Surface Physics:

A View of the Top

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Surface Science

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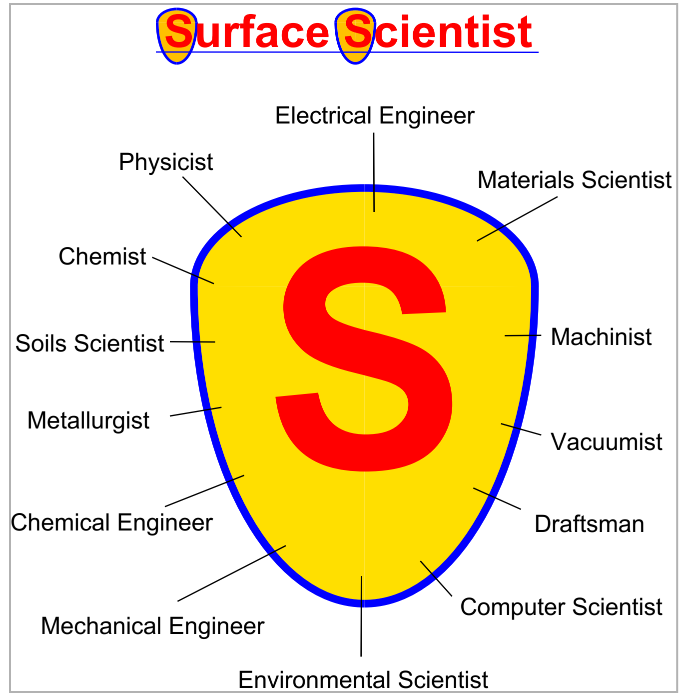
The study of the physical and chemical properties of solid surfaces and interfaces.



Surface Physics - part of condensed matter physics

Surface Chemistry - part of physical chemistry

Materials Science

Electrical Engineering

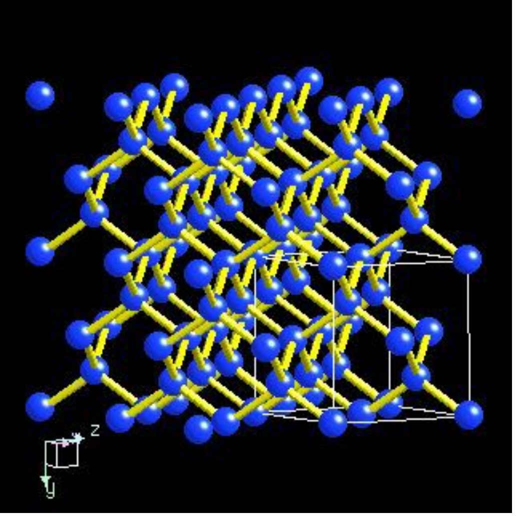
Chemical Engineering

others…

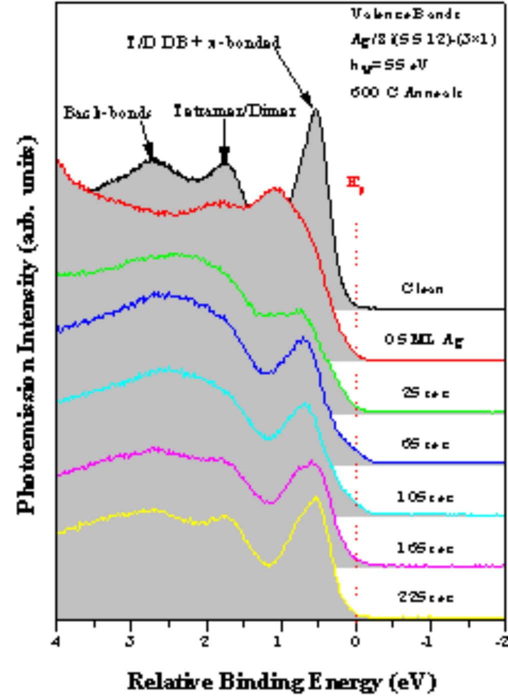
Nanoscience

Surfaces/Interfaces

- Technological ties with semiconductor industry, petroleum industry, high T_c superconductors, tribology, environmental issues, much more…
- Requires a wide variety of experimental skills
- Combines both laboratory work and work at major facilities
- Many techniques must be applied to a given system in order to completely characterize it

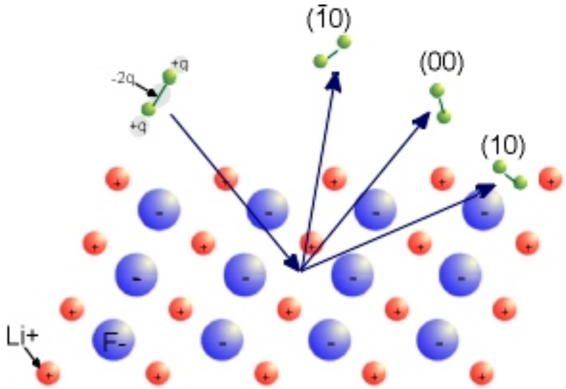


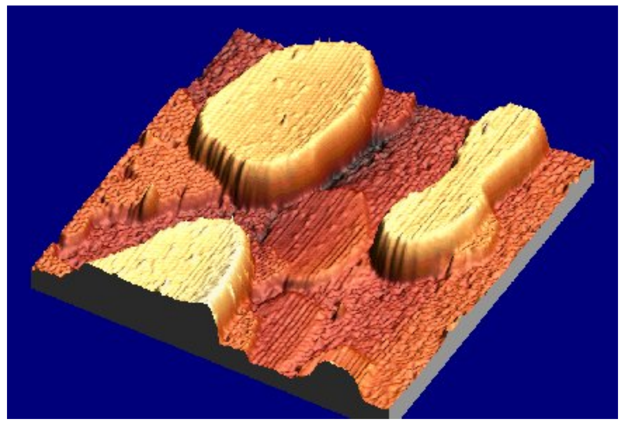
Surface Science is concerned with:



- Geometric structure

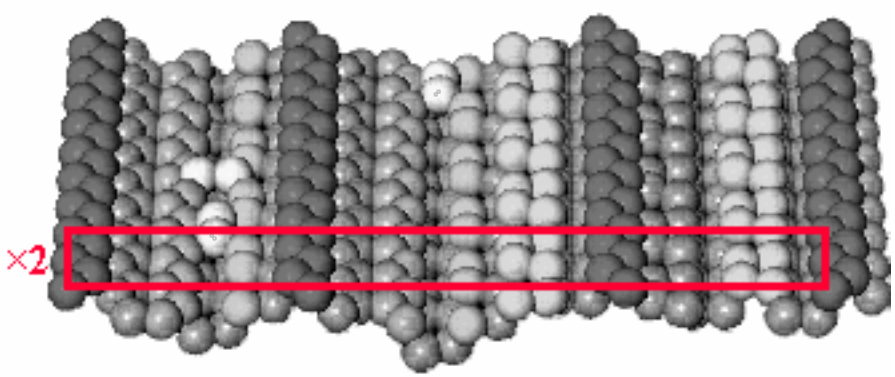
- Particle-Surface Interactions



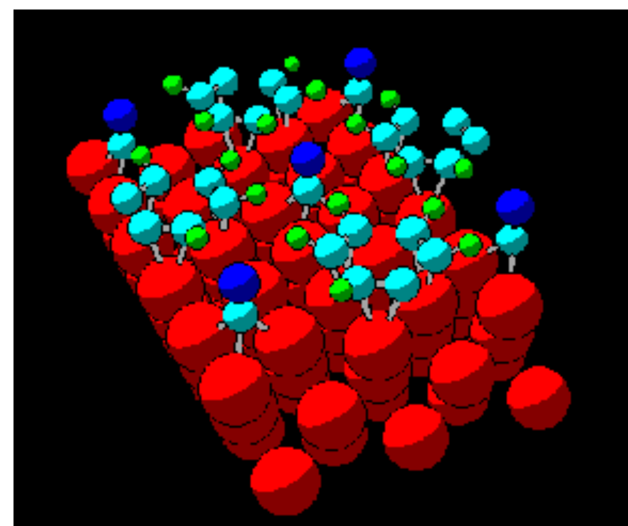


- Electronic structure

- Effects of radiation damage

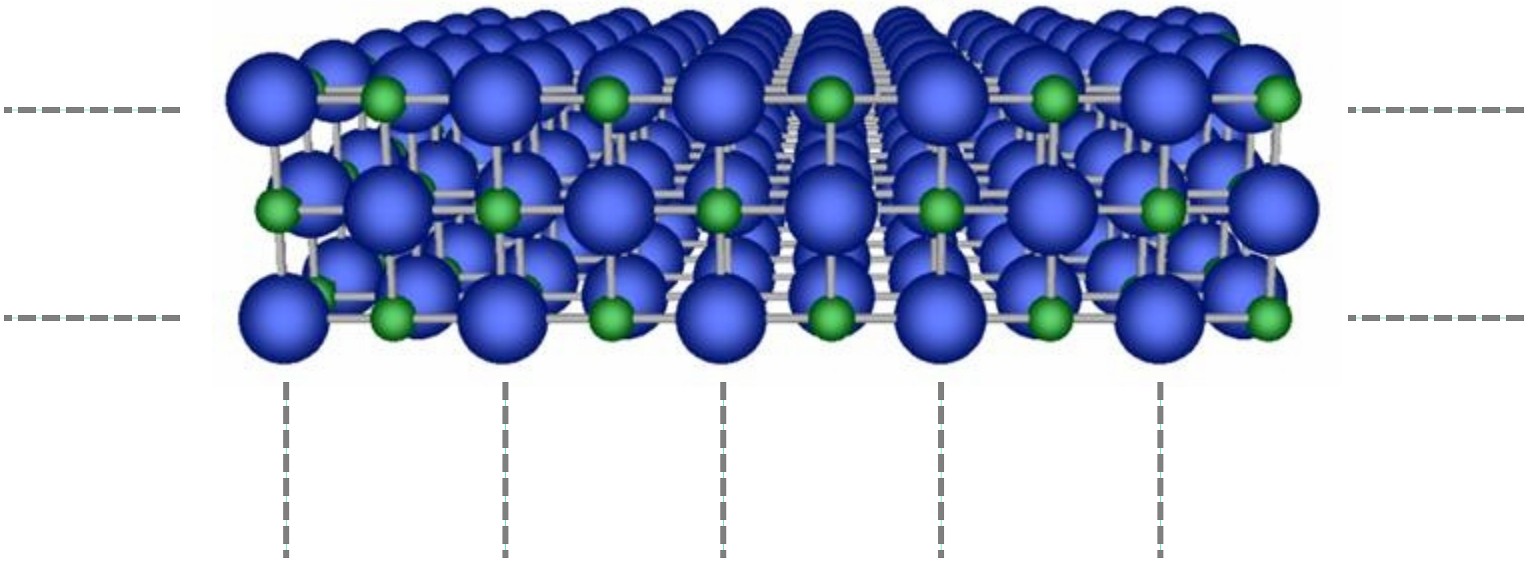


- Chemical surface reactions



Surface Structures

Almost side view

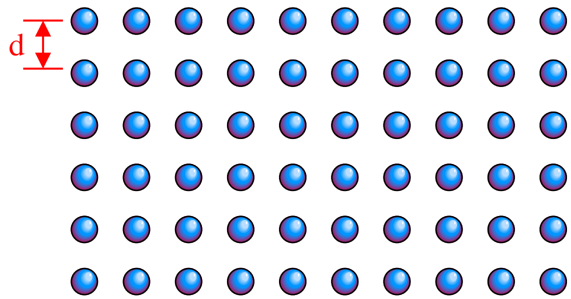


- A solid is composed of atoms with infinite periodicity in 3-dimensions
- The periodicity is broken at a surface

Surface Structures

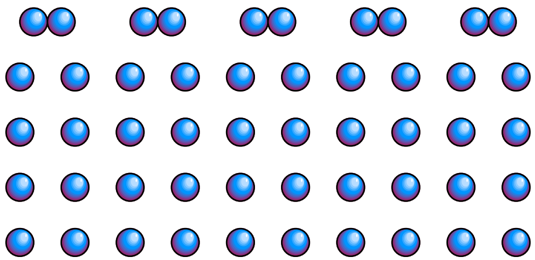
side view

Bulk-terminated Surface



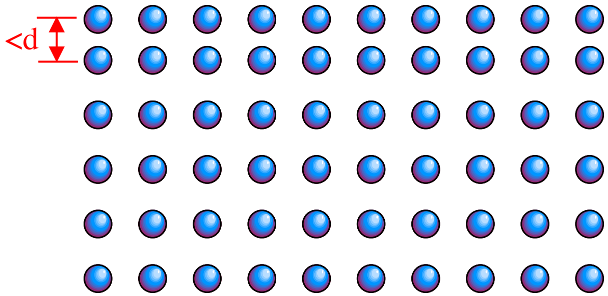
- Surface atoms are in bulk-like positions
- It's as though the surface were simply cut

Reconstructed Surface



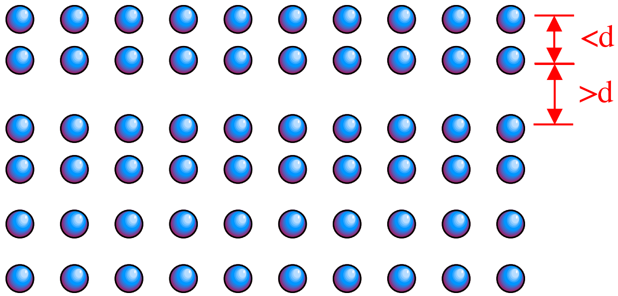
- Surface atoms are moved laterally, as well as in the perpendicular direction
- Reconstruction can involve many atomic layers

Relaxed Surface



- Surface layer is moved uniformly into, or away from, the bulk material in the perpendicular direction, i.e., $d_{12} \neq d_{bulk}$

Oscillatory Relaxation



- The relaxation extends into the first few atomic layers
- Relaxation oscillates between inward and outward

Surface Science

Relaxations and reconstructions lead to new phenomena at surfaces, such as:

1. Unique chemical reactions – catalysis, etching, atomic layer deposition
2. Unique electronic properties – novel devices, quantum computation
3. Ability to adsorb molecules in unique configurations – new materials
4. ???

Experiment vs. Theory

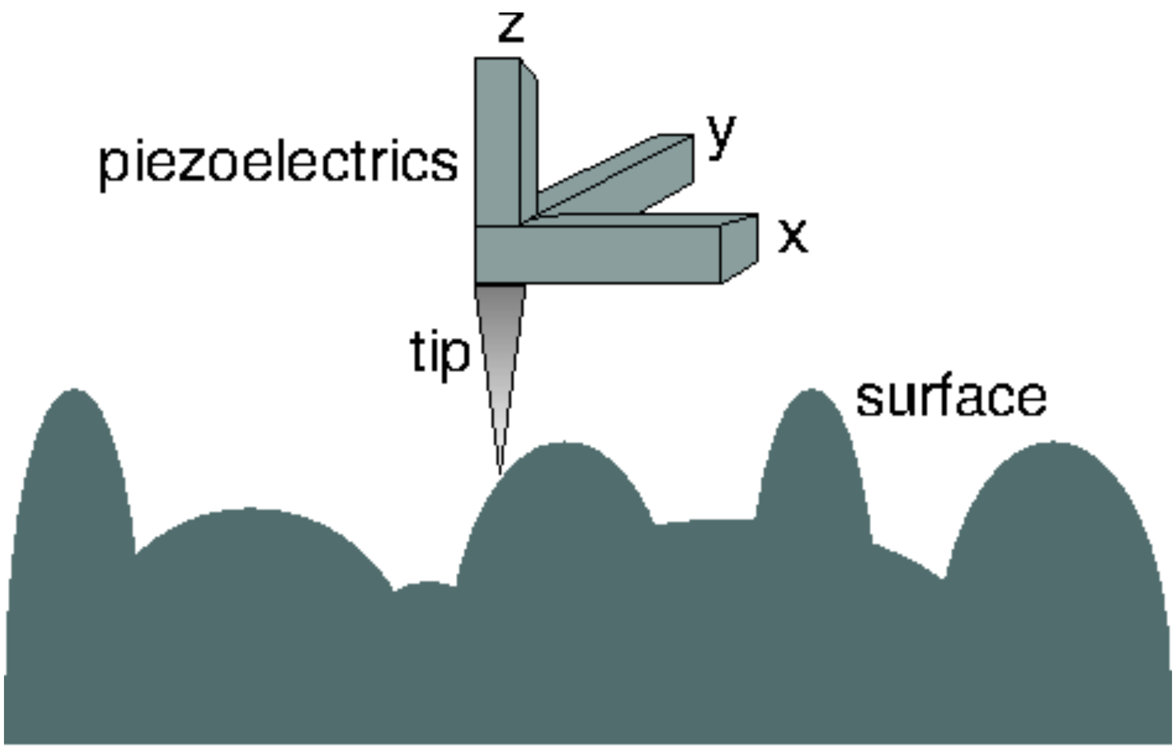
Duke's Laws

1. All theories are wrong

2. All experiments measure something

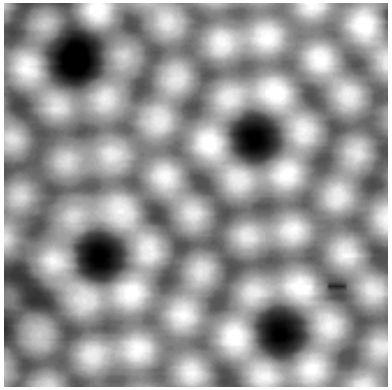
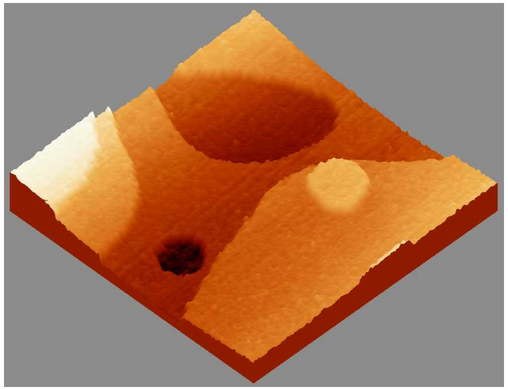
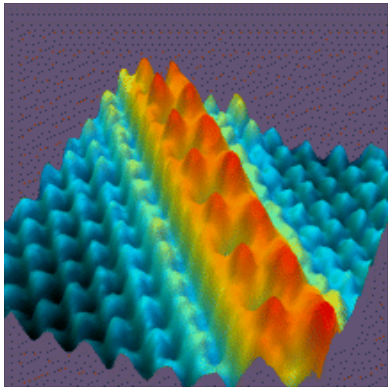
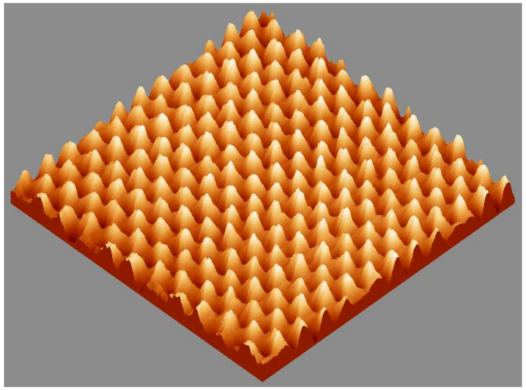
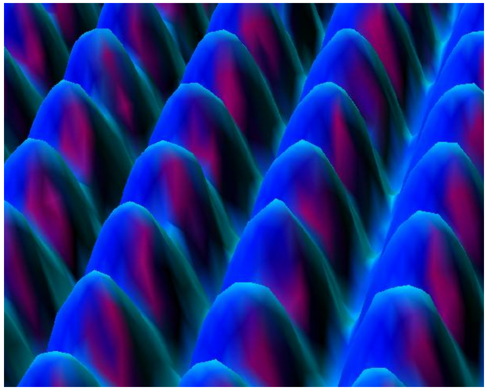
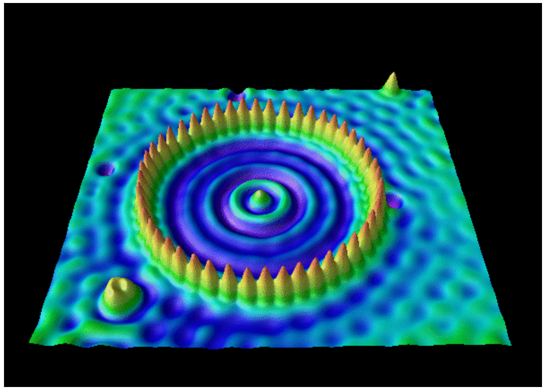
Scanning Tunneling Microscopy (STM)

- 1986 Nobel prize in Physics (Binning and Rohrer, IBM Zurich)

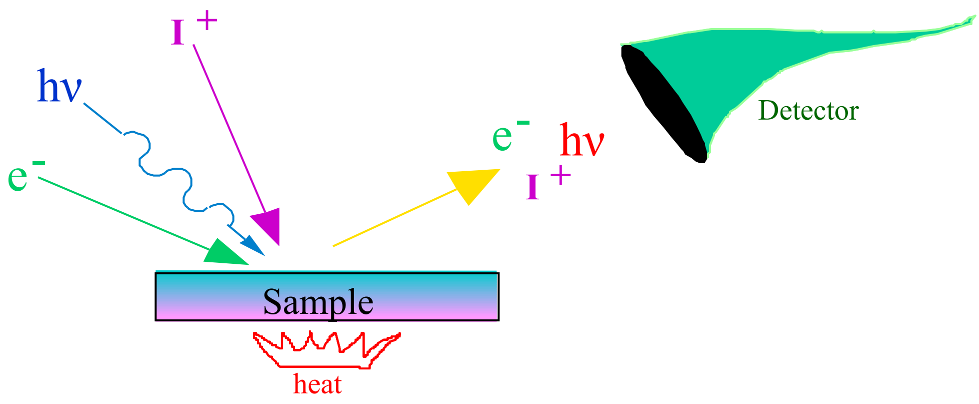


- Measures electron density at a surface with atomic resolution

Scanning Tunneling Microscopy (STM)

Atomic resolution	Metal surfaces	Novel systems
		
Clean silicon	Gold	Cesium nanowire
		
Graphite	Cold nickel	Quantum corral

Generic
Surface Spectroscopy



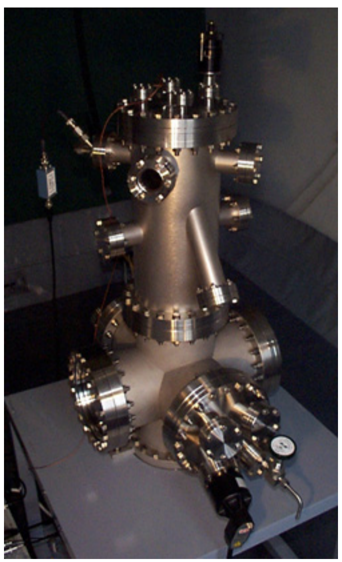
- Particles can be: electrons, ions, photons, atomic or molecular particles, heat, others…
- Experiments are designed to probe outermost few Å's of surface
- Techniques in our laboratory include x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), ion scattering spectroscopy (ISS), electron stimulated desorption (ESD), scanning tunneling microscopy (STM), and others...

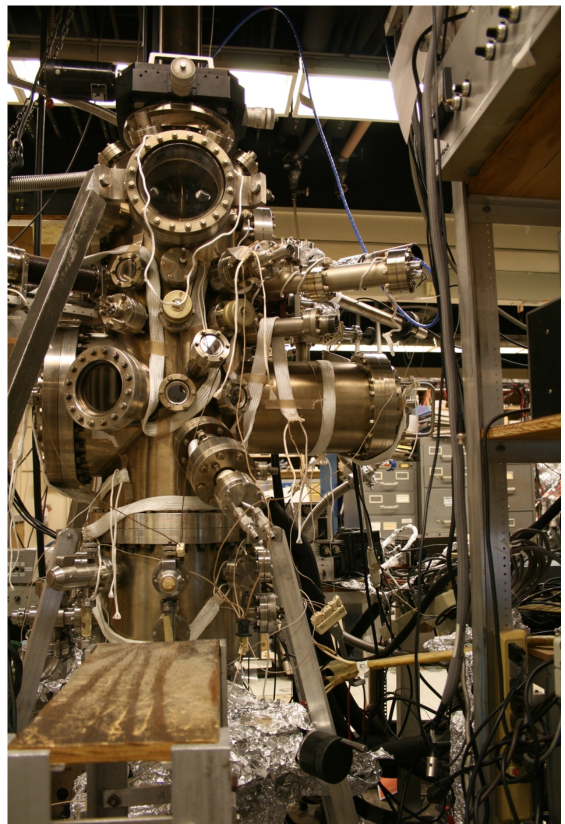
A few techniques:

STM	RBS	TYP
AFM	EELS	EXAFS
NSOM	HREELS	NEXAFS
LEED	PES	SEXAFS
AES	ARPES	PED
ESD	ARUPS	XPS
ESDIAD	RHEED	ESCA
PSD	TEM	SPV
PSDIAD	STEM	LERS
ISS	REM	SAM
LEIS	TED	MQS
MEIS	HREM	TDS
HEIS	AREELS	TPS
ICISS	UPS	TPD
ALICISS	IPS	SXPS
SIMS	CITS	FIM

Ultra-High Vacuum (UHV)

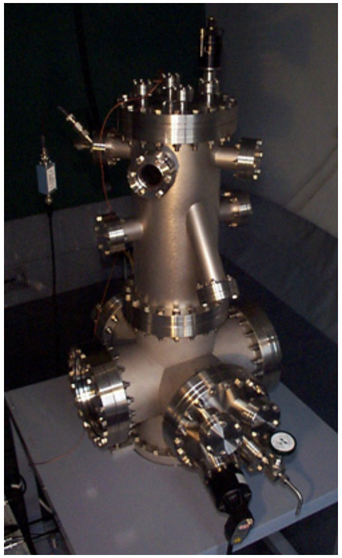
- On the order of 1 x 10^{-10} torr
- UHV is achieved with all-metal chambers that are baked to remove water and other adsorbed gases from the walls, and are evacuated with oil-free pumps
- **Why do we need UHV?**

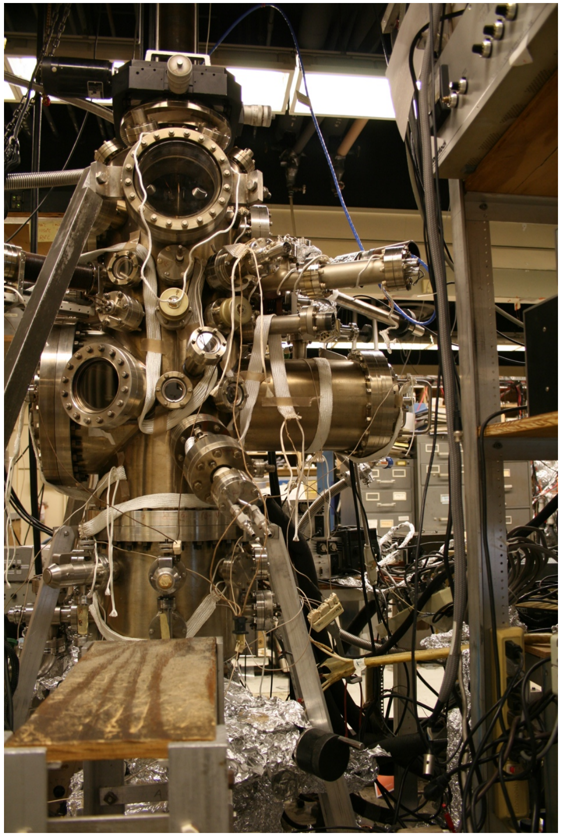




Ultra-High Vacuum (UHV)

- On the order of 1×10^{-10} torr
- UHV is achieved with all-metal chambers that are baked to remove water and other adsorbed gases from the walls, and are evacuated with oil-free pumps
- **Needed to insure that surfaces remain clean**



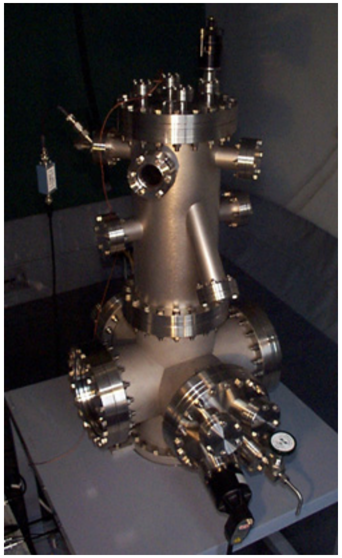


Vacuum Requirements

Ultra-High Vacuum (UHV)

- On the order of 1×10^{-10} torr
- Needed to insure that surfaces remain clean
- UHV is achieved with all-metal chambers that are baked to remove water and other adsorbed gases from the walls, and are evacuated with oil-free pumps
- Unit of exposure is defined as:

$$1 \text{ Langmuir} = 1 \text{ L} = 1 \times 10^{-6} \text{ torr-seconds}$$

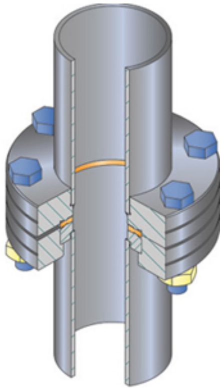


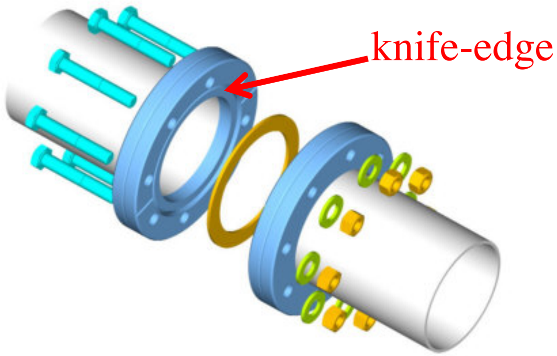
- This corresponds to each surface atom seeing one gas molecule if all molecules stick, then 1 L will completely cover the surface
- Thus, a sample can be left in UHV for:

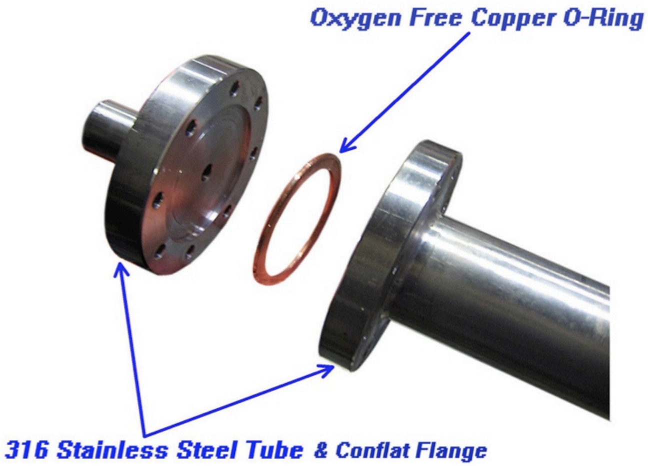
$$10^{-6} \text{ torr-sec}/10^{-10} \text{ torr} = 10^{4} \text{ seconds} = 2.7 \text{ hours}$$

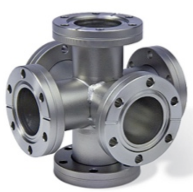
Ultra-High Vacuum (UHV)

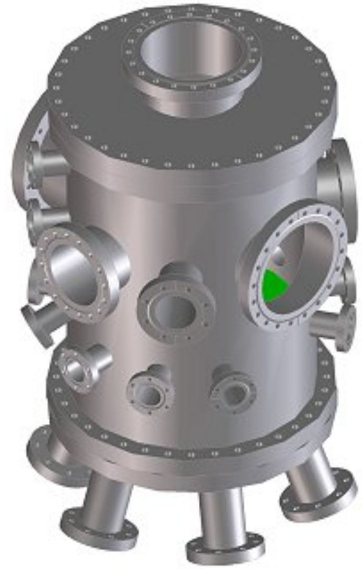
CONFLAT flanges

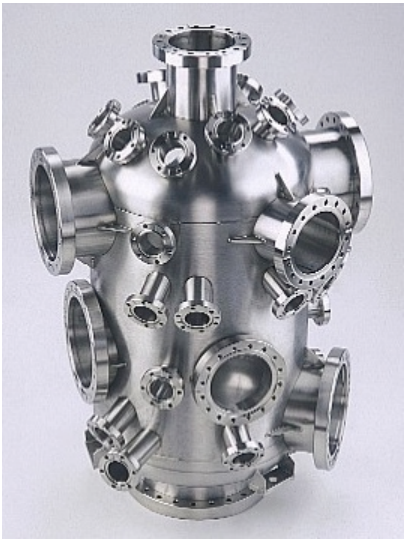






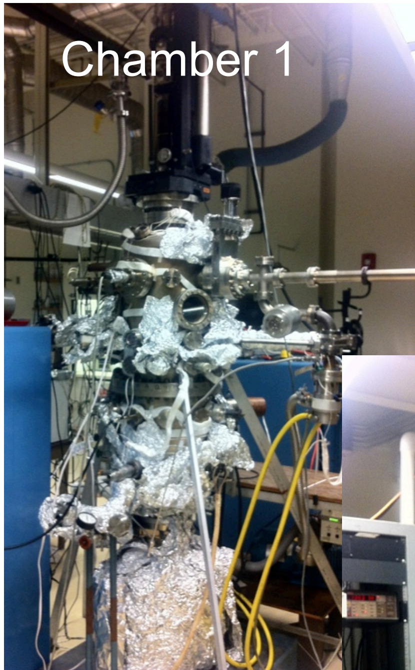


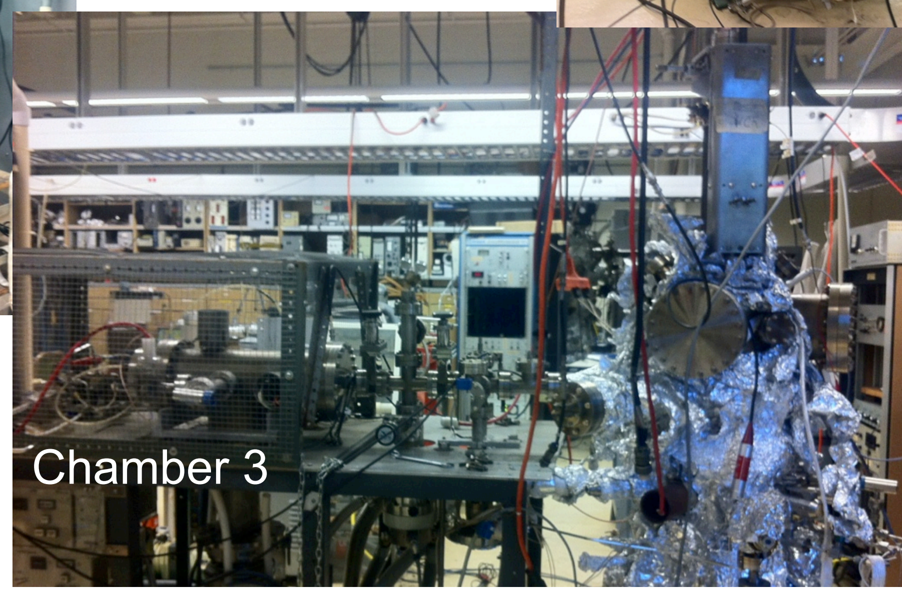





The Yarmoff Lab

The Yarmoff Lab





The Yarmoff Group

UNIVERSITY OF CALIFORNIA UCRIVERSIDE

Current Graduate Students
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Haoshan “Shawn” Zhu

Current Undergrads
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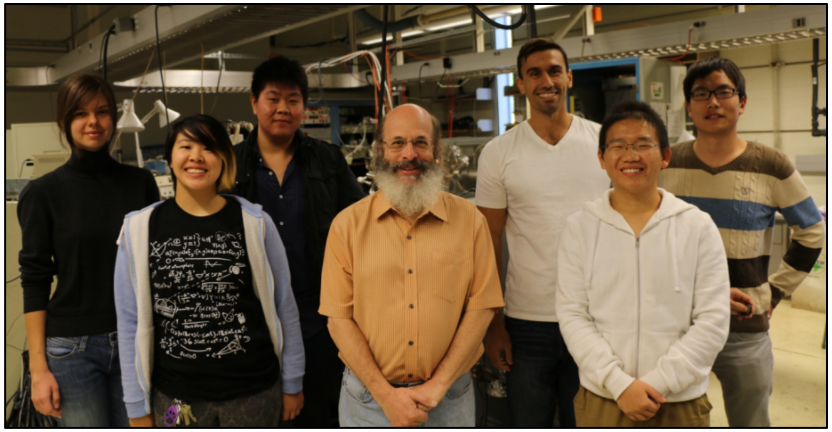
Summer Intern
Bradley Erwin



Former Postdocs
Snow Balaz - *now at Youngstown State University*
Prasanta Karmakar - *now at Bhaba Atomic Research Centre*
David Shuh - *now at LBNL*

Former Graduate Students
C. Wayne Lo - *Applied Materials*
Varoujan Chakarian - *KLA Tencor*
Tom D. Durbin - *UCR Center for Environmental Research*
Kristine A. H. German - *Xerox Webster Research Center*
Wei Kevin Wang - *Ericsson*
Patrick R. Varekamp - *IBM*
Chris B. Weare - *Microsoft*
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S. Roger Qiu - *Lawrence Livermore National Laboratory (LLNL)*
Ye Yang - *KLA Tencor*
Frank Liu - *Lehigh University*
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Weimin Zhou - *UCR Dept. of Physics & Astronomy*

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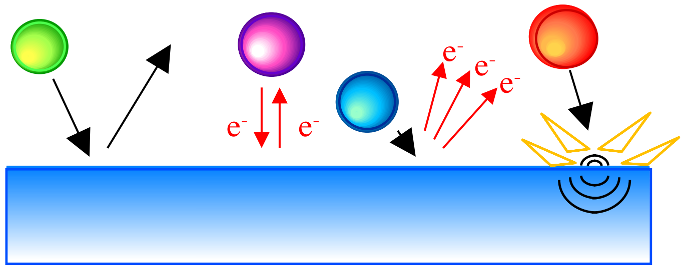
Jing Shi - *UC Riverside*

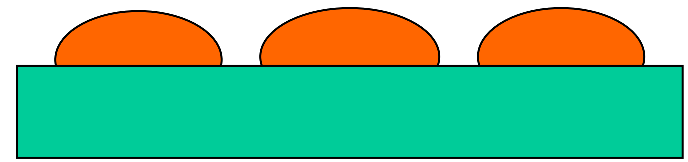
Funding:
National Science Foundation
Army Research Office
Center for Nanoscale Innovation for Defense
UCR College of Natural and Agricultural Sciences

Projects

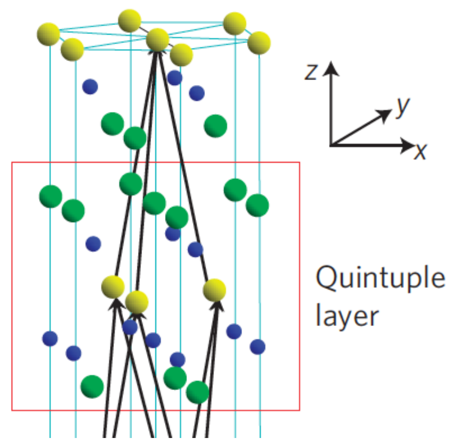
Ion-surface interactions



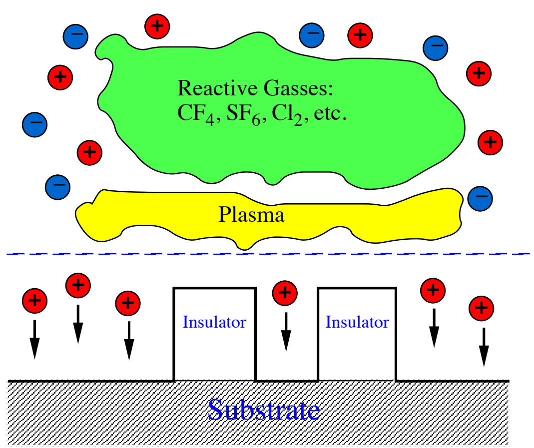
Fabrication and characterization of nanomaterials



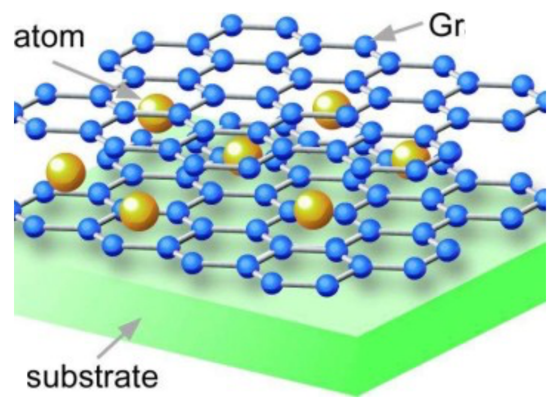
Surface structure of topological insulators



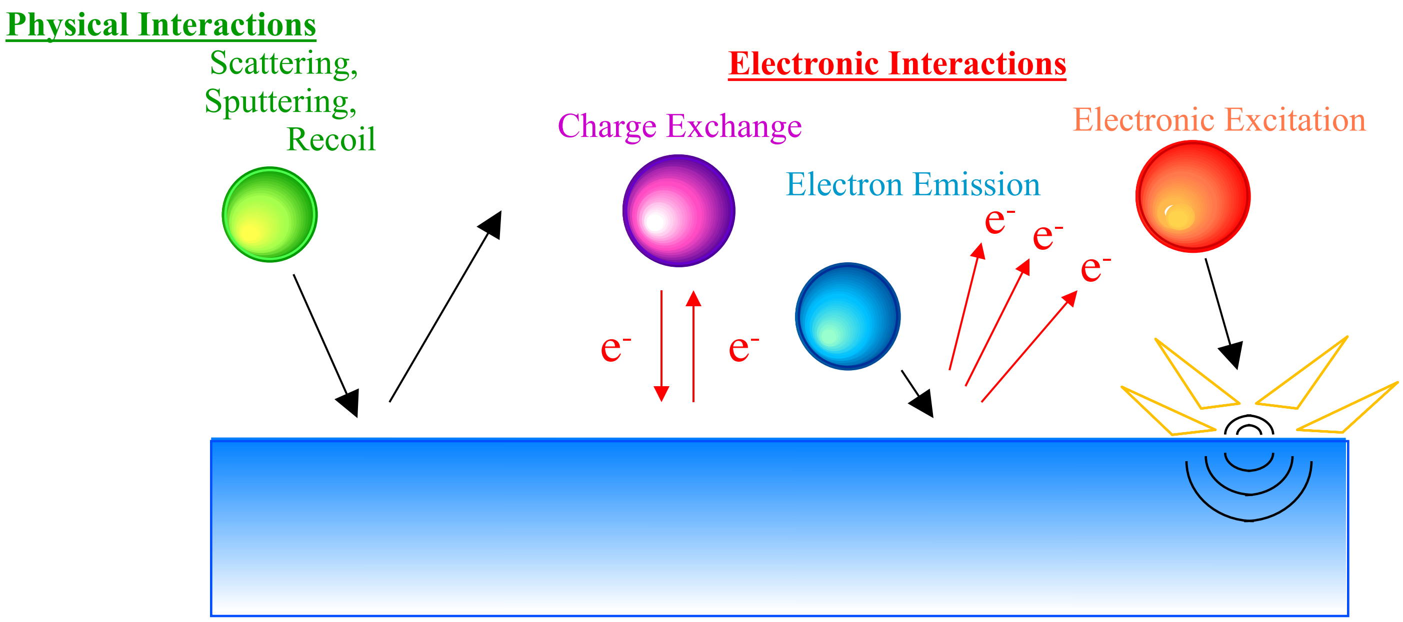
Semiconductor surface etching



Defects and intercalation in graphene



Ion-Surface Interactions



- Ion-surface interactions are important in many technical applications, such as:

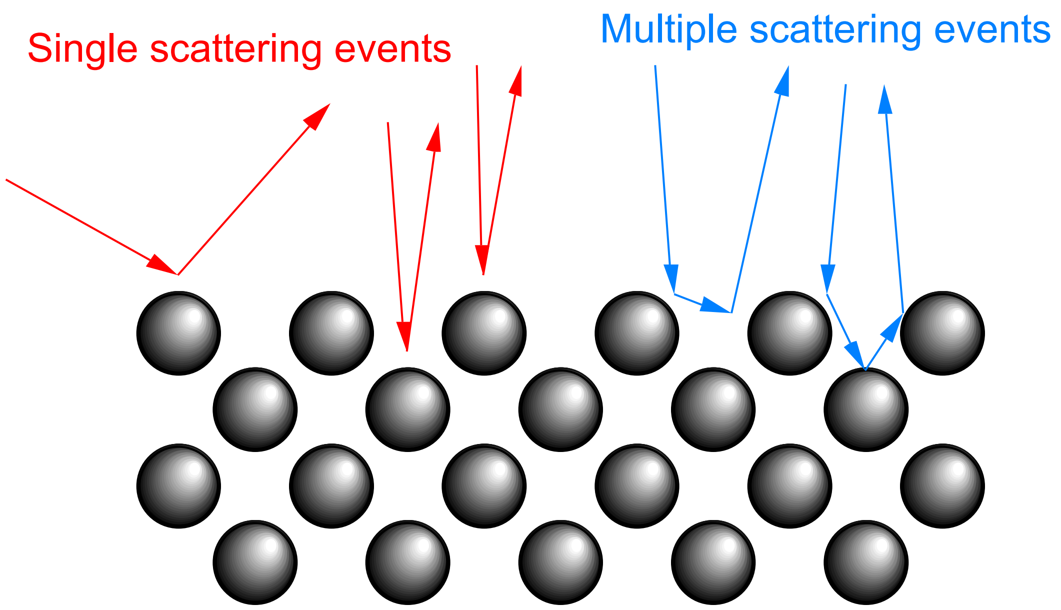
  Surface Chemical Reactions
  Plasma Processing
  Secondary Ion Mass Spectrometry (SIMS)
  Ion Implantation
  Stimulated Desorption (ESD, PSD,…)

- Ion-surface interactions can be classified as:

  Physical Interactions
  Scattering, sputtering, recoiling, etc.
  → Energy loss is due to *elastic scattering*

  Electronic Interactions
  Charge transfer (neutralization, ionization)
  Electronic excitation (substrate, projectile)
  Electron emission
  → Energy loss is due to *inelastic scattering*

Ion Scattering Spectroscopy



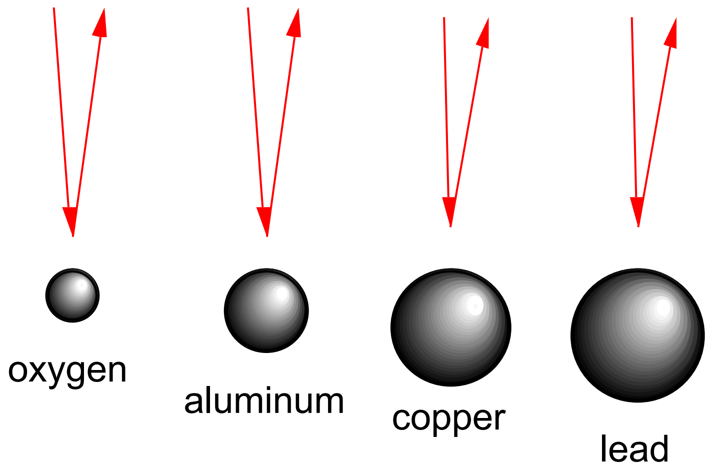
Binary collision approximation (BCA):

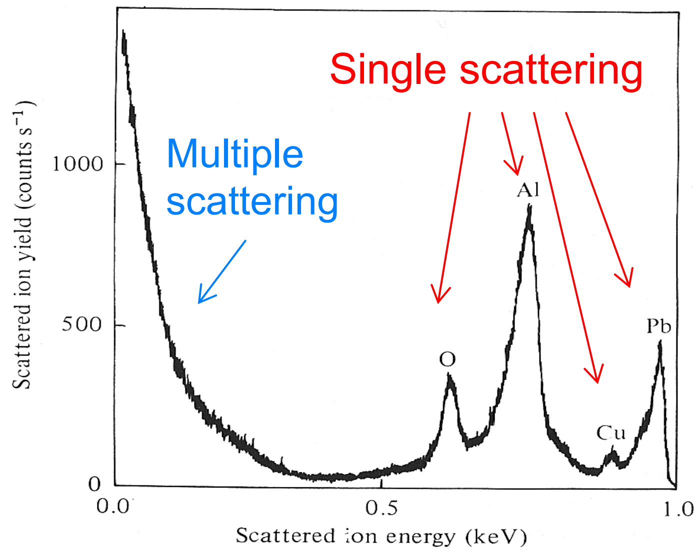
- Ions interact with one substrate atom at time
- Sequence of binary collisions with target atoms positioned at lattice sites

What would a measurement of the energy of the scattered ions tell you about the surface?

Ion Scattering Spectroscopy

Single scattering events





E. Taglauer and W. Heiland, Appl. Phys. **9**, 261 (1976).

The energy spectrum provides the mass distribution of surface atoms.

Binary collision approximation (BCA):

- Ions interact with one substrate atom at time
- Sequence of binary collisions with target atoms positioned at lattice sites
- Single scattering peak (SSP) is seen for each type of surface atom.

Elastic energy loss during single collision:

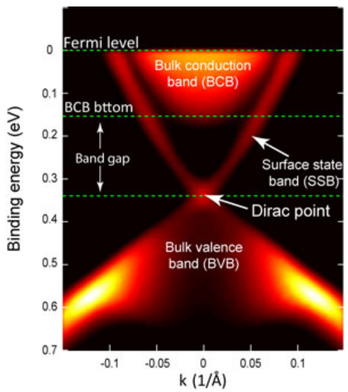
$$\frac{E_S}{E_0} = \left[\frac{\cos\theta \pm \left[\left(\frac{M_T}{M_P} \right)^2 - \sin^2\theta \right]^{1/2}}{1 + \left(\frac{M_T}{M_P} \right)} \right]^2$$

E_0 – incident energy
E_S – scattered energy
θ – scattering angle
M_T – mass of target atom
M_T – mass of projectile

Topological Insulators

- Topological Insulator's are insulators in the bulk, but conduct along the surface or edge via topological surface states (TSS).

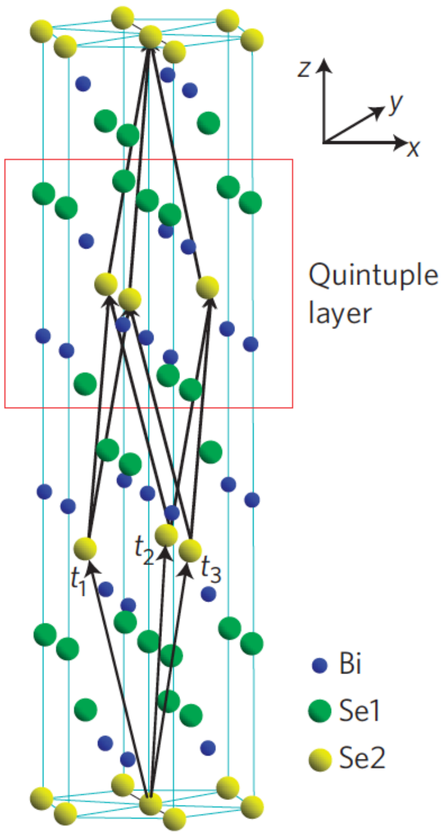
- Applications include:
  - Spintronics devices
  - Quantum computing
  - Superconductors
  - More…



- $(Bi,Sb)_2(Te,Se)_3$ family of compounds are TI's that are 2D materials composed of Quintuple Layers.

- The TSS of Bi_2Se_3 form a simple Dirac cone, its has a practical band gap of 0.3 eV, and it's easy to grow single crystals.

- Problems exist with these materials, however, including the aging effect.

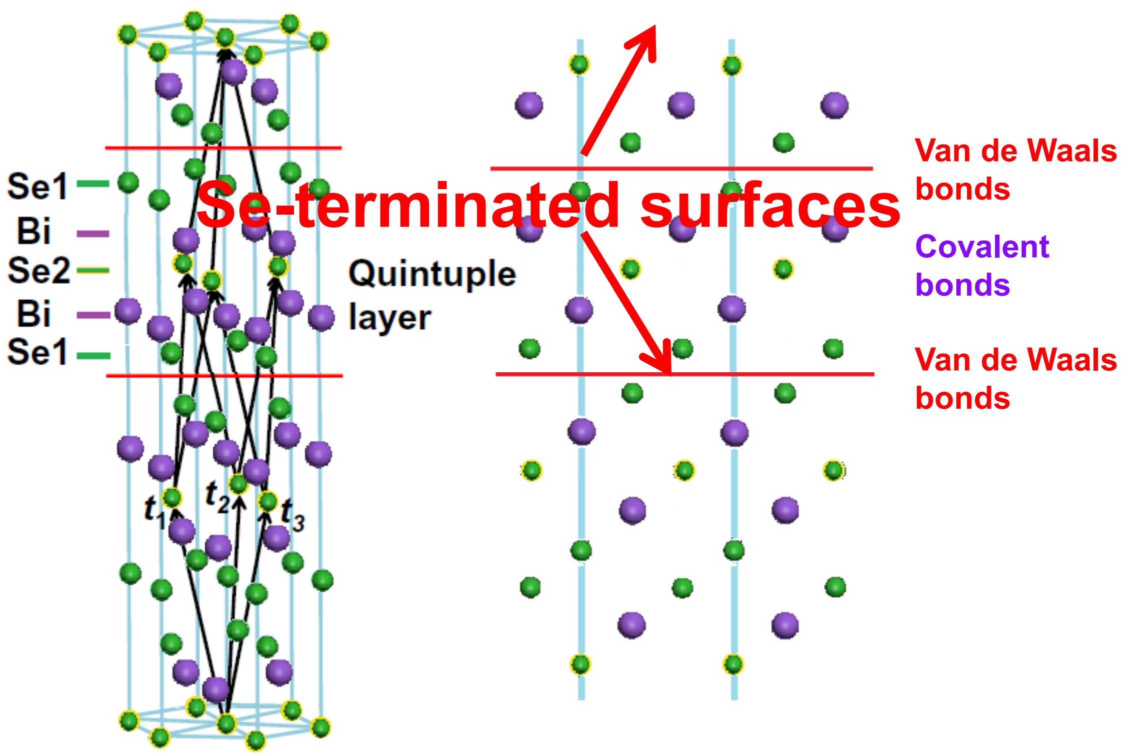


Bi_2Se_3

Crystal Structure

Quintuple layer structure

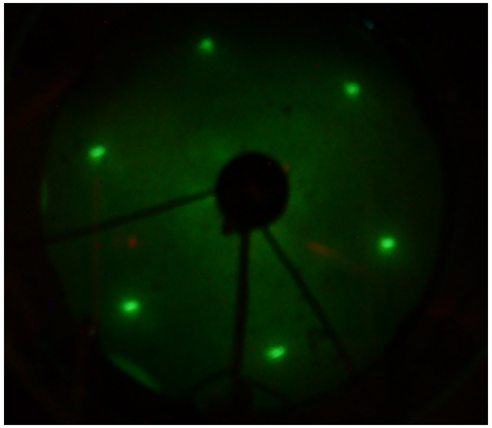
- view from side



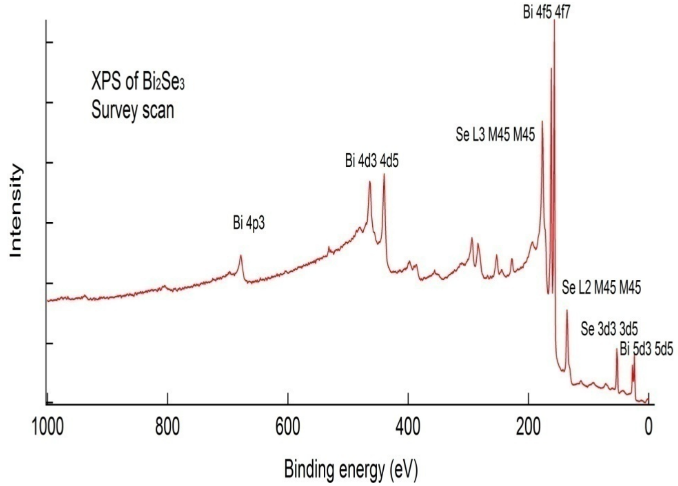
Surface analysis measurements

Following *in situ* cleaving

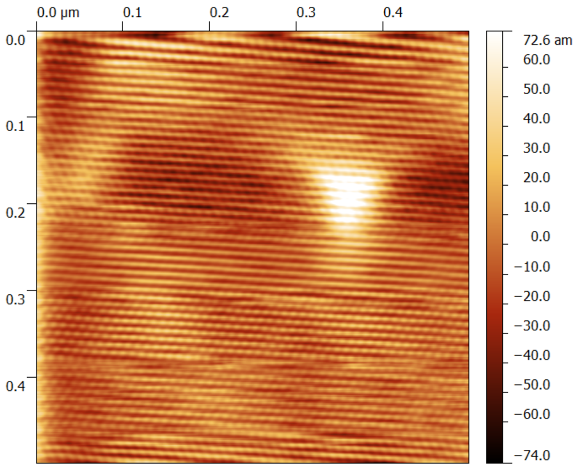
Low energy electron diffraction (LEED)



X-ray photoelectron spectroscopy (XPS)



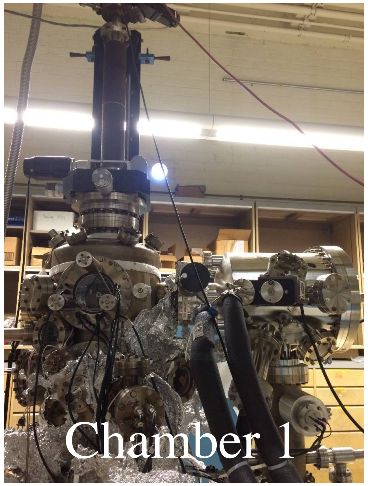
Scanning tunneling microscopy (STM)

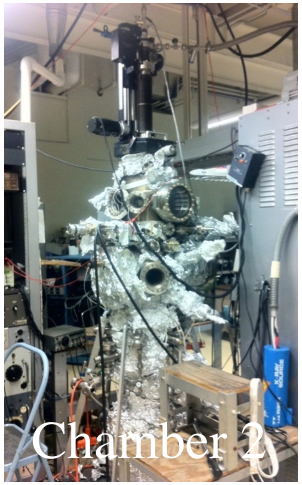


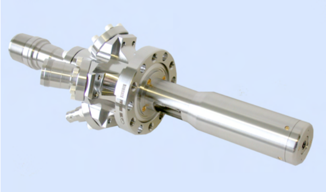
- Sample is well-ordered single crystal with 1x1 unit cell
- No detectable contamination
- Atomic resolution with sub-surface triangular defects seen, consistent with the literature

Thanks to Ludwig Bartels for the STM images

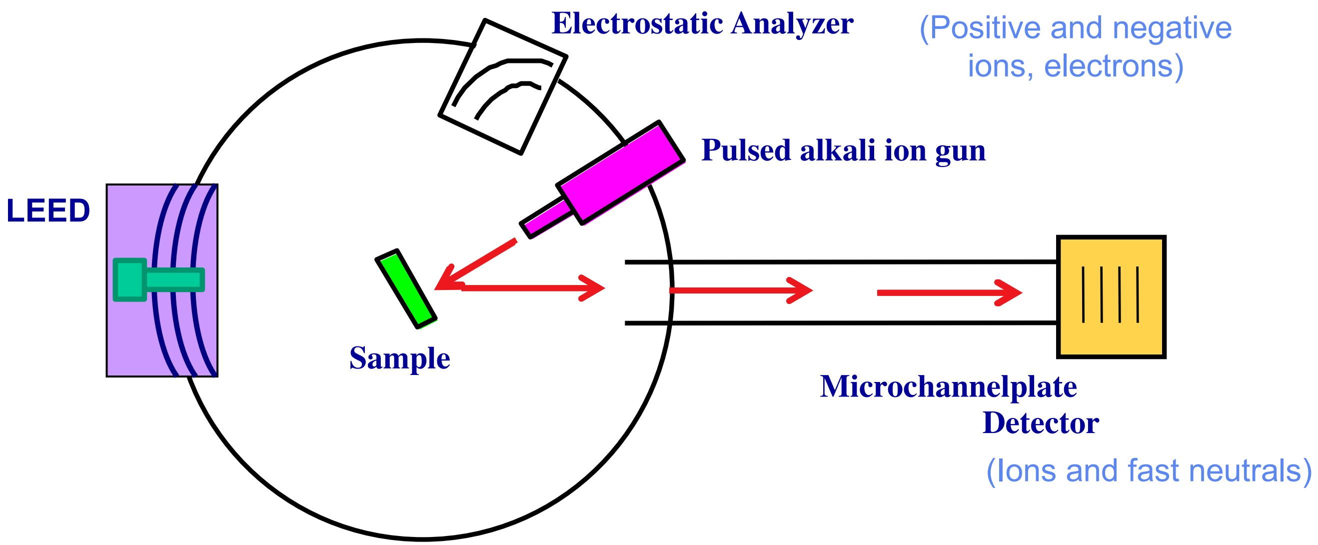
Experimental setup







Kimball Physics IGS-4



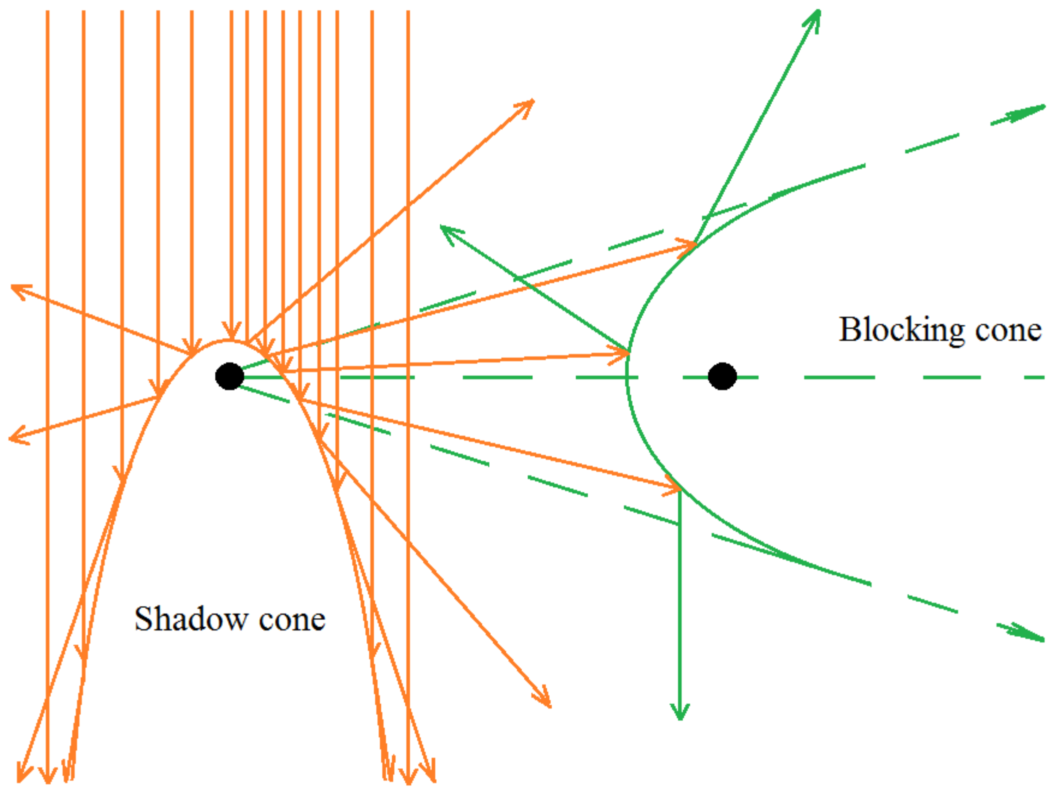
Time-of-flight (TOF) spectroscopy

- Pulsed ion beam: frequency 80 kHz, pulse width ~40 ns
- All scattered particles collected so that neutralization does not play a role
- Fluence kept to less than 1% of a ML to limit damage

Chamber 1: Sample orientation and scattering angle variable, sample transfer with attached MBE chamber

Chamber 2: Cooling with LN_2 or LHe

Shadow and Blocking Cones



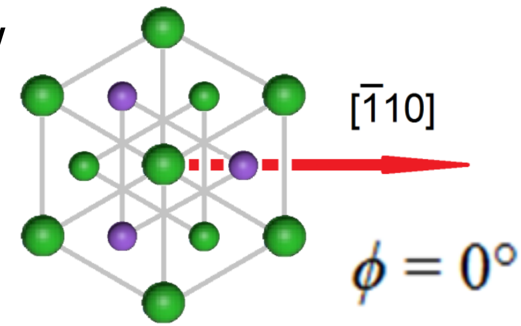
- A shadow cone is the region behind a target atom from which the incoming beam is excluded due to scattering
- A blocking cone is the region behind a first layer target atom from which the ions scattered from below are excluded
- They are constructed by mapping out all possible trajectories

Double Alignment Orientation

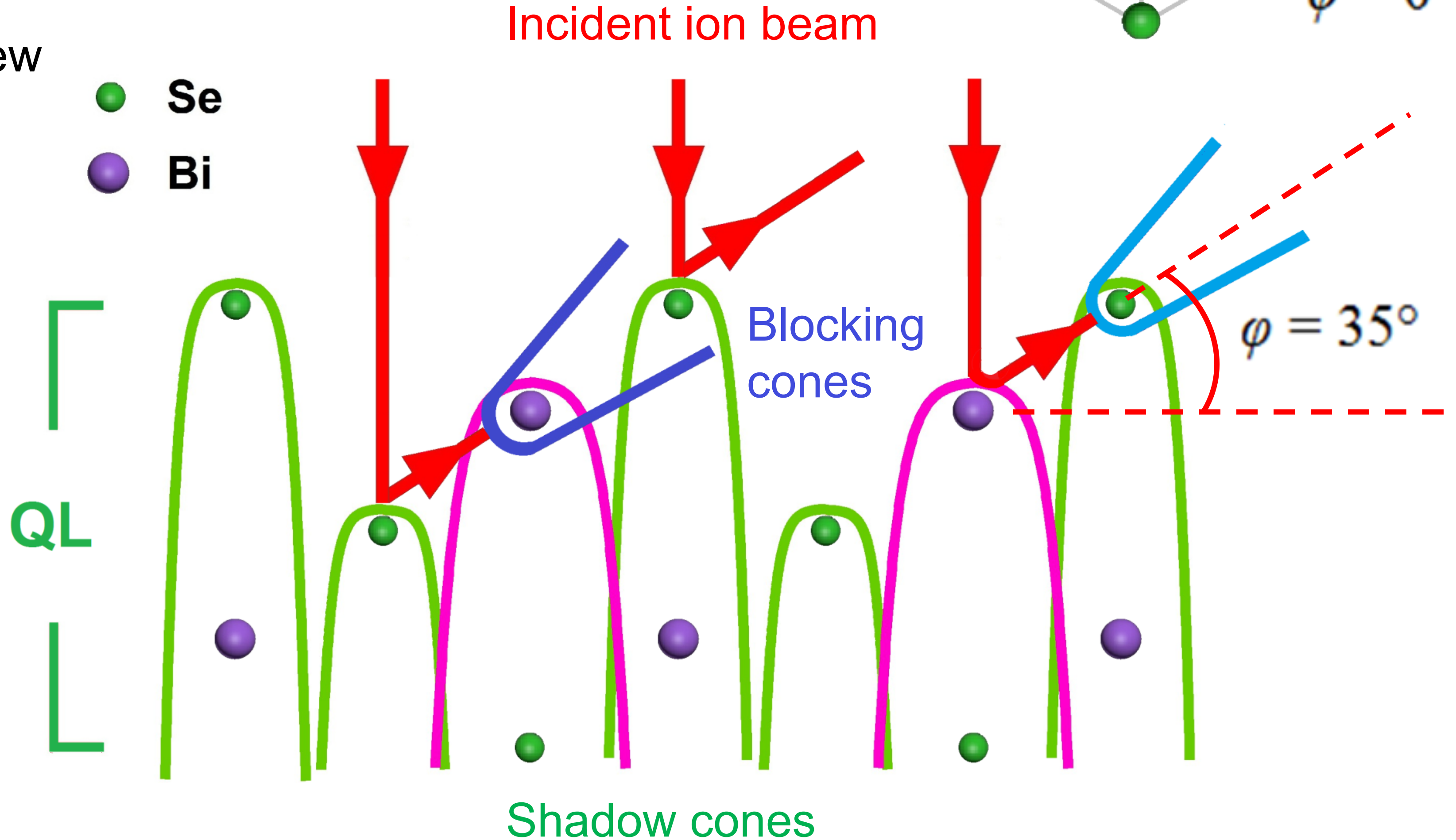
Polar angle: $\phi = 35°$

Azimuth: $\varphi = 0°$

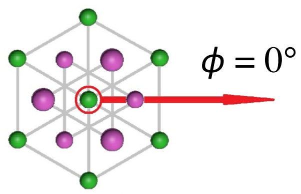
Top view



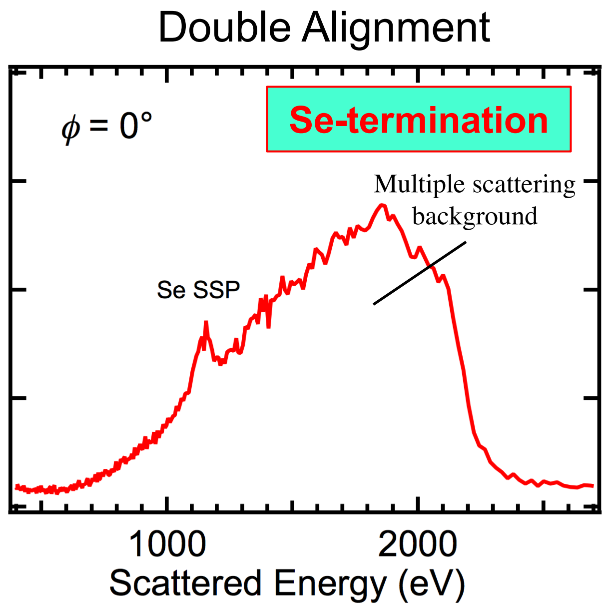
Side view

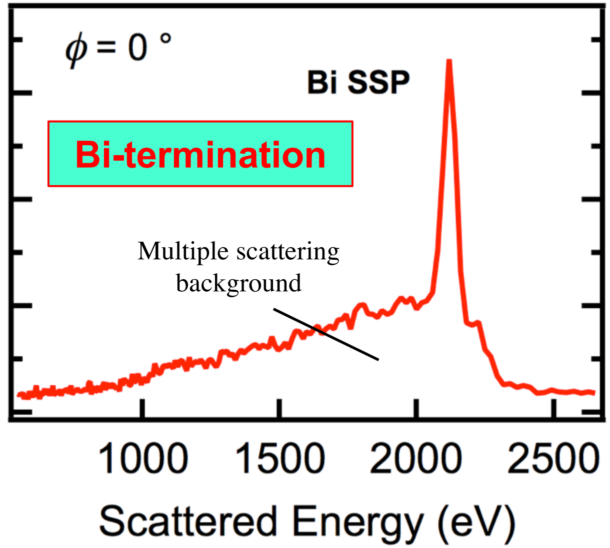


Double Alignment

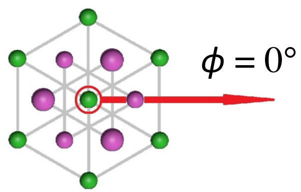


- In <u>double alignment</u>, the samples can show either Se or Bi-termination

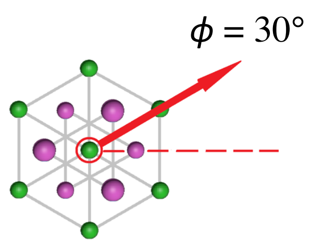




Double/Single Alignment

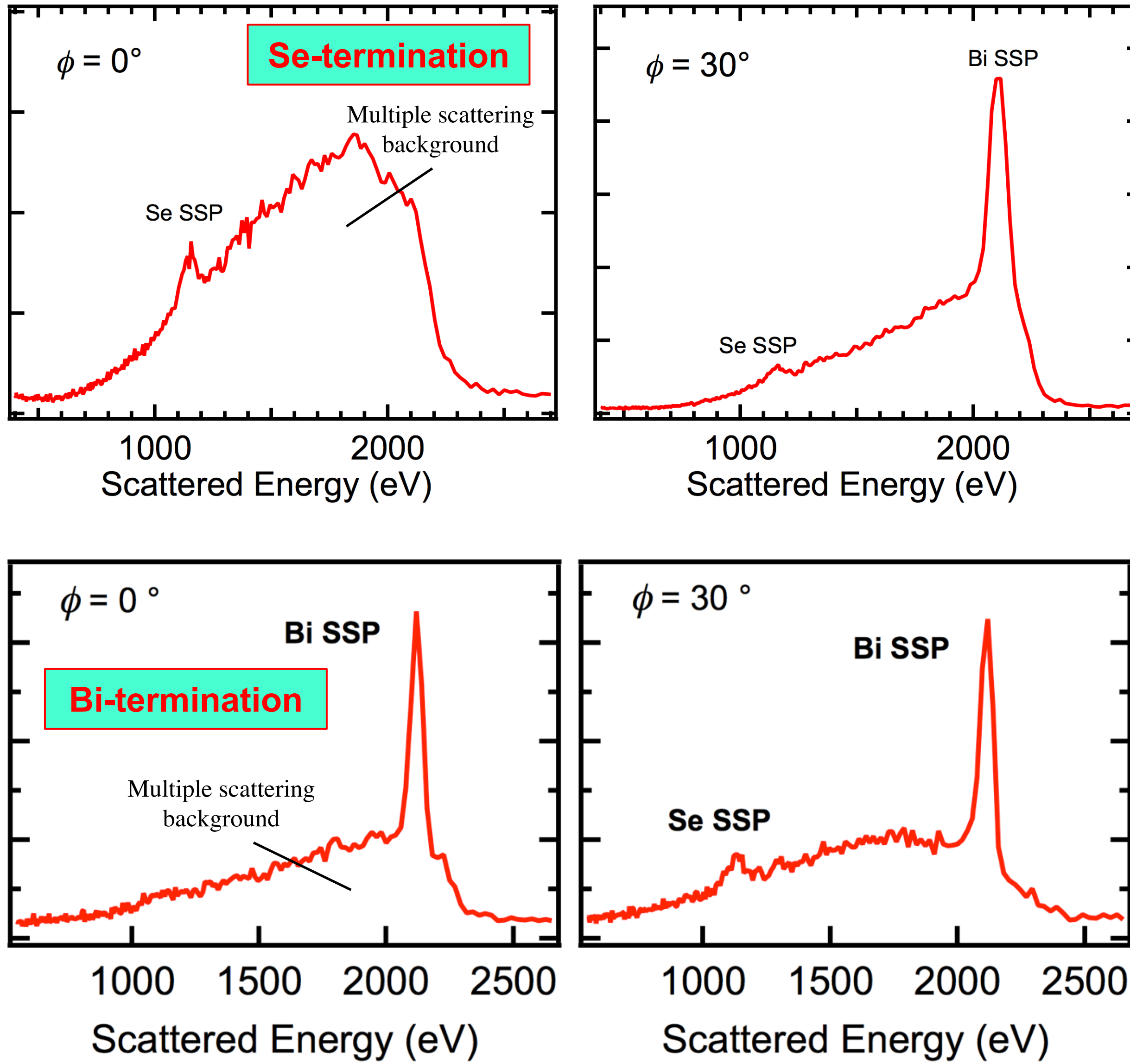


- In <u>double alignment</u>, the samples can show either Se or Bi-termination



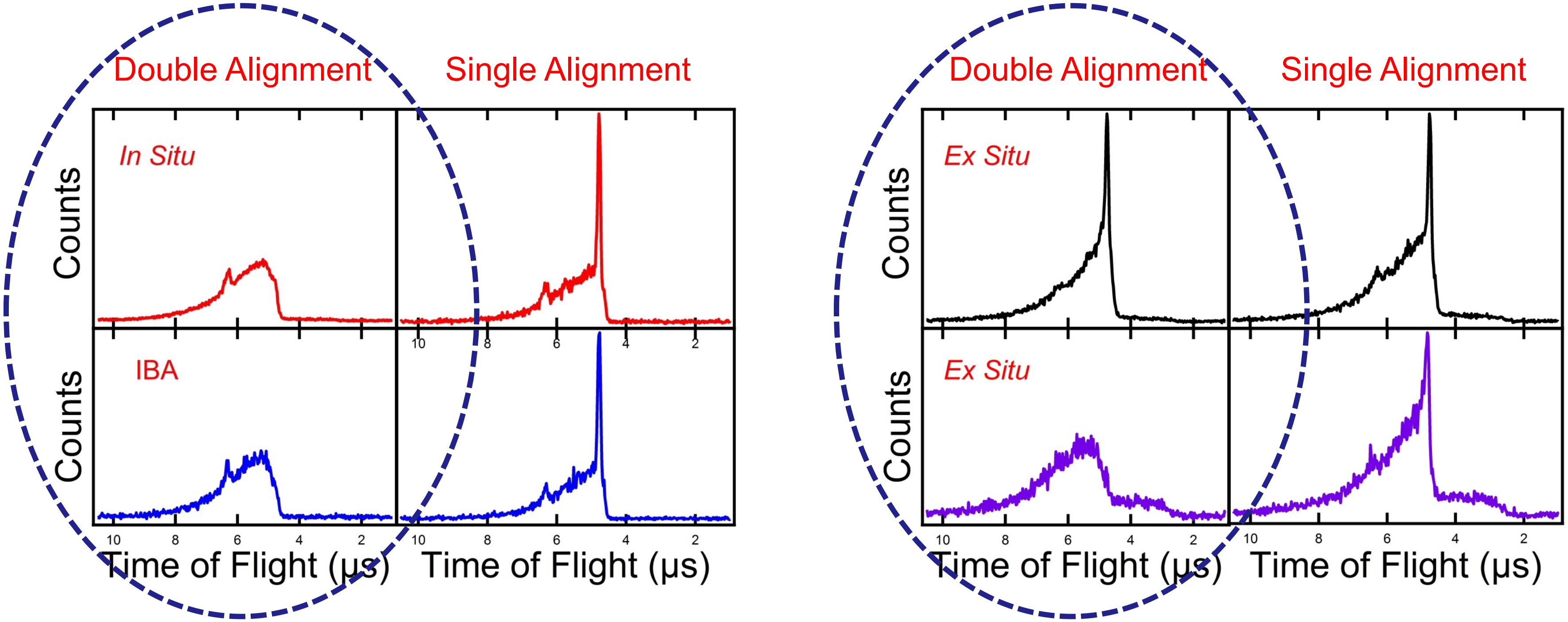
- Rotating by 30° leads to a <u>single alignment</u> orientation that reveals the 2nd layer atoms

Double Alignment | Single Alignment



Sample Preparation methods:

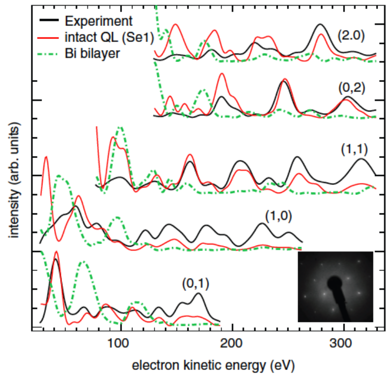
1. ***In situ* cleaving** in UHV
2. **Ion bombardment and annealing (IBA)**
3. ***Ex situ* cleaving** in air using scotch or carbon tape



- *In situ* cleaving and IBA both lead to Se-termination
- More detailed measurements of the angular distribution of scattered ions indicate the same surface atomic structure

- *Ex situ* cleaving leads to either Se- or Bi-termination

Other recent work



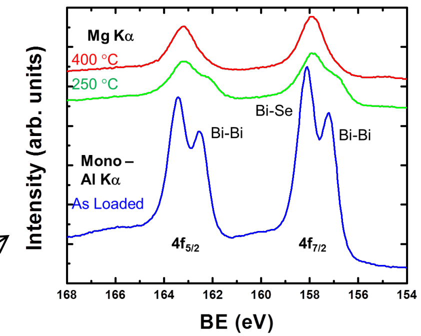
There are mixed reports in the literature.

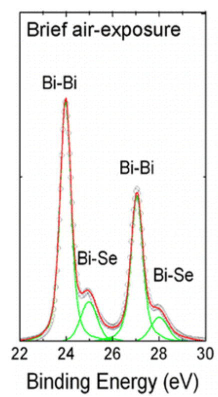
Se-terminated
LEED and x-ray diffraction
de Rios, et al., Phys. Rev. B **88**, 041404 (2013)

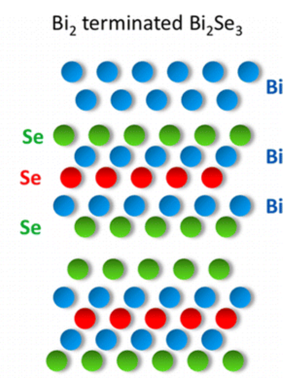
50-50 mixture of Te- and Bi-terminations
STM
Coelho, et al., Nano Lett. **13**, 4517 (2013)

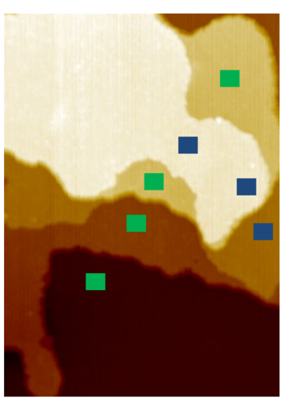
Sometimes Se, sometimes Bi
XPS
Hewitt, et al., J. Vac. Sci. Technol. B **32**, 04E103 (2014)

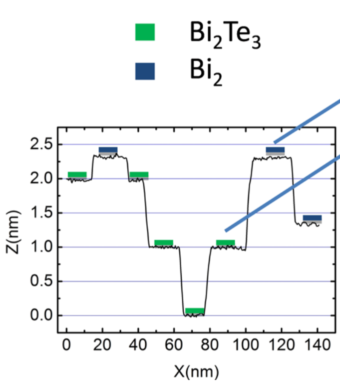
Air exposure leads to Bi termination
Synchrotron XPS
Edmonds, et al., J. Phys. Chem. C **118**, 20413 (2014)

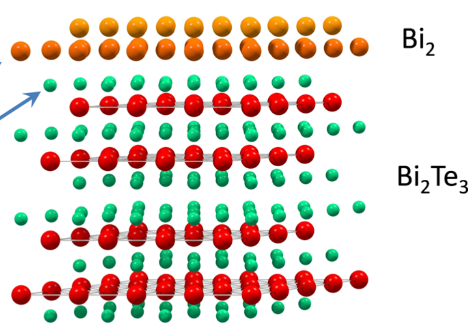












Conclusions

Contamination Effects the Surface Structure

- The surface of *ex situ* cleaved samples can be either Se-terminated or Bi-terminated. The termination change may be related to intercalation of atmospheric contaminants.

- The samples that are cleaved *in situ* or prepared by IBA have minimal contamination and are Se-terminated.

Future Directions

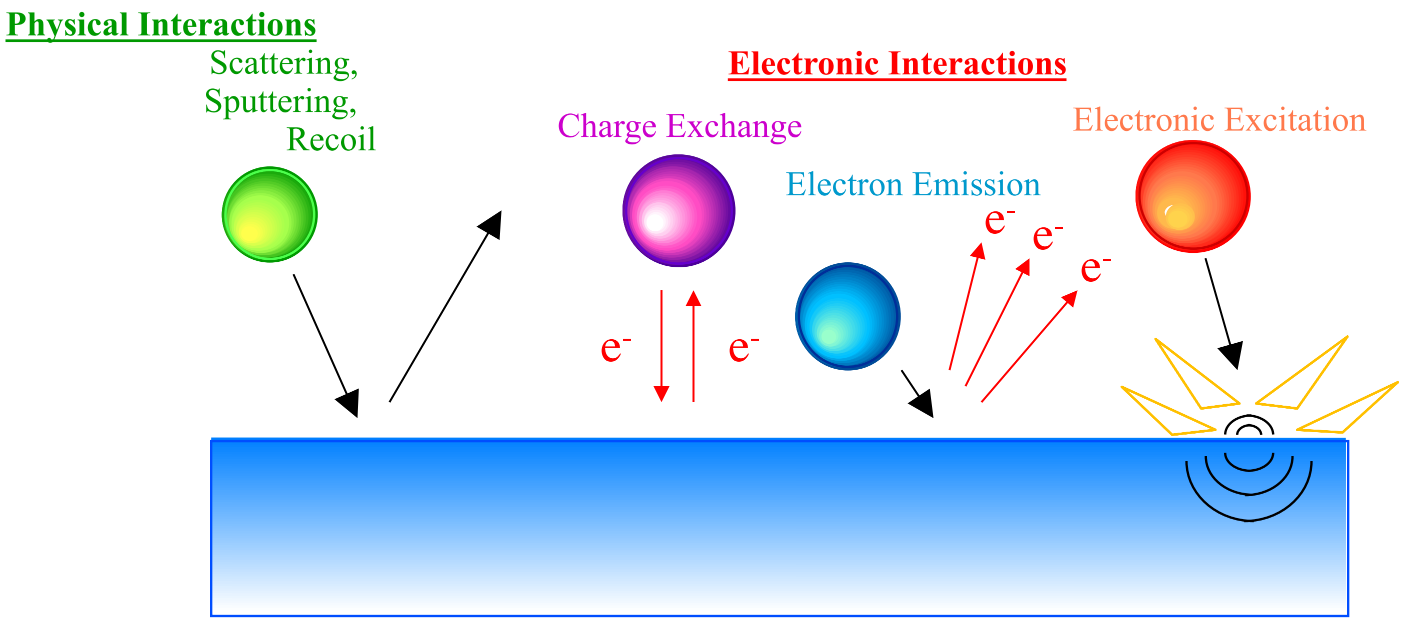
- Alter the stoichiometry and other parameters in the sample preparation to investigate how this affects the termination.

- Exposure the clean surface to reactants, such as O_2, H_2O, N_2O, halogens, etc., to monitor how surface contamination leads to a termination change.

- Grow materials by molecular beam epitaxy (MBE).

- Investigate other related materials.

Ion-Surface Interactions



- Ion-surface interactions are important in many technical applications, such as:

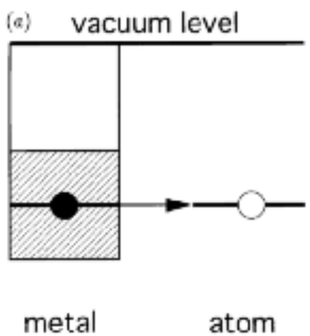
  Surface Chemical Reactions
  Plasma Processing
  Secondary Ion Mass Spectrometry (SIMS)
  Ion Implantation
  Stimulated Desorption (ESD, PSD,…)

- Ion-surface interactions can be classified as:

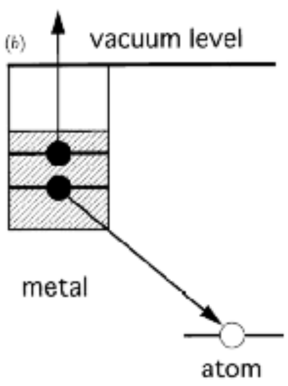
  Physical Interactions
  Scattering, sputtering, recoiling, etc.
  → Energy loss is due to *elastic scattering*

  Electronic Interactions
  Charge transfer (neutralization, ionization)
  Electronic excitation (substrate, projectile)
  Electron emission
  → Energy loss is due to *inelastic scattering*

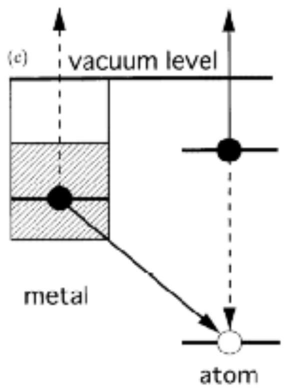
Charge transfer processes in ion-surface collisions



Resonant charge transfer (RCT)



Auger neutralization



Auger de-excitation

- Resonant charge transfer (RCT) of electrons between atomic and metal states at constant energy

  Ionization/affinity level overlaps conduction band:

  alkali, halogen, oxygen ions

  Reversible; final charge state determined along exit trajectory

- Auger processes involve the relaxation of the excited atom-surface system

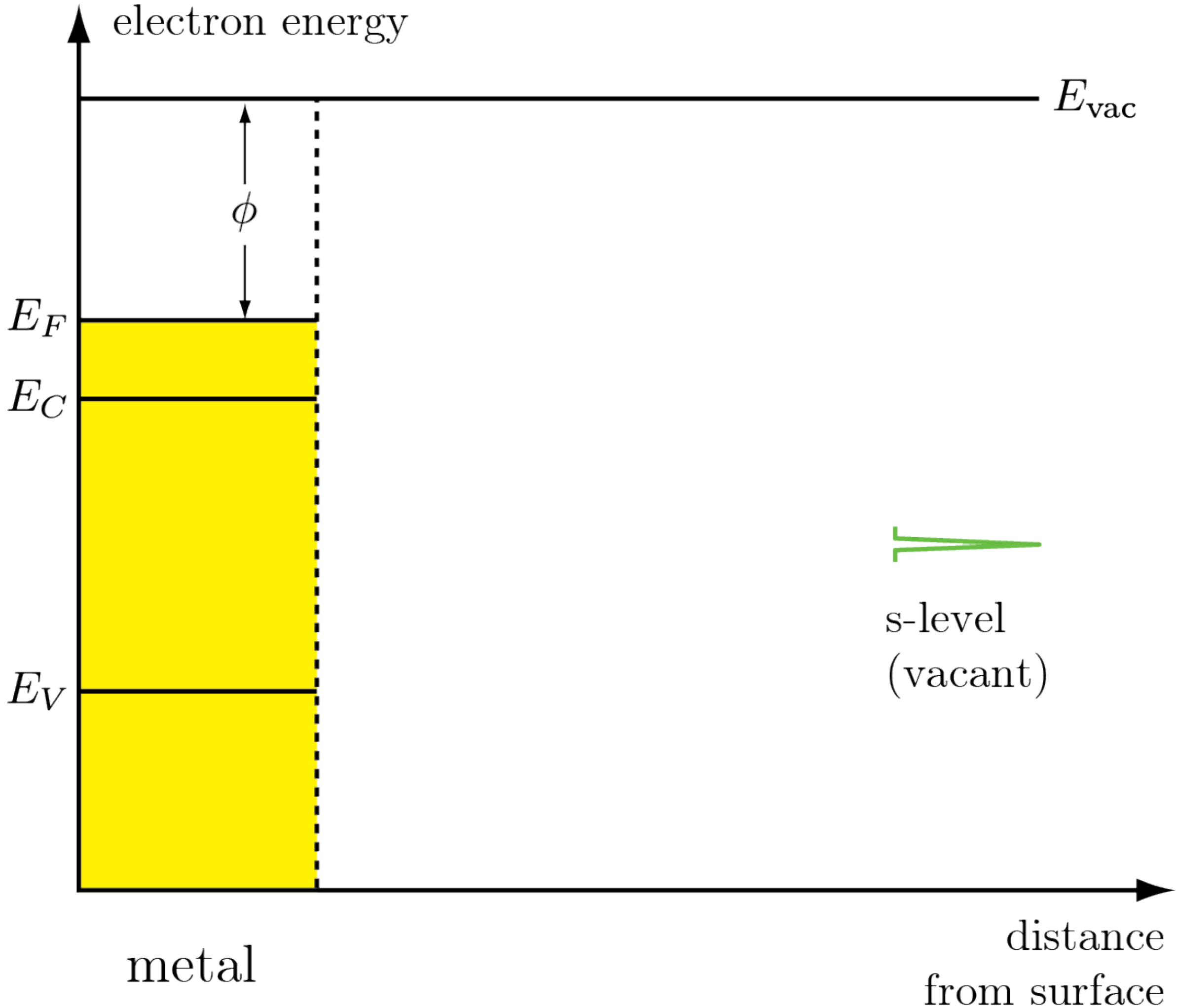
  Ionization level below conduction band:

  noble gas ions

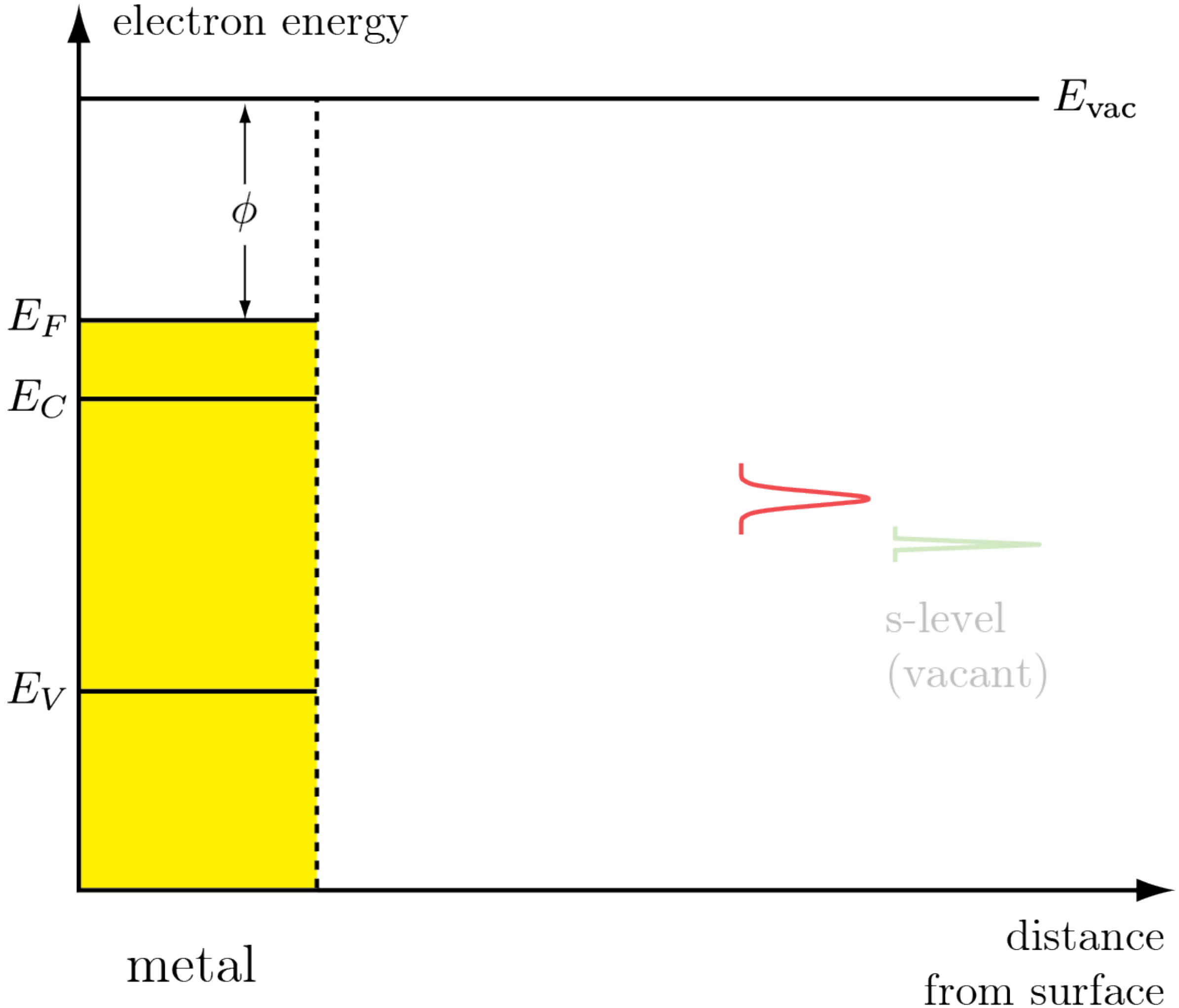
  Irreversible; neutralization can occur anytime during scattering

- Other processes involve inner shell electrons of the projectile and of the target surface

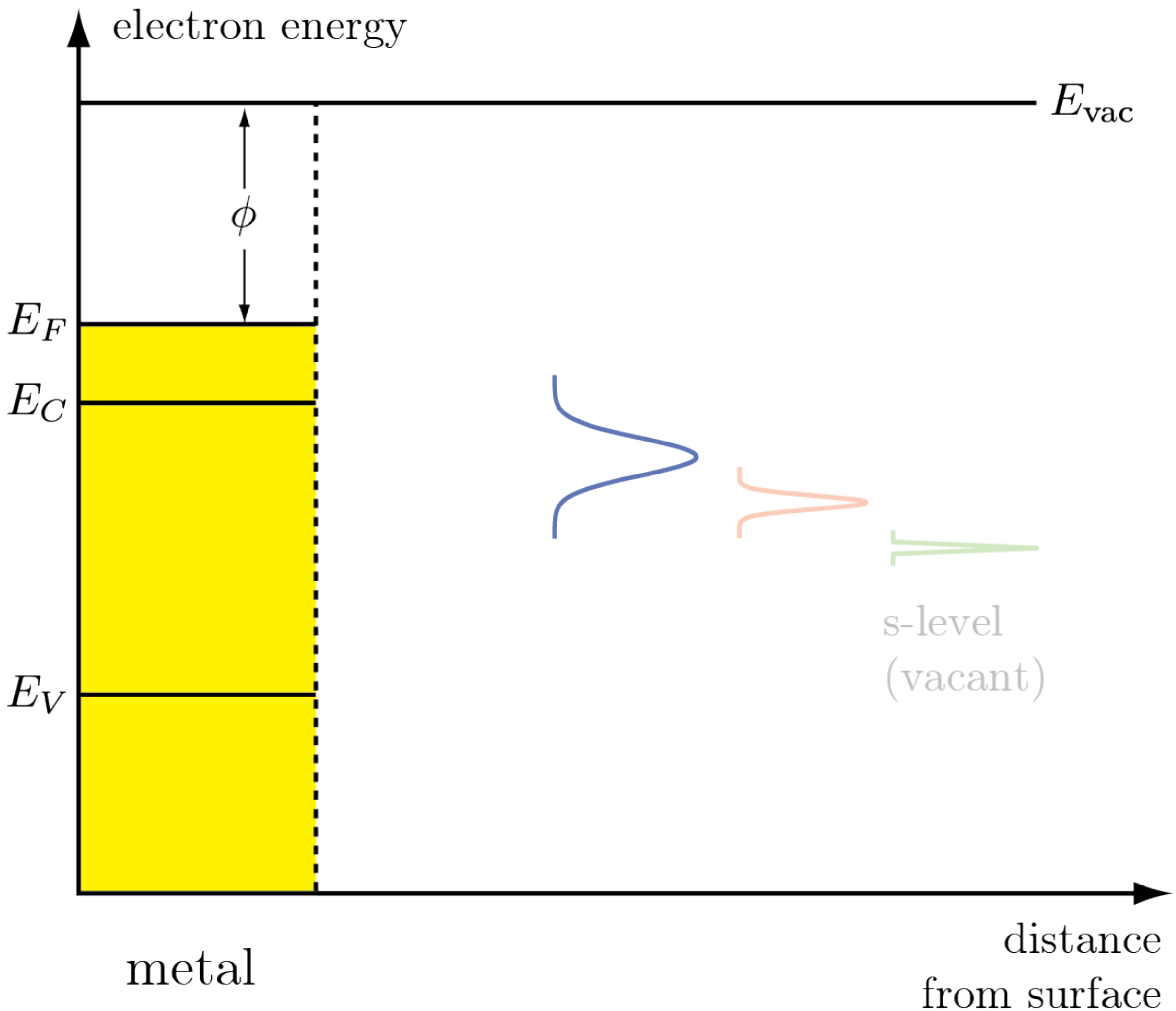
Resonant Charge Transfer (RCT)



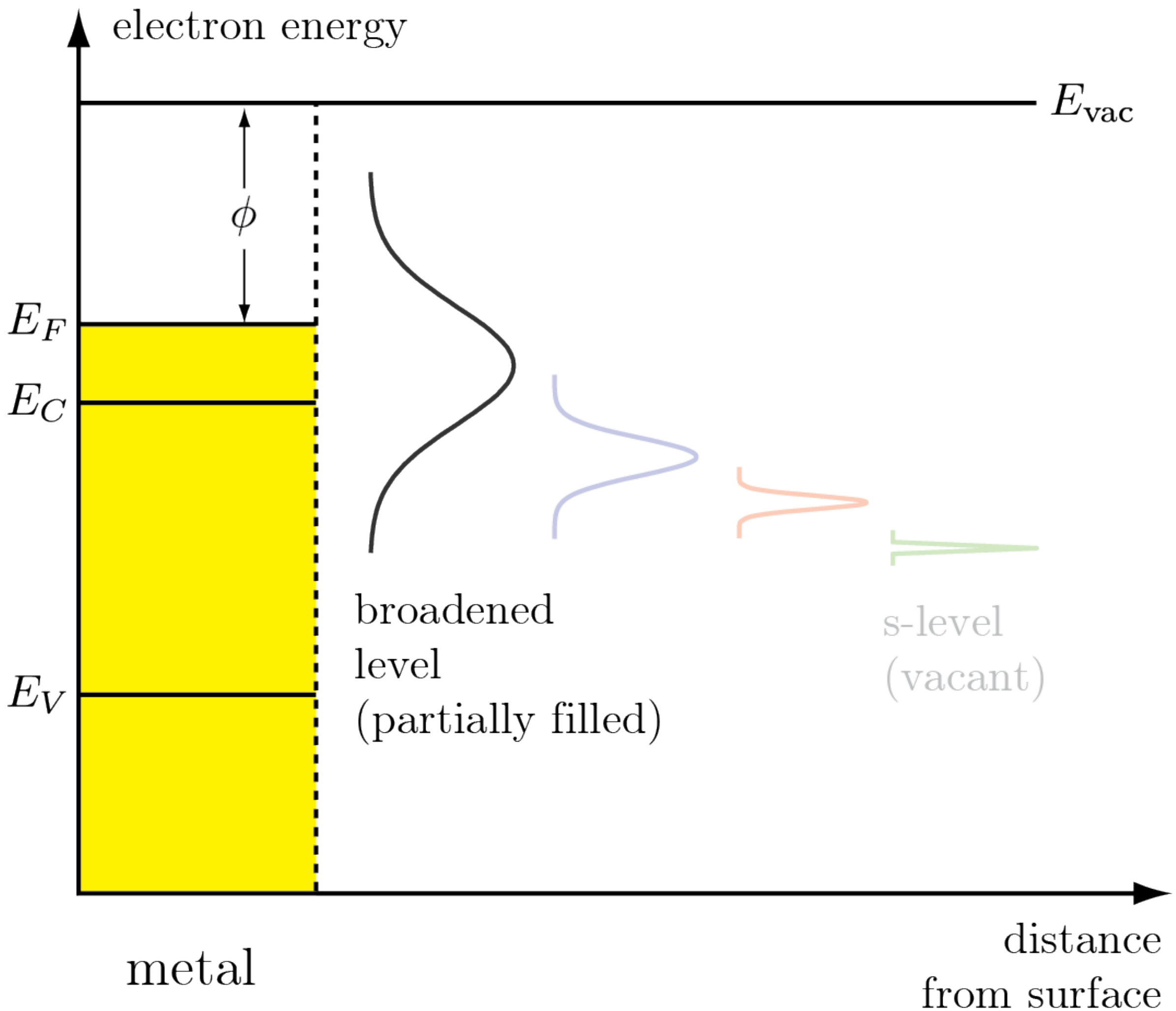
Resonant Charge Transfer (RCT)



Resonant Charge Transfer (RCT)

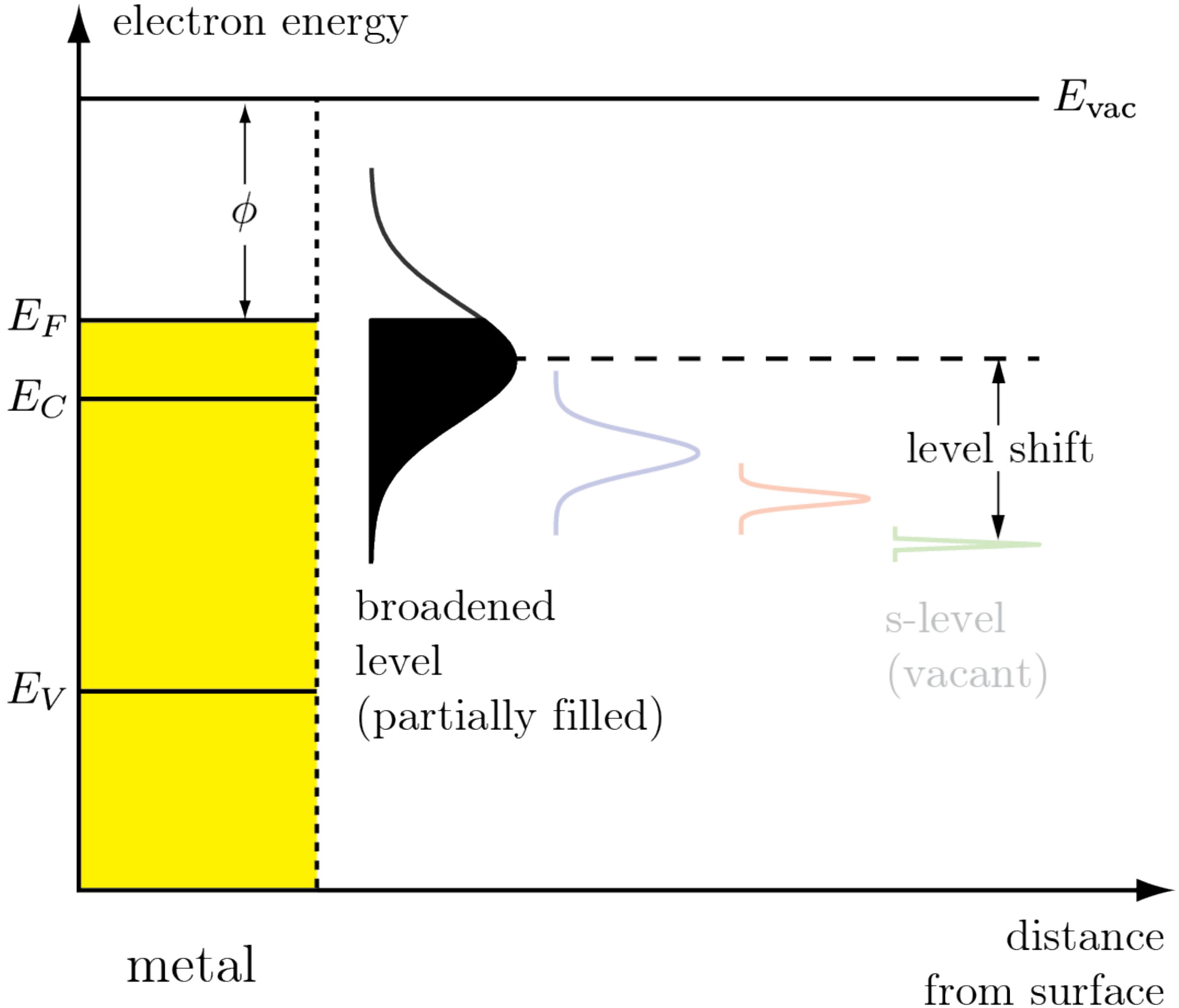


Resonant Charge Transfer (RCT)



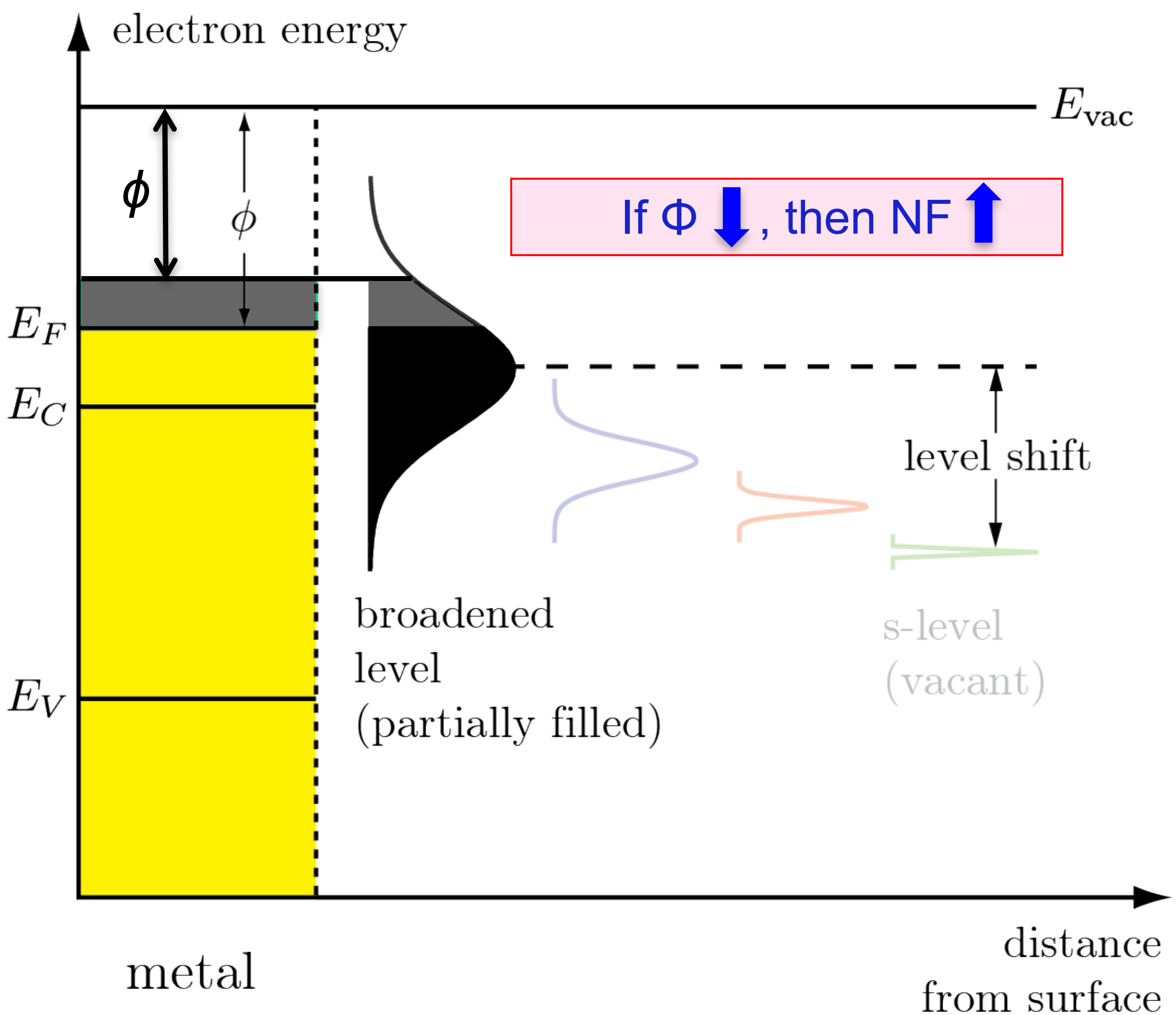
Resonant Charge Transfer (RCT)

- The neutral fraction (NF) is determined at an effective "freezing distance" along the exit trajectory, which is typically within a few Å's of the surface.
- The "freezing distance" depends on velocity, electronic structure, etc.



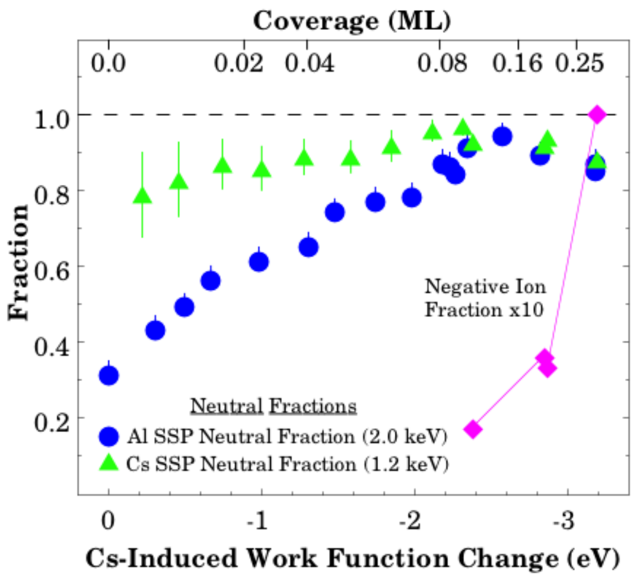
Resonant Charge Transfer (RCT)

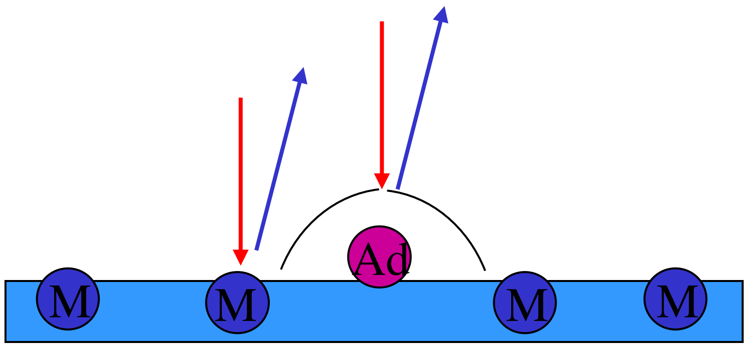
- A change in surface work function leads to a change in the measured neutral fraction
- If the work function is lowered, then the scattered alkali neutral fraction will increase, and vice versa.



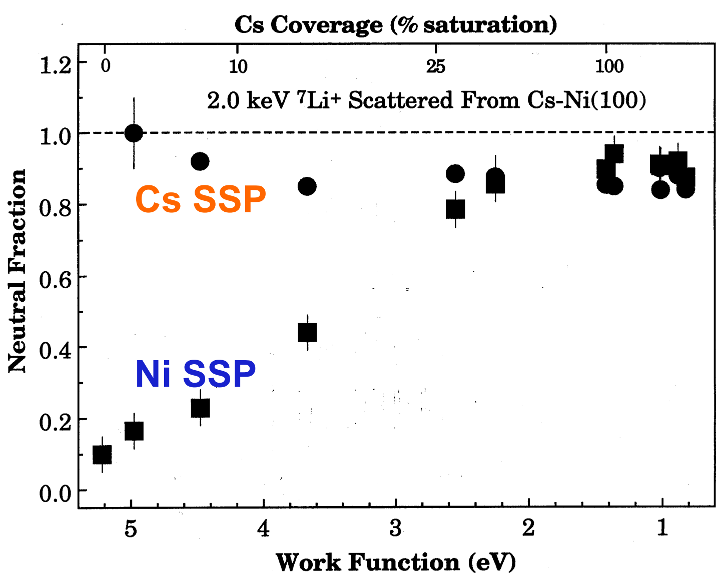
$^7Li^+$ scattered from Cs/Metal Surfaces

Cs/
Al





Cs/
Ni

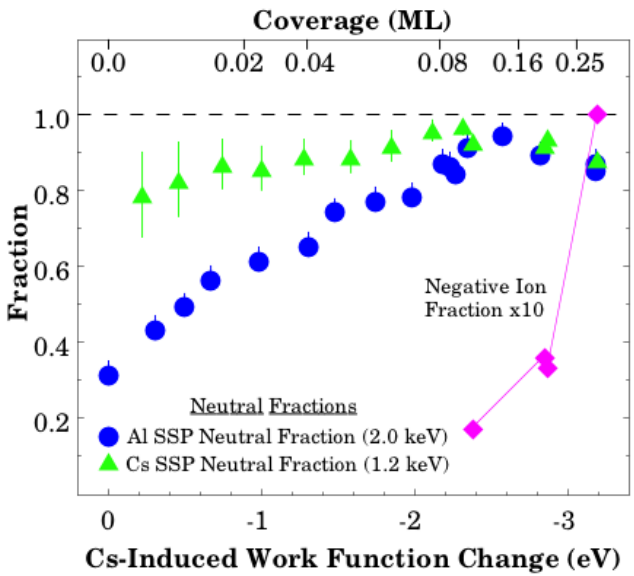


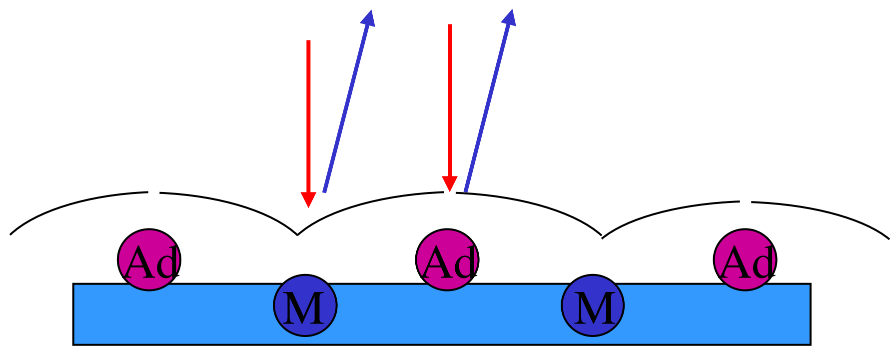
- At low Cs coverages, there are big differences in neutral fractions for scattering from substrate and adsorbate sites
  - Alkalis form isolated dipoles
  - The surface LEP is *inhomogeneous*

C.B. Weare and J.A. Yarmoff, J. Vac. Sci. Technol. A **13**, (1995) 1421; Surf. Sci. **348**, (1996) 359; Nucl. Instrum. Meth. B **125**, 262 (1997).

$^7Li^+$ scattered from Cs/Metal Surfaces

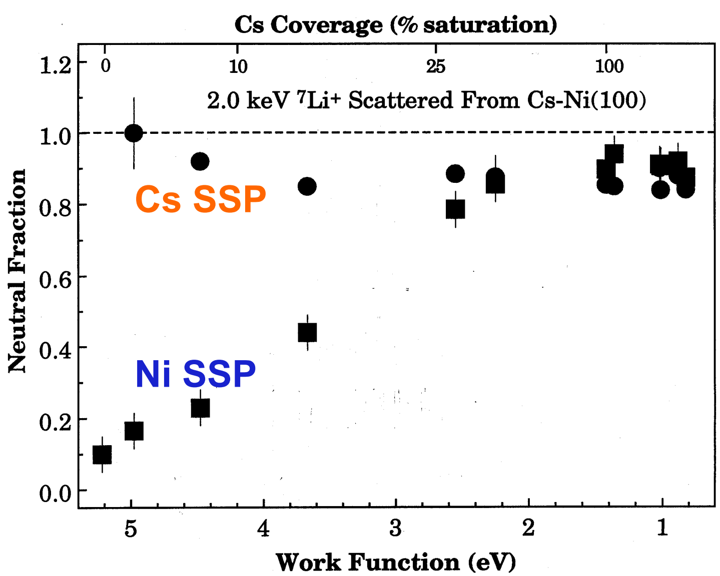
Cs/
Al





- For high Cs coverages, the neutral fractions are nearly equal
  - Alkalis form a dipole sheet
  - The surface LEP is *homogeneous*

Cs/
Ni

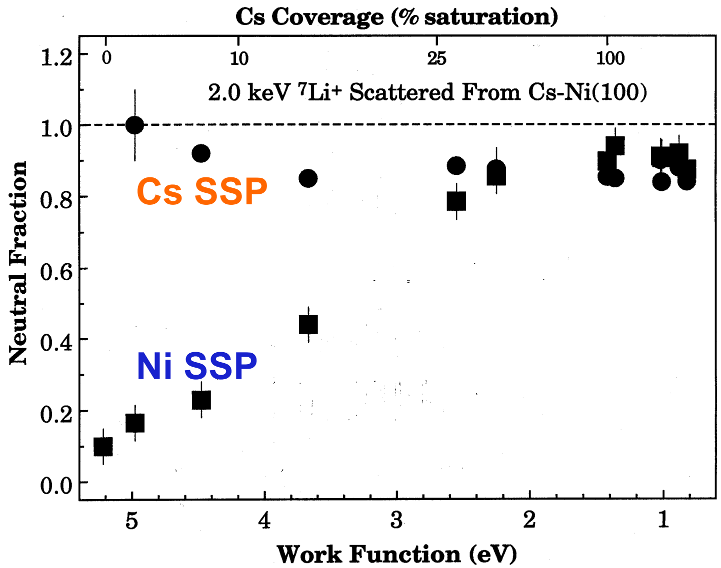


- Similar behavior seen for many systems

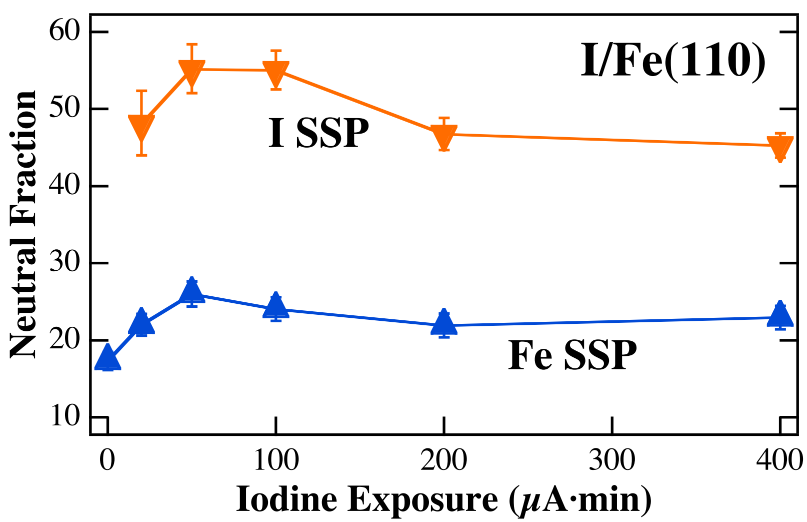
C.B. Weare and J.A. Yarmoff, J. Vac. Sci. Technol. A **13**, (1995) 1421; Surf. Sci. **348**, (1996) 359; Nucl. Instrum. Meth. B **125**, 262 (1997).

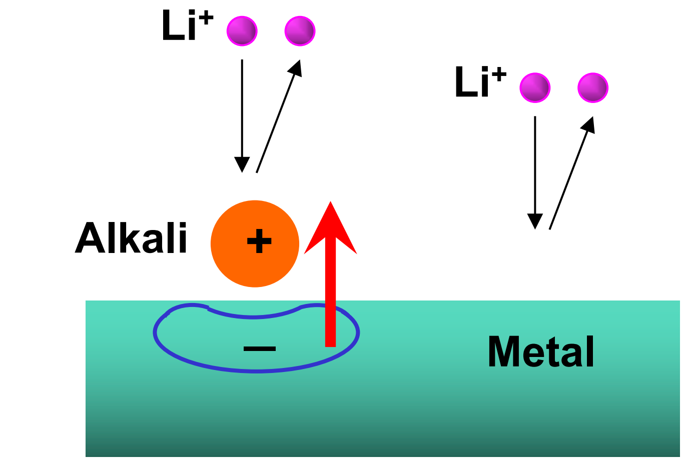
$^7Li^+$ scattered from Charged Adatoms

Cs/Ni

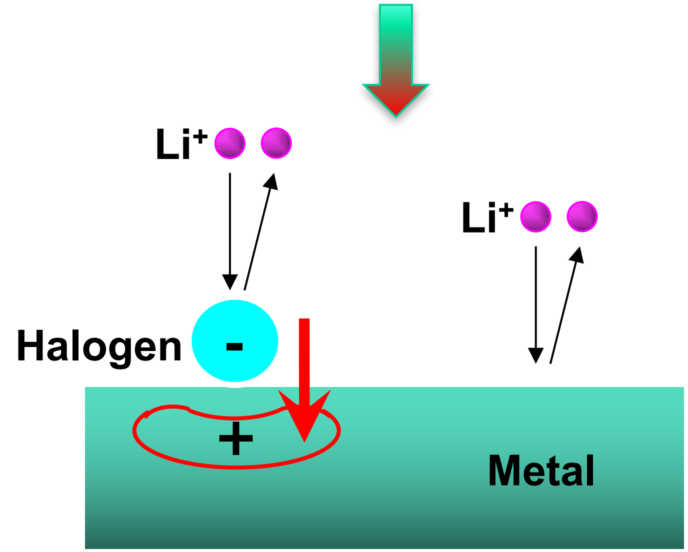


I/Fe





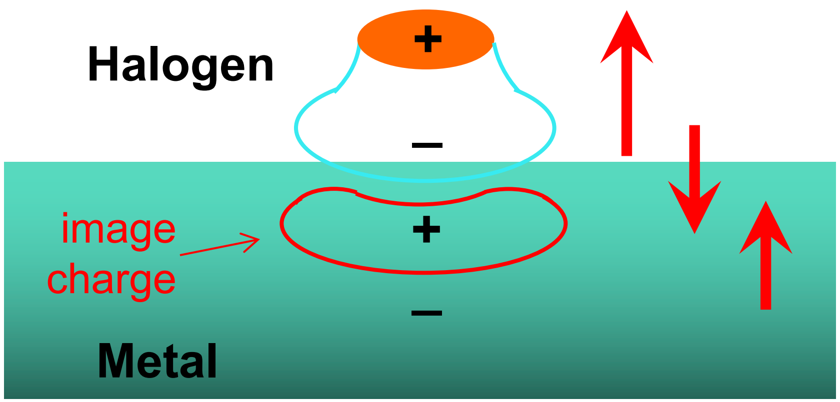
Switch polarity?



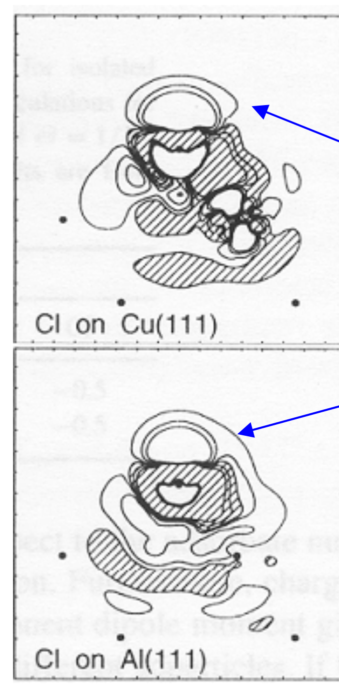
Y. Yang, Z. Sroubek and J. A. Yarmoff, Phys. Rev. Lett. **91**, 086104 (2003); Phys. Rev. B **69**, 045420 (2004); Surf. Sci. **573**, 335 (2004).

Halogen adatoms

Halogen adatoms are polarizable



Electron Density Calculations

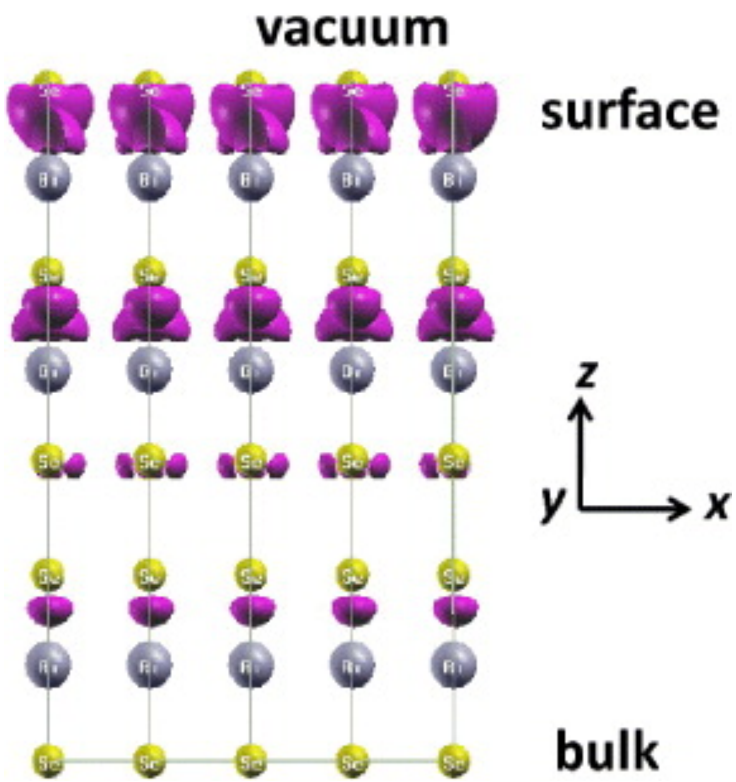


Deficiency of charge above the halogen

- Overall, adsorbed halogens are negatively charged.
- The negative charge is, however, attracted to its image charge in the metal.
- This leads to a positively charged region at the top of the adsorbate, and a combination of three dipoles so that the potential at top of the halogen adatom is reduced from the substrate, similar to an alkali adatom.

M. Scheffler and C. Stampfl, in *Handbook of Surface Science*, edited by K. Horn and M. Scheffler (Elsevier Science B. V., 2000), Vol. 2, p. 285.

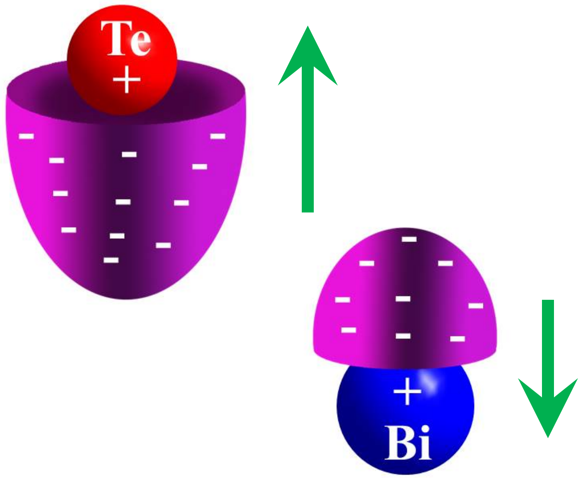
Spatial charge distribution near E_F

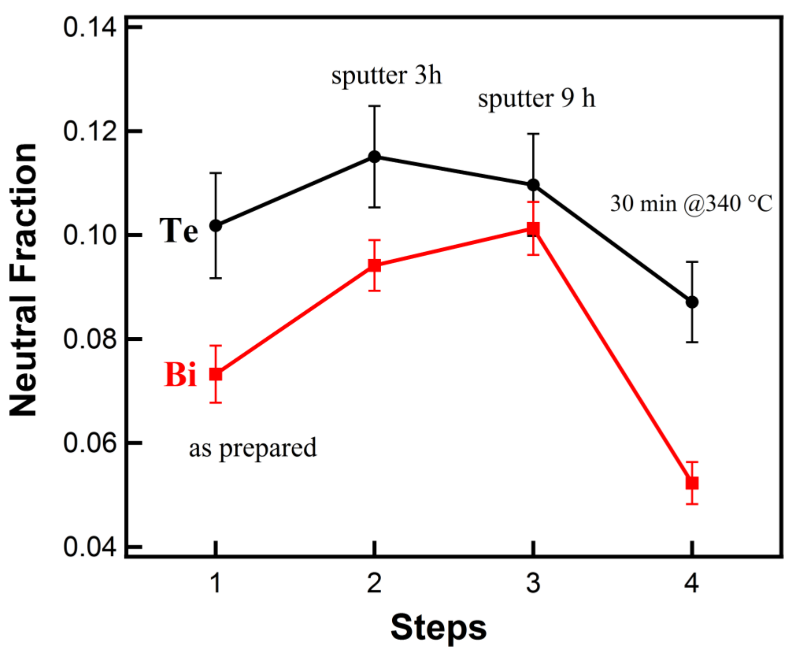


- The spatial charge distribution within an energy window of 10 meV around the Fermi level.
- The electron charge from the Topological Surface States (TSS) is positioned between the outermost Se or Te atoms and the Bi atoms.

Wei Zhang, Rui Yu, Hai-Jun Zhang, Xi Dai and Zhong Fang, New J. Phys. **12**, 065013 (2010).

Spatial charge distribution near E_F

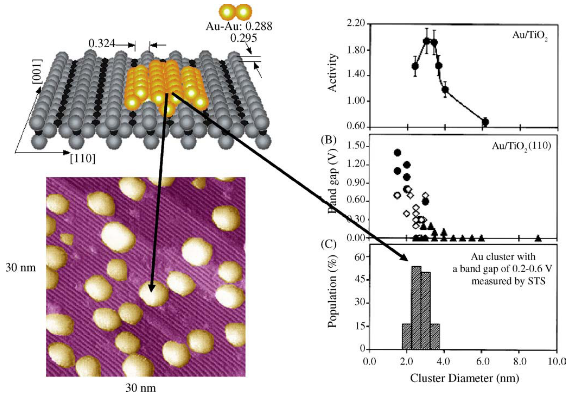




- Charge is accumulated in between the Te and Bi atoms, leading to
  - An upward dipole above the Te atoms leads to a reduced local work function and larger neutral fraction.
  - A downward dipole above the Bi atoms leads to an increased local work function and smaller neutral fraction.
- When the surface is disordered by sputtering, the neutral fraction difference is reduced.
- When the order is restored by annealing, the neutral fraction difference returns.

> Neutralization in alkali LEIS confirms the rearrangement of charge at the TI surface due to the TSS.

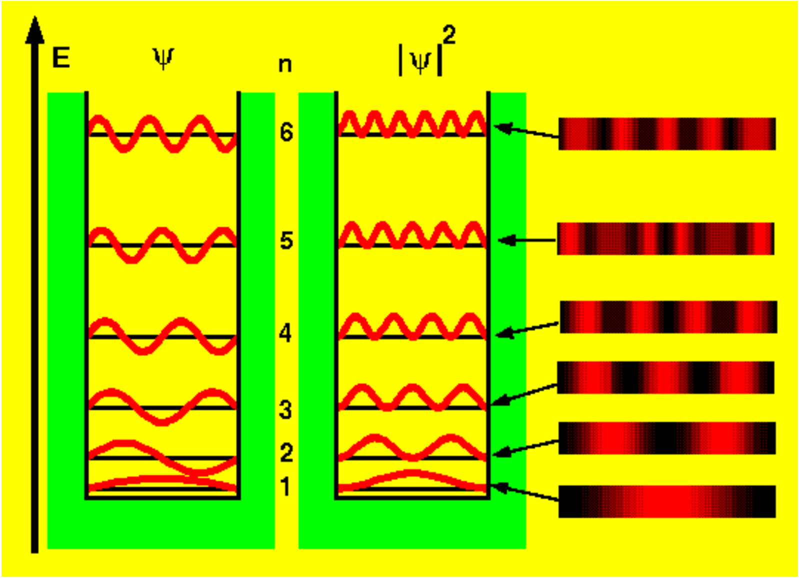
Nanoclusters



M.S. Chen and D.W. Goodman,
Catal. Today **111**, 22 (2006).

- The fabrication and characterization of metal nanoclusters is an important problem in fundamental science and advanced technology.
- The quantum-size behavior of nanomaterials enables their use in applications such as quantum computing and as catalysts.
- To fully exploit the potential of materials on the nanoscale, their basic physical and electronic properties must be understood.

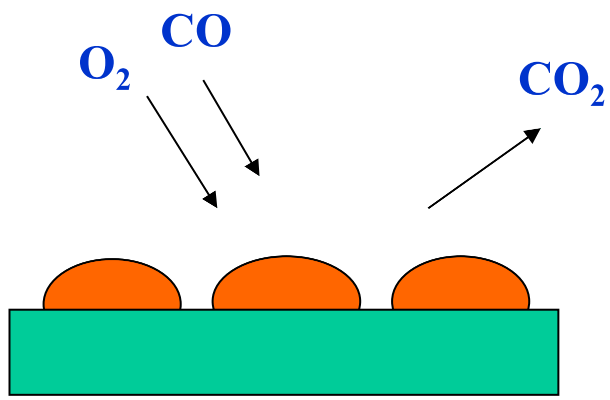
Confined states:
Particle in a box

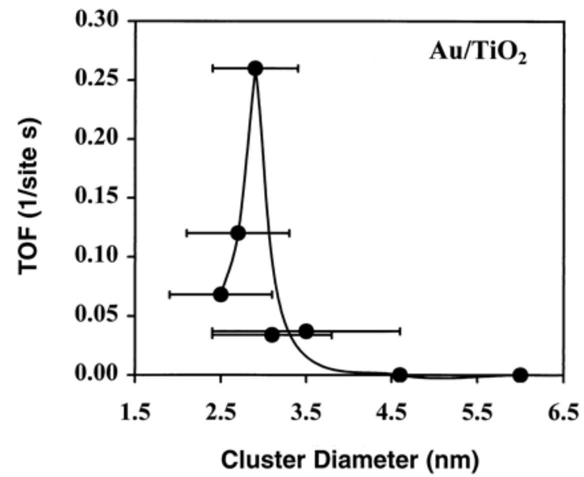


Catalysis with Nanoclusters

Oxidation of CO

$CO + \frac{1}{2}O_2 \rightarrow CO_2$

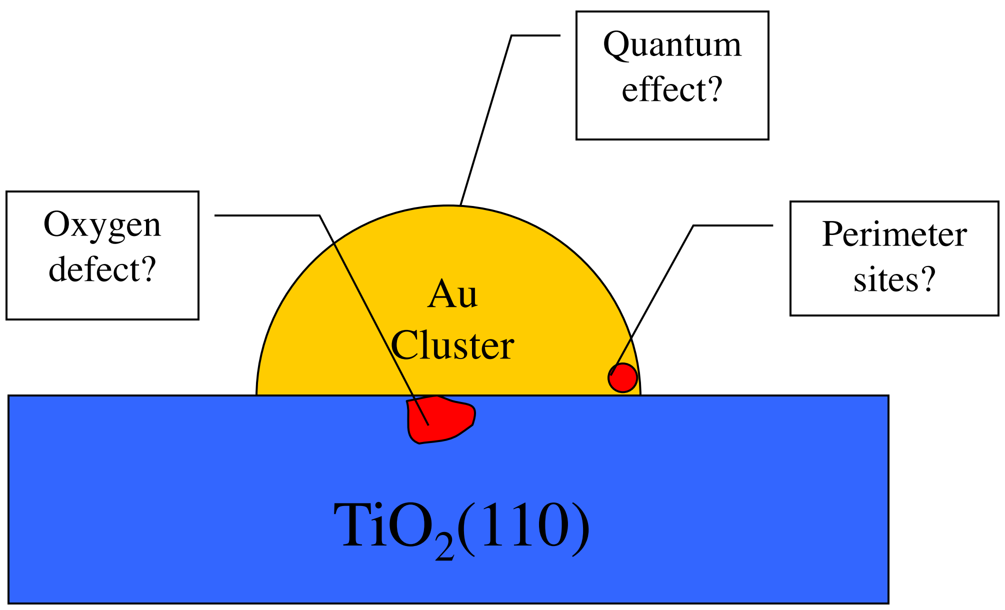




M. Valden, X. Lai, and D.W. Goodman, Science **281**, 1647 (1998)

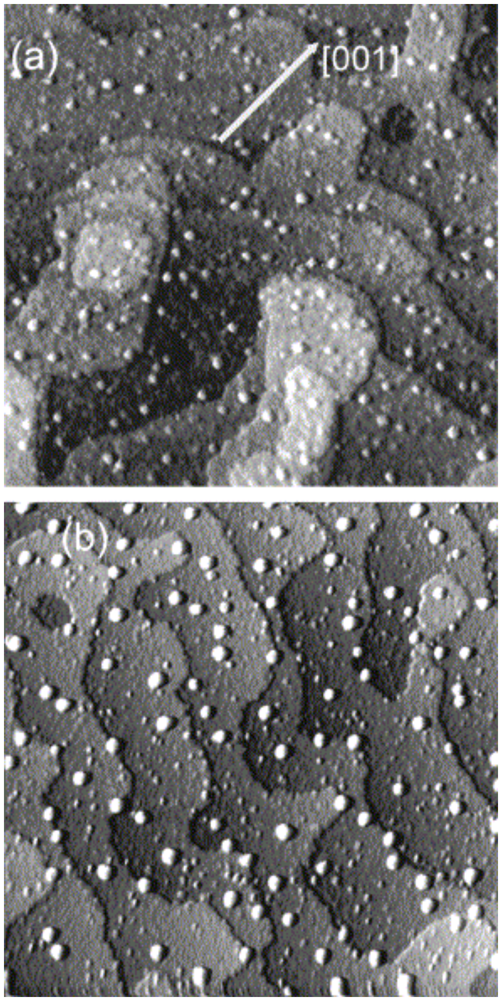
Why are the reactions enhanced in the presence of metal nanoclusters?

Still a mystery.



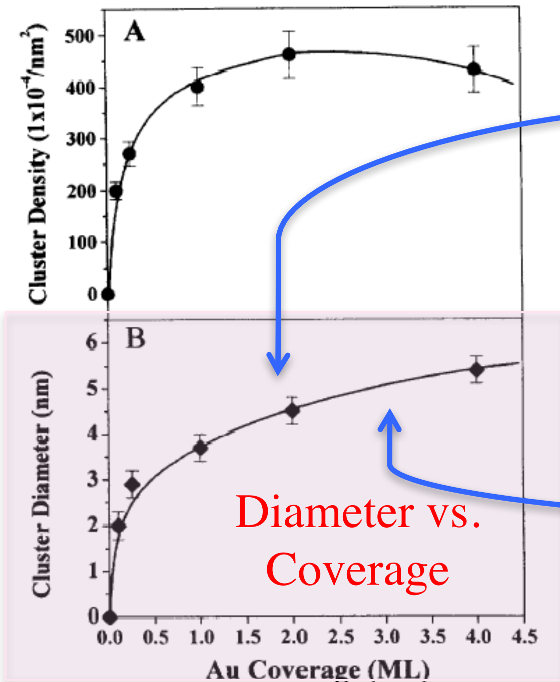
Au Nanocrystals grown on TiO_2(110)

STM images



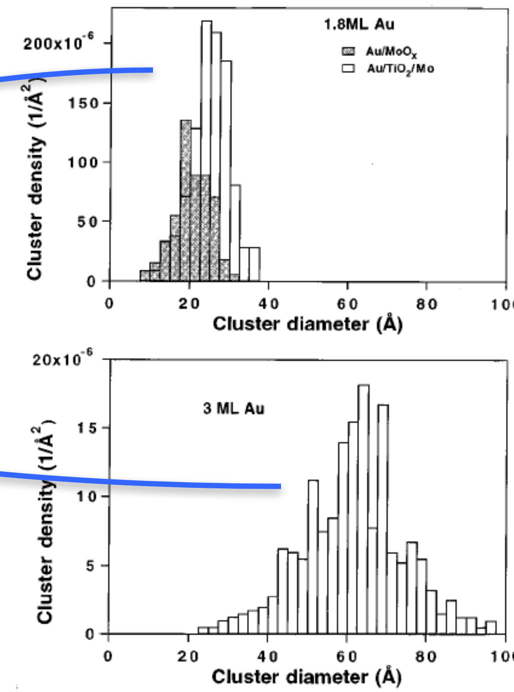
C.E.J. Mitchell, A. Howard, M. Carney and R.G. Egdell, Surf. Sci. **490**, 196 (2001).

Cluster density and diameter



X. Lai, T.P. St. Clair, M. Valden and D.W. Goodman, Prog. Surf. Sci. **59**, 25 (1998).

Cluster size distribution

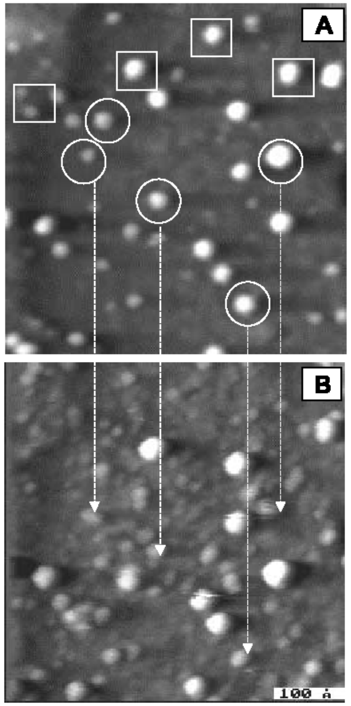


C. Xu, W.S. Oh, G. Liu, D.Y. Kim and D.W. Goodman, J. Vac. Sci. Technol. A **15**, 1261 (1997).

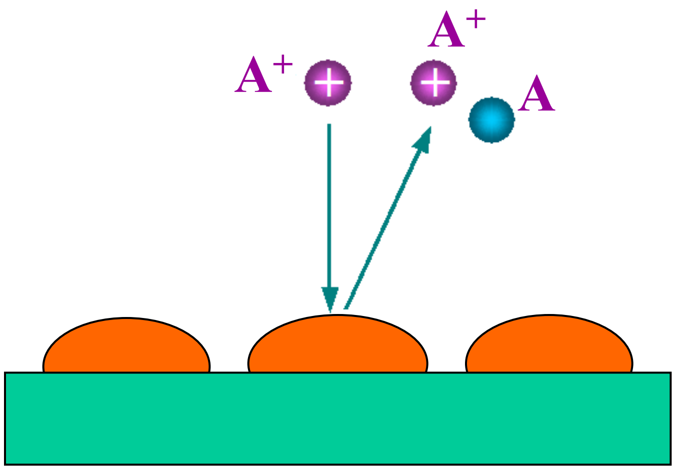
Ion Scattering from Nanocrystals

- The confined states in the nanostructure overlap the ionization level of the scattered alkali.

Au Nanocrystals grown on $TiO_2(110)$

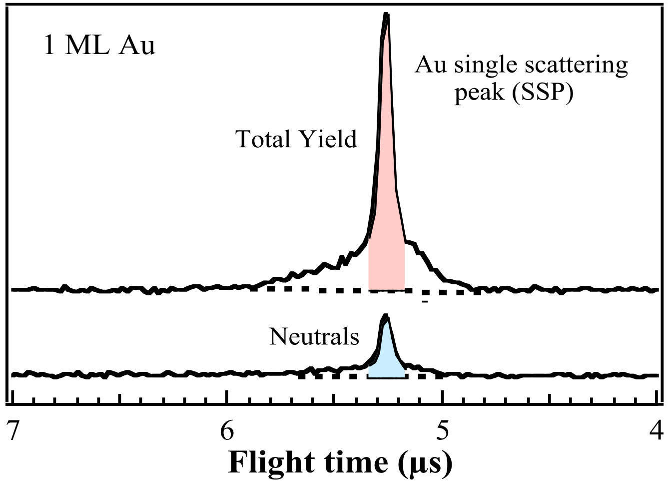


A. Kolmakov and D.W. Goodman, Surf. Sci. Lett. **490**, L597 (2001).

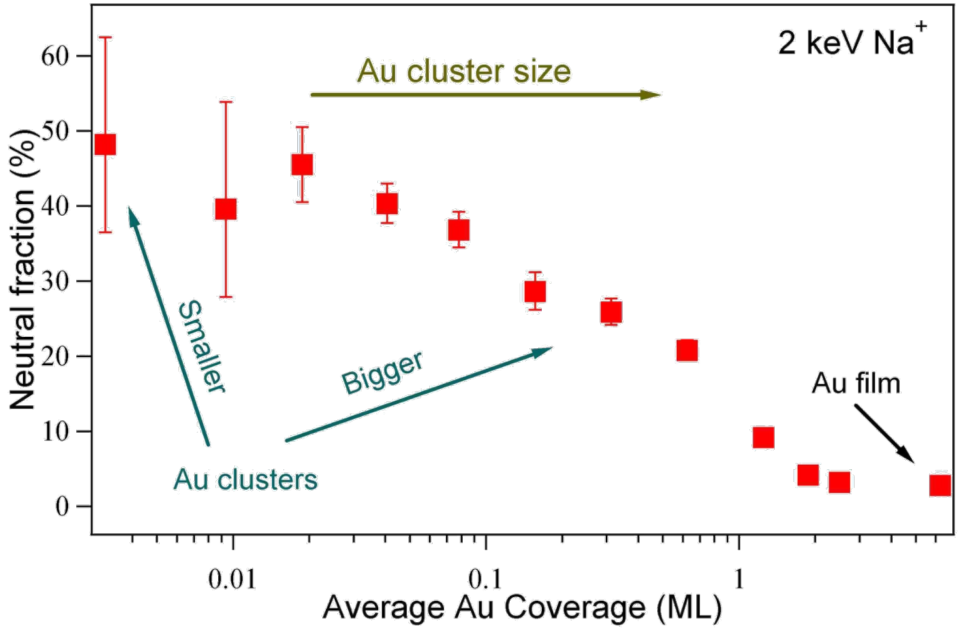


Measure fraction of ions that are neutralized - provides information on quantum-confined states

TOF spectra for Na^+ scattering



Na^+ Neutral Fraction vs. Au Deposition



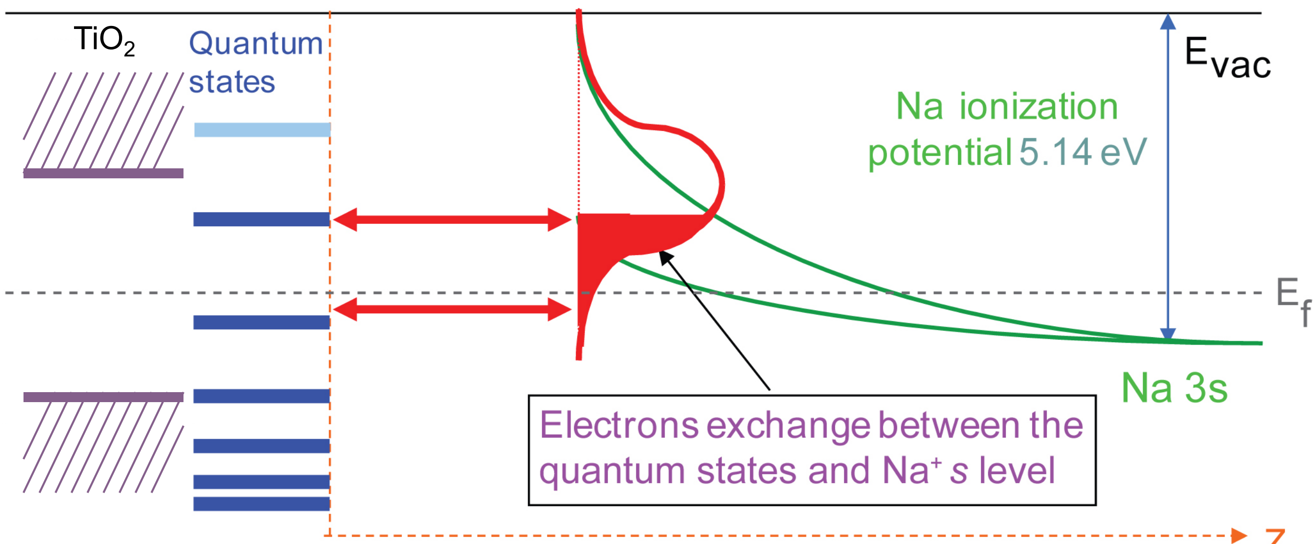
- Larger Au coverages corresponds to larger cluster sizes.

  1 ML refers to the amount of Au (arranged in a close-packed array) required to cover the substrate completely with a single atomic layer. For Au with a bulk density of 19.3 g/cm^3, the thickness of such a layer is 2.6 Å.

- As the average size of the Au nanoclusters increases, the neutral fraction decreases.
- For coverages of 5 ML and above, the neutral fraction has converged to that of bulk Au.
- The large neutral fractions suggest that the confined quantum states in the small Au nanoclusters interact with the Na ions.

G. F. Liu, Z. Sroubek and J. A. Yarmoff, Phys. Rev. Lett. **92**, 216801 (2004).

Resonant Charge Transfer for Au Nanoclusters

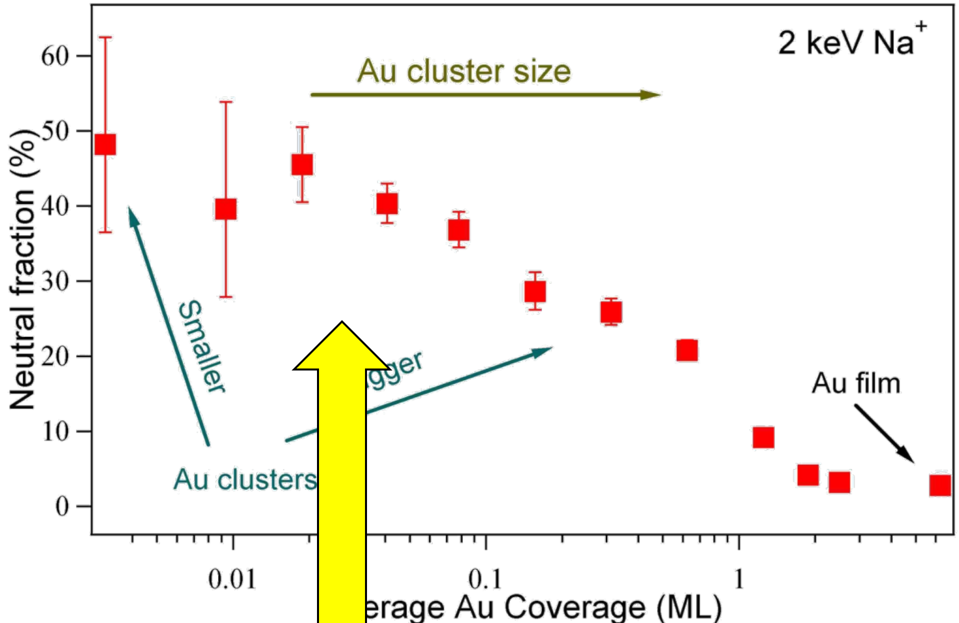


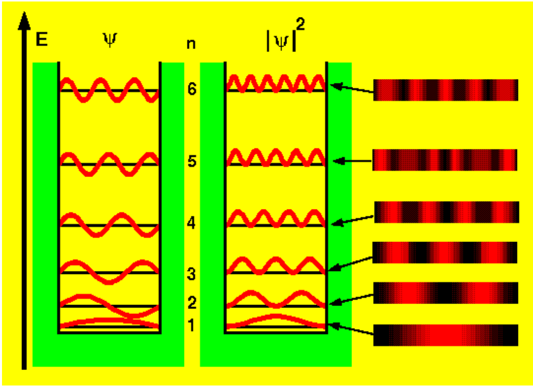
Not drawn to scale.

- For Au nanoclusters, the confined quantum states overlap the Na *s* level, leading to neutral fractions up to ~50%.
- There are discrete confined states in small Au clusters, and Au clusters presumably are negatively charged, filling these states.

J. Li, X. Li, H.-j. Zhai, L.-S. Wang, Science ***299*** *(2003) 864;*
A. Sanchez et al., J. Phys. Chem. A ***103*** *(1999) 9573.*

Neutral Fraction as a function of Au Nanocrystal Size





Confined states:
Particle in a box

- For Au nanoclusters, the confined quantum states overlap the Na *s* level, leading to neutral fractions up to ~50%.
- There are discrete confined states in small Au clusters, and Au clusters presumably are negatively charged, filling these states.

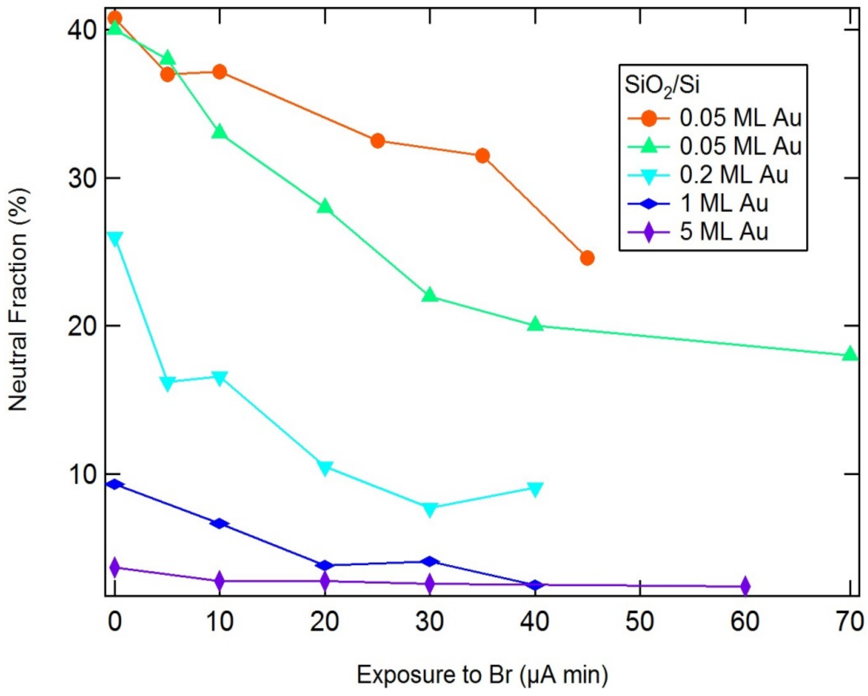
Adsorption of Br_2 on Au nanoclusters grown on SiO_2

- Br_2 produced in a solid state electrochemical cell
- Br_2 exposed to
  - Au foil Doesn't stick!
  - SiO_2 Doesn't stick!
  - Au nanoclusters on SiO_2 Sticks!!!!!!

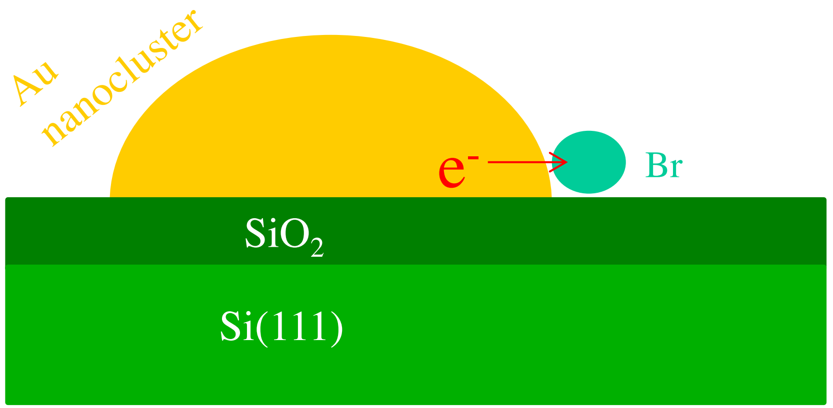
Br-Br bond breaking is catalyzed by Au nanoclusters!!!

Adsorption of Br_2 on Au nanoclusters grown on SiO_2

2.5 keV Na^+ scattered from Au nanoclusters

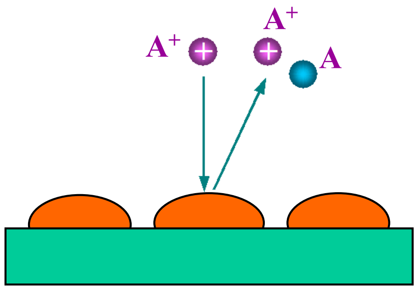


- Charge removal from nanoclusters by adsorbed Br

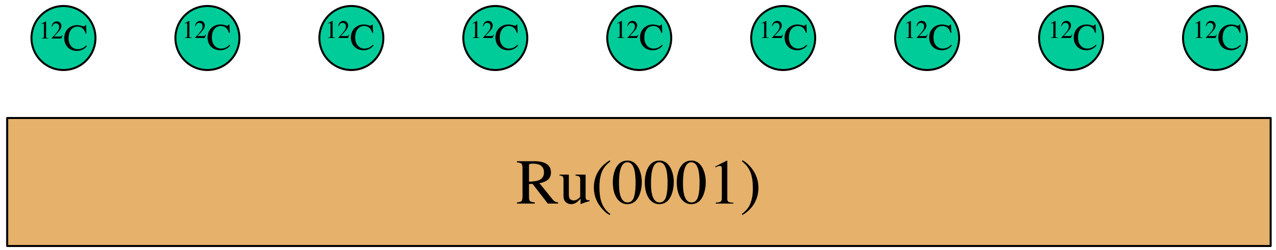


Conclusions - Nanoclusters

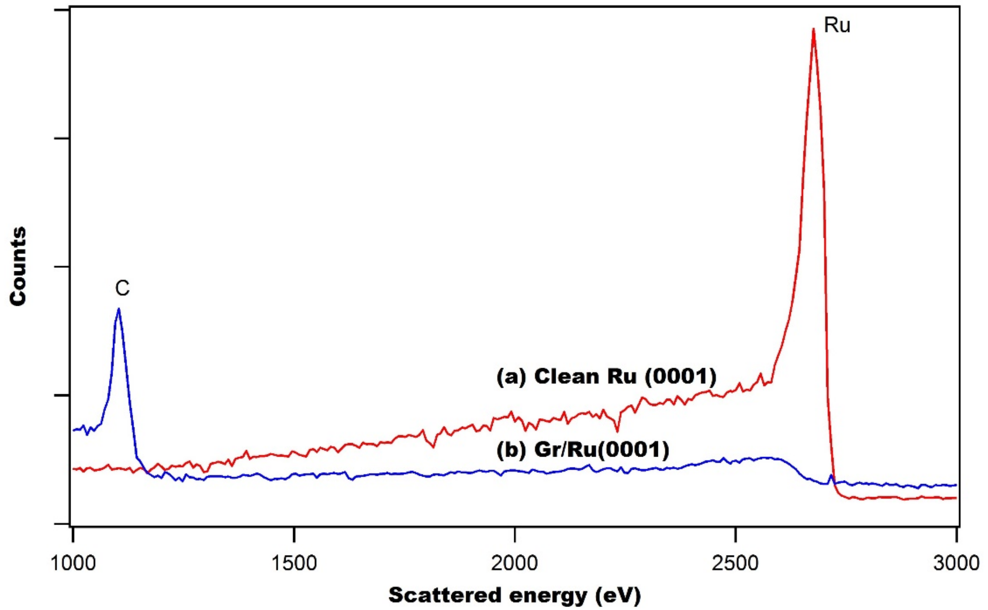
- ✓ Alkali ion scattering probes the local electronic structure at a surface.
- ✓ The neutralization in scattering from nanoclusters is sensitive to the size of the clusters.
- ✓ Au nanoclusters act to break intramolecular bonds, the first step in catalysis.
- ✓ Active clusters can be formed by ion bombardment.
- ✓ Increasing the surface temperature of Au/SiO_2 leads to surface diffusion and agglomeration.
- ✓ Clusters grown by BLAG depend on amount of metal deposited and thickness of the buffer layer.



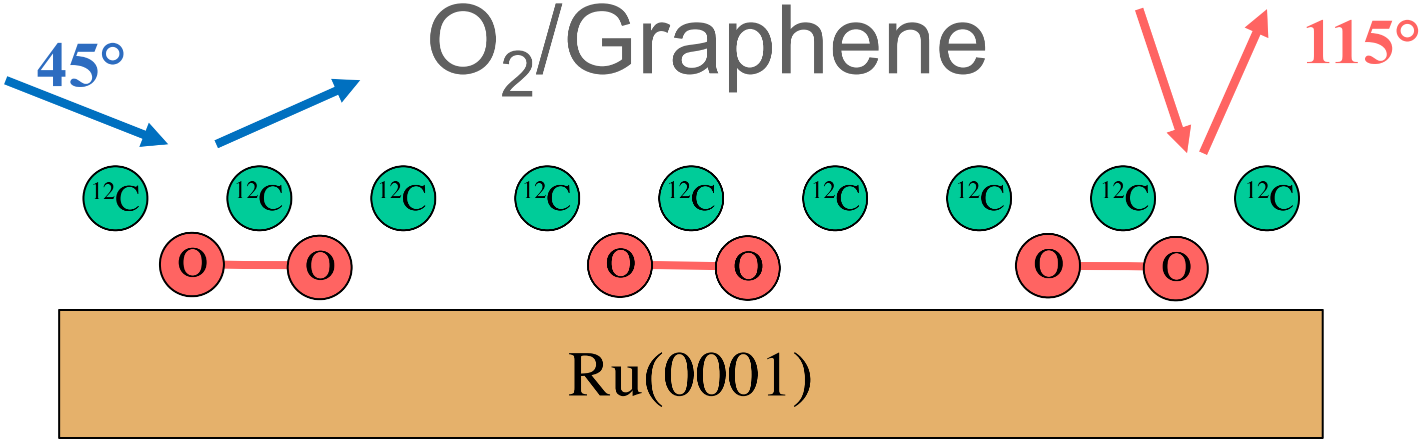
Graphene



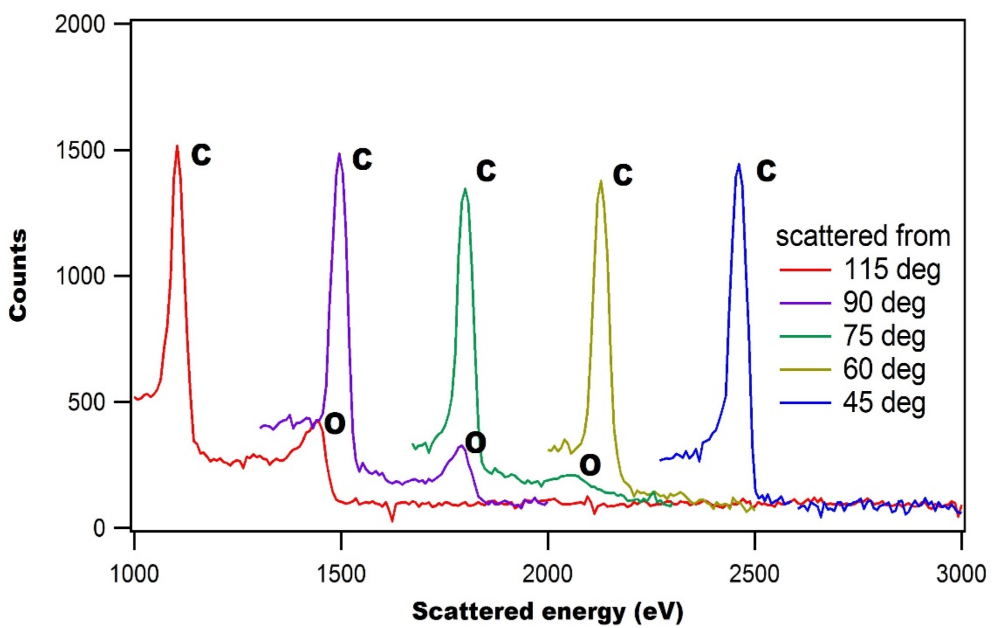
- Single layer Gr is grown onto a Ru(0001) substrate by CVD.



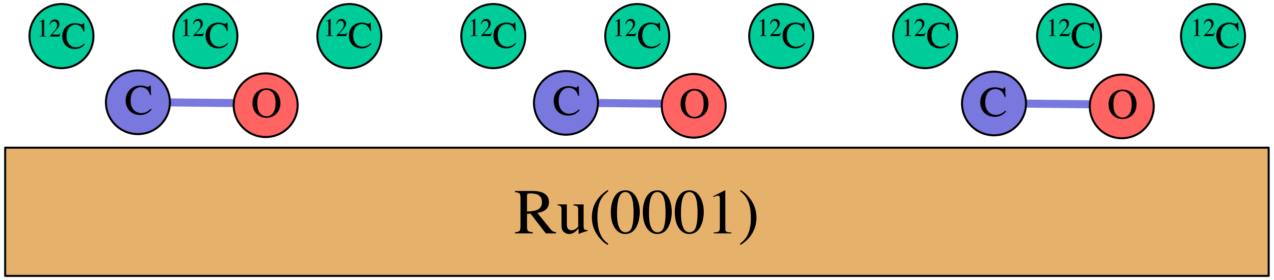
O_2/Graphene



- Single layer Gr is grown onto a Ru(0001) substrate by CVD.
- When exposed to O_2, LEIS shows that the molecules intercalate between the Gr and the substrate.

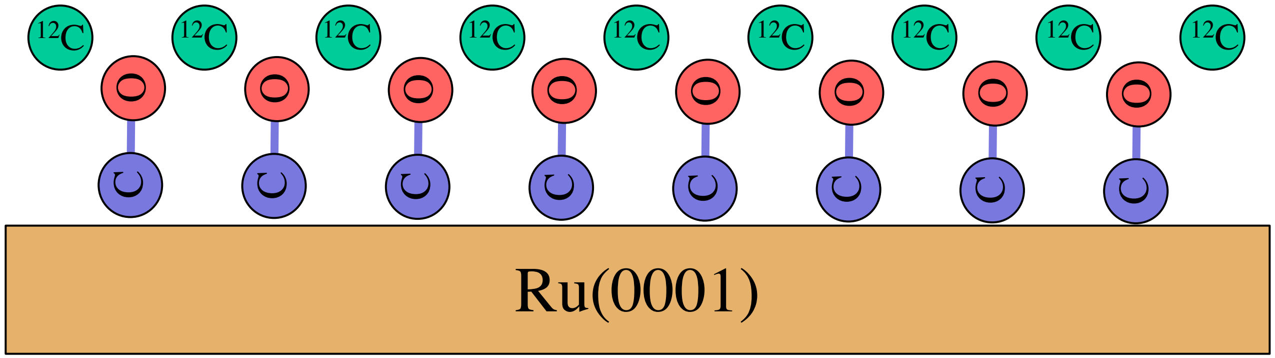


CO/Graphene



- Single layer Gr is grown onto a Ru(0001) substrate by CVD.
- When exposed to CO, LEIS shows that the molecules initially intercalate between the Gr and the substrate.

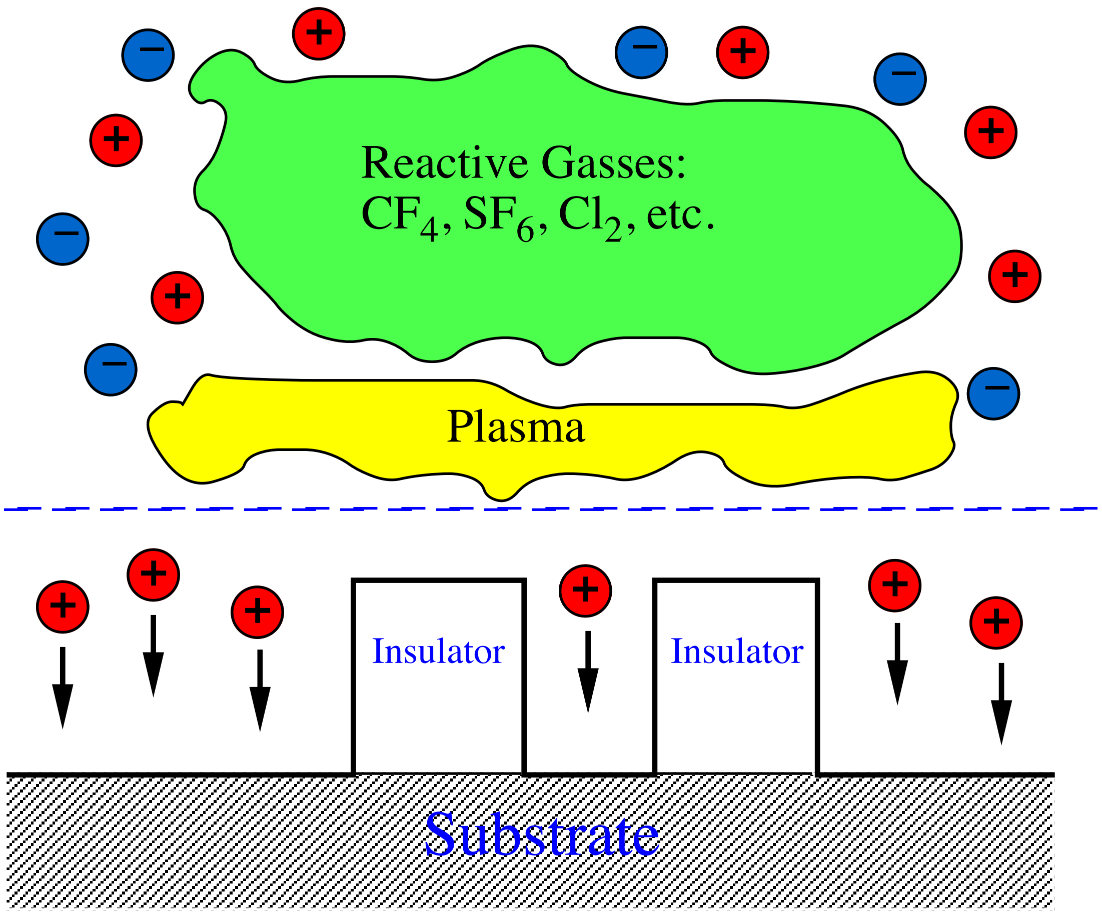
CO/Graphene



- Single layer Gr is grown onto a Ru(0001) substrate by CVD.
- When exposed to CO, LEIS shows that the molecules initially intercalate between the Gr and the substrate.
- When the coverage is increased, the CO molecules reorient to become upright.

Dry Processing of Semiconductors

- Reactive Ion Etching (RIE)
- Chemical Vapor Deposition (CVD)



Chemical process results in a high degree of selectivity

Etching of Si

$$Si + 4\,F^* \rightarrow SiF_4\ (gas)$$

Etching of GaAs

Low temperatures:

$$GaAs + 3\,Cl_2 \rightarrow$$

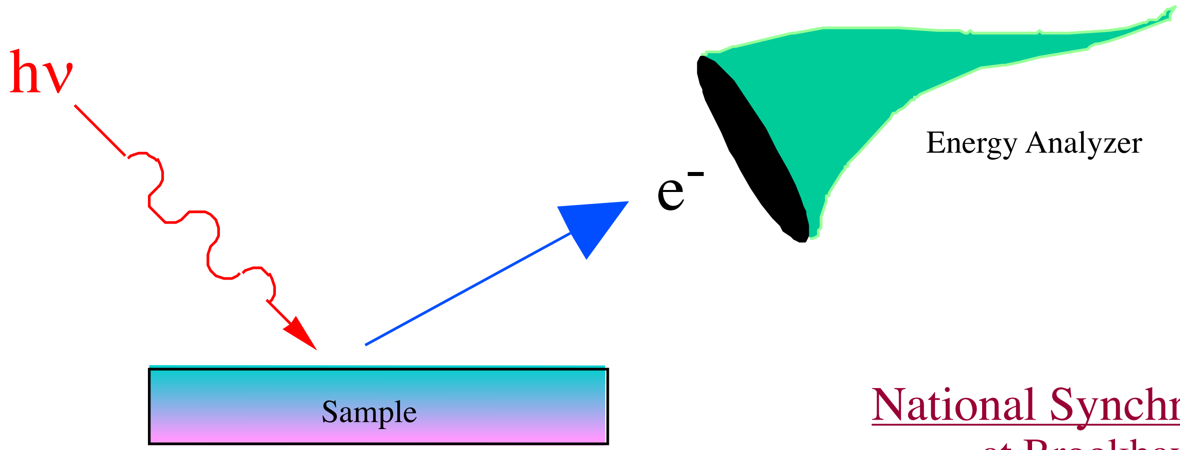
$$GaCl_3\ (gas) + AsCl_3\ (gas)$$

High temperatures:

$$GaAs + 1/2\,Cl_2 \rightarrow$$

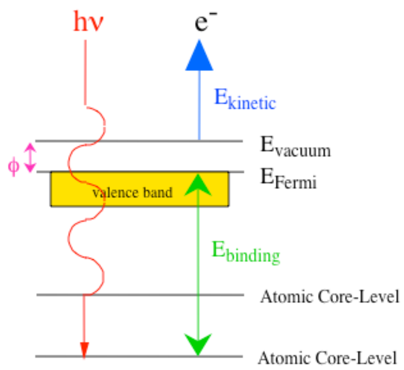
$$GaCl\ (gas) + 1/x\ As_x\ (gas)$$

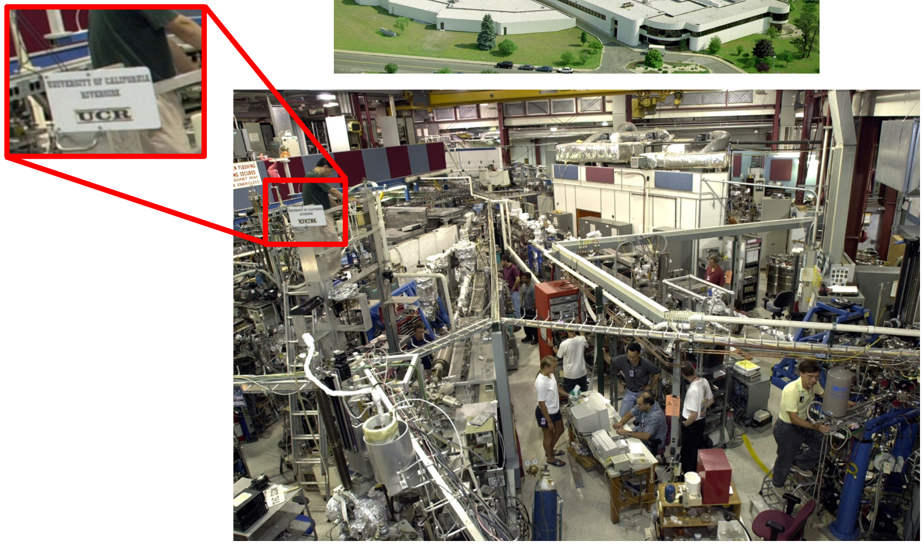
Soft X-Ray Photoelectron Spectroscopy (SXPS)



National Synchrotron Light Source (NSLS)
at Brookhaven National Laboratory

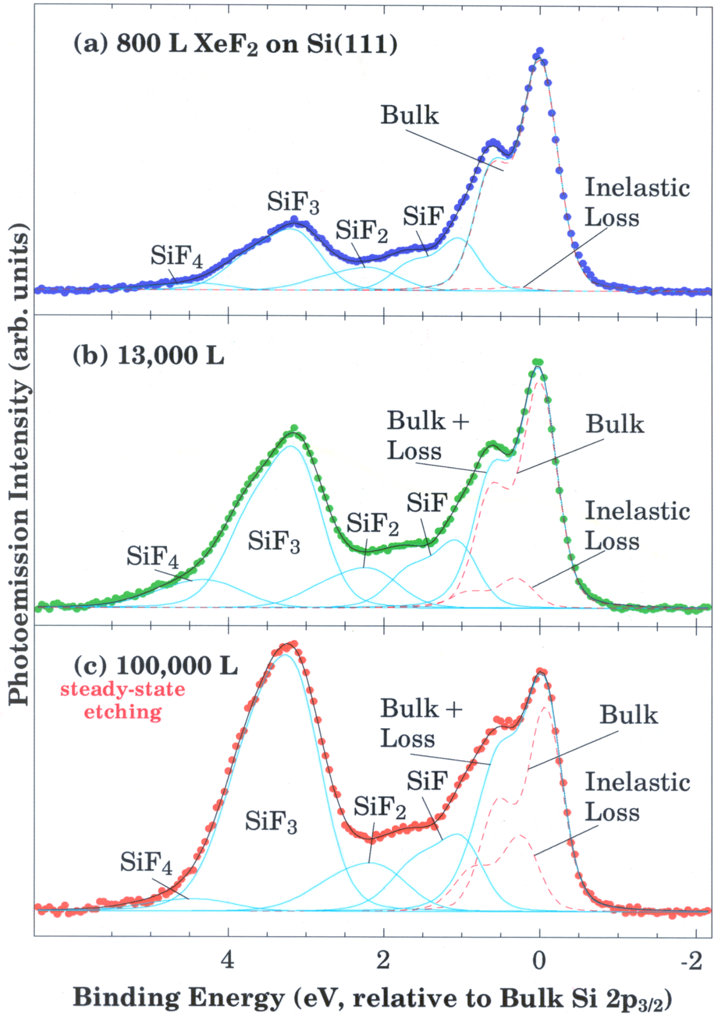
- $E_{kinetic} = h\nu - E_{binding} - \phi$
- Measures filled Density-of-States

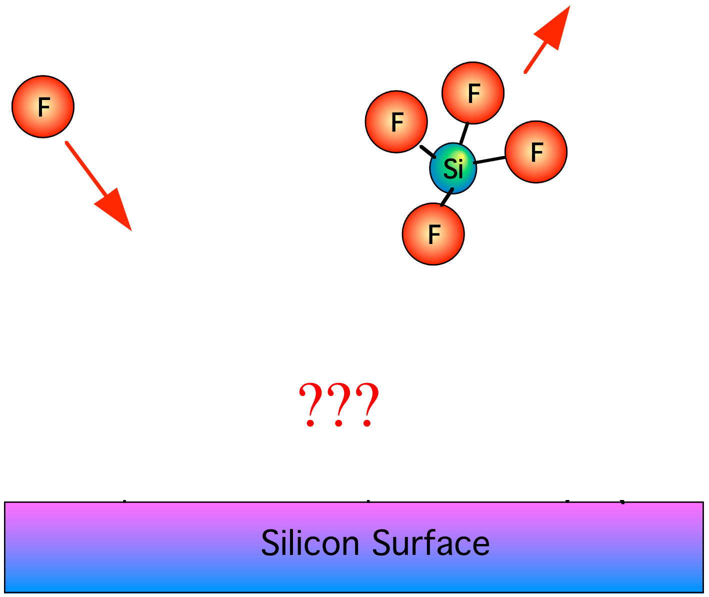




Fluorine etching of Si

Soft X-ray Photoelectron Spectroscopy

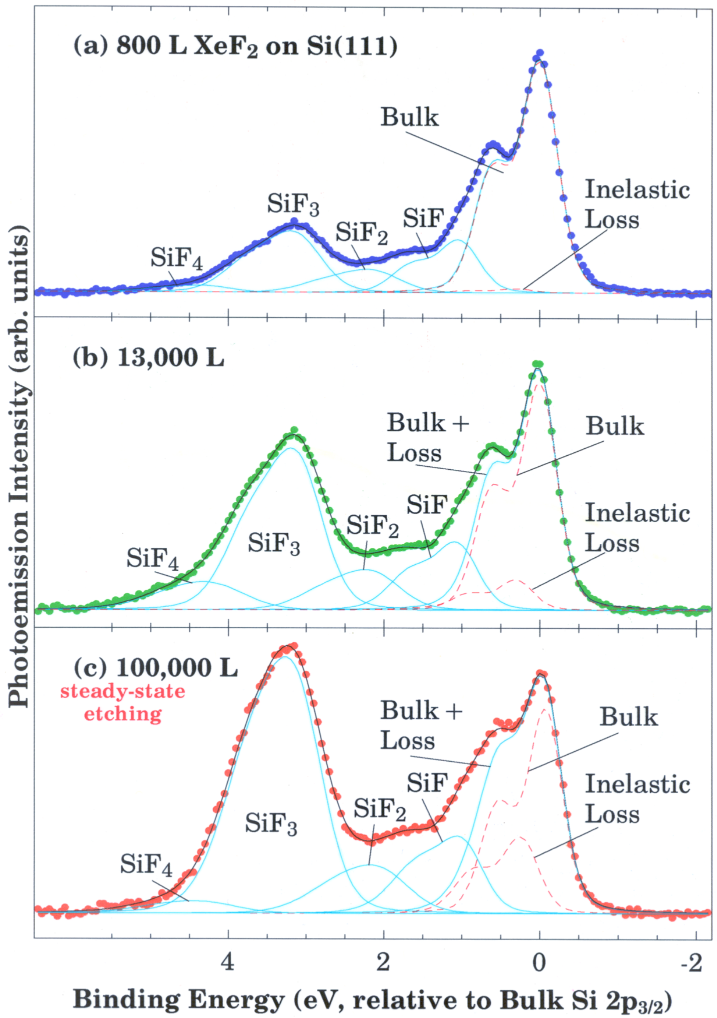


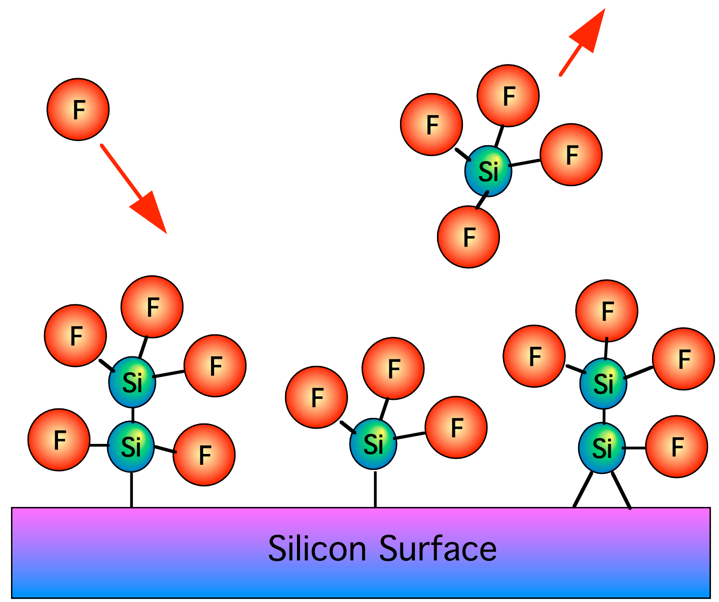


- Fluorine goes down, SiF_4 comes off
- Si forms tetrahedral bonds, just like carbon
- What structure does the fluorosilyl groups have while attached to the surface?

Fluorine etching of Si

Soft X-ray Photoelectron Spectroscopy





- Surface is covered with fluorosilyl "trees", terminated by SiF_3
- Atomic fluorine reacts with adsorbed SiF_3 to form gaseous SiF_4
- Atomic fluorine reacts with trees to form gaseous Si_2F_6 and Si_3F_8
- In order to accommodate the trees, the surface is macroscopically roughened

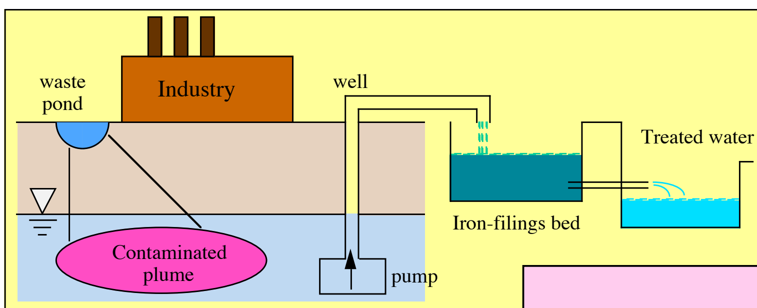
Use of surface chemical reactions for environmental remediation

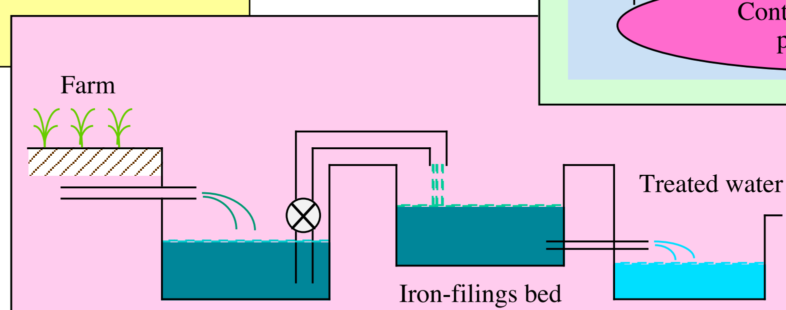
Environmental Problem

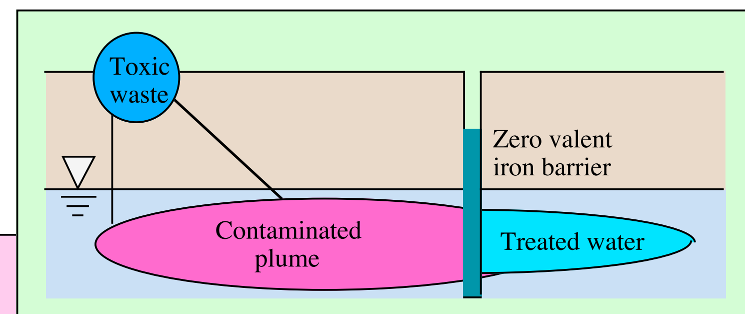
- Oxidized forms of several toxic trace elements (e.g., SeO_4^{2}, CrO_4^{2}, UO_2^{2+}) are soluble in water and mobile in the environment.
- These ions have contaminated groundwaters throughout the United States and the world. For example, at many DOE sites it is a critical cleanup issue.

Environmental Solution

- Zero valent iron (ZVI) can be used to reduce mobile forms of toxic elements in water to insoluble forms, presumably via a surface redox reaction.
- In general, the reduced forms are less toxic and less mobile.
- There are various ways in which to implement this process:

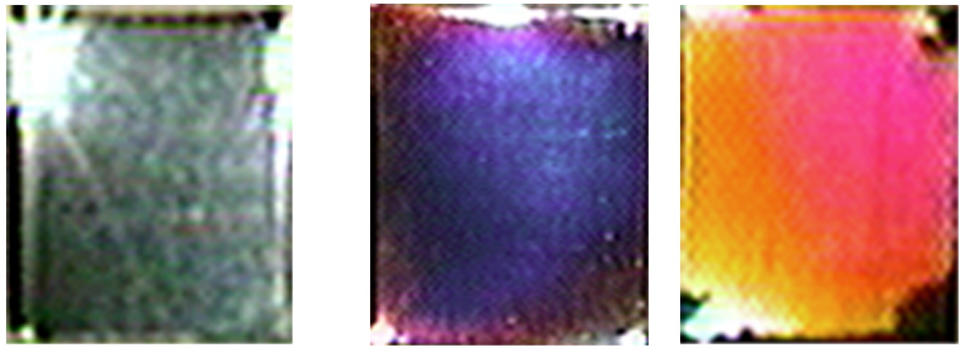






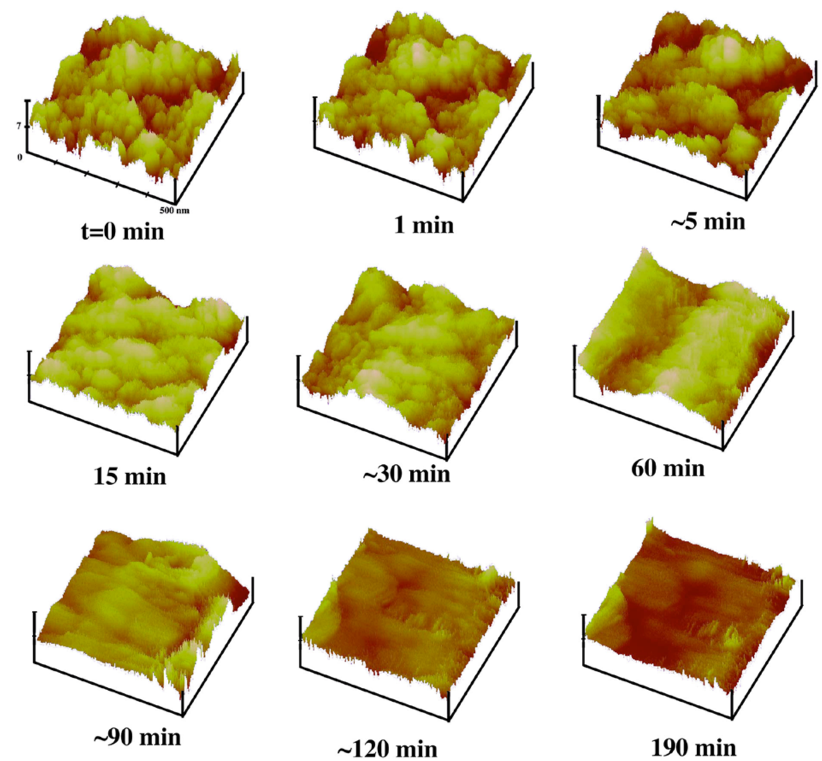
Iron foils reacted in a Uranyl Nitrate Solution

Fe foil before reaction

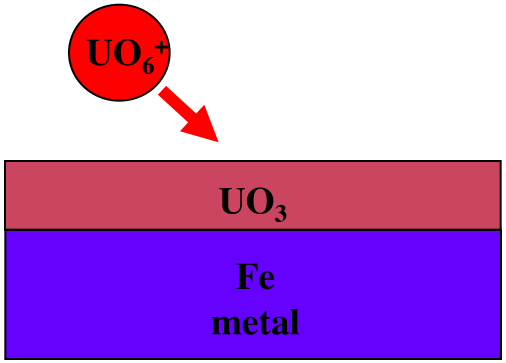


Fe foils following reaction appear iridescent

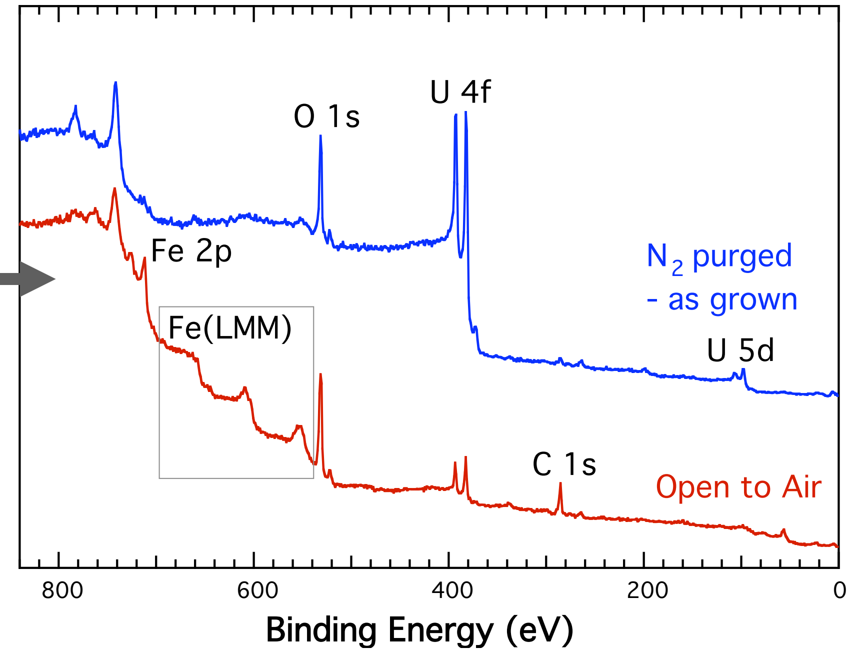
The surface of an iron foil was monitored with *in situ* STM in a solution containing uranyl nitrate. The 500x500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. XPS analysis showed that the smooth morphology is due to the deposition of UO_3.



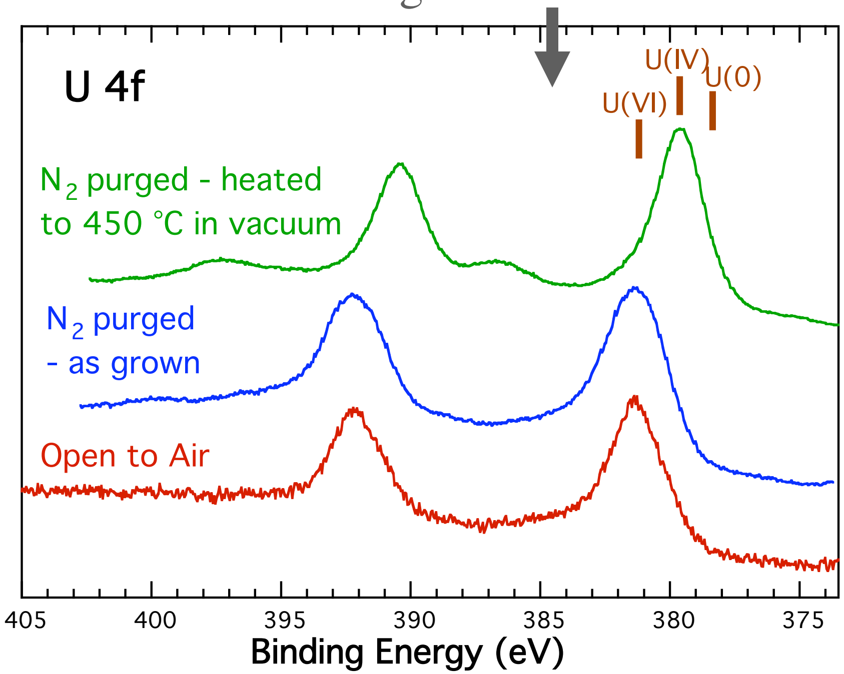
X-Ray Photoelectron Spectroscopy (XPS)



Wide scan



High-resolution scan



- Films of U(VI) oxide grow under both conditions.
- Much more U is deposited with N_2 purging, as no Fe is visible

  - this is due to carbonate formation from dissolved CO_2 when open to air
- When heated in vacuum, surface of films reduce to UO_2
- As-grown material was identified as “Schoepite”

Surface Science

Thank you!!