A Molecular Level Investigation of the Electron Beam Induced Deposition of Methylcyclopentadienylplatinum(IV)-trimethyl

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Outline

• Background / Motivation
• Experimental Approach
• Surface Chemistry and Kinetics (500eV)
• Incident Energy Dependence (σ(E))
• Summary
The ability to focus electron beams into small spots, control electron beam fluence and raster the beam makes EBID an ideal method for growing a wealth of different nanostructures.
Examples of EBID

Freestanding Pt wire grown from MeCpPtMe$_3$

Pt wire grown on SiO$_2$ from MeCpPtMe$_3$


Pt wire, 4 μm long, grown between Au electrodes on Si / SiO$_2$ substrate from MeCpPtMe$_3$

W(CO)$_6$ on C films

van Dorp et al., JVST B, 2007, 2210.

Rh grown on graphite from [RhCl(PF$_3$)$_2$]


Frabboni et al., Physica E, 2007, 265.

Botman et al., Nanotechnology, 2006, 3779.
**Motivation**

The fundamental surface processes that are responsible for electron beam induced deposition of nanostructures are not well understood.

- Many questions about EBID process
  - Chemical reaction at the surface?
  - Incident electron energy dependence?

- If we can better understand the chemistry, we can:
  - Choose precursors more selectively
  - Improve deposition purity (carbon)
  - Improve purification techniques
  - Increase metallic characteristics
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Our Approach

• To understand the EBID process using well established surface analytical techniques
  
  – Adsorbing a nanometer scale film of EBID precursor to a substrate provides a “clean” environment for in situ observation
  
  – Surface coverage can be controlled
  
  – An UHV environment enables analysis of gas phase products
  
  – A film, on the order of cm² in area, can be analyzed using common surface analytical techniques
Experimental Notes

Substrate
- Chemically un-reactive towards precursor

Film
- Thin!!! (1-3 Monolayer regime so that each precursor molecule experience the same electron flux)

Electron Beam
- Broad and defocused (uniform irradiation)
**Broad Beam Surface Irradiation**

Production of a film over a large surface area enables traditional surface analytical techniques to probe the EBID process.

![Diagram showing electron beam irradiating a gold substrate with a Pt-containing molecule, leading to a film formation on the substrate.](image)
We have studied the electron stimulated reactions of the well-known Pt precursor, Trimethyl(methylcyclopentadienyl)platinum(IV), adsorbed onto gold using the above techniques:
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RAIRS Analysis of Dissociation Kinetics

- Time resolved *in situ* RAIRS analysis shows loss of $\nu$(C-H) intensity with increasing electron beam irradiation.

RAIRS analysis shows loss of $\nu$(C-H) intensity with increasing electron beam irradiation.
Adsorption of MeCpPt(IV)Me₃ onto Gold Substrate – Controlling film thickness

Film thickness, \( d \), calculated from attenuation of Au(4f) signal

\[
d = \lambda \cos(\theta) \ln\left( \frac{I}{I_0} \right)
\]

\( d \) = adsorbate thickness
\( \lambda \approx 2 \text{nm} \) for Au(4f) photoelectron
\( \theta = 54^\circ \) photoelectron take-off angle
\( I = \text{Au(4f) area} \)

Influence of Dosing Time on Film Thickness

\[ P_{\text{dosing}} = 1 \times 10^{-6} \text{ Torr} \]

\( d_{\text{ave}} = 0.96 \text{nm} \)

Experiments Conducted in this Regime

XPS and MS

Dosing Time (seconds)
Production of Amorphous Platinum/Carbon Film

XP spectra of sputter deposited platinum on gold

Substrate heated to room temperature leaving electron beam irradiation product

Electron beam irradiation for 20 sec (20 μA, 500eV)

MeCpPt(IV)Me₃ adsorbed onto gold substrate (~195K)
Influence of e⁻ Beam Irradiation on Surface Composition of Adsorbate Layer

The XP spectra of the C(1s), Au(4f), and Pt(4f) regions shows:

- No loss of platinum from surface
- Shift in platinum environment from precursor to product

MeCpPt(IV)Me₃ is stable under x-ray irradiation for >2hrs
XPS Analysis of Dissociation Kinetics

Quantification of the deconvoluted Pt(4f) region fit to exponential decay shows first order kinetics.

Decay profiles show that the observed rate constant increases with increasing target current.
Signal Resolution vs. Signal Intensity

- High resolution / low intensity emphasizes elemental environment
  - 22eV Pass Energy

- Low resolution / high intensity emphasizes stoichiometry
  - 90eV Pass Energy
The C:Pt ratio of 10 XP spectra of the MeCpPtMe3 prior to e- beam irradiation is representative of the initial stoichiometric ratio of 9 carbon atoms to 1 platinum atom. The stoichiometric loss of 1 carbon atom as a result of irradiation is independent of film thickness. The C:Pt ratio after e- beam irradiation decreases to a ratio of 8:1, indicating the loss of 1 carbon atom per molecule as a result of irradiation.
Electron beam irradiation results in the production of counts (a.u.) corresponding to the production of hydrogen and methane.

MS capable of measuring individual masses as a function of time.
Kinetic Analysis of Methane Production

- Tracking methane production during electron beam irradiation fit to exponential decay
- $m/z = 15$ is a unique mass representative of methane
- Methane loss fit to first order kinetics indicates an increase in the observed rate constant with increasing target current
Dissociation by Pt-CH₃ Cleavage

Analogous compound decomposes via production of identical gas phase products
Complementary Techniques

\[ \sigma = \frac{k_{\text{obs}}}{I_{\text{target}}} \times A \]

<table>
<thead>
<tr>
<th>Technique</th>
<th>(\sigma) cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>1.37E-16</td>
</tr>
<tr>
<td>RAIRS</td>
<td>4.32E-16</td>
</tr>
<tr>
<td>MS (MeCpPtMe(_3))</td>
<td>9.75E-17</td>
</tr>
<tr>
<td>MS (CpPtMe(_3))</td>
<td>1.02E-16</td>
</tr>
</tbody>
</table>

\[ \sigma_{\text{ave, 500eV}} = 2.2 \times 10^{-16} \text{ cm}^2 \]

XPS, RAIRS, and MS provide comparable \(\sigma\) values though they measure different processes.
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Dependence on Incident Electron Energy Observed Using XPS

Electron Beam Energy

Counts (a.u.)

Electron Energy (eV)

Binding Energy (eV)

Above XP spectra: 25 μA, t=60 sec

Optimal σ between 100-200 eV suggests electron impact ionization process
Dependence on Incident Electron Energy Observed Using MS

\[ \sigma_{60\text{eV}} < \sigma_{200\text{eV}} > \sigma_{2000\text{eV}} \]

MS supports XPS results
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• Electron beam irradiation of surface adsorbed MeCpPt(IV)Me₃ results in the formation of platinum atoms embedded in an amorphous carbon film via an electron impact process in which bond cleavage releases hydrogen and methane.

• Each precursor molecule that undergoes electron stimulated decomposition losses exactly one carbon atom.

A UHV surface science approach can provided valuable information on reaction rates and fundamental chemical processes involved in EBID
<table>
<thead>
<tr>
<th>Technique</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>Reasonable quantification</td>
<td>Central atom must change oxidation state</td>
</tr>
<tr>
<td>AES</td>
<td>Destructive (Not applicable)</td>
<td></td>
</tr>
<tr>
<td>Mass Spectrometry</td>
<td>Good Quantification</td>
<td>Duty Cycle Slow</td>
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<tr>
<td>(a) TPD</td>
<td></td>
<td>Decomposition may compete with desorption</td>
</tr>
<tr>
<td>(b) Analysis of desorbing species</td>
<td>Simple reasonable quantification</td>
<td>Indirect monitor of surface processes</td>
</tr>
<tr>
<td>IR (reflection)</td>
<td>Parent can easily be monitored</td>
<td>Poor Sensitivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Modest Quantification</td>
</tr>
</tbody>
</table>
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Thank you
Solution to Au satellites

The graph shows XPS intensity (arb. units) versus binding energy (eV) for Au (4f) and Pt (4f) peaks. The intensity for Au peaks is multiplied by 1, while that for Pt peaks is multiplied by 5. The graph includes peaks for different compounds, including Au and PtMeCpPtMe₃, and indicates the presence of secondary satellites for Au. The binding energy scale ranges from 70 to 75 eV.
Electron Source: Flood Gun

- **Why use a flood gun?**
  - Uniform electron beam over a wide area (necessary for XPS and RAIRS)
  - High target current
  - Relatively broad range of Energies (40 – 500 eV)

Electron Flood Gun can produce:
(a) 40 - 500 eV electrons
(b) 5 - 150 µA target currents
Sample

Cu leads provide for heating and cooling (100K-450K)

Type K thermocouple

Au Substrate (~195 K)

Manipulator
X-ray Photoelectron Spectroscopy (XPS)

Ejected Photoelectron

\[ \text{Vacuum Level} \]

\[ \text{2p} \]

\[ \text{2s} \]

\[ \text{hν} \]

\[ \text{KE} \]

\[ \text{BE} = hν - \text{KE} \]

\[ \text{hν} \]

\[ \text{1s} \]

\[ \text{Counts (a.u.)} \]

\[ \text{Binding Energy (eV)} \]

\[ \text{Counts (a.u.)} \]

\[ \text{Binding Energy (eV)} \]

\[ \text{XPS enables quantitative determination of chemical composition and effective oxidation state} \]

\[ \text{Reduction of Pt indicated by peak shift to lower BE} \]

\[ \text{Pt(4f)} \]

\[ \text{Pt}^\text{Parent} \quad \text{Pt}^\text{Product} \]
Reflection Absorption Infrared Spectroscopy (RAIRS)

FT-IR Beam
Ultra-High Vacuum
Detector

Reflective Au

MeCpPtMe$_3$
vibrational structure

ν(C-H)

IR Intensity (a.u.)

Wavenumber (cm$^{-1}$)

ν(C-H)

IR Intensity (a.u.)

Wavenumber (cm$^{-1}$)

Electron Irradiation Time (sec)
↓
1200
240
0

0.01 Abs

0.001 Abs
Mass Spectrometry (MS)

MS was used to:

• Verify purity of organometallic precursor

• Observe gaseous products of EBID

• Ensure cleanliness of UHV

Electron bombardment within the MS creates ionized fragments representative of species present in the gas phase.
How does Film Thickness Influence the Process?

Methane area independent of film thickness

σ independent of film thickness
Substrate Dependence?

All experiments conducted at ~195K with 20μA target current and 200eV electron energy