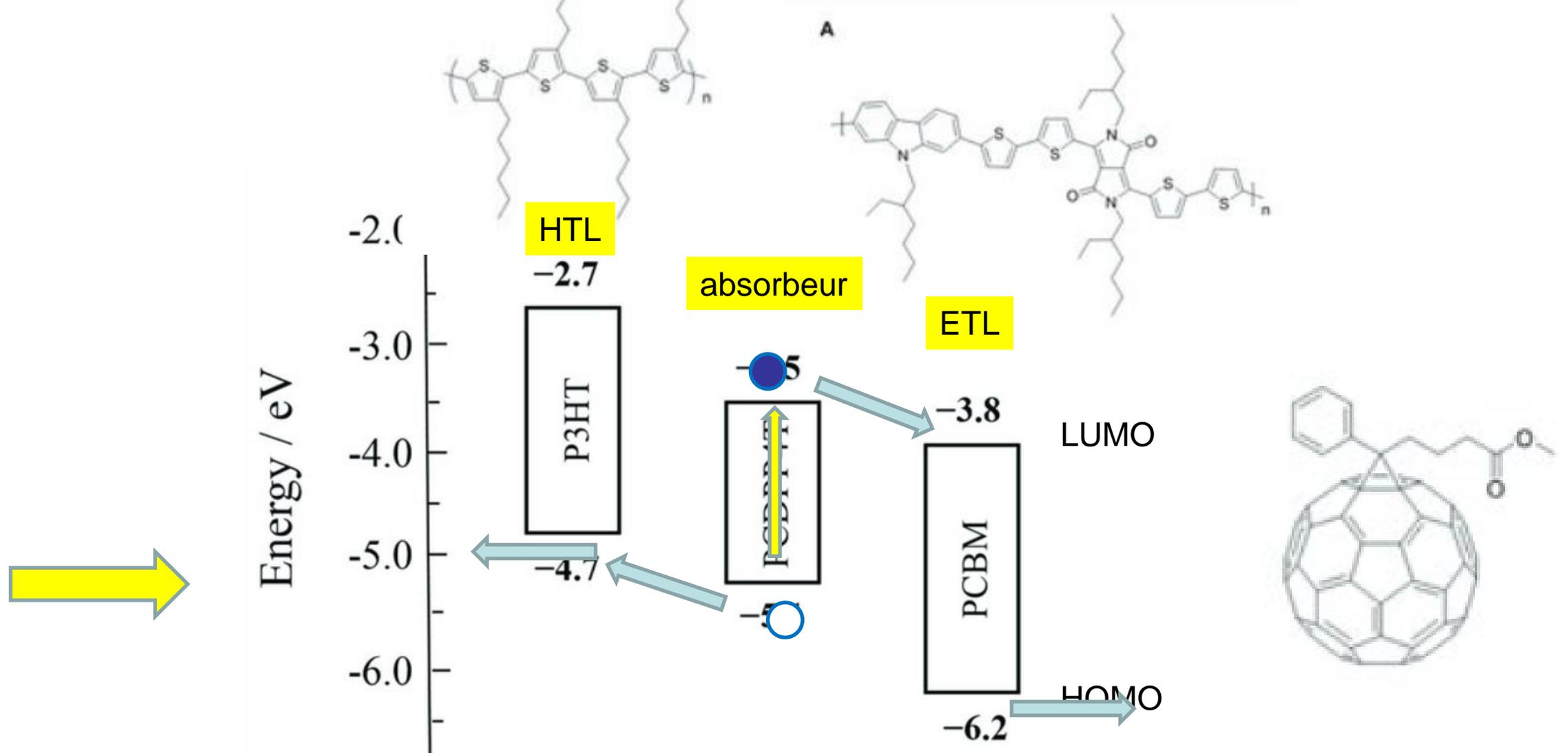
Clé des avancées récentes

Exemple des cellules CIGS



Par courtoisie : Dr. K. Ramanathan et al.,
NREL, EMRS 2004

Application au photovoltaïque organique



HTL : couche transporteuse de trous
 ETL: couche transporteuse d'électrons

Transparents de réserve

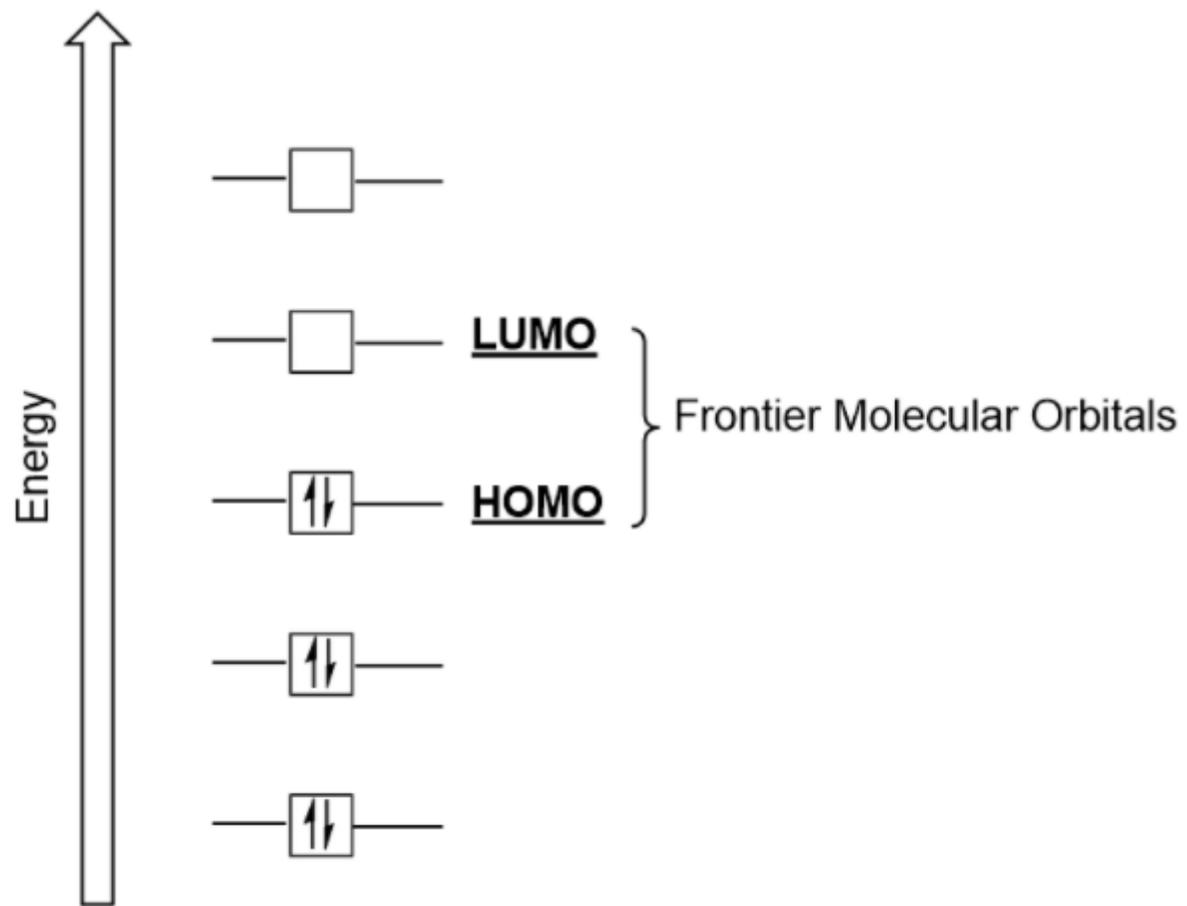
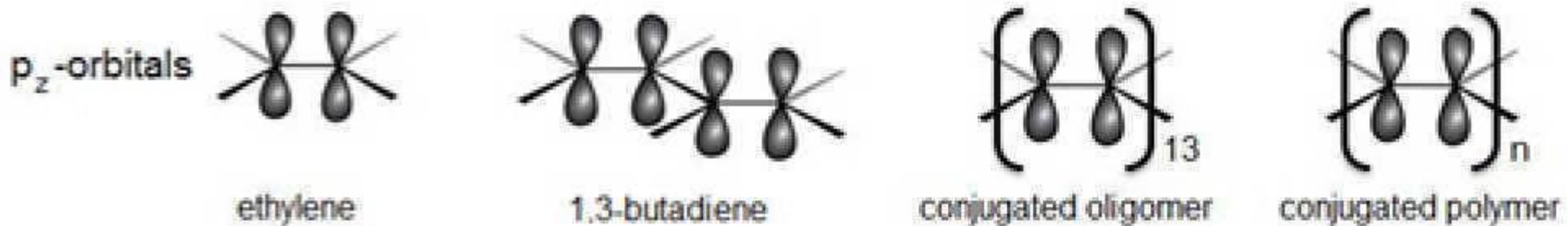
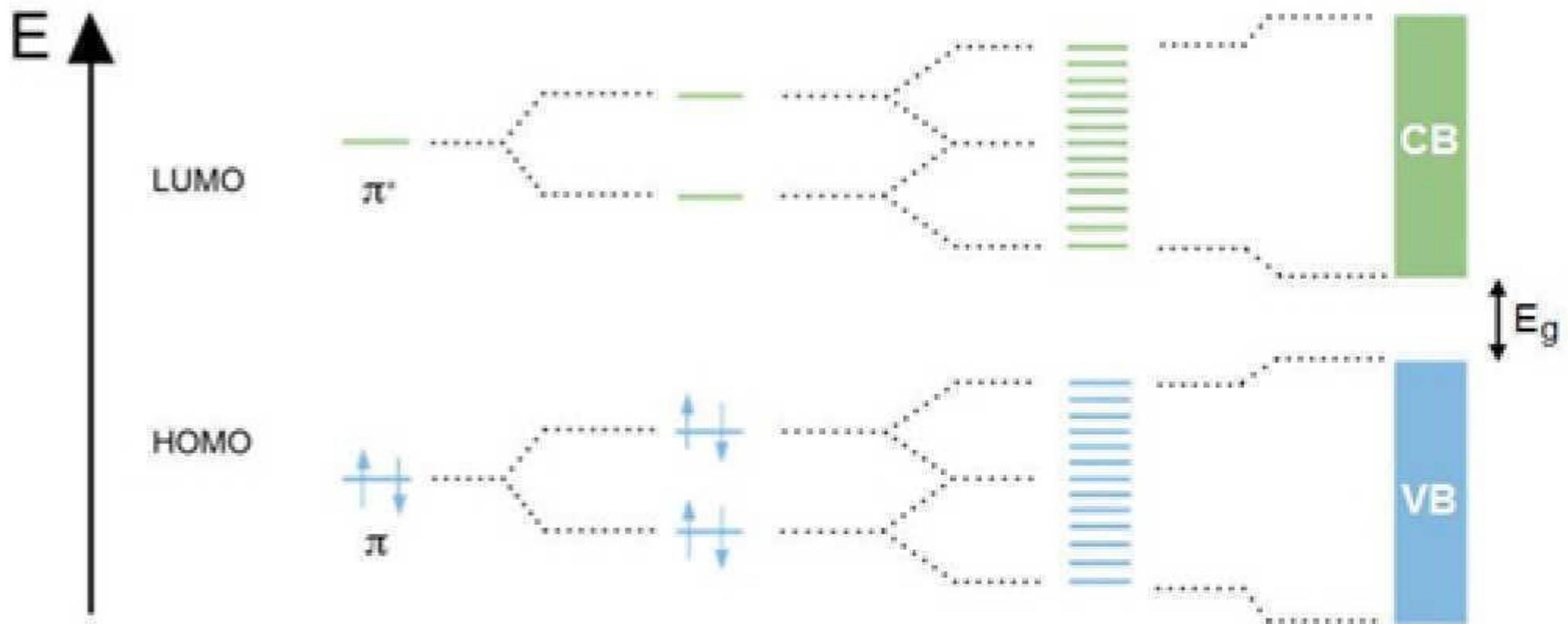
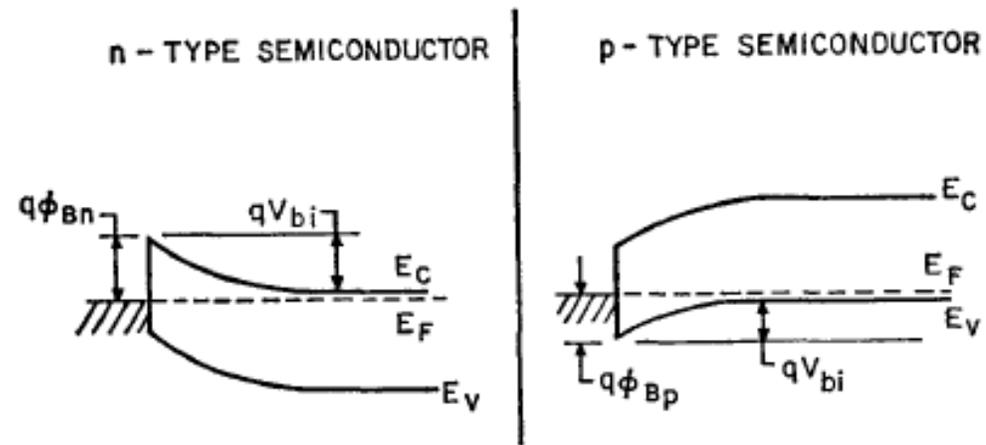
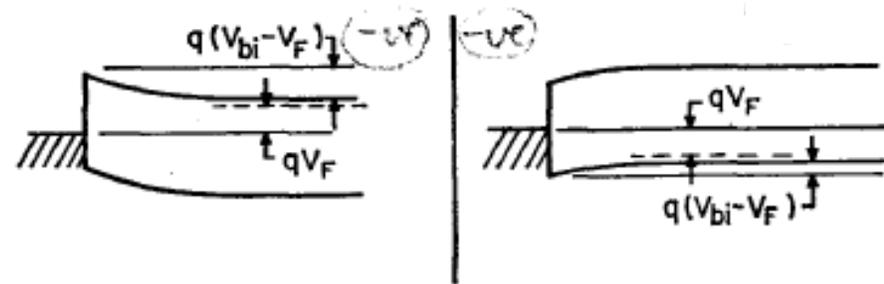


Figure 9.26 "Frontier molecular orbitals HOMO and LUMO."

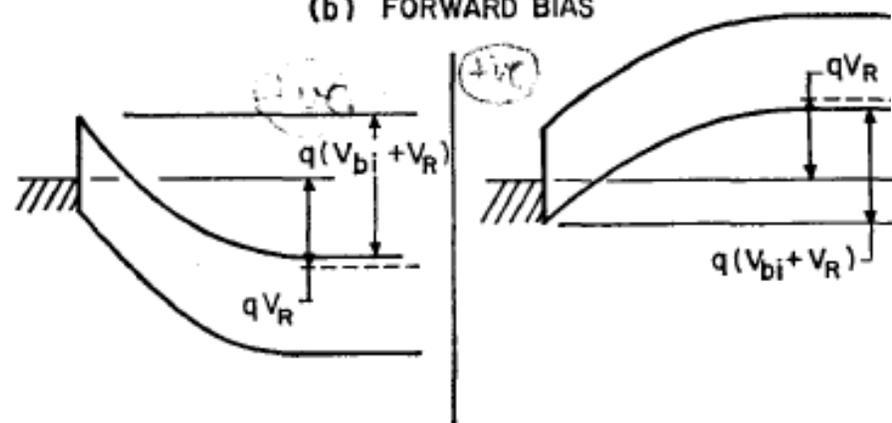




(a) THERMAL EQUILIBRIUM



(b) FORWARD BIAS



(c) REVERSE BIAS