ORDERED SUPRAMOLECULAR POLYTHIOPHENE STRUCTURES ON PASSIVATED SILICON SURFACES

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Background

- The functionalization of semiconductor surfaces with organic molecules is a necessary step in the development of hybrid organic-semiconductor structures.

- A significant challenge to organic layer formation is the fact that semiconducting surfaces exhibit a large number of dangling bonds which suppress the diffusivity of adsorbed molecules and can even break the molecules apart via the formation of Si-C bonds.

- Recently it has been shown that these problems can be overcome by depositing the molecules onto a passivated surface.*

Silicon Substrate

Si(111) has a complex stable $7 \times 7$ reconstruction, which reduces the number of dangling bonds from 49 to 19 for each $7 \times 7$ unit cell.

Still not good enough! Can’t provide a surface with enough mobility for molecule diffusion.
\[ \sqrt{3} \text{ surface} \]

Compared to the highly reactive Si(111) (7 × 7) surface, a monolayer Ag layer passivates the surface which allows the supramolecular ordering of TPA on Si(111).*

STM image of the \( \sqrt{3} \)-Ag surface. 100Å × 100Å


Thiophene Deposition

- Thiophene based molecules are of considerable interest in organic semiconductor research due to their efficient conjugation and the chemical stability.

- Thiophene thin films exhibit reasonably high mobilities ($\mu_h \sim 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)*

- In addition to non-conjugated layers, thiophene based molecules have been used as precursors in surface-confined polymerization experiments.

*Takimiya et al., J.AM.CHEM.SOC.128, 2006 12605
Experiment

- All measurements are performed in UHV system with a base pressure $\sim 2 \times 10^{-10}$ Torr.

- Si(111) wafers use a annealing sequence to attain $7 \times 7$ reconstruction.

- The $\sqrt{3}$ surface is formed by deposition of one monolayer of silver onto the clean Si surface at 580 °C. Layer formation confirmed with low energy electron diffraction (LEED).

- TBTTA molecules deposited and Auger electron spectroscopy (AES) was used to verify the coverage.
Supermolecular structures at RT

- Three supramolecular domains consistent with the 3-fold symmetry of $\sqrt{3}$ lattice
- “Raster noise” in many images suggest additional molecules moving on the surface
- Structures only stable under certain bias conditions
Unit Cell

Long side: (15±1) Å
Short side: (10±1) Å
Angle: (70±2)°

320 Å x 320 Å (-1.11 V 500 pA)

10 nm
Intermolecular Interactions

- TBTTA on Highly oriented pyrolytic graphite (HOPG) exhibits very similar unit cell*

- On HOPG, DFT calculations indicate ordering determined entirely by Van der Waals interactions between molecules.

Type II structures at RT

- Do observe second (type II) structures at RT
- The periodicity is (9±0.5)Å
- More stable under range of bias conditions
Effect of annealing

- Silver layer limits temperature to 400°C
- Above 160°C molecular layer decomposes

Auger indicates no stoichiometric change after anneal at this temperature.
Summary:

➢ The v3 surface does provide a high mobility template for TBT TA adsorption.

➢ Molecules form 2-d structures on v3 surface at RT. Structures are quite fragile and can decompose readily under STM imaging.

➢ Size and symmetry of unit cell suggests Van der Waals interaction the driving force.

➢ Defects in v3 structure can limit the size of domains.

➢ Another (type II) structure observed at room temperature.

➢ Do see changes after annealing.
THANK YOU FOR YOUR ATTENTION!

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Molecular structure of terephthalic acid (TPA).
Possible covalent structure

A recent research indicated that a Ullman dehalogenation reaction followed with C-C coupling can be performed on Ag(111) surface after the absorption of TBTTA when thermal energy was applied.*

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