Surface Analysis of Organic Monolayers using FTIR and XPS

Michael Toole
Jamie Nipple

Advisor: Professor David Janes
Graduate Mentors: Patrick Carpenter
Adina Scott

Presentation Outline

- Introduction to Self-Assembled Monolayers (SAMs)
- Introduction to Surface Analysis (FTIR/XPS)
- Applications of SAMs
- Method #1: Solution Immersion
- Method #2: Molecular Self-Assembly
- Method #3: Electrochemical Reduction
- Summary of Findings
- Future Outlook
- Questions

Introduction: Organic Monolayers

Self-Assembled Monolayers

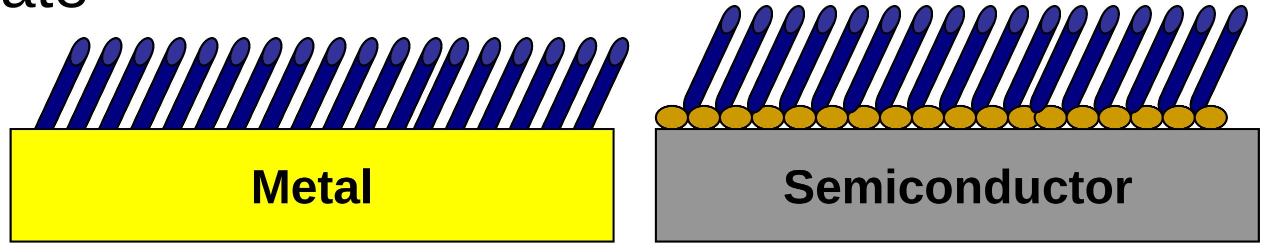
- •Single layer of molecules
- •Form spontaneously
- •Well-defined structure
- •Covalently bonded
- •Bound to metal (Au, Ag, Cu) or semiconductor (GaAs, Si) substrate

GaAs (100) Substrate

- •Alkanethiol molecules (-SH)
- •Form S-As covalent bond

Si (111) Substrate

- •Benzene molecules (-C_6H_{12})
- •Form Si-C covalent bond



Graphics Source: Patrick Carpenter

Preparation Techniques

- Molten Deposition
  - Melt alkanethiols to 100-200 °C
  - Deposit onto GaAs substrate
  - Relatively effective
  - Not usable on all alkanethiols

- Activated NH_4OH Immersion
  - Similar to solution immersion
  - Etch with NH_4OH
  - Allow to purge for 20 hours at room temperature

- Solution Immersion
  - Etch substrate with HCL
  - Rinse with DI H_2O
  - Deposit substrate into solution
  - Dry on hotplate (~8 hours)

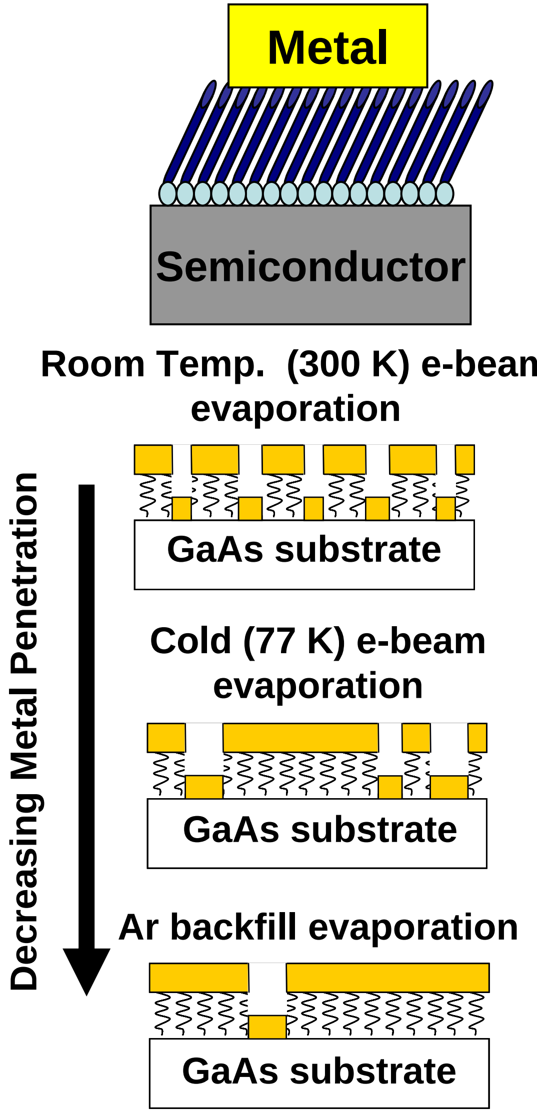
- Electrochemical Reduction
  - Reduce aryl diazonium salts ($C_6N_2BF_4$) on Si
  - Causes a radical reaction
  - Useful for benzene monolayers

Purpose: Creation on nanoscale transistors

Problems: Metal penetration

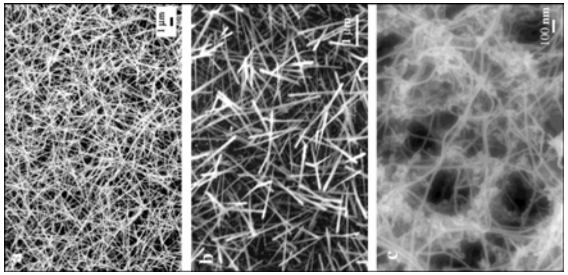
Contacting Techniques

- Basic Principles:
  - Face substrate away from metal
  - Heat metal until reaches gaseous phase
  - Hot metal reaches substrate and is deposited
- Standard (300K): Pressure in chamber pumped down to 10-7 Torr and then sample deposited
- Cold (77K): Sample cooled with liquid nitrogen and slowly deposited
- Ar Backfill: Backfilled with Ar gas to slow KE



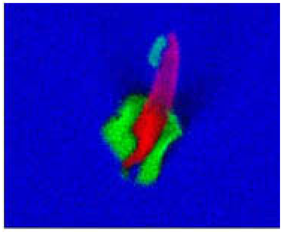
Graphics Source: Patrick Carpenter

- Scanning Electron Microscopy (SEM)
  - Topography
  - Morphology
  - Composition
  - Atomic arrangement
- Auger Electron Spectroscopy (AES)
  - Elemental composition and concentration
  - Mapping of elements
  - Depth-profiling
- Ellipsometry
  - Layer thickness
  - Composition
  - Topography
  - Optical constants

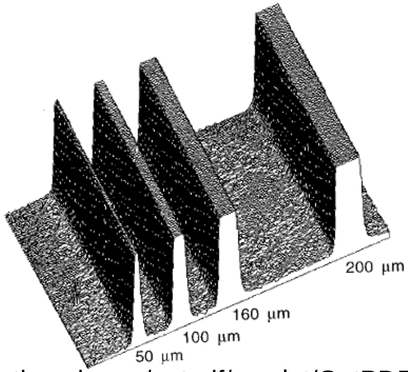


http://www3.interscience.wiley.com/cgi-bin/fulltext/76509302/PDFSTART

Color Composite Auger Map

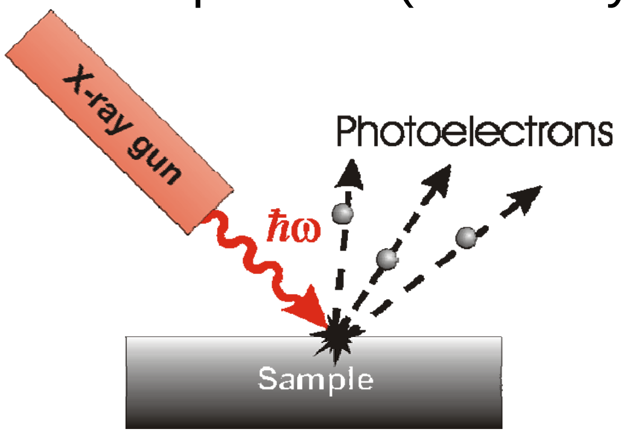


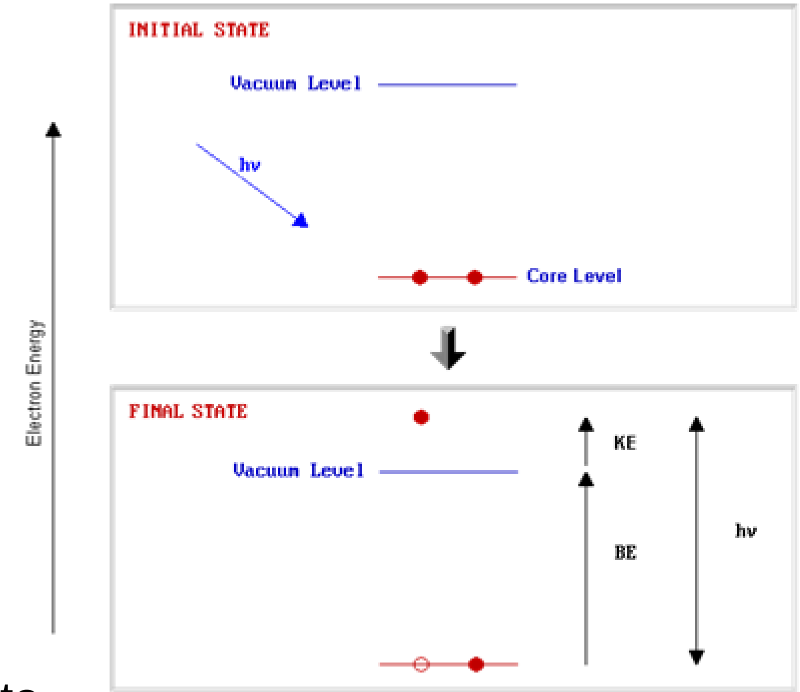
www.mate.calpoly.edu/.../images/aesimage.jpg



http://scitation.aip.org/getpdf/servlet/GetPDFServlet?filetype=pdf&id=RSINAK000067000008002930000001&idtype=cvips&prog=normal

- Uses photons (soft x-rays 200-2000 eV) to remove core electrons from sample = Photoemission



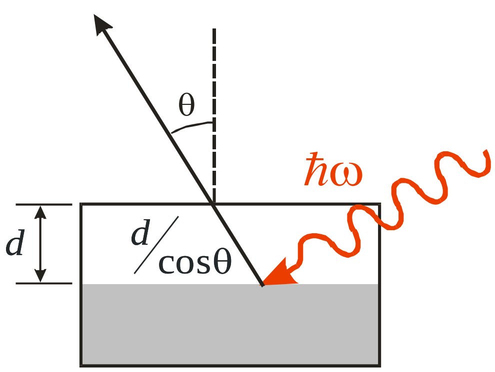


Images by Dmitry Zemlyanov (Purdue University)

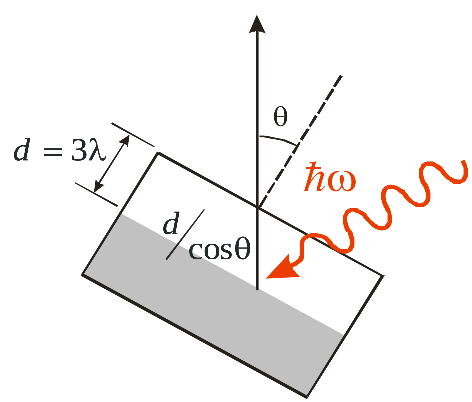
- Produces photoelectron spectrum by measuring the kinetic energy distribution of emitted photoelectrons
- Differences between the ionized electron and neutral electron = Binding energy (BE) which is direct measure of energy required to remove concerned electron
- Determines elemental concentration and electronic state of sample surface

- Binding energy is dependent on:
  - Level at which photoemission is occurring
  - Formal oxidation state of the atom
  - Local and chemical environment

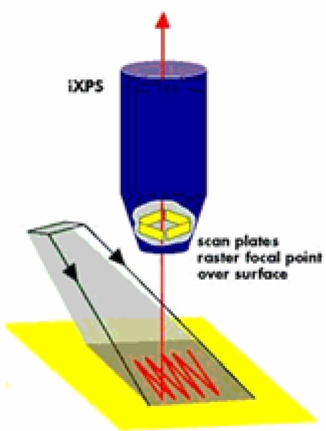
  * A change in the oxidation state or the environment will result in a chemical shift
- Other XPS capabilities



Depth-profiling



Angle Resolved XPS



X-Y Mapping

Images by Dmitry Zemlyanov (Purdue University)

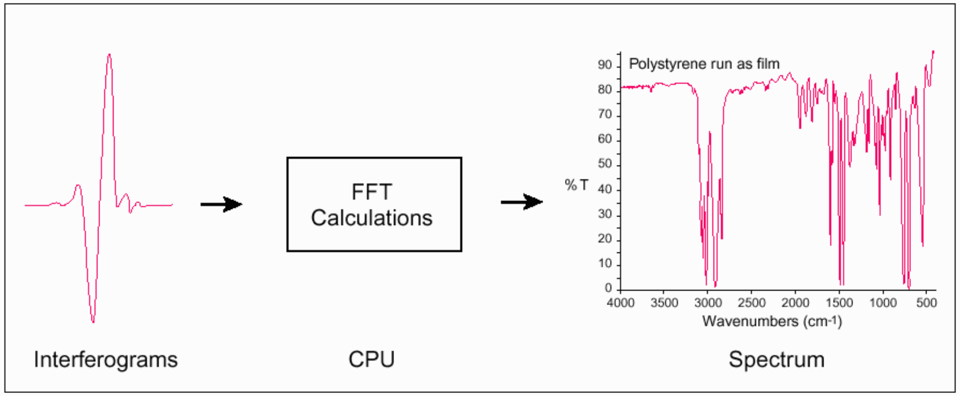
Basic Principle

- Fire IR-rays at sample
- Atoms (Bonds) within sample vibrate with specified frequencies

Uses of FTIR

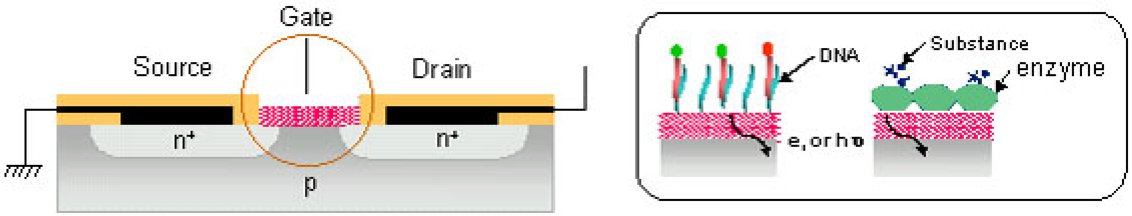
- Chemical Analysis
    - Match to known spectra
    - Match chemical groups
- Electronic Information
    - Measure optical conductivity
    - Determine whether metal, insulator, superconductor, semiconductor

$$W(x) \equiv \frac{2I(x) - I(0)}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} G(k) e^{ikx} dk$$



Images by http://spectroscopy.lbl.gov/FTIR-Martin/FTIR-Martin_files/frame.htm

- Biological Sensors



http://www.coe.waseda.ac.jp/osaka/B-e.html

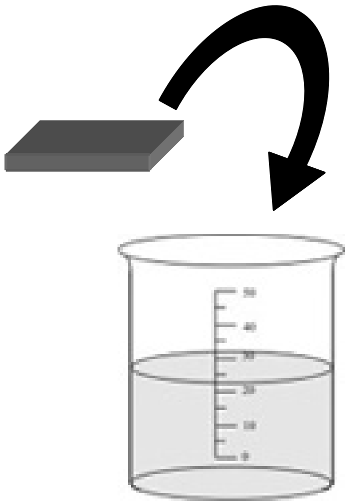
  - Biosensing system based on molecular recognition
- Electrochemistry
  - Sensors use monolayers to impart selectivity onto an electrode
  - Monitors pH, inorganic species, and organic molecules
- Molecular Electronics
  - Nanoscale insulators and dielectrics
  - Molecular switches
  - Rectifiers
  - Field effect transistors

Research Purpose Statement

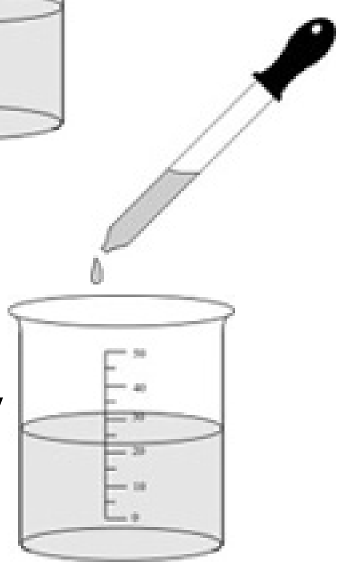
- Use XPS and FTIR to characterize the surface of samples fabricated using three different techniques
- Analyze the results to determine elemental composition, percent oxidation, and atomic bonding
- Determine the effectiveness of each fabrication technique

Deposition Method #1: Solution Immersion

Native oxide etch with HCL



Addition of NH_4OH, deposit sample, dry on hotplate



Substrate: GaAs (100)

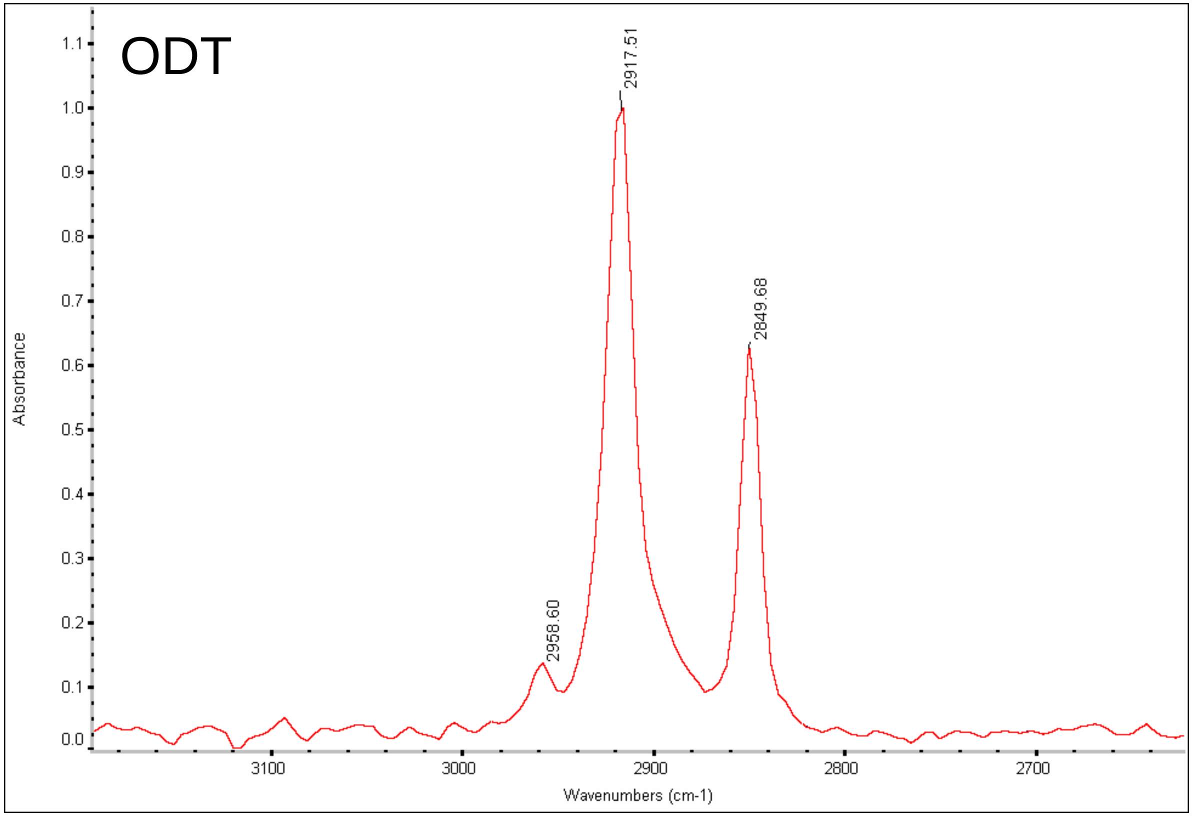
Organic Molecule: 1-Octadecanethiol (ODT)

Covalent Bond: S-As

Procedure:

1) Oxide etched from GaAs using 1:9 HCL:DI solution
2) 5 mM molecule prepared, 5% (by volume) of 30% NH_4OH was added for continuing etching
3) Substrate then submerged into solution
4) Samples then purged with N_2 gas for 1 minute
5) Samples dried on 50° hotplate for 8 hours
6) Samples rinsed with ethanol after drying
7) Sample re-dried with N_2 gas

Solution Immersion: FTIR Analysis



Peaks Present

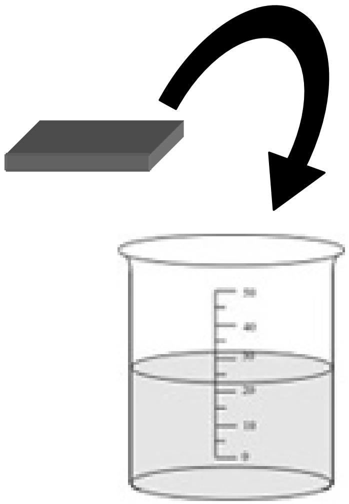
- CH_2 peak (2917.51 cm^{-1})
- CH_2 peak (2849.68 cm^{-1})
- CH_3 peak (2958.60 cm^{-1})

Indicates

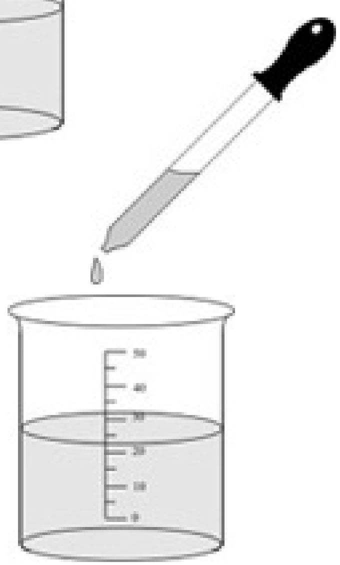
- Fairly well ordered monolayer as shown by semi-sharp peaks and lower wavenumbers

Deposition Method #2: Molecular Self-Assembly

Native oxide etch with NH_4OH



Addition of NH_4OH, deposit sample, dry at room temperature



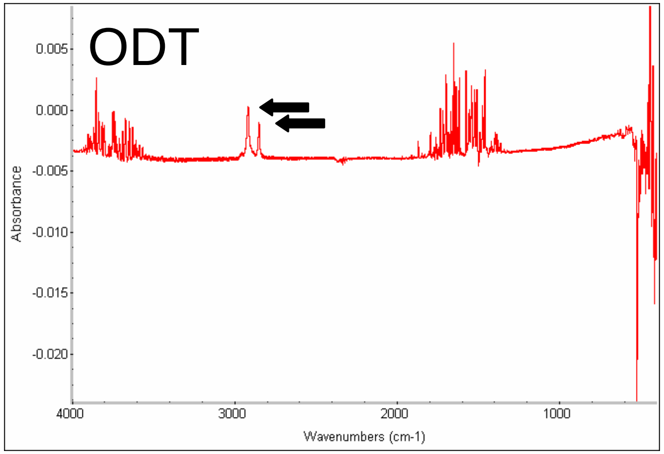
Substrate: GaAs (100)

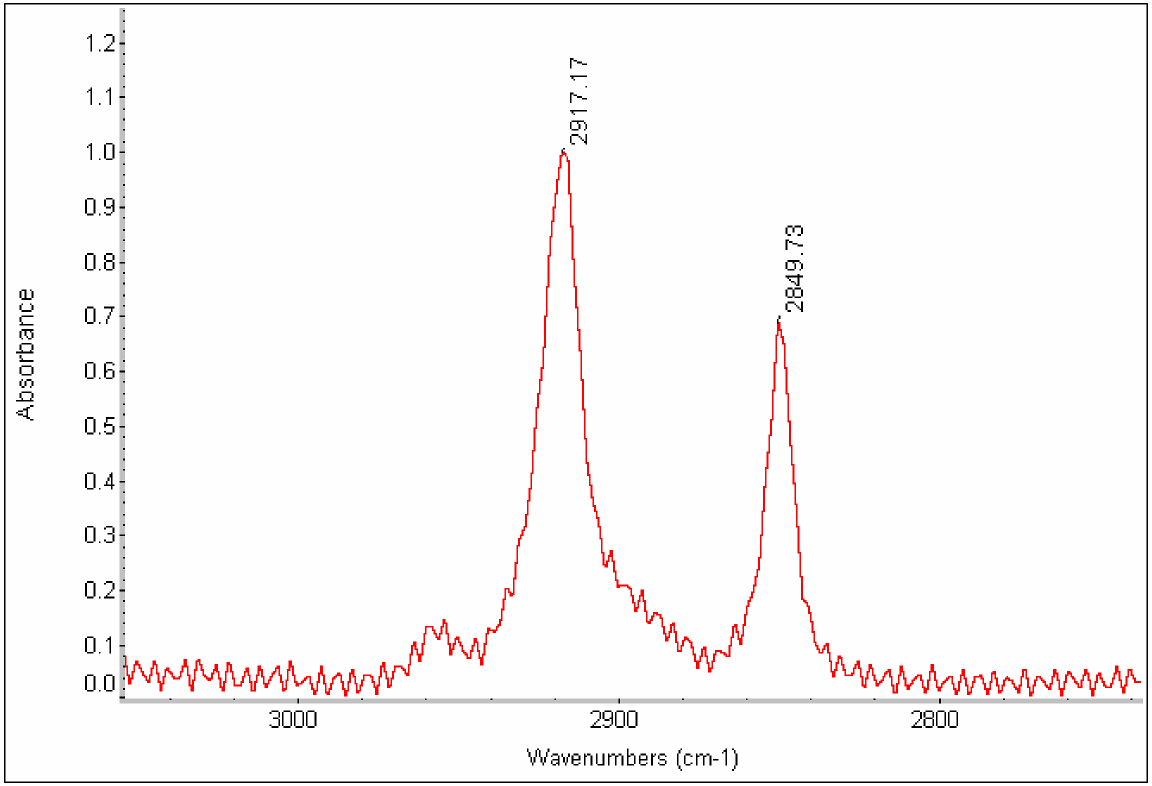
Organic Molecule: 1-Octadecanethiol (ODT) and XYL

Covalent Bond: S-As

Procedure:

1) Oxide etched from GaAs using NH_4OH
2) 5 mM molecule prepared, 5% (by volume) of 30% NH_4OH was added for continuing etching
3) Substrate then submerged into solution
4) Samples then purged with N_2 gas for 1 minute
5) Samples dried at room temperature for 20 hours
6) Samples rinsed with ethanol after drying
7) Sample re-dried with N_2 gas

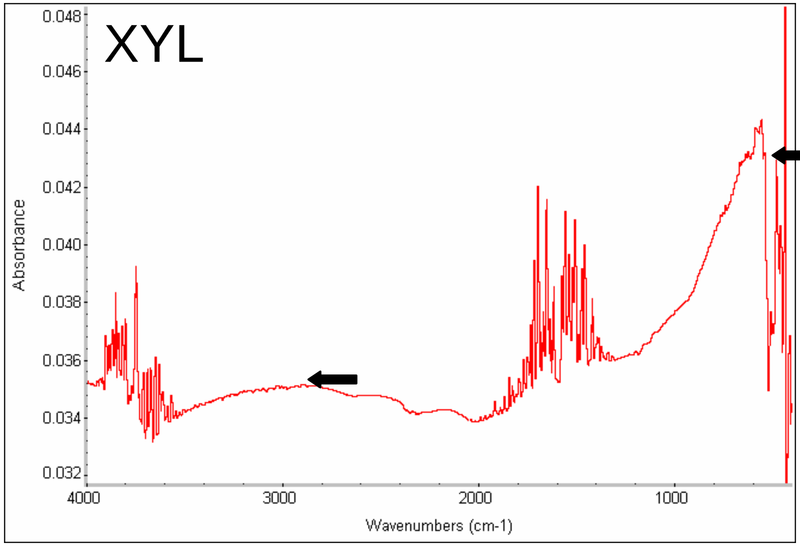




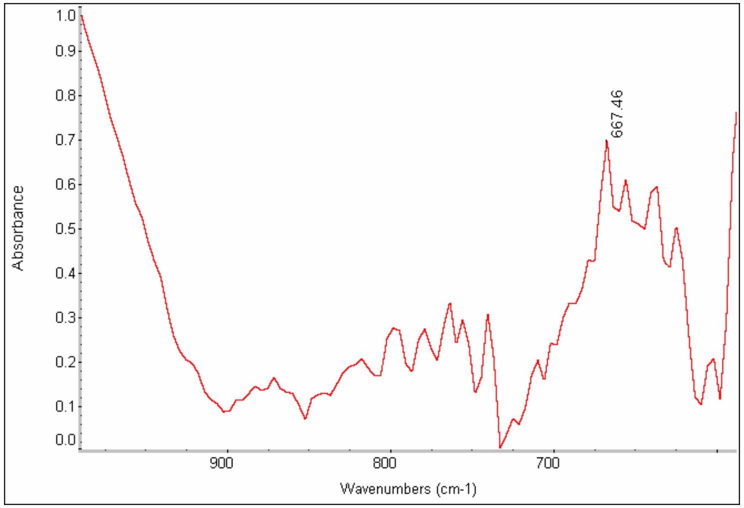
Octadecanethiol

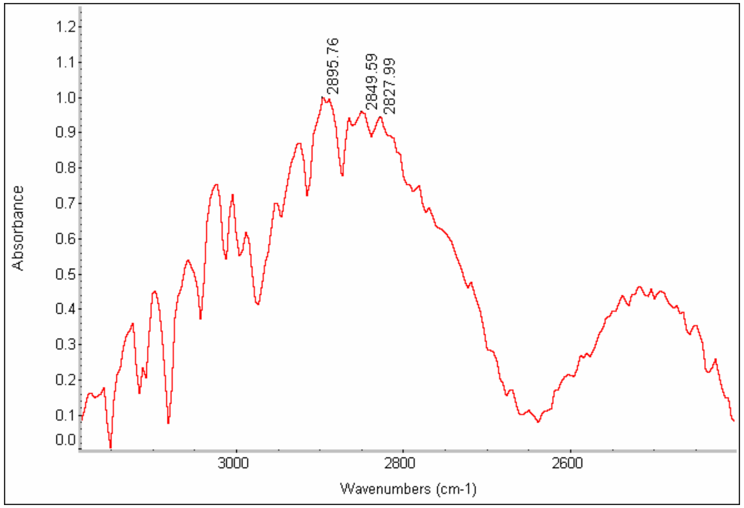
- Expected: C-H_3 Stretch ~2850-3000cm^{-1}

  C-H_2 Stretch ~1465cm^{-1}
- Peak present at 2917.17cm^{-1}, 2849.73cm^{-1}
- Peaks indicates successful monolayer formation
- Sharp peaks indicate highly ordered monolayer



Expanded Spectrum

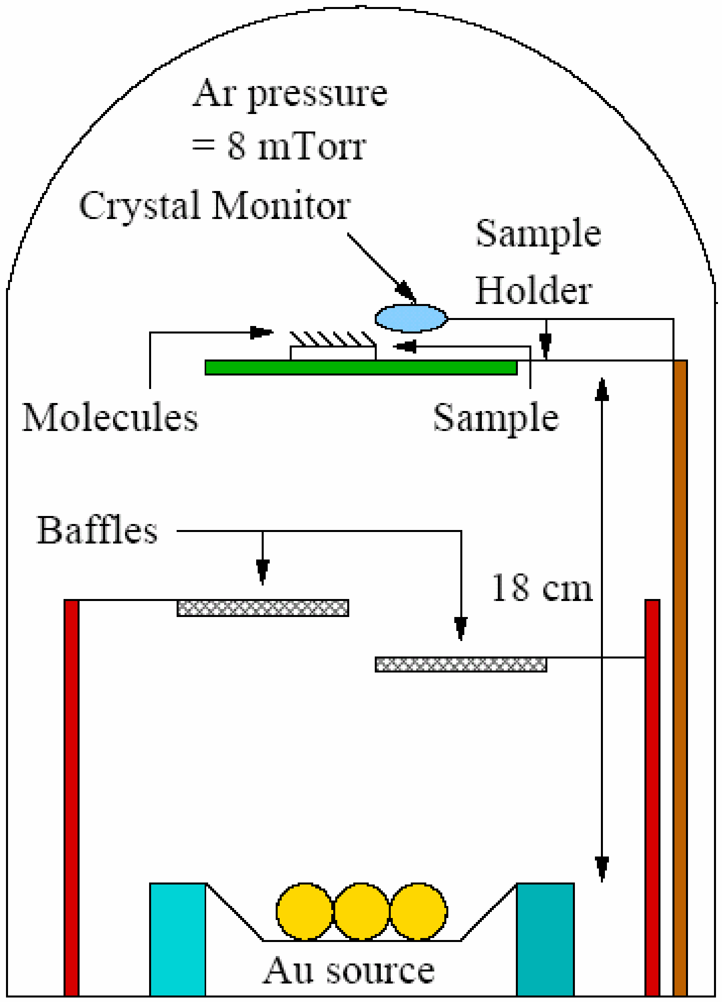




XYL

- Expected: C-H_3 Stretch ~2850-3000cm^{-1}

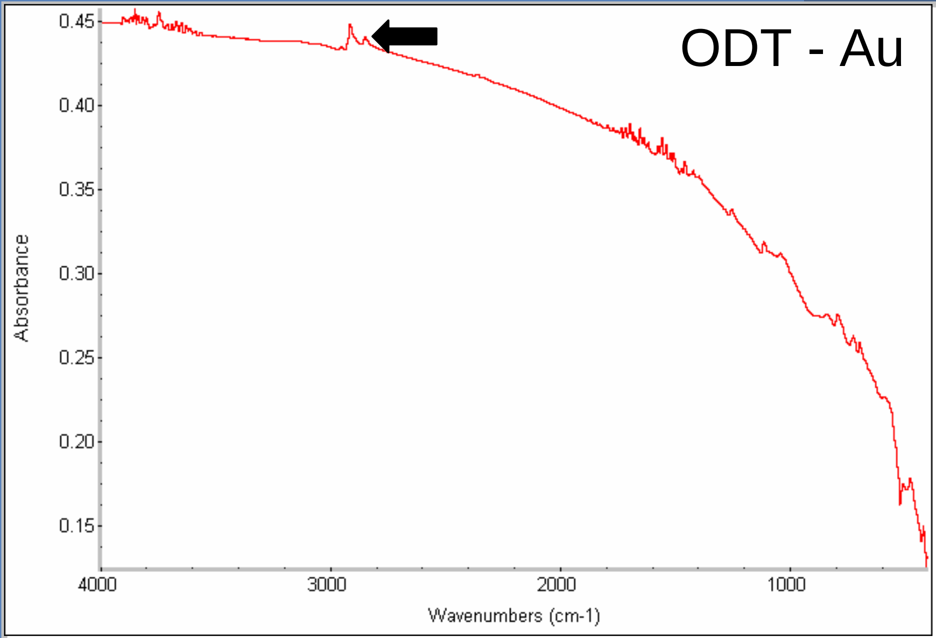
  C-H_2 Stretch ~1465cm^{-1}
- Peak present at 2895.26cm^{-1}, 2849.59cm^{-1}
- Peaks indicates successful monolayer formation
- Semi-Sharp peaks indicate semi-ordered monolayer



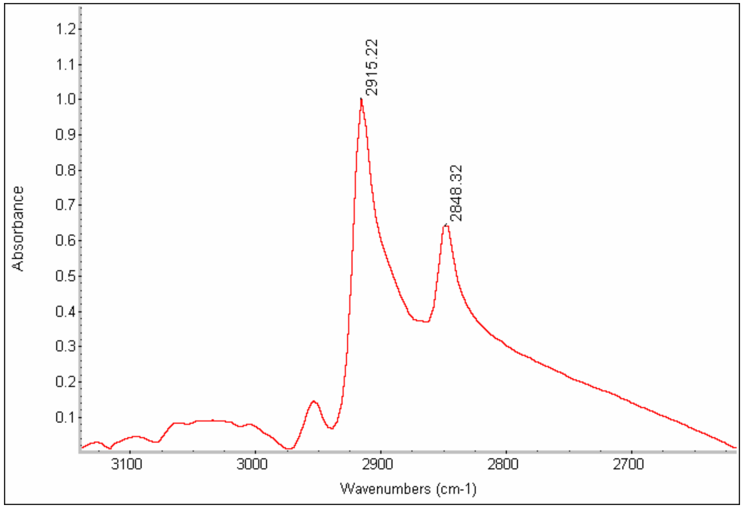
Graphics Source: Patrick Carpenter

Indirect Evaporation Procedure

1) Substrate is faced away from metallic source and cooled
2) Argon is backfilled into the chamber during deposition
3) Metallic Au is heated
4) Argon slows the kinetic energy of evaporated Au particles
5) Reduced kinetic energy results in a lower quantity of penetration
6) A thin layer of Au is evaporated on the ODT organic monolayer



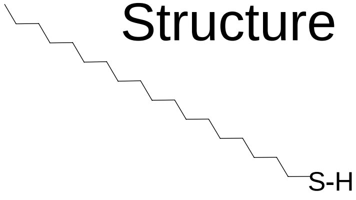
Expanded Spectrum



Octadecanethiol contacted with Au

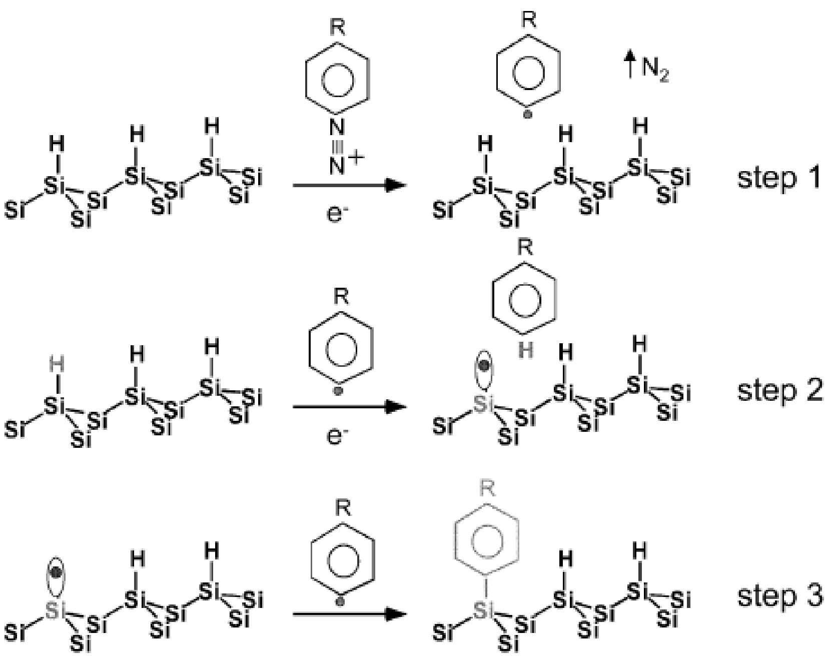
- Expected: C-H_3 Stretch ~2850-3000cm^{-1}
  C-H_2 Stretch ~1465cm^{-1}
- Peak present at 2915.22cm^{-1}, 2848.32cm^{-1}
- Correlates to peaks at 2917.17cm^{-1}, 2849.73cm^{-1}
- Indicates successful monolayer formation
- Indicates successful contact with Au

Molecular Structure

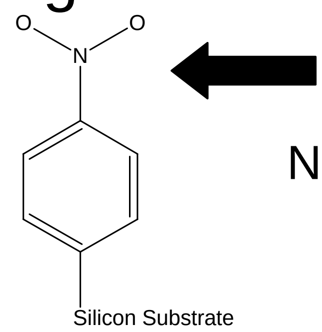


Deposition Method #3: Electrochemical Reduction

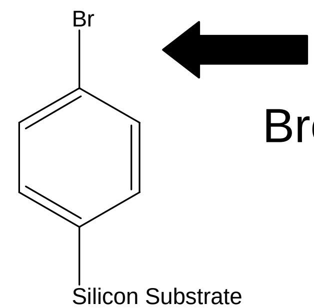
- Electrochemical reduction of aryl diazonium salts ($C_6N_2BF_4$) on Si(111) by promoting a radical reaction



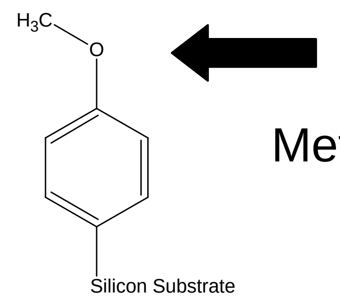
P. Allongue et al. / Journal of Electroanalytical Chemistry 550/551 (2003) 161/174



Nitrobenzene “NB”

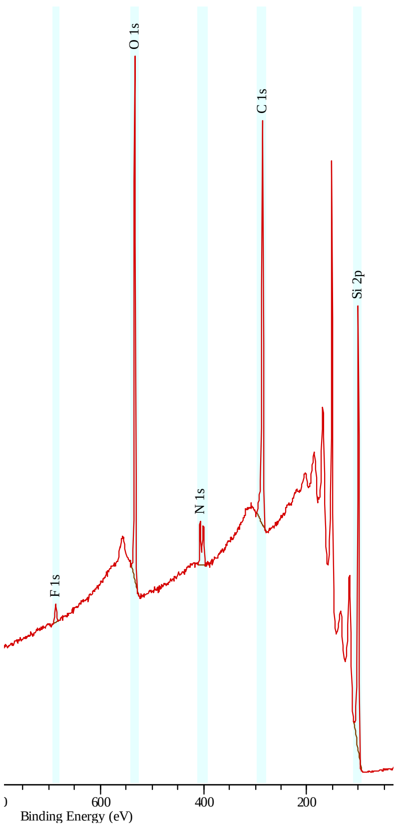


Bromobenzene “BB”



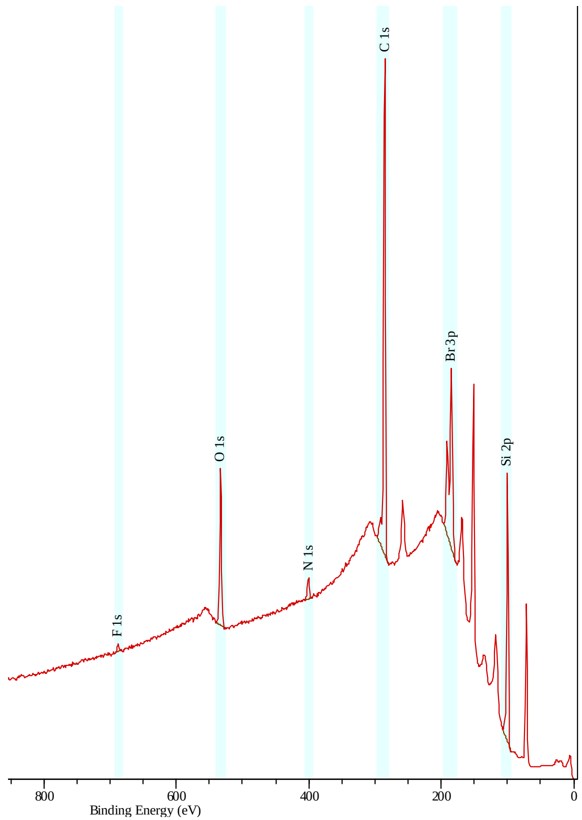
Methoxybenzene “MB”

NB Wide



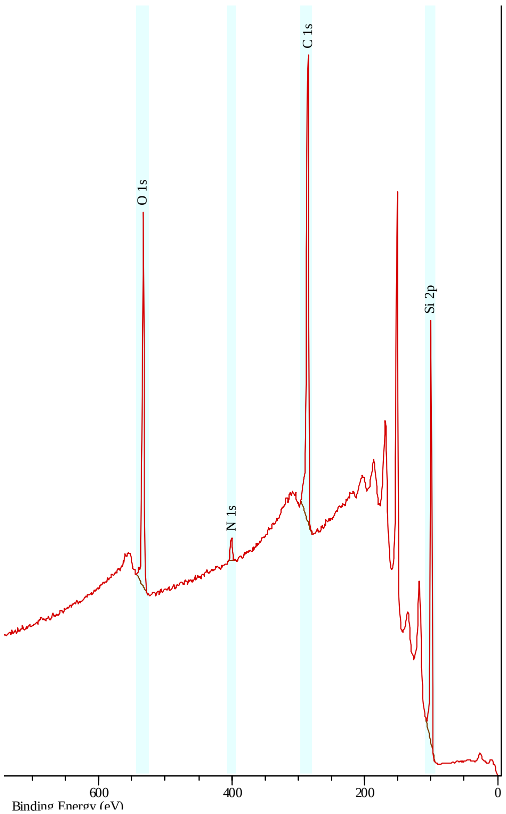
Name	Pos.	FWHM	Area	At%
O 1s	533	2.91125	23154.0	15.76
C 1s	286	3.13313	20026.4	39.95
N 1s	406	3.06303	4163.0	4.61
F 1s	687	3.154	909.7	0.41
Si 2p	100	2.54496	16079.8	39.26

BB Wide



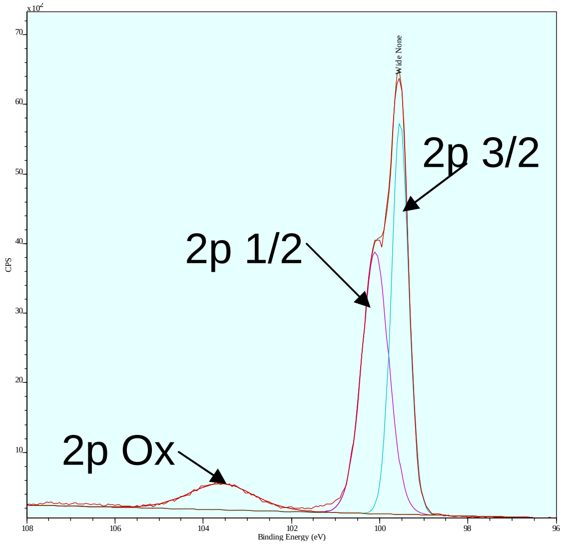
Name	Pos.	FWHM	Area	At%
O 1s	533	3.06708	8831.5	6.38
C 1s	285	2.80737	26758.3	56.60
N 1s	400	3.19643	1254.1	1.47
F 1s	687	2.94095	412.9	0.20
Br 3p	184	3.80632	17167.9	7.22
Si 2p	100	2.48349	10863.7	28.13

MB Wide

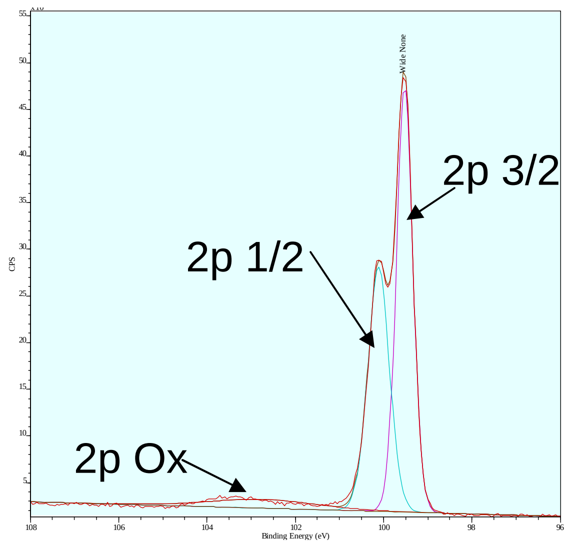


Name	Pos.	FWHM	Area	At%
O 1s	533	3.09062	18332.9	12.87
C 1s	285	3.31614	24542.7	50.48
N 1s	400	3.23162	1129.4	1.29
Si 2p	100	2.49079	14042.9	35.36

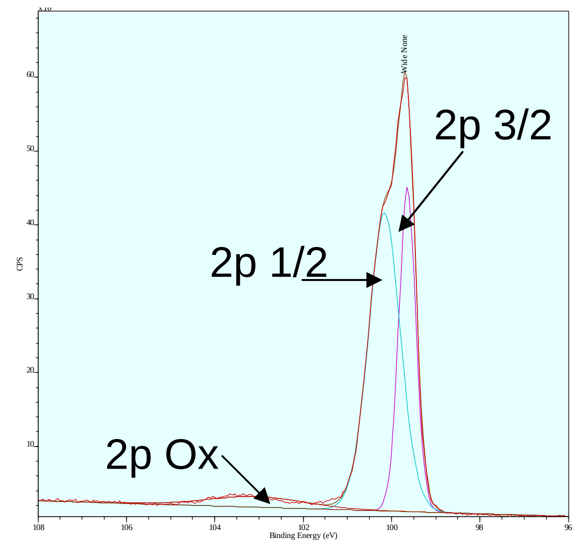
- Expanded view of Si 2p



Nitrobenzene



Bromobenzene



Methoxybenzene

2p Ox: sample oxidation (red)
2p 1/2: spin-orbit splitting (teal)
2p 3/2: spin-orbit splitting (purple)

- Sample Oxidation

NB	Position	% Conc.
Si 2p 1/2	101.1	45.29
Si 2p 3/2	99.5	43.75
Si 2p Ox	103.6	10.96

Surface Oxidation: 4.3%

BB	Position	%Conc.
Si 2p 1/2	100.1	39.89
Si 2p 3/2	99.5	53.01
Si 2p Ox	102.7	7.10

Surface Oxidation: 1.99%

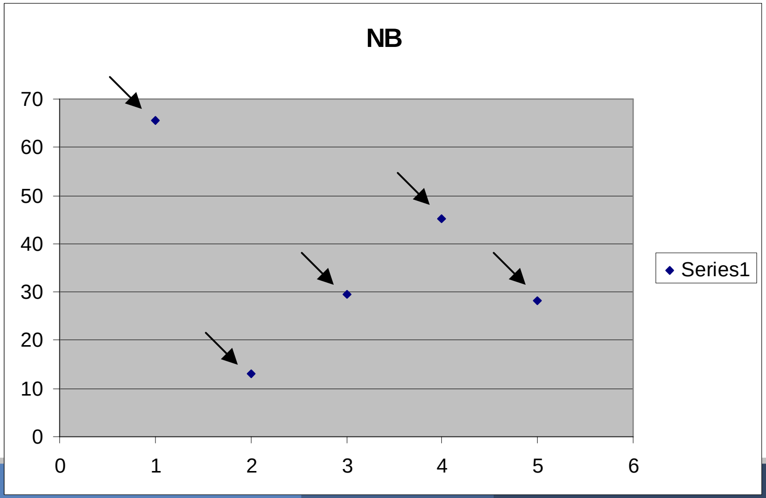
MB	Position	% Conc.
Si 2p 1/2	101.1	59.31
Si 2p 3/2	99.6	34.29
Si 2p Ox	103.0	6.40

Surface Oxidation: 2.26%

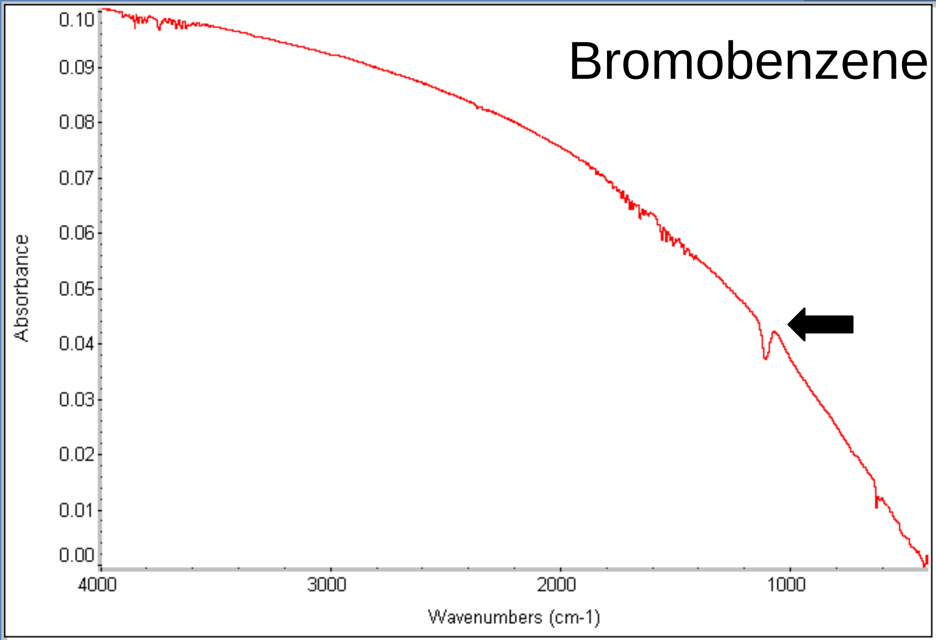
- Surface Characterization: Depth Information

$$N_{elastic} = N_0\left(1 - \exp\left\{-d/\lambda\cos\theta\right\}\right)$$

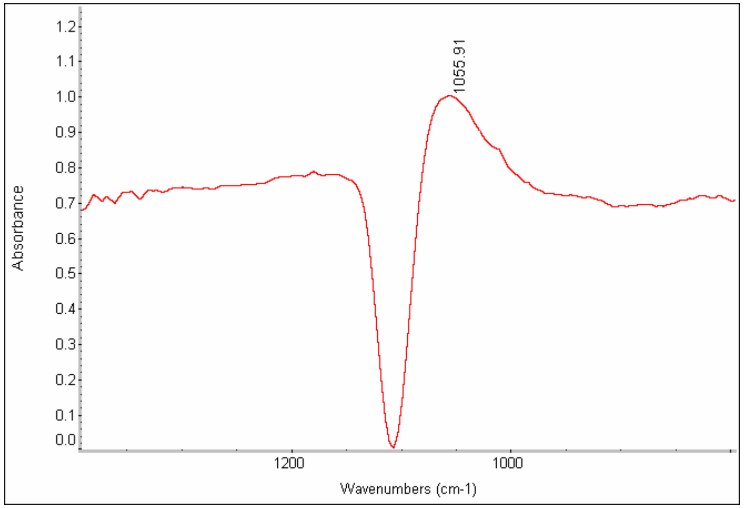
NB	% Si 2p Ox	% Si 2p +1	d	BB	% Si 2p Ox	% Si 2p+1	d	MB	% Si 2p Ox	% Si 2p+1	d
0	4.3	35.96	**65.6**		1.99	27.14	**80.71**		2.26	34.1	**83.83**
-30.06	4.88	35.38	**13.05**		2.02	27.11	**17.1**		1.88	34.49	**19.16**
-45	5.59	34.67	**29.61**		3.17	24.96	**34.12**		3.52	32.84	**36.23**
-59.94	7.27	32.99	**45.27**		4.59	24.54	**48.85**		4.01	32.35	**62.49**
-75.06	11.11	29.15	**28.1086**		4.7	24.43	**48.03**		4.86	31.5	**54.46**



Graph is not linear: Islands of oxidation on sample surface



Expanded Spectrum



Bromobenzene

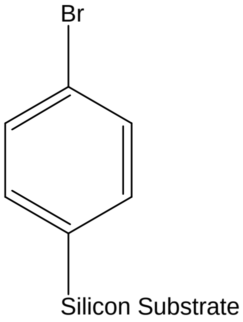
- Expexted: C-Br peak ~560-620cm^{-1}

  Aromatic =CH_2 ~2950-3050cm^{-1}

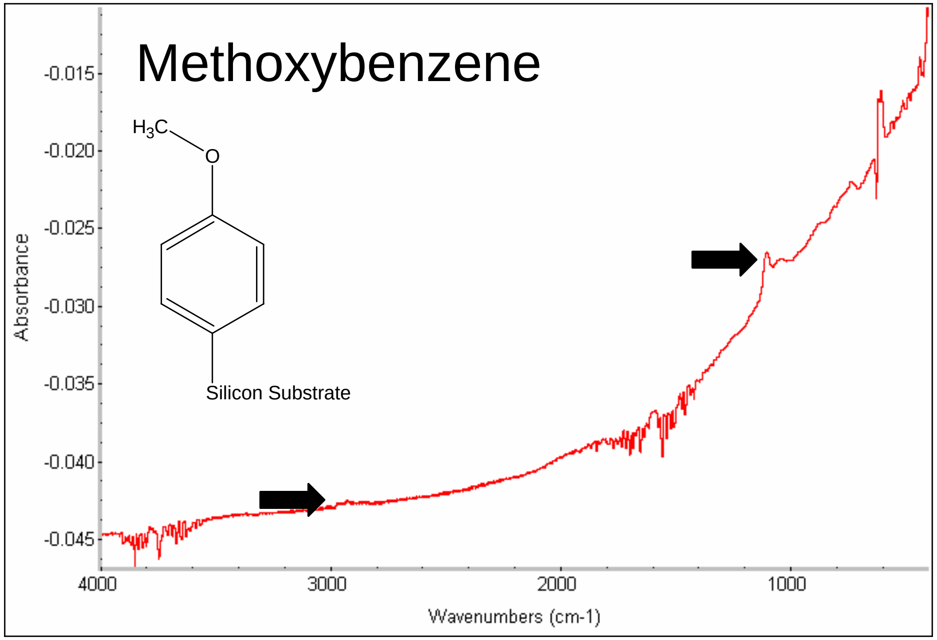
  Aromatic C=C ~1475-1600cm^{-1}

- Peak present at 1055.91cm^{-1}
- Indicates oxidation of substrate
- No conclusive monolayer formation

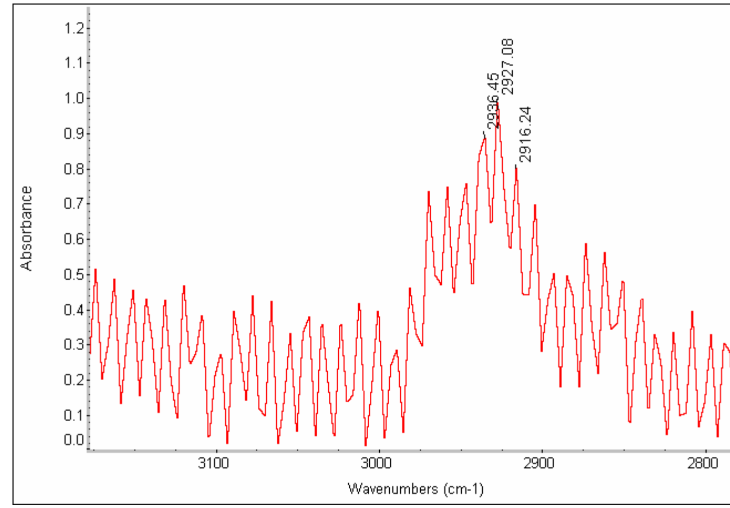
Molecular Structure

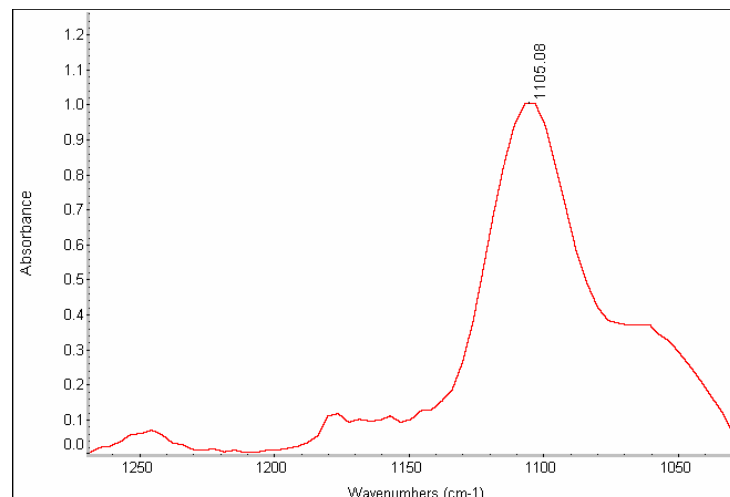


Electrochemical Deposition: FTIR Analysis



Expanded Spectrum





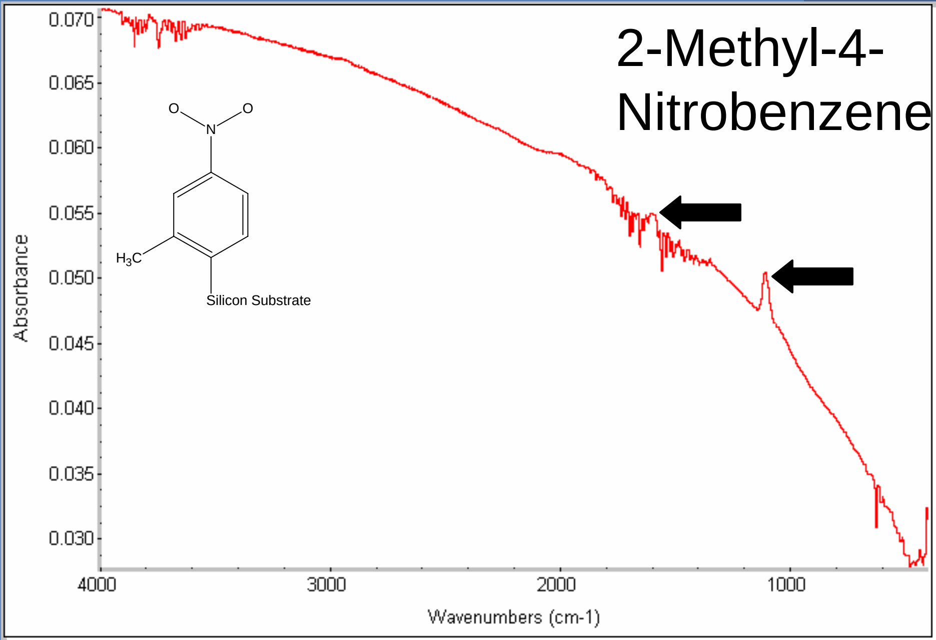
Methoxybenzene

- Expected: O–CH_3 ~2900-3000cm-1

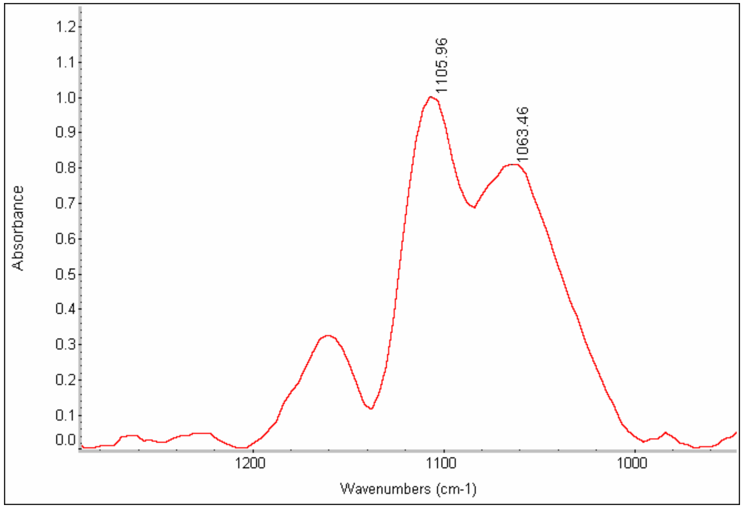
  Aromatic C=C ~1475-1600cm^{-1}
- Peak present at 1105.08 cm^{-1}
- Indicates oxidation of substrate
- Peaks present at 2936.45, 2927.08, 2916.24cm^{-1}
- Indicates successful monolayer formation

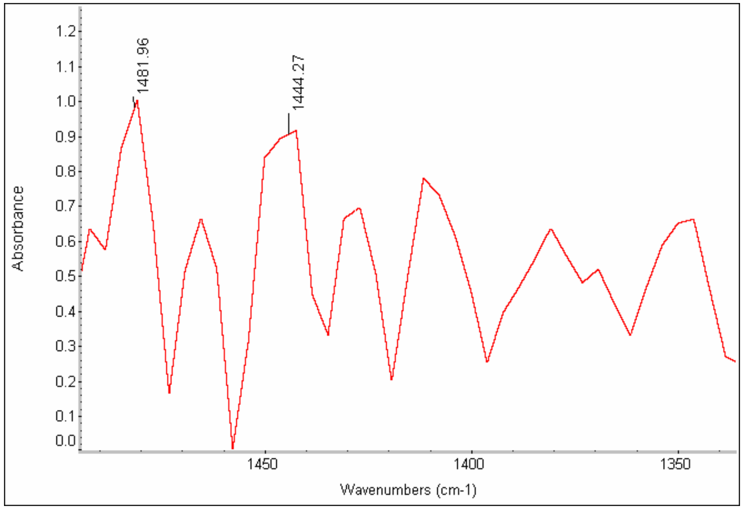
INAC NCN

Electrochemical Deposition: FTIR Analysis



Expanded Spectrum



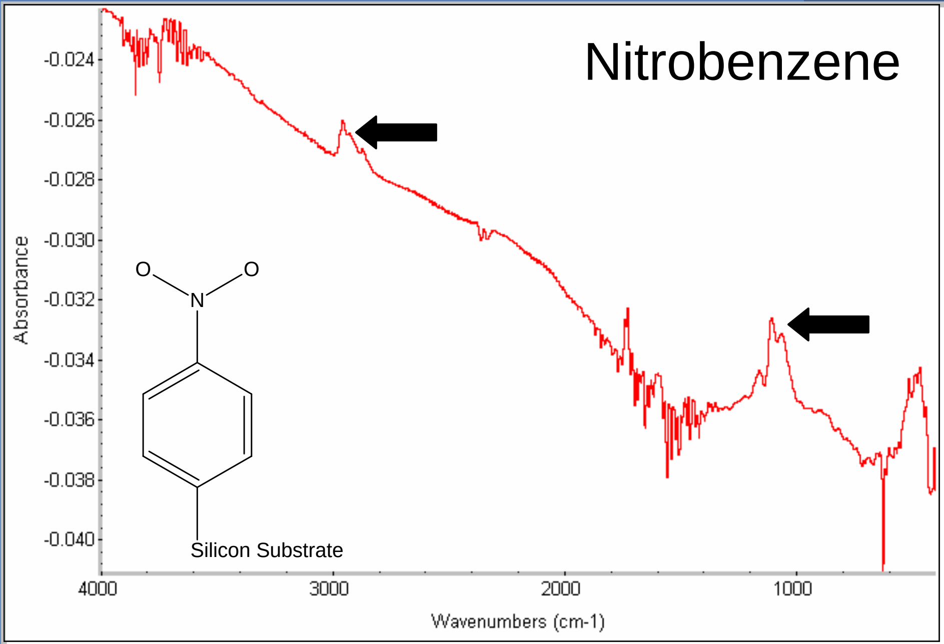


2-Methyl-4-Nitrobenzene

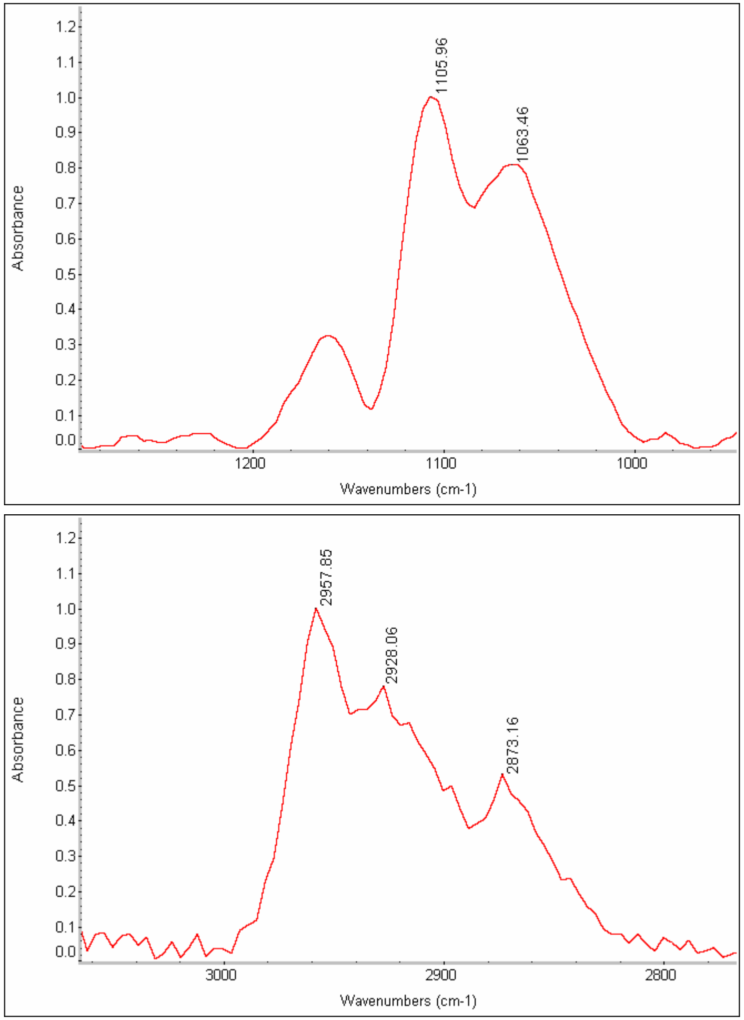
- Expected: N-O_2 peak ~1460cm^{-1}

  Amine N-H_2 peak ~1350cm^{-1}
- Peak present at 1105.98cm^{-1}
- Indicates oxidation of substrate
- No other peaks present
- No conclusive monolayer formation

Electrochemical Deposition: FTIR Analysis



Expanded Spectrum



Nitrobenzene

- Expected: N-O_2 peak ~1460cm^{-1}

  Amine N-H_2 peak ~1350cm^{-1}
- Peak present at 1105.96cm^{-1} (Oxidation)
- Peaks present at 2957.85, 2908.06cm^{-1}
- Indicates semi-successful monolayer formation
- Broad peaks indicate unordered or multiple layers

Summary of Results

- Solution immersion and self-assembly method were both effective in monolayer formation

- Self-assembly method with NH_4OH is more effective for monolayer formation upon GaAs (100) as shown by peak intensity

- Contacting molecule with Au resulted in a highly-ordered, low-penetrated compound when using self-assembly method

- FTIR of nitrobenzene and methoxybenzene indicate semi-successful monolayer formation on Si (111), although multiple layers may have been present on nitrobenzene

- FTIR of bromobenzene and 2-methyl-4-nitrobenzene indicate no indication of successful monolayer formation on Si (111)

- XPS results indicate successful monolayer formation of all the functional groups tested

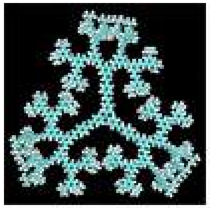
- XPS indicate show ~2-4% oxidation upon substrates when using the electrochemical reduction method, often in islands

Future Outlook of SAMs

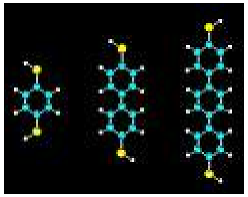
- Extension of two-dimensional capabilities into three dimensions
  - Carbon nanotubes
  - Nanoparticles
  - Dendrimers
  - Molecular wires

www.ewels.info

nanobot.blogspot.com



www.cdtltd.co.uk



www.physics.purdue.edu

- Molecular level control of integrated molecular systems will result in useful nanodevices
- Concern
  - Long-term stability and robustness of alkanethiol chemistry
    - Research possible systems with more robust bonds or use new alkyl chains
  - Functional device yield

A special thanks to…

- NASA
- INAC
- SURI 2006
- Purdue University
- Professor David Janes
- Patrick Carpenter and Adina Scott

Any Questions?