UC RIVERSIDE UNIVERSITY OF CALIFORNIA

Prof. Jory A. Yarmoff
Department of Physics

Surface Science

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

Surface Physics - part of condensed matter physics

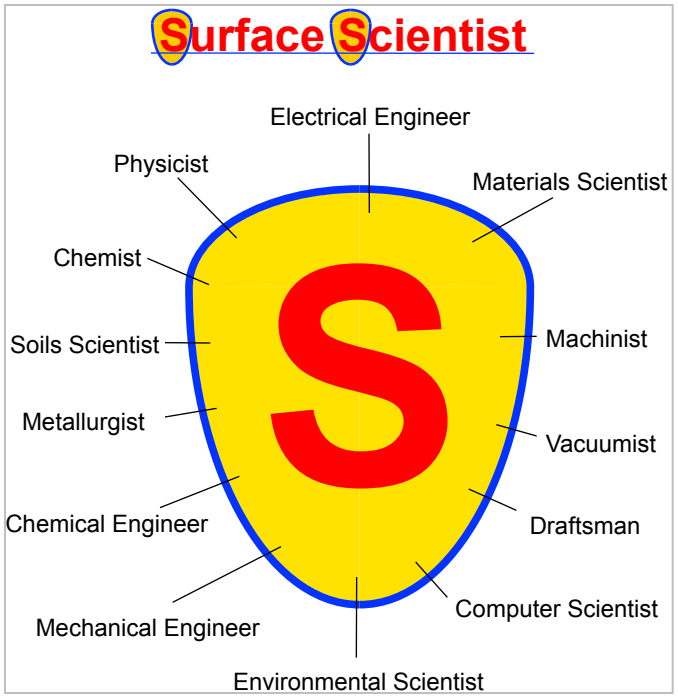
Surface Chemistry - part of physical chemistry

Materials Science

Electrical Engineering

Chemical Engineering

others...

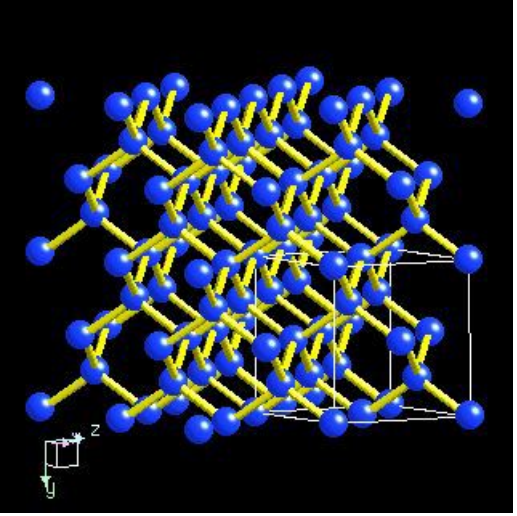


Nanoscience

Surfaces/Interfaces

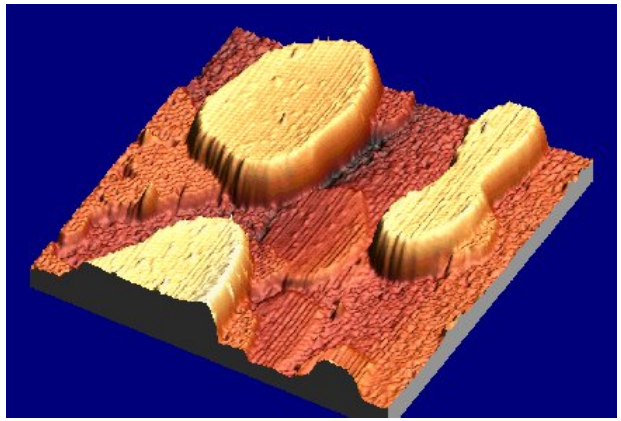
- Technological ties with semiconductor industry, petroleum industry, high T_c superconductors, tribology, environmental issues, much more…
- Requires a wide variety of experimental skills
- Combines both laboratory work and work at major facilities
- Many techniques must be applied to a given system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

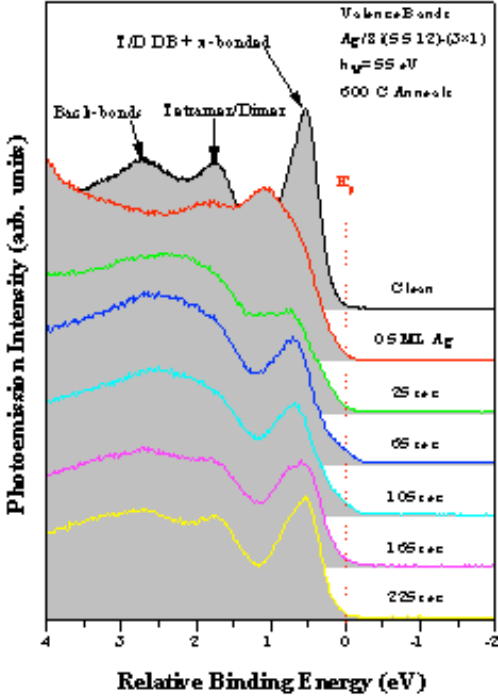
Surface Science is concerned with:



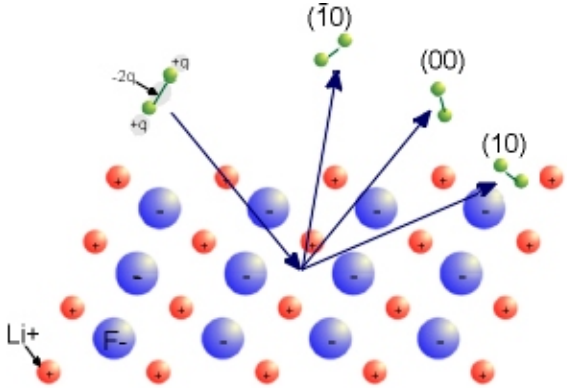
- Geometric structure

- Particle-Surface Interactions

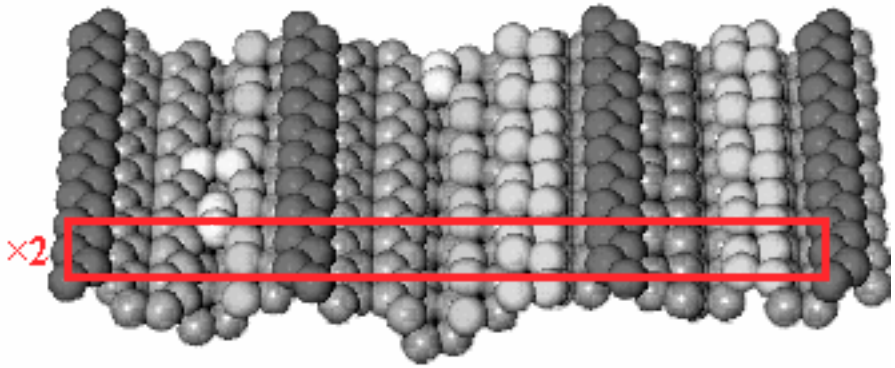




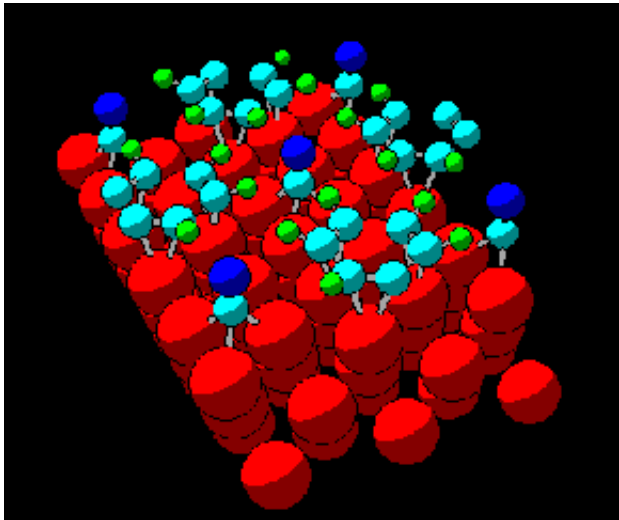
- Electronic structure



- Effects of radiation damage

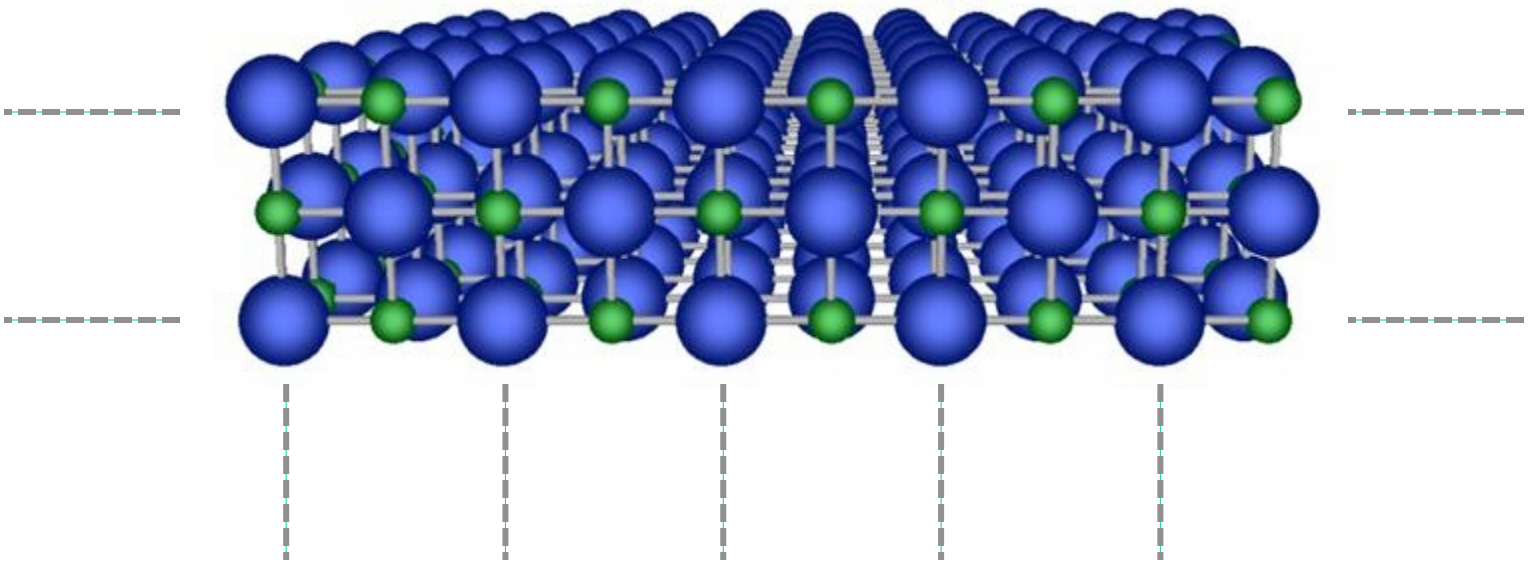


- Chemical surface reactions



Surface Structures

Almost side view

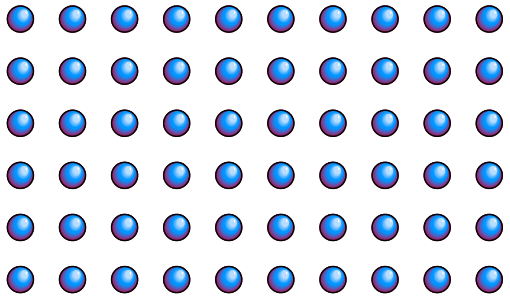


- A solid is composed of atoms with infinite periodicity in 3-dimensions
- The periodicity is broken at a surface

Surface Structures

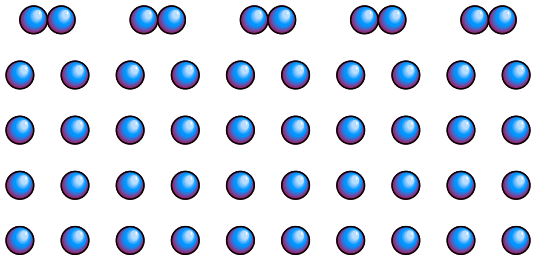
side view

Bulk-terminated Surface



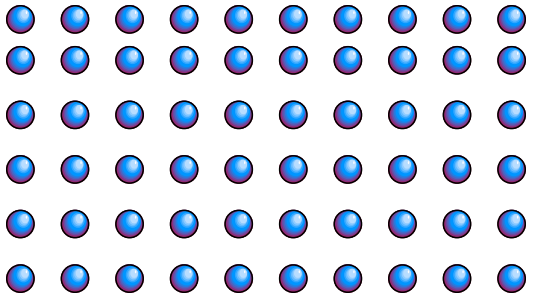
- Surface atoms are in bulk-like positions
- It's as though the surface were simply cut

Reconstructed Surface



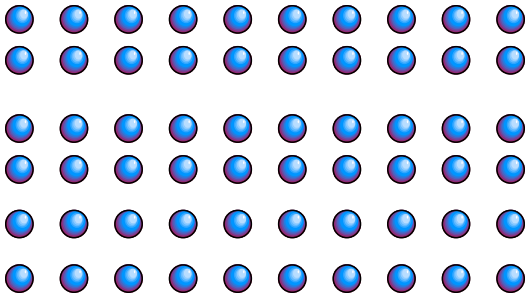
- Surface atoms are moved laterally, as well as in the perpendicular direction
- Reconstruction can involve many atomic layers

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

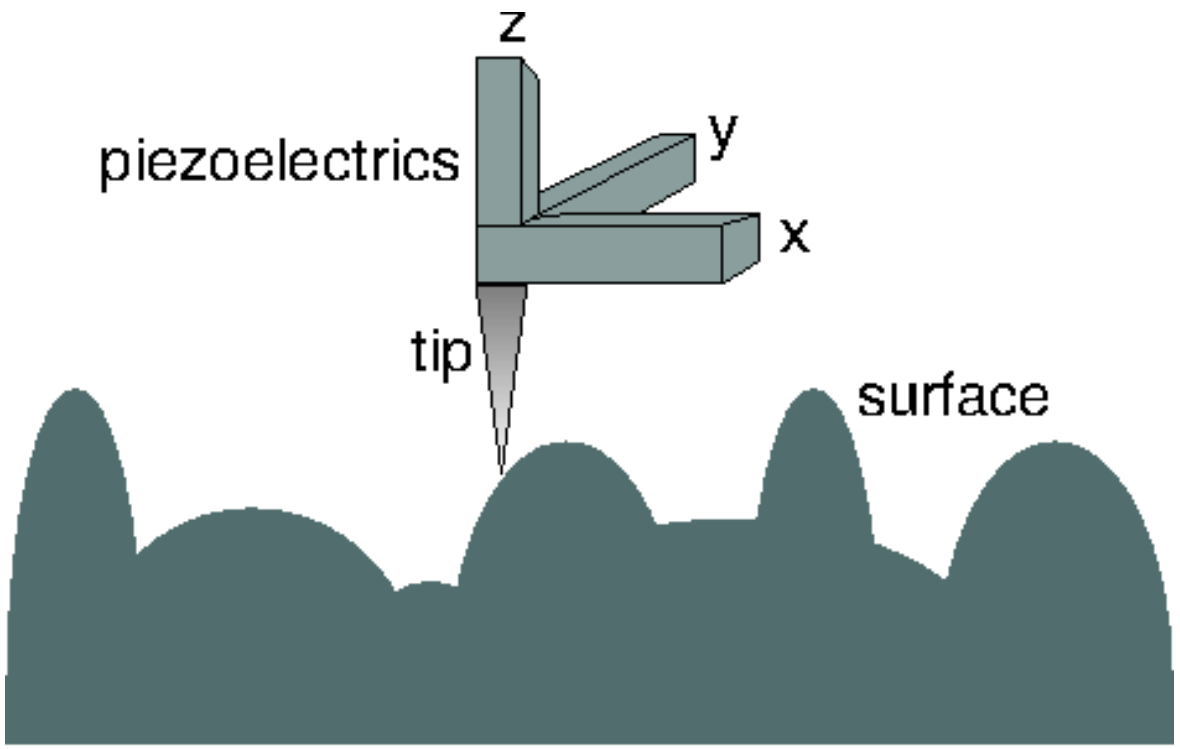
Surface Science

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

1. Unique chemical reactions – catalysis
2. Unique electronic properties – novel devices
3. Ability to adsorb molecules in unique configurations
4. ???

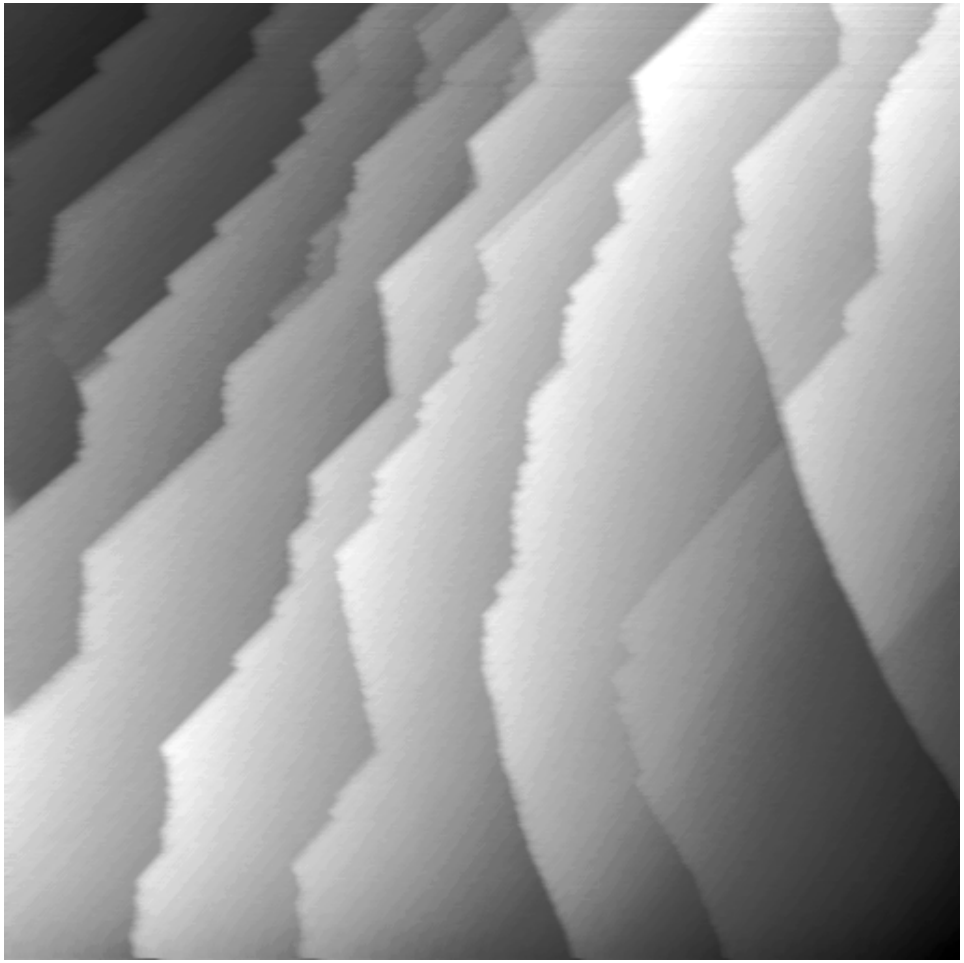
Scanning Tunneling Microscopy (STM)

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

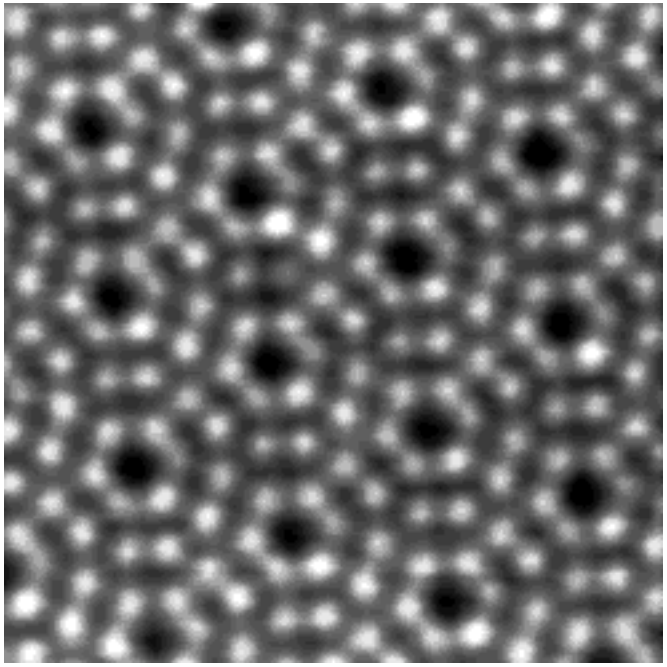


- Measures electron density at a surface with atomic resolution

STM of Silicon (111) Surfaces

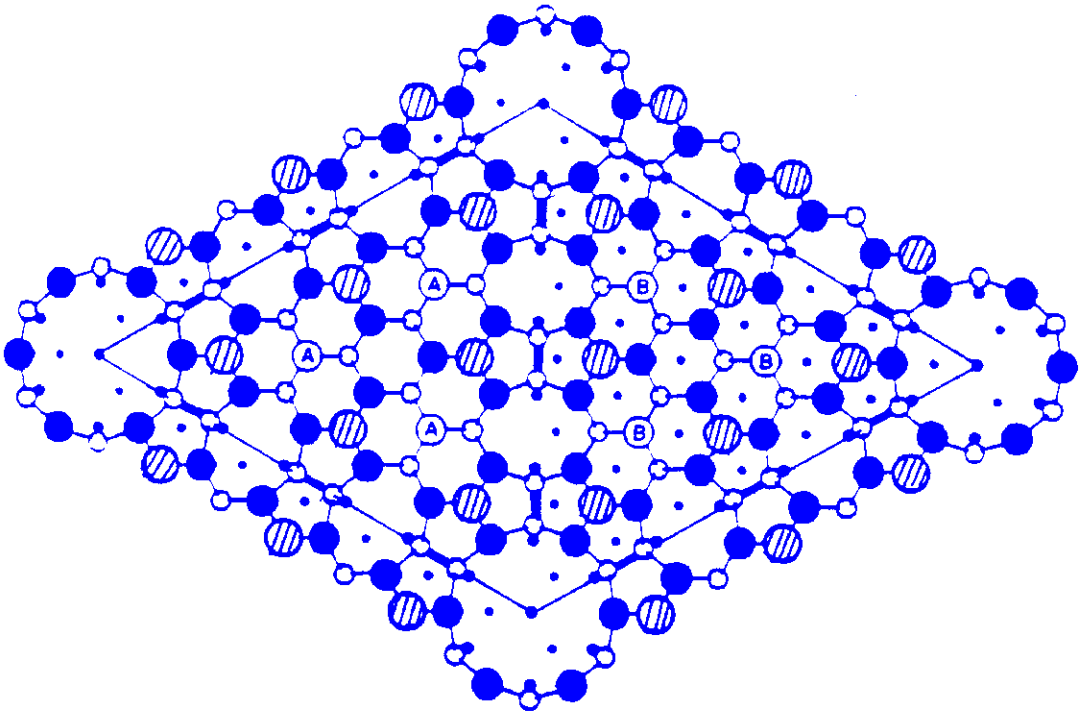


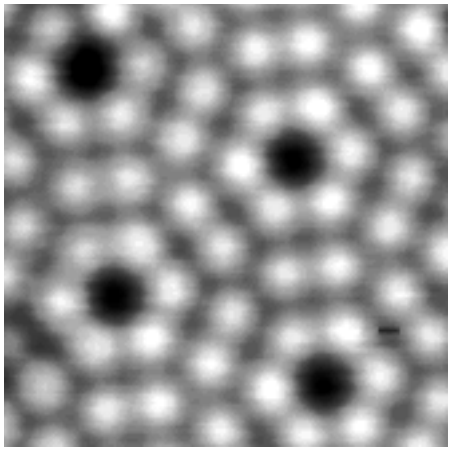
Large scale image showing atomic height steps

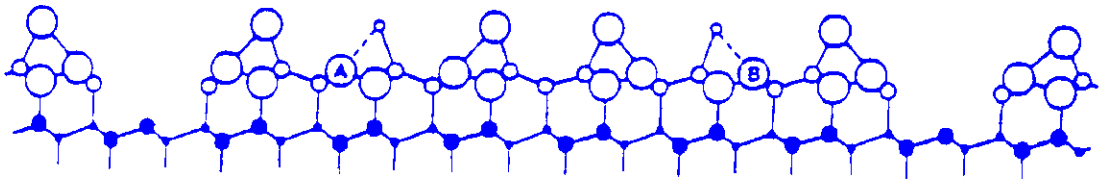


Finer scale image showing
atomic resolution

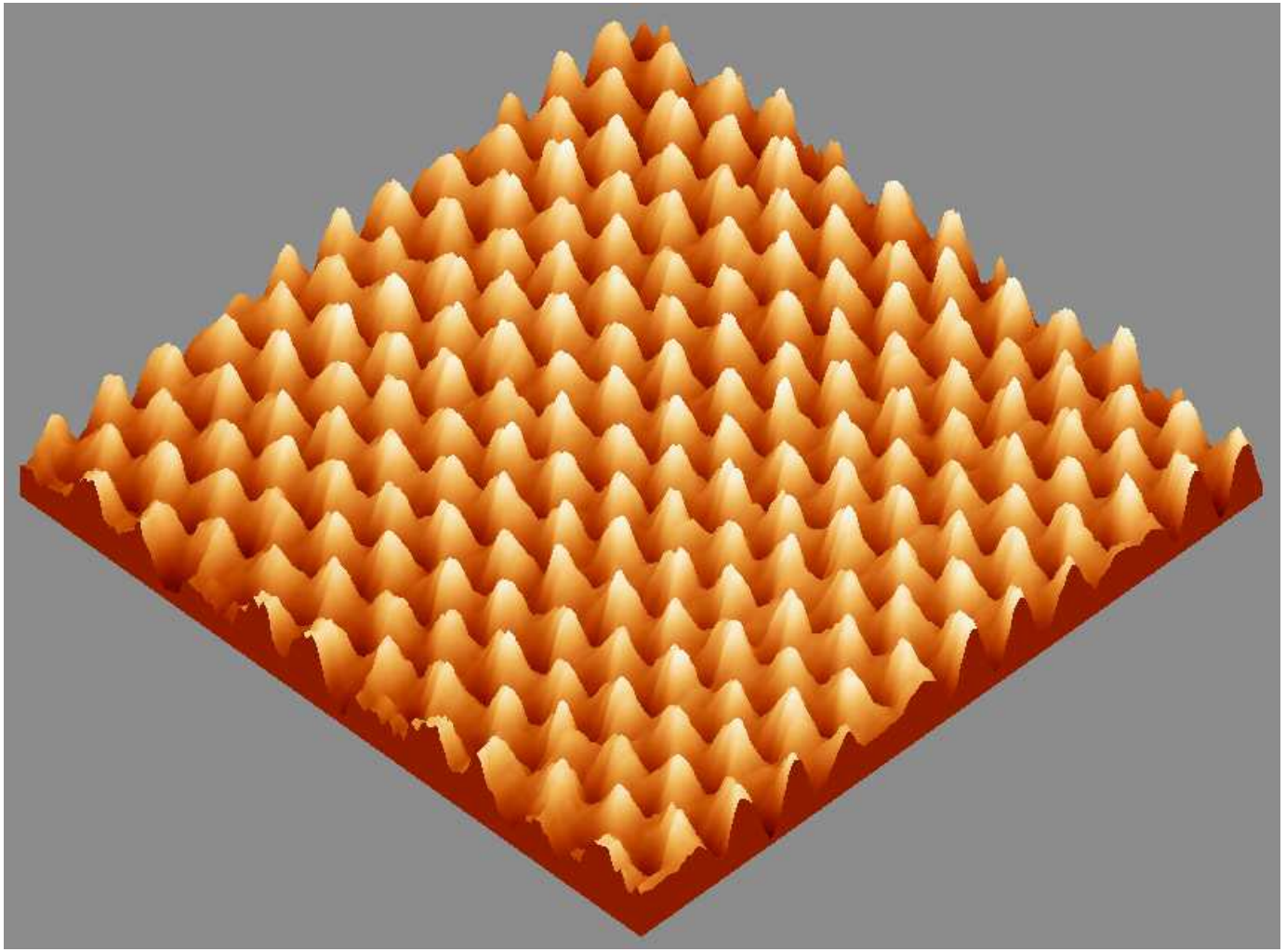
Si(111) Dimer-Adatom-Stacking Fault Reconstruction



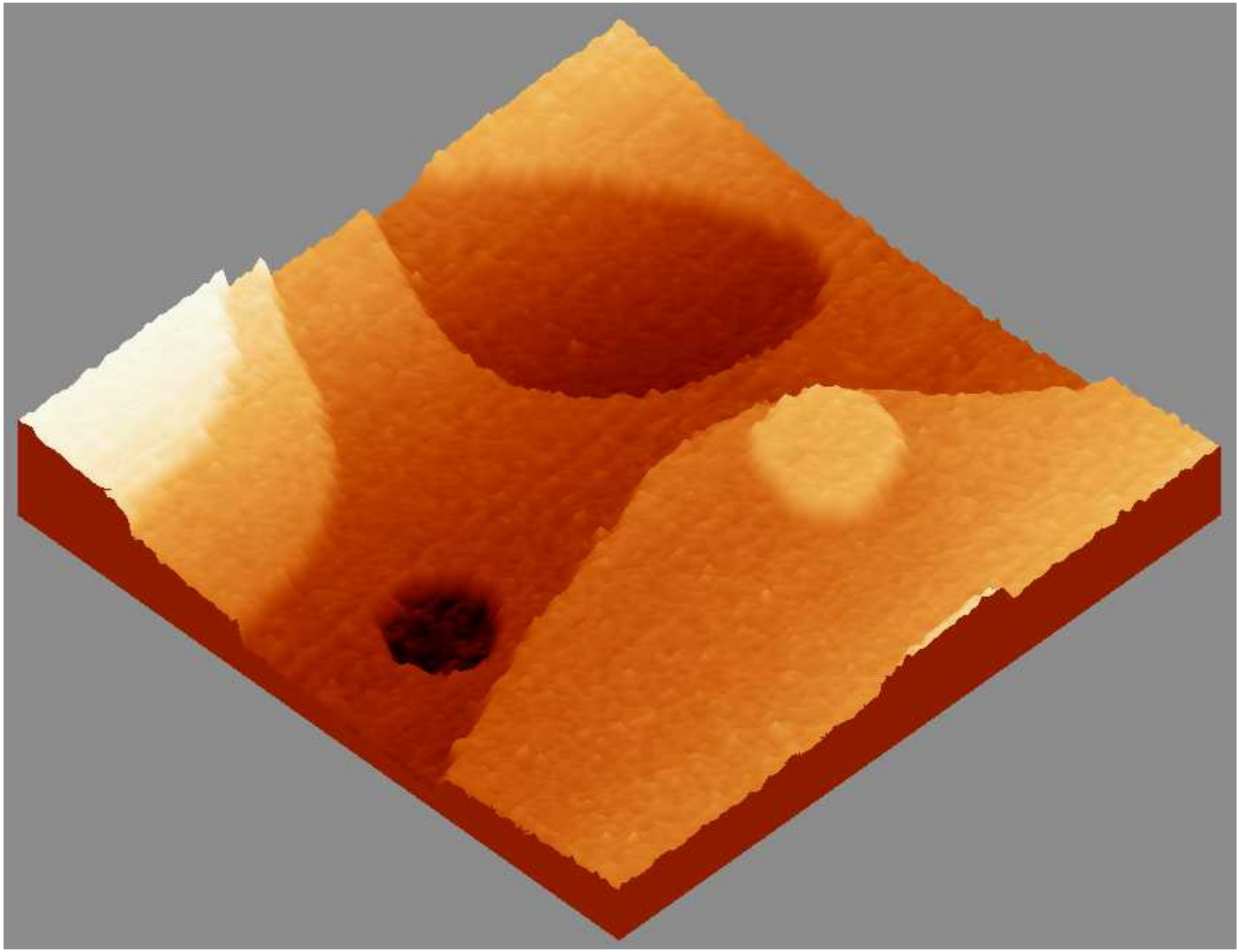




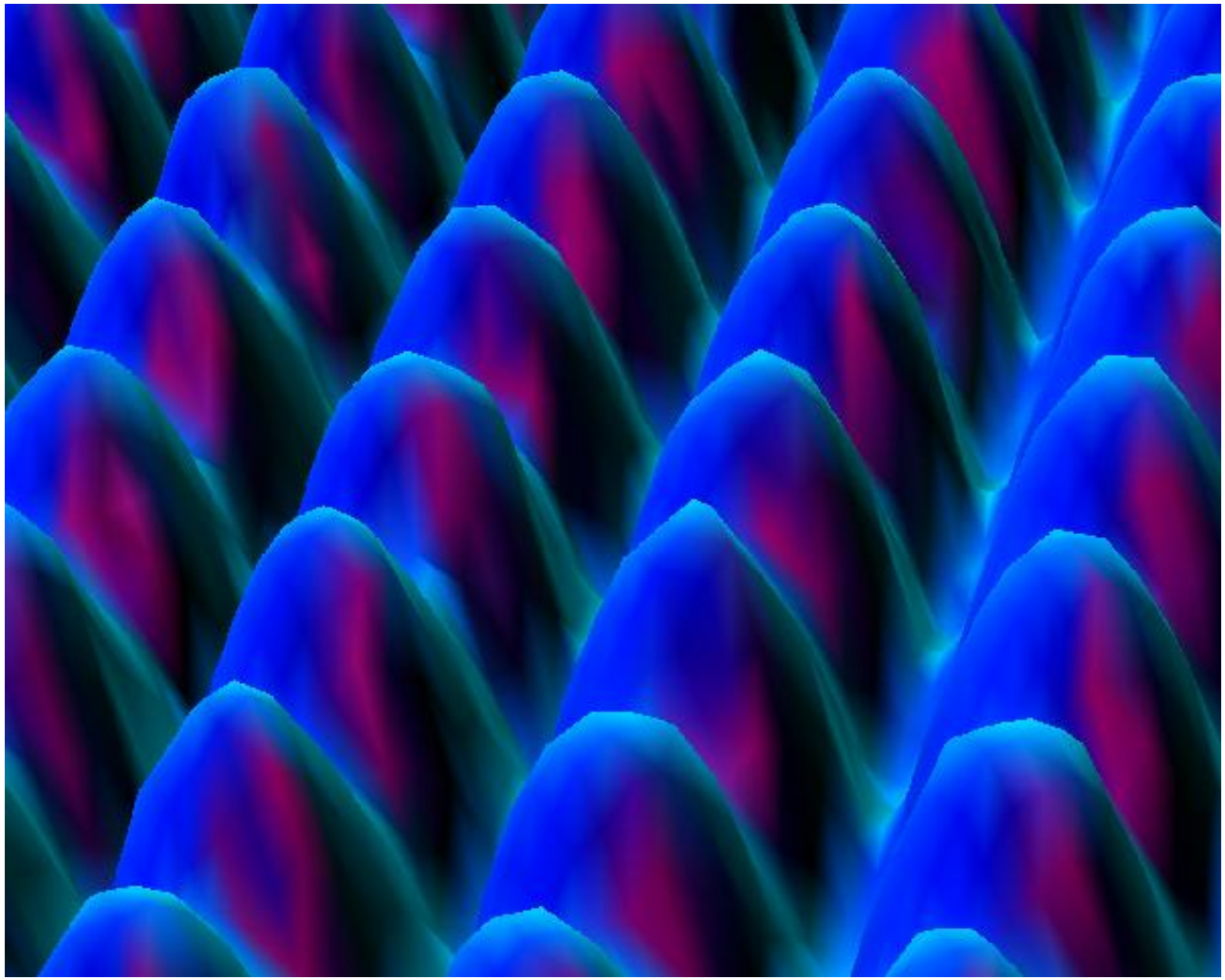
Graphite Surface (in air)



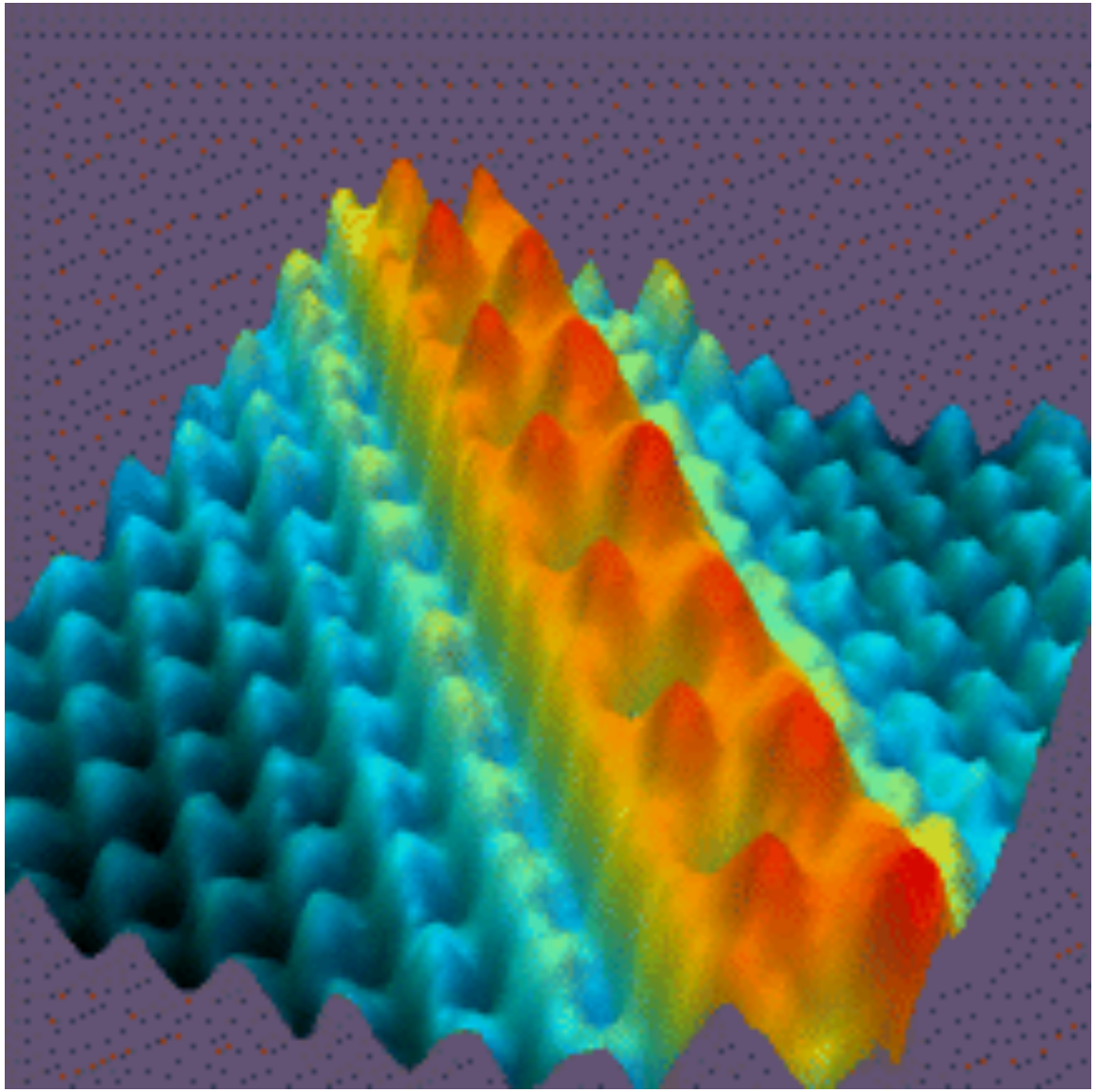
Gold Surface



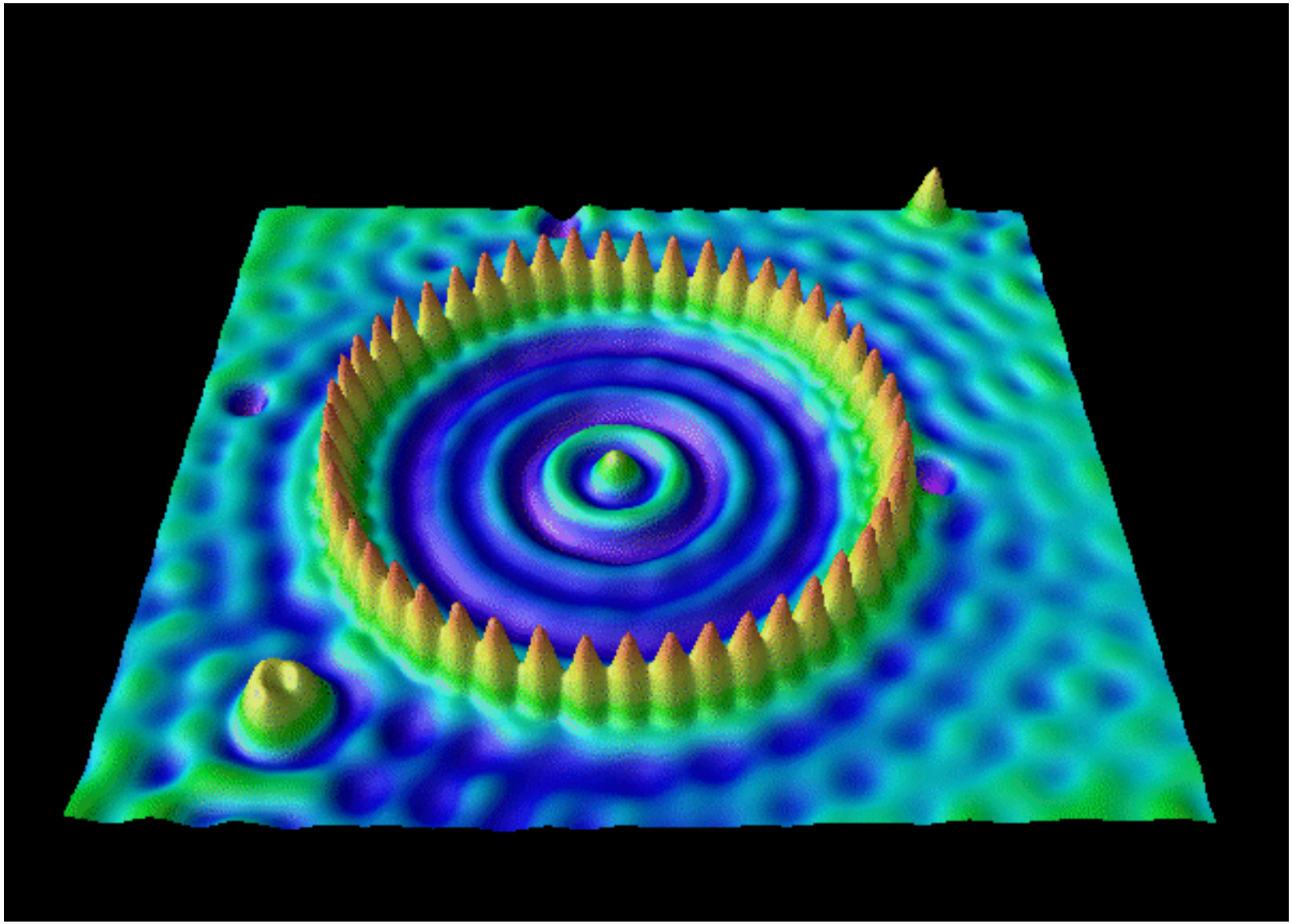
Nickel single crystal at low temperature



“Nanowire” of Cs on a GaAs surface



“Quantum corral” formed from Xe adsorbed on Ni

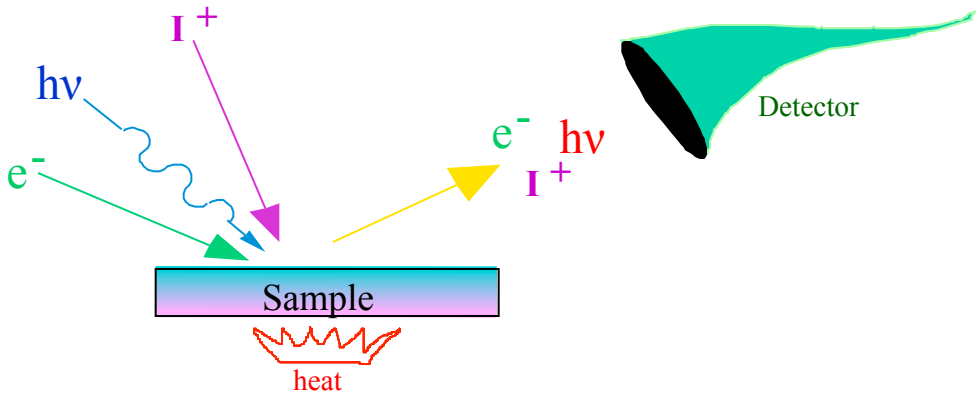


Experiment vs. Theory

Duke's Laws

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

Generic Surface Spectroscopy



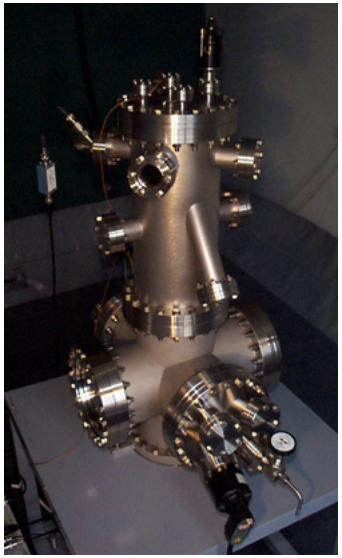
- Particles can be: electrons, ions, photons, atomic or molecular particles, heat, others…
- Experiments are designed to probe outermost few Å's of surface
- Techniques in our laboratory include x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), ion scattering spectroscopy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

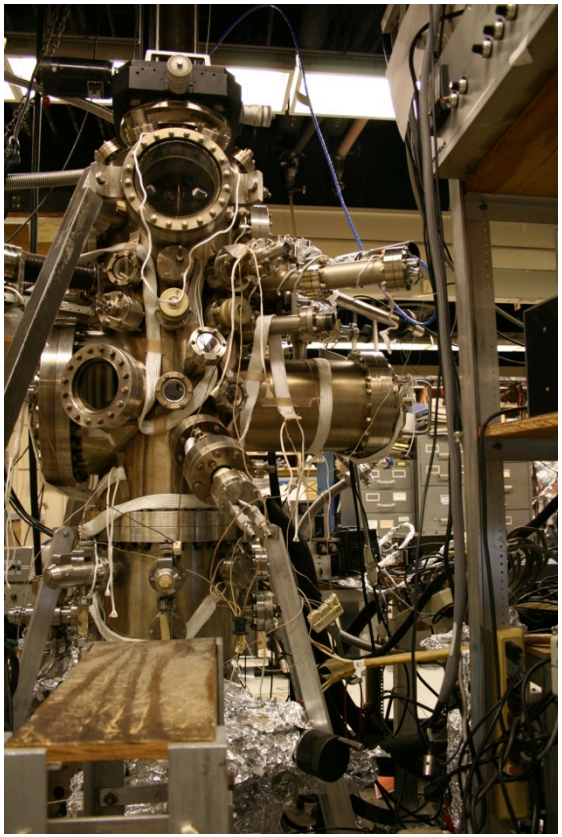
A few techniques:

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)

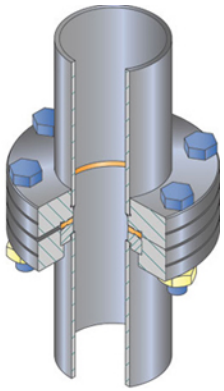
- Better than 1 x 10^{-10} torr
- Needed to insure that surfaces remain clean
- UHV is achieved with all-metal chambers that are baked to remove water and other adsorbed gases from the walls, and are evacuated with oil-free pumps

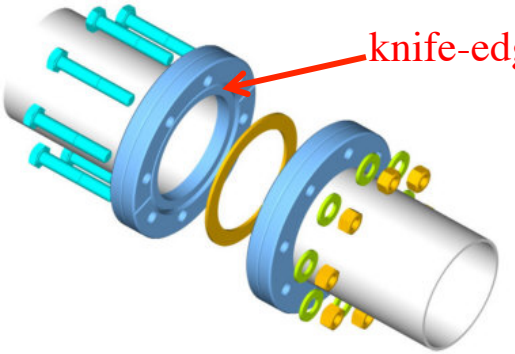


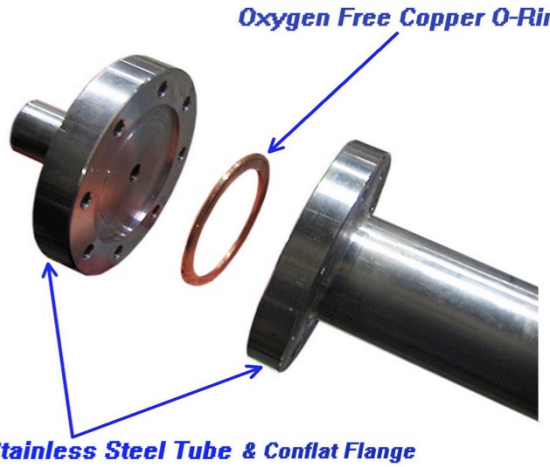


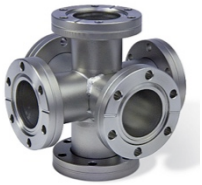
Ultra-High Vacuum (UHV)

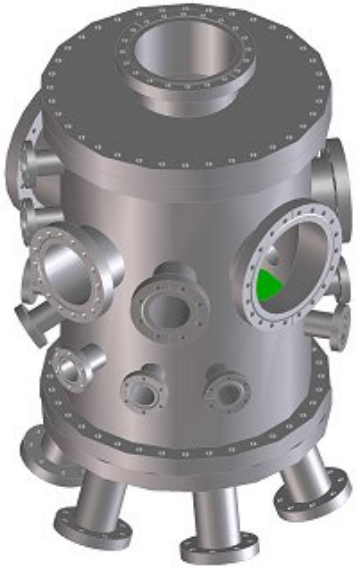
CONFLAT flanges

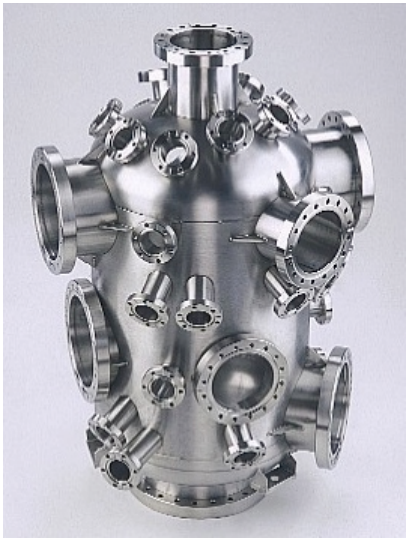






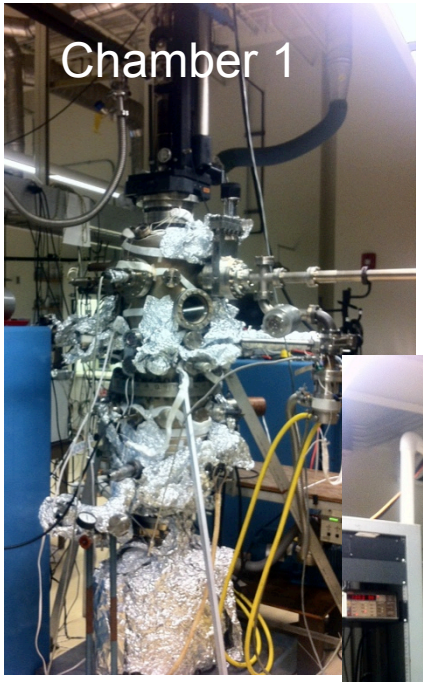


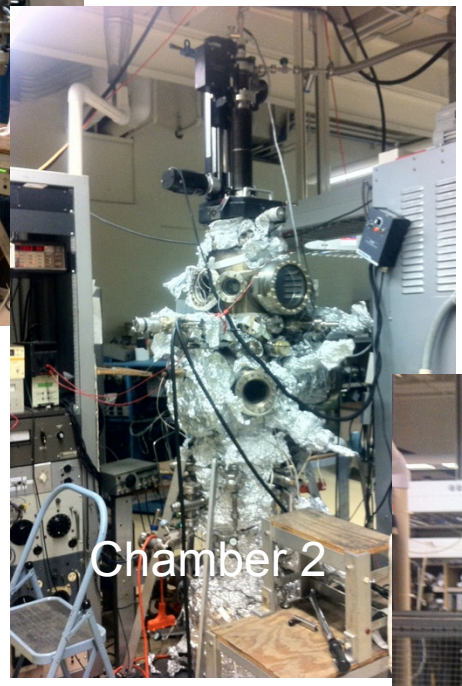


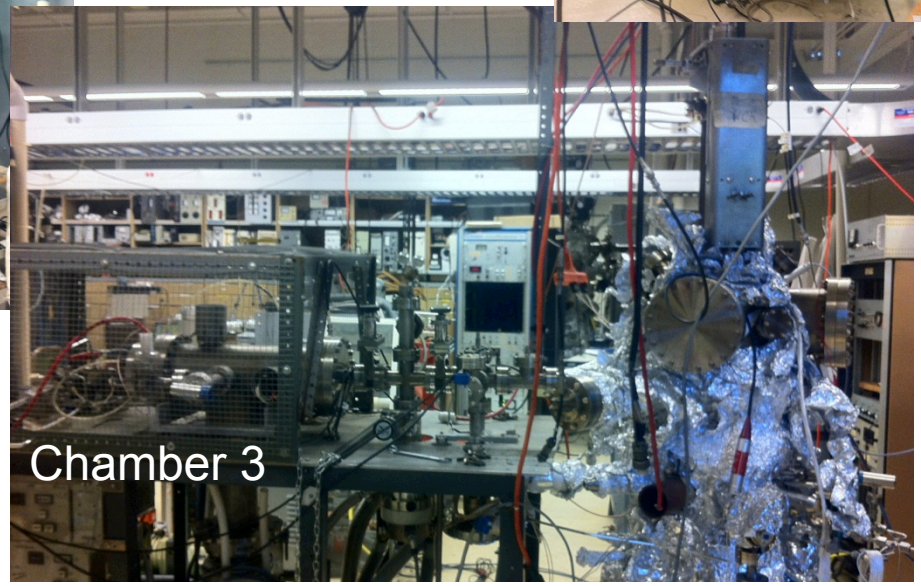


The Yarmoff Lab

The Yarmoff Lab







The Yarmoff Group

UC RIVERSIDE UNIVERSITY OF CALIFORNIA

Current Graduate Students
Alex Arjad
Xiaoxiao He
Weimin Zhou

Current Undergrads
Josiah Keagy
Aron Pedigo

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 Gann - *Georgia Institute of Technology*

Collaborators
Zdenek Sroubek - *Academy of Sciences, Czech Republic*
Regina Ragan - *UC Irvine*
Ruqian Wu - *UC Irvine*
Richard Osgood - *Columbia*

Funding:
National Science Foundation

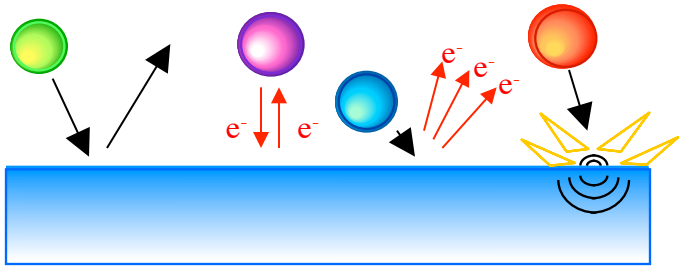
Army Research Office

Center for Nanoscale Innovation for Defense

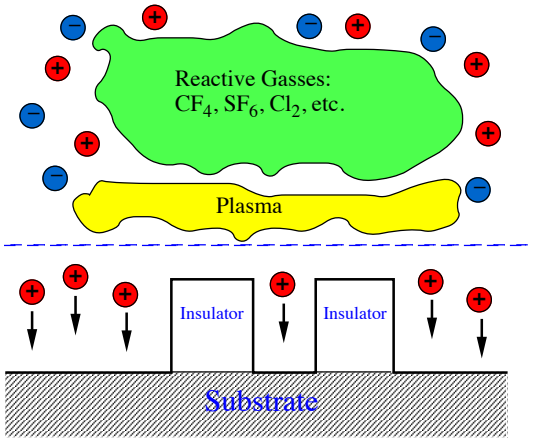
UCR College of Natural and Agricultural Sciences

Projects

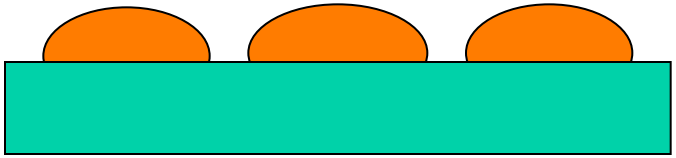
Ion-surface interactions



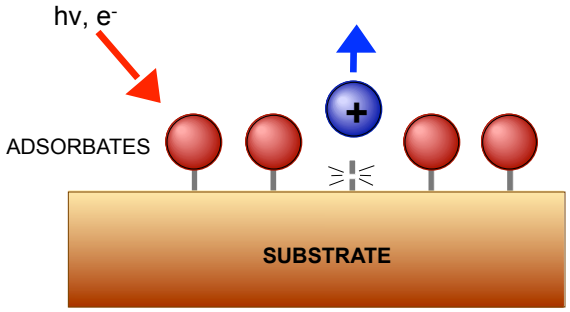
Semiconductor surface etching



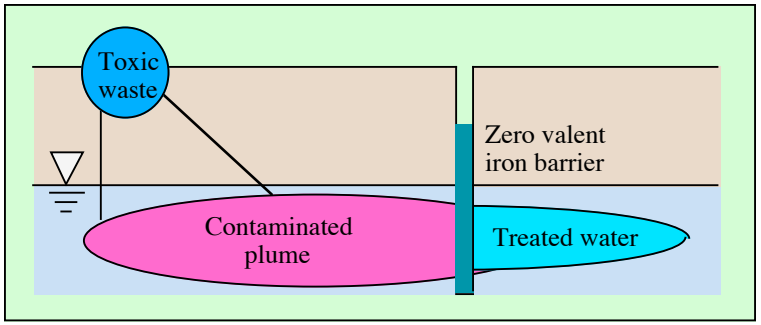
Fabrication and Characterization of Nanomaterials



Radiation damage to surfaces

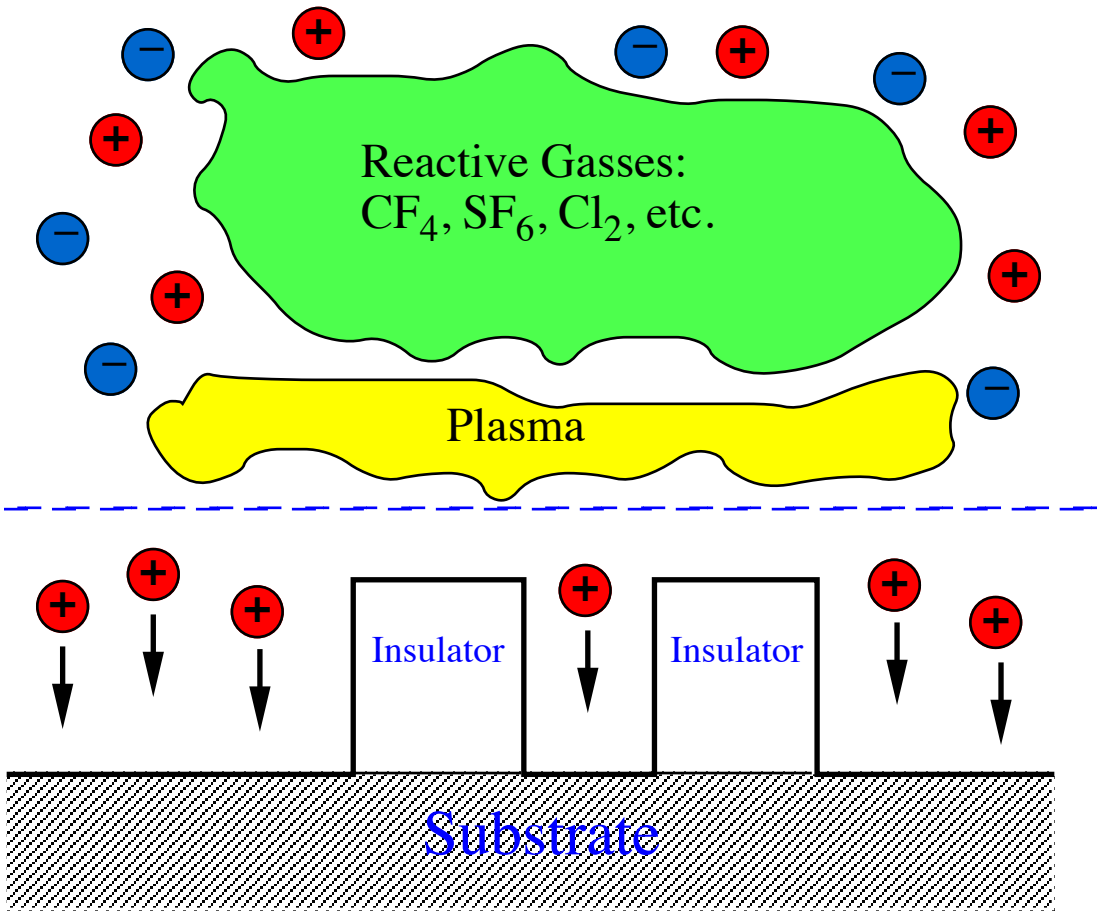


Environmental surfaces



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:

$$GaAs + 3\ Cl_2 \rightarrow$$

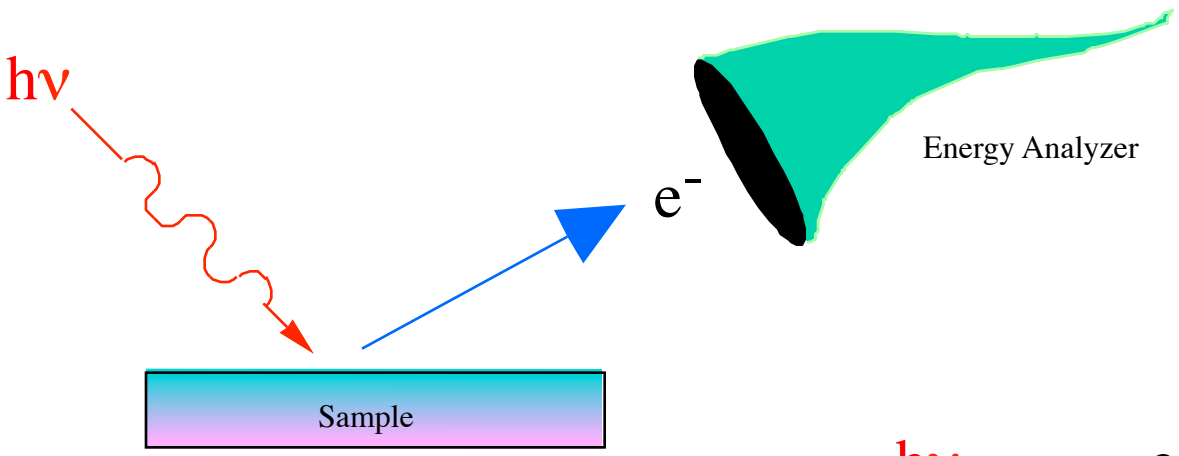
$$GaCl_3\ (gas) + AsCl_3\ (gas)$$

High temperatures:

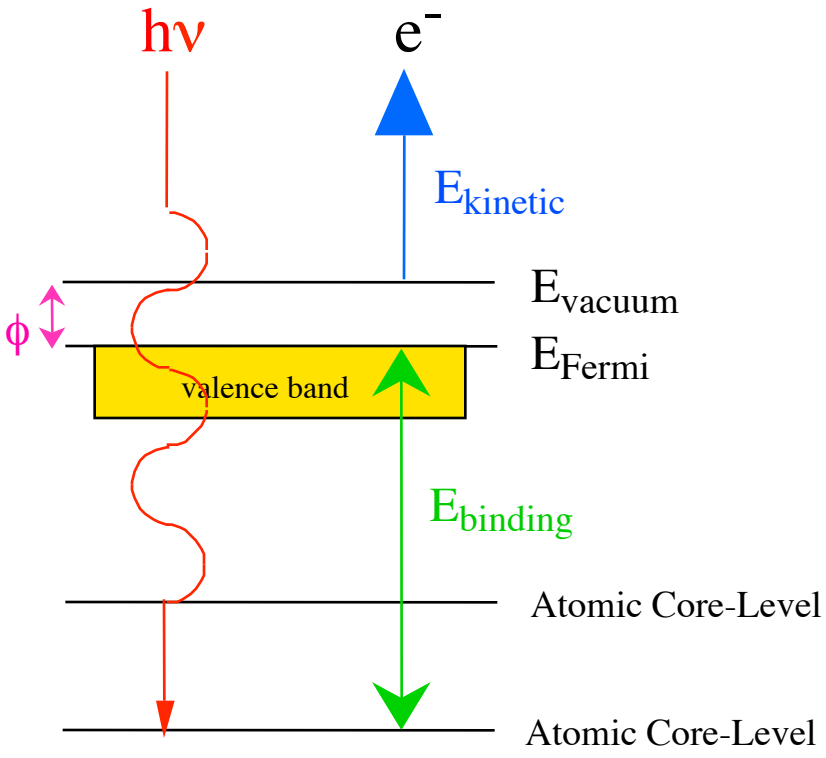
$$GaAs + 1/2\ Cl_2 \rightarrow$$

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

Soft X-Ray Photoelectron Spectroscopy (SXPS)

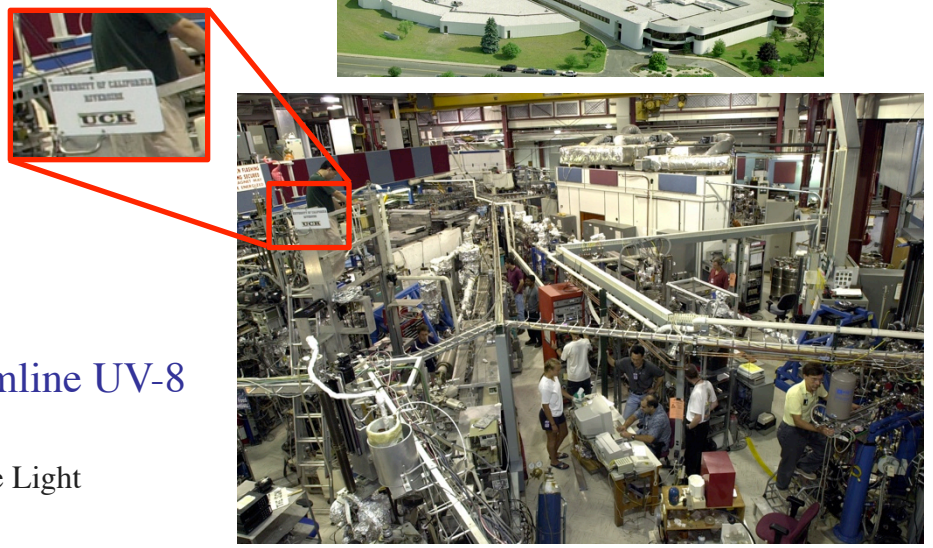


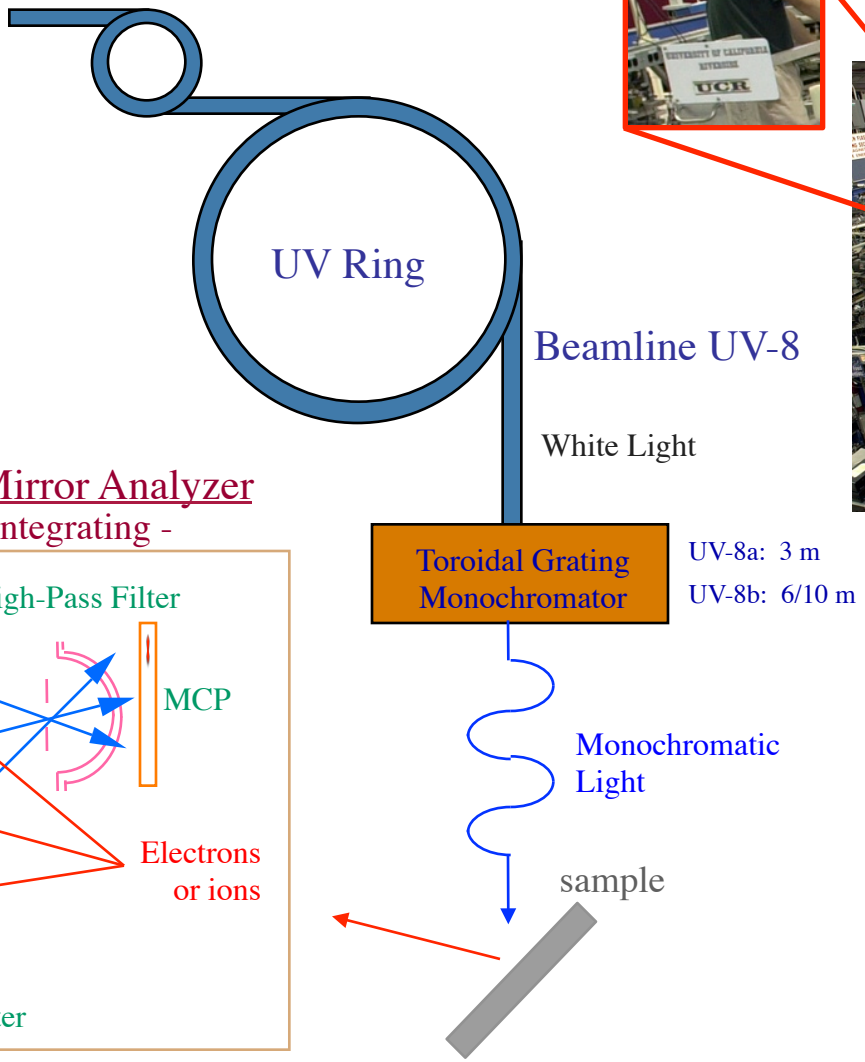
- $E_{kinetic} = h\nu - E_{binding} - \phi$
- Measures Filled Density-of-States (DOS)
- Sampling Depth is determined by $E_{kinetic}$
  (e.g., for $E_{kinetic}$ = ~25 eV, l = ~3 Å)



National Synchrotron Light Source (NSLS)

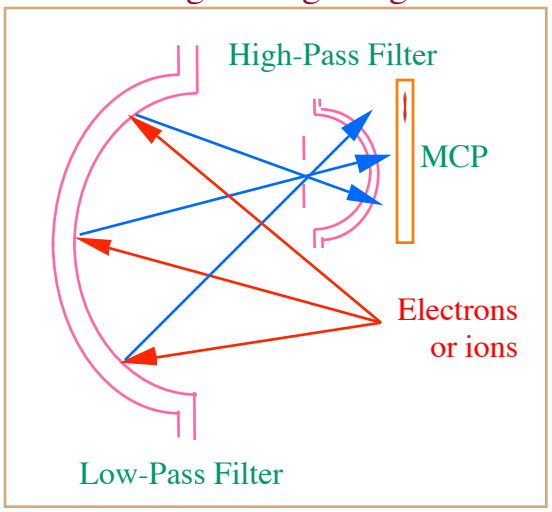
at Brookhaven National Laboratory



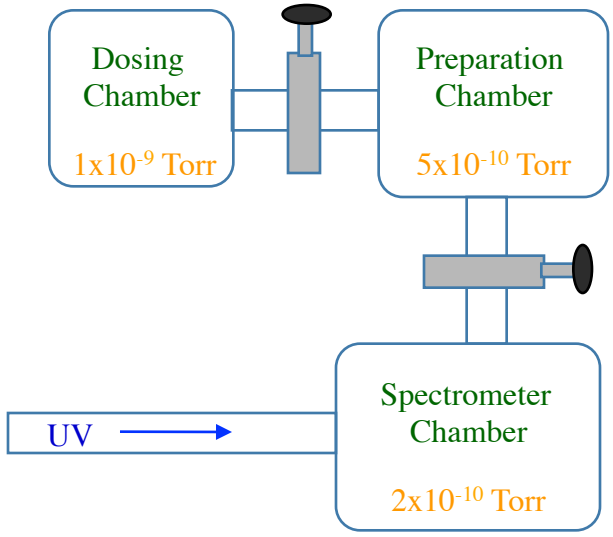


Ellipsoidal Mirror Analyzer

- Angle-Integrating -

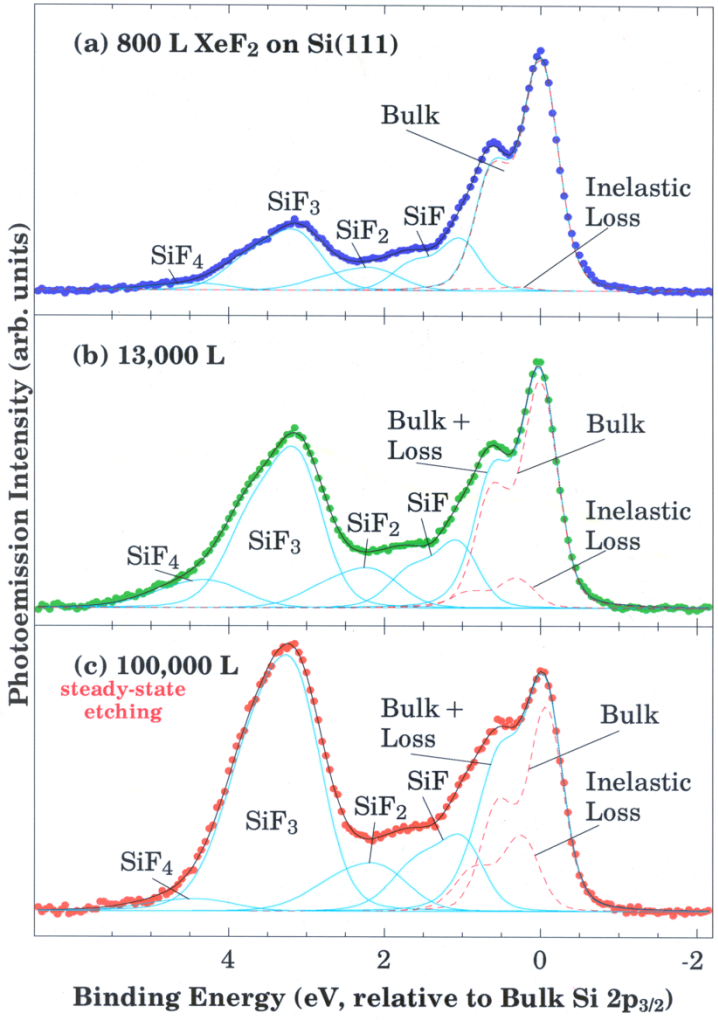


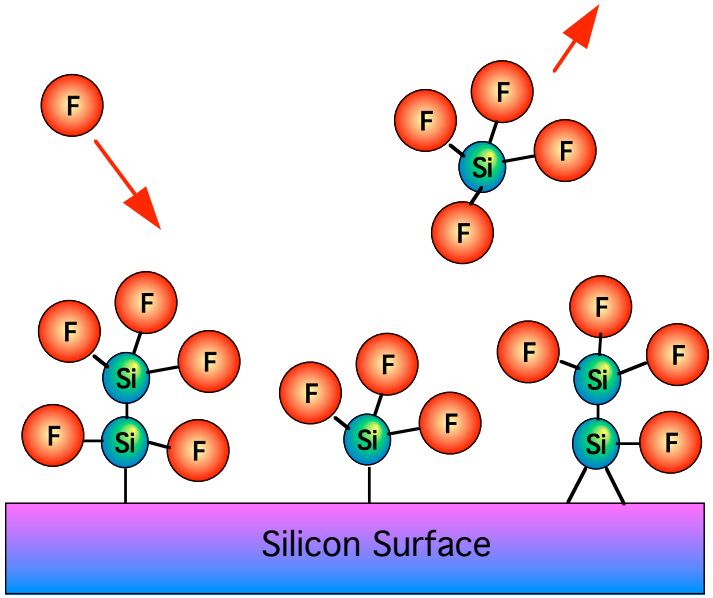
Sample Transfer System



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

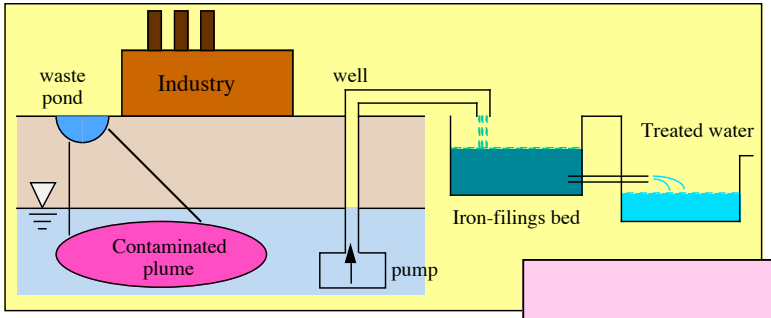
Use of surface chemical reactions for environmental remediation

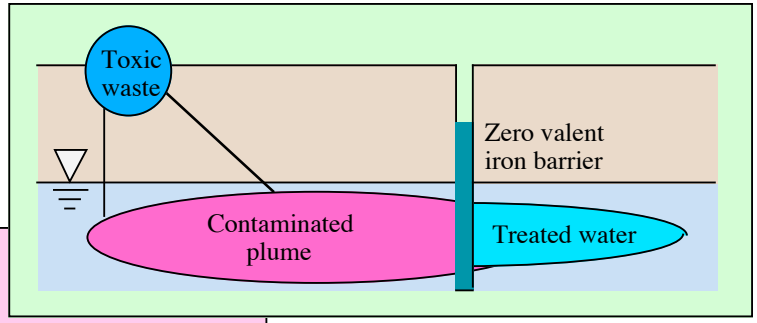
Environmental Problem

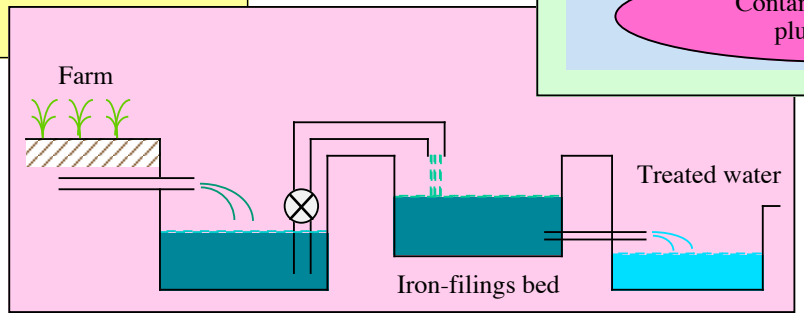
- Oxidized forms of several toxic trace elements (e.g., SeO_4^{2}, CrO_4^{2}, UO_2^{2+}) are soluble in water and mobile in the environment.
- These ions have contaminated groundwaters throughout the United States and the world. For example, at many DOE sites it is a critical cleanup issue.

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:

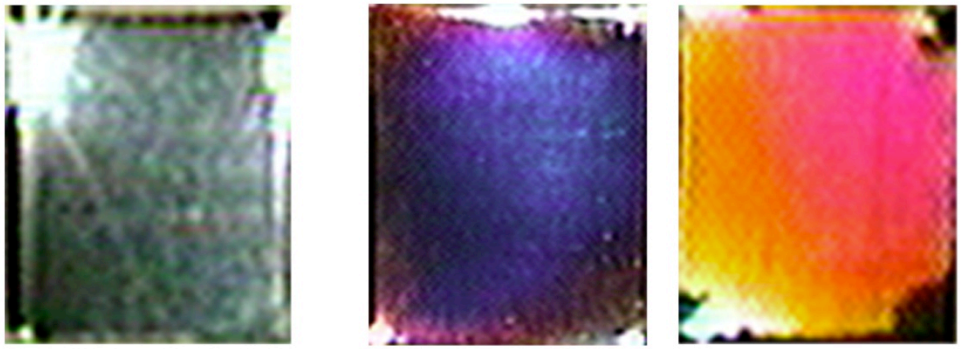






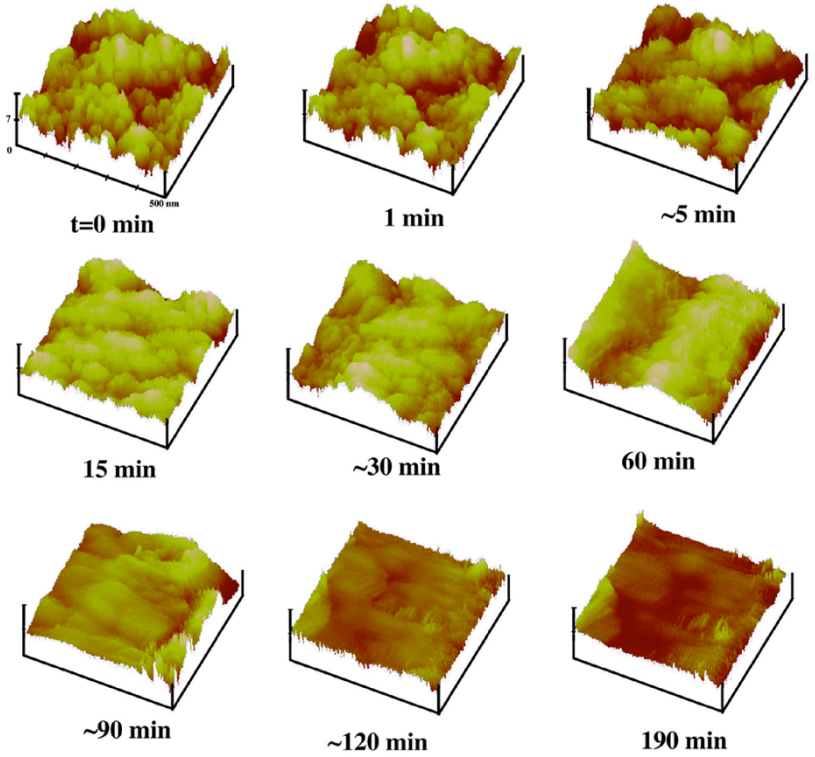
Iron foils reacted in a Uranyl Nitrate Solution

Fe foil before reaction

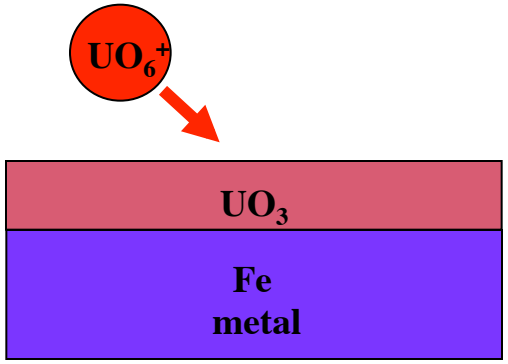


Fe foils following reaction appear iridescent

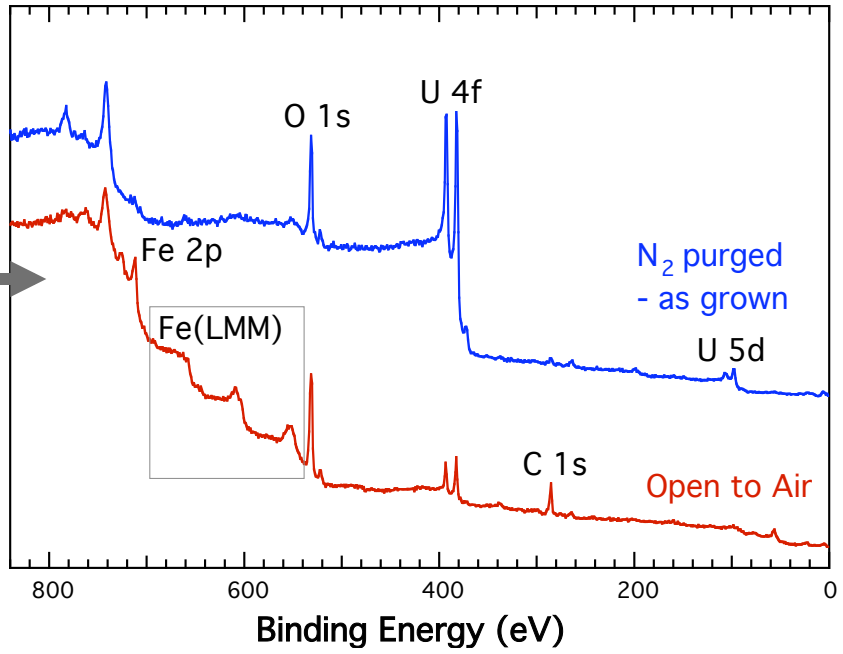
The surface of an iron foil was monitored with *in situ* STM in a solution containing uranyl nitrate. The 500x500 nm images show the rough surface, characteristic of a native iron oxide, becoming smoother as the reaction proceeds. XPS analysis showed that the smooth morphology is due to the deposition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



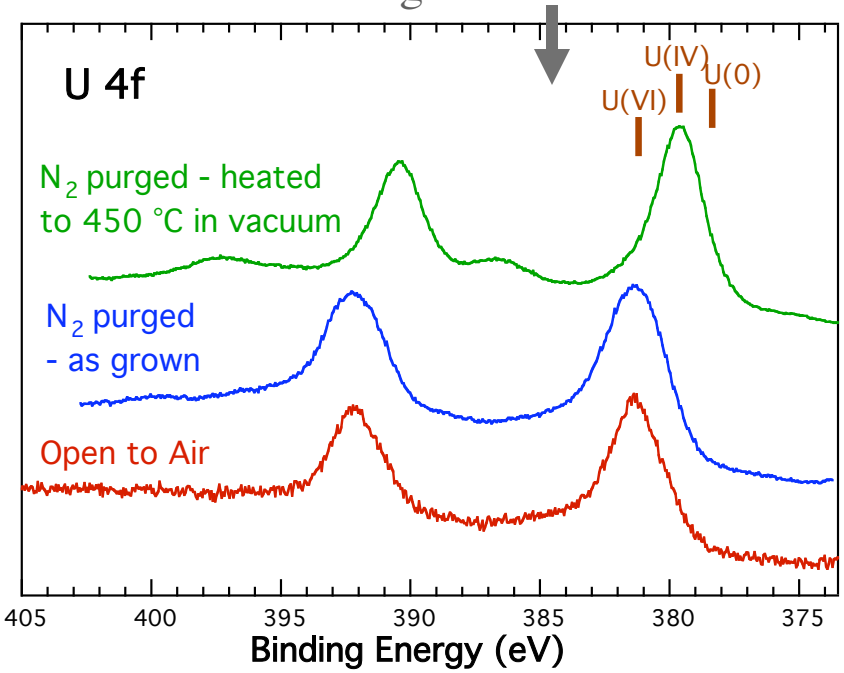
X-Ray Photoelectron Spectroscopy (XPS)



Wide scan



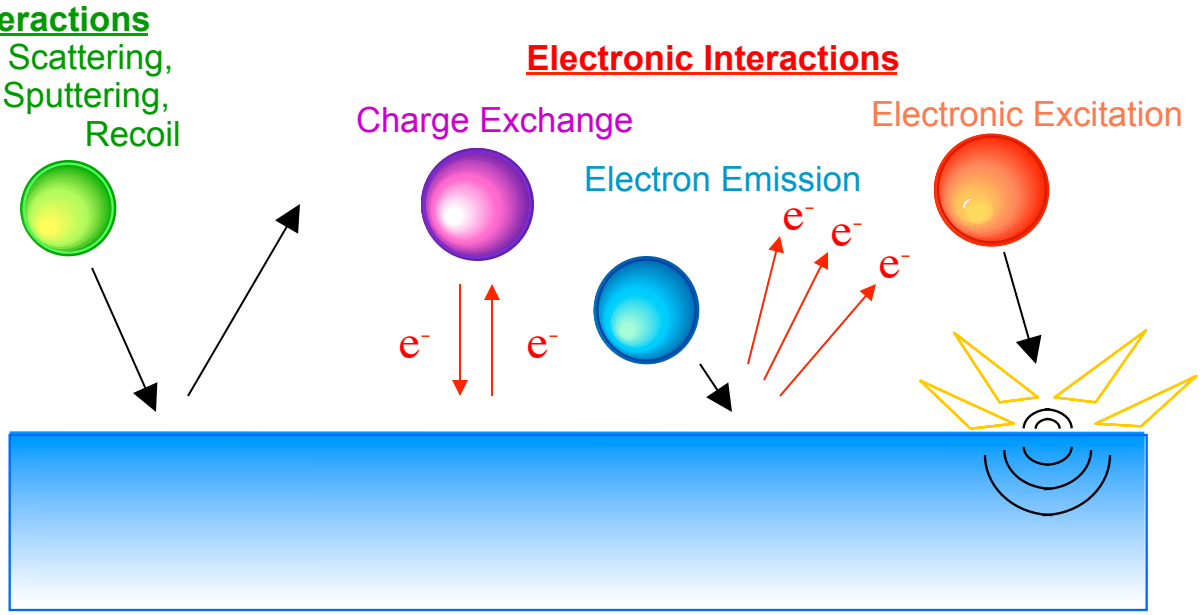
High-resolution scan



- 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

Ion-Surface Interactions



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

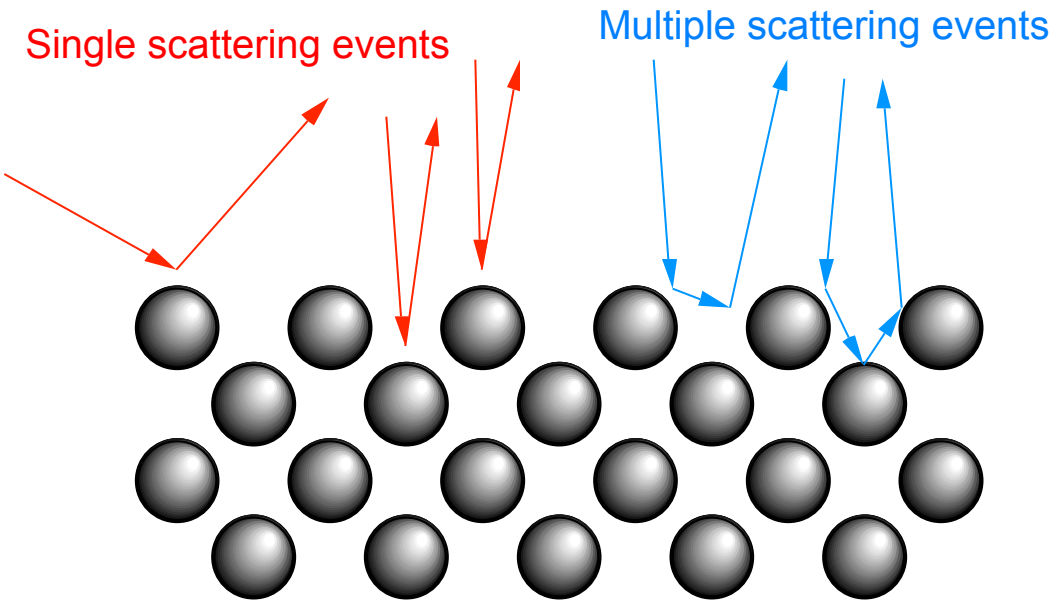
  Surface Chemical Reactions
  Plasma Processing
  Secondary Ion Mass Spectrometry (SIMS)
  Ion Implantation
  Stimulated Desorption (ESD, PSD,…)

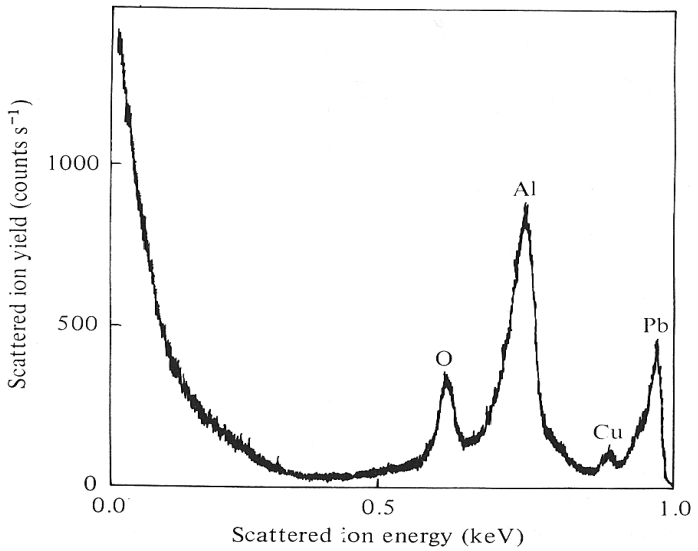
- Ion-surface interactions can be classified as:

  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





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

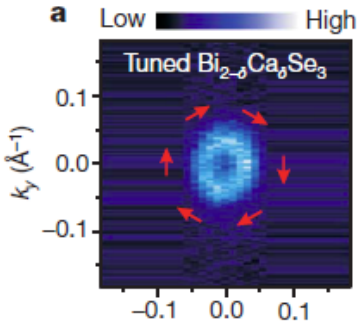
Binary collision approximation (BCA):

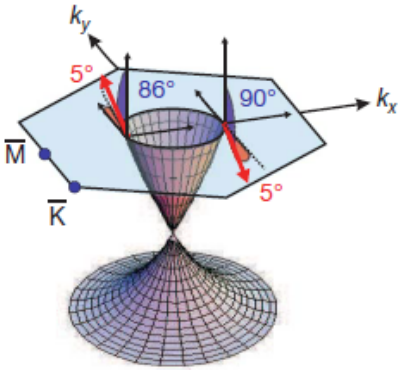
- Ions interact with one substrate atom at time
- Scattering is a sequence of binary collisions with target atoms positioned at lattice sites
- Elastic and inelastic energy losses are decoupled
  - Elastic energy lost during a single collision
  - Continuous inelastic energy losses are roughly proportional to distance traveled in crystal
- Single scattering peak (SSP) seen for each type of surface atom

Surface Studies of Topological Insulators

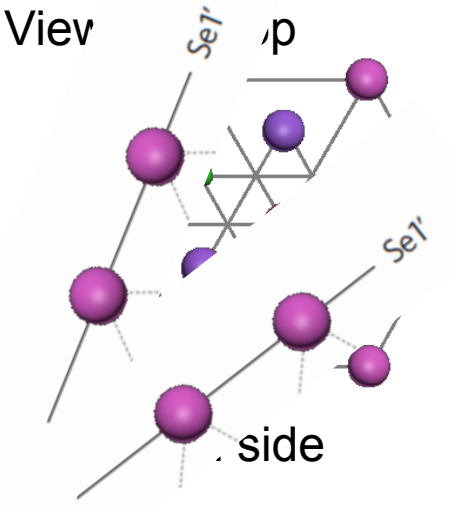
Bi_2Se_3:

- 3D topological insulator (TI)
- Have strong spin-orbit interactions that give rise to robust surface states

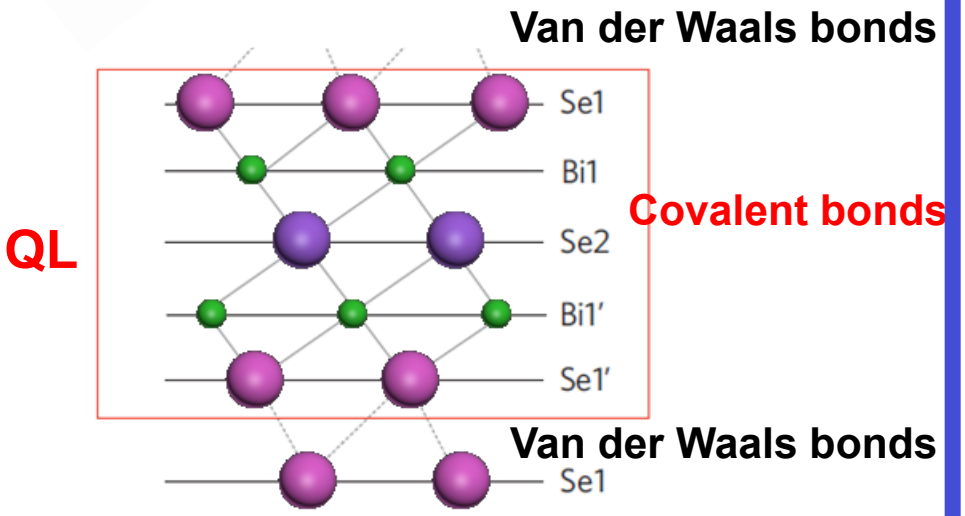




D. Hsieh et al. , NATURE, Vol 460(1101), 27 August 2009

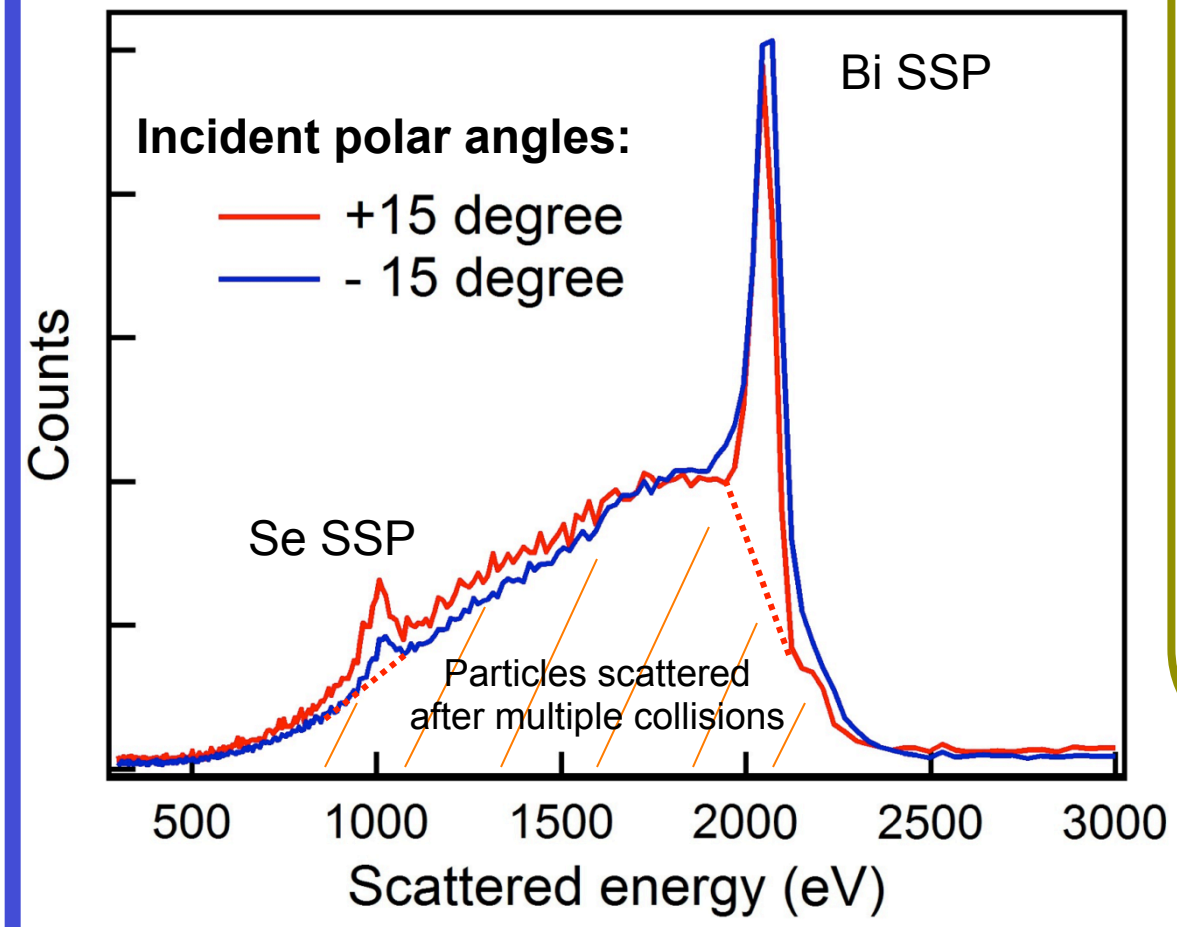


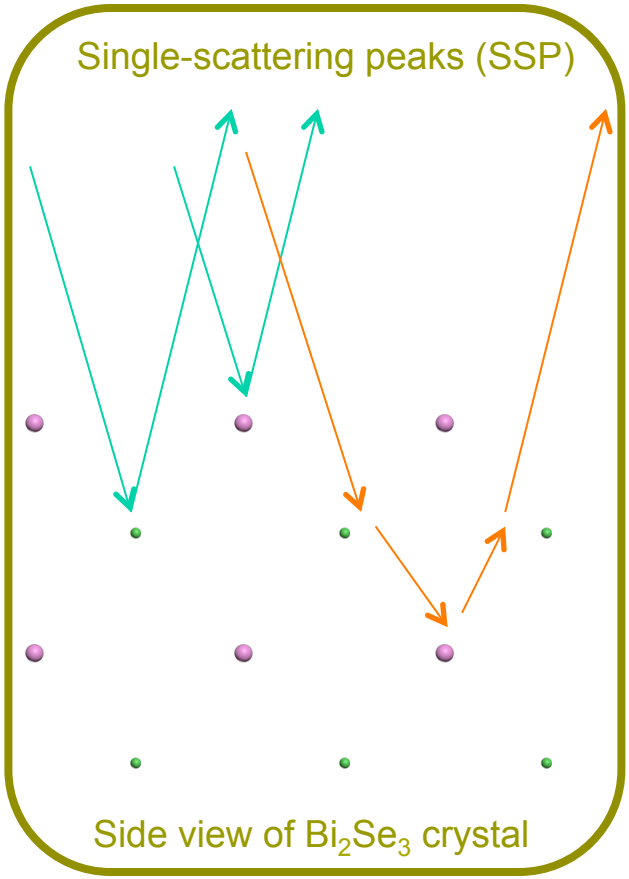
1st layer
2nd layer
3rd layer



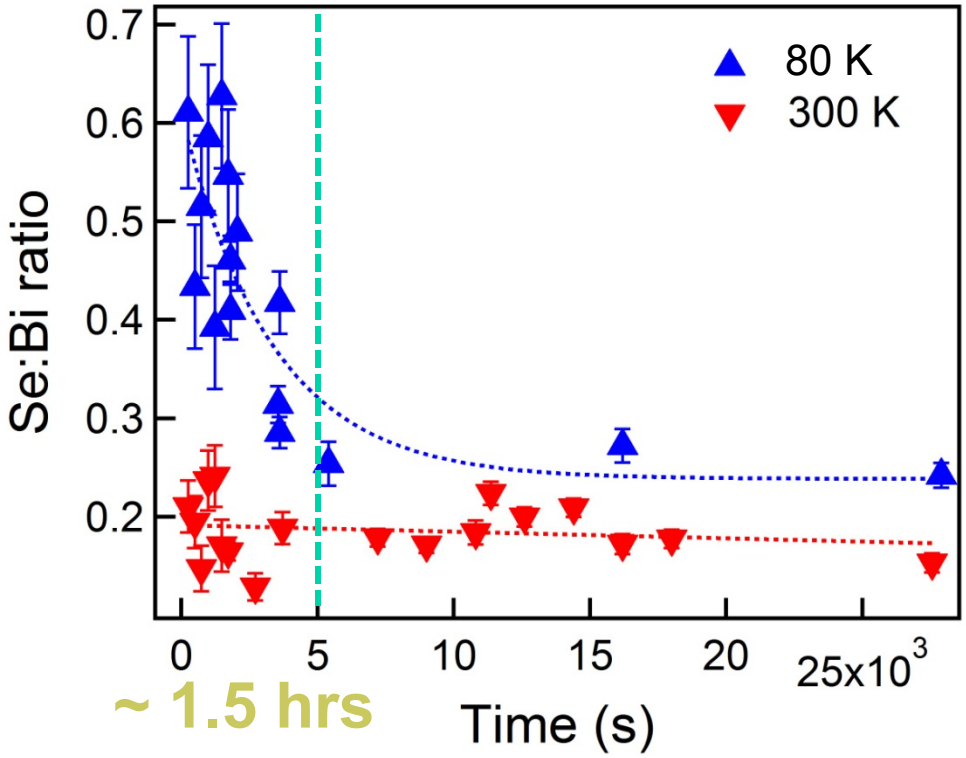
Ion Scattering Spectra

Time-of-flight (TOF) spectra for 3.0 keV Na^+ ions scattered from Bi_2Se_3 at room temperature, with an incident azimuthal angle of ϕ = 12.5°





Time dependence

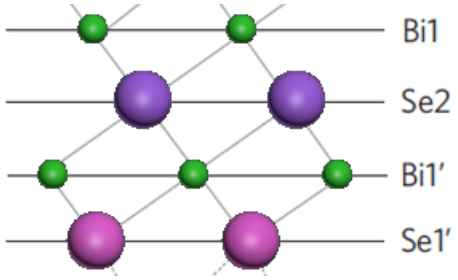


Time dependnce of Se:Bi ratio at an altitude angle φ=0° and an azimuth angle ϕ= 12.5°

- An exponential drop of the Se:Bi ratio at 80 K, which ends up matching the room temperature value after about 1.5 hours.

- The surface becomes Bi-rich more slowly at 80 K than at room temperature.

Conclusions



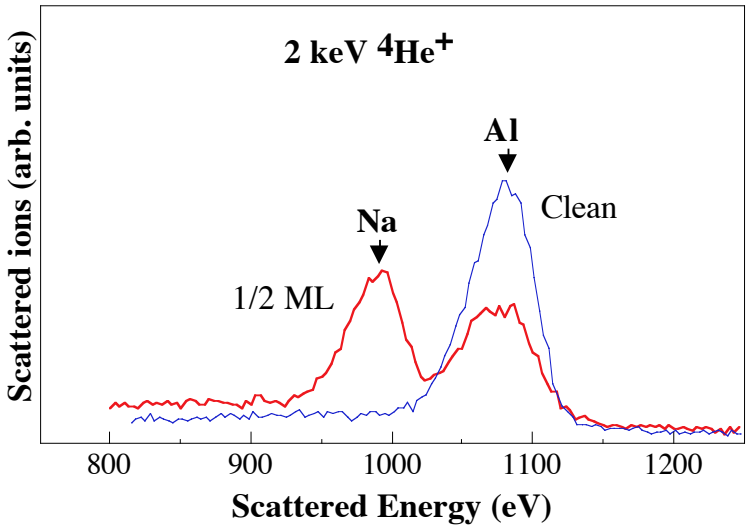
- Se is located beneath surface Bi atoms.
- As Bi_2Se_3 has quintuple layers (QLs) held together by weak van der Waals bonds, it has been assumed that a Se termination results when cleaved.
- The LEIS spectra indicate a surface terminated with Bi, although some Se is still present.
- We need further experiments to ascertain the mechanism causing Se depletion and/or Bi enhancement.

ISS Energy Spectra

Na adsorbed on Al(100)

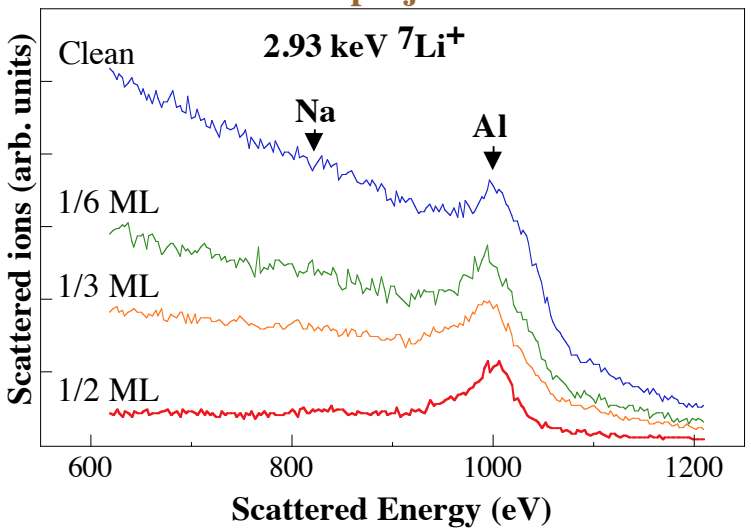
- Electrostatic analyzer employed
- Sensitive only to scattered ions

Traditional ISS



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

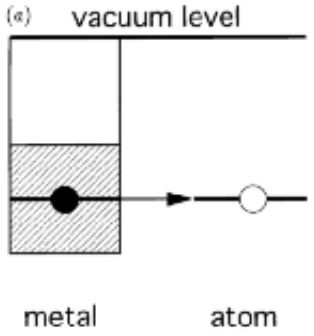
Alkali projectile



- 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-metal surface collisions

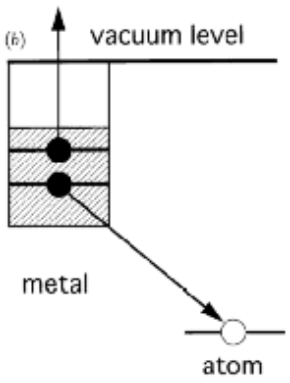


Resonant charge transfer (RCT)

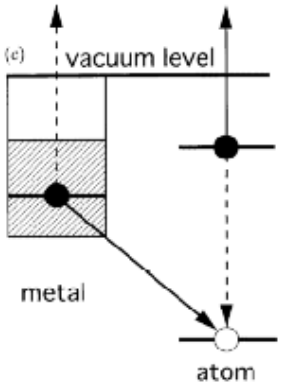
- Resonant charge transfer (RCT) of electrons between atomic and metal states at constant energy

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

  Reversible; final charge state determined along exit trajectory



Auger neutralization



Auger de-excitation

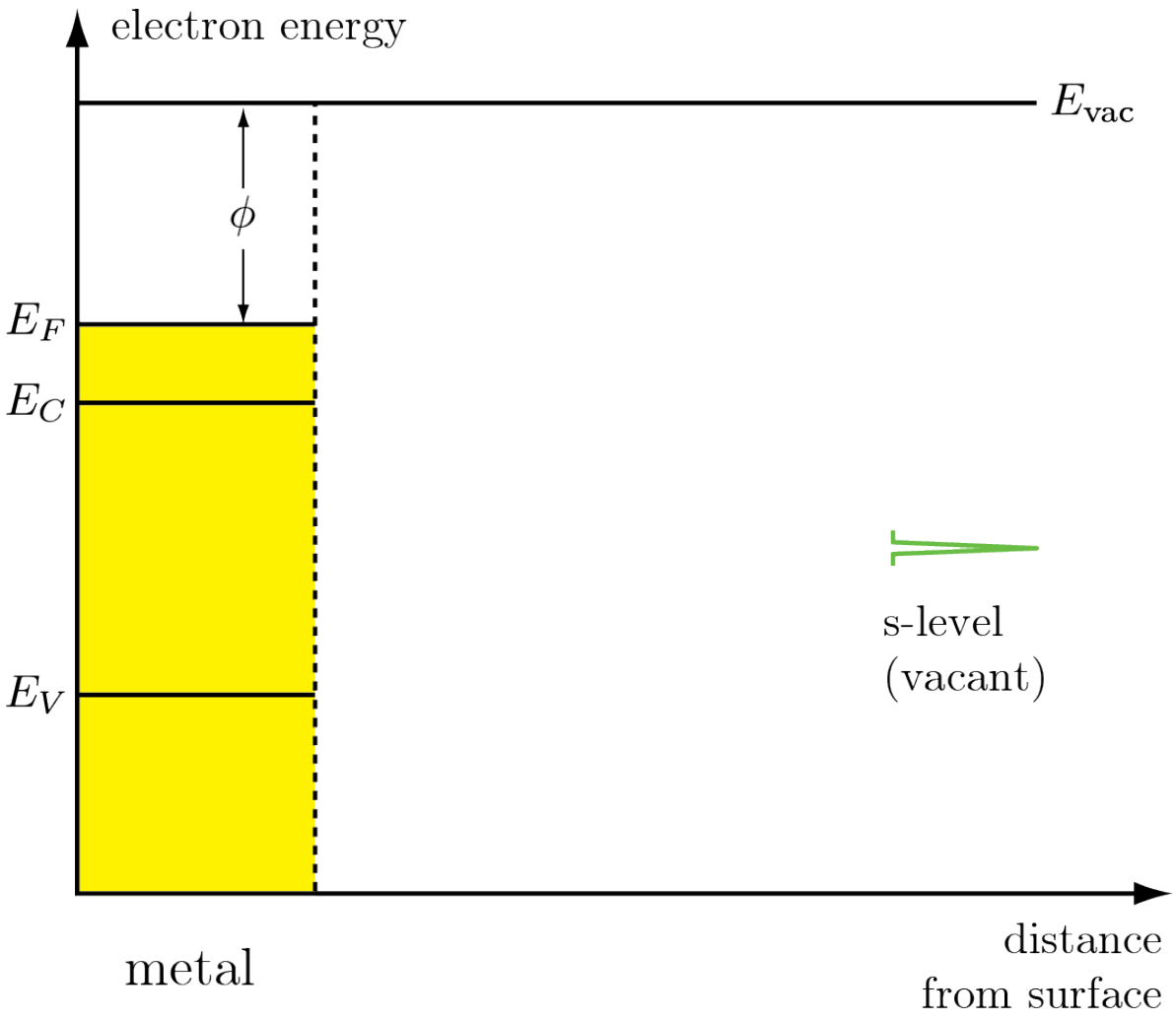
- Auger processes involve the relaxation of the excited atom-surface system

  Ionization level below conduction band:
  noble gas ions

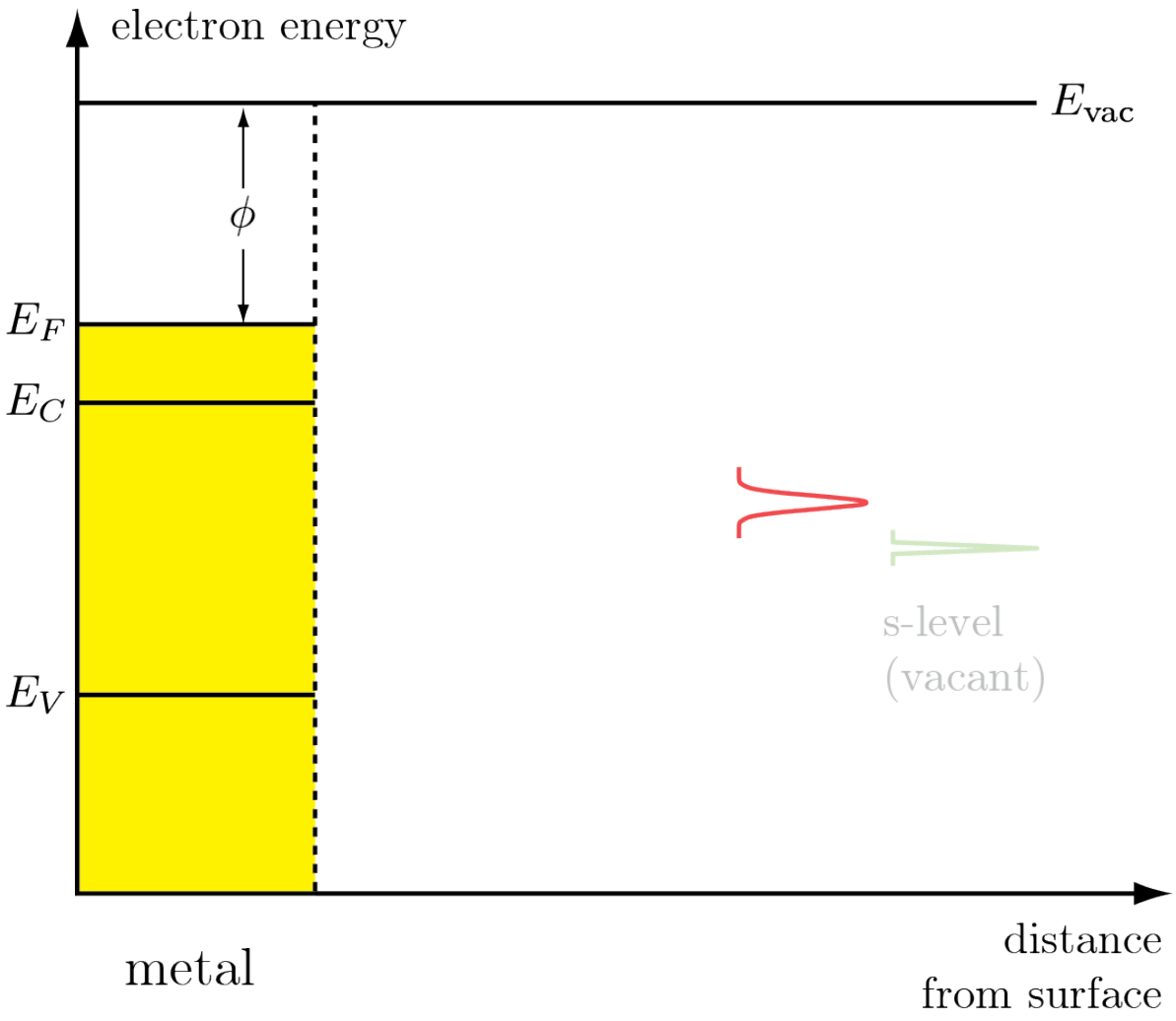
  Irreversible; neutralization can occur anytime during scattering

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

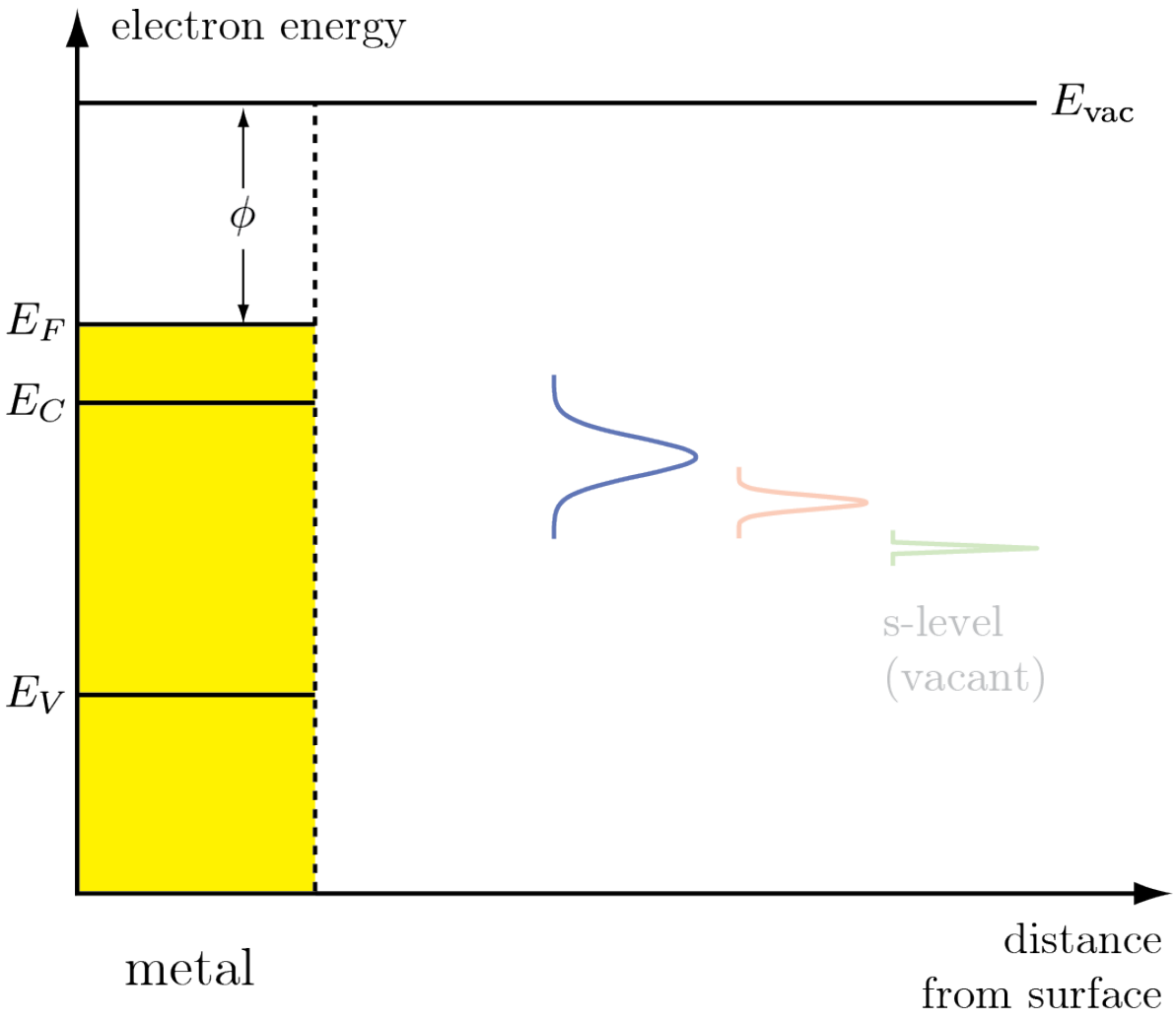
Resonant Charge Transfer (RCT)



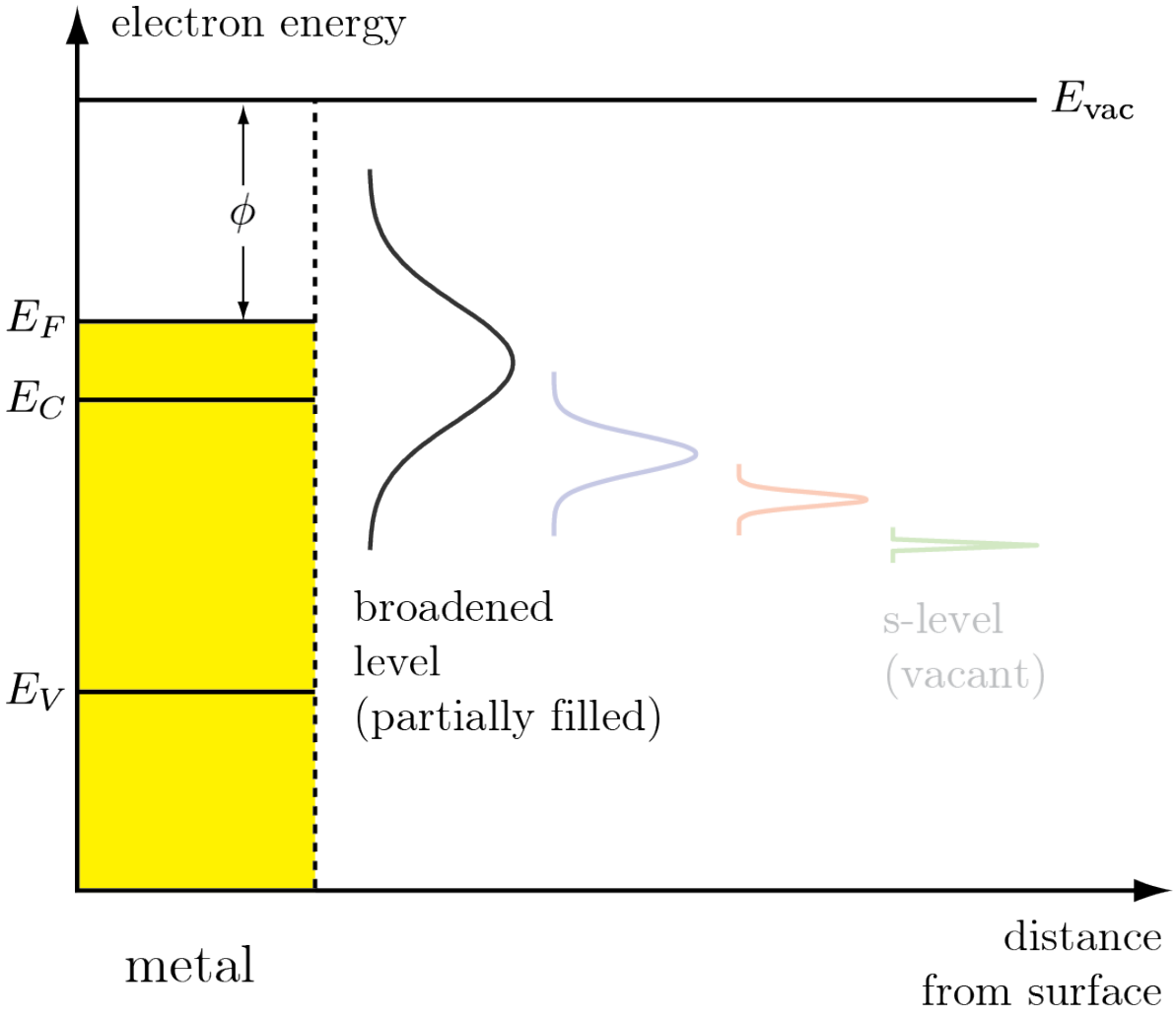
Resonant Charge Transfer (RCT)



Resonant Charge Transfer (RCT)

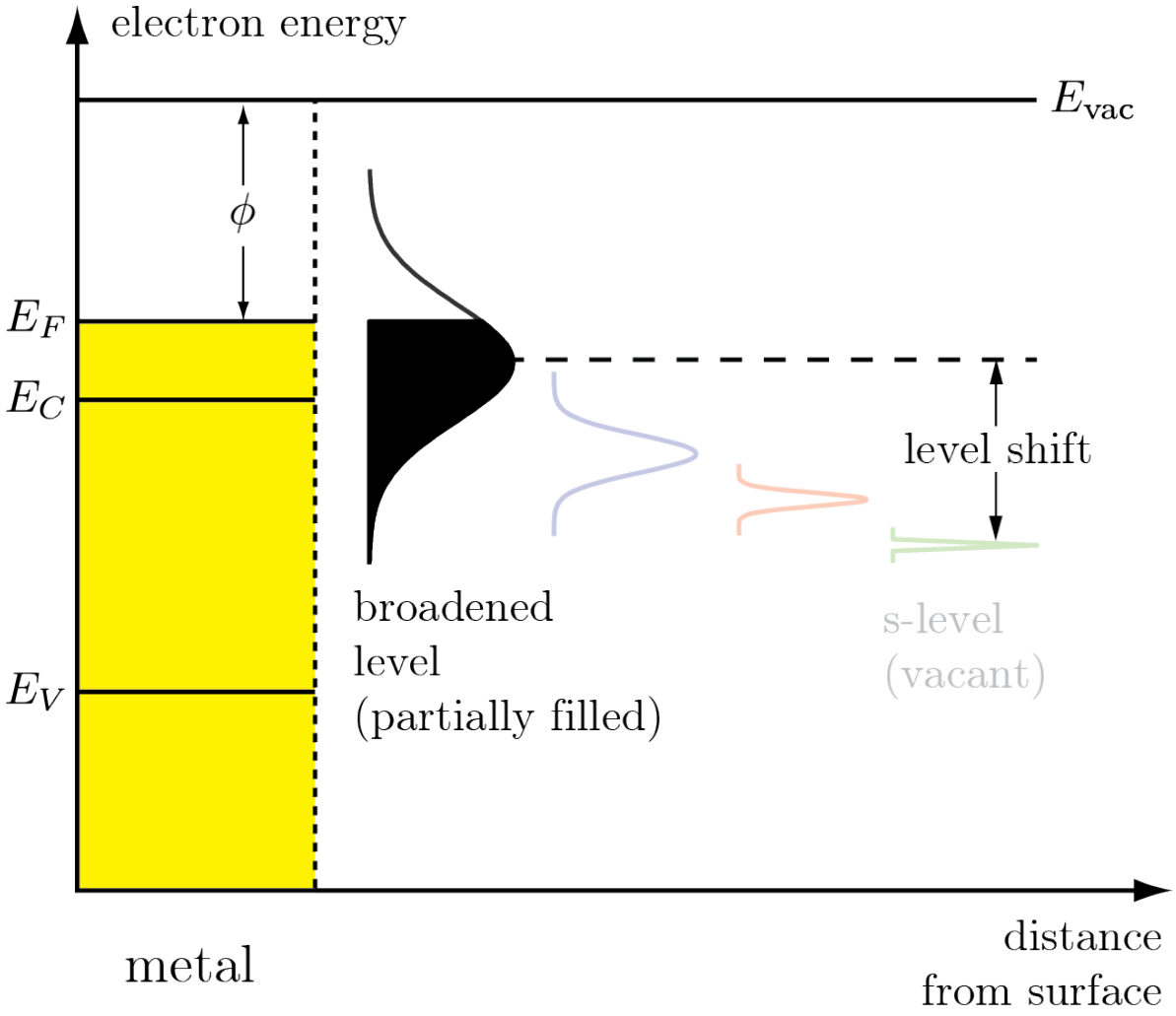


Resonant Charge Transfer (RCT)



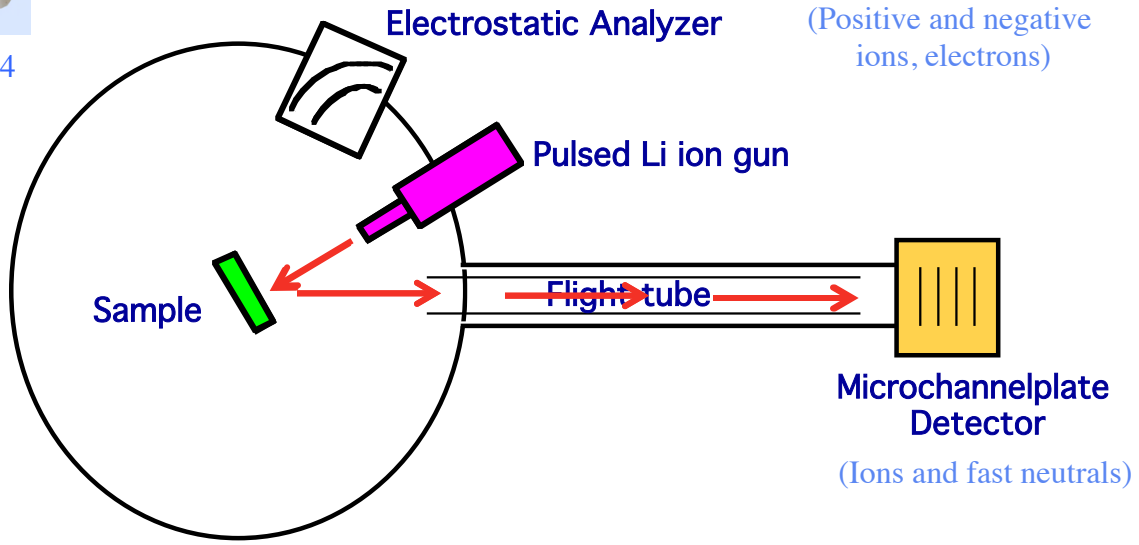
Resonant Charge Transfer (RCT)

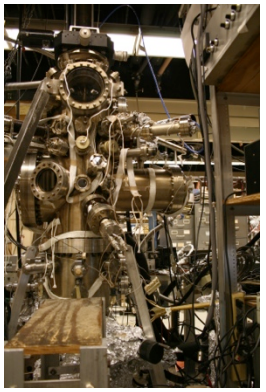
- The neutral fraction (NF) is determined at an effective "freezing distance" along the exit trajectory, which is typically within a few Å's of the surface.
- The "freezing distance" depends on velocity, electronic structure, etc.



Kimball Physics IGS-4

Experimental setup



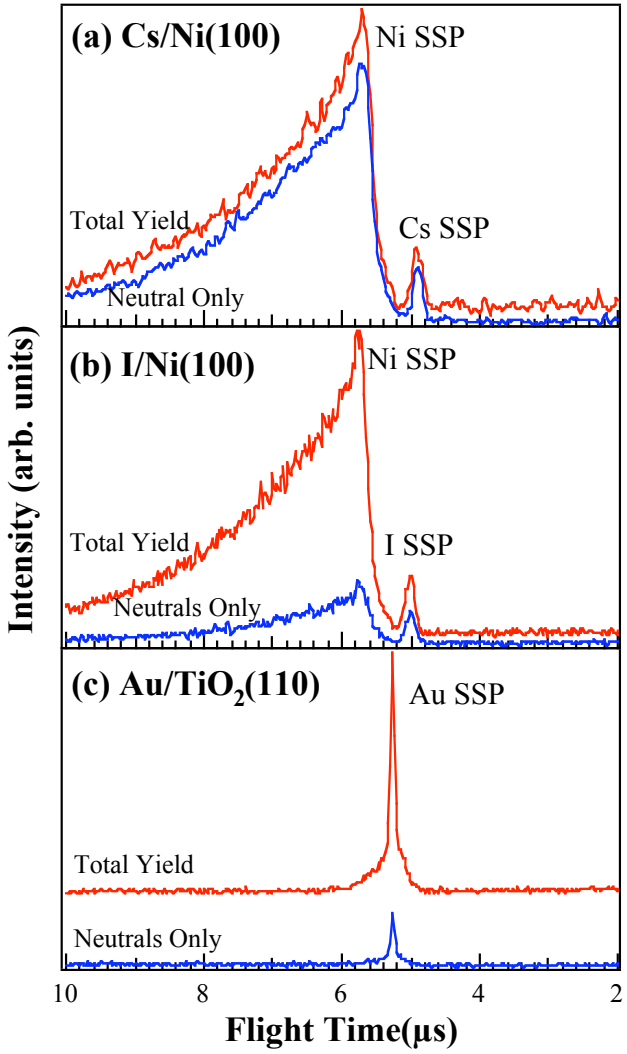


- Pulsed ion beam: frequency 80 kHz, pulse width ~40 ns
- Incidence/emission angle can be varied; Scattering angle fixed at 150°-168°
- Voltage placed on the "Flight tube" or deflection plates to remove scattered ions

- 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 Spectra

- More energetic particles arrive at the detector more quickly.
- "Total Yield" and "Neutrals Only" spectra are shown, from which a neutral fraction can be determined.

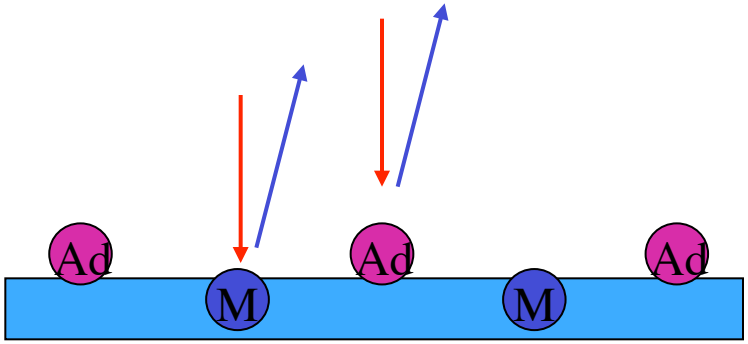


$^{7}Li^{+}$ scattered at 168° from cesium-covered Ni(100).

$^{7}Li^{+}$ scattered at 168° from iodine-covered Ni(100).

$^{23}Na^{+}$ scattered at 135° from Au nanocrystals grown on TiO_2(110).

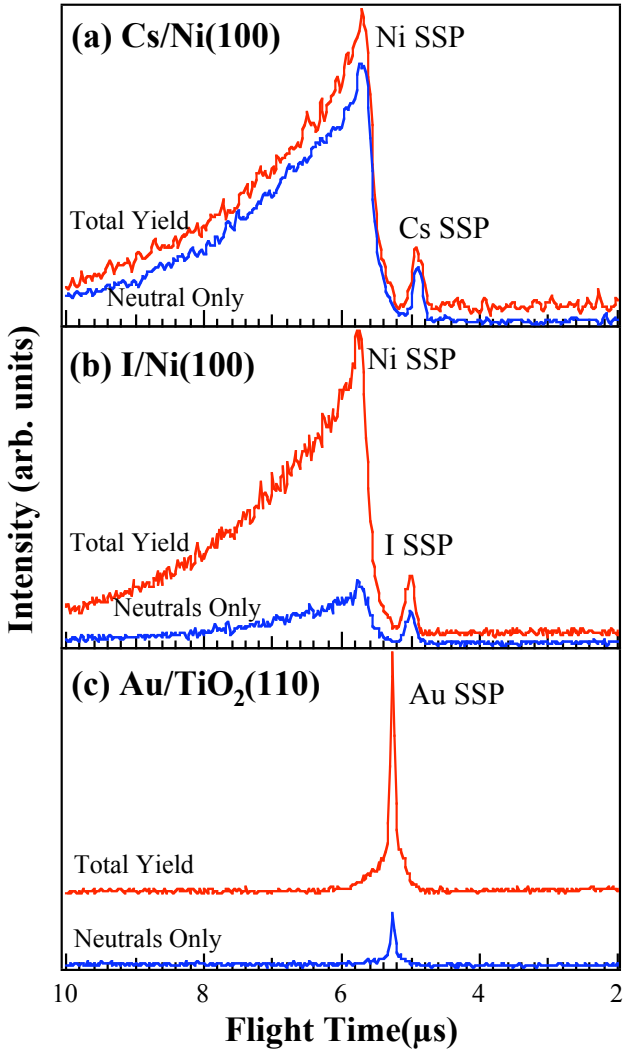
Single Scattering



The energy of a single scattering peak (SSP) is a function of the target mass. Thus, the adsorbate (Cs, I, Au) SSP's are clearly separated from the substrate (Ni, TiO_2) SSP.

Time of Flight Spectra

- More energetic particles arrive at the detector more quickly.
- "Total Yield" and "Neutrals Only" spectra are shown, from which a neutral fraction can be determined.



$^{7}Li^{+}$ scattered at 168° from cesium-covered Ni(100).

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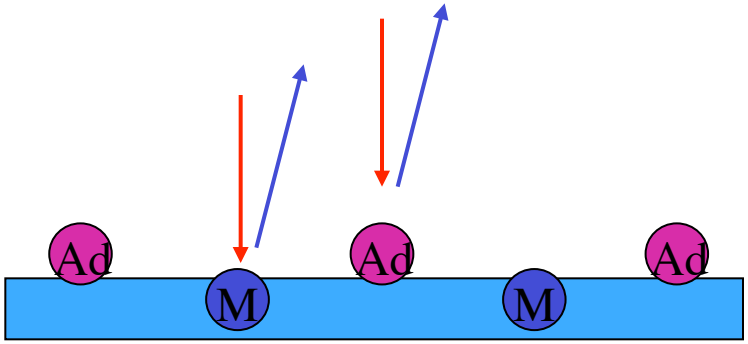
$^{23}Na^{+}$ scattered at 135° from Au nanocrystals grown on TiO_2(110).

Neutral Fractions

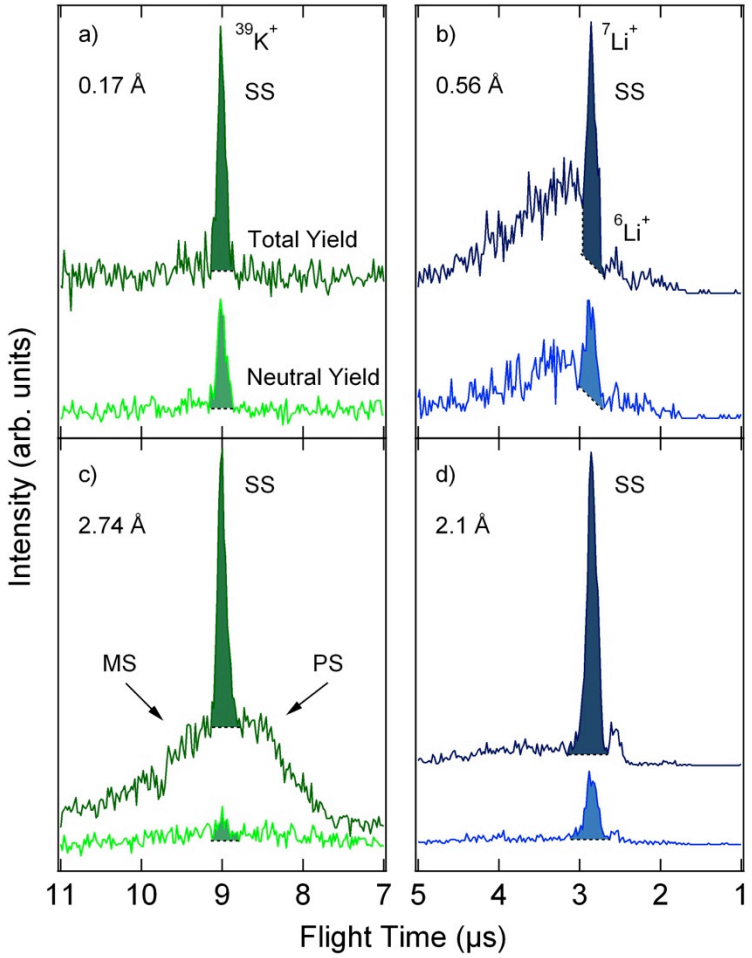


- Separate neutral fractions can be measured for scattering from adsorbate and substrate sites
- The neutral fraction for a given feature is determined by dividing the neutral yield spectra (1000 V on flight tube) by the total yield spectra (flight tube at ground).

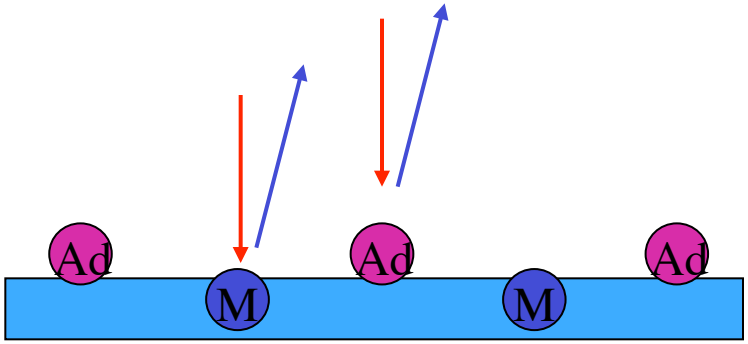
Time of Flight Spectra

- More energetic particles arrive at the detector more quickly.
- "Total Yield" and "Neutrals Only" spectra are shown, from which a neutral fraction can be determined.

$^{39}K^+$ and $^{7}Li^+$ scattered from Au-covered SiO_2/Si(111)



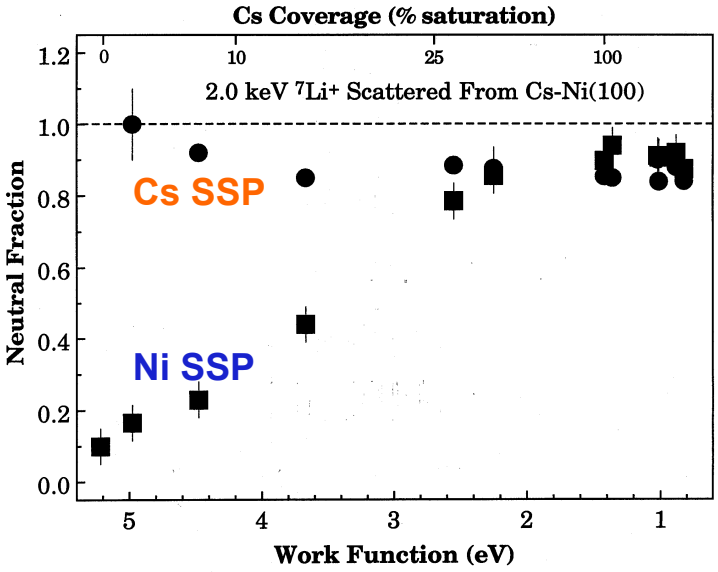
Neutral Fractions

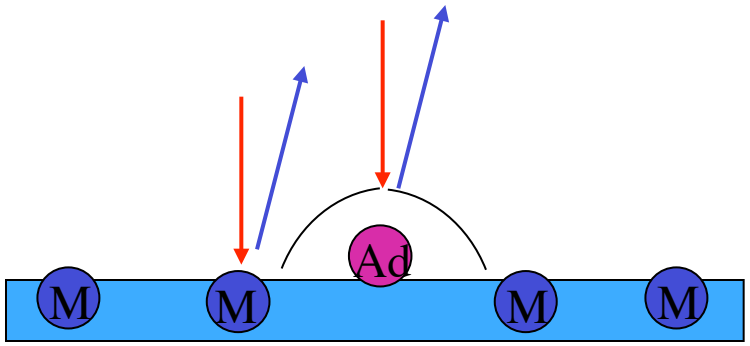


- Separate neutral fractions can be measured for scattering from adsorbate and substrate sites
- The neutral fraction for a given feature is determined by dividing the neutral yield spectra (1000 V on flight tube) by the total yield spectra (flight tube at ground).

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

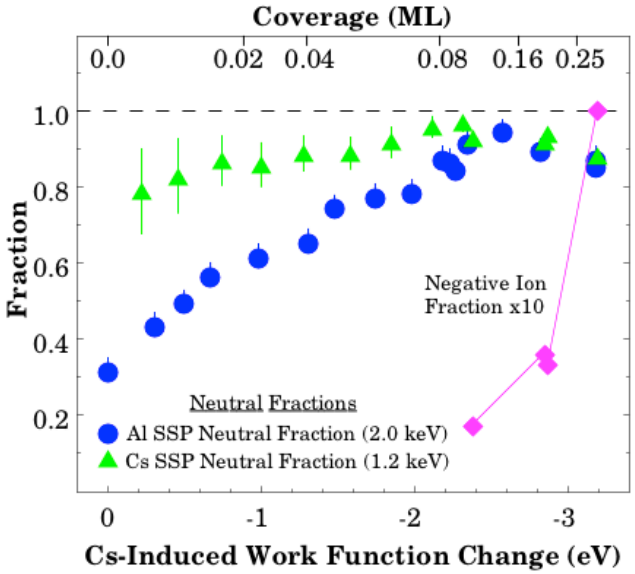
Cs/ Ni





- 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*

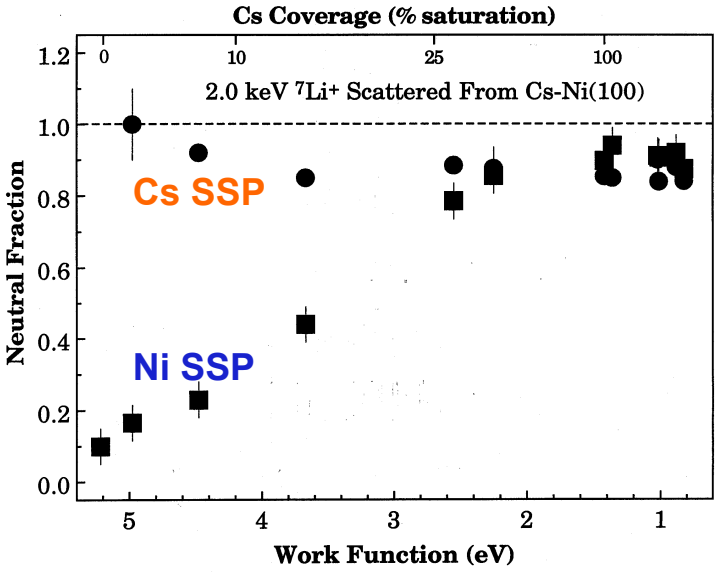
Cs/ Al

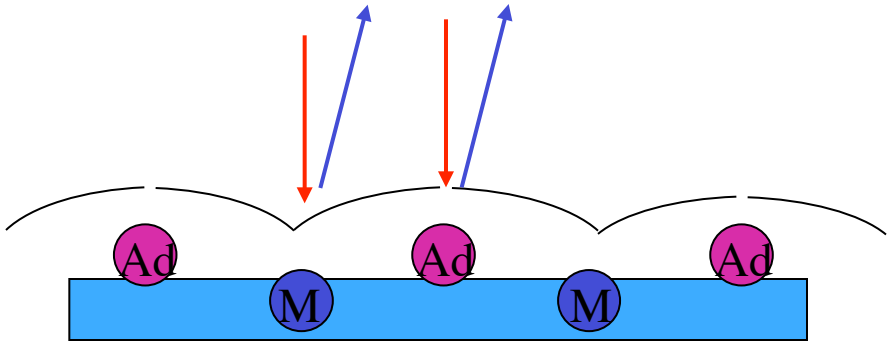


C.B. Weare and J.A. Yarmoff, J. Vac. Sci. Technol. A 13, (1995) 1421; Surf. Sci. 348, (1996) 359; Nucl. Instrum. Meth. B 125, 262 (1997).

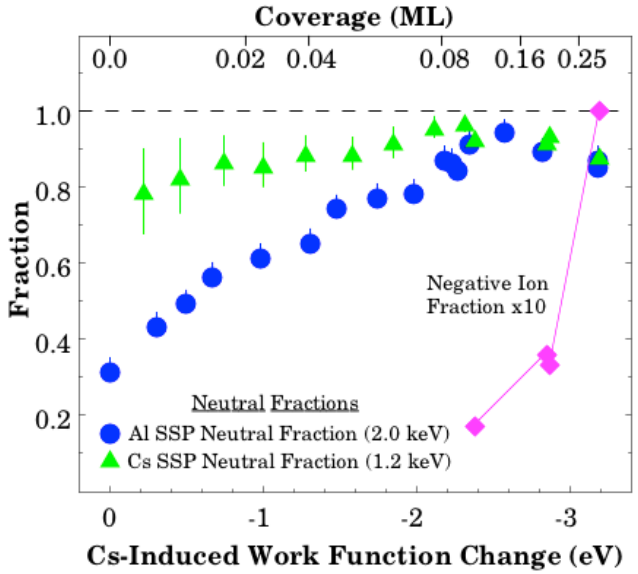
$^{7}Li^{+}$ scattered from Cs/Metal Surfaces

Cs/ Ni





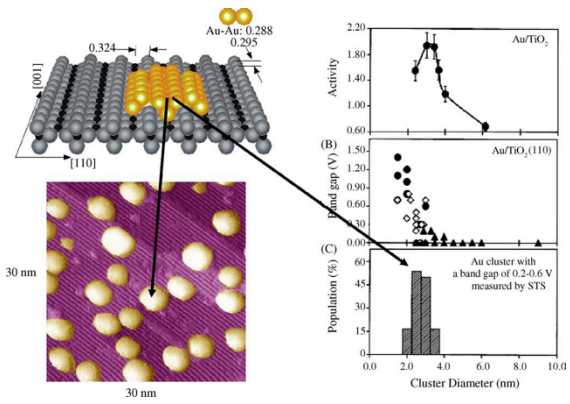
Cs/ Al



- For high Cs coverages, the neutral fractions are nearly equal
  - Alkalis form a dipole sheet
  - The surface LEP is *homogeneous*
- At the largest coverages, negative Li^{-} ions may be formed.
- 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).

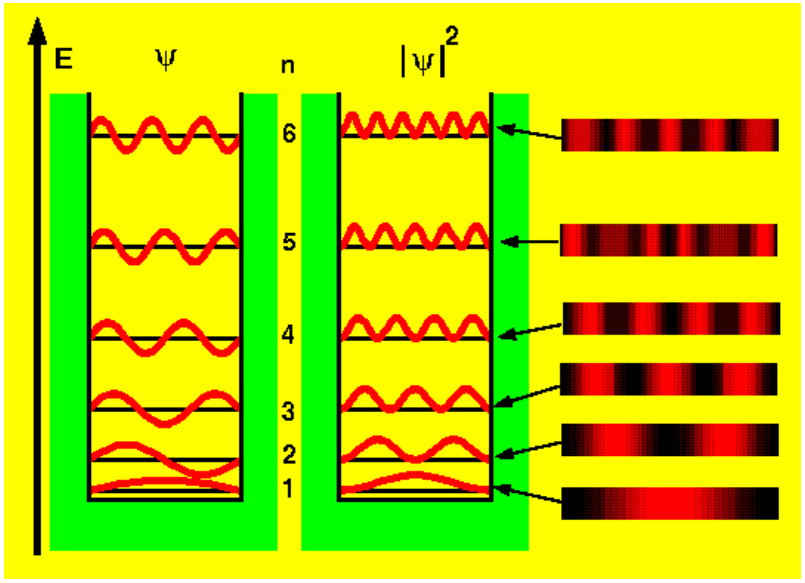
Nanoclusters



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.

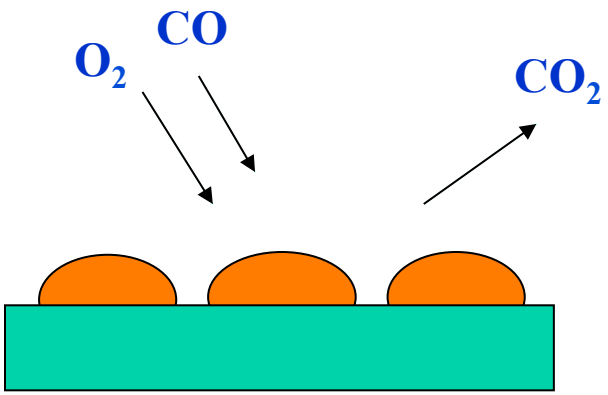
Confined states:
Particle in a box

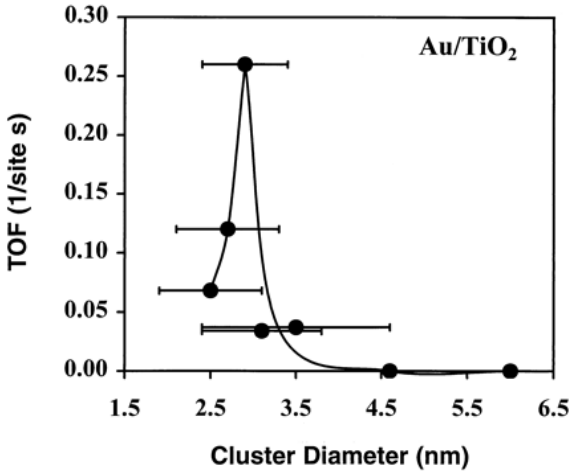


Catalysis with Nanoclusters

Oxidation of CO

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

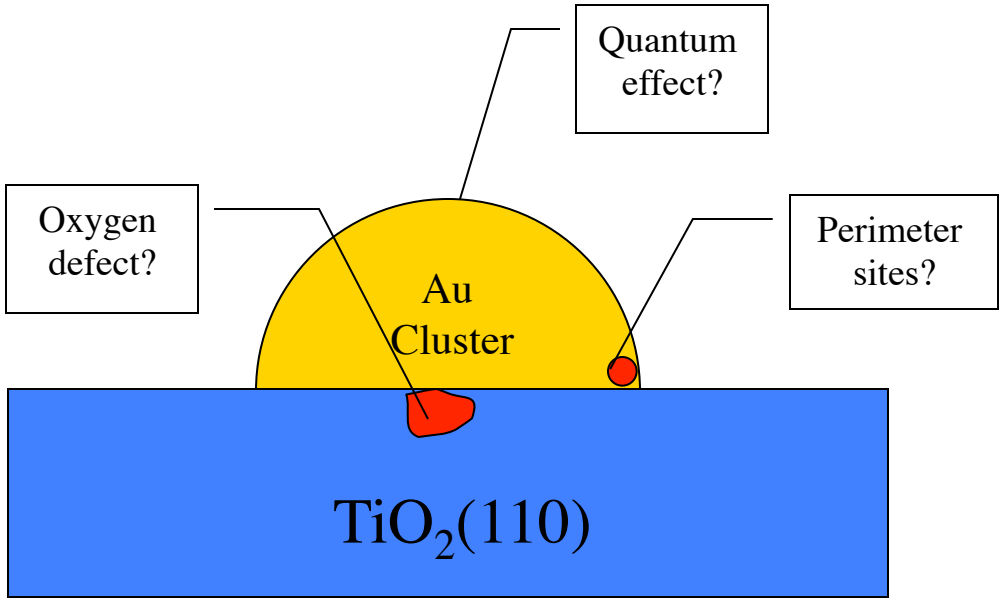




M. Valden, X. Lai, and D.W. Goodman, Science **281**, 1647 (1998)

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

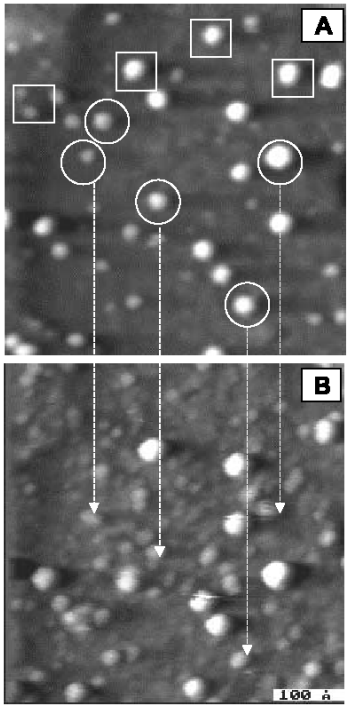
Still a mystery.



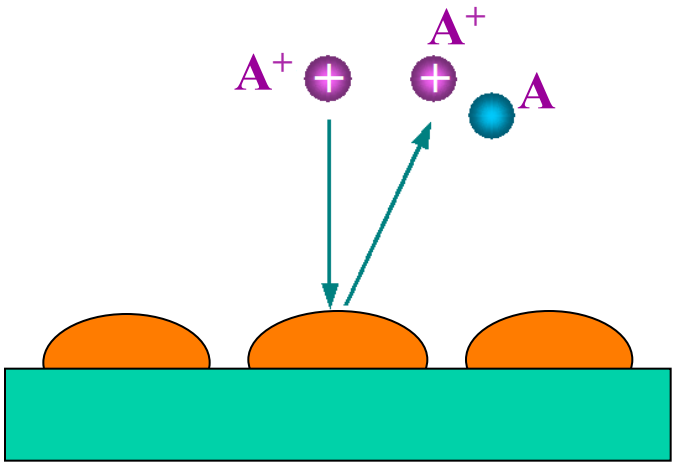
Ion Scattering from Nanocrystals

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

Au Nanocrystals grown on TiO_2(110)

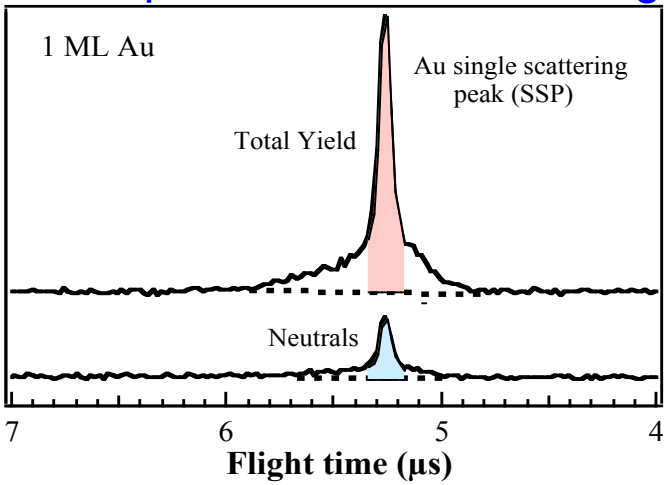


A. Kolmakov and D.W. Goodman, Surf. Sci. Lett. **490**, L597 (2001).



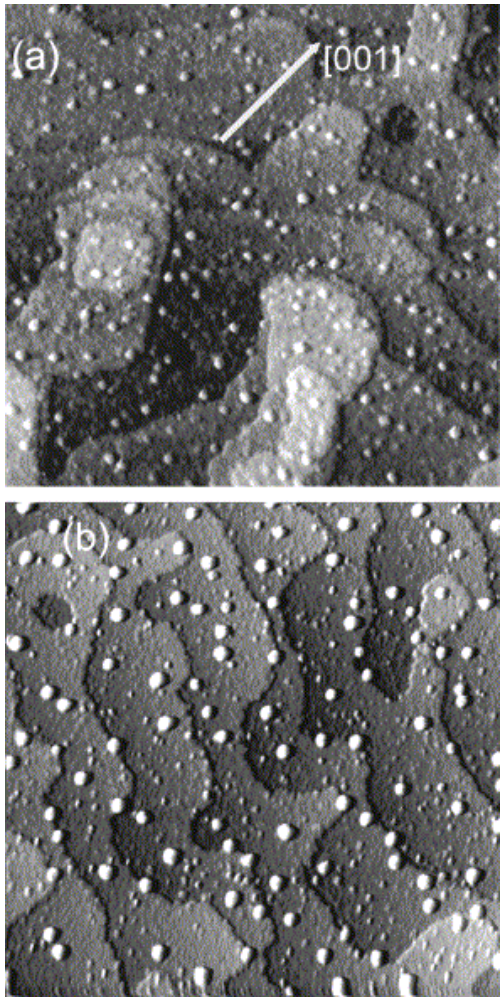
Measure fraction of ions that are neutralized - provides information on quantum-confined states

TOF spectra for Na^+ scattering



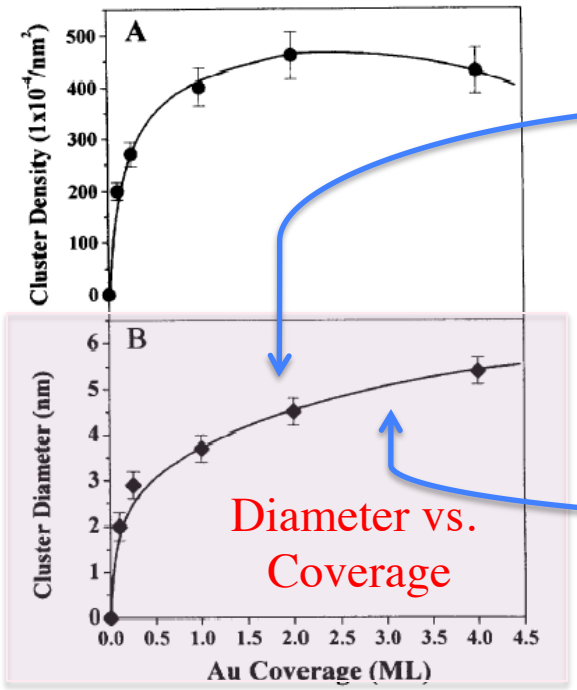
Au Nanocrystals grown on TiO_2(110)

STM images



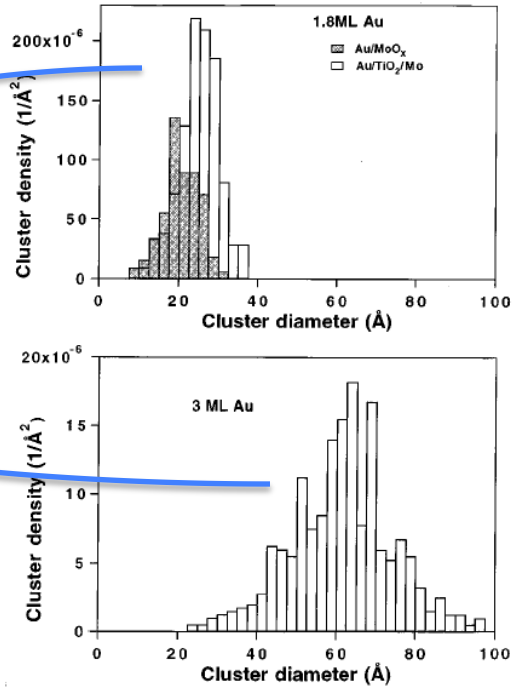
C.E.J. Mitchell, A. Howard, M. Carney and R.G. Egdell, Surf. Sci. **490**, 196 (2001).

Cluster density and diameter



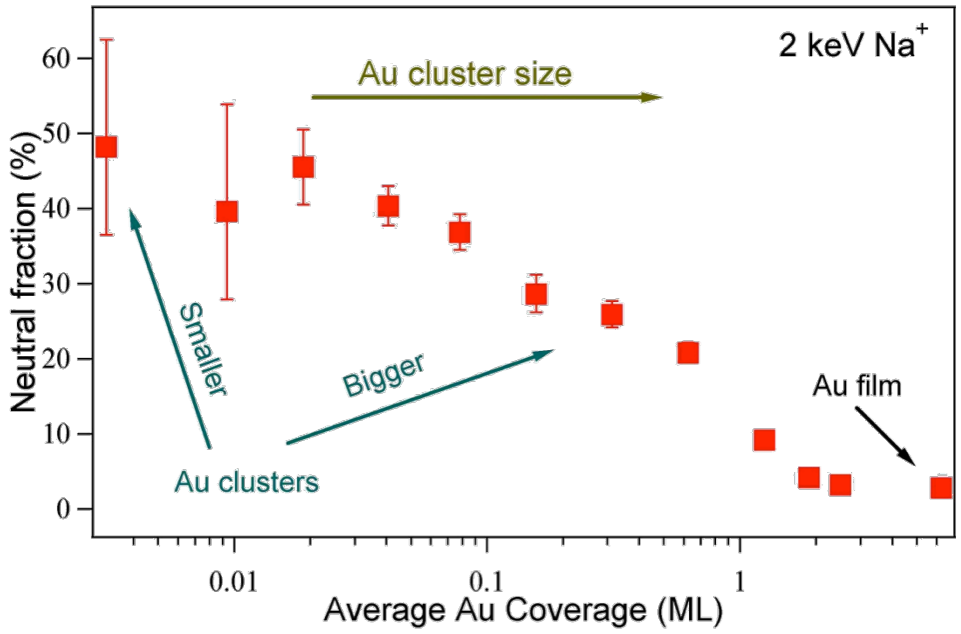
X. Lai, T.P. St. Clair, M. Valden and D.W. Goodman, Prog. Surf. Sci. **59**, 25 (1998).

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).

Na^+ Neutral Fraction vs. Au Deposition



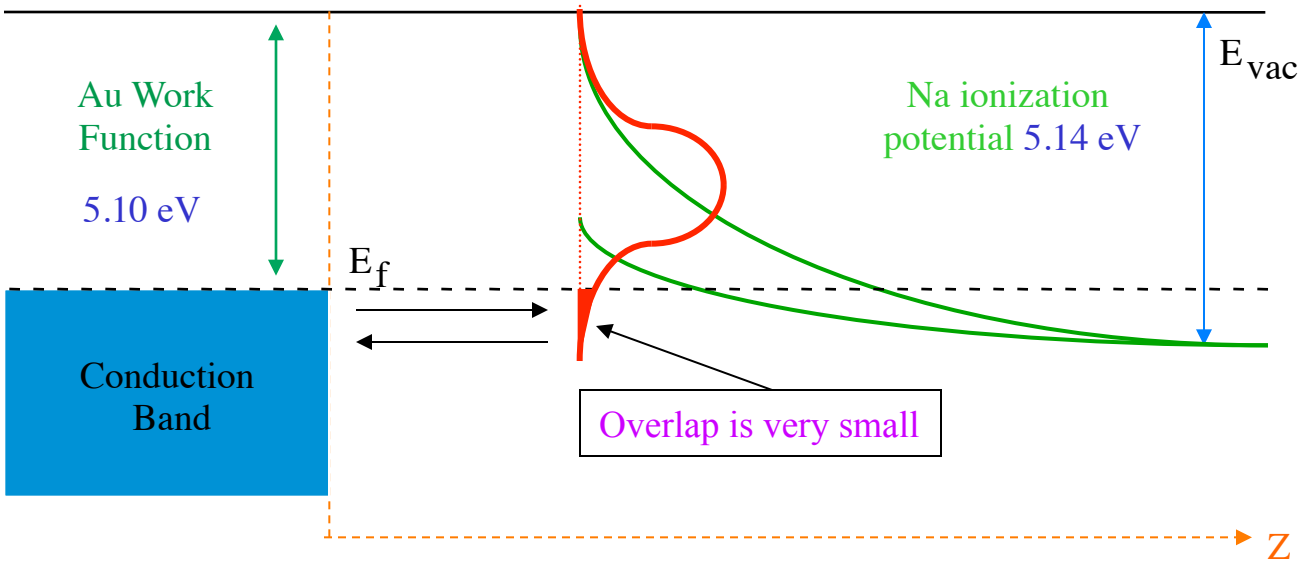
- Larger Au coverages corresponds to larger cluster sizes.

  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.

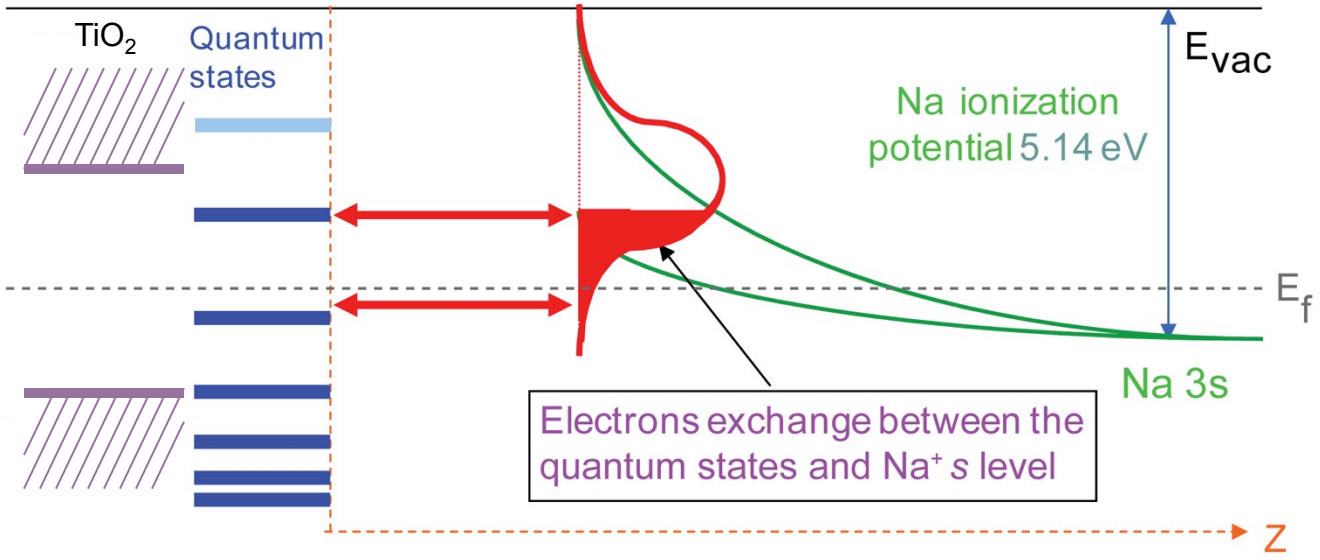
G. F. Liu, Z. Sroubek and J. A. Yarmoff, Phys. Rev. Lett. **92**, 216801 (2004).

Resonant Charge Exchange for Au Metal



- For Au metal, or a bulk-like film, the overlap between the conduction band and the Na *s* level is small, leading to a neutral fraction of ~2%

Resonant Charge Transfer for Au Nanoclusters

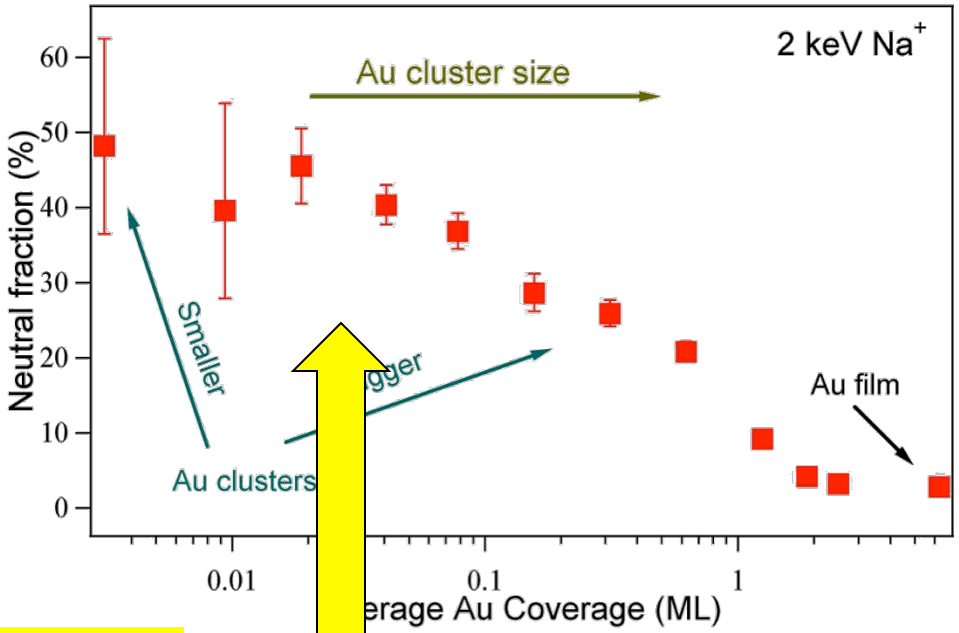


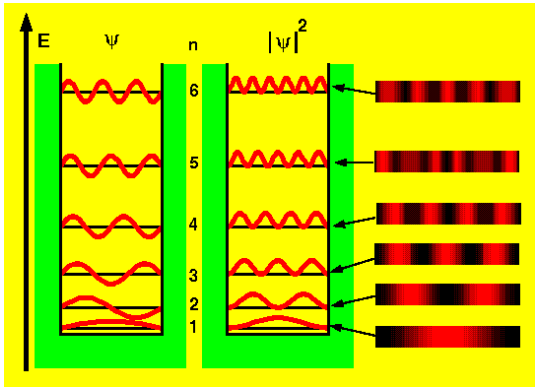
Not drawn to scale.

- 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

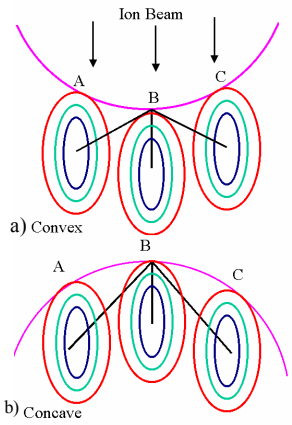


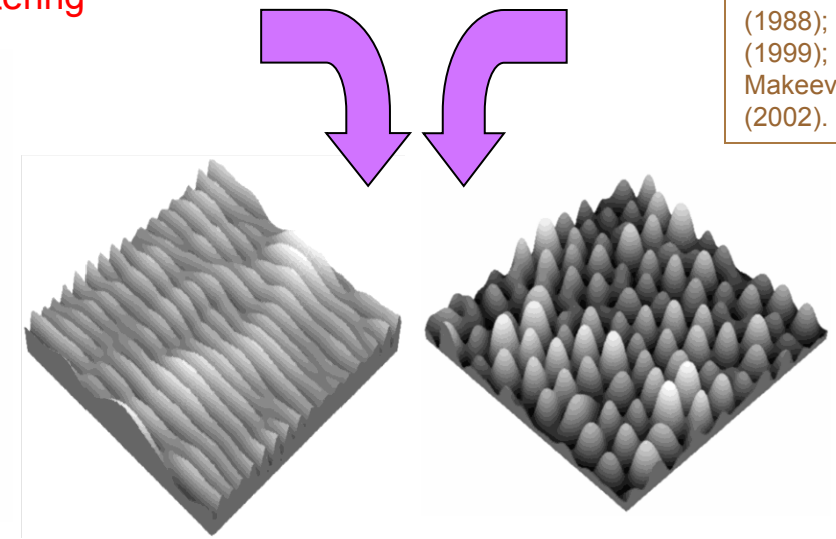


Confined states:
Particle in a box

Nanoscale patterning via Sputtering

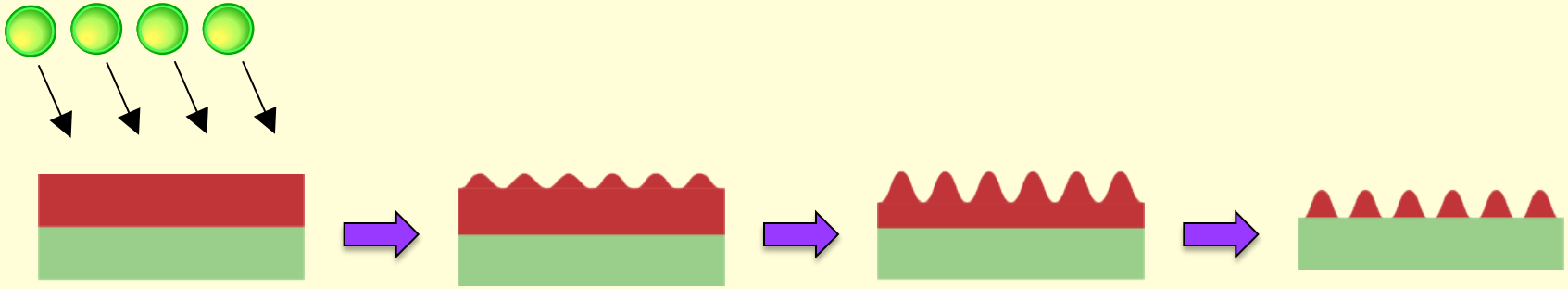
Curvature dependent sputtering





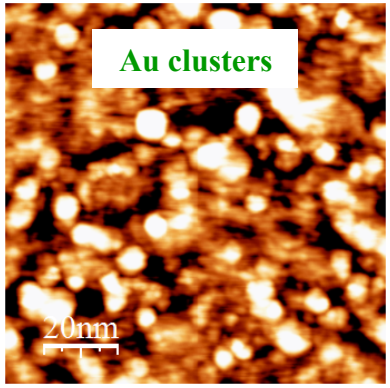
R. Bradley, et al., J. Vac. Sci. Technol. A **6**,2390 (1988); S. Facsko, et al., Science **285**, 1551 (1999); Phys. Stat. Sol. (b) **224**, 537 (2001); M. Makeev, et al., Nucl. Instrum. Meth. B **197**, 185 (2002).

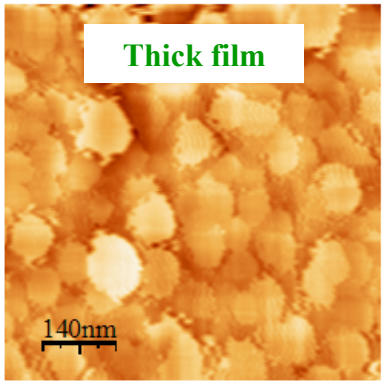
Sputter a thin film to produce clusters of one material on an insulating matrix

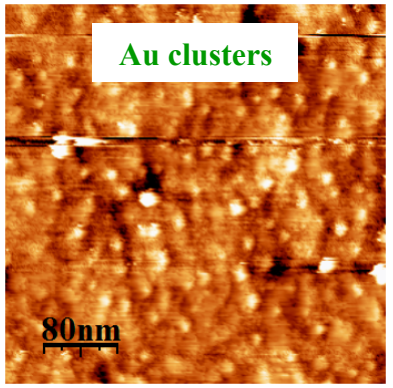


Using Ion Beams to Fabricate Nanocrystals

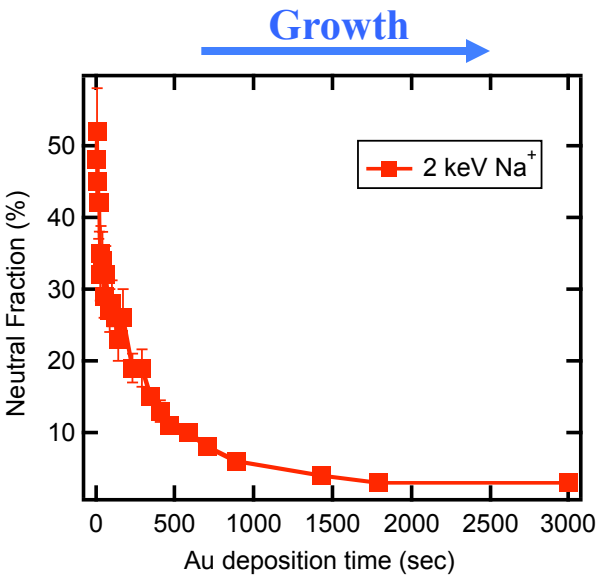
Au nanocrystals grown by evaporation onto TiO_2 substrate

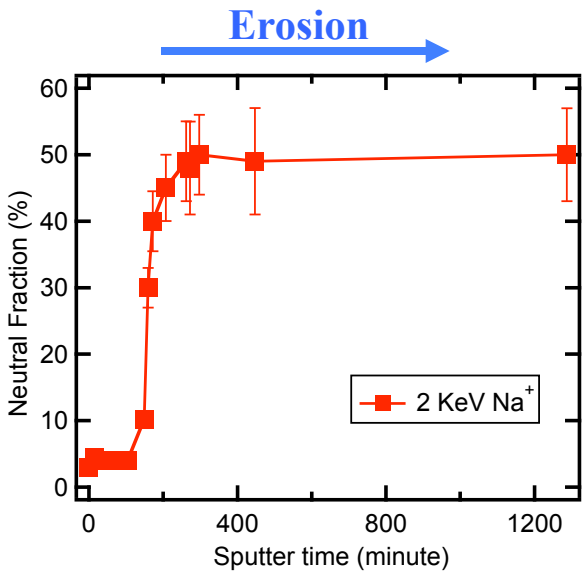






Au nanocrystals formed by sputtering with Ar^+ ions





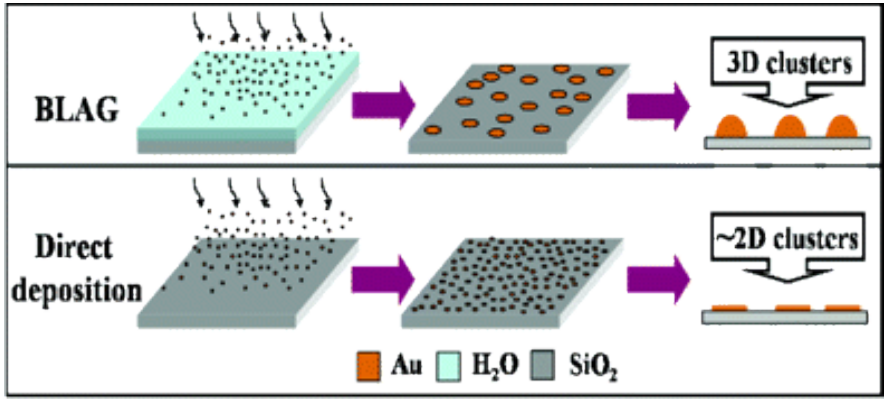
- The erosion and surface diffusion of Au due to ion bombardment forms nanoclusters.
- As the average cluster size decreases with ion fluence, the Na NF increases.
- The confined states in the small Au nanoclusters couple to the Na ions, as during deposition. z

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

BLAG (Buffer Layer Assisted Growth)

Novel way to grow metal clusters:

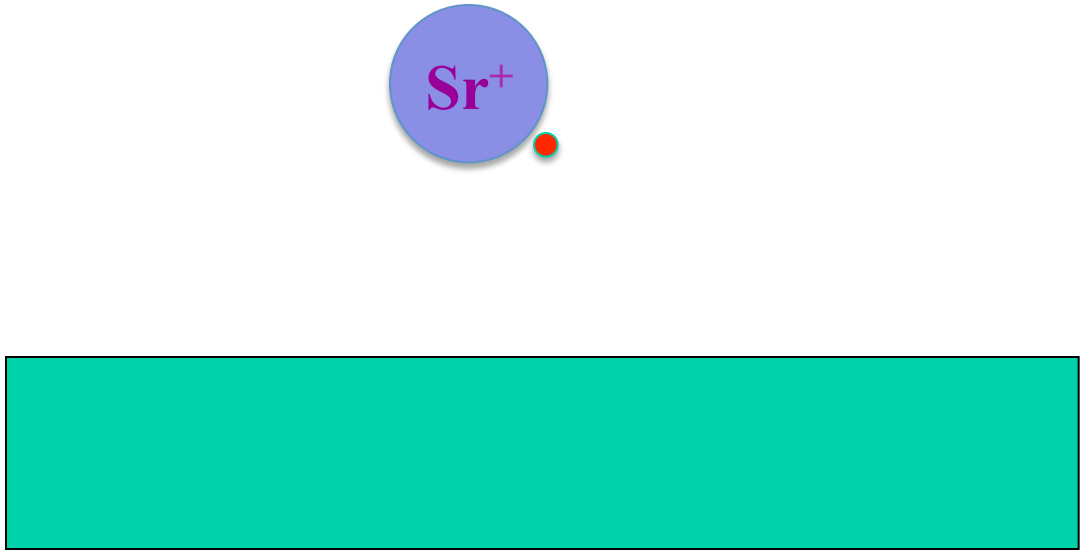
- Grow “anything” on “anything”
- Can control size and density
- Higher height to diameter ratio (~0.5) than direct deposit (~0.2)
- The thermally hot metal atoms do not react with the substrate during evaporation



J.H. Weaver, et al., Surf. Sci. ***557*** *(2004) 1*

Multi-Electron Effects in Ion Scattering

- Singly charged alkaline earth ion has one valence electron
- This electron acts as a spin-impurity, leading to Kondo resonance at E_F
- As the ionization level crosses E_F, a mixed-valent state is formed, whose occupancy has a very strong temperature dependence



H. X. Shao, P. Nordlander, and D. C. Langreth, Phys. Rev. Lett. **77**, 948 (1996);
J. Merino and J. B. Marston, Phys. Rev. B **58**, 6982 (1998).

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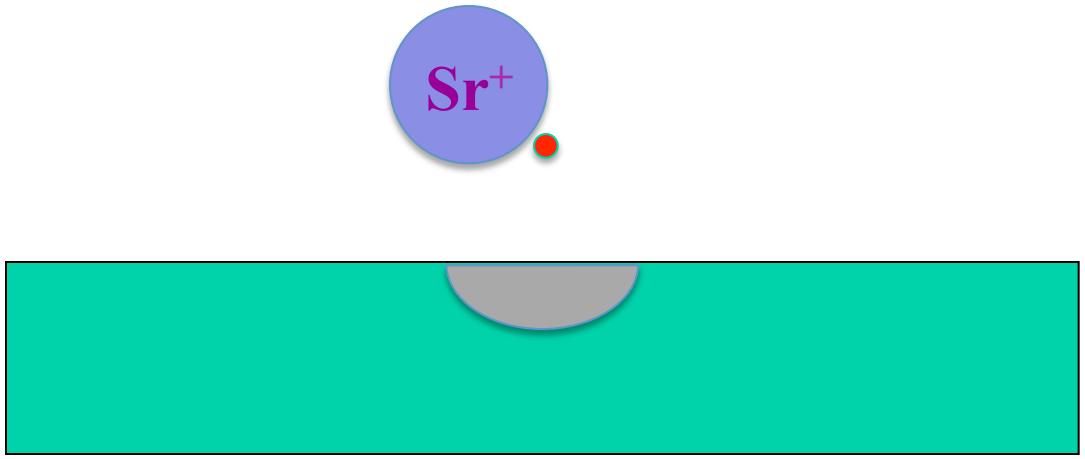

H. X. Shao, P. Nordlander, and D. C. Langreth, Phys. Rev. Lett. **77**, 948 (1996);
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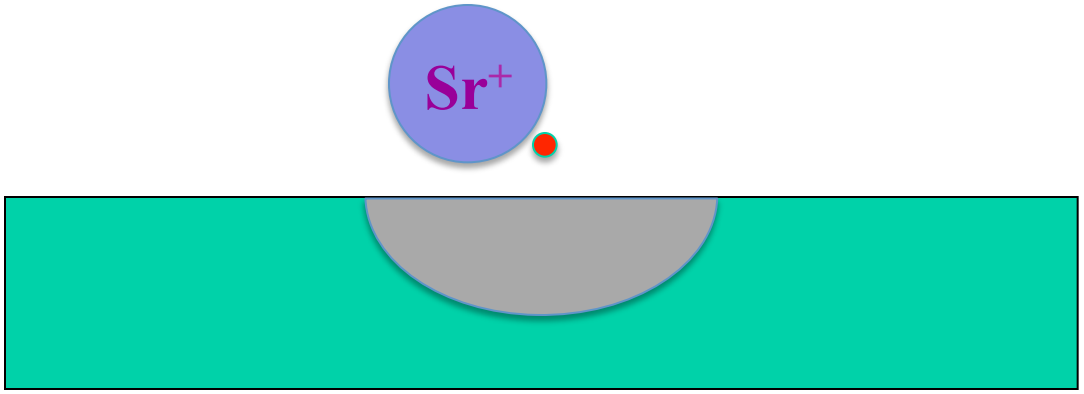

H. X. Shao, P. Nordlander, and D. C. Langreth, Phys. Rev. Lett. **77**, 948 (1996);
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- A singly charged alkaline earth ion has one valence electron
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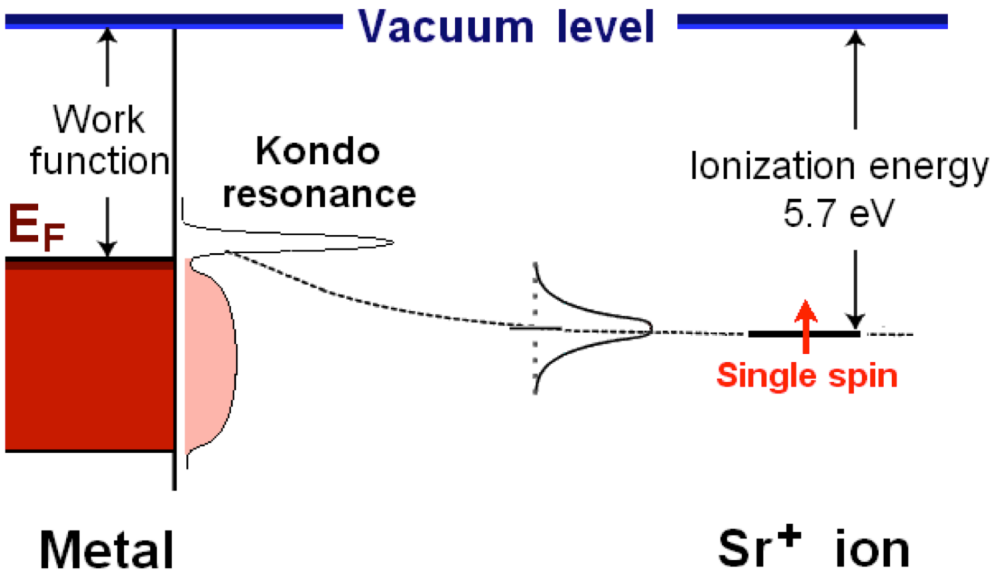
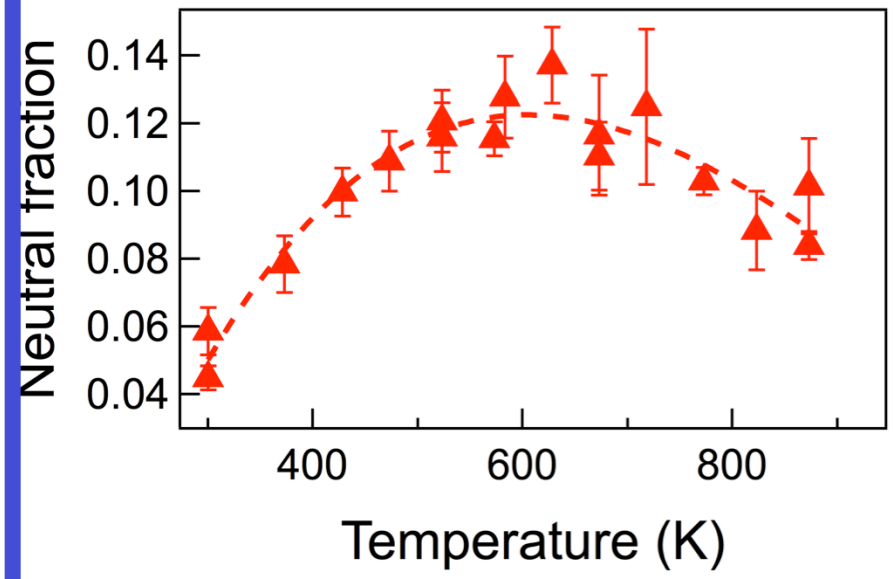


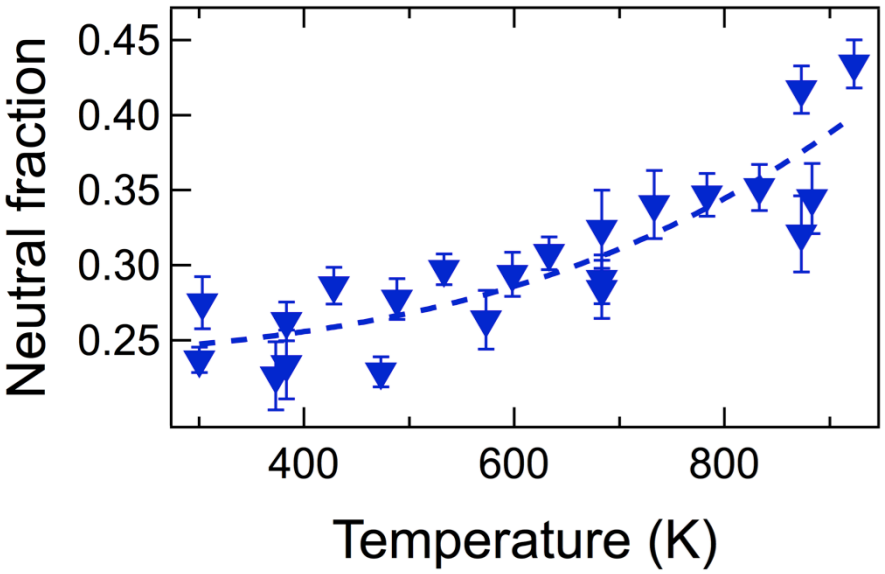
Neutral Fraction vs. Temperature

Sr^+ - *single valence electron*



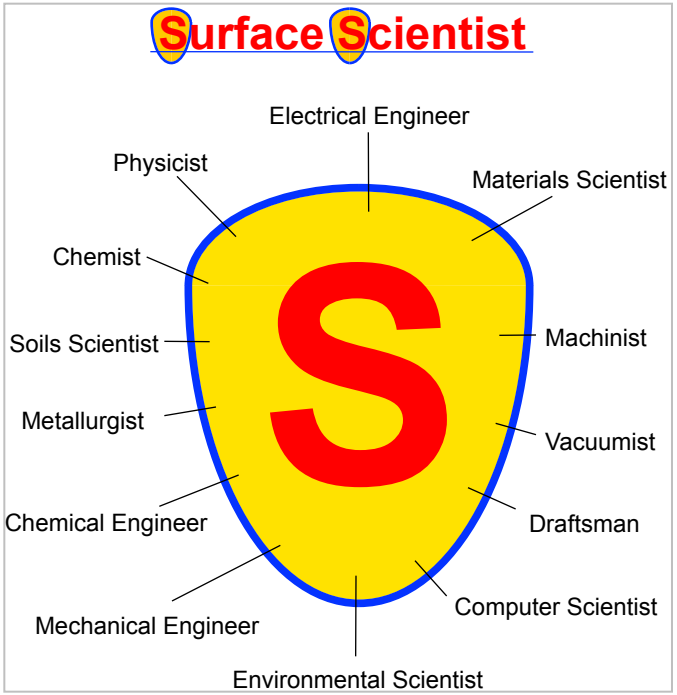
- Rise in NF with temperature can be explained as the normal expectation for RCT as states above E_F are populated
- Decrease in NF above 600 K can only be explained via correlated electron physics

Ga^+ - *pair of valence electrons*



- Rise in NF with temperature can be explained as the normal expectation for RCT as states above E_F are populated

X. He and J.A. Yarmoff, Phys. Rev. Lett. **105**, 176806 (2010).

Surface Science

Thank you!!