

# Surface Science

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

Surface Physics - part of condensed matter physics

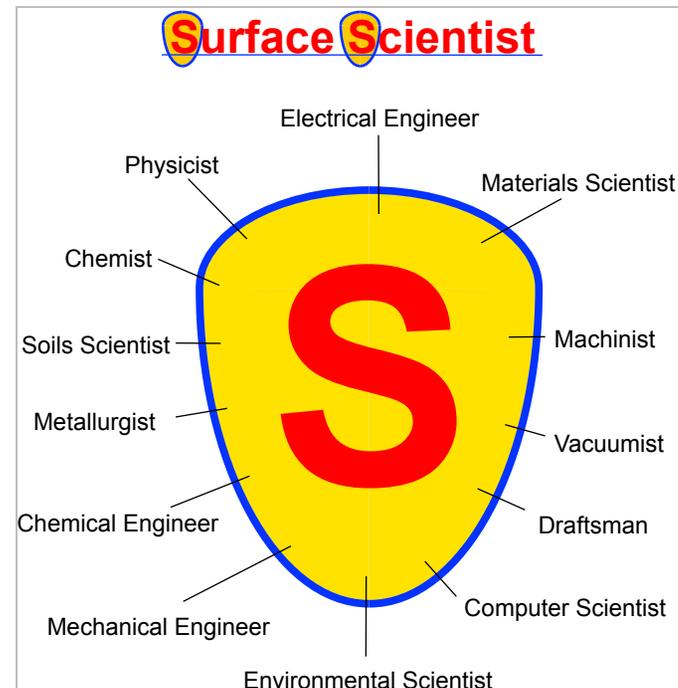
Surface Chemistry - part of physical chemistry

Materials Science

Electrical Engineering

Chemical Engineering

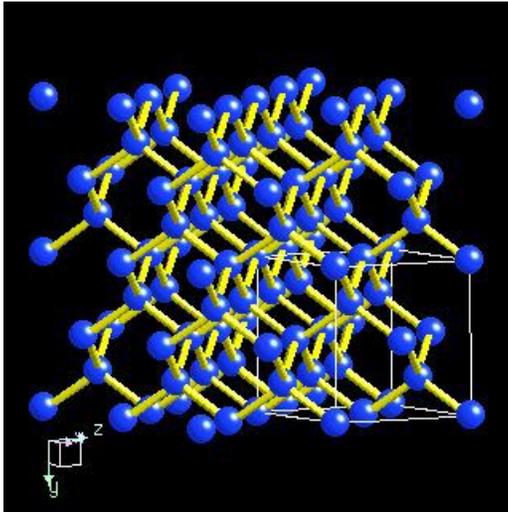
others...



# Nanoscience

## Surfaces/Interfaces

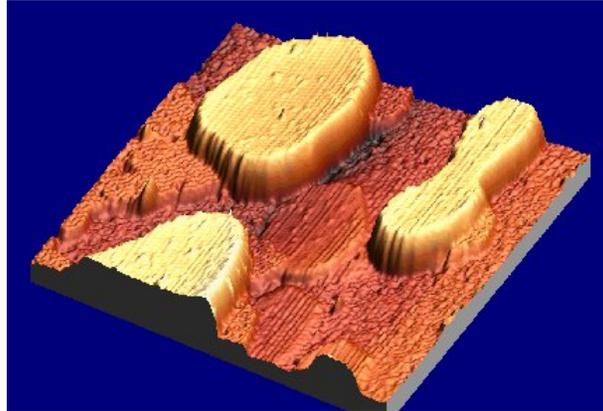
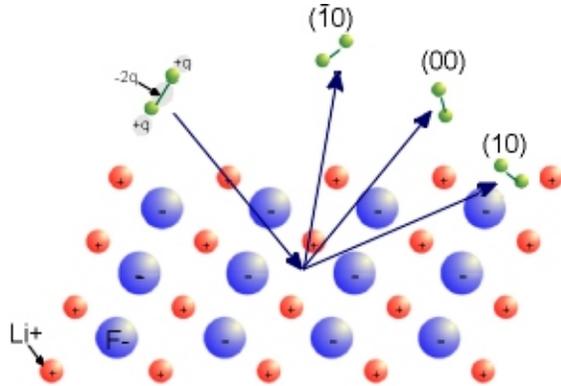
- Technological ties with semiconductor industry, petroleum industry, high  $T_c$  superconductors, tribology, environmental issues, much more...
- Requires a wide variety of experimental skills
- Combines both laboratory work and work at major facilities
- Many techniques must be applied to a given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



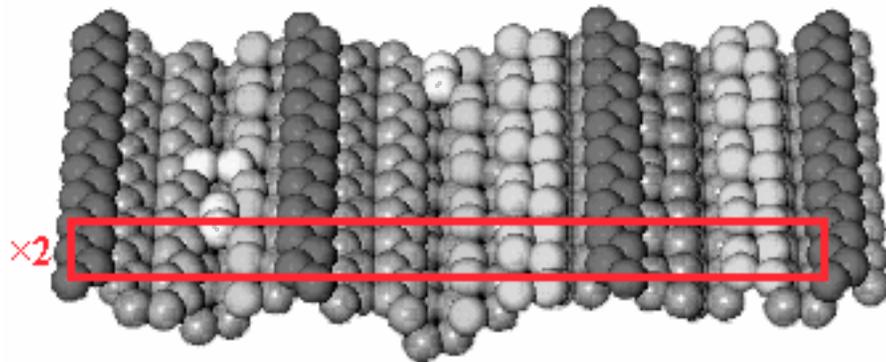
# Surface Science is concerned with:

- Geometric structure

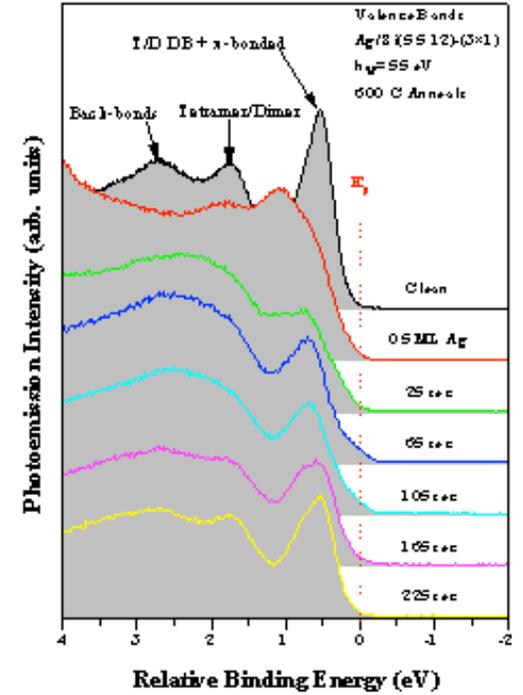
- Particle-Surface Interactions



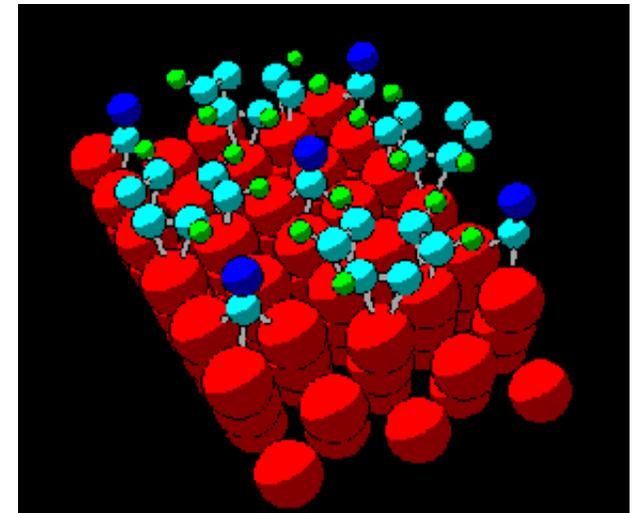
- Effects of radiation damage



- Chemical surface reactions

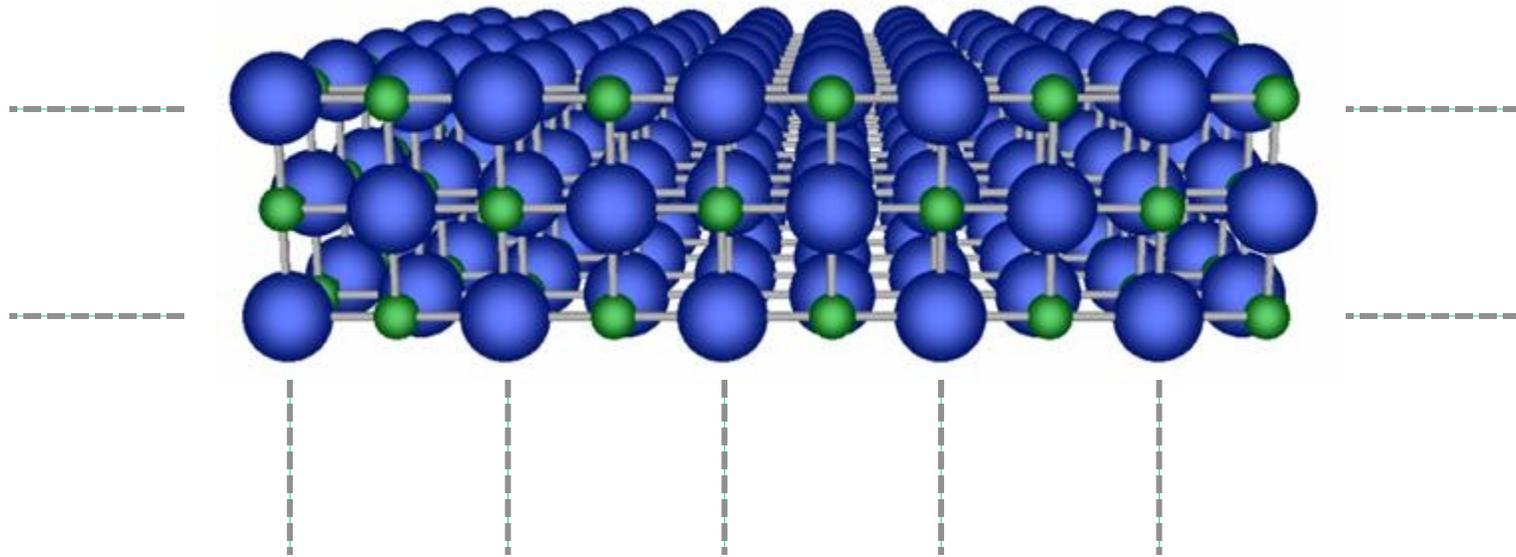


- Electronic structure



# Surface Structures

Almost side view

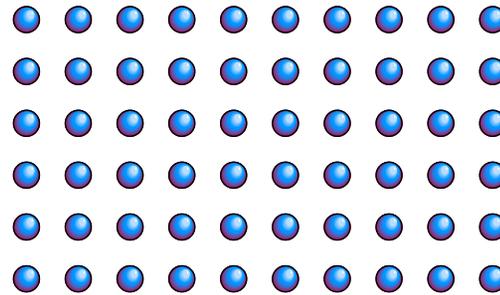


- A solid is composed of atoms with infinite periodicity in 3-dimensions
- The periodicity is broken at a surface

# Surface Structures

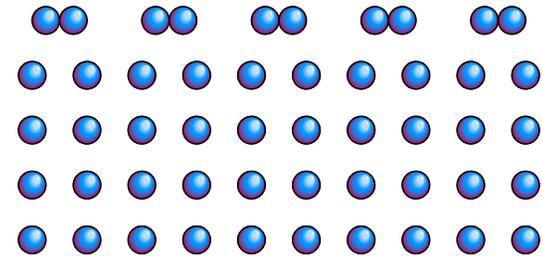
side view

## Bulk-terminated Surface



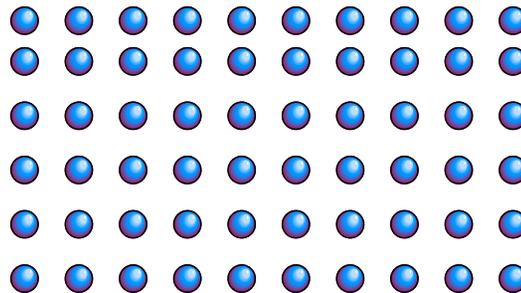
- Surface atoms are in bulk-like positions
- It's as though the surface were simply cut

## Reconstructed Surface



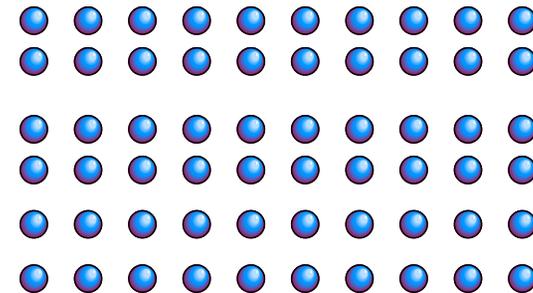
- Surface atoms are moved laterally, as well as in the perpendicular direction
- Reconstruction can involve many atomic layers

## Relaxed Surface



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

## 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
2. Unique electronic properties – novel devices
3. Ability to adsorb molecules in unique configurations
4. ???



## Experiment vs. Theory

### Duke's Laws



1. All theories are wrong
2. All experiments measure something

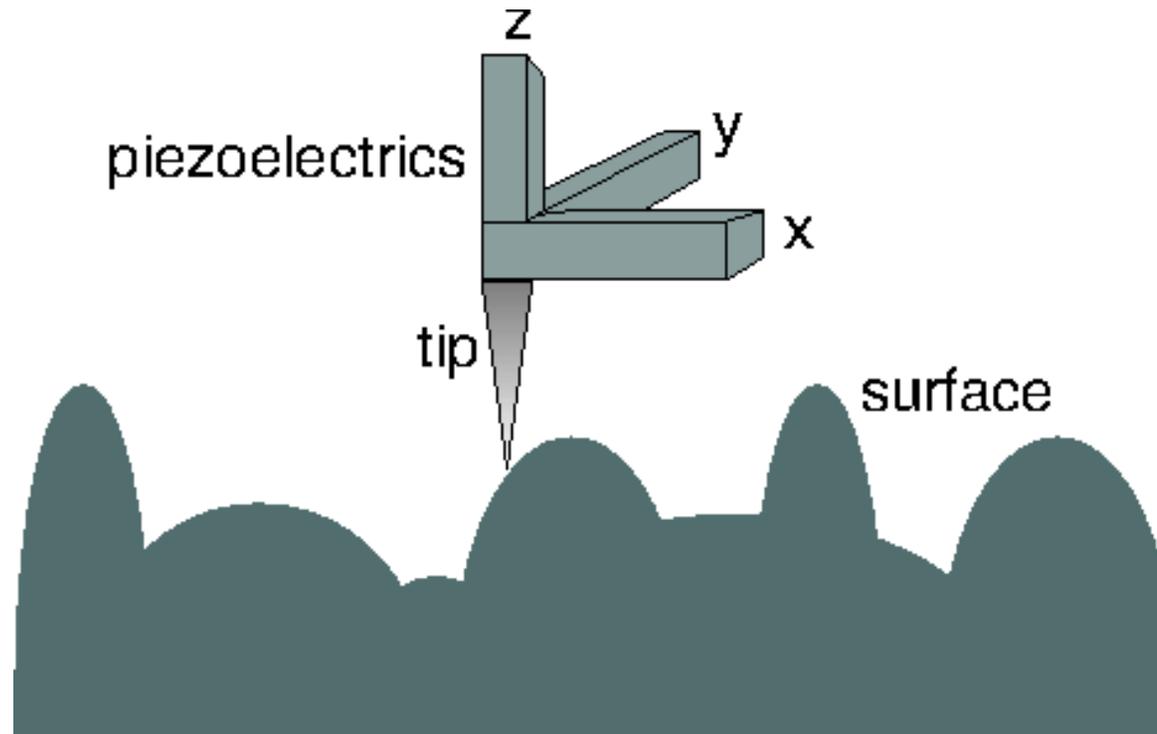


**Experiment**



## Scanning Tunneling Microscopy (STM)

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

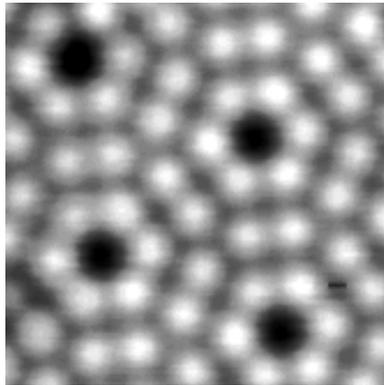


- Measures electron density at a surface with atomic resolution

# Scanning Tunneling Microscopy (STM)

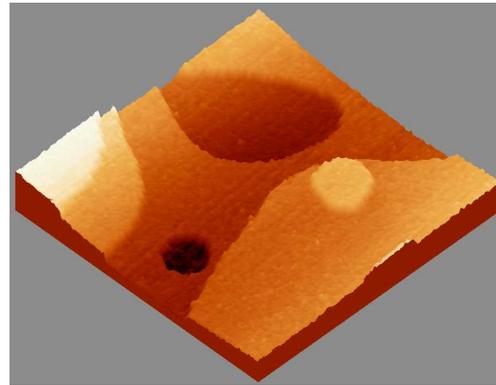


## Atomic resolution



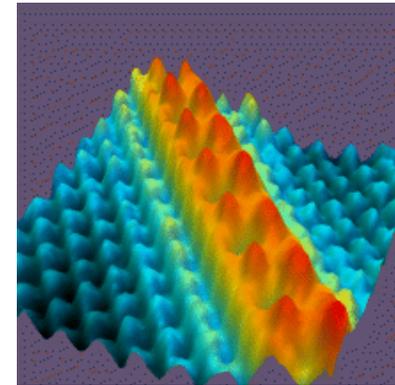
Clean silicon

## Metal surfaces

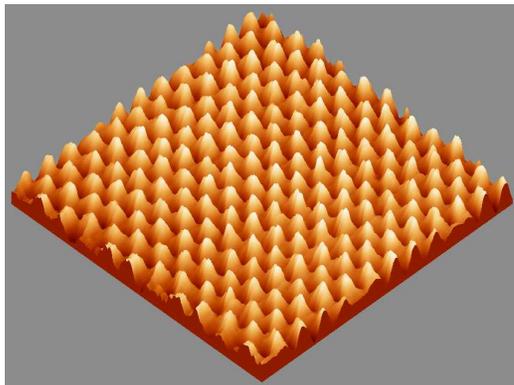


Gold

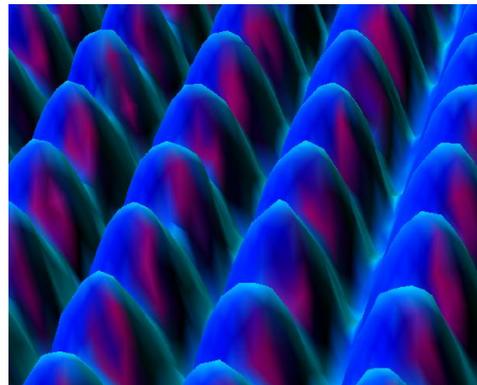
## Novel systems



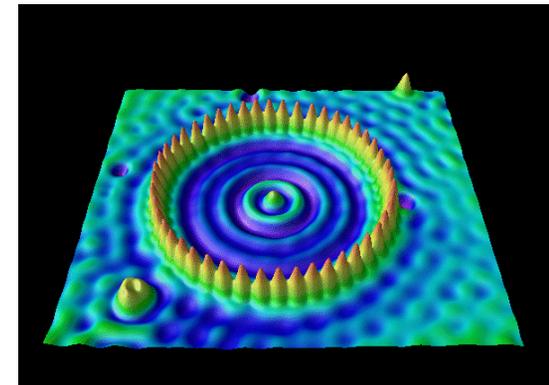
Cesium nanowire



Graphite

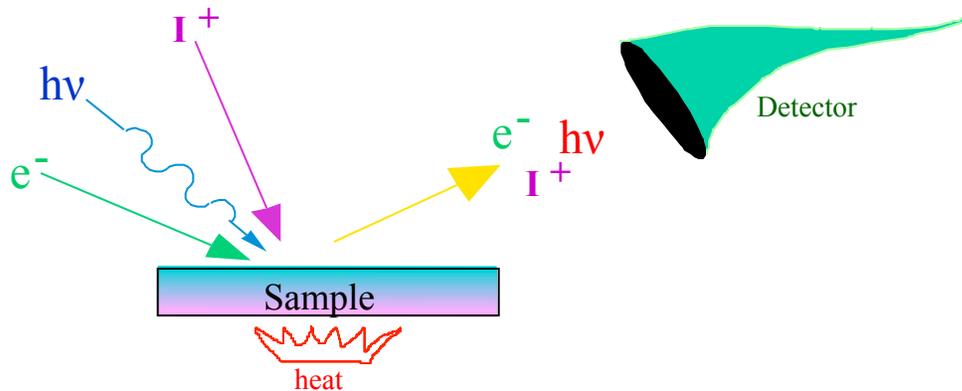


Cold nickel



Quantum corral

# Generic Surface Spectroscopy



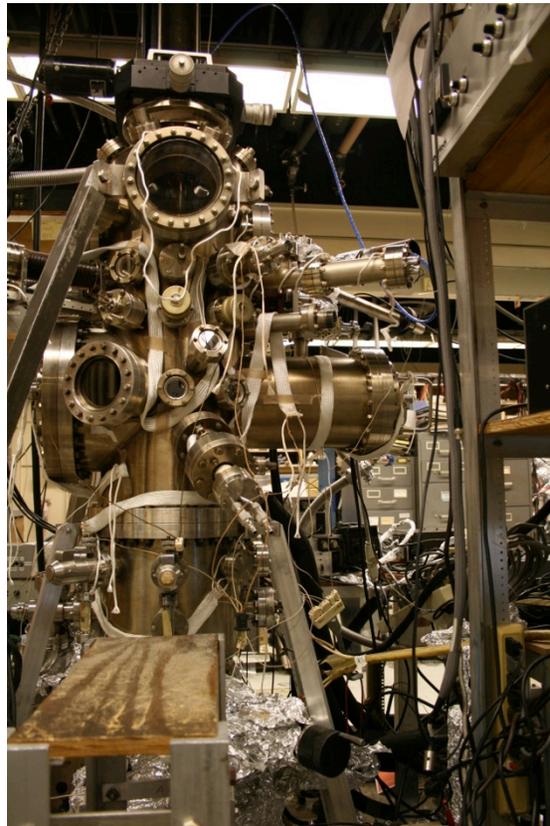
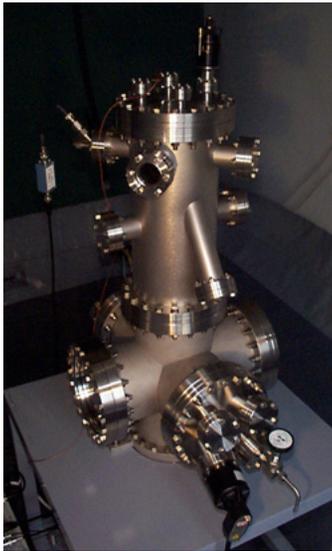
- Particles can be: electrons, ions, photons, atomic or molecular particles, heat, others...
- Experiments are designed to probe outermost few Å's of surface
- Techniques in our laboratory include x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), ion scattering spectroscopy (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	LEERS
ISS	REM	SAM
LEIS	TED	MQS
MEIS	HREM	TDS
HEIS	AREELS	TPS
ICISS	UPS	TPD
ALICISS	IPS	SXPS
SIMS	CITS	FIM

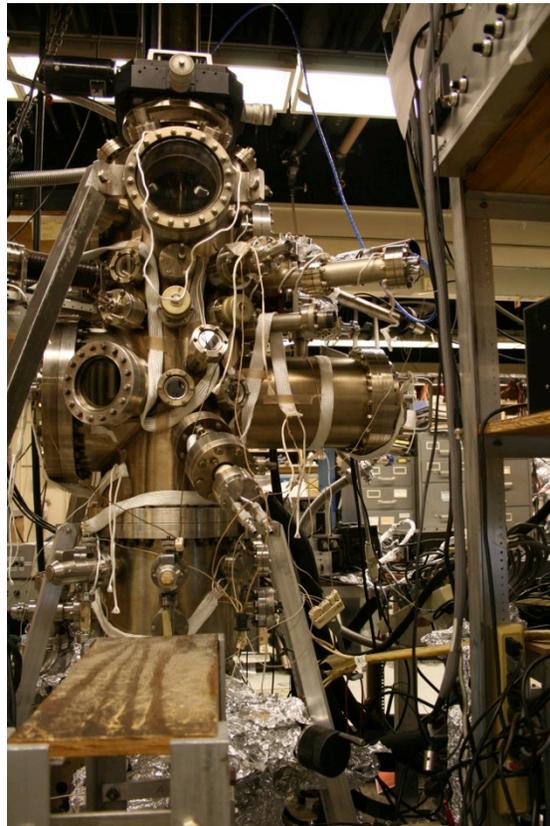
## Ultra-High Vacuum (UHV)

- Better than  $1 \times 10^{-10}$  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  $1 \times 10^{-10}$  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)

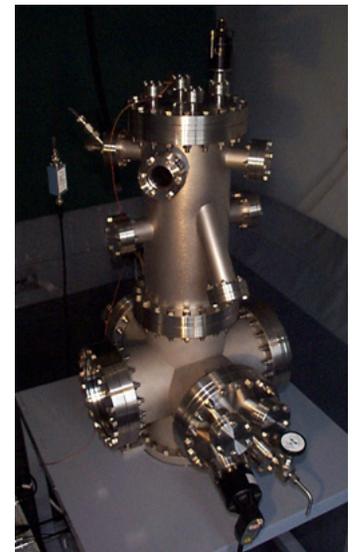
- On the order of  $1 \times 10^{-10}$  torr or better
- Needed to insure that surfaces remain clean
- UHV is achieved with all-metal chambers that are baked to remove water and other adsorbed gases from the walls, and are evacuated with oil-free pumps

- Unit of exposure is defined as:

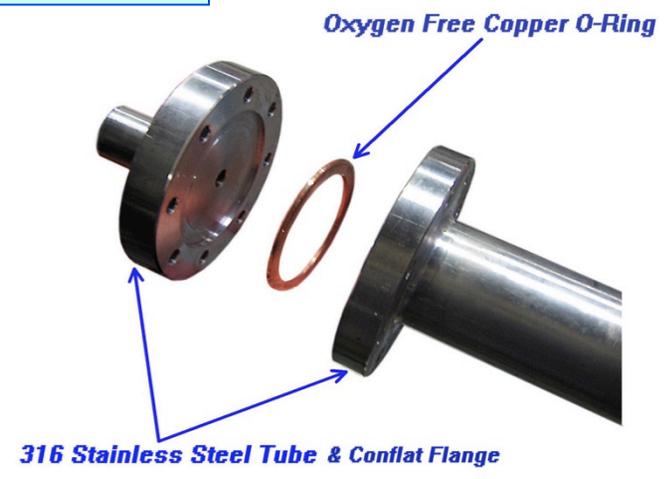
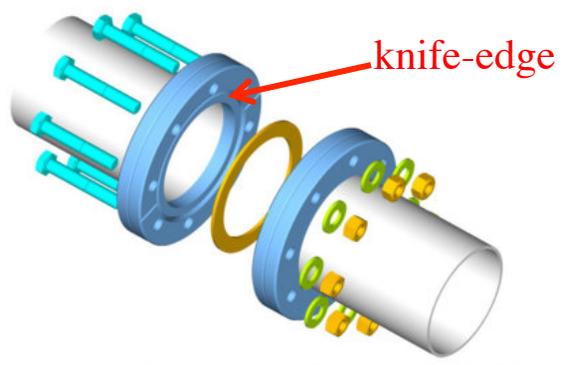
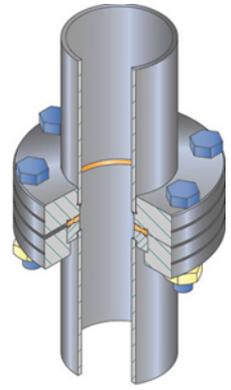
$$1 \text{ Langmuir} = 1 \text{ L} = 1 \times 10^{-6} \text{ torr-seconds}$$

- 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:

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



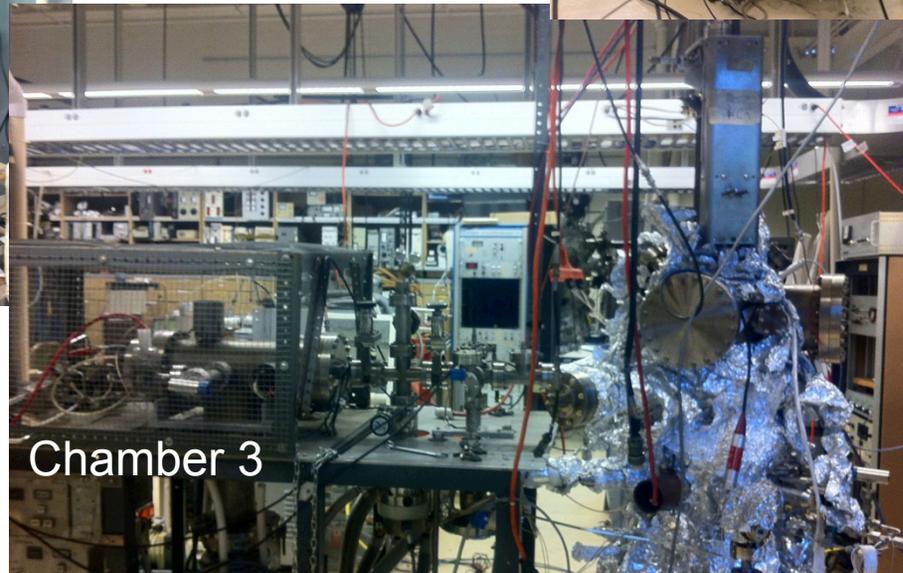
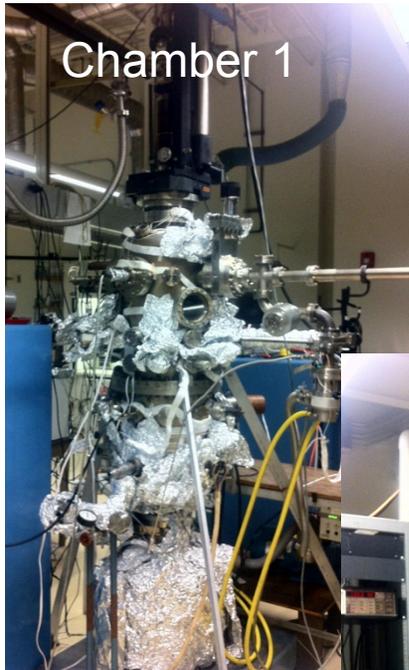
# Ultra-High Vacuum (UHV) CONFLAT flanges



# The Yarmoff Lab



# The Yarmoff Lab



# The Yarmoff Group

## Current Graduate Students

Weimin Zhou, Chris Salvo  
Tianbai Li, Selcuk Temiz  
Fatemeh Barati

## Current Undergrads

Josiah Keagy, Ugne Dargyte  
Mario Gorgees, Daniel Ryan

## Former Postdocs

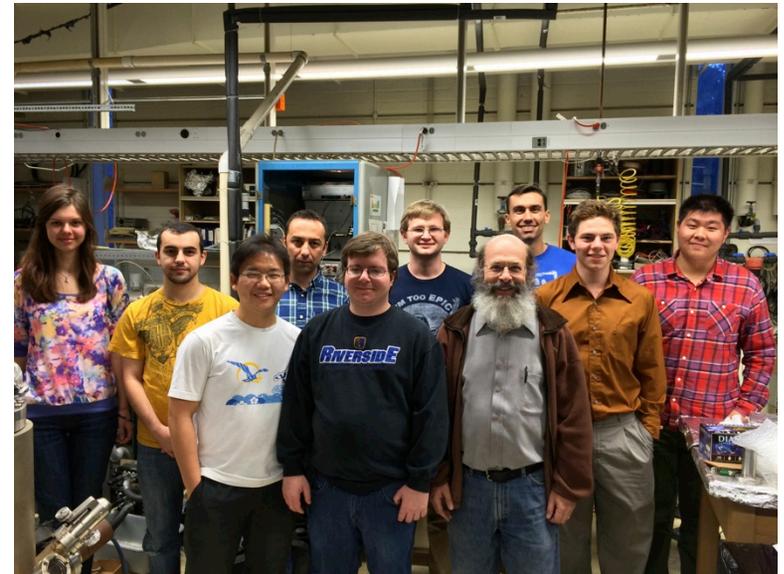
Snow Balaz - *now at Ohio State*  
Prasanta Karmakar - *now at Bhaba Atomic Research Centre*  
David Shuh - *now at LBNL*

## 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*  
William C. Simpson - *California State University, Sacramento*  
S. Roger Qiu - *Lawrence Livermore National Laboratory (LLNL)*  
Ye Yang - *KLA Tencor*  
Frank Liu - *Lehigh University*  
Victor Chen - *Medical College of Wisconsin*  
Reuben D. Gann - *Georgia Institute of Technology*  
Xiaoxiao He - *KLA Tencor*  
Alex Arjad - *searching*

## Collaborators

Zdenek Sroubek - *Academy of Sciences, Czech Republic*  
Regina Ragan, Ruqian Wu - *UC Irvine*  
Jing Shi - *UC Riverside*



## Funding:

National Science  
Foundation



Army Research  
Office



Center for Nanoscale  
Innovation for  
Defense

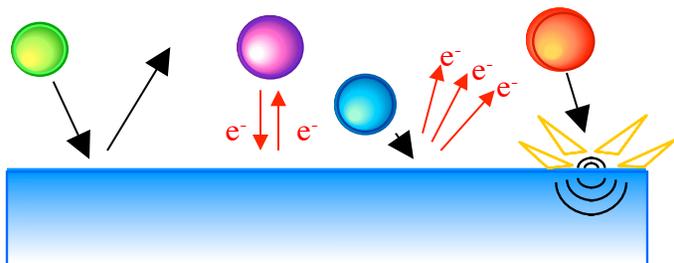


UCR College of  
Natural and  
Agricultural Sciences

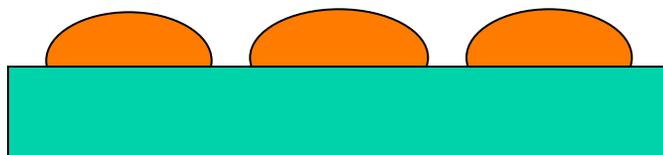


# Projects

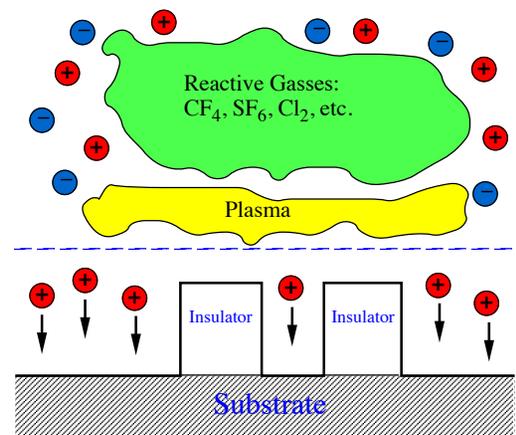
## Ion-surface interactions



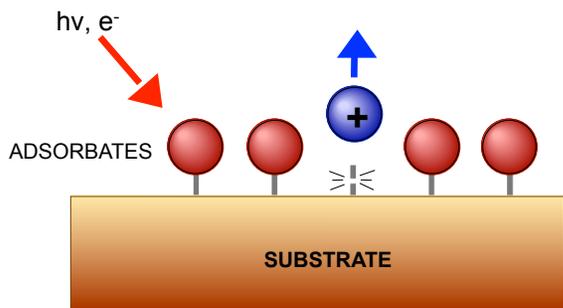
## Fabrication and Characterization of Nanomaterials



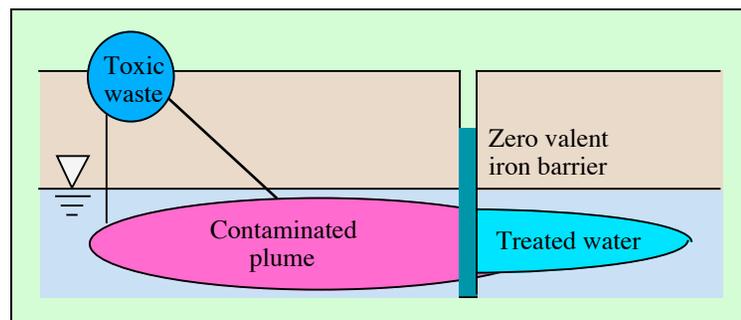
## Semiconductor surface etching



## Radiation damage to surfaces



## Environmental surfaces



# Ion-Surface Interactions

## Physical Interactions

Scattering,  
Sputtering,  
Recoil



## Electronic Interactions

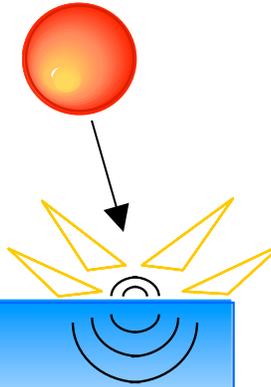
Charge Exchange



Electron Emission



Electronic Excitation



- 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

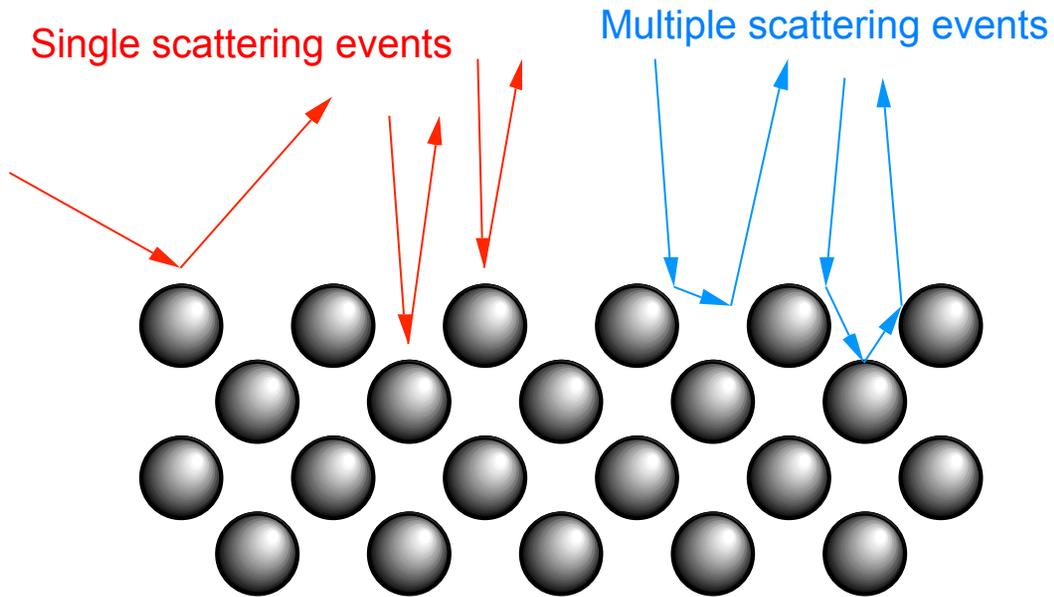
Charge transfer (neutralization, ionization)

Electronic excitation (substrate, projectile)

Electron emission

→ Energy loss is due to *inelastic scattering*

# Ion Scattering Spectroscopy



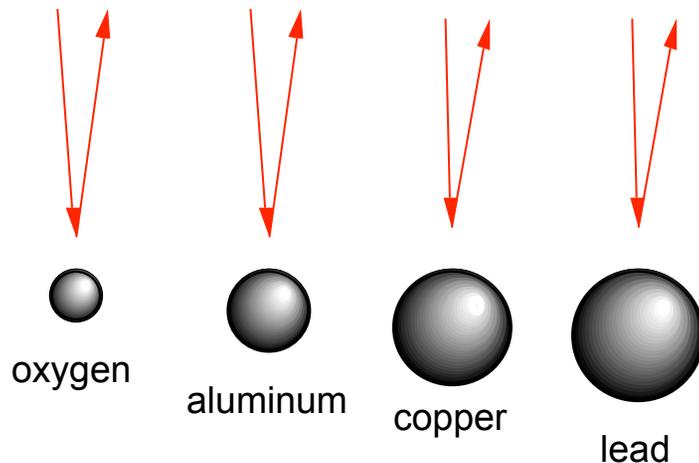
## Binary collision approximation (BCA):

- 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

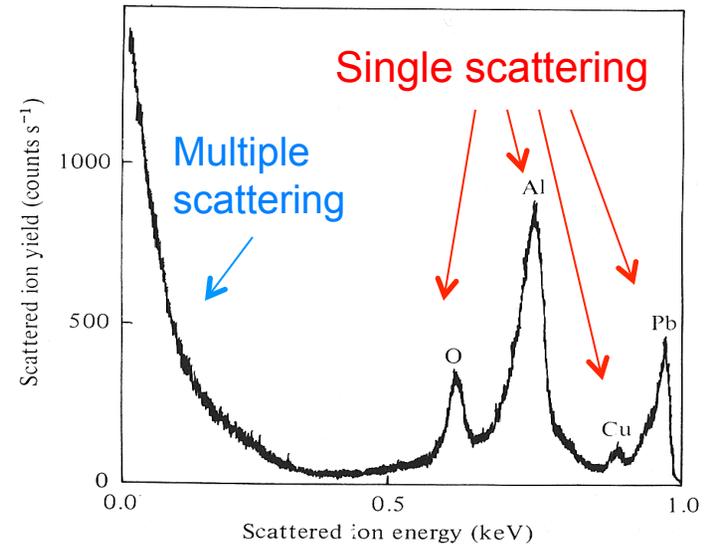
## Single scattering events



**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.



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

### Elastic energy loss during single collision:

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

$E_S$  - scattered energy  
 $E_0$  - incident energy  
 $\theta$  - scattering angle  
 $M_T$  - mass of target atom  
 $M_P$  - mass of projectile

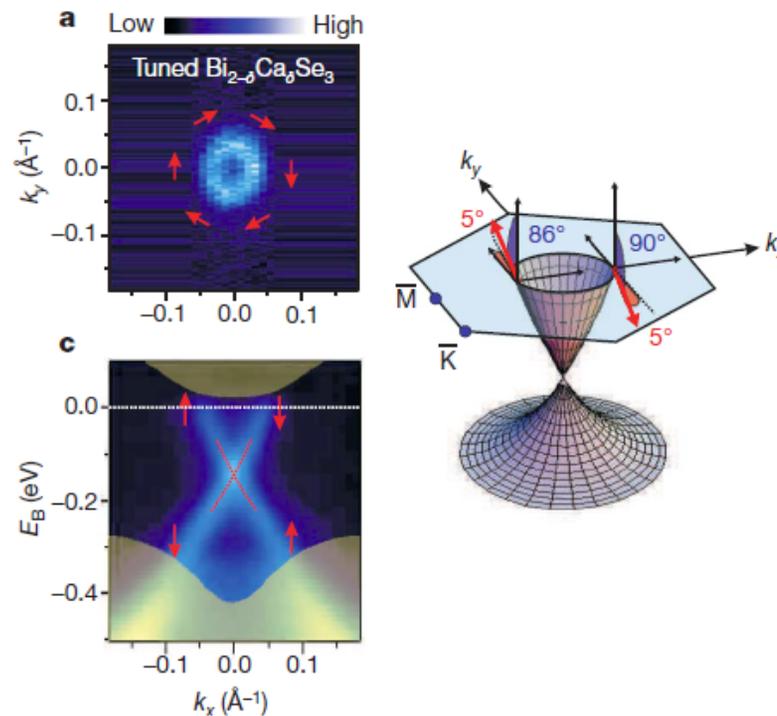
# Topological Insulators



- $(\text{Bi,Sb})_2(\text{Te,Se})_3$  family of compounds

# Topological Insulators

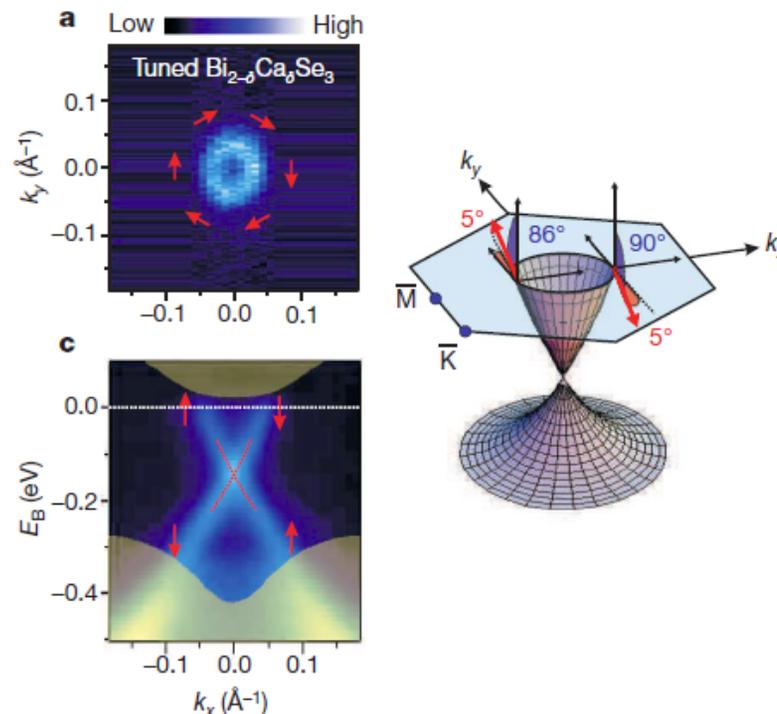
- $(\text{Bi,Sb})_2(\text{Te,Se})_3$  family of compounds
- Promising materials for spintronics, quantum computing



D. Hsieh, et al., Nature **430**, 1101 (2009).

# Topological Insulators

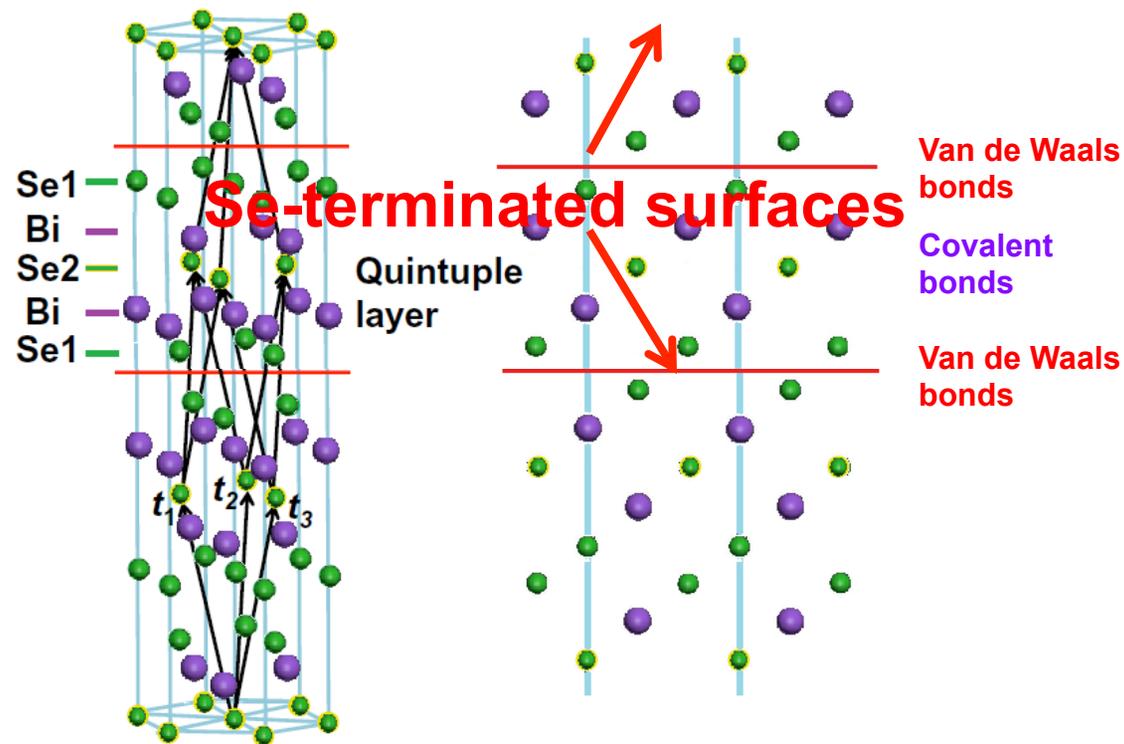
- $(\text{Bi,Sb})_2(\text{Te,Se})_3$  family of compounds
- Promising materials for spintronics, quantum computing
- Problems exist with these materials, including the aging effect



D. Hsieh, et al., Nature **430**, 1101 (2009).

# Topological Insulators

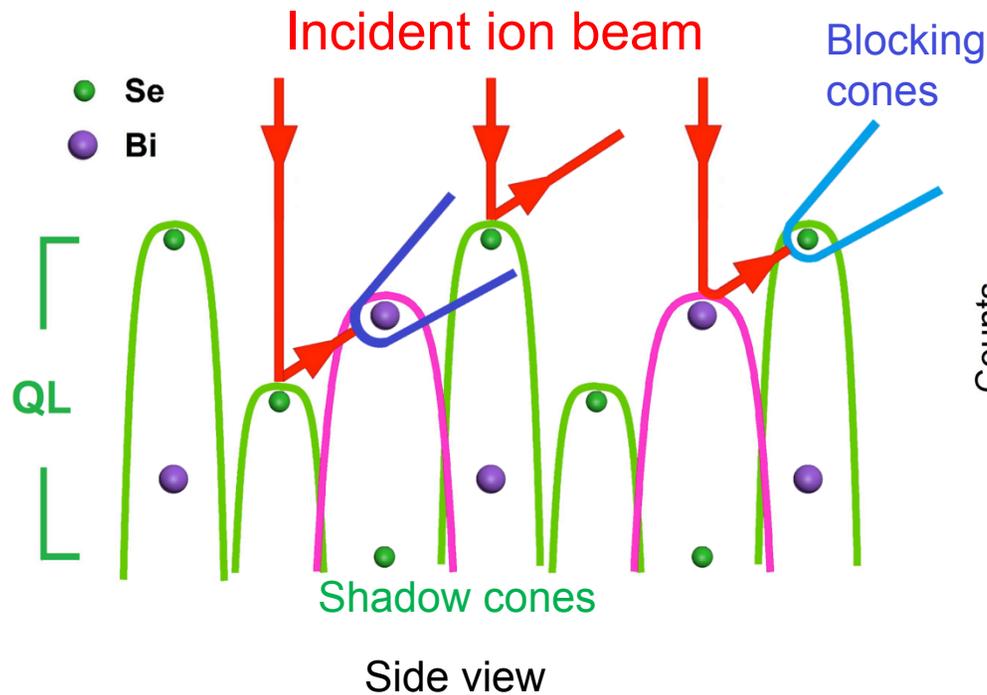
- $(\text{Bi,Sb})_2(\text{Te,Se})_3$  family of compounds
- Promising materials for spintronics, quantum computing
- Problems exist with these materials, including the aging effect
- Quintuple layer (QL) structure



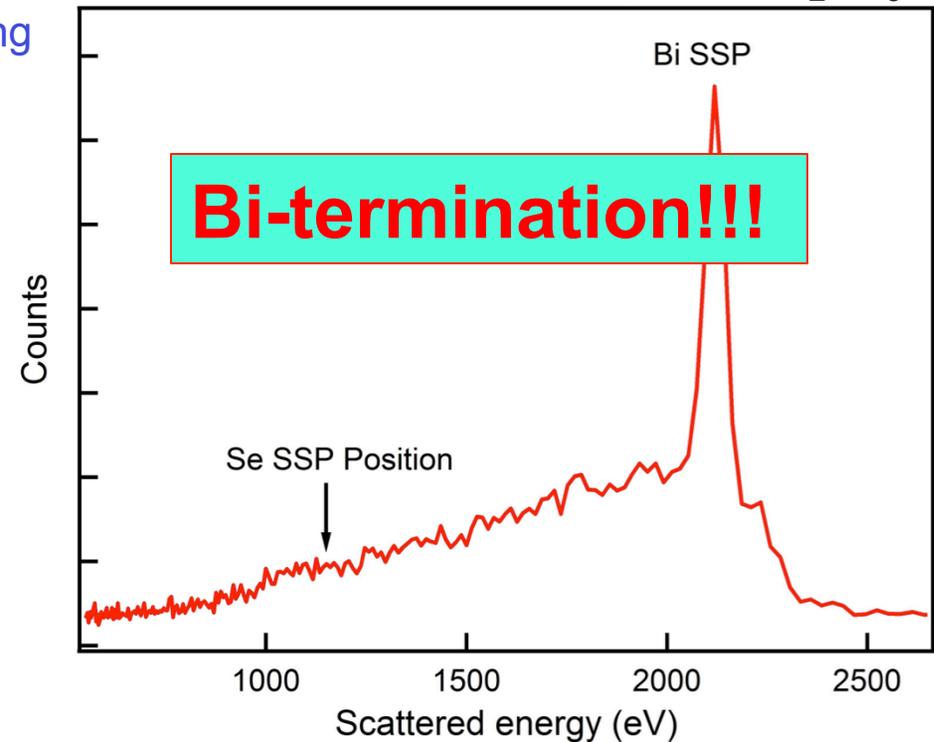
# Double Alignment Orientation

Polar angle:  $\phi = 35^\circ$

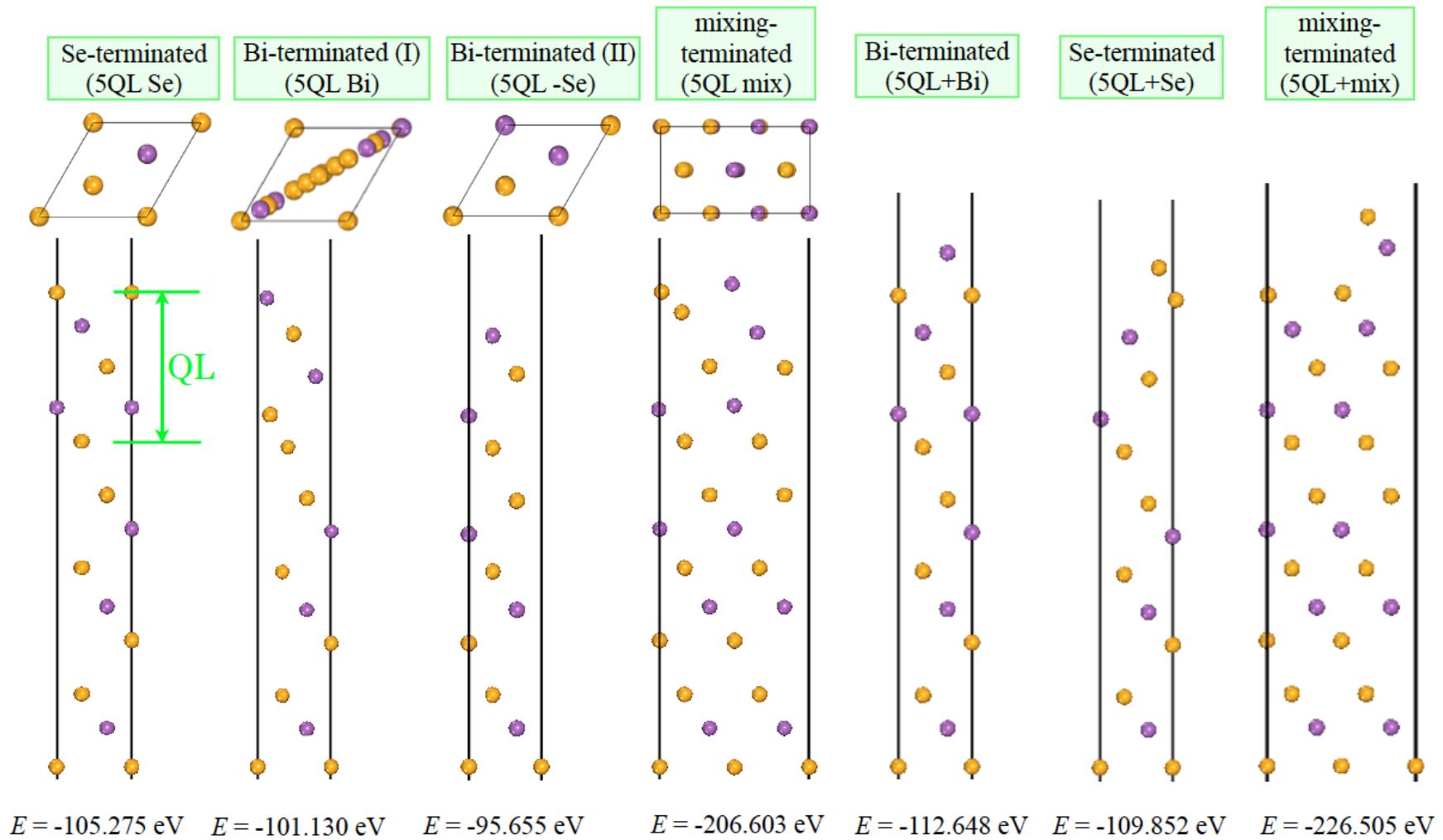
Azimuth:  $\varphi = 0^\circ$



3.0 keV  $\text{Na}^+$  ion scattering from  $\text{Bi}_2\text{Se}_3$



## Bi<sub>2</sub>Se<sub>3</sub> Surface (5QL)

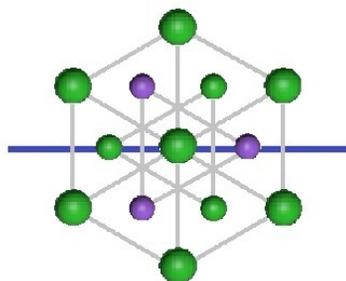


Single bilayer of Bi on top of  $\text{Bi}_2\text{Se}_3$  is the most stable

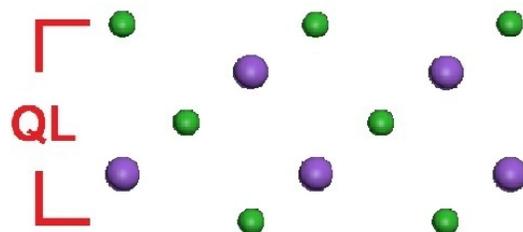
- Extra Bi
- Se
- Bi

## Crystal structure

View from top



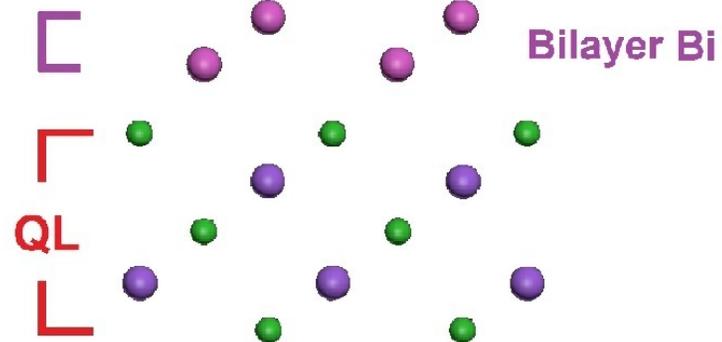
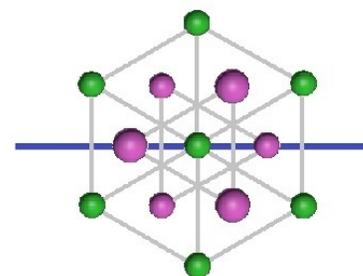
View from side



Total energy

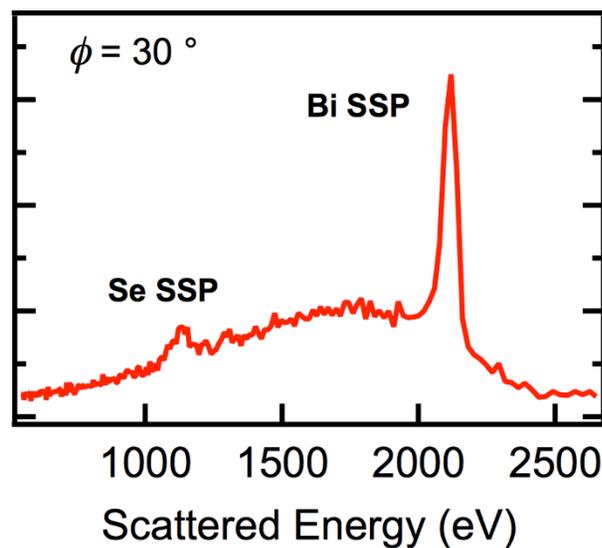
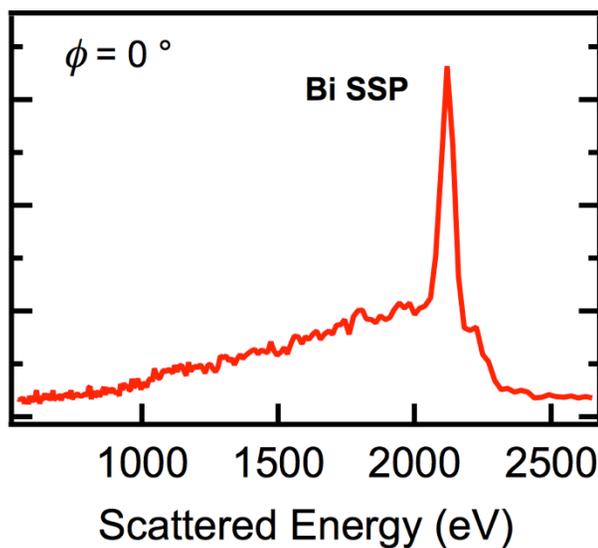
-105.3 eV

Bi /  $\text{Bi}_2\text{Se}_3$   
(5QL + bilayer Bi)



-123.0 eV

# Changing Orientation

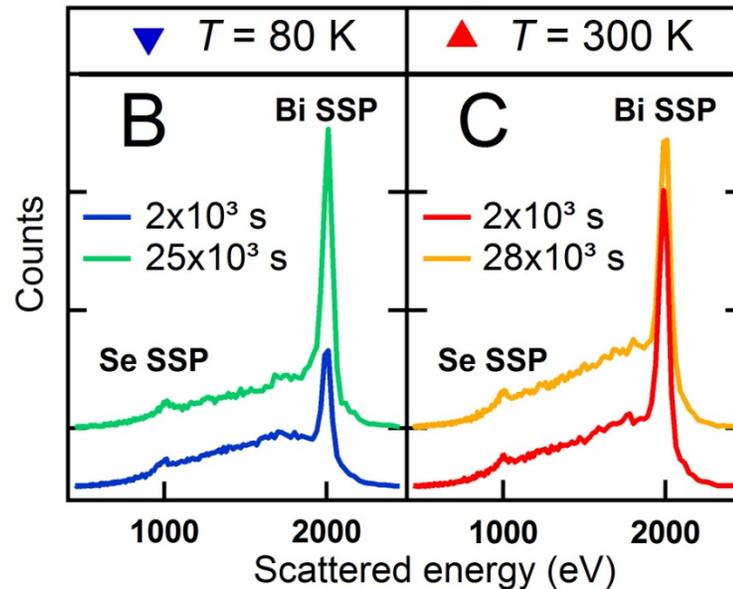


- Changing to a single alignment orientation reveals subsurface Se

# Temperature & Time dependence

3.0 keV Na<sup>+</sup> scattering from Bi<sub>2</sub>Se<sub>3</sub>, with emission angles of  $\phi = -12.5^\circ$ ,  $\varphi = 60^\circ$

Cleaved at temperatures of



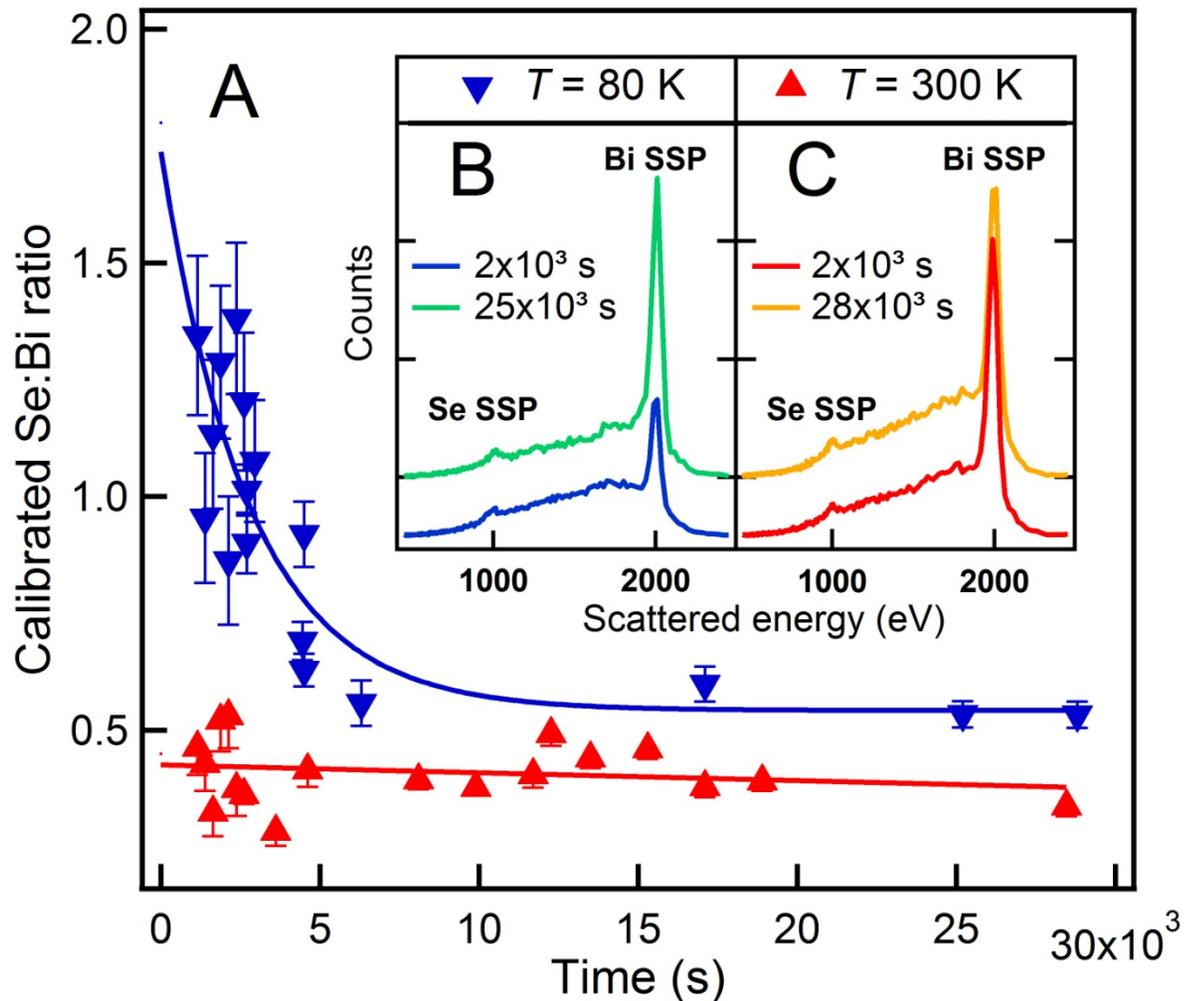
At 80 K, Bi peak increases with time.

At 300 K, no obvious changes in peak shapes.

Non-total blocking direction

# Temperature & Time dependence

Calibrated Se:Bi ratio vs. time

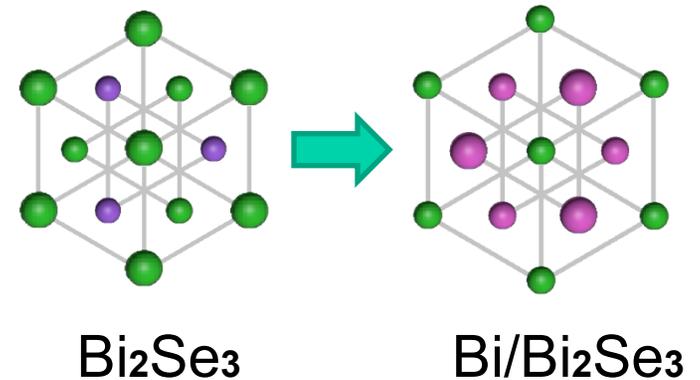


The Se:Bi ratio drops exponentially at 80 K, matching the 300 K value after about 1 hour (time constant = 2775 s).

Se:Bi ratios from Kalypso simulations:

$1.27 \pm 0.09$

$0.36 \pm 0.03$

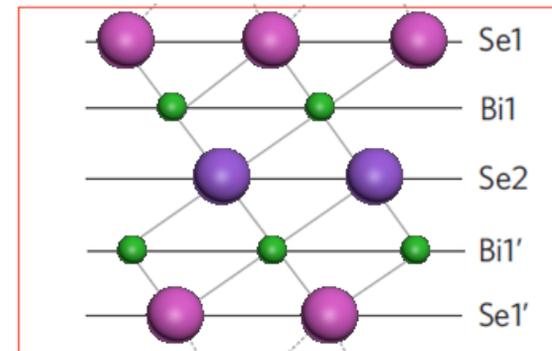


Surface termination changes more slowly at 80 than at 300 K.

Thermally activated process, such as diffusion of surface species, leads to Bi-termination.

## Depletion of surface Se or enrichment of surface Bi?

- Depletion of Se
  - Desorption of Se to form  $\text{Se}_2$  or  $\text{Se}_4$  moieties
  - Removal of all Se from a QL leaves a Bi bilayer behind



- Enrichment of Bi
  - Diffusion of Bi
  - Transports to the surface as a surfactant

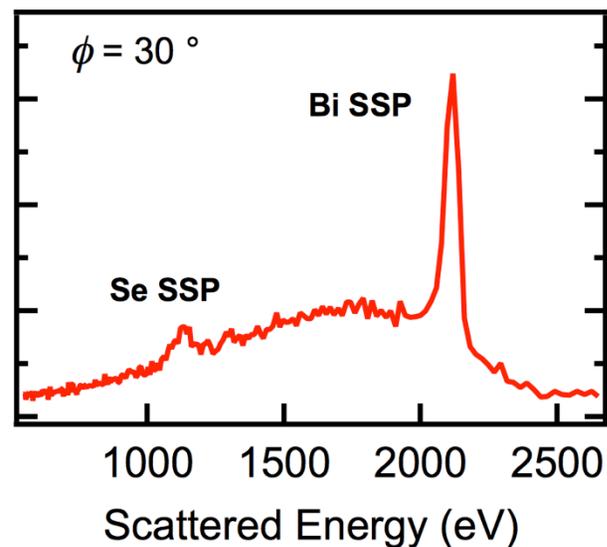
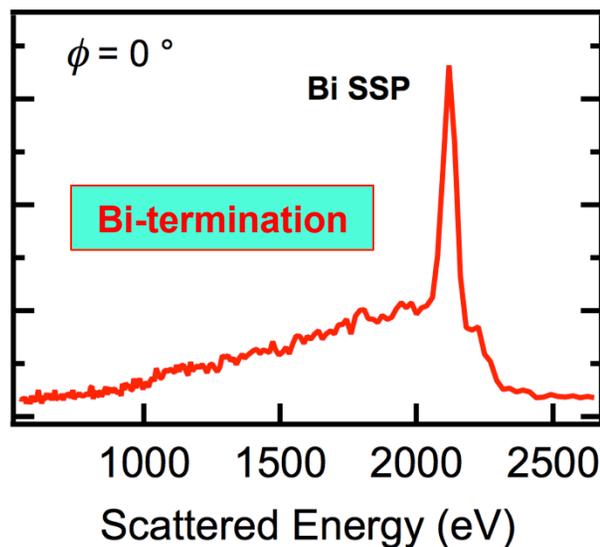
But, wait...



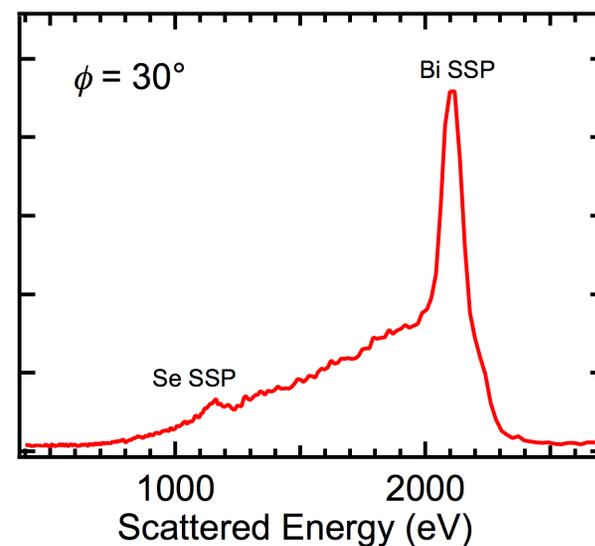
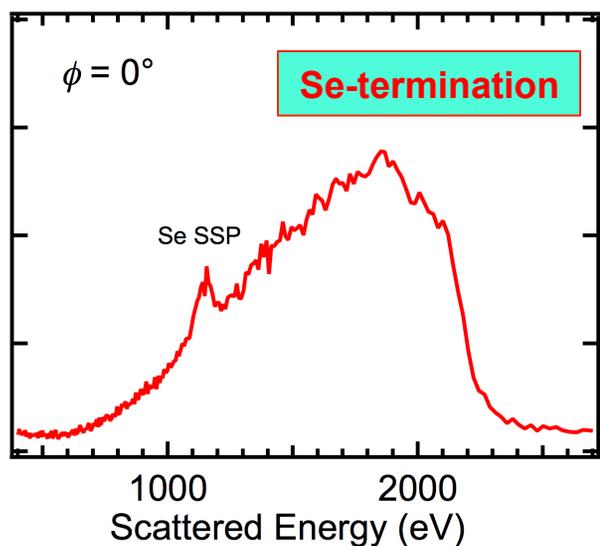
# The Halloween NIGHTMARE

- New graduate student
- Se termination revealed

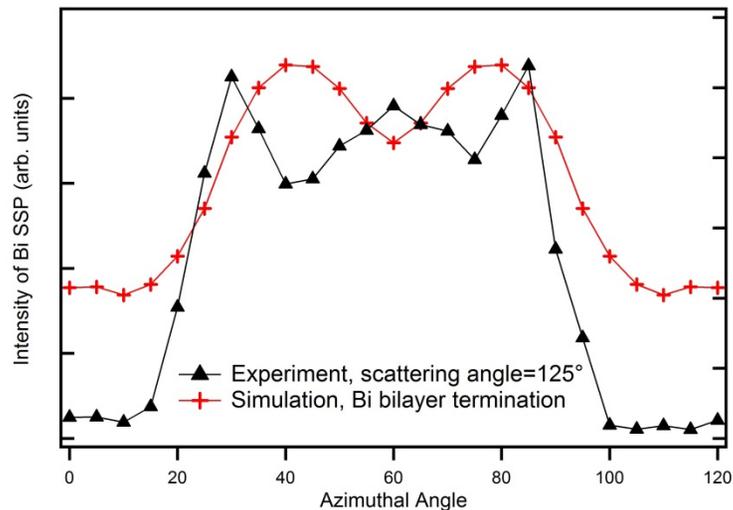
Xiaoxiao He



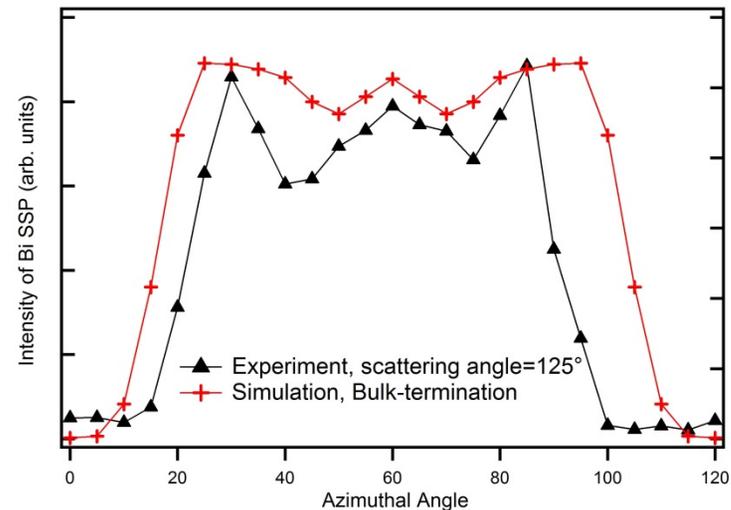
Weimin Zhou



## Bi Bilayer Termination



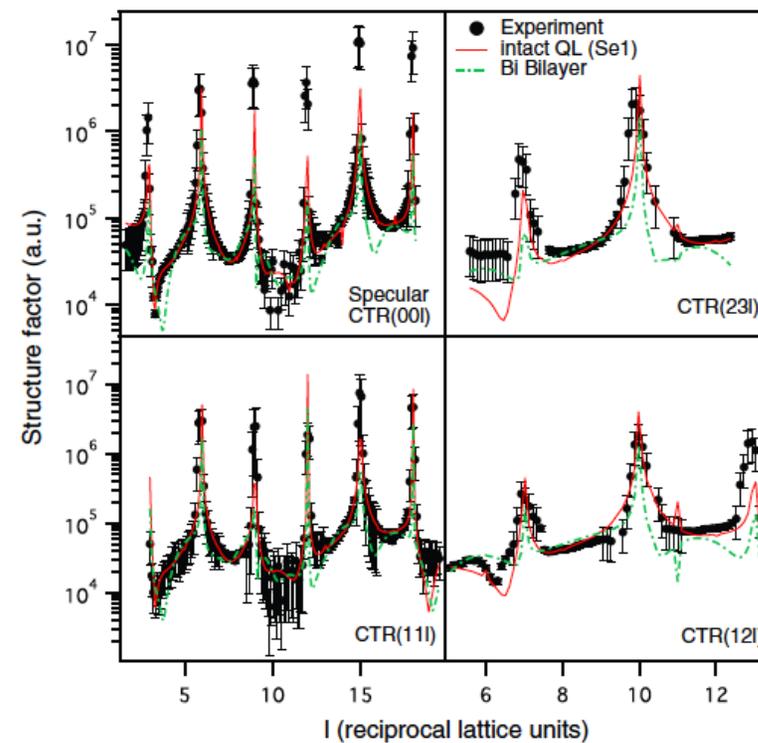
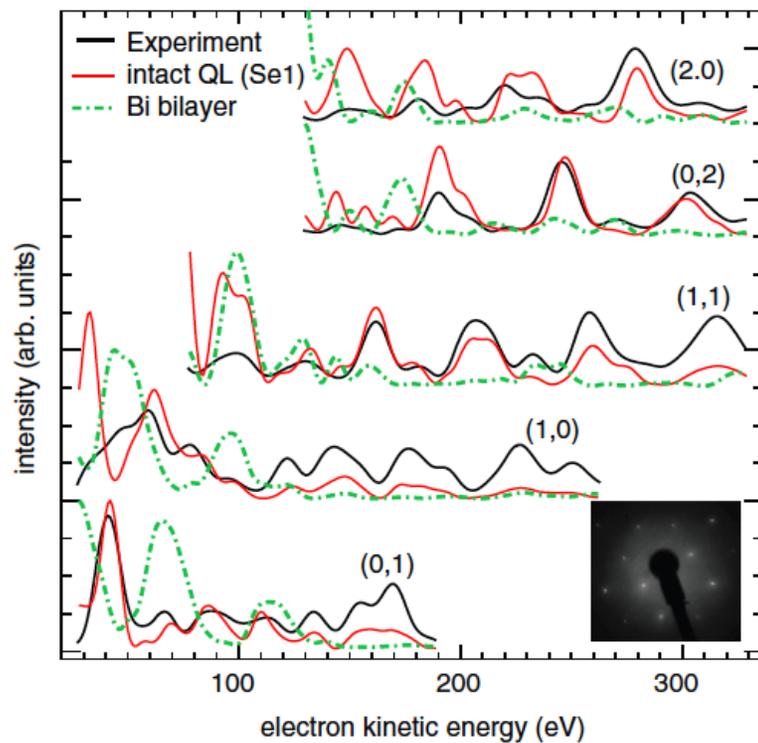
## Bulk Se-Termination



- Simulation package is Kalypso.
- Experimental data is collected from an *in-situ* cleaved surface that is Se rich.
- The experimental Bi intensity dependence on azimuthal angle seems to **support bulk-termination**, but the match is not yet satisfactory.
- We are still working to optimize the model to better fit the experimental data and determine the specific surface structure.

# Other recent work

- Combined low energy electron and x-ray diffraction study
- Indicates a **Se-terminated** surface

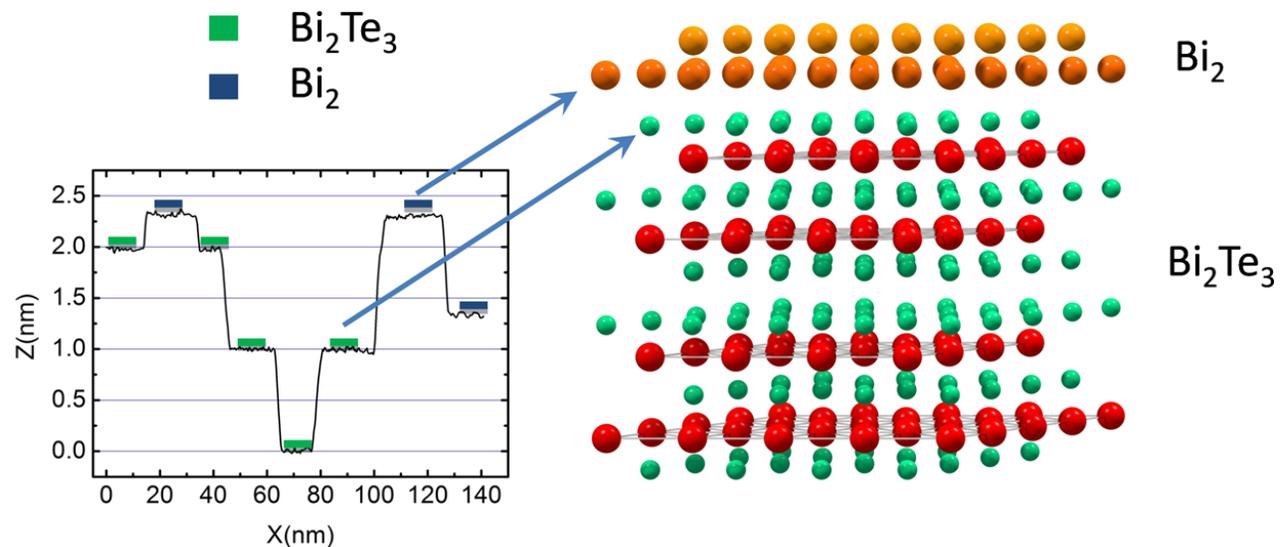
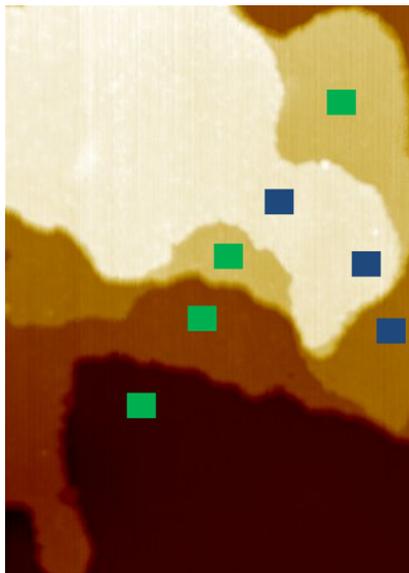


de Rios, et al., Phys. Rev. B **88**, 041404(R) (2013)

# Other recent work



- STM study of  $\text{Bi}_2\text{Te}_3$  prepared by sputtering/annealing in UHV
- Indicates an approximate 50-50 mixture of Bi and Te terminations



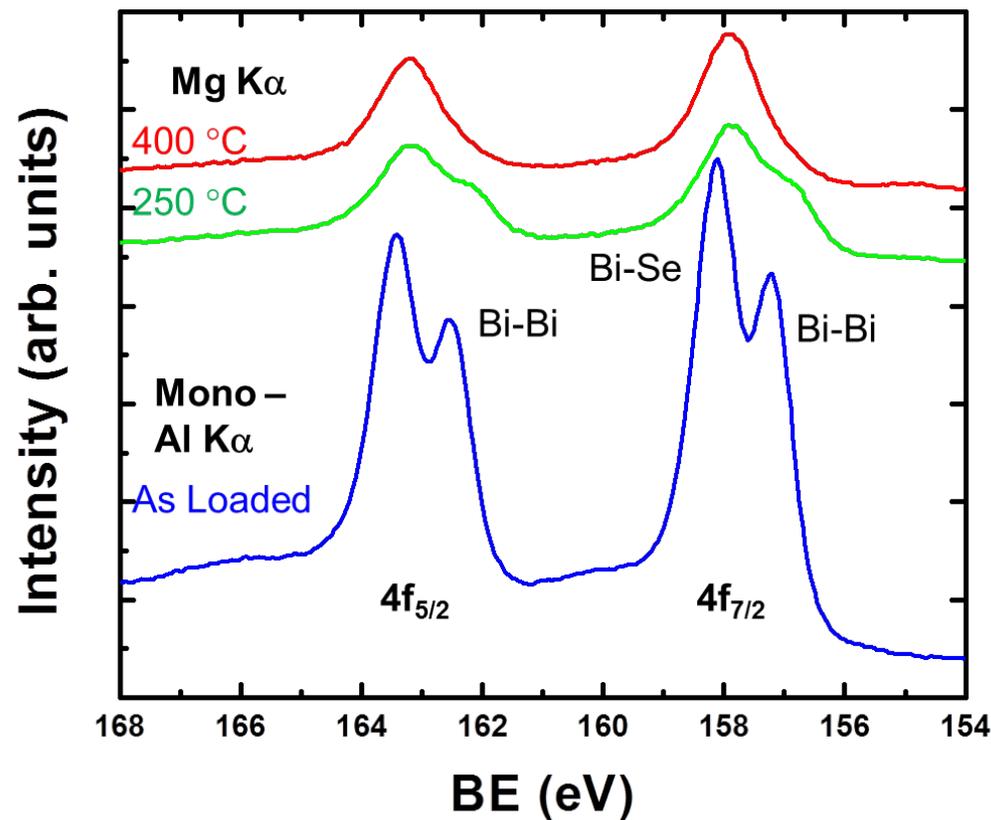
Coelho, et al., Nano Lett. **13**, 4517–4521 (2013)

# Other recent work



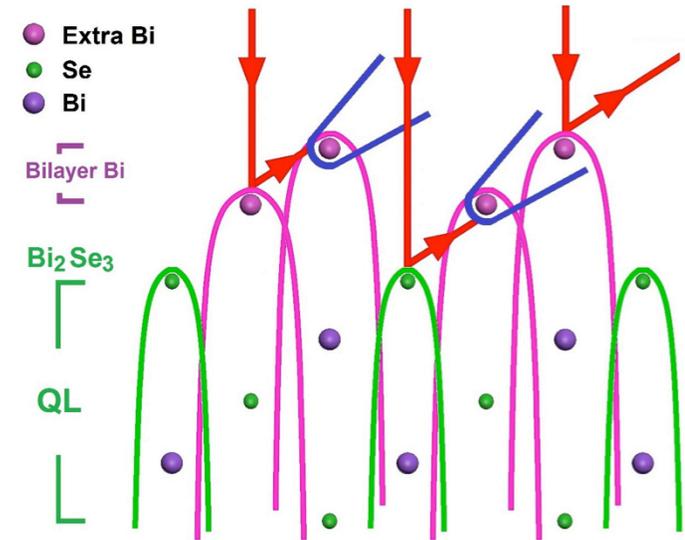
For about half of the cleaves, XPS shows a doublet in the Bi 4f level

- The high BE component matches that of  $\text{Bi}_2\text{Se}_3$
- The low BE component matches that of Bi metal

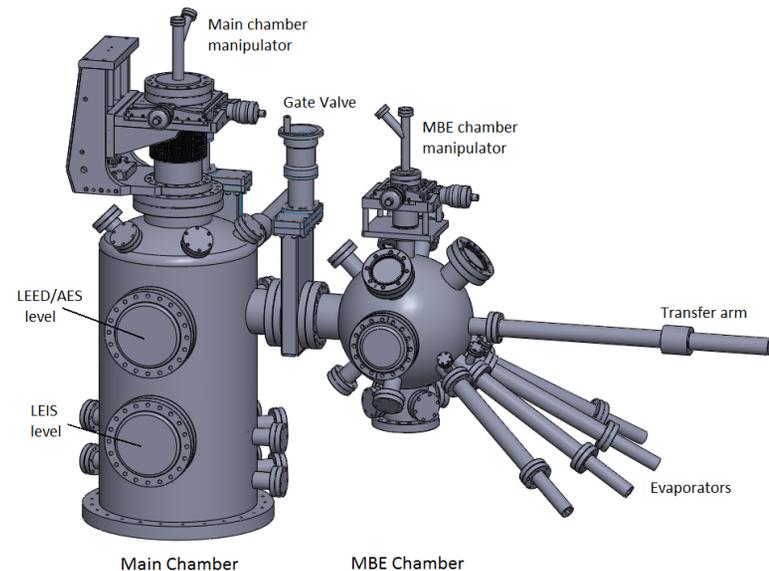


# Conclusions: Surface Termination of $\text{Bi}_2\text{Se}_3$ UCR

- $\text{Bi}_2\text{Se}_3$  is comprised of quintuple layers (QLs) held together by weak van der Waals bonds, so it has been assumed that a Se termination results when cleaved.
- The LEIS spectra (*sometimes?*) indicate a surface terminated with Bi after cleaving at room temperature.
- DFT shows that addition of a Bi bilayer is more stable.
- Measurements at  $\text{LN}_2$  temperature suggest that surface does cleave to form a Se-termination, but that atomic diffusion leads to a change.



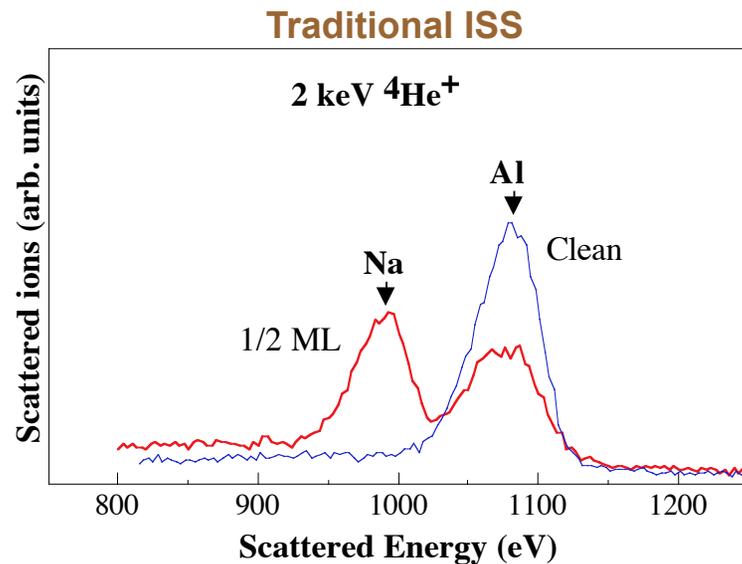
- Alter the stoichiometry and other parameters in the sample preparation to investigate how this affects the termination
- Use LEIS to measure a complete surface structure of cleaved materials
- Measure time dependence at liquid He temperatures
- Investigate other related materials
- Grow materials by MBE
- Investigate surface adsorption, chemical reactions
- Use the neutralization in LEIS to detail electronic properties
- Investigate effects of e-beam radiation



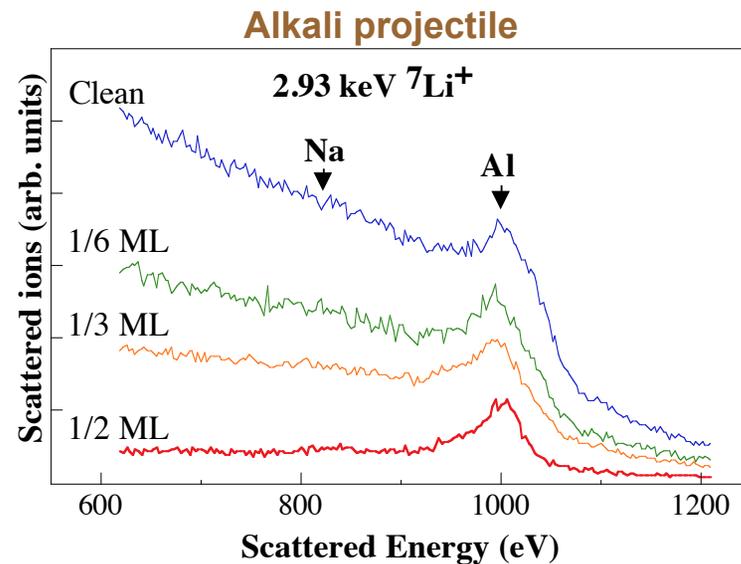
# ISS Energy Spectra

Na adsorbed on Al(100)

- Electrostatic analyzer employed
- Sensitive only to scattered ions



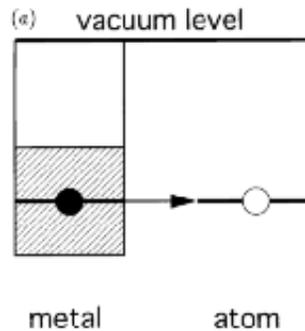
- Single scattering peaks (SSP) seen for Na and Al surface atoms.



- Where is the Na?

K.A.H. German, C.B. Weare, P.R. Varekamp, J.N. Andersen and J.A. Yarmoff, Phys. Rev. Lett. **70**, 3510 (1993).

# Charge transfer processes in ion-surface collisions

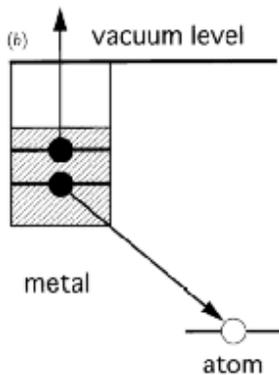


**Resonant charge transfer (RCT)**

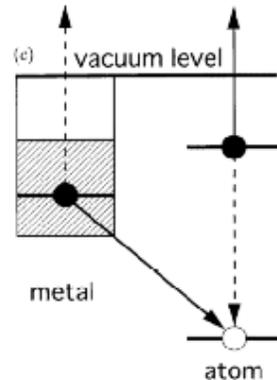
- **Resonant charge transfer (RCT)** of electrons between atomic and metal states at constant energy

*Ionization/affinity level overlaps conduction band:  
alkali, halogen, oxygen ions*

Reversible; final charge state determined along exit trajectory



**Auger neutralization**



**Auger de-excitation**

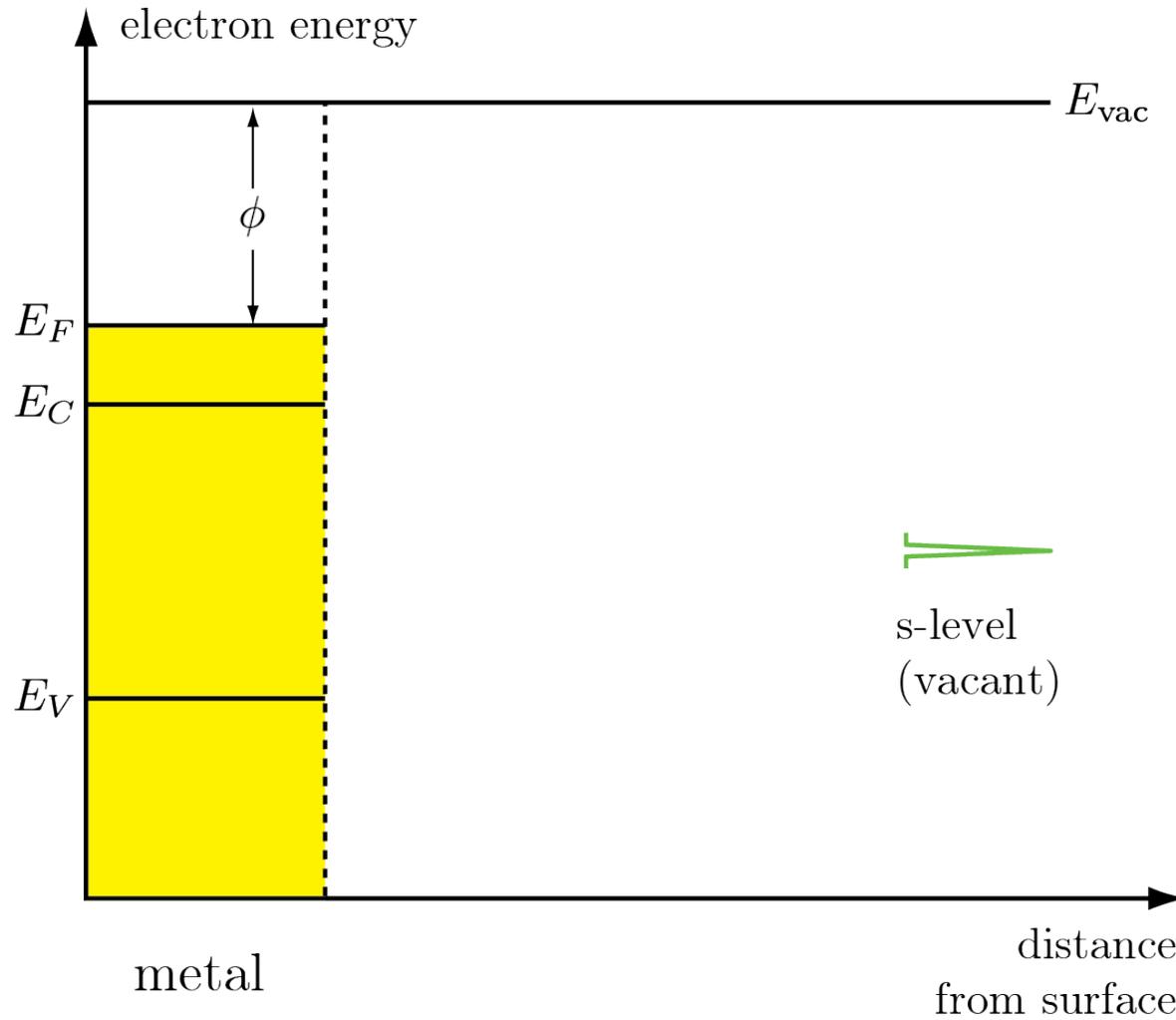
- **Auger processes** involve the relaxation of the excited atom-surface system

*Ionization level below conduction band:  
noble gas ions*

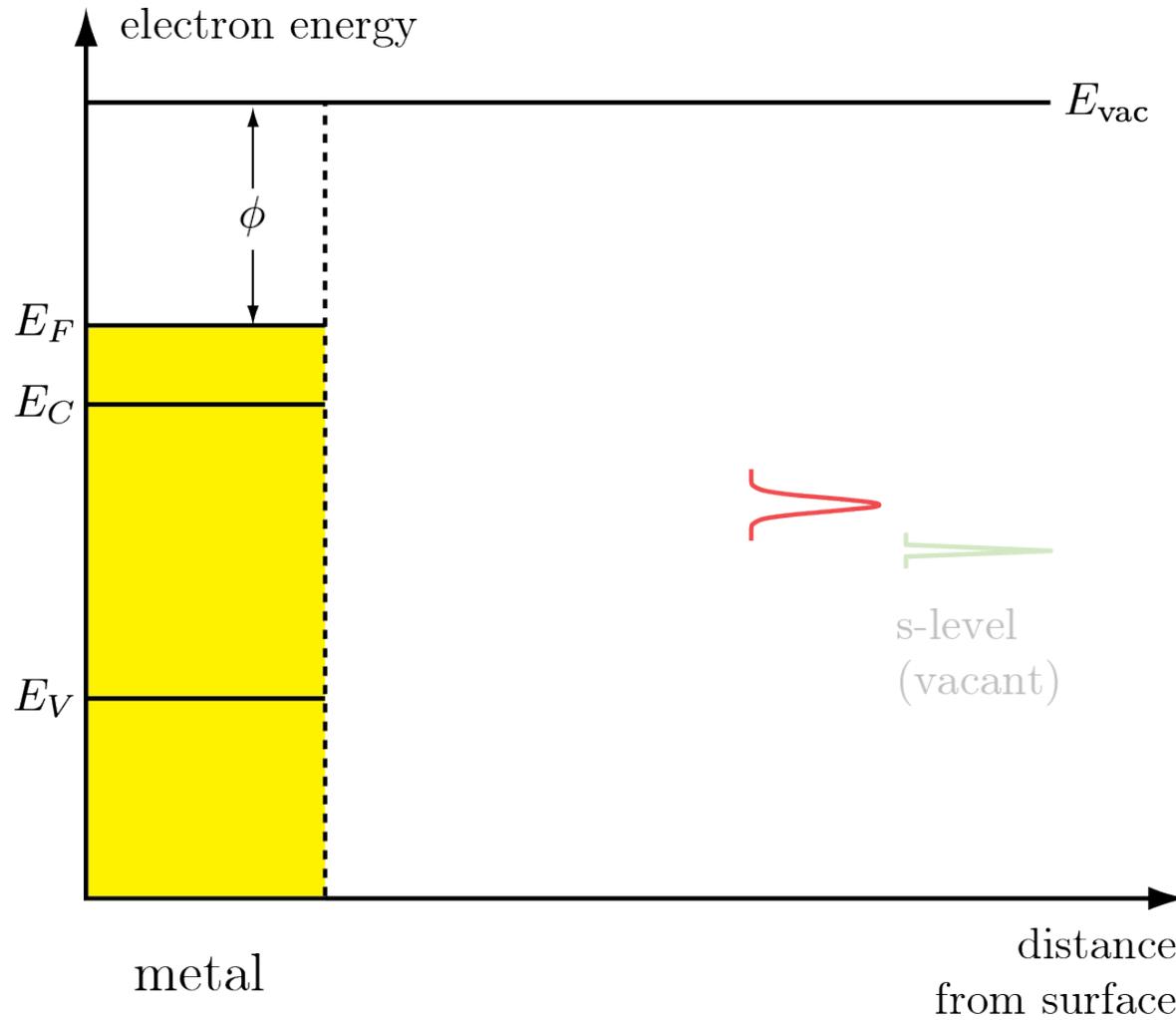
Irreversible; neutralization can occur anytime during scattering

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

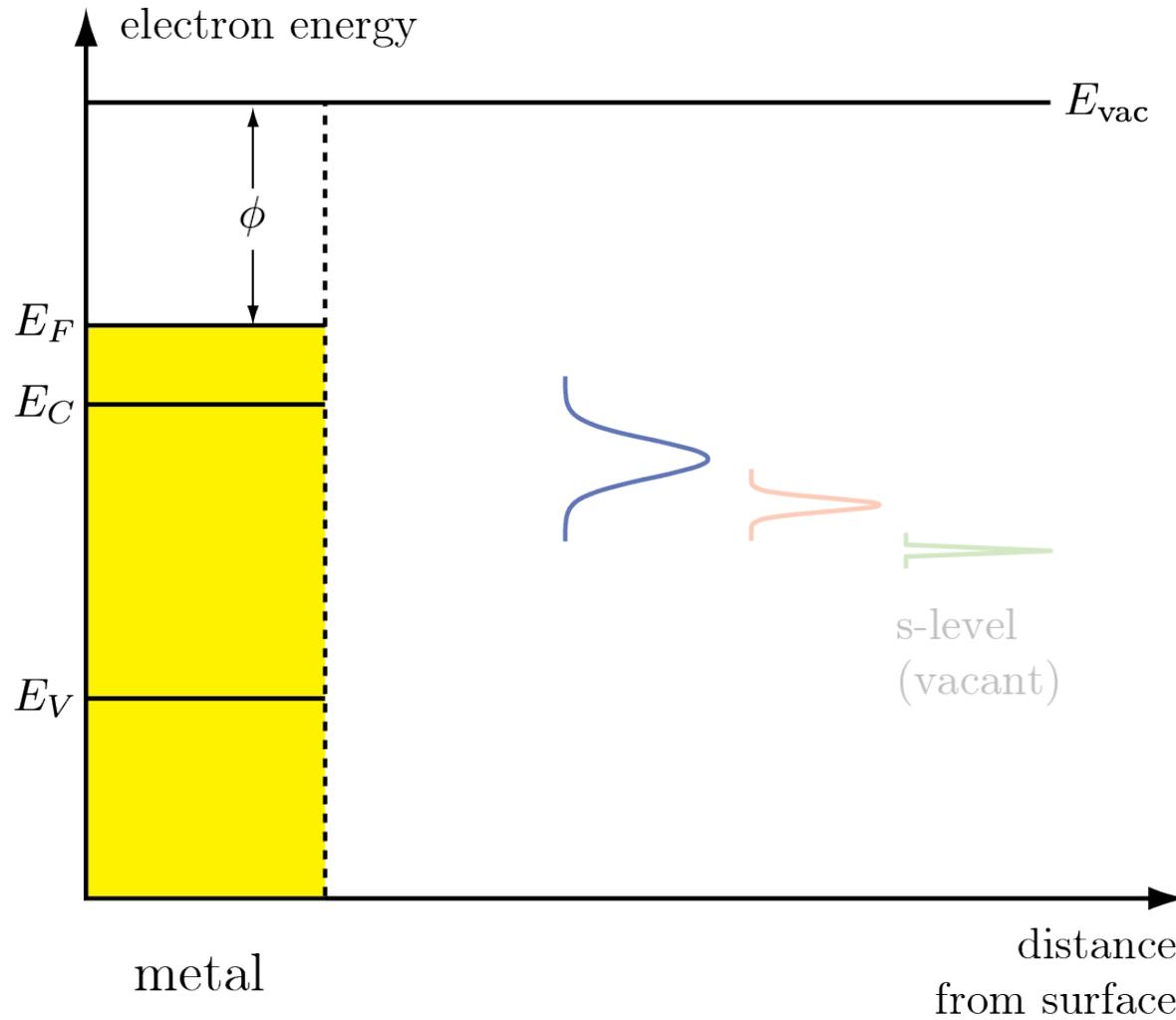
# Resonant Charge Transfer (RCT)



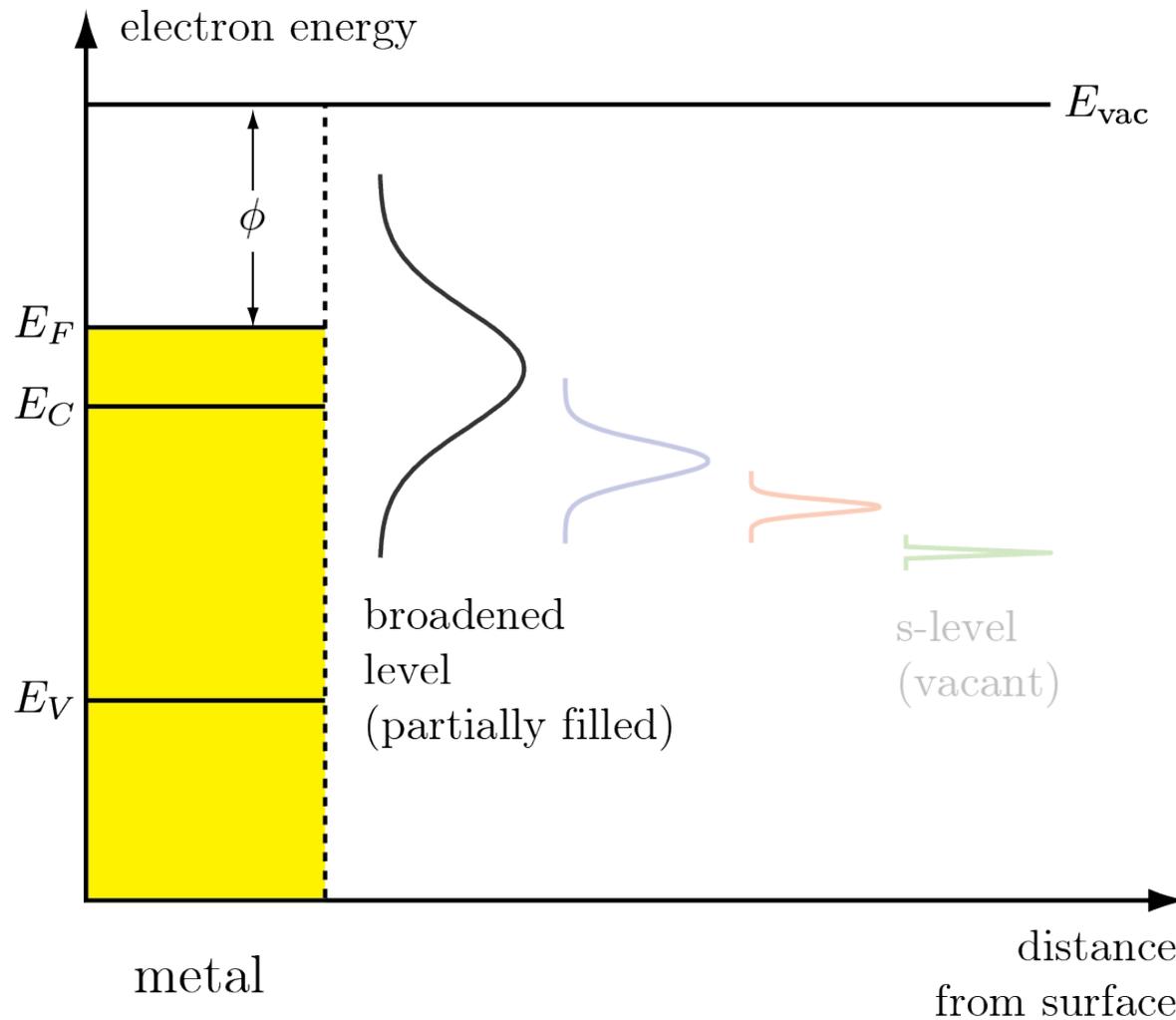
# Resonant Charge Transfer (RCT)



# Resonant Charge Transfer (RCT)

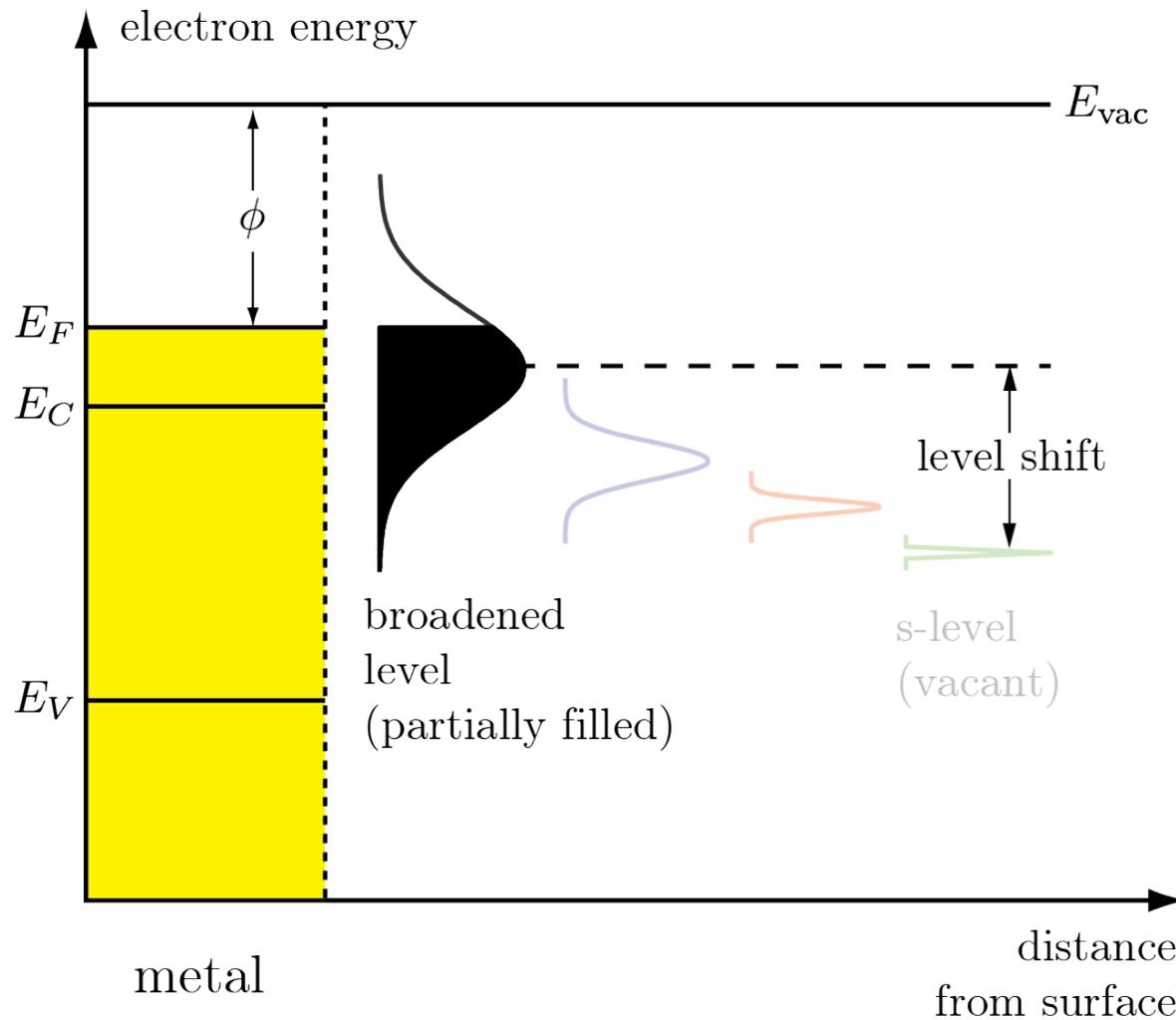


# Resonant Charge Transfer (RCT)



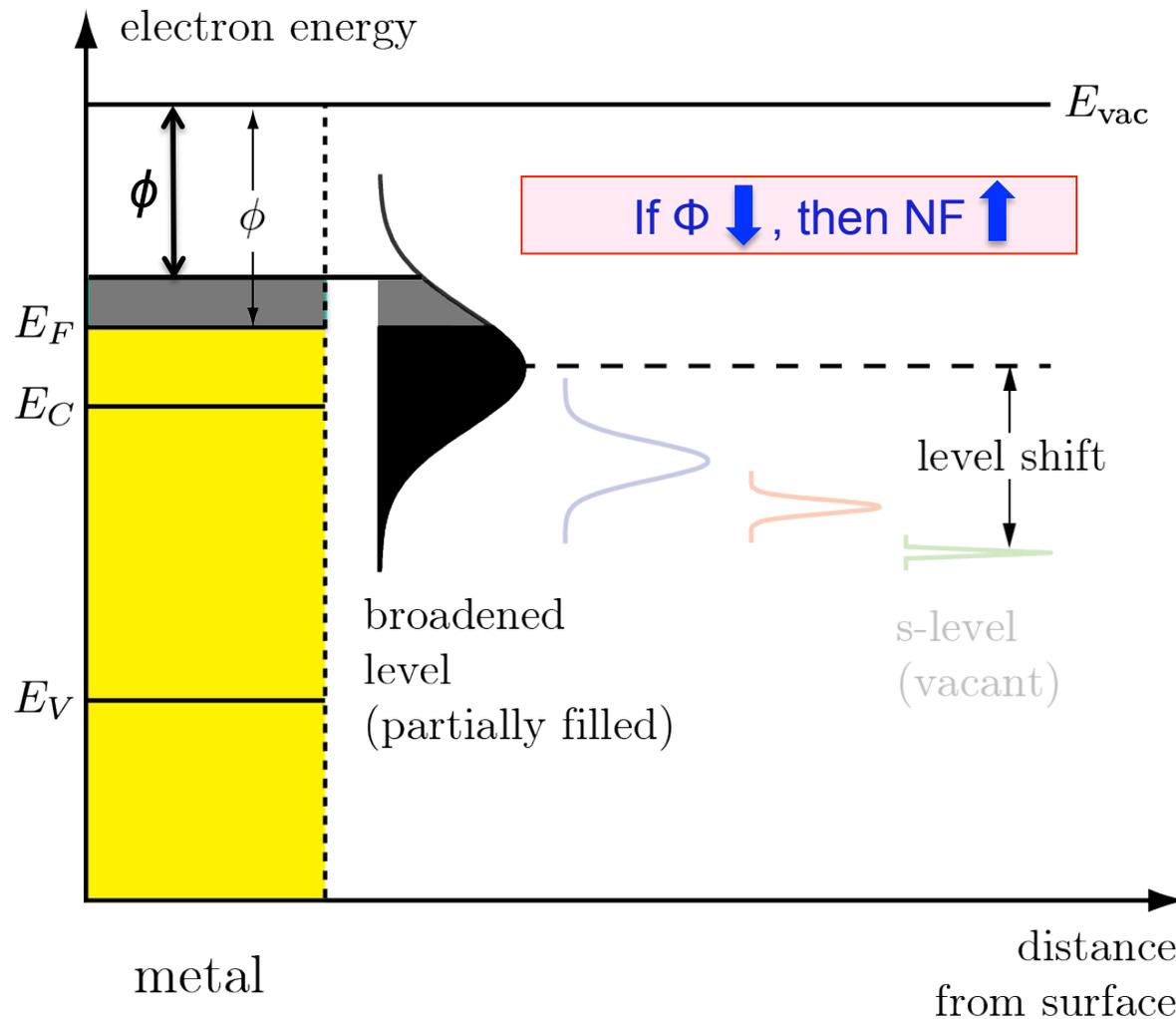
# Resonant Charge Transfer (RCT)

- The neutral fraction (NF) is determined along the exit trajectory, typically within a few Å' s of the surface.
- The NF is dependent on the occupancy of states at the Fermi energy.



# Resonant Charge Transfer (RCT)

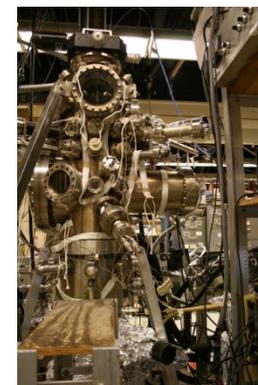
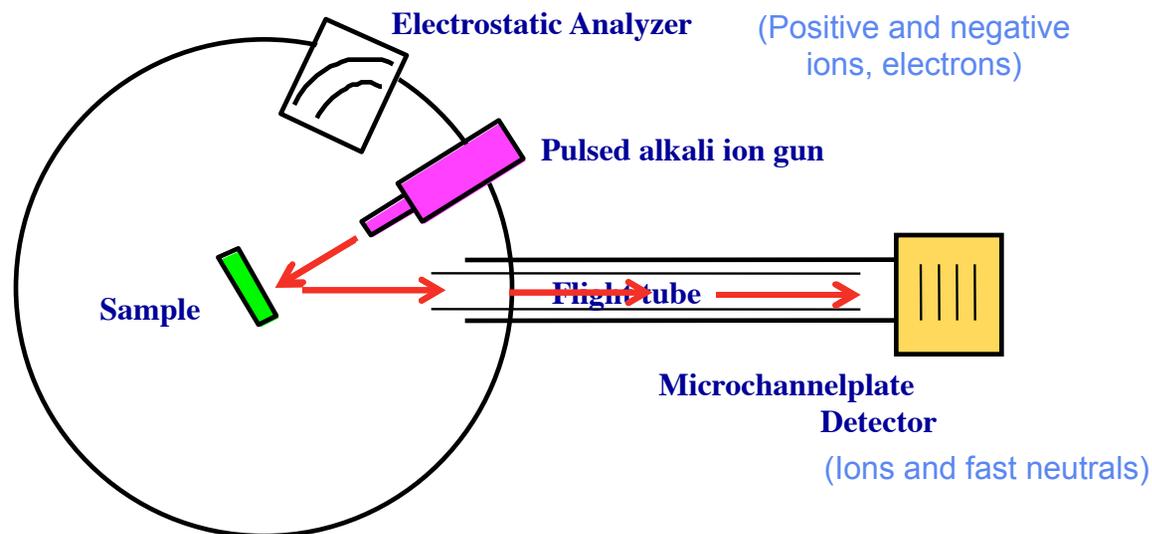
- A change in surface work function leads to a change in the measured neutral fraction
- If the work function is lowered, then the scattered alkali neutral fraction will increase, and vice versa.



# Experimental setup

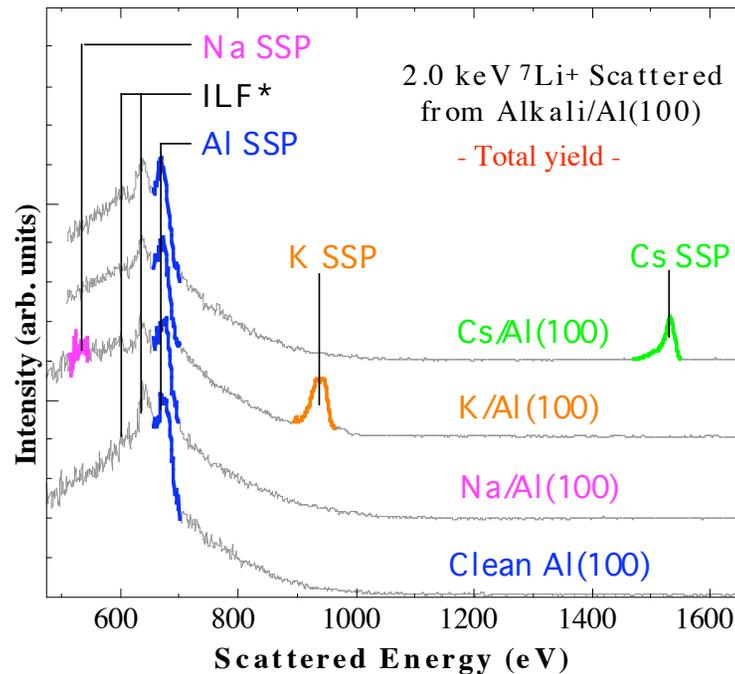


Kimball Physics IGS-4

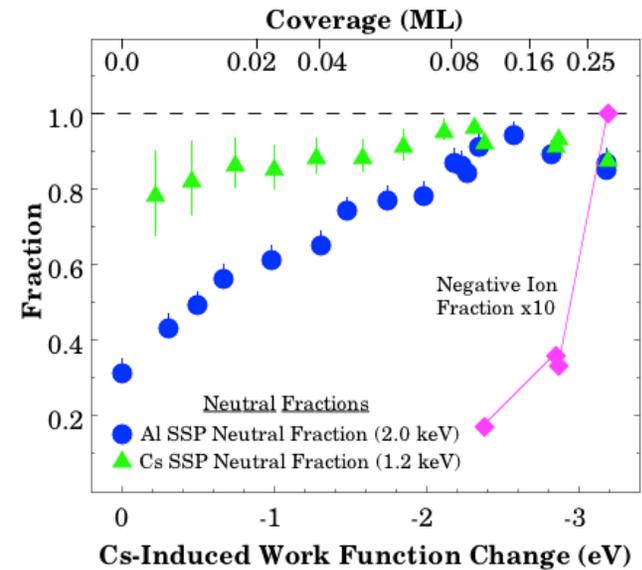


- Pulsed ion beam: frequency 80 kHz, pulse width ~40 ns
- Incidence/emission angle can be varied; Scattering angle fixed at 150°-168°
- Voltage placed on the “Flight tube” or deflection plates to remove scattered ions
- Ion bombardment/annealing cycles are used to clean the samples
- LEED, AES and/or XPS used for sample characterization
- Alkali adsorbates deposited from SAES getters
- Iodine and bromine deposited from solid-state electrochemical cells
- Metals deposited from W-filament evaporators
- Work function change measured from the energy shift of the secondary electron cutoff

# Time-of-flight (TOF) spectra and Neutral Fractions



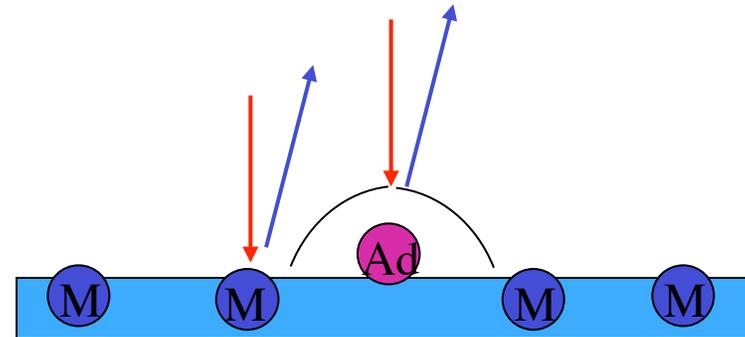
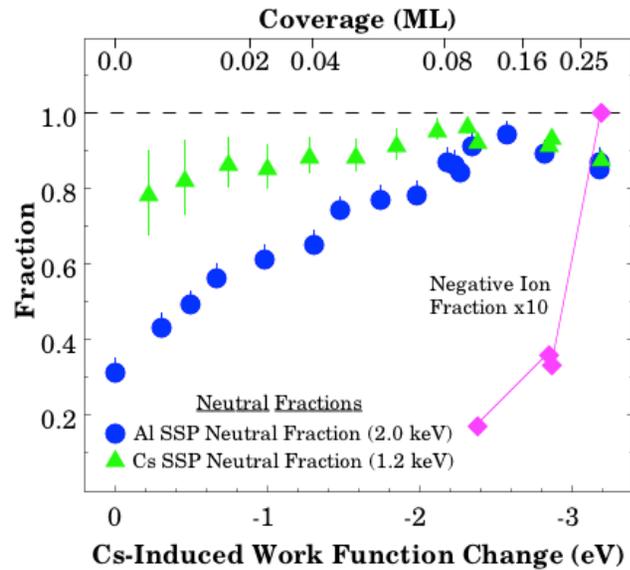
Cs/  
Al



- Total-yield spectra for scattered 2.5 keV  ${}^7\text{Li}^+$  collected with flight tube at ground.
- Neutrals-only spectra collected with a 150 V bias voltage on flight tube.
- Single scattering peaks (SSP) integrated after subtracting the multiple scattering background.
- Neutral fractions are determined by dividing the neutrals-only SSP by the total-yield SSP.

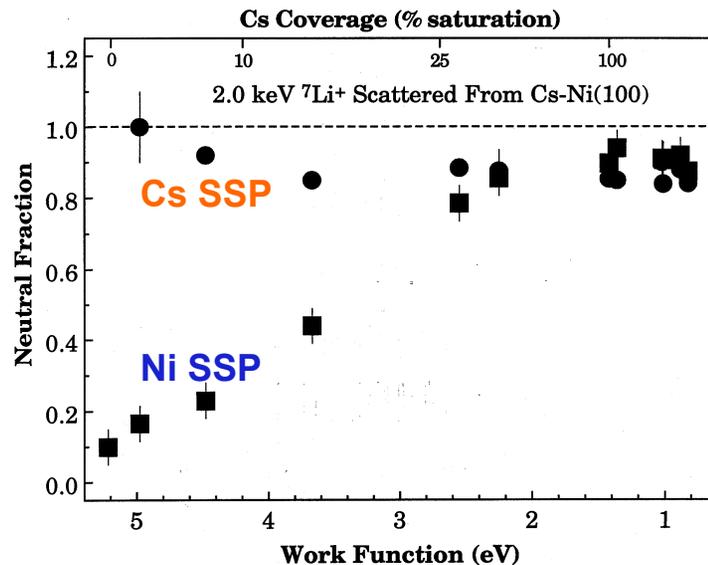
# ${}^7\text{Li}^+$ scattered from Cs/Metal Surfaces

Cs/  
Al



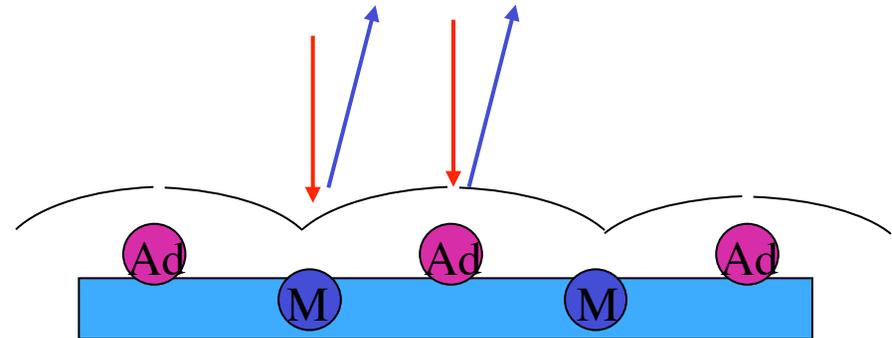
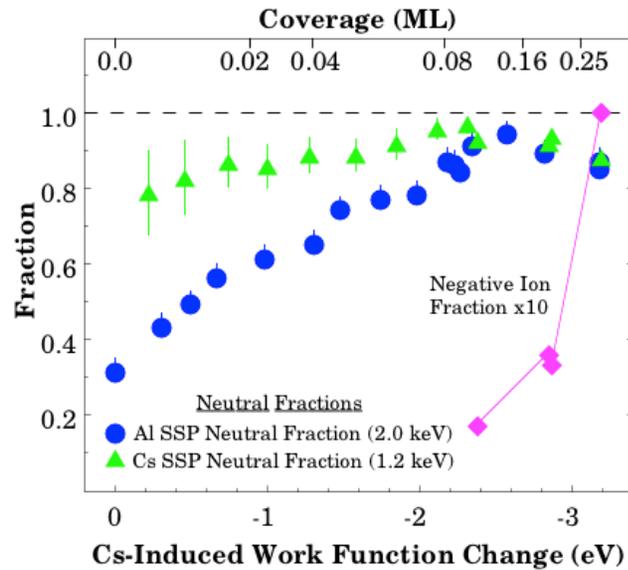
- At **low Cs coverages**, there are big differences in neutral fractions for scattering from **substrate** and **adsorbate** sites
  - Alkalis form **isolated dipoles**
  - The surface LEP is **inhomogeneous**

Cs/  
Ni



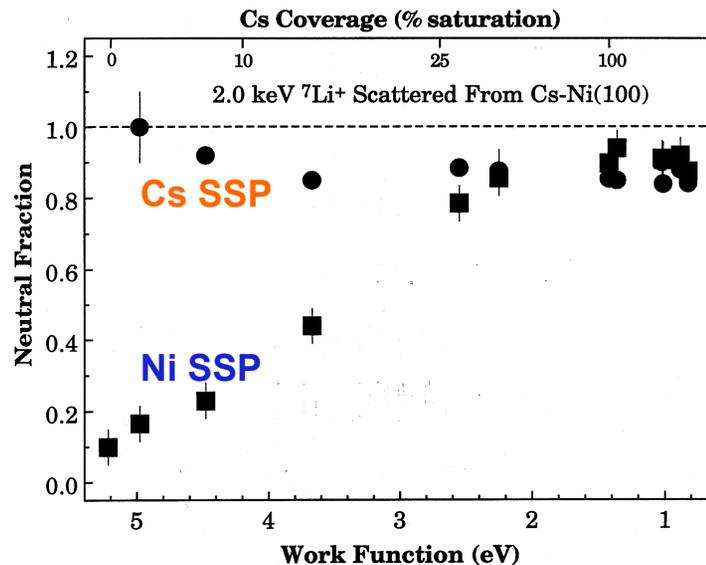
# ${}^7\text{Li}^+$ scattered from Cs/Metal Surfaces

Cs/  
Al



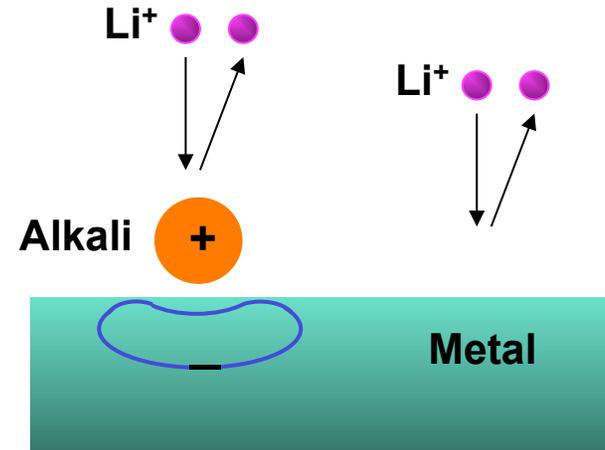
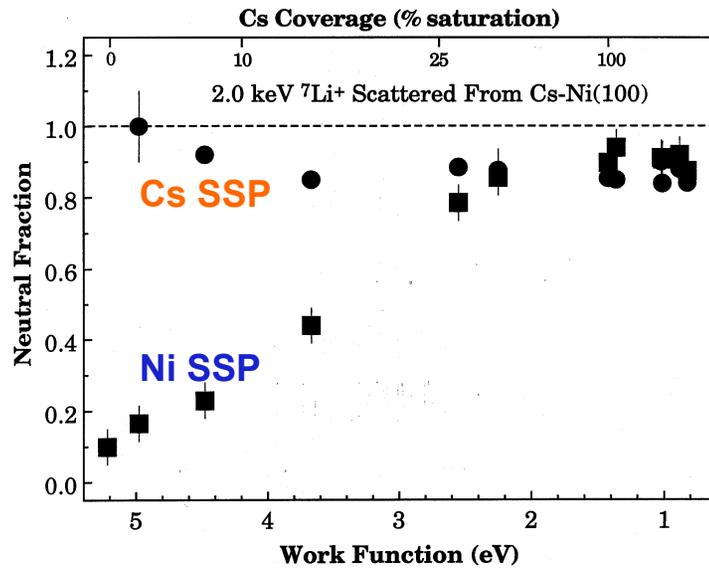
- For **high Cs coverages**, the neutral fractions are nearly equal
  - Alkalis form a **dipole sheet**
  - The surface LEP is **homogeneous**
- Similar behavior seen for many systems

Cs/  
Ni

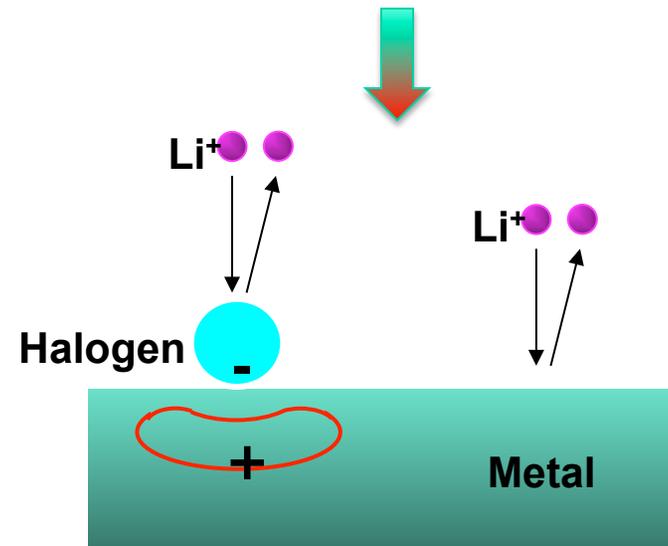


# ${}^7\text{Li}^+$ scattered from Charged Adatoms

Cs/  
Ni



Switch polarity?



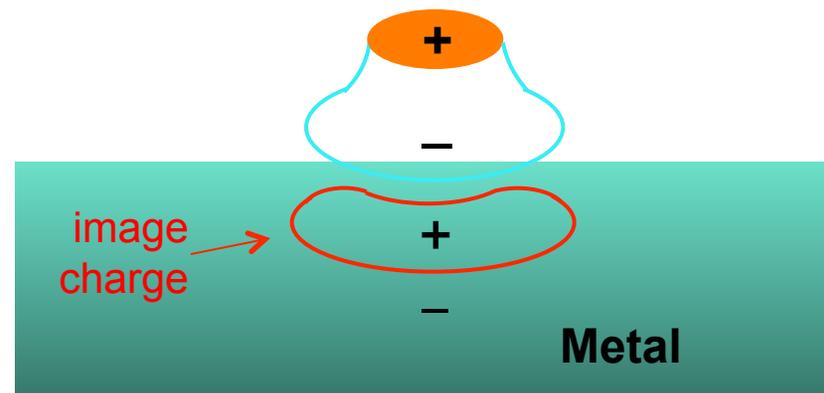
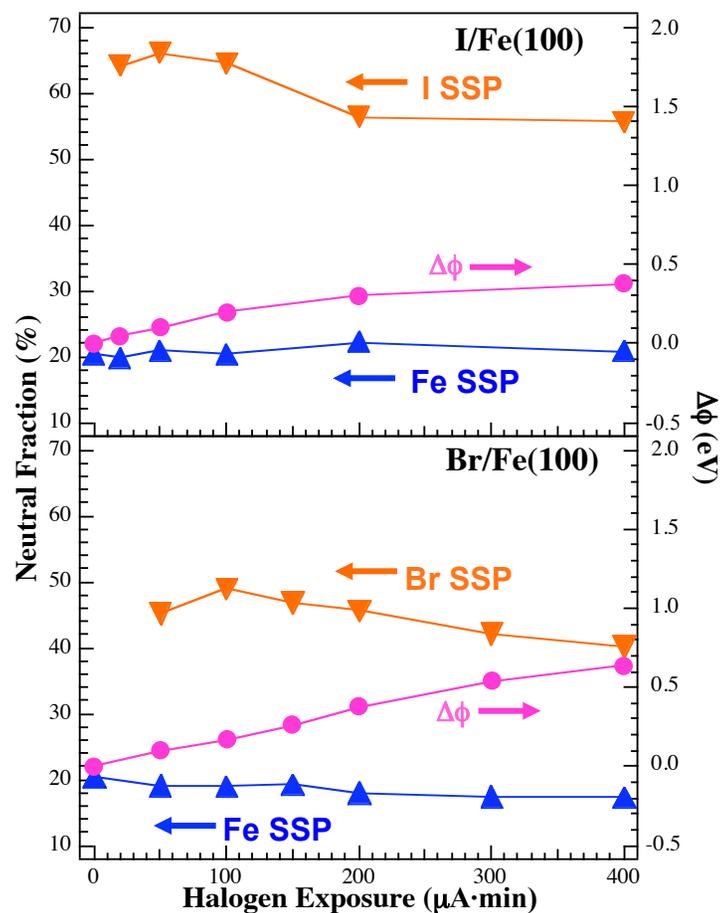
Halogen SSP  
Neutral Fraction

<

Metal SSP  
Neutral Fraction

???

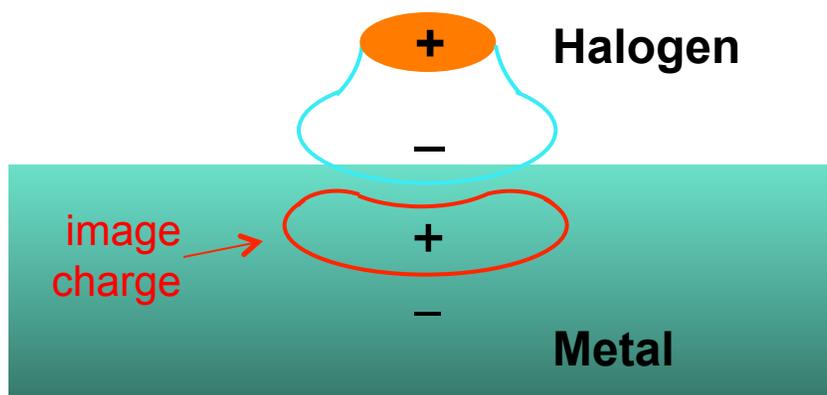
# ${}^7\text{Li}^+$ scattered from halogen-covered metals



- › Overall, adsorbed halogens are negatively charged
- › However, the negative charge is 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

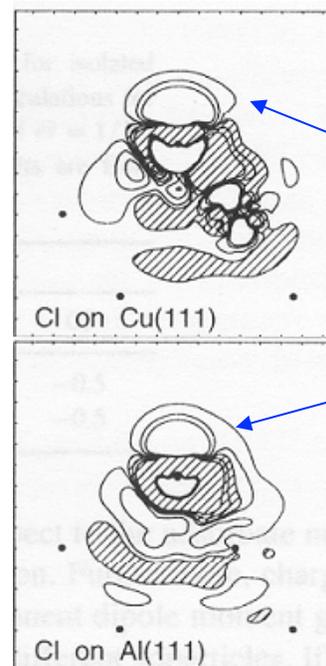
- Iodine/bromine adsorption *increases* the surface work function  $\Phi$  of Fe(100).
- Neutral fraction of the halogen SSP is *much larger* than that of the Fe SSP.

# Halogen atoms are polarizable



- › Overall, adsorbed halogens are negatively charged
- › However, the negative charge is 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

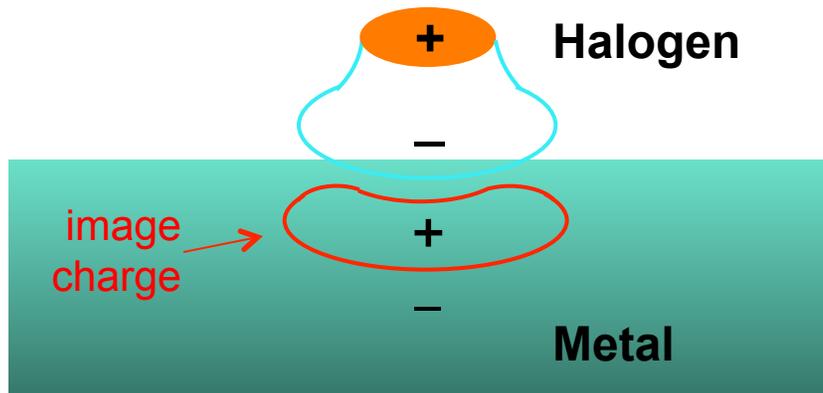
## Electron Density Calculations



Deficiency of charge above the halogen

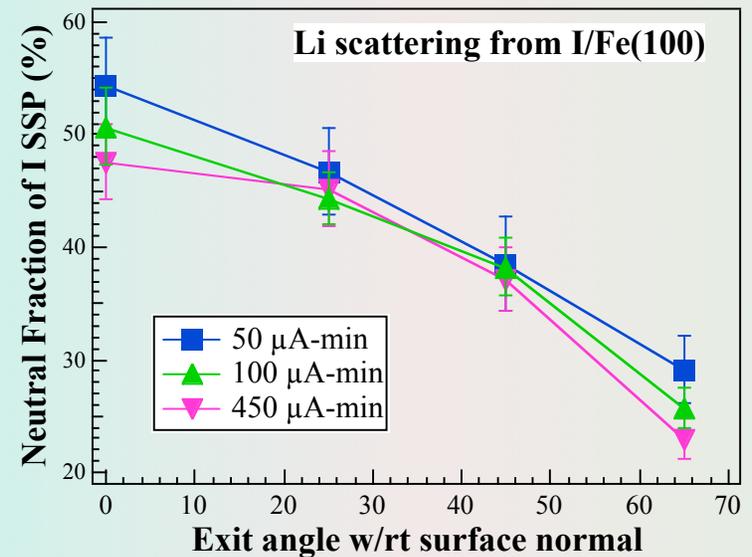
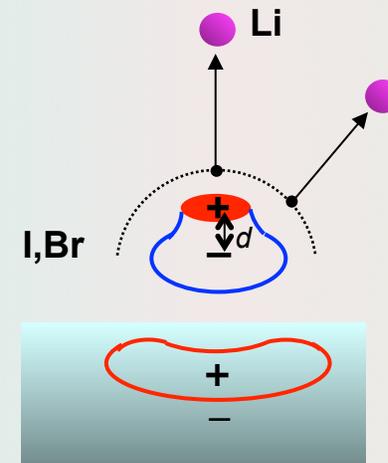
M. Scheffler and C. Stampfl, in *Handbook of Surface Science*, edited by K. Horn and M. Scheffler (Elsevier Science B. V., 2000), Vol. 2, p. 285.

# Halogen atoms are polarizable

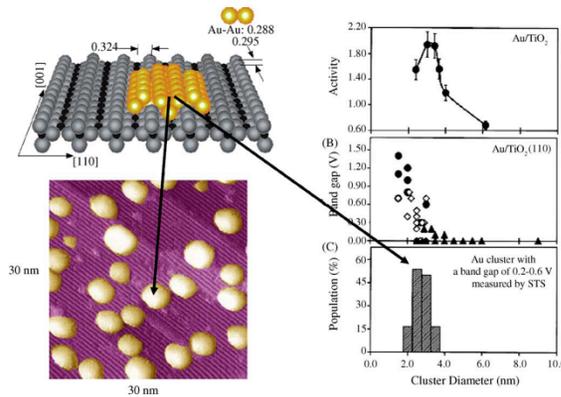


- Overall, adsorbed halogens are negatively charged
- However, the negative charge is attracted to its image charge in the metal
- This leads to a positively charged region at the top of the adsorbate, and a combination of three dipoles

## Angular dependence of the neutral fraction



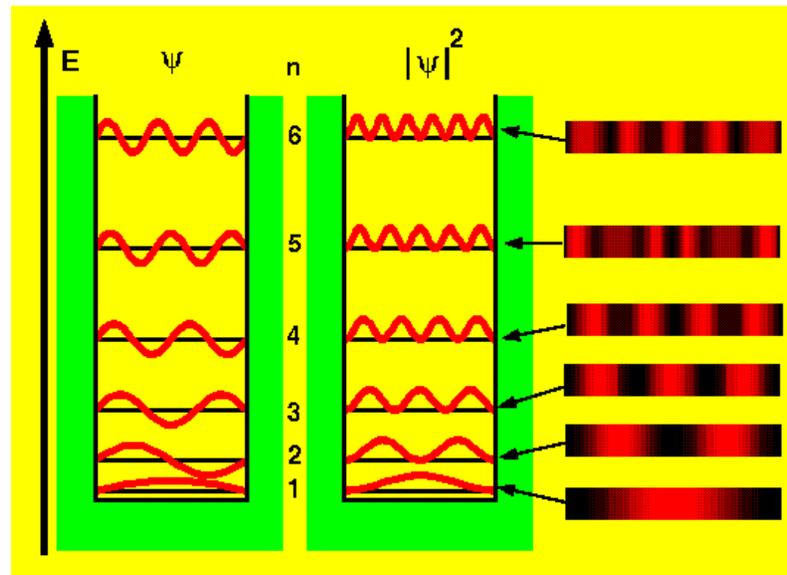
# Nanoclusters



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

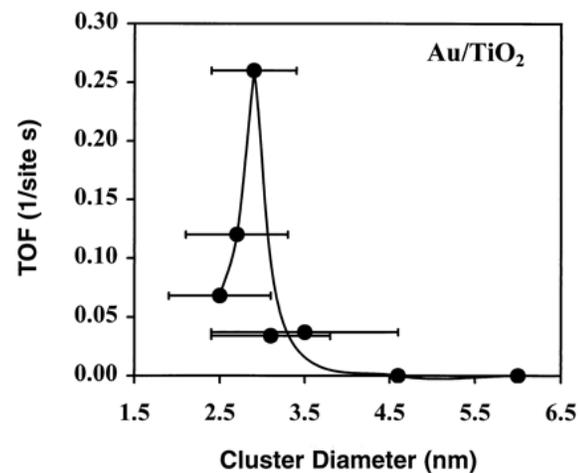
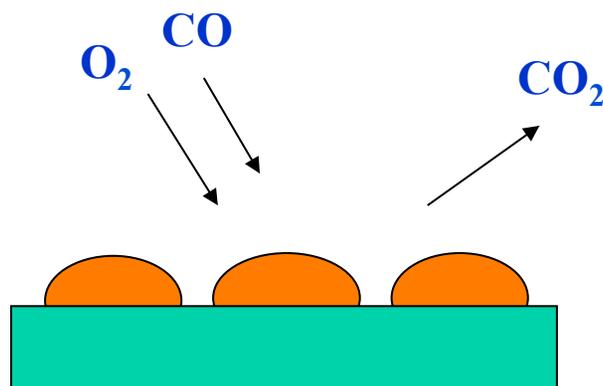
- The fabrication and characterization of metal nanoclusters is an important problem in fundamental science and advanced technology.
- The quantum-size behavior of nanomaterials enables their use in applications such as **quantum computing** and as **catalysts**.
- To fully exploit the potential of materials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

Confined states:  
Particle in a box



# Catalysis with Nanoclusters

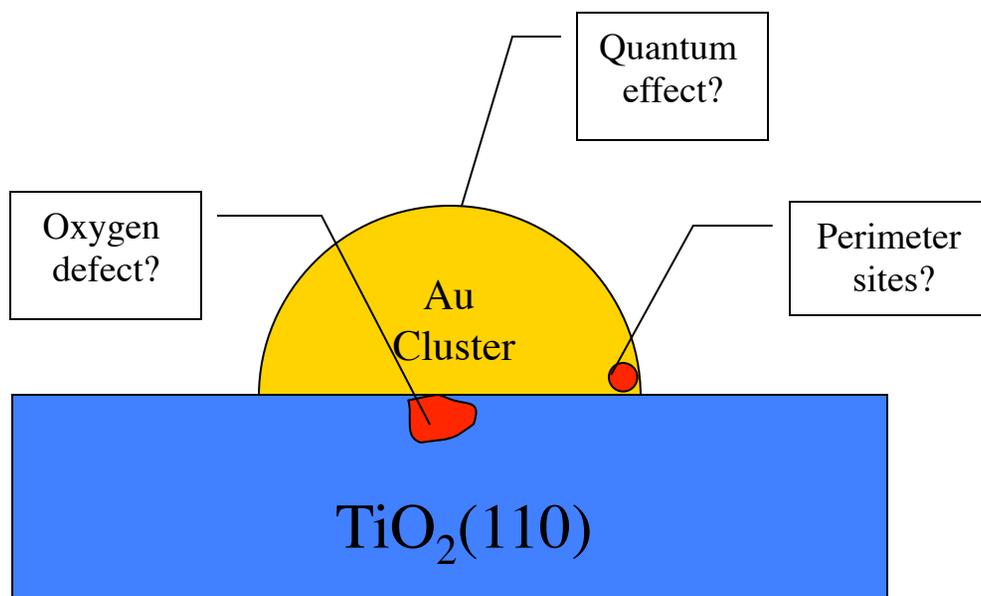
## Oxidation of CO



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

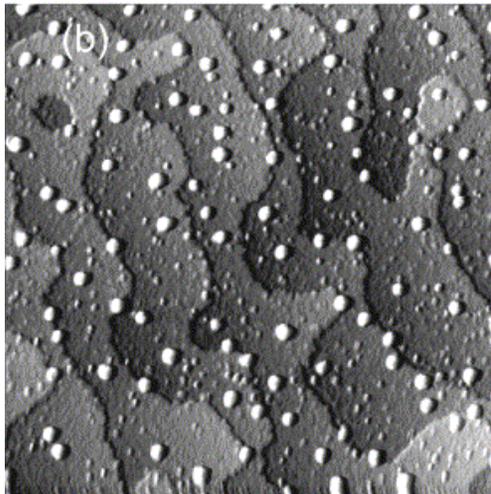
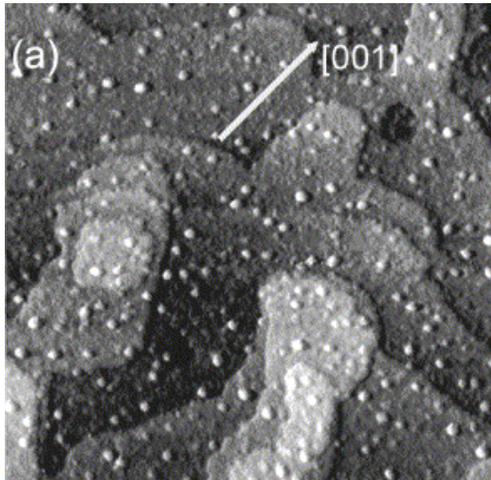
Why are the reactions enhanced in the presence of metal nanoclusters?

Still a mystery.

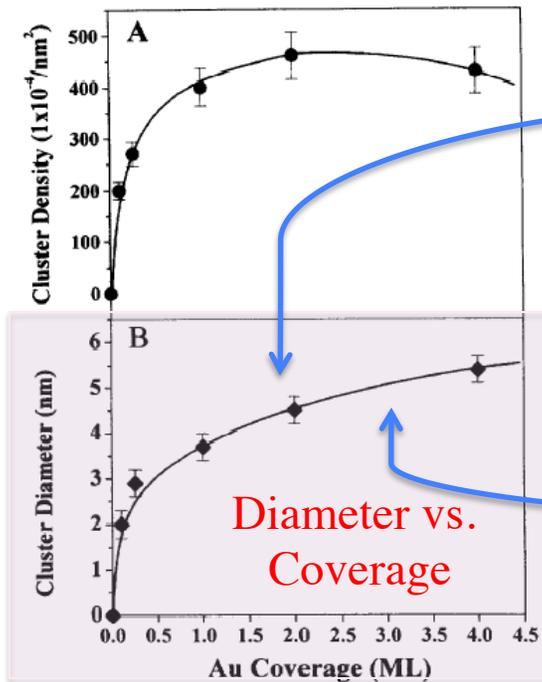


# Au Nanocrystals grown on TiO<sub>2</sub>(110)

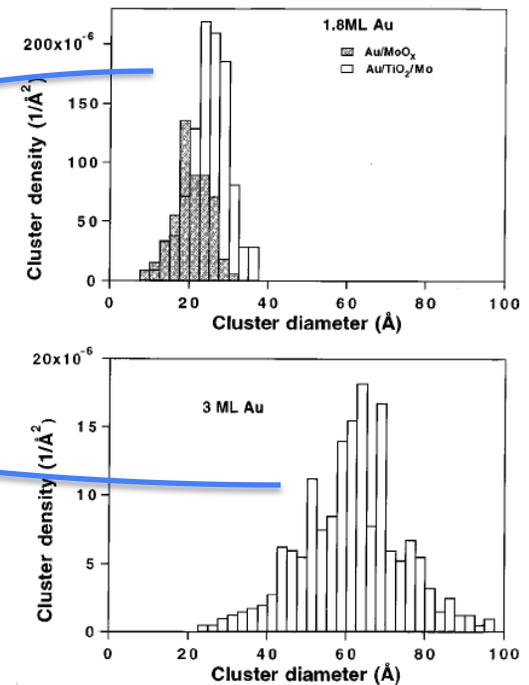
STM images



Cluster density and diameter



Cluster size distribution



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

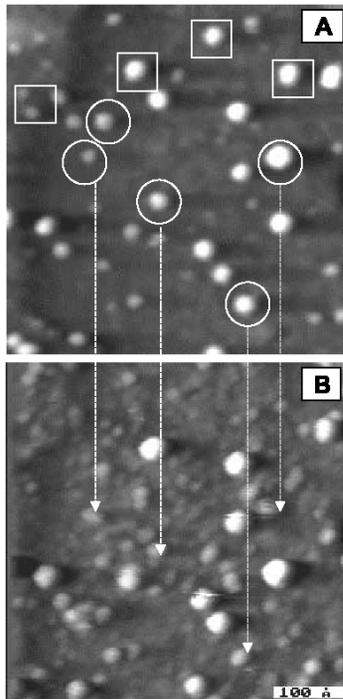
C. Xu, W.S. Oh, G. Liu, D.Y. Kim and D.W. Goodman, *J. Vac. Sci. Technol. A* **15**, 1261 (1997).

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

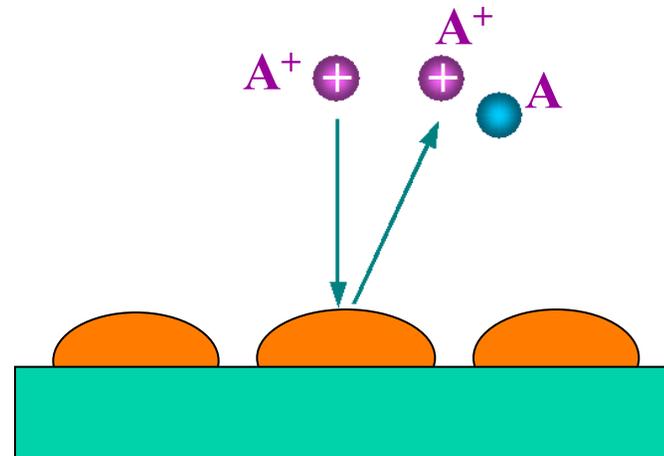
# Ion Scattering from Nanocrystals

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

## Au Nanocrystals grown on $\text{TiO}_2(110)$

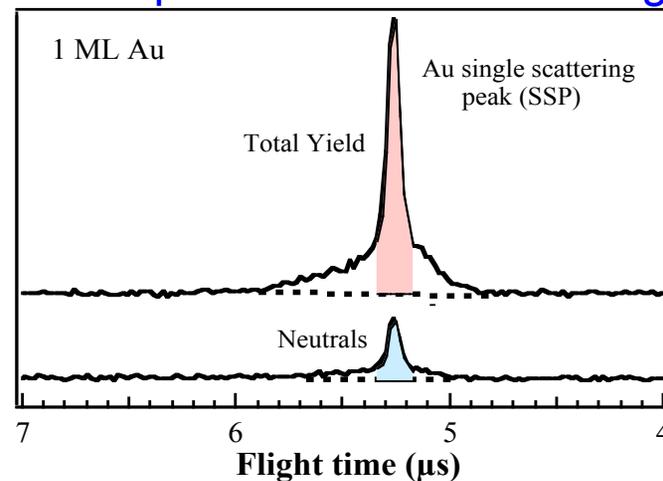


A. Kolmakov and D.W. Goodman, *Surf. Sci. Lett.* **490**, L597 (2001).

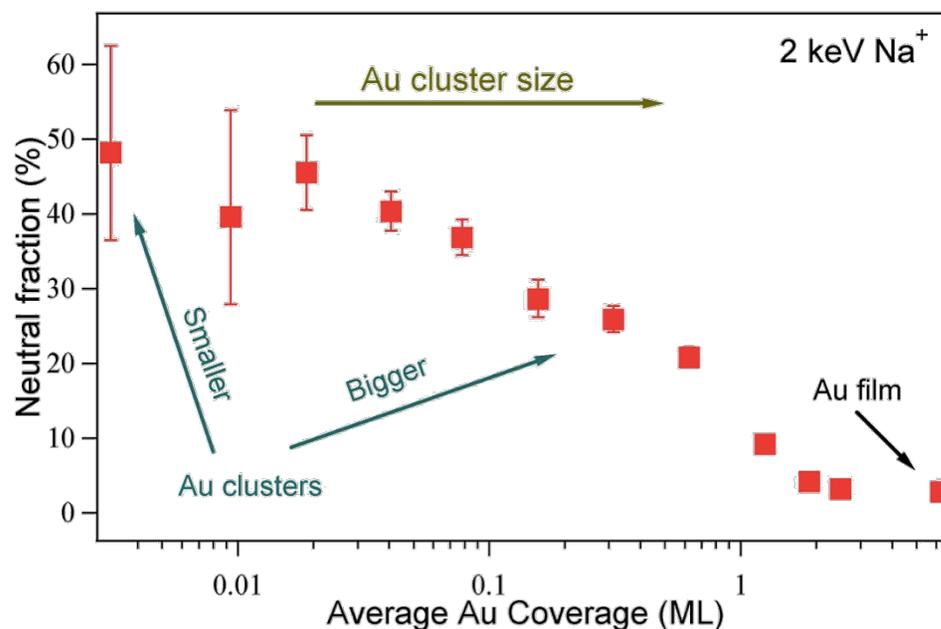


Measure fraction of ions that are neutralized - provides information on quantum-confined states

## TOF spectra for $\text{Na}^+$ scattering



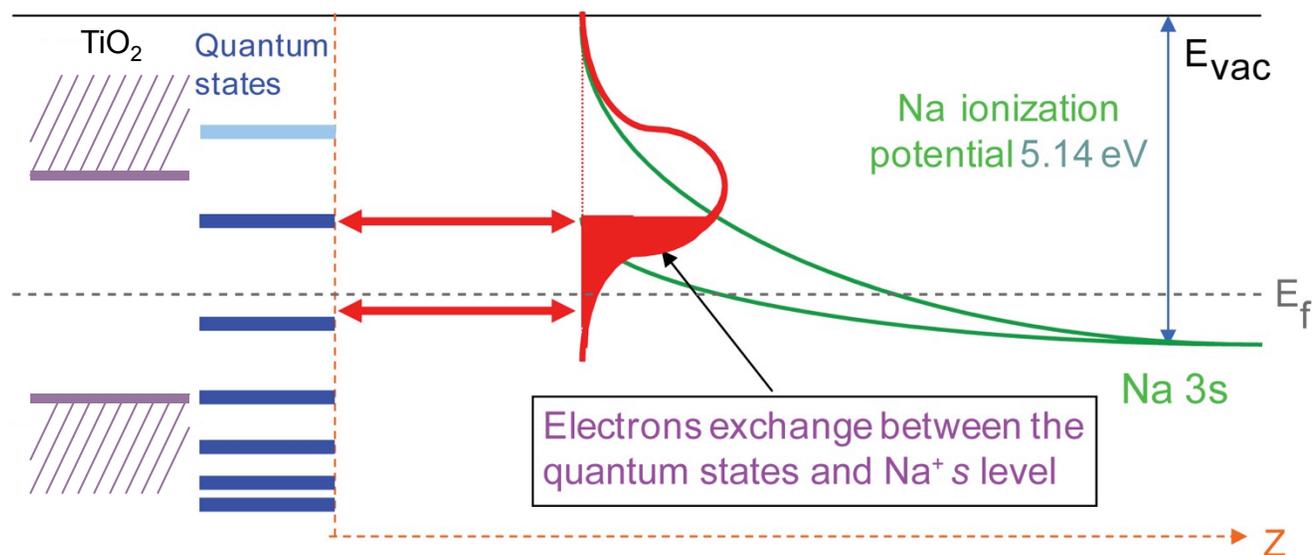
## Na<sup>+</sup> Neutral Fraction vs. Au Deposition



- 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<sup>3</sup>, 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

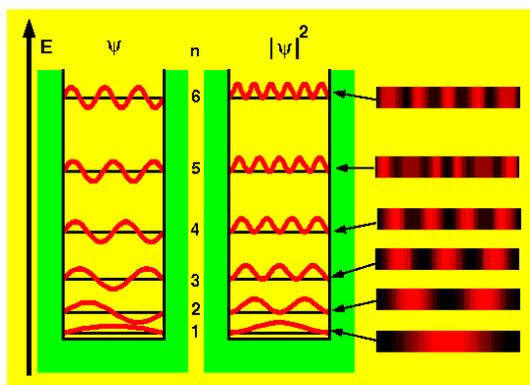
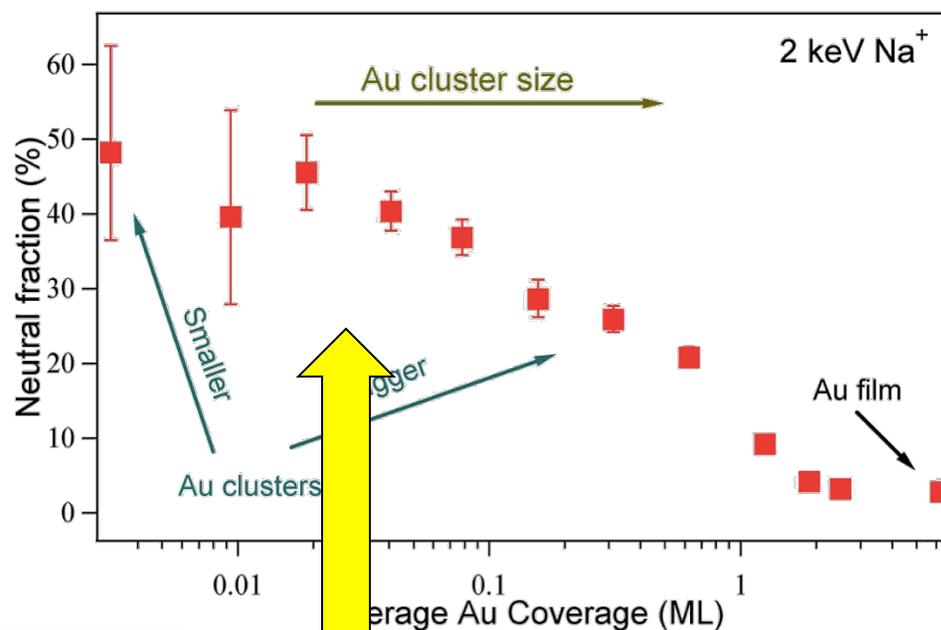


Not drawn to scale.

- For Au nanoclusters, the confined quantum states overlap the Na  $s$  level, leading to neutral fractions up to  $\sim 50\%$ .
- 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.*

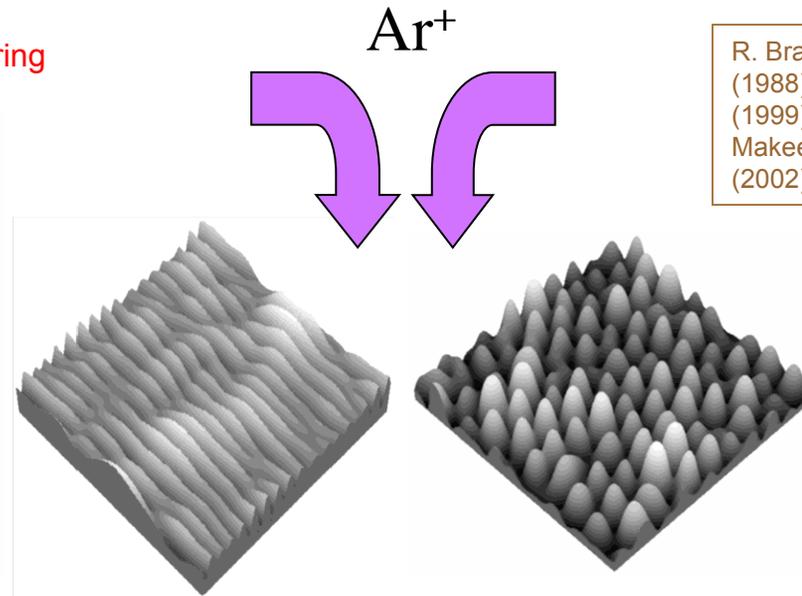
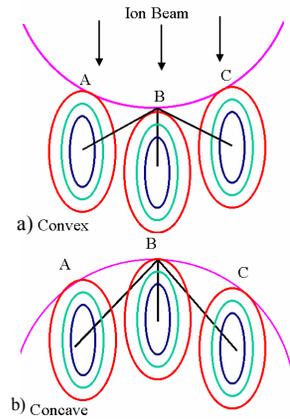
# Neutral Fraction as a function of Au Nanocrystal Size



Confined states:  
Particle in a box

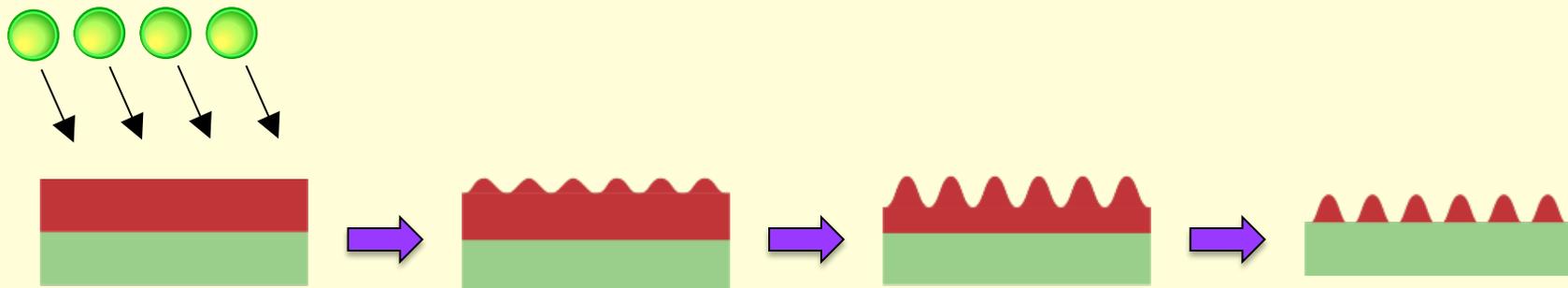
# Nanoscale patterning via Ion Bombardment (Sputtering)

## Curvature dependent sputtering



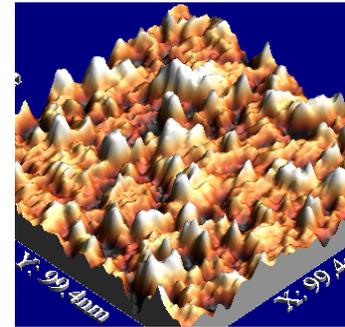
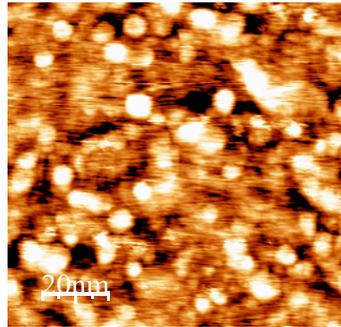
R. Bradley, et al., *J. Vac. Sci. Technol. A* **6**,2390 (1988); S. Facsko, et al., *Science* **285**, 1551 (1999); *Phys. Stat. Sol. (b)* **224**, 537 (2001); M. Makeev, et al., *Nucl. Instrum. Meth. B* **197**, 185 (2002).

Sputter a thin film to produce clusters of one material on an insulating matrix

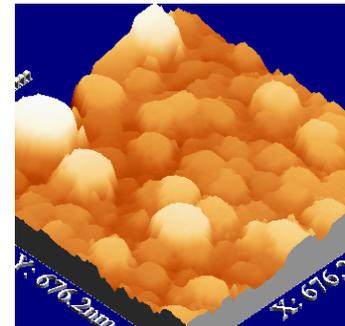
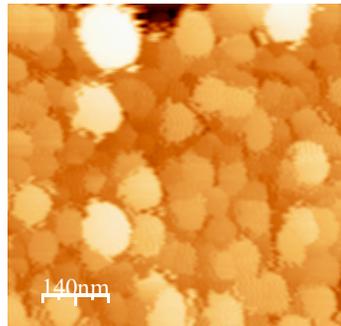


# STM topography of Au on TiO<sub>2</sub>(110)

- **Deposition:** 2-dimensional islands are initially formed up to a certain critical coverage. Above the critical coverage, 3-dimensional islands grow.

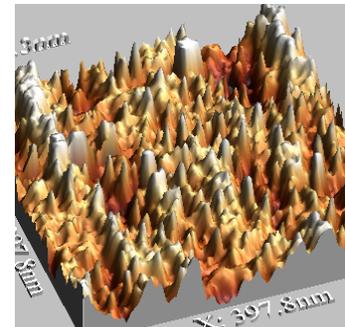
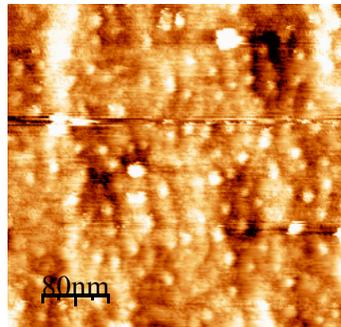


0.01 ML  
deposited Au



60 ML  
deposited Au

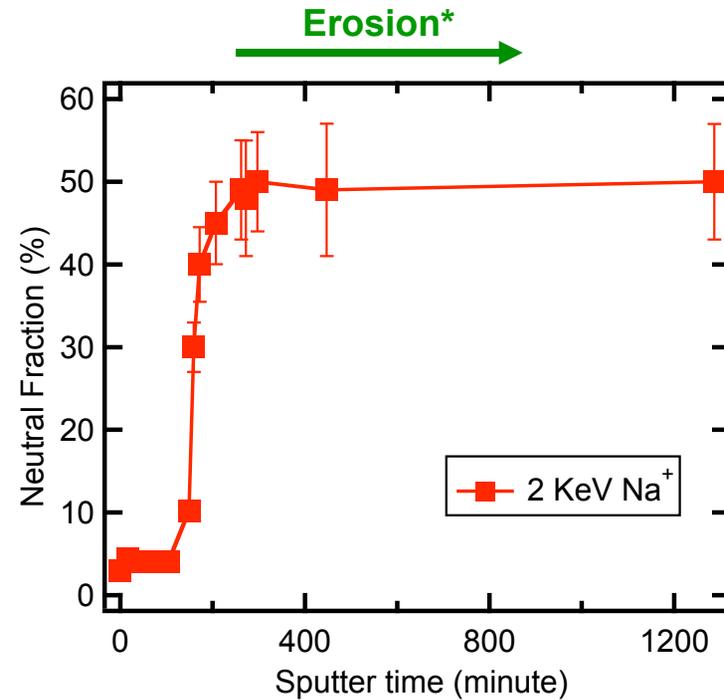
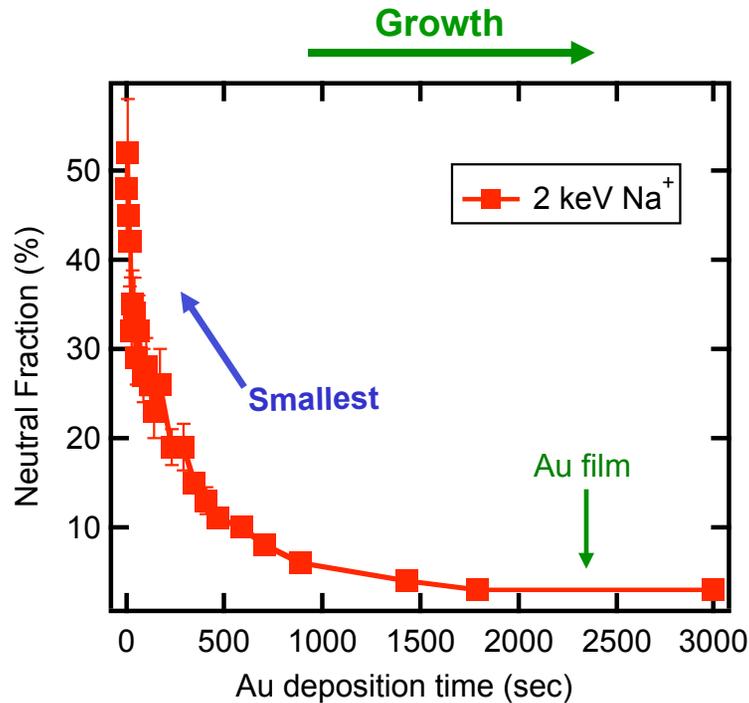
- **Sputtering:** The interplay between curvature dependent sputtering and surface diffusion forms the Au nanoclusters.



After sputtering  
60 ML Au film at  
an Ar<sup>+</sup> fluence of  
 $5 \times 10^{16}$  ions/cm<sup>2</sup>

# Au Deposition vs. Sputtering

Neutral fraction (NF) of singly scattered 2 keV Na<sup>+</sup> ions

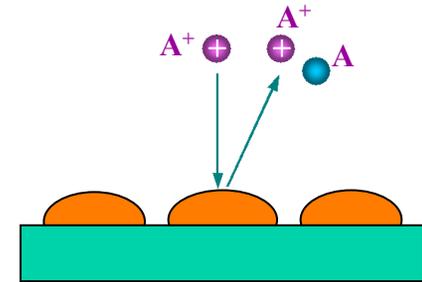


- The erosion and surface diffusion of Au due to ion bombardment forms nanoclusters.
- As the average cluster size decreases with ion fluence, the Na NF increases.
- This demonstrates that the confined quantum states in the small Au nanoclusters couple to the Na ions, as observed during deposition.

\*P. Karmakar, G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **98**, 215502 (2007).

# Conclusions - Nanoclusters

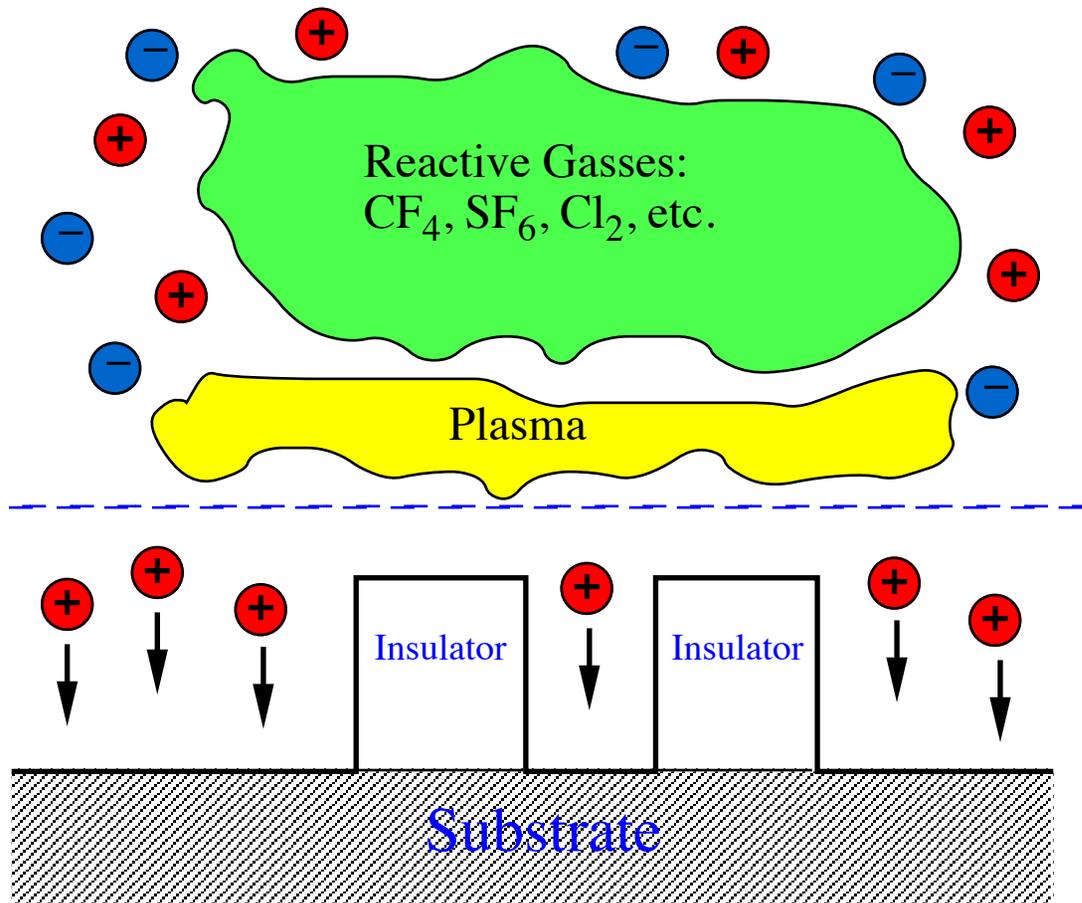
- ✓ Alkali ion scattering probes the local electronic structure at a surface.
- ✓ The neutralization in scattering from nanoclusters is sensitive to the size of the clusters.
- ✓ Sputtering of a thin film is a promising new method for nanocluster formation.



# Dry Processing of Semiconductors



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



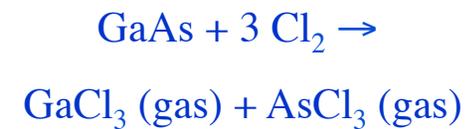
**Chemical process results  
in a high degree of  
selectivity**

## Etching of Si

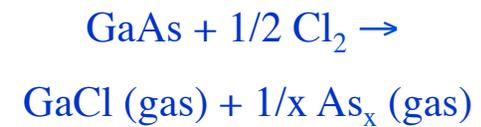


## Etching of GaAs

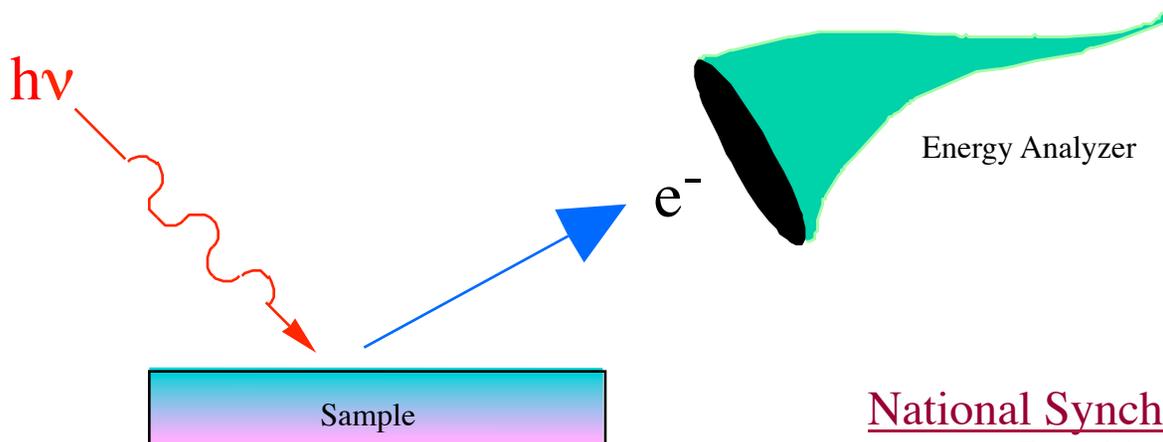
Low temperatures:



High temperatures:

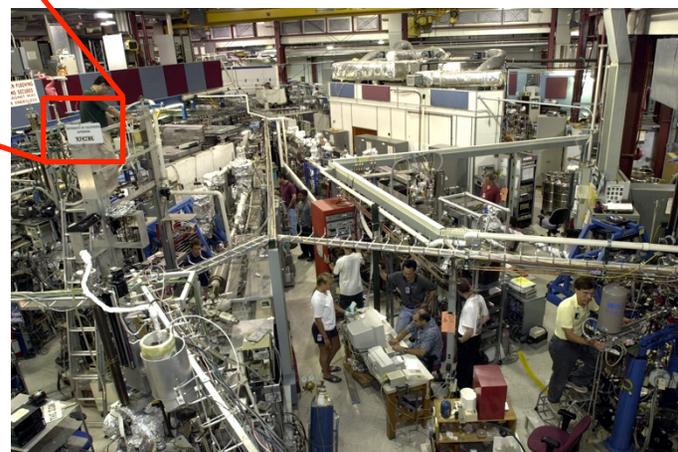
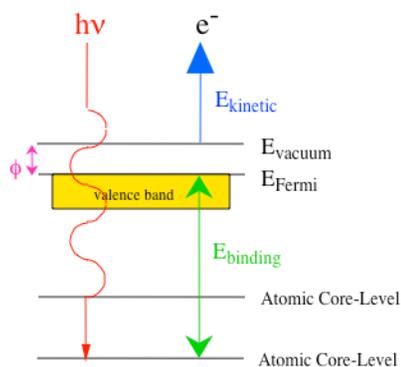


# Soft X-Ray Photoelectron Spectroscopy (SXPS)



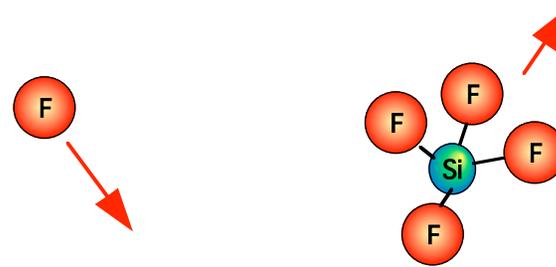
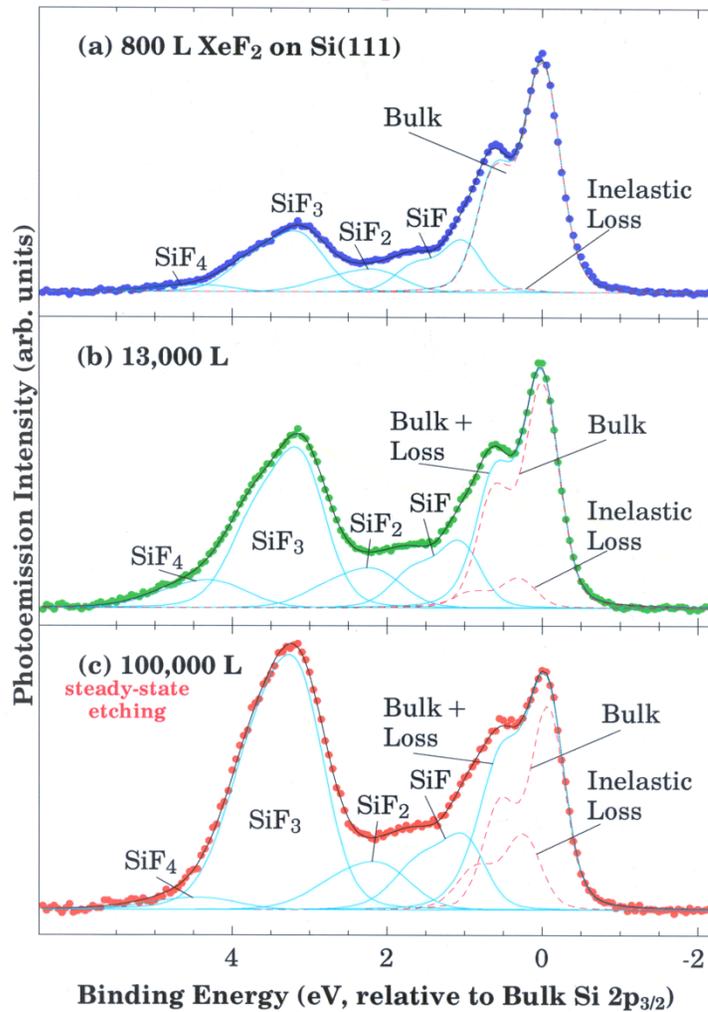
National Synchrotron Light Source (NSLS)  
at Brookhaven National Laboratory

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



# Fluorine etching of Si

## Soft X-ray Photoelectron Spectroscopy



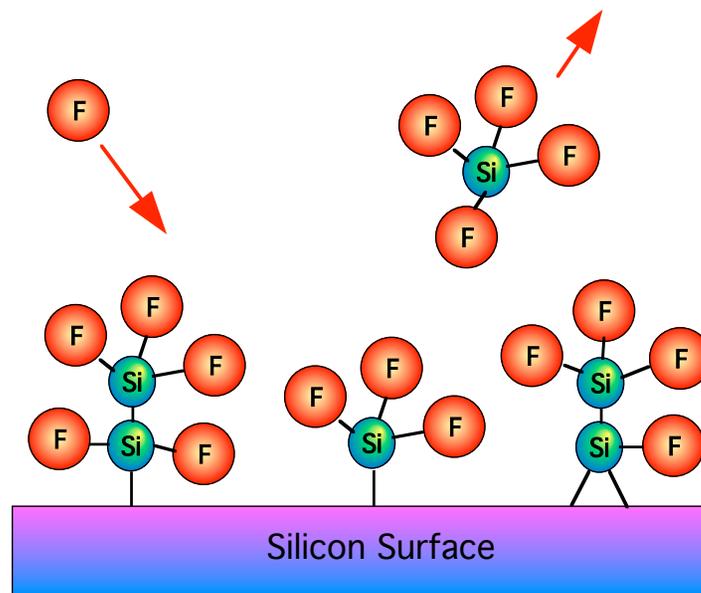
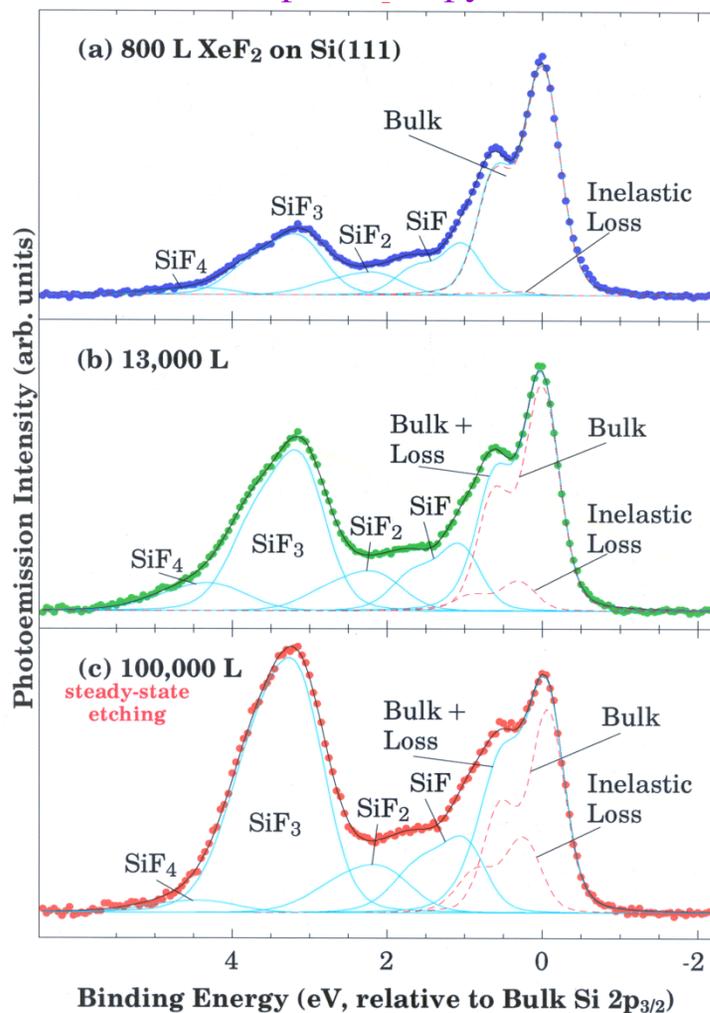
???

Silicon Surface

- Fluorine goes down, SiF<sub>4</sub> 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<sub>3</sub>
- Atomic fluorine reacts with adsorbed SiF<sub>3</sub> to form gaseous SiF<sub>4</sub>
- Atomic fluorine reacts with trees to form gaseous Si<sub>2</sub>F<sub>6</sub> and Si<sub>3</sub>F<sub>8</sub>
- In order to accommodate the trees, the surface is macroscopically roughened

# Use of surface chemical reactions for environmental remediation

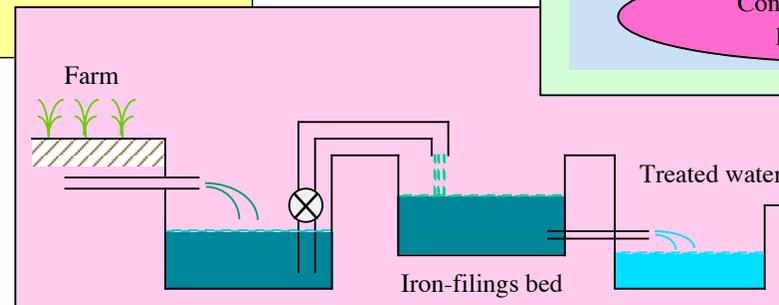
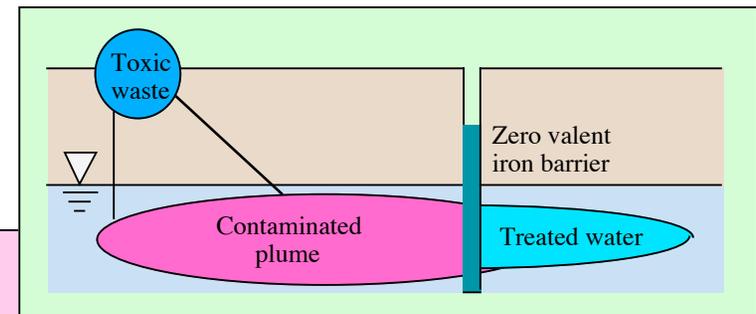
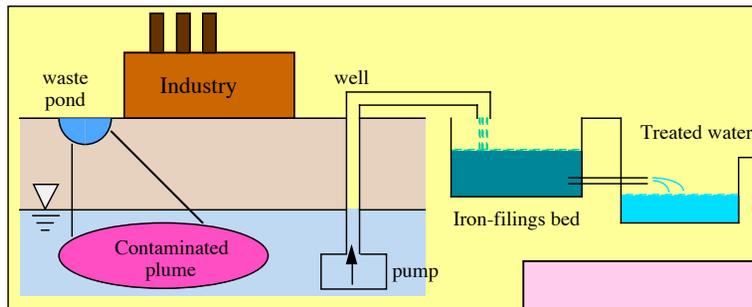


## Environmental Problem

- Oxidized forms of several toxic trace elements (e.g.,  $\text{SeO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{UO}_2^{2+}$ ) 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

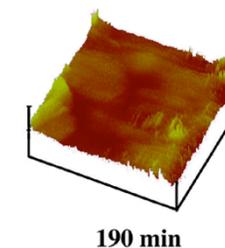
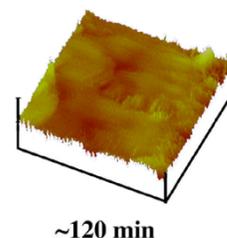
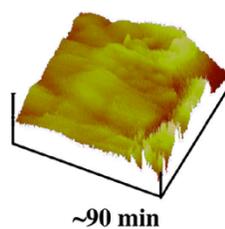
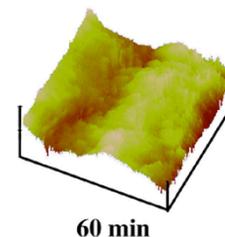
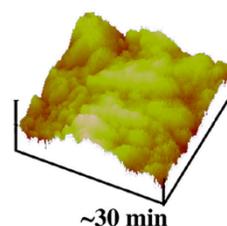
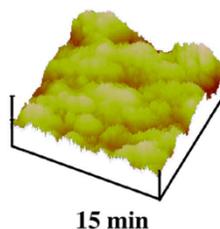
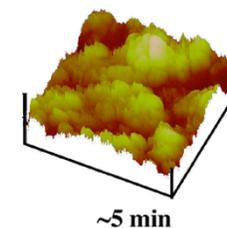
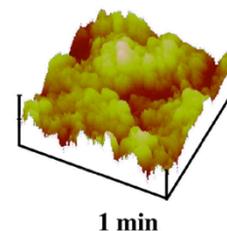
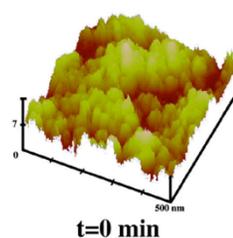


Fe foil before  
reaction

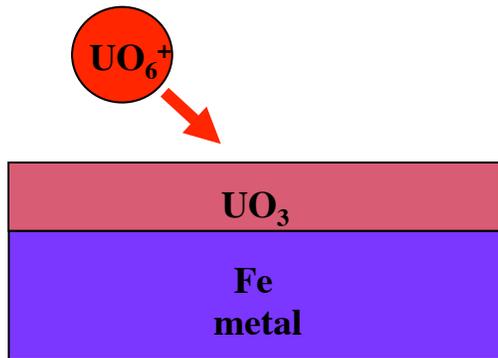


Fe foils following  
reaction appear  
iridescent

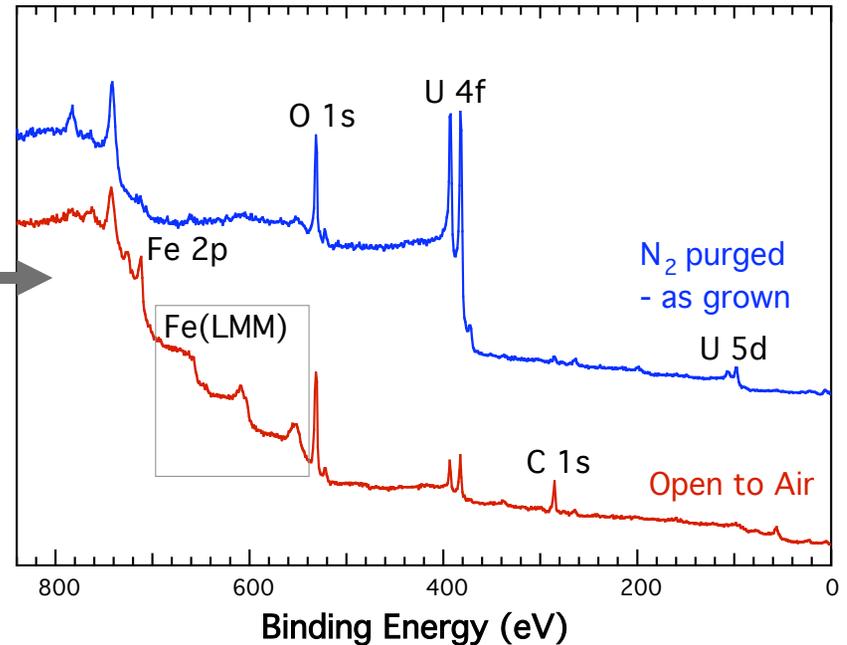
The surface of an iron foil was monitored with *in situ* STM in a solution containing uranyl nitrate. The 500x500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. XPS analysis showed that the smooth morphology is due to the deposition of  $\text{UO}_3$ .



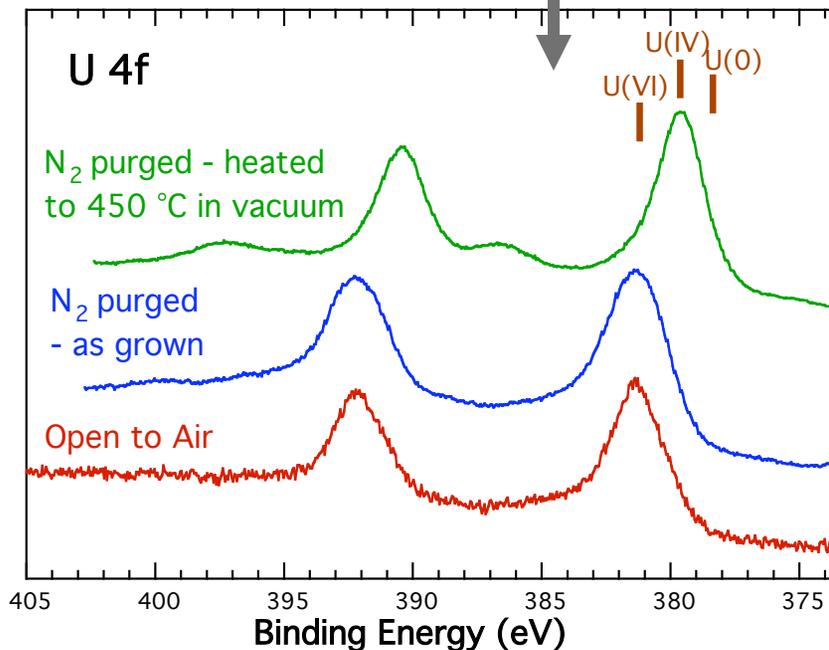
# X-Ray Photoelectron Spectroscopy (XPS)



Wide scan



High-resolution scan



- Films of U(VI) oxide grow under both conditions.
- Much more U is deposited with N<sub>2</sub> purging, as no Fe is visible  
- this is due to carbonate formation from dissolved CO<sub>2</sub> when open to air
- When heated in vacuum, surface of films reduce to UO<sub>2</sub>
- As-grown material was identified as “Schoepite”

# Surface Science

Thank you!!

