

Introduction to Self-Assembled Monolayers and Biosensors

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Advisor: Professor David Janes

- Introduction to Self-Assembled Monolayers (SAMs)
- Introduction to SAM Surface Analysis Techniques
- Introduction to Biosensors
- Self-Assembled Monolayer Biosensors
- Experimental Design
- Solving Future Problems
- Questions

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

Examples

GaAs (100) Substrate

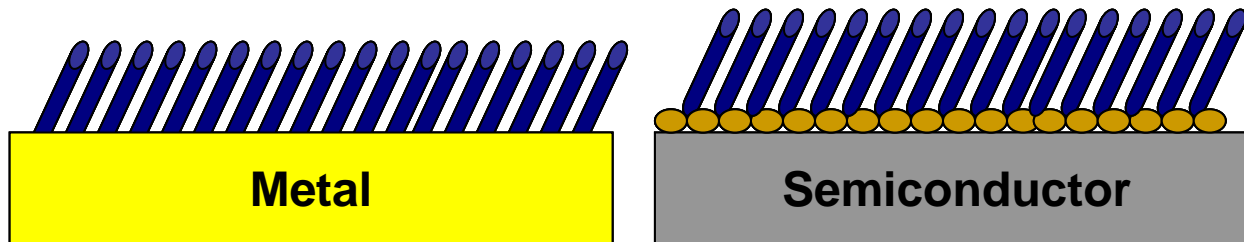
- Alkanethiol molecules (-SH)
- Form S-As covalent bond

Au Substrate

- Alkanethiol molecules (-SH)
- Form S-Au covalent bond

Si (111) Substrate

- Benzene molecules (-C₆H₁₂)
- Form Si-C covalent bond

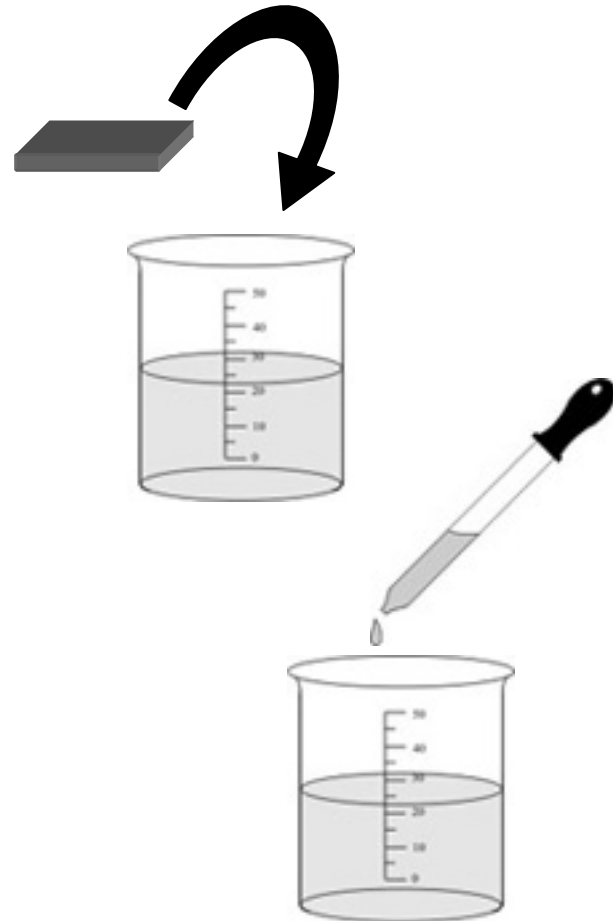


Graphics Source: Patrick Carpenter

Preparation Techniques

• Molten Deposition

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



• Solution Immersion

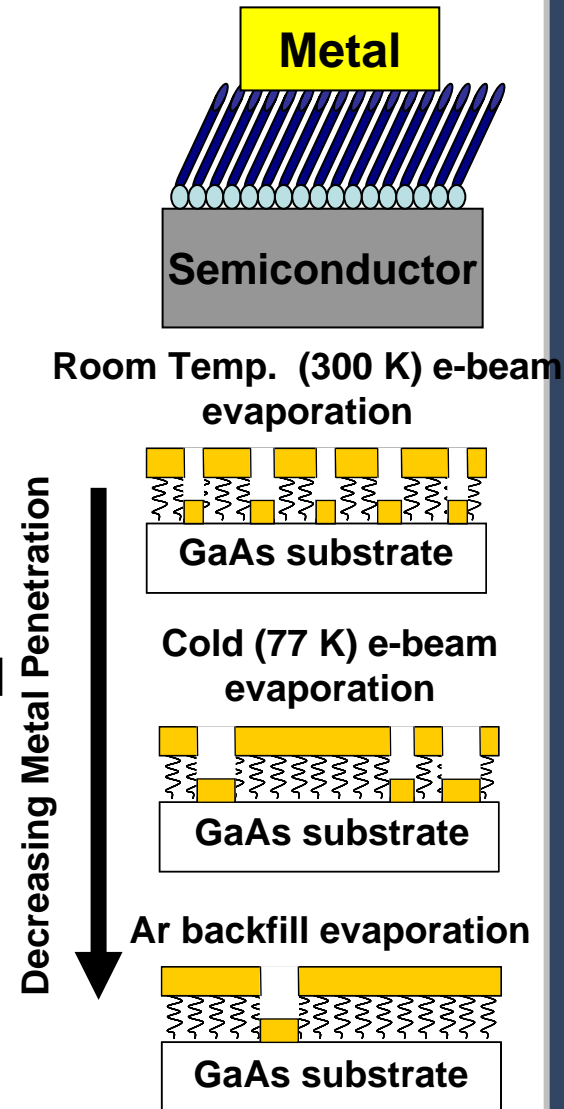
- Etch substrate with HCl
- Rinse with DI H₂O
- Deposit substrate into solution
- Dry on hotplate (~8 hours)

Purpose: Creation of nanoscale transistors

Problems: Metal penetration

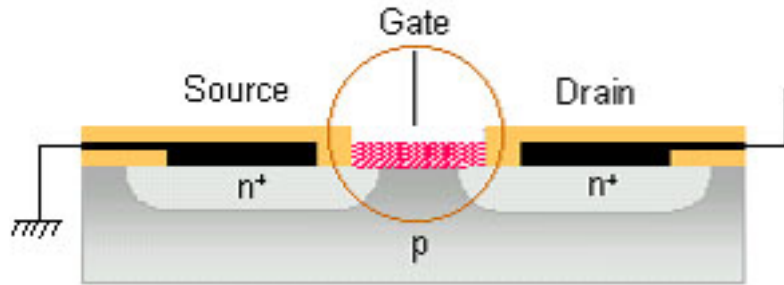
Contacting Techniques

- 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

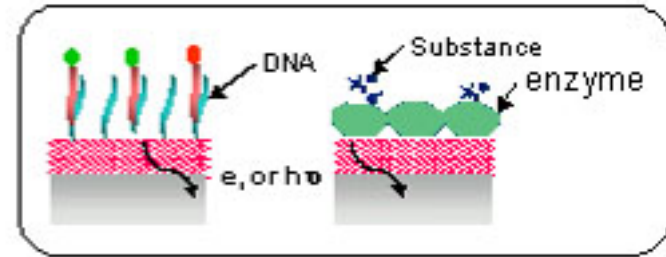


Graphics Source: Patrick Carpenter

- Biological Sensors

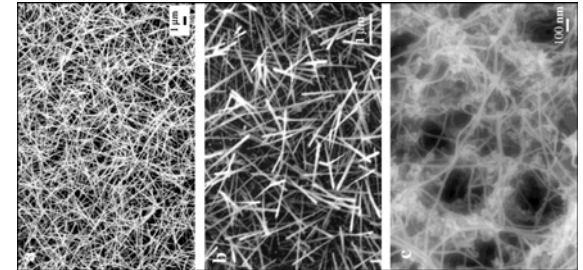


<http://www.coe.waseda.ac.jp/osaka/B-e.html>



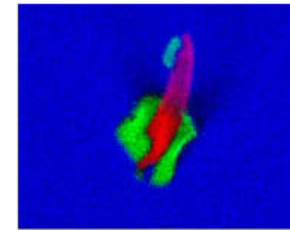
- Biosensing system based on molecular recognition
- Electrochemistry
 - Sensors use monolayers to impart selectivity onto an electrode
 - Monitors pH, inorganic species, and organic molecules
- Molecular Electronics
 - Nanoscale insulators and dielectrics
 - Molecular switches
 - Rectifiers
 - Field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

- 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

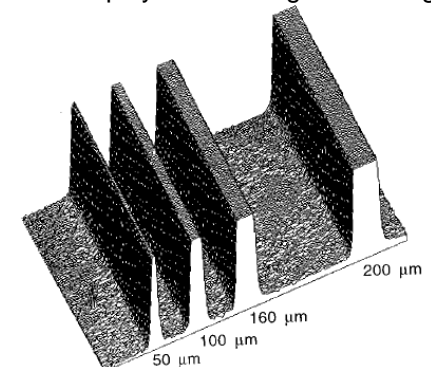


<http://www3.interscience.wiley.com/cgi-bin/fulltext/76509302/PDFSTART>

Color Composite Auger Map



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



<http://scitation.aip.org/getpdf/servlet/GetPDFServlet?filetype=pdf&id=RSINAK00006700000800293000001&idtype=cvips&prog=normal>

- X-Ray Photoemission Spectroscopy
 - Uses photons (200-2000 eV)
 - Removes core electrons
 - Formal oxidation state
 - Local and chemical environment

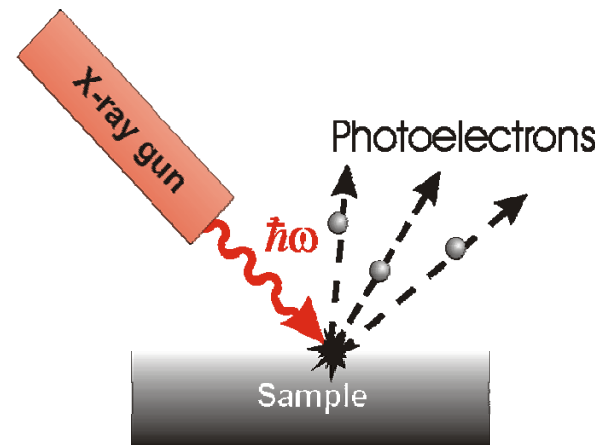


Image by
Dmitry Zemlyanov
(Purdue University)

- Fourier Transmission Infrared Spectroscopy
 - Uses infrared rays
 - Bonds vibrate with specific frequencies
 - Match with various chemical groups

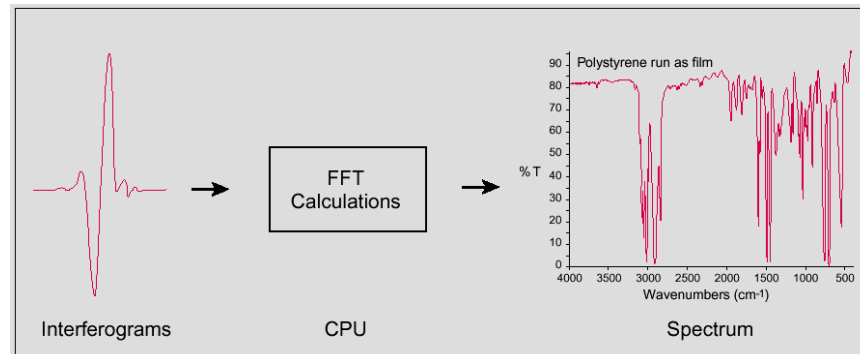


Image by http://spectroscopy.lbl.gov/FTIR-Martin/FTIR-Martin_files/frame.htm



Image by
http://www.medicine.oulu.fi/anat/files/images/human_body2.jpg

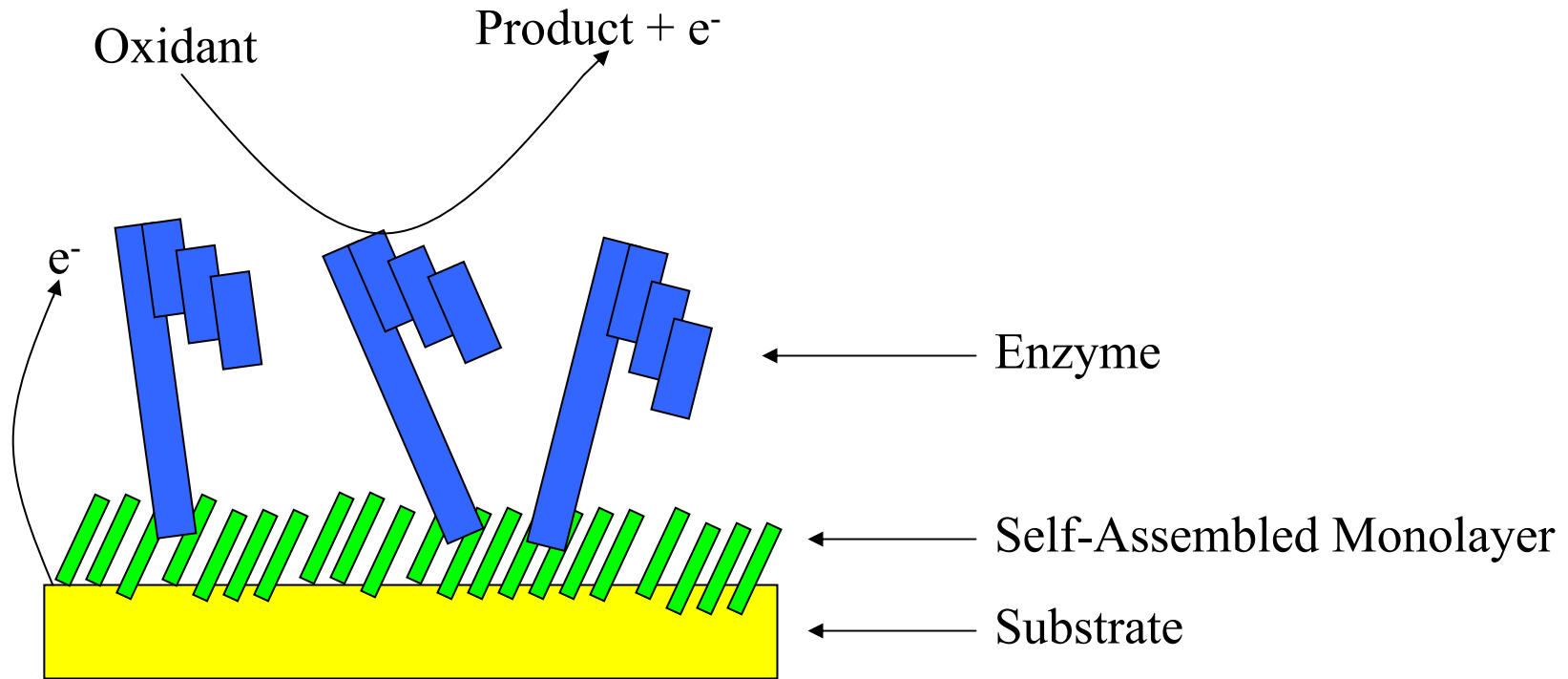
Purpose: To detect chemicals in the body

Procedure

- Determine molecule of interest
- Find corresponding enzyme
- Design device

Keys to Success

- Enzymes are highly specific
- Nearly all molecules are reduced or oxidized allowing for various electric measurements



Measured via Amperometry, Potentiometry, Volammetry

Various Types

- Carbon nanotubes
- Self-assembled monolayers
- Quantum dots

Advantages

- Easy to make
- Miniaturization is simple
- Diversity
 - Flexibility due to varying head groups of SAM
 - Flexibility due to varying length of SAM
- Environment
 - Relatively organized and thus predictable
 - Protection from many outside chemicals by SAM
 - SAM can mimic lipid-bilayer environment of cell
- Testing
 - Minimal amount of biomolecule required
 - Electrical readings easy to take

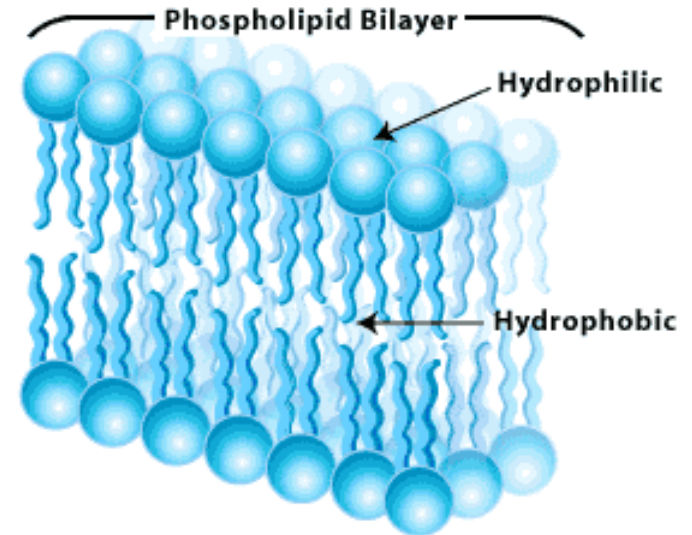
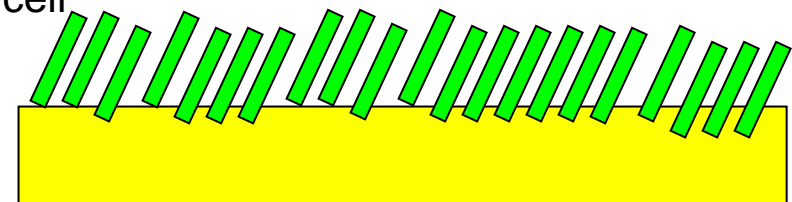
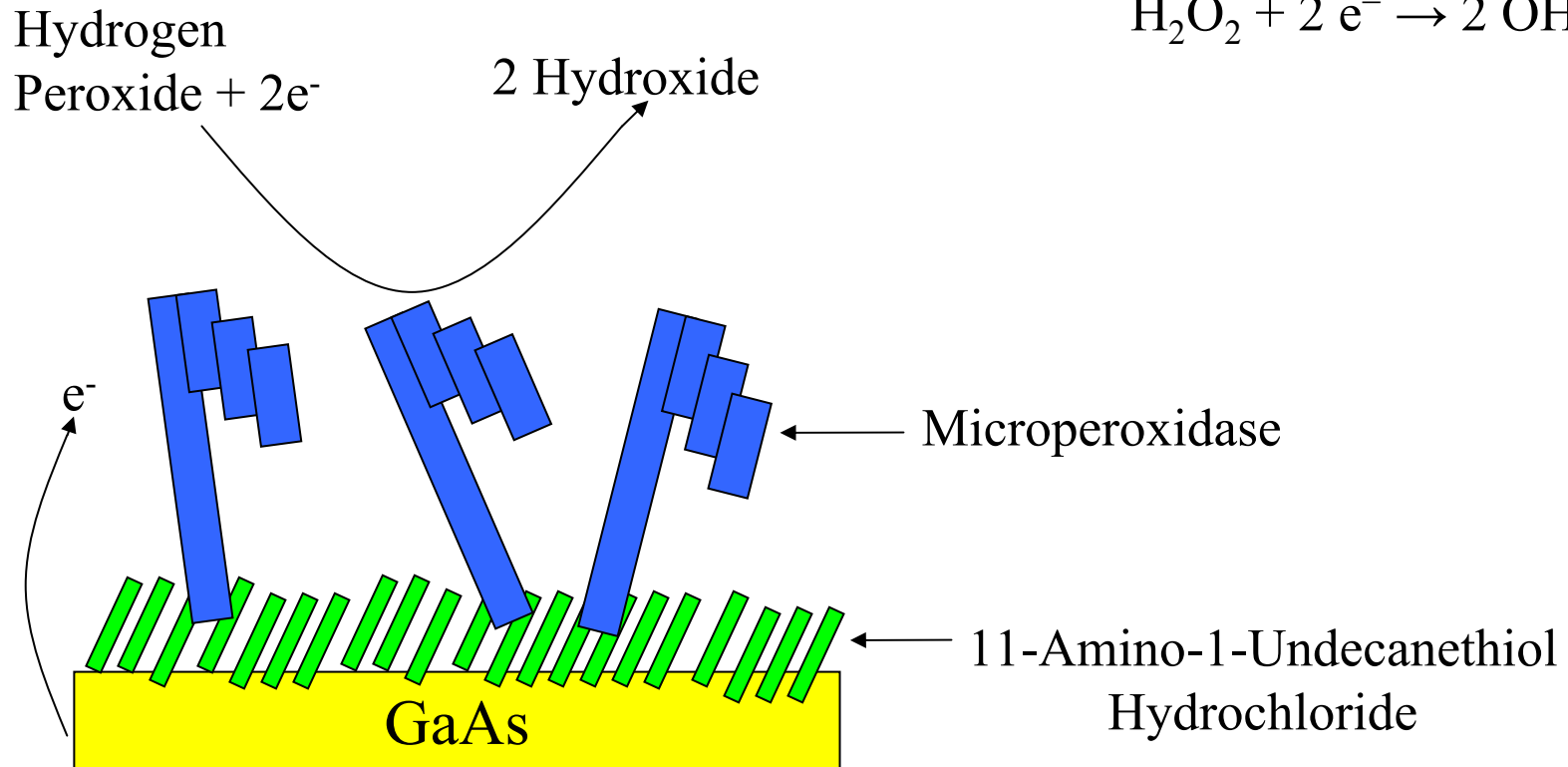
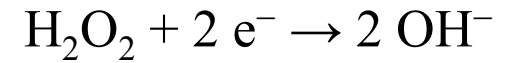


Image by:
<http://www.bioteach.ubc.ca/Bio-industry/Inex/graphics/lipidbilayer.gif>



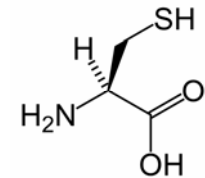
Net Reaction



Unique features of GaAs

- Advantages

- Can work in dry environment / electron gas studies
- High electron mobility
- Highly specific sulfur chemistry
- Chemistry applicable to biological systems with cysteine



- Disadvantages

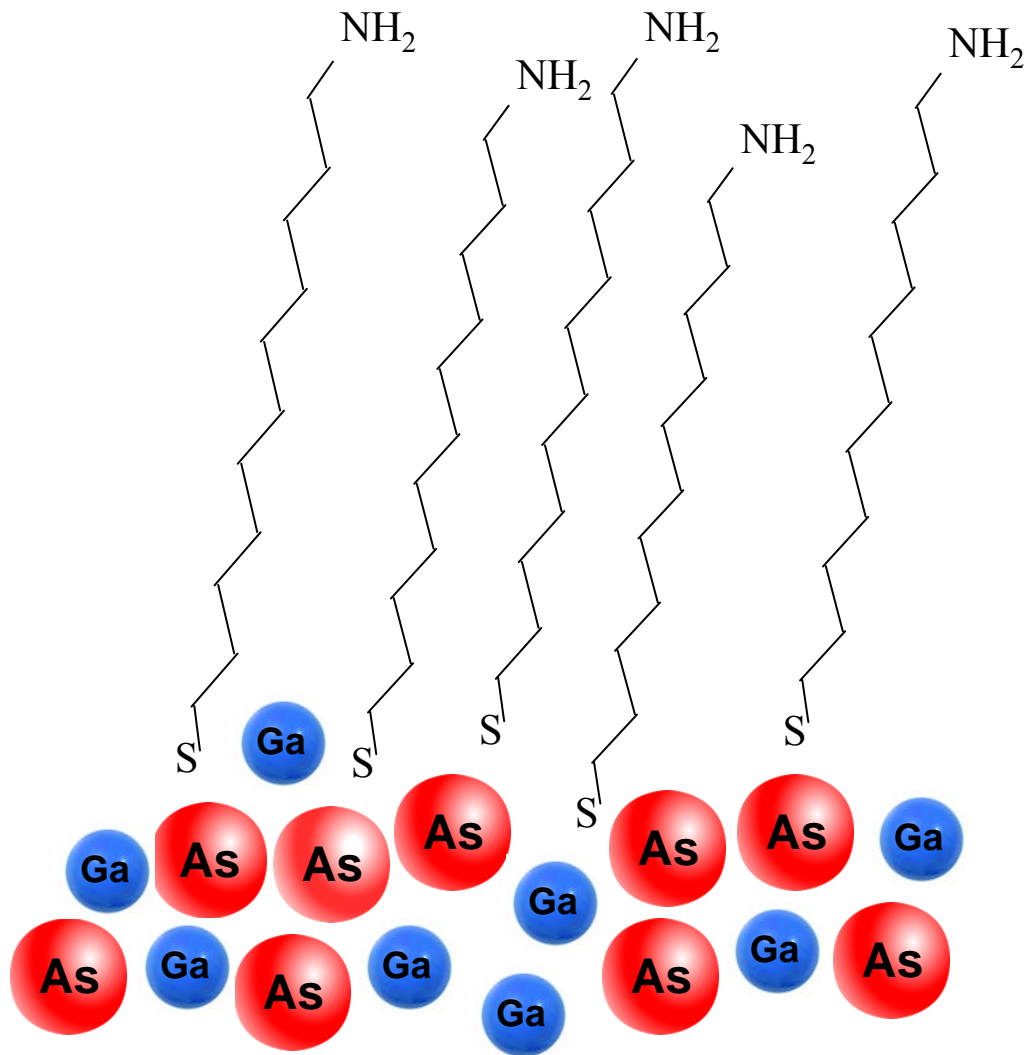
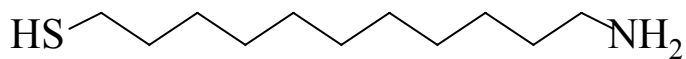
- Oxidizes extremely easily
- Few studies on passivation of GaAs in physiological solutions
- Few studies on GaAs biosensors

GaAs

Bond Formation

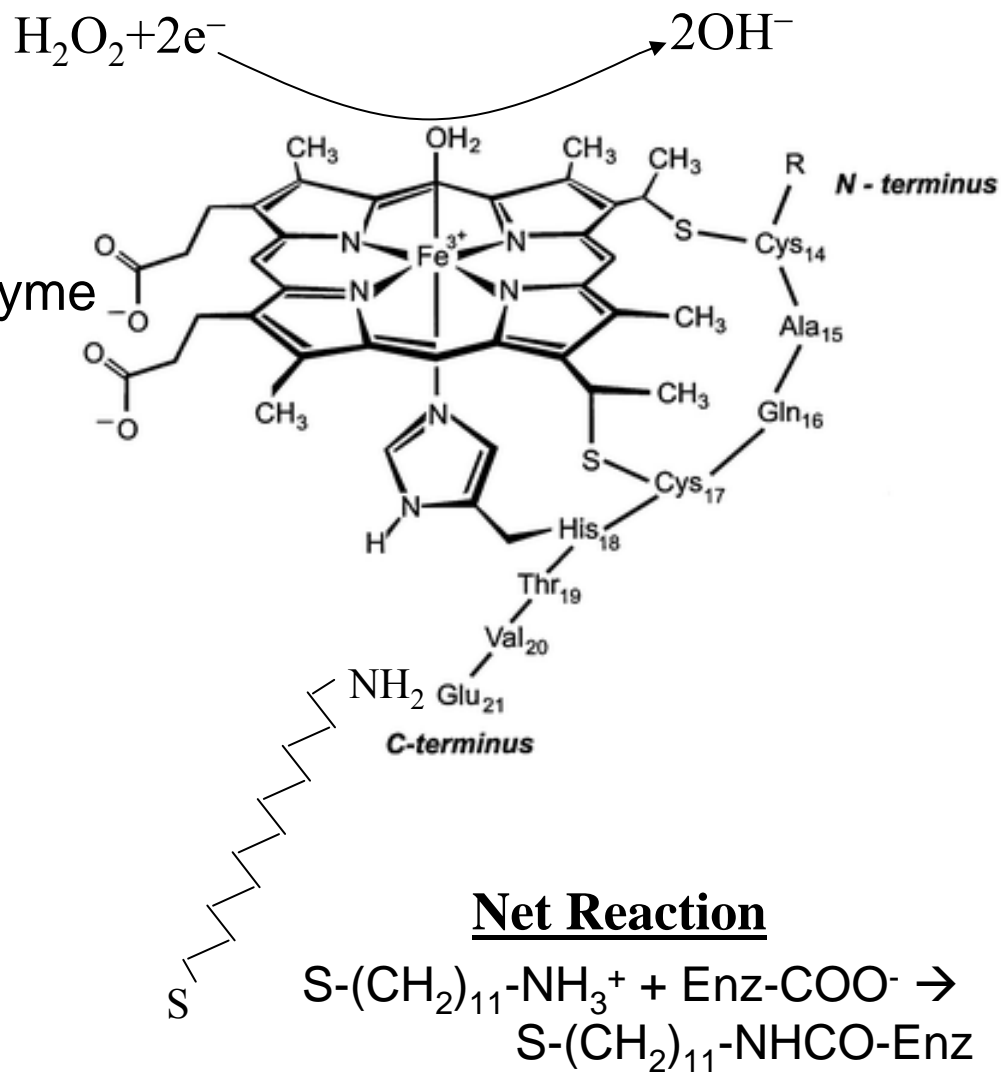
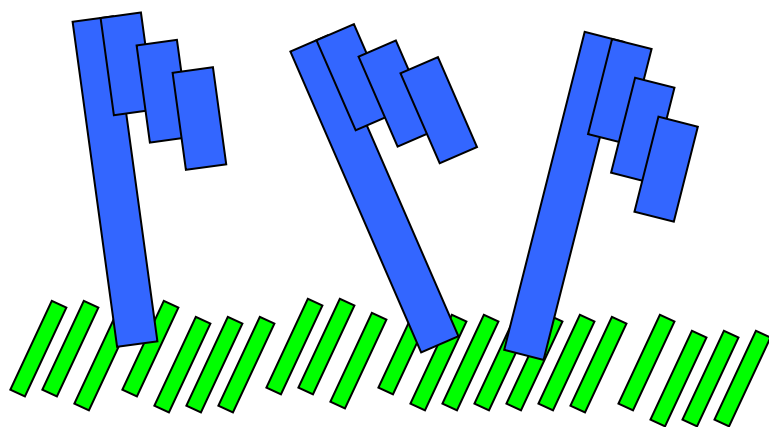
- Arsenic of GaAs
- Sulfur of Alkanethiol SAM
- Forms a As-S Bond

11-Amino-1-Undecanethiol
Hydrochloride



Bond Formation

- Amino group of SAM
- Terminal carboxyl group of enzyme
- Forms an amide bond



- FTIR

- Analysis of bare GaAs
- Analysis of GaAs with amine-terminated monolayer
- Analysis of GaAs with monolayer and protein

- Ellipsometry

- No bare GaAs due to quick photo-oxidation
- Analysis of GaAs with amine-terminated monolayer
- Analysis of GaAs with monolayer and protein

- Cyclic Voltamagram

Problems

- Physiological solutions
- Sensor pollution

Solutions

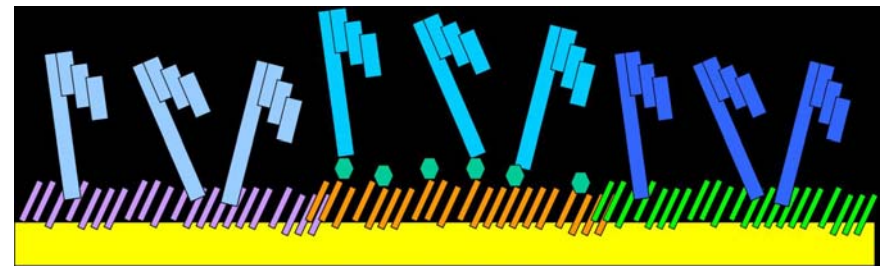
- Filter solution prior to detection
- Data analysis

Future Goal

- Multi-sensors
- Instantaneous feedback



Image by
<http://www.securacell.com/images/multiple%20vials.jpg>



Multi-sensor with various enzyme detectors

A special thanks to...

- NASA
- INAC
- SURI 2007
- Purdue University
- Professor David Janes

