SAND2011-7010C

Evaluation of the Residue from Microset on Various Metal Surfaces

CASS
October, 2011
Sandia National Laboratories
Livermore, CA

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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/cm^3

Coe-Flex Polysulfide Impression Material Type 2
MSDS - base – fillers TiO_2,SiO_2 - density 1.3-1.6 g/cm^3
- catalyst – cupric hydroxide, TiO_2, SiO_2, 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

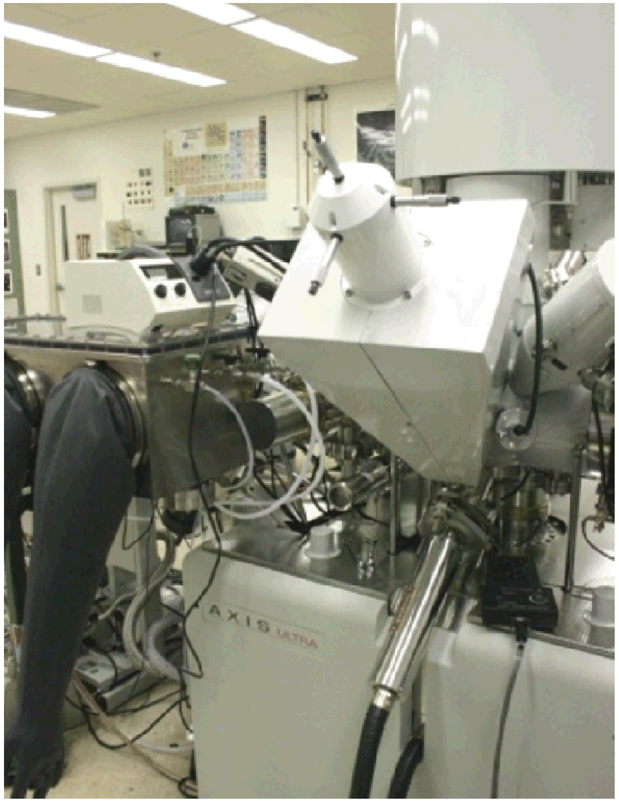
X-ray Photoelectron Spectroscopy (XPS)
UV Photoelectron Spectroscopy (UPS)
Auger Emission Spectroscopy (AES)
Time-of-Flight-Secondary Ion Mass Spectrometry (ToF-SIMS)
(All are equipped for imaging (elemental mapping) and depth profiling)

Scanning Probe Microscopy (AFM)
Profilometry
Scanning Kelvin probe

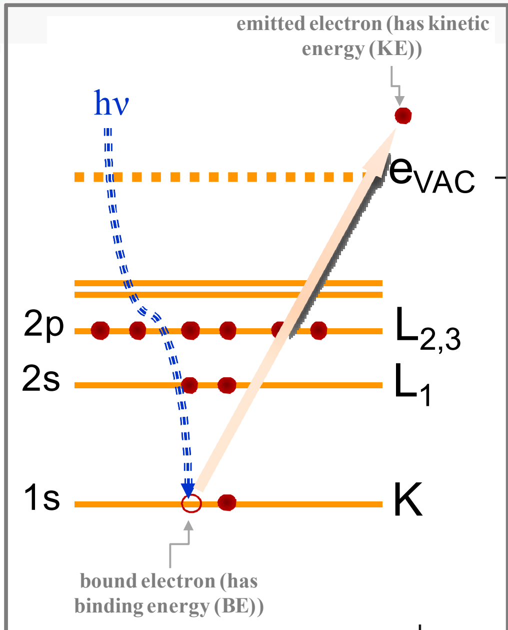
Electrochemistry
Spin coating
UV/Vis

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

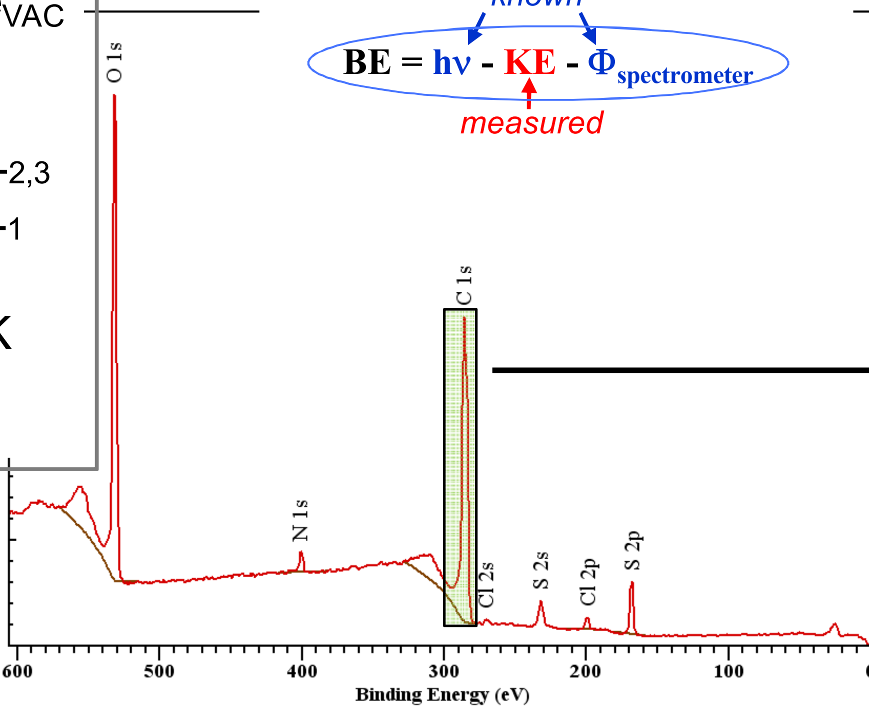


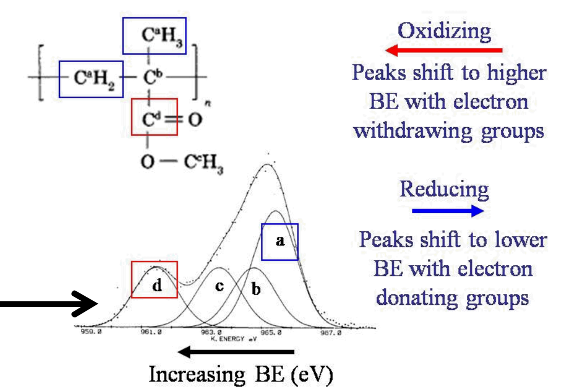
X-Ray Photoelectron Spectroscopy



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

known
measured





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

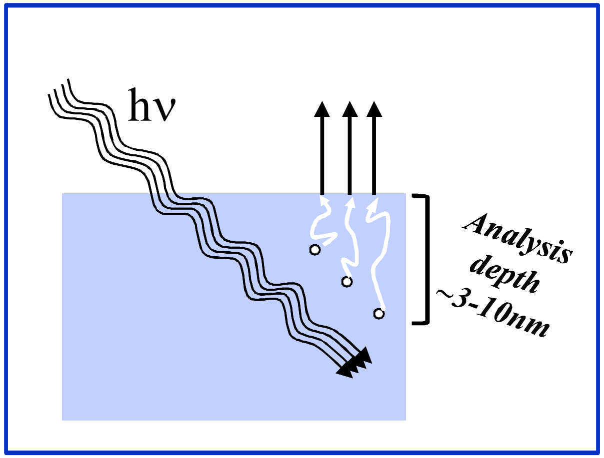
- **Binding Energy (BE) shifts relate to local chemical environment.**

- **Binding Energy (BE) relates to elemental identification.**
- **Peak area relates to atomic abundance in near surface.**

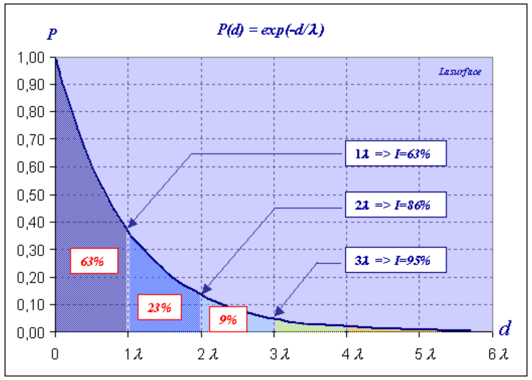
X-Ray Photoelectron Spectroscopy

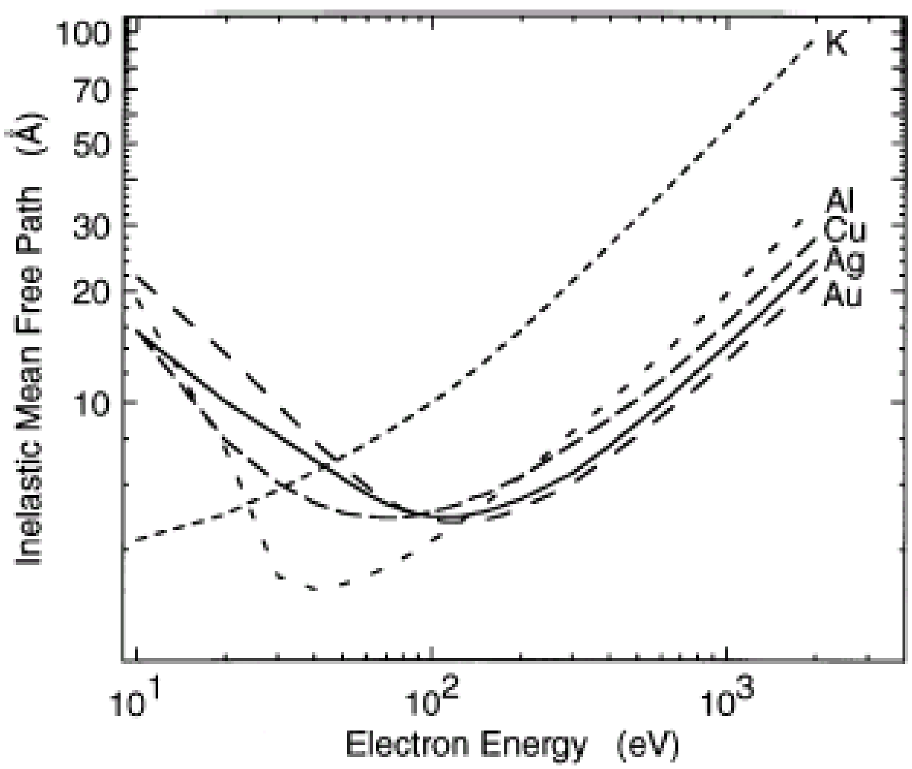
Inelastic mean free path (IMFP or λ): the average distance between inelastic collisions for an electron in a particular material

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



Analysis depth is 3x(IMFP)





Substrates and Experimental Methods

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

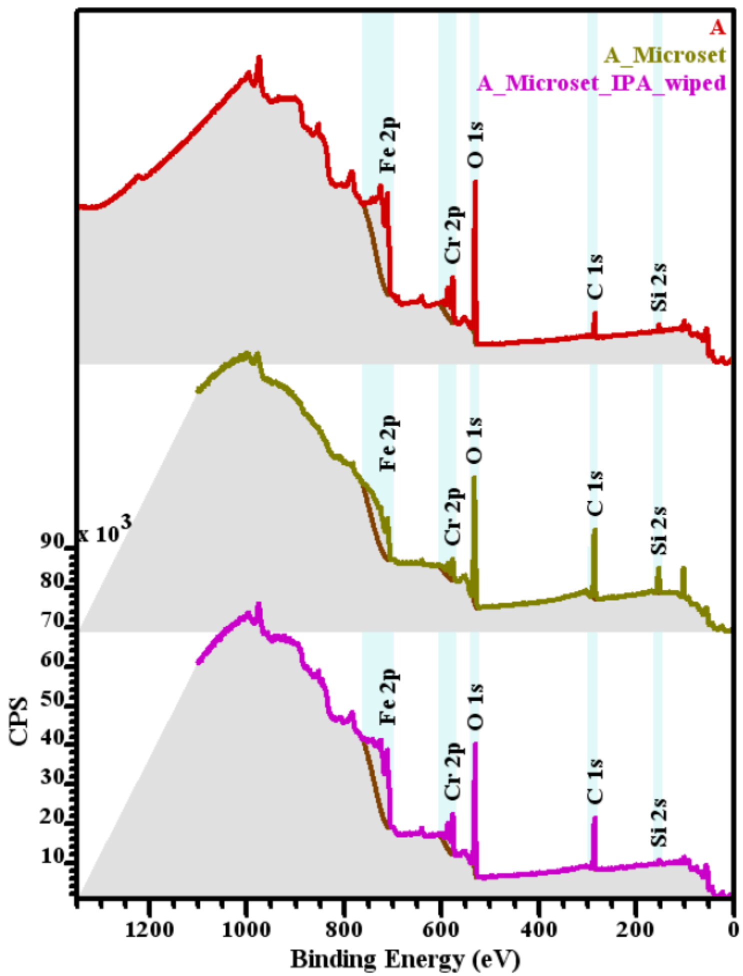
Table A. Expected bulk compositions of the metal substrates.

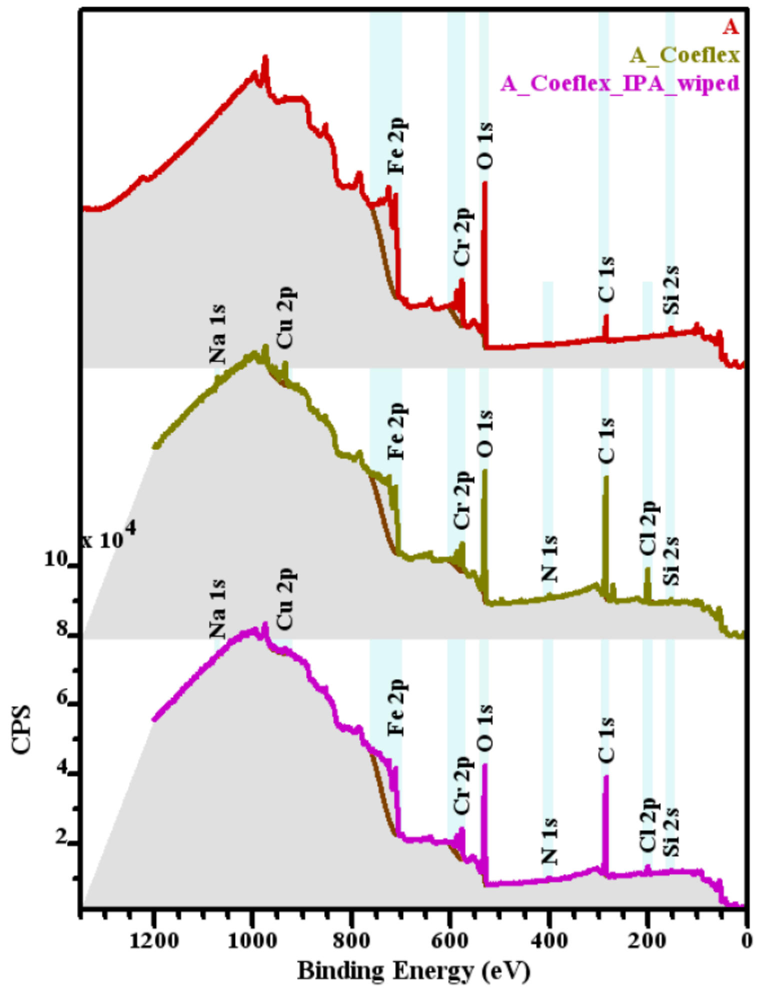
	Si	Fe	Cu	Mn	Mg	Cr	Ni
304	1	rem.		2		18-20	8-10.5
304L	1	rem.		2		18-20	8.0-12.0
316	1	rem.		2		16-18	10.0-14
316L	1	rem.		2		16-18	10.0-14
21-6-9		rem.		8.0-10		19-21.5	5.5-7.5
Ti / 6Al / 4V		0.25					
Al 6061	0.4-0.8	0.7	0.15-0.4	0.15	0.8-1.2	0.04-0.35	
Al 7075	0.4	0.5	1.2-2	0.3	2.1-2.9	0.18-0.28	

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

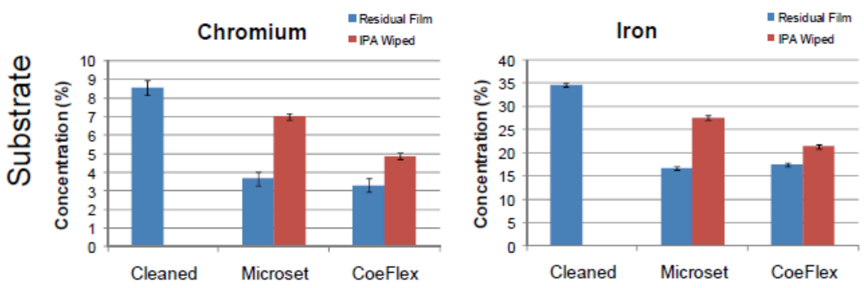
1. Cleaning the substrate.
2. Applying Microset (or Coe-Flex).
3. Allowing time for replicate curing.
4. Marking the location of the Microset (or Coe-Flex) followed by removal of the replicate by peeling it away from the surface.
5. XPS analyses was performed on three locations of the pristine substrate 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.

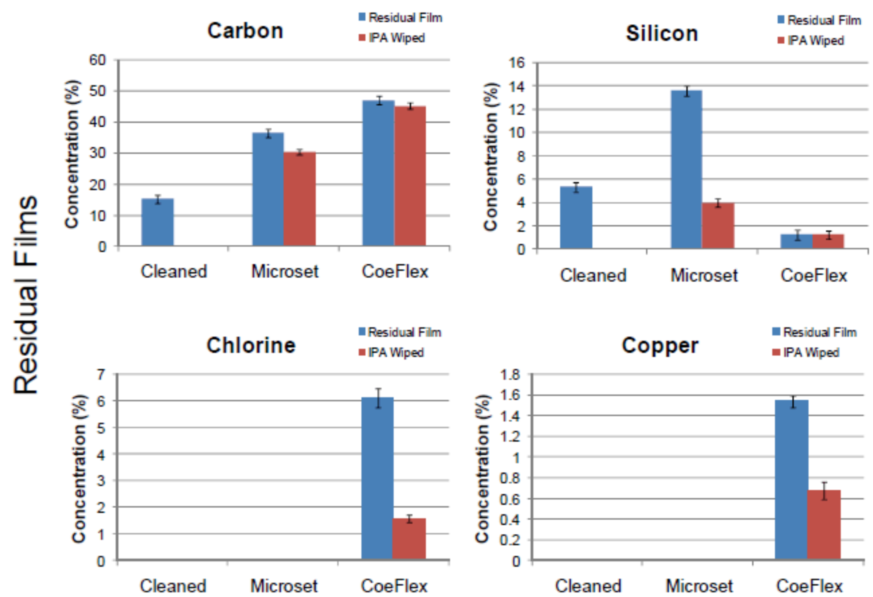
Example Spectra for 304 Stainless Steel





Example - 304 stainless steel





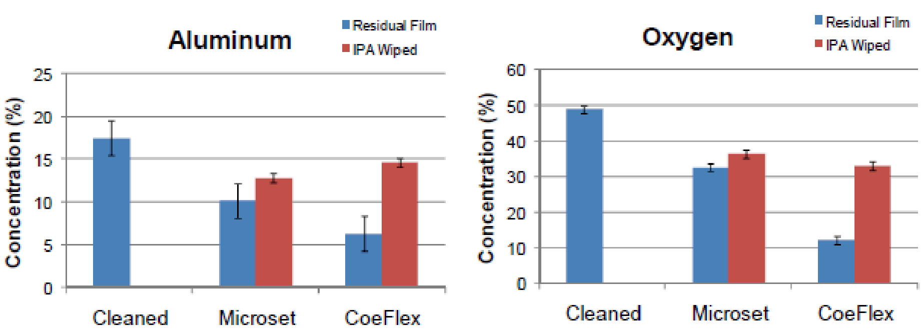
<u>Concentration of Substrate Species</u>

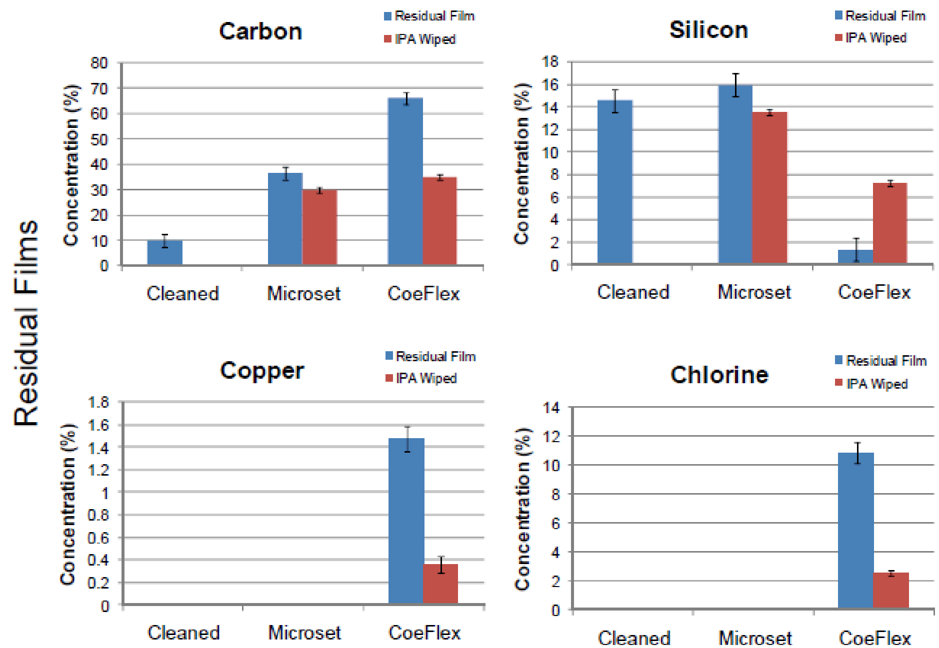
Substrate elements attenuated by residual films.
Intensity increases after cleaning with isopropanol.

<u>Concentration of Contaminant Species</u>

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





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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

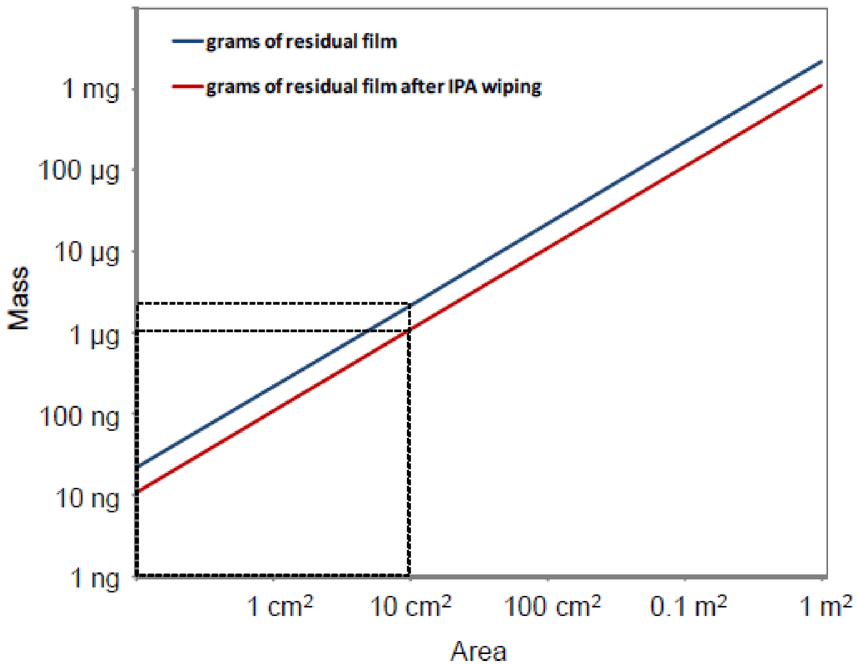
Microset application is simple, easy, and repeatable
…gun application with static mixers.

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.)

Use of Microset is being implemented.



Residual film assumed to have a thickness of 2 nm and a density of 1.1 g/cm^3

Acknowledgements

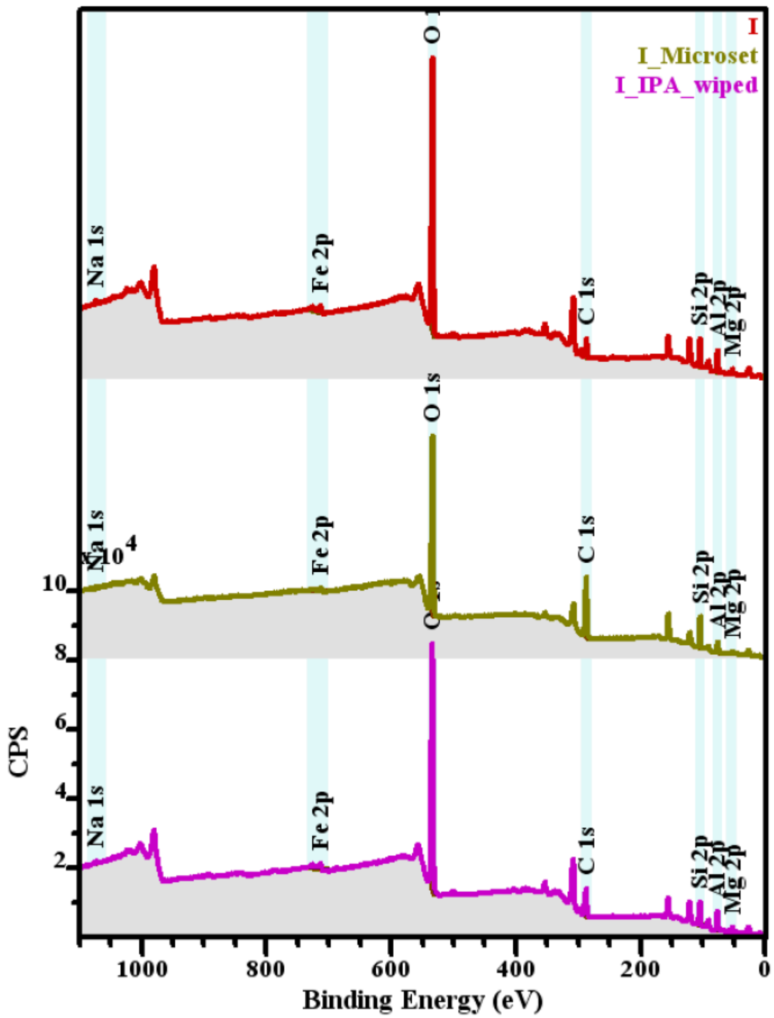
Jim Aubert
Bill Wallace
Tony Ohlhausen

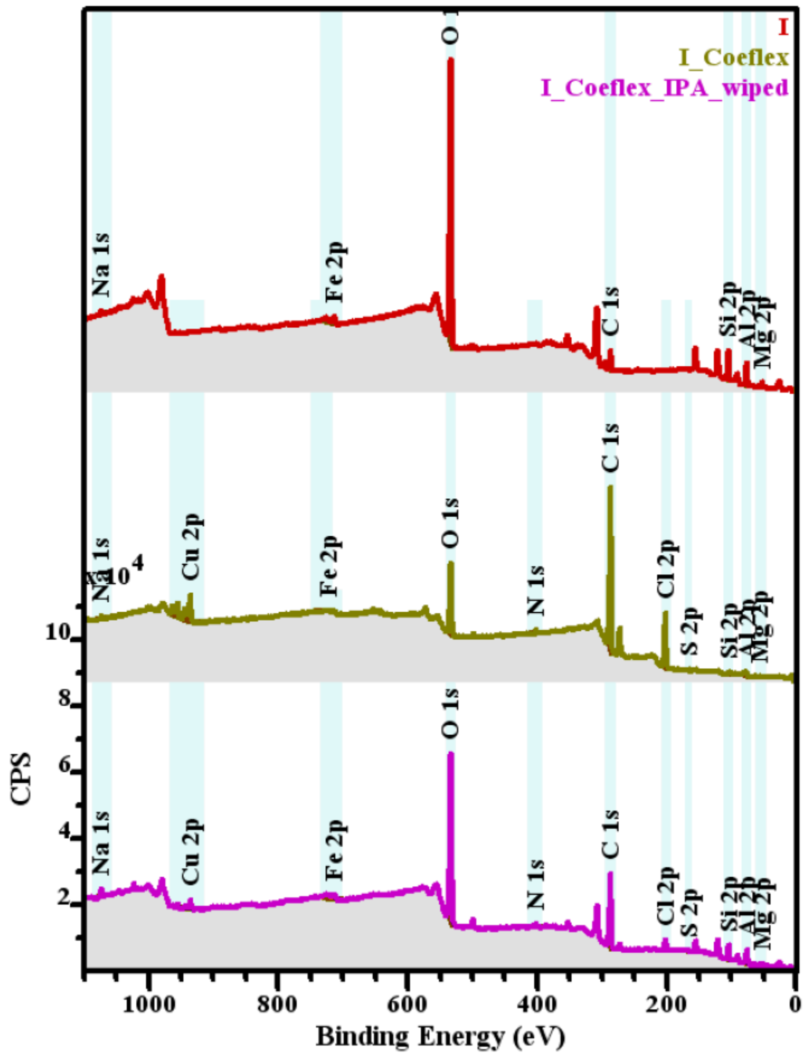
Mike Kelly

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

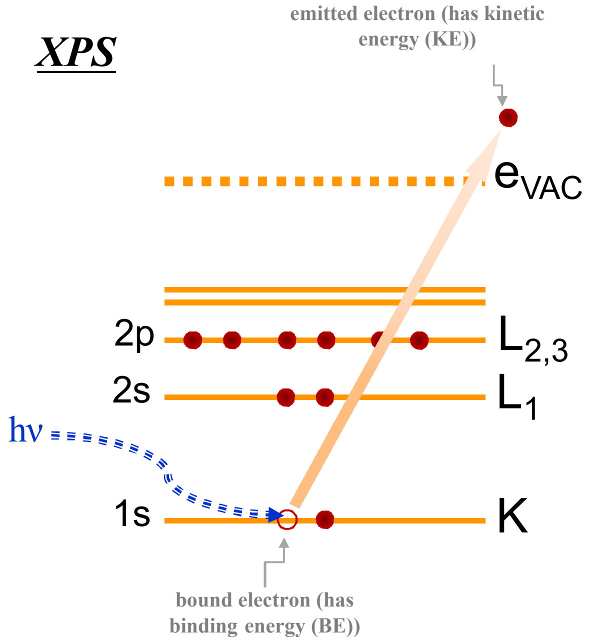
ellipsometry

	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 -

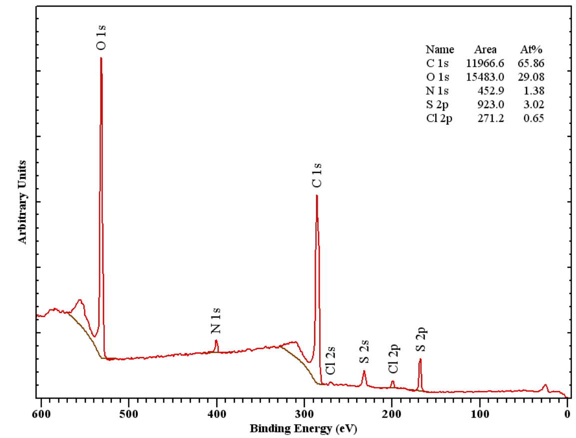


$$BE = h\nu - KE - \Phi_{spectrometer}$$

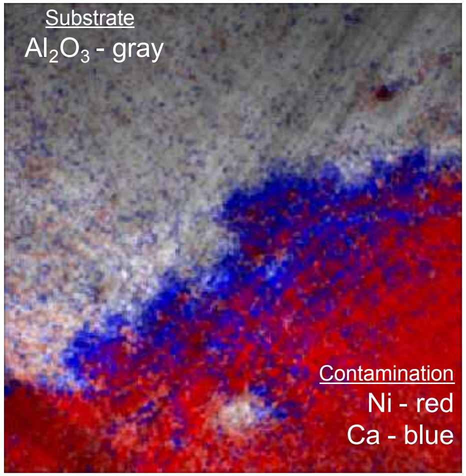
The inelastic mean free path (IMFP or λ) of an emitted electron makes XPS a very surface sensitive technique.

Compositional Analysis

(identification and quantification)

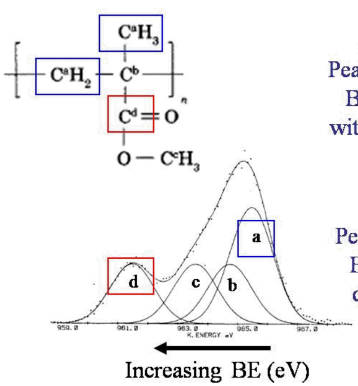


Chemical Imaging



Peak Fitting for Chemistry

(valence and chemical environment)



Oxidizing

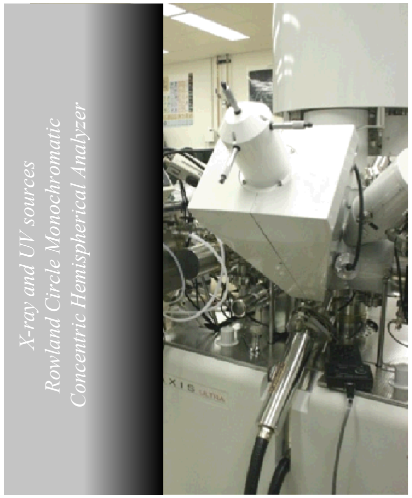
Peaks shift to higher BE with electron withdrawing groups

Reducing

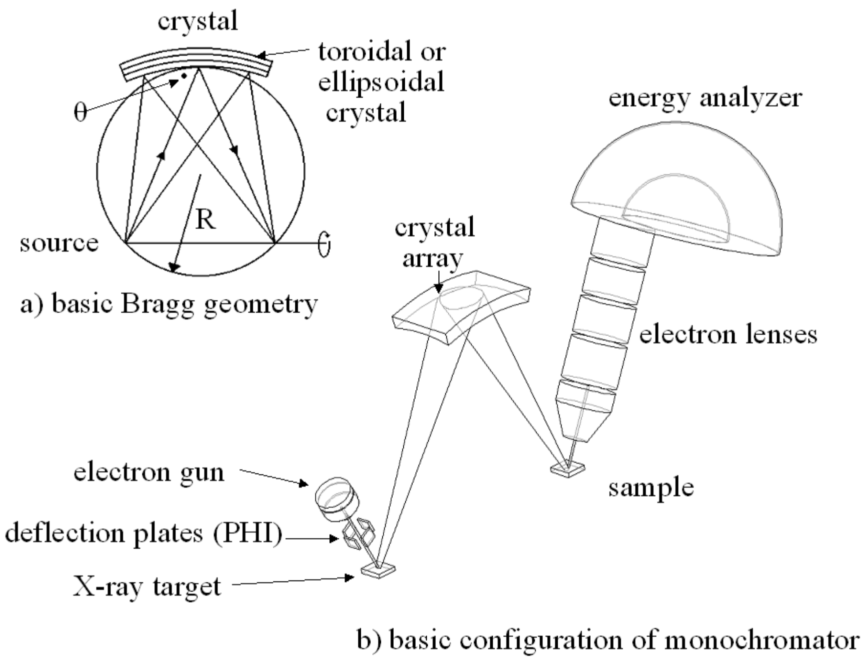
Peaks shift to lower BE with electron donating groups

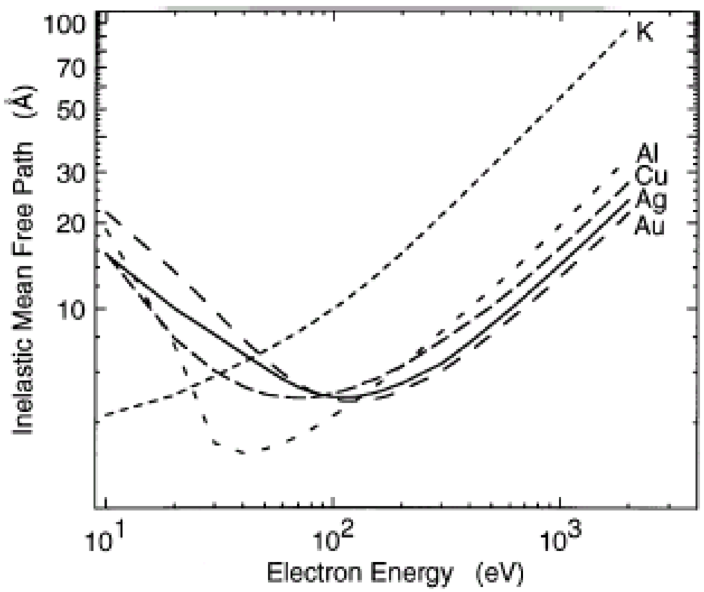
Pijpers, Donners, *J. Polym. Sci. Chem. Ed.* (1985) **23**, 453.

Kratos Axis Ultra DLD



Monochromatic X-ray source





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