EUV Processes in Tin-oxo Cages—A Computational Chemistry Perspective

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Metal oxide systems and oxo clusters

EUV Atomic Cross sections
(100 Mb = 1 Å²)

B. Cardineau, Frontiers of Nanoscience, 11, 327 (2018)

K Sakai et al., JVSTB, 36, 06J504 (2018)
Prototypical cage

180 mJ/cm²


50 nm HP

Y. Zhang et al., *JM3*, 16(2), 23510, (2017)

34 mJ/cm²

J Haitjema et al., *JM3*, 16(3), 1 (2017)

A good platform of computational material engineering
Quantum Chemistry Calculations

• Density functional theory
  – The ‘work horse’
  – Proven—accurate for non-degenerate molecules
  – PBE0/def2-TZVP//def2-SVP

• Q-Chem
  – Commercially available
  – Optimized for performance
Electron driven chemistry

- Photoionization
- Electron attachment
- Impact ionization
Terminology

Ligand

Belt-R

Side-R
Electron driven chemistry

Photoionization

Impact ionization

Electron attachment
Sn-C cleavage driven chemistry

2+ → 3+ + e⁻

2.8 eV

0.60 eV

2+ → 3+ + e⁻

2.8 eV

+
The story of two R groups

1.23 eV

0.60 eV

Cleaving off belt-R

Cleaving off side-R
The story of two R groups

2+ 1.23 eV

3+ 0.60 eV

3+ 1.78 eV

3+ 1.67 eV

2.16 eV

0 eV

1.23 eV

1.67 eV

0.60 eV

Cleaving off belt-R +

Cleaving off side-R +
First or second order?

Photoionization

Electron attachment

Impact ionization
Electron driven chemistry

- Photoionization
- Impact ionization
- Electron attachment
Electron attachment

Lowest Unoccupied Molecular Orbital

Electrostatic potential (V)
Sn-C cleavage driven chemistry

Ligand

R-groups

4.42 eV

3.35 eV

1.13 eV

2.8 eV

0.06 eV

+ + –

+ –

+ + –

+ + –

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The story of two R-groups

An excited state is needed

- 0.74 eV

- 0.06 eV
  Energy in Sn-C stretching modes at room temperature: 0.18 eV

Cleaving off side-R

Cleaving off belt-R
Excited states

- 0 eV
- 0.74 eV
- 0.87 eV
- 1.25 eV

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First or second order?
A tale of two mechanisms
Process selectivity and reaction order

• Ionization
  – Extra energy is needed for cleavage
  – Side methyl groups are more unstable.
  – Order is incident energy dependent
  – **Happens closer to the EUV absorption site**

• Electron attachment
  – Side methyl groups: extra excitation needed
  – Belt methyl groups: could be spontaneous
  – **Could happen further away**
Into the future

• Devise strategies to engineer process selectivity

• Explore methods for bond breaking process suitable for large molecules to model relative reaction speeds
Thank you

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