PMR 5251

Assessment of Mechanical Behavior of Materials using Machine Learning Approach

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Materials Characterization

Encyclopedia of materials characterization:surfaces, interfaces, thinfilms/C. Richard Brundle,Charles A.Evans, Jr., Sham Wilson., 1992
ISBN CL7506-9168-9

" Though a wide range of analytical techniques is covered in this volume there are certain traits common to many of them. Most involve either electrons, photons, or ions as a probe beam strikingthe materialto be analyzed.The beam interactswith the matéria linsome way,and insome of the techniques the *changes* induced inthe beam (energy, intensity, and angular distribution) are monitored after the inter- action, and analytical information is derived from the observation of these changes. In other techniques the information used for analysis comes from elec- trons, photons, or ions that are ejected from the sample under the stimulation of the probe beam. In many situations several connected processes may be going on more or less simultaneously, with a particular analytical technique picking out only one aspect, e.g., the extent of absorption of incident light, or the kinetic energy distributionof ejected electrons "

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Compilation of Comparative Information on the Analytical Techniques Discussed in This Volume

Article No.	Technique	Main information: Elemental	Chem. state	Phase	Defects	Structure	Image	Other	Depth probed (typical)	Width probed (typical)	Trace capability (typical)	Types of solid sample (typical)	Vacuum needed ?	Commercial Instrument cost	Usage	Service available
2.1	Light Microscopy				•		•	•	Variable	0.2 µm	—	All	N	1	1	Y
2.2	SEM				•		•		sub µm	10 nm	—	Cond., coated ins.	Y	2	1	Y
2.3	STM				•	•	•		sub Å	1 Å	—	Conductors	N	2	3	Y
2.3	SFM				•	•	•		sub Å	1 nm	—	All	N	2	2	Y
2.4	TEM			•	•	•	•		200 nm*	5 nm	—	All; <200 nm thick	Y	3	2	Y
3.1	EDS	•					•		1 µm	0.5 µm	500 ppm	All; $Z > 5$	Y	2	2	Y
3.2	EELS	•	•				•		20 nm*	1 nm	Few %	All; <30 nm thick	Y	2	3	N
3.3	Cathodo-luminescence		•		•			•	10 nm–µm	1 µm	ppm	All; semicond. usually	Y	1	3	N
3.4	STEM			•	•	•	•		100 nm*	1 nm	—	All; <200 nm thick	Y	3	3	N
3.5	EPMA	•					•		1 µm	0.5 µm	100 ppm	All; flat best	Y	3	2	Y
4.1	XRD			•	•	•			10 µm	mm	3%	Crystalline	N	2	1	Y
4.2	EXAFS	•				•			Bulk*	mm	Few %	All	Y/N	—	3	N
4.3	SEXAFS	•				•			1 nm	mm	Few %	Surface and adsorbate	Y	—	3	N
4.3	NEXAFS	•	•			•			1 nm	mm	Few %	Surface and adsorbate	Y	—	3	N
4.4	XPD	•	•			•			3 nm	150 µm	1%	Single crystal	Y	3	3	N
4.5	LEED				•	•			1 nm	0.1 mm	—	Single crystal	Y	—	2	N
4.6	RHEED				•	•			1 nm	0.02 mm	—	Single crystal	Y	—	2	N
5.1	XPS	•	•						3 nm	150 µm	1%	All	Y	3	1	Y
5.2	UPS		•			•			1 nm	mm	—	All	Y	—	3	N
5.3	AES	•	•				•		2 nm	100 nm	0.1%	All, inorganic usually	Y	3	1	Y

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5.4	REELS	•	•				•		2 nm	100 nm	—	All	Y	—	3	N
6.1	XRF	•							10 µm	mm	0.1%	All	N	2	1	Y
6.2	TXRF	•					•		3 nm	cm	ppb–ppm	Trace heavy metals	Y	3	3	Y
6.3	PIXE	•					•		Few µm	100 µm	10 ppm	All	Y	3	3	Y
7.1	Photo-luminescence		•		•		•	•	Few µm	Few µm	ppb	All, semicond. usually	N	1	2	N
7.2	Modulation Spectroscopy		•		•		•	•	1 µm	100 µm	ppm	All, semicond. usually	N	2	3	N
7.3	VASE							•	1 µm	cm	—	Flat thin films	N	2	3	Y
8.1	FTIR		•		•			•	Few µm	20 µm	Variable	All	N	2	1	Y
8.2	Raman Scattering		•		•			•	Few µm	1 µm	Variable	All	N	2	2	Y
8.3	HREELS		•			•			2 nm	mm	1%	All; flat cond. best	Y	3	3	N
8.4	NMR		•	•		•			Bulk	—	—	All; not all elements	N	3	3	N
9.1	RBS	•			•	•			To 2 µm	mm	0.01–10%	All	Y/N	3	2	Y
9.2	ERS							•	1 µm	mm	0.01%	H containing	Y	—	3	N
9.3	MEIS	•			•	•			1 nm	mm	0.1%–10%	All; usually single crystal	Y	3	3	N
9.4	ISS	•							3 Å	150 µm	50 ppm–1%	All	Y	—	3	Y
10.1	Dynamic SIMS	•					•		2 nm	1 µm	ppb–ppm	All, mostly semicond.	Y	3	1	Y
10.2	Static SIMS	•	•				•		3 Å	100 µm	Few %	All, mostly polymer	Y	3	2	Y
10.3	SALI	•	•						3 Å	100 nm	ppb–ppm	All, mostly inorg.	Y	3	3	N

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10.4	SNMS	•							1.5 nm	cm	50 ppm	Flat conductors	Y	2	2	Y
10.5	LIMS	•	•						100 nm	2 µm	1–100 ppm	All	Y	3	2	Y
10.6	SSMS	•							3 µm	cm	0.05 ppm	Sample forms electrode	Y	—	2	Y
10.7	GDMS	•							100 nm	cm	ppt–ppb	Sample forms electrode	Y	3	2	Y
10.8	ICPMS	•							5 µm	mm	ppt	All	Y	2	1	Y
10.9	ICPOES	•							5 µm	mm	ppb	All	Y	1	1	Y
11.1	Neutron Diffraction			•		•			Bulk	—	—	Crystalline	N	—	3	N
11.2	Neutron Reflectivity							•	Up to mm	—	—	Flat polymer films	N	—	3	N
11.3	NAA	•							Bulk	—	ppt–ppm	Trace metals	N	2	3	Y
11.4	NRA	•							10–100 nm	10 µm	10–100 ppm	All; $Z < 21$	Y	—	3	Y
12.2	Optical Scatterometry							•	—	mm	—	Flat smooth films	N	1	3	Y
12.3	MOKE						•	•	30 nm	0.5 µm	—	Magnetic films	N	1	2	N
12.4	Adsorption							•	Outer atoms	—	—	Large surface area	Y	—	2	N

Notes: This table should be used as a "quick reference" guide only.
* Measured in transmission.
Commercial Instrument cost: These are typical costs; large ranges depending on sophistication and accessories: 1 means < \$50k; 2 means \$50–300k; 3 means >\$300k. "—" means no complete commercial instrument.
Usage: Numbers refer to usage for anaylsis of solid materials. 1 means Extensive; 2 means medium; 3 means not common.
Trace capability: Guide only. Often very material/conditions dependent. "—" means not used for trace components.

Materials Characterization

- **Bulk/Elemental**
  - Qualitative
    - Major/Minor: IC†, ICP-AES, NAA, OES, SSMS, XRS
    - Trace/Ultratrace: ESR†, FT-IR**, IC†, ICP-AES, IR**, NAA, OES, SSMS
  - Quantitative
    - Major/Minor: AAS, IC†, ICP-AES, IGF†, NAA, OES, SSMS, XRS
    - Trace/Ultratrace: AAS, COMB†, ESR†, FT-IR**, IC†, ICP-AES, IGF†, IR**, NAA, OES, SSMS
- **Microanalysis/Structure**
  - Crystal structure/Phase ID: ESR*, TEM, XRD
  - Phase distribution/Morphology: EPMA, IA, OM, SEM, TEM
  - Elemental: AES, EPMA, SEM, TEM
  - Defects: SEM*, TEM, XRD
- **Surface analysis**
  - Elemental: AES, LEISS, RBS, SIMS, XPS
  - Molecular/Compound: FT-IR*, RS*, SIMS*, XPS

Fig. 1 Flow chart of inorganic solids: metals, alloys, semiconductors. Acronyms are defined in Table 10.

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Materials Characterization

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- **Bulk/Elemental**
  - Qualitative
    - Major/Minor: FT-IR†*, IC†, ICP-AES, IR†*, OES, RS†*, SSMS, XRS
    - Trace/Ultratrace: FT-IR†*, IC†, ICP-AES, IR†*, NAA, OES, SSMS
  - Quantitative
    - Major/Minor: AAS, FT-IR†*, IC†, ICP-AES, IR†*, OES, RS†*, SSMS, XRS
    - Trace/Ultratrace: AAS, FT-IR†*, IC†, ICP-AES, IR†*, NAA, OES, SSMS
- **Microanalysis/Structure**
  - Crystal structure/Phase ID: TEM, XRD
  - Phase distribution/Morphology: EPMA, IA, OM, SEM, TEM
  - Elemental: AES, EPMA, SEM, TEM
  - Defects: SEM*, TEM
- **Surface analysis**
  - Elemental: AES, LEISS, RBS, SIMS, XPS
  - Molecular/Compound: FT-IR*, IR*, RS*, SIMS*, XPS†

Fig. 2 Flow chart of inorganic solids: glasses, ceramics. Acronyms are defined in Table 10.

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Materials Characterization

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Bulk/Macroanalysis

- Elemental
  - Qualitative
    - Major/Minor: COMB†, FT-IR*, IC†, ICP-AES, IR*, NAA, OES, RS*, SSMS, XRS
    - Trace/Ultratrace: COMB†, ESR*, FT-IR*, IC†, ICP-AES, IR*, NAA, OES, SSMS
  - Quantitative
    - Major/Minor: AAS, COMB†, FT-IR*, IC†, ICP-AES, IR*, ISE†, NAA, OES, RS*, SSMS, XRS
    - Trace/Ultratrace: AAS, COMB†, ESR†, FT-IR*, IC†, ICP-AES, IGF†, IR*, ISE†, NAA, OES, SSMS
- Molecular/Compound
  - Qualitative
    - Major/Minor: FT-IR, IC†*, IR, RS, TEM, XRD
    - Trace/Ultratrace: FT-IR, IC†*, IR
  - Quantitative
    - Major/Minor: FT-IR, IC†*, IR, RS, XRD
    - Trace/Ultratrace: FT-IR, IC†*, IR

Structure

- Crystal structure: TEM, XRD
- Molecular structure: ESR†, FT-IR, IR, NMR†, RS
- Defects: SEM*, TEM, XRD

Microanalysis

- Elemental: AES, EPMA, SEM, TEM
- Phase distribution/Morphology: EPMA, IA, OM, SEM, TEM

Surface analysis

- Elemental: AES, LEISS, RBS, SIMS, XPS
- Molecular/Compound: FT-IR*, IR*, RS*, SIMS†, XPS†

Fig. 3 Flow chart of inorganic solids: minerals, ores, slags, pigments, inorganic compounds, effluents, chemical reagents, composites, catalysts. Acronyms are defined in Table 10.

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Materials Characterization

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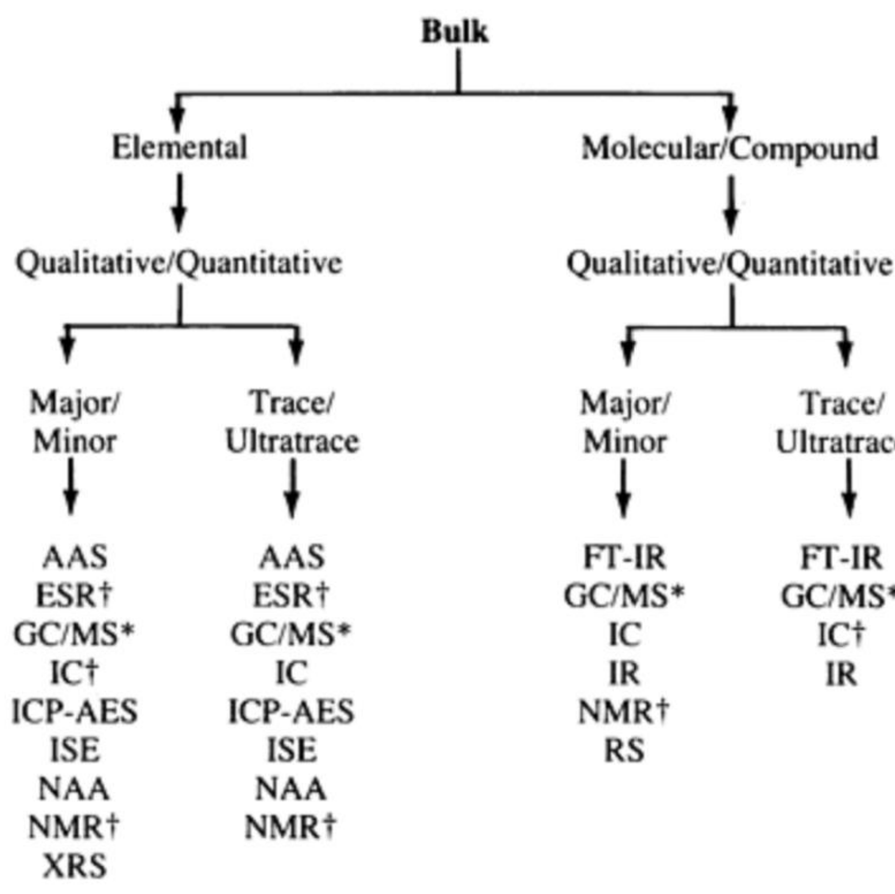

Fig. 4 Flow chart of inorganic liquids and solutions: water, effluents, leachates, acids, bases, chemical reagents. Acronyms are defined in Table 10.

Materials Characterization

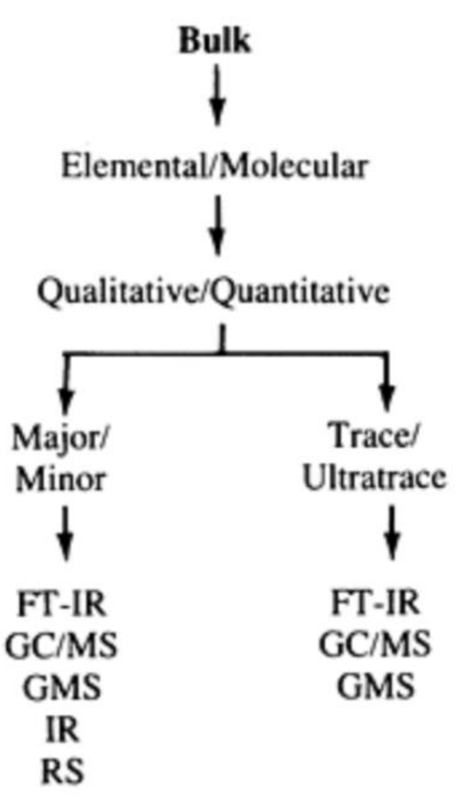

Fig. 5 Flow chart of inorganic gases: air, effluents, process gases. Acronyms are defined in Table 10.

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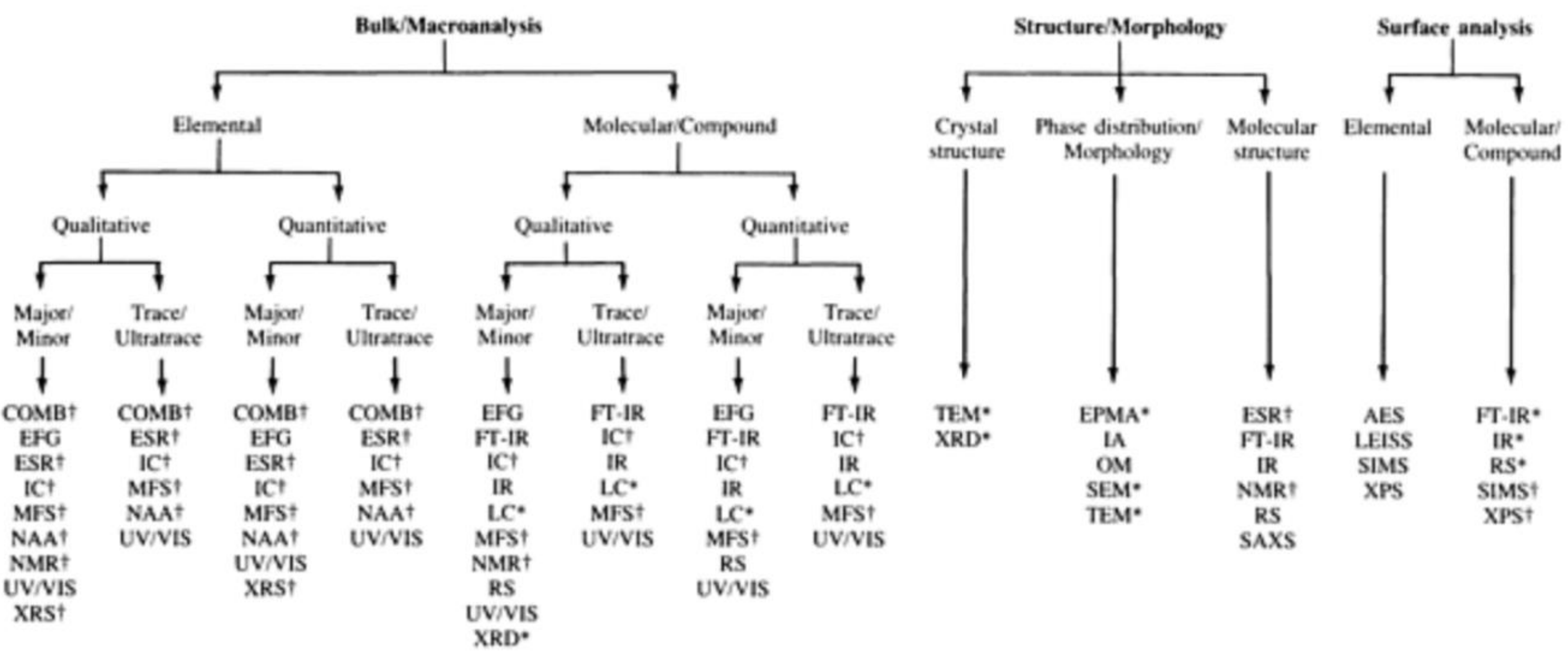

Fig. 6 Flow chart of organic solids: polymers, plastics, epoxies, long-chain hydrocarbons, esters, foams, resins, detergents, dyes, organic composites, coal and coal derivatives, wood products, chemical reagents, organometallics. Acronyms are defined in Table 10.

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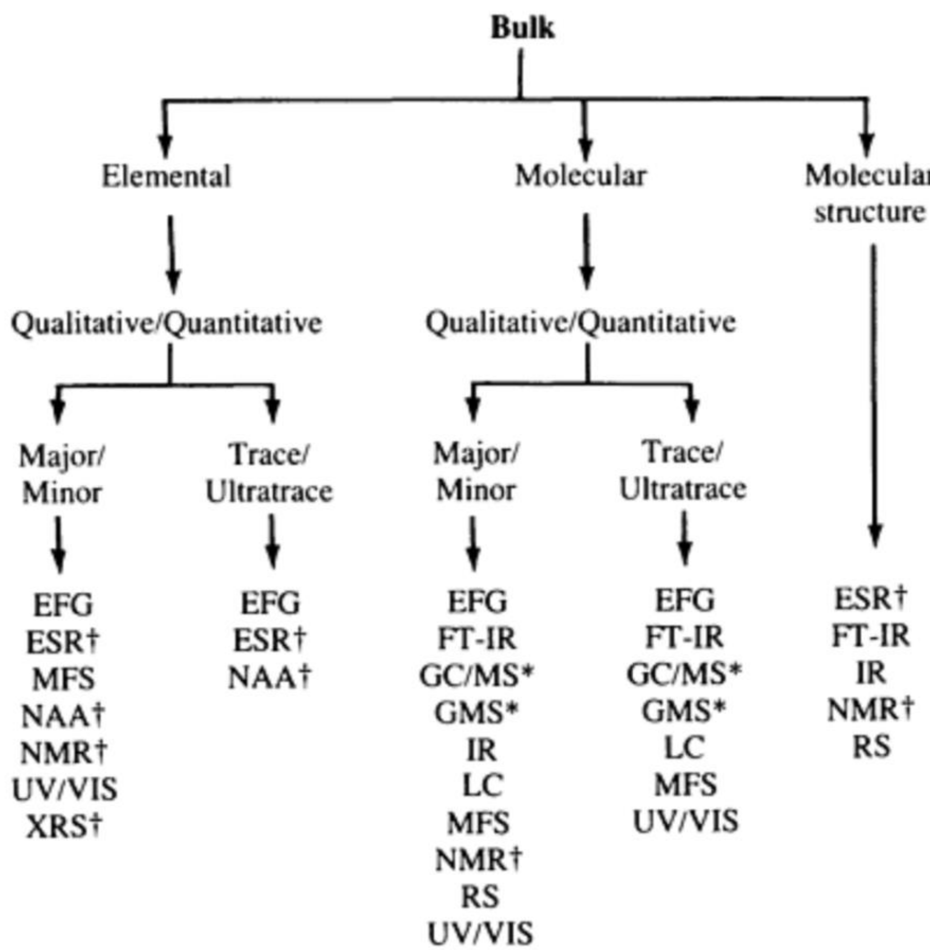

Fig. 7 Flow chart of organic liquids and solutions: hydrocarbons, petroleum and petroleum derivatives, solvents, reagents. Acronyms are defined in Table 10.

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Fig. 8 Flow chart of organic gases: natural gas, effluents, pyrolysis products, process gas. Acronyms are defined in Table 10.

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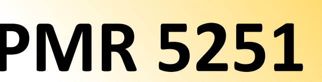
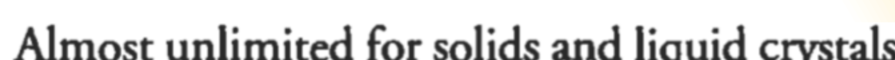


Light Microscopy

The light microscope uses the visible or near visible portion of the electromagnetic spectrum; light microscopy is the interpretive use of the light microscope

the first polished metal and metal-alloy specimens were prepared and viewed with the intention of correlating their structures with their properties



Range of samples characterized	Almost unlimited for solids and liquid crystals
Destructive	Usually nondestructive; sample preparation may involve material removal
Quantification	Via calibrated eyepiece micrometers and image analysis
Detection limits	To sub-ng
Resolving power	0.2 μm with white light
Imaging capabilities	Yes
Main use	Direct visual observation; preliminary observation for final characterization, or preparative for other instrumentation
Instrument cost	$2,500–$50,000 or more
Size	Pocket to large table

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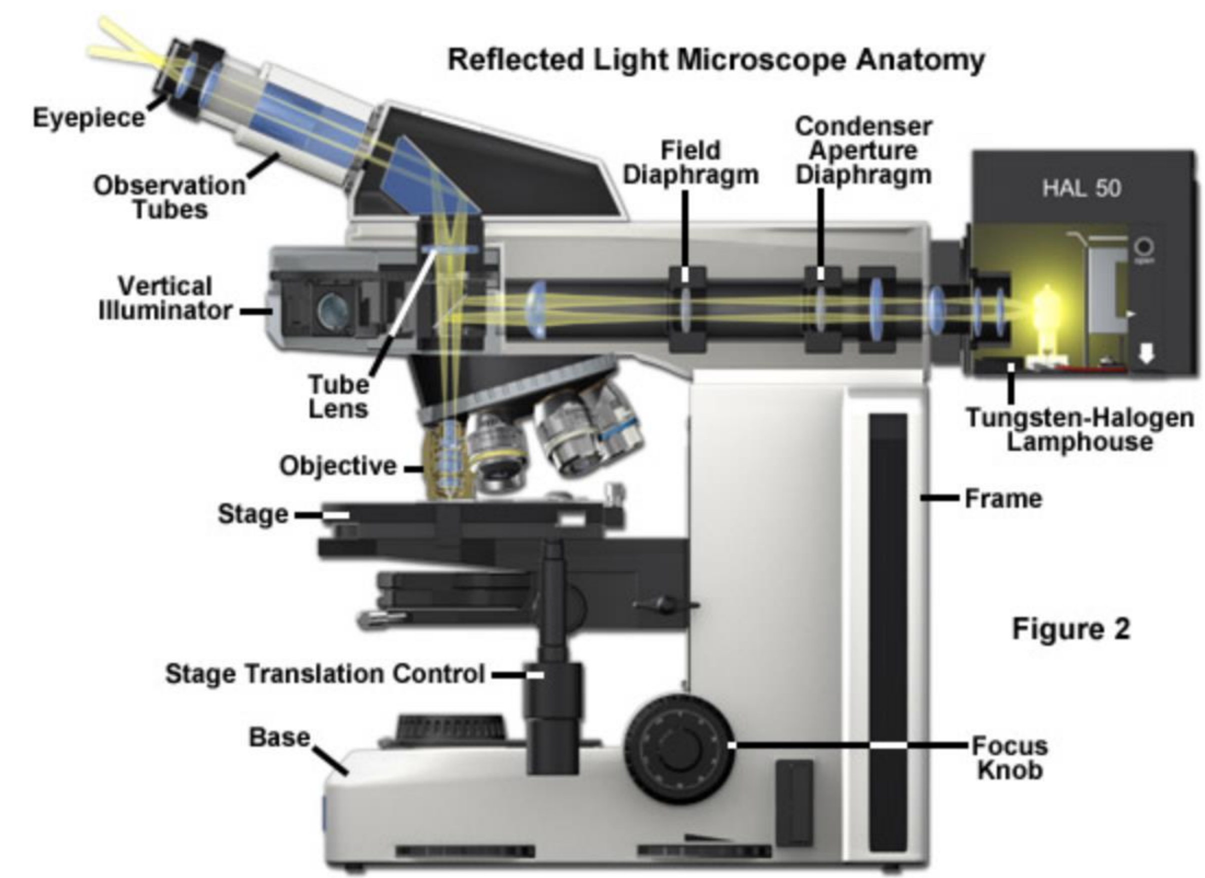
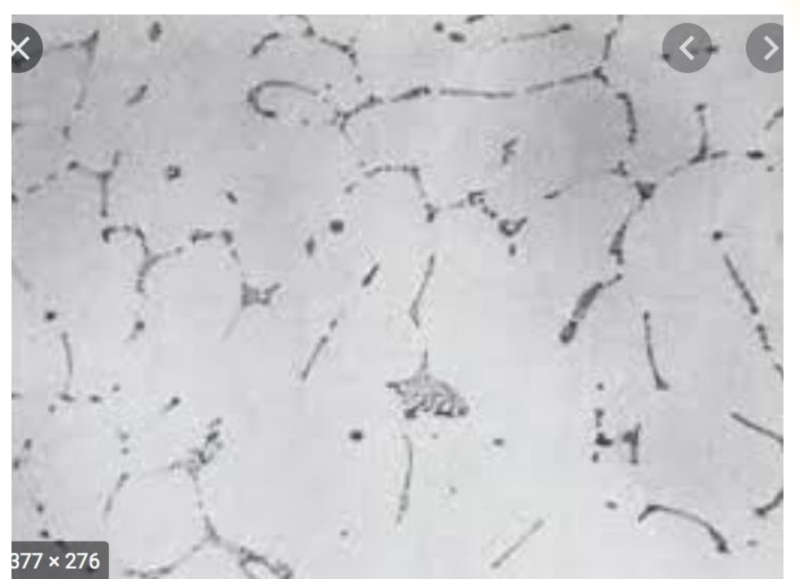
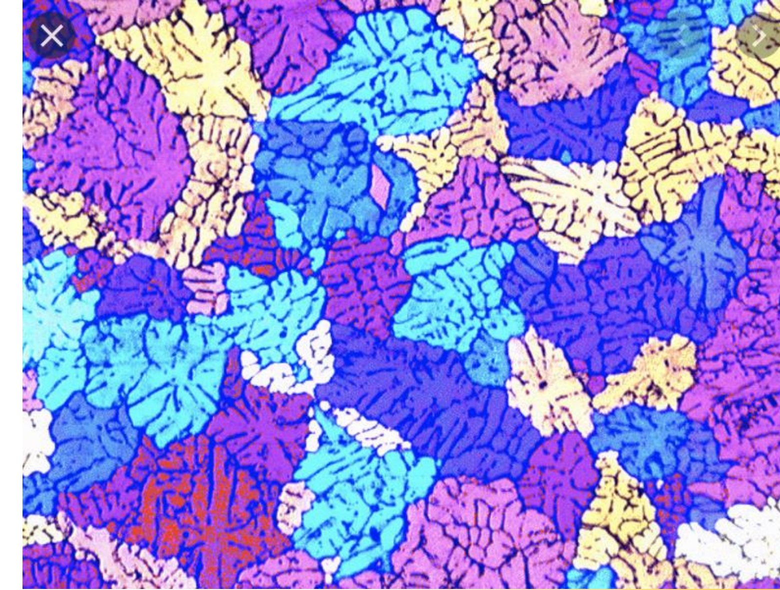
Light Microscopy

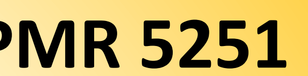




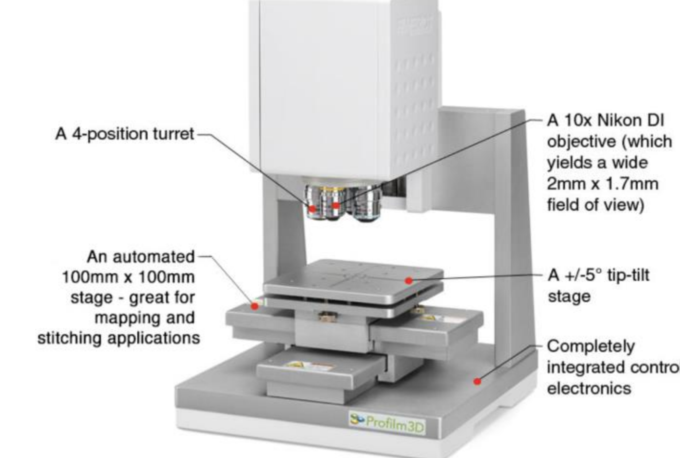
Al alloys

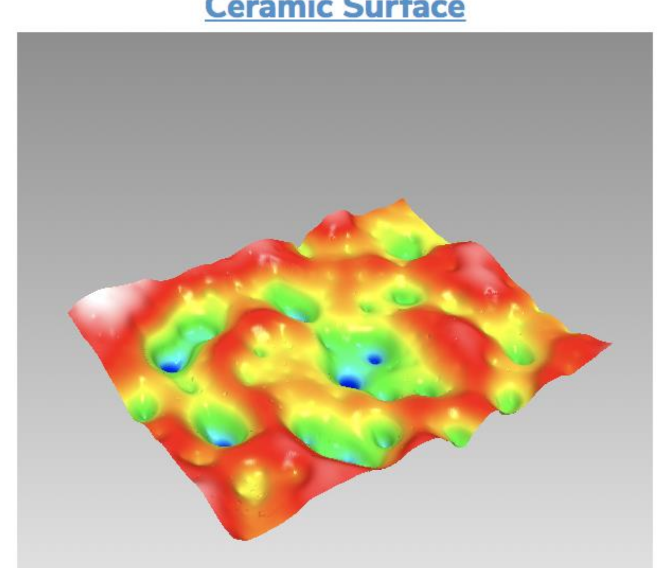


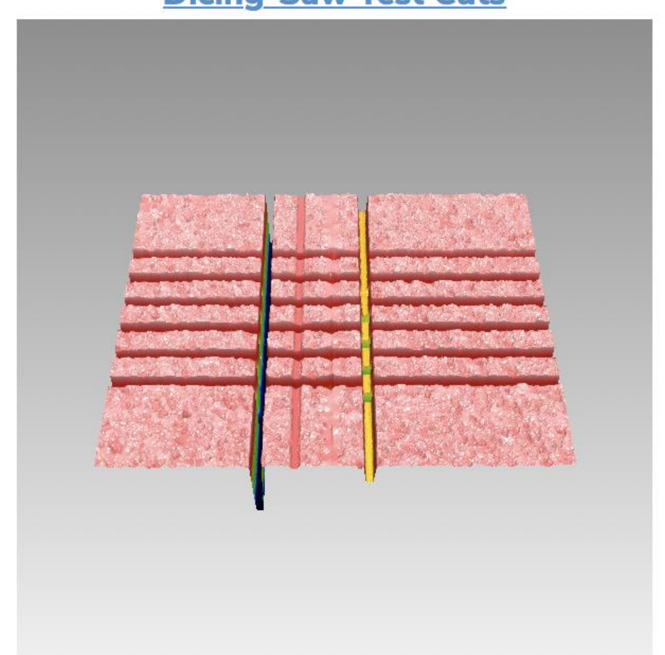
http://zeiss-campus.magnet.fsu.edu/articles/basics/reflected.html

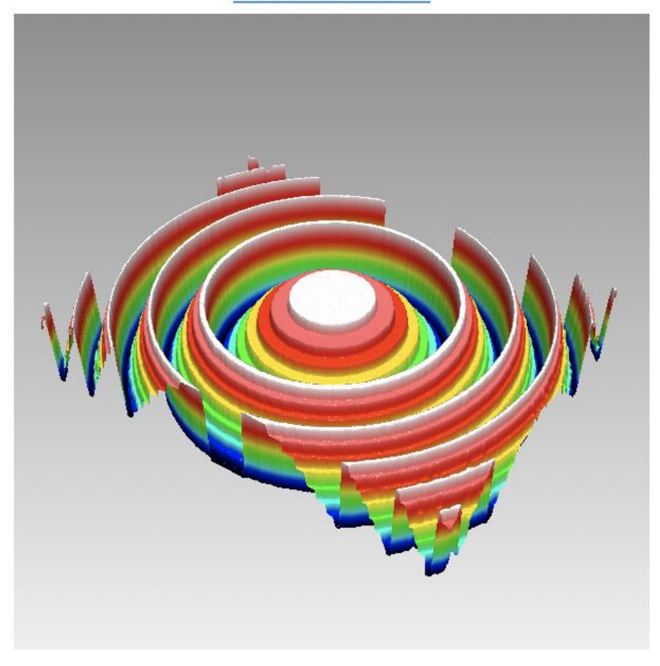


Profilometer



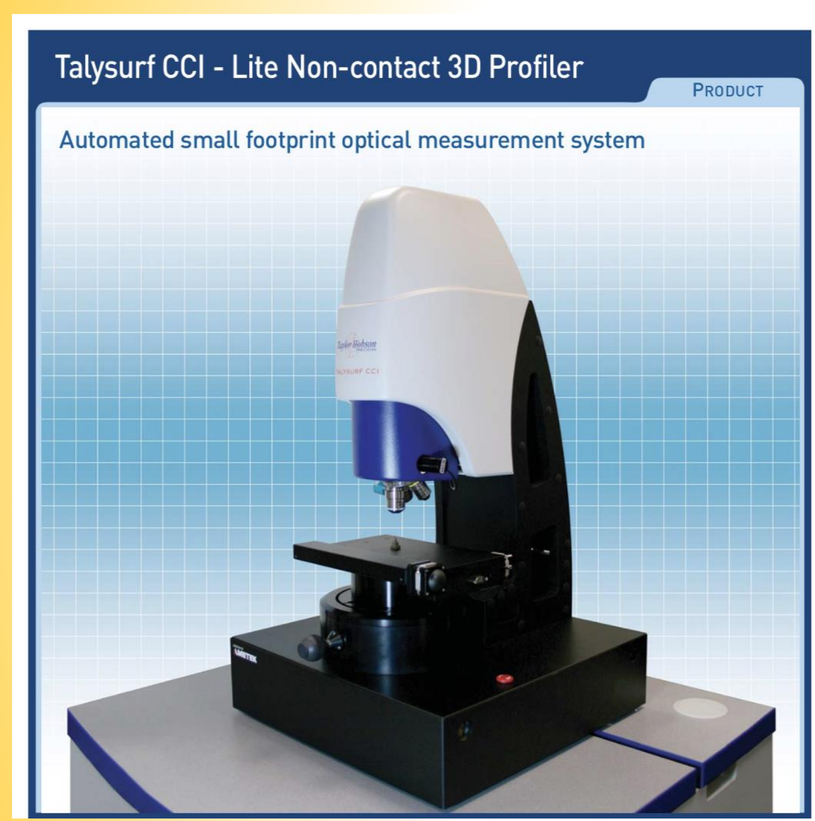


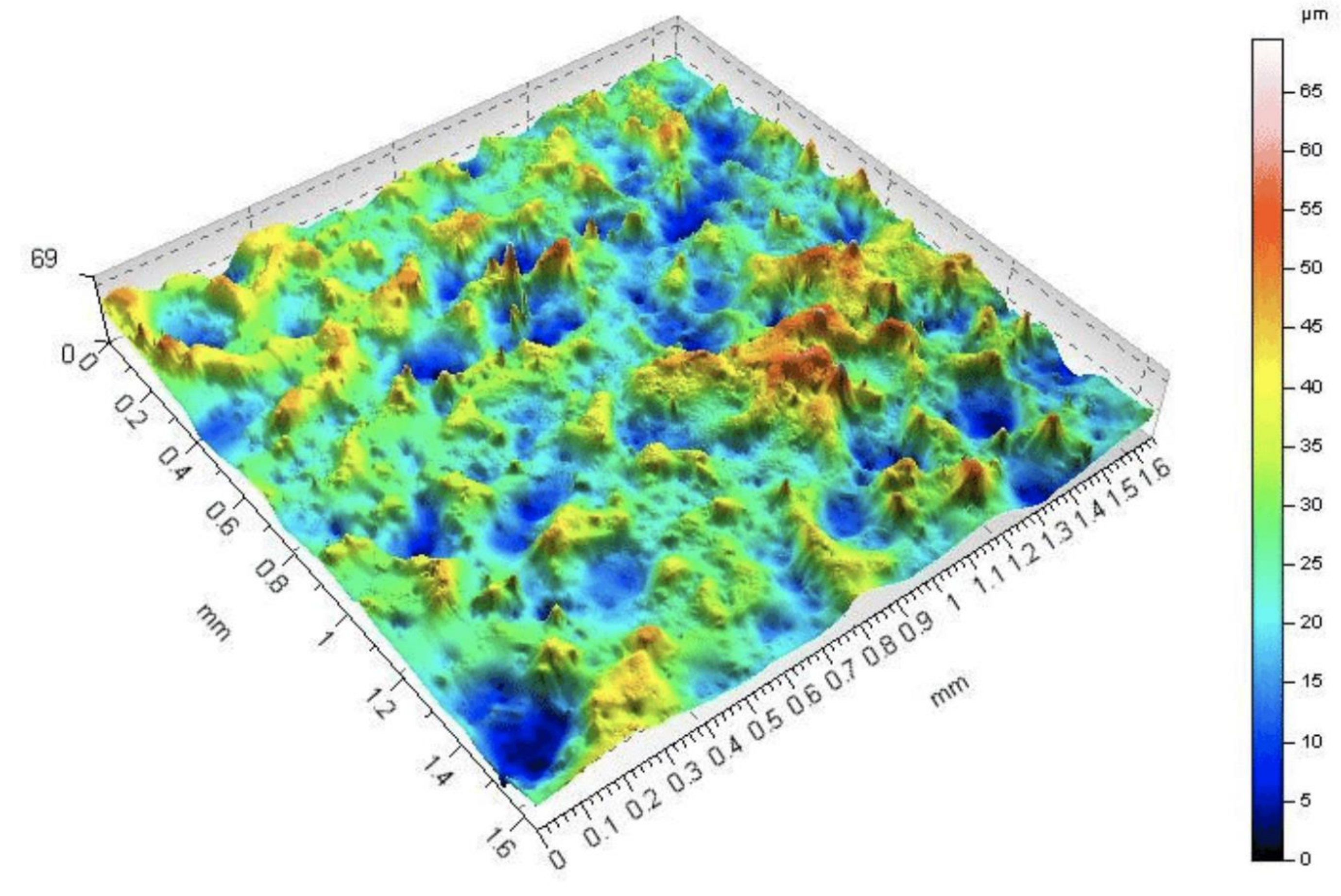




https://www.filmetrics.com/profilometers/profilm3d?gclid=EAIaIQobChMIzNvtpOT_6wIVS4CRCh2Lhg99EAAYASAAEgKqXPD_BwE

Profilometer

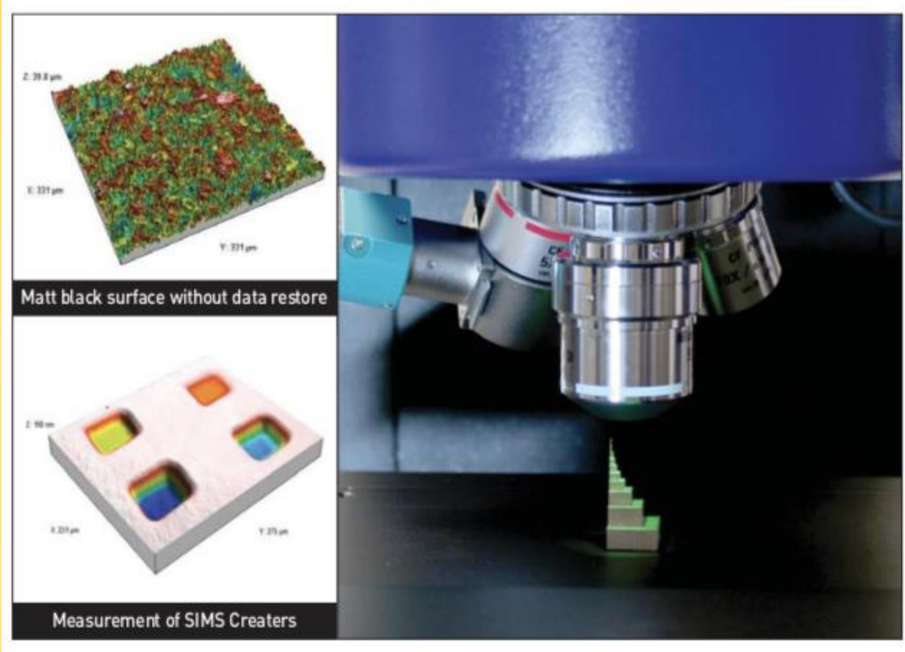




View of 3D on machined surface made by Talysurf CCI Lite-Taylor Hobson scanning profilometer type

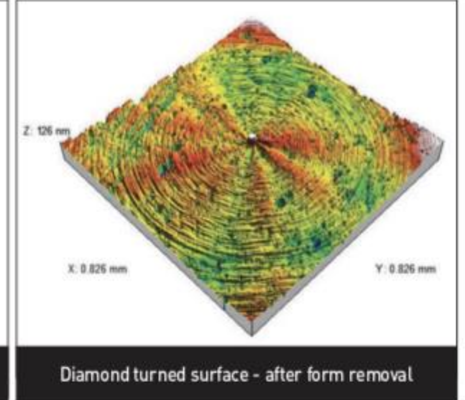
https://www.researchgate.net/figure/ew-of-3D-on-machined-surface-made-by-Talysurf-CCI-Lite-Taylor-Hobson-scanning_fig1_313649778

Profilometer



Z: 11.7 µm
X: 0.826 mm
Y: 0.826 mm

Diamond turned surface - measured using auto fringe find and auto range



Diamond turned surface - after form removal

Talysurf CCI Lite System Specifications	
Measurement technique	Coherence Correlation Interferometry
Vertical range (Z)	2.2 mm as standard (>10 mm with Z-stitching)
Vertical resolution [max]	0.01 nm [0.1 Å]
Noise floor (Z)	<0.08 nm [0.8 Å] [1]
Repeatability of surface RMS (Z)	<0.02 nm [0.2 Å] [2]
Max. Measurement area (X, Y)	6.6 mm (>75 mm with X, Y stitching)
Number of measurement points	1024 x 1024 standard
Optical resolution (X, Y)	0.4 - 0.6µm (surface dependent)
Step height repeatability	<0.1%
Surface reflectivity	0.3% - 100%
Measurement time	5-40 seconds (typical)

[1] As demonstrated by multiple measurements on a levelled fused silica optical flat
[2] As demonstrated by 1 sigma Std Dev of 20 Sq (RMS) measurements on SiC flat

Scanning Electron Microscopy - SEM

The Scanning Electron Microscope (SEM) is often the first analytical instrument used when a "quick look" at a material is required and the light microscope no longer provides adequate resolution. In the SEM an electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area. As the beam interacts with the sample it creates various signals (secondary electrons, inter- nal currents, photon emission, etc.), all of which can be appropriately detected. These signals are highly localized to the area directly under the beam.

Main use	High magnification imaging and composition (elemental) mapping
Destructive	No, some electron beam damage
Magnification range	10×–300,000×; 5000×–100,000× is the typical operating range
Beam energy range	500 eV–50 keV; typically, 20–30 keV
Sample requirements	Minimal, occasionally must be coated with a conducting film; must be vacuum compatible
Sample size	Less than 0.1mm, up to 10 cm or more
Lateral resolution	1–50 nm in secondary electron mode
Depth sampled	Varies from a few nm to a few μm, depending upon the accelerating voltage and the mode of analysis
Bonding information	No
Depth profiling capabilities	Only indirect
Instrument cost	$100,000–$300,000 is typical
Size	Electronics console 3 ft. × 5 ft.; electron beam column 3 ft. × 3 ft.

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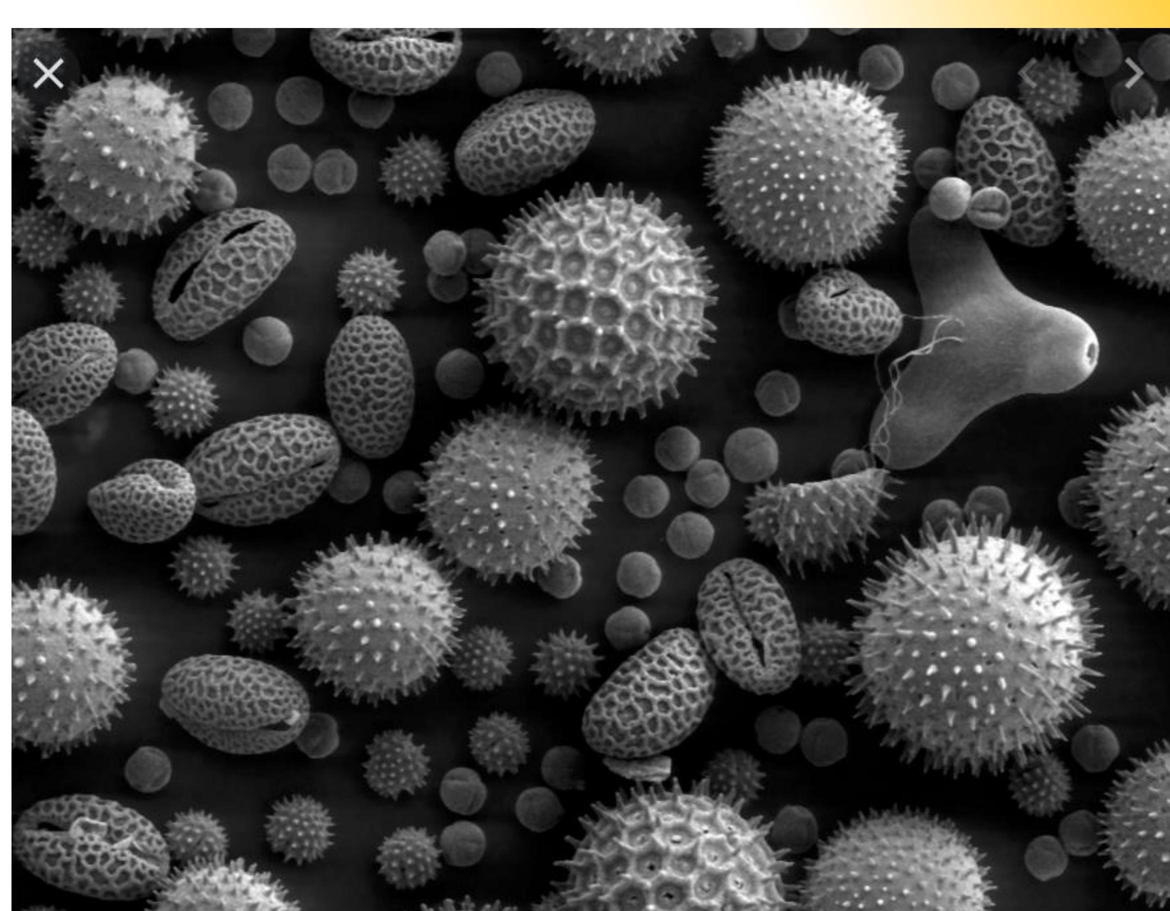
Scanning Electron Microscopy - SEM



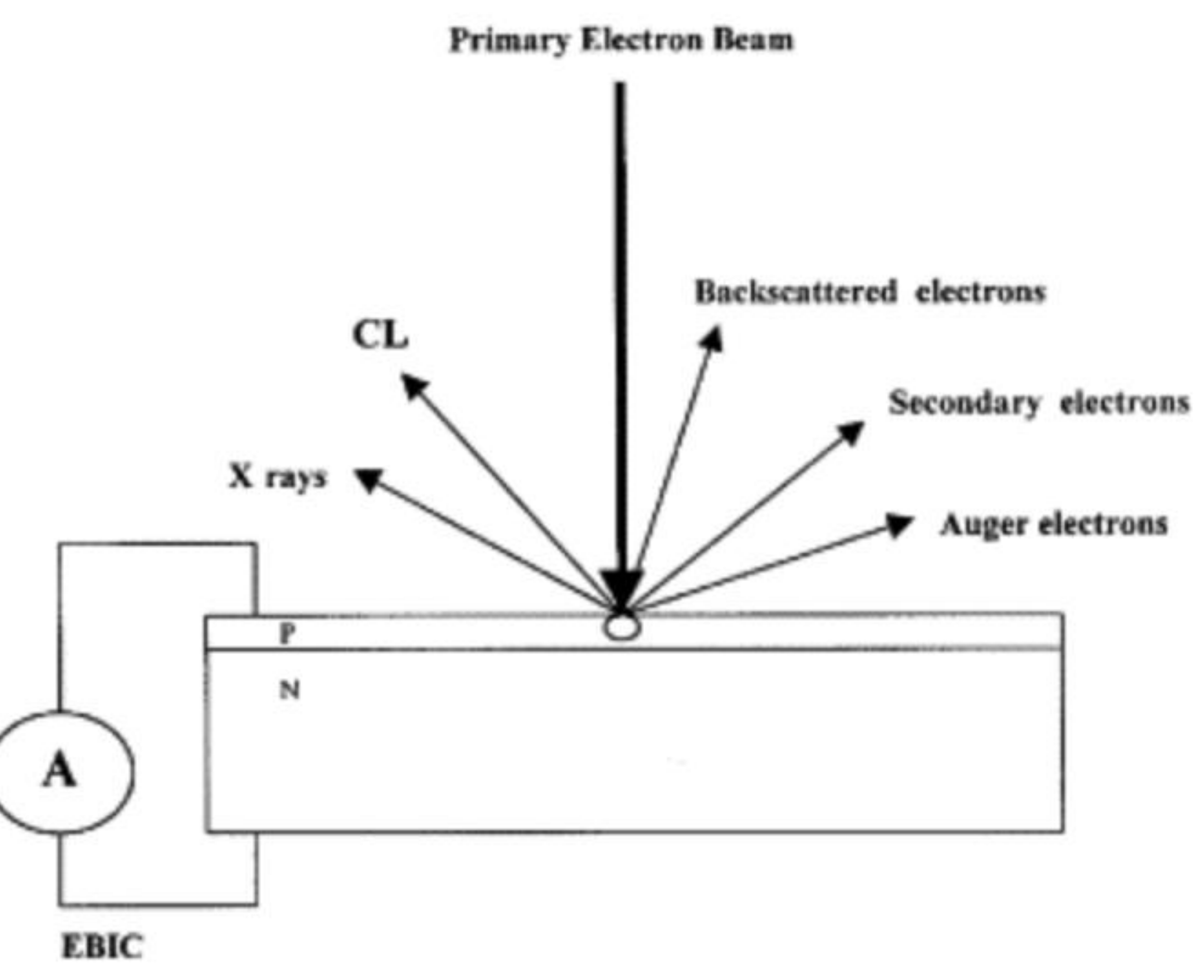
Scanning Electron Microscopy - SEM

Simplified electron beam-sample interaction: secondary electrons, auger electrons, light photons and X-rays are emitted from the sample when this is struck by fast incoming electrons. Transmitted electrons can remain unscattered, or be elastically or inelastically scattered.

Primary fast electrons
Auger electrons
Secondary electrons
X rays
Light
Elestically scattered electrons
Unscattered electrons
Inelastically scattered electrons

https://www.researchgate.net/figure/Simplified-electron-beam-sample-interaction-secondary-electrons-auger-electrons-light_fig5_289520567

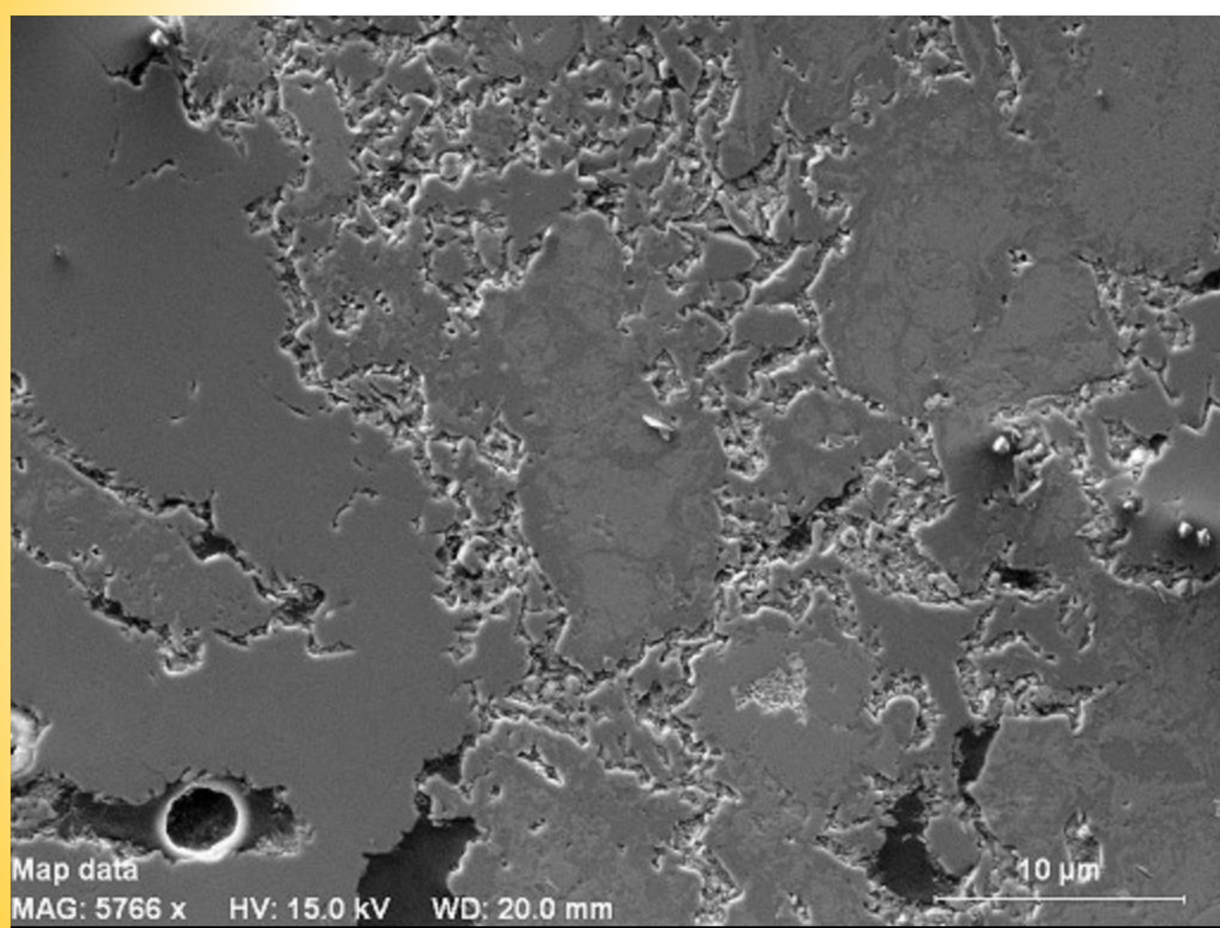
Scanning Electron Microscopy - SEM



https://www.sciencedirect.com/topics/medicine-and-dentistry/secondary-electrons

Scanning Electron Microscopy - SEM

Secondary electrons

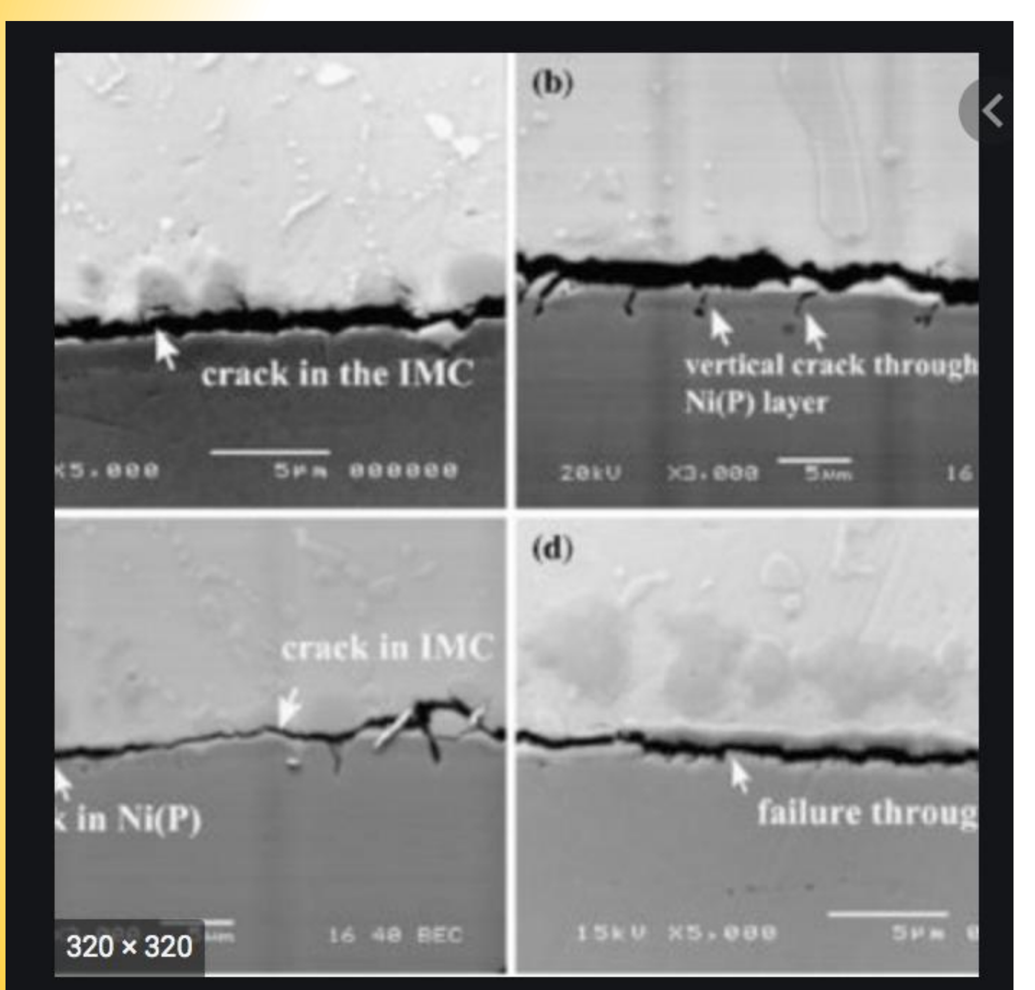


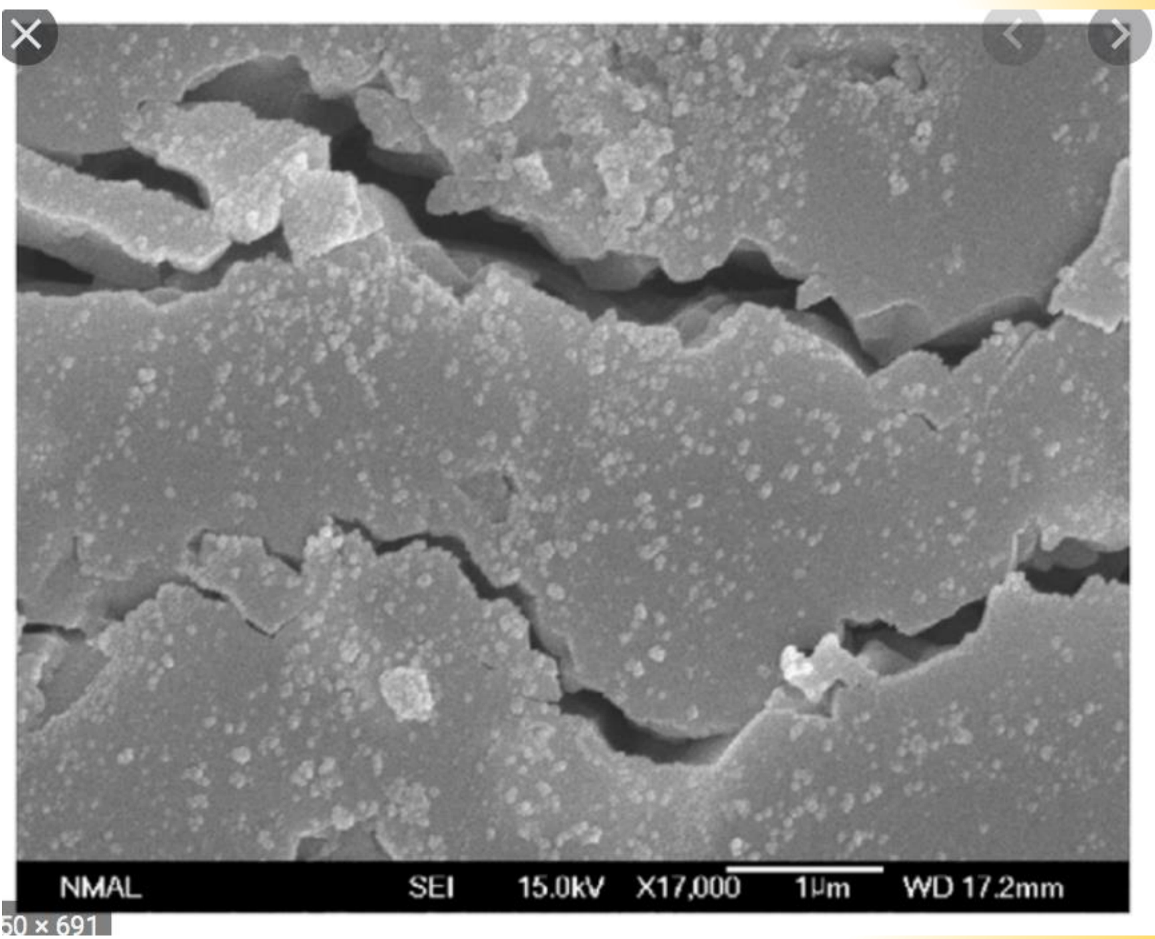
http://minerva.union.edu/hollochk/sem/se.html

This is an image of an aluminum copper alloy formed using backscattered electron imaging. The light area is mostly copper and the dark area is mostly aluminum.

Scanning Electron Microscopy - SEM

Surface Analysis





Scanning Electron Microscopy - SEM

EDS and WDS

Energy dispersive spectrometers (**EDS**) sort the X-rays based on their energy; while wavelength dispersive spectrometers (**WDS**) sort the X-rays based on their wavelengths.

Table 3110. Comparison between EDS and WDS techniques.

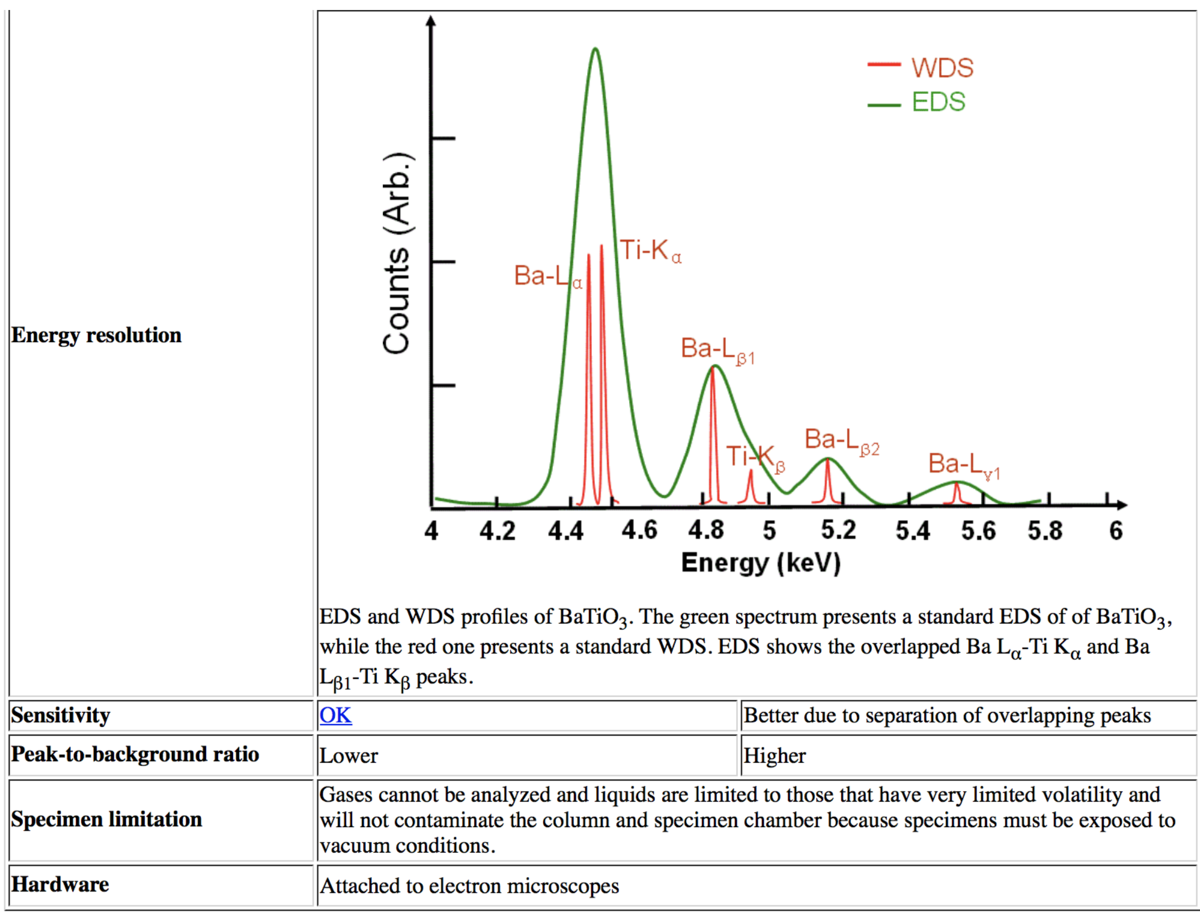
	EDS	**WDS**
Full name	Eenergy dispersive X-ray spectroscopy	Wavelength dispersive X-ray spectroscopy
Principle	Measures the energy of X-ray photon	Determine the wavelength of X-ray
Spectrum range	Measures across a broad range of energies in the spectrum	Measures specific regions within the spectrum
Efficiency	More efficient for an unknown specimen	More efficient for the concentration of specific, known element
Speed	Quicker for large energy ranges	Slower for large energy ranges
Throughput of X-rays	Lower	Higher
Spatial resolution	The same	
	Lower: ~ 125 eV	Higher: ~5-10 eV

https://www.globalsino.com/EM/page3110.html

EDS and WDS

Energy dispersive spectrometers (**EDS**) sort the X-rays based on their energy; while wavelength dispersive spectrometers (**WDS**) sort the X-rays based on their wavelengths.

https://www.globalsino.com/EM/page3110.html



Energy resolution	EDS and WDS profiles of $BaTiO_3$. The green spectrum presents a standard EDS of of $BaTiO_3$, while the red one presents a standard WDS. EDS shows the overlapped Ba L_α-Ti K_α and Ba $L_{\beta 1}$-Ti K_β peaks.	
Sensitivity	OK	Better due to separation of overlapping peaks
Peak-to-background ratio	Lower	Higher
Specimen limitation	Gases cannot be analyzed and liquids are limited to those that have very limited volatility and will not contaminate the column and specimen chamber because specimens must be exposed to vacuum conditions.	
Hardware	Attached to electron microscopes	

PMR 5251

Field Emission Electron Microscopy FIB e EBSD

https://www.imri.uci.edu/content/fei-quanta-3d-feg-dual-beam-semfib-0

Electron Source & Operating HT: Field emission gun 1kV~30kV
Electron beam resolution
•High-vacuum
1.2 nm at 30 kV (SE)
2.5 nm at 30 kV (BSE)*
2.9 nm at 1 kV (SE)
•Low-vacuum
1.5 nm at 30 kV (SE)
2.5 nm at 30 kV (BSE)
2.9 nm at 3 kV (SE)

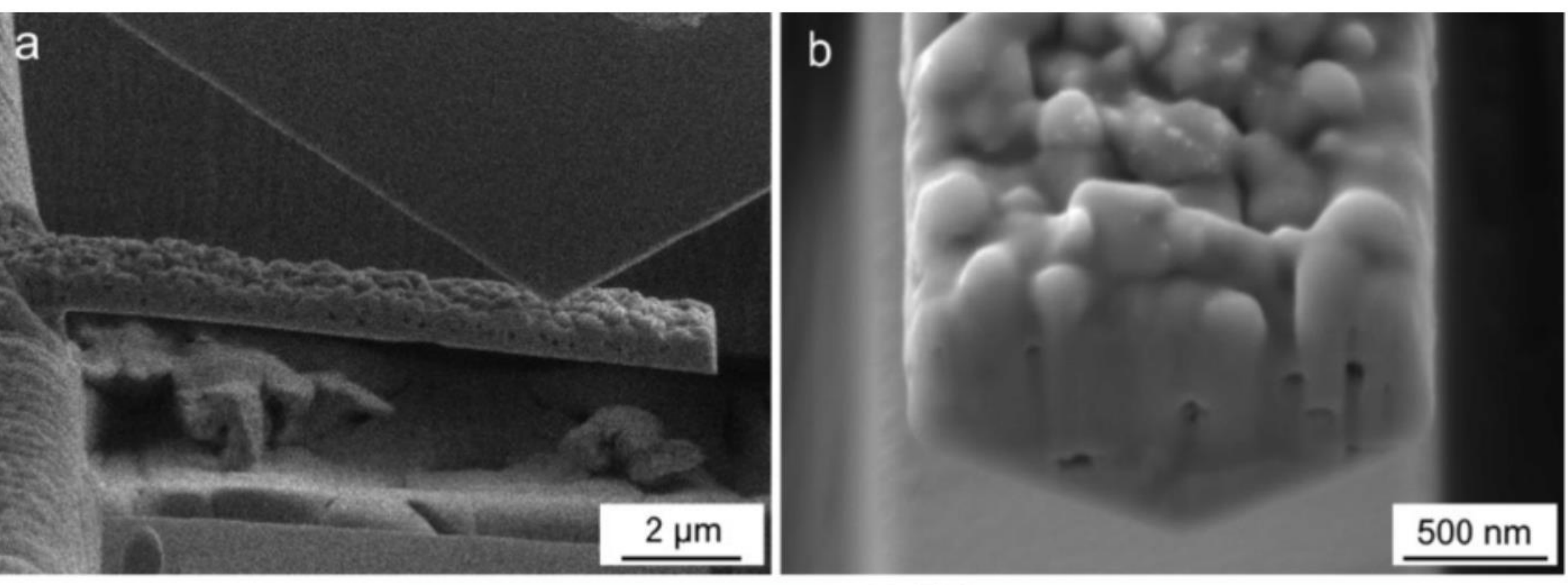
•Extended low-vacuum mode (ESEM)
1.5 nm at 30 kV (SE)
Focus Ion Beam resolution:
•7 nm at 30 kV at beam coincident point (5 nm achievable at optimal working distance)
Electron optics
•High-resolution field emission – SEM column optimized for high-brightness/ high-current
•60 degree objective lens geometry with through-the-lens differential pumping and heated objective apertures
Ion optics
•High-current ion column with Ga liquid-metal ion source
•Acceleration voltage: 2 – 30 kV
•Probe current: 1 pA – 65 nA in 15 steps
•15-position aperture strip
•Magnification 40 x – 1280 kx in "quad" mode at 10 kV
Detectors and Attachments:
•Everhardt-Thornley SED
•Low-vacuum SED (used in low vacuum)
•Gaseous SED (GSED) (used in ESEM mode)
•Solid-State BSED
•Gaseous analytical BSED (GAD) (used for low-vacuum analytical applications)
•EDS: Oxford silicon drift detector (50 mm^2) and INCA software
•HKL EBSD (Electron Backscatter Diffraction) systems

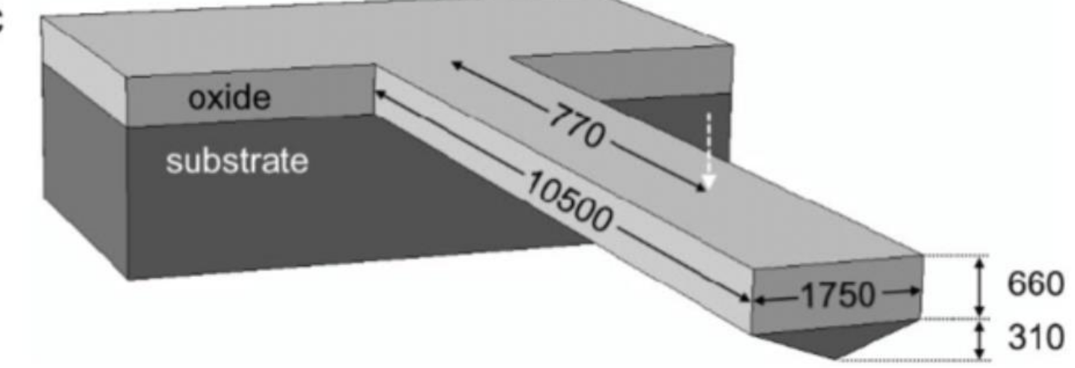
Field Emission Electron Microscopy FIB

http://www.soest.hawaii.edu/AEMC/instruments/aemc_helios.htm

FIB preparation of an electron-transparent thin section of a meteorite sample.

Field Emission Electron Microscopy FIB





SEM images of FIB milled cantilever, showing (a) side view during bending test and (b) front view prior to test (sample tilted at 55˚with55˚with respect to horizontal axis); (c) Model for FE simulation (dimensions in nm)

https://www.researchgate.net/figure/SEM-images-of-FIB-milled-cantilever-showing-a-side-view-during-bending-test-and-b_fig5_337946048

Field Emission Electron Microscopy

EBSD

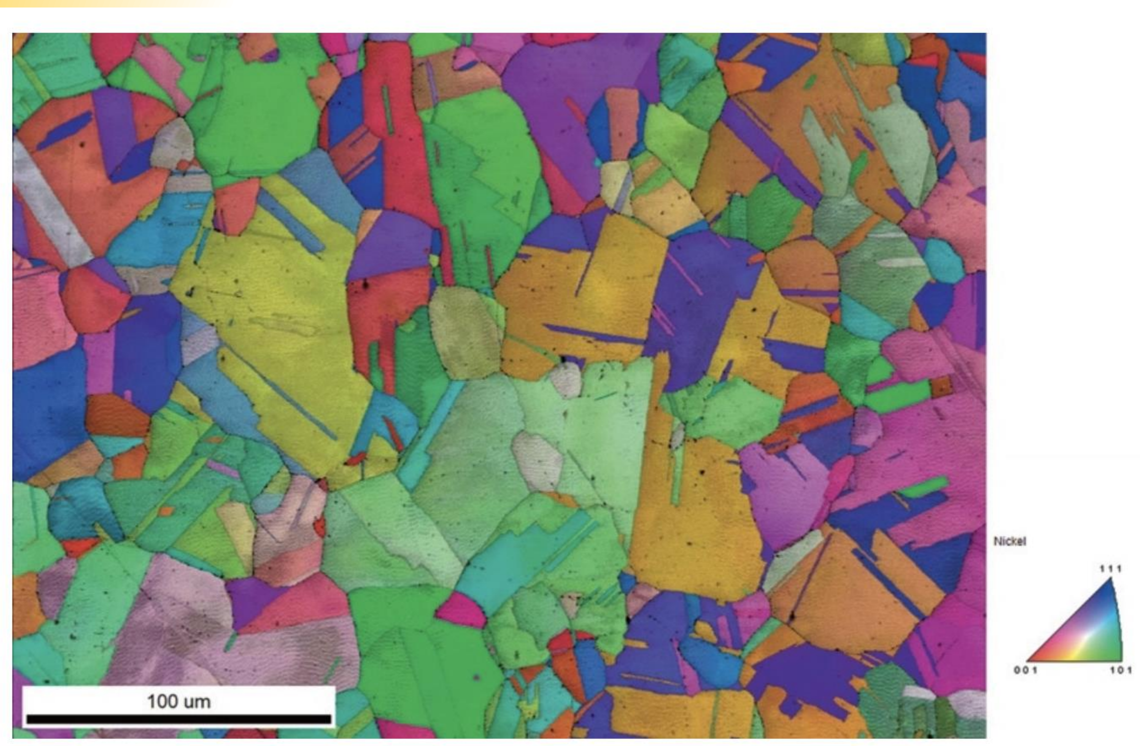


Figure 1. *EBSD IQ + IPF map from a Ni superalloy collected at 3,000 indexed points per second at 11 nA with 99.6% indexing success.*

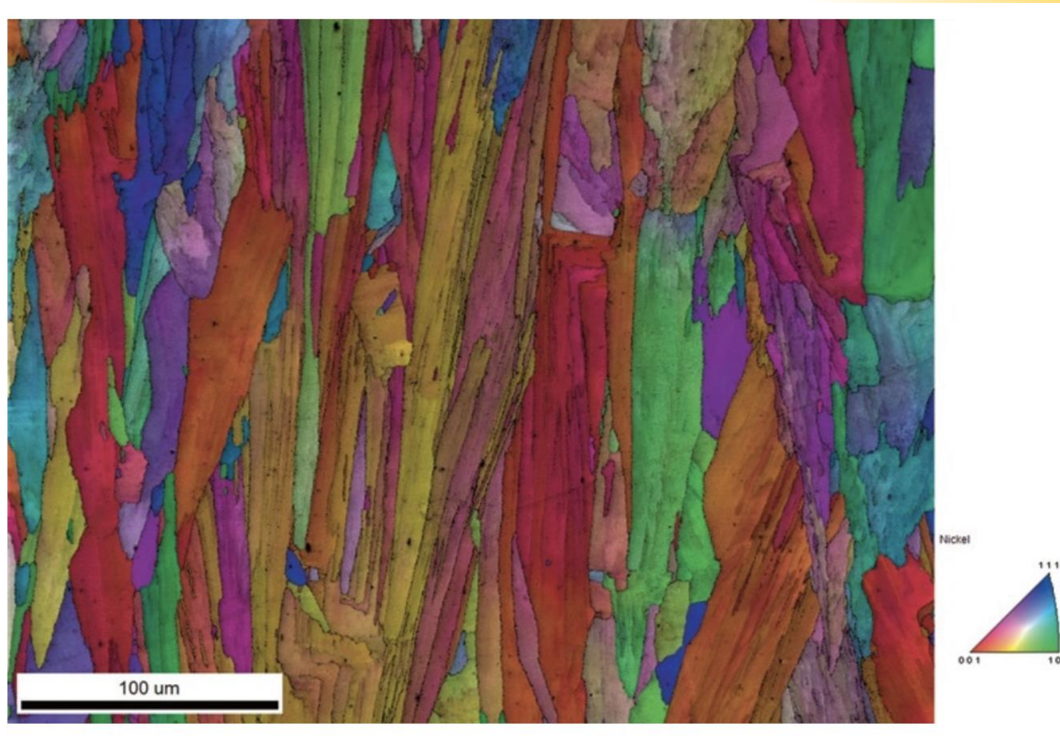


Figure 2. *EBSD IQ + IPF map from an additively manufactured IN718 alloy collected at 4,500 indexed points per second.*

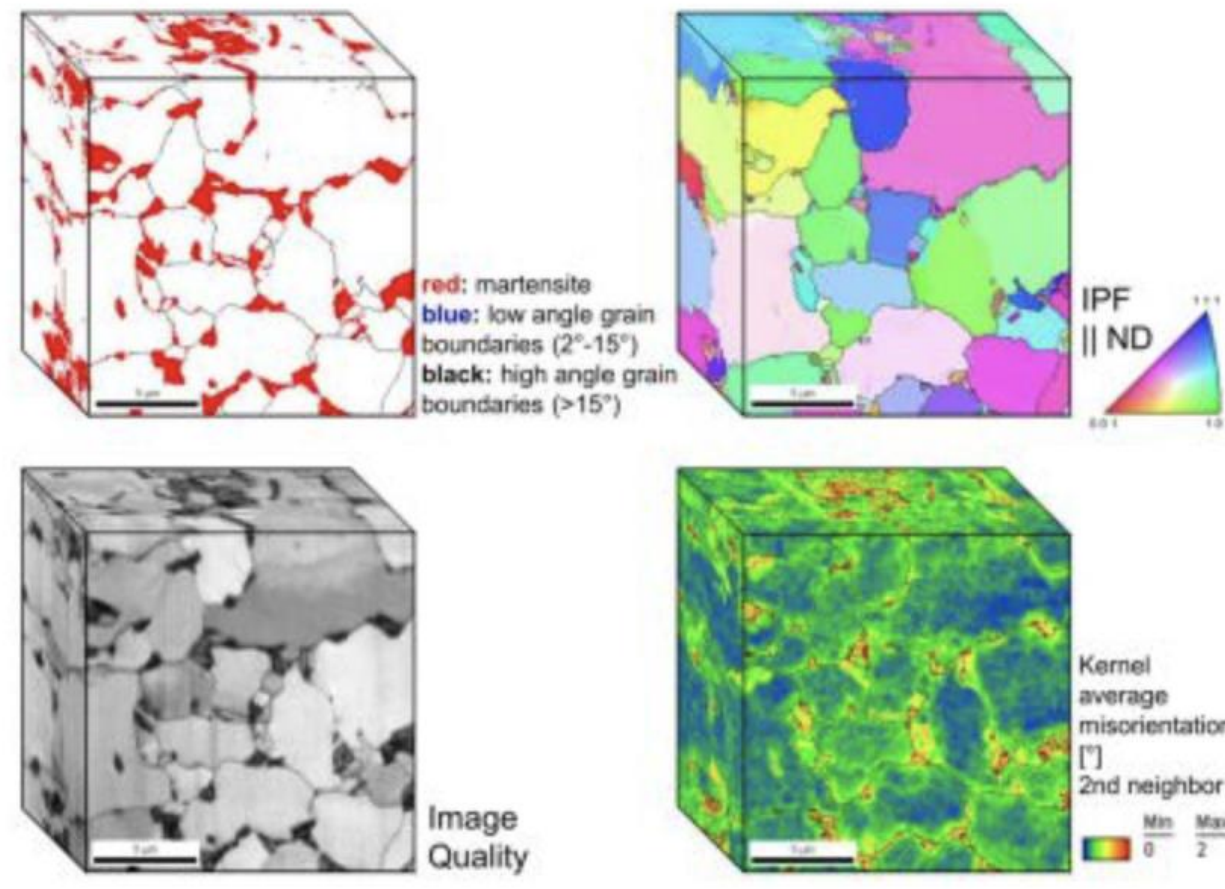
https://www.azom.com/article.aspx?ArticleID=17966

Field Emission Electron Microscopy
EBSD

Figure 3. *EBSD IQ + IPF map from a deformed ferritic steel sample.*

https://www.azom.com/article.aspx?ArticleID=17966

Field Emission Electron Microscopy EBSD

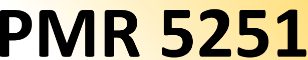


Dual phase steel microstructure revealed by 3D EBSD.

http://www.dierk-raabe.com/ebsd-and-3d-ebsd/

ESCOLA POLITÉCNICA DA USP

Field Emission Electron Microscopy EBSD



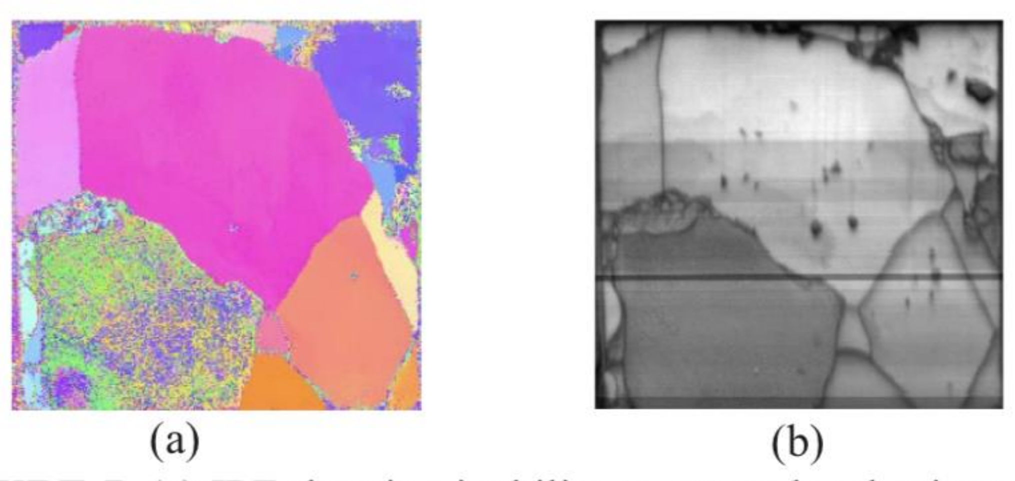


FIGURE 7. (a) IPF showing inability to assess local orientation texture for $HfAl_3$ grains, (b) greyscale image showing overall grain structure.

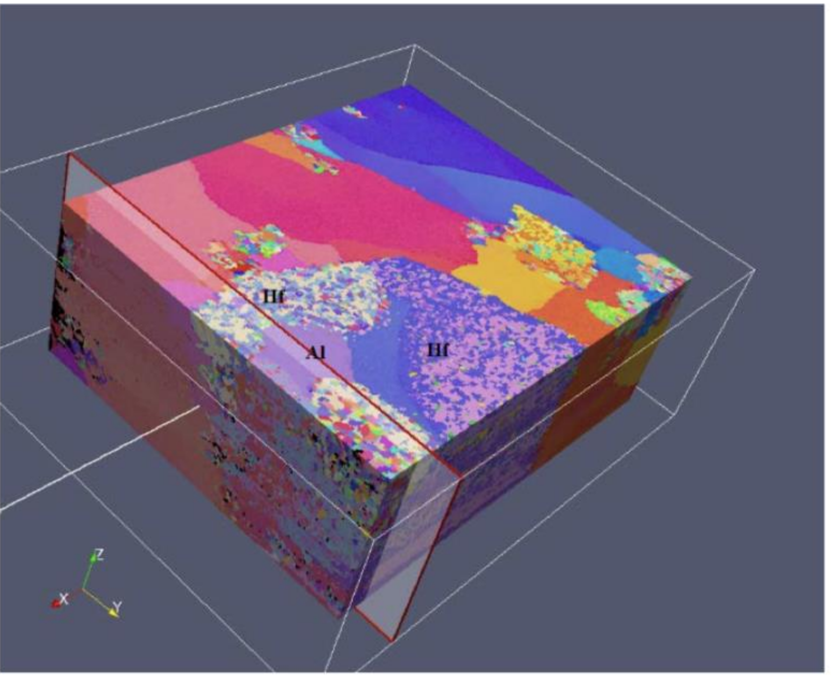


FIGURE 10. The 3D recontruction model to show the Al grain surrounded by $HfAl_3$ grains.

https://www.osti.gov/servlets/purl/1358236

Transmission Electron Microscopy - TEM

In Transmission Electron Microscopy (TEM) a thin solid specimen ***(5*** 200 nm thick) is bombarded in vacuum with a highly-focused, monoenergeticbeam of elec- trons. The beam is of sufficient energy to propagate through the specimen. A series of electromagneticlenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of sample that con- tain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. Analysis of transmit- ted electron images yields information both about atomic structure and about defects present in the ma

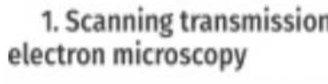
Range of elements	TEM does not specifically identify elements measured
Destructive	Yes, during specimen preparation
Chemical bonding information	Sometimes, indirectly from diffraction and image simulation
Quantification	Yes, atomic structures by diffraction; defect characterization by systematic image analysis
Accuracy	Lattice parameters to four significant figures using convergent beam diffraction
Detection limits	One monolayer for relatively high-Z materials
Depth resolution	None, except there are techniques that measure sample thickness
Lateral resolution	Better than 0.2 nm on some instruments
Imaging/mapping	Yes
Sample requirements	Solid conductors and coated insulators. Typically 3-mm diameter, < 200-nm thick in the center
Main uses	Atomic structure and Microstructural analysis of solid materials, providing high lateral resolution
Instrument cost	\$300,000–\$1,500,000
Size	100 ft.^{2} to a major lab

Transmission Electron Microscopy - TEM

TEM

Spectroscopy

Imaging

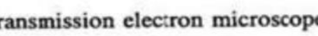


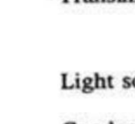
Diffraction

1. Scanning transmission electron microscopy
2. 3D electron tomography

1. X-ray energy dispersive spectroscopy
2. Electron energy loss spectroscopy
3. TEM-cathodoluminescenece microscopy

1. Selected area electron diffraction
2. Nano beam electron diffraction
3. Convergent beam electron diffraction





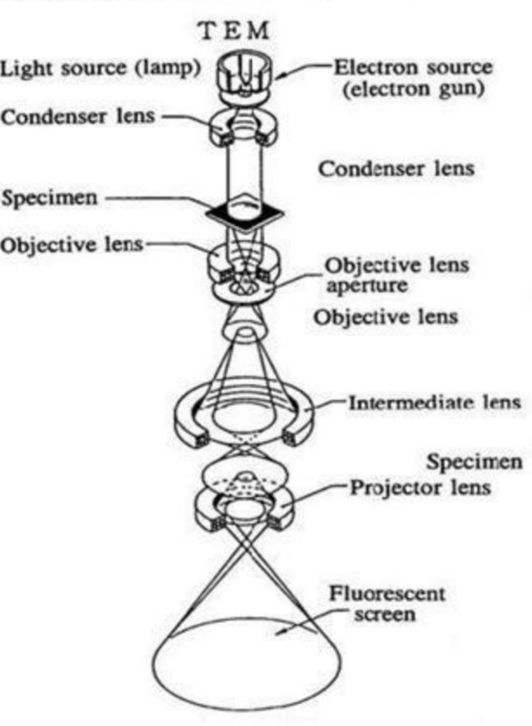


Fig 1

Incident Beam

Specimen

Objective Lens

Diffraction Pattern

Image Plane

Fig 2

Fig 1 - General layout of a TEM describing the path of electron beam in a TEM (Taken from JEOL 2000FX Handbook)

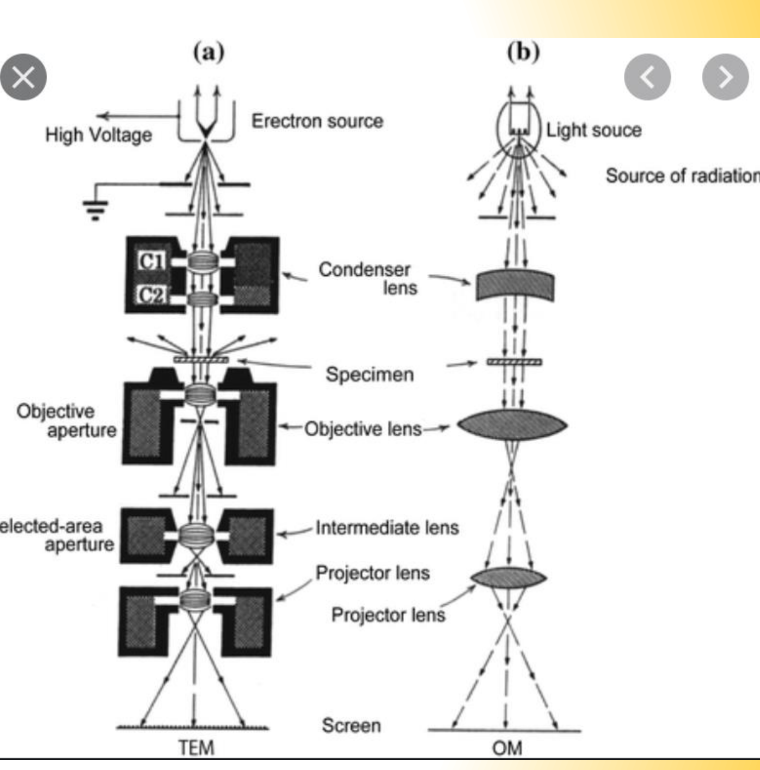
Fig 2 - A ray diagram for the diffraction mechanism in TEM

https://www.sciencedirect.com/topics/materials-science/transmission-electron-microscopy

Transmission Electron Microscopy - TEM

PMR 5251

TEM



https://www.youtube.com/watch?v=D3JY4LgyX6Q

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Transmission Electron Microscopy - TEM

PMR 5251

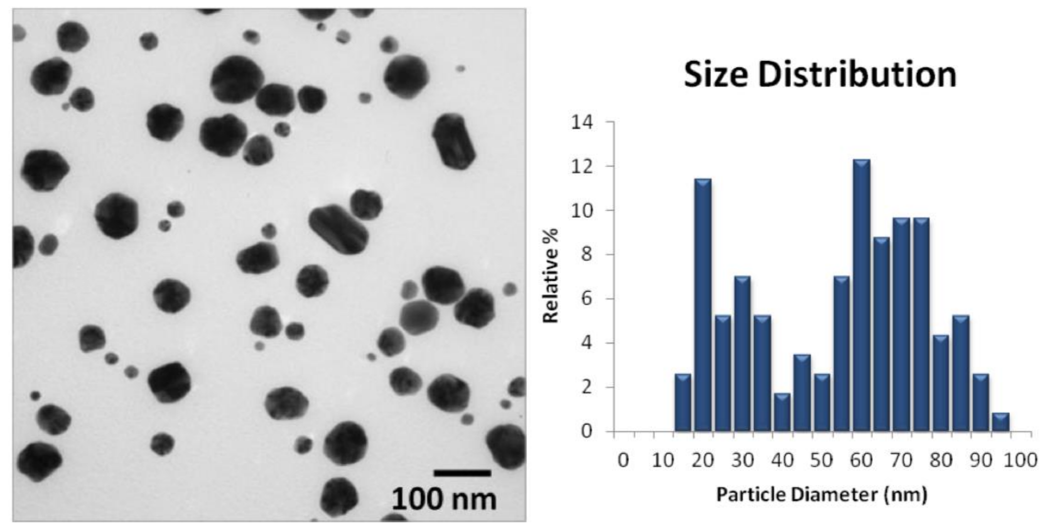
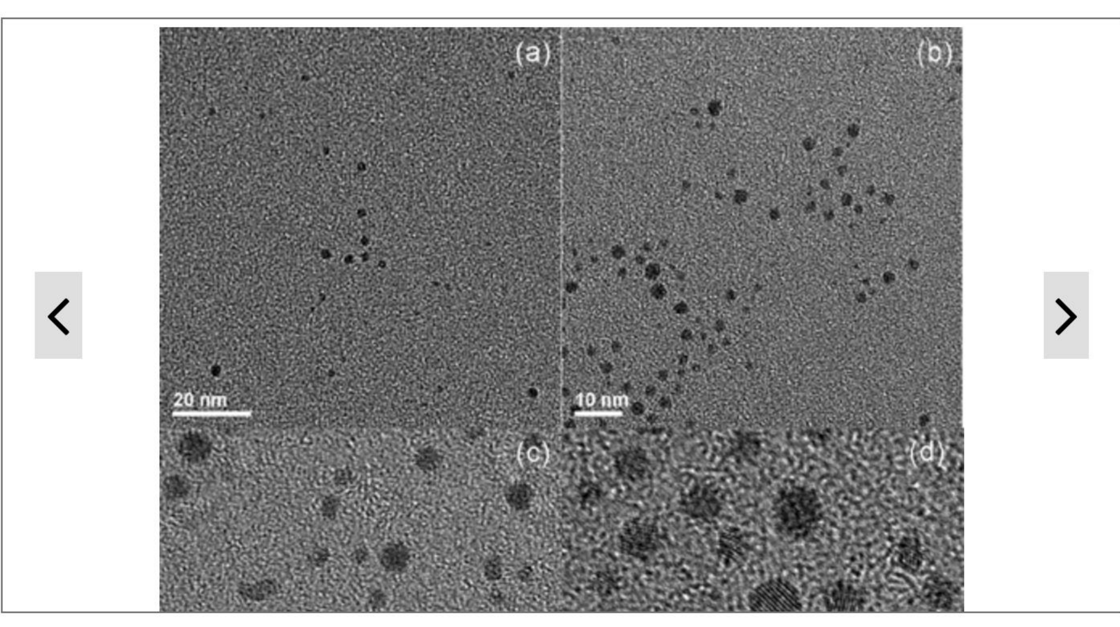


Figure 3. For particles that are size and shape polydisperse, a size distribution can be obtained by measuring each particle diameter at a fixed angle. The random orientation of particles allows for a statistical measure of the size distribution to be generated.



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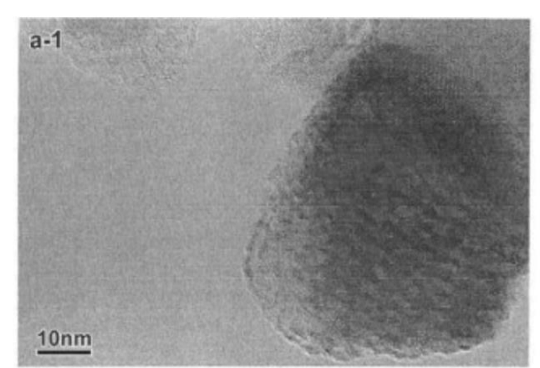
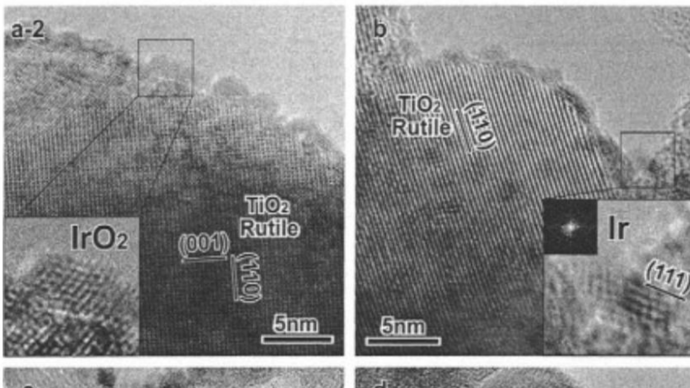
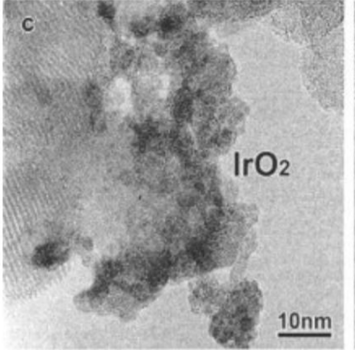
Cite This: *Langmuir* 2008, 24, 20, 11350-11360

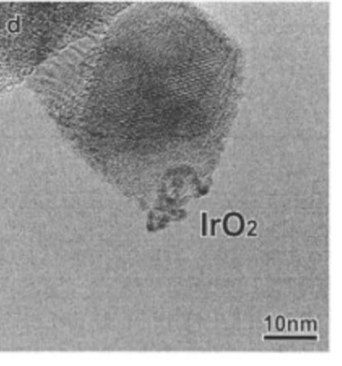
http://50.87.149.212/sites/default/files/nanoComposix%20Guidelines%20for%20TEM%20Analysis.pdf

Transmission Electron Microscopy - TEM









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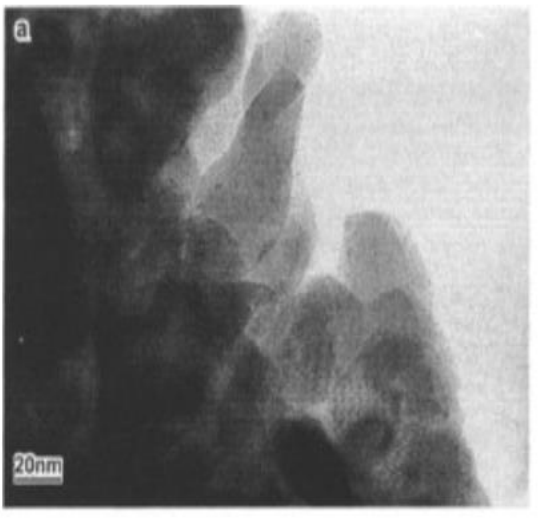
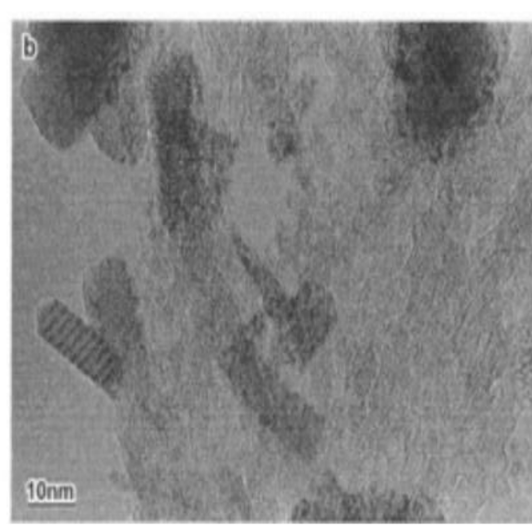




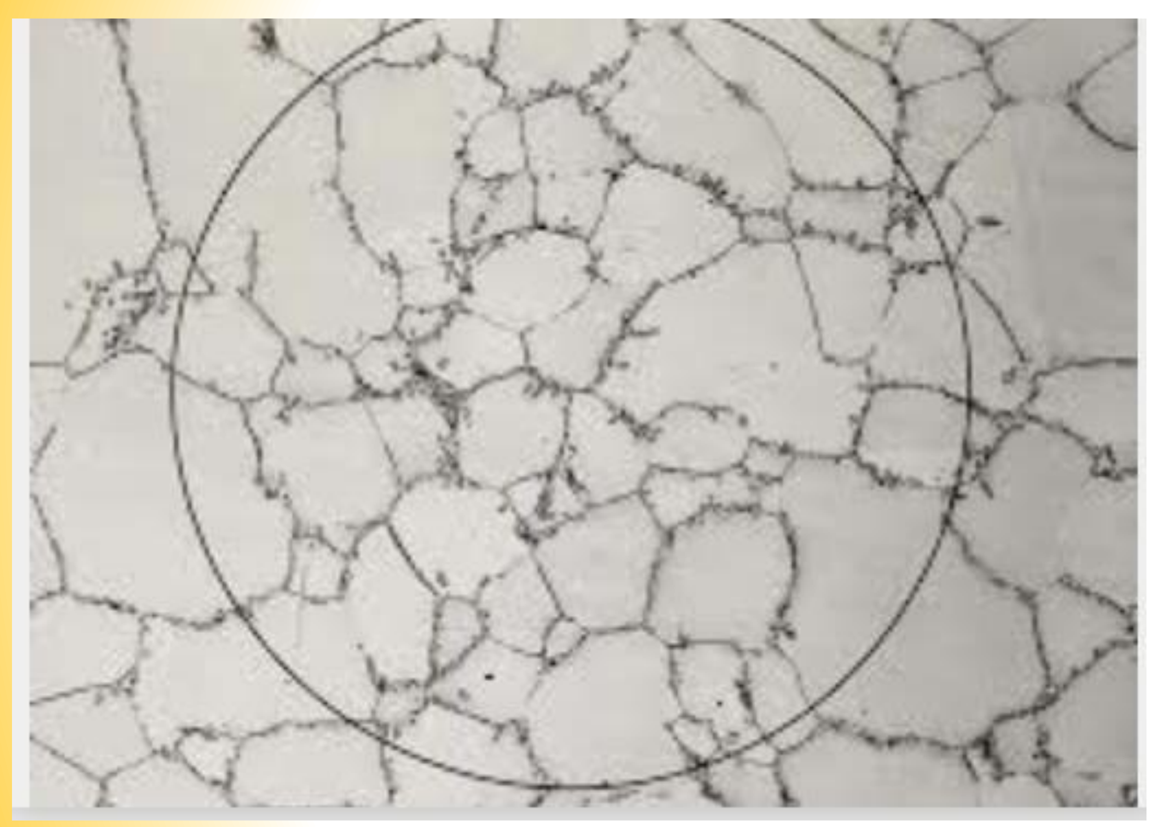
Download full-size image

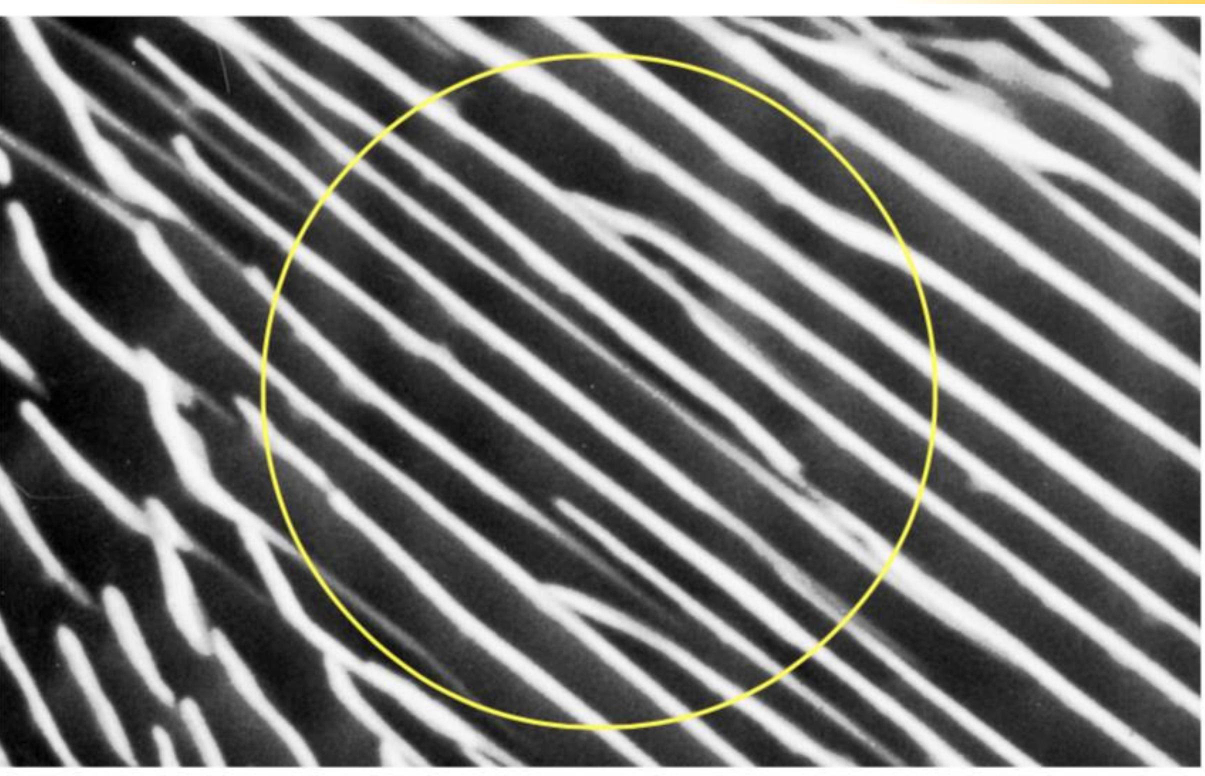
Fig. 4. (a) TEM image of Ir/Fe_2O_3 prepared by DP and (b) TEM image of Ir/Al_2O_3 prepared by DP.

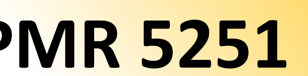
Fig. 5. TEM images of the Ir/TiO_2 catalysts prepared by the DP method followed by the pretreatment at 523 K (a-1) prepared at pH 8 and calcined in air, (a-2) prepared at pH 8 and calcined in air, (b) prepared at pH 8 and calcined in the hydrogen stream, (c) prepared at pH 3 and calcined in air, (d) prepared at pH 5 and calcined in air.

https://www.sciencedirect.com/topics/chemistry/tem-image

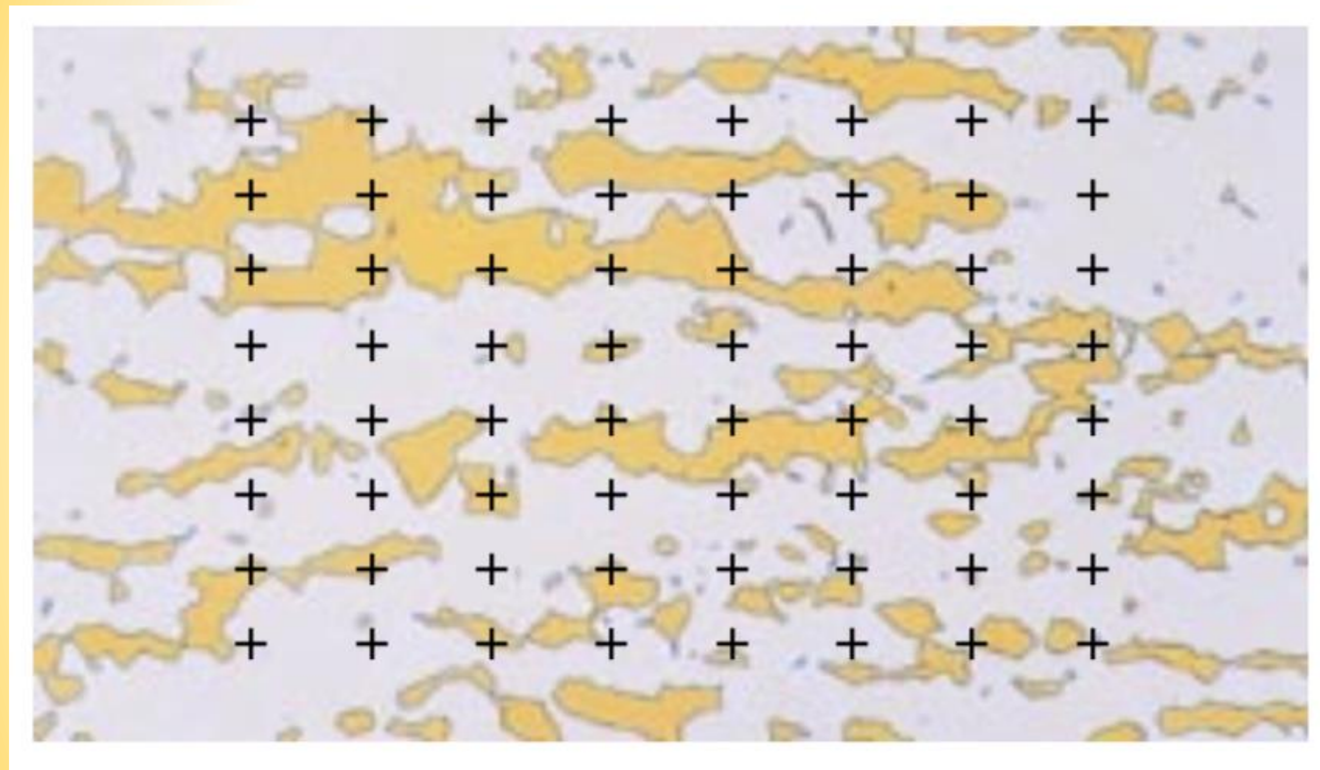
Quantitative Metallography

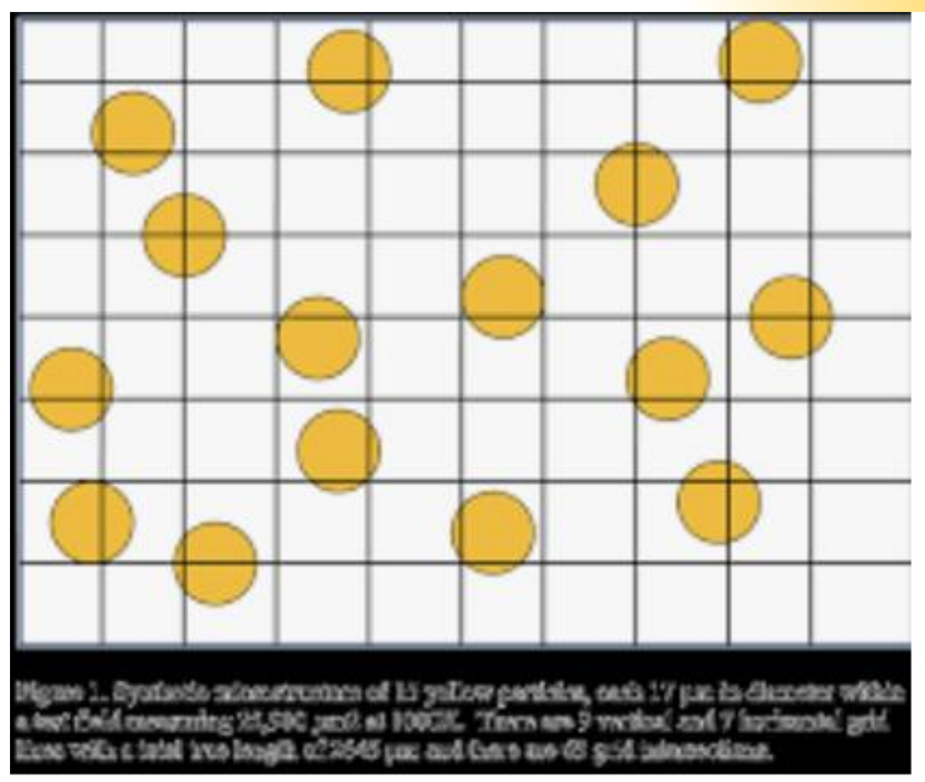






Quantitative Metallography

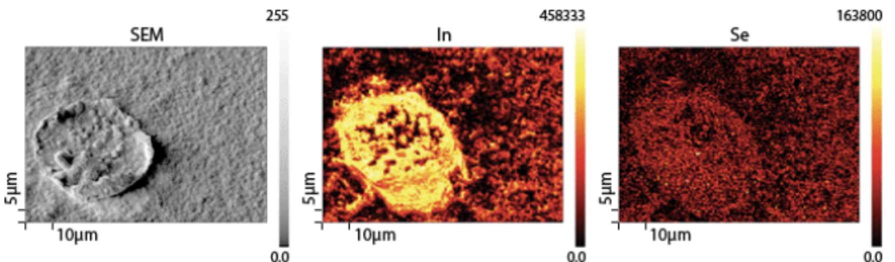




Introduction to Quantitative Metallography
George Vander Voort

Auger

Field Emission Auger Electron Spectroscopy with Scanning Auger Microscopy



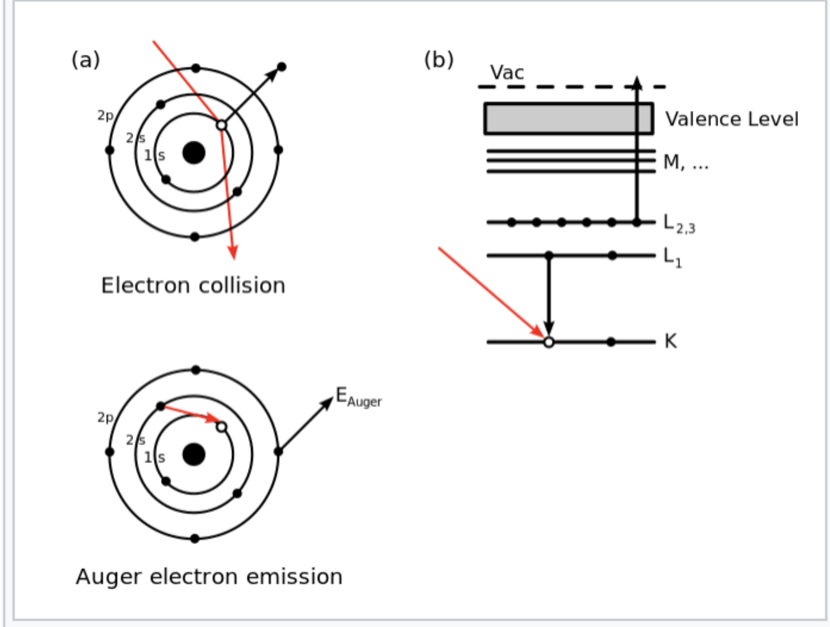
(a) SEM and (b&c) SAM images of a surface defect in Cu(In,Ga)SeS. SAM analysis shows the defect to be an In-rich region (b), indicating that the likely origin was an "In-spit" during precursor deposition that was subsequently selenized during downstream processing (c).

In Auger electron spectroscopy (AES), we bombard a sample surface with a focused beam of high-energy (2- to 10-kV) electrons. The incident electrons lose energy to the sample atoms, generating Auger electrons that have discrete kinetic energies characteristic of the emitting atoms.

https://www.nrel.gov/materials-science/auger-electron.html

Auger

The **Auger effect** is a physical phenomenon in which the filling of an inner-shell vacancy of an atom is accompanied by the emission of an electronfrom the same atom.[1] When a core electron is removed, leaving a vacancy, an electron from a higher energy level may fall into the vacancy, resulting in a release of energy. Although most often this energy is released in the form of an emitted photon, the energy can also be transferred to another electron, which is ejected from the atom; this second ejected electron is called an **Auger electron**.

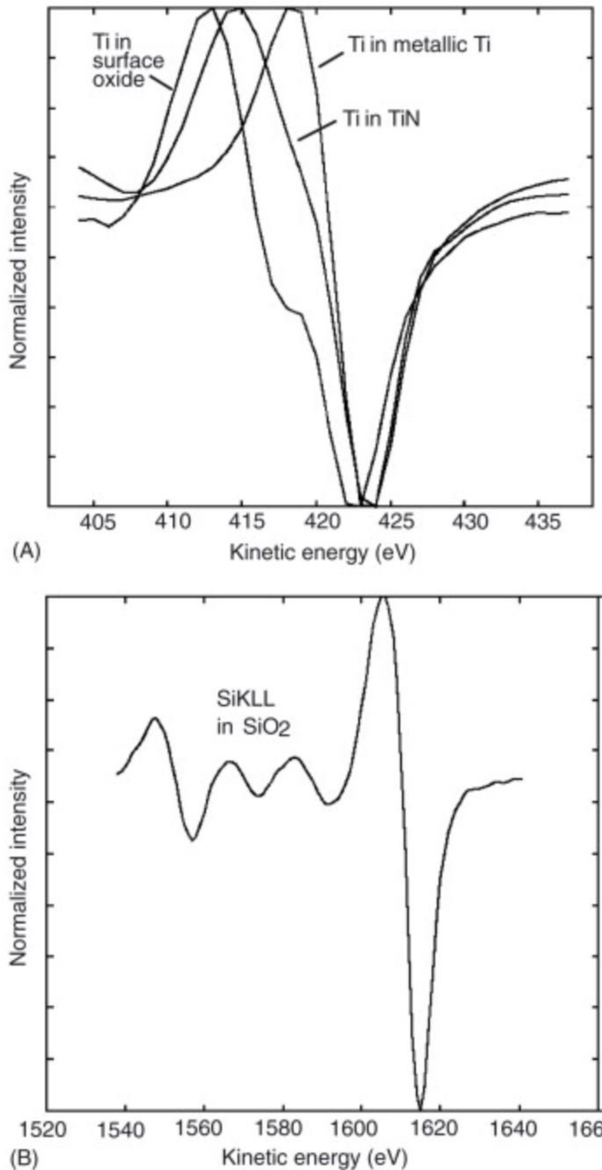


Two views of the Auger process. (a) illustrates sequentially the steps involved in Auger deexcitation. An incident electron (or photon) creates a core hole in the 1s level. An electron from the 2s level fills in the 1s hole and the transition energy is imparted to a 2p electron which is emitted. The final atomic state thus has two holes, one in the 2s orbital and the other in the 2p orbital. (b) illustrates the same process using X-ray notation, $KL_1L_{2,3}$.

Auger electron spectroscopy involves the emission of Auger electrons by bombarding a sample with either X-rays or energetic electrons and measures the intensity of Auger electrons that result as a function of the Auger electron energy. The resulting spectra can be used to determine the identity of the emitting atoms and some information about their environment.

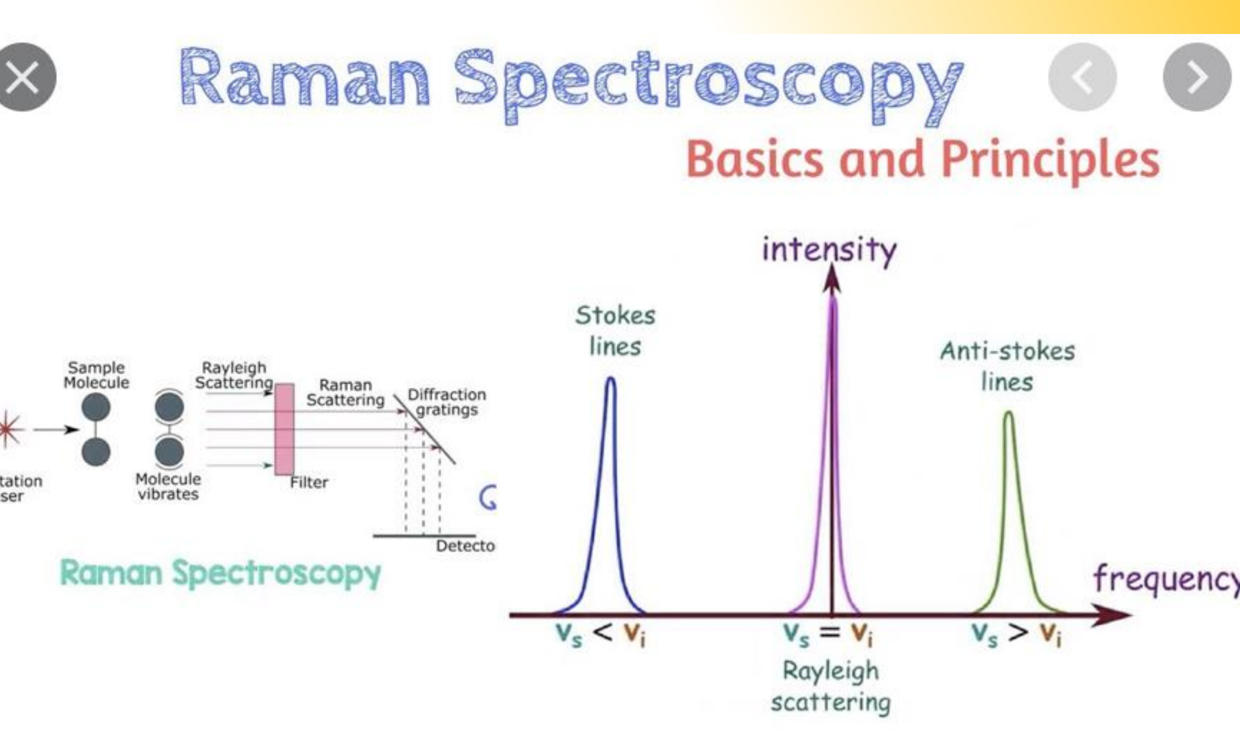
https://www.sciencedirect.com/topics/medicine-and-dentistry/auger-electron-spectroscopy

Auger



Download full-size image

Figure 7. (A) Ti $L_3M_{23}V$ $d(N(E) \times E)/dE)$ Auger spectra of a Ti surface oxide, TiN, and metallic Ti. (B) Si KLL $d(N(E) \times E)/dE)$ Auger spectra of silicon dioxide. (Reproduced with permission from ULVAC-PHI.)



https://www.mt.com/br/pt/home/applications/L1_AutoChem_Applications/Raman-Spectroscopy.html

Raman

Raman spectroscopy is a **spectroscopic** technique typically used to determine vibrational modes of molecules, although rotational and other low-frequency modes of systems may also be observed.

hυ

hυ

Δ

$E_1=E_2$ $E_1>E_2$

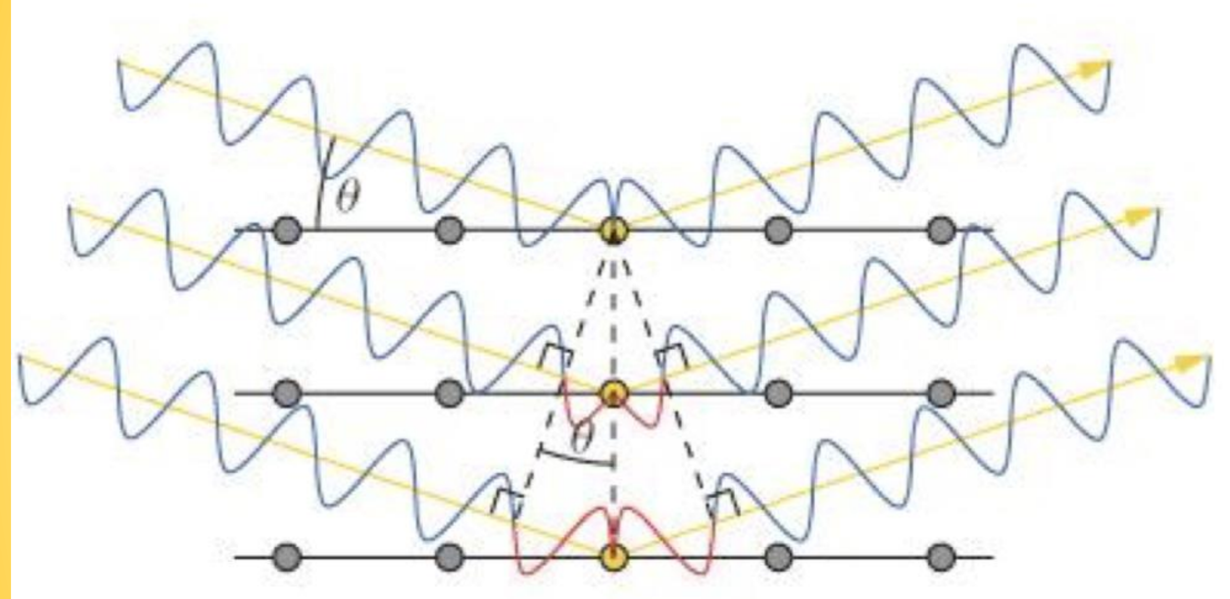
R H C=C H R

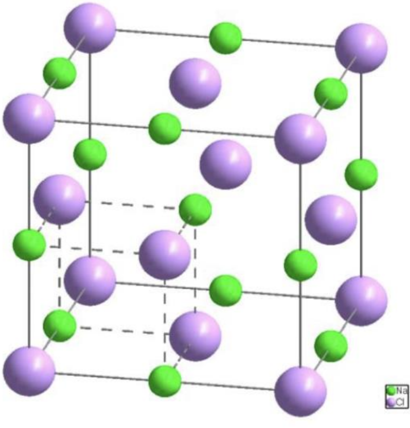
Raman Shift (cm^{-1})

https://www.mt.com/br/pt/home/applications/L1_AutoChem_Applications/Raman-Spectroscopy.html

X-Ray Diffraction

Lei de Bragg





NaCl – fcc lattice

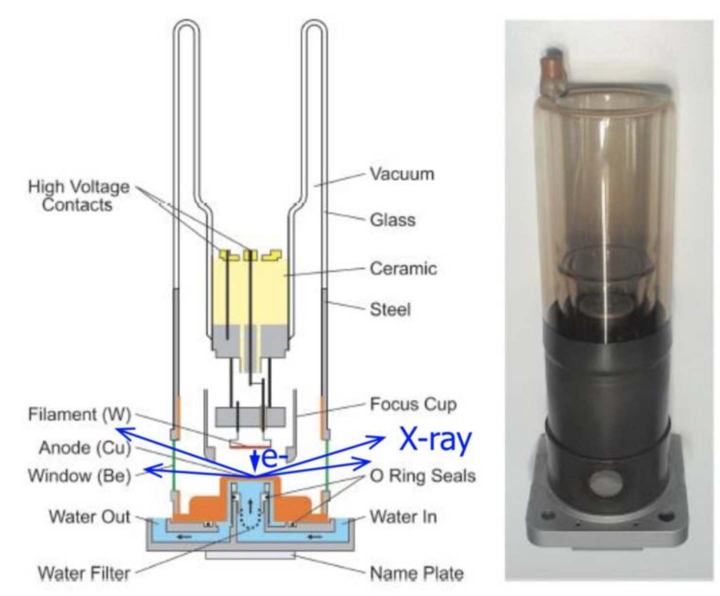
Fm-3m
a= 5.64 Å

Bragg:
In sodium chloride there appear
To be no molecules represented by NaCl. The equality in number of sodium and chloride atoms is arrived at by a chess-board pattern of these atoms; it is a result of geometry and no of a pairing off of the atoms

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2014_2015/elena_willinger__fundamental_of_x-ray_diffraction__141107.pdf

X-Ray Diffraction

Conventional X-ray laboratory source



Electrostatic potential 20 to 60 kV

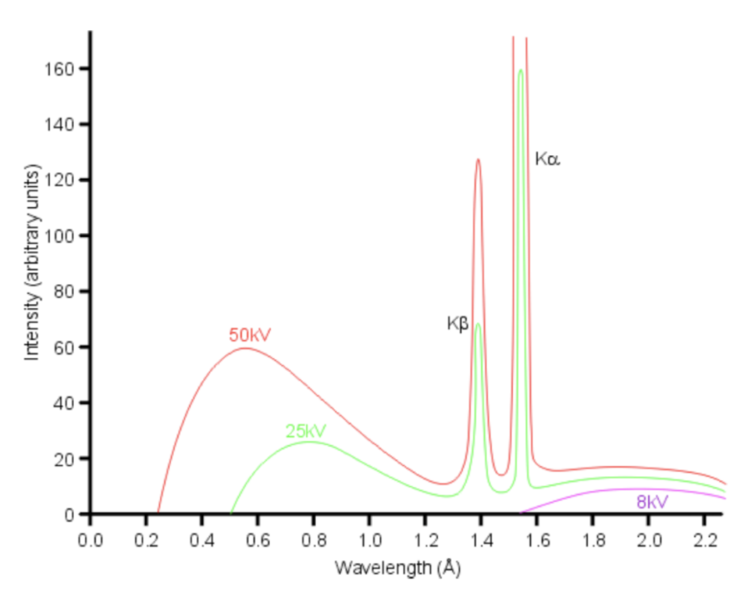
Anode current 10 to 50 mA

Input power ~ 0.5 to 3 kW

Only 0.1% transforms into X-ray beam

The wavelengths, most commonly used in crystallography: 0.5-2.5 Å

A typical x-ray spectrum from a Cu target



$$eV = h\nu = \frac{hc}{\lambda}$$

$$\lambda_c = \frac{12.4}{V, kV}\ \text{Å}$$

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2014_2015/elena_willinger__fundamental_of_x-ray_diffraction__141107.pdf

X-Ray Diffraction

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

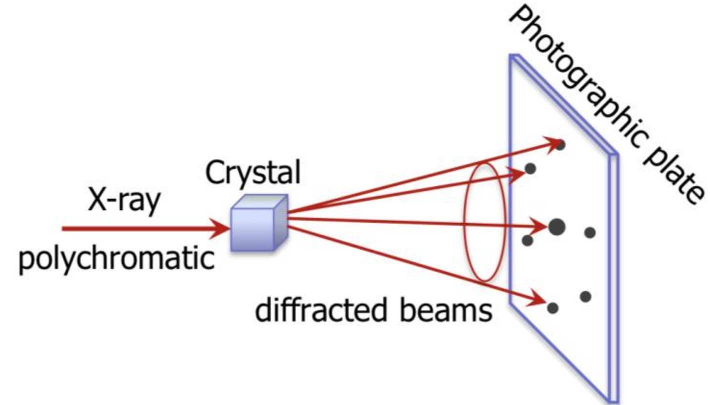
Table 1.1: Bravais lattices in three-dimensions.

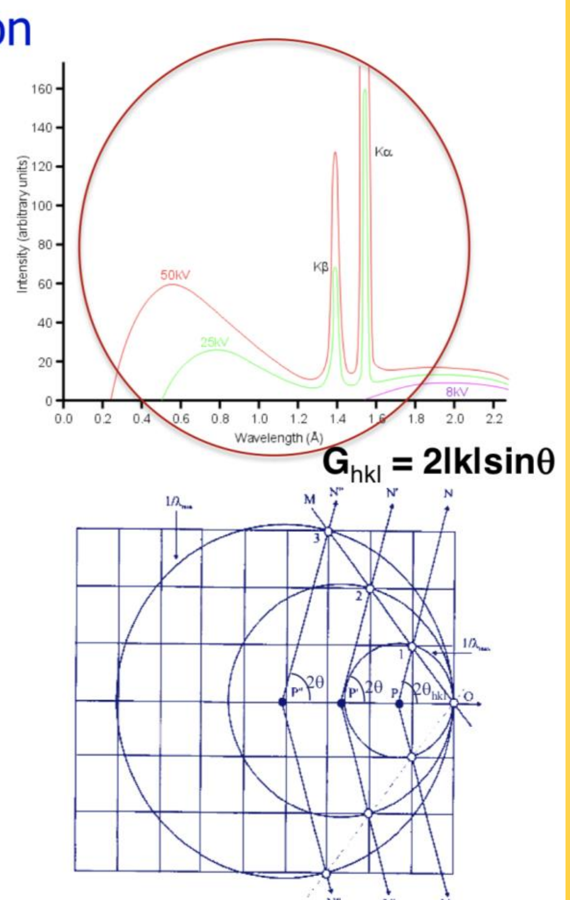
Laue diffraction

$$2d_{hkl}\sin\theta_{hkl} = \lambda$$

θ_{hkl} is fixed ⟶ polychromatic radiation

The crystal position is fixed





http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2014_2015/elena_willinger__fundamental_of_x-ray_diffraction__141107.pdf

X-Ray Diffraction

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2014_2015/elena_willinger__fundamental_of_x-ray_diffraction__141107.pdf

AuCu- face-centred cubic (F), fcc
disordered solid solution

Fm-3m
a= 3.872 Å

AuCu3- primitive cubic (P)
ordered solid solution

Pm-3m
a= 3.747 Å

Au
Cu

Intensity
111
200
220
311
222
2 theta
Wavelength: 1.54056
43.700, 10289
h, k, l = 2, 0, 0

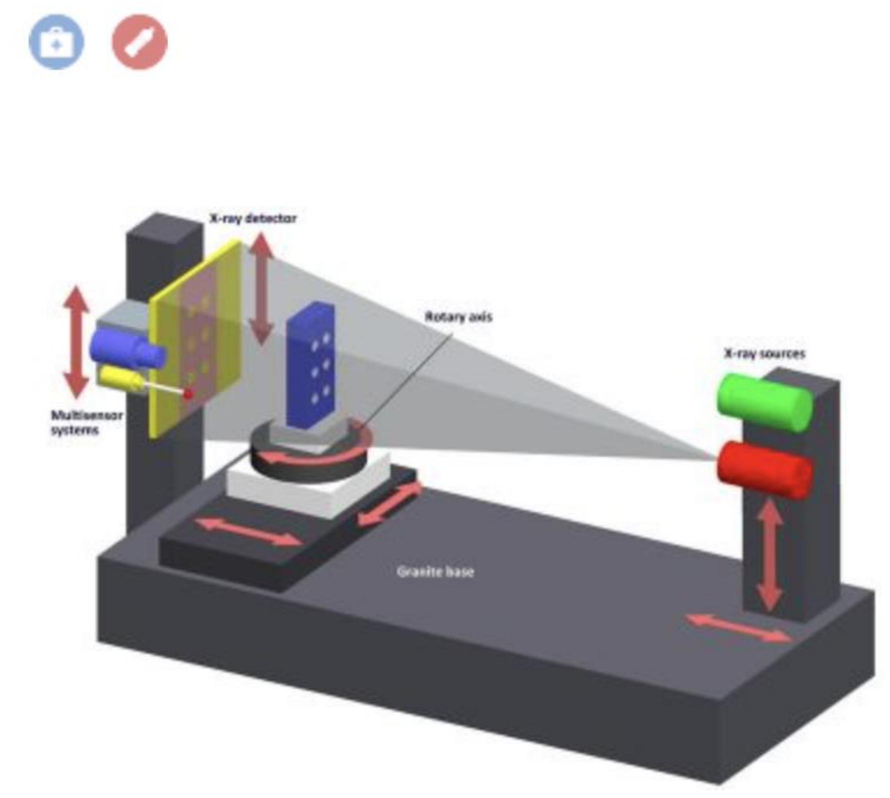
Intensity
100
110
111
200
210
211
220
300
310
311
2 theta
Wavelength: 1.54056
60.179, 10413
h, k, l = 2, 1, 1

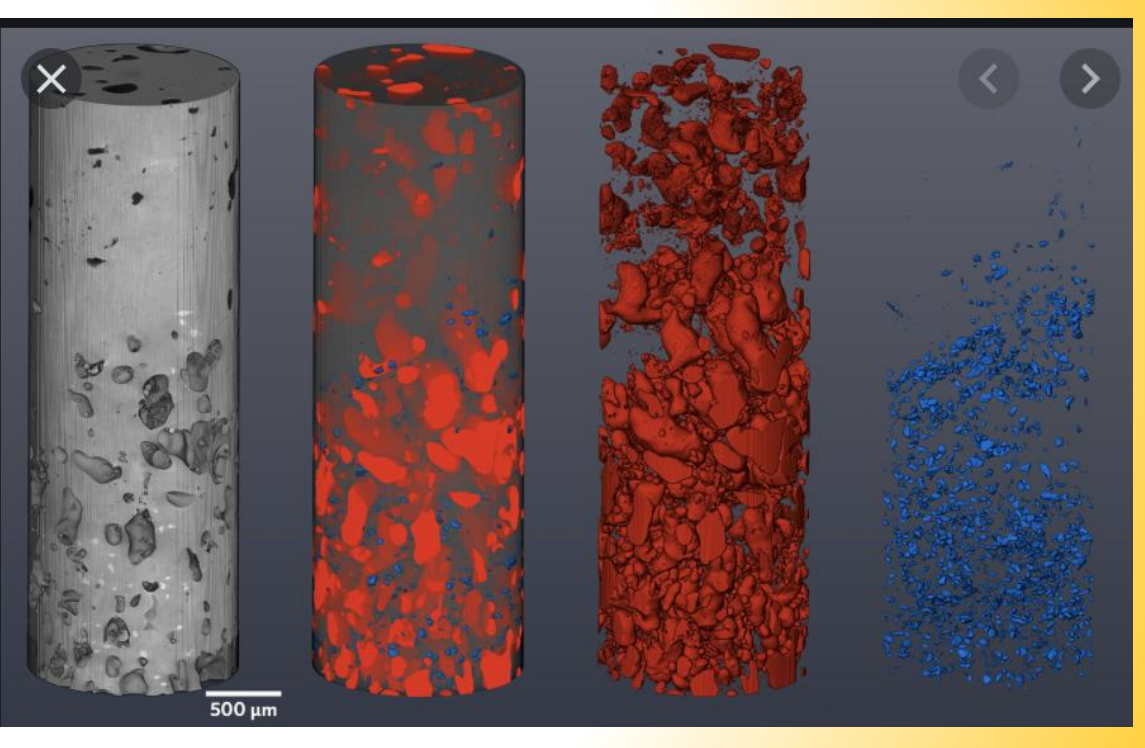
X-Ray Diffraction

	Aeris	Empyrean range	X'Pert³ MRD	X'Pert³ MRD XL
	Benchtop X-ray diffractometer	Multipurpose X-ray diffractometers for your analytical needs	Versatile research & development XRD system	Versatile research, development & quality control XRD system
	More details ›	More details ›	More details ›	More details ›
Technology				
X-ray Diffraction (XRD)	✔	✔	✔	✔
Measurement type				
Particle shape		✔		
Particle size		✔		
Crystal structure determination	✔	✔		
Phase identification	✔	✔	✔	✔
Phase quantification	✔	✔	✔	✔
Contaminant detection and anal...		✔		
Epitaxy analysis		✔	✔	✔
Interface roughness		✔	✔	✔
3D structure / imaging		✔		
Thin film metrology		✔	✔	✔
Residual stress		✔	✔	✔

X-Ray Tomography

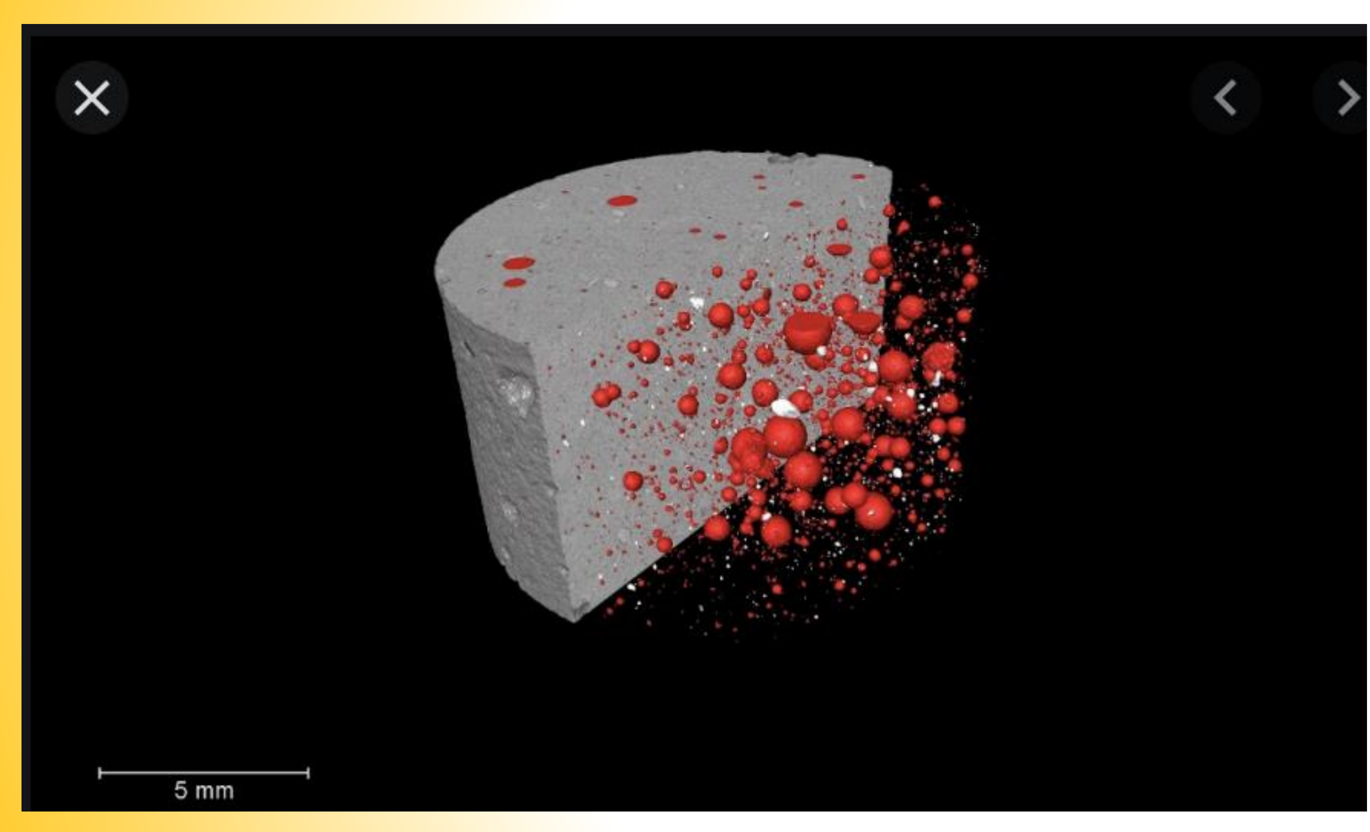
A NEW SENSOR: X-RAY COMPUTED TOMOGRAPHY

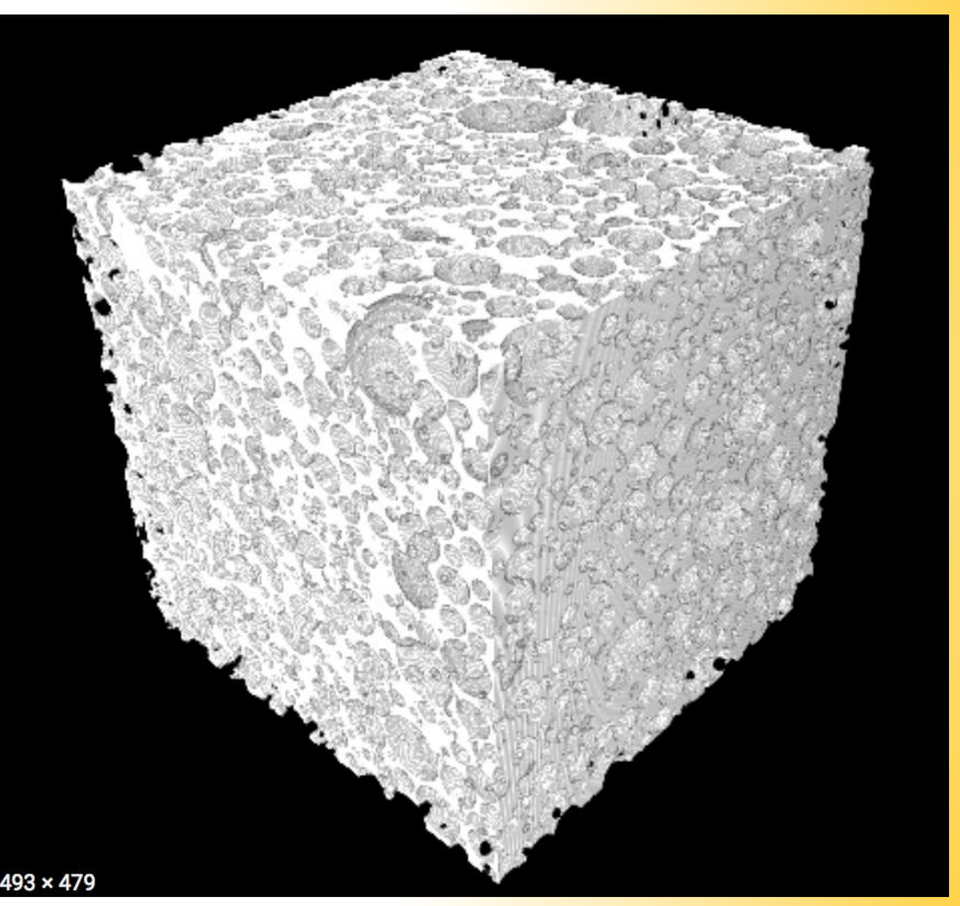




https://werthinc.com/a-new-sensor-x-ray-computed-tomography/

X-Ray Tomography





https://www.thermofisher.com/br/en/home/materials-science/xps-technology/multi-technique-workflow.html?cid=2020-ms-xps-multitechnique&utm_source=google&utm_medium=cpc&utm_campaign=2020-ms-xps-multitechnique&gclid=EAIaIQobChMI6K333aT_6wIVigaRCh05PA7NEAAYASAAEgIcmPD_BwE

Technique	**XPS** X-ray photoelectron spectroscopy	**ISS** Ion scattering spectroscopy	**REELS** Reflected electron energy loss spectroscopy	**UPS** UV photoelectron spectroscopy	**Raman** Raman spectroscopy	**AES** Auger electron spectroscopy
Probe	X-ray photons	Noble gas ions (He, Ne, Ar)	Electrons	UV photons	Light photons	Electrons
Detected	Electrons	Noble gas ions (He, Ne, Ar)	Electrons	Electrons	Light photons	Electrons
Collected data	Quantified elemental and chemical state composition. All elements can be detected except H & He	Elemental composition of outer atomic layer only. Detect elements heavier than probe ion	Electronic structure and hydrogen detection	Valence band electron meaasurement. Electronic property measurement	Raman-active vibrational modes of bonds in sample, which can be a fingerprint of the material/ compound	Elemental composition. Some chemical state information for certain compounds

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https://www.thermofisher.com/br/en/home/materials-science/xps-technology/multi-technique-workflow.html?cid=2020-ms-xps-multitechnique&utm_source=google&utm_medium=cpc&utm_campaign=2020-ms-xps-multitechnique&gclid=EAIaIQobChMI6K333aT_6wIVigaRCh05PA7NEAAYASAAEgIcmPD_BwE

XPS
ISS
REELS
UPS
Raman
AES

Typical analysis area

~µm²
~mm²
~mm²
~mm²
~µm²
~nm²

Typical analysis depth range

1 nm
5 nm
10 nm
1 µm

https://www.thermofisher.com/br/en/home/materials-science/xps-technology/multi-technique-workflow.html?cid=2020-ms-xps-multitechnique&utm_source=google&utm_medium=cpc&utm_campaign=2020-ms-xps-multitechnique&gclid=EAIaIQobChMI6K333aT_6wIVigaRCh05PA7NEAAYASAAEgIcmPD_BwE

	XPS	ISS	REELS	UPS	Raman	AES
Types of experiments	Measuring surface composition, depth profiling, interface chemistry, coating conformity, defect ID	Elemental surface composition, monolayer coverage measurement, segregation	Lowest unoccupied state measurement, band gap measurement, hydrogen detection	Work function measurement, valence band energy levels, valence band fingerprint	Molecular structure, compound identification, defect ID	Defect review, small structure analysis
Materials classes						
Metals	✓	✓	✓	✓		✓
Oxides	✓	✓	✓	✓	✓	✓
Ceramics	✓	✓	✓	✓	✓	✓
Polymers	✓		✓	✓	✓	✓
Nanomaterials	✓		✓	✓	✓	✓
Powders	✓		✓	✓	✓	✓
Glasses	✓	✓	✓	✓	✓	✓
Bio-materials	✓		✓	✓	✓	✓
Semiconductors	✓	✓	✓	✓	✓	✓

Hardness

1.2.8 Hardness Measurements

Meyer
Projected area

$$H = \frac{P}{A}$$

Universal (Martens)
Actual area

$$HM = \frac{F}{4h^2 \sin\theta / \cos^2\theta} = \frac{F}{26.43\, h^2}$$ Vickers indenter

$$HM = \frac{P}{3\sqrt{3}h^2 \tan\theta / \cos\theta}$$ Berkovich indenter

h measured from specimen free surface

Brinell
Actual area

$$BHN = \frac{2P}{\pi D\left(D - \sqrt{D^2 - d^2}\right)}$$

D = Diameter of indenter
d = diameter of residual impression

Vickers
Actual area

$$HV = \frac{2P}{d^2} \sin\frac{136°}{2} = 1.8544 \frac{P}{d^2}$$

$$HV = 0.094495\, H$$

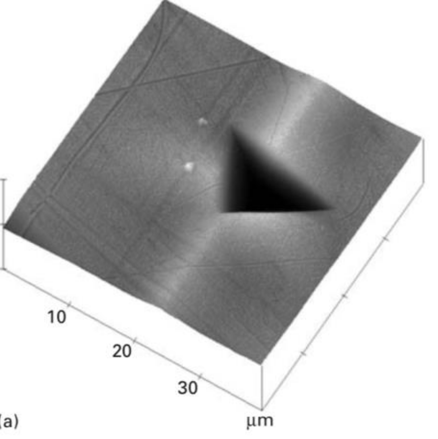
P = kgf
d = Length of diagonal mm
1 kgf = 9.806 N

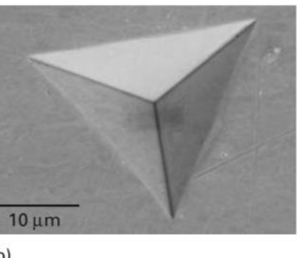
Knoop
Projected area

$$KHN = \frac{2P}{d^2\left[\cot\frac{172.5}{2} \tan\frac{130}{2}\right]}$$

d = Length of long diagonal of residual impression

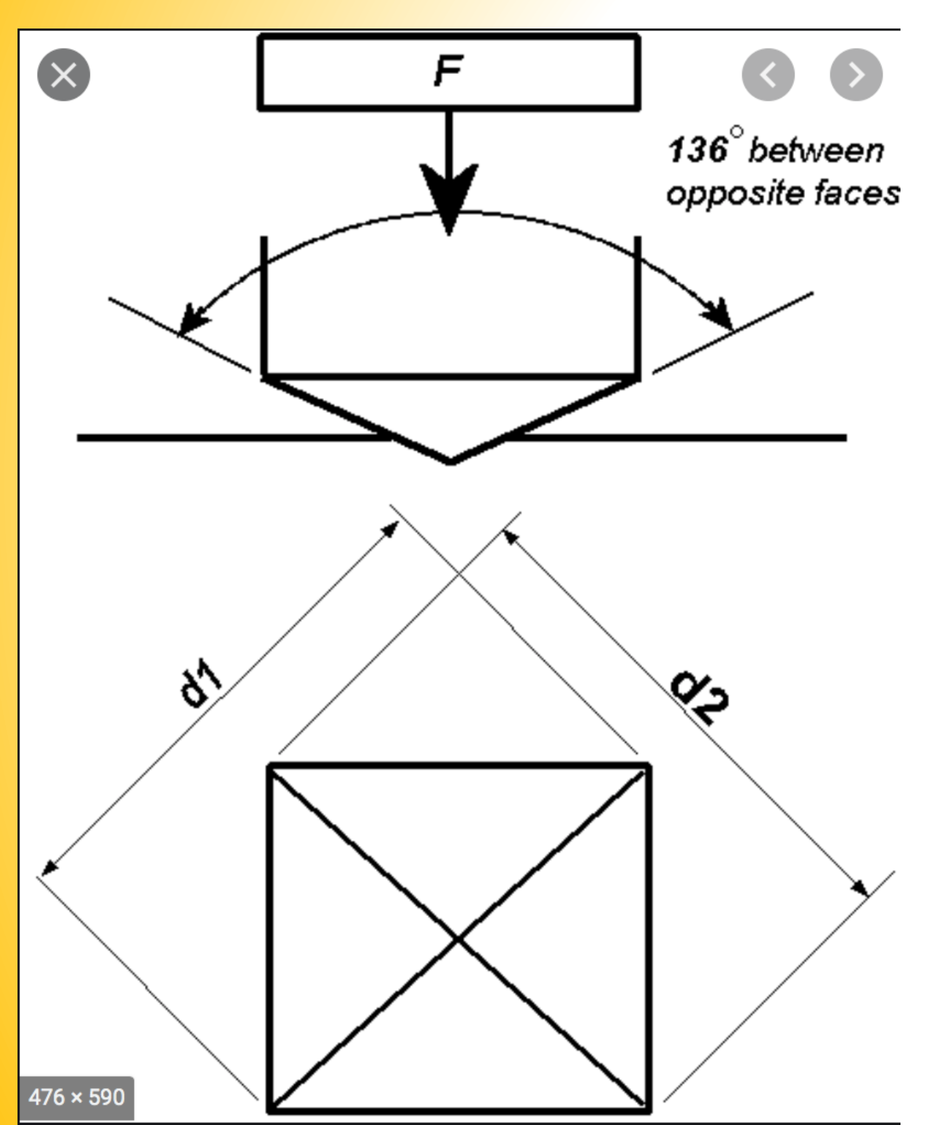
Fig. 3.42 An impression made by means of Berkovich indenter in a copper sample. (From X. Deng, M. Koopman, N. Chawla, and K. K. Chawla, *Acta Mater.*, 52 (2004) 4291.) (a) An atomic force micrograph, which shows very nicely the topographic features of the indentation on the sample surface. The scale is the same along the three axes. (b) Berkovich indentation as seen in an SEM.

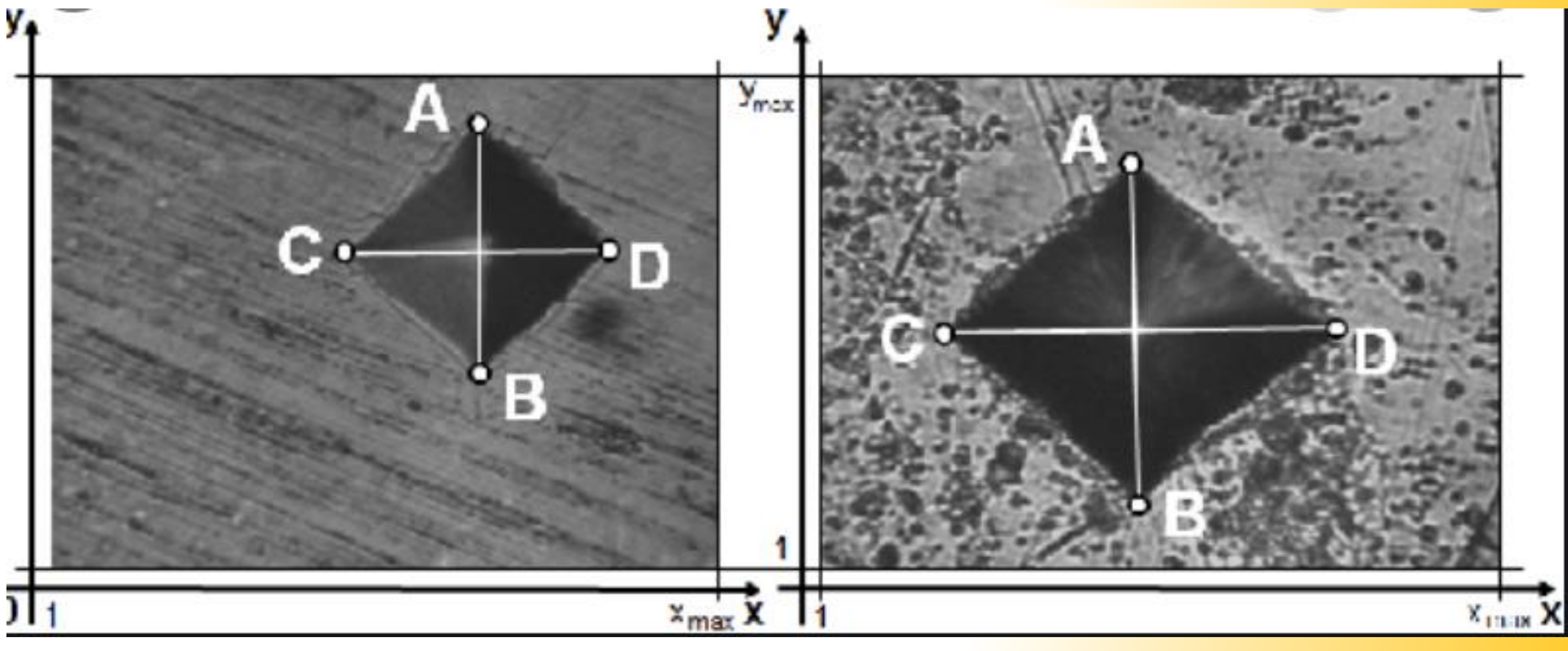




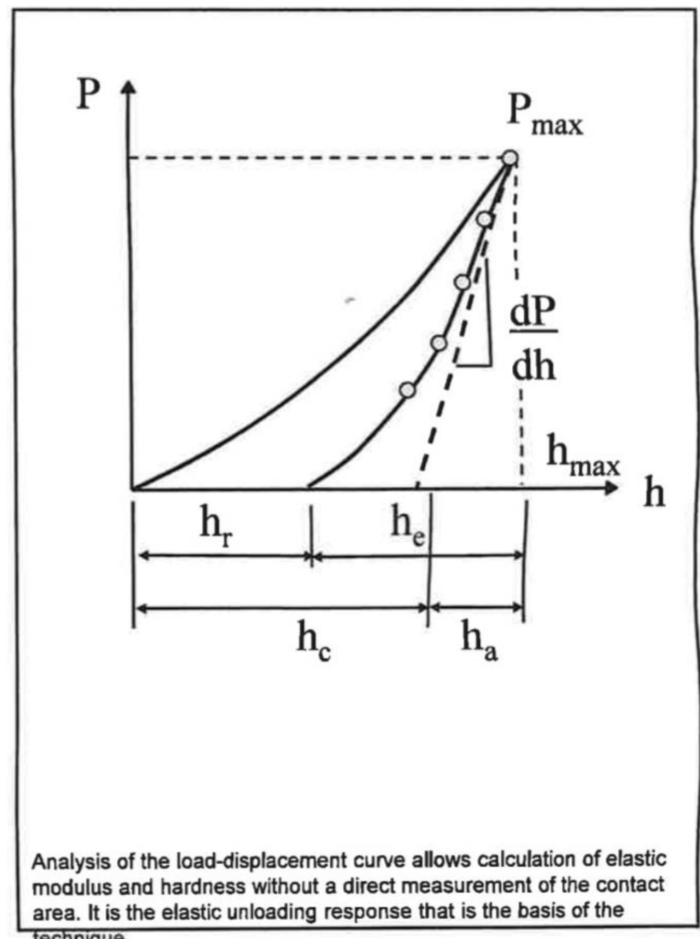
(b)

Hardness





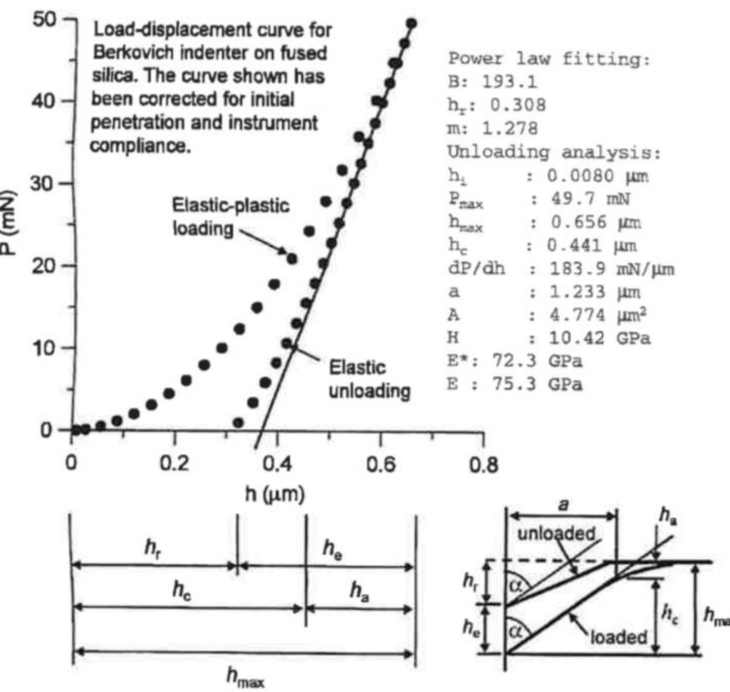
Instrumented Indentation



Analysis of the load-displacement curve allows calculation of elastic modulus and hardness without a direct measurement of the contact area. It is the elastic unloading response that is the basis of the technique.

1.3.1 Load-Displacement Curve

Nanoindentation is conventionally performed using instrumented indentation whereby the load and the indenter displacement are recorded during the indentation process. Both loading and unloading responses are recorded in the form of a load-displacement curve.



Although most nanoindenters are load-controlled machines, it is conventional practice to plot the load on the vertical axis and the displacement on the horizontal axis. The load displacement curve must be corrected for contact depth determination, instrument compliance, and indenter tip shape (area function) before during analysis for the determination of *E* and *H*.

Instrumented Indentation

1.3.2 Theoretical Analysis

The load-displacement curve is used to determine the depth of contact by using the elastic unloading data (even if the contact involves plastic deformation). The actual indenter is conveniently modelled as an equivalent conical indenter. The equations of contact are:

$$P = \frac{2}{\pi} E^* h_e^2 \tan\alpha' \qquad (1)$$

$$h = \left(\frac{\pi}{2} - \frac{r}{a}\right) a \cot\alpha' \quad r \le a$$

At $r = 0$, $h = h_e$:

$$h_e = \frac{\pi}{2} a \cot\alpha'$$

α' is the combined angle of the cone and the sides of the residual impression

At $r = a$, $h = h_a$:

$$h_a = \left(\frac{\pi}{2} - 1\right) a \cot\alpha'$$

From which we obtain:

$$h_a = \left(\frac{\pi - 2}{\pi}\right) h_e \text{ and: } h_t = h_c + h_a$$

Thus:

$$h_t = h_c + \frac{\pi - 2}{\pi} h_e$$

From Eqn. 1:

$$\frac{dP}{dh} = 2E^* \frac{2}{\pi} h_e \tan\alpha'$$

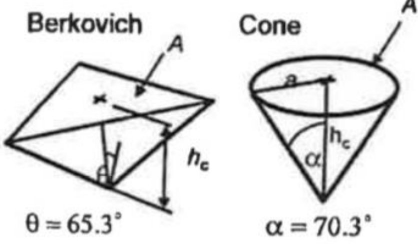
$$P = \frac{1}{2} \frac{dP}{dh} h_e$$

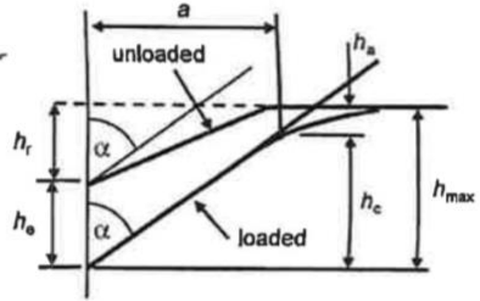
$$h_e = P \frac{2}{dP/dh}$$

Thus:

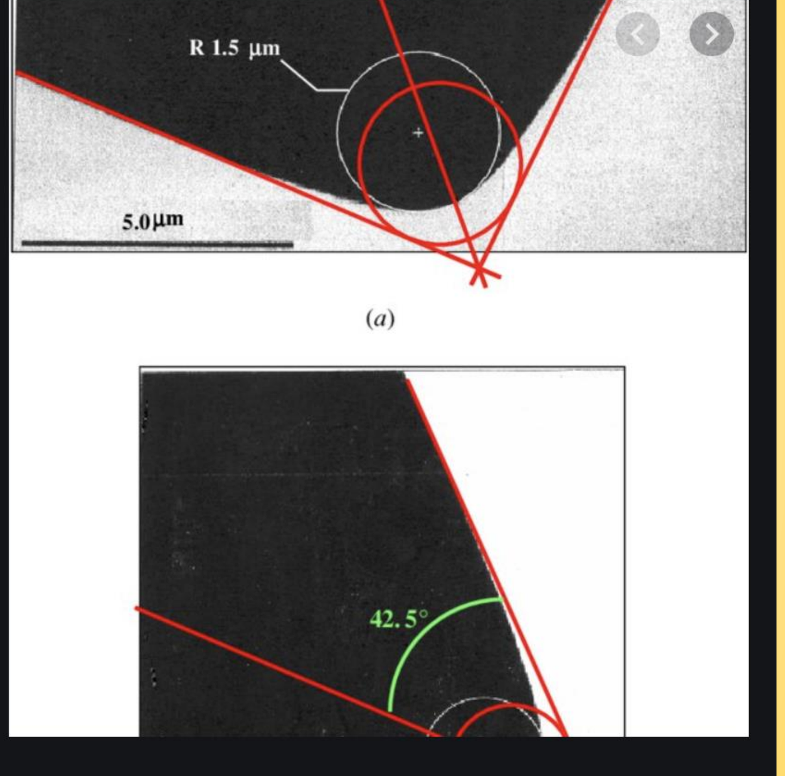
$$h_{max} = h_c + \left[\frac{2(\pi - 2)}{\pi}\right] \frac{P}{dP/dh}$$

h_{max}, P_{max} and dP/dh are all obtained from measurements and so h_c can be determined.





Calculation of H	Calculation of E*
$A = 3\sqrt{3} h_c^2 \tan^2\theta$	$P = \frac{2}{\pi} E^* h_e^2 \tan\alpha$
$= 24.5 h_c^2$	$\frac{dP}{dh} = 2\frac{2}{\pi} E^* h_e \tan\alpha$
	$h_e = \frac{\pi}{2} a \cot\alpha$
	$\frac{dP}{dh} = 2E^* \frac{2}{\pi} \frac{\pi}{2} a$
	$= 2E^* a$
$H = \frac{P}{A}$	$E^* = \frac{dP}{dh} \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}}$



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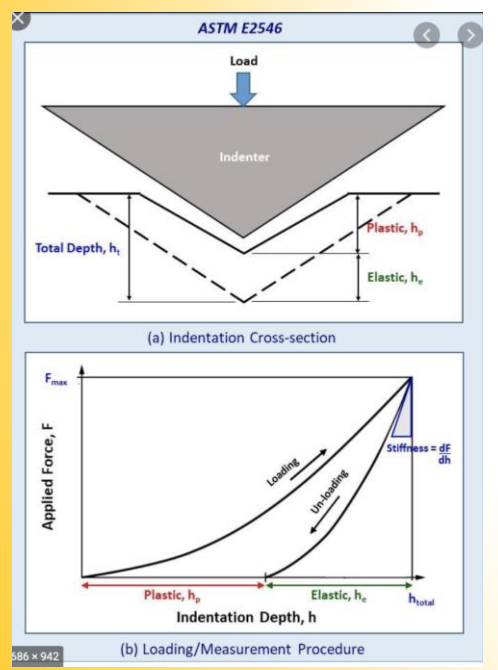
Instrumented Indentation

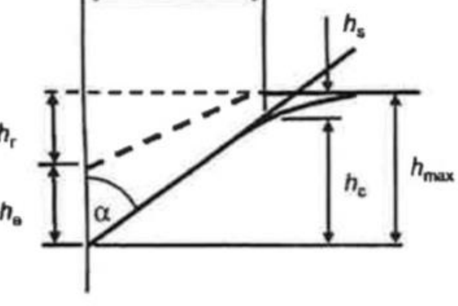


1.3.3 Oliver and Pharr Method

Two of the most important physical properties of materials are elastic modulus and hardness. In nanoindentation, the depth of penetration of a diamond indenter is measured along with the prescribed load. The resulting load-displacement response typically shows an elastic-plastic loading followed by an elastic unloading. The elastic equations of contact are then used in conjunction with the unloading data to determine the elastic modulus and hardness of the specimen material.

Berkovich geometry

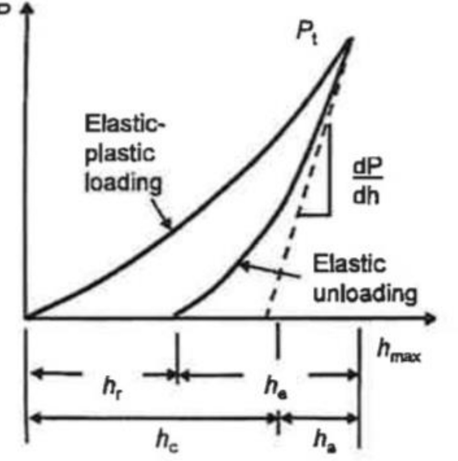
Residual impression of Berkovich indenter in hardened steel.



The three-sided Berkovich indenter is the most popular choice of geometry for nanoindentation testing. The contact depth (as measured from the total depth of penetration) is given by:

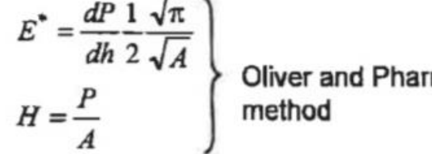
$$h_c = h_{max} - \varepsilon \frac{P_{max}}{dP/dh}$$

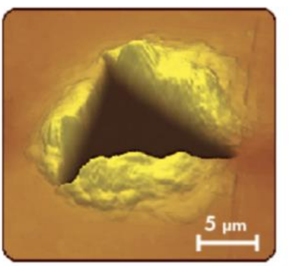
The factor ε depends upon the indenter shape. Once h_c is known, the area of contact A is found from the geometry of the indenter.



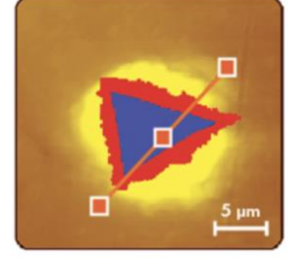
Elastic modulus is given by: $E^* = \frac{dP}{dh}\frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A}}$

Hardness is calculated from: $H = \frac{P}{A}$

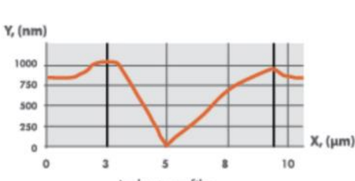




Indent on the titanium surface (99%)

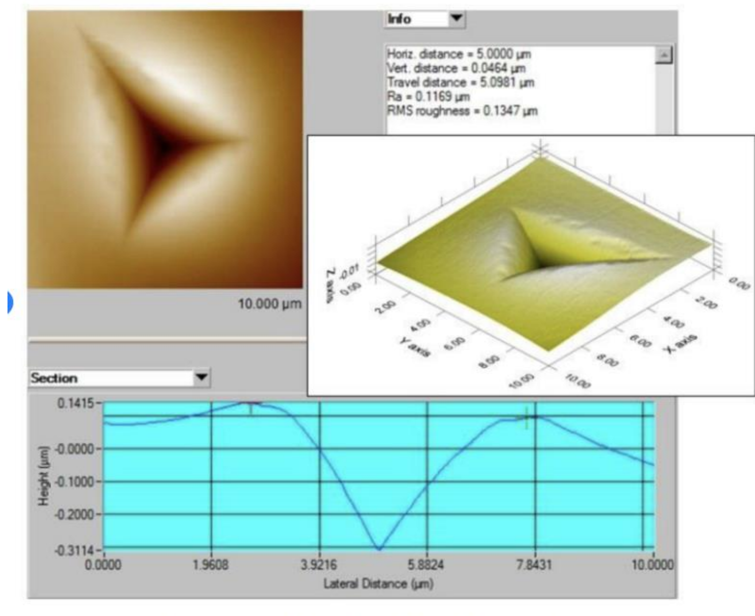


Example of automated area calculation



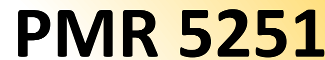
Indent profile

http://nanoscan.info/eng/methods/hardness-measurement-over-the-residual-indent-image



2D and 3D view (axis dimensions, µm) of the plastic nano-indentation imprint with the corresponding line scan and median roughness for the blend film with 20 wt. % of chitosan.

https://www.researchgate.net/figure/2D-and-3D-view-axis-dimensions-mm-of-the-plastic-nano-indentation-imprint-with-the_fig4_257998720



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