PRINCETON UNIVERSITY

Microscopy and Spectroscopy to Characterize Processed Materials

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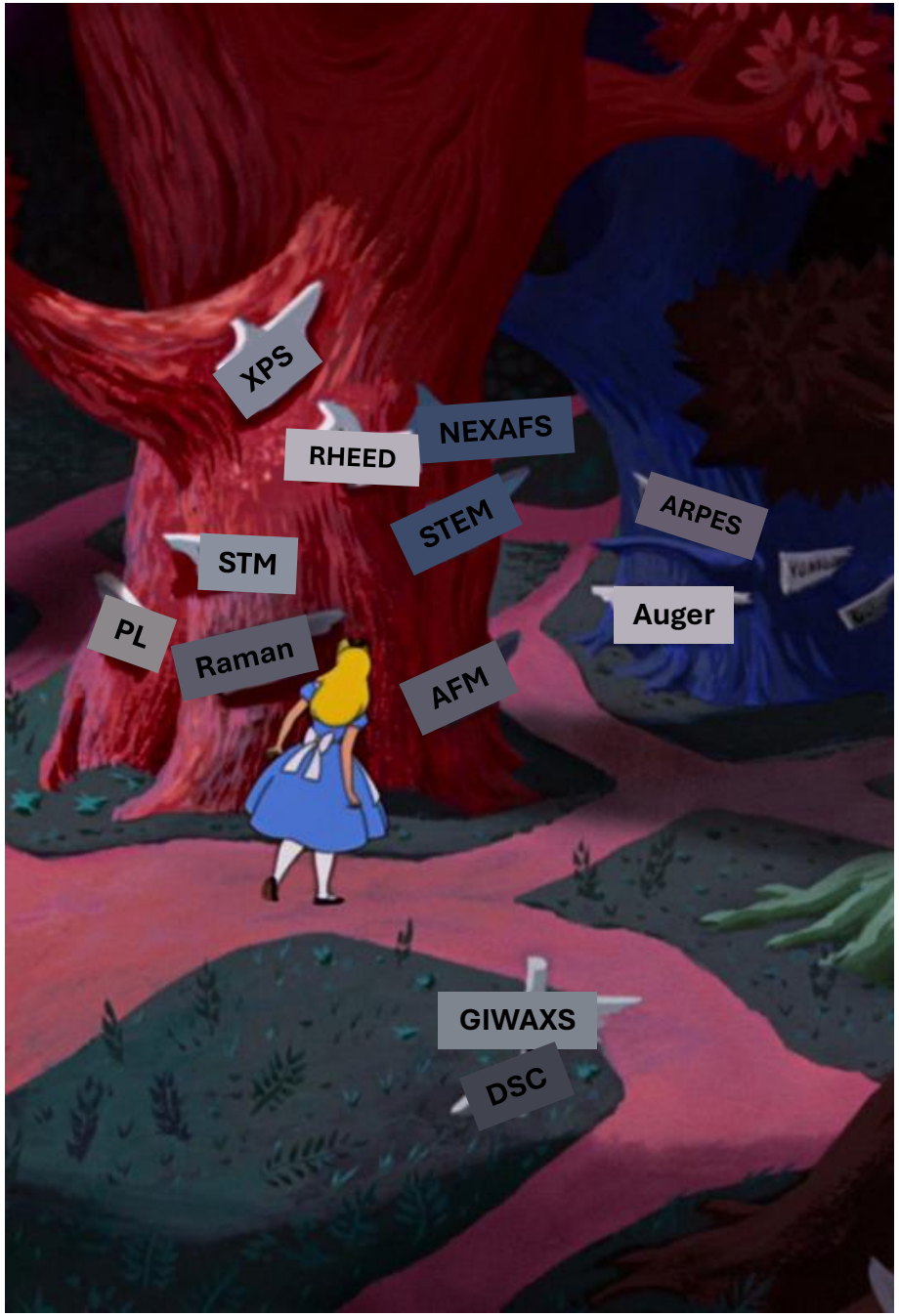
Which characterization technique is the right one for my material?

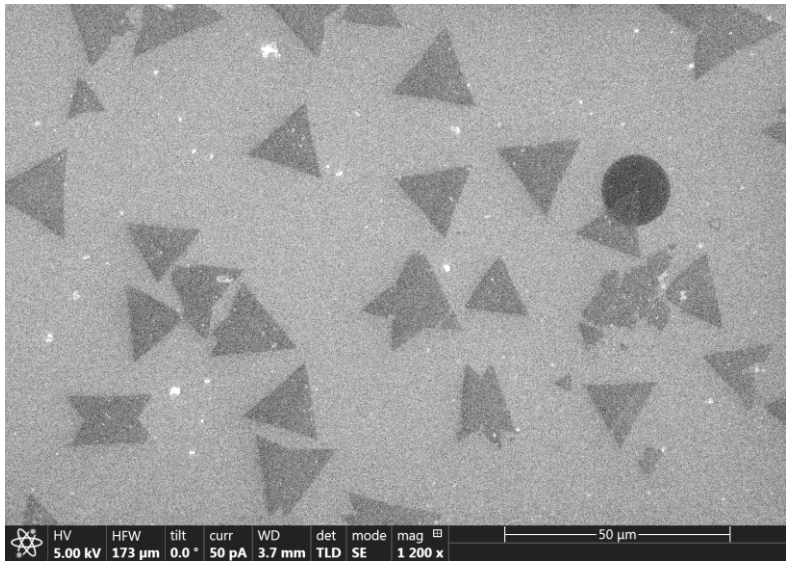
That depends a great deal on what it is you want to learn!

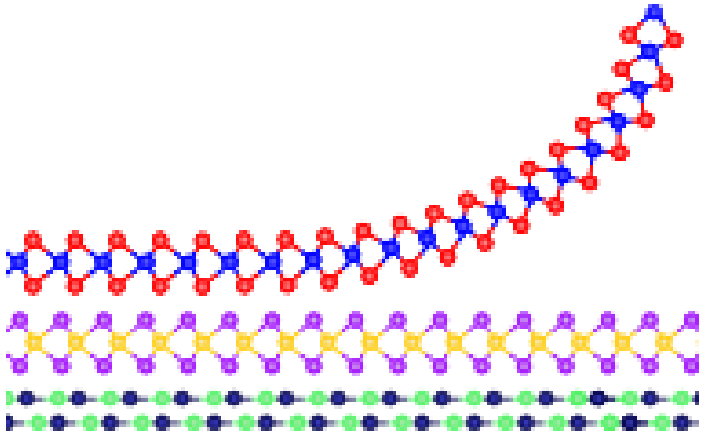
This lecture: a brief roadmap to this dense forest of materials science characterization techniques

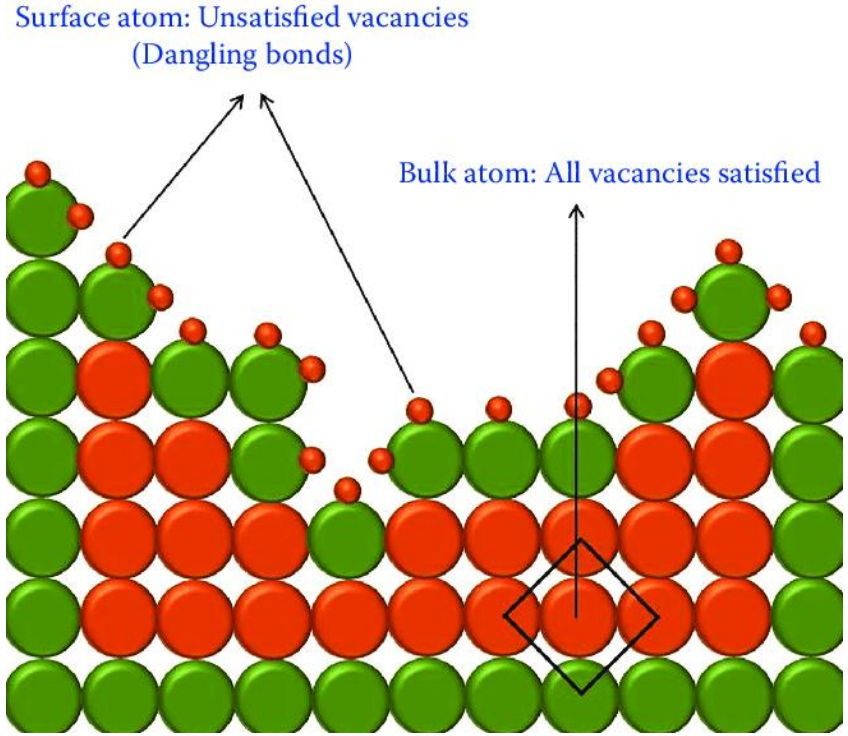


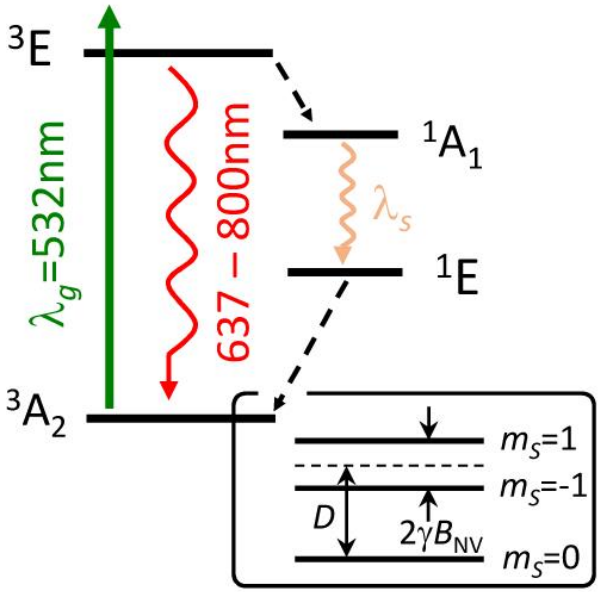
Practical considerations

- Size
- Thickness (/thinness, substrate)
- Surface vs. bulk
- Resolution (spatial, energy, etc…)



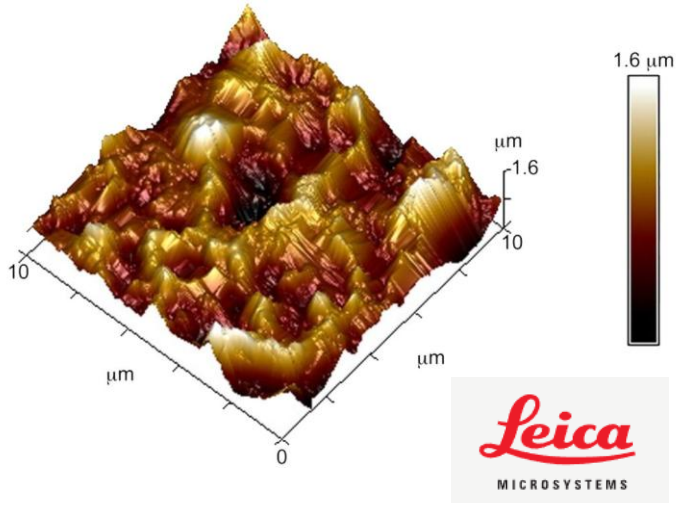


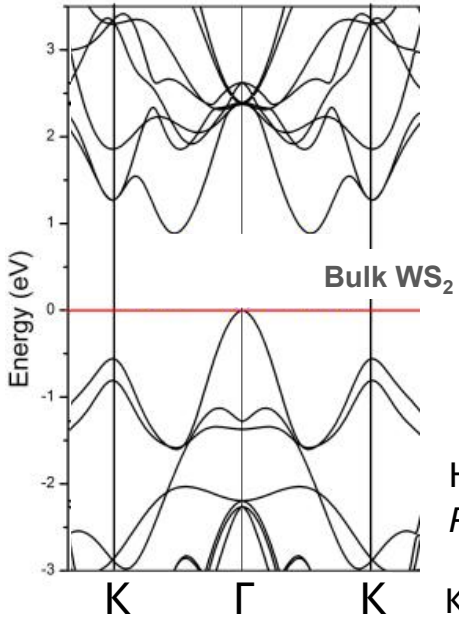




Philosophical considerations

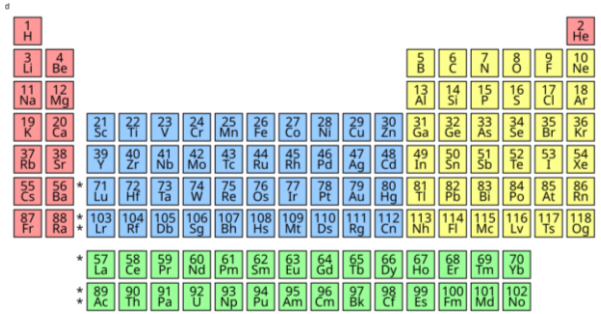
- Morphology
- Composition
- Lattice structure
- Electronic structure
- Dynamics, light-matter interactions

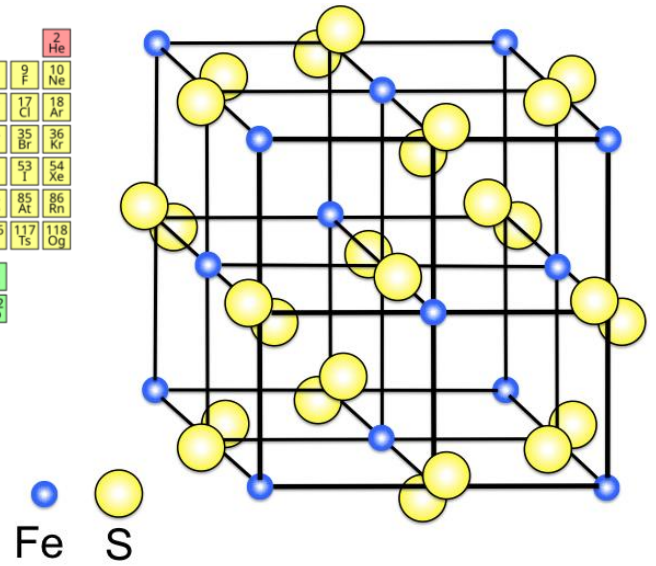


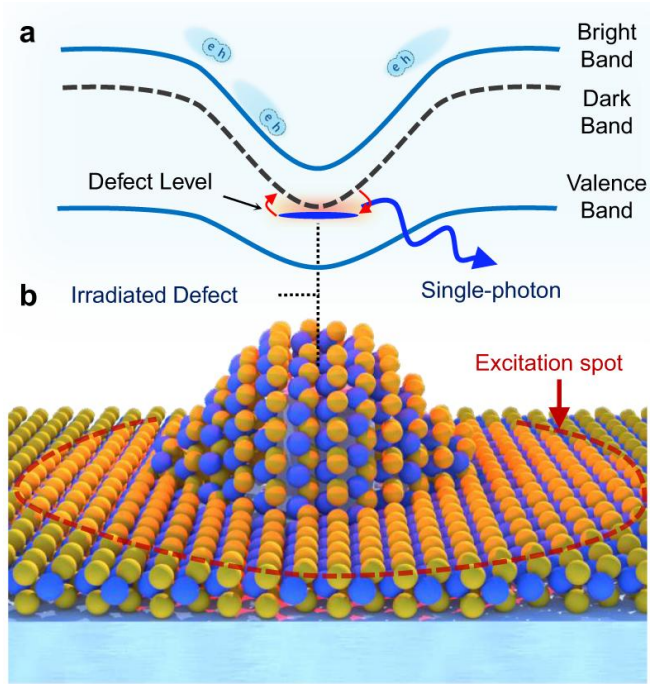


H. Terrones et al. *Sci Rep*. **3**, 1549 (2013)

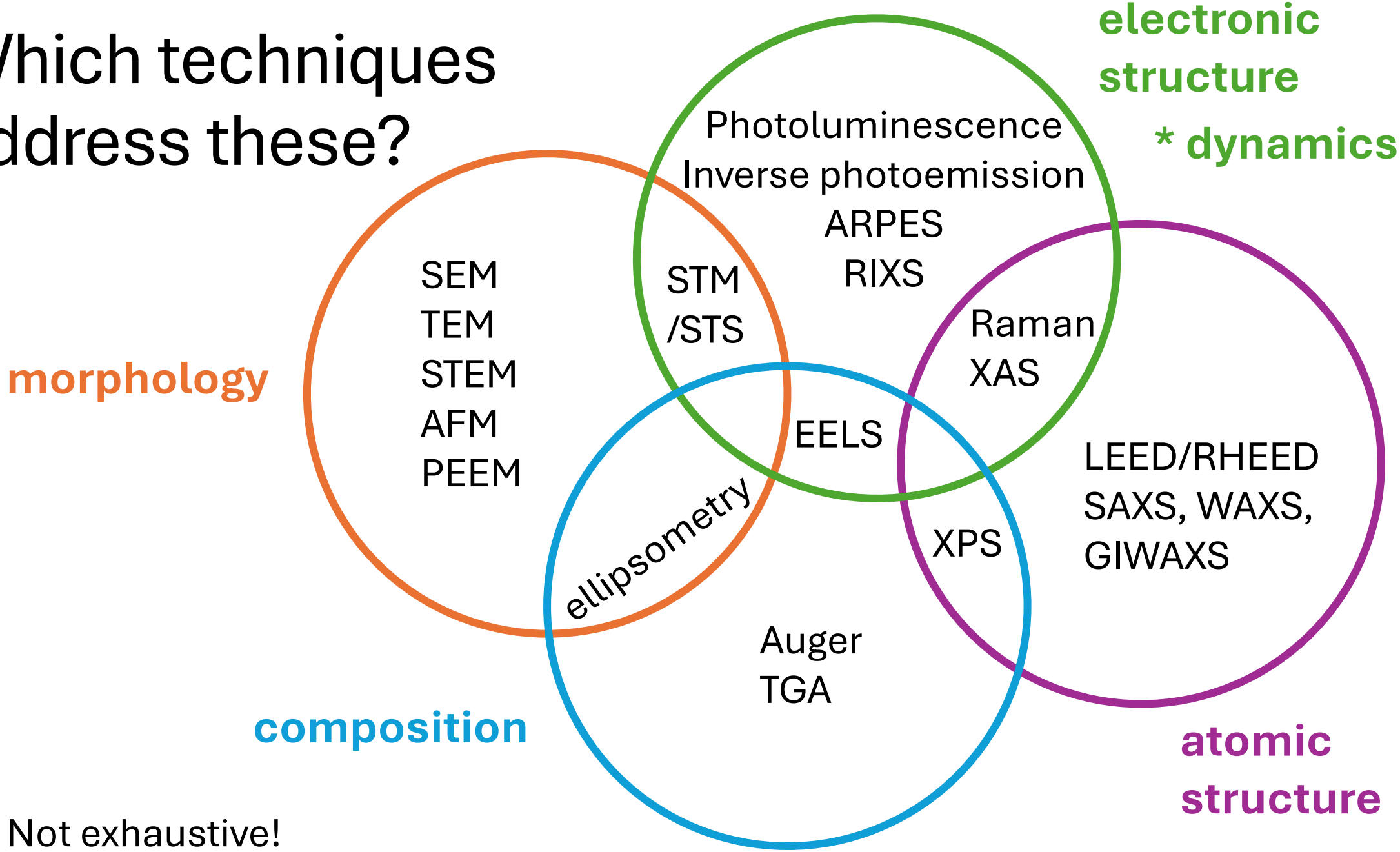
K. Parto et al. *Nat. Commun.* 12, 2, 3585 (2021)







Which techniques address these?



Not exhaustive!

Techniques by type of probe

optical
Photoluminescence
Raman
XAS, NEXAFS
Ellipsometry
Reflectivity

photoelectric
XPS/UPS
ARPES
PEEM

scanning probe
STM
AFM
SNOM
Tip-enhanced Raman

time-resolved
PL, Raman
XAS
XPS, ARPES
PEEM
STM, SNOM
RIXS
…

electron
LEED/RHEED
Auger
EELS
Inverse photoemission
(S)(T)EM

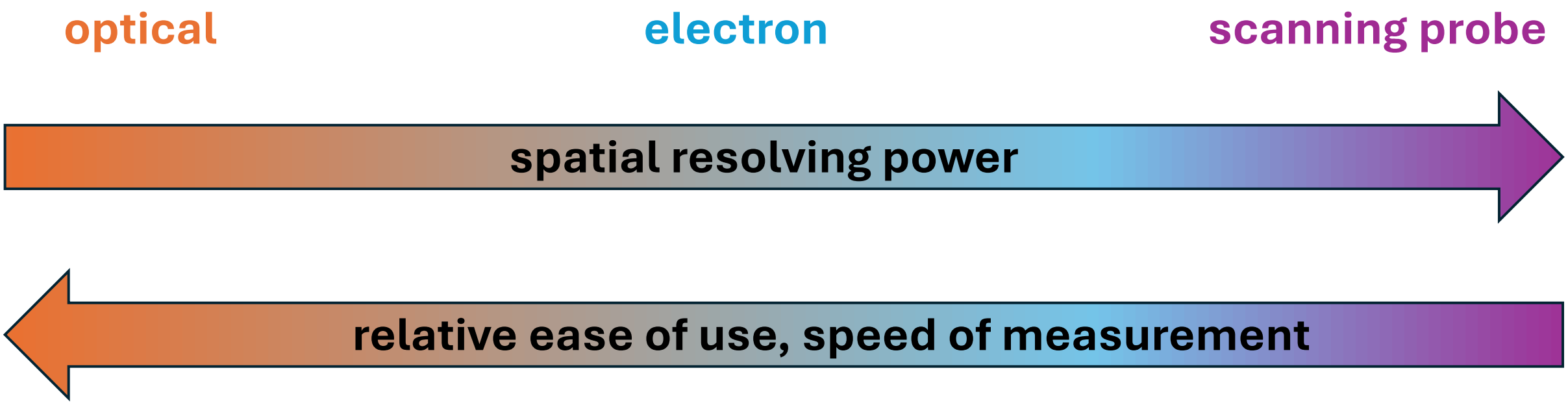
scattering
SAXS, WAXS, GIWAXS
RIXS
Neutron

thermal
DSC
TGA
TPD

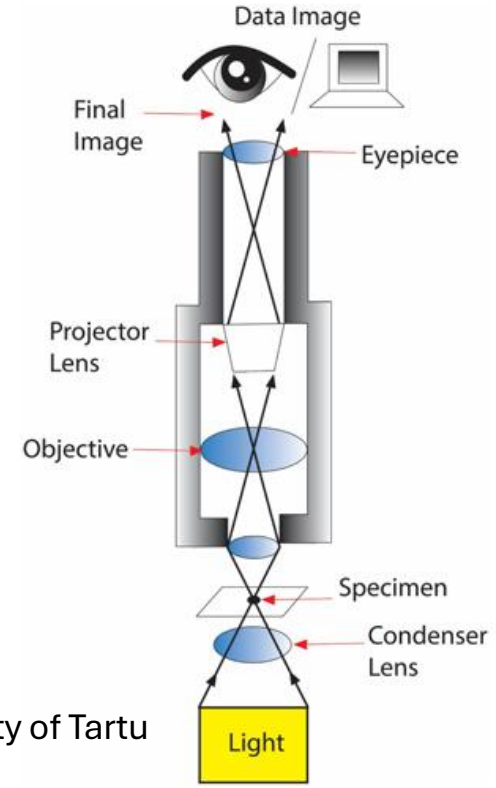
Not exhaustive!

Microscopy

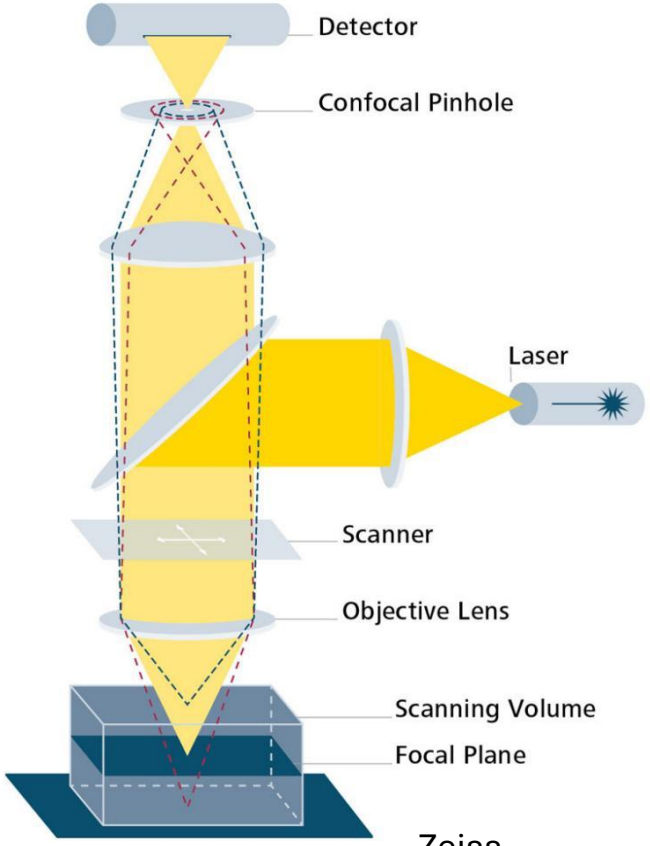
Magnify and resolve small features



Optical microscopy



University of Tartu



Zeiss

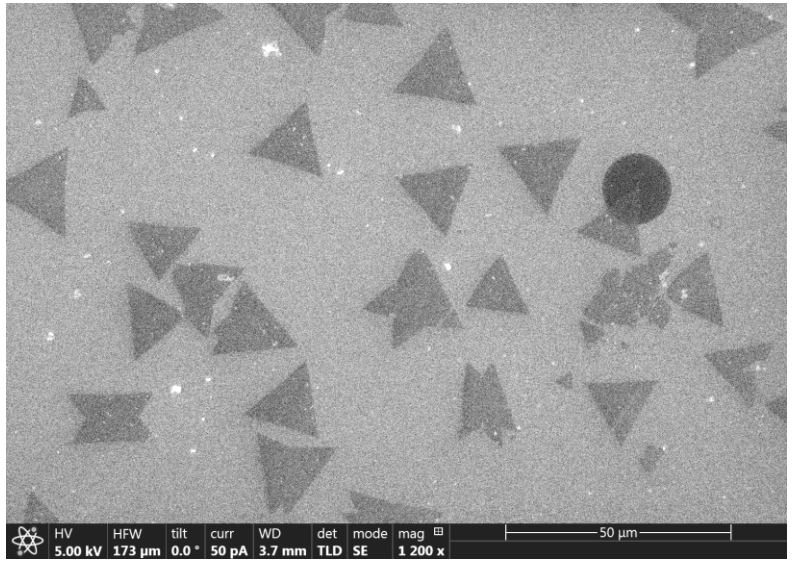
- Resolution down to ~200 um if perfect
- Consider: if your sample is very thin, it may have very poor optical contrast!

- Can be easily coupled with lasers to combine microscopy with laser spectroscopic approaches

Electron Microscopy

- Use a beam of electrons to illuminate a sample, a series of electro-optic lenses to focus and control the beam
- Resolution typically few to 10s of nm depending on system
- Vacuum techniques, samples should be reasonably conductive (or sputter coated)
- Consider checking out https://myscope.training/ to practice aligning imaging columns

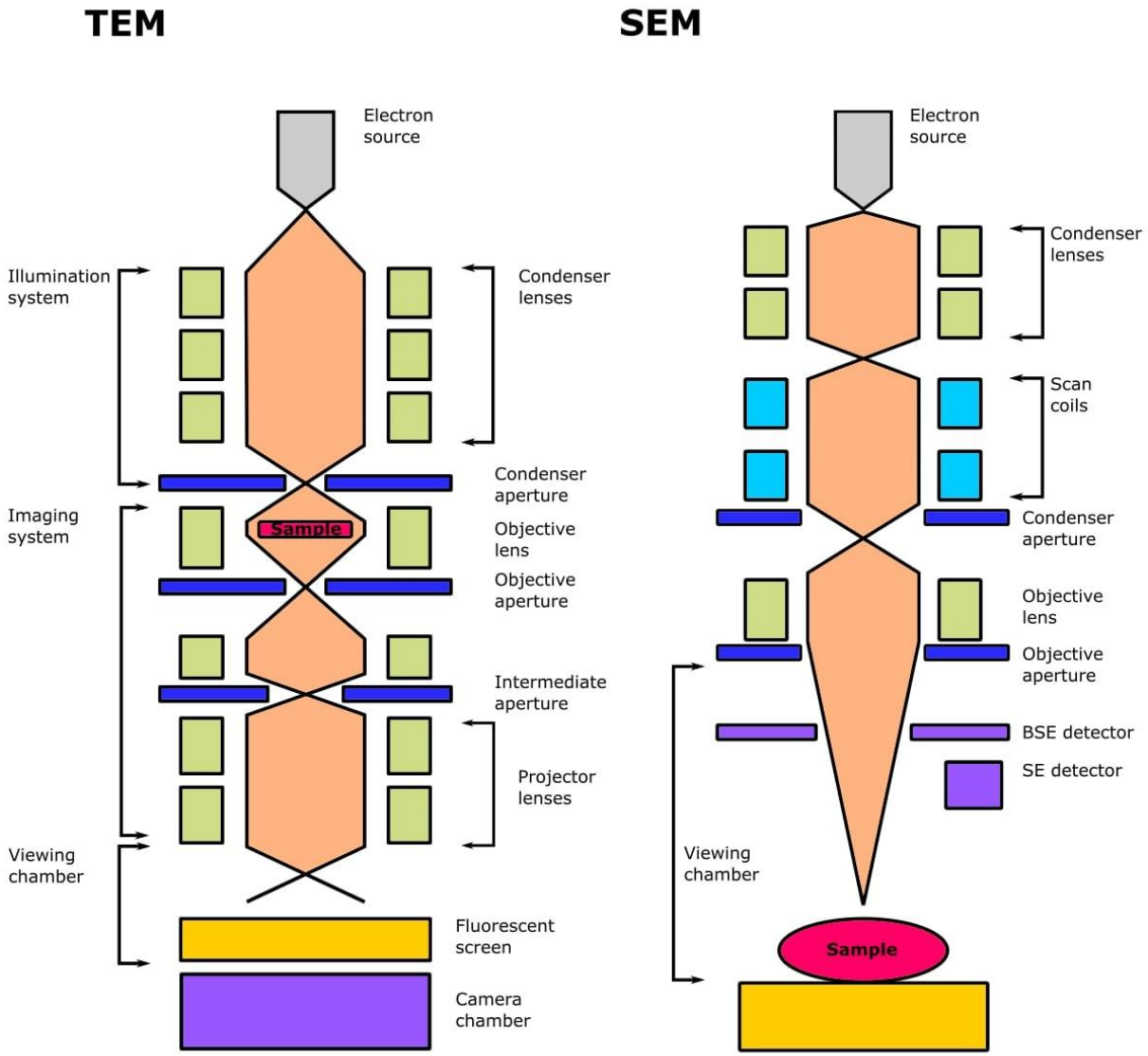
MYSCOPE
MICROSCOPY TRAINING



Monolayer WS_2 grown flakes in SEM

Electron Microscopy

- Transmission vs. scanning
- TEM: electrons transmit and are imaged to a camera, where contrast is governed by electrons scattered/absorbed by the sample
- SEM: detect secondary and backscattered electrons from the sample surface
- TEM can offer higher resolution, but samples must be thin and prepared on special grids (tricky)
- STEM variation combines both – same sample requirements as TEM, but can achieve higher resolution



Thomas Warwick

Scanning Probe Microscopy

A very diverse family of techniques typically capable of achieving sub-nm resolution of features on the surface of materials

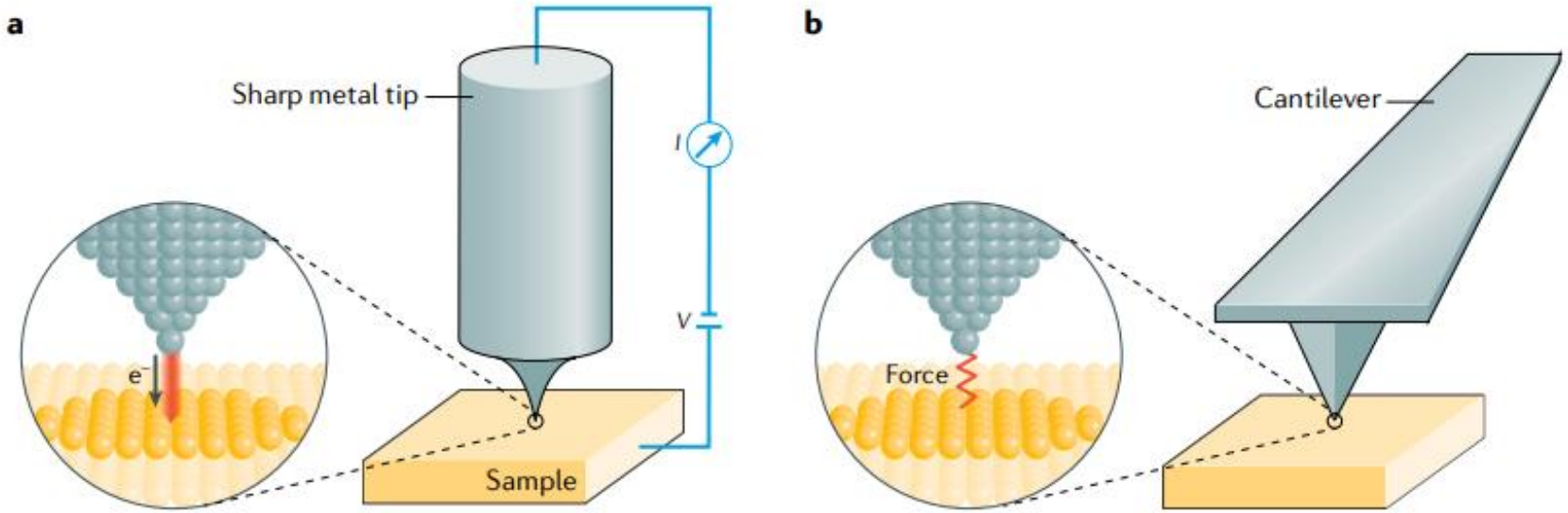
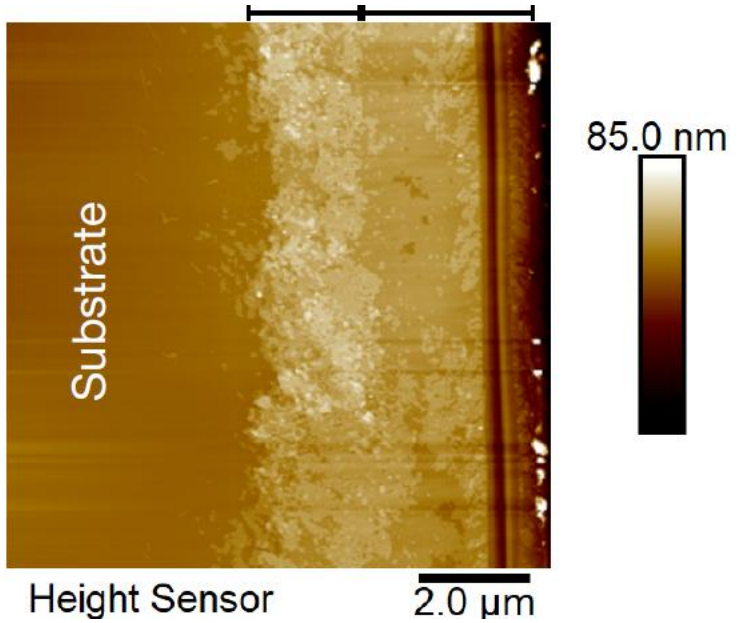


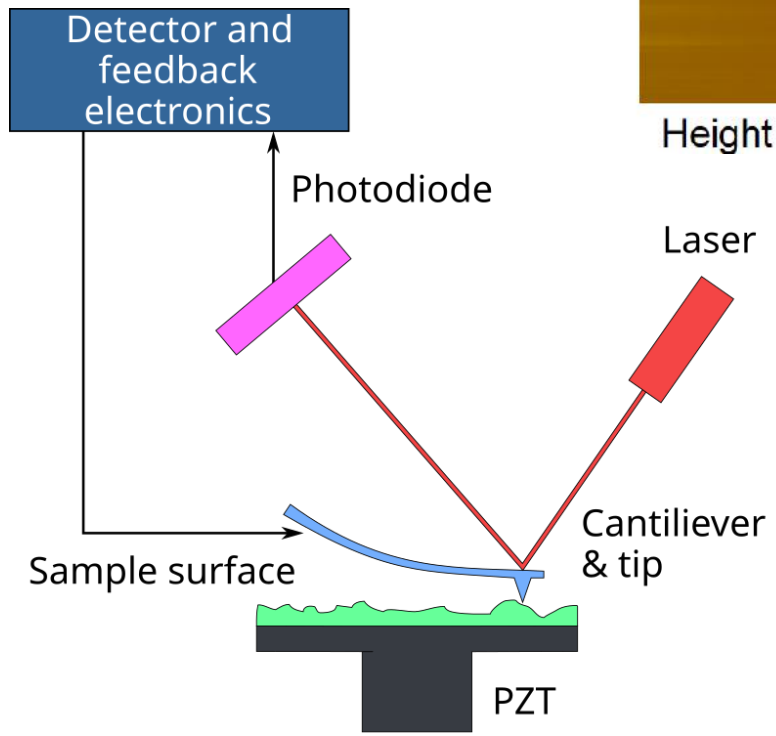
Fig. 1 | **Basic set-up for scanning probe microscopy.** Scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) both use a tip to scan the sample. Both techniques use different feedback signals to maintain constant tip–sample interaction, but their basic principle of operation and image acquisition mechanisms are similar. **a** | STM collects the tunnelling current between the tip apex and the sample when a bias voltage is applied. **b** | AFM detects local forces and corresponding mechanical parameters through a spring-like cantilever.

K. Bian et al., *Nature Reviews Methods Primers*. 1, 36 (2021)

Atomic Force Microscopy

- In contact AFM, the tip directly contacts the surface, providing a highly sensitive probe of surface roughness (sub nm)
- Ambient technique suitable for a range of samples from conducting to insulating



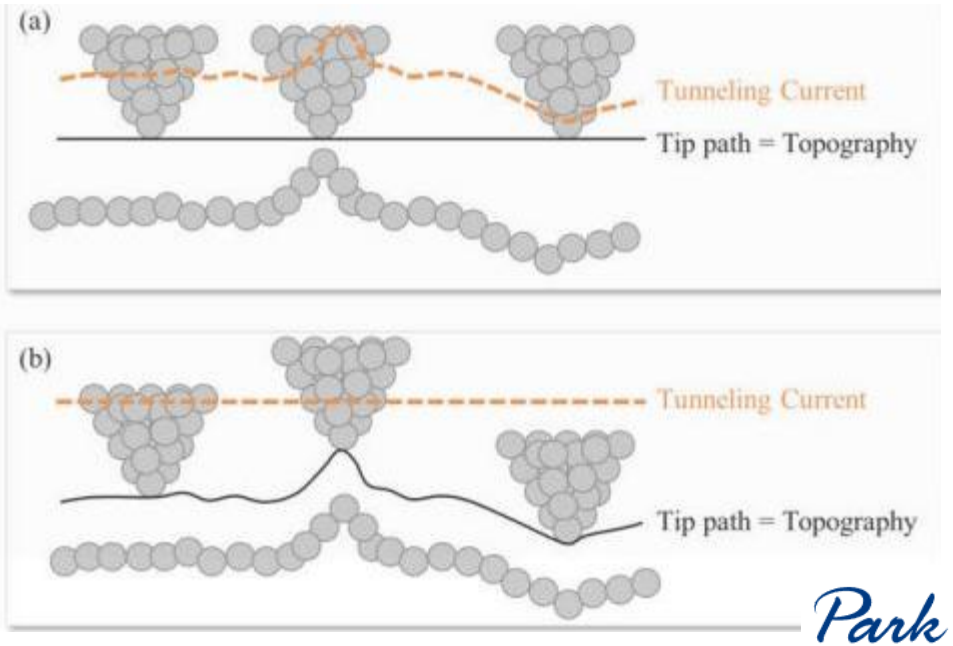


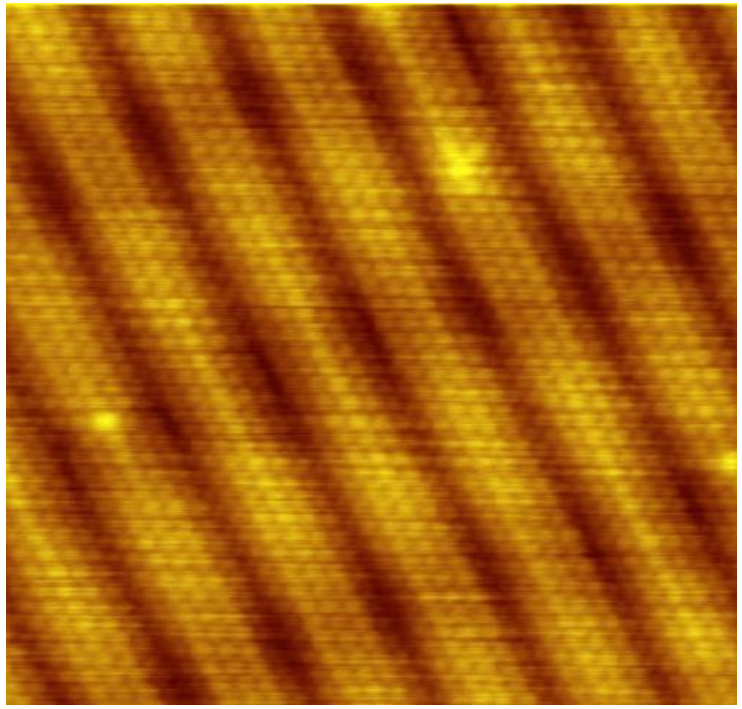
Scanning Tunneling Microscopy

- Most typically requires an ultrahigh vacuum environment and cryogenically cooled temperatures
- Strict: sample must have a clean surface and be conductive at these temperatures. Also, slow!

Constant height mode

Constant current mode

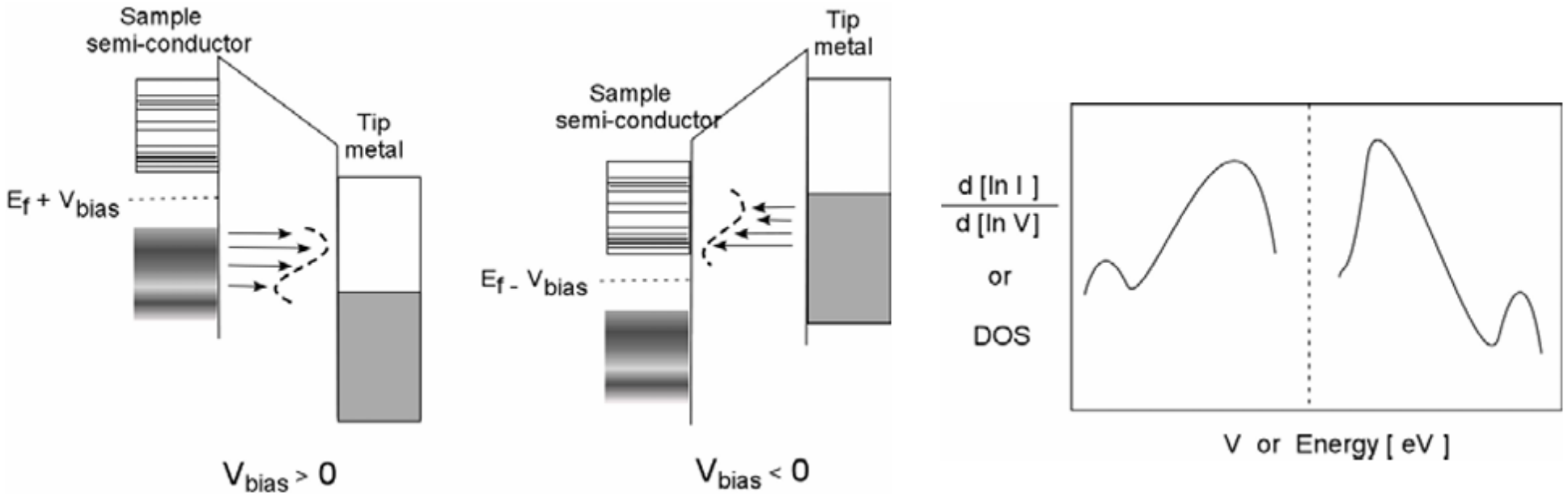




Au (100) surface (Erwin Rossen)

Scanning Tunneling Spectroscopy

- Bias voltage allows current flow between tip and sample without contact via quantum tunneling through the barrier
- To map the local density of states, fix the tip height and measure the change in electron tunneling current as a function of electron energy (tip bias)

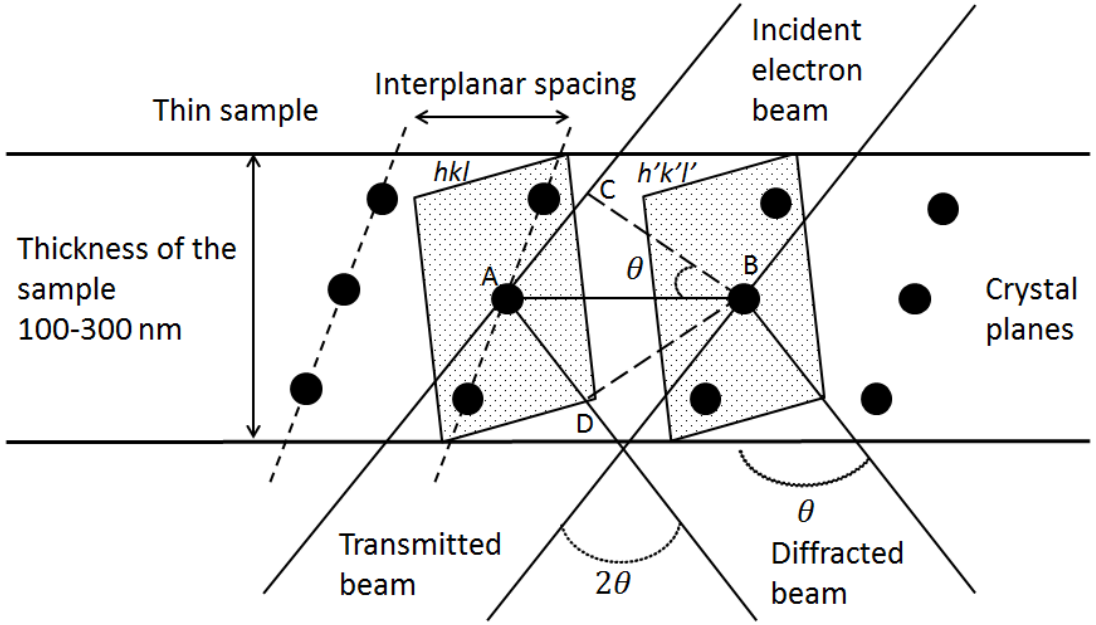


U Washington, Nanoscience on the tip

Electron Diffraction

- Sensitive approach for measuring crystal lattice structure
- Ultrahigh vacuum technique
- Can be destructive to the sample
- There are also x-ray diffraction + scattering related variants (SAXS, WAXS, GIWAXS)

→*(should I use electrons or x-rays? If the sample is small or thin (2D), you must use electrons. If the sample is thicker/3D, go for x-rays)*



M. A. Asadabad and M. J. Eskandari. *Modern Electron Microscopy in Physical and Life Sciences*, 2016.

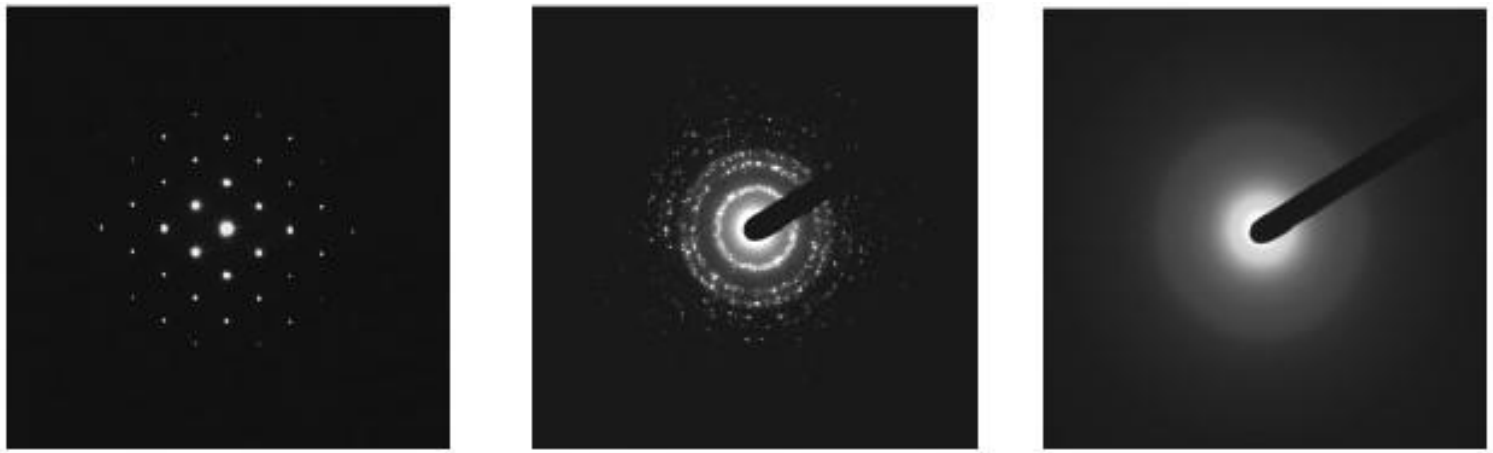
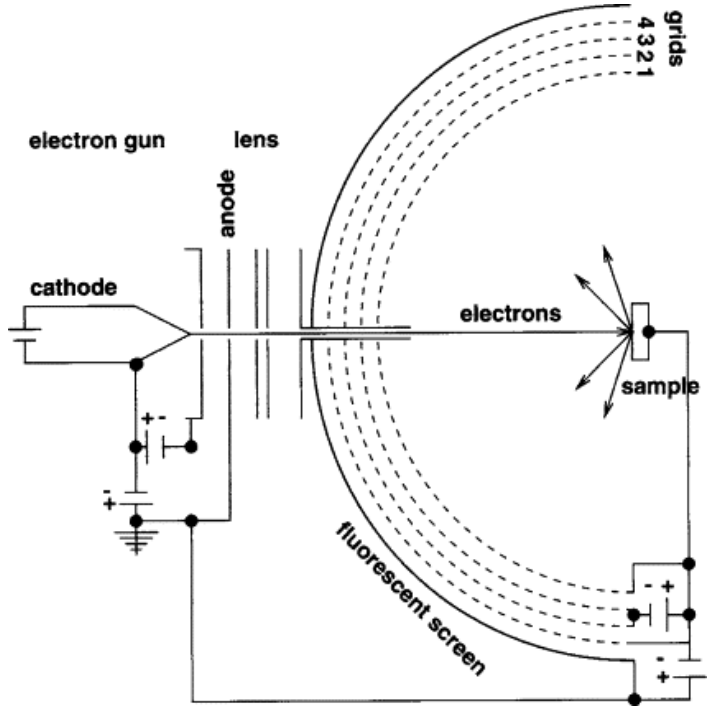


Fig. 4. Example of diffraction patterns: Crystalline Si (left), polycrystalline Si (centre), and quarts glass (right)

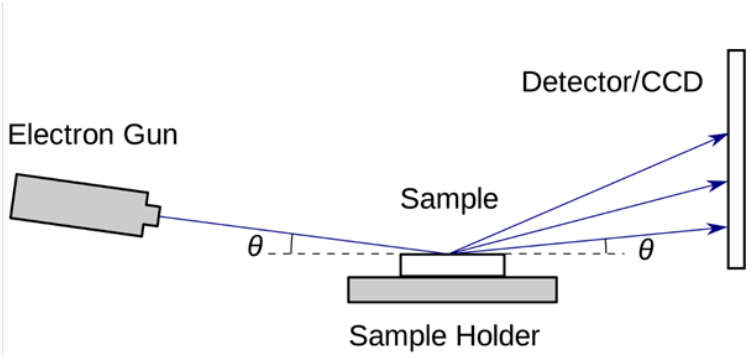
https://www.mst.or.jp/Portals/0/en/en_ed.html

LEED, RHEED

- LEED (Low-Energy Electron Diffraction) and RHEED (Reflection High-Energy Electron Diffraction) are both powerful tools for observing surface crystal, growth, and cleanliness
- The lower energy range of LEED (~10-200 eV) compared to RHEED (~keV) makes it more surface sensitive (can identify surface reconstruction)
- The grazing reflection geometry of RHEED is more amenable for in situ measurements during growth or processing



LEED geometry

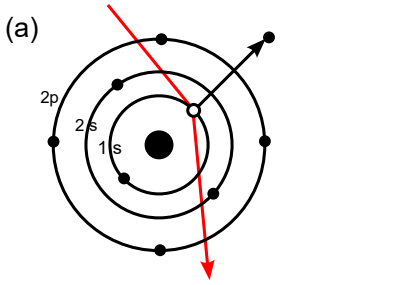


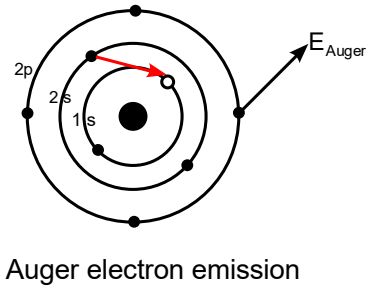
RHEED geometry

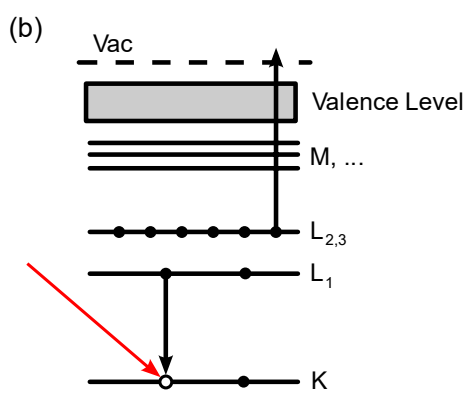
Elemental Analysis with Electrons

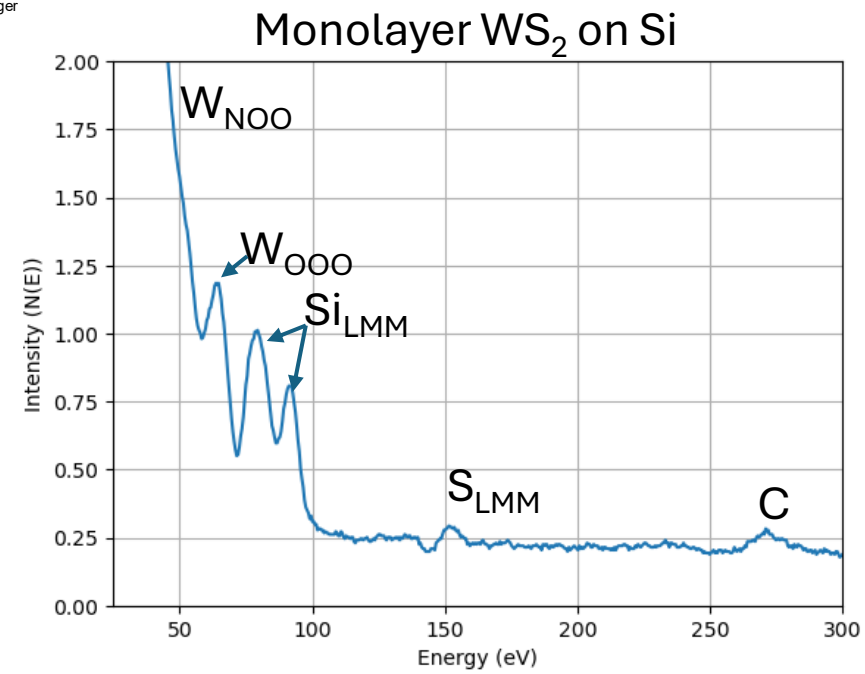
Auger electron spectroscopy

- Relaxation of outer shell electron to a core hole leads to emission of Auger electrons with characteristic energies
- Auger transitions are labeled according to the shells involved in the process
  - Process to the right would be labeled $KL_1L_{2,3}$
- Transition energies are element specific but subject to shifts based on chemical environment
- Surface-sensitive vacuum technique often coupled with LEED/RHEED instruments



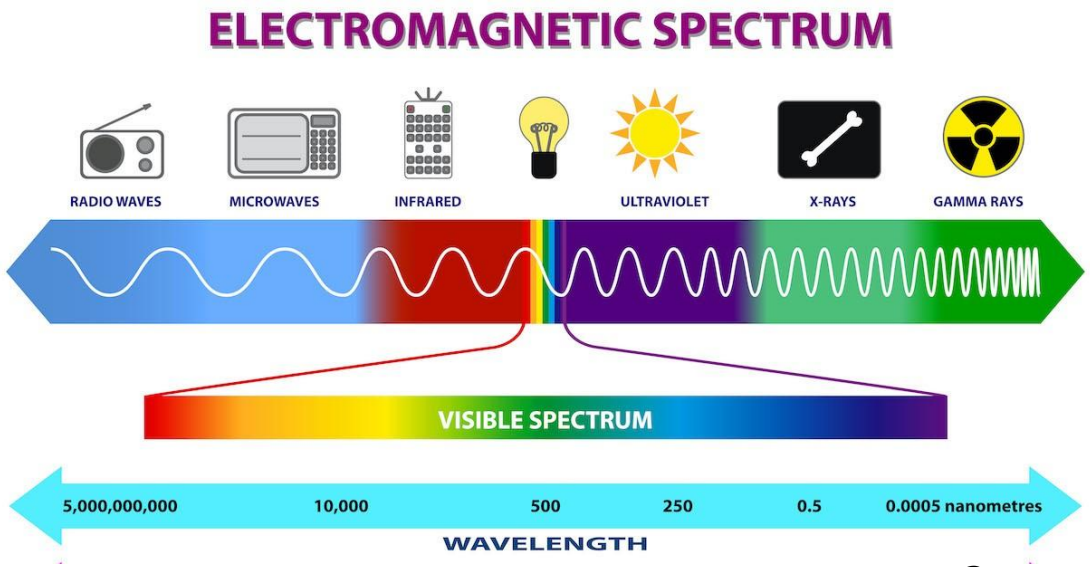




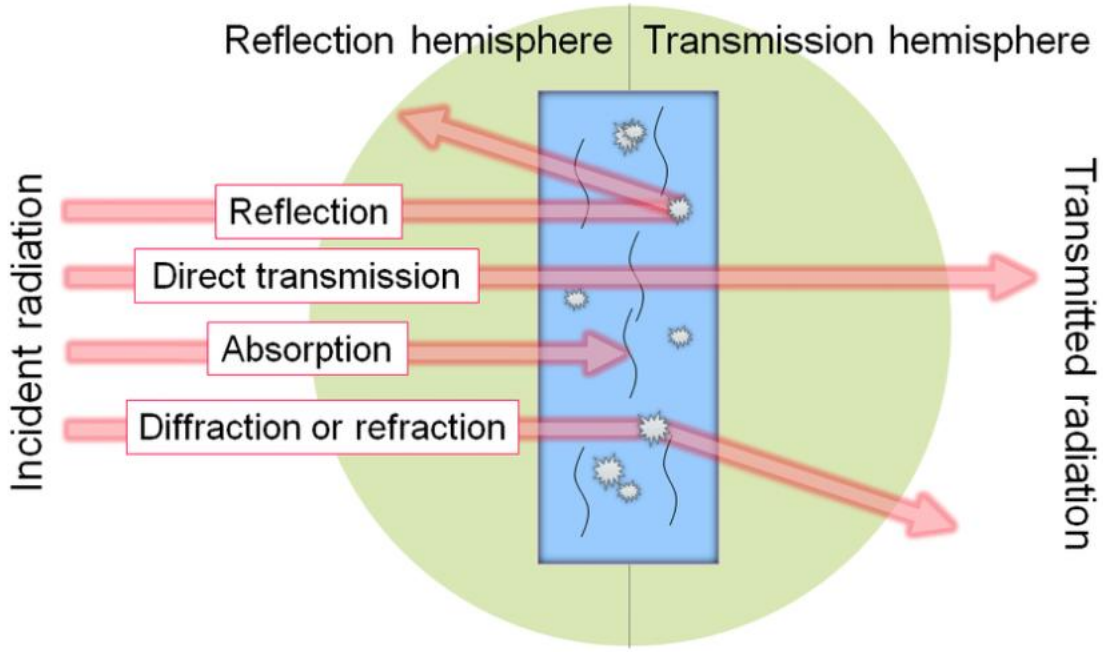


Spectroscopy

- Using electromagnetic radiation to probe the properties of matter (often electronic)
- Broadly categorized either by the range of the electromagnetic spectrum used, or by the type of interaction (absorption, fluorescence, Raman, etc.)



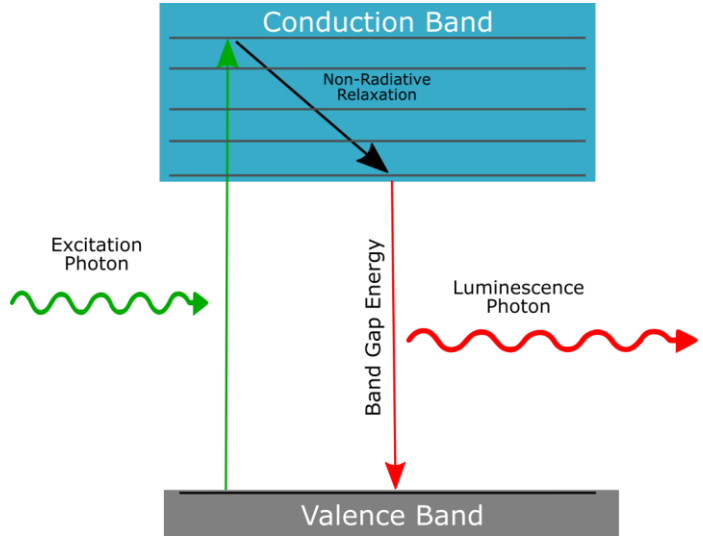
Getty

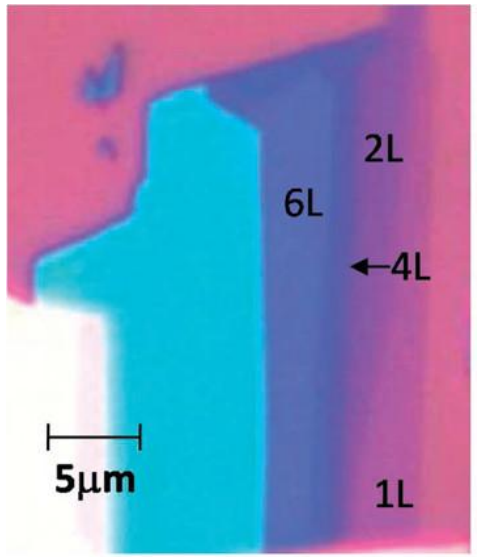


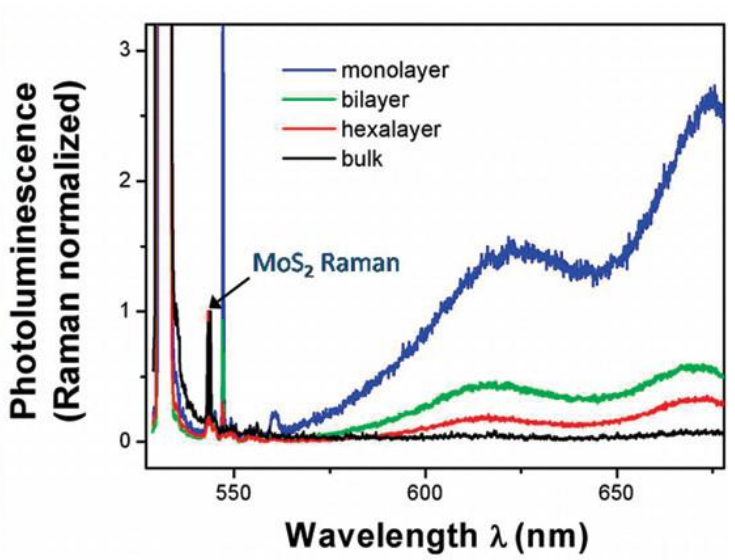
Kari Hyll

Optical Photoluminescence

- Used to probe optical band gaps and optical transition energies for semiconducting systems
- Easy to perform with visible lasers in commercial instruments, does not carry surface cleanliness requirements of other techniques
- Note that indirect band gap semiconductors may have weak signatures…
- Time-resolved photoluminescence is a popular variant in which the optical excitation is synchronized with photoluminescence recording



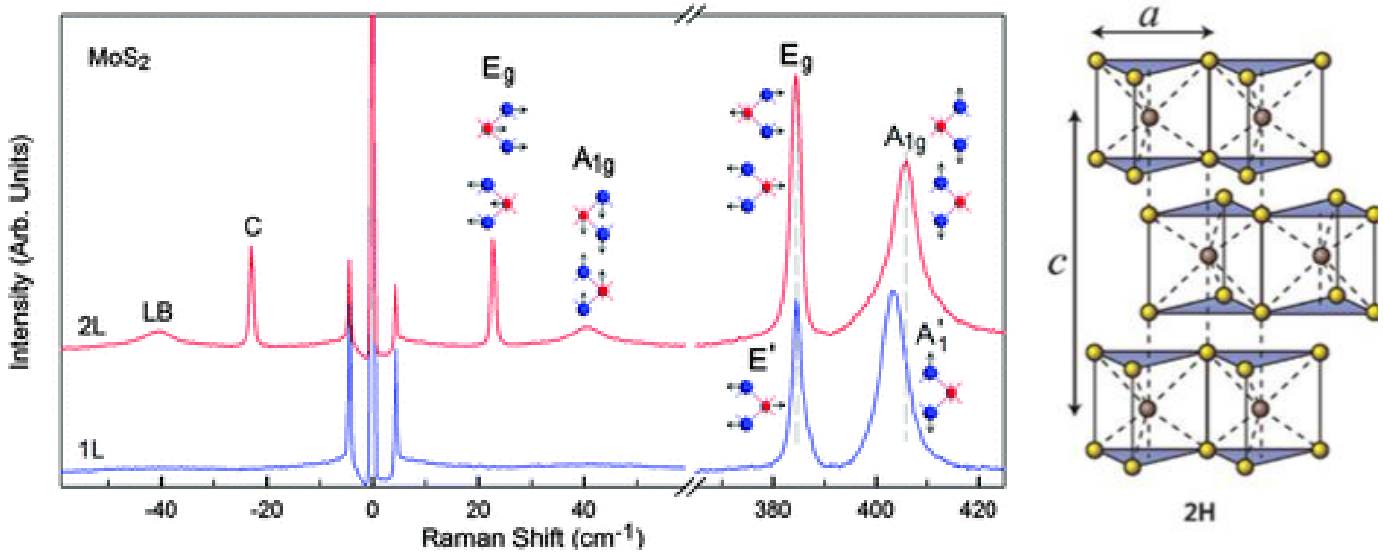


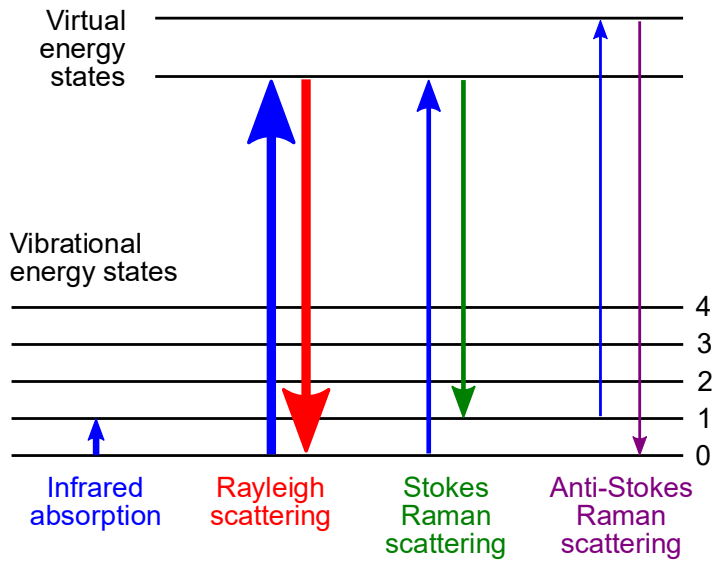


A. Splendiani, *Nano Lett*. 10, 4, 2010

Raman Spectroscopy

- Visible, IR, UV, or x-ray light can be used
- Inelastic scattering with material phonons: Raman scattering
- Sensitive to material vibrational modes
- Can be very useful for identifying number of layers in low-dimensional/thin materials



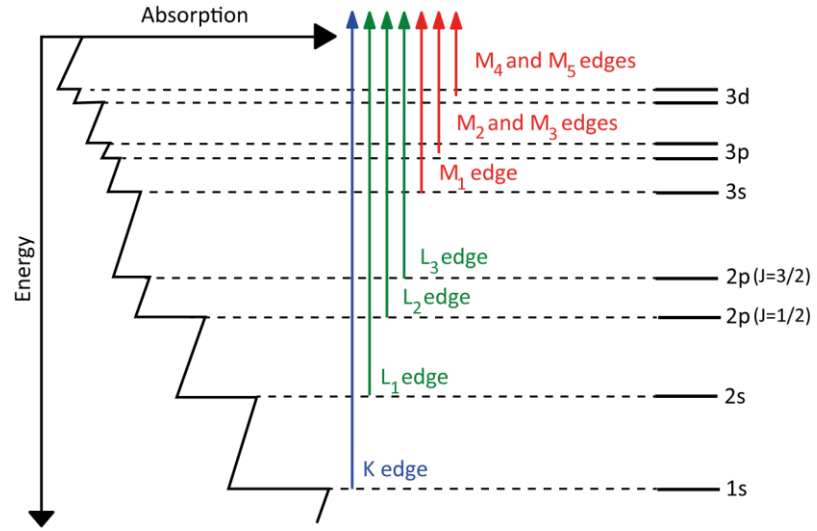


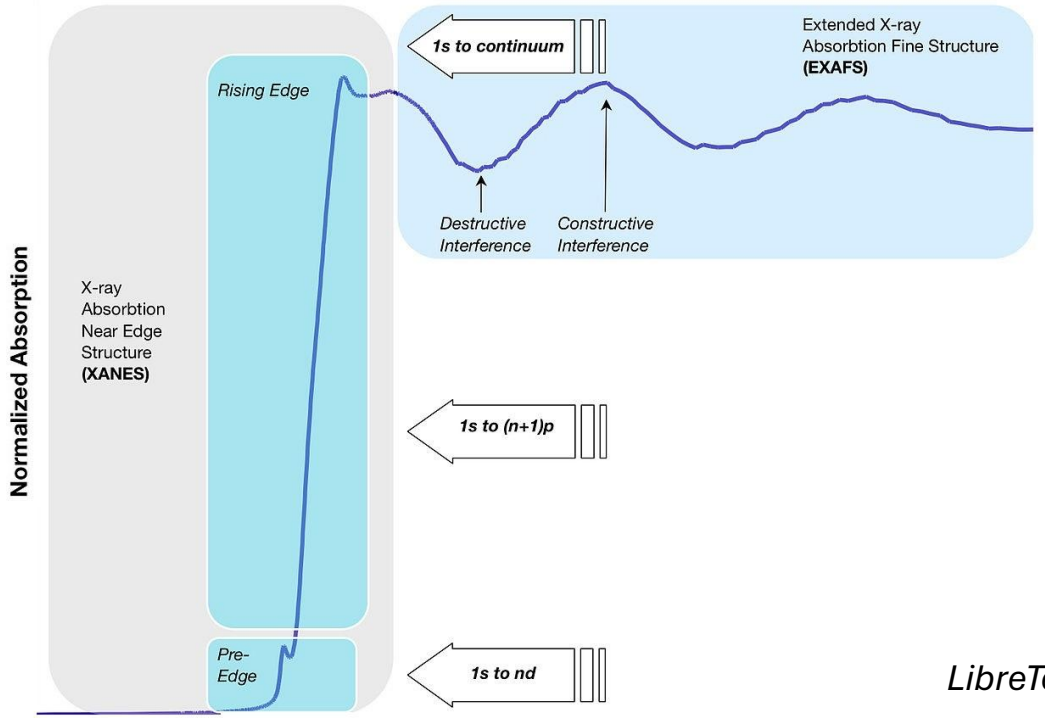
Wikipedia: Raman spectroscopy

X. Zhang et al, *Chem. Soc. Rev.* 9, 2015

Absorption Spectroscopies

- For static approaches, x-ray techniques are the most powerful (XAS, NEXAFS). Time-resolved approaches can be done with lower energy photons
- Very sensitive to local atomic arrangements, oxidation states, etc.
- For absorption, samples should be thin (consider: x-ray damage, signal-to-noise…). Usually, reflective geometry can also be an option for thicker samples
- Signals can be surprisingly complex to analyze! Energy shifts and pre-edge features hold the desired information

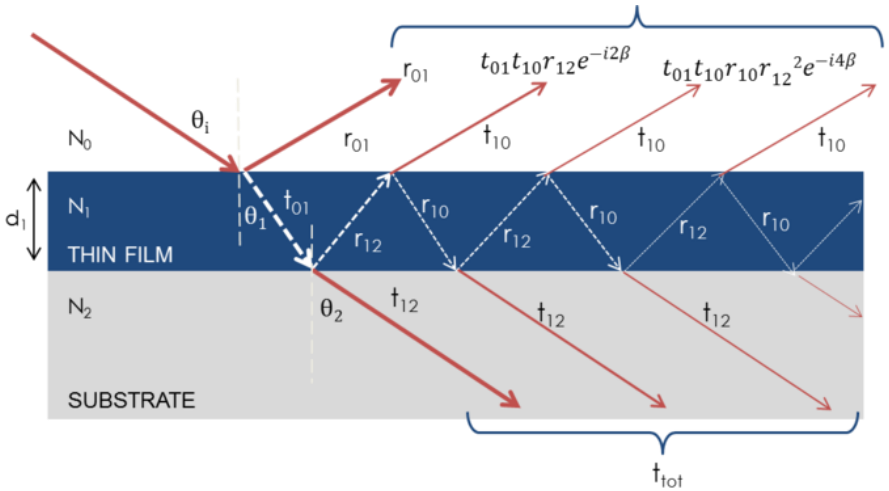


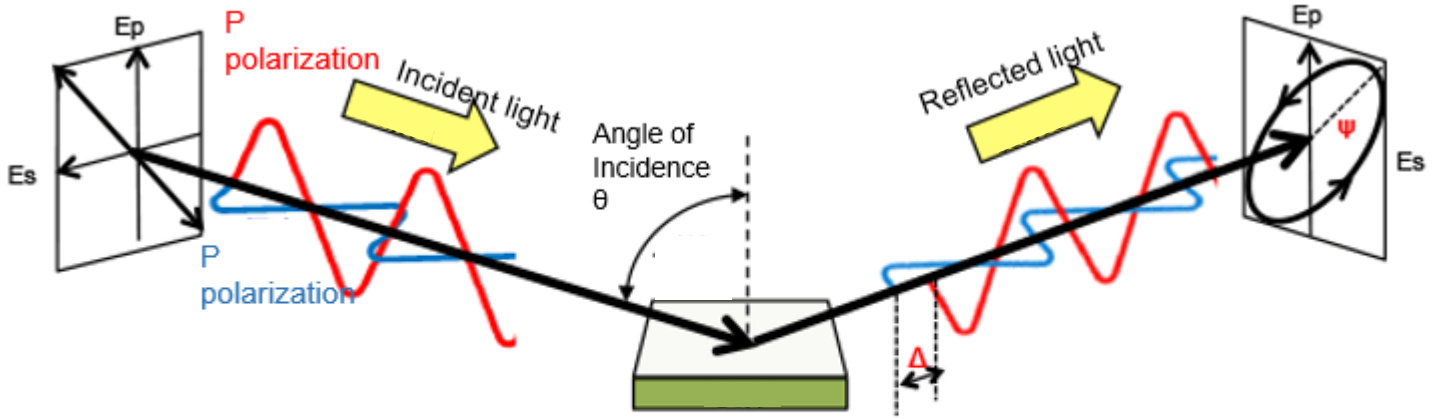


LibreTexts: XANES

Ellipsometry

- Used for probing the optical properties of thin films (complex refractive index, dielectric function)
- ! Note assumption that sample is optically homogeneous, isotropic, and not rough on surface





Measures changes in polarization state of incident light and reflected light

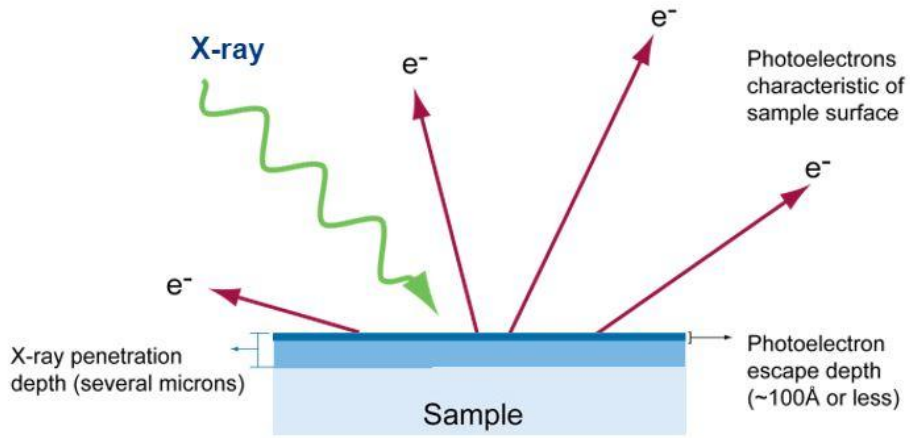
Δ: Phase difference between S polarization and P polarization

Ψ: Reflection amplitude ratio angle of S polarization and P polarization

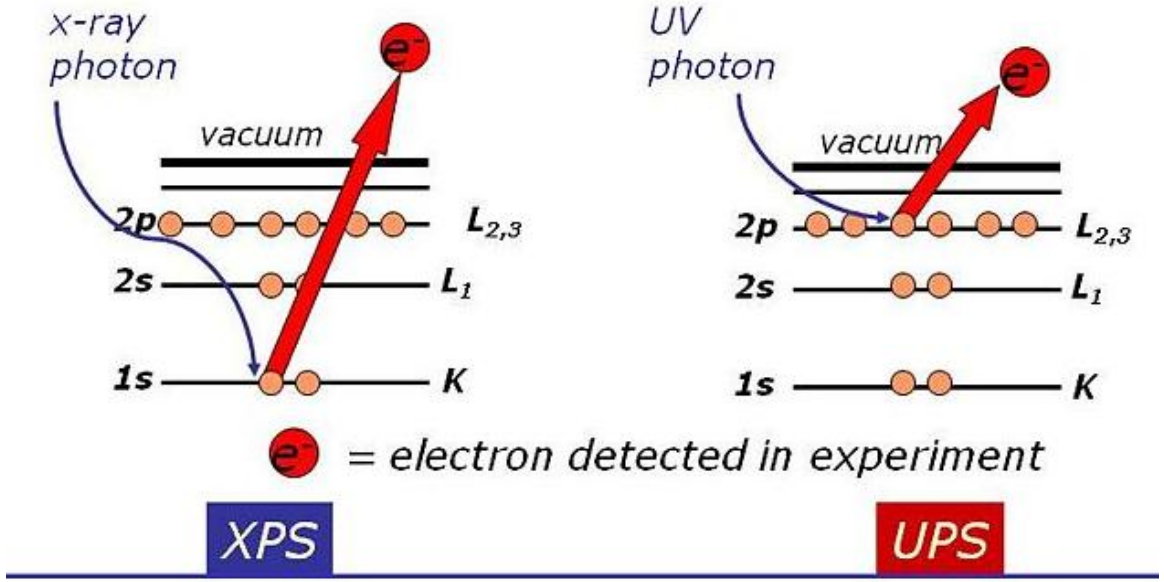
ULVAC

Photoemission – XPS/UPS

- Sensitive probe of the occupied energy levels of a material
- Ultraviolet UPS typically done at 21 eV (He lamp)
- Higher energy XPS (e.g., Al Kα) is element-specific – exact recorded energies of core levels are sensitive to local environment
- Requires ultrahigh vacuum environment
- Likely easy to access basic capabilities



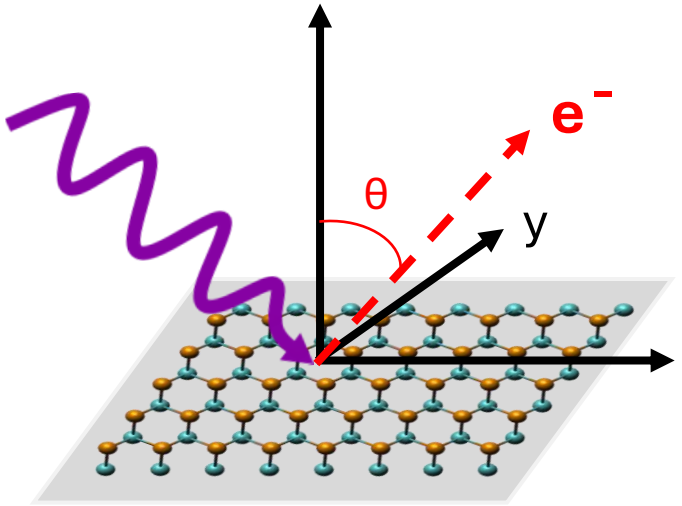
eurofins



Clean Energy wiki

Photoemission - ARPES

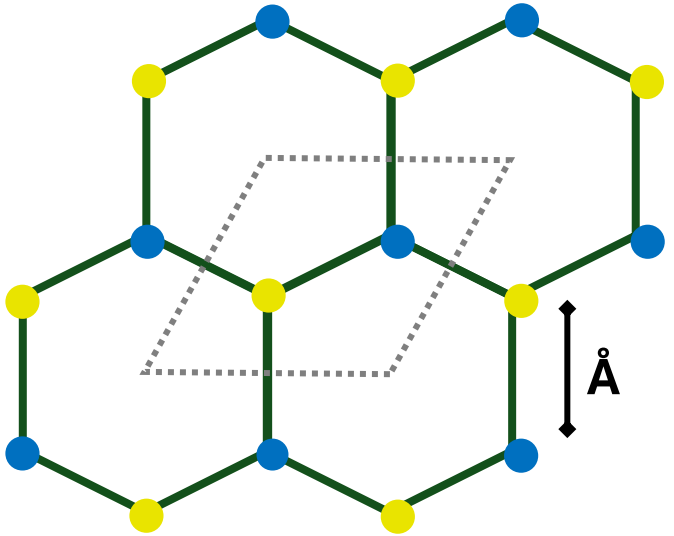
- Photon in, electron out technique that directly records momentum space information by recording angles of emission
- Ultrahigh vacuum technique; very surface sensitive
- Requires a single crystalline sample with clean surface and not too insulating material or conductive substrate
- Can be performed with a high energy lamp light source, but specialized equipment typically means going to a synchrotron



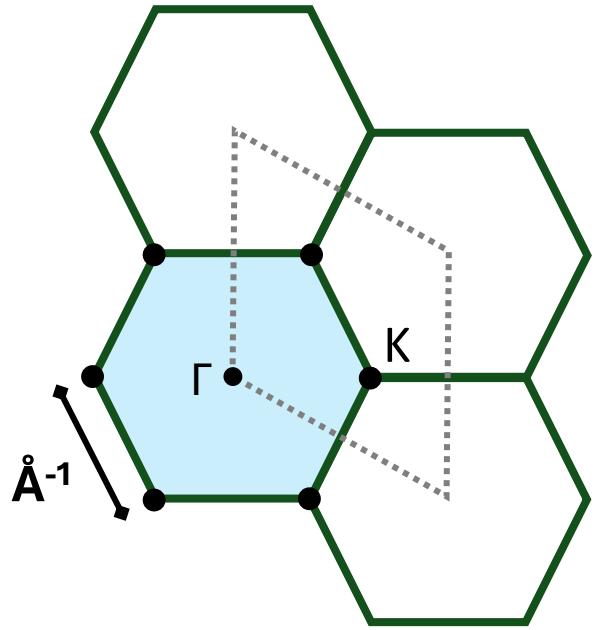
$$E_{kin} = h\upsilon - W - E_B$$

$$k_{\parallel} = (2m_e E_{kin})^{1/2} \sin\theta/\hbar$$

Real Space

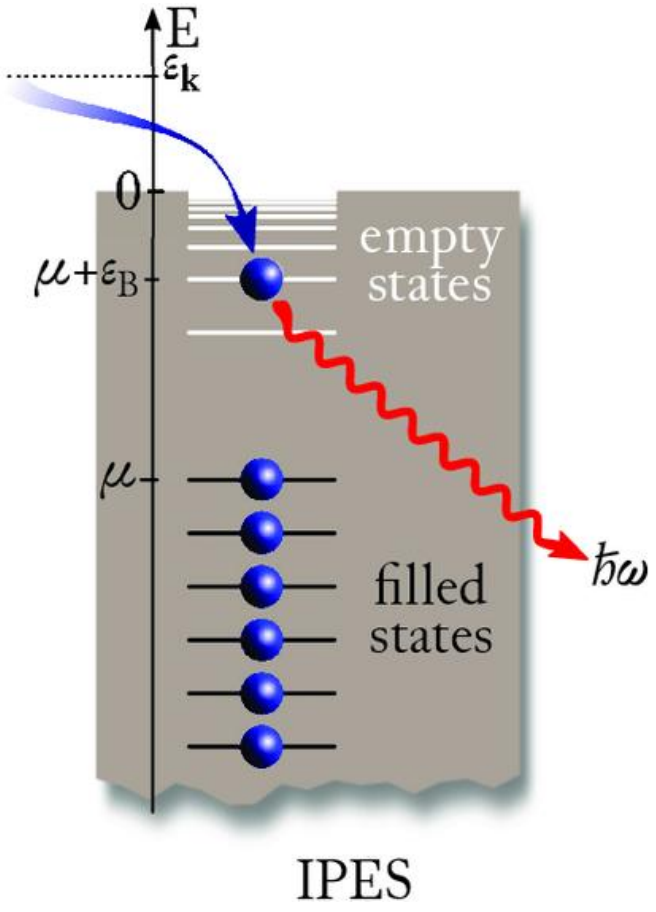


Reciprocal Space



Inverse Photoemission Spectroscopy

- Electron in, photon out technique
- Monochromatic electron source impinges on the sample, a small number relax into formerly unoccupied states by emission of a photon
- Relatively simple way to record basic excited state energy information if time resolution is not needed and coarse energy resolution is OK (~1 eV)



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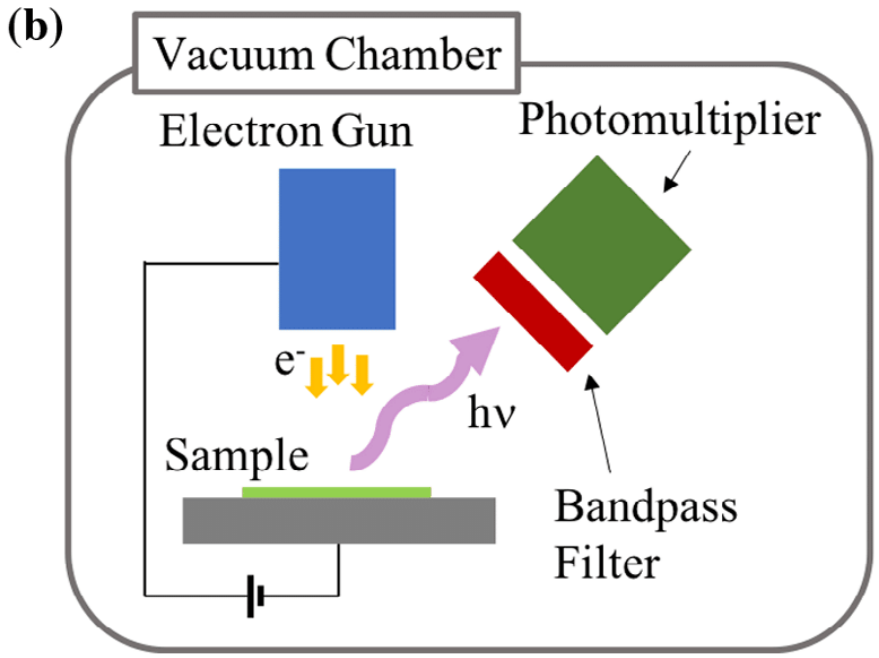
Marco Vanzini

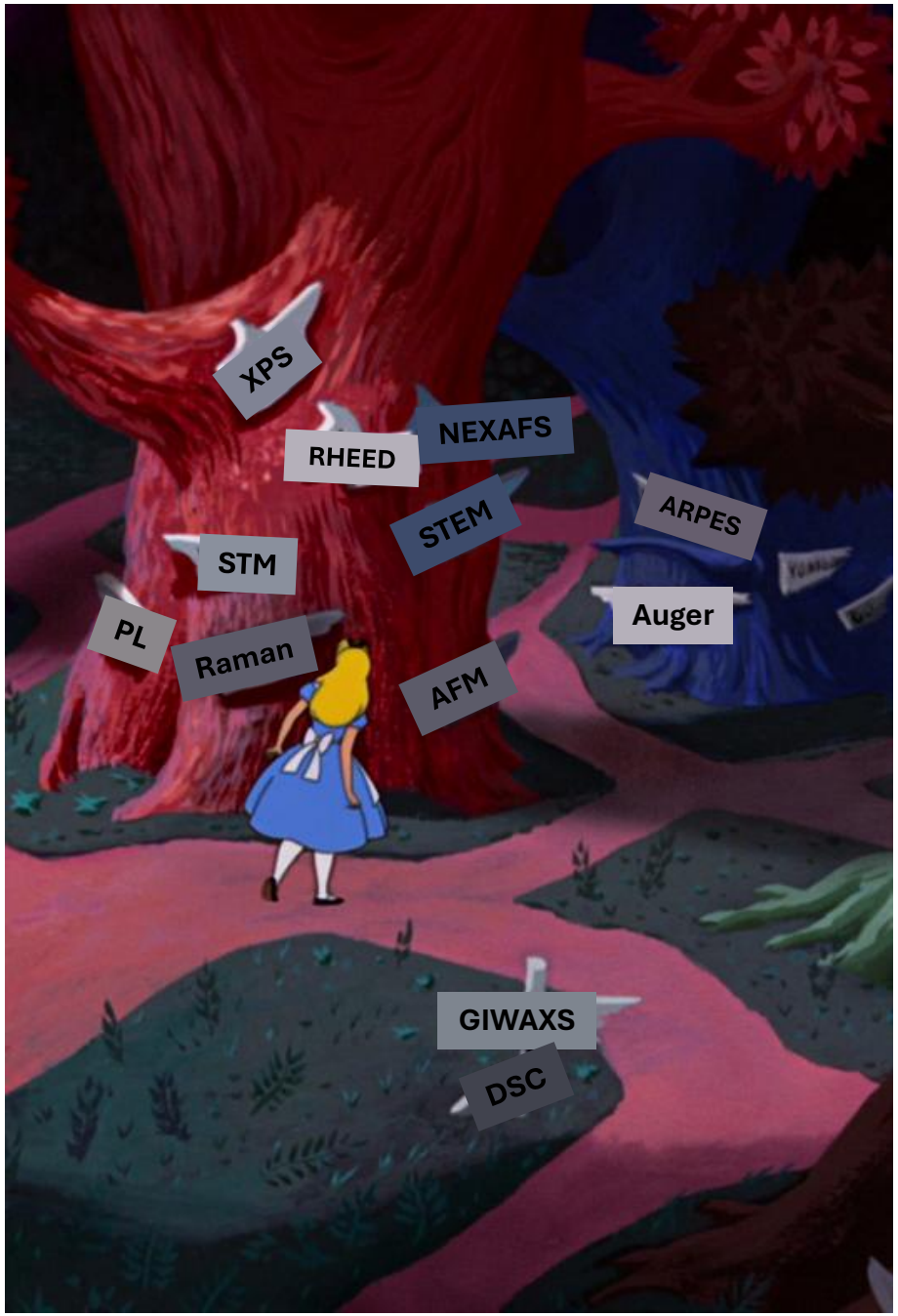


S. Kim et al., *Science and Technology of Advanced Materials* 2018, 19(1):486-494

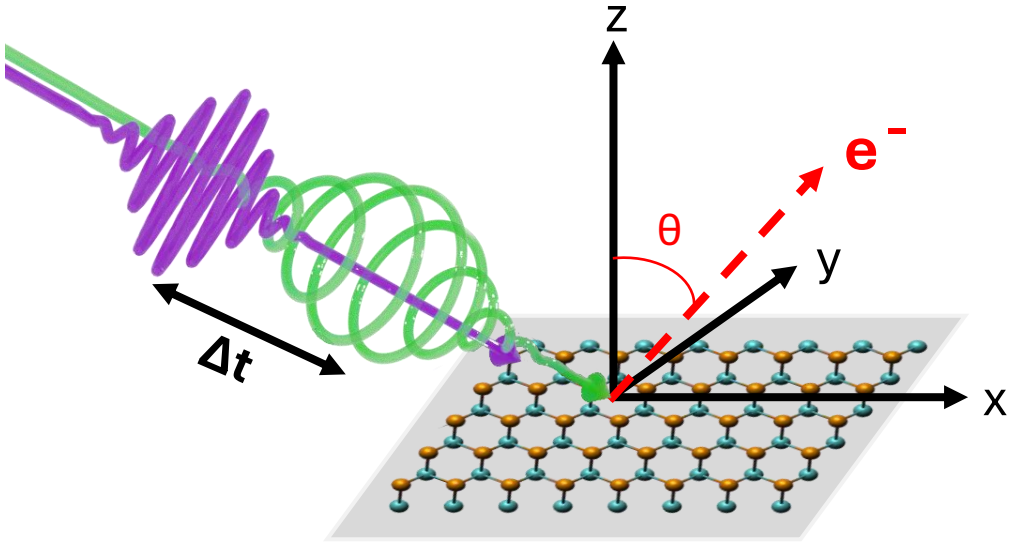
Which characterization technique is the right one for my material?

That depends a great deal on what it is you want to learn!

Much more that lies beyond this talk!
(Come talk to me about time-resolved spectroscopies)

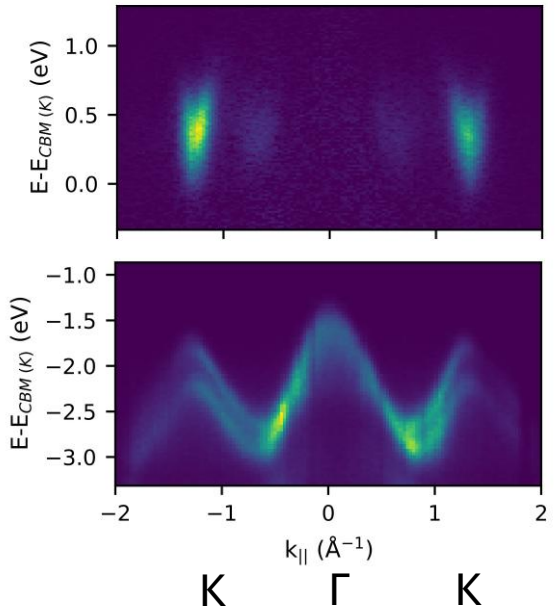


Time-resolved photoemission

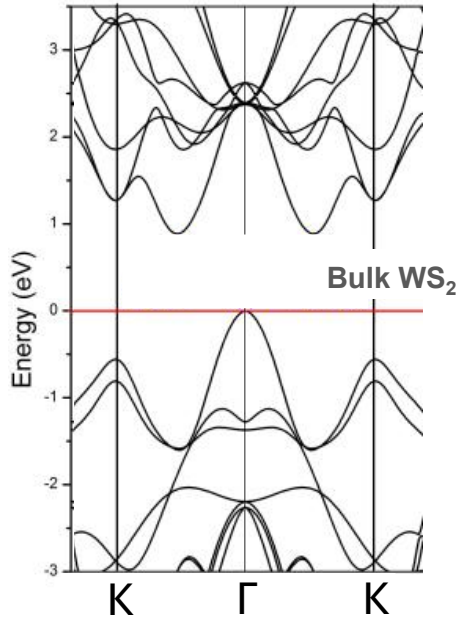


$$E_{kin} = h\upsilon_{probe} - W - E_{BE}$$

$$k_{\parallel} = (2m_e E_{kin})^{1/2} \sin\theta/\hbar$$



A. Kunin et al. *Phys. Rev. Lett.* **130**, 046202 (2023)



H. Terrones et al. *Sci Rep.* **3**, 1549 (2013)

- Directly visualize electrons (and holes, as depletion) in momentum space and map the occupied band structure vs. time
- Space charge effects typically become limiting factor for energy resolution and sensitivity