Challenges in Experimental Surface Analysis of Plasma-Facing Materials

Bruce E. Koel

Department of Chemical and Biological Engineering,
Princeton University
NSTX Collaborator, Princeton Plasma Physics Laboratory (PPPL)

BPSFG, PPPL
June 29, 2011

PRINCETON
Chemical and Biological Engineering

PPPL
PRINCETON PLASMA PHYSICS LABORATORY

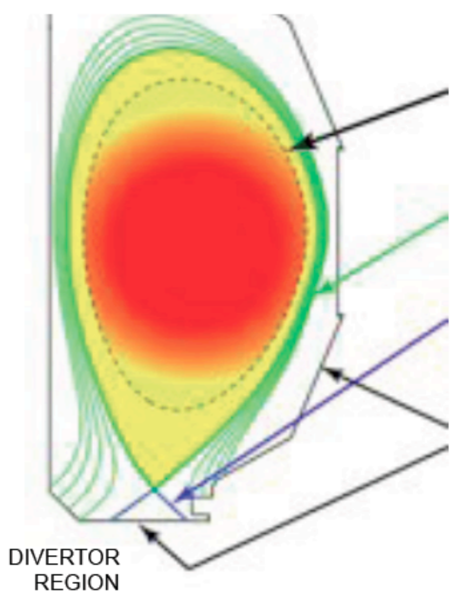
Plasma Facing Materials for Fusion

National Spherical Torus Experiment - NSTX

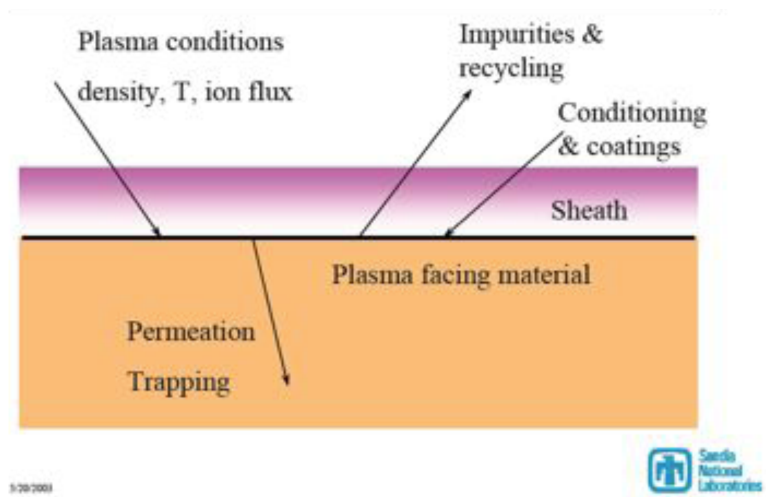
The Central Issue: How to interface a 100 million degree burning plasma to its room temperature surroundings?

Magnetic topology ‘diverts’ most PMI away from plasma to minimize plasma contamination but also concentrates heat load in space.

Low plasma density and size limitations lead to high edge gradients and repetitive relaxations or ‘ELMS’ that concentrate heat load in time as well !



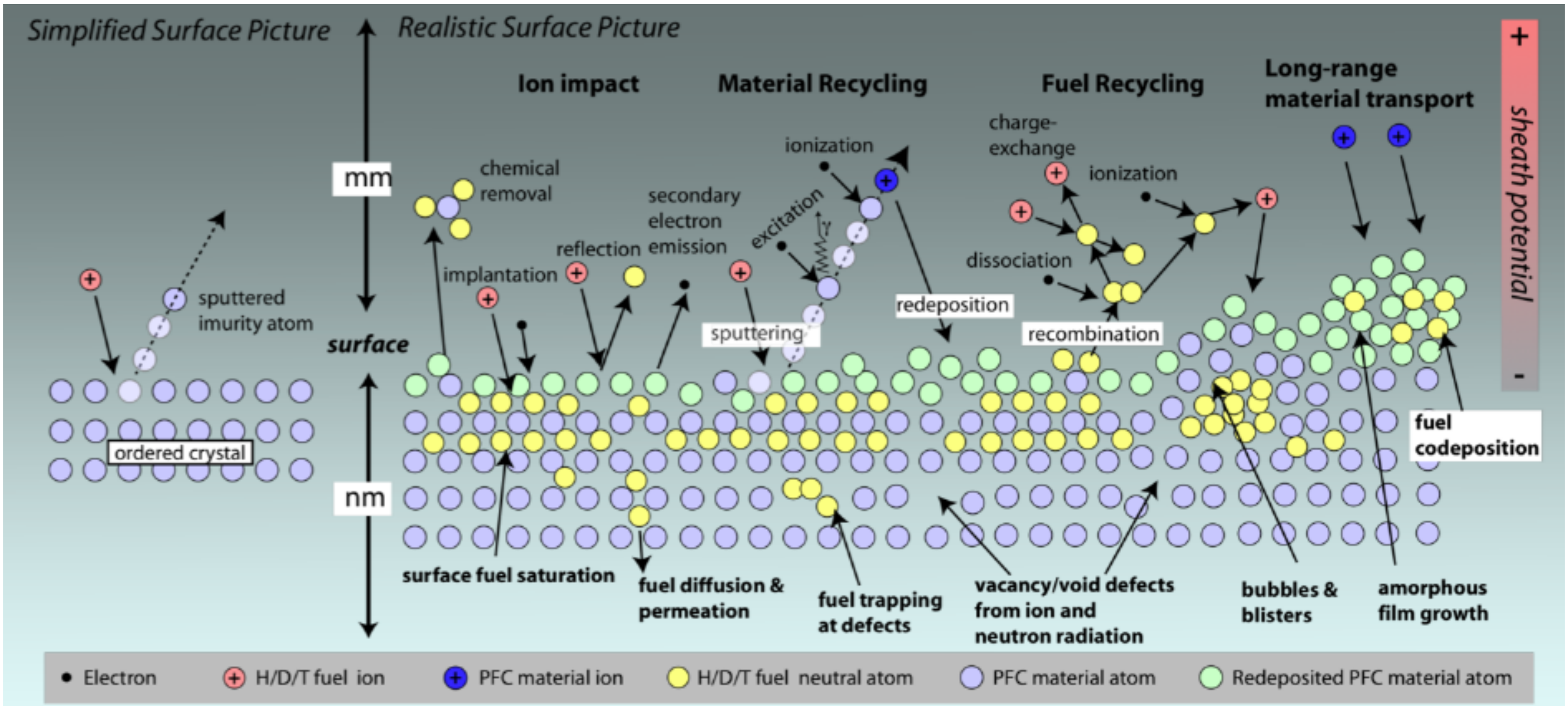
- Physics of the formation, structure and stability of the edge plasma.
- Plasma and impurity transport in the Scrape-of-Layer (open field lines).
- Tritium retention and plasma material interactions.
- Erosion and decomposition of plasma facing materials and components.
- Dust generation, safety.



Sandia National Laboratories

M. Ulrickson

Surface Interactions at the Plasma-Materials Interface



Whyte and Wirth, unpublished

Surface Science in the Koel group

New insights and materials from studies of structure and reactions at interfaces

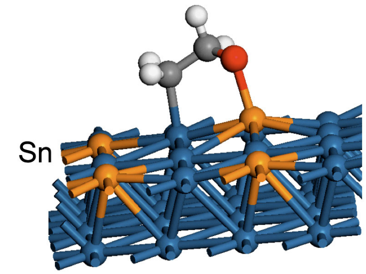
Selective hydrogenation catalysis: Controlling selectivity in reactions over Sn-Pt surface alloys

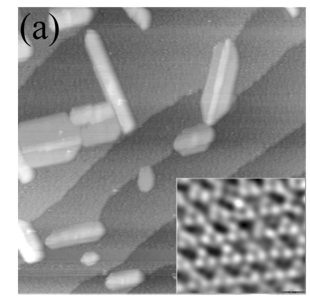
Oxide nanostructures: Properties and reactivity of SnO_2 films and nanocrystals

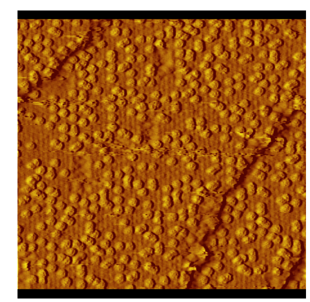
Alloy electrodes: Novel Au-Pd_3Fe(111) alloys for oxygen reduction in PEM fuel cells

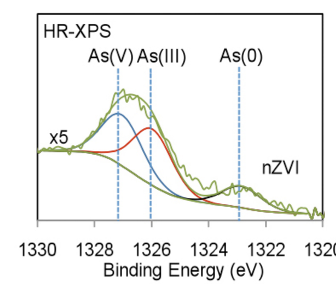
Liquid-solid interfaces: Development of Rutherford backscattering as a probe for nanometer characterization of electrodes in solution under potential control

Metal sorption on Fe nanoparticles: As sequestration by iron np for environmental remediation









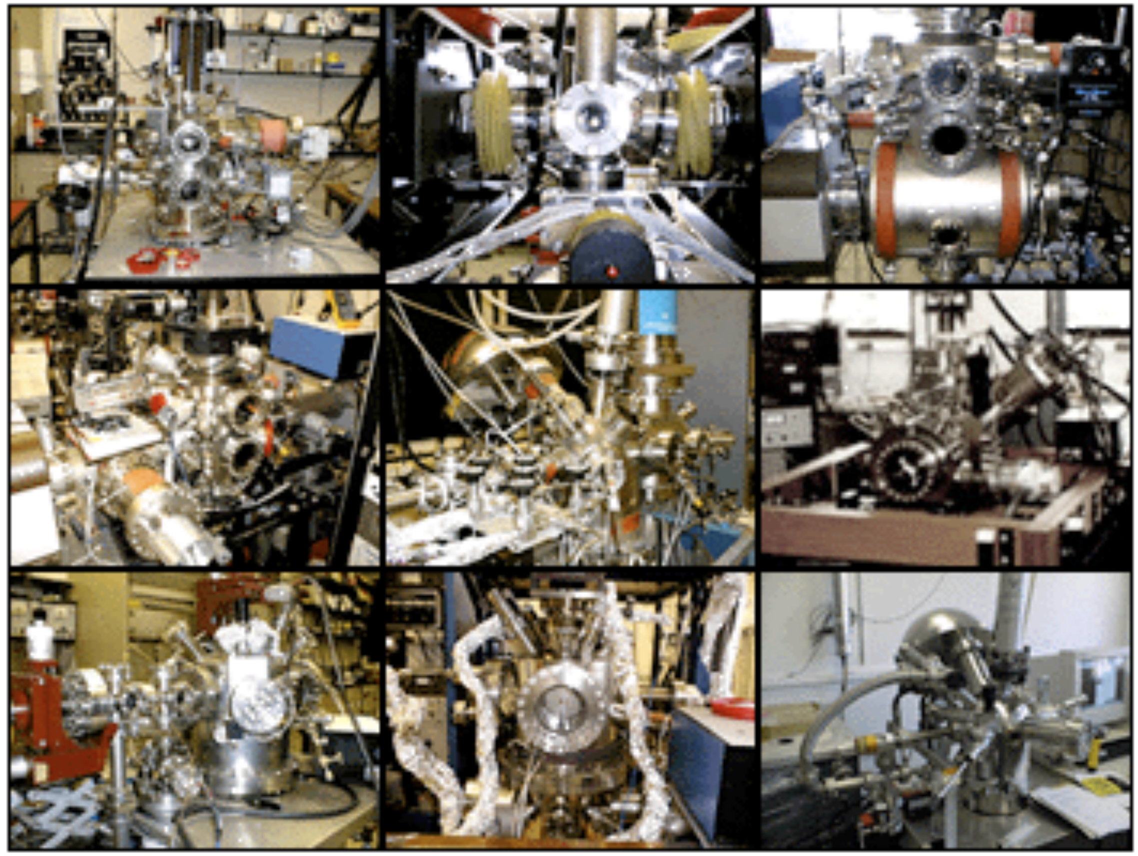
Surface Science of Materials Challenges for PMI

- **Liquid metal surfaces**
  - – Li, Ga, Sn, Li-Sn eutectics
  - – Segregation in binary and ternary alloys
  - – Chemical reactions on alloy surfaces
- **Solid-solid and solid-liquid interfaces**
  - –Metal-metal and metal-oxide adhesion energies
  - –Influence of surface nanostructure, grain size, morphology, native and applied coatings
- **Plasma processing of materials**
  - –Ion-surface scattering, implantation, sputtering
  - –Radical-surface interactions (D chemistry)
  - –Electron-stimulated processes

Surface Science - Methodology

Surface Analytical Methods

- ✓ AES (Auger electron spectrosco
- ✓ SAM (Scanning Auger electron r
- ✓ LEED (Low energy electron diffra
- ✓ RHEED (Reflection high energy
- ✓ XPS (X-ray photoelectron spectr
- ✓ XPD (X-ray photoelectron diffrac
- ✓ LEIS (Low energy ion scattering)
- ✓ ALISS (Alkali ion scattering) —
- ✓ RBS (Rutherford backscattering
- ✓ HREELS (High-resolution electro
- ✓ FTIR (Fourier transform infrared
- ✓ TPD (Temperature-programmed
- ✓ STM (Scanning tunneling micros

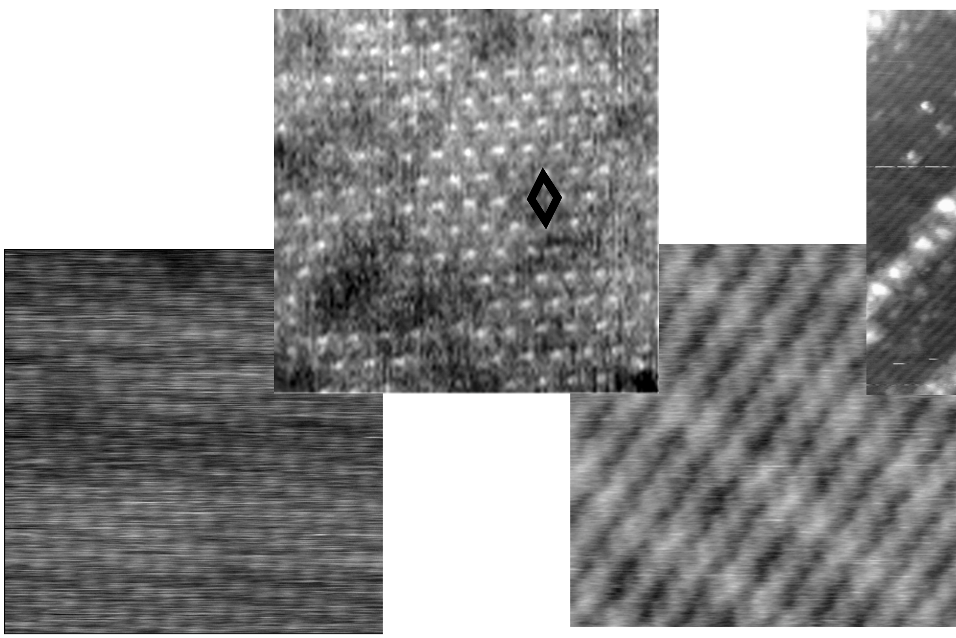


Approach

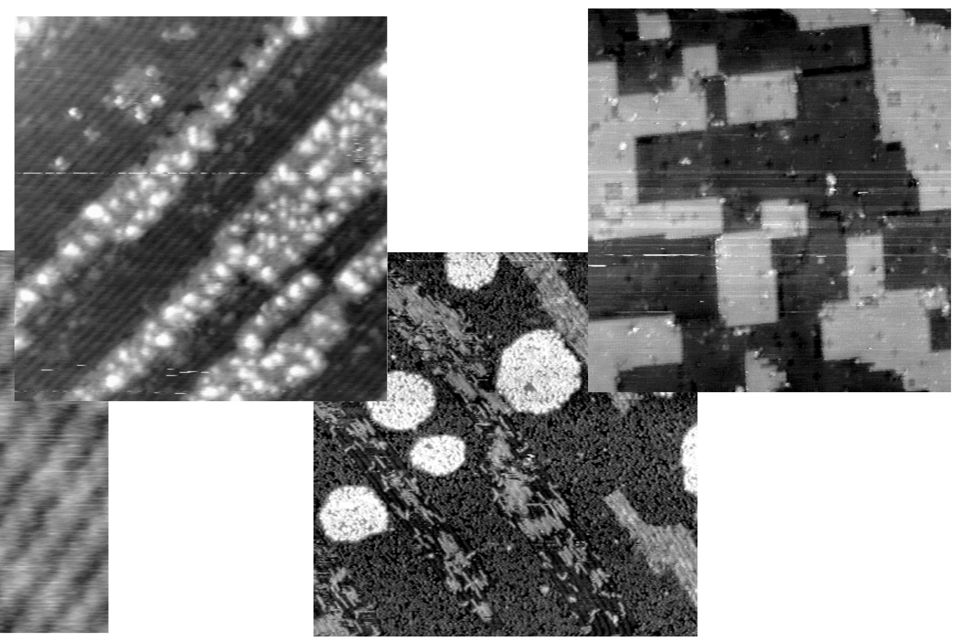
- Well-defined single crystals and thin films formed by vapor deposition
- Composition and structure, thermal and chemical transformations
- Reaction mechanisms, intermediates, and *reactive-sites*

Nucleation, growth, and alloying of Ge films on Pt

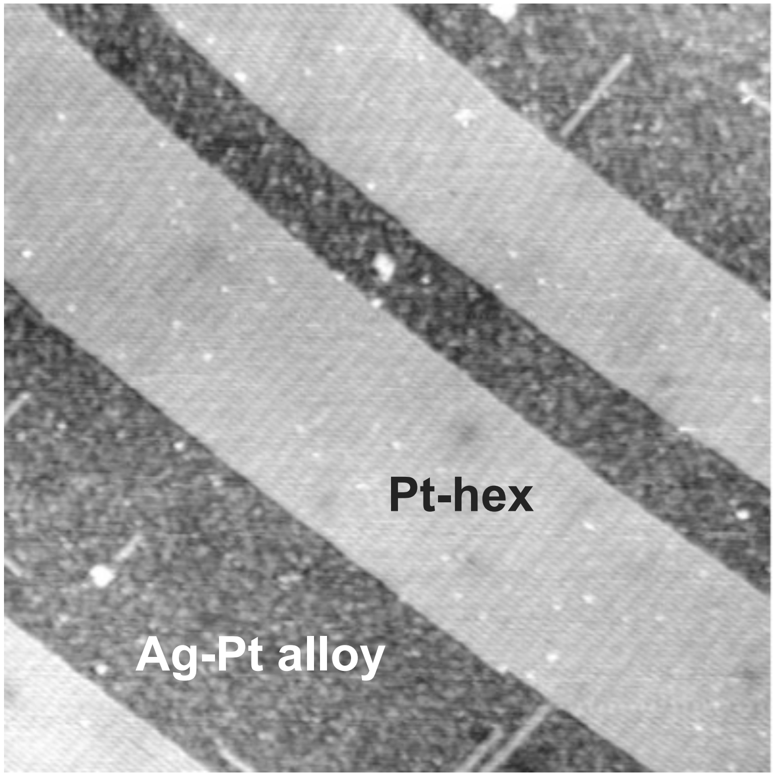
Ge on Pt(111)



Ge on Pt(100)

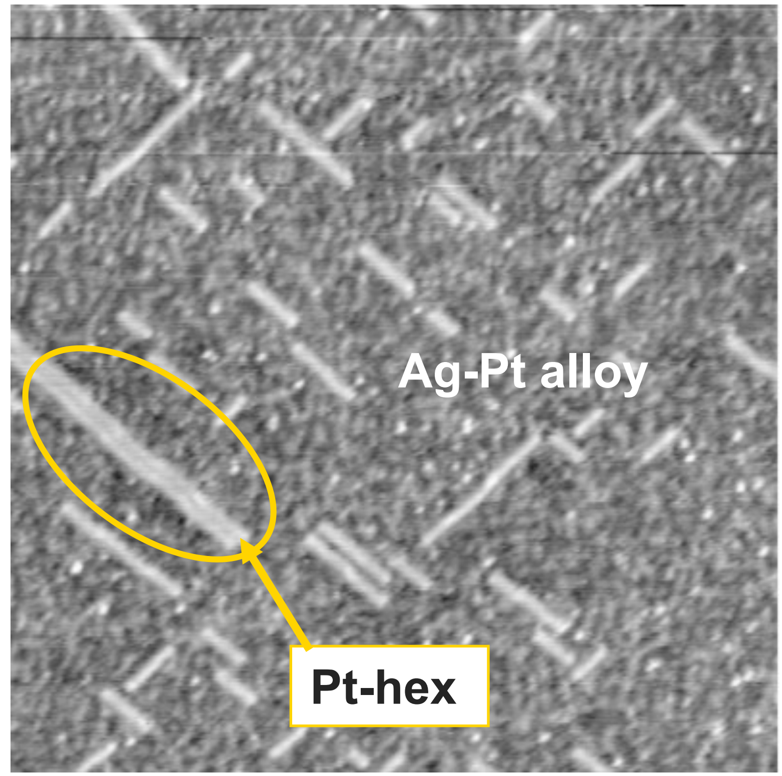


Co-existence of Ag-Pt alloy and pure-Pt hex domains



(150 nm)^2

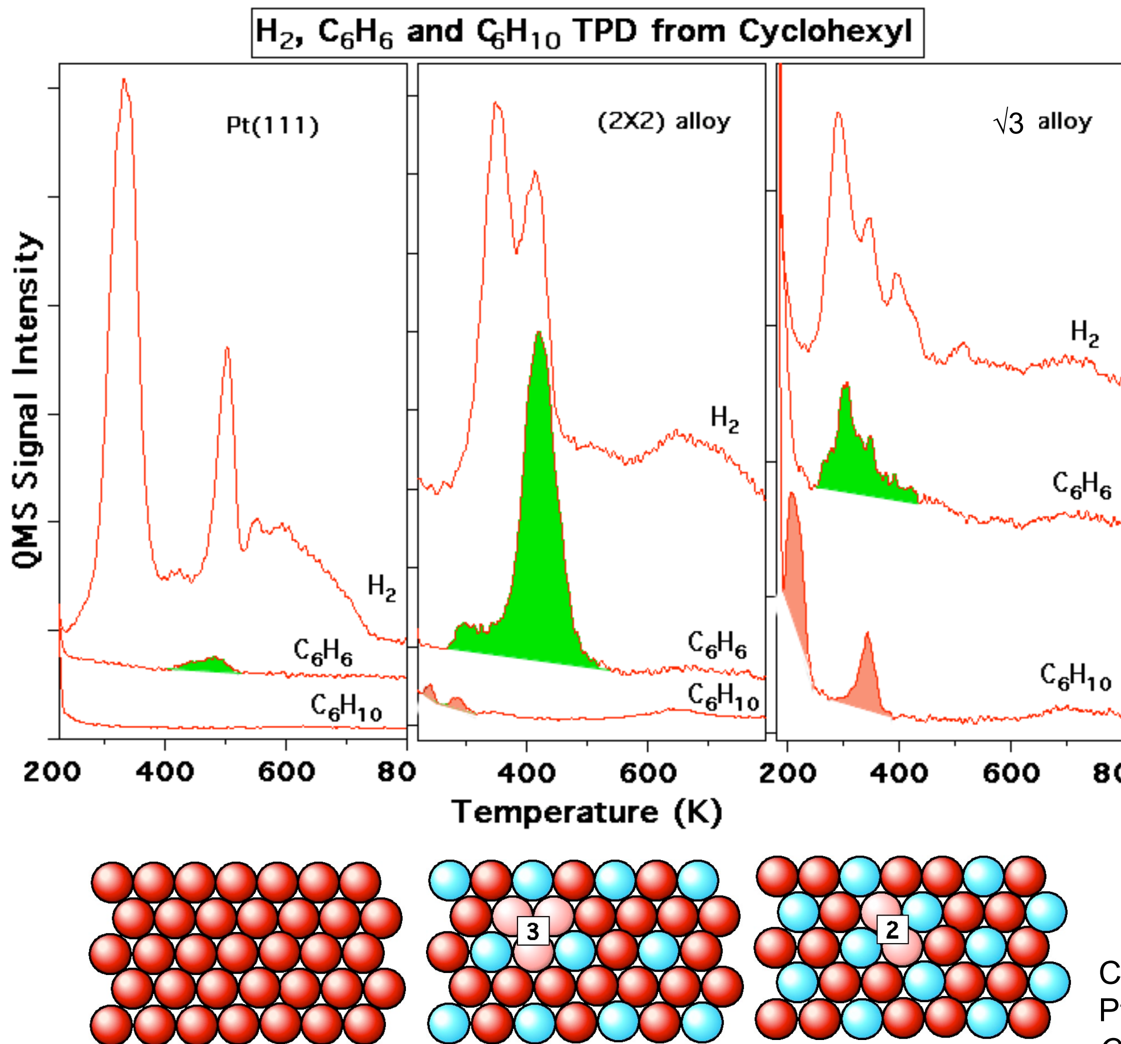
Ag-Pt-alloy phases appear darker, distinguished from pure-Pt hex phases for 0.25-ML Ag on Pt(100) after annealing to 900 K

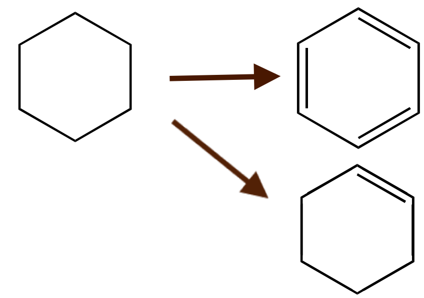


(75 nm)^2

Single-unit-cell-wide Pt(100)-hex domains surrounded by Ag-Pt alloy phase in thermodynamic equilibrium

Site-directed chemistry: 3-fold Pt sites on PtSn alloys yield benzene

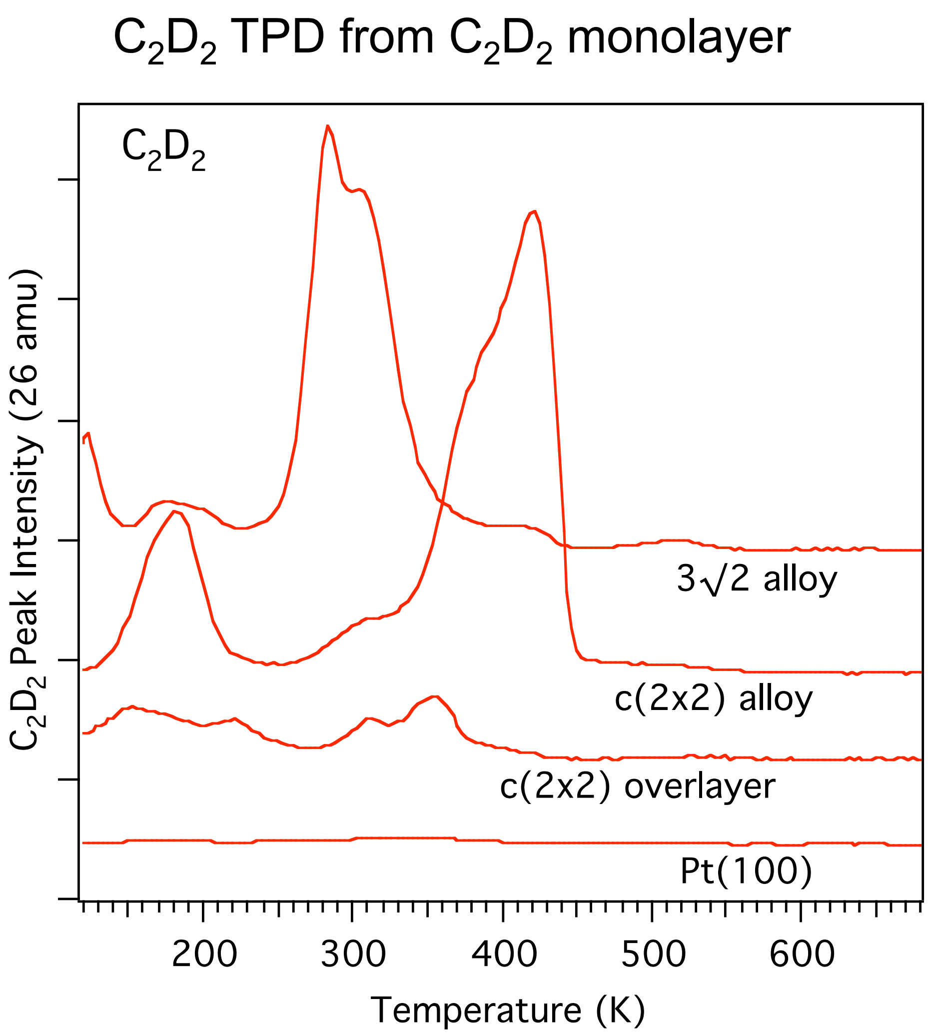


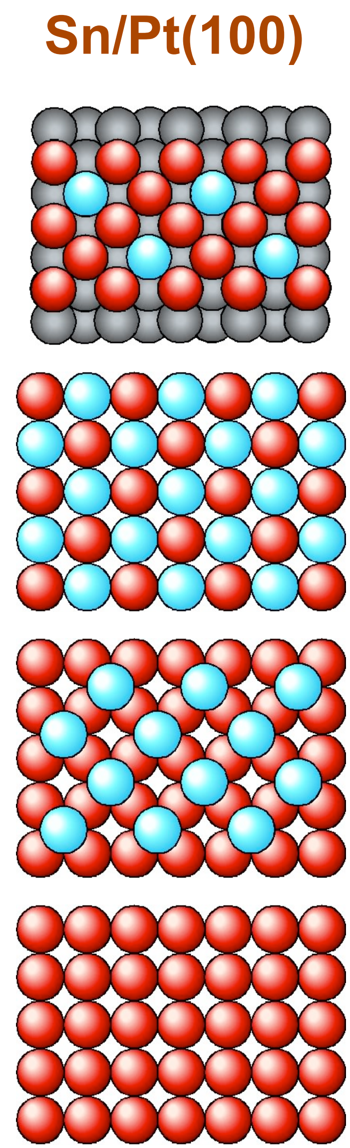


Cyclohexane conversion probed by cyclohexyl radicals from electron-induced dissociation (EID)

Ch. 2 "Structure, Characterization and Reactivity of Pt-Alloy Surfaces", B. E. Koel, in *Model Systems in Catalysis: From Single Crystals and Size Selected Clusters to Supported Enzyme Mimics,* R. M. Rioux (Ed.), (Springer, 2010), pp. 29-50.

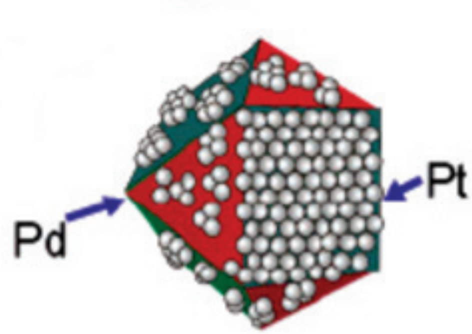
Sn-adatoms are more effective than alloyed-Sn in blocking sites

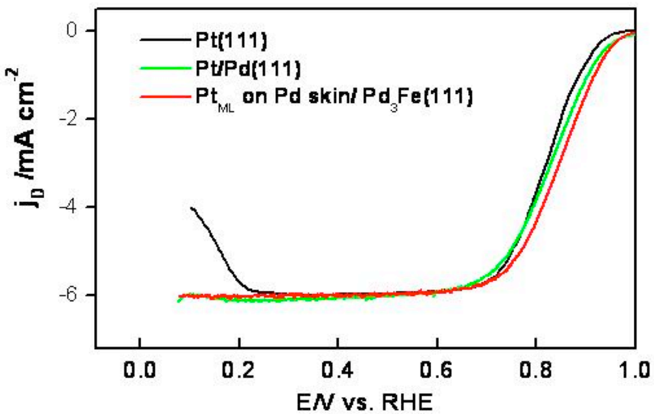


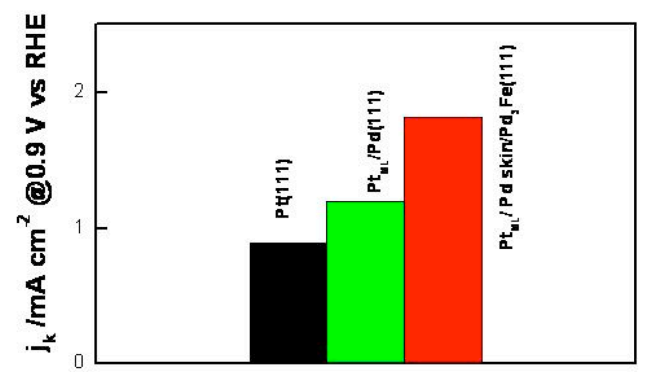


Improving the O_2 reduction reaction rate in fuel cells using novel alloy electrodes

Well-defined $Pd_3Fe(111)$ single-crystal alloy

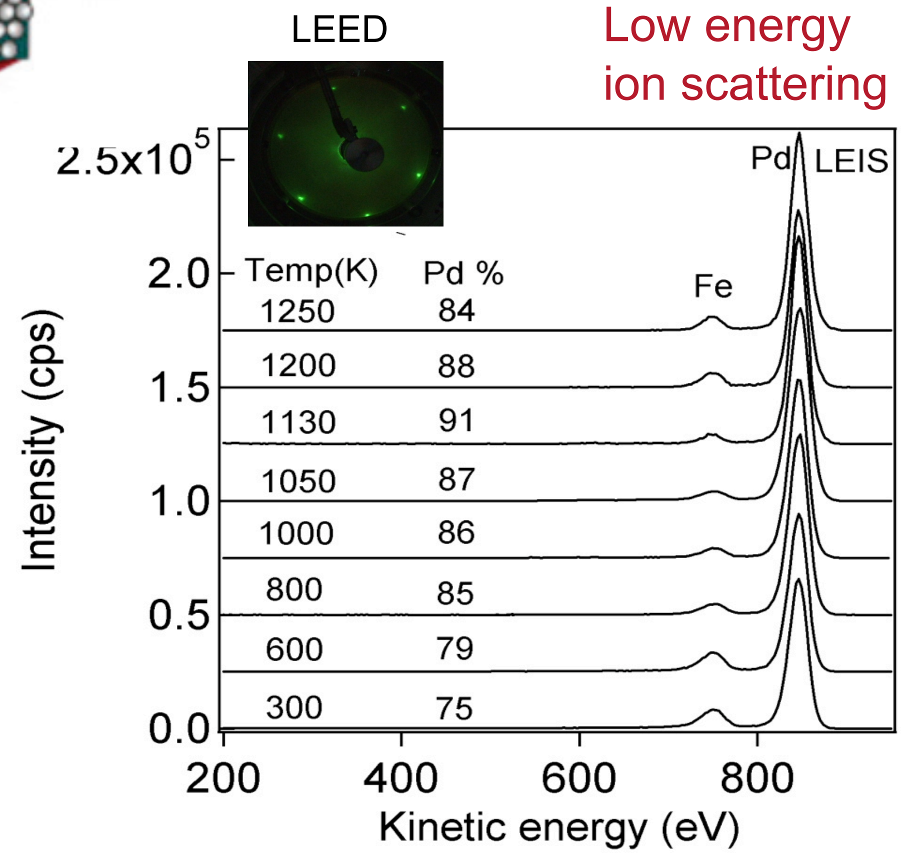






Annealing causes Pd segregation

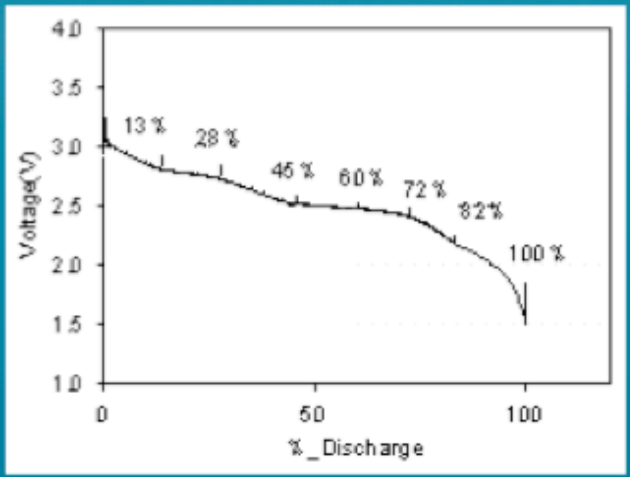
Low energy ion scattering



Zhou, et al., *J. Amer. Chem. Soc.*, **131**, 12755 (2009)

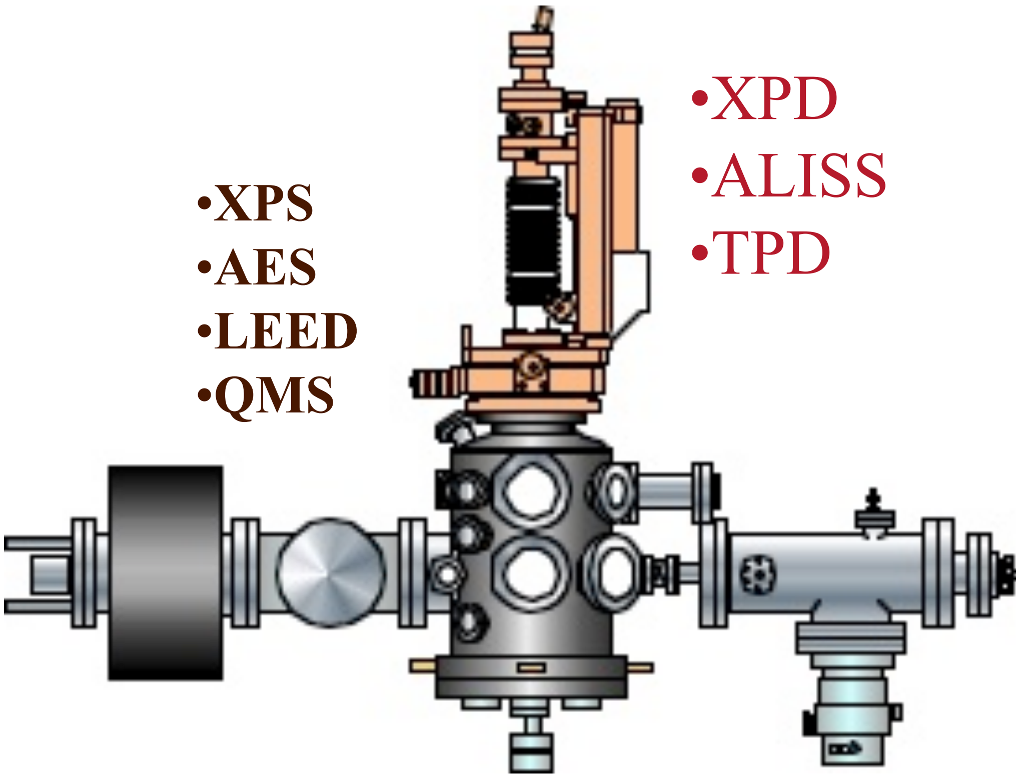
Electrode Reaction of Li / SVO Battery

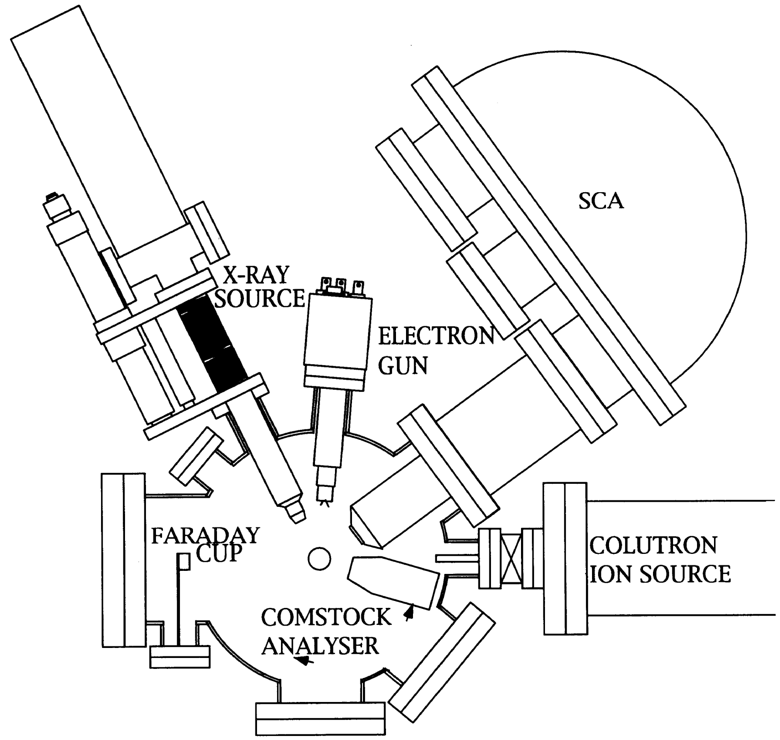
- Cathode half reaction
  - Silver reduction
    $Ag_2V_4O_{11} + 2Li^+ + 2e^- \rightarrow Li_2V_4O_{11} + 2Ag$
  - Vanadium reduction
    $Li_2V_4O_{11} + 5Li^+ + 5e^- \rightarrow Li_7V_4O_{11}$
- Anode half reaction
  - Lithium oxidation
    $Li \rightarrow Li^+ + e^-$
- Full cell reaction
  $Ag_2V_4O_{11} + 7Li \rightarrow Li_7V_4O_{11} + 2Ag$



©2003 Quallion LLC
Confidential & Proprietary Information of Quallion LLC

XPS/XPD/LEIS/ALISS instrument

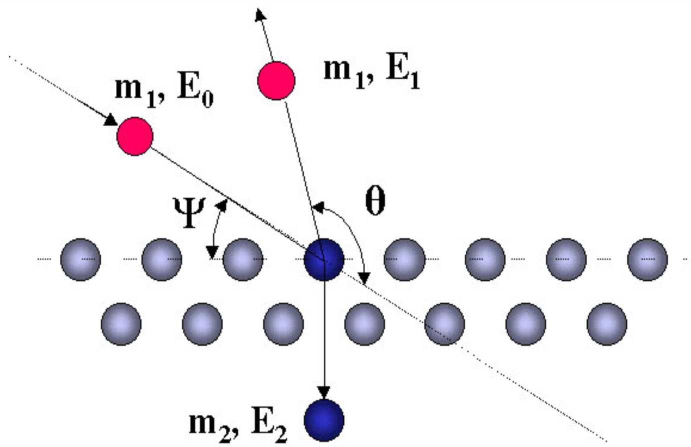




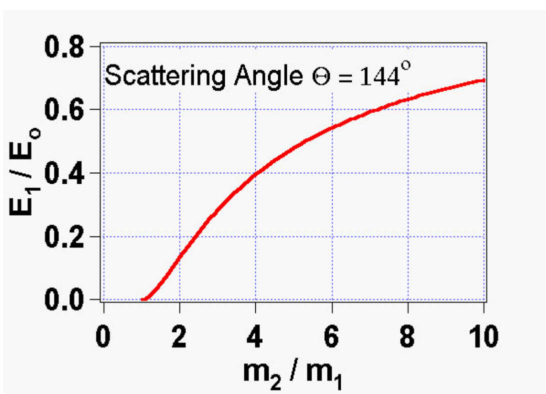
- **Li deposition**
  Resistive heating of Li in crucible or SAES getter source

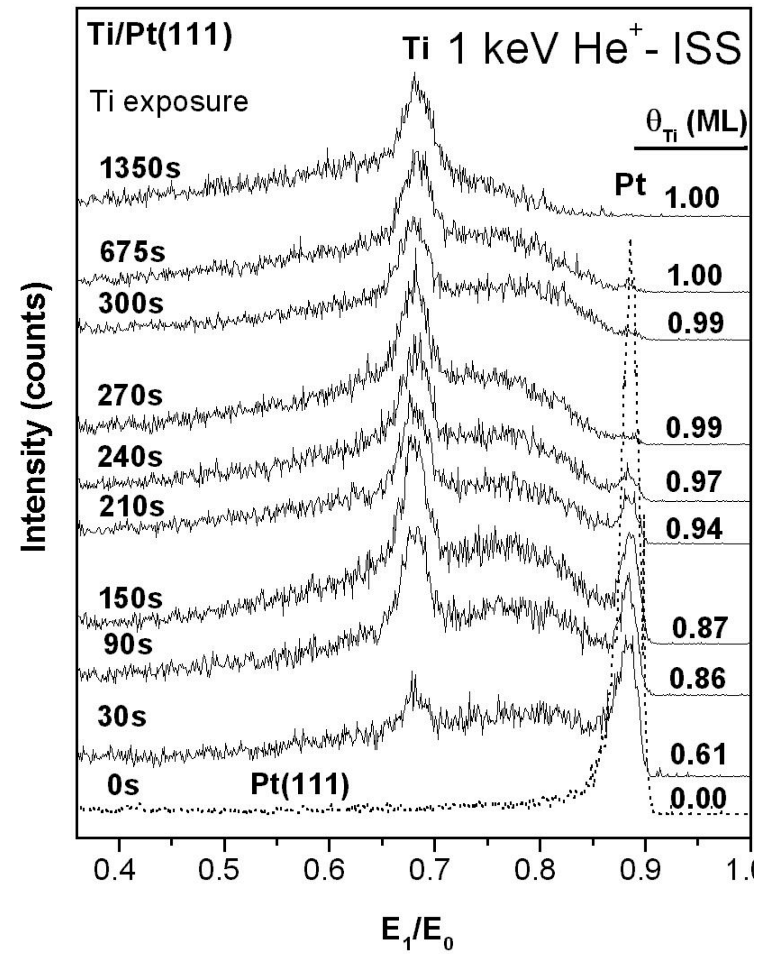
- **Li film growth**
  Deposition of submonolayer or thicker Li films om vacuum or reactive gas environments and heat substrate to high temperature

Low Energy Ion Scattering (LEIS or ISS)



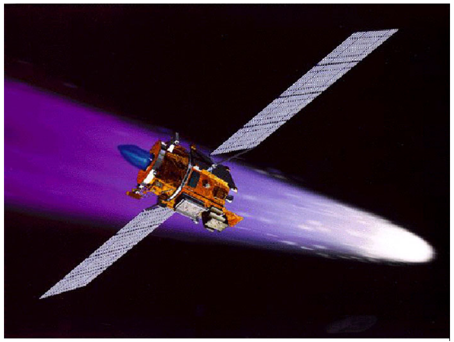
$$\frac{E_1}{E_o} = \left(\frac{\cos\theta + \sqrt{m_2^2 / m_1^2 - \sin^2\theta}}{1 + (m_2/m_1)} \right)^2$$

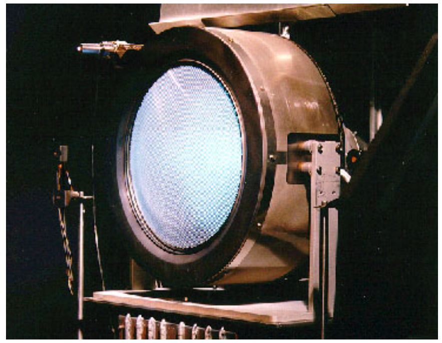


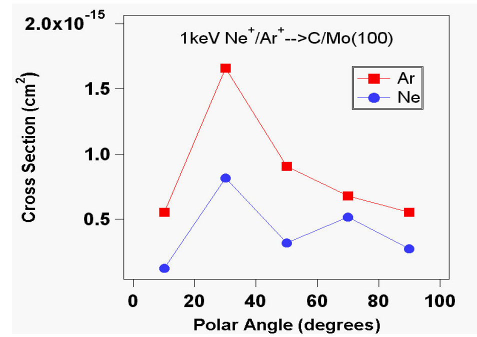


Elemental composition of ONLY the top-most atomic layer

Desorption of Adsorbed Carbon on Mo(100) by Noble Gas Ion Sputtering: Validation of Ground Test Measurements of Ion Engine Lifetime



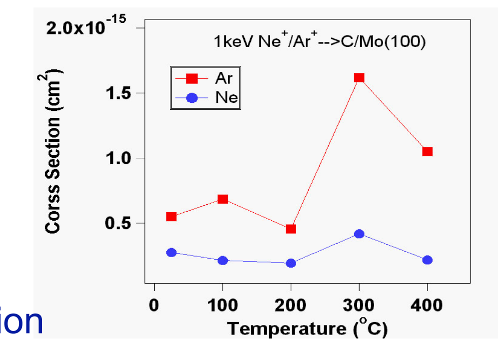




Sputtering of adsorbed carbon is important in surface cleaning and in ground testing of ion thruster lifetimes

Ion sputtering desorption cross section is used to characterize how efficiently surface atoms are removed

Does carbon deposited during ground testing artificially reduce the Mo grid sputtering rates and thus increase estimates of grid lifetime?



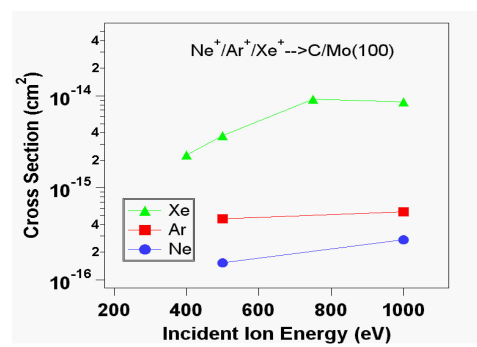
Desorption for C on Mo(100) increase with mass of impinging ion

C desorption maximum at an incident angle of 30°

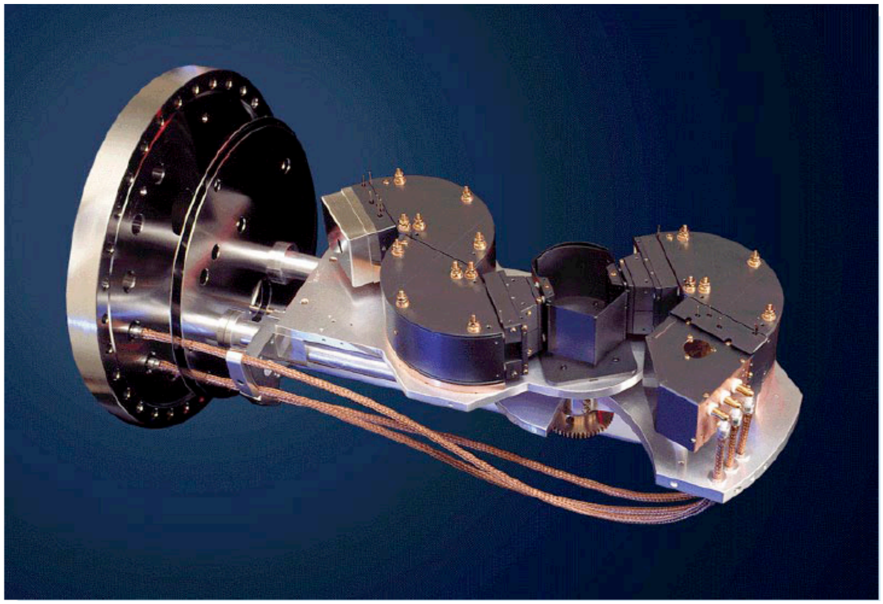
C desorption maximum at 300°C

C desorption increases with ion energy

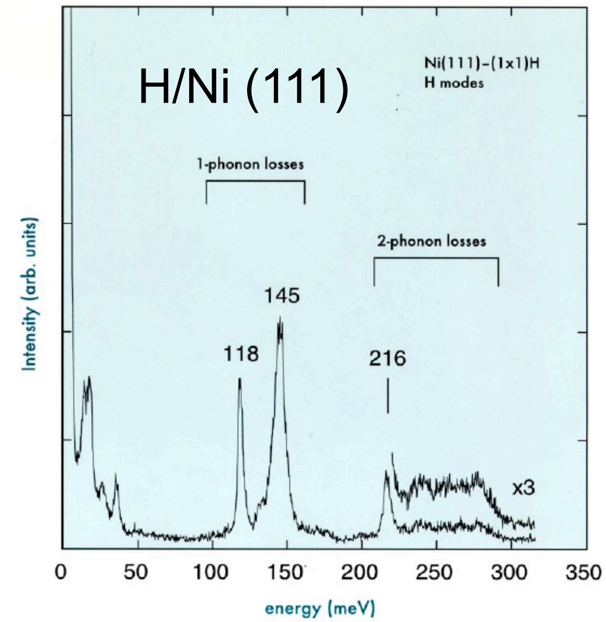
Deposited carbon does not reduce Mo grid erosion rate during ground testing. The measured lifetime can be used with confidence in predicting engine wear in space.

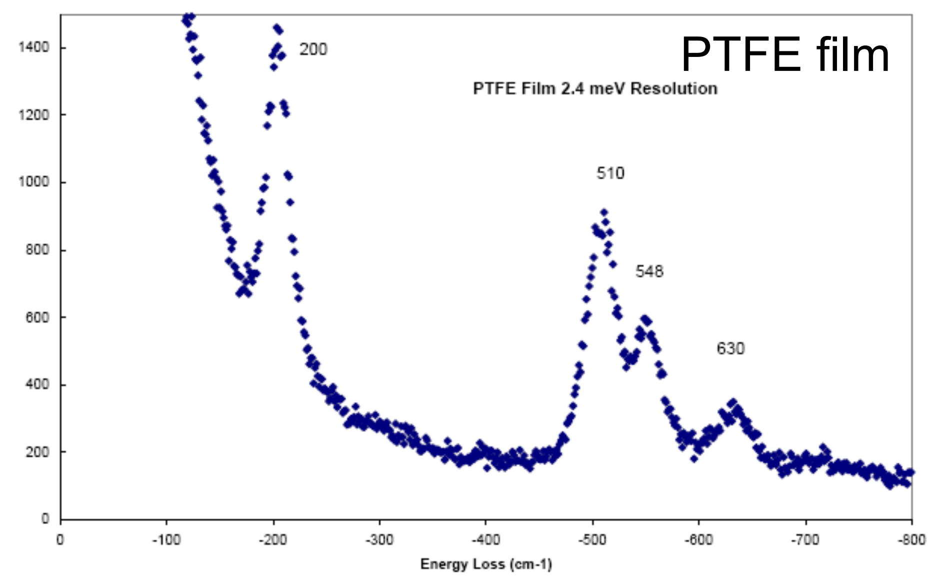


Surface vibrations from HREELS



Multichannel Electron Energy Analyzer (Model ELS5000 MCA)



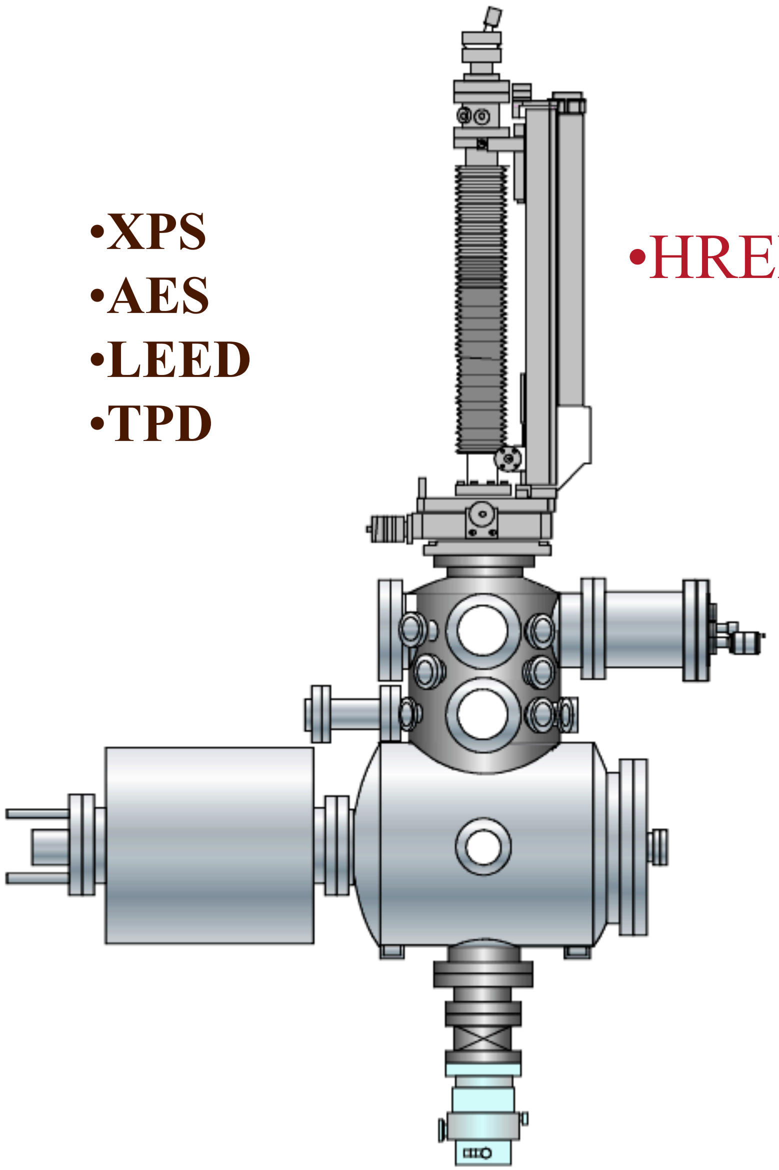


High Resolution Electron Energy Loss Spectroscopy (HREELS)

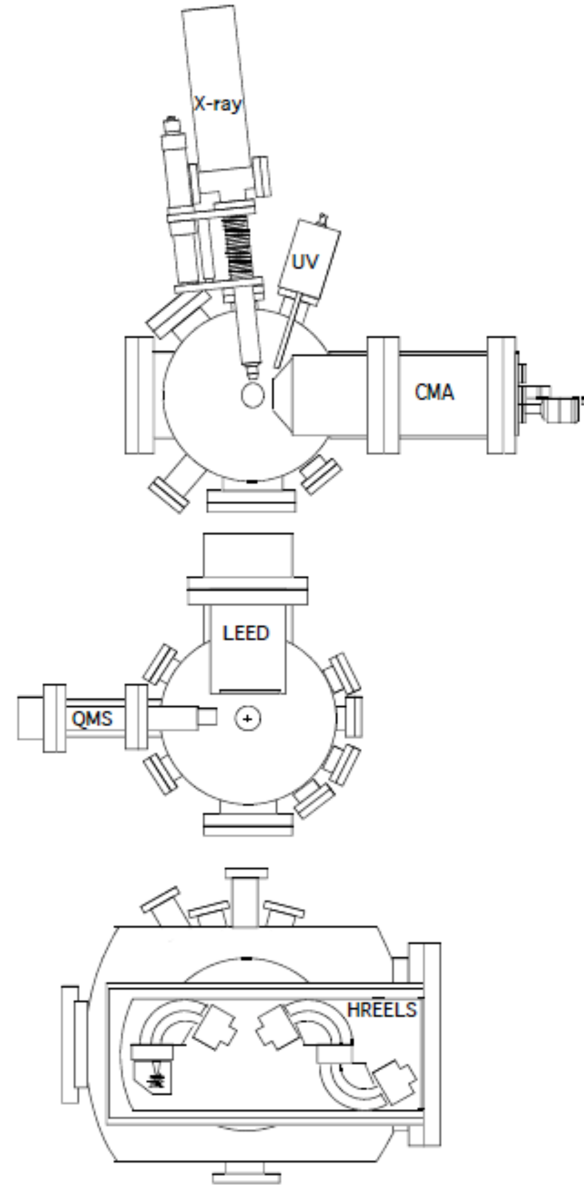
www.lktech.com

HREELS instrument

- XPS
- AES
- LEED
- TPD

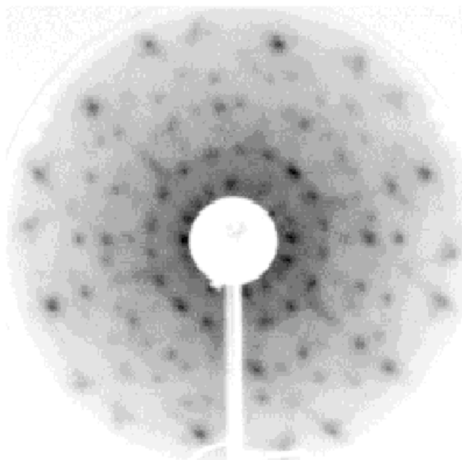


- HREELS



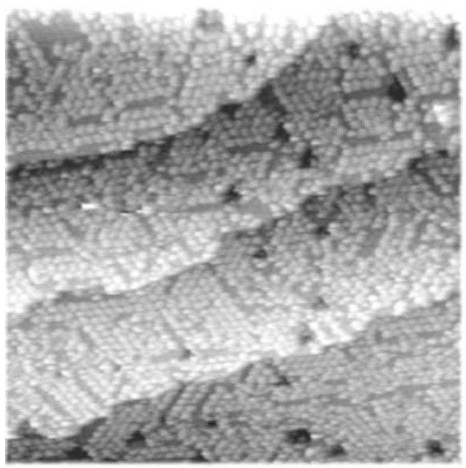
Structure-reactivity relationships for tin oxide thin films

LEED



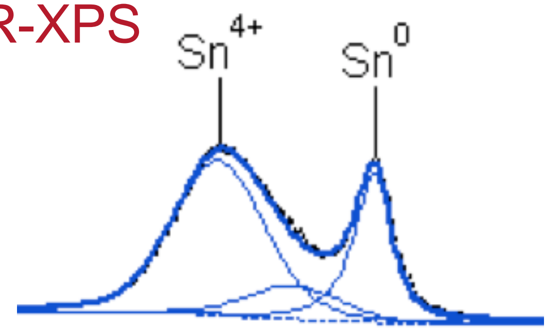
Incommensurate SnO_x monolayer

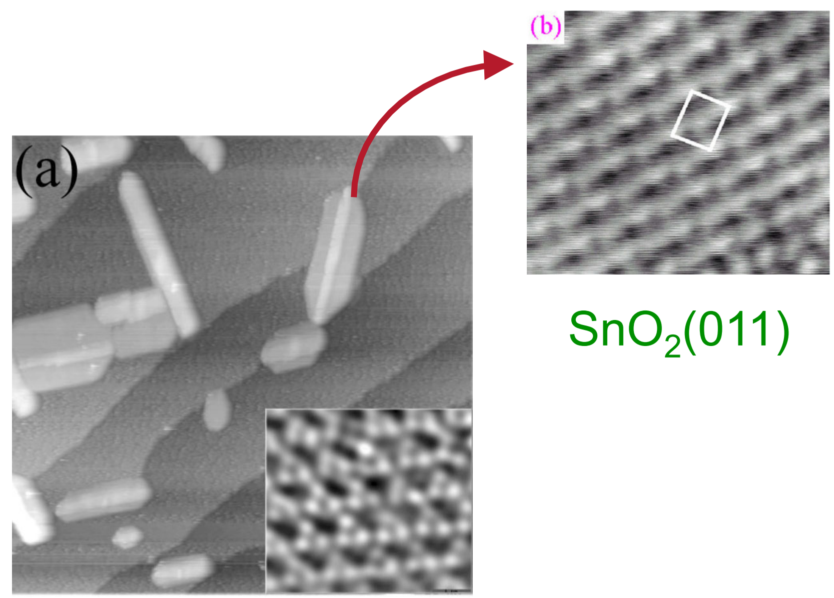
STM



(5x5) SnO_x monolayer

HR-XPS





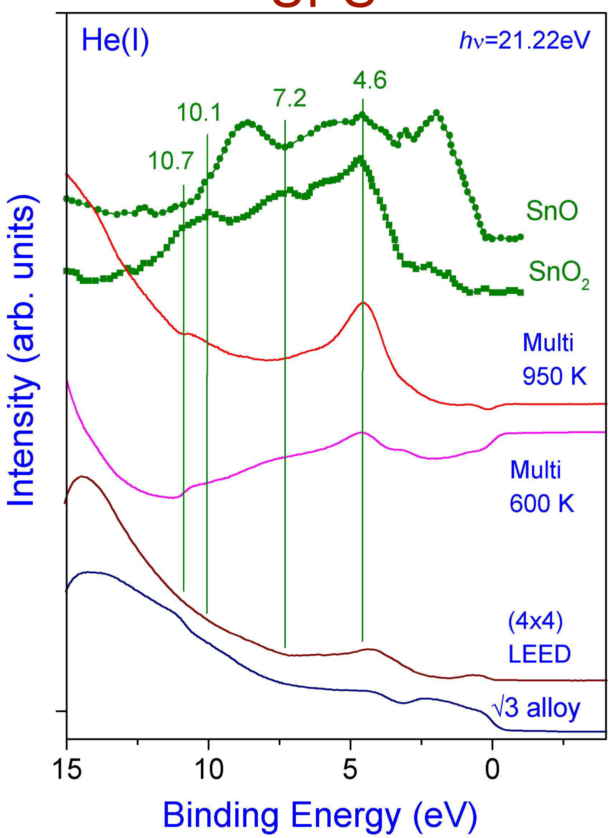
$SnO_2(011)$

(4x4) SnO_2 multilayer

Batzill, et al., *Phys. Rev. B,* **69**, 165403 (2004)

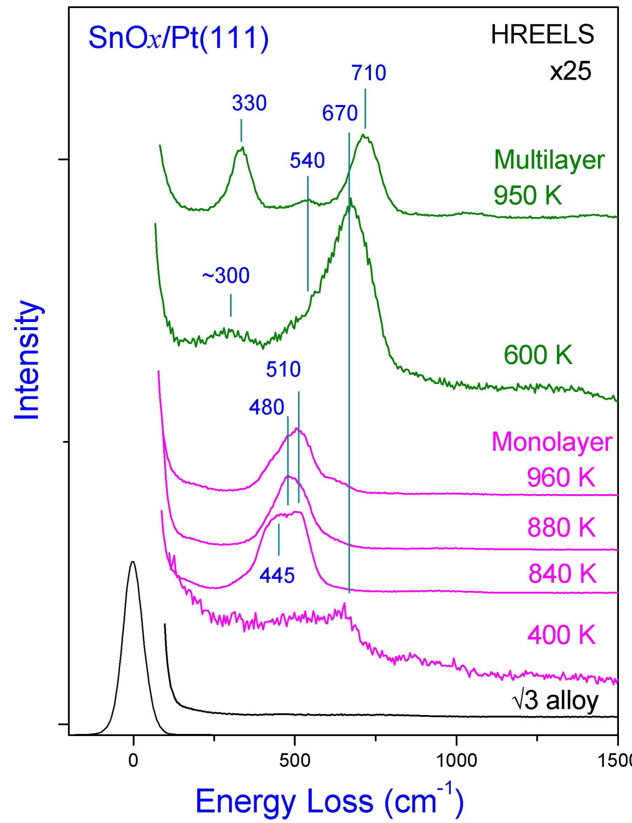
Electronic and vibrational properties of SnO_x films

UPS



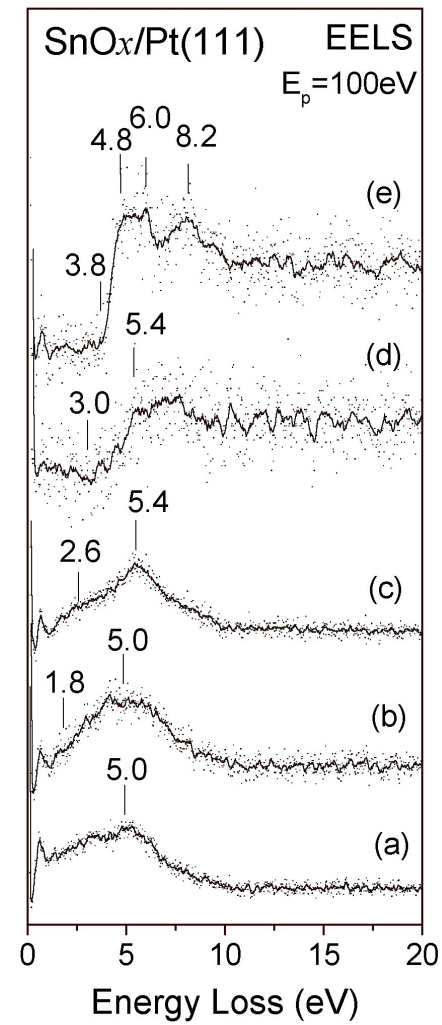
Valence band DOS

HREELS



Vibrations/phonons

EELS

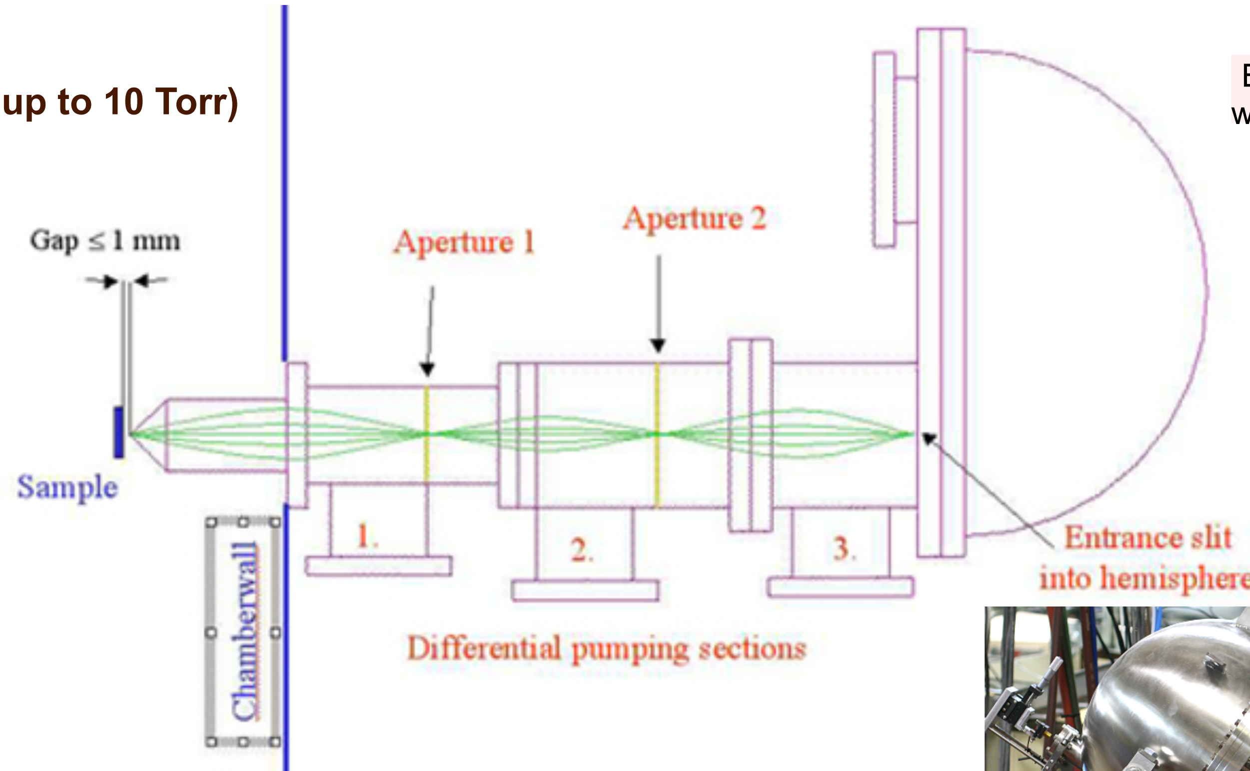


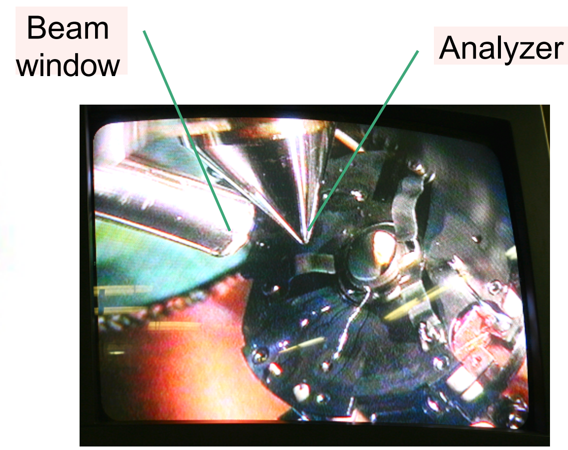
Electronic/optical transitions

Princeton Surface Science

HPPES: *In-situ* reactivity of SnO_x films at 10 Torr

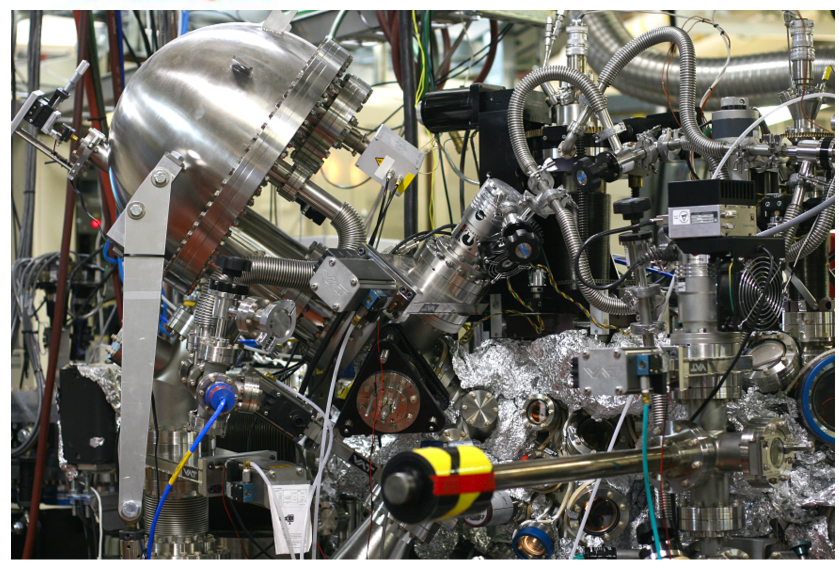
(up to 10 Torr)





High Pressure Photoemission Spectroscopy (HPPES)

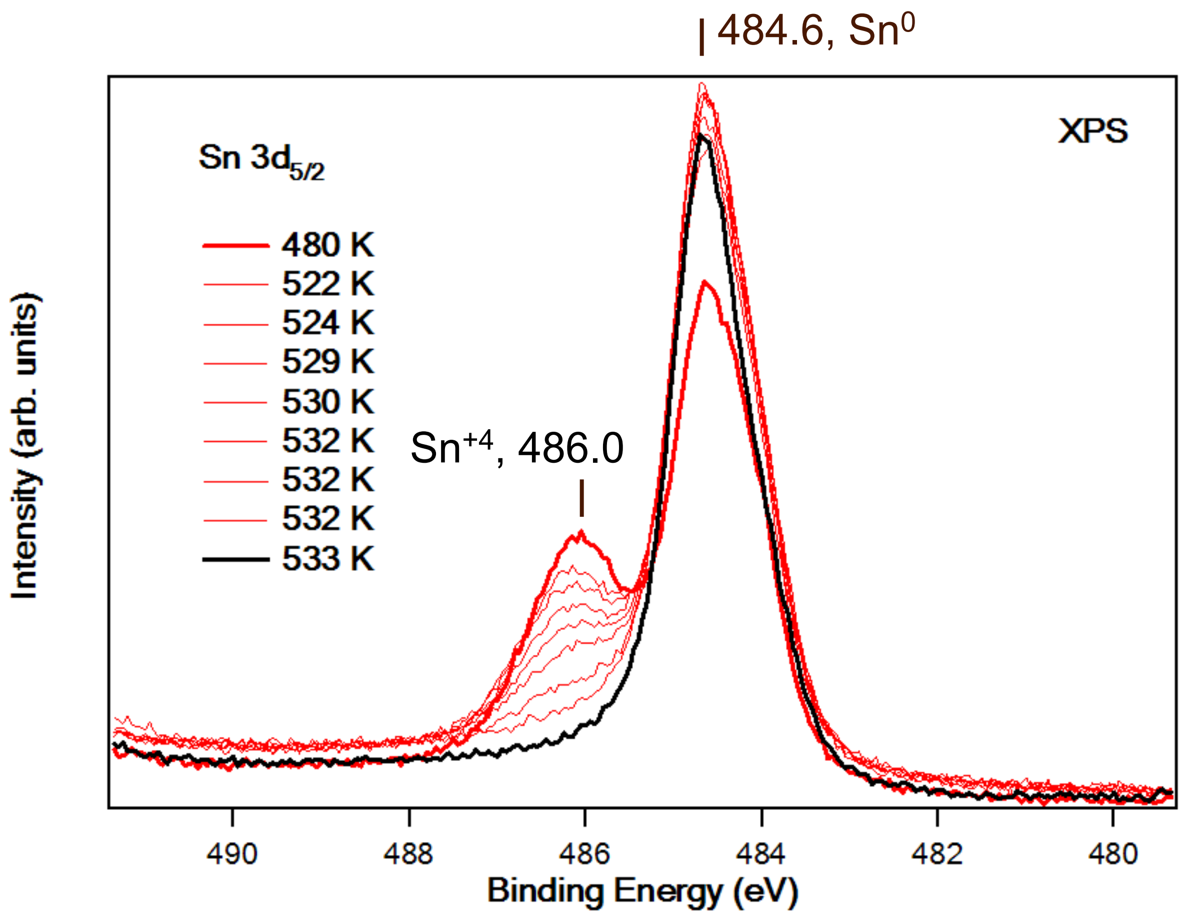
Beamline 11.0.2
Advanced Light Source (ALS)
Lawrence Berkeley National Laboratory

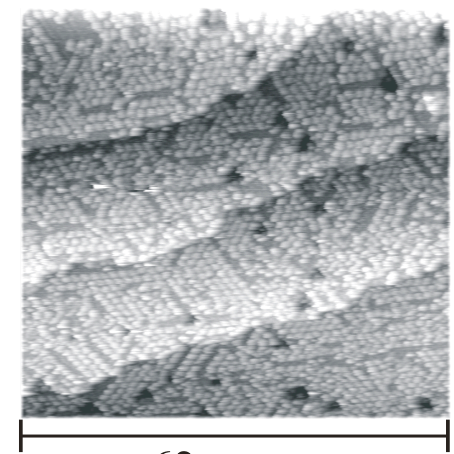


Schematic courtesy of Miguel Salmeron
Bluhm, et al., J. Electron. Spectrosc. Relat. Phenom. **2006**, 150, 86

H_2 reduction of the (5x5)-SnO_x monolayer film

2.1 Torr H_2, 520 K, 10 min

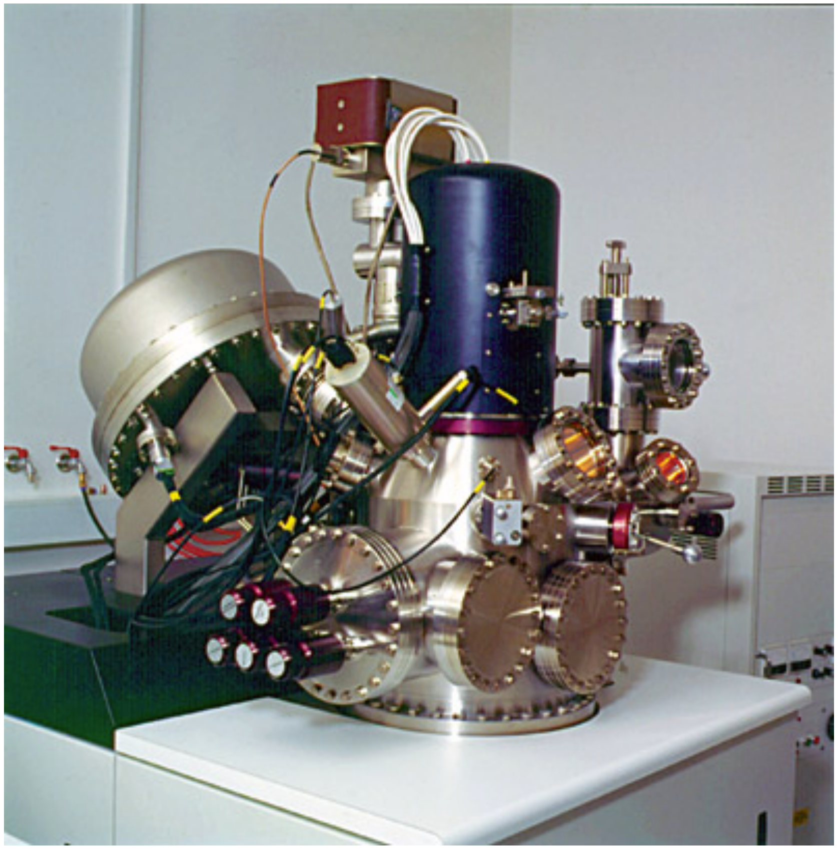




1.5 nm "nanodots"

Less reactive than the (4x4) monolayer: 2.2 Torr H_2, 450 K, 5 min

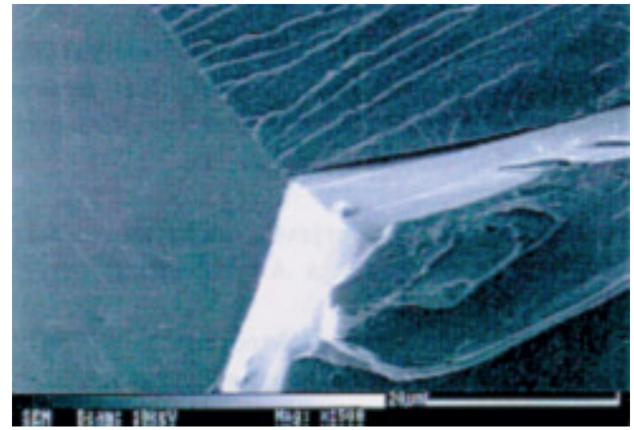
SAM imaging of polycrystalline surfaces and segregation

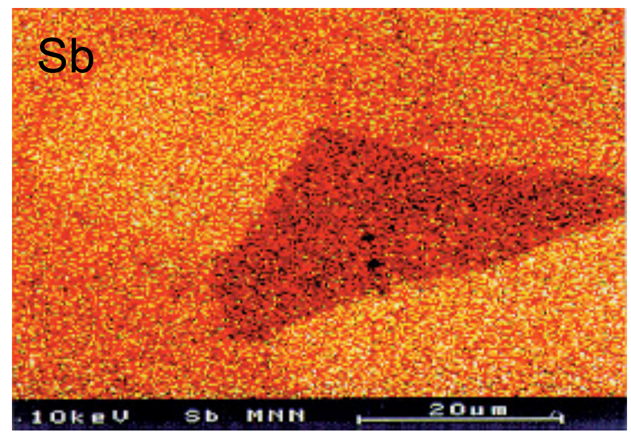


Scanning Auger Electron Microscopy (SAM)

VG-Scientific Microlab 310F with AES, SAM, SEM, XPS

SEM picture of the intercrystalline surface of a Fe-Si-Sn alloy, fractured in UHV

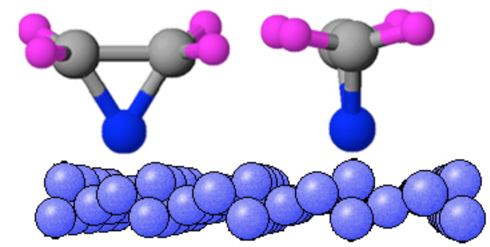


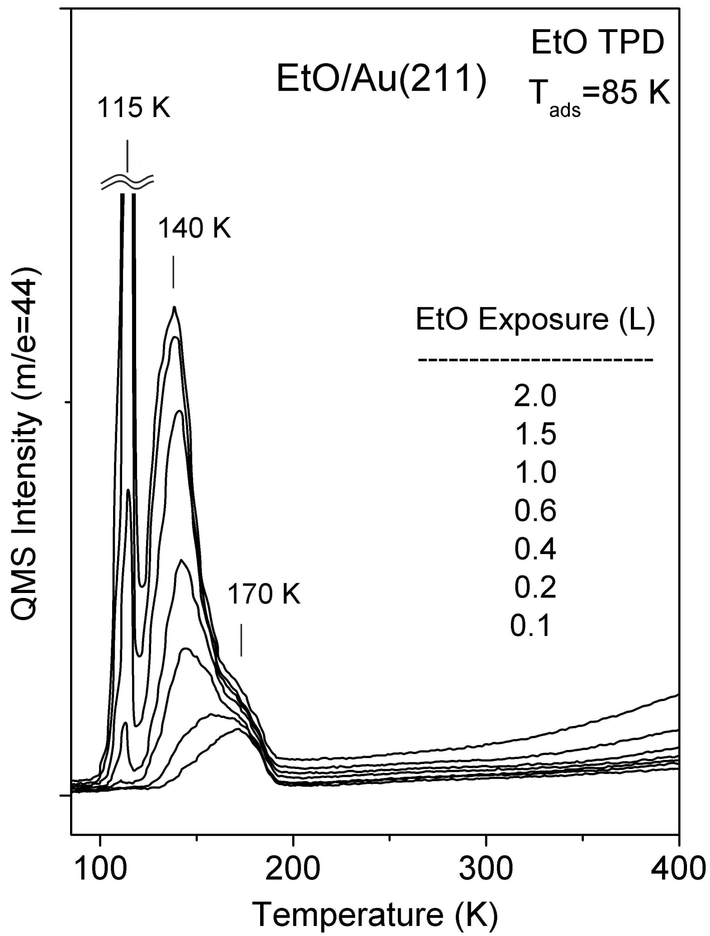


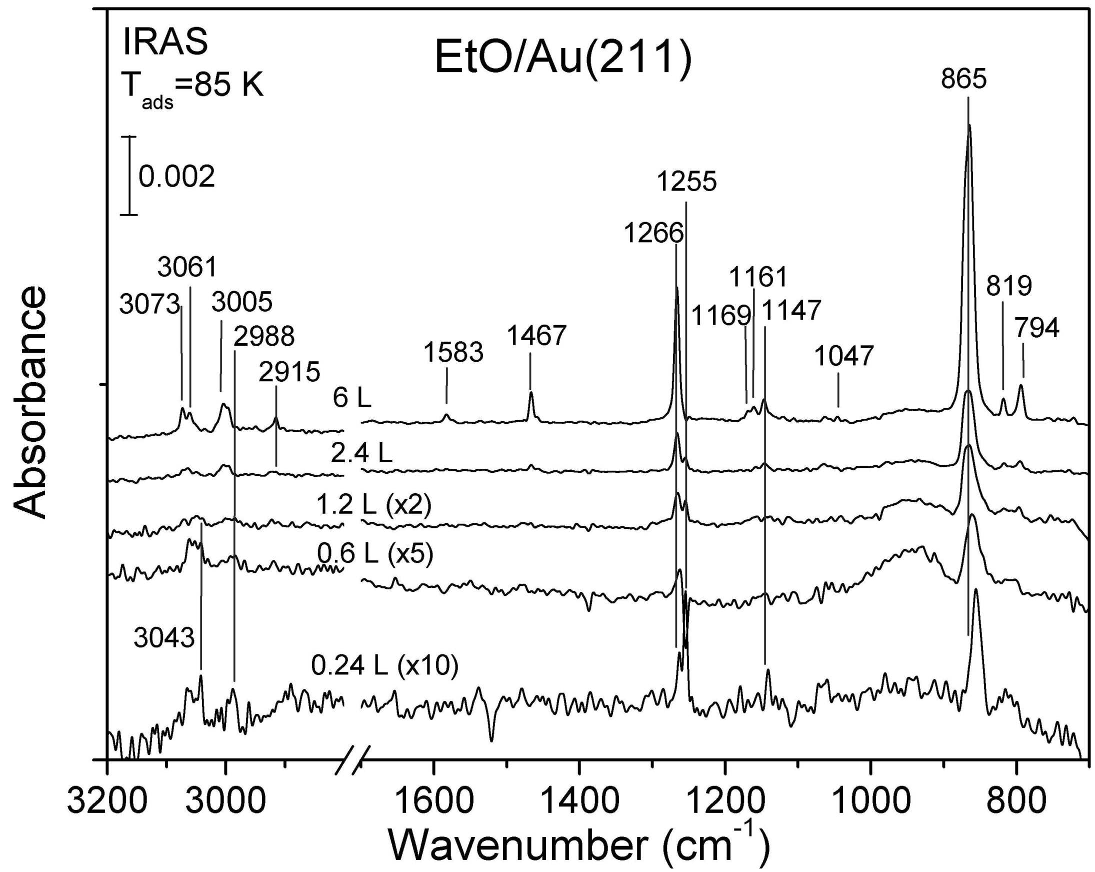
SAM picture of the surface of steel containing 0.05 % Sb steel, showing how segregation depends on grain orientation

www.imt.si

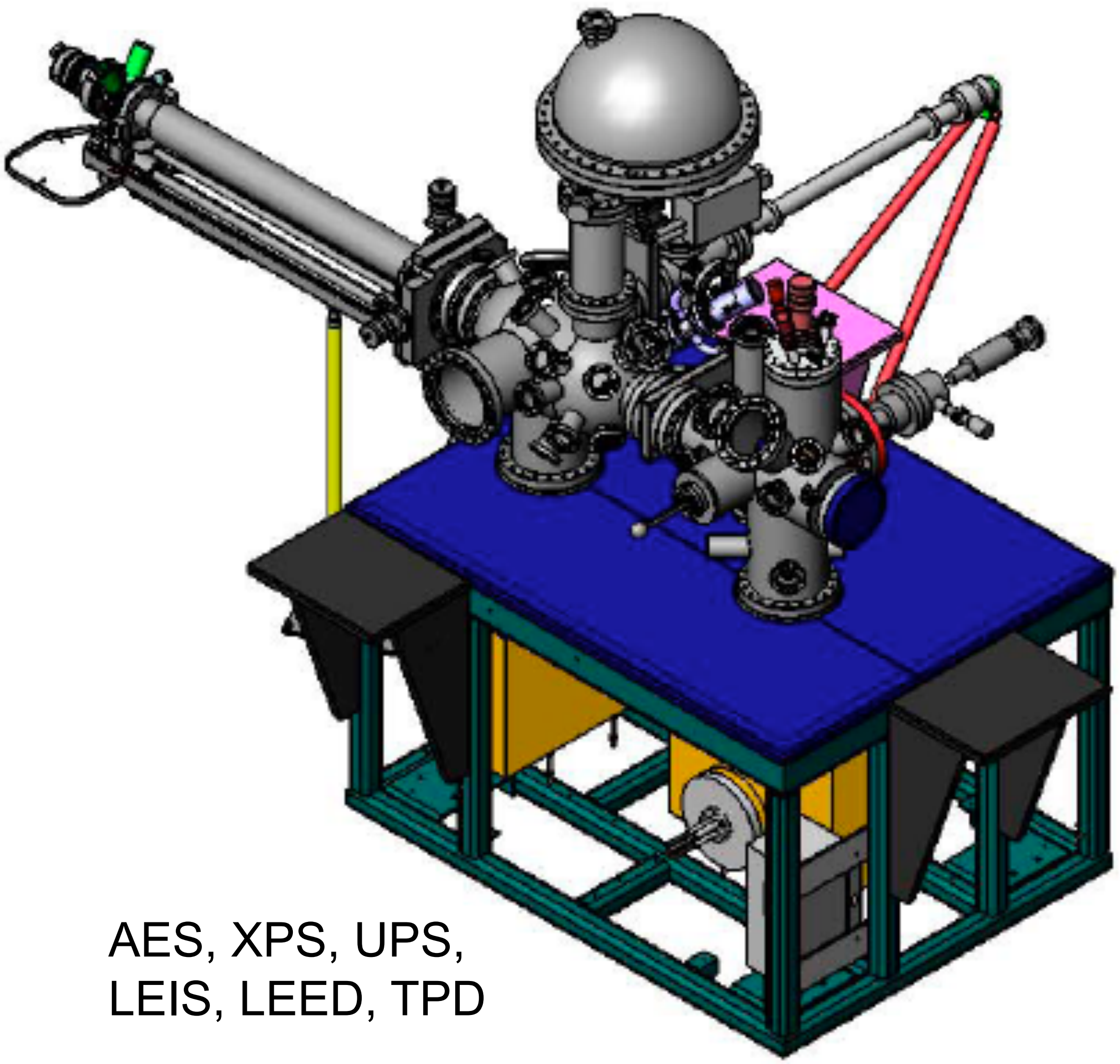
Ethylene Oxide (EtO) on Au(221)



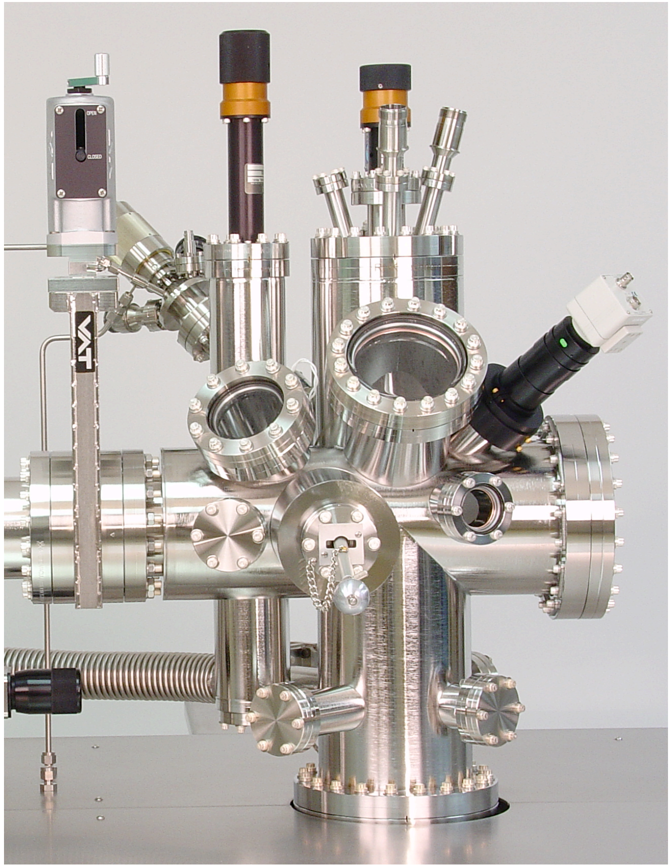




Scanning tunneling microscopy (STM)



AES, XPS, UPS,
LEIS, LEED, TPD

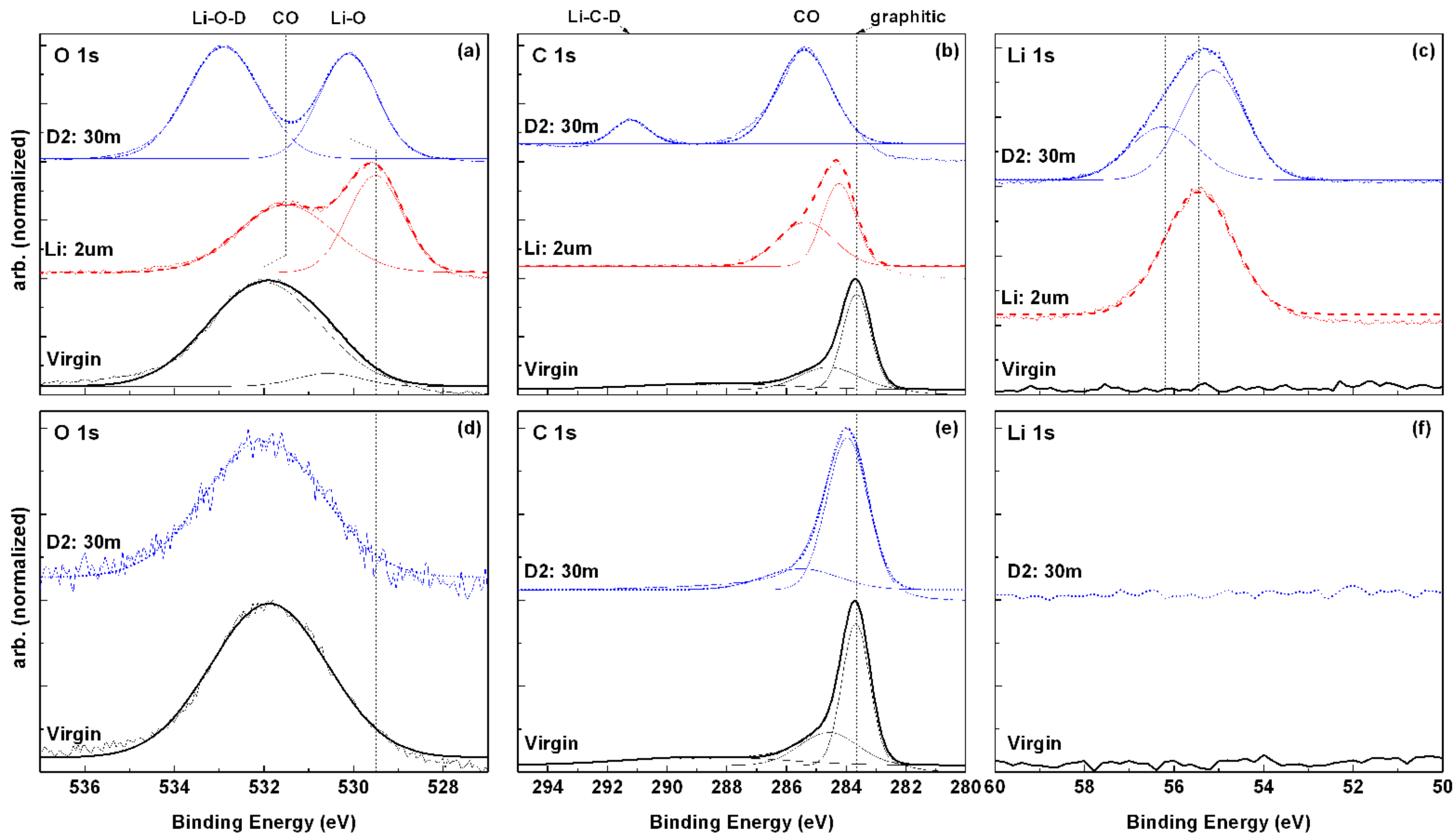


RHK UHV3000 STM

XPS controlled laboratory studies

w/ Li

w/o Li

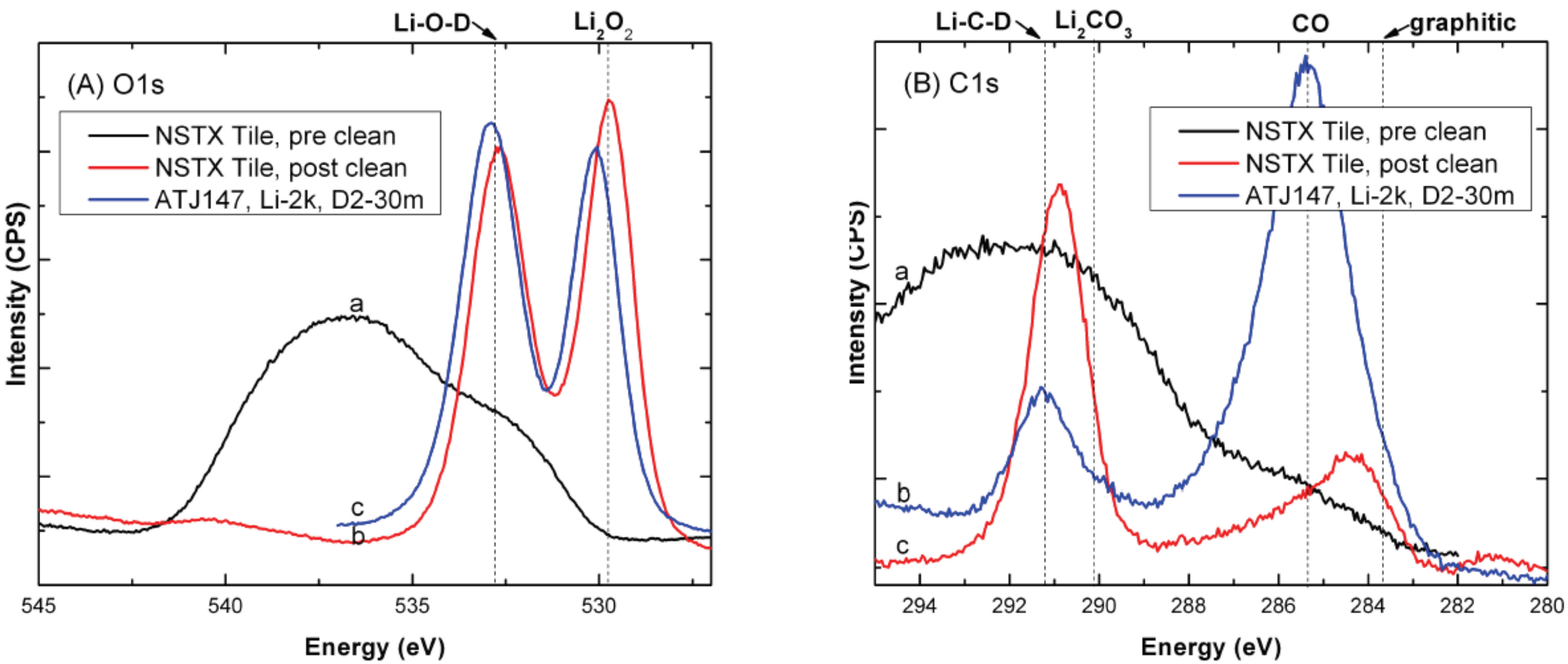


Changes in speaks indicates a chemical change.

JP, CT - Purdue

Princeton Surface Science

Offline experiments vs post mortem tiles.



After cleaning procedures (sputtering, annealing), post mortem tiles exhibit peaks resembling those of offline, controlled experiments.

JP, CT - Purdue

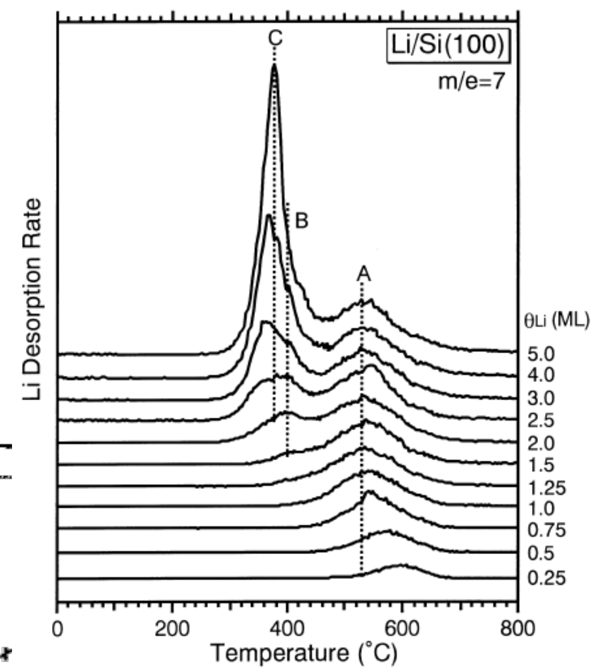
Princeton Surface Science

Temperature Programmed Desorption (TPD)

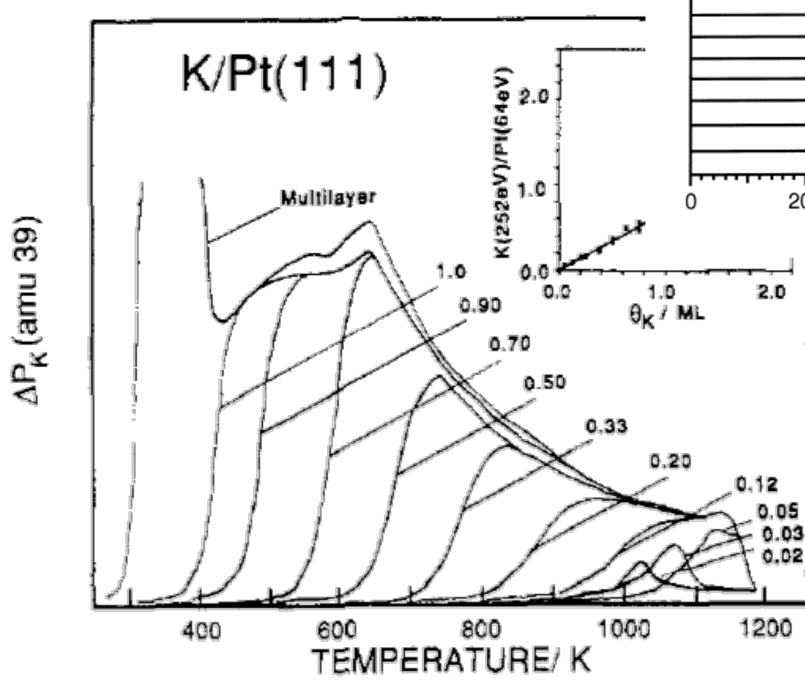
Temperature Programmed Desorption (TPD)

- Heat sample while detecting the evolved gas using a mass spectrometer.
  - — As temperature increases species desorb and are detected as an increase in pressure
  - — Temperature of peak maximum provides information on the binding energy of the desorbing species

Measure and calculate Li adhesion energy from TPD, e.g. Li on Mo



S. Hongo



B.Koel

H atom - Surface Chemistry

Semiconductors

- Silicon
  - 1. Boland, J.J., *Surf. Sci.*, 261, 17, (1992)
  - stability of 3 phases of hydrogenated Si(100) to addition of H atoms correlates inversely to the bond strain
  - 2. Koleske, D.D., Gates, S.M., Schultz, J.A., *J. Chem. Phys.,* 99(7), 5619, (1993)
  - H abstracts D adsorbed on Si(100) with an E_a=0.8 kcal/mol
- Gallium Arsenide
  - 1. Creighton, J.R., *JVSTA,* 8(6), 3984, (1990)
  - H etches GaAs(100); prefers As and abstracts up to 15% of the surface arsenic
  - 2. Qi, H.; Gee, P.E.; Nguyen, T.; Hicks, R.F.
  - sticking coeff = 0.1 to 1.0 from 303 to 433 K on GaAs(100)
- Misc
  - Chang, R.P.H.; Chang, C.C.; Darack, S.
  - Selective etching rates for H plasmas: Si/SiO_2=30, GaAsO/GaAs=2; In/P(in InP)<1

Metal Single Crystals

- Copper
  - 1. Sandl, P; Bischler, U.; Bertel, E.
  - S=.18 on Cu(110); subsurface adsorption possible
- Nickel
  - 1. Bischler, U.; Bertel, E.
  - One dimensional chain reconstructions observed on Ni(110)
  - 2. Johnson, A.D.; Maynard, K.J.; Daley, S.P; Yang, Q.Y.; Ceyer, S.T.
  - H atoms have S=0.05 into the bulk of Ni(111)

H Atom Chemistry with Atomic and Molecular Adsorbates

Eley Rideal mechanisms observed for several reactions

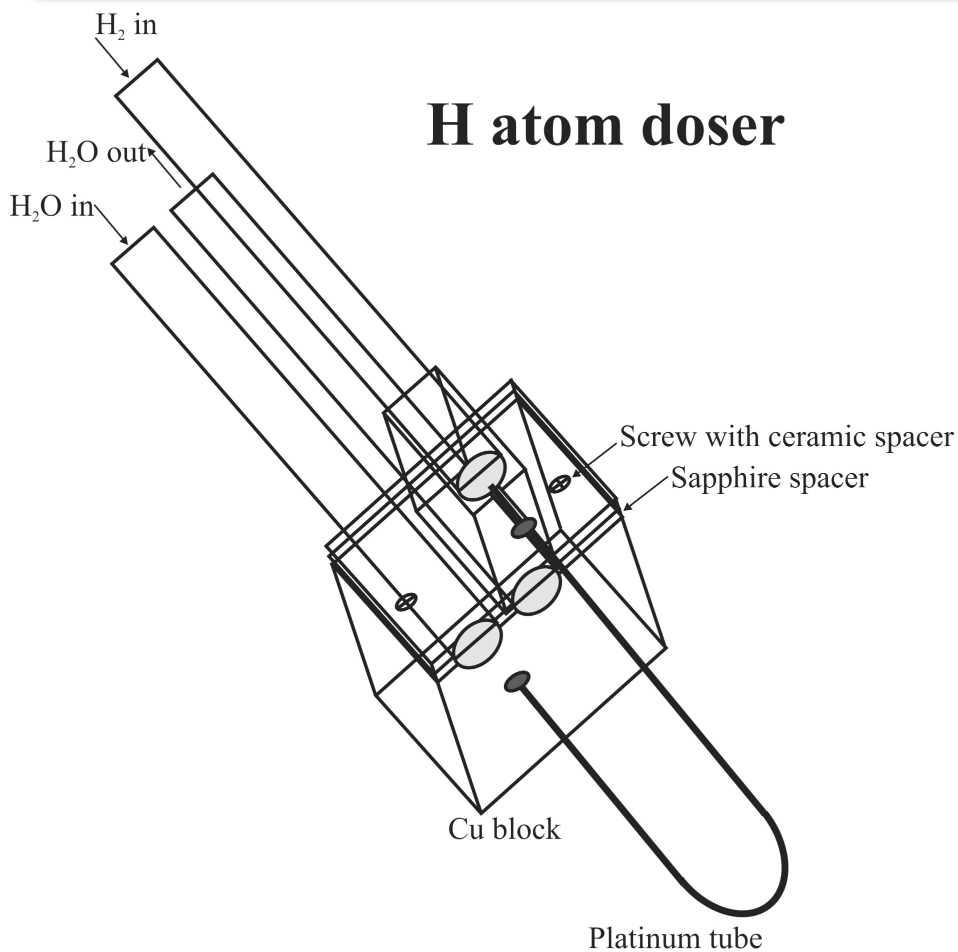
Atomic Adsorbates

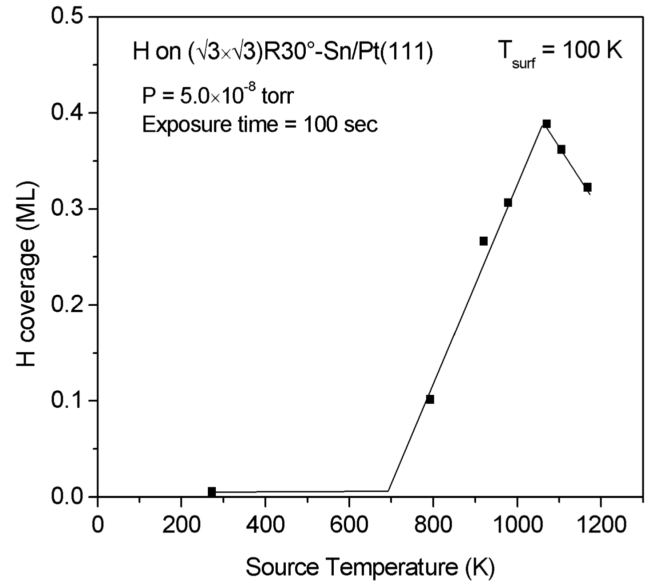
- Chlorine
  - — 1. Zhou, X.L.; White, J.M.; Koel, B.E. *Surf. Sci.*, 218, 201, (1989)
  - — Cl blocks the adsorption of H on Ag(111)
  - — 2. Jackson, B.; Persson, M.; Kay, B.D. *J. Chem. Phys.*, 100, 7687, (1994)
  - — H(g)+ Cl(a)/Au(111) is shown to have a very small (few%) probability of forming HCl
- Oxygen
  - — 1. Xie, J.; Mitchell, W.J.; Lyons, K.J.; Wang, Y.; Weinberg, W.H. *JVSTA*, 12(4), 2210, (1994)
  - — up to 50% of the surface O can be removed as water from Ru(100)-*p*(1x2)-O
- Carbon
  - — 1. Biener, J.; Schenk, A.; Winter, B.; Lutterloh, C.; Schubert, U.A.; Kuppers, J. *Surf. Sci.*, 307-309, 228, (1994)
  - — chemical erosion of graphite by H

Molecular Adsorbates

- n-butane
  - — Nicholas, J.E.; Vaghjiani, G.L. *J.Chem.Phys.*, 91, 5121, (1989)
  - — calculates graph of reaction cross section of H+ n butane.
- ethylene, benzene
  - — Xi, M.; Bent, B.E. *JVSTB,* 10, 2440, (1992)
  - — cross sections: 18 A^2 for D/ethylene; 15 A^2 for D/benzene

Design of clean H atom doser





H coverage calibration:

C_2H_4 on Pt(111) at 300 K produces 0.25-ML CCH_3 that fully dehydrogenates in TPD

J. Phys. Chem. 92 (1988) 2862

UHV-compatible Plasma Source: tectra microwave/ECR atom, ion and atom/ion hybrid source

Atom source

Atom flux: >2x1016 atoms/cm2/s at 10cm

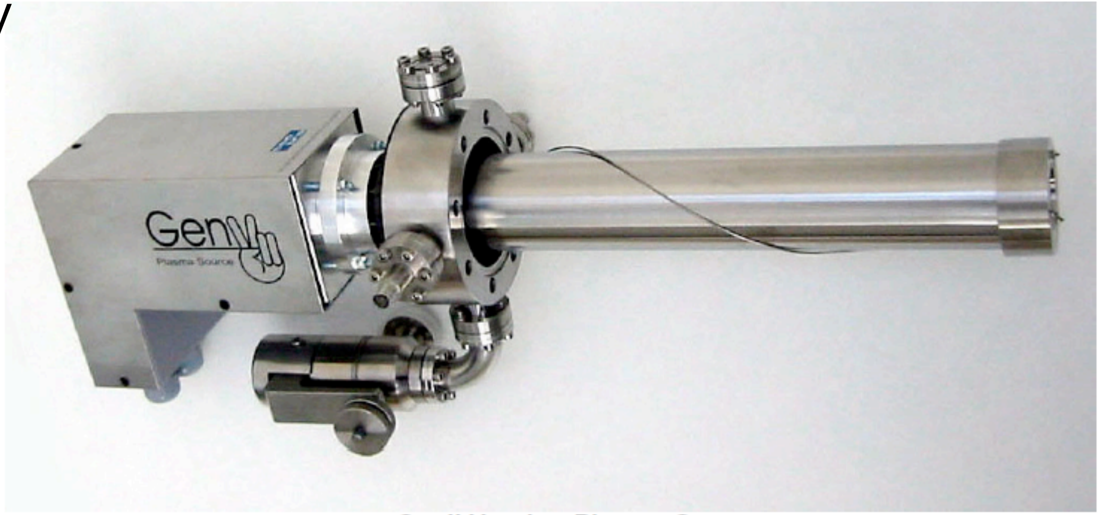
Nitrogen, Oxygen, Hydrogen (any most other non-condensible gases)

Working pressure: 1x10-8 mbar

Ion source

Ion current density: >2mA/cm2 at 1.3keV and >0.05mA/cm2 at <100eV at 120mm distance

Ion energy: 25eV - 2000eV



R.Anton, T. Wiegner, W. Naumann, M. Liebmann, C. Klein, C. Bradley, Rev. Sci. Instr. Feb 2000

Liquid Metals in Fusion

Liquid Metals of Interest: Li, Ga, Sn

Alloys Studied: Li-Al, Li-Cu, Li-Sn

Fundamental Questions: What is the composition of the Liquid Surface?
(as most of the sputtered erosion originates at the surface).

Atoms with lower surface tension tend to segregate (Oxygen, Fluorine have the tendency to segregate) and Li segregates in Sn-Li.

Segregation effects the sputter flux composition- Sputtering rate Vs Segregation rate?-At high sputter rates, the effect is transient leading to an equilibrium sputter flux resembling bulk composition.

Sputtering of dynamically evolving surface is challenging and not known.

Also known that the erosion rate at higher temperatures for liquid metals is greater than what can be attributed to the sum of independent sputter and evaporation fluxes- Need explanation!

Oxidation of Sn droplets

TAKAYUKI MIMA, HIRONORI TAKEUCHI, SHIGEO ARAI, KEISUKE KISHITA, KOTARO KURODA, AND HIROYASU SAKA,” In Situ Observation of Oxidation of Liquid Droplets of Tin and Melting Behavior of a Tin Particle Covered With a Tin Oxide Layer,” MICROSCOPY RESEARCH AND TECHNIQUE 72:223–231 (2009)

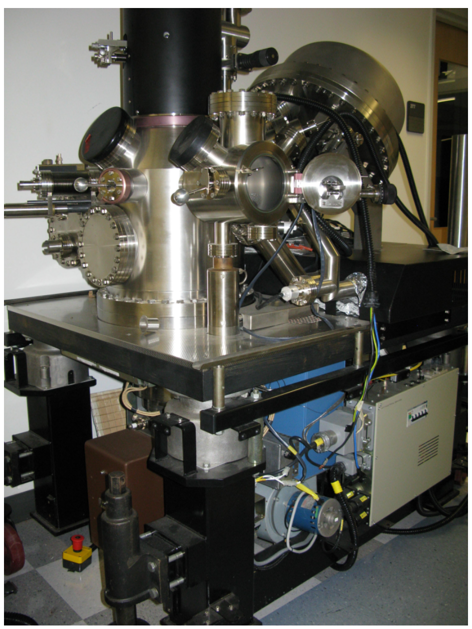
In many processes involving real materials, the liquid phase plays a very important role. One of the most typical examples is solidification: many properties of solidified products are determined when materials transform from the liquid phase into the solid phase. To obtain better properties of solid materials, the liquid-to-solid reaction, that is solidification, must be controlled carefully. For this purpose, it is vital to have a detailed knowledge of the structure and behavior of the solid-liquid (S-L) interface.

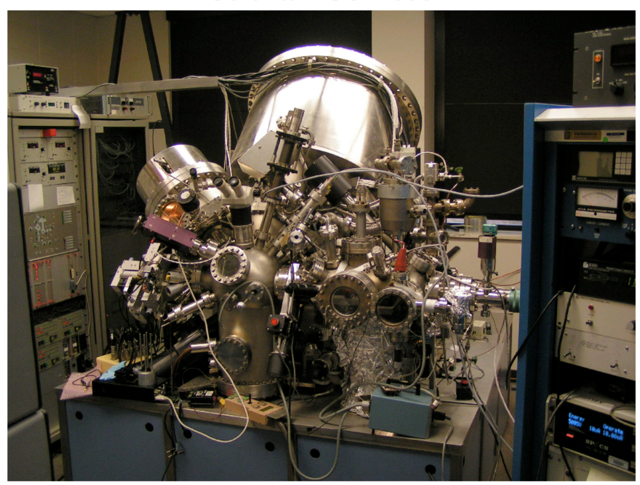
CONCLUSIONS

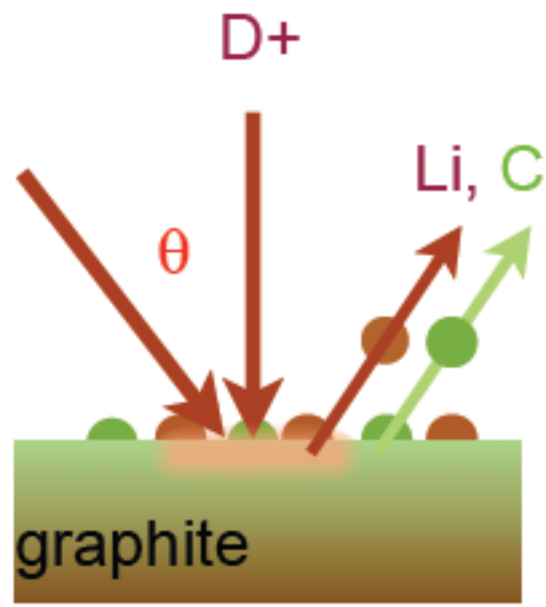
1. The solid-liquid interface in Sn was atomically rough.
2. The contact angle of a solid Sn was larger than 90^0. This is in sharp disagreement with previous results.
3. It was shown that this discrepancy cannot be explained by an increase in the internal pressure of Sn due to the formation of Sn3O4 layer.
4. Possible reasons for this discrepancy were discussed in terms of change in various interfacial and/or surface energies due to the presence of oxygen atoms.

Proposed Work – Surface Sciences Group

- Utilize the Scanning Auger Microprobe (SAM) and XPS to characterize the surface of lithiated ATJ graphite.
- Use the chemical shifts in the KVV transition of Li at 39 eV to produce separate maps of Li and LiO.
  - Obtain a clean spectrum of bulk Li
  - Evaporated films
    - Lithium oxide films on graphite, how do they respond to H?
    - Lithium hydride films on graphite, how do they respond to O?





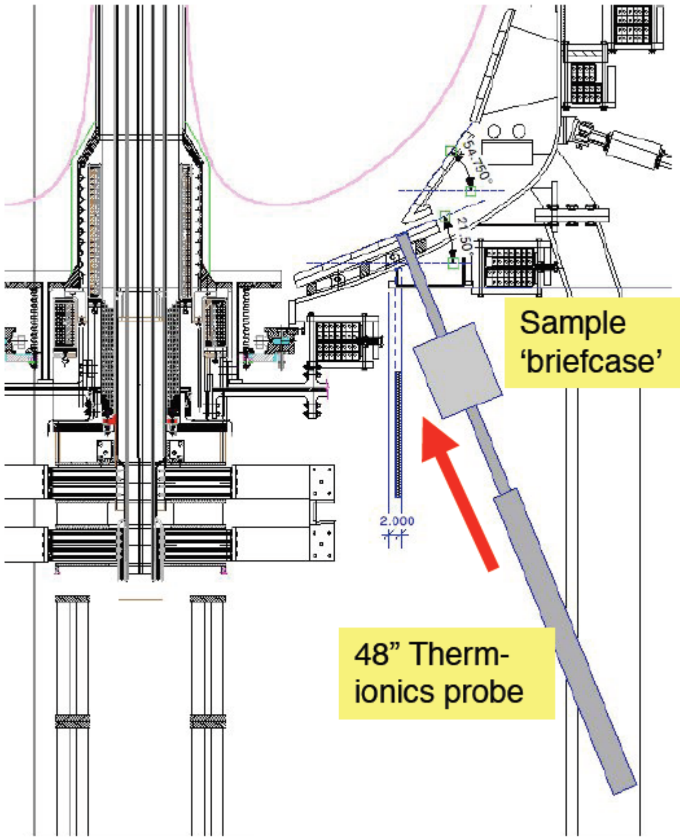


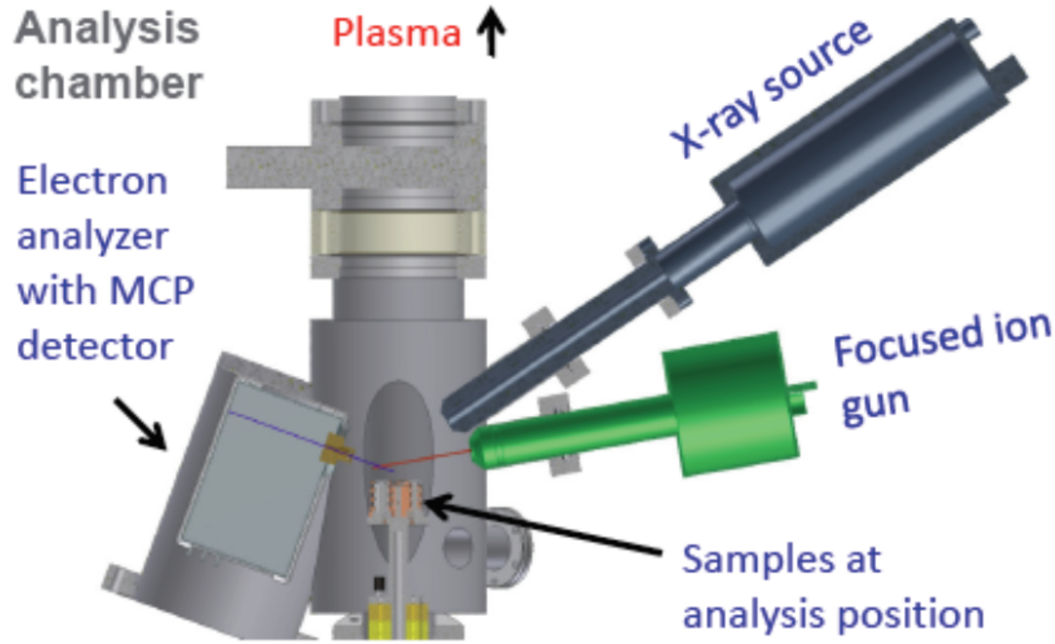
JP Allain

Proposed Work – Surface Science Group

- A differentially pumped ion gun can be used as a source of H+, D+, or O + for ion-induced chemistry studies, and can also produce Ar+ for sputtering applications.
- Determine utility of reflection electron energy-loss spectroscopy (RHEELS) obtained in SAM for detecting and imagine H-rich phases.
- Employ electron stimulated desorption (ESD) of D+ caused by incidient electron beam to obtain additional chemical information.
- Temperature programmed desorption (TPD) can be used to determine energetics of surface processes; H and D concentrations in the Li film and desorbed products of chemical reactions, and the Li adhesion energy.
- Surface science investigations of reactions and processes on sufaces of Li, Ga, Sn and Li+Sn eutectics, using a wide range of ion scattering probes and electron spectroscopy for surface analysis.

Tokamak *in-situ* diagnosis of PMI: measure dynamic response





DRS (direct recoil spectroscopy)
TDS (measure H/D retention)
XPS (chemical bonding states)
LEISS (ion scattering spectroscopy)

NSTX Materials Analysis and Particle Probe (MAPP), with in-vacuo surface analysis. FY2011 and FY2012 NSTX experimental campaigns.

PPPL

PRINCETON PLASMA PHYSICS LABORATORY