Metal Organic interfaces

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Milano, 15-18 Novembre 2011

Outline

• general concepts
• energetics
• Interfaces: tailoring
• injection mechanisms
Metal-semiconductor contacts

\[ E_{\text{VACUUM}} \quad \] \\
\[ E_F \quad \] \\
\[ \text{HOMO} \quad \text{LUMO} \]

metal \quad \text{semiconductor}

\( \Phi_{\text{Be}} \) \text{ barrier to electron injection}

\( \Phi_{\text{Bh}} \) \text{ barrier to hole injection}

Thermal Equilibrium (1)

@Thermal Equilibrium a common Fermi level is established by means of \textit{charge transfer}...

\[ E_{F1} \quad \] \\
\[ E_{F2} \]

..from higher lying to lower lying Fermi level
Thermal Equilibrium (2)

Interface dipoles (1)

Barrier $\Phi_{Be}$ and $\Phi_{Bh}$ do change!!
Interface dipoles (1)

Barriers $\Phi_{Bo}$ and $\Phi_{Bh}$ do change!!

Interface dipoles (2)
Spectroscopical techniques

(a) UPS
(b) XPES
(c) XAS
(d) IPES

Kahn Adv. Mat. 2003 15 271
Zahn, Chemical Reviews, 2007, Vol. 107, No. 4 1181

Interface interaction strength

<table>
<thead>
<tr>
<th>Example of interface</th>
<th>Interaction type</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble gas atoms or saturated hydrocarbons on clean metal surfaces</td>
<td>Physisorption, absence of charge transfer</td>
<td>59, 61-63</td>
</tr>
<tr>
<td>π-conjugated molecules and polymers on organic or passivated metal surfaces</td>
<td>Physisorption, possible integer electron charge transfer through tunneling</td>
<td>22, 68</td>
</tr>
<tr>
<td>π-conjugated molecules on non-reactive clean metal surfaces</td>
<td>Weak chemisorption, possible partial charge transfer</td>
<td>21, 80</td>
</tr>
<tr>
<td>(π-conjugated) molecules on reactive clean metal surfaces</td>
<td>Strong chemisorption, covalent bonding between molecule and metal, (partial) charge transfer</td>
<td>20</td>
</tr>
<tr>
<td>(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces</td>
<td>Strong chemisorption, covalent bond at specific sites of the molecule and metal, (partial) charge transfer, surface dipole</td>
<td>24, 97</td>
</tr>
</tbody>
</table>
Metal/organic interfaces:

Metal/organic interfaces:
Real Metal surfaces: pushback effect

![Diagram](attachment:image.png)

Real Metal surfaces: pushback effect
Real Metal surfaces: pushback effect

Metal/organic interfaces:
Physisorptive regime

Physisorptive regime
Physisorptive regime: who cares $\Phi_B$?

$$n_j \propto N_{\text{eff}} \exp^{\Phi_B/kT}$$

$$\rho = \frac{en_1}{\left( \frac{x}{L_1} + 1 \right)^2}$$

$$L_1 \propto \sqrt{\frac{\phi_{\text{th}}}{n_1}}$$

Fig. 8.3. Density of electrons and rise in potential near an Ohmic contact. $L_1$ is the Debye length for the density $n_0$.

Physisorptive regime: image charge

Rose Photoconductivity and allied problems 1963
Clean Metal/molecule interfaces: weak chemisorption

Induced Density of states model

In organic molecule CNL accounts for:
• all Molecular Orbitals
• Metal induced orbitals broadening -> midgap states
Charge Neutrality Level

\[ \Delta_{\text{DIS}} = \frac{4\pi e^2 D(E_F) d}{A} (\phi_M - \text{CNL} - \Delta_{\text{DIS}}) \]

\[ \Downarrow \]

\[ \begin{align*}
\Delta_{\text{DIS}} &= (1 - S_{\text{MO}})(\phi_M - \text{CNL}) \\
S_{\text{MO}} &= \frac{1}{1 + 4\pi e^2 D(E_F) d/A}
\end{align*} \]
CNL: Theory vs Experiment

<table>
<thead>
<tr>
<th></th>
<th>CNL</th>
<th>EF</th>
<th>$\phi_{0}$ (theoretical)</th>
<th>$\Delta$ (theoretical)</th>
<th>$\Delta$ (experimental)</th>
<th>$\phi_{0}$ (theoretical)</th>
<th>$\phi_{0}$ (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTCDA</td>
<td>4.8</td>
<td>7.3 (6.8)</td>
<td>5.1 [6]</td>
<td>0.16</td>
<td>0.25</td>
<td>0.2 [6]</td>
<td>2.45</td>
</tr>
<tr>
<td>PTCBI</td>
<td>4.4</td>
<td>6.7 (6.2)</td>
<td>5.0 [7]</td>
<td>0.16</td>
<td>0.30</td>
<td>0.4 [7]</td>
<td>2.20</td>
</tr>
<tr>
<td>CBP</td>
<td>4.05</td>
<td>6.8 (6.3)</td>
<td>4.9 [10]</td>
<td>0.50</td>
<td>0.43</td>
<td>0.5 [10]</td>
<td>2.33</td>
</tr>
<tr>
<td>CuPc</td>
<td>4.0</td>
<td>5.7 (5.2)</td>
<td>5.3 [31]</td>
<td>0.30</td>
<td>0.91</td>
<td>1.2 [31]</td>
<td>1.31</td>
</tr>
<tr>
<td>α-NPD</td>
<td>4.1</td>
<td>6.0 (5.5)</td>
<td>5.14 [32]</td>
<td>0.33</td>
<td>0.70</td>
<td>0.86 [32]</td>
<td>1.56</td>
</tr>
<tr>
<td>α-NPD</td>
<td>5.4</td>
<td>6.4 (33)</td>
<td>0.87</td>
<td>1.3 [33]</td>
<td>1.47</td>
<td>1.9 [33]</td>
<td></td>
</tr>
<tr>
<td>Alk2</td>
<td>3.65</td>
<td>6.3 (5.8)</td>
<td>5.2 [6]</td>
<td>0.58</td>
<td>0.65</td>
<td>0.65 [6]</td>
<td>1.75</td>
</tr>
<tr>
<td>BCP</td>
<td>3.65</td>
<td>6.9 (6.6)</td>
<td>–</td>
<td>0.42</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
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Strong chemical interaction @ Interface
Chemisorption

Chemisorption: Alq3/Mg (1)

Unexpected electron flow!!
Chemisorption: Alq3/Mg (2)

Chemistry induced electronic states formation: a new Mg:Alq3 organometallic complex

Interface energetics: summary

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Integer charge transfer

IDIS and partial C.T.

Chemical reactions @ interface
### Polymers on metal

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Solvents "passivates" metals-> no intimate metal organic contact
- no IDIS nor chemical reaction

### Metal on Polymers

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*Intimate* metal organic contact is *possible* due to (Ultra) High Vacuum metal evaporation
Metal-Polymers-Metal interfaces

- ICT barriers < 0.3/0.4 eV
- Band bending?

**Pushback:**
Pt Ef=5.65eV

**IDIS dipole**

**Chemical reaction**

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[**Metal/Small molecule**] – [**Small molecule/metal**] interfaces

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**Integer charge transfer**

**IDIS and partial C.T.**

**Chemical reactions @ interface**

*Intimate* metal organic contact is *possible*
due to (Ultra) High Vacuum *metal and molecule* evaporation
Molecules: Clean Vs. contaminated metal

The contaminated metal has the smaller work function but also yields the lower hole barrier.

Contaminants give:
- a pushback effect
- a less intimate contact (hence less ISID)
Effect of deposition technique

- Vacuum deposited *vs* liquid phase deposition: *solvents/air passivates interfaces*

- Metal upon Organics *vs* Organics upon Metal

![Metal Diffusion](image)

*But often this does not give different electrical behavior…*

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Materials

**Theory…**

**practice…**
ITO (I)

\[
\begin{align*}
\text{In}_2\text{O}_3 & \quad \text{ITO (I)} \\
\text{In}_{2(1-x)}\text{Sn}_{2x}\text{O}_{3+x} & \quad \text{ITO (II)}
\end{align*}
\]

\[\varepsilon = 1 - \left( \frac{\omega_p}{\omega} \right)^2, \quad \omega_p = \left( \frac{ne^2}{\varepsilon g m} \right)^{1/2} \]

\(\omega > \omega_p, \varepsilon > 0 \quad \rightarrow \quad \text{transparent insulator} \)

\(\omega < \omega_p, \varepsilon < 0 \quad \rightarrow \quad \text{reflective conductor} \)

\(\omega_p \ \text{ITO} \approx 900\text{nm} \)
Interface functionalization

Salaneck J. Appl. Phys., Vol. 84, No. 12, 15 December 1998

**Table 1.** Work function, sheet resistance, and root-mean-square (rms) surface roughness of ITO for the different surface treatments.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Work function (eV)</th>
<th>Sheet resistance (Ωsq)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>4.5</td>
<td>16.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Mechanical paper rubbing</td>
<td>4.2</td>
<td>16.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Mechanical Teflon rubbing</td>
<td>4.2</td>
<td>16.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>4.35</td>
<td>15.5</td>
<td>3.4</td>
</tr>
<tr>
<td>RCA (no IPA)</td>
<td>4.35</td>
<td>19.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Dry cleaning: O₂ plasma (5'/10'/15')</td>
<td>4.6</td>
<td>18.5/23.5/32.5</td>
<td>8.8/4.8/3.8</td>
</tr>
<tr>
<td>Ar plasma (5'/10'/15')</td>
<td>4.5/4.5/4.55</td>
<td>16.7/17.1/17.0</td>
<td>10.9/15.4/23.0</td>
</tr>
<tr>
<td>Combined: Asperox (20'/O₂ plasma (10')</td>
<td>4.6</td>
<td>27.7</td>
<td>6.0</td>
</tr>
<tr>
<td>O₂ plasma (10'/Asperox (20')</td>
<td>4.7</td>
<td>&gt;30.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Interface functionalization**

- PEDOT PSS on ITO:
Interface functionalization: multilayer

From single large $\Phi_B$ to many smaller $\Phi_{Bi}$

Interface functionalization (4)

polar SAM on ITO

Khodabakhsh Ad.Funct.Mat. 14 2004 1205
**Doping**

Walzer et al. Chemical Reviews, 2007, Vol. 107, No. 4

**Doping**

Leo, JOURNAL OF APPLIED PHYSICS 106, 103711 2009
Charge injection

Classic models

Through the barrier:
Fowler-Nordheim \( J = BF^2 \exp \left( -\frac{b}{F} \right) \)
Needs bands and triangular barrier

Over the barrier:
Richardson-Schottky \( J = A' T^2 \exp \left( -\frac{\Delta - cF^{1/2}}{kT} \right) \)
Does not take hopping into account
Injection in organics

Ingredients:
- hopping transport
- Schottky effect
- Energetic disorder


Schottky effect (1)

\( \Delta \Phi_B \propto \exp \sqrt{F} \)

- \( F: \) \( 10^5 \text{ V/cm} \rightarrow 2 \times 10^6 \text{ V/cm} \)
- \( V: \) 1 V \( \rightarrow 20 \text{ V su 100nm} \)
- \( \Delta \Phi_B: \) 0.06 V \( \rightarrow 0.28 \text{ V} \)
- \( X_{\text{max}}: \) 3.2nm \( \rightarrow 0.7 \text{ nm} \)
Hopping & image potential

Ingredients:
- hopping transport
- Schottky effect
- Energetic disorder

excitation

thermalization

collection

backflow

E_F

Thermalization length

Ingredients:
- hopping transport
- Schottky effect
- Energetic disorder

High mobility
Eg inorganics

low mobility
Eg. organics

E_F

Under thermal equilibrium

\[ \text{Injection } (\propto \mu) \]

\[ \text{Recombination with image charge } (\propto \mu) \]

Ingredients:
- hopping transport
- Schottky effect
- Energetic disorder

Under Applied voltage

\[ \text{Injection } (\propto \mu) \]

\[ \text{Recombination with image charge } (\propto \mu) \]

Ingredients:
- hopping transport
- Schottky effect
- Energetic disorder
Injection & mobility

For a given energetics, the larger the mobility, the higher the injection efficiency


\[
J = q\mu N_0 F \exp \left( -\frac{\Phi_B}{kT} + \beta_s \sqrt{F} \right) \Psi(F')
\]

\[
\beta_s = \left[ \frac{q^3}{4\pi\varepsilon(kT)^2} \right]^{0.5}
\]

Correction term
backflow effect

Schottky barrier lowering

Ingredients:
- hopping transport
- Schottky effect
- Energetic disorder
Disorder & injection

The higher the disorder, the lower $\Phi_B$

\[
J = q\mu N_0 F \exp \left( - \frac{\Phi_B - \frac{1}{2} \sigma^2}{kT} + \beta_s \sqrt{F} \right) \Psi(F)
\]
Disorder & injection

\[ J = q\mu N_0 F \exp \left[ - \frac{\Phi_B - \frac{1}{2}\sigma^2}{kT} + (\beta_s + \beta_\sigma)\sqrt{F} \right] \Psi(F) \]

\[ \beta_\sigma = \frac{2^{3/2}}{3} \left[ \frac{q\sigma^2}{(kT)^3} \right]^{0.5} \]

Marohn Phys. Rev. Lett. 2007 66101

Disorder & injection

Enhanced disorder at interface:
(eg. Due to Disordered polar SAM)
Injection is not the most difficult step
But! Image charge attenuates interface disorder..... So what?!

Baldo PhysRevB 64(2001) 85201
Organic Organic interfaces

- Low charge density -> no pillow effect
- Active forces:
  - Van der Waals
  - Electrostatic interaction
  - Repulsion forces
- Degree of interaction
  - CT@gnd state (*eg. alkyl chains prevent intimate contact*)
  - Orbital mixing @gnd state (short range interaction)
  - Polarizations (long range interaction)


The End