Measurements and Characterization Tutorial

Surface Analysis Characterization: Fundamentals and Applications to PV

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Tutorial Outline

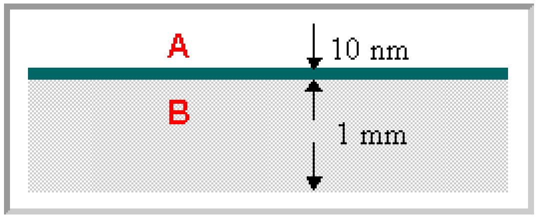
- What is surface analysis?
- What are the various surface analysis tools available within the surface analysis team?
- What is meant by surface sensitivity and why does it make surface analysis techniques unique and yet complementary to other techniques within M&C?
- Applications of the techniques toward furthering PV progress from team research projects, intra-division collaborations, industrial support/collaborations

What is Surface Analysis?

Surface analysis involves probing a sample with various chemical or physical probes and detecting the various characteristic emitted species to yield information about a surface. Typical probes include photon, electron or ion beams.

Surface Sensitivity

- Many analytical techniques used in materials characterization are “bulk” techniques in the sense that they give a composite measurement of the atoms in a sample.



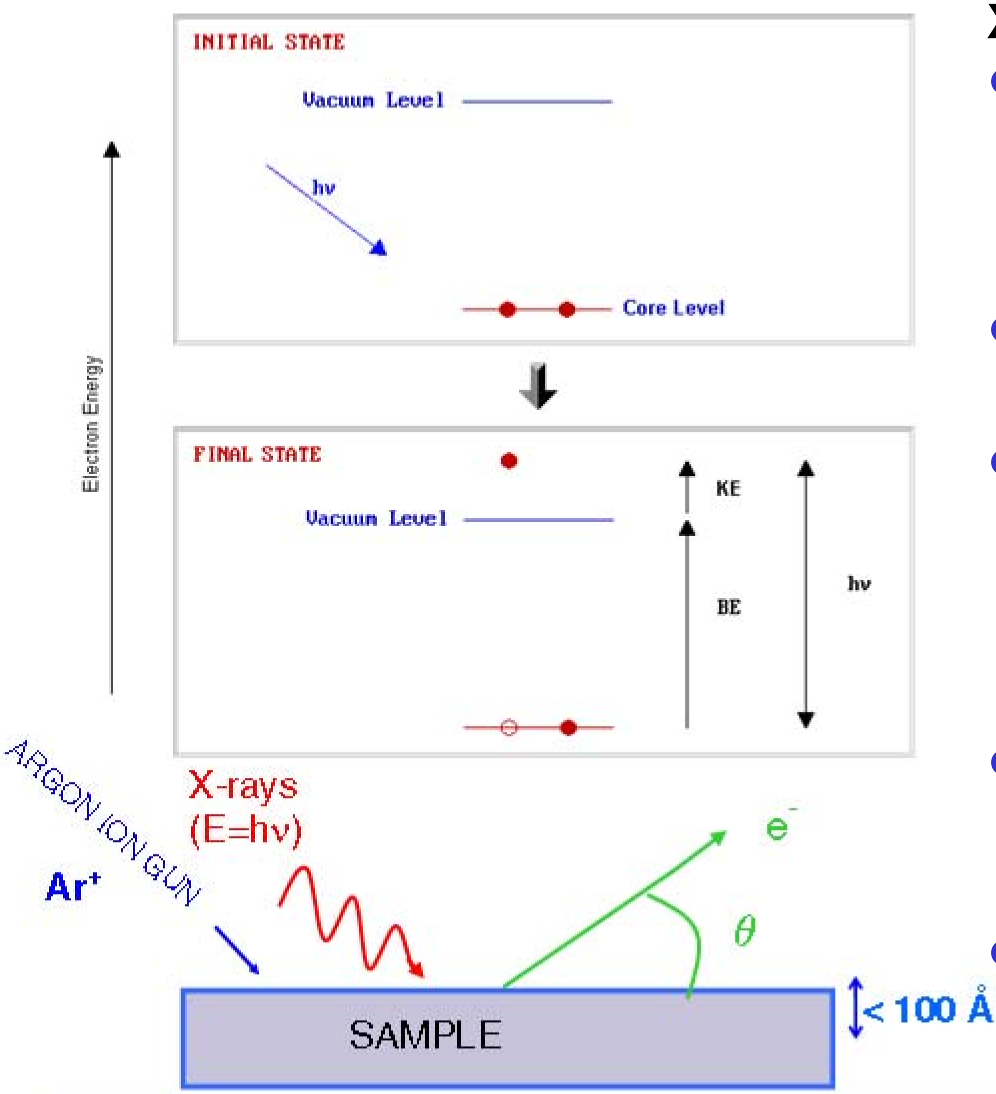
- In contrast, a surface sensitive technique preferentially provides more sensitivity to atoms near the surface than in the bulk away from the surface i.e. the majority of the signal originates from the surface region.

Surface Analysis Team Capabilities

Technique	Excitation Source/ Signal Detected	Elements Detected	Detection Limits	Depth Resolution	Lateral Resolution
Auger Electron Spectroscopy (AES)	Focused Electron Beam/ Auger Electrons	Li to U	0.5 at.%	0-100Å* *Auger electron escape depth	150Å
X-ray photoelectron Spectroscopy (XPS/ESCA)	Monochromatic X-rays/ Photoemitted electrons and Auger electrons	Li to U	0.5 at.%	0-100Å	26μm
Secondary Ion Mass Spectrometry (SIMS)	Primary Ions (Cs, O, Ar)/ Secondary Ions	H to U All elements and isotopes	To 1 pp**b** (at/cm^3)	<100Å	0.3μm
Static SIMS *or* Time-of-Flight SIMS (TOF-SIMS)	Primary Ions (Ar, Ga, O)/ Secondary Ions	H to U All elements and isotopes	To 1 pp**m** (at/cm^3)	<50Å	<0.2μm

X-Ray Photoelectron Spectroscopy (XPS)

(Photoemission Spectroscopy or ESCA (Electron Spectroscopy for Chemical Analysis)

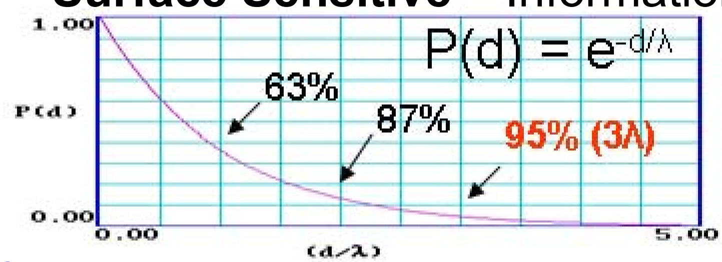


$KE = h\nu - BE - \Phi_s$

$BE = h\nu - KE - \Phi_s$

XPS Basics:

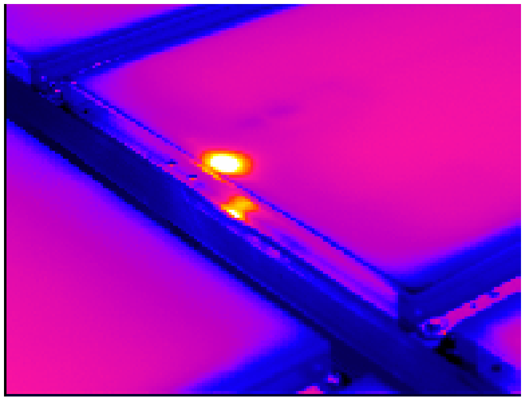
- **Qualitative and Quantitative Information** - Photoelectrons occur at binding energies characteristic of elements present and at intensities proportional to their concentrations
- **Chemical State Analysis –** BE sensitive to valence states and molecular environments
- **Surface Sensitive –** Information depth < 100Å

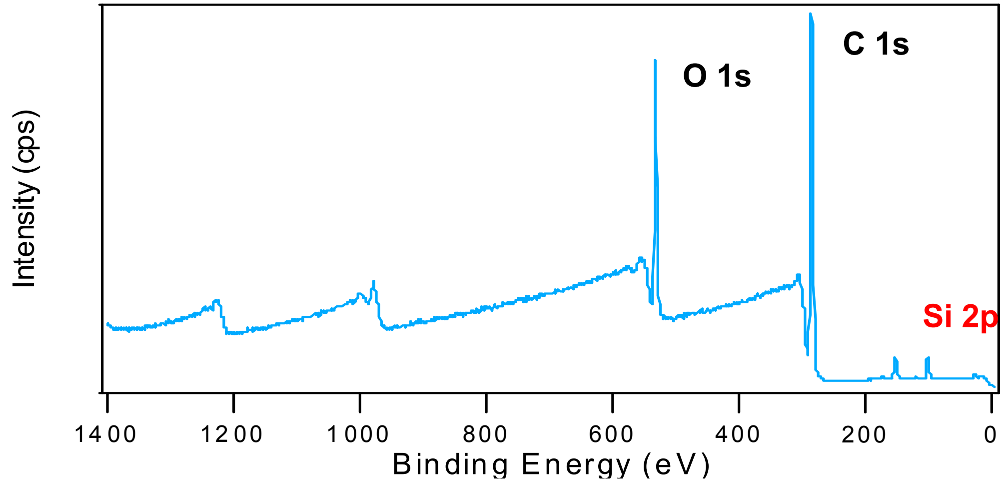


- **Angle Resolved XPS –** Grazing take-off angles enhances fraction of signal from surface confined species
- **Depth Profiling/Imaging –** Analyzer "scans" to produce images

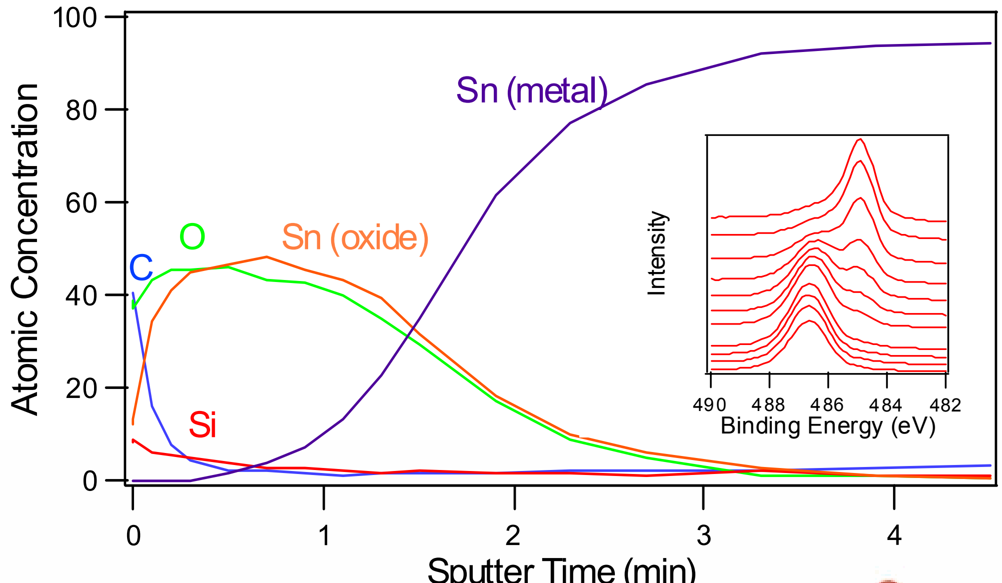
Applications of XPS to PV at NREL

- Adhesive coated buss bar material used in PV modules started to exhibit thermal hot spots in the field

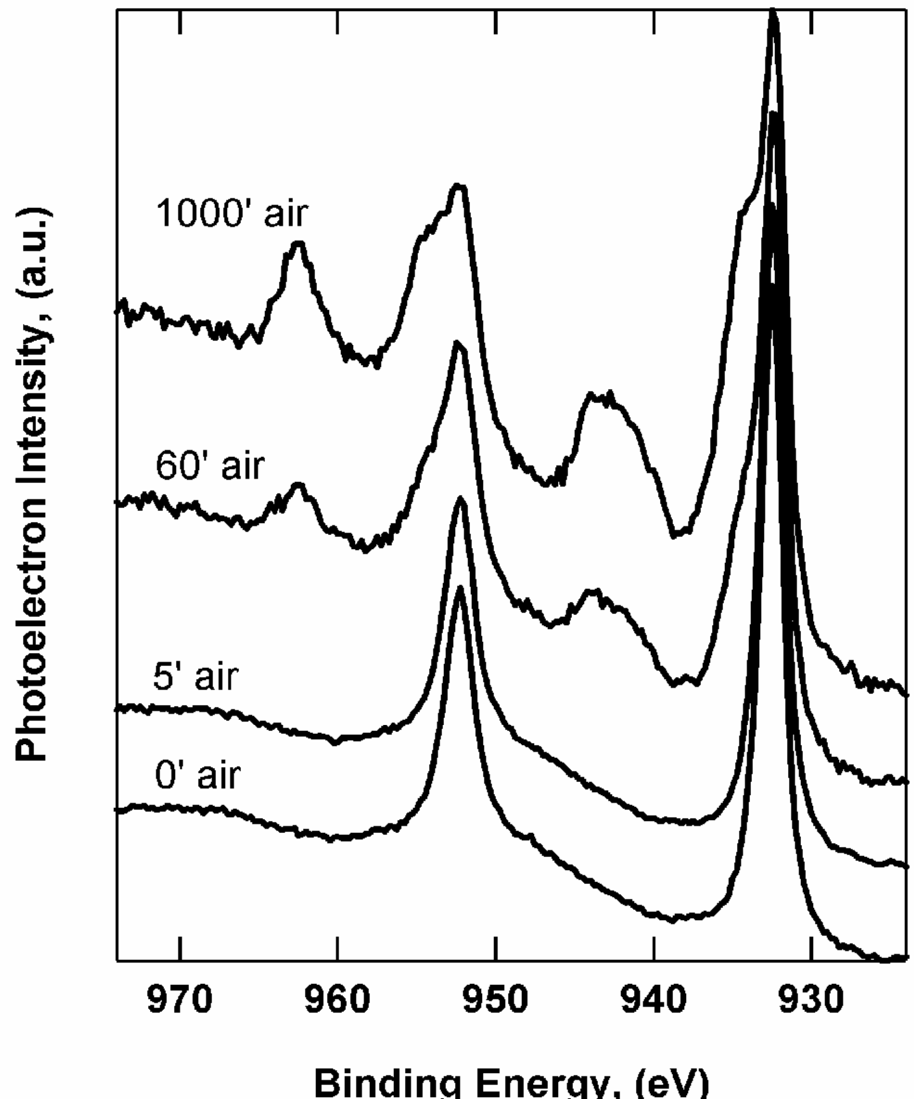




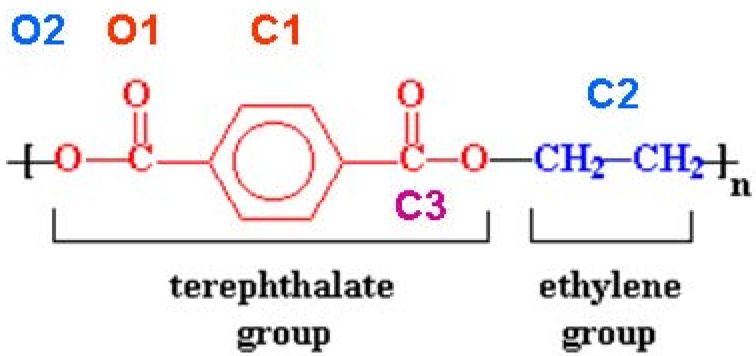
- XPS examination of new buss bar quickly shows evidence of silicone release liner transfer on adhesive side and metal side of tape
- Depth profile of metal side shows layer of silicone material on top of oxidized tin and distinguishes tin oxide from metallic tin

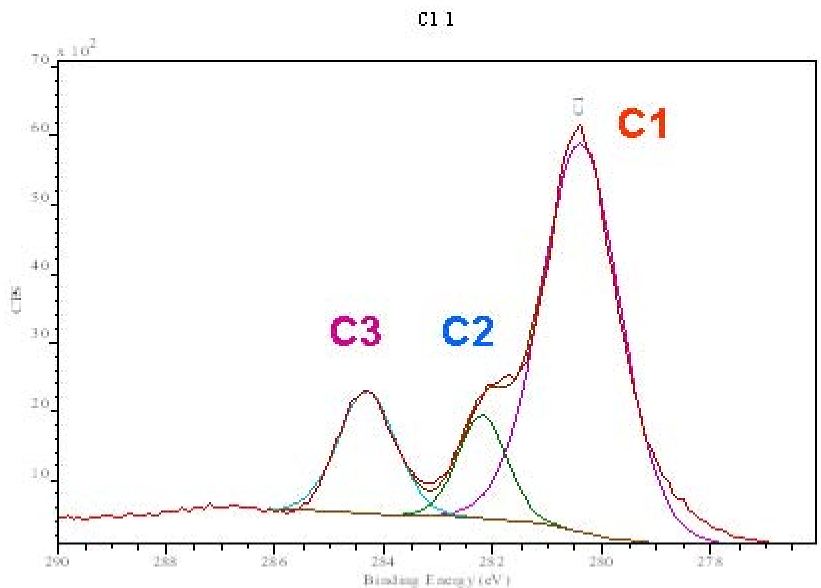


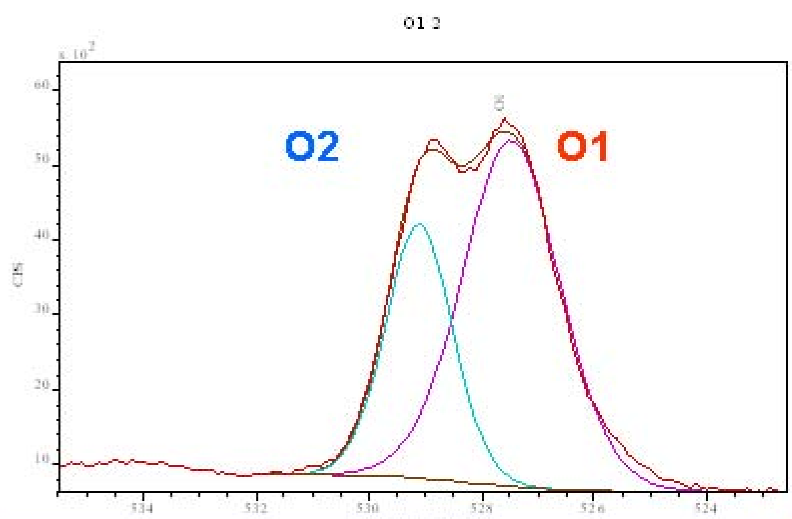
- CuInGaSe (CIGS) compounds represent an important class of PV absorber materials
- Experiments conducted using new integrated system in surface analysis lab
- Freshly etched surface using ammonia solution showed exclusive presence of Cu^{+1} but exposure to air showed gradual conversion of Cu^{+1} to Cu^{+2}



- New polymer backsheet materials under investigation for PV packaging applications
- Polyethylene terphthalate (PET):

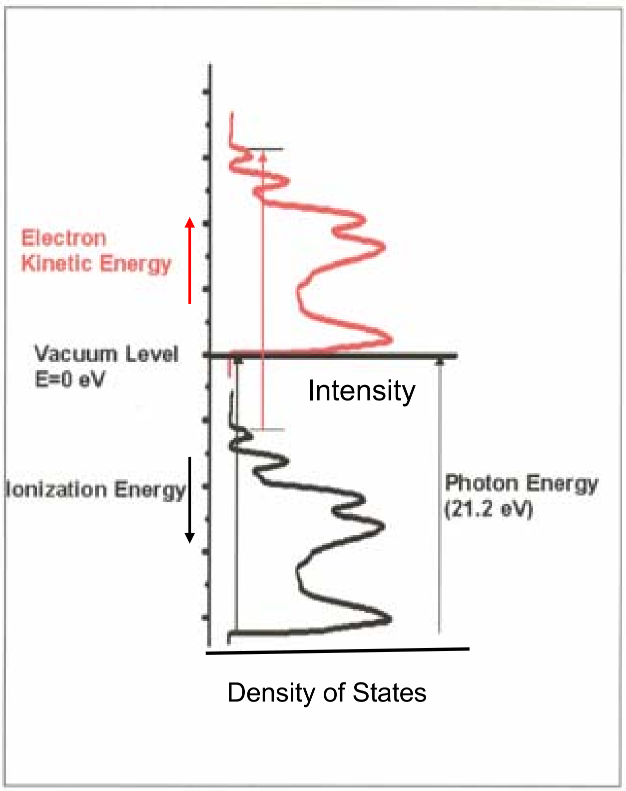






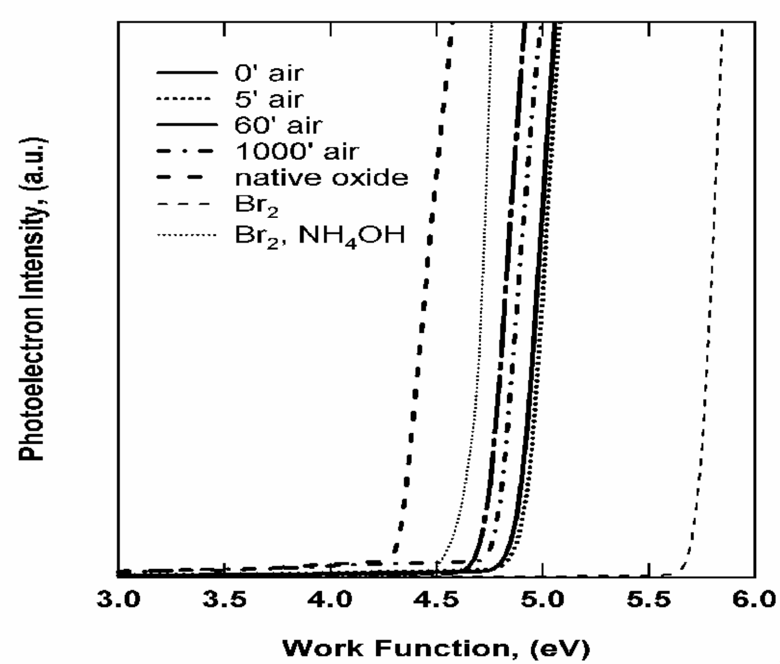
- Three clearly resolved forms of carbon and two resolved forms of oxygen evident in high resolution XPS scans
- Chemical functionalities can be altered by plasma and/or other treatments to enhance subsequent adhesion to PV encapsulants or other materials

Ultraviolet Photoelectron Spectroscopy (UPS)

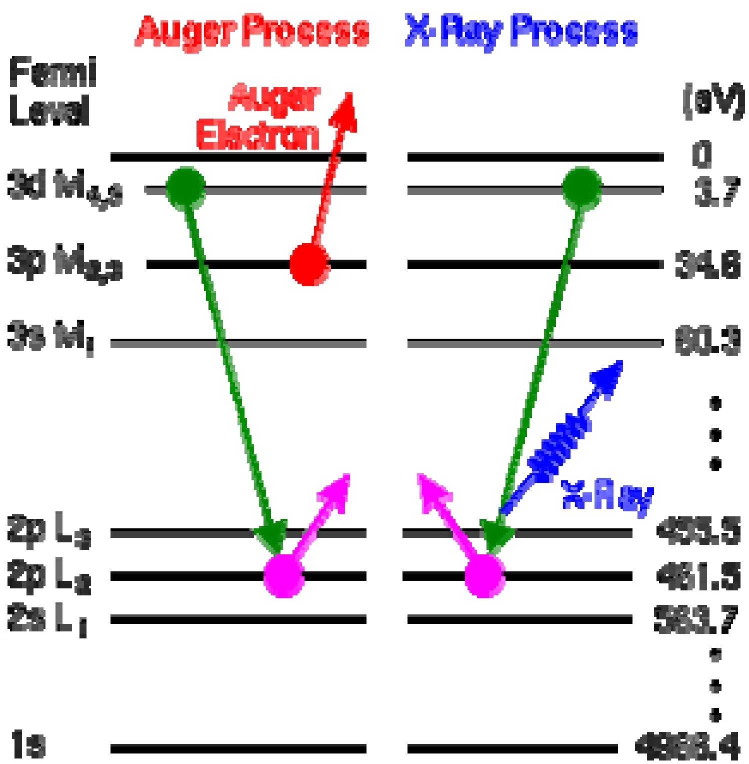


UPS Basics:

- **Chemical Bonding Information** - UPS probes only valence band energy levels and hence valence band (bonding) electrons
- **Work Function Determination –** Sensitive to surface contamination or adsorbed layers
- **Surface Sensitive –** Low mean escape depth



Auger Electron Spectroscopy (AES)



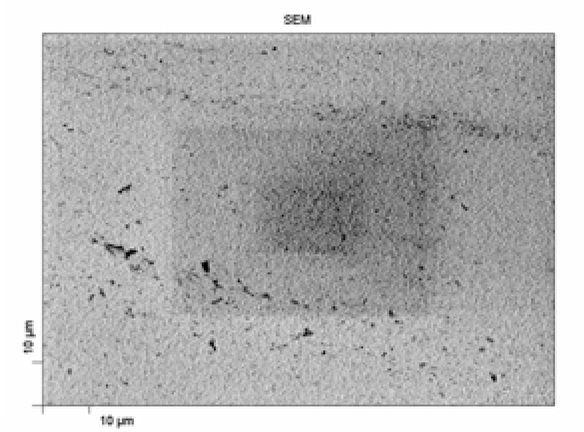
AES Basics:

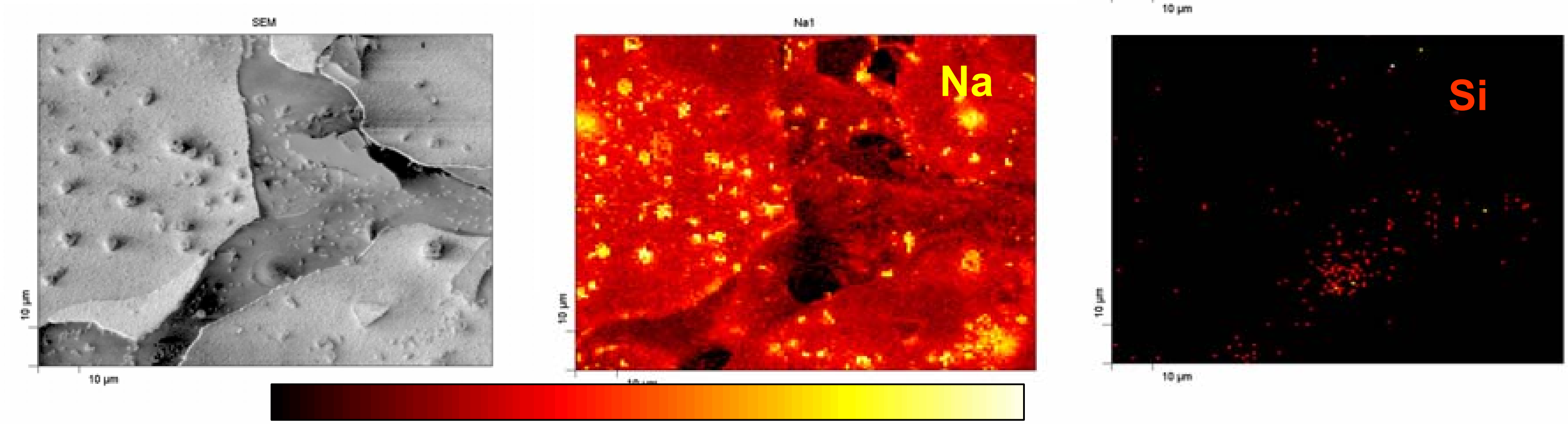
- **Qualitative and Quantitative Information** - Auger electrons occur at kinetic energies characteristic of elements present and at intensities proportional to their concentrations
- **Surface Sensitive –** Information depth limited to < 100Å
- **Small feature analysis –** Electron beam enables small spot size (15nm) and large magnification – point feature <u>and</u> composite analysis!
- **Depth Profiling –** Achieved by sputtering the surface with Ar^+ ions. Useful for bulk analysis, diffusion, junctions, etc.
- **Elemental Mapping and Line Scans** – Achieved by rastering (map) or scanning electron beam and setting analyzer to detect selected elements

Applications of AES to PV at NREL

- Thin conducting oxide coated glass is used routinely in PV modules
- Tin oxide/glass delamination has been observed. Failure traditionally believed to be due to penetration of alkali metals through the diffusion barrier
- Stressing TCO/glass in the lab results in delamination and formation of nodules
- Nodules revealed to be Na in AES map

TIN OXIDE (≈8500 Å)
DIFFUSION BARRIER (≈1500 Å)
SODA LIME GLASS (3mm)





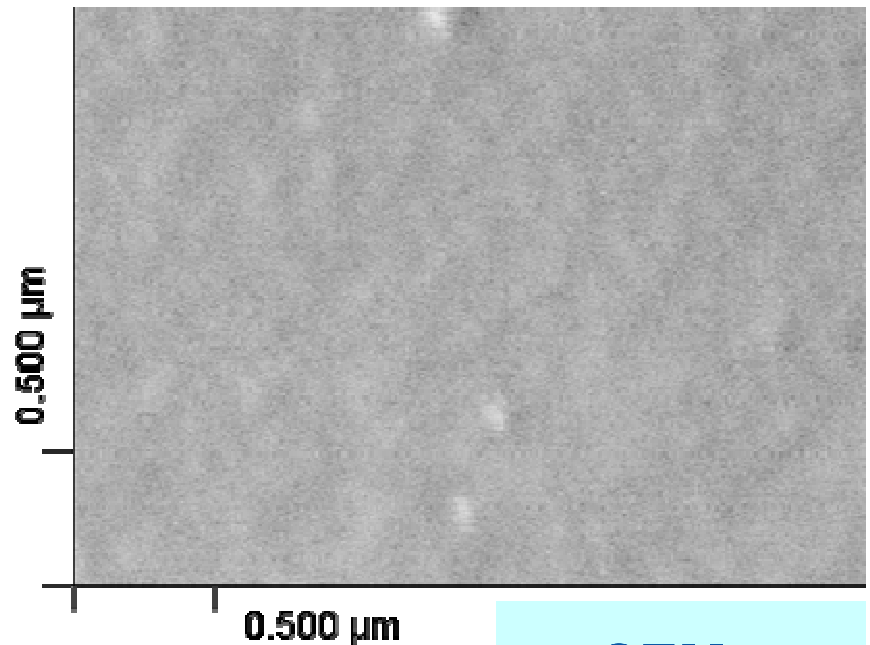
Increasing concentration

Cu-Mediated Surface Morphology of CdTe(111)-B

Process Steps

- **0.25% Br/MeOH Etch, (Glovebox)**
- **300C UHV anneal, (XPS)**
  ➔ stoichiometric surface

CdTe Surface



SEM

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Process Steps

- 0.25% Br/MeOH Etch, (Glovebox)
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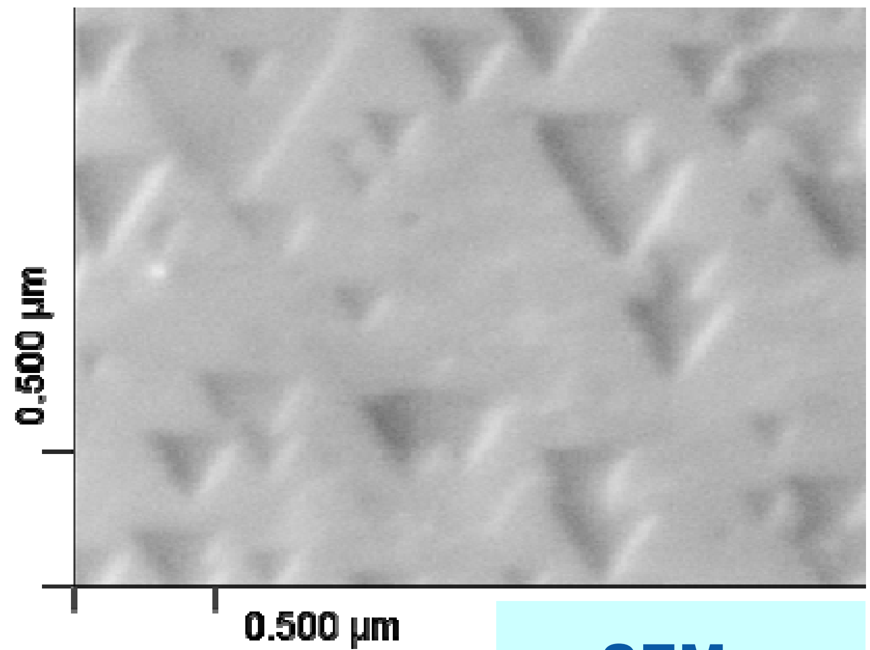
- 150 Å Cu, 300C (Dep. Chamber)
  - ➔ Cu segregates at surface
  - ➔ [111] surface w/ terraces

CdTe Surface



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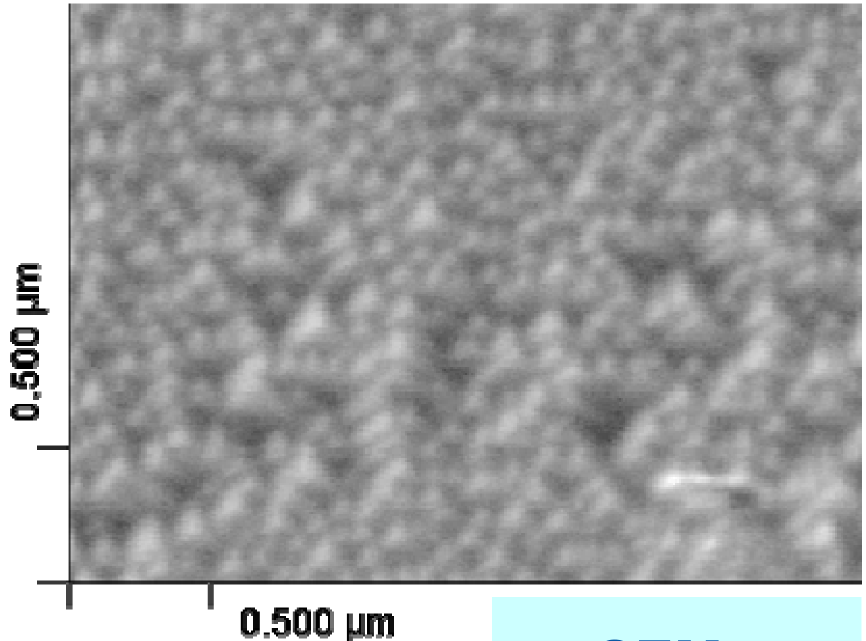
- **300C Anneal, 3 Hr. (XPS)**
  - ➔ **Cu diffuses into bulk**
  - ➔ **nanoscale [110] facets form**

CdTe Surface



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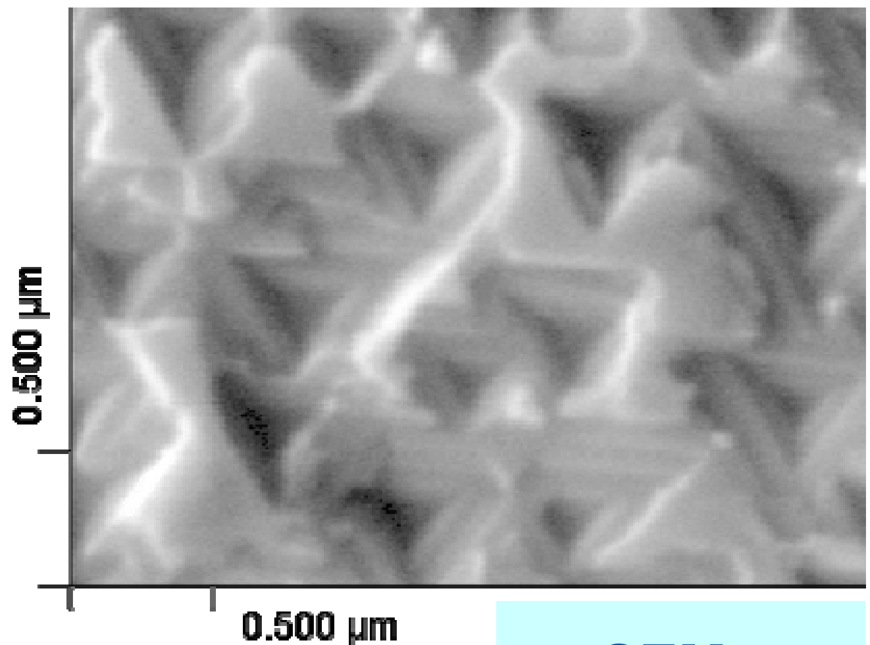
- **300 Å Cu, 300C (Dep. Chamber)**
  - ➔ **[111] facets reappear**
  - ➔ **triangular pits**

CdTe Surface



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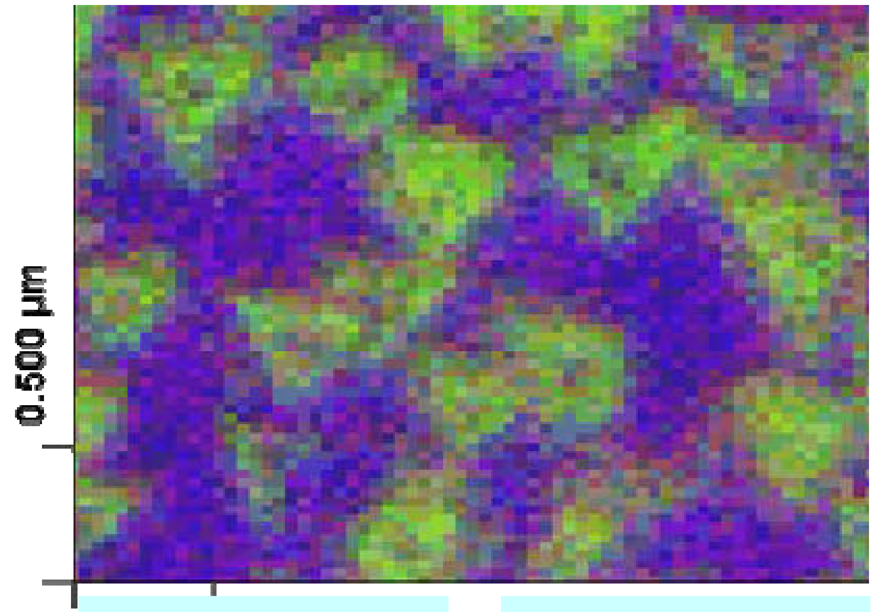
CdTe Surface

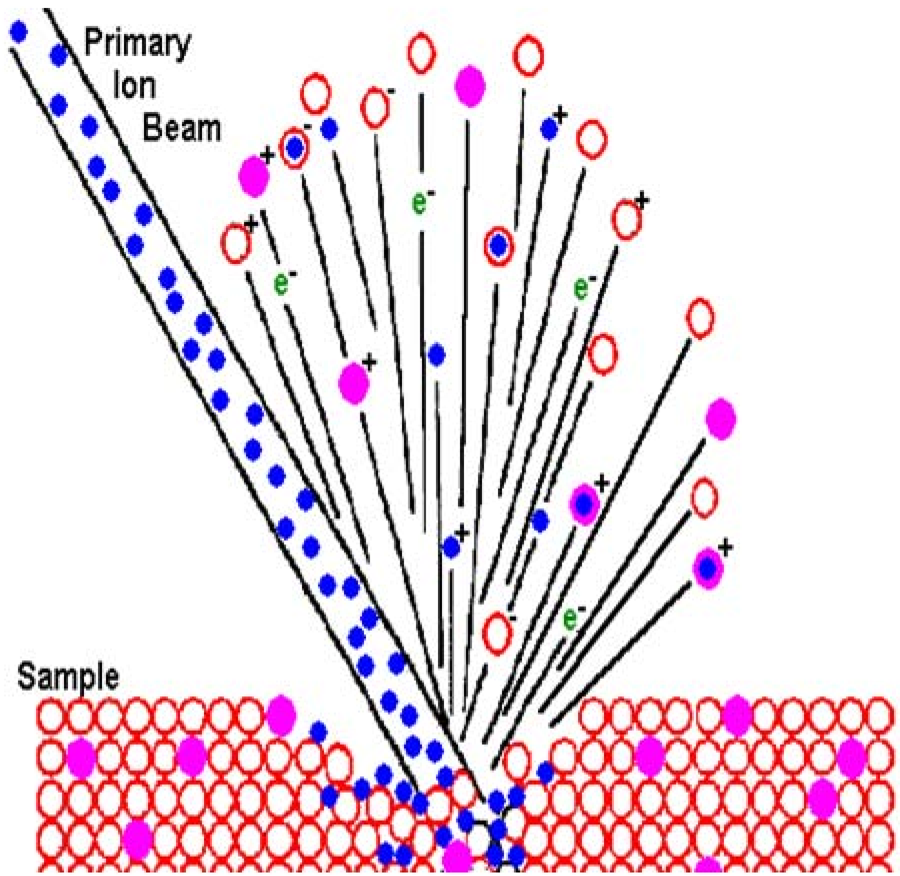


Cd Te Cu

AES map

Cu segregates on CdTe(111)-B and stabilizes [111] planes.

Secondary Ion Mass Spectrometry (SIMS)

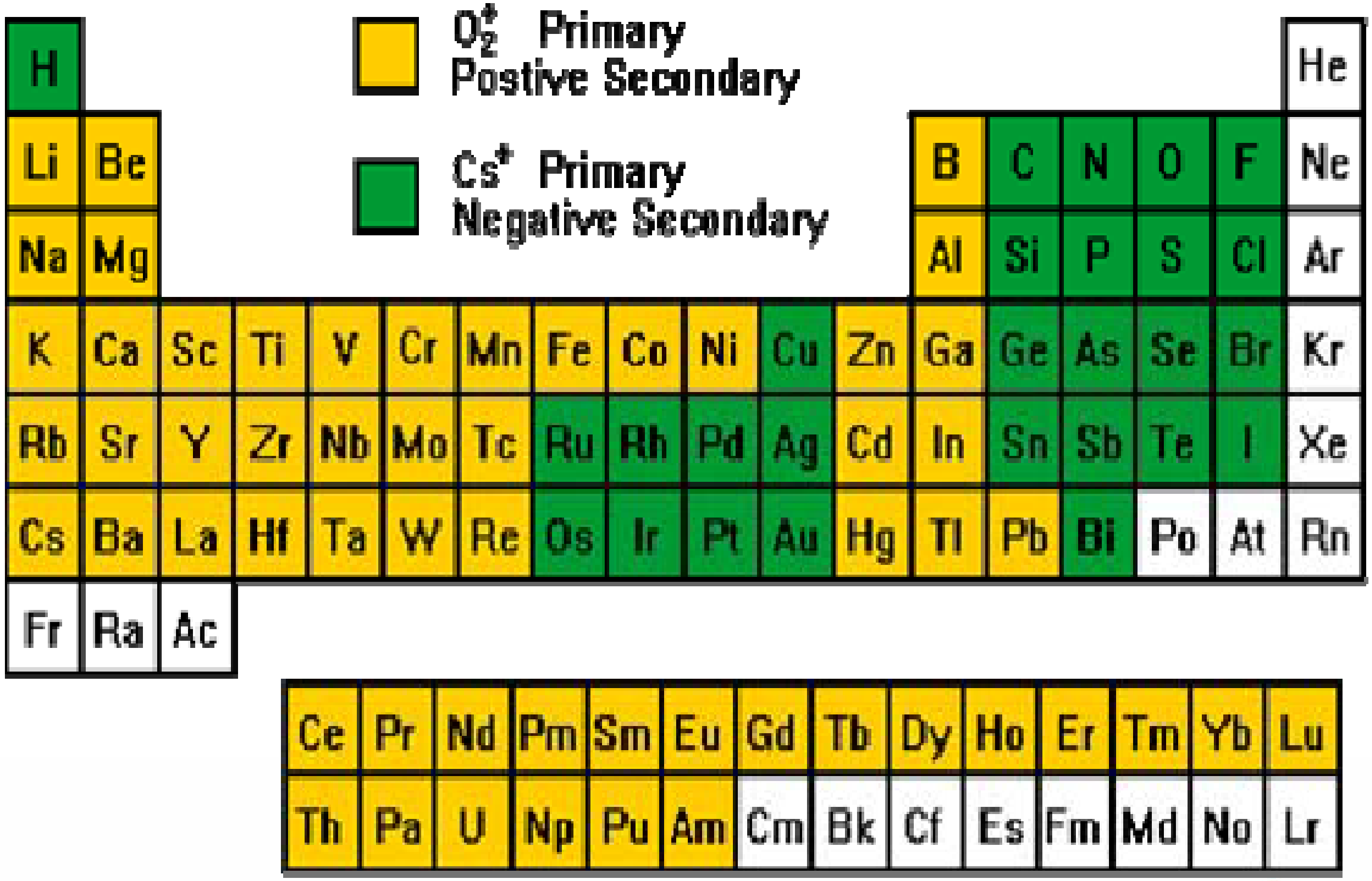


Qualitative and Quantitative Information - Secondary ions occur at m/z ratios unique to the originating elements or molecular species. Ion yields are extremely matrix dependent (standards required for quantitation!)

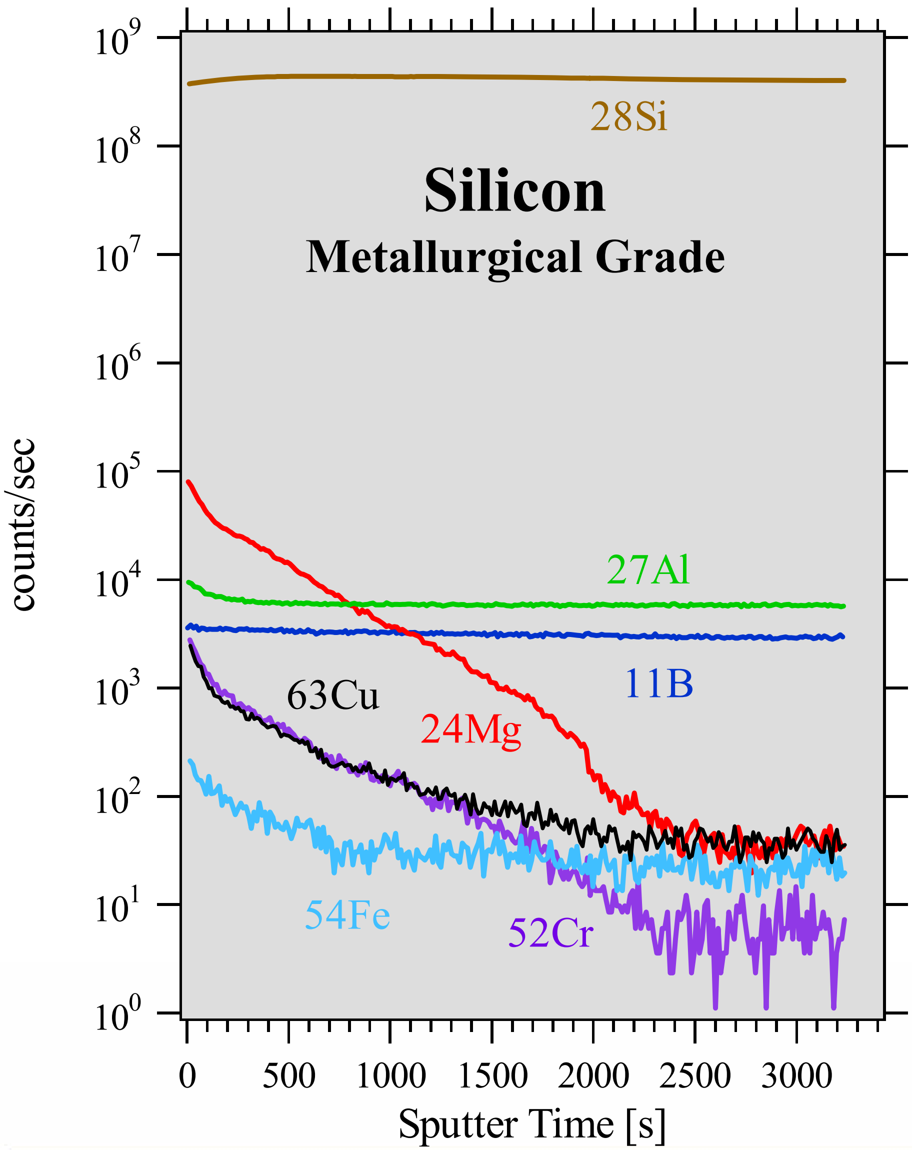
- **Detection of Hydrogen –** Unique to SIMS
- **Examination of Isotopes –** diffusion experiments using D_2O for example
- **Ultimate Surface Sensitivity –** Monolayer sampling depths
- **High Mass Resolution (m/Δm) -** Important to distinguish species with close m/z values
- **Superior Detection Limits –** ppm to ppb
- **Small feature analysis –** Raster size: 50 to 500 µm. Analysis size: 10 to 100 µm enables “ion imaging”
- **Depth Profiling –** Since emitted ions are examined (in contrast to AES & XPS) very fast sputter rates possible (upwards of 3000Å/min)

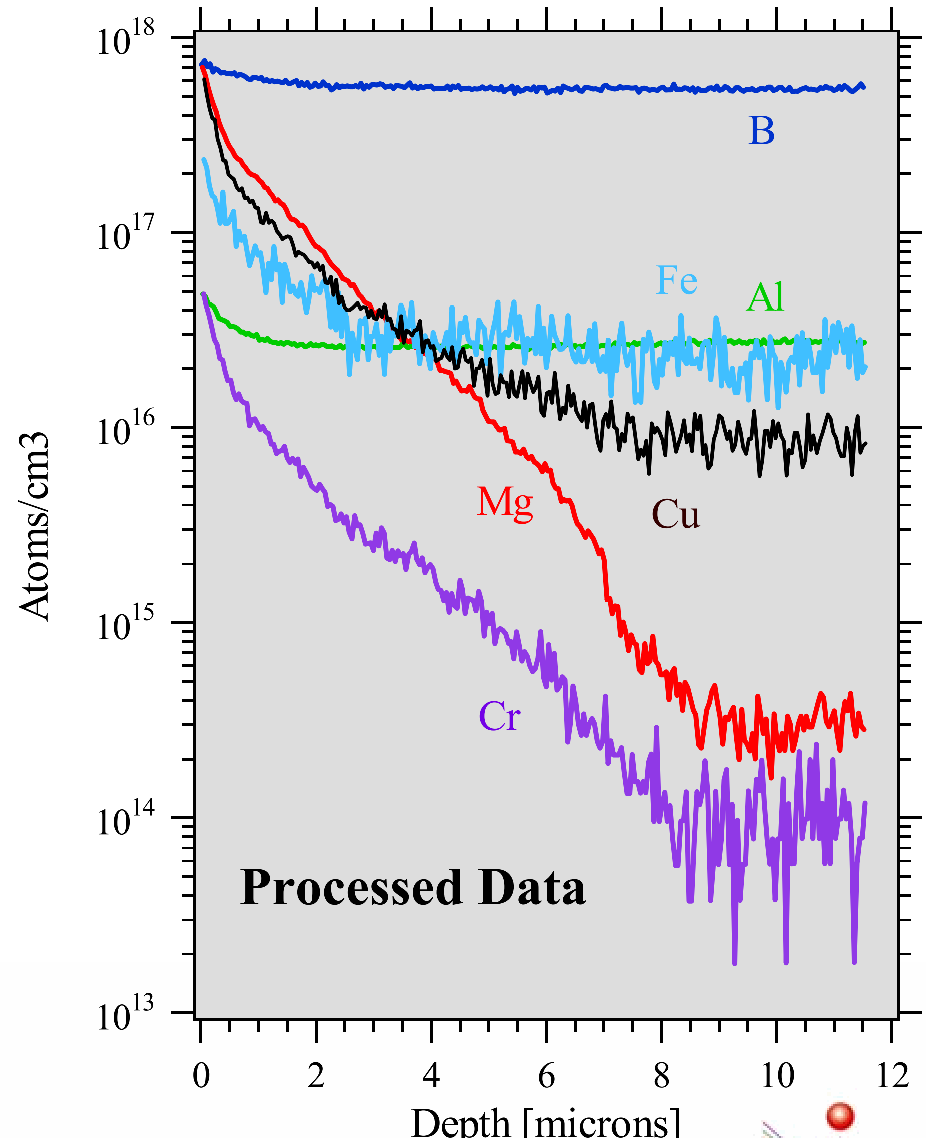
Positive and Negative Ion Yield vs. Periodic Table

- O_2 beam
  ↑ + ion yield
- Cs beam
  ↑ - ion yield

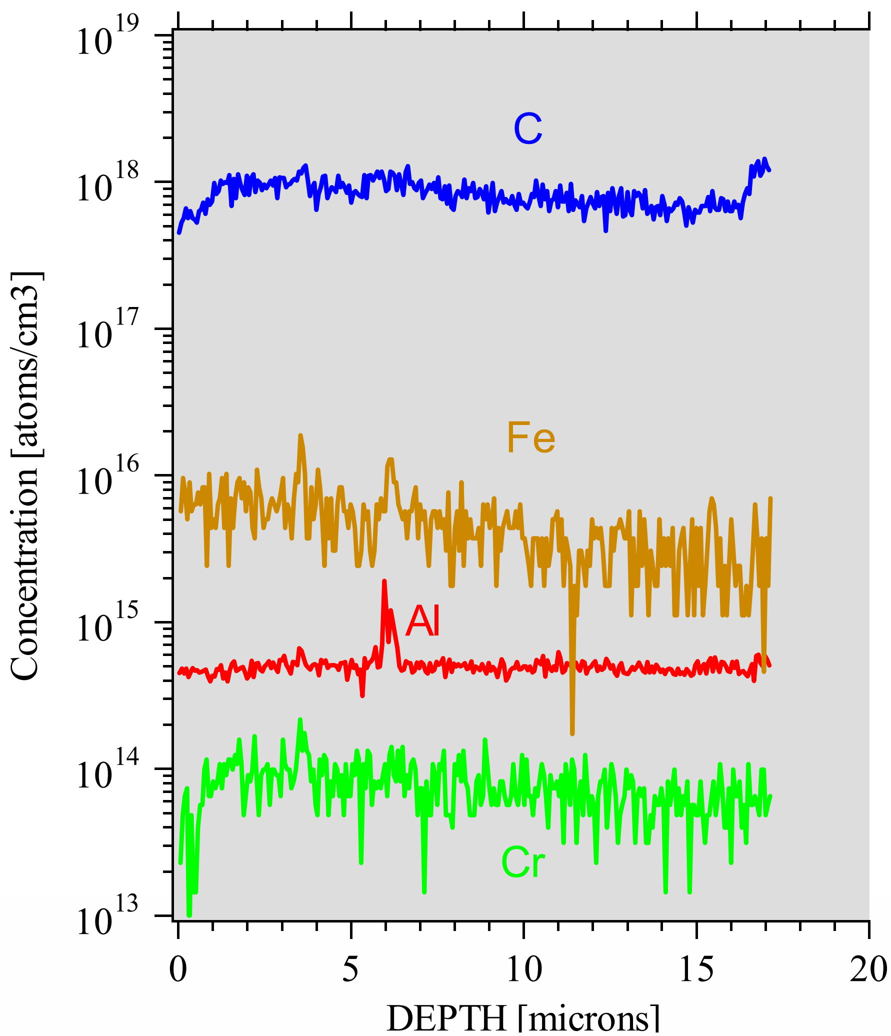


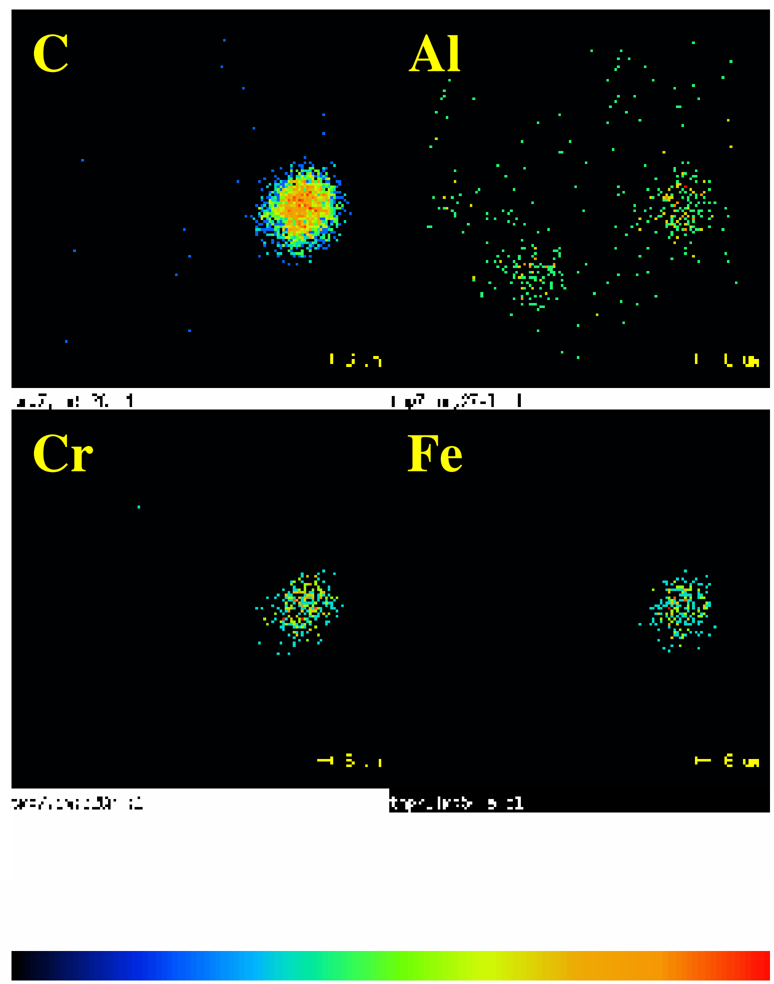
Applications of SIMS to PV at NREL



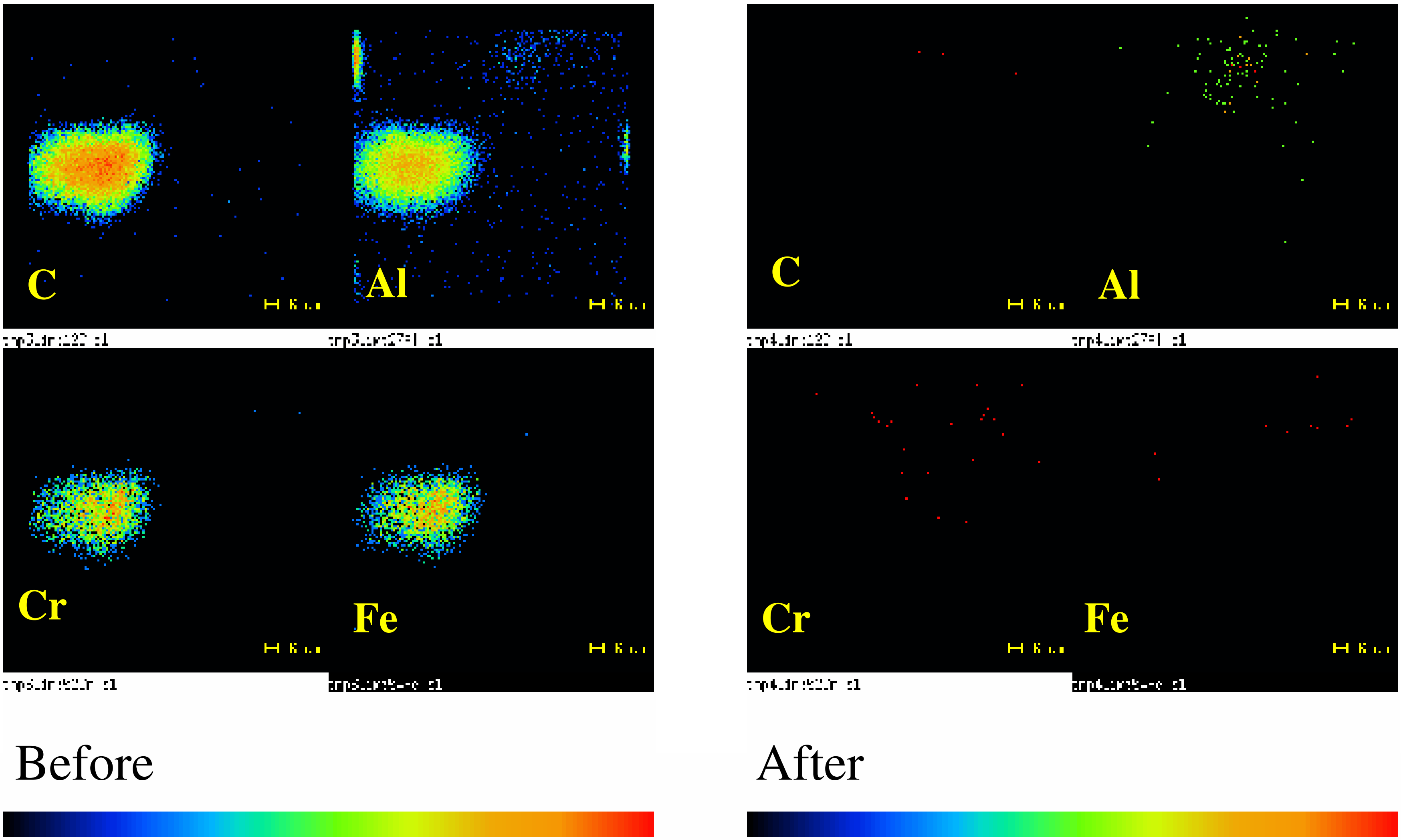


SIMS Depth Profile and Post Scanning Ion Image





Scanning Ion Images: Before and After O_2 Depth Profile



Conclusions

- Surface analysis provide levels of surface sensitivity not possible with other techniques
- Degree of surface sensitivity determined by nature of specific technique
- Surface analytical techniques provide qualitative and quantitative information as well as spatial information and bulk depth profiles
- Surface analytical data is rich in chemical information such as valence state or molecular environment, bonding information, surface “cleanliness” and more
- Surface analysis is routinely used at NREL to enable fundamental research, intra-division collaborative work and industrial support all designed to further PV progress

Acknowledgements

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- Bob Reedy
- Glenn Teeter
- Matt Young
- Sally Asher (Team Leader)