ThermoFisher SCIENTIFIC

The design of an integrated XPS/Raman spectroscopy instrument for co-incident analysis

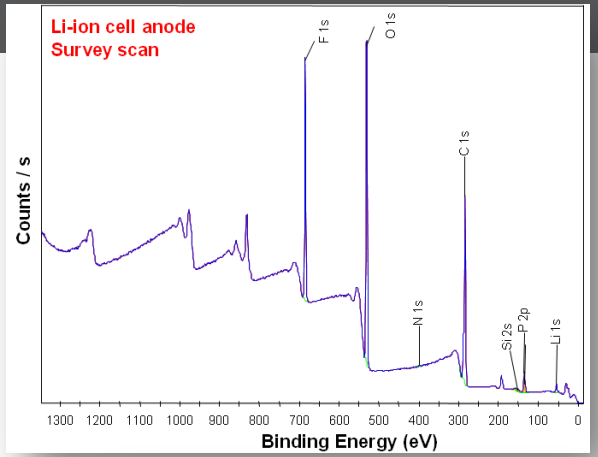
Tim Nunney

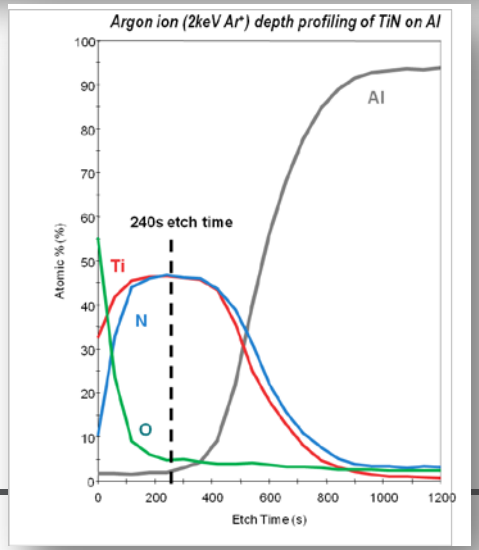
XPS Surface Analysis

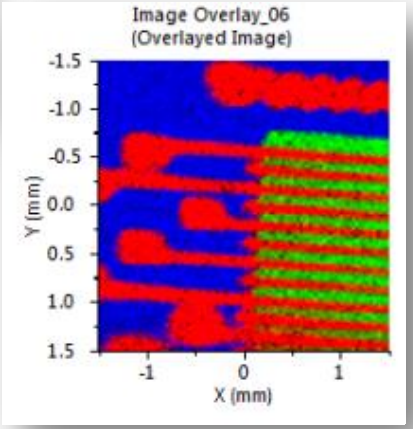
XPS
- Understand the surface chemistry

Imaging XPS
- Locate it on the surface

Depth Profiling
- Understand variation from surface to bulk



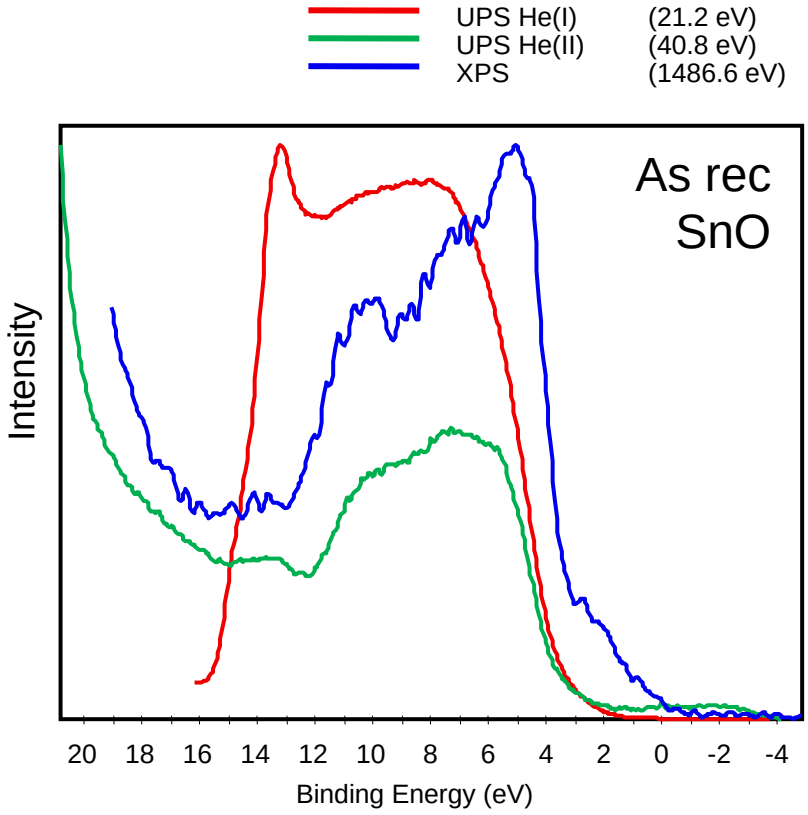




ThermoFisher SCIENTIFIC

XPS + ...

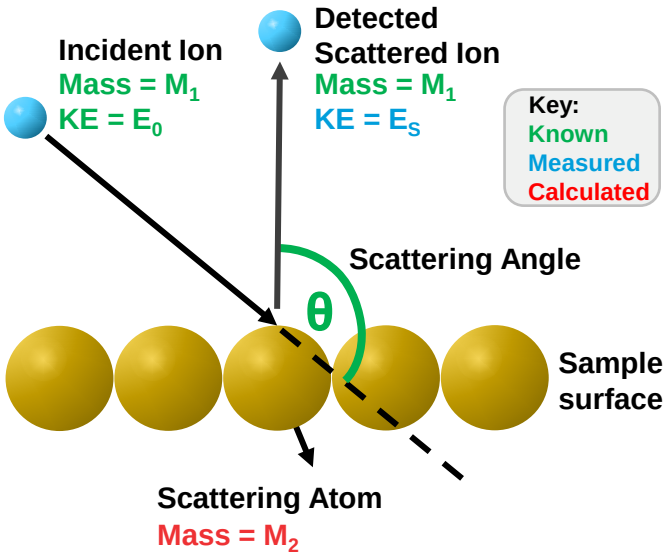
- UV Photoelectron Spectroscopy

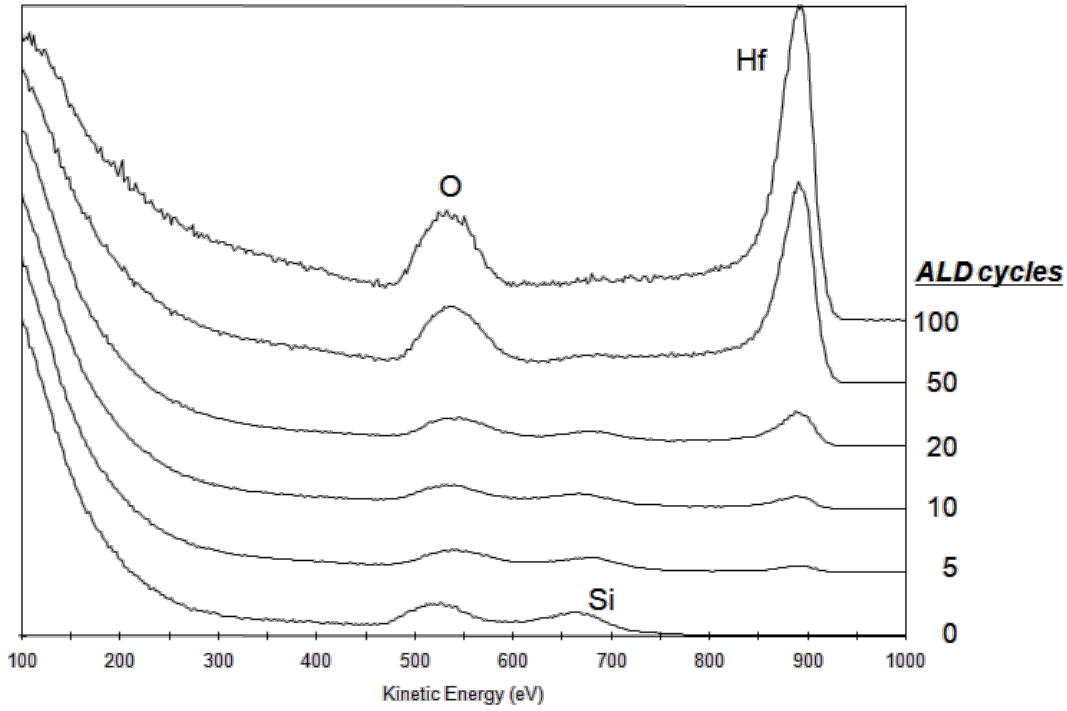


ThermoFisher SCIENTIFIC

XPS + ...

- UV Photoelectron Spectroscopy
- Ion Scattering Spectroscopy

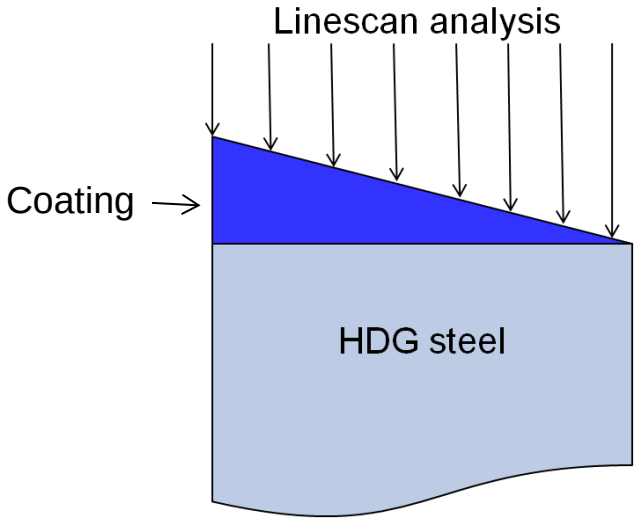


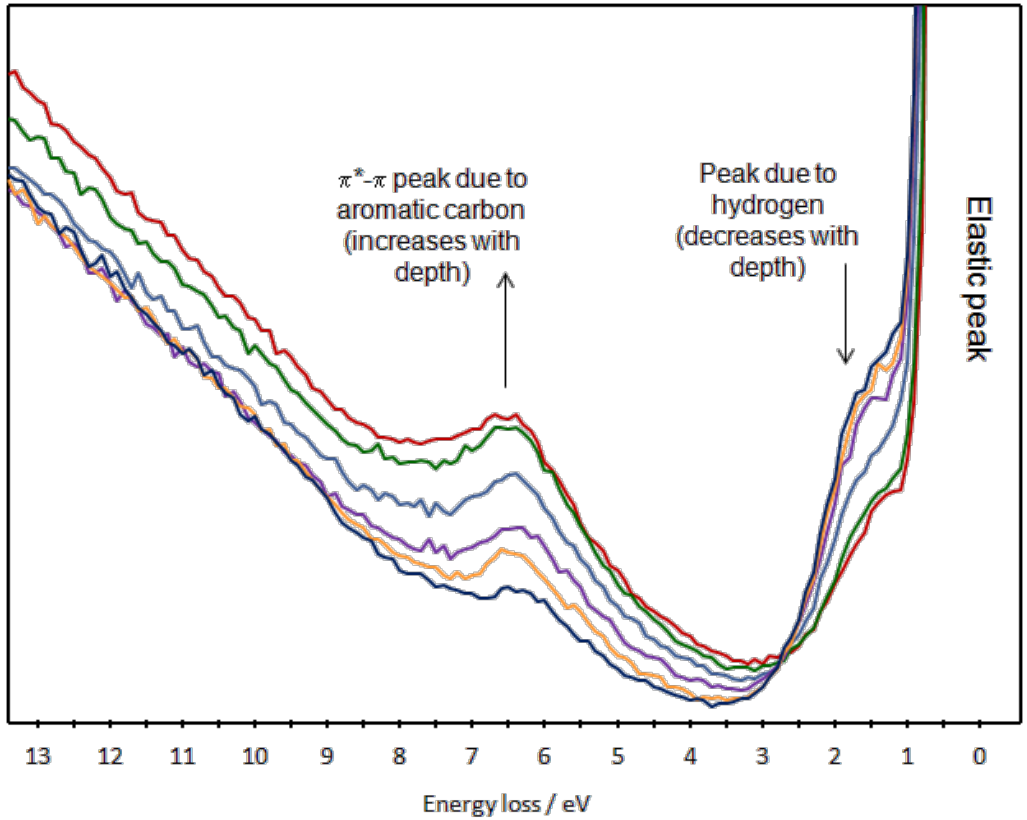


ThermoFisher SCIENTIFIC

XPS + ...

- UV Photoelectron Spectroscopy
- Ion Scattering Spectroscopy
- REELS





ThermoFisher SCIENTIFIC

(Some) other analysis techniques

XPS

Quantitative chemical state

Very surface sensitive

EDS

High spatial resolution imaging

Rapid image analysis

Raman

Chemical bonding information

Structural information

FTIR

Chemical bonding information

Molecular 'fingerprint'

XRF

Elemental composition

High sensitivity

XRD

Structural information

Crystallinity and composition

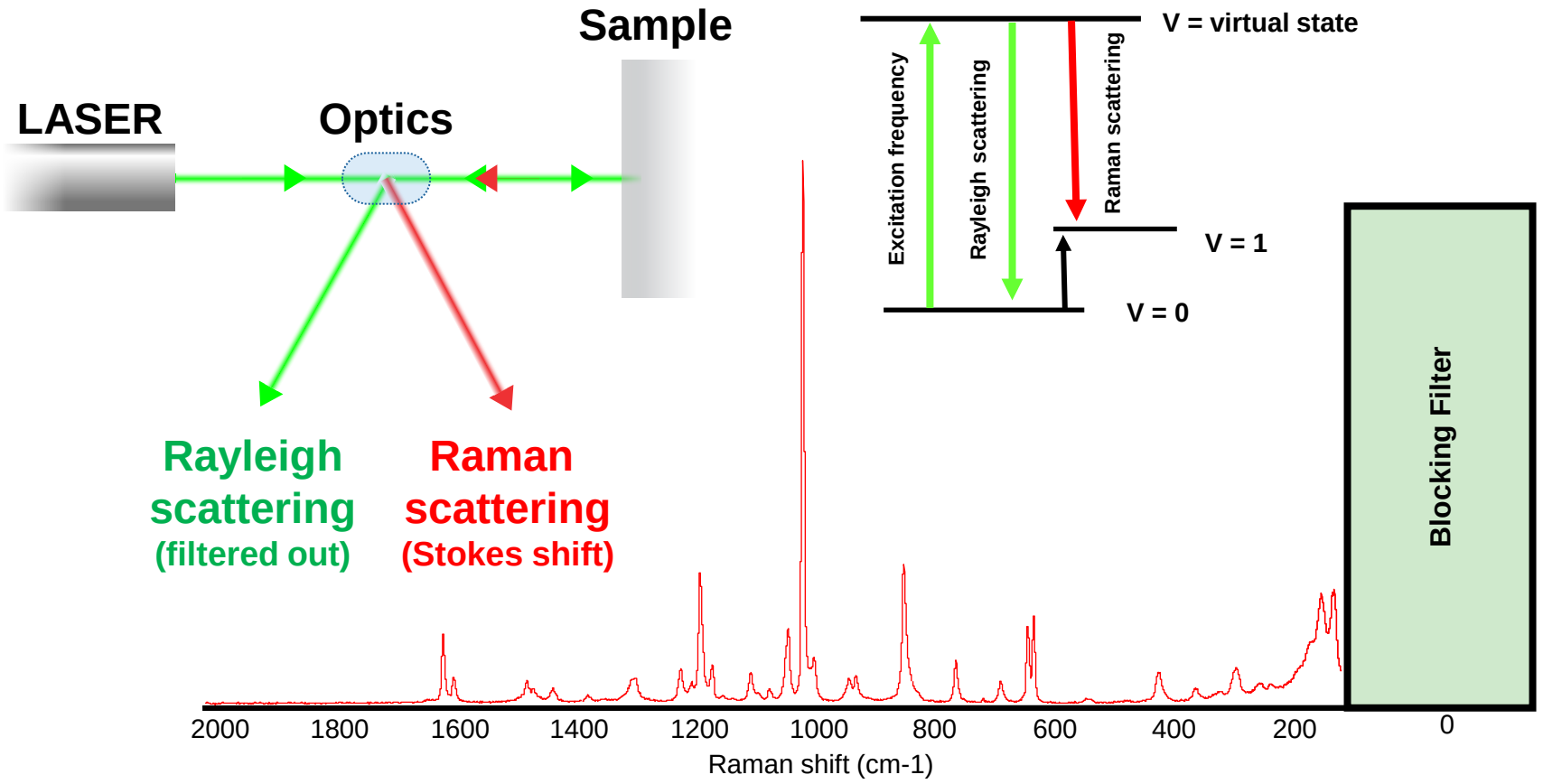
ThermoFisher SCIENTIFIC

Other techniques

XPS	EDS	Raman	FTIR	XRF	XRD
Quantitative chemical state Very surface sensitive	High spatial resolution imaging Rapid image analysis	Chemical bonding information Structural information	Chemical bonding information Molecular ‘fingerprint’	Elemental composition High sensitivity	Structural information Crystallinity and composition

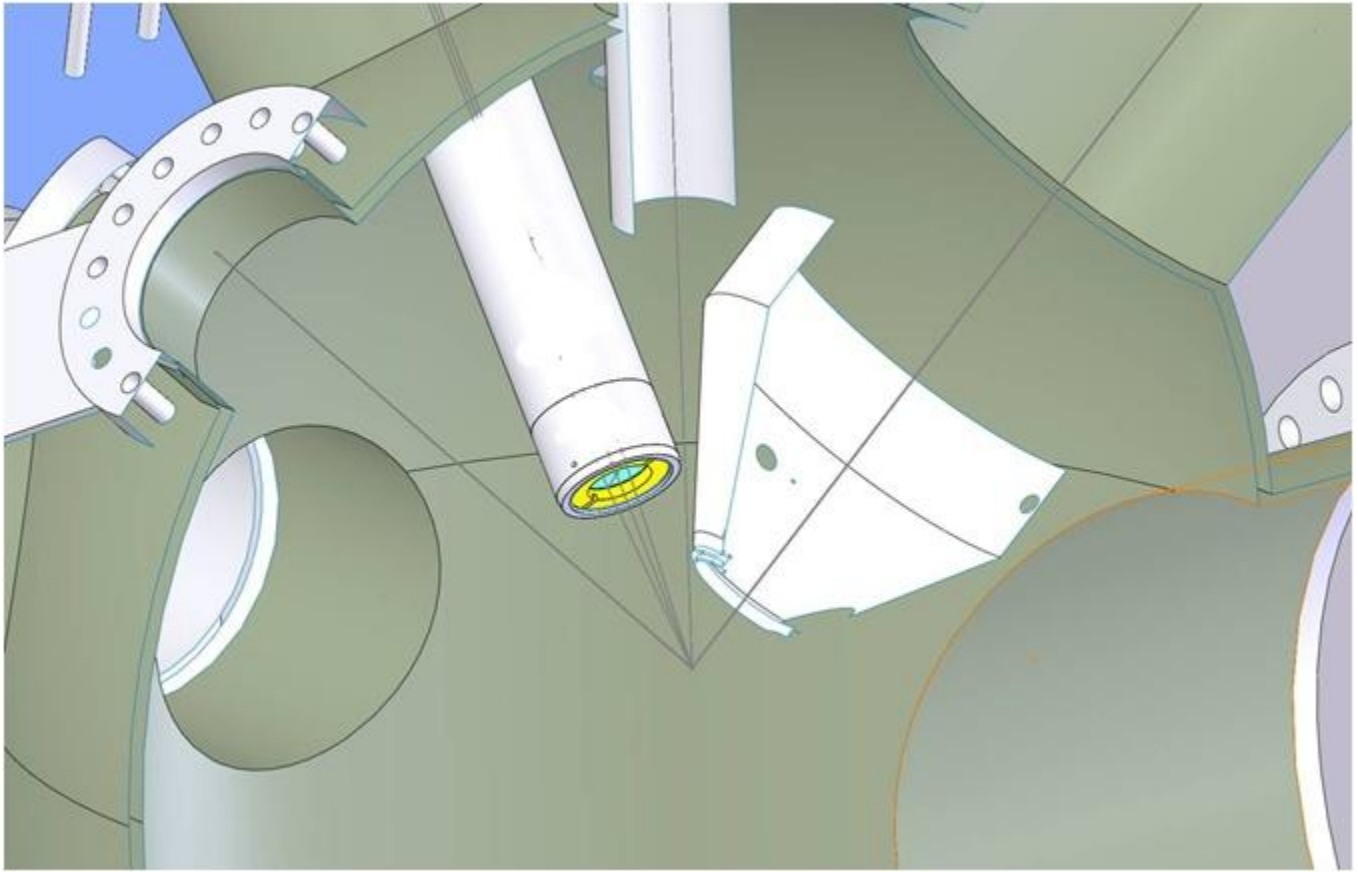
ThermoFisher SCIENTIFIC

Raman Spectroscopy



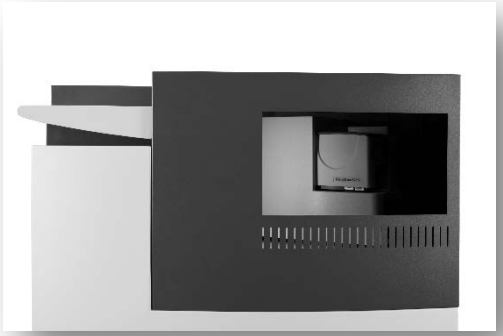
ThermoFisher SCIENTIFIC

XPS-Raman



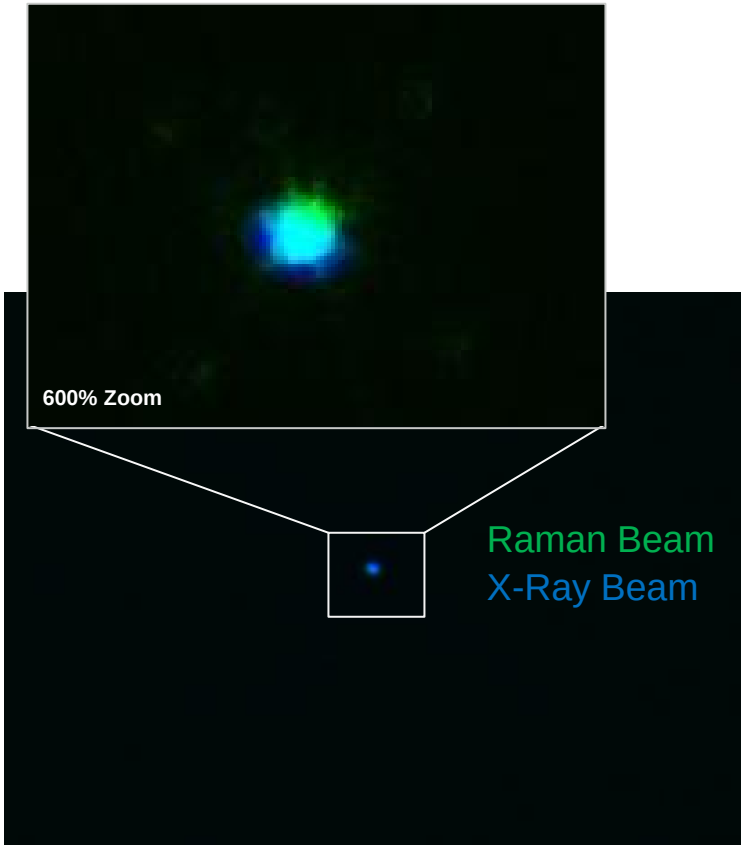
ThermoFisher SCIENTIFIC

XPS with iXR Raman Spectrometer



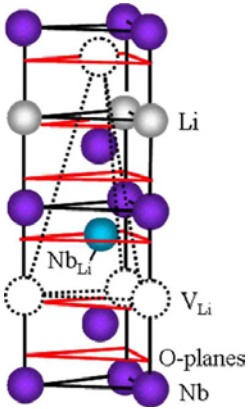
- Integration of small form factor Thermo Scientific™ iXR Raman spectrometer with
  - Thermo Scientific™ Theta Probe and
  - Thermo Scientific™ Nexsa XPS systems
- Allows simultaneous acquisition of Raman & XPS data
- Correlated analysis position
  - No need to move the sample to acquire data
  - Analysis area is matched
- Software control allows complex hybrid experiments

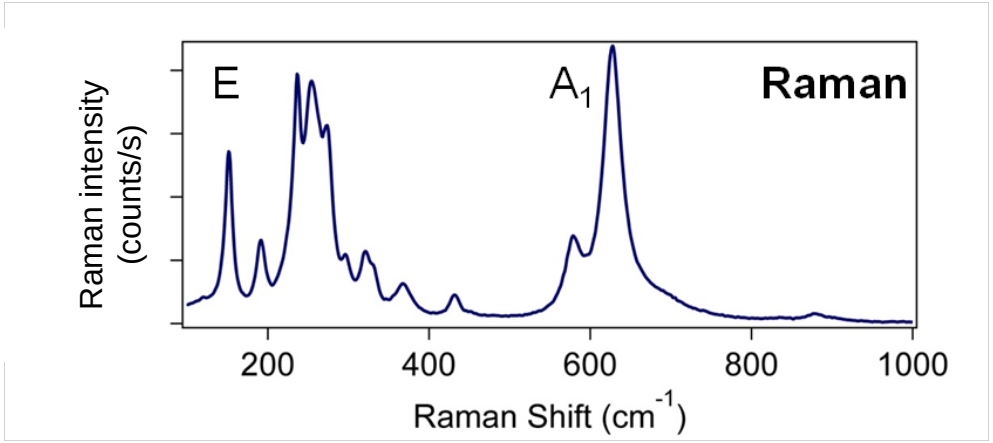
Co-alignment of analysis positions



ThermoFisher SCIENTIFIC

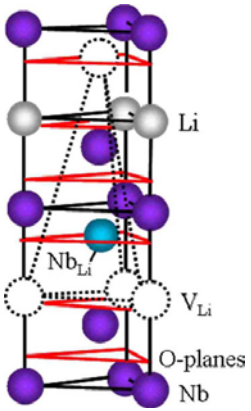
Lithium niobate

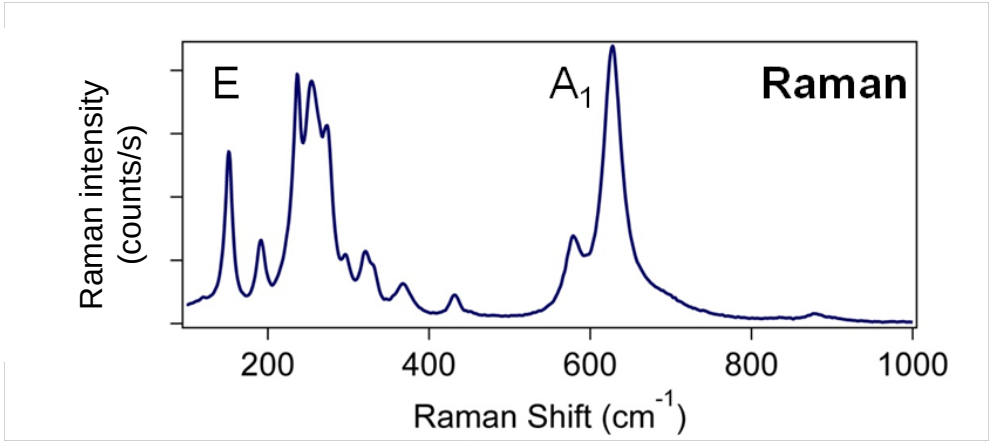


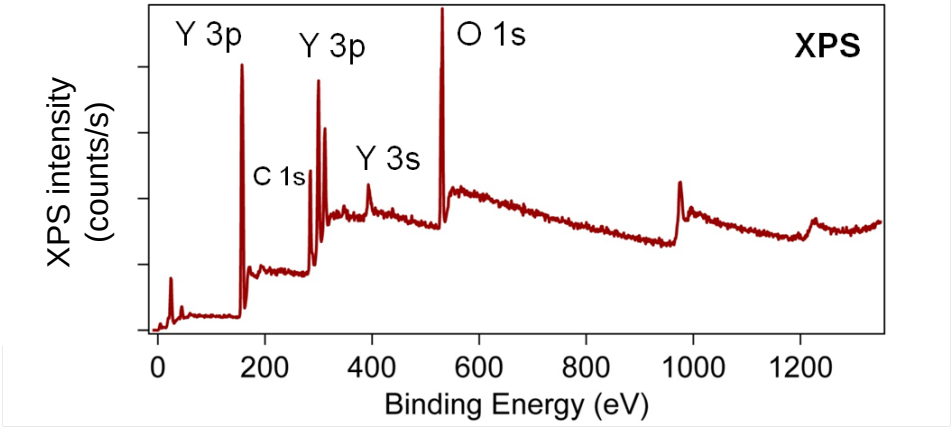


ThermoFisher SCIENTIFIC

Lithium niobate...?





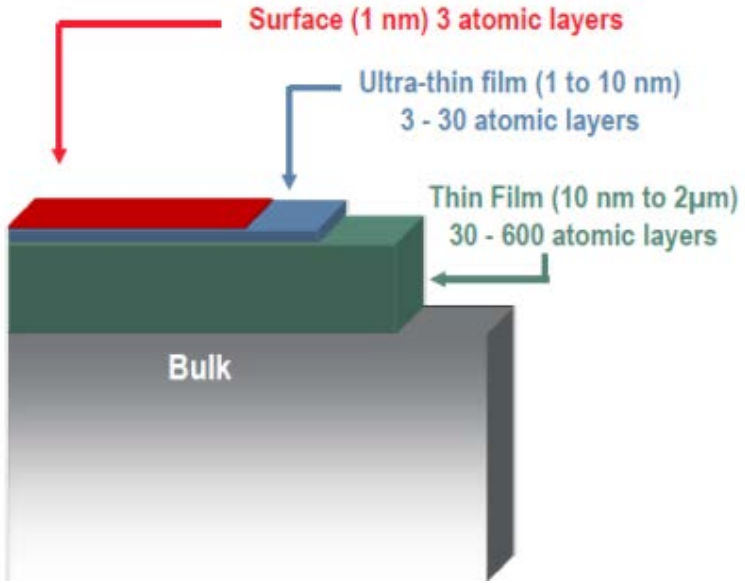


ThermoFisher SCIENTIFIC

Bulk vs surface

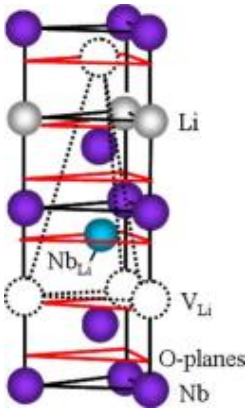
- For strongly absorbing materials such as semiconductors, the Raman signal is acquired from a volume defined by the Raman penetration depth and the diameter of the laser beam
- A lower laser wavelength gives smaller penetration and provides chemical information closer to the samples surface
- Nominal XPS sampling depth is ≤ 10 nm

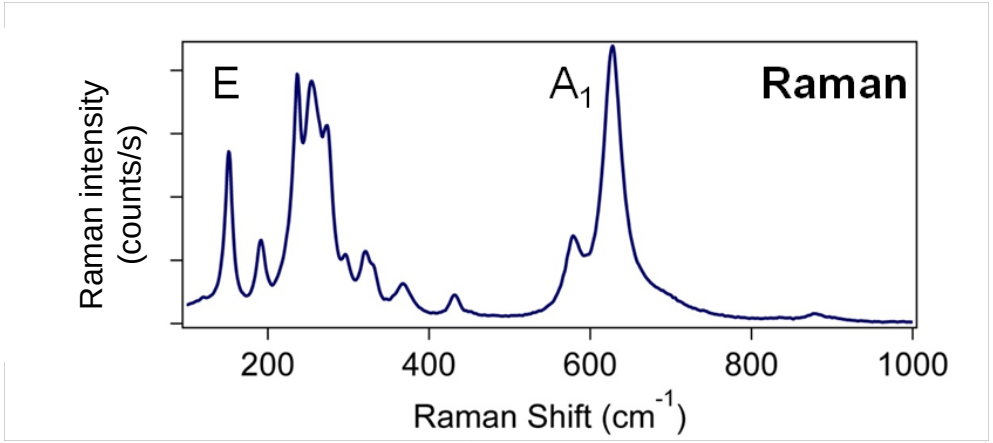
Laser Wavelength (nm)	Penetration Depth in Si (nm)	Penetration Depth in Ge (nm)	Penetration depth in a transparent Polymer Film (nm)
633	3000	30	>5000
514	760	19	>5000
488	570	18	>5000
457	310	18	>5000
325	10	9	>5000
244	6	7	>5000



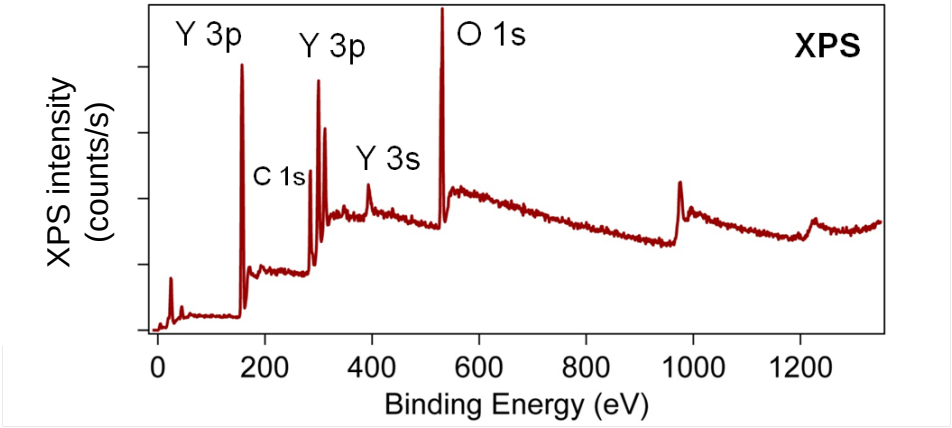
ThermoFisher SCIENTIFIC

Lithium niobate with yttrium oxide coating





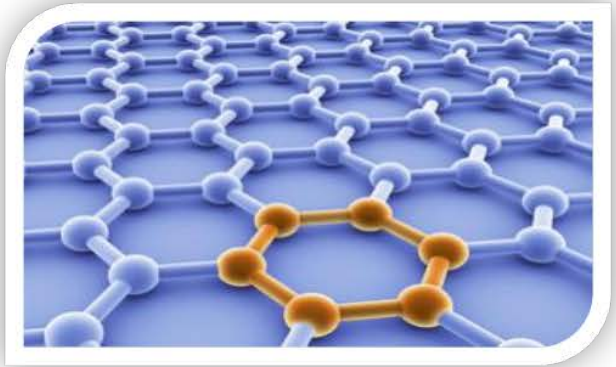
Bulk



Surface

ThermoFisher SCIENTIFIC

Applications Area: Carbon



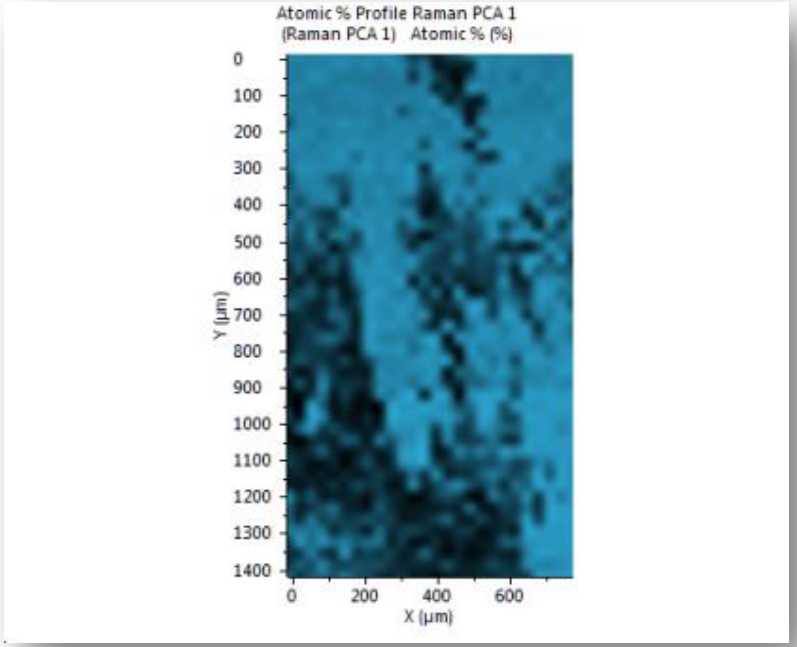
- Information from Raman / XPS / EDS
  - Layer thickness
  - CNT morphology
  - Contaminant ID
  - Chemical modification ID

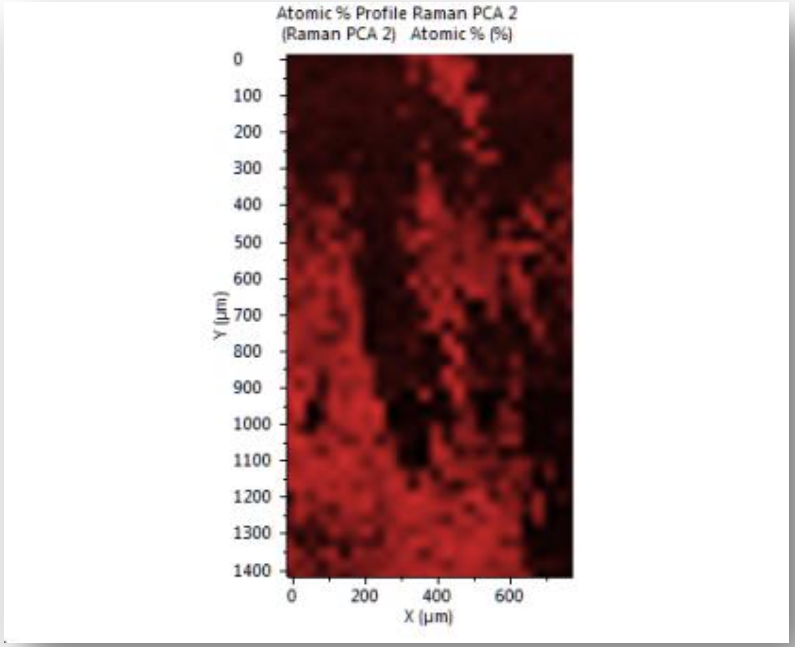
- Problems
  - Graphene layers
  - Catalyst contamination
  - Chemical modification success
  - QA/QC production

- Example solutions
  - Layer characterisation
  - Modification quantification
  - Nanotube characterisation
  - Contaminant quantification

ThermoFisher SCIENTIFIC

Graphene on SiO_2

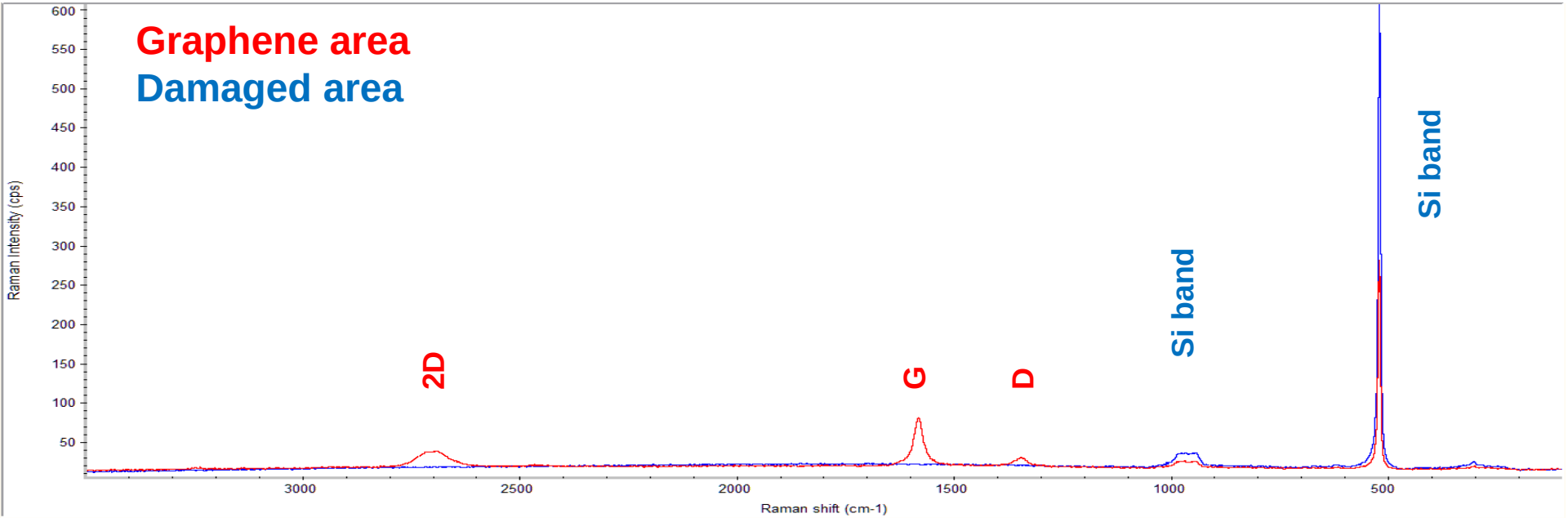




Raman imaging of damaged graphene layer deposited on a silicon wafer
(Mapping controlled through Avantage software)

ThermoFisher SCIENTIFIC

Graphene – PCA analysis of map



No graphene signal from damage zone

8 mW
50 µm pinhole
15 x 10s acquisitions

ThermoFisher SCIENTIFIC

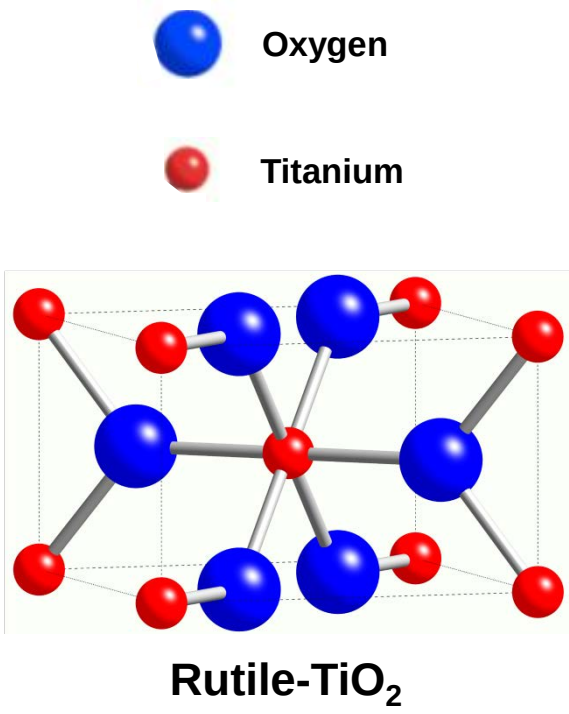
Graphene - XPS

Both areas are contaminated by the adhesive material in the container that the sample was face down on. Not visible in Raman, but easy to see in XPS.

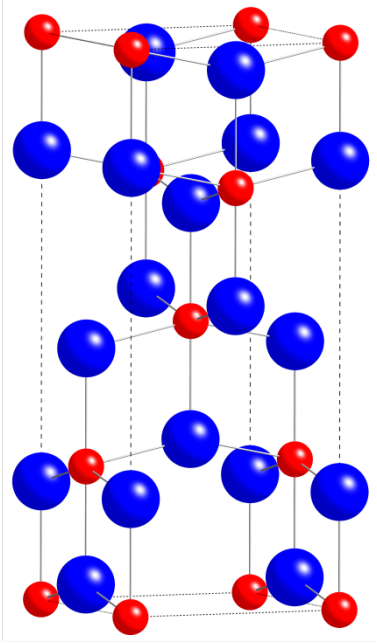
ThermoFisher SCIENTIFIC

TiO_2 powders

- Titanium dioxide (TiO_2)
  - Material of great interest due to its application in heterogeneous catalysis, dye-sensitised solar cells, bone implants and self-cleaning windows, amongst others
  - Frontier material in the development of nanotechnology, nanoparticles, nanorods etc. fabricated to improve application properties
  - Most abundant polymorphs are rutile and anatase
  - Degree of mixing between two polymorphs influences material properties, such as catalytic activity



Rutile-TiO_2



Anatase-TiO_2

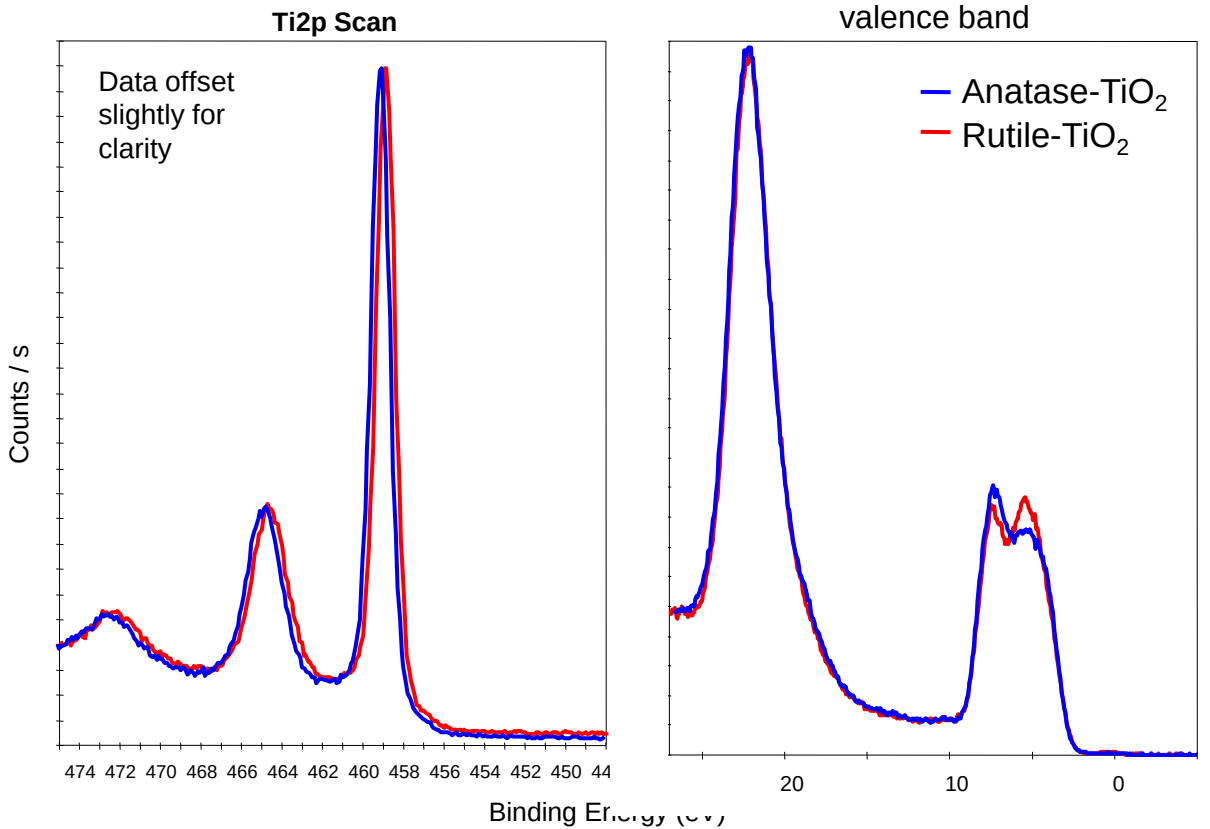
ThermoFisher SCIENTIFIC

TiO_2 powders

XPS of single polymorph

- Core level XPS spectra show identical elemental and chemical composition for pure anatase and pure rutile samples

- There is a slight variation in peak shape of valence band, however this is not conducive to easy quantification of the amount of polymorph.

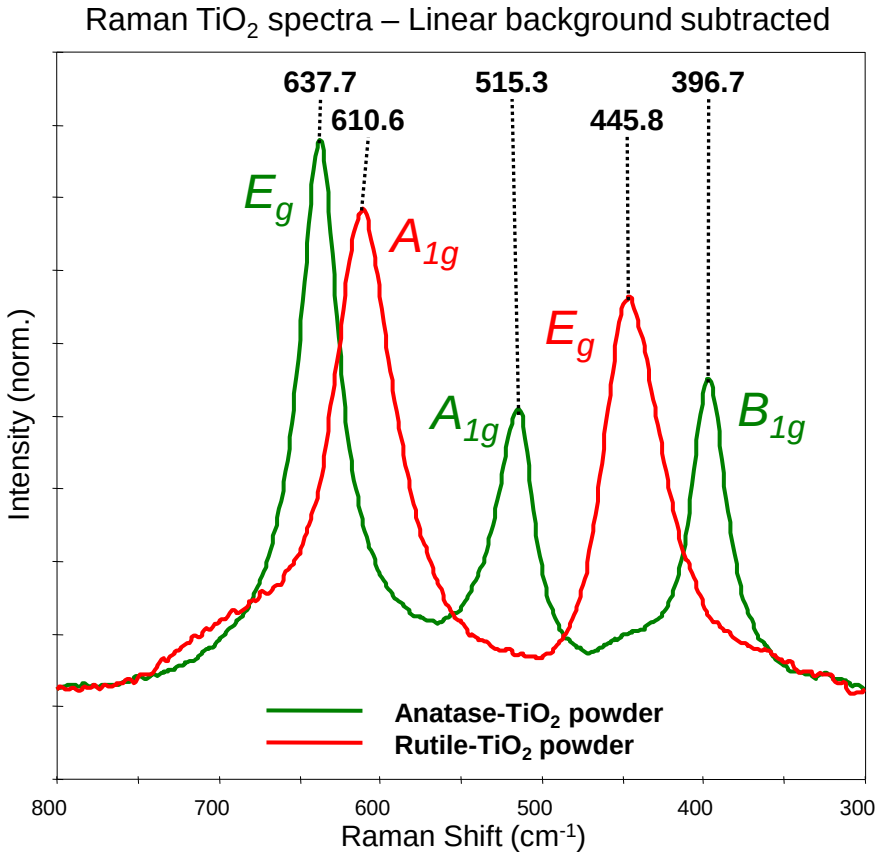


ThermoFisher SCIENTIFIC

TiO_2 powders

- Raman spectra were acquired from pure anatase-TiO_2 and rutile-TiO_2 powders

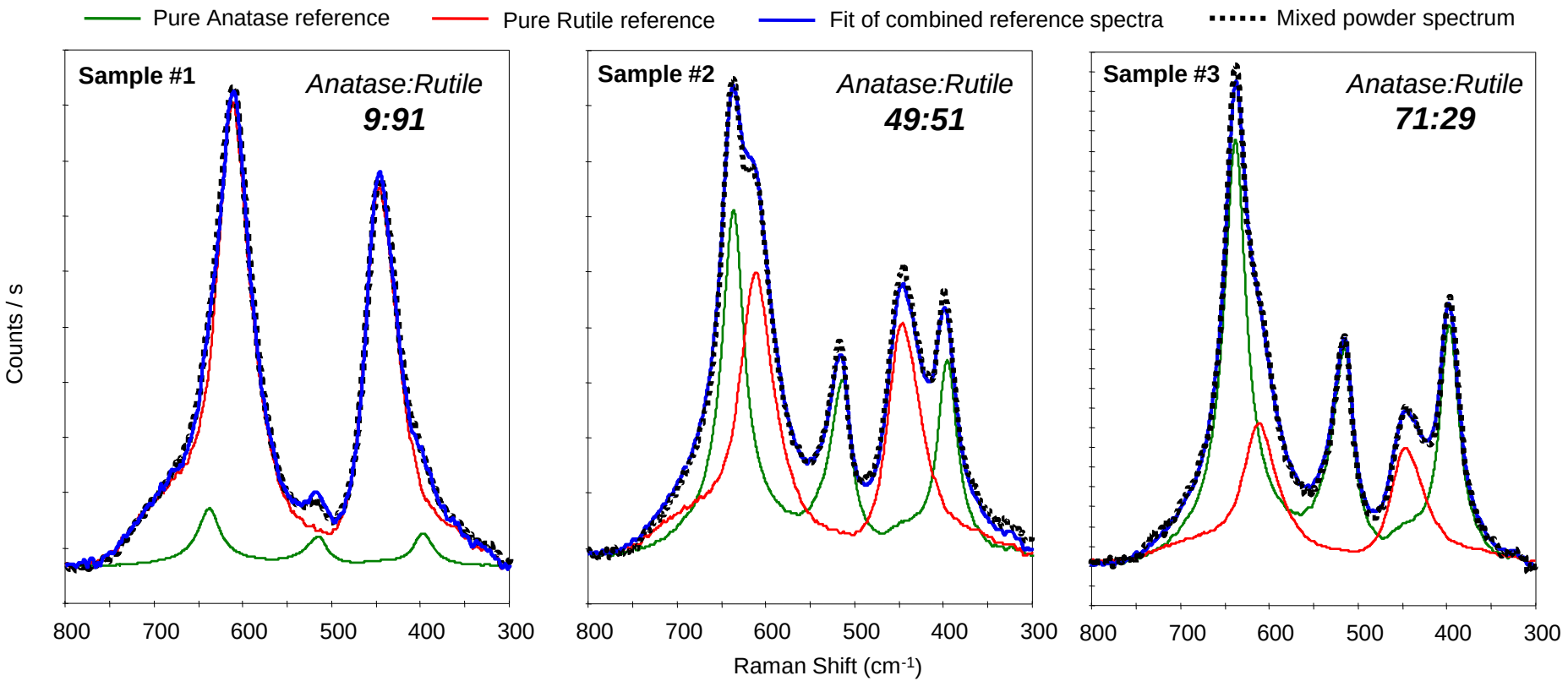
- Pure spectra can be used as reference for determining the composition of powders with different proportions of anatase and rutile



ThermoFisher SCIENTIFIC

TiO_2 powders

Raman spectroscopy of mixed powders



ThermoFisher SCIENTIFIC

Summary

- Adding extra analytical techniques increases the information that can be obtained.
- Matching the technique to the application is important
- Having co-incident analysis points ensures that the data is collected from the same point on the sample, but...
- ...consideration must be made of variations between analysis volumes.
- Offers opportunities for
  - Bulk – surface studies
  - Carbon nanomaterials
  - Coating analysis
  - .....