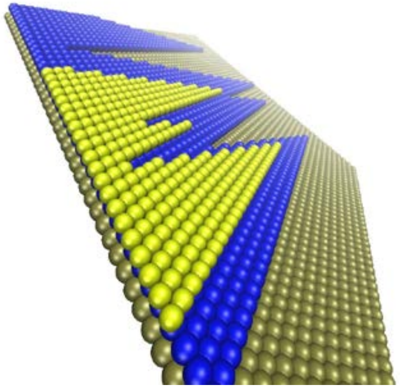
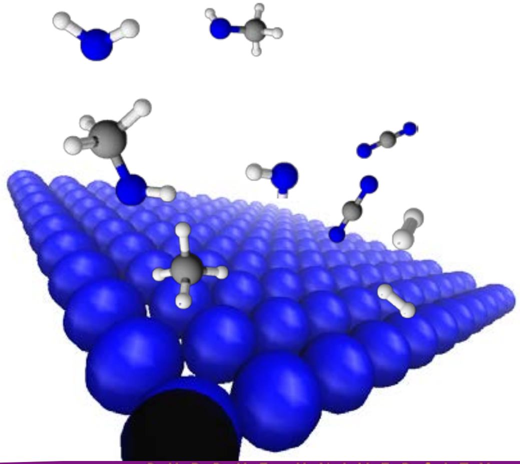
Nanotechnology for Aerospace Research: *surface science applications*

Dmitry Zemlyanov
dzemlian@purdue.edu

Surface Characterization Facility at Birck Nanotechnology Center, BRK 1077, Purdue University





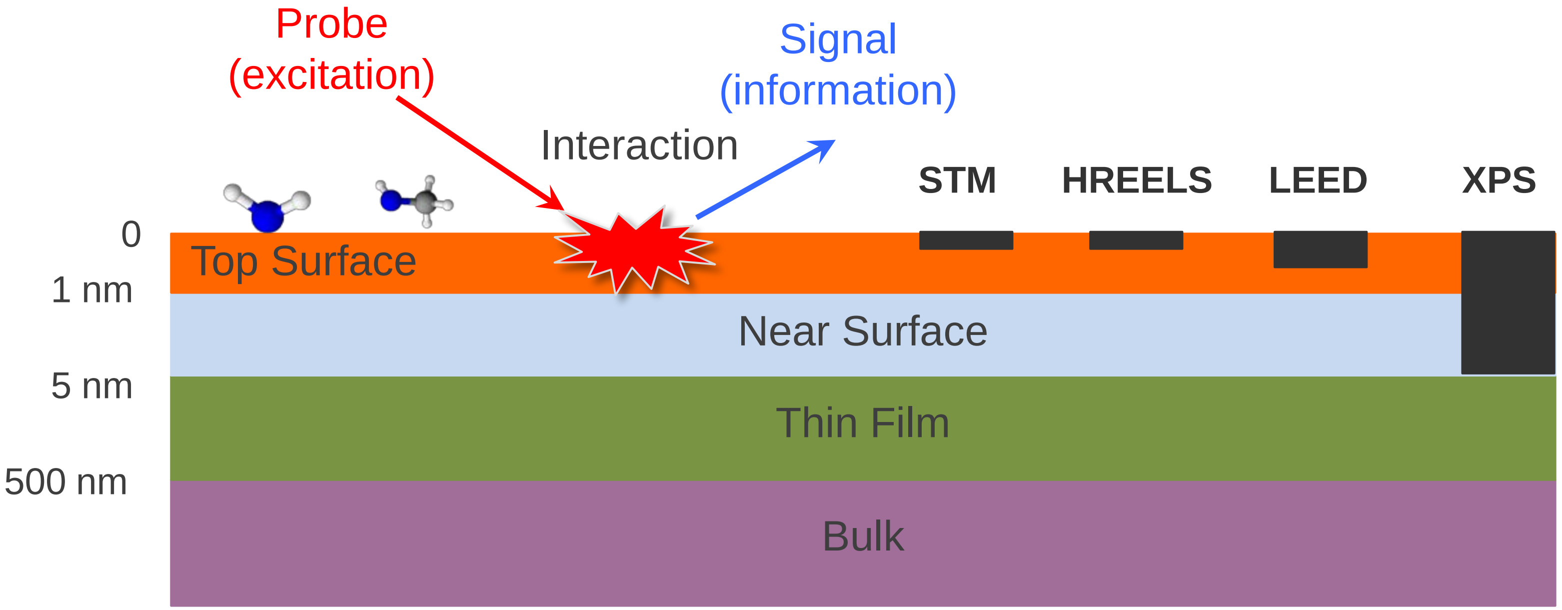
Why Surface Science?

Knowledge and control of surfaces becomes critical for many modern technologies. Rational design of interfaces requires an ability to determine the surface structure and chemical composition at the atomic scale.

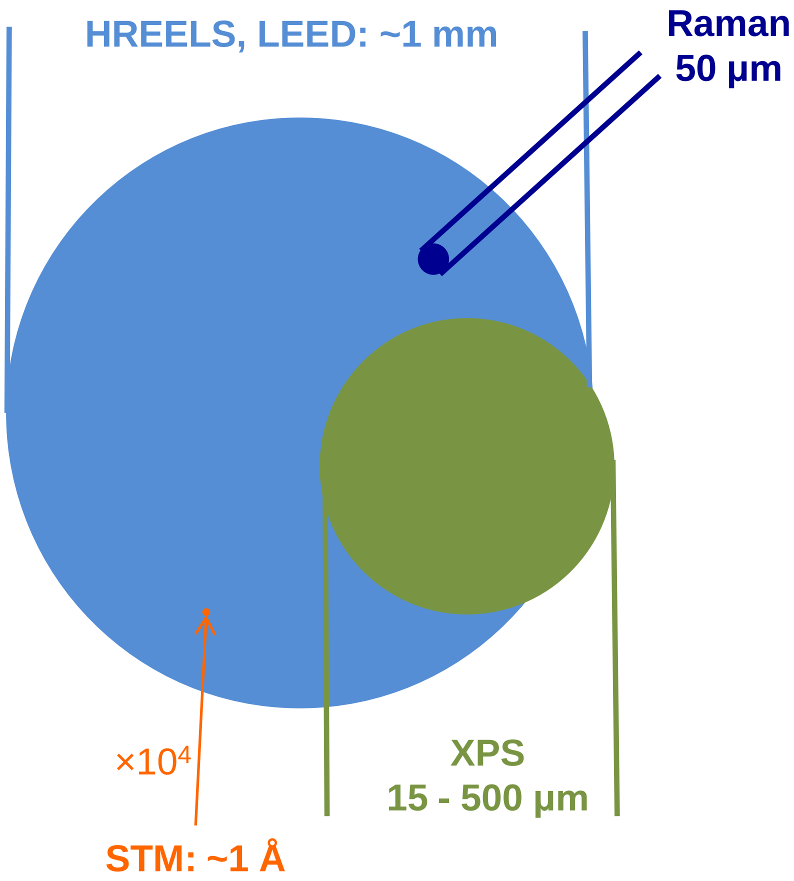
Techniques & Surface Sensitivity

- Scanning Tunneling Microscopy (STM)
- High-Resolution Electron Energy Loss Spectroscopy (HREELS)
- Low Energy Electron Diffraction (LEED)
- X-ray Photoemission Spectroscopy (XPS)

Information depth of the techniques



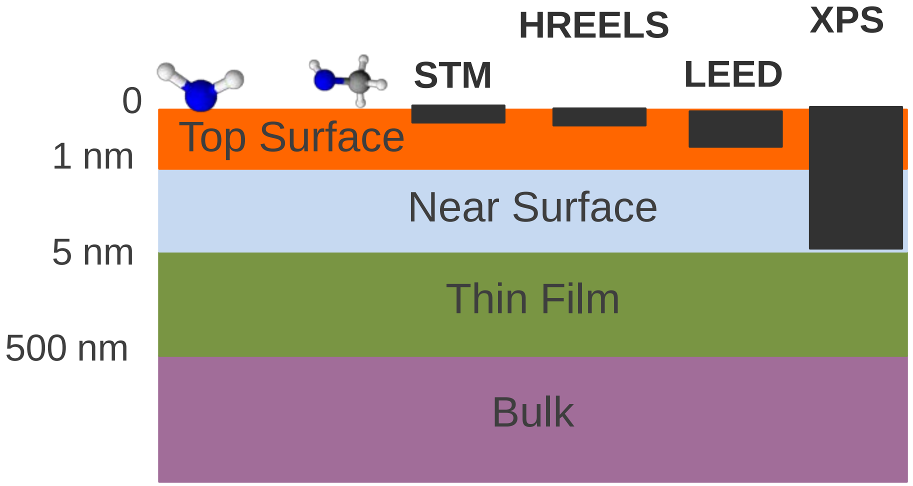
Spatial resolution of the techniques



Techniques & Surface Sensitivity

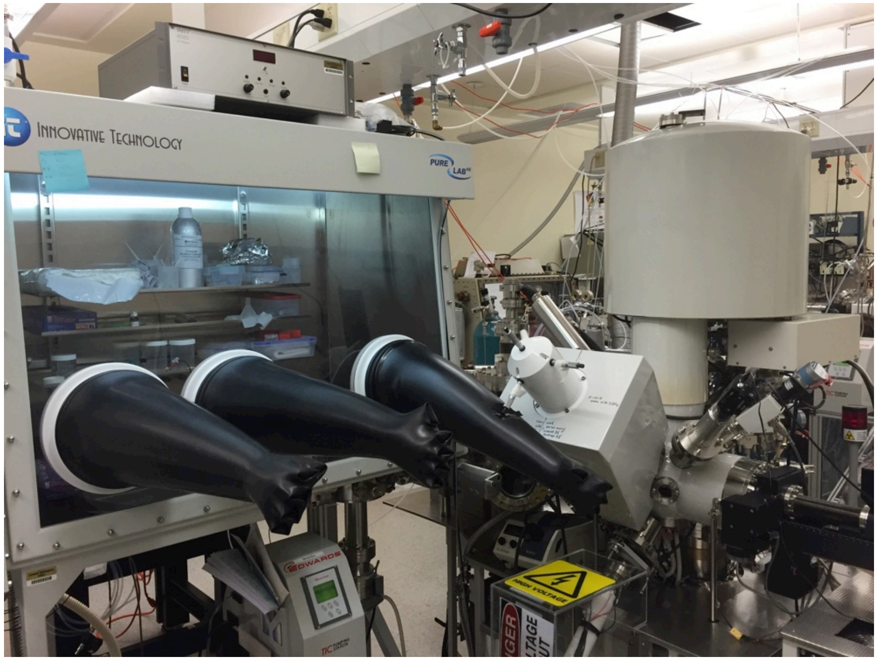
- Scanning Tunneling Microscopy (STM)
  - atomic structure
- High-Resolution Electron Energy Loss Spectroscopy (HREELS)
  - vibrational spectra, < 1% ML
- Low Energy Electron Diffraction (LEED)
  - surface structure, microscopic
- X-ray Photoemission Spectroscopy (XPS)
  - chemical composition and element chemical state

Information depth of the techniques



Surface Characterization Facility at Birck Nanotechnology Center, BRK 1077

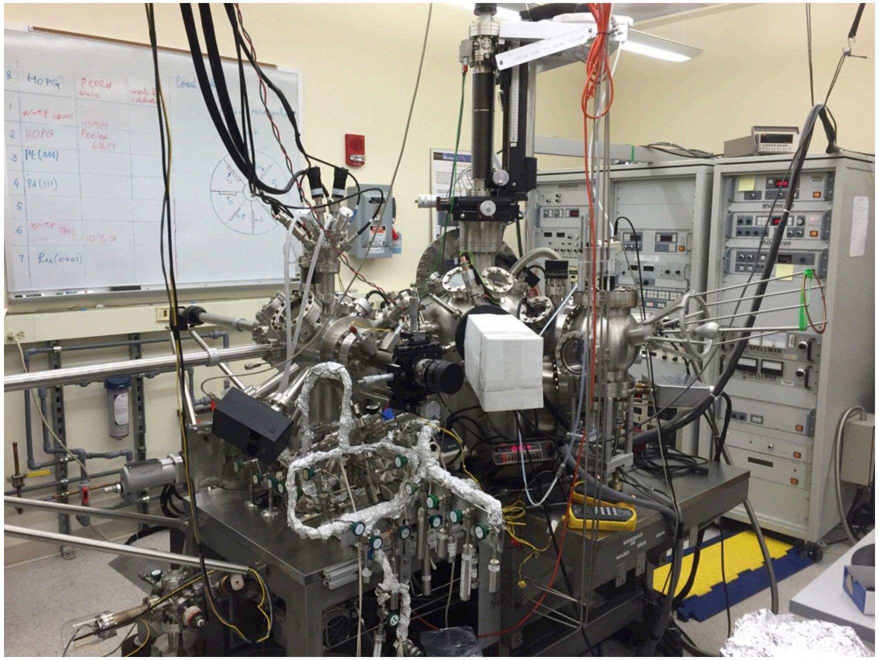
Kratos Axis Ultra DLD Imaging XPS



Dedicated XPS system:

- Monochromatic X-ray source;
- Charge neutralizer (any vacuum-compatible sample can be studied);
- Real time imaging XPS;
- Reaction cell (6 bar, 1000°C);
- Sputtering gun (coronene for non-destructive depth profiling);
- UPS (ultra-violet photoemission spectroscopy);
- Attached Ar-filled glove-box.

Omicron Surface Analysis Cluster



Multi-tool instrument:

- XPS, HREELS, LEED;
- State-of-art UHV STM/AFM;
- UHV treatment chamber;
- Gas manifolds for UHV ALD ;
- E-beam evaporator.

Outline

- Thin film measurement/characterization: graphene/Cu, BN, MoS_2 – *XPS & STM*

Inspired by 2D electronics, thermal management, catalytic applications

Collaborators: Prof. Gary Chen (Industrial Engineering); Prof. Timothy Fisher (Mechanical Engineering); Dr. Andrey Voevodin (AFRL)

- Oxidation of phoshorene (black phosphorus)

Inspired by 2D electronics applications

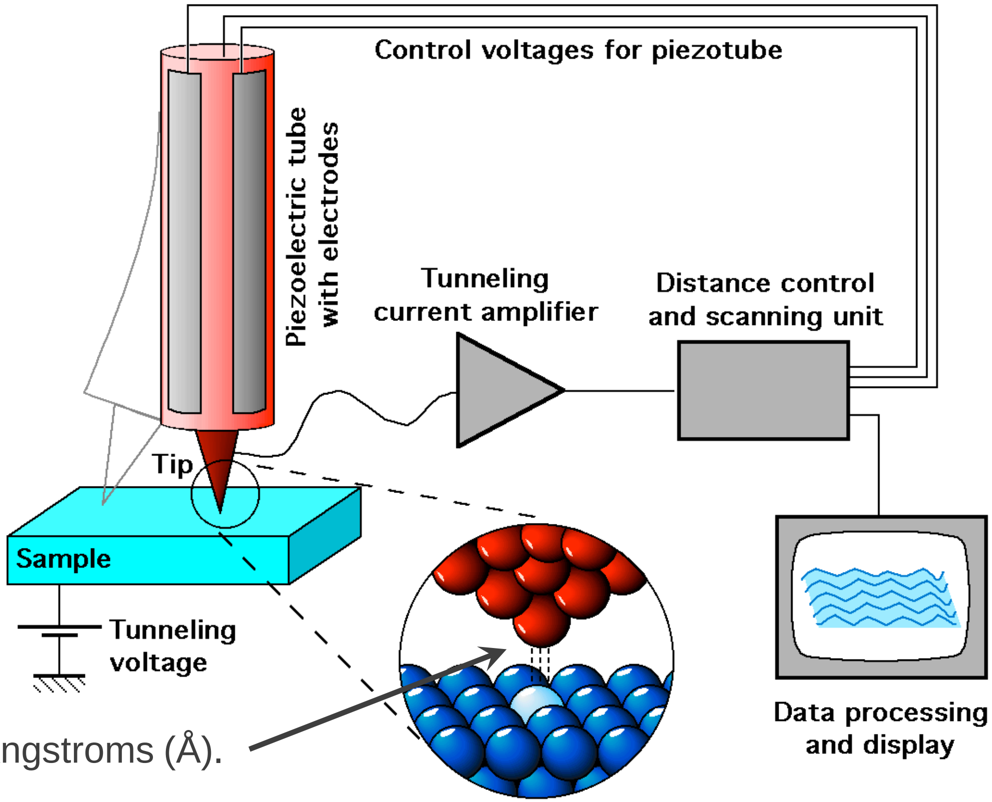
Collaborators: Prof. Peide Ye (Electrical and Computer Engineering)

- Depth profiling

Inspired by 2D electronics, thin films, catalysis

Collaborators: Prof. Fabio Ribeiro (Chemical Engineering); Prof. Christophe Copéret (ETH)

Basic Principles of STM



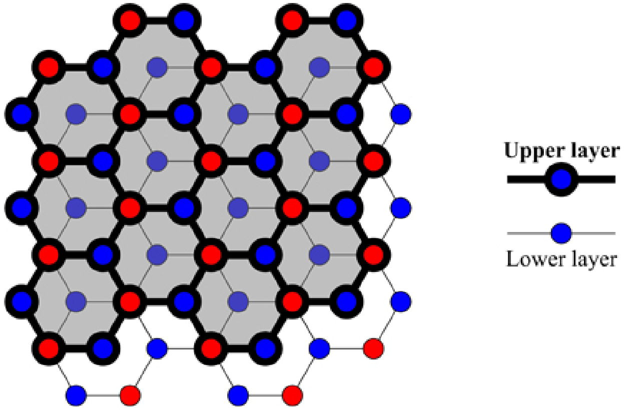
Distance, d, is a few Angstroms (Å).

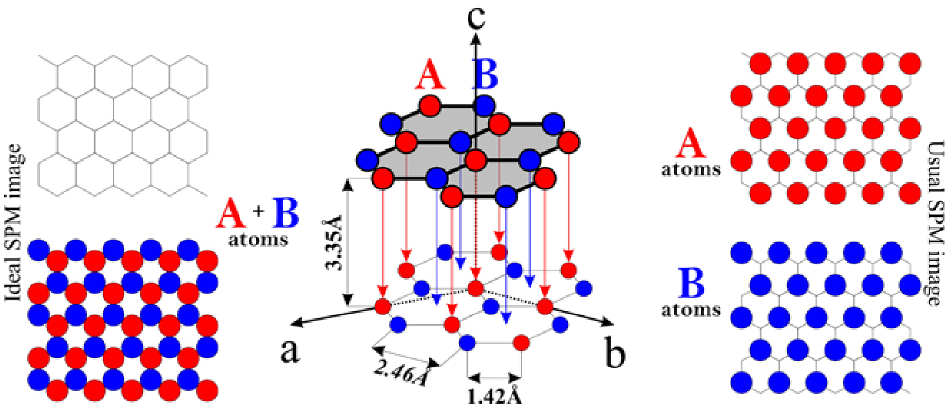
- When a bias voltage (mV - V) is applied, electrons tunnel between the tip and sample. A tunneling current is in the range of 10 pA to 10 nA.
- Tunneling current is proportional to $e^{-2\kappa d}$ and decreases by a factor of ~10 when d is increased by 1 Å.
- Using a feedback look, we try to keep the tunneling current constant (constant distance between the tip and the surface(???)).

The STM schematics is by Michael Schmid - Michael Schmid, TU Wien; adapted from the IAP/TU Wien STM Gallery, CC BY-SA 2.0 at, https://commons.wikimedia.org/w/index.php?curid=180388

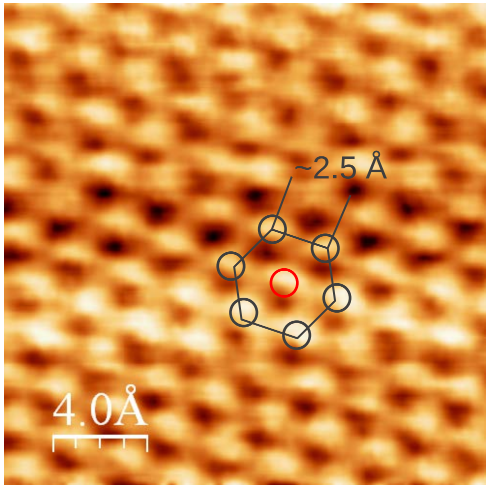
Graphene by *STM*

Structure of highly oriented pyrolytic graphite (HOPG)

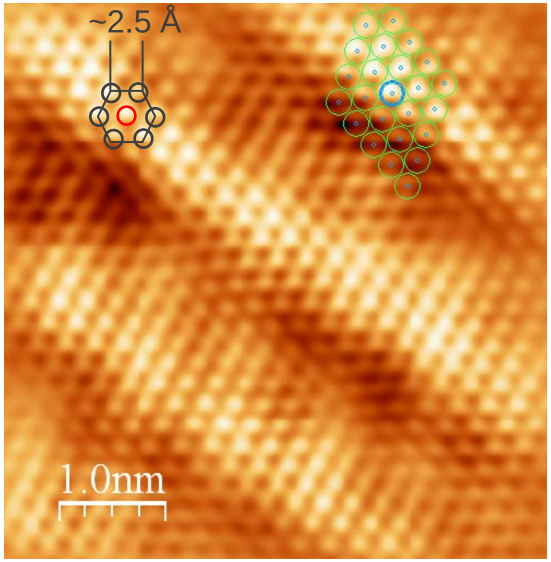




STM image of HOPG



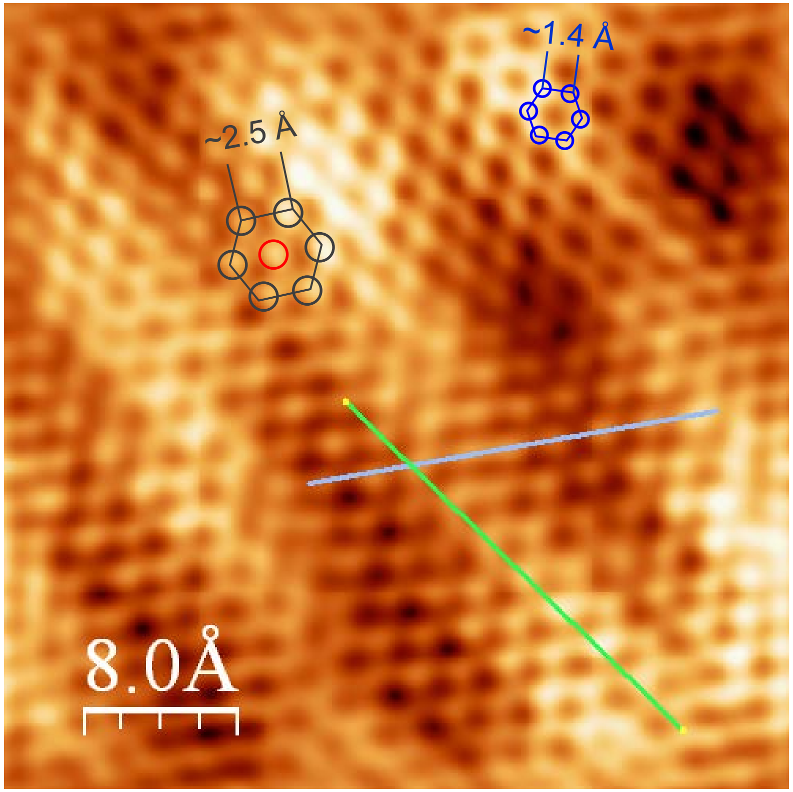
STM image of a few layers of graphene on a Cu foil



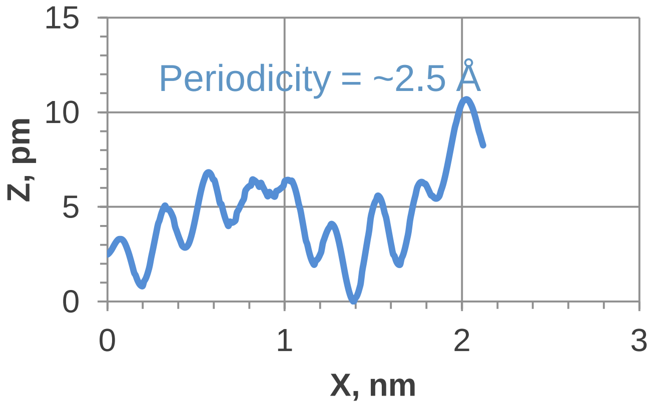
The sample provided by Prof. Gary Chen

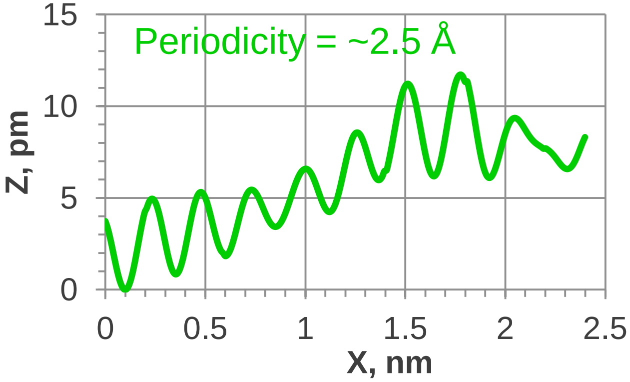
Graphene – *STM*

STM image of a few layers of graphene on a Cu foil
with areas of single layer graphene



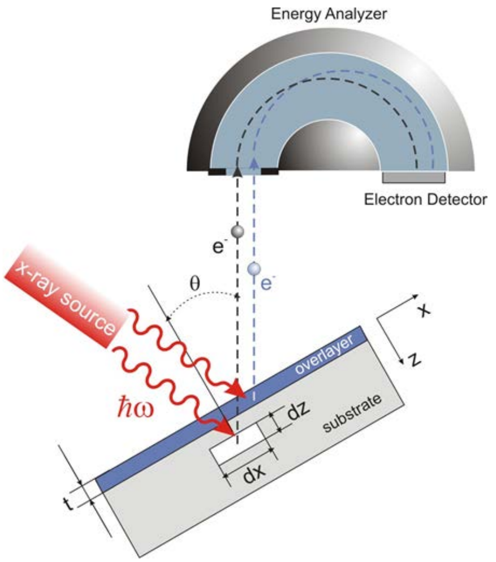
The sample provided by Prof. Gary Chen



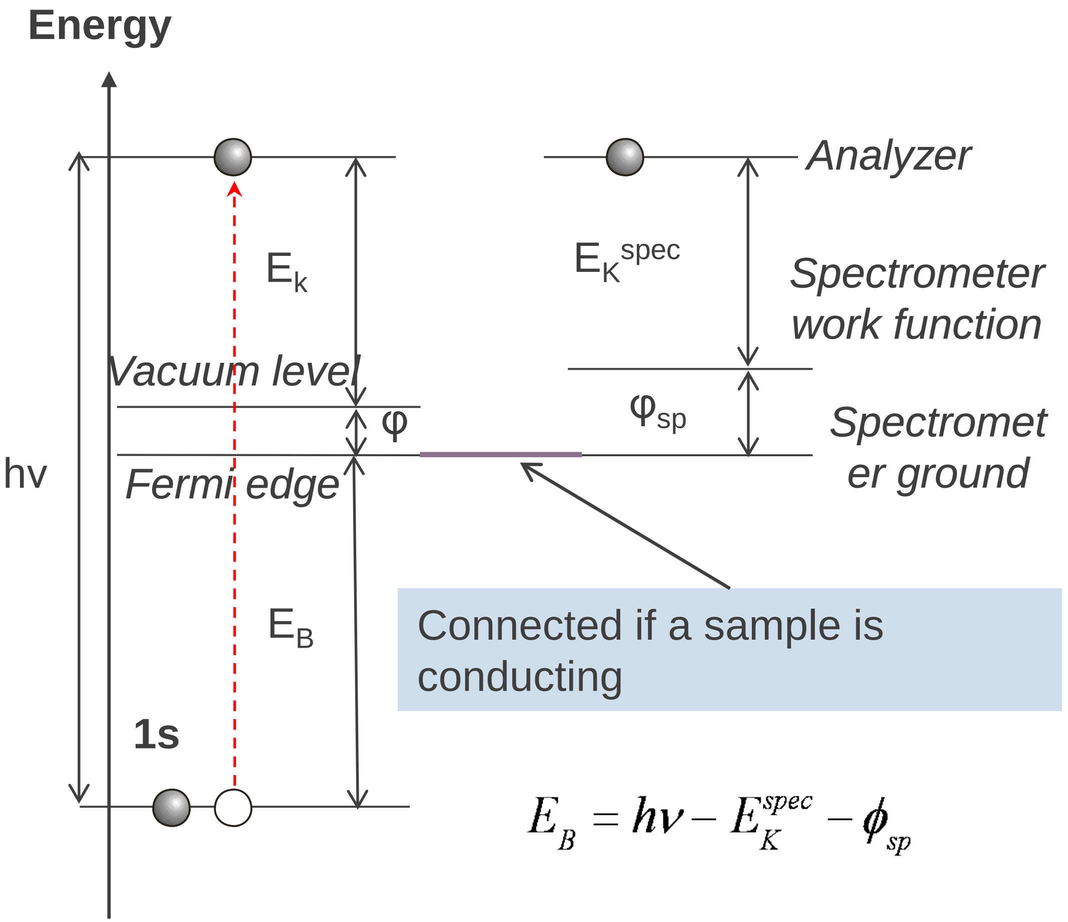


Graphene – *XPS*

Basic Principles of XPS



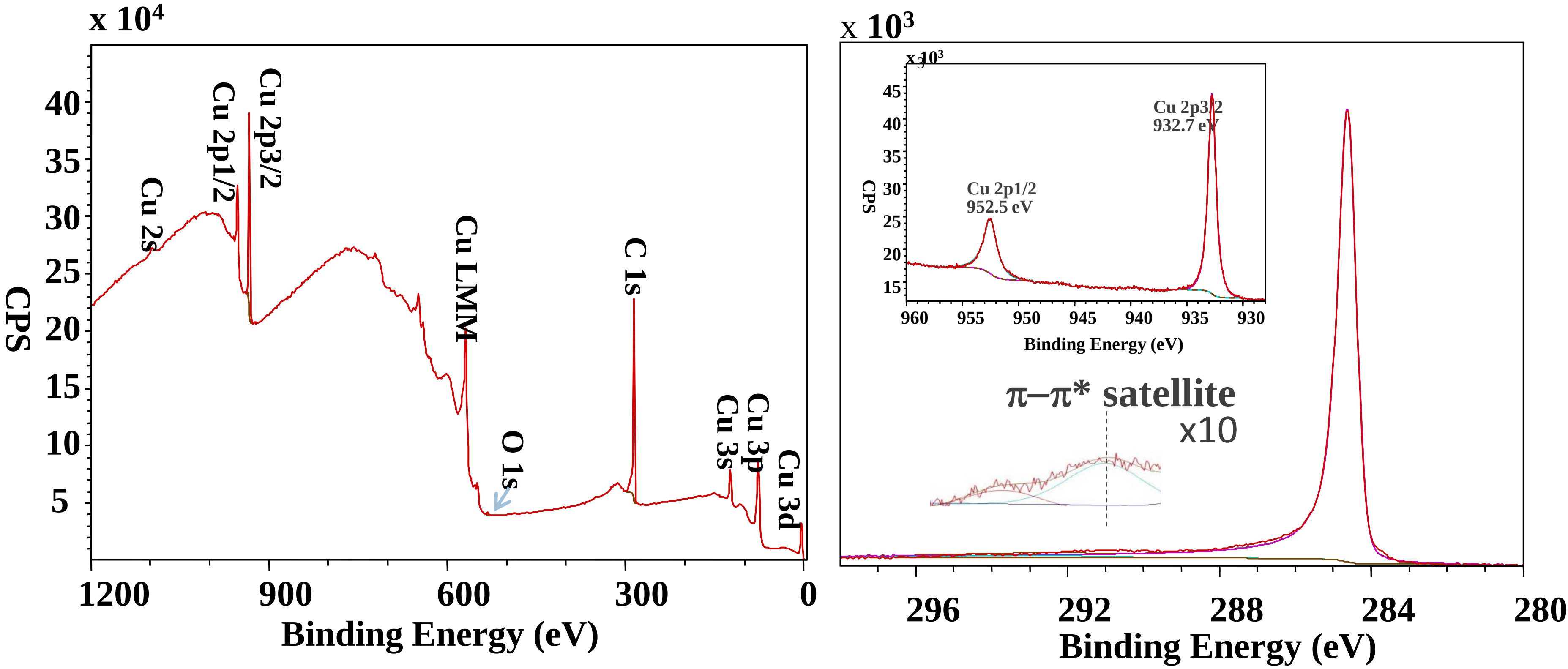
The process of using photons (light) to remove electrons from a bulk material is called ***photoemission***.



Connected if a sample is conducting

$$E_B = h\nu - E_K^{spec} - \phi_{sp}$$

Graphene – *XPS*



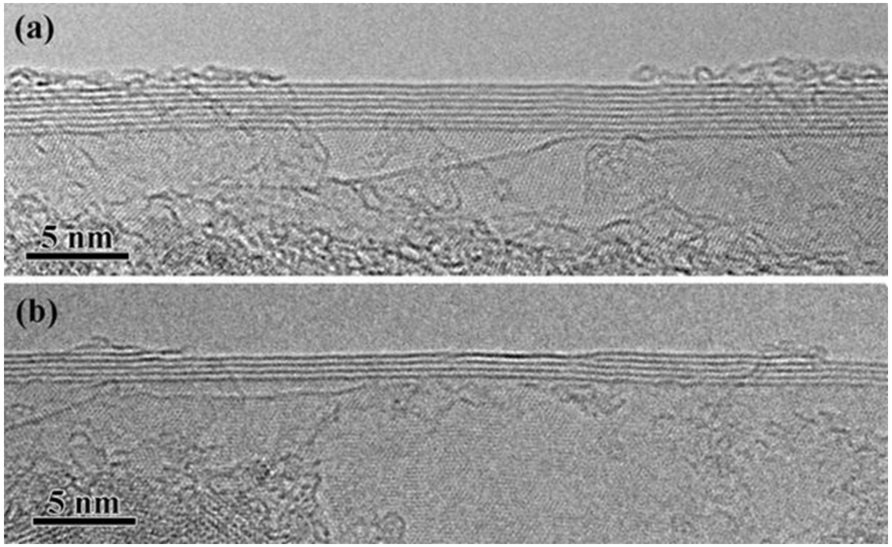
Survey and high resolution XPS spectra of few layer graphene.
Growth conditions: H_2:CH_4 =10:1; 3 min – H_2 + 1min – H_2/CH_4 mixture.

$$\frac{N_{C1s}(\theta)}{N_{Cu2p}(\theta)} = \frac{\rho_{graphene} \times \frac{d\sigma_{C1s}}{d\Omega} \times \Lambda_e^{graphene}(E_{C1s})}{\rho_{Cu} \times \frac{d\sigma_{Cu2p}}{d\Omega} \times \Lambda_e^{Cu}(E_s)} \times \frac{1-\exp\left(\frac{-t}{\Lambda_e^{graphene}(E_{C1s})\cos\theta}\right)}{\exp\left(\frac{-t}{\Lambda_e^{graphene}(E_{Cu2p})\cos\theta}\right)}$$

8 layers of graphene

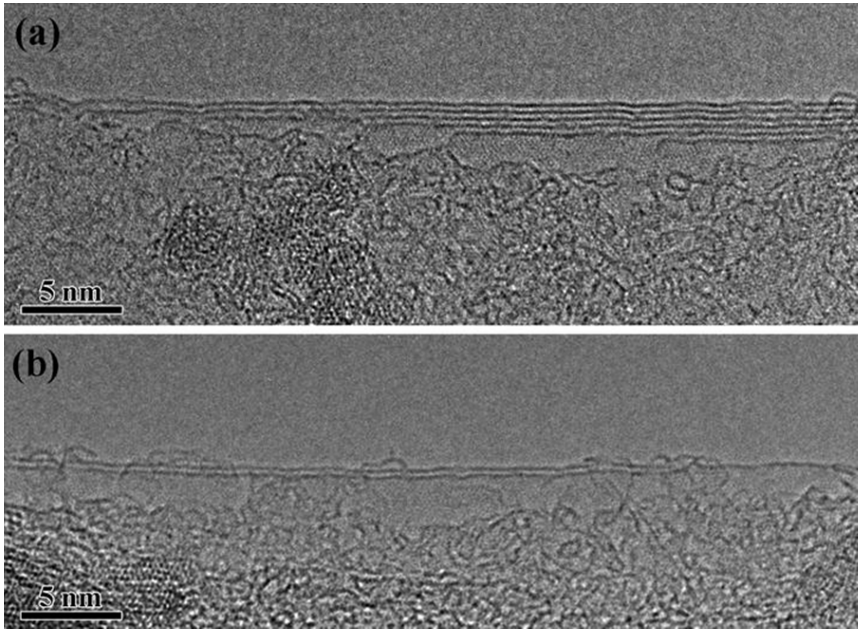
In collaboration with Prof. Timothy Fisher and Prof. Andrey Voevodin

Graphene – *XPS*



TEM image of few layer graphene.

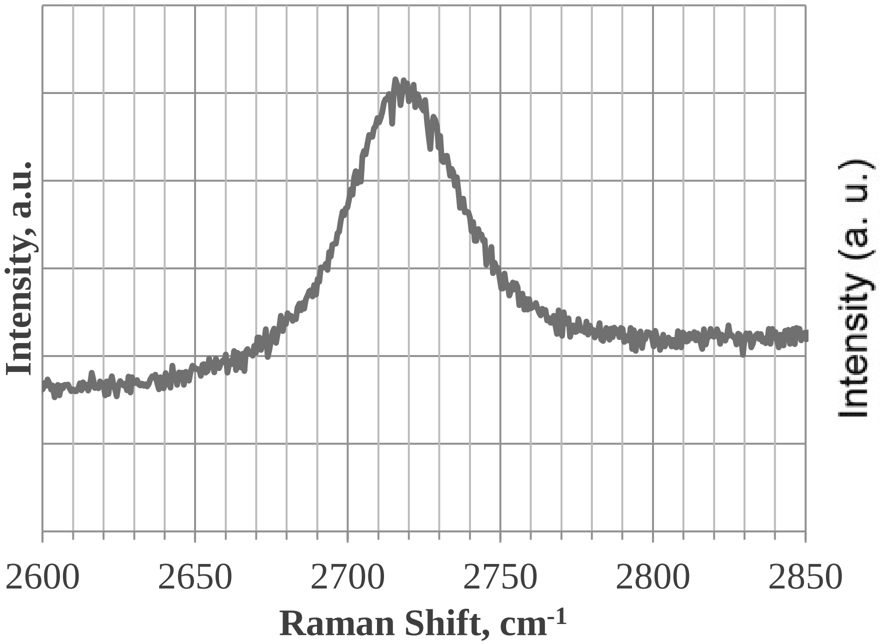
Growth conditions: H_2:CH_4 =10:1; 3 min – H_2 + 1min – H_2/CH_4 mixture.

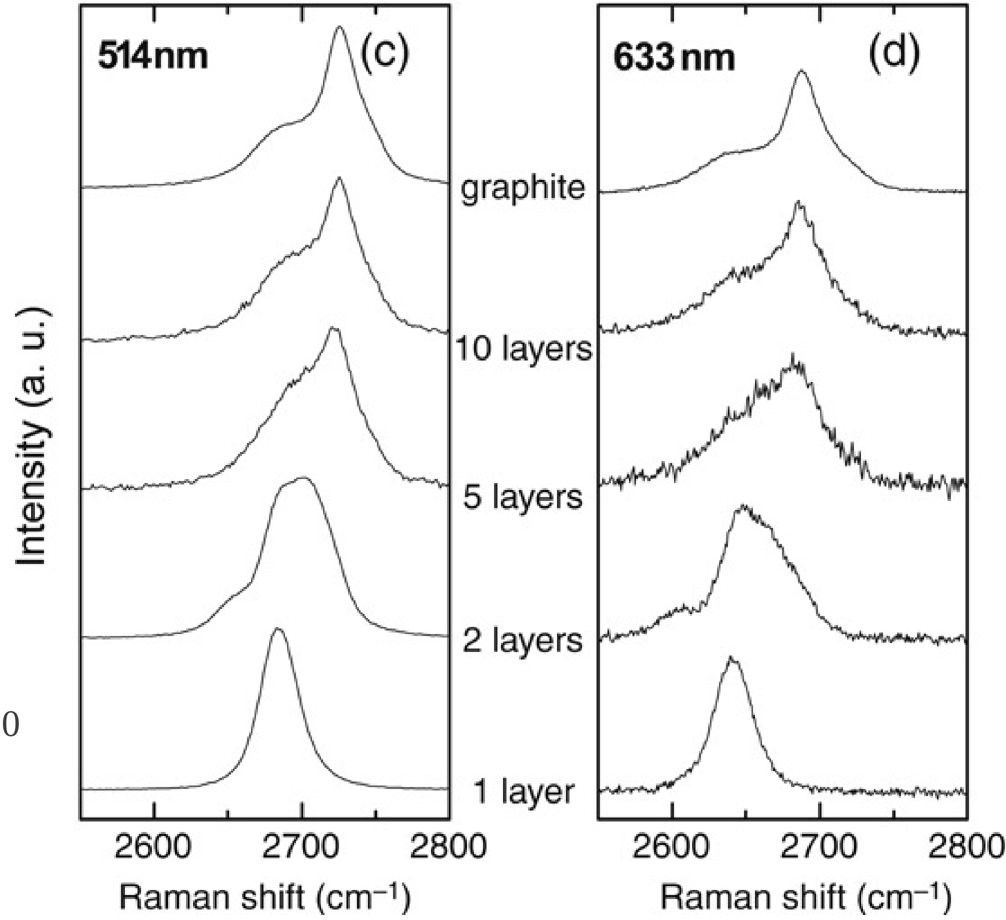


TEM shows anywhere from 1 to 6 graphene layers. XPS measured 2.9 layer of graphene.

XPS: 8 layers of graphene!!!
TEM: ~7 layers of graphene!!!

Graphene – *XPS*



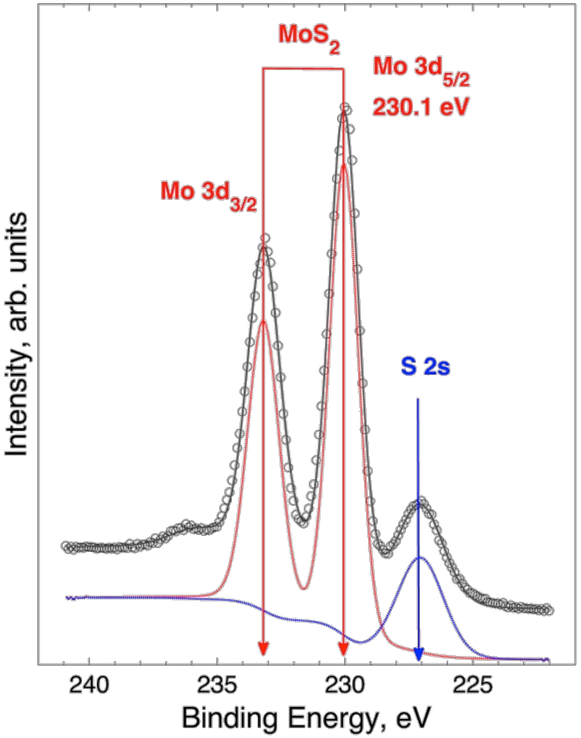


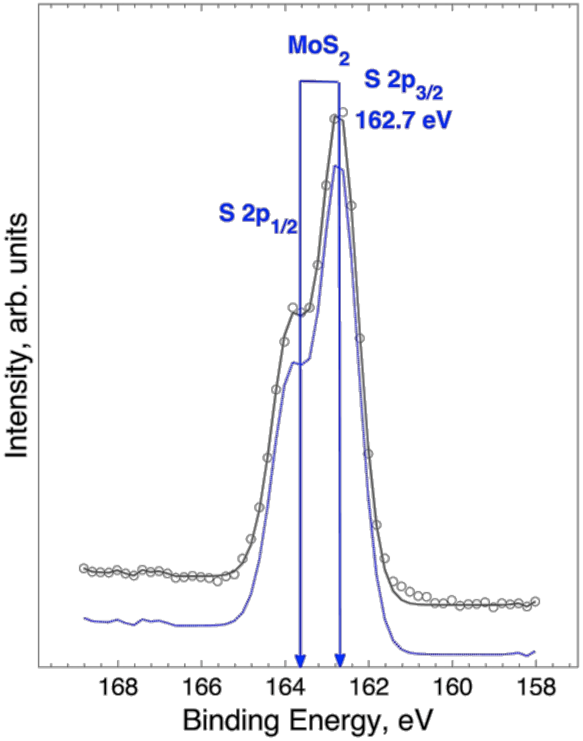
Raman (488 nm) of few layer graphene. Growth conditions: H_2:CH_4 =10:1; 3 min – H_2 + 1min – H_2/CH_4 mixture.

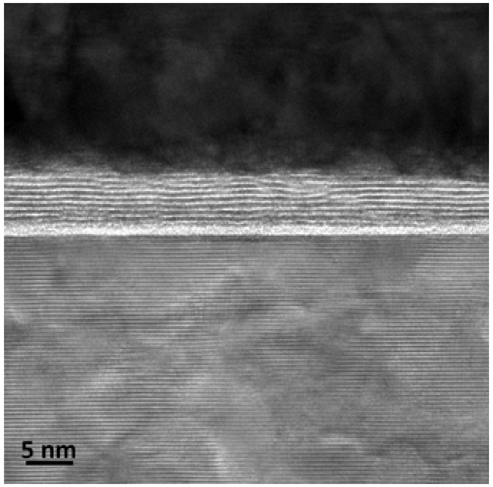
XPS: 8 layers of graphene!!!
TEM: 7 layers of graphene!!!

In collaboration with Prof. Timothy Fisher and Prof. Andrey Voevodin

MoS_2/sapphire – *XPS*





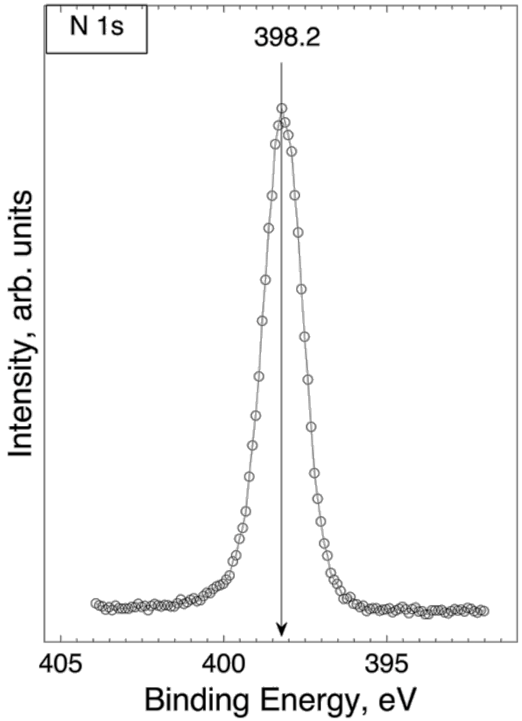


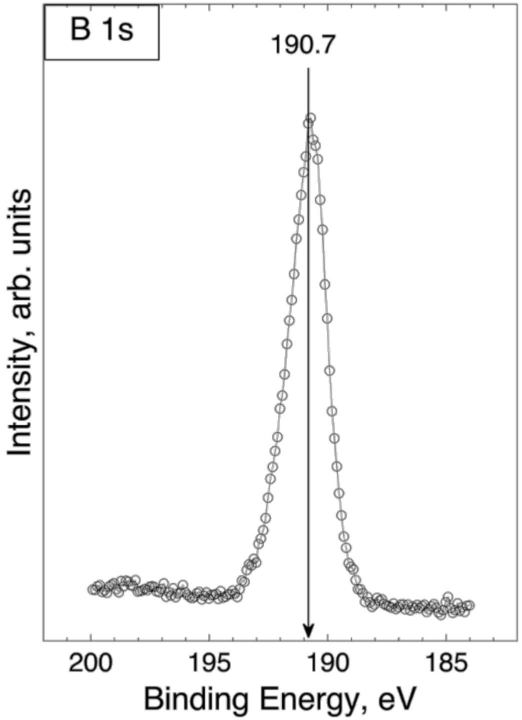
The ratio between sulfur and molybdenum was 2.1±0.1.

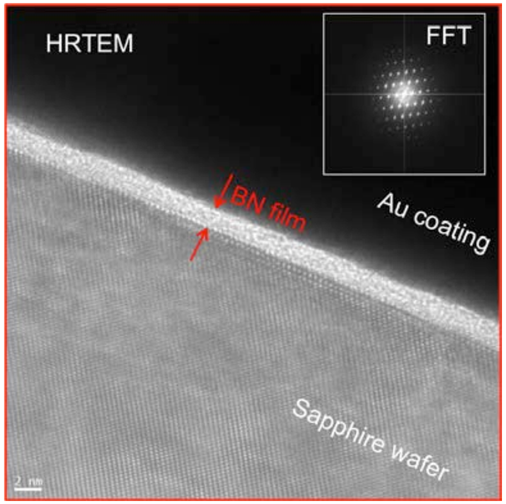
XPS: 5.7±0.7 layers (depending on an analysis spot)
TEM: 7-8 layers

In collaboration with Prof. Timothy Fisher and Prof. Andrey Voevodin

BN/sapphire – *XPS*







The ratio between nitrogen and boron was 0.8.

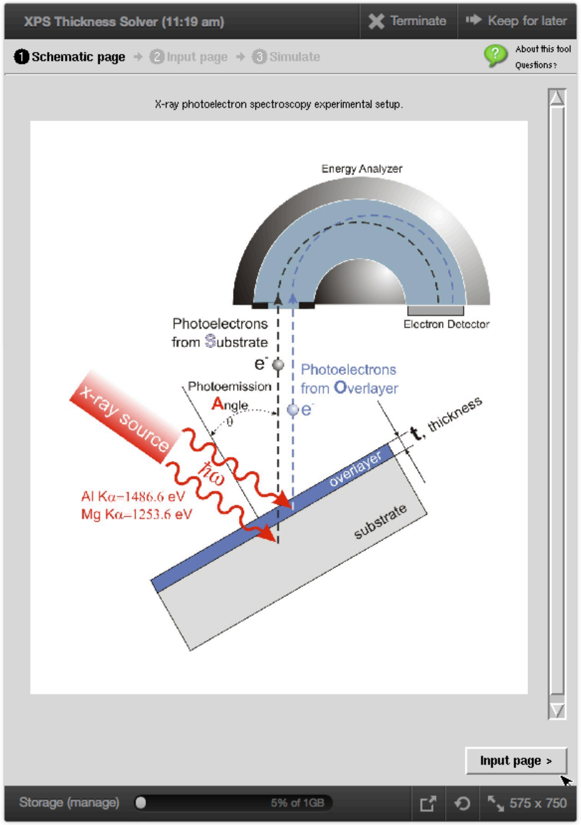
XPS: 2.0±0.2 nm
TEM: 1.5-18 nm

In collaboration with Prof. Timothy Fisher and Prof. Andrey Voevodin

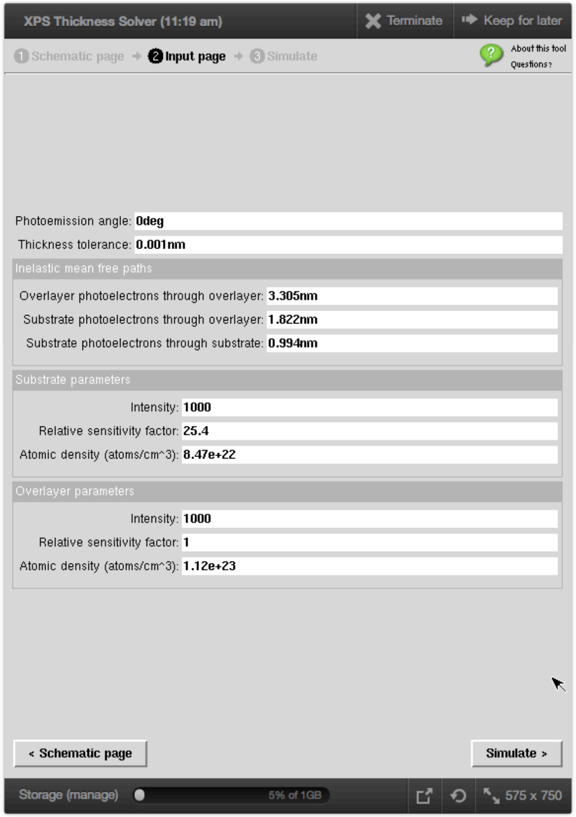
2D materials – *XPS*

$$\frac{N_{C1s}(\theta)}{N_{Cu2p}(\theta)}=\frac{\rho_{graphene}\times\frac{d\sigma_{C1s}}{d\Omega}\times\Lambda_e^{graphene}(E_{C1s})}{\rho_{Cu}\times\frac{d\sigma_{Cu2p}}{d\Omega}\times\Lambda_e^{Cu}(E_s)}\times\frac{1-\exp\left(\frac{-t}{\Lambda_e^{graphene}(E_{C1s})\cos\theta}\right)}{\exp\left(\frac{-t}{\Lambda_e^{graphene}(E_{Cu2p})\cos\theta}\right)}$$

XPS Thickness Solver



X-ray photoelectron spectroscopy experimental setup.



Photoemission angle: 0deg

Thickness tolerance: 0.001nm

Inelastic mean free paths

Overlayer photoelectrons through overlayer: 3.305nm

Substrate photoelectrons through overlayer: 1.822nm

Substrate photoelectrons through substrate: 0.994nm

Substrate parameters

Intensity: 1000

Relative sensitivity factor: 25.4

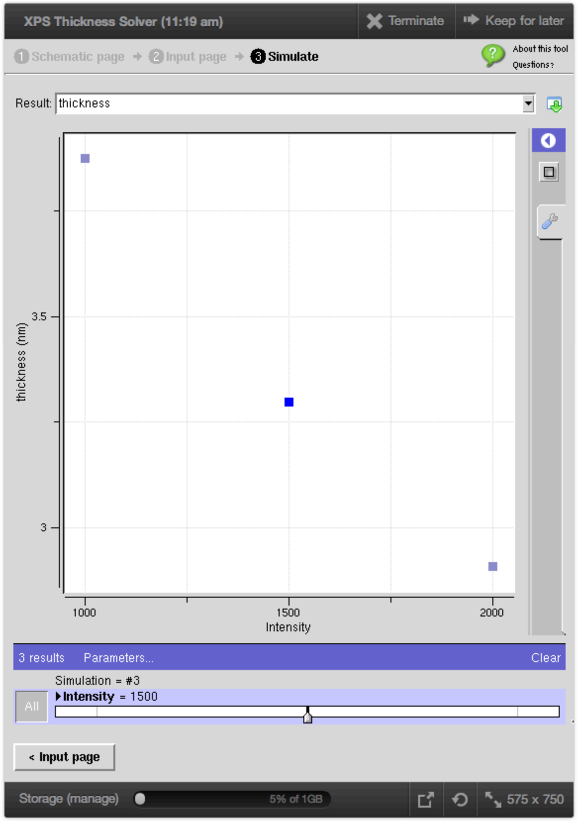
Atomic density (atoms/cm^3): 8.47e+22

Overlayer parameters

Intensity: 1000

Relative sensitivity factor: 1

Atomic density (atoms/cm^3): 1.12e+23



Result: thickness

Simulation = #3

Intensity = 1500

Kyle Christopher Smith; David A Saenz; Dmitry Zemlyanov; Andrey A Voevodin (2012), "XPS Thickness Solver," http://nanohub.org/resources/xpsts. (DOI: 10.4231/D3N29P603).

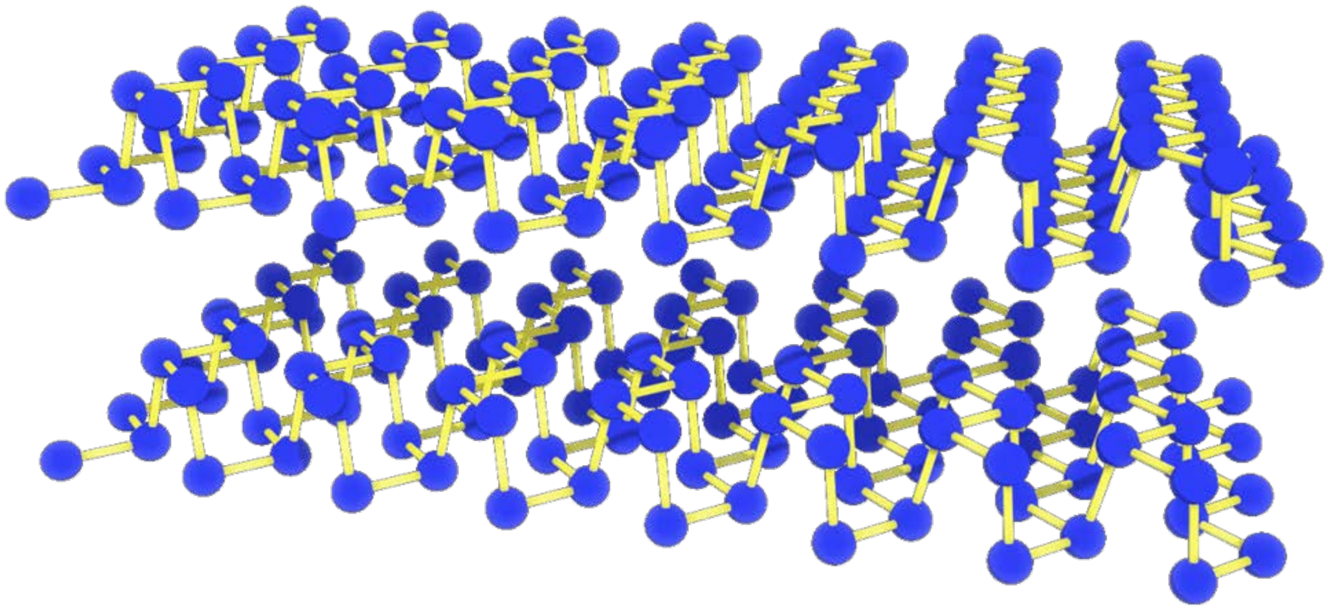
2D materials – *STM and XPS*

- Identification of graphene by STM
- Measurement of average thicknesses of a few layers of graphene, MoS_2 and BN by XPS

Phosphorene degradation (black phosphorus) - *XPS*

What is Phosphorene?

- 2D Layered Material
- Puckered Honeycomb Structure
- Stacking of Monolayer ‘Phosphorene’
- Potential application - microelectronics

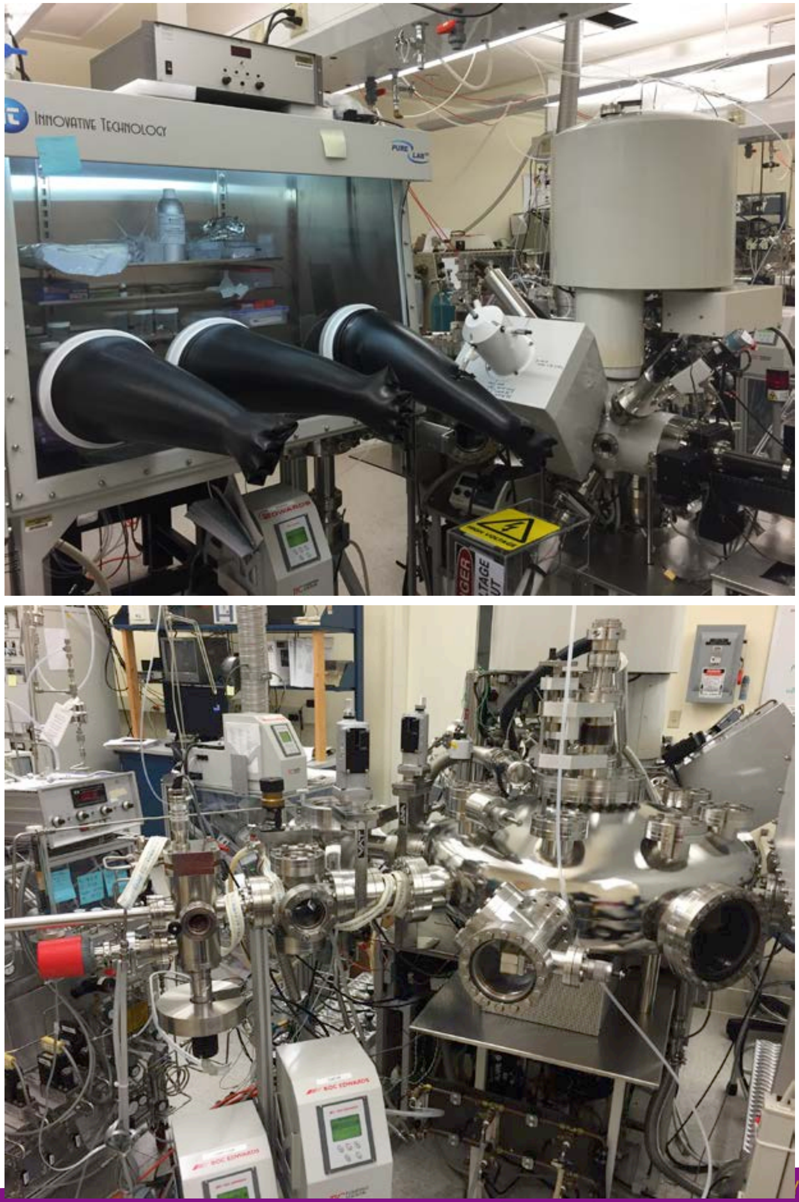


In collaboration with Prof. Peide Ye

Phosphorene degradation (black phosphorus) - *XPS*

- Sample cleaved in the inert environment (glove box);
- Possible degradation sources: oxygen (O_2) and water (H_2O) – treatment in the reaction cell;
- All transfers were done under UHV without contact to air.

Kratos Axis Ultra DLD Imaging XPS

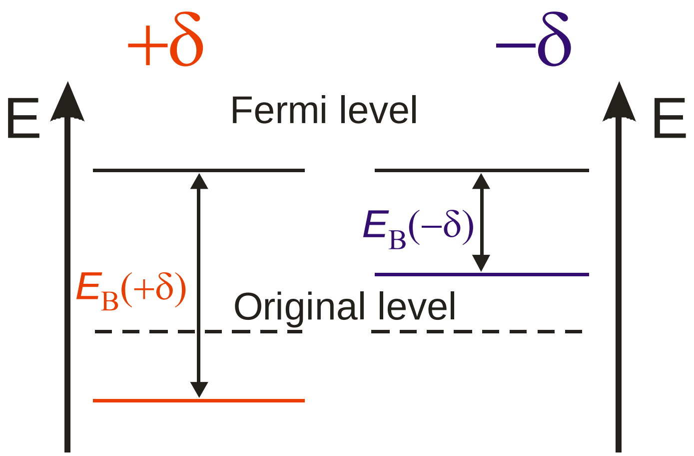


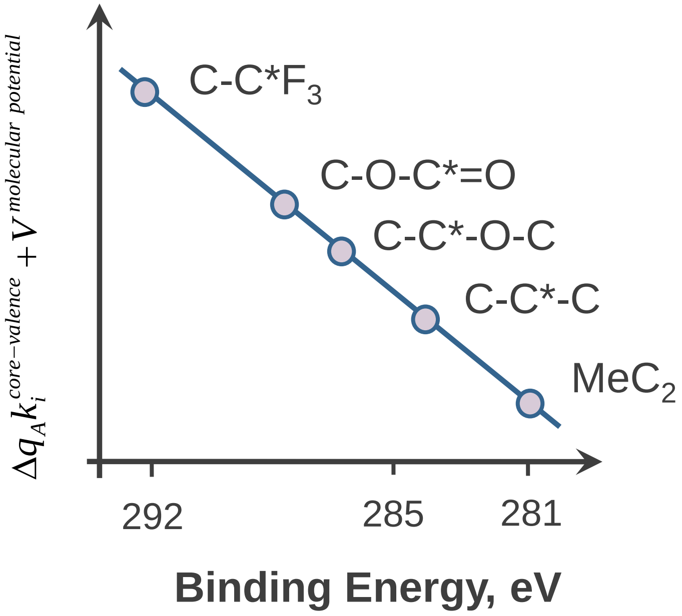
In collaboration with Prof. Peide Ye

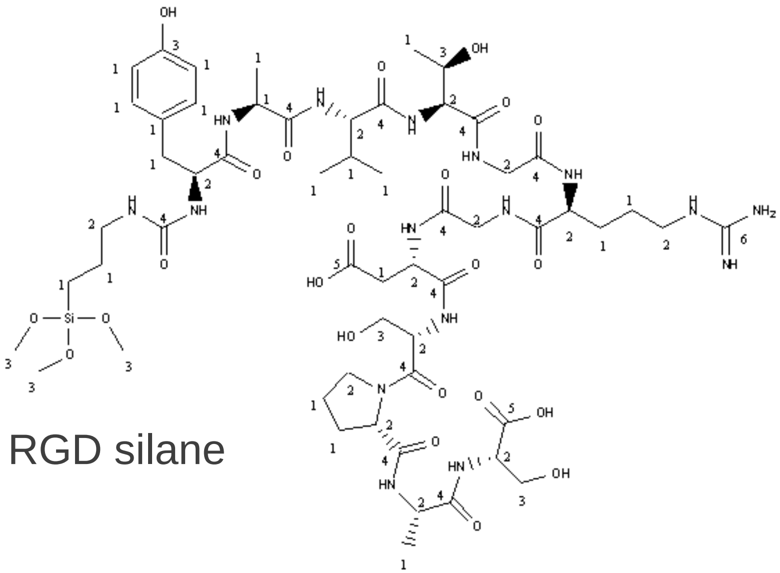
Phosphorene degradation (black phosphorus) - *XPS*

Why XPS?

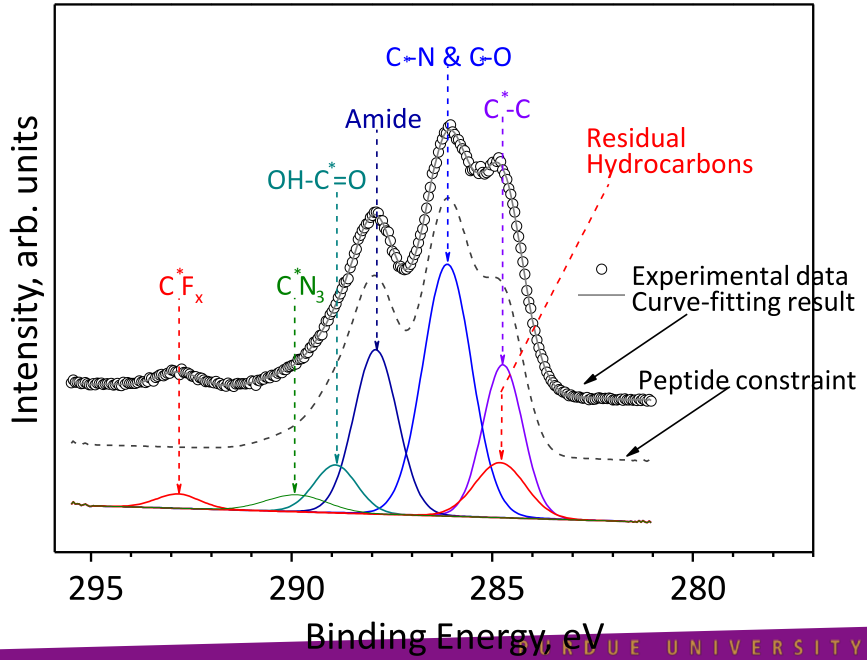
Chemical Shift





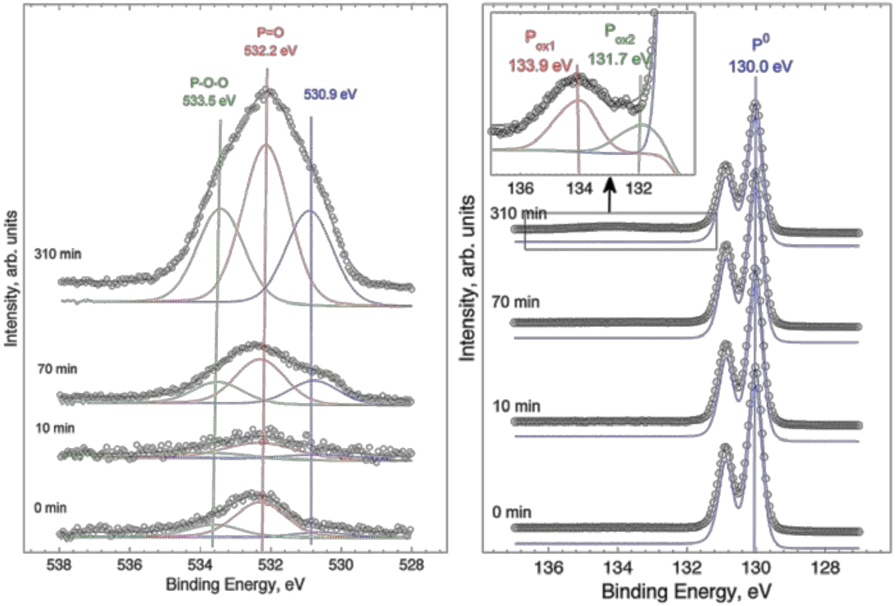


RGD silane

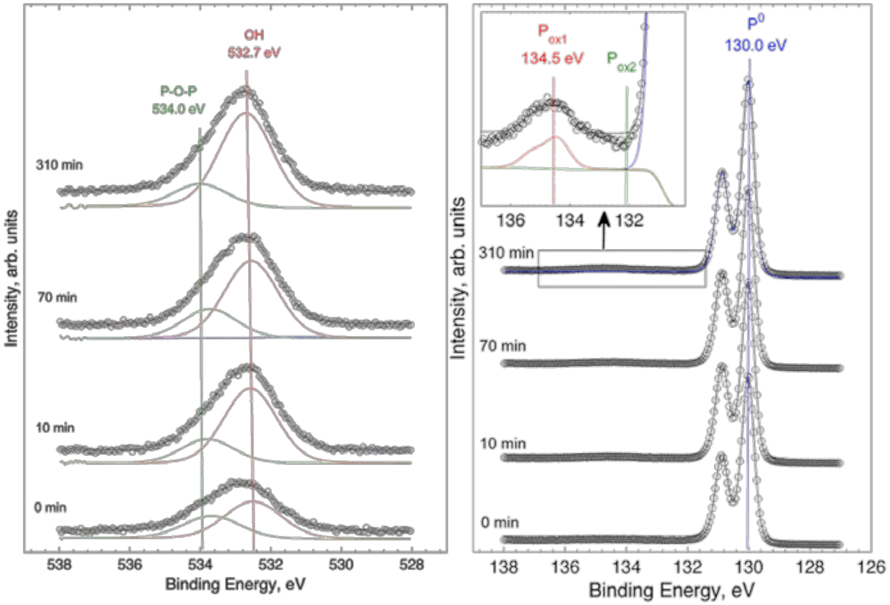


Phosphorene degradation (black phosphorus) - *XPS*

5% O_2/Ar at room temperature



5% H_2O/Ar at room temperature



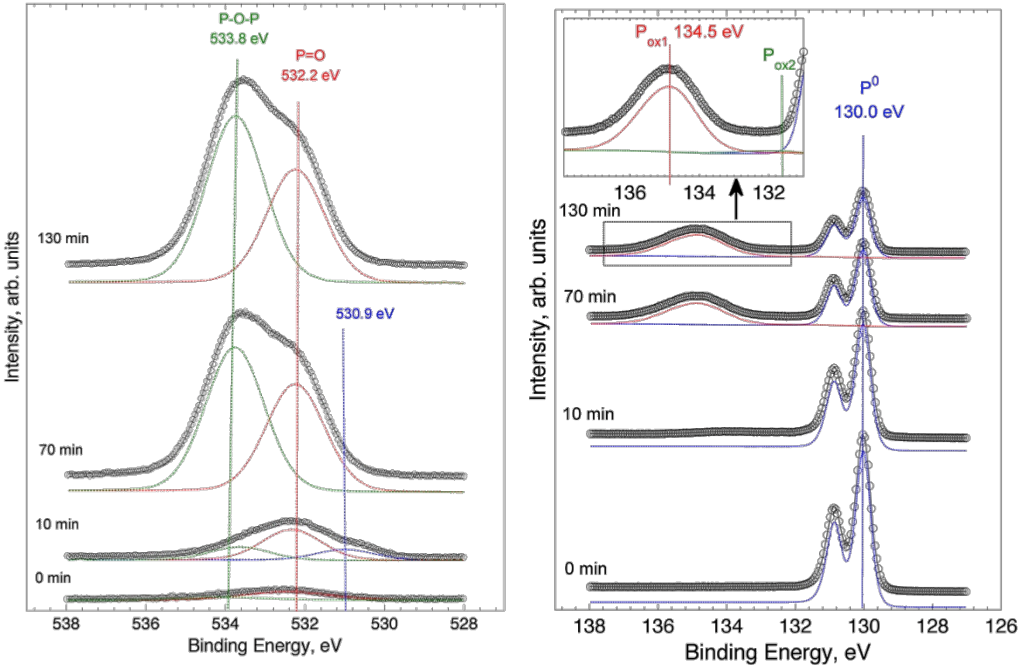
- P has three chemical states: the major product was P_4O_{10}.
- The P-O-P and O=P components were detected in the O 1s spectrum

- P has two chemical states: the major product was like-HPO_3.
- The P-O-P and P-O-H components were detected in the O 1s spectrum

In collaboration with Prof. Peide Ye

Phosphorene degradation (black phosphorus) - *XPS*

$5\%O_2$ & $2.3\%H_2O$ in Ar Treatment



- The major product was P_4O_{10}.
- The P-O-P and O=P components were detected in the O 1s spectrum

In collaboration with Prof. Peide Ye

Phosphorene degradation (black phosphorus) - *XPS*

XPS result can be quantified in the terms of coverage and/or oxide thickness

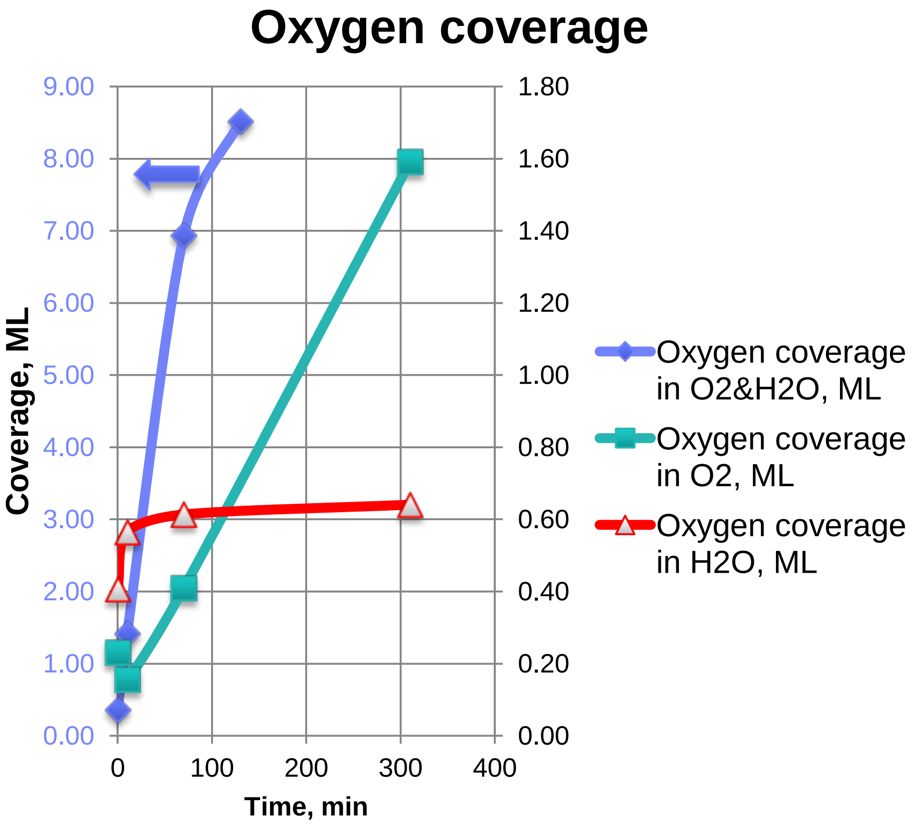
$$Coverage \equiv \frac{s_{adlayer}}{s_{substrate}} = \frac{N_{adlayer}(\theta)}{N_{substrate}(\theta)} \frac{\frac{d\sigma_{substraye}}{d\Omega} \times \Lambda_e^{substrate}(E_{substrate})\cos\theta}{\frac{d\sigma_{adlayer}}{d\Omega} \times d}$$

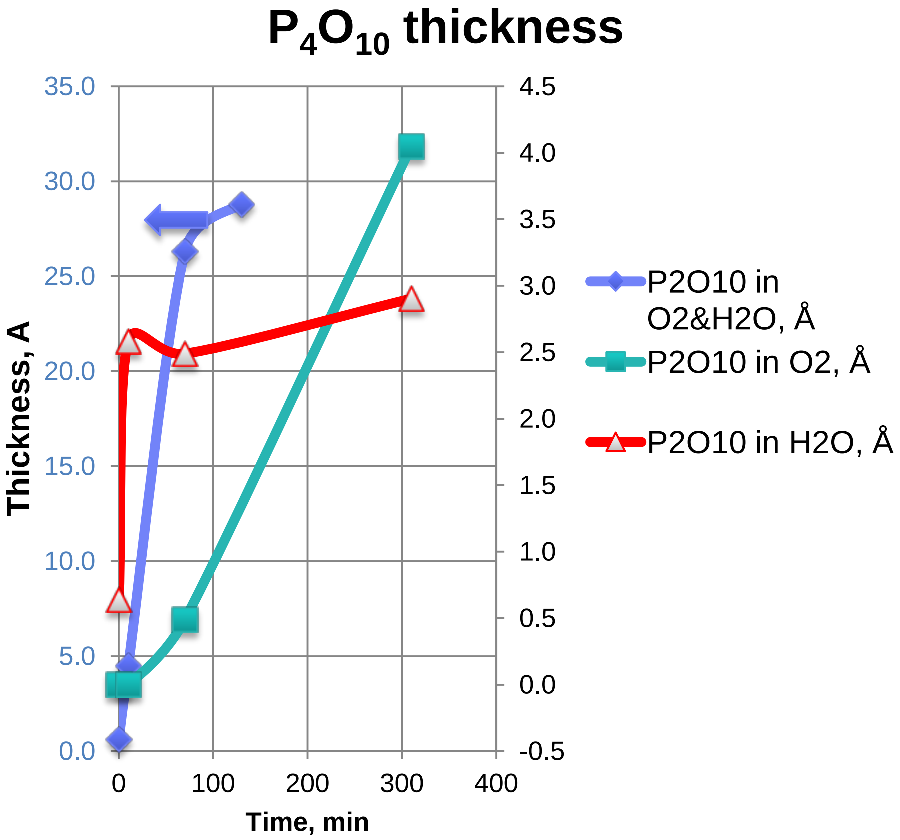
$$\frac{N_l(\theta)}{N_s(\theta)} = \frac{\rho_{overl} \times \frac{d\sigma_l}{d\Omega} \times \Lambda_e^{overl}(E_l)}{\rho_{subst} \times \frac{d\sigma_s}{d\Omega} \times \Lambda_e^{subst}(E_s)} \times \frac{1 - \exp\left(\frac{-t}{\Lambda_e^{overl}(E_l)\cos\theta}\right)}{\exp\left(\frac{-t}{\Lambda_e^{overl}(E_s)\cos\theta}\right)}$$

In collaboration with Prof. Peide Ye

Phosphorene degradation (black phosphorus) - *XPS*

5%O_2 & 2.3%H_2O in Ar Treatment



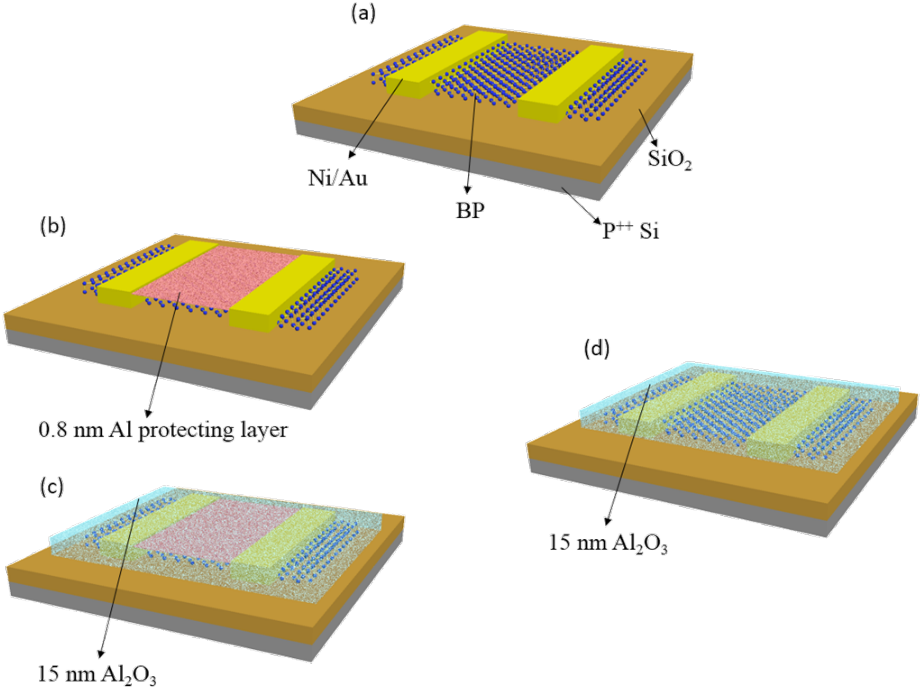


- Oxidation rate in O_2+H_2O is about 10× higher than with only O_2 or H_2O, respectively.

In collaboration with Prof. Peide Ye

Phosphorene degradation (black phosphorus) - *XPS*

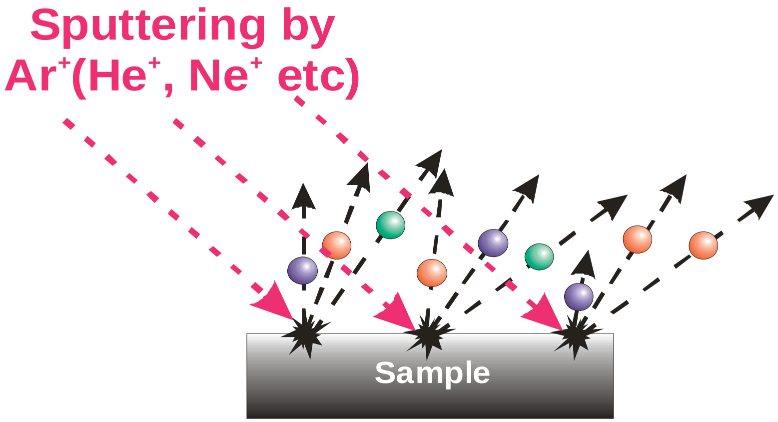
- In steam, the productions is like-HPO_3.
- In oxygen and wet oxygen the productions is P_4O_{10}.
- Oxidation rate in wet oxygen is about 10× higher than with only oxygen or water respectively. Intermediates (like-HPO_3?) make the oxidation much faster.

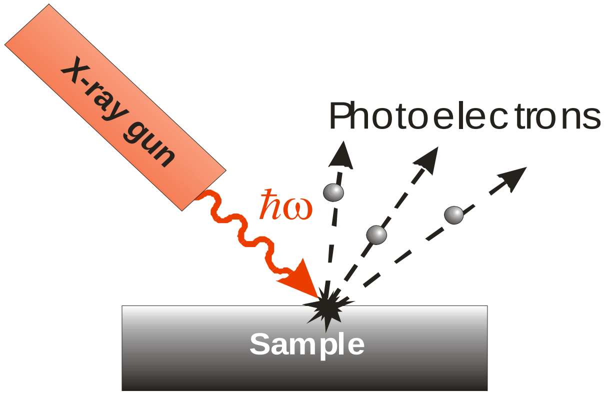


(a) Schematic view of a fabricated back-gate modulated BP FET. (b) Prior to ALD integration on BP, a 0.8 nm Al protecting layer was pre-deposited on BP surface and waited to be oxidized in ambient condition. (c) 15 nm Al2O3 was then deposited with TMA and water as precursors at 200 ºC. (d) 15 nm Al2O3 was directly deposited with TMA and water as precursors at 200 ºC without applying 0.8 nm Al protecting layer.

In collaboration with Prof. Peide Ye

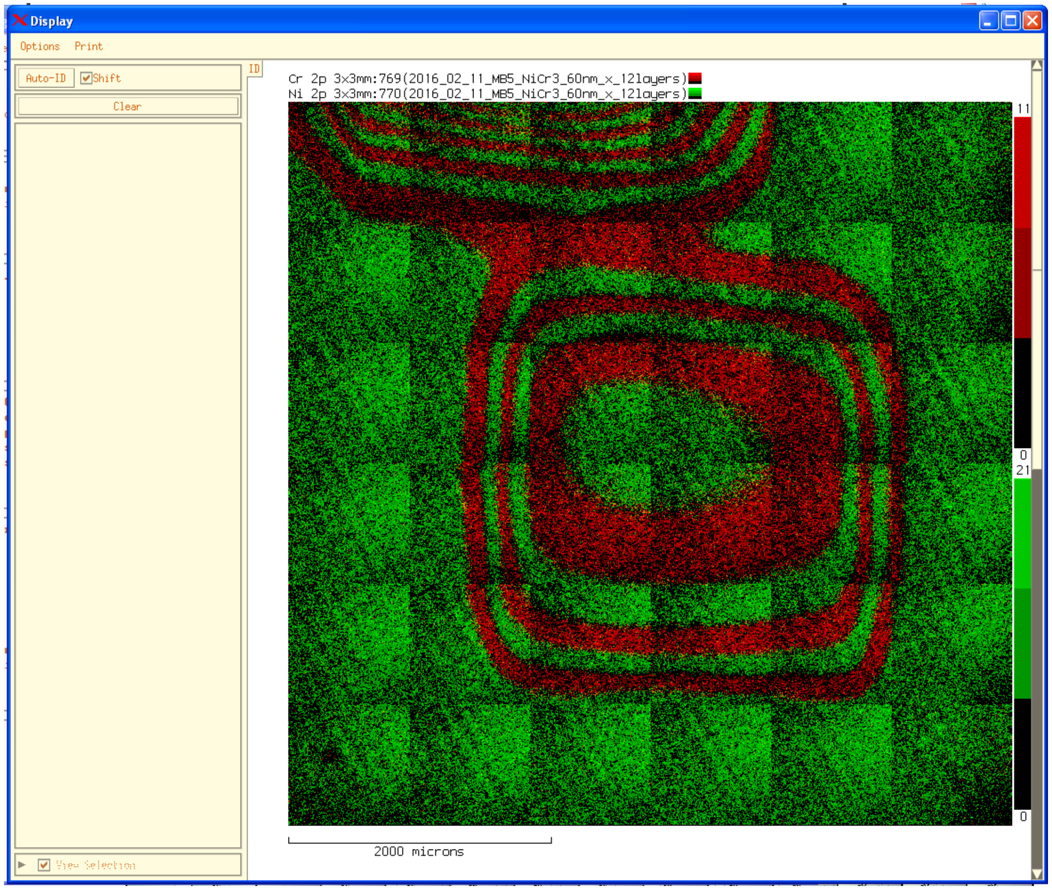
Depth Profiling - *XPS*





Depth profiling by ion sputtering is destructive methods

Depth Profiling - *XPS*



Cr 2p 3x3mm:769(2016_02_11_MB5_NiCr3_60nm_x_12layers) 🟥
Ni 2p 3x3mm:770(2016_02_11_MB5_NiCr3_60nm_x_12layers) 🟩

2000 microns


Ni – 65 nm

Cr – 60 nm

Ni – 65 nm

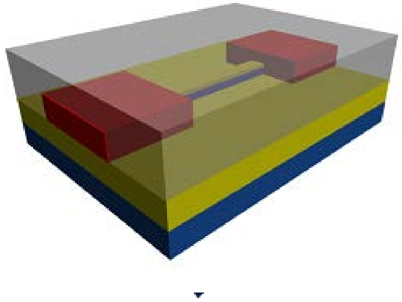
Cr – 60 nm

Ni – 65 nm

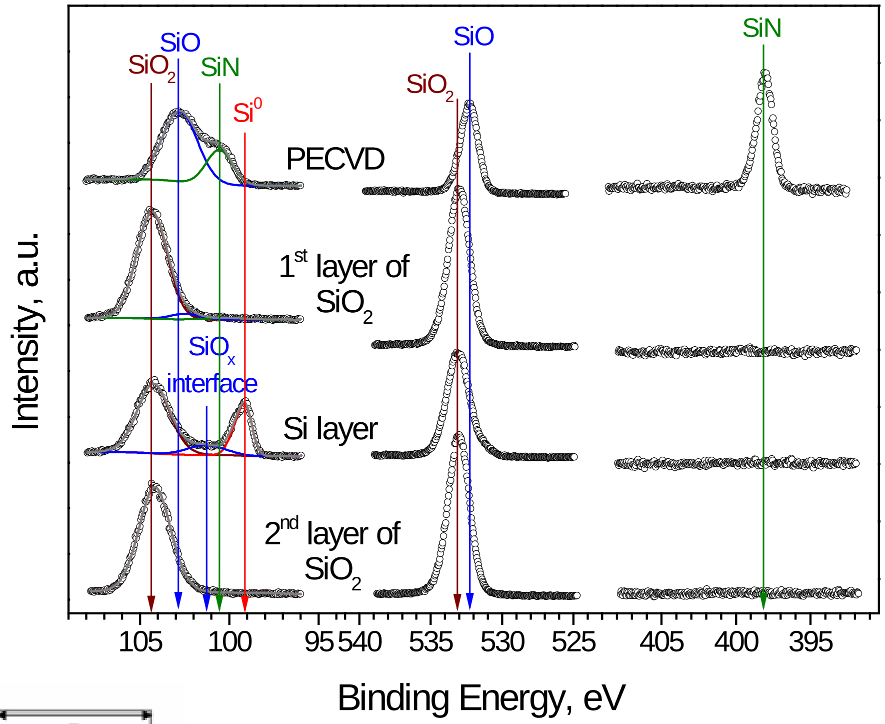
Cr – 60 nm

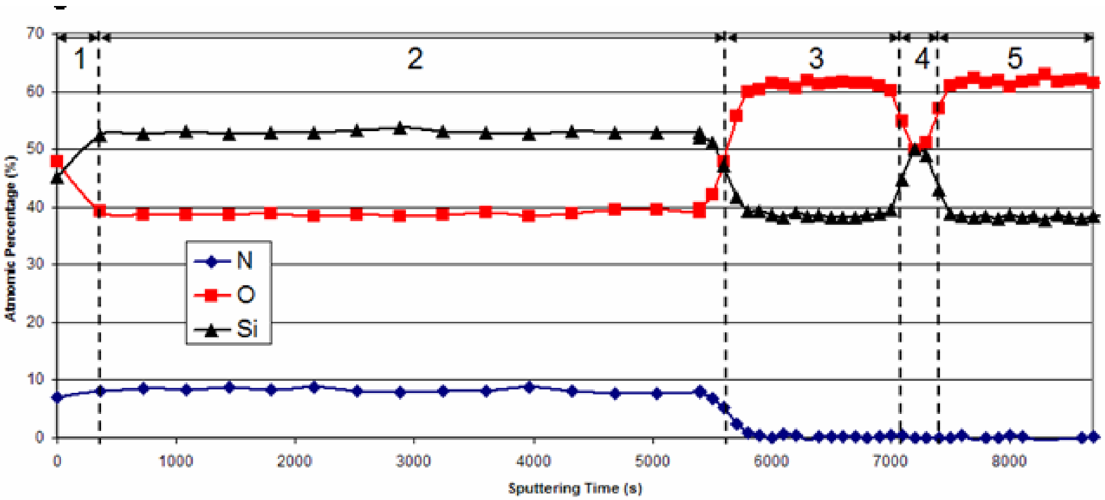
Si wafer

Depth Profiling - *XPS*

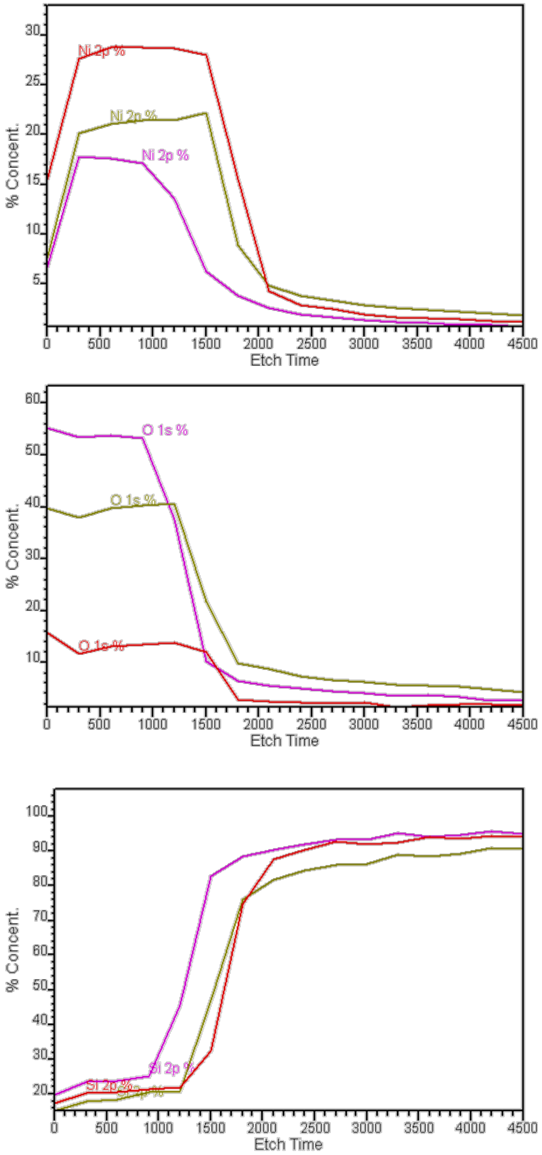


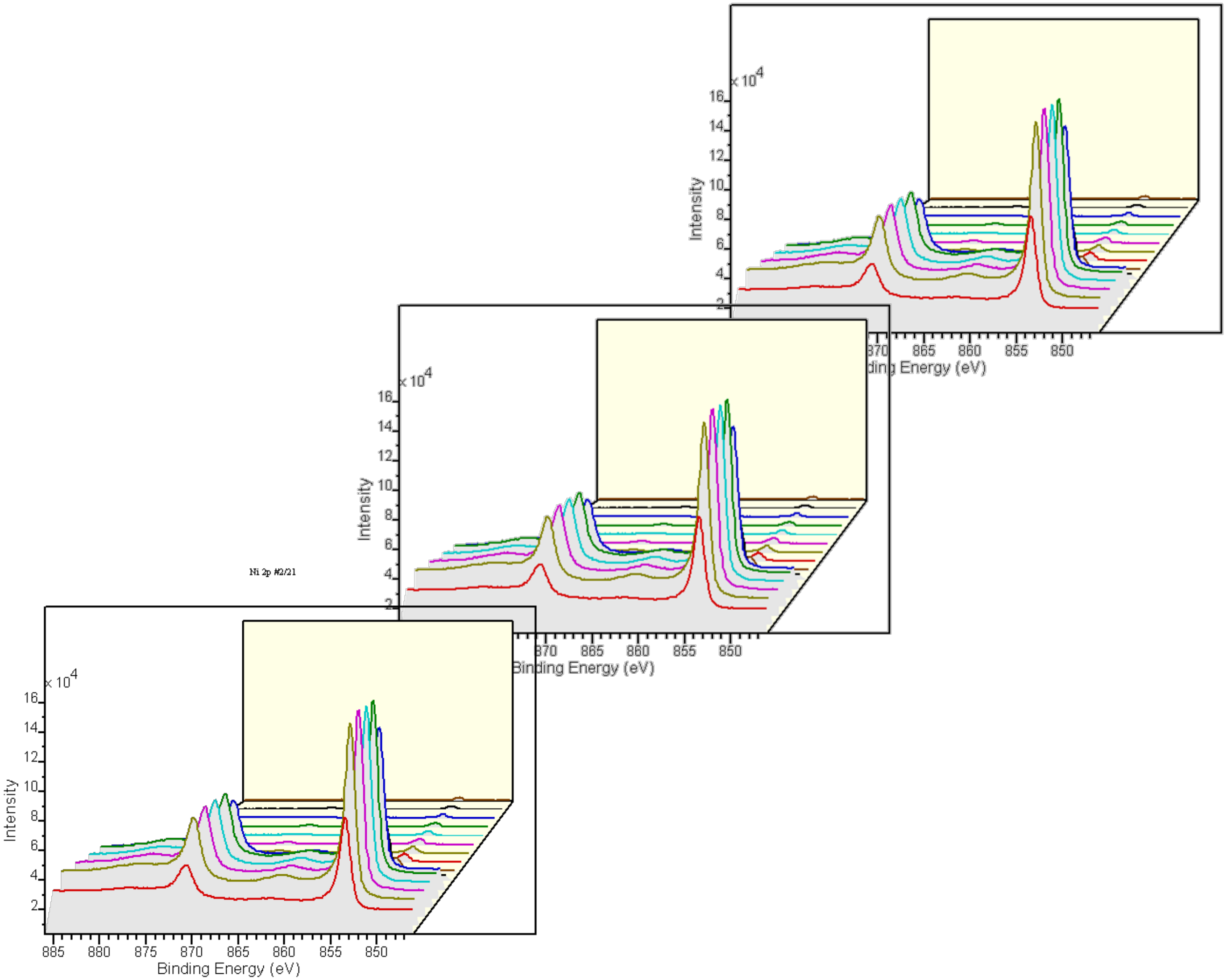
- 🟨 Silicon Dioxide
- 🟦 Silicon
- 🟥 Platinum
- ⬜ PECVD Oxide





Depth Profiling - *XPS*





Sample 2: Ni-rich layer without thermal treatment

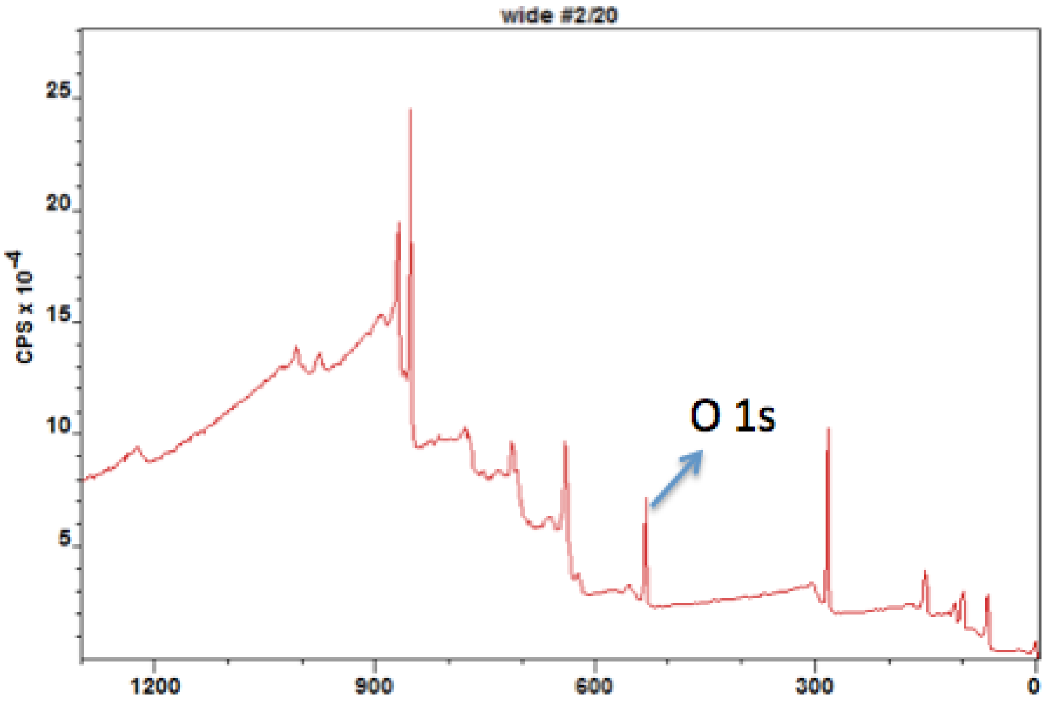
Sample 3: Ni-rich layer with 350°C thermal treatment in H_2 flow for 12 h

Sample 4: Ni-rich layer with 700°C thermal treatment in H_2 flow for 12 h

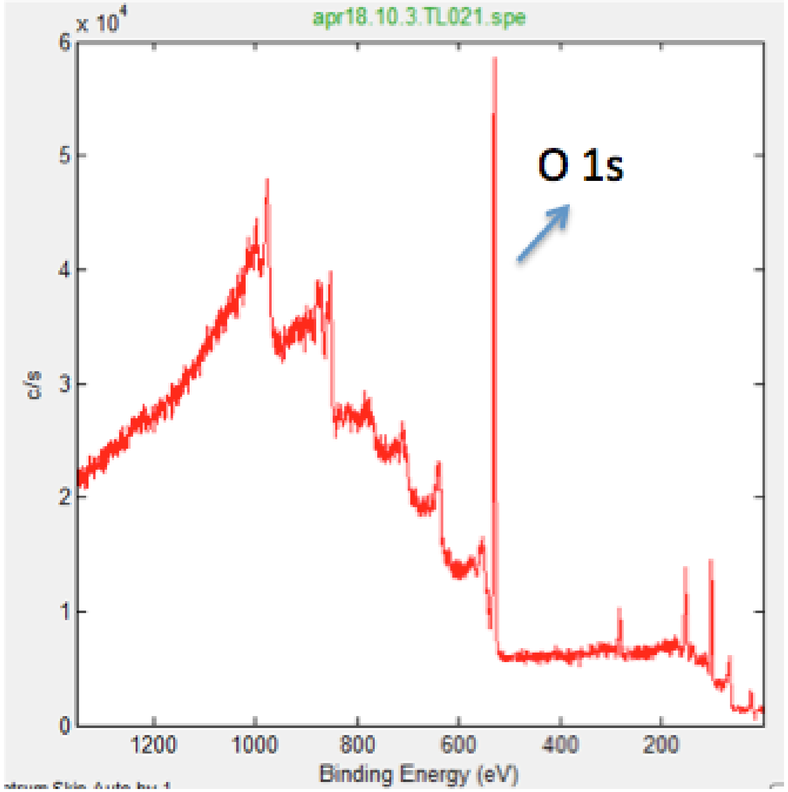
In collaboration with Prof. Fabio Ribeiro and Prof. Christophe Copéret

Depth Profiling - *XPS*

Inert XPS (Conducting in Purdue)

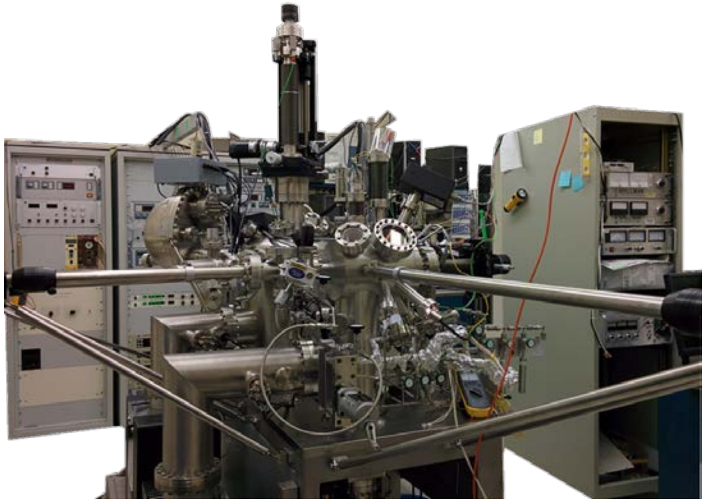


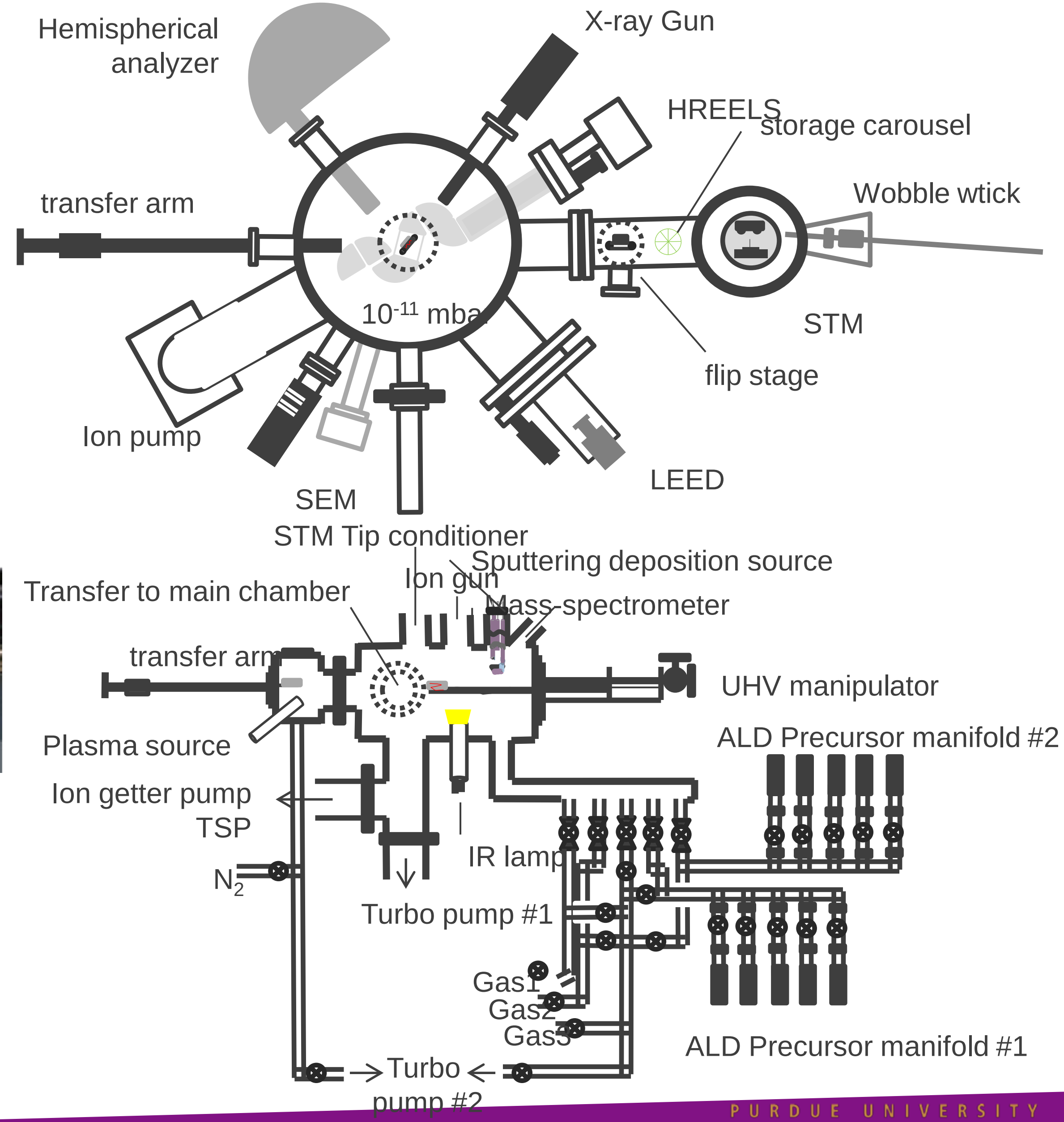
Normal XPS (Conducting in EPFL)



In collaboration with Prof. Fabio Ribeiro and Prof. Christophe Copéret

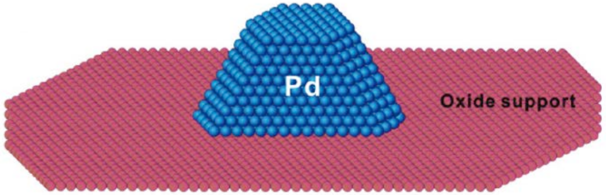
Surface Analysis Cluster

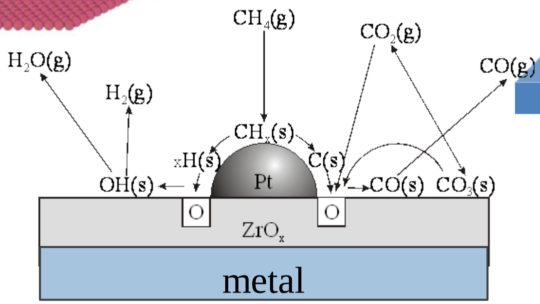




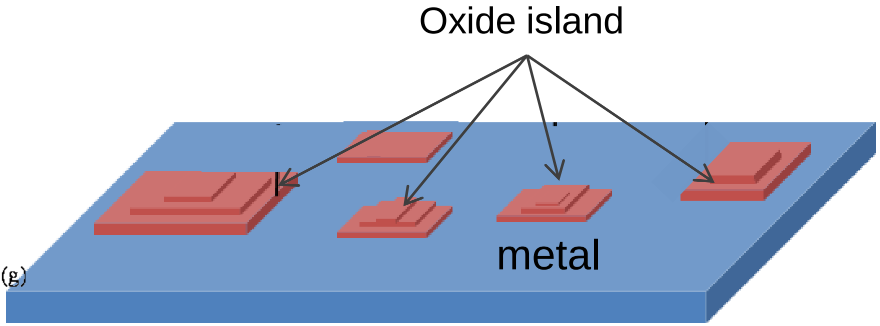
Regular catalyst

Flat model catalyst



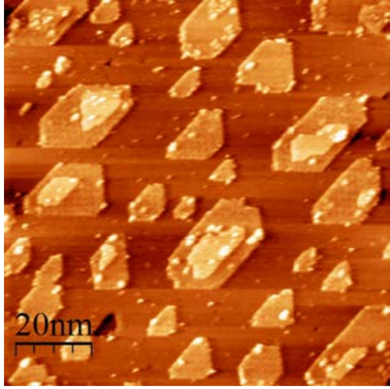


Reverse model catalyst



- Model catalysts can be readily studied by the surface analysis tools.
- Active phase is “open” for analysis
- Reverse catalysts allow to control an oxide island perimeter and “enhance” boundary effects.

ALD: Examples of substrates and precursors

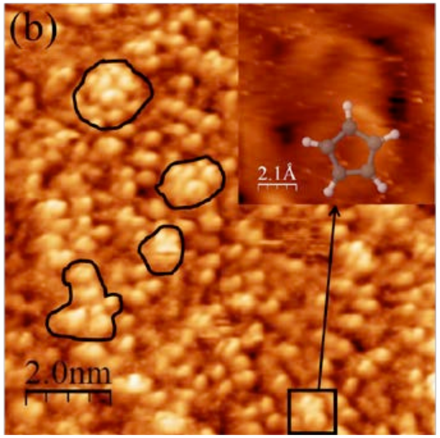


- **Single crystals used as substrates:** Pt(111), Pd(111), Cu(111), TiO_2(110).

- **Precursors:** Trimethylaluminum (TMA), bis(η_5-cyclopentadienyl)iron (ferrocene), palladium(II) hexafluoroacetylacetonate ($Pd(hfac)_2$), diethylzinc, zirconium-t-butoxide ($Zr^{+IV}(OC_4H_9)_4$), etc.

- **Model Catalysts:** Al_2O_3/Pt(111), Al_2O_3/Pd(111), Al_2O_3/Cu(111), ZrO_x/Pd(111), ZrO_x/Cu(111), ReO/Pt(111), FeO/Pt(111), TiO_x/Pt(111), PdZn/Pd(111), Pd/TiO_2(110), etc.

1. Gharachorlou et al. ACS APPLIED MATERIALS & INTERFACES, 6 (2014), p.14702
2. Detwiler et al. JOURNAL OF PHYSICAL CHEMISTRY C, 119 (2015), p. 2399
3. Gharachorlou et al. ACS APPLIED MATERIALS & INTERFACES, 7 (2015), p. 16428
4. Detwiler et al. SURFACE SCIENCE, 640 (2015), p. 2
5. Paul et al. CHEMISTRY OF MATERIALS, (2015) 10.1021/acs.chemmater.5b01778
6. Gharachorlou et al. JOURNAL OF PHYSICAL CHEMISTRY C, 119 (2015), p. 19059



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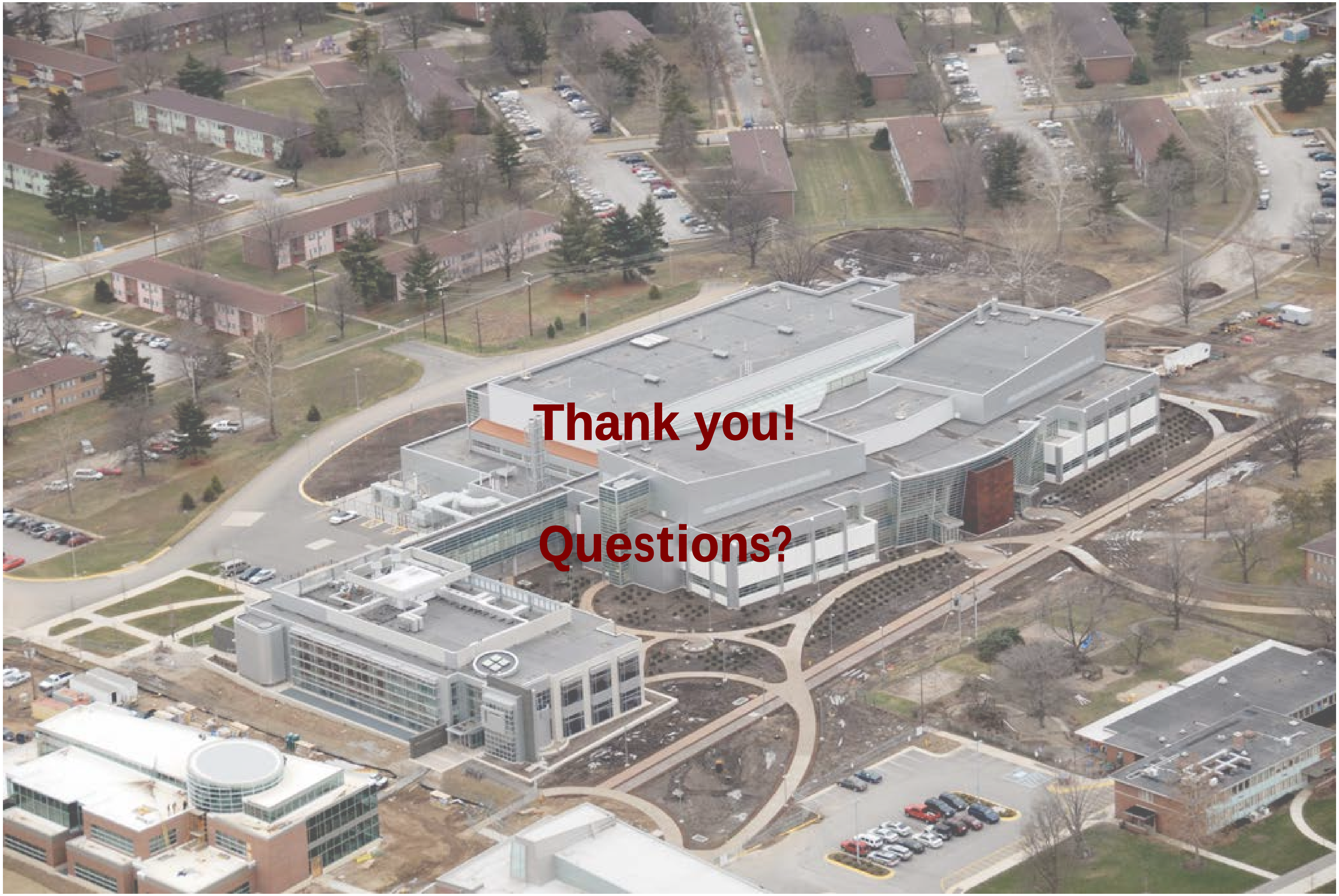

Thank you!

Questions?

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