Electron Beam Induced Deposition (EBID) of Nanostructured Materials

Joshua Wnuk, Justin Gorham, D. Howard Fairbrother

Department of Chemistry, Johns Hopkins University, Baltimore, MD

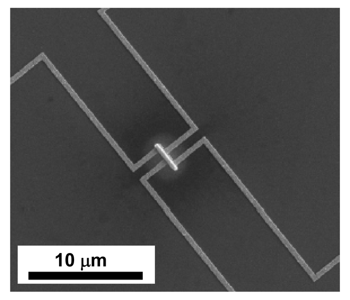
Introduction

Electron Beam Induced Deposition (EBID) is capable of creating 2-D and 3-D nanostructures an order of magnitude smaller than current lithographic techniques.

Advantages of EBID:
- Size limited only by secondary electron ejection
- Wide range of possible precursor compounds

Current disadvantages:
- Little is currently known about fundamental deposition and growth processes
- Lack of insight into chemical processes means that deposits often contain large amounts of undesirable contamination

Project Goals:
- To gain insight into the EBID mechanism
- To use knowledge of fundamental processes to optimize the efficiency and purity of EBID deposits

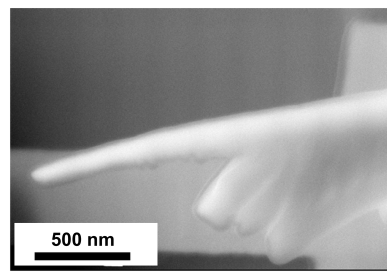


Platinum wire deposited across Au leads using $MeCpPtMe_3$

Two projects are currently underway utilizing EBID in the Fairbrother Lab:

Deposition of platinum using methylcyclopentadienyl-platinum(IV)trimethyl ($MeCpPtMe_3$)

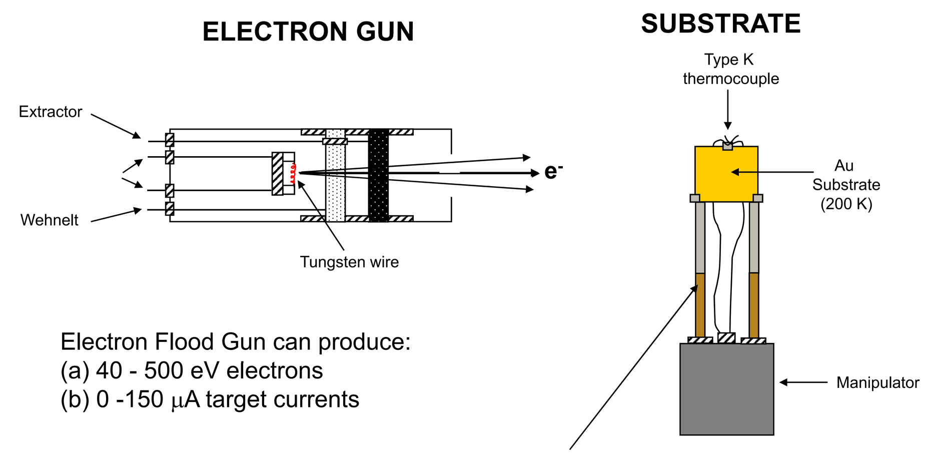
Synthesis of amorphous Carbon:Nitride (*a*:C:N) films from diaminopropane



Three dimensional structure formed using EBID of $W(CO)_6$

Experimental

All EBID experiments are conducted in ultra-high vacuum (UHV) using an electron flood gun (FG). The FG produces a uniform beam of electrons at a well defined energy.

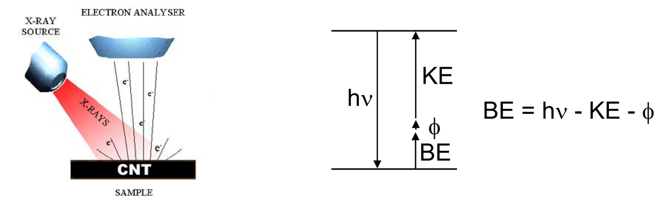


Electron Flood Gun can produce:
(a) 40 - 500 eV electrons
(b) 0 -150 µA target currents

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

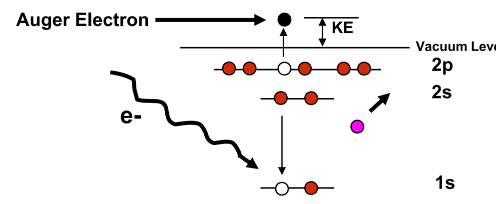
X-ray Photoelectron Spectroscopy (XPS)

XPS provides information about the material's elemental composition, oxidation states and film thickness.



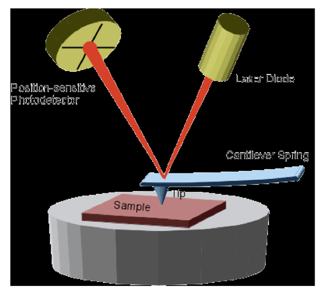
Auger Electron Spectroscopy (AES)

The focused, high energy electron beam generated by the AES is used for depositing structures and making spectroscopic measurements.



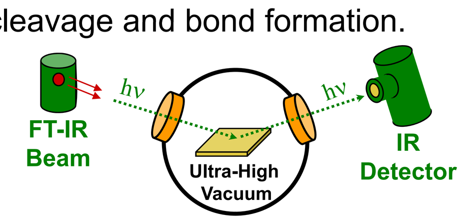
Atomic Force Microscopy (AFM)

The use of AFM enables us to characterize the morphology and structure of the deposited material.



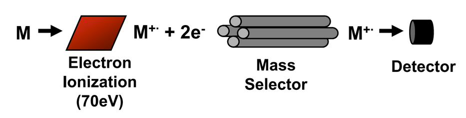
Reflection Absorption Infrared Spectroscopy (RAIRS)

The vibrational spectra of molecules adsorbed to a mirrored substrate provides information about bond cleavage and bond formation.

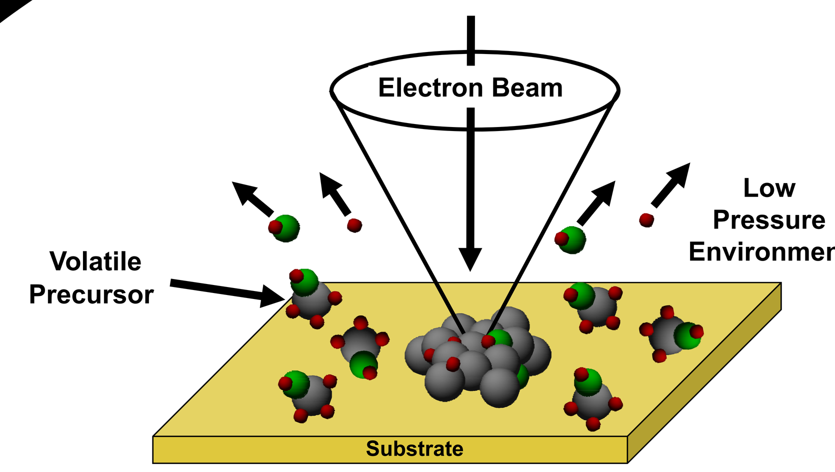


Mass Spectrometry (MS)

The MS measures the partial pressure of gases within the vacuum chamber.

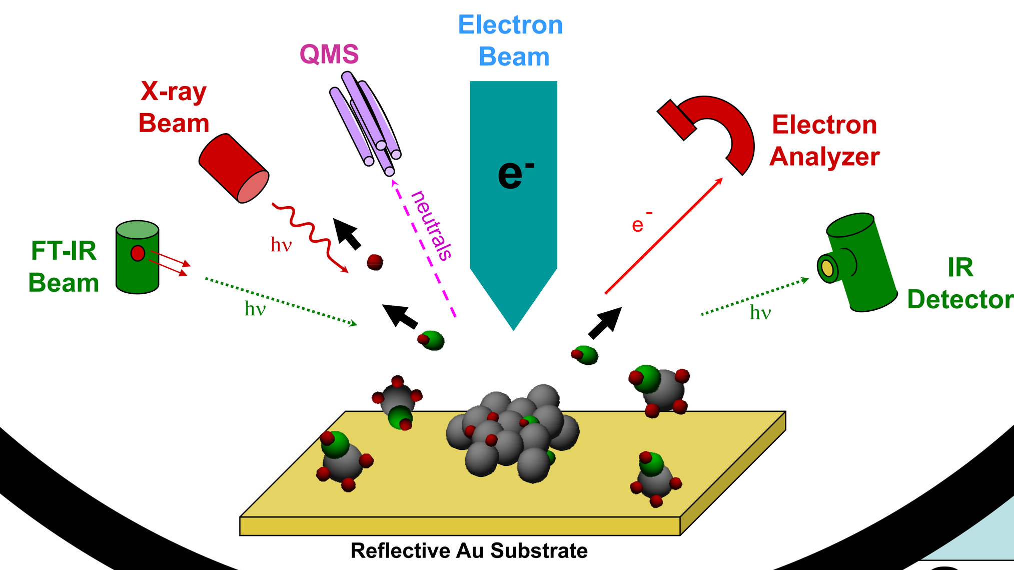


The Process

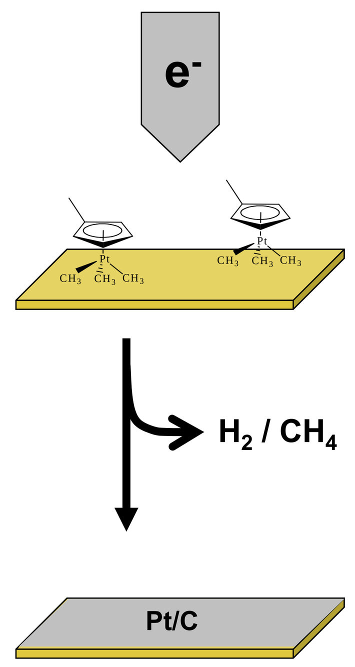


The ability to focus an electron beam to a small spot size, control electron fluence, and raster the beam makes EBID ideal for growing a wealth of different nanostructures

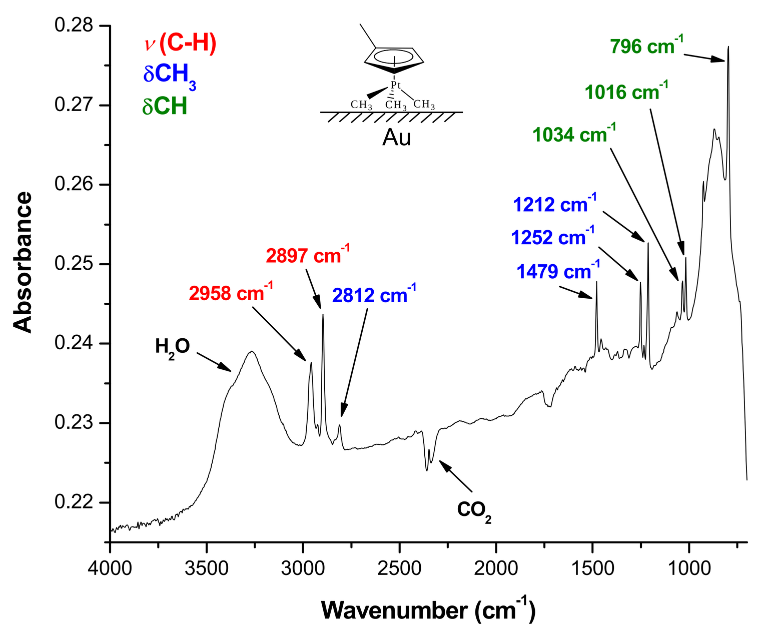
Our Experimental Approach



Deposition of Pt from an Organometallic Precursor

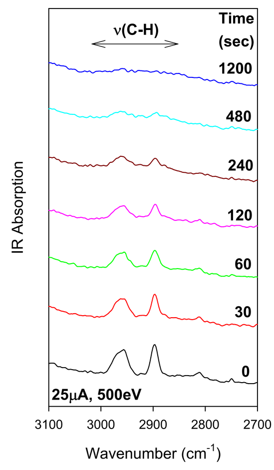


Reflection Absorption Infrared Spectroscopy

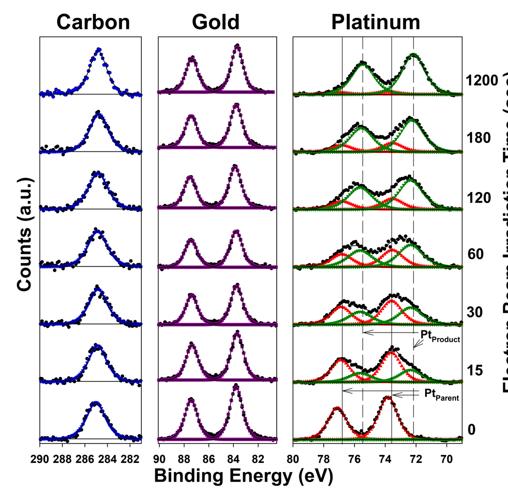


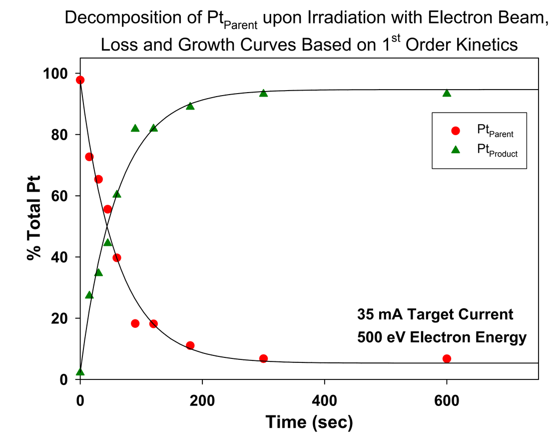
RAIRS spectrum of $MeCpPtMe_3$ adsorbed onto gold substrate measured using a merucry/cadmuim/telluride (MCT) detector.

The loss of hydrocarbon stretching modes with increased electron beam exposure suggests that the organic ligands are degraded by the incident beam.



X-ray Photoelectron Spectroscopy

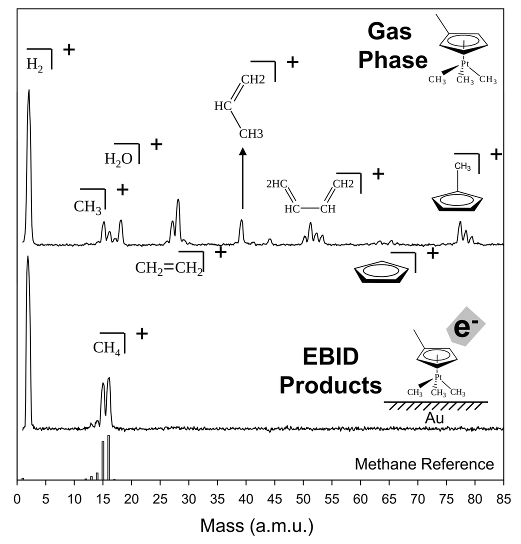


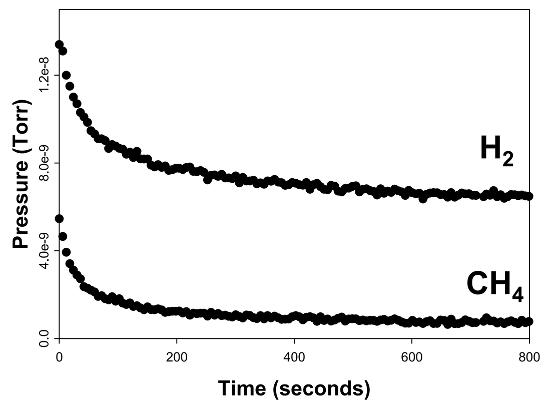


- Deconvolution of the Pt(4f) region allows for calculation of the reaction kinetics.
- There is little observable change in the carbon region suggesting that while the parent compound readily decomposes with electron beam exposure, the resultant film is a mixture of carbon and platinum.

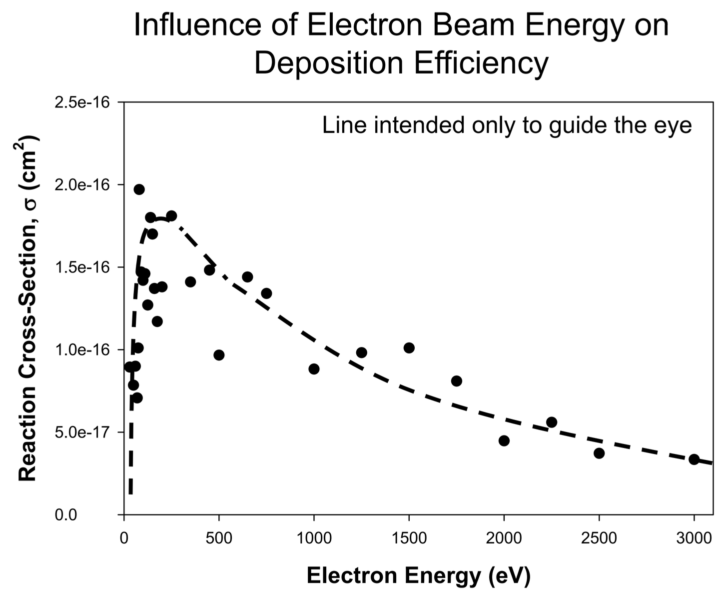
Mass Spectroscopy

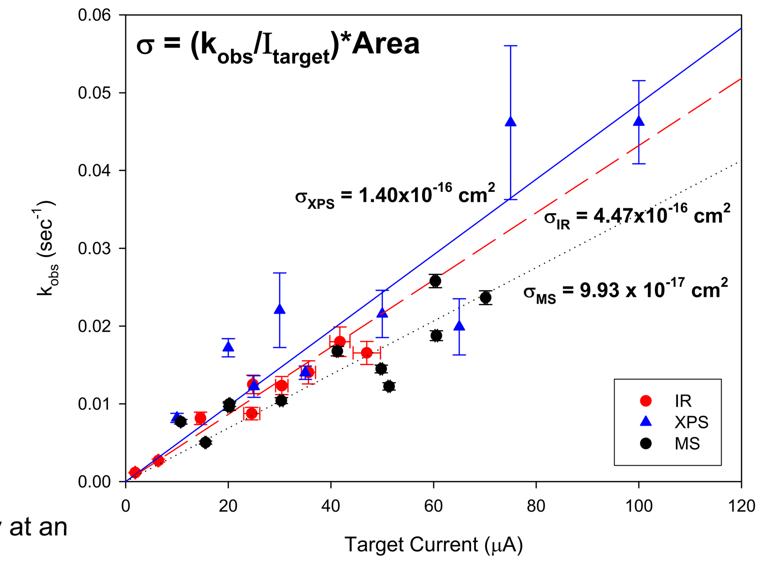
Electron irradiation of the $MeCpPtMe_3$ dosed substrate results in the loss of hydrogen and methane and can be fit to a 1[st] order loss process.





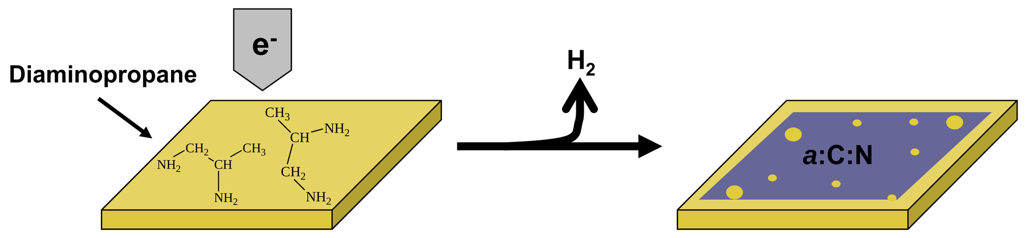
The change in partial pressure of H_2 and CH_4 with time enable measurement of the reaction kinetics.



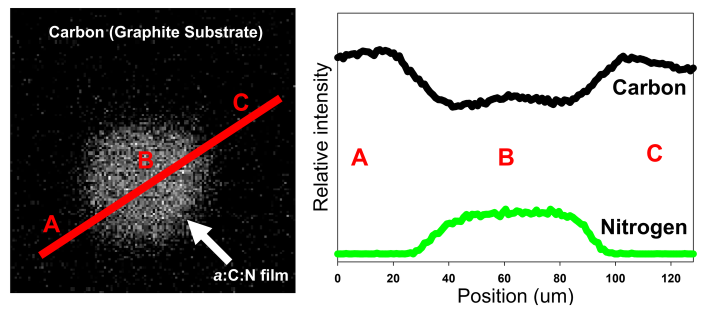


- Electron stimulated decomposition of $MeCpPtMe_3$ reaches maximum efficiency at an incident electron energy of approximately 150 eV
- This suggests dissociation by electron impact (**$M + e^- \rightarrow M^+ \rightarrow$ Decomposition)**

Amorphous Carbon:Nitride (*a*:C:N) Film Deposition

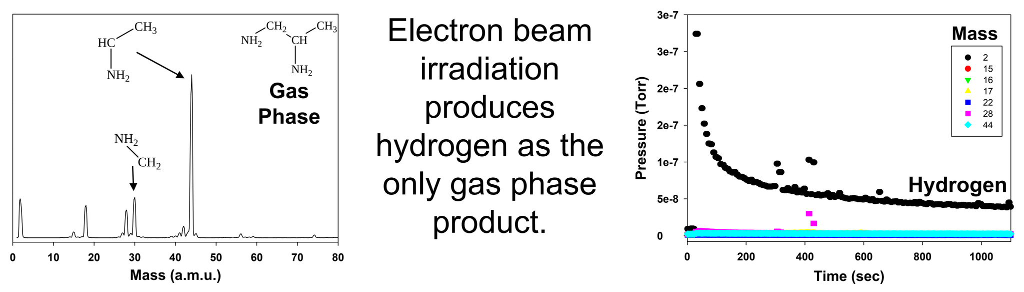


Scanning Auger Electron Spectroscopy



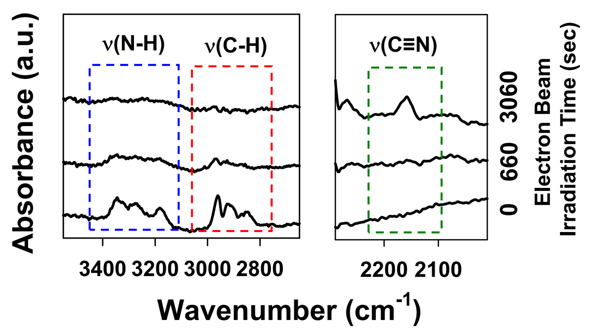
a:C:N film deposited on graphite at room temperature using a focused electron beam at 1.5 keV in the presence of diaminopropane.

Mass Spectrometry



Electron beam irradiation produces hydrogen as the only gas phase product.

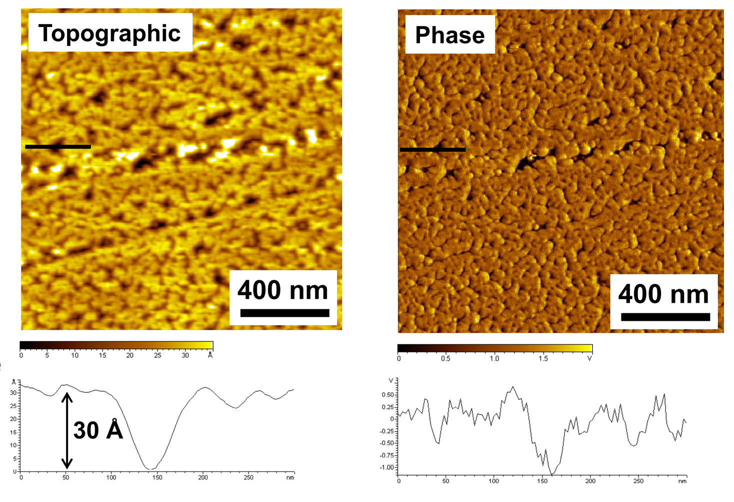
Reflection Absorption Infrared Spectroscopy

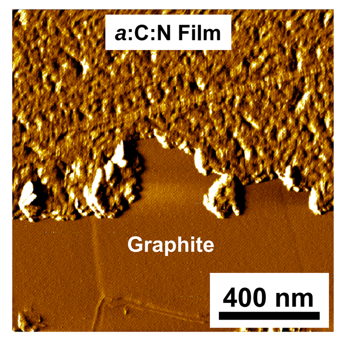


Electron beam irradiation results in loss of the C-H and N-H stretching modes and the formation of a C≡N bond.

Atomic Force Microscopy of *a*:C:N Film

a:C:N film is amorphous and porous as seen by voids in the film through which the substrate is visible. Phase image indicates film softer than substrate





The AFM tip "plows" away the *a*:C:N film to reveal graphite below.

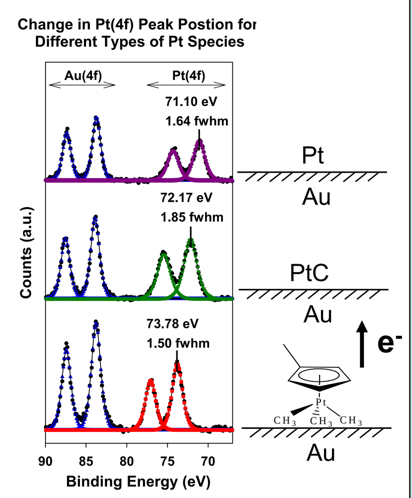
Summary

Amorphous Carbon Nitride Deposition:

- Electron beam irradiation of diaminopropane produces an amorphous carbon:nitride film producing hydrogen gas as the only by-product of reaction
- Electron stimulated reactions lead to C≡N bond formation in deposited *a*:C:N film
- AFM reveals that films are amorphous and porous

Platinum Film Growth from an Organometallic Precursor:

- Kinetics of electron beam induced deposition are 1[st] order with relationship to electron fluence; comparable reaction rate obtained from XPS, IR and MS
- Deposited films contain a large concentration of carbon
- Evidence supports formation of a platinum/carbonaceous film with loss of hydrogen; XPS data suggests one methane molecule desorbs per Pt precursor
- Dependence on incident electron energy suggests optimal bond cleavage energy of approximately 150 eV



Future Work

Amorphous Carbon Nitride Deposition:

- Quantitative analysis of growth kinetics
- Influence of electron energy of growth kinetics
- Deposition of nanostructured films with well defined chemical composition
- Materials properties of deposited films (hardness, friction, biocompatibility

Platinum Film Growth from an Organometallic Precursor:

- Investigate other organometallic precursors (e.g. $AuMe_2(acac)$)
- Influence of chemical composition on materials properties (conductivity)
- Purification of metallic deposit using radicals to remove carbon