

Evaluation of the Residue from Microset on Various Metal Surfaces

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Sandia National Laboratories

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Defect Replication

Use a mold to cast a reverse replica of defects (scratches, dents, etc.) on a material surface.

The mold can later be used for measurements of the defect and for documentation.



Replicating compounds

What is the residual contamination and how much is left?

Microset 101RT Synthetic Rubber Replicating Compound

MSDS – siloxanes, silicones, glycol, silica, carbon, and complexed platinum - density 1.1 g/cm³



Coe-Flex Polysulfide Impression Material Type 2

MSDS - base – fillers TiO₂, SiO₂ - density 1.3-1.6 g/cm³
- catalyst – cupric hydroxide, TiO₂, SiO₂, chlorinated fatty acid ester



Table 3. Relative atomic concentrations of Microset and Coe-Flex as measured by XPS.

	[C]	[Si]	[O]	[Cl]	[S]	[Cu]	[Na]	[Ti]	[N]
Microset	50	30	20						
Coe-Flex	70	4	10	10	2	1	< 1	< 1	< 1

Surface Analysis Lab Capabilities

X-ray Photoelectron Spectroscopy (XPS)

UV Photoelectron Spectroscopy (UPS)

Auger Emission Spectroscopy (AES)

Time-of-Flight-Secondary Ion Mass Spectrometry
(ToF-SIMS)

(All are equipped for imaging (elemental mapping) and
depth profiling)

Scanning Probe Microscopy (AFM)

Profilometry

Scanning Kelvin probe

Electrochemistry

Spin coating

UV/Vis

Synchrotron-based techniques

Variable kinetic energy XPS

Near Edge X-Ray Absorption Fine Structure
(NEXAFS)

Imaging NEXAFS

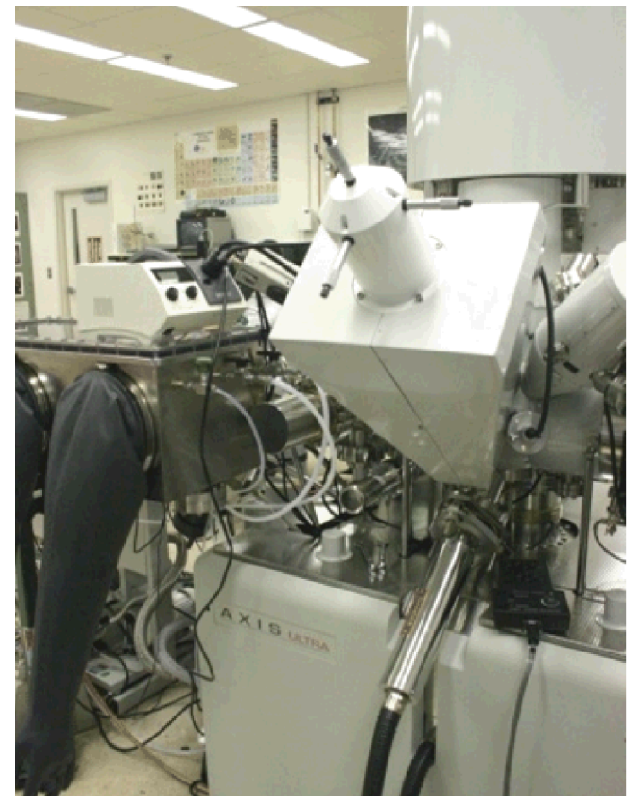
XPS/UPS – AES/ISS *in situ* capabilities

inert atmosphere sample transfer

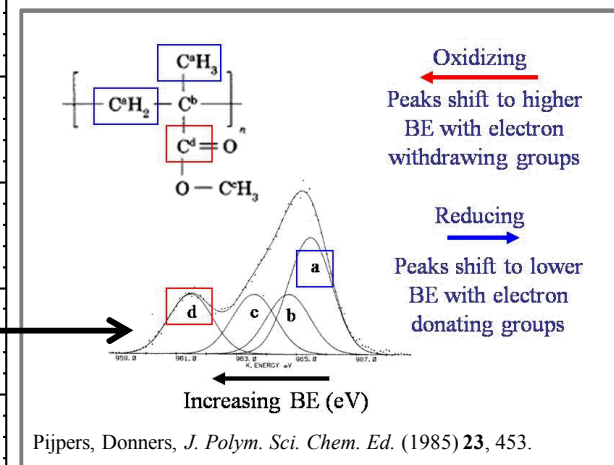
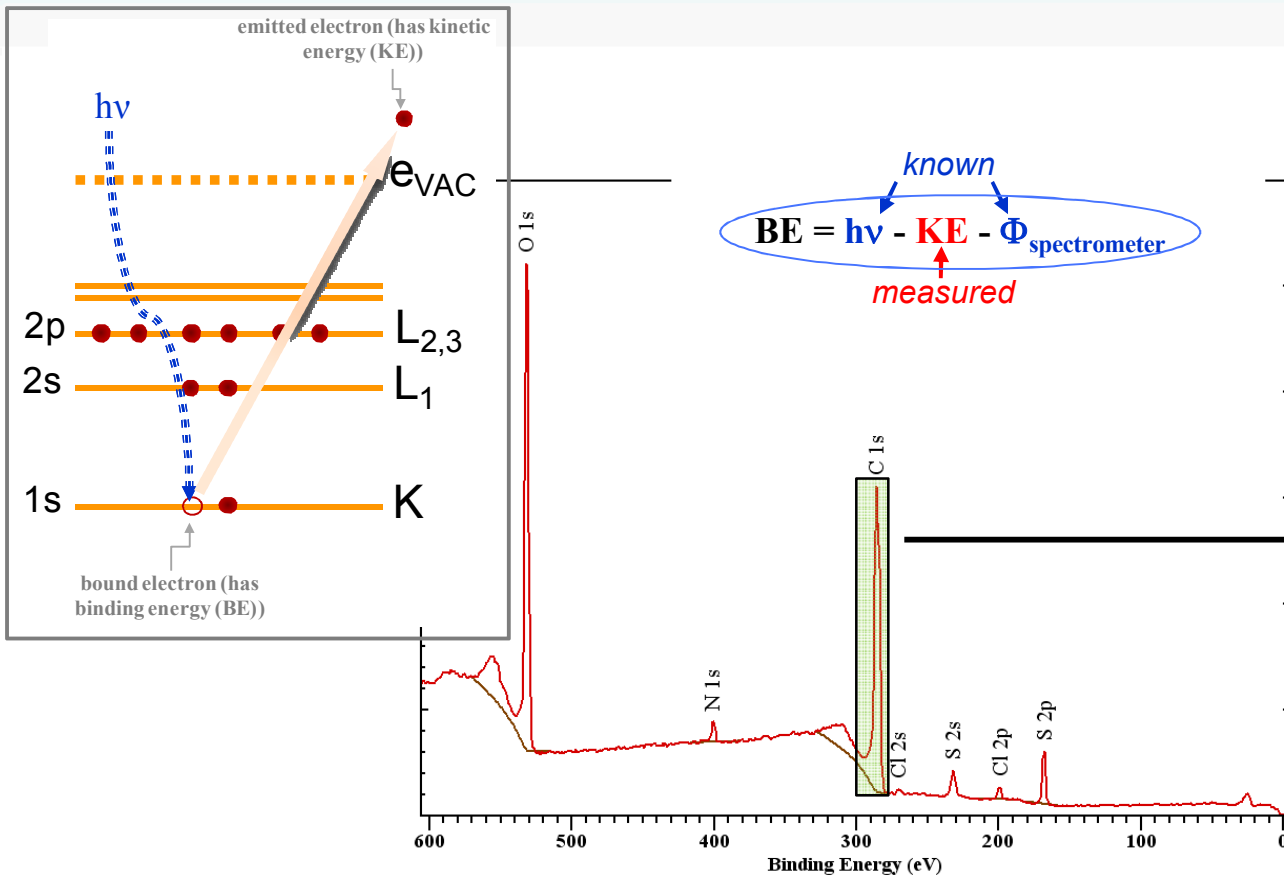
thermal evaporation

e-beam evaporation

thermal processing



X-Ray Photoelectron Spectroscopy



➤ Binding Energy (BE) relates to elemental identification.

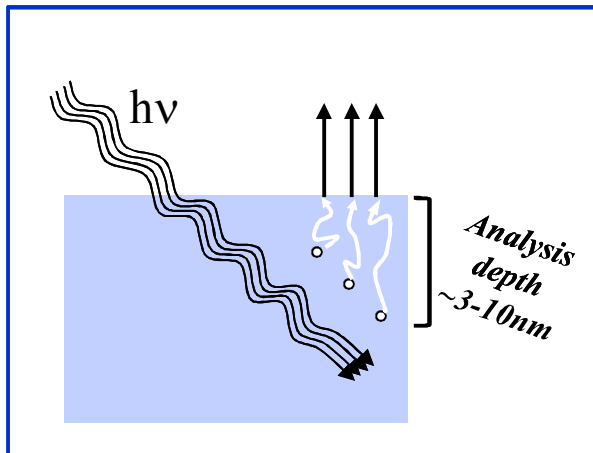
➤ Peak area relates to atomic abundance in near surface.

➤ Binding Energy (BE) shifts relate to local chemical environment.

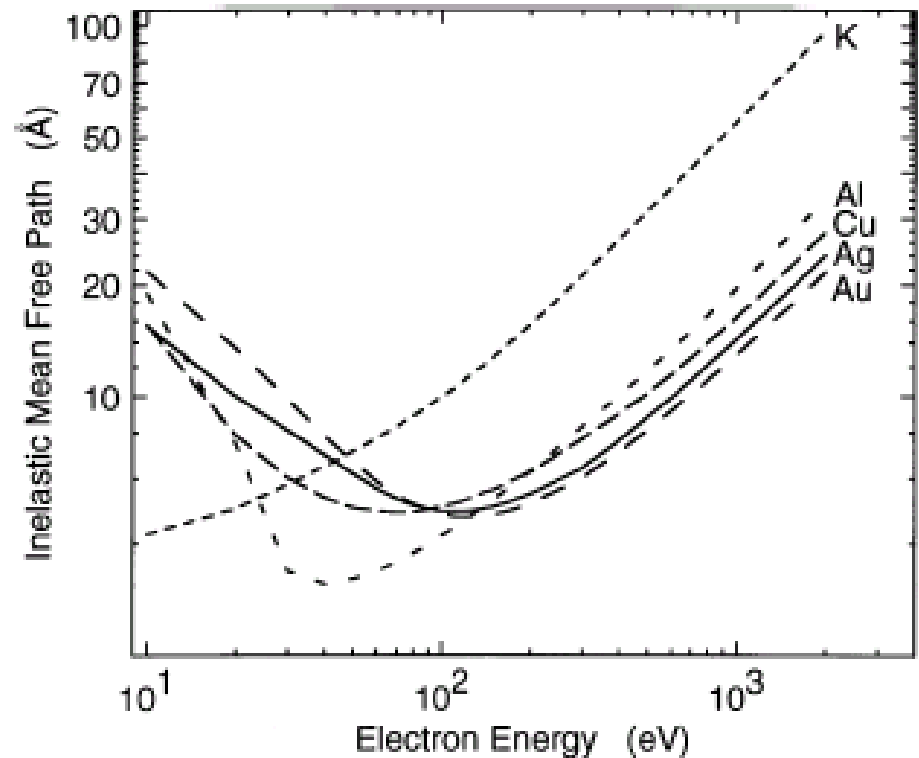
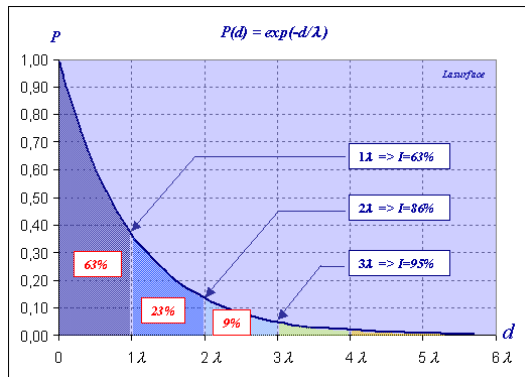
X-Ray Photoelectron Spectroscopy

Inelastic mean free path (IMFP or λ): the average distance between inelastic collisions for an electron in a particular material

The IMFP is dependent on the initial kinetic energy of the electron and the nature of the medium.



Analysis depth is $3\times(\text{IMFP})$



Substrates and Experimental Methods

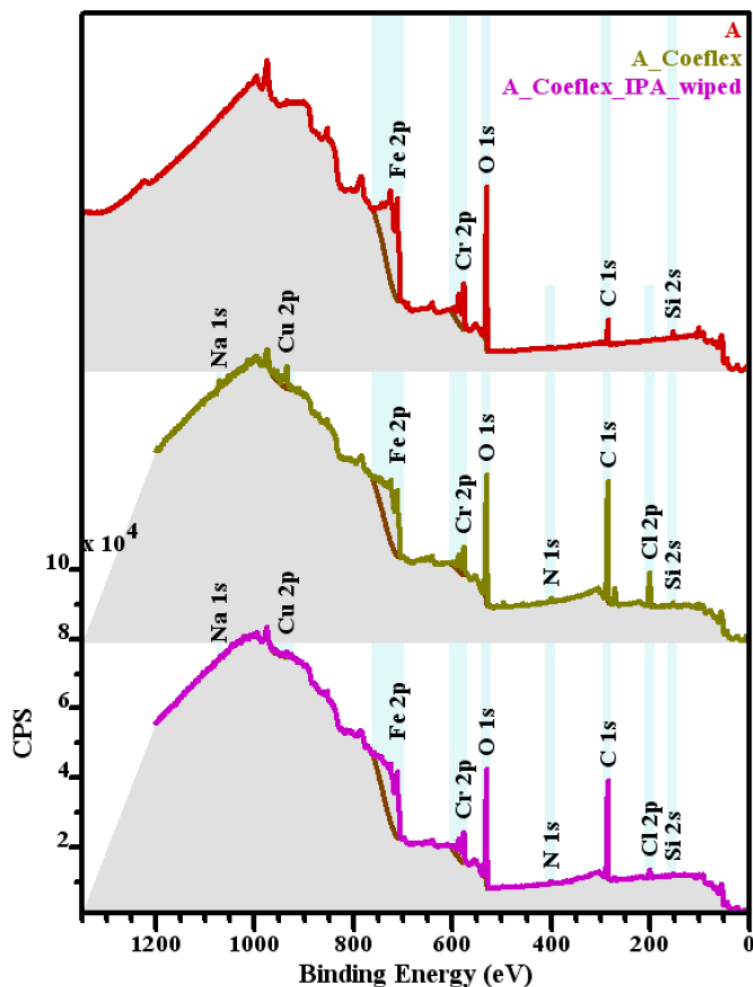
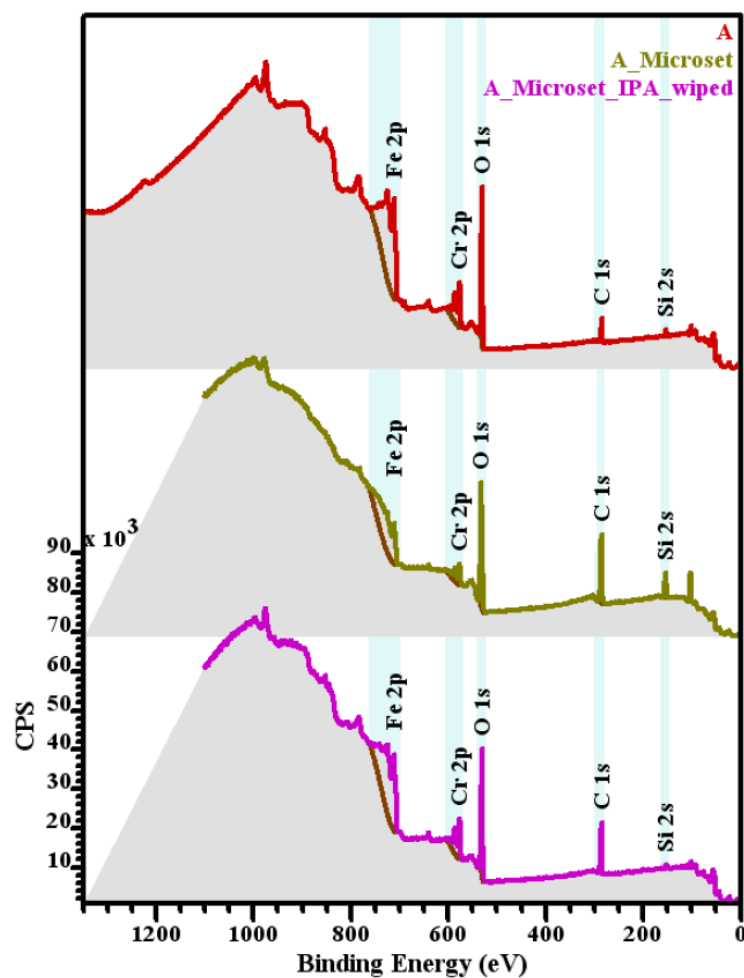
Table A. Expected bulk compositions of the metal substrates.

I.D.	Material
A	304
B	304L
C	316
D	316L
E	21-6-9
F	Ti-Al alloy
G	Ti / 6% Al / 4% V
H	Al 6061-T6 Bare
I	Al 7075-T6 Bare
J	Al 6061-T6 Anodized
K	Al 7075-T6 Anodized
L	Al 6061-T6 Alodine 1997
M	Al 7075-T6 Alodine 1997
N	Al 6061-T6 Alodine 047
O	Al 6061-T6 Alodine-new 2004

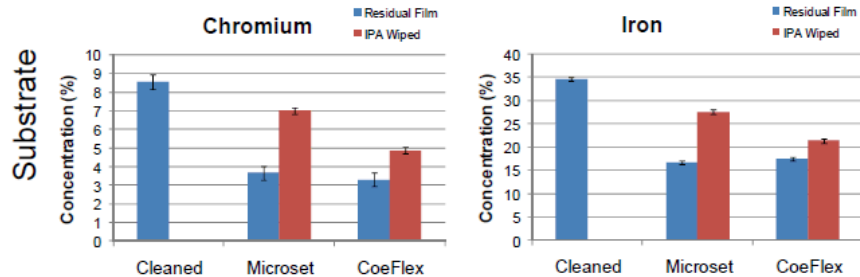
	Si	Fe	Cu	Mn	Mg	Cr	Ni
304	1	rem.		2		18-20	8-10.5
304L	1	rem.		2		18-20	8.0-12.0
316	1	rem.		2		16-18	10.0-14
316L	1	rem.		2		16-18	10.0-14
21-6-9		rem.		8.0-10		19-21.5	5.5-7.5
Ti / 6Al / 4V		0.25					
Al 6061	0.4-0.8	0.7	0.15-0.4	0.15	0.8-1.2	0.04-0.35	
Al 7075	0.4	0.5	1.2-2	0.3	2.1-2.9	0.18-0.28	
cont.	Zn	V	Ti	Mo	Al	other	
304						x	
304L						x	
316				2.0-3		x	
316L				2.0-3		x	
21-6-9						x	
Ti / 6Al / 4V		3.5-4.5	rem.		5.5-6.75	x	
Al 6061	0.25		0.15		rem.	x	
Al 7075	5.1-6.1		0.2		rem.	x	

1. Cleaning the substrate.
2. Applying Microset (or Coe-Flex).
3. Allowing time for replicate curing.
4. Marking the location of the Microset (or Coe-Flex) followed by removal of the replicate by peeling it away from the surface.
5. XPS analyses was performed on three locations of the pristine substrate surface as well as three locations within the region where Microset (or Coe-Flex) had been applied.
6. Samples were then removed from the analysis chamber and were wiped with a Kimwipe soaked in isopropanol
7. Three locations in the Microset (or Coe-Flex) region were then reanalyzed.

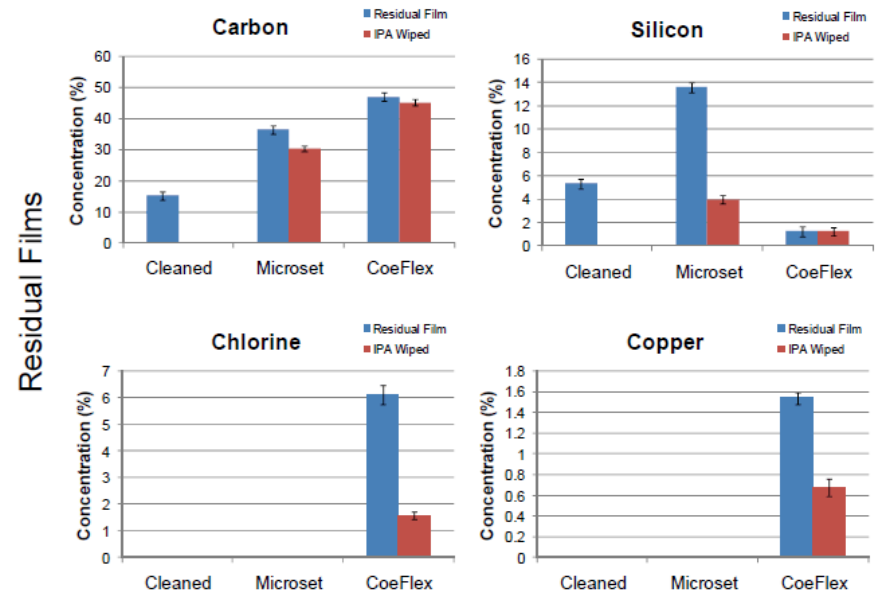
Example Spectra for 304 Stainless Steel



Example - 304 stainless steel

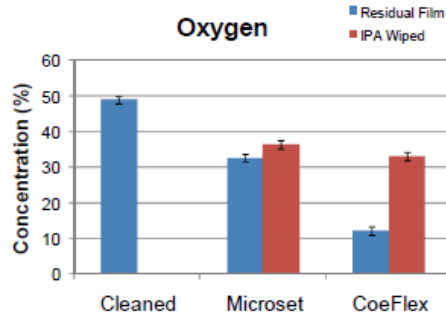
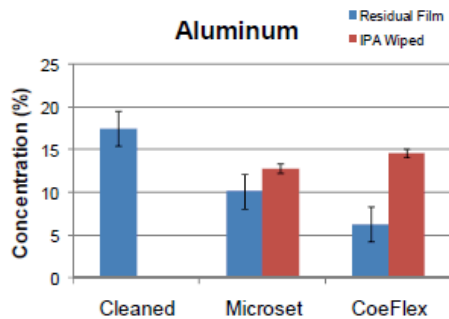


Concentration of Substrate Species
 Substrate elements attenuated by residual films.
 Intensity increases after cleaning with isopropanol.

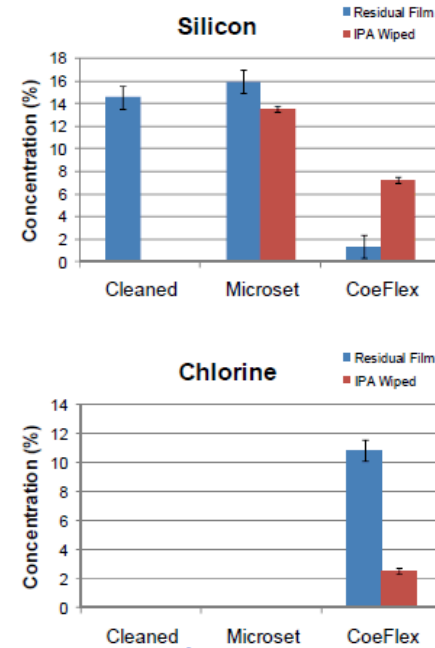
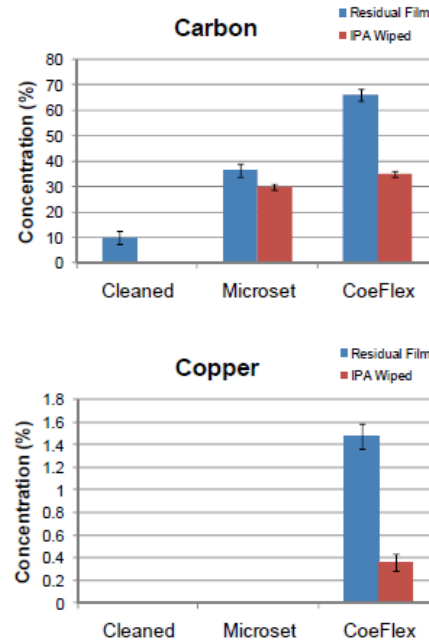


Concentration of Contaminant Species
 Contaminant emission increases by residual films.
 Intensity decreases after cleaning with isopropanol.
 Microset leaves Si and C.
 CoeFlex leaves C, Cu, and Cl.

Example – Al 7075-T6



Residual Films



Concentration of Substrate Species

Substrate elements attenuated by residual films.
Intensity increases after cleaning with isopropanol.

Concentration of Contaminant Species

Contaminant emission increases by residual films.
Intensity decreases after cleaning with isopropanol.

Microset leaves Si and C.
CoeFlex leaves C, Cu, and Cl.

Estimation of the Residual Film Thicknesses

$$\frac{I_{obs}}{I_{ideal}} = \exp\left(\frac{-d}{\lambda \sin\theta}\right)$$

I_{obs} = the intensity from the substrate elemental component with the residual film present

I_{ideal} = the intensity of the substrate under ideal/clean conditions

d = thickness of the residual film (nm)

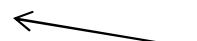
λ = effective attenuation length of the escaping photoelectron (nm)

θ = take-off angle

	Microset residual film thickness (nm)	Microset film after wiping with IPA (nm)	Coe-Flex residual film thickness (nm)	Coe-Flex film after wiping with IPA (nm)	Element used for calculation
A	2.5	0.6	2.8	1.7	Cr
B	2.4	1.8			Cr
C	2.3	1.8			Cr
D	1.9	0.6			Cr
E	2.7	0.8			Cr
F	1.1	0.5			Al
G	3.6	2.1			Fe
H	2.3	1.8			Cr
I	1.6	0.9	3.1	0.5	Al
J	1.8	0.8	3.4	0.8	Al
K	2.1	1.2			Al
L	2.1	0.8			Cr
M	2.3	1.5			Cr
N	2.3	2.1			Cr
O	1.2	1.2			Cr
Avg.	2.1 ± 0.6	1.2 ± 0.6	3.1 ± 0.3	1.0 ± 0.6	

Thicknesses were also evaluated by ellipsometry for several samples, and showed similar results to those obtained by XPS.

Alodined aluminum are effectively chromium substrates (from an XPS perspective).



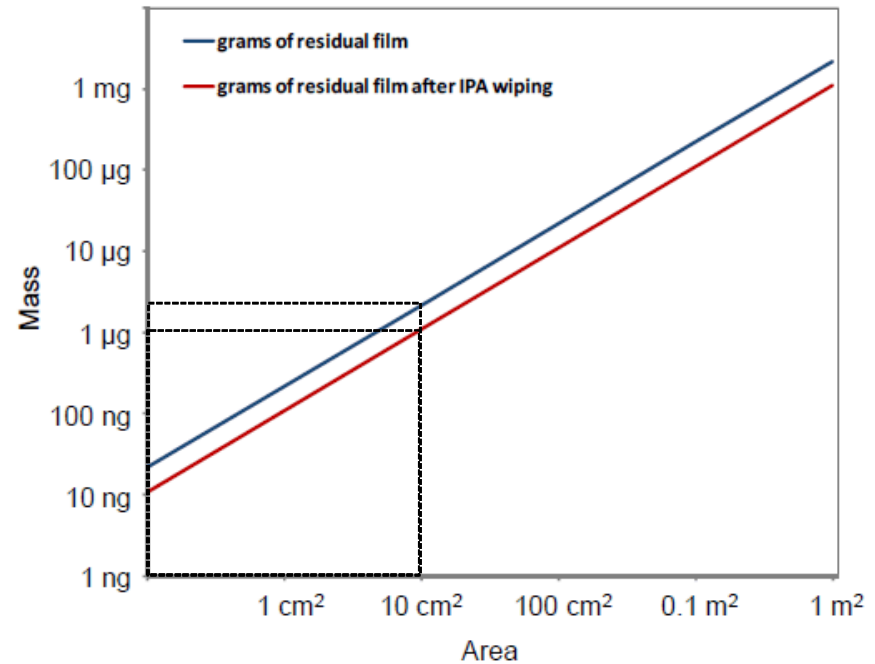
Conclusions

Microset application is simple, easy, and repeatable
...gun application with static mixers.

Coe-Flex cure depends on user
...ratio of base:catalyst
...mix time
...application

Microset leaves thin contaminant film containing Si and C.
Coe-Flex leaves thin contaminant film containing Cu and Cl.

Microset and Coe-Flex residual film thicknesses can be
effectively reduced by wiping with isopropanol.
(Other solvents may be more effective.)



Residual film assumed to have a thickness of 2 nm
and a density of 1.1 g/cm³

Acknowledgements

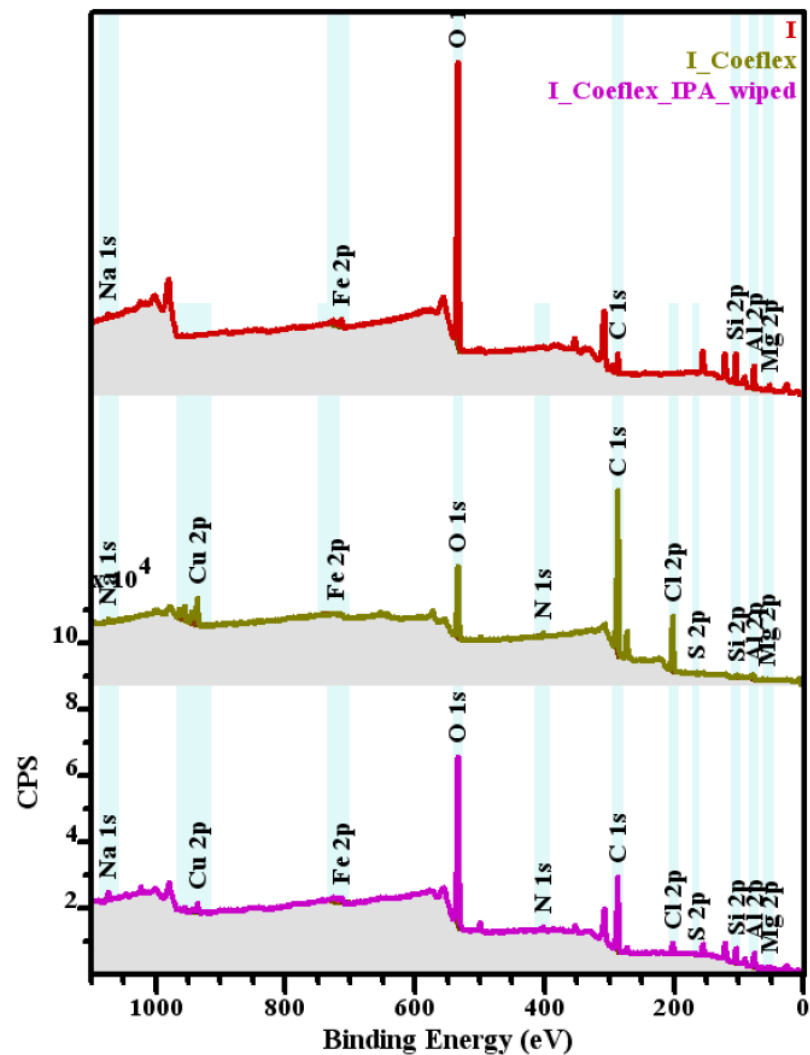
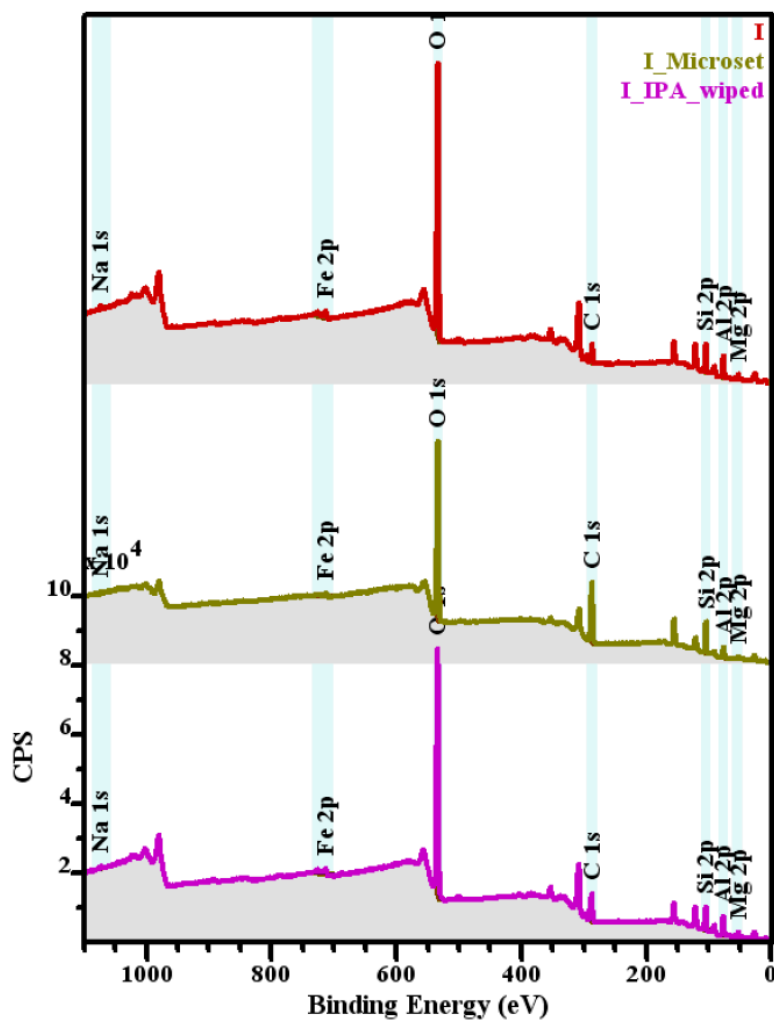
**Jim Aubert
Bill Wallace
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Mike Kelly

**Dale Huber
Andrew Price**

**Eddie Lopez
Alice Kilgo
Patti Sawyer**

Example Spectra for Aluminum Sample



roughness

	RMS Roughness (nm)
A	12 ± 4
B	15 ± 4
C	12 ± 3
D	No data
E	9 ± 1
F	No data
G	160 ± 50
H	2900 ± 400
I	100 ± 10
J	500 ± 160
K	270 ± 70
L	430 ± 200
M	670 ± 170
N	3100 ± 200
O	3400 ± 600

ellipsometry

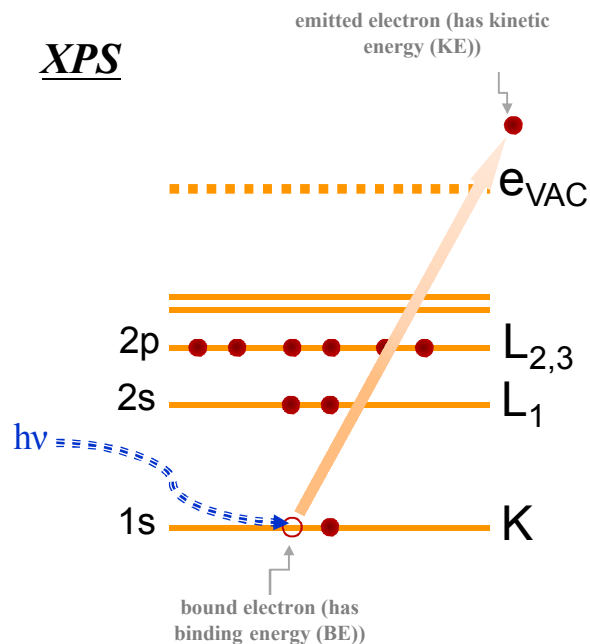
	Thickness (nm)
E	
E/Coe-Flex	2.3 ± 1
E/Microset	2.6 ± 1
B	
B/Coe-Flex	22 ± 1
B/Microset	2 ± 1
C	
C/Coe-Flex	8 ± 1
C/Microset	1.8 ± 1
I	
I/Coe-Flex	28 ± 2
I/Microset	2.4 ± 1

Conclusions

XPS characterizes core level electrons

- Chemical Analysis – Chemical Environment – Oxidation State – Electronic Environment -

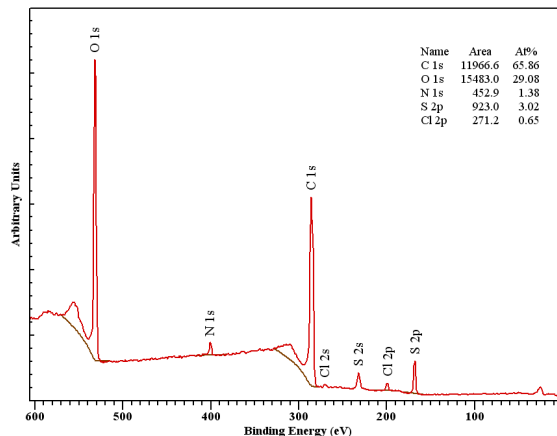
XPS



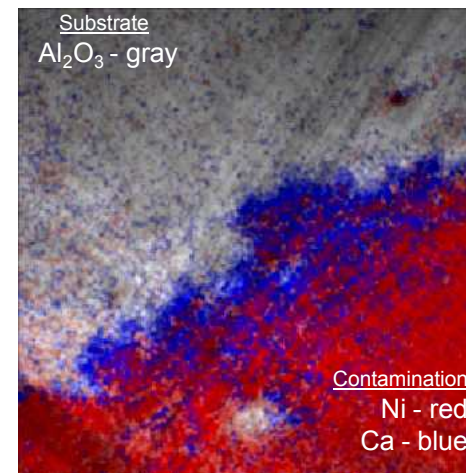
$$BE = h\nu - KE - \Phi_{\text{spectrometer}}$$

The inelastic mean free path (IMFP or λ) of an emitted electron makes XPS a very surface sensitive technique.

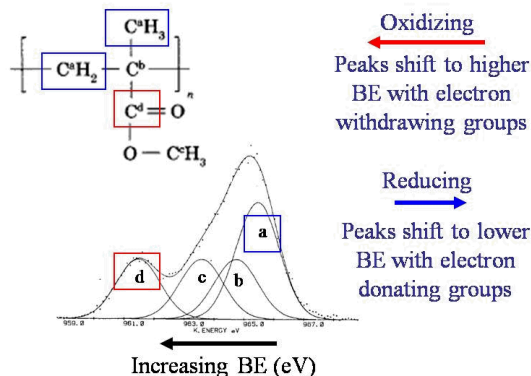
Compositional Analysis (identification and quantification)



Chemical Imaging

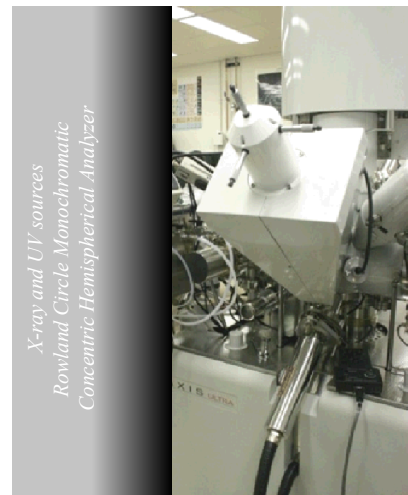


Peak Fitting for Chemistry (valence and chemical environment)

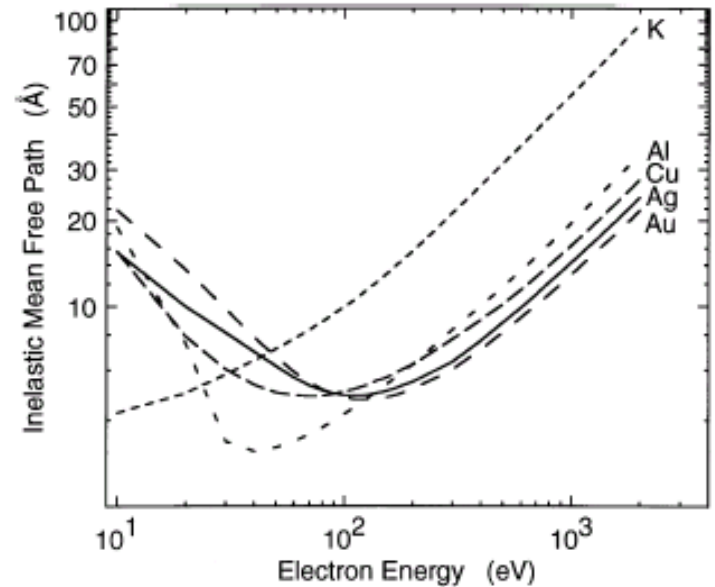
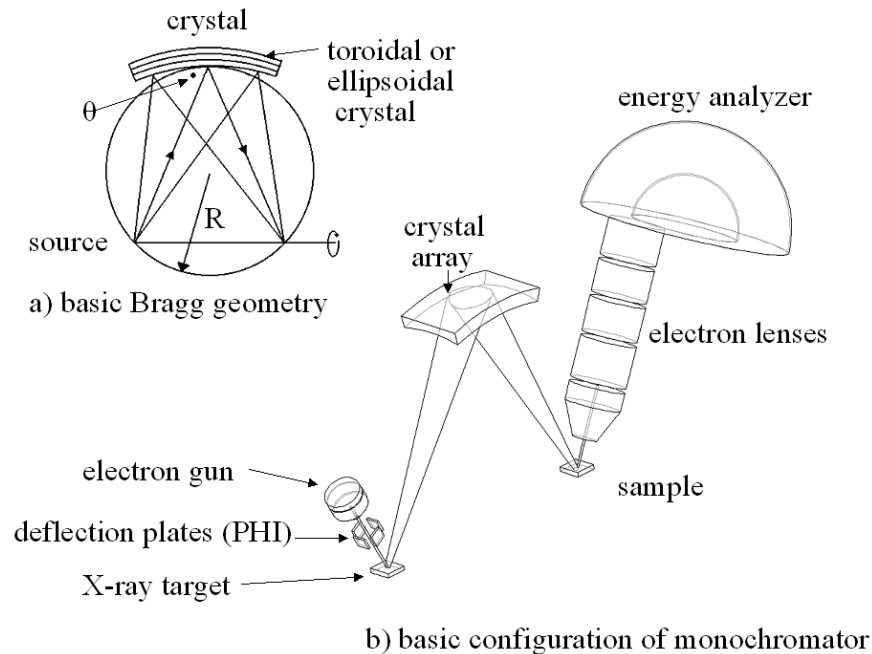


Pijpers, Donners, *J. Polym. Sci. Chem. Ed.* (1985) **23**, 453.

Kratos Axis Ultra DLD



Monochromatic X-ray source



I.W. Drummond, Chapter 5, *XPS: Instrumentation and Performance*, Briggs and Grant, 2003.