Band Offsets At Interfaces of Current Interest

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OUTLINE

- Introduction
- Band Offset : What is it? Why is it important?
- Conventional Band Offset Theories - Blame it on the "interface states"
- What's wrong with the "interface states" explanation?
- Let's ask the chemists how to solve this solid state physicists' problem!
- Implications for Current Technological Interfaces
  - Metal-organic and organic-organic interfaces
  - High-K Oxide/Si interfaces

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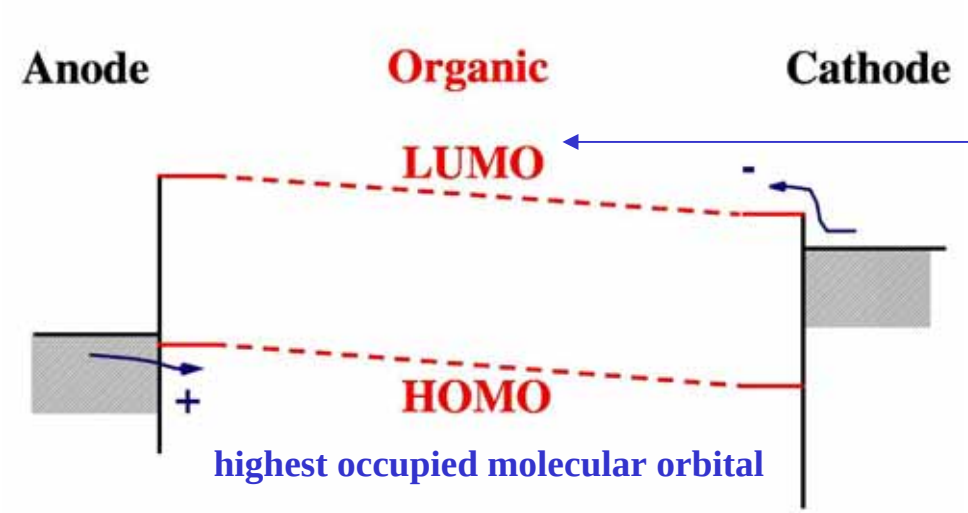
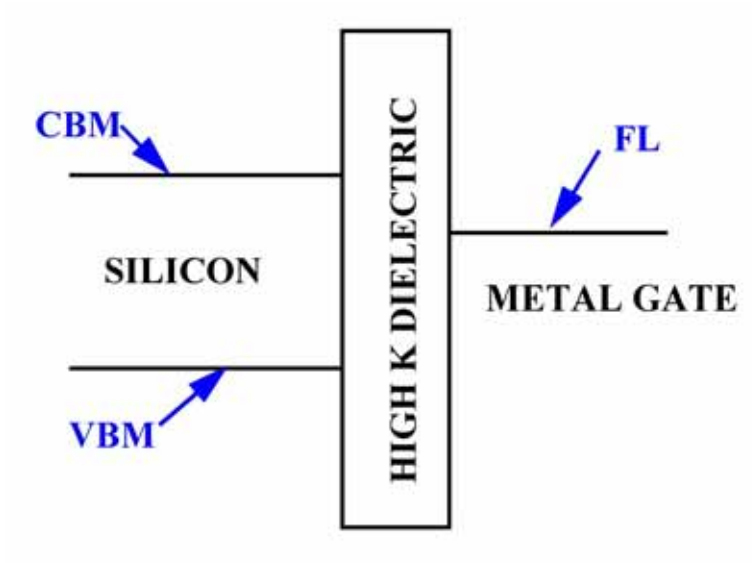
Material Interfaces of Current Interest

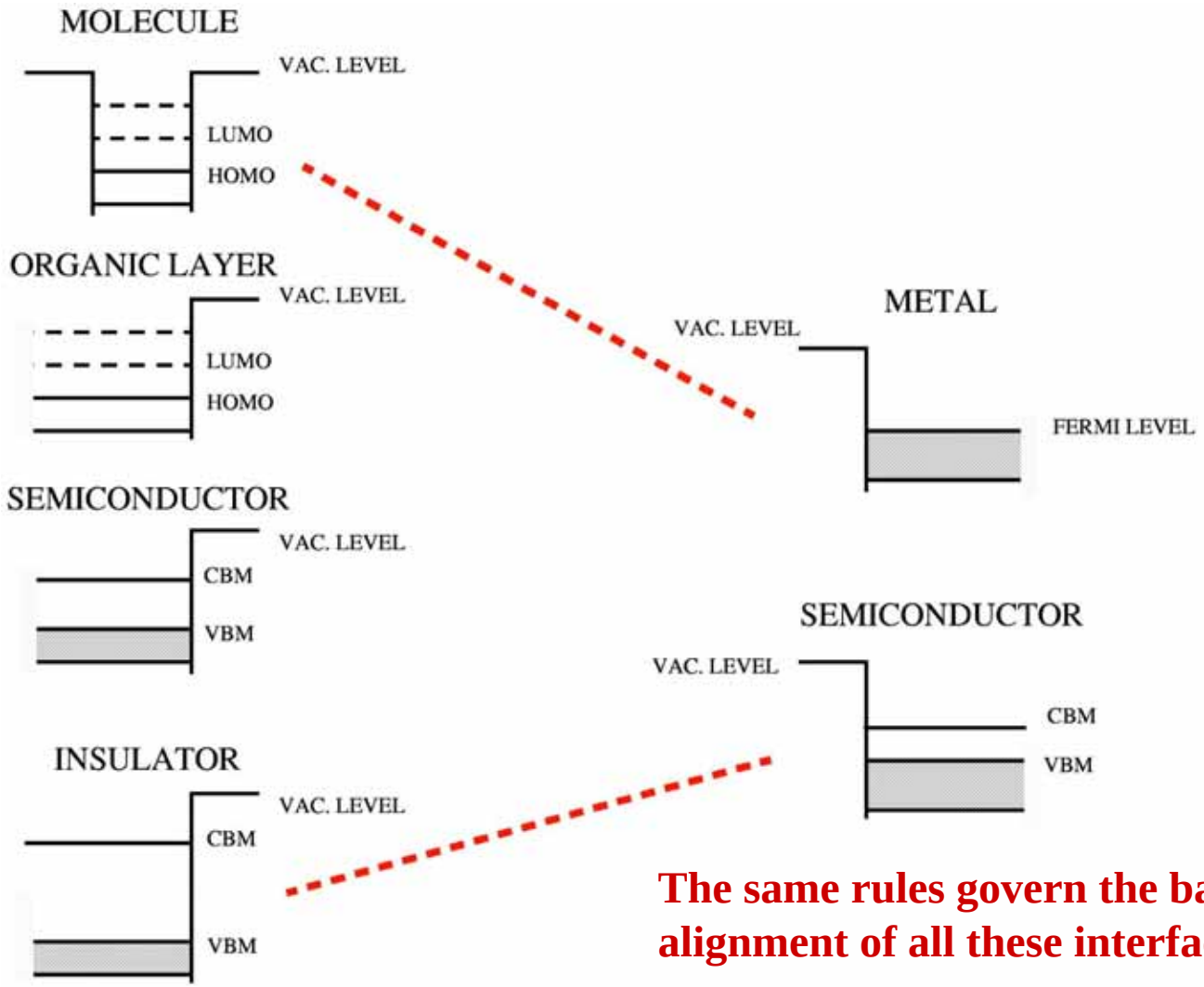


"Organic LE Device"

MOSFET with
High K Insulator



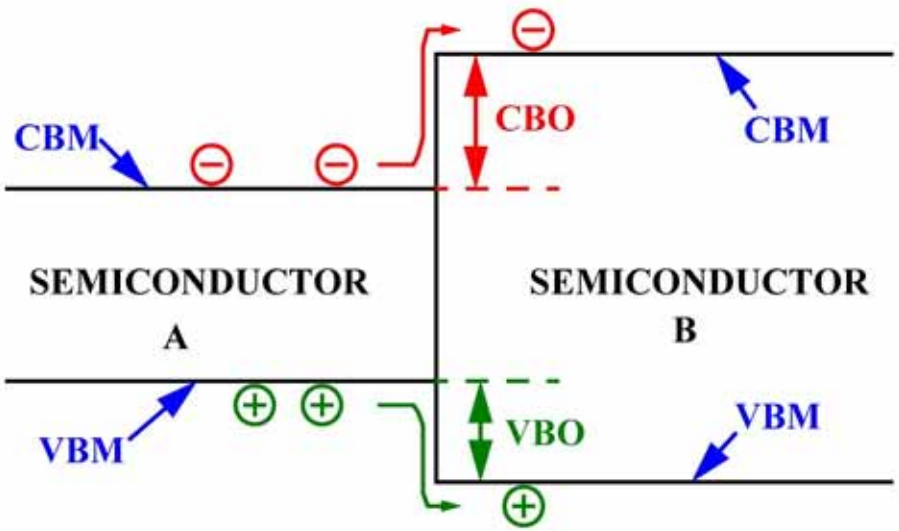
Band Alignment (Offset) Problem

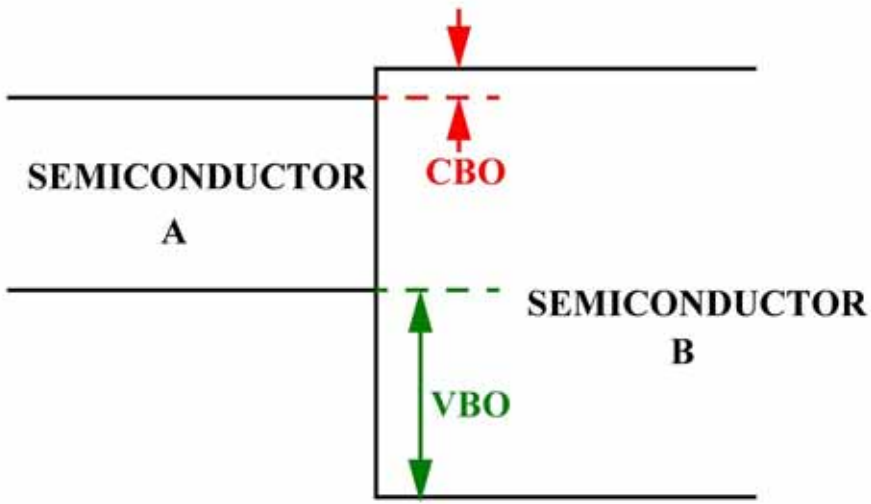


The same rules govern the band alignment of all these interfaces!

Band Offset and Schottky Barrier Height

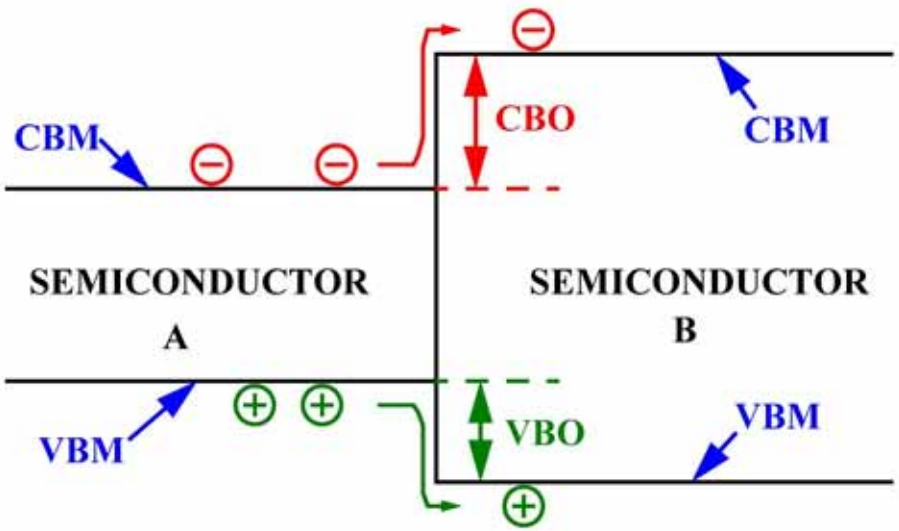
Semiconductor Heterojunction



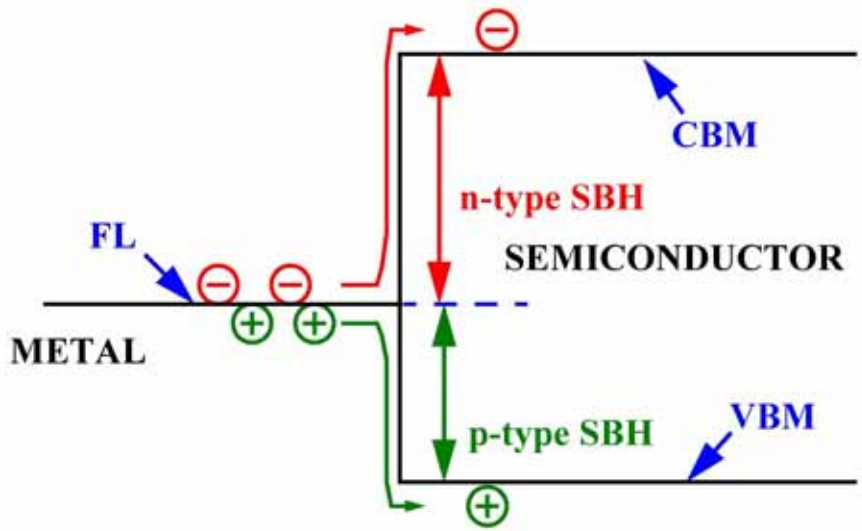


Band Offset and Schottky Barrier Height

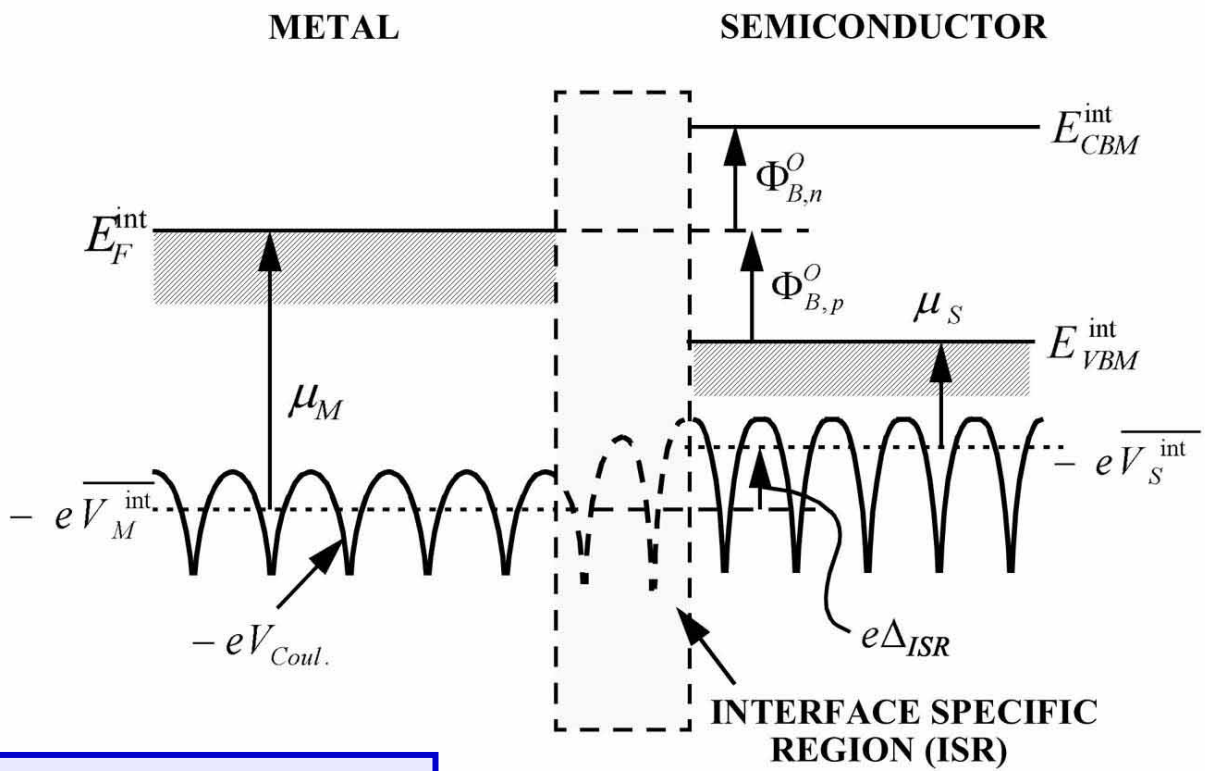
Semiconductor Heterojunction



Schottky Barrier



Electrostatic Potential And Schottky Barrier Height



$$\Phi_{B,p}^{o} = \mu_M - \mu_S - e\Delta_{ISR}$$

bulk terms

interface term

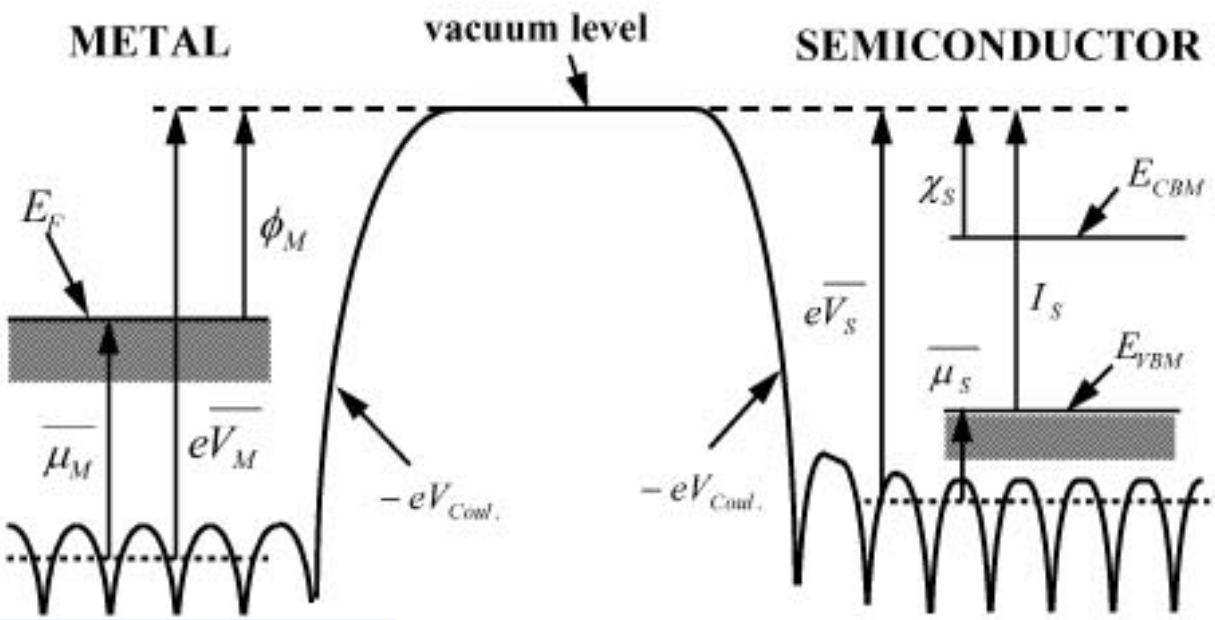
Inside the ISR:

(1) Electrostatic potential is continuous

(2) Charge distribution is such that the interface energy is minimized

The "Schottky-Mott" Relationship

"ISOLATED METAL AND SEMICONDUCTOR"



Schottky-Mott Relationship

$$\Phi^{o}_{B,n} = \phi_M - \chi_S$$

n-SBH — **metal w.f.** — **semiconductor electron affinity**

= "FREEZE THE CHARGE DISTRIBUTION"

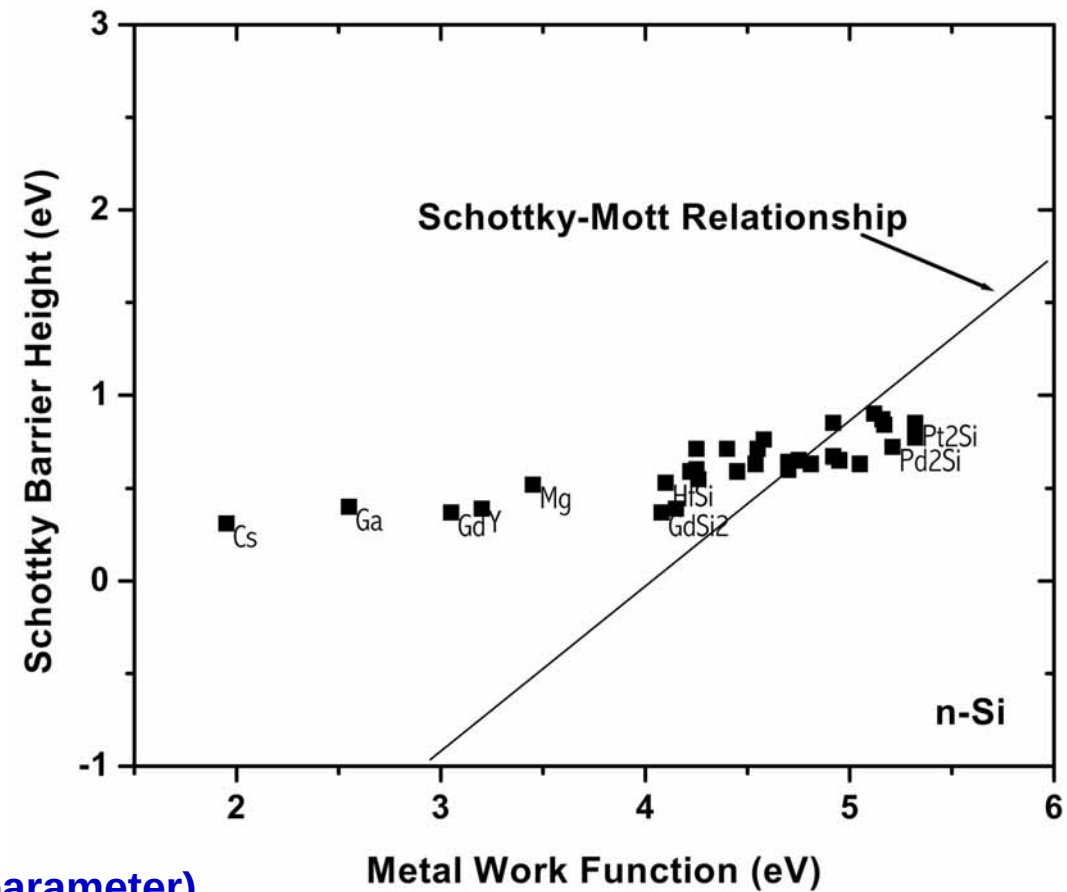
The Fermi Level Pinning Phenomenon

Schottky-Mott Prediction

$$S_\Phi \equiv \frac{\partial \Phi^o_{B,n}}{\partial \phi_M} = 1$$

Experimental Observation

$$S_\Phi \approx 0.1 - 0.3$$



Interface behavior parameter (S-parameter) reflects how strongly the SBH depends on the metal (work function).

Interface Chemistry

Non-Interactive Schottky-Mott Model:

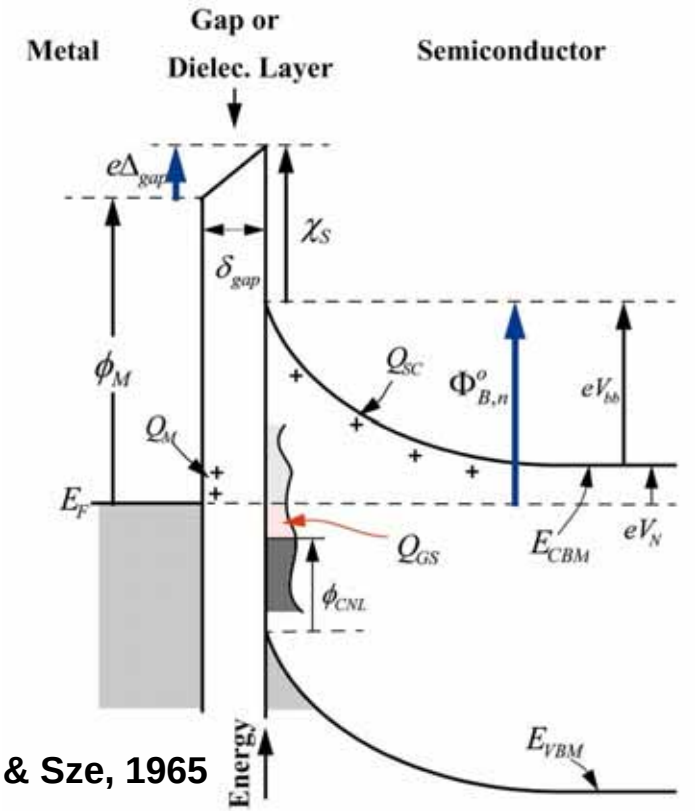
$$\Phi_{B,n}^{o} = \phi_M - \chi_S$$

FL pinning suggests Interface Interaction:

$$\Phi_{B,n}^{o} = \phi_M - \chi_S + e\Delta_{gap}$$

interface dipole

Interface Gap States: Fixed-Separation Model



Cowley & Sze, 1965

$$\Phi^o_{B,n} = \gamma_{GS}(\phi_M - \chi_S) + (1-\gamma_{GS})(E_g - \phi_{CNL})$$

$$\gamma_{GS} = \left(1 + e^2 \delta_{gap} D_{GS}\, \varepsilon_{gap}^{-1}\right)^{-1} \Leftrightarrow S_\Phi$$

Conditions for systematic analysis:

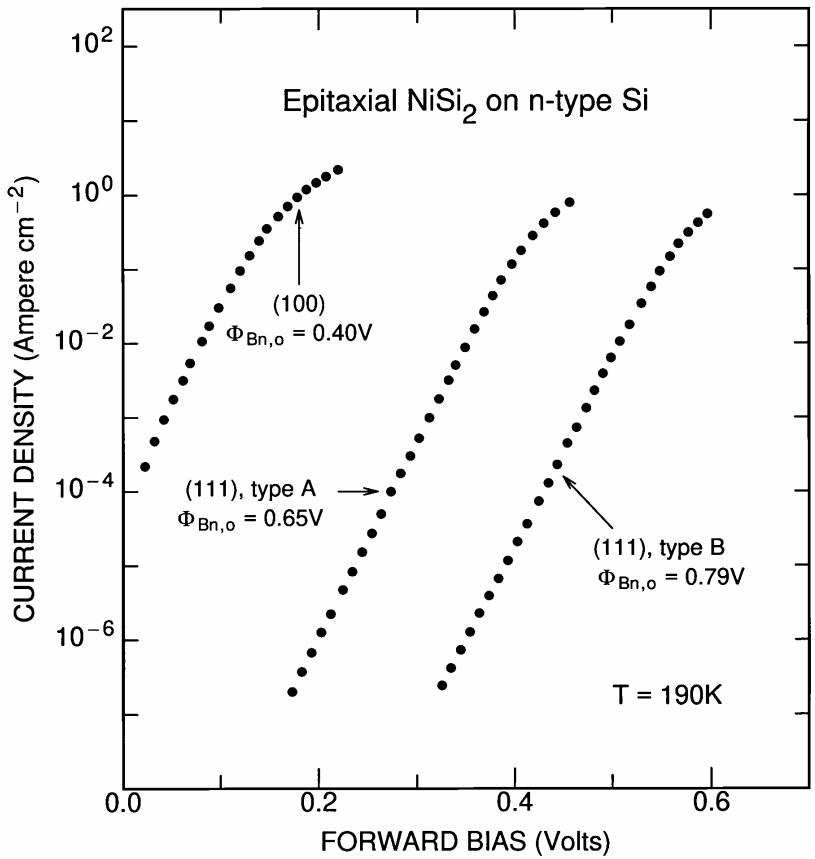
(1) Interface states are independent of the metal.

(2) Interface gap (distance) is large, > 1nm.

$$\Phi^o_{B,n} = \phi_M - \chi_S + e\Delta_{gap}$$

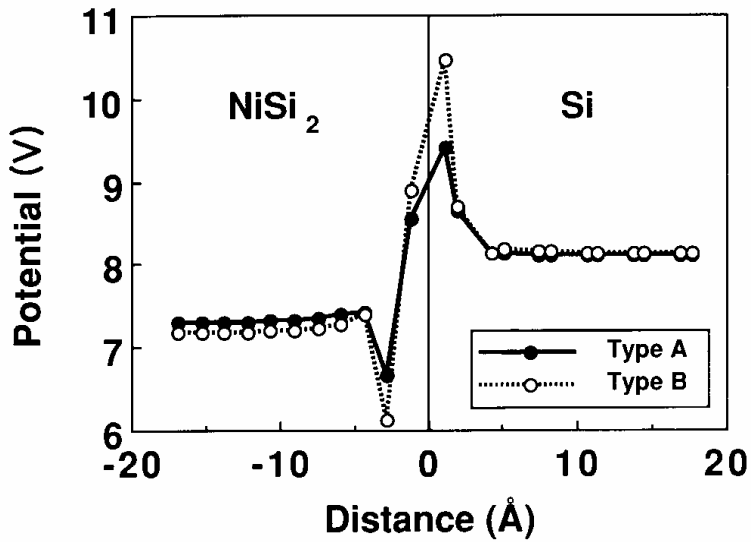
$$\| \quad (\phi_{CNL} - \Phi^o_{B,n}) \frac{e^2 D_{gs} \delta_{gap}}{\varepsilon_{gap}}$$

Single Crystal Schottky Barriers



Schottky barrier height depends on interface structure !

Ab initio calculations reproduced the experimental A-B difference



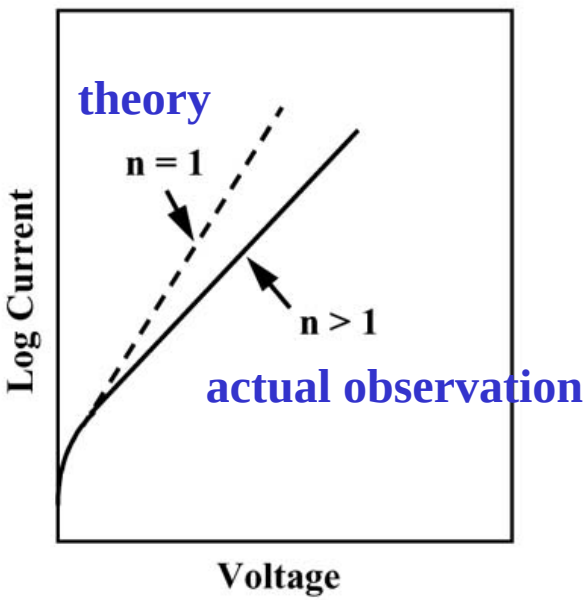
Fujitani and Asano 1990

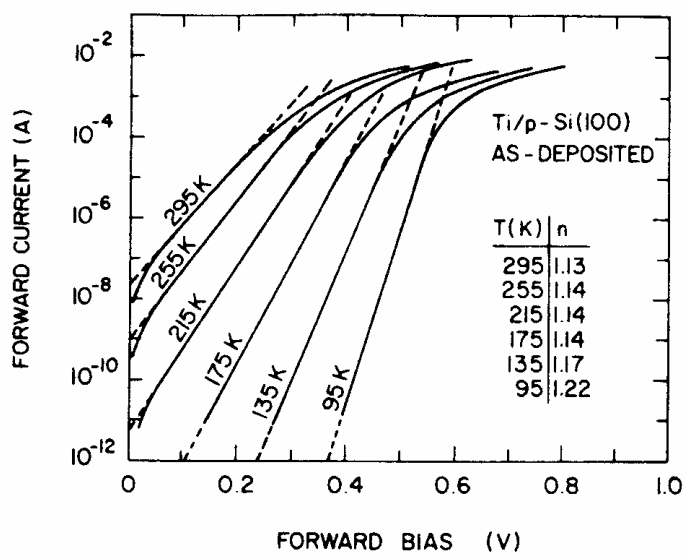
Ideality Factor

Thermionic Emission Theory

$$I_{SB}(V_a) = AA^*T^2 \exp(-\frac{e\Phi_{B,n}}{k_BT}) \left[\exp(\frac{eV_a}{nk_BT}) - 1\right]$$

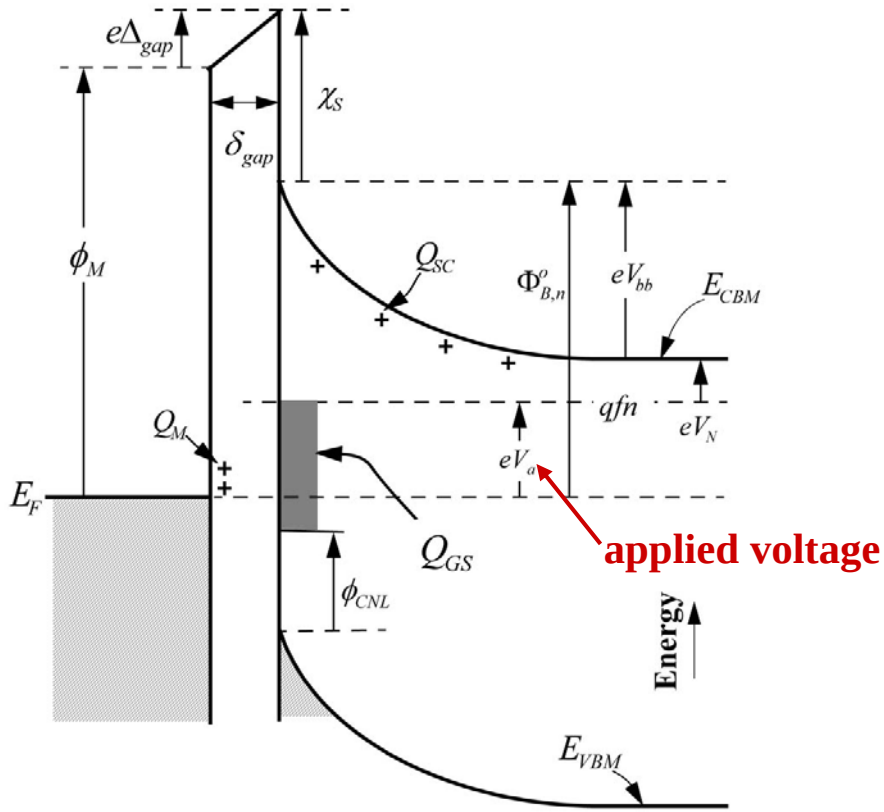
n: ideality factor





Aboelfotoh, 1988

Interface Gap State Model With Applied Bias Voltage



$$\frac{\partial \Phi^{o}_{B,n}}{\partial V_a} = \frac{e^2 \delta_{gap} D_{GS} \varepsilon^{-1}_{gap}}{1 + e^2 \delta_{gap} D_{GS} \varepsilon^{-1}_{gap}}$$

$$n \equiv \left[1 - \frac{\partial \Phi^{o}_{Bn}}{e \partial V_a} \right]^{-1}$$

$$= 1 + e^2 \delta_{gap} D_{GS} \varepsilon^{-1}_{gap}$$

Fixed Separation Model: Internal Inconsistency

Predictions of Fixed Separation Model

$$S_\Phi = \left(1 + e^2 \delta_{gap} D_{GS} \, \varepsilon_{gap}^{-1} \right)^{-1}$$

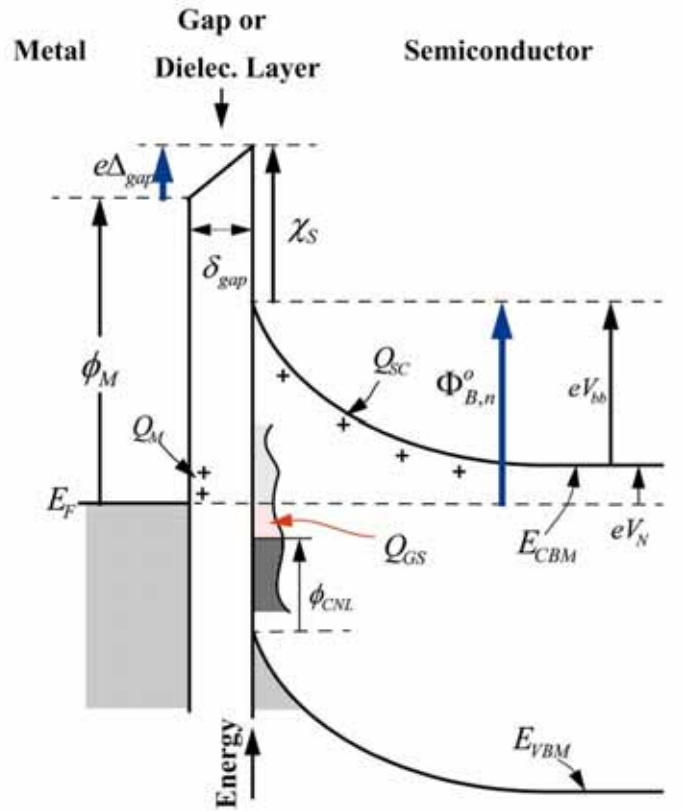
$$\Rightarrow \quad n = S_\Phi^{-1}$$

$$n = 1 + e^2 \delta_{gap} D_{GS} \varepsilon_{gap}^{-1}$$

But for most semiconductors,

$$n \approx 1 \qquad S_\Phi < 0.3 \quad \Rightarrow \quad n << S_\Phi^{-1}$$

Interface Gap States: Fixed Separation Model



$$\Phi^o_{B,n} = \phi_M - \chi_S + e\Delta_{gap}$$

$$= (\phi_{CNL} - \Phi^o_{B,n})\frac{e^2 D_{gs}\delta_{gap}}{\varepsilon_{gap}}$$

$$\Phi^o_{B,n} = \gamma_{GS}(\phi_M - \chi_S) + (1-\gamma_{GS})(E_g - \phi_{CNL})$$

$$\gamma_{GS} = \left(1 + \frac{e^2\delta_{gap}D_{GS}}{\varepsilon_{gap}}\right)^{-1} \Leftrightarrow S_\Phi$$

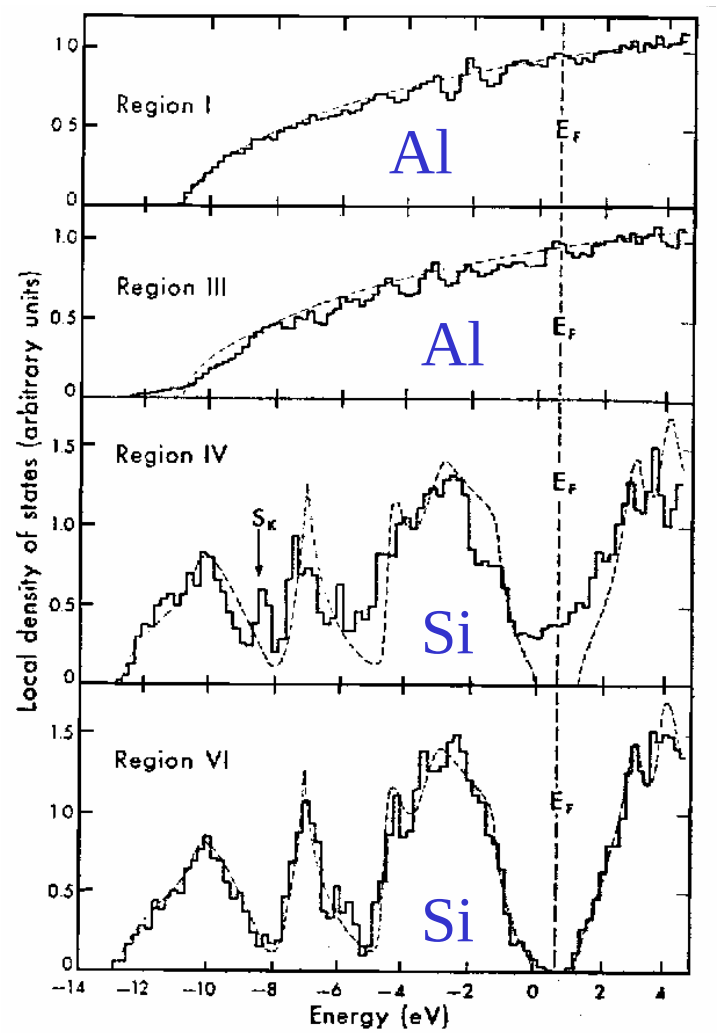
Conditions for systematic analysis:

~~(1) Interface states are independent of the metal.~~

~~(2) Interface gap (distance) is large, > 1nm.~~

Metal Induced Gap States (MIGS)

Louie 1977



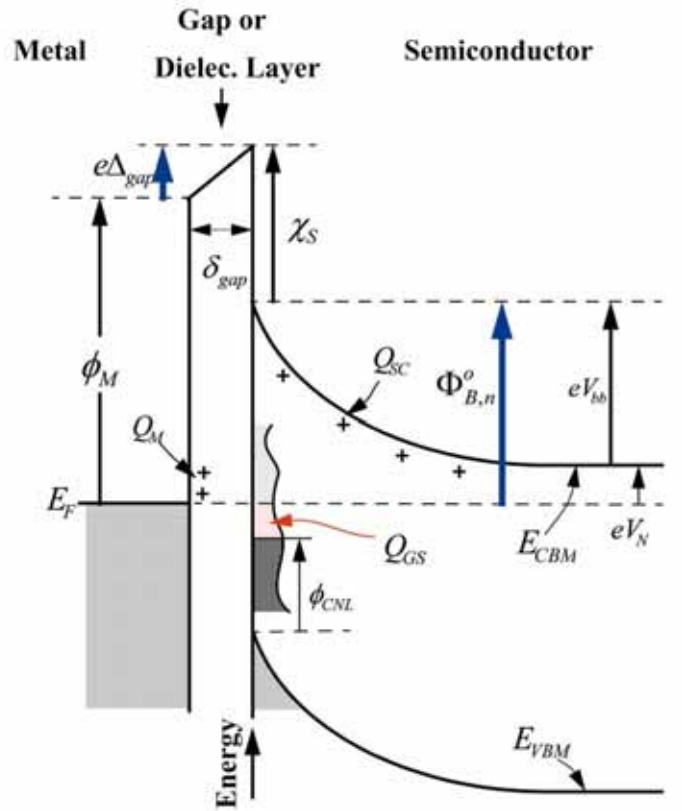
MIGS penetration depth found to be:

~0.1nm for ionic semiconductors

~0.3nm for covalent semiconductors

Charge transfer occurs over single atomic plane, i.e. bonding.

Interface Gap States: Fixed Separation Model



$$\Phi^o_{B,n} = \phi_M - \chi_S + e\Delta_{gap}$$

$$= (\phi_{CNL} - \Phi^o_{B,n})\frac{e^2 D_{gs}\delta_{gap}}{\varepsilon_{gap}}$$

$$\Phi^o_{B,n} = \gamma_{GS}(\phi_M - \chi_S) + (1-\gamma_{GS})(E_g - \phi_{CNL})$$

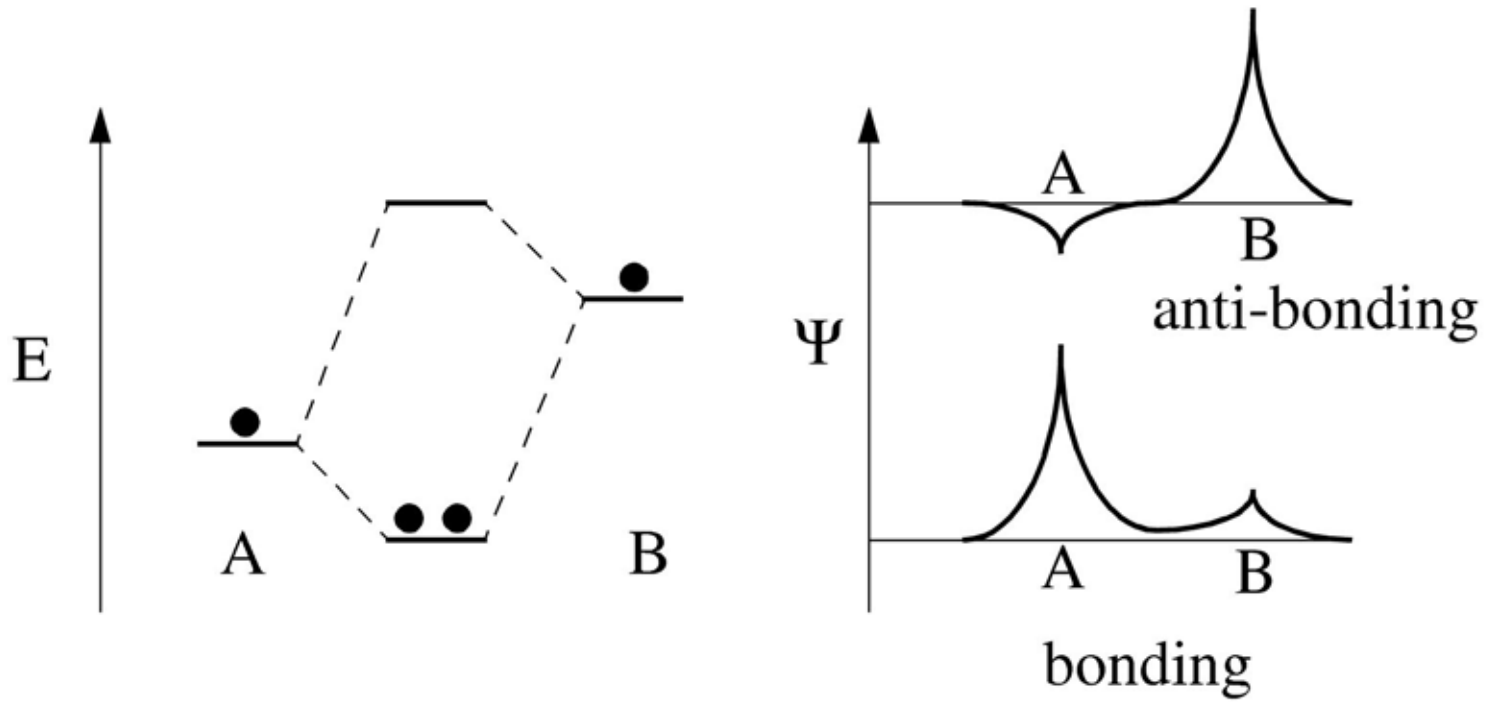
$$\gamma_{GS} = \left(1 + \frac{e^2\delta_{gap}D_{GS}}{\varepsilon_{gap}}\right)^{-1} \Leftrightarrow S_\Phi$$

Conditions for systematic analysis:

~~(1) Interface states are independent of the metal.~~

~~(2) Interface gap (distance) is large, > 1nm.~~

Simple Picture of Bond Polarization



Electrochemical Potential Equalization Method

total energy of a multi-atomic molecule

$$E_{tot}(Q_A, Q_B, ...Q_N) = \sum_{i=A}^{N}(E_i^o + U_i Q_i + Y_i Q_i^2 / 2 + ...) + \sum_{i \neq j} \frac{Q_i Q_j J_{ij}}{2}$$

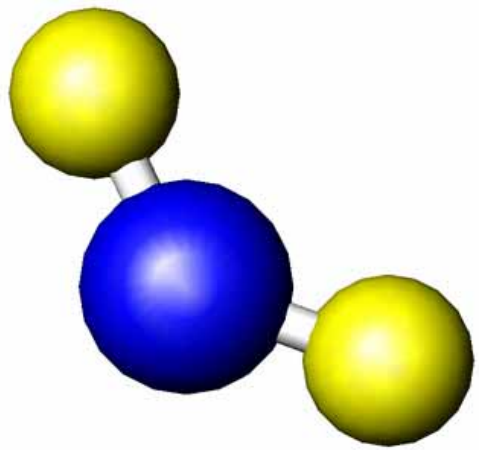
$$U_A = \frac{\chi_A + I_A}{2}$$

$$Y_A = I_A - \chi_A$$

χ : electron affinity

I : ionization potential

Q_A : net charge on atom A



minimize the energy, subject to $\sum_{i=A}^{N} Q_i = 0$

$$\mu_A = \frac{\partial E_{tot}}{\partial Q_A}$$ **electrochemical potential**

$$\mu_A = \mu_B = ... = \mu_N$$

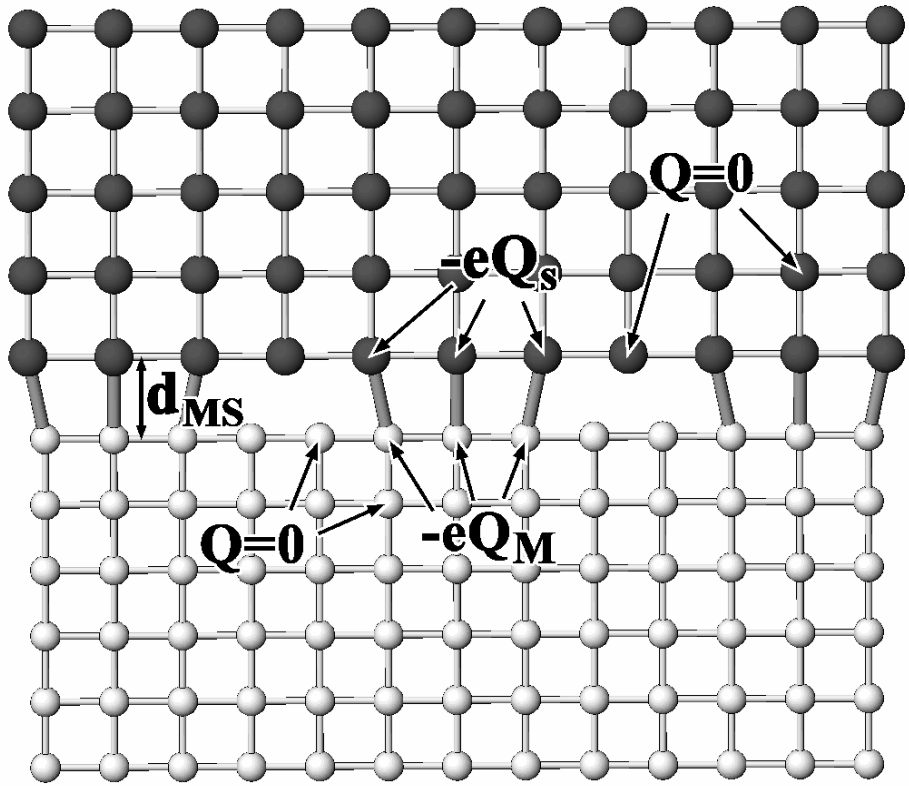
to get $Q_A, Q_B, ..., Q_N$

Treating A Metal-Semiconductor Interface As A Gigantic Molecule

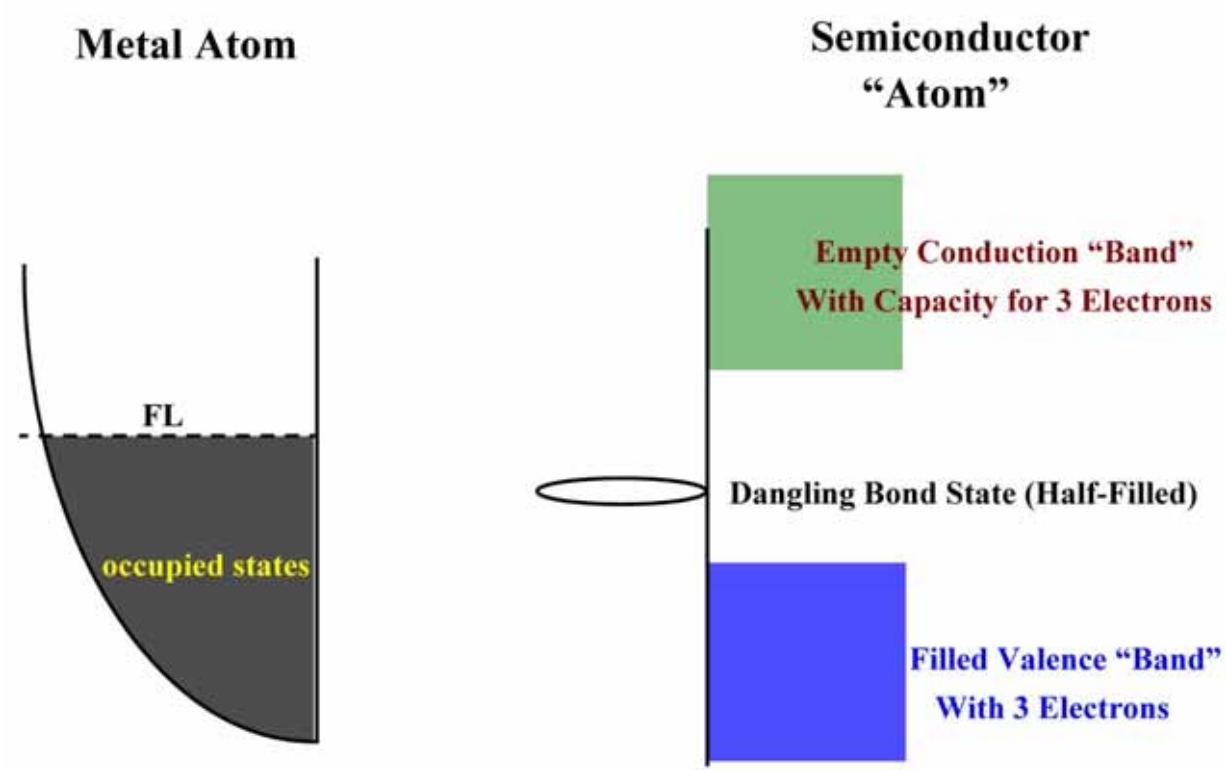
Assume bond density, N_B

Assume charge transfer only for these bonds

Assume bond polarization is interface dipole



Metal-Semiconductor Interface Bonds



First, break bonds!

Bond Polarization At MS Interfaces

TOTAL ENERGY

$$E_{ISR} = \sum_{i}^{N_M} (E_M^O + U_M Q_{M_i} + \frac{1}{2} Y_M Q_{M_i}^2) + \sum_{i}^{N_S} (E_S^O + U_S Q_{S_i} + \frac{1}{2} Y_S Q_{S_i}^2) + \sum_{i \neq j}^{N_M} \frac{Q_{M_i} Q_{M_j} J_{M_i M_j}}{2} + \sum_{i \neq j}^{N_S} \frac{Q_{S_i} Q_{S_j} J_{S_i S_j}}{2} + \sum_{i,j}^{N_M, N_S} Q_{M_i} Q_{S_j} J_{M_i S_j}$$

CHARGE TRANSFER

$$Q_S = \frac{U_M - U_S}{Y_S + Y_M - 2J_{MS} + 4J_{MM} + 4J_{SS}}$$

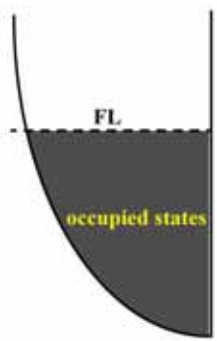
Converted Into

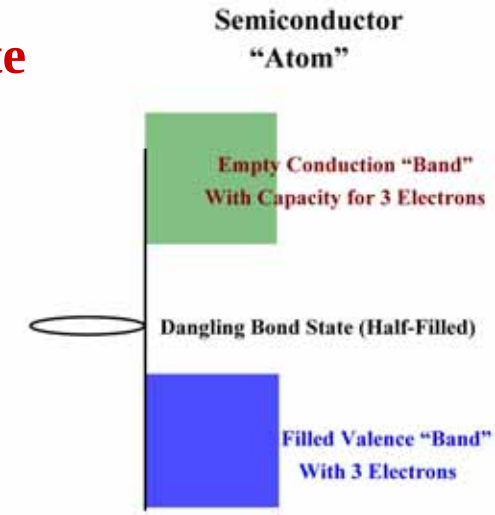
broken-bond state

$$Q_S = \frac{I_S - \phi_M - E_B}{E_g + \kappa}$$

hardness

electrostatic interaction





Bond Polarization At MS Interfaces

$$\Phi_{B,n}^{o} = \gamma_B(\phi_M - \chi_S) + (1-\gamma_B)(E_g - E_B)$$

$$\gamma_B = 1 - \frac{e^2 N_B d_{MS}}{\varepsilon_{it}(E_g + \kappa)}$$

Interface gap states model :

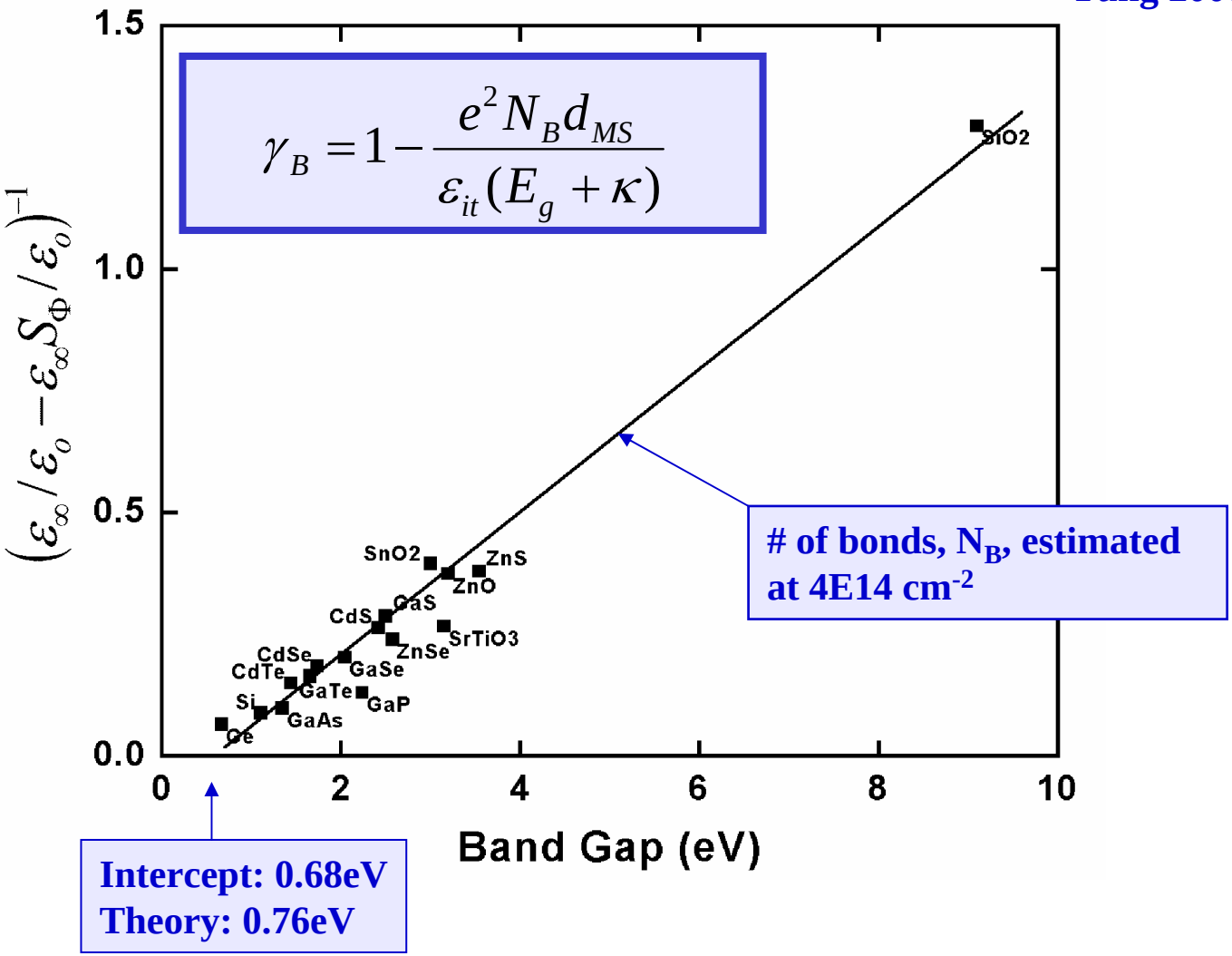
$$\Phi_{B,n}^{o} = \gamma_{GS}(\phi_M - \chi_S) + (1-\gamma_{GS})(E_g - \phi_{CNL})$$

$$\gamma_{GS} = \left(1 + \frac{e^2 \delta_{gap} D_{GS}}{\varepsilon_{gap}}\right)^{-1}$$

Bond Polarization Theory Of SBH

Tung 2000

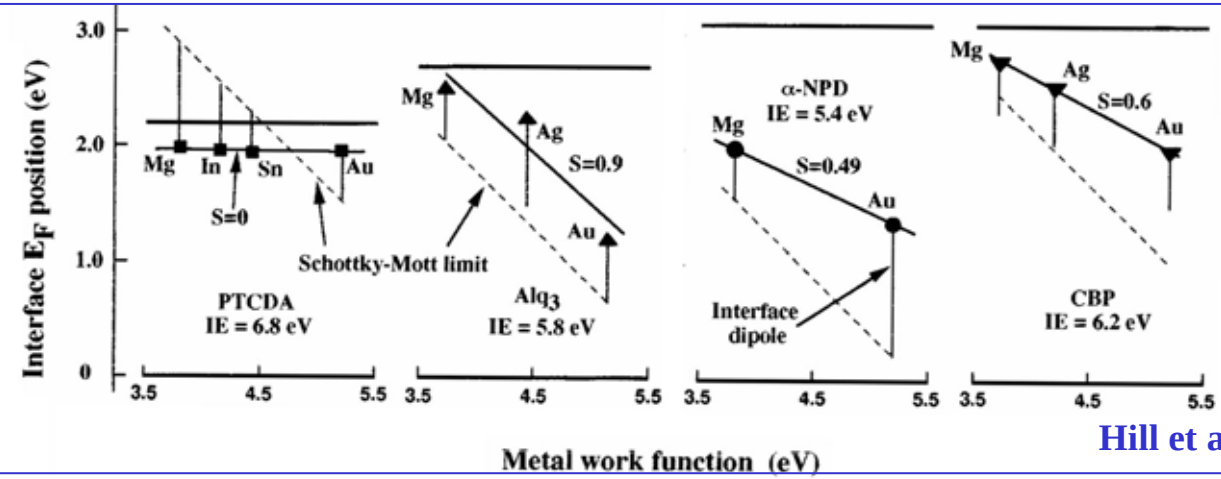
$$\gamma_B = 1 - \frac{e^2 N_B d_{MS}}{\varepsilon_{it}(E_g + \kappa)}$$



# of bonds, N_B, estimated at 4E14 cm^{-2}

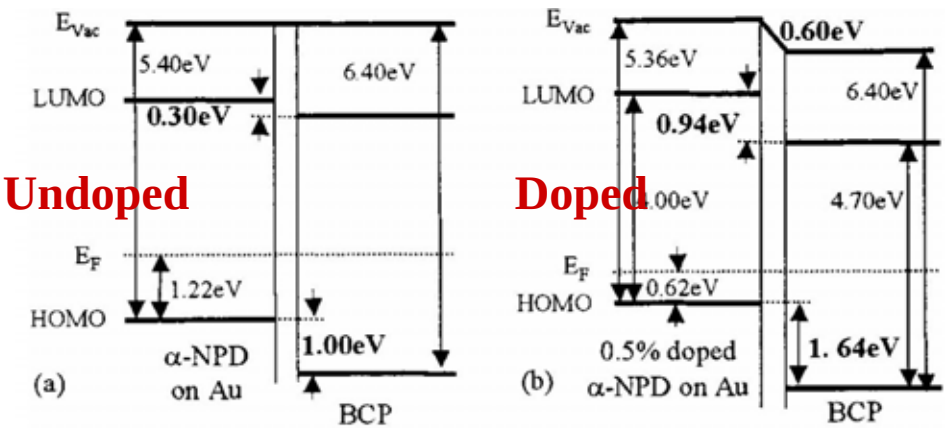
Intercept: 0.68eV
Theory: 0.76eV

"Band"-Alignment At Organic Interfaces



Metal-Organic

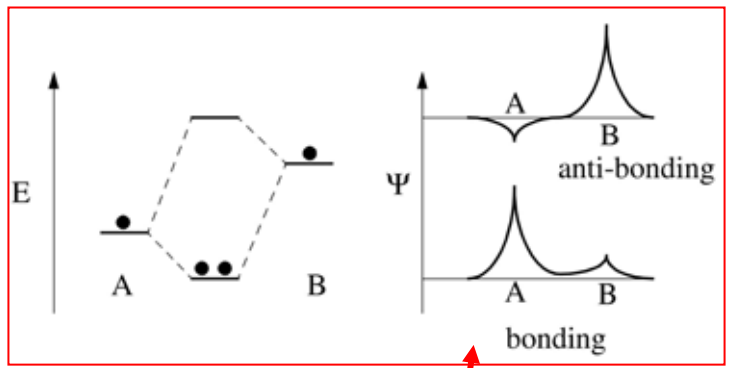
Hill et al., APL 73, 662 (1998)

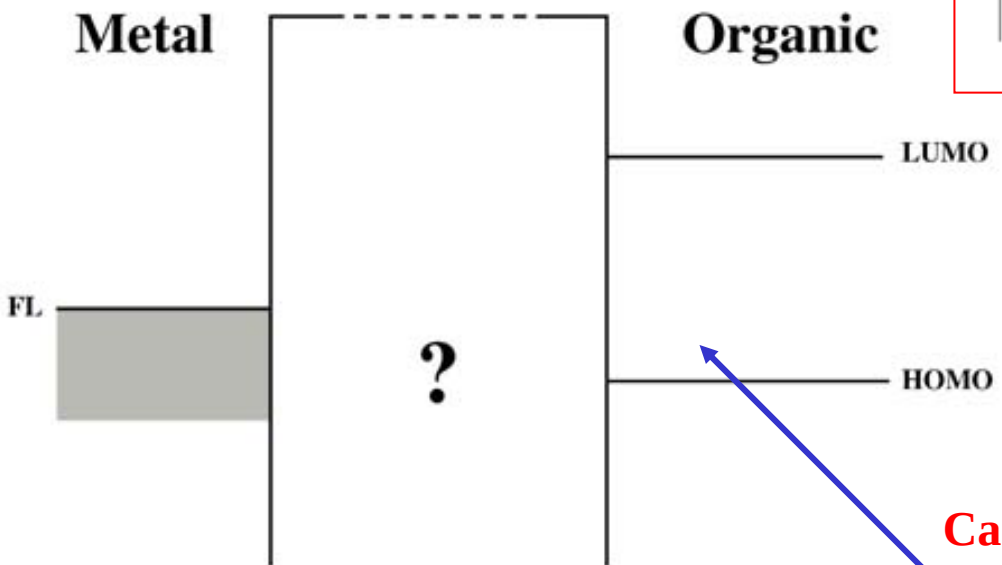


Organic-Organic

Gao & Kahn, APL 82, 4815 (2003).

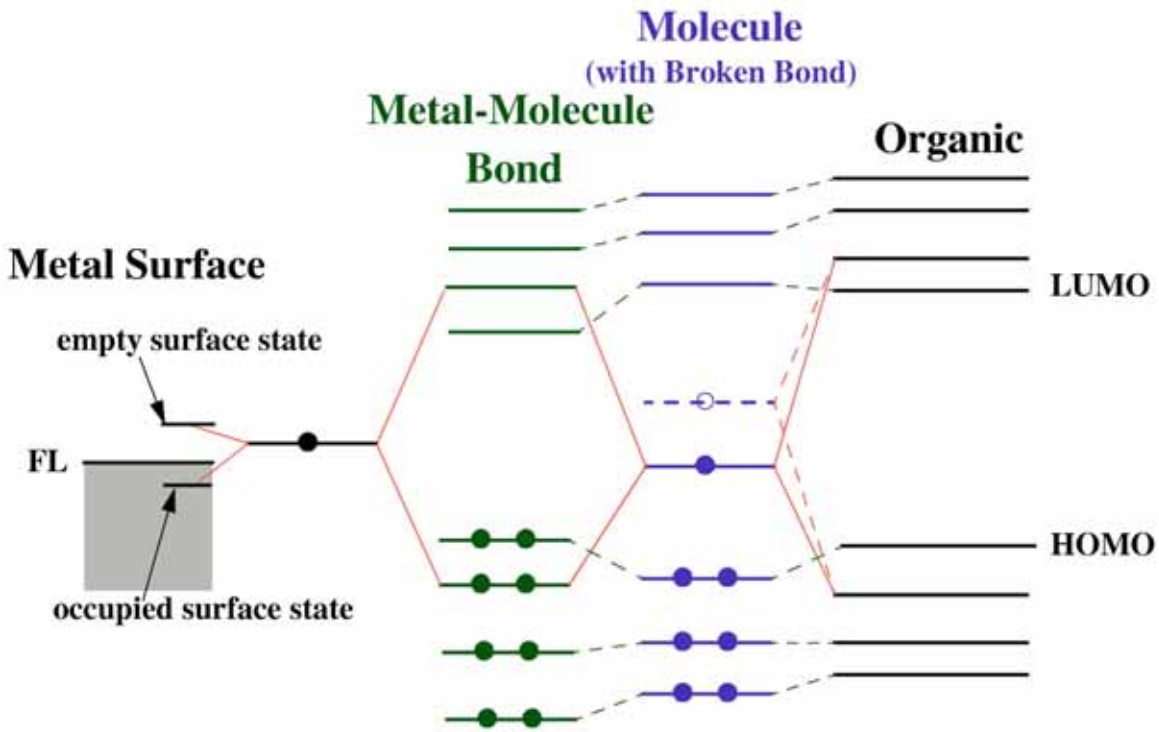
Interface Dipole At Organic Interface



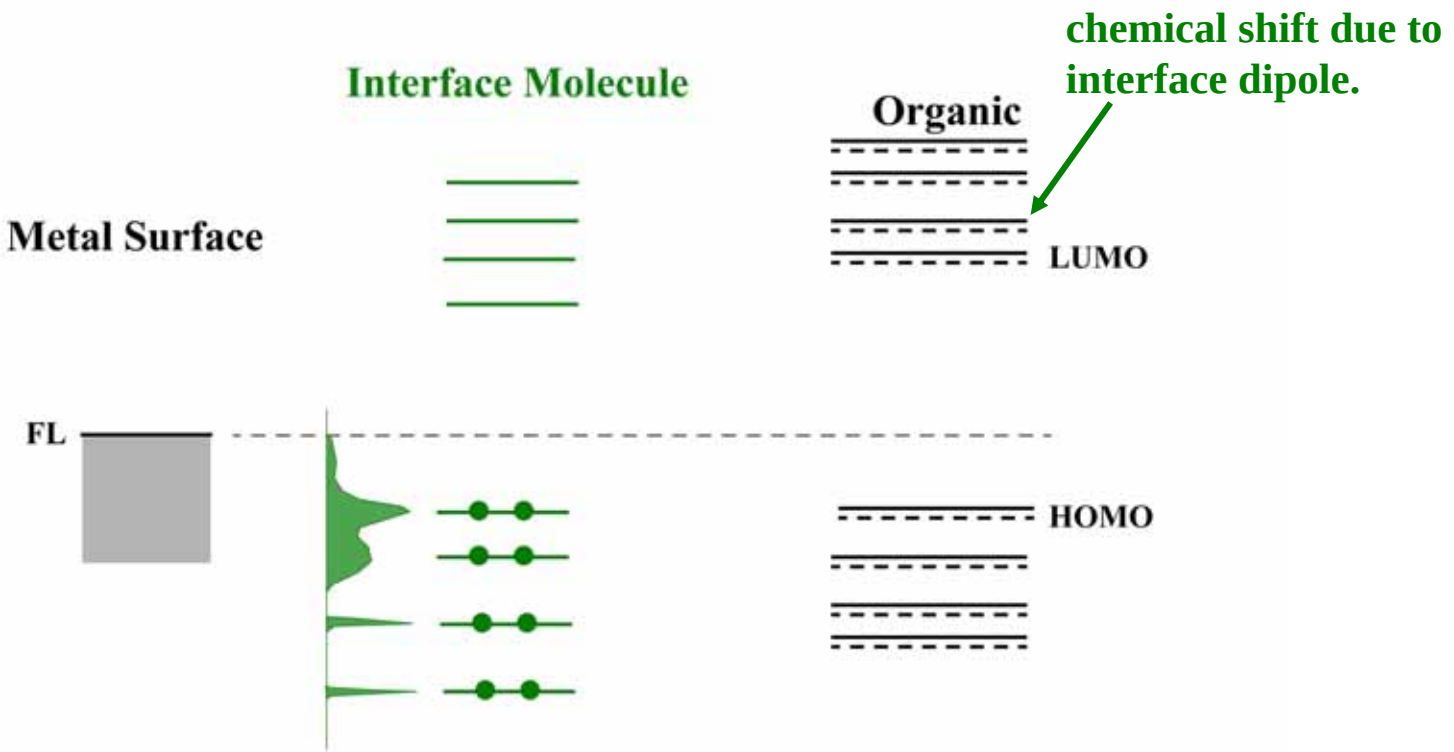


Can't use this bonding picture, because there're no unpaired electrons on perfect molecules!

The FBTFB Picture of Interface Dipole Formation



The FBTFB Picture of Interface Dipole Formation



$$\Phi_{hole} = \gamma_B (I - \phi_M) + (1 - \gamma_B) E_B \qquad \gamma_B = 1 - \frac{e^2 N_B d_{it}}{\varepsilon_{it}(E_H + \kappa)}$$

First-Break-Then-Form-Bond (FBTFB) Picture of Interface Dipole Formation

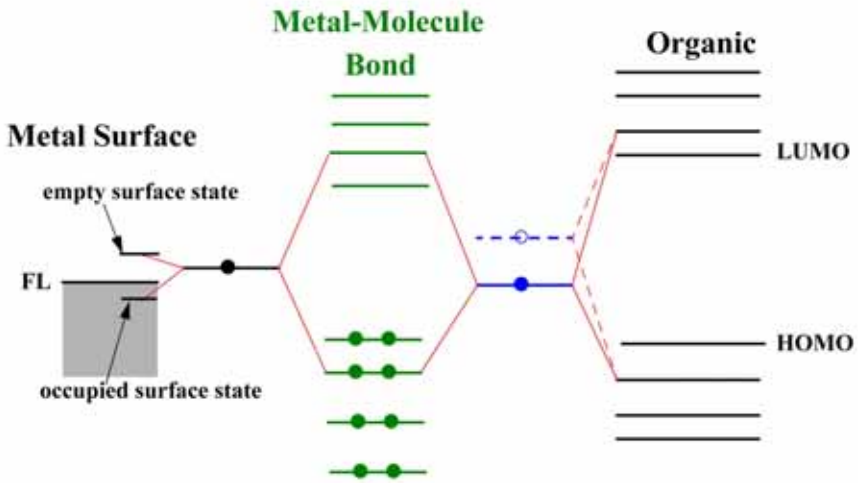
SALIENT FEATURES

Apparent pinning at orbital energy of the bond which has been broken.

No interface gap states needed to pin the Fermi level.

Bonding configuration matters.

Metal states matter.



$$\Phi_{hole} = \gamma_B (I - \phi_M) + (1 - \gamma_B) E_B$$

CAVEATS

Change in work function associated with bond breaking has been neglected.
Polarization of molecule has been neglected.
Different bonding configurations for different interfaces (different metals).
More than one bonding configurations possible at one interface.