Surface Chemistry and Reaction Dynamics of Electron Beam Induced Deposition Processes

2nd FEBIP Workshop
Thun, Switzerland 2008

Howard Fairbrother
Johns Hopkins University
Baltimore, MD, USA
Outline

• Background / Motivation
• Experimental Approach
  – Analytical techniques and electron source
• Surface Chemistry and Kinetics
• Electron Stimulated Dissociation Mechanism
• Summary & Outlook
Electron Beam Induced Deposition

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.
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 reactions at the surface?
  • $\sigma_{\text{reaction}}(E)$?

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

• Background / Motivation
• Experimental Approach
• Surface Chemistry and Kinetics (500eV)
• Electron Stimulated Dissociation Mechanism
• Summary
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 cm$^2$ in area, can be analyzed using common surface analytical techniques
Broad Beam Surface Irradiation

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

Gold Substrate (~195K)

Why gold?
**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 – 500eV)

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

Type K thermocouple

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

Au Substrate (~195 K)

Manipulator
• We have studied the electron stimulated reactions of the well-known Pt precursor, Trimethyl(methylcyclopentadienyl)-platinum(IV), adsorbed onto gold using the above techniques:
X-ray Photoelectron Spectroscopy (XPS)

XPS enables quantitative determination of chemical composition and effective oxidation state.

Reduction of Pt indicated by peak shift to lower BE.
Reflection Absorption Infrared Spectroscopy (RAIRS)

FT-IR Beam

Ultra-High Vacuum

IR Detector

ν(C-H) MeCpPtMe₃ vibrational structure

IR Intensity (a.u.)

3000 2500 2000 1500 1000

Wavenumber (cm⁻¹)

0.01 Abs

ν(C-H)

IR Intensity (a.u.)

3100 3000 2900 2800 2700

Wavenumber (cm⁻¹)

0.001 Abs

Ultra-High Vacuum

Reflective Au

Electron Irradiation Time (sec)

1200

240

0
Mass Spectrometry (MS)

Electron bombardment within the MS creates ionized fragments representative of species present in the gas phase.

MS was used to:
- Verify purity of organometallic precursor
- Observe gaseous products of EBID
- Ensure cleanliness of UHV
Outline

• Background / Motivation
• Experimental Approach
• Surface Chemistry and Kinetics (fixed electron energy = 500eV)
• Electron Stimulated Dissociation Mechanism
• Summary
Adsorption of MeCpPt(IV)Me₃ onto Gold Substrate – Controlling film thickness

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

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

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

Influence of Dosing Time on Film Thickness

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

$d_{ave} = .96\text{nm}$

XPS and MS Experiments Conducted in this Regime

CH₃ CH₃ CH₃

Au
Production of Amorphous Platinum/Carbon Film

XP spectra of sputter deposited platinum on gold

![Graph showing binding energy vs counts (a.u.)](image)

- **Counts (a.u.)**
- **Binding Energy (eV)**

Substrate heated to room temperature leaving electron beam irradiation product

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

MeCpPt(IV)Me$_3$ 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 change in film thickness as determined by Au(4f) attenuation
- Shift in platinum environment from precursor to product

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

• Low resolution / high intensity emphasizes stoichiometry
Evidence for Carbon Loss During Irradiation

- The C:Pt ratio of 10 XP spectra of the MeCpPt(IV)Me₃ prior to e⁻ beam irradiation is representative of the initial stoichiometric ratio of 9 carbon atoms to 1 platinum atom.

- 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.
Gas Phase Products

MS capable of measuring individual masses as a function of time

Counts (a.u.)

Mass (a.m.u.)
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
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>1.40E-16</td>
</tr>
<tr>
<td>MS (m/z=15)</td>
<td>9.75E-17</td>
</tr>
</tbody>
</table>

\[ \sigma_{\text{ave}, 500\text{eV}} = 2.28E-16 \text{ cm}^2 \]

XPS, RAIRS, and MS provide similar \( \sigma \) values though they measure different processes.
How does Film Thickness Influence the Process?

Methane area independent of film thickness

\( \sigma \) independent of film thickness
Surface Chemistry

- 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.
Outline

• Background / Motivation
• Experimental Approach
• Surface Chemistry and Kinetics (500eV)
• Electron Stimulated Dissociation Mechanism
• Summary
Dependence on Incident Electron Energy Observed Using XPS

Electron Beam Energy
- Above XP spectra: 25μA, t=60 sec

Optimal σ between 100-200eV 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
Dissociative Ionization Process

Decomposition products
Substrate Dependence?

All experiments conducted at ~195K with 20μA target current and 200eV electron energy
A UHV surface science approach can provide valuable information on reaction rates and fundamental chemical processes involved in EBID.
Exptl. Requirements

Substrate
- Chemically unreactive 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)
<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>
</tr>
<tr>
<td>(a) TPD</td>
<td></td>
<td>Decomposition may compete with desorption</td>
</tr>
<tr>
<td>(b) Analysis of desorbing</td>
<td>Simple reasonable quantification</td>
<td>Indirect monitor of surface processes</td>
</tr>
<tr>
<td>species</td>
<td>Parent can easily be monitored</td>
<td>Poor Sensitivity</td>
</tr>
<tr>
<td>IR (reflection)</td>
<td></td>
<td>Modest Quantification</td>
</tr>
</tbody>
</table>
Acknowledgements

• Joshua Wnuk, Johns Hopkins University
• Justin Gorham, Johns Hopkins University
• Willem van Dorp, Rutgers University
• Ted Madey, Rutgers University
• Kees Hagen, Delft University of Technology