Influence of Interface Dipole Potentials on the Growth-morphology at organic/metal and organic/semiconducting interfaces

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Outline

• Introduction to the investigated system
• Experimental details:
  - LEED and XPS/UPS
  - Tetracene and ZnPc on GaSe passivated Si(111)

• Interpretation
• Conclusions
Substrate: GaSe half-sheet passivated Si(111)

Properties:
- The GaSe half-sheet saturates all dangling bonds on the Si(111)-surface
- The GaSe half-sheet provides a van der Waals-like surface termination
- Nearly flatband conditions, no Fermi-level pinning then usually found on silicon surfaces
- Stable against a lot of deposits and ambient air

Deposits properties:
- Interesting candidates for opto-electronic device manufacture
- Stable and planar molecules with no decomposition during evaporation
- Easy to evaporate under UHV-conditions
#1 System:
Tetracene on GaSe passivated Si(111)
Morphological properties of the Tetracene interface

Deposition of Tetracene on Si(111):GaSe at room temperature

<table>
<thead>
<tr>
<th>Structure</th>
<th>b₁ [Å]</th>
<th>b₂ [Å]</th>
<th>α⁺ [°]</th>
<th>α [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.3</td>
<td>13.5</td>
<td>77</td>
<td>102</td>
</tr>
<tr>
<td>2</td>
<td>5.3</td>
<td>27</td>
<td>81</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>4.37</td>
<td>54.2</td>
<td>85</td>
<td>95</td>
</tr>
</tbody>
</table>

Two planar and one more bulk-like structure
UPS measurements: stepwise deposition of Tetracene onto Si(111):GaSe at room temperature

1. Band bending in the substrate (submonolayer coverage)
2. No indication of energetic shifts of the overlayer
3. Formation of an interface dipole potential of $\delta = 0.45$ eV
#2 System:
ZnPc on GaSe passivated Si(111)
Morphological properties of the ZnPc interface

LEED-pattern obtained during room temperature deposition of ZnPc

Outer 6 spots: planar ZnPc in a centered rectangular configuration with three domains and lattice parameters:

\[ a_1 = 14.4 \text{Å} \text{ and } a_2 = 25.0 \frac{\text{Å}}{\sqrt{3}} \times 14.4 \text{Å} \]

Inner 12 spots: facet-spots of ZnPc

Formation of a 13x13 overlayer structure with respect to the substrate
The stripes are in agreement with the model, because of a twofold symmetry of the LUMO. This twofold symmetry and the highly ordered structure can lead to a stripe formation in the empty state images. Therefore, STM and LEED are in well agreement.
Electronic properties of the ZnPc interface

UPS spectra obtained during the deposition of ZnPc

1. Band bending is observable for the substrate and the overlayer
2. Formation of an interface dipole potential $\delta$
Band energy diagram includes:
- band bending of the Si-substrate
- band bending of ZnPc
- formation of dipole layers

“Build in” dipole potential of the passivation layer

Interface dipole $\delta$
## Summary of interface properties

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<th>ZnPc</th>
<th>Tetracene</th>
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<td><strong>Growth morphology:</strong></td>
<td>planar: a=14.4Å and b=25Å</td>
<td>3 modifications: two planar and a preferred tilted structure</td>
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<td><strong>LEED and STM</strong></td>
<td></td>
<td></td>
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<td><strong>Interface dipole potential:</strong> UPS</td>
<td>Yes, 0.54eV</td>
<td>Yes, ≈0.45eV</td>
</tr>
<tr>
<td><strong>Band bending: substrate</strong></td>
<td>Yes, 0.26eV</td>
<td>Yes, ≈0.25 eV</td>
</tr>
<tr>
<td><strong>Band bending: overlayer</strong></td>
<td>Yes, 0.22eV</td>
<td>No</td>
</tr>
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</table>

**Sideview:**

- **planar ZnPc**
- **tilted Tetracene**
- **Si(111):GaSe**

**Why does ZnPc grow completely flat lying and Tetracene not?**
Possible molecular interactions

a) molecule - molecule
b) molecule-edge - molecule-edge

a) and b) represents bulk interactions which are only van der W aals like; $I_a > I_b$.

c) molecule - substrate
d) molecule-edge - substrate
e) electrostatic interaction

c) and d) represent van der W aals like interactions between the adsorbed molecule and the Si-substrate, usually smaller than $I_a$ and $I_b$.
e) Is an additional possible interaction, resulting from a charge transfer at the interface
Why does ZnPc grow flat lying and Tetracene not?

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<td>Charge per molecule</td>
<td>≈1.04e</td>
<td>≈0.25e</td>
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<tr>
<td>Electrostatic attraction (q•δ)</td>
<td>≈0.56eV/molecule</td>
<td>≈0.1eV/molecule</td>
</tr>
<tr>
<td>Heat of sublimation</td>
<td>≈0.5eV/molecule</td>
<td>≈1.1eV/molecule</td>
</tr>
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<td>≈ molecule -molecule interaction</td>
<td></td>
<td></td>
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**Table:**

- **ZnPc:**
  - 0.5eV/mol
  - Less than the heat of sublimation (~0.1-0.4 eV)
  - Planar growth: first layer and multilayers

- **Tetracene:**
  - 1.1eV/mol
  - Greater than the heat of sublimation (~0.1-1.0 eV)
  - For Tetracene bulk-like growth is favoured

**Note:**

Edge interactions are smaller than the interactions discussed above!
1. The experiments show a different growth behaviour for Tetracene and ZnPc on GaSe passivated Si(111)
   a) Tetracene grows in a more bulk-like structure
   b) ZnPc shows a planar growth-mode

2. The different growth-morphologies are a result of different electronic properties of the interface

3. The planar growth of ZnPc is stabilized by the electrostatic interaction between the first layer and the substrate

➤ Control of the first layer is the crucial step towards defined interface engineering!