SURFACE SCIENCE WESTERN

ISO 9001:2015

Western

X-ray Photoelectron Spectroscopy (XPS)
Auger Electron Spectroscopy (AES)

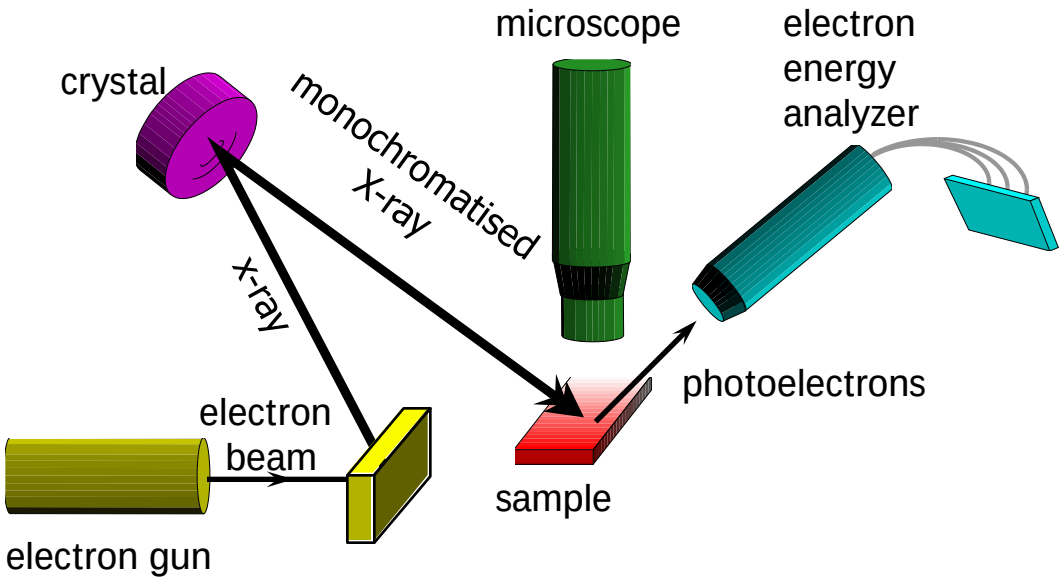
Dr. Sridhar Ramamurthy

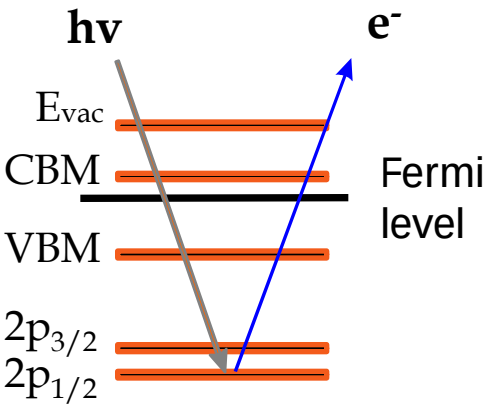
Senior Research Scientist, Surface Science Western

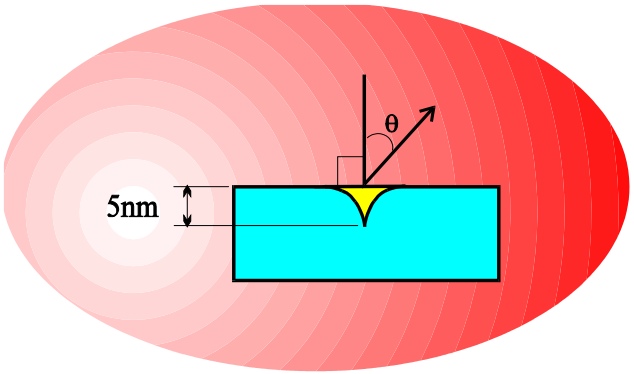
Adjunct Research Professor, Department of Mechanical and Materials Engineering, Western University

SURFACE SCIENCE WESTERN

X-ray Photoelectron Spectroscopy







B.E. = hν - K.E. - ϕ

-surface elements

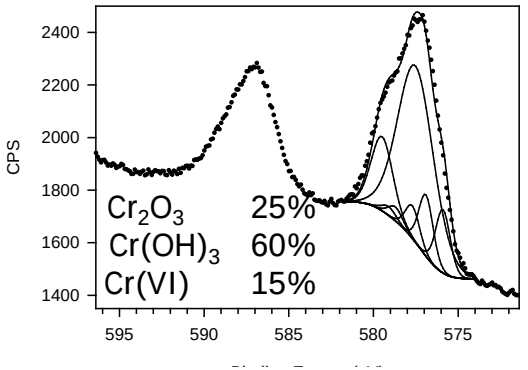
-chemical states

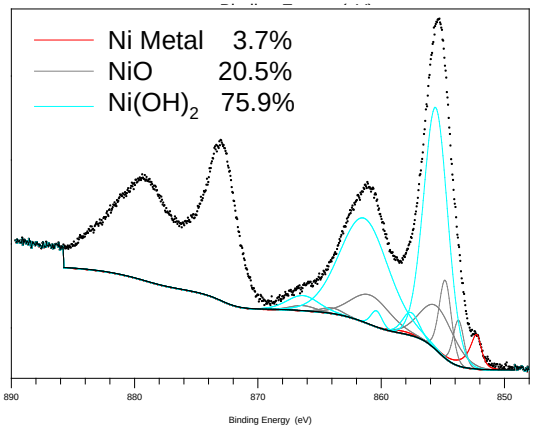
Semiconductor energy levels

SURFACE SCIENCE WESTERN

X-ray Photoelectron Spectroscopy

- Elemental and chemical state analysis of the outer surface of a solid samples
- Effective probing depth 5-10 nm
  - Varies slightly with sample composition
  - Can be varied with electron take-off (or sample) angle
- Detects elements from lithium to uranium
  - Quantitative
  - 0.01 to 0.5 atomic % detection limits
- Examples of chemical information that can be obtained
  - Metal oxides, hydroxides, carbides
  - Silicone, silica, silicon nitride or elemental silicon,
  - Fluorocarbon or fluoride,
  - Chromium 0, III or VI





SURFACE SCIENCE WESTERN

Kratos AXIS Supra Spectrometer

SURFACE SCIENCE WESTERN

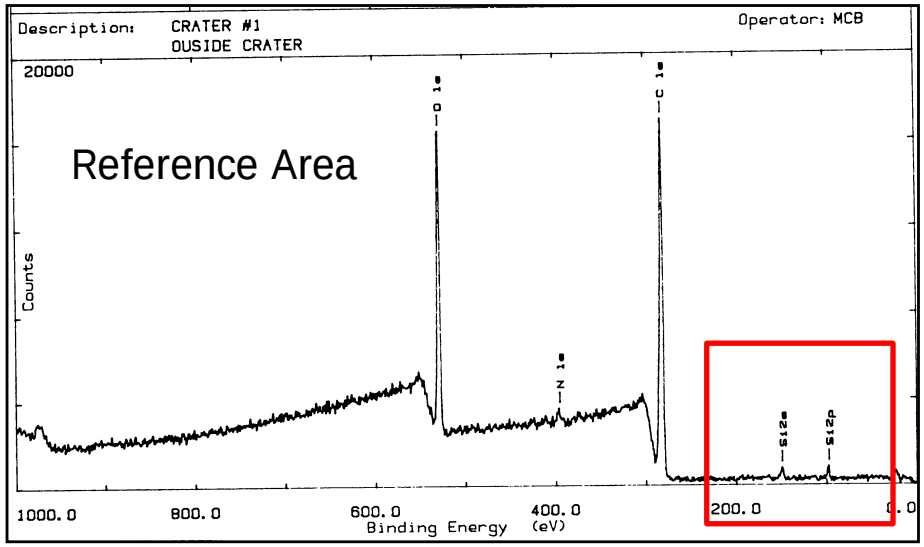
Kratos AXIS Supra Spectrometer

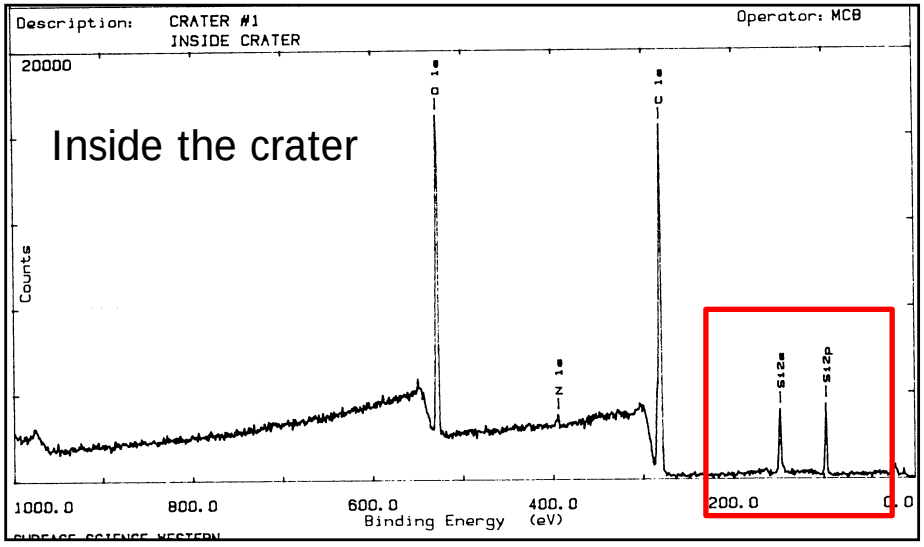
- Large area – 300x700 µm, 110, 55, 27 µm selected area spots
- Variable angle sample orientation (angle resolved analysis)
- High precision automated stage for remote or non-attended operation
- Depth profiling with both monoatomic Ar^+ and gas cluster beams (up to $Ar3000^+$)
- Interfaced to a glove box for chemical preparation under inert atmosphere
- Analysis of sample sizes up to 30 mm x 75 mm and up to 10 mm thick (can do larger samples on Nova instrument)
- Elemental and chemical imaging, small spot analysis
- Multiple X-ray sources including monochromatic Al Kα, monochromatic Ag Lα, He(I) and He(II)
- In-situ fracturing at low temperature
- Sample heating (800° C) and cooling (-100° C)
- Ion scattering spectroscopy (ISS) equipped

SURFACE SCIENCE WESTERN

XPS Analysis of Crater Defects

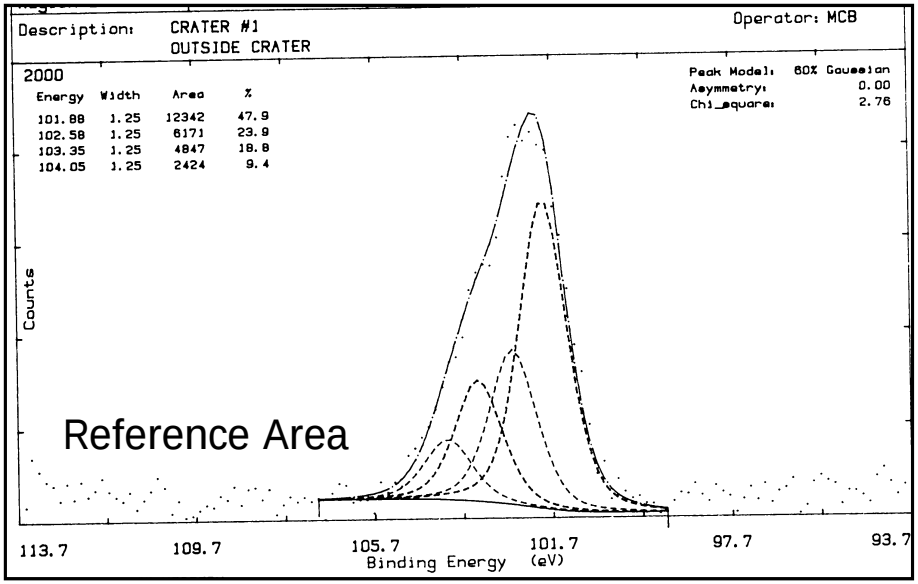
- Crater defects on a car bumper (Zenoy substrate)
- Optical and SEM/EDX analysis revealed no significant differences between the crater area and a reference area of coating
- XPS, a much more surface sensitive technique, was used.

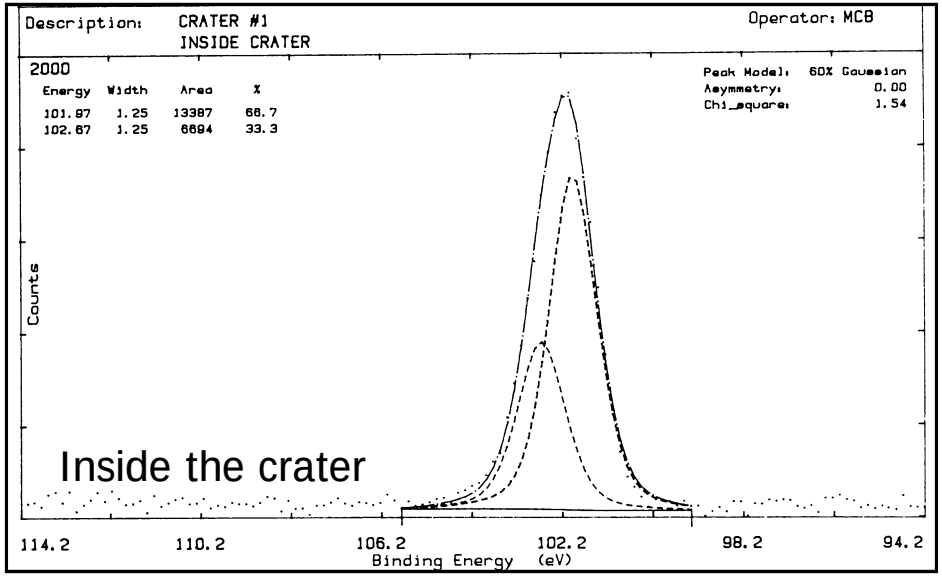




SURFACE SCIENCE WESTERN

XPS Analysis of Crater Defects



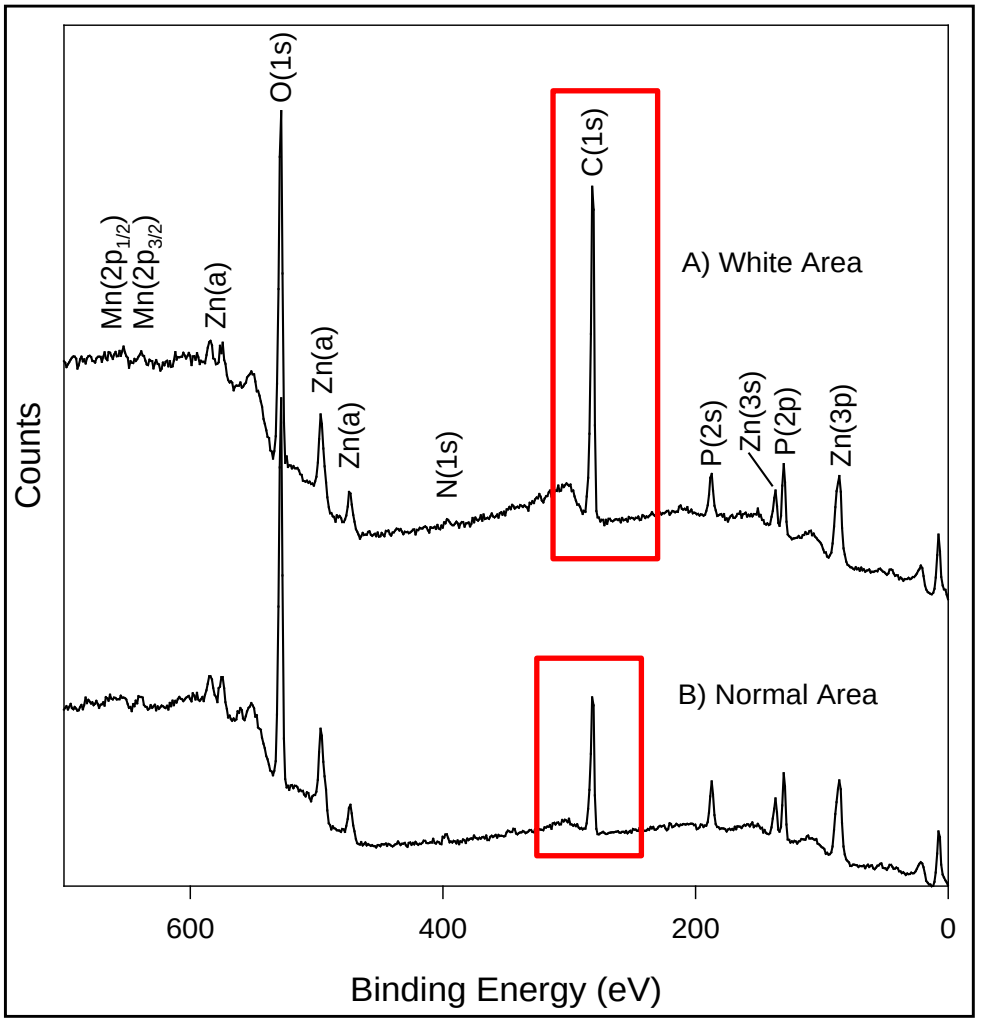


- Two species of silicon were observed on the reference area - silicone and silica
- High resolution Si 2p spectra confirmed the presence of a single species of silicon in the crater - silicone
- improper mixing of additives may be responsible for the crater formation.

SURFACE SCIENCE WESTERN

XPS Analysis of Phosphated Steel

- A customer was finding large defective areas of e-coat on a zinc plated and phosphated steel.
- It had been noticed that white areas on the unpainted phosphated steel were of roughly the same size as that of the defects.
- Analysis of the white areas by XPS showed an increase in carbon compared to a normal area of phosphate coating
- The cause of the defects was then tracked to a organic compound on the surface of the phosphated steel.



SURFACE SCIENCE WESTERN

Estimation of Oxide Thickness

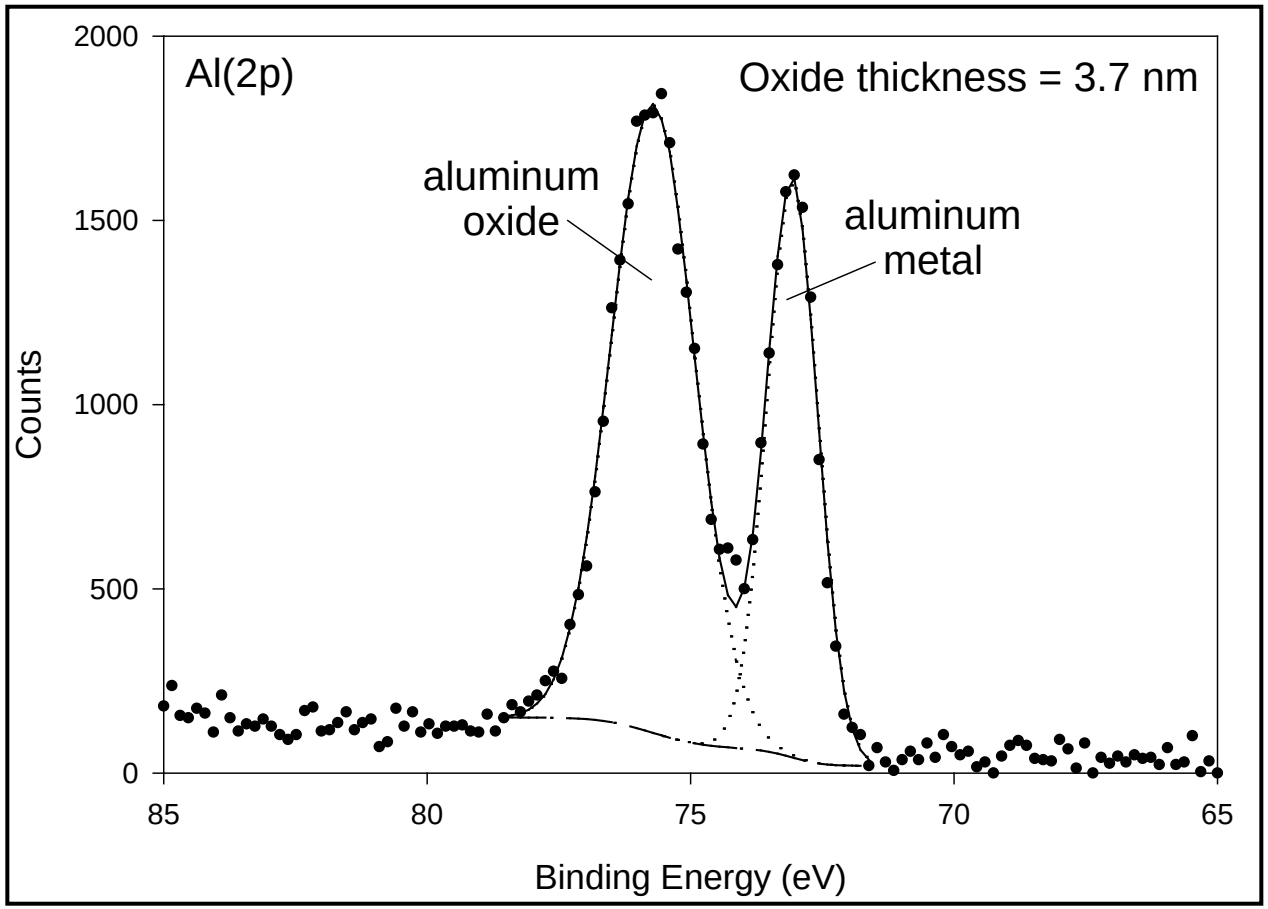
- Usually, the binding energies of the oxide and the metallic species are separated by a few electron volts.
- Thus, when the oxide is thin (< 9 nm), it is possible to distinguish the contribution from both oxide and metal photoelectrons.
- For aluminum, oxide thickness (d) is given as:

$$d\ (nm) = 2.8 \ln ((1.4(I_o/I_m))+1)$$

  - where I_o and I_m are the intensities (peak areas) of the oxide and metal photoelectron peaks respectively.

SURFACE SCIENCE WESTERN

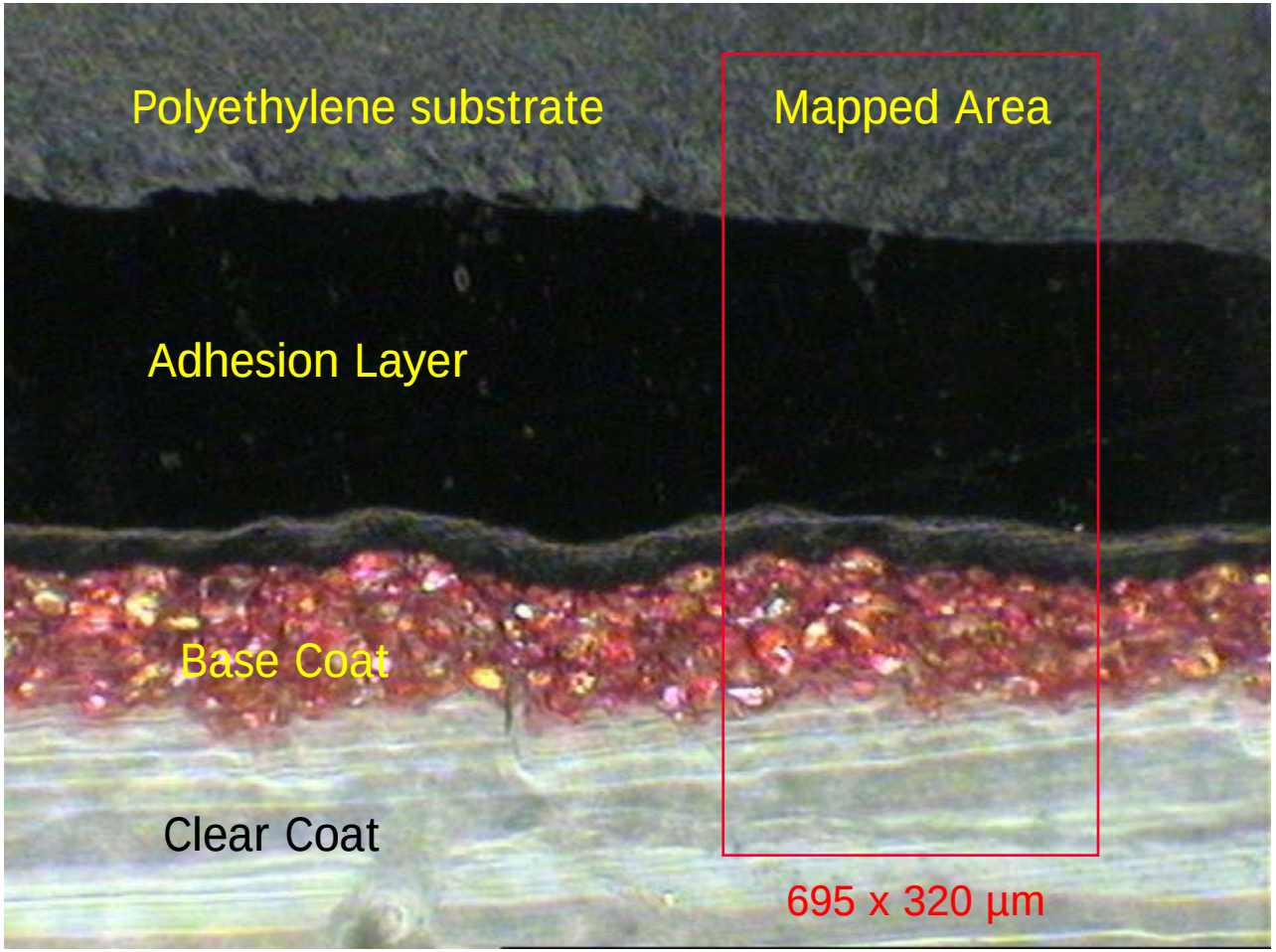
Estimation of Oxide Thickness



High resolution Al 2p spectrum of an aluminum surface. The aluminum metal and oxide peaks shown can be used to determine oxide thickness, in this case 3.7 nm

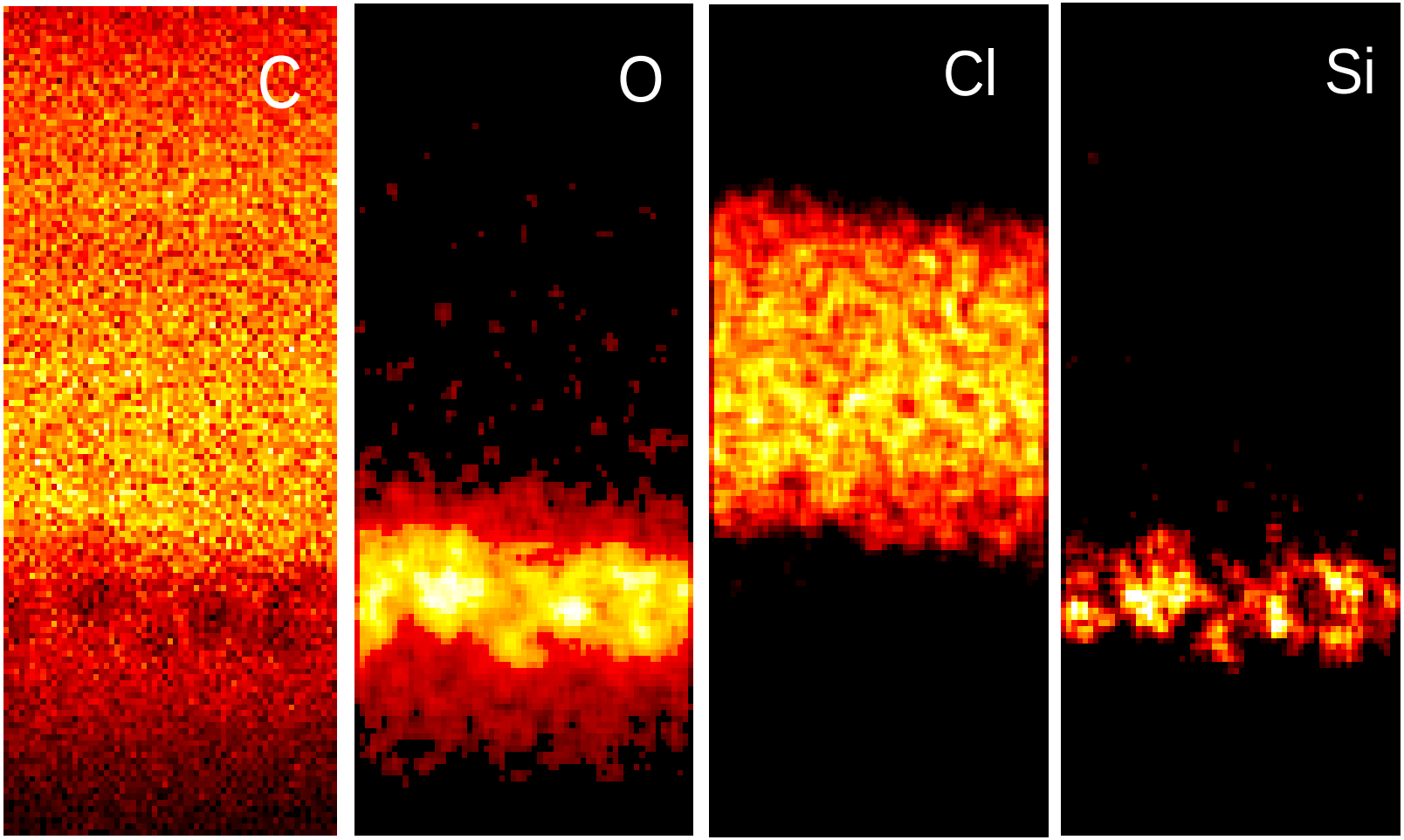
SURFACE SCIENCE WESTERN

XPS Imaging – Paint Cross-Section



SURFACE SCIENCE WESTERN

XPS Imaging – Paint Cross-Section

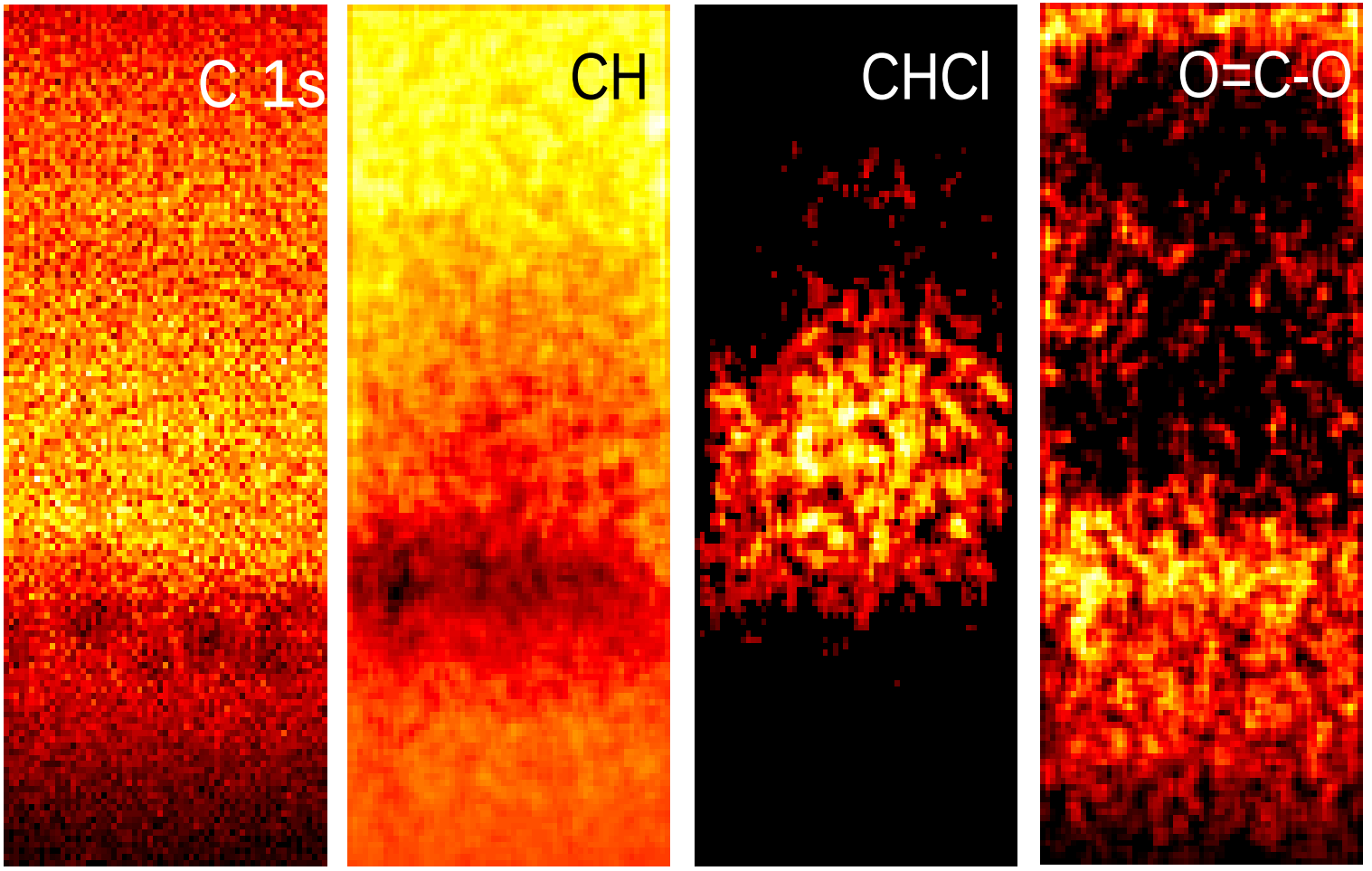


695 x 320 µm

Elemental XPS Maps using C 1s, O 1s, Cl 2p and Si 2p signals

SURFACE SCIENCE WESTERN

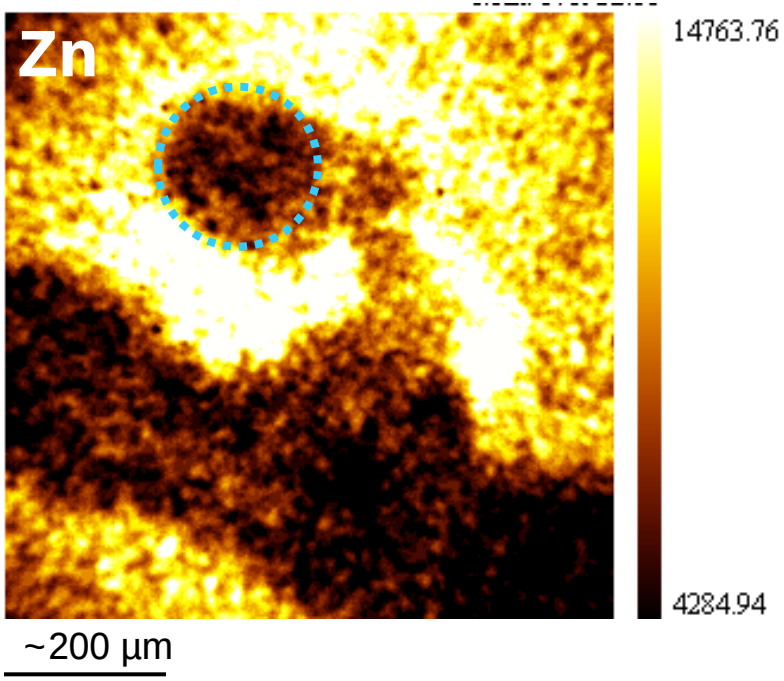
XPS Imaging – Paint Cross-Section



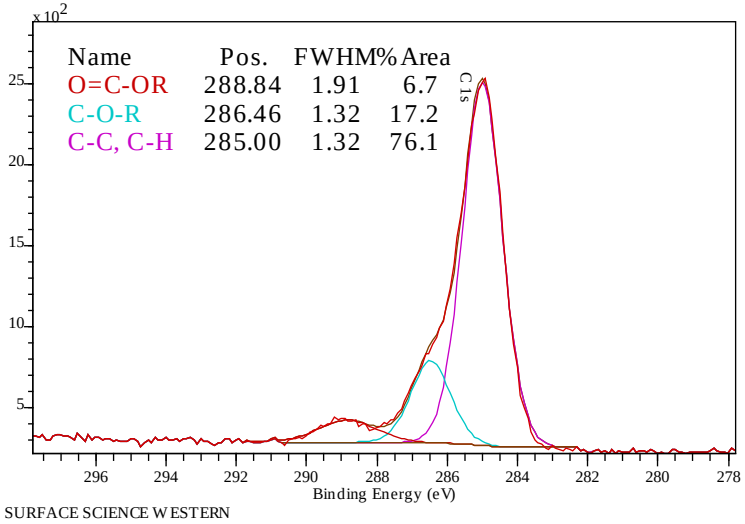
695 x 320 µm

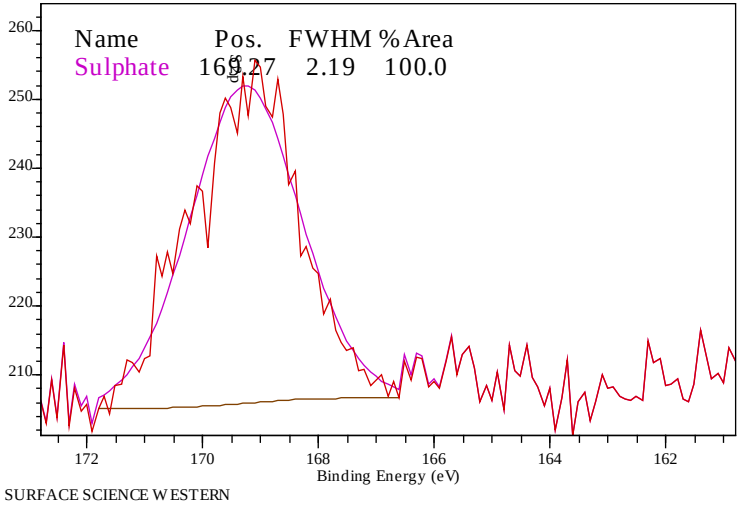
C 1s Chemical State Maps

XPS Spot Mode From Images



Zinc $2p_{3/2}$ Photoelectron Image
Corrosion Test Panel





XPS C 1s and S 2p high resolution spectra collected from a 220 µm spot.

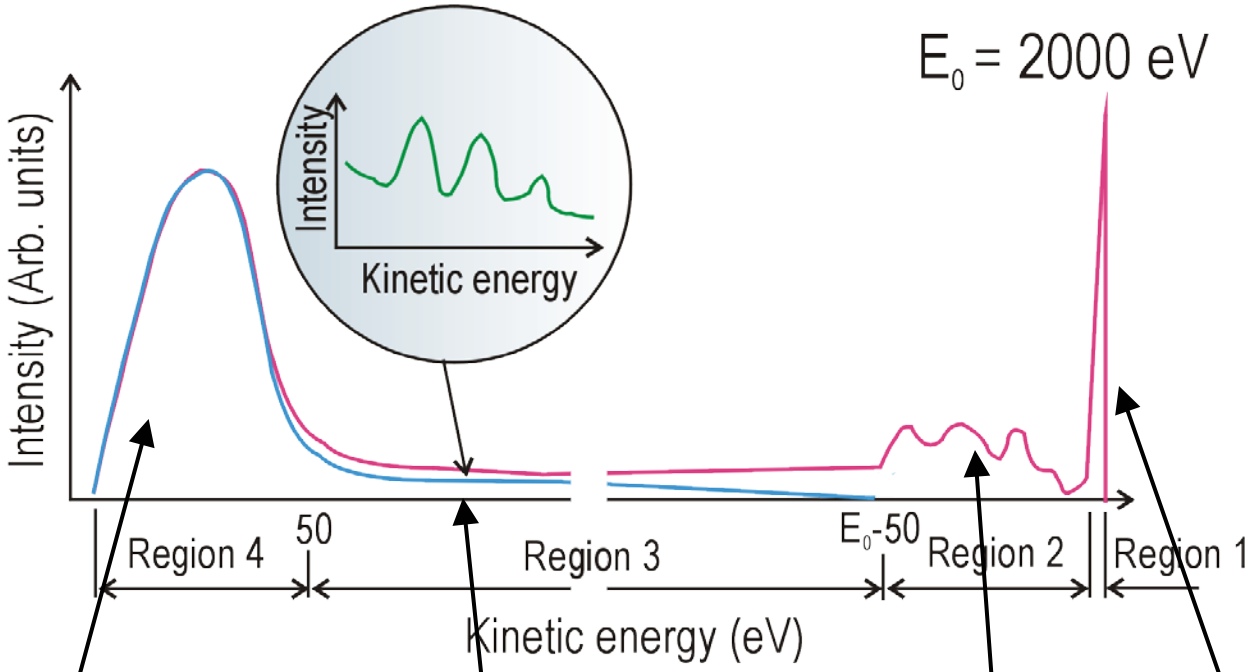
SURFACE SCIENCE WESTERN

XPS Summary

- Elemental and chemical state information from the outer 5-10 nm of a solid surface
- Most of solid samples can be analyzed
- Quantifiable
- All elements detectable except H and He with detection limits of 0.01 to 0.5 at. %
- Imaging and depth profiling of elements and/or chemical states

SURFACE SCIENCE WESTERN

Auger Electron Spectroscopy



"True secondaries" or slow peak (electrons which have undergone a number of collisions).

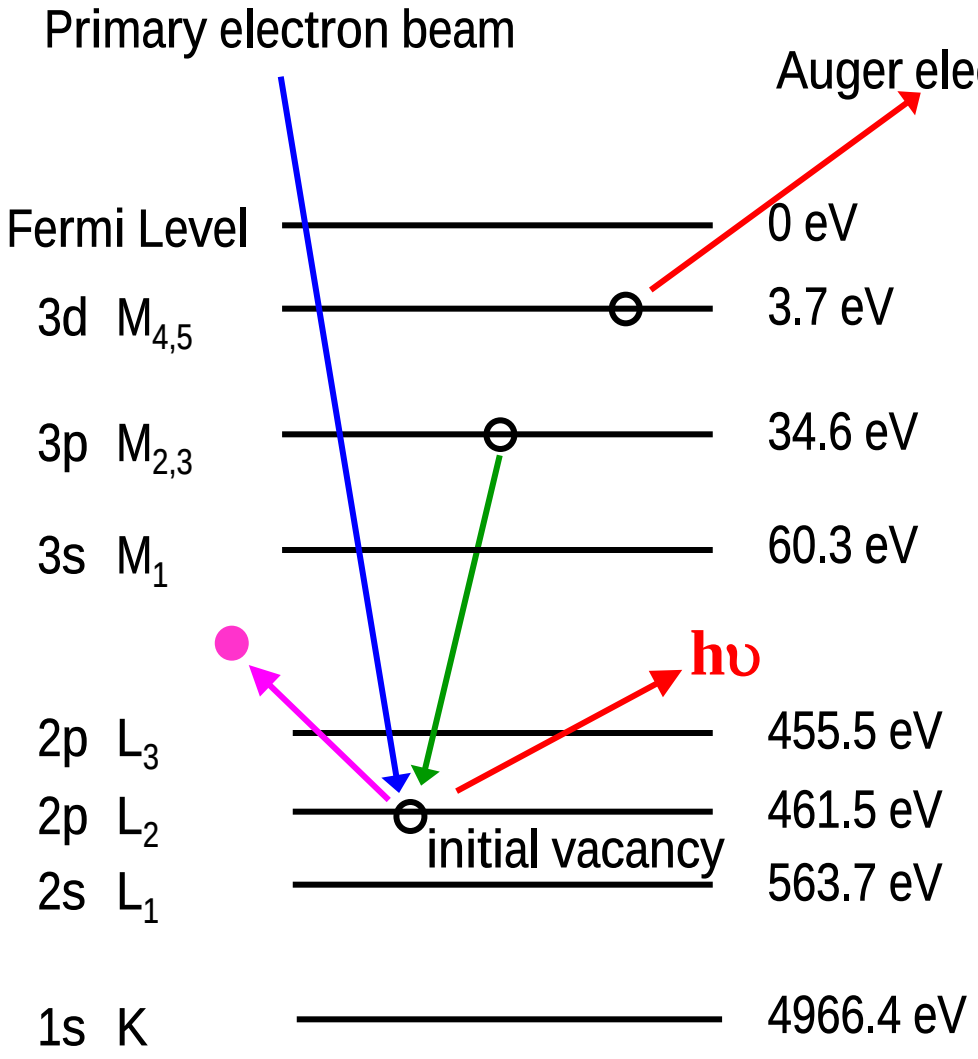
Auger peak (doesn't shift with E_p)

Plasmon loss peak (energy loss from excited plasma vibrations)

Elastic peak (electron reflected with almost no loss of energy)

SURFACE SCIENCE WESTERN

Auger Electron Spectroscopy

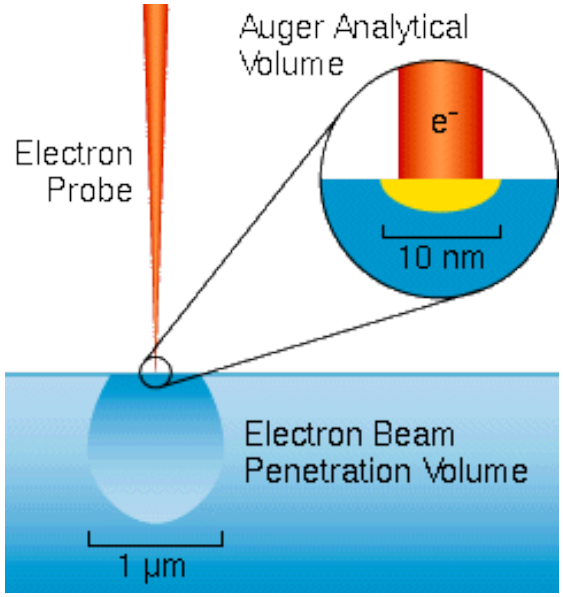


For Titanium:

$E_{Auger} \approx E_{L2} - E_{M2,3} - E_{M4,5}$

$\approx 461.5\ eV - 34.6\ eV - 3.7\ eV$

$\approx 423.2\ eV$



Also known as Scanning Auger Microscopy (SAM)

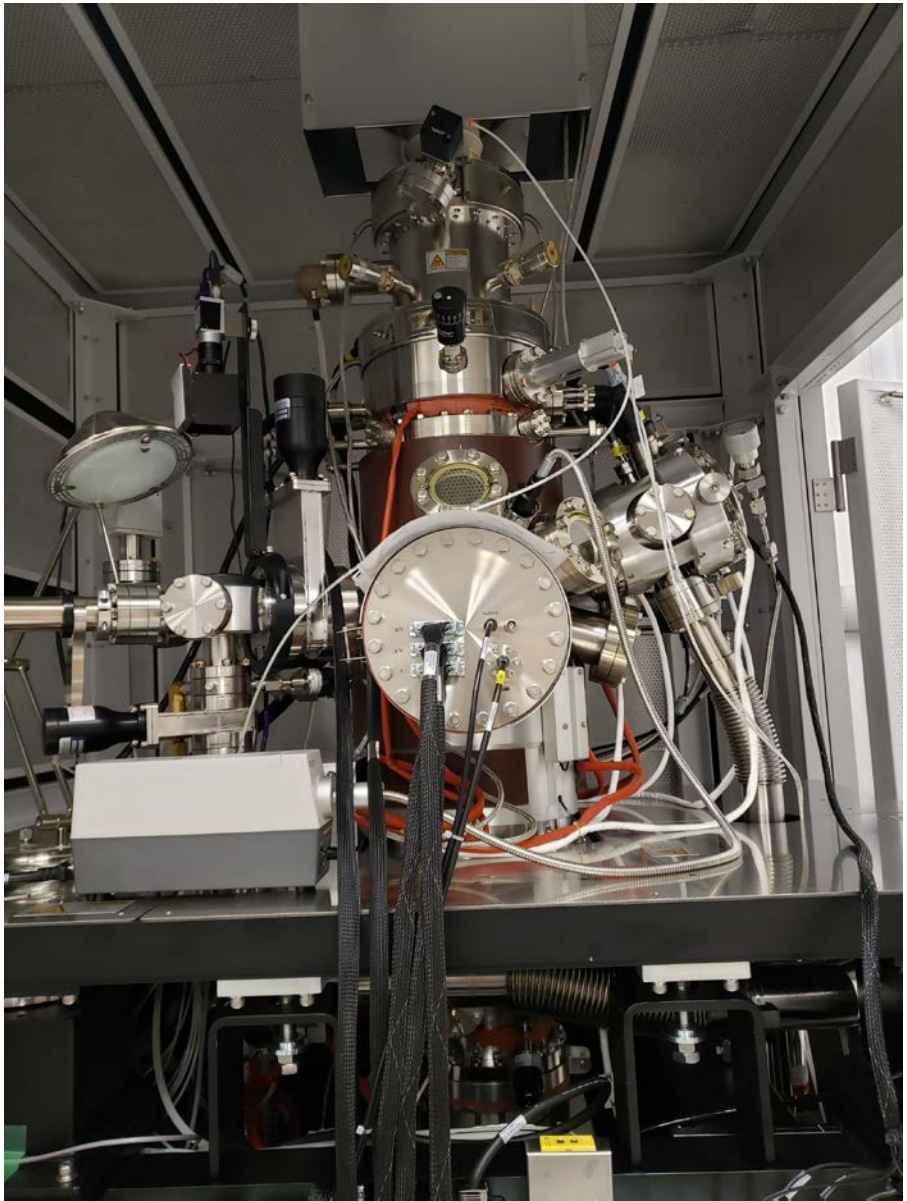
SURFACE SCIENCE WESTERN

Auger Characteristics

- Depth probed: 0.5 - 5 nm (typically 0.5- 3 nm)
- All elements except H and He
- Non-destructive, except to electron beam sensitive materials and during depth profiling
- Elemental analysis, semi-quantitative without standard; quantitative with standards
- Absolute sensitivity: 0.1 at. % (1000 ppm) or lower for most elements, depending on the matrix
- Small spot analysis
- Line scans
- Depth profiling in combination with ion beam sputtering
- Imaging/mapping due to scanning system
- Vacuum (UHV) compatible samples

SURFACE SCIENCE WESTERN

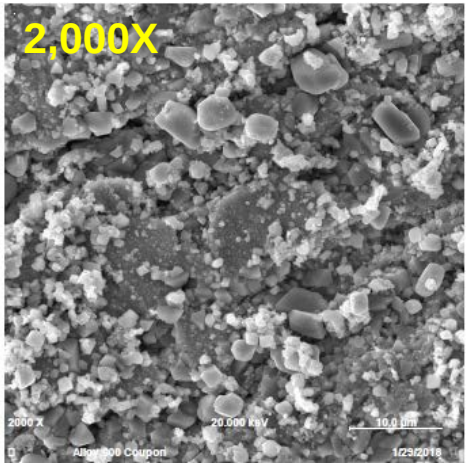
PHI 710 Scanning Auger Nanoprobe



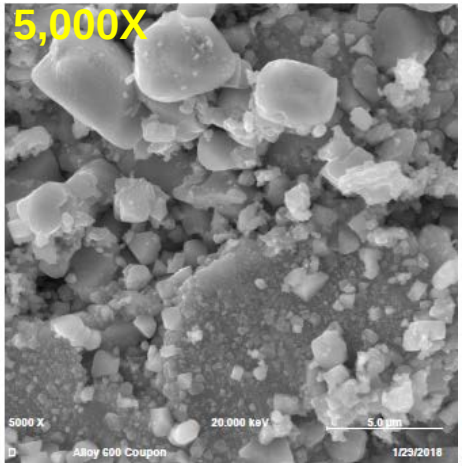
- 25 kV Schottky thermal field emission electron source
- ~ 4 nm SE dark space resolution (25 kV, 1 nA)
- ~ 8 nm Auger spatial resolution (20 kV, 1 nA)
- 8 channel coaxial cylindrical mirror analyzer (eliminates topography induced artifacts)
- High Energy Resolution Mode – enables chemical state analysis
- Floating column argon ion gun - surface cleaning, depth profiling, and charge neutralization
- In-situ parking and fracture stage

Oxidized Alloy 600 Coupon

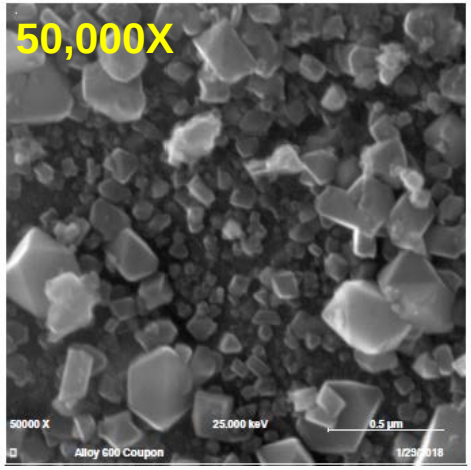
- Alloy 600: (~ 70% Ni, 15% Cr and 10% Fe)
- Exposed to a high temperature and high-pressure autoclave for ~10 years.
- Contains crystals/deposits on surface ranging from a few µm to a few nm.



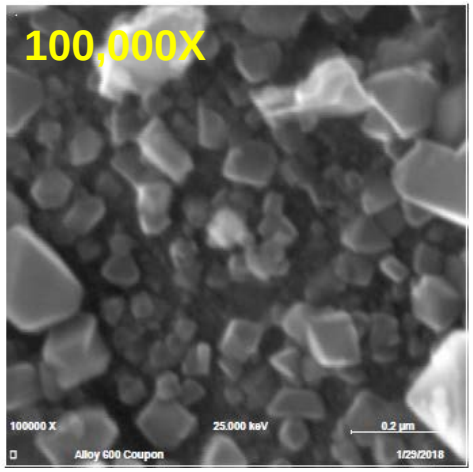
10 µm



5 µm



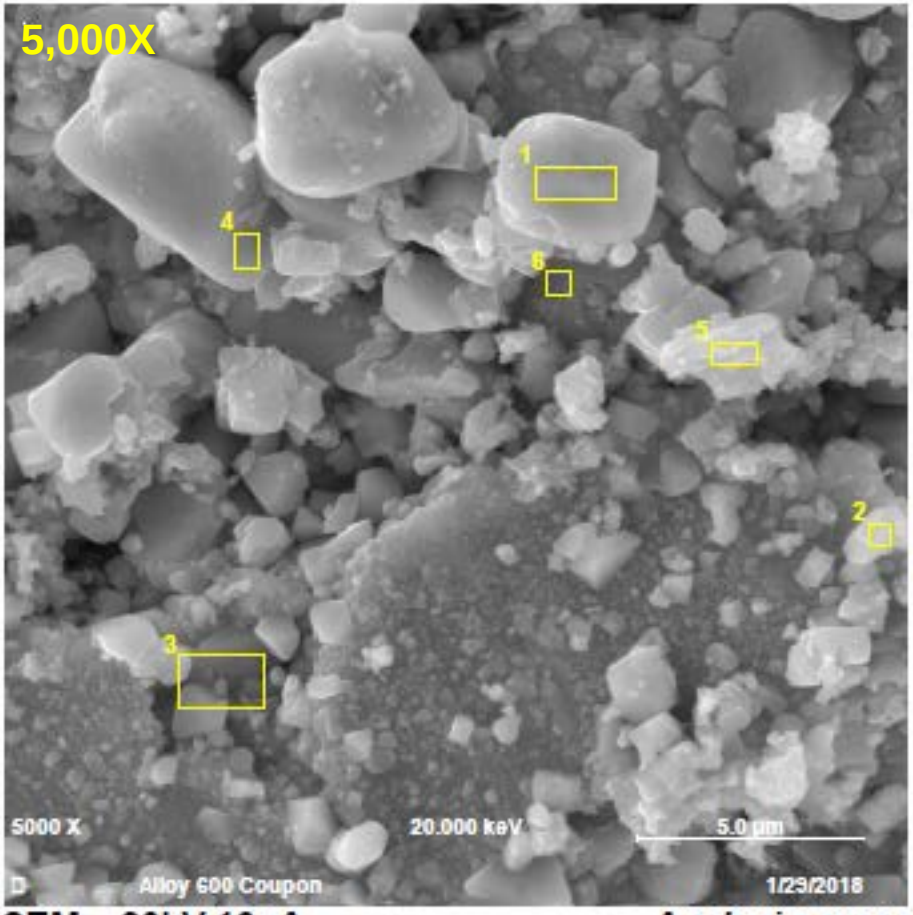
500 nm



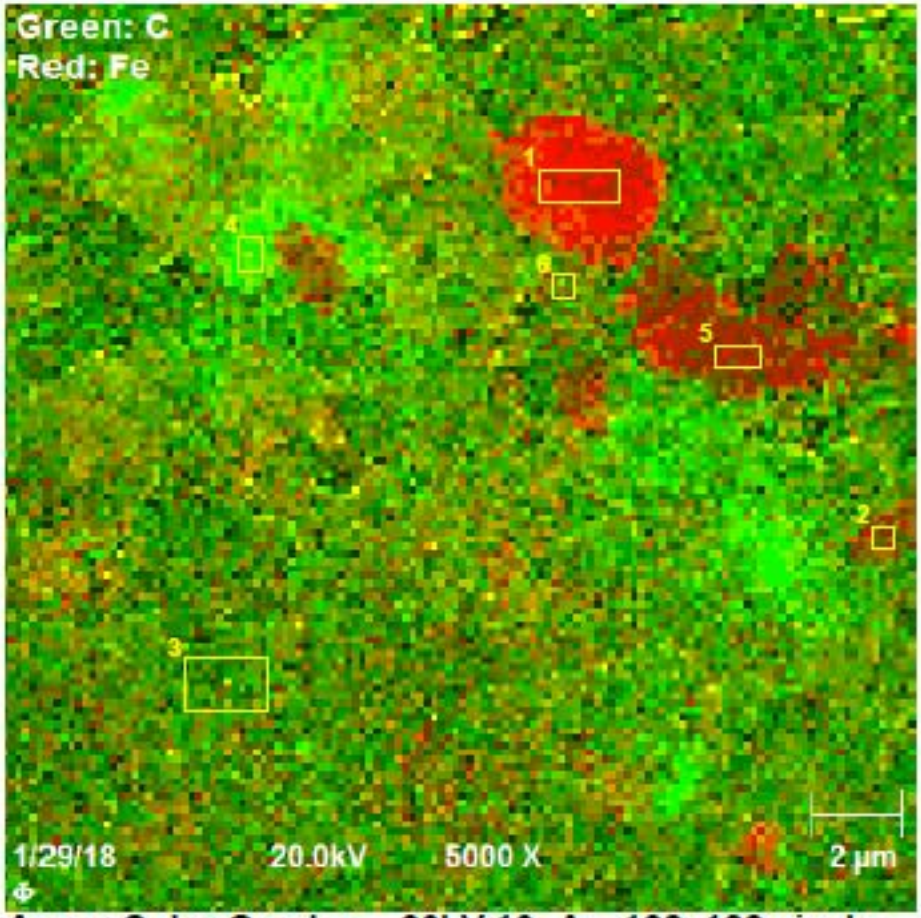
200 nm

SURFACE SCIENCE WESTERN

Oxidized Alloy 600 Coupon



SEM 20kV 10nA *Analysis areas*



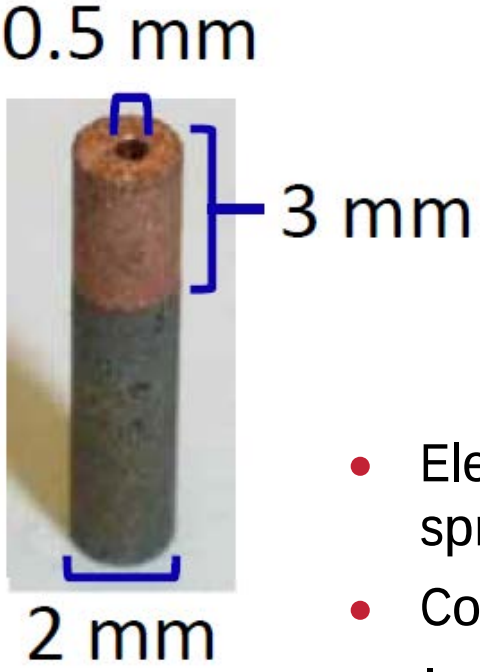
Auger Color Overlay 20kV 10nA 128x128 pixels
Green: C Red: Fe

Analysis Area Selection:

Area 1: "High" Fe
Area 2: "High" Ni
Area 3: "High" Al
Area 4: "High" C
Area 5: "High" Cr
Area 6: "High" S

SURFACE SCIENCE WESTERN

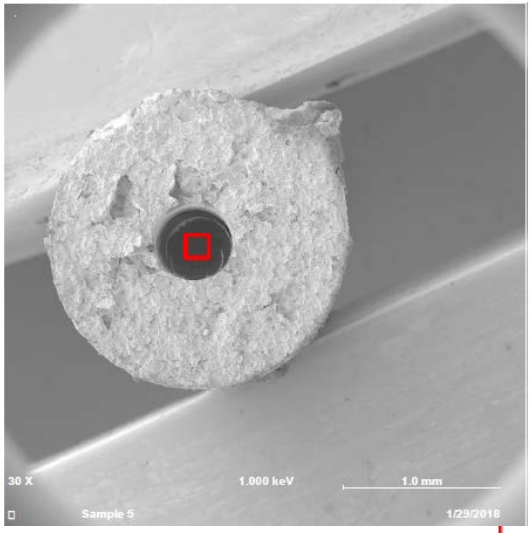
Copper Coated Steel

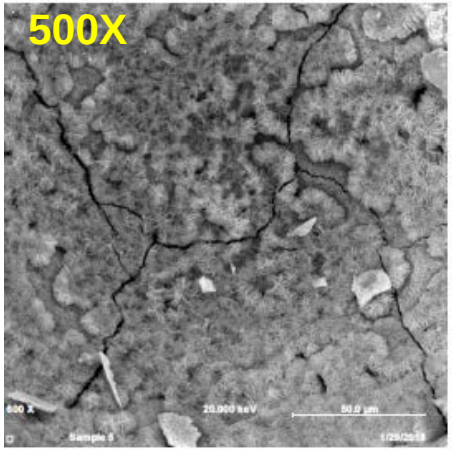


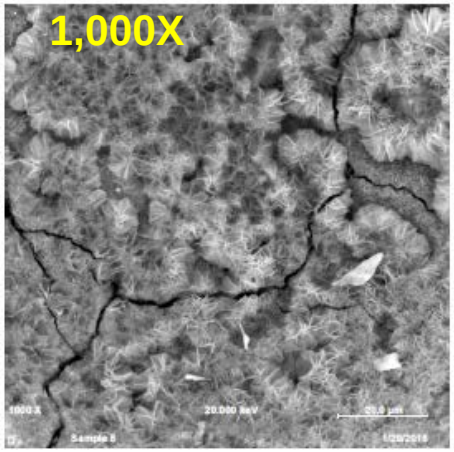
- Electrodeposited Cu on steel, with the upper cold spray Cu broken off (~ 0.2 mm Cu left on steel)
- Corroded 38 hours in oxygenated 3 M NaCl
- Iron(III) oxides (α-/β-/γ-FeOOH, γ-Fe_2O_3) are expected to be present inside the hole

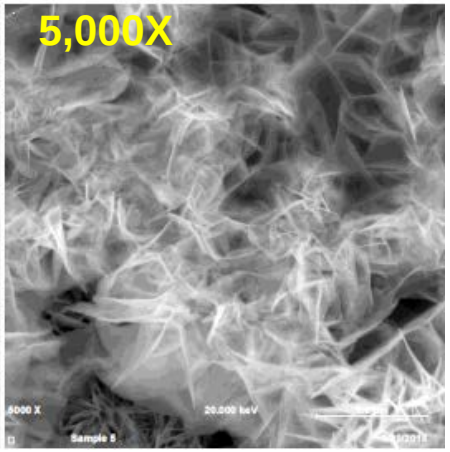
SURFACE SCIENCE WESTERN

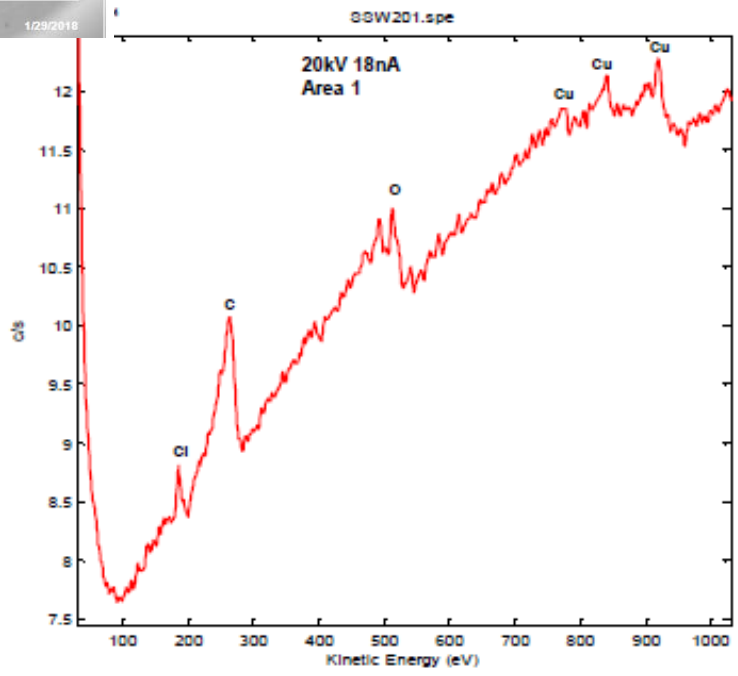
Copper Coated Steel

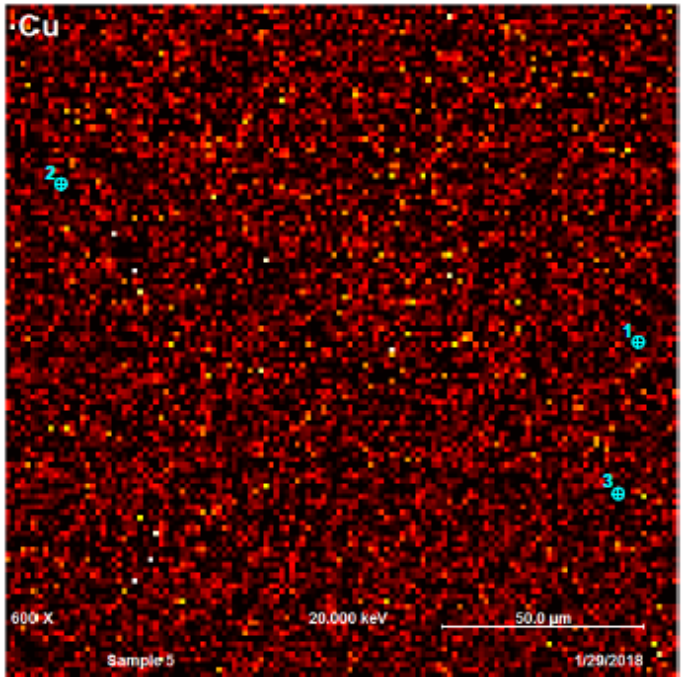






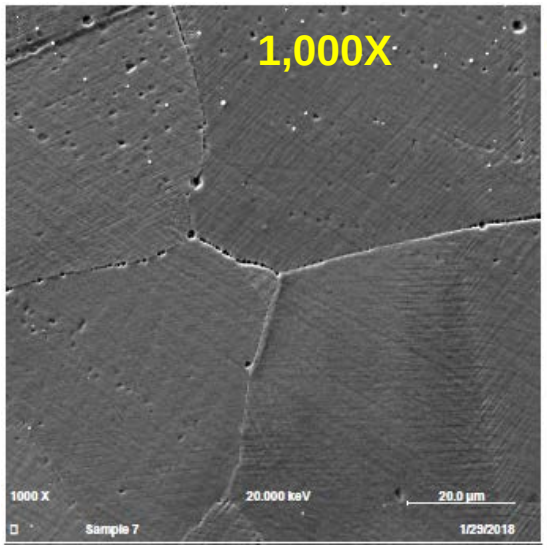


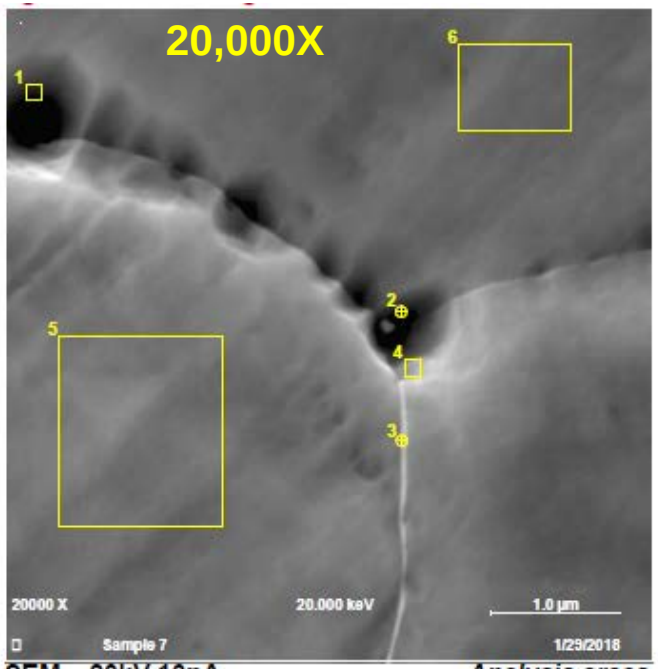




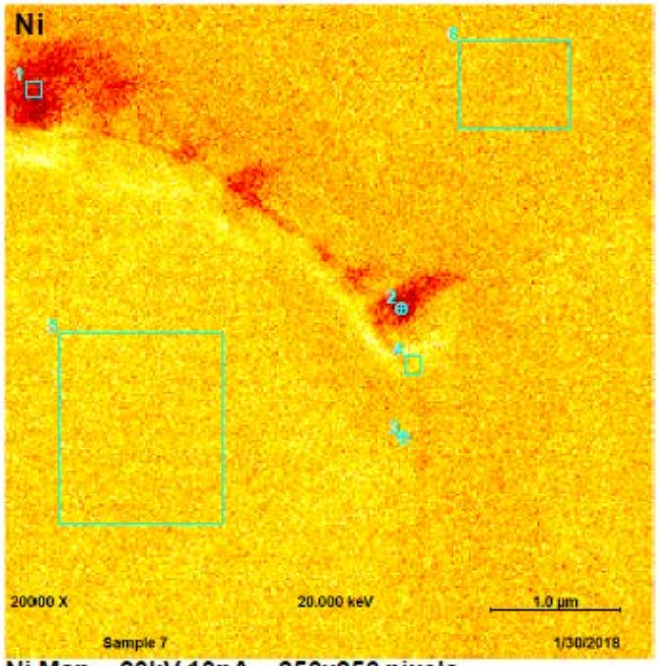
Hastelloy G-35 Coupon

- 58% Ni, 33% Cr, 8.1% Mo, 2% Fe, W, Co and other trace elements
- Sample polished to 1 µm diamond paste and exposed for 6 hours in 1 M HCl + 2 M NaCl solution at 75 °C
- AES analysis conducted to investigate corrosion at the grain boundaries





SEM 20kV 10nA *Analysis areas*

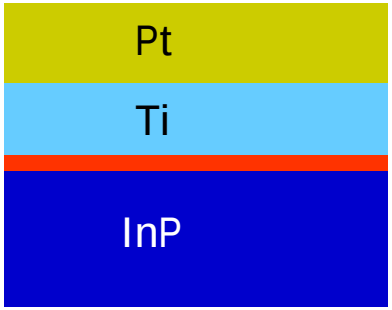


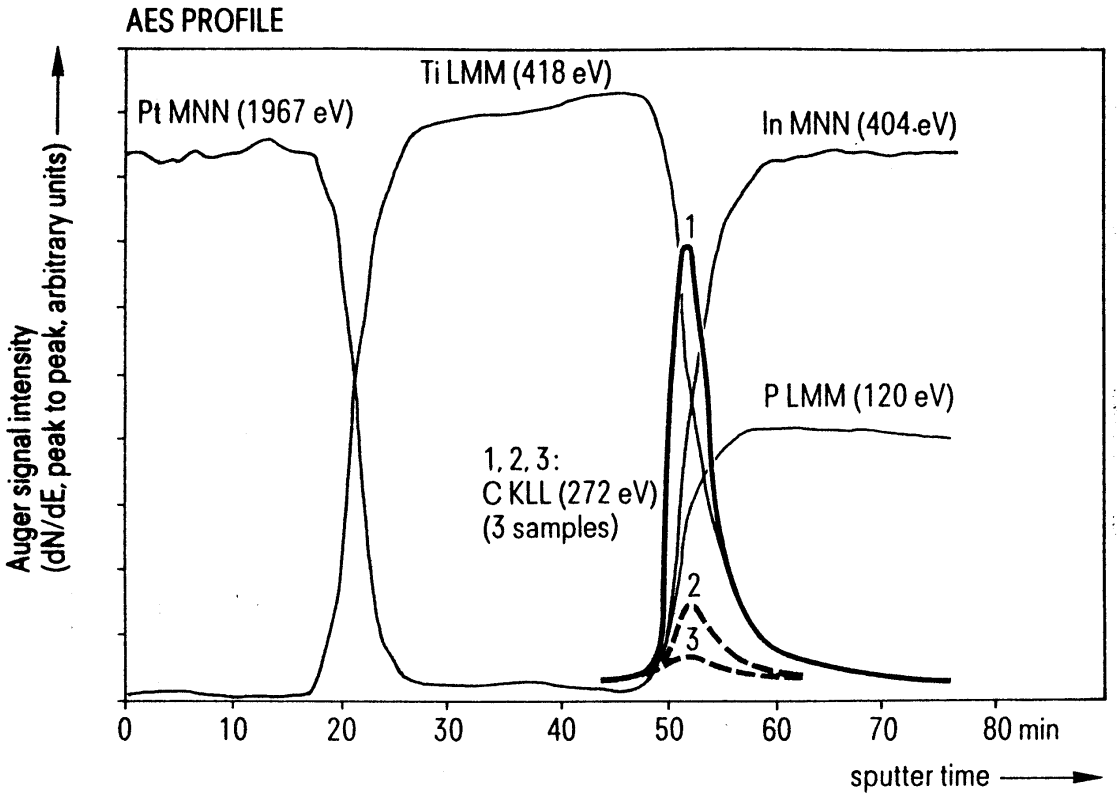
Ni Map 20kV 10nA 256x256 pixels
Thermal Pseudocolor Image *32.77 min.*

Analysis Area Selection:
Areas 1-2: "Low" Ni
Area 3: Grain Boundary
Area 4: "High" Mo
Area 5: Slightly Higher Ni
Area 6: Slightly Higher Cr & Mo

Auger Depth Profiling

Pt/Ti/InP Sample





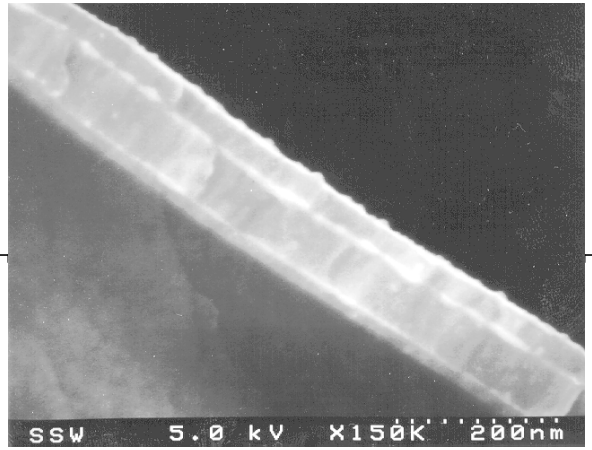
For each element, an Auger peak is selected for acquiring its intensity at each depth.

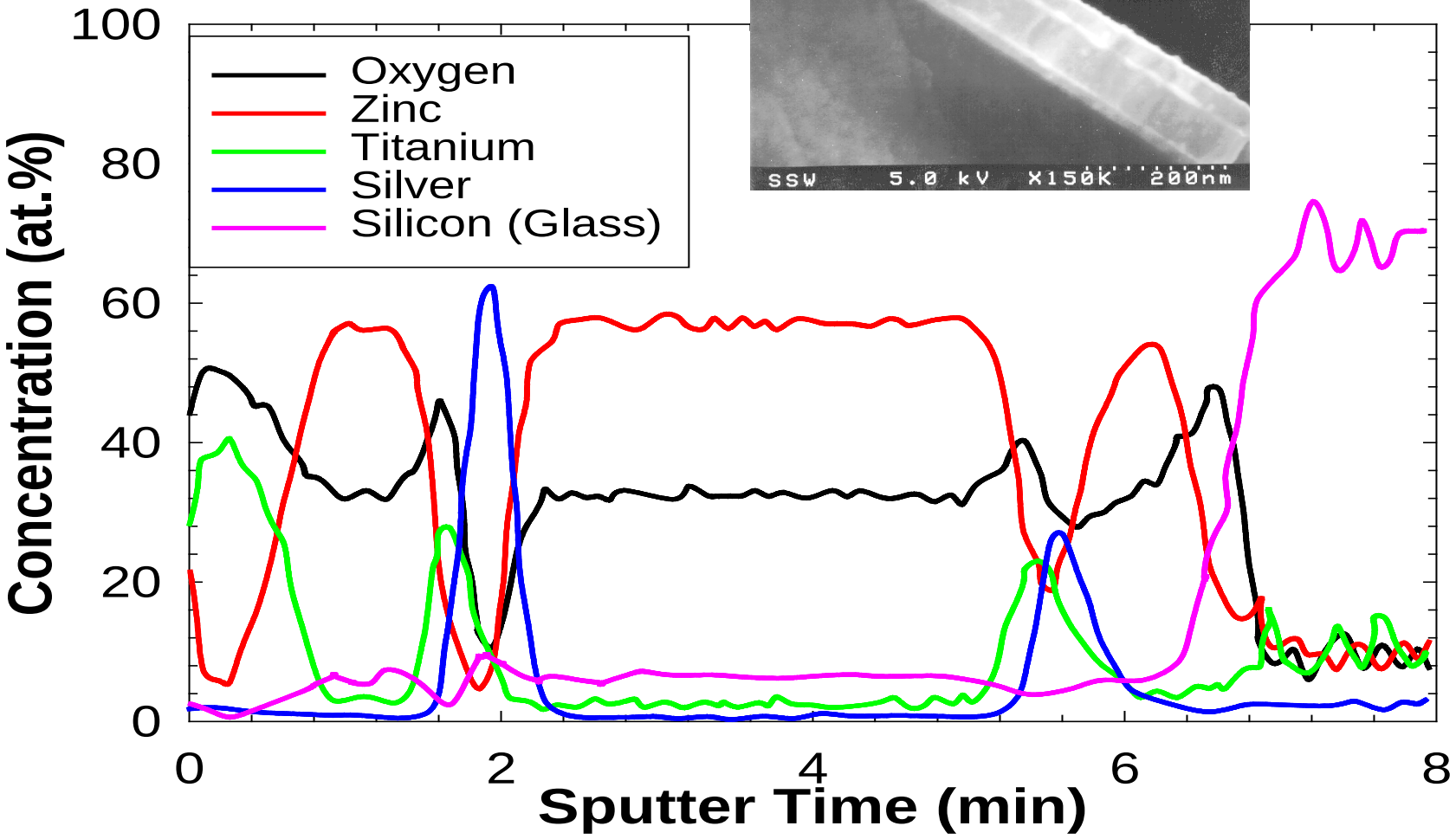
Pt: MNN at 1697 eV
C: KLL at 272 eV
O: LMM at 120 eV
Ti: LMM at 418 eV
In: MNN at 404 eV

Carbon contamination at the interface

SURFACE SCIENCE WESTERN

Auger Depth Profiling





SURFACE SCIENCE WESTERN

Auger Summary

- Very high spatial resolution (~ 10 nm) for Auger analysis, from the outer 2-3 nm of sample surface
- Much smaller analysis volume compared to SEM/EDX
- Elemental composition and some chemical state information
- Relatively high sensitivity for lower z elements
- Depth profiling, mapping, small spot analysis, and line scans

SURFACE SCIENCE WESTERN

Thank You!

SURFACE SCIENCE WESTERN

Phone: (519) 661-2173
Fax : (519) 661-3709
999 Collip Circle, LL31
The University of Western Ontario
Research & Development Park
London, Ontario, Canada N6G 0J3