AMC 2024

2024 ADVANCED MATERIALS CHARACTERIZATION *workshop*

Optical Characterization Methods
Part I

Julio A. N. T. Soares
Materials Research Laboratory
University of Illinois at Urbana-Champaign

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Optical Characterization

Light properties

Light-matter interation

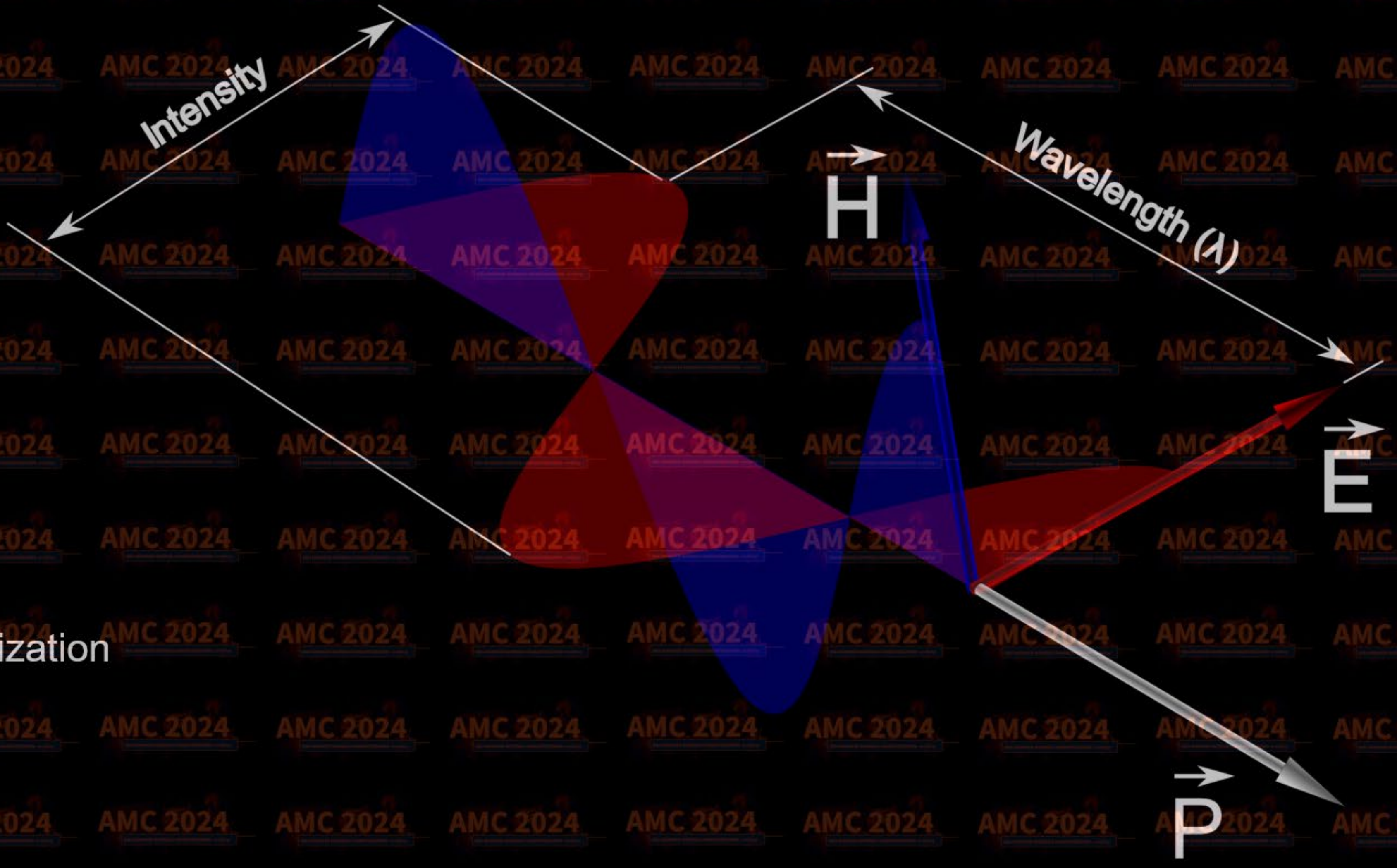
Instrumentation and methods

Application examples

Strengths and limitations

Complementary techniques

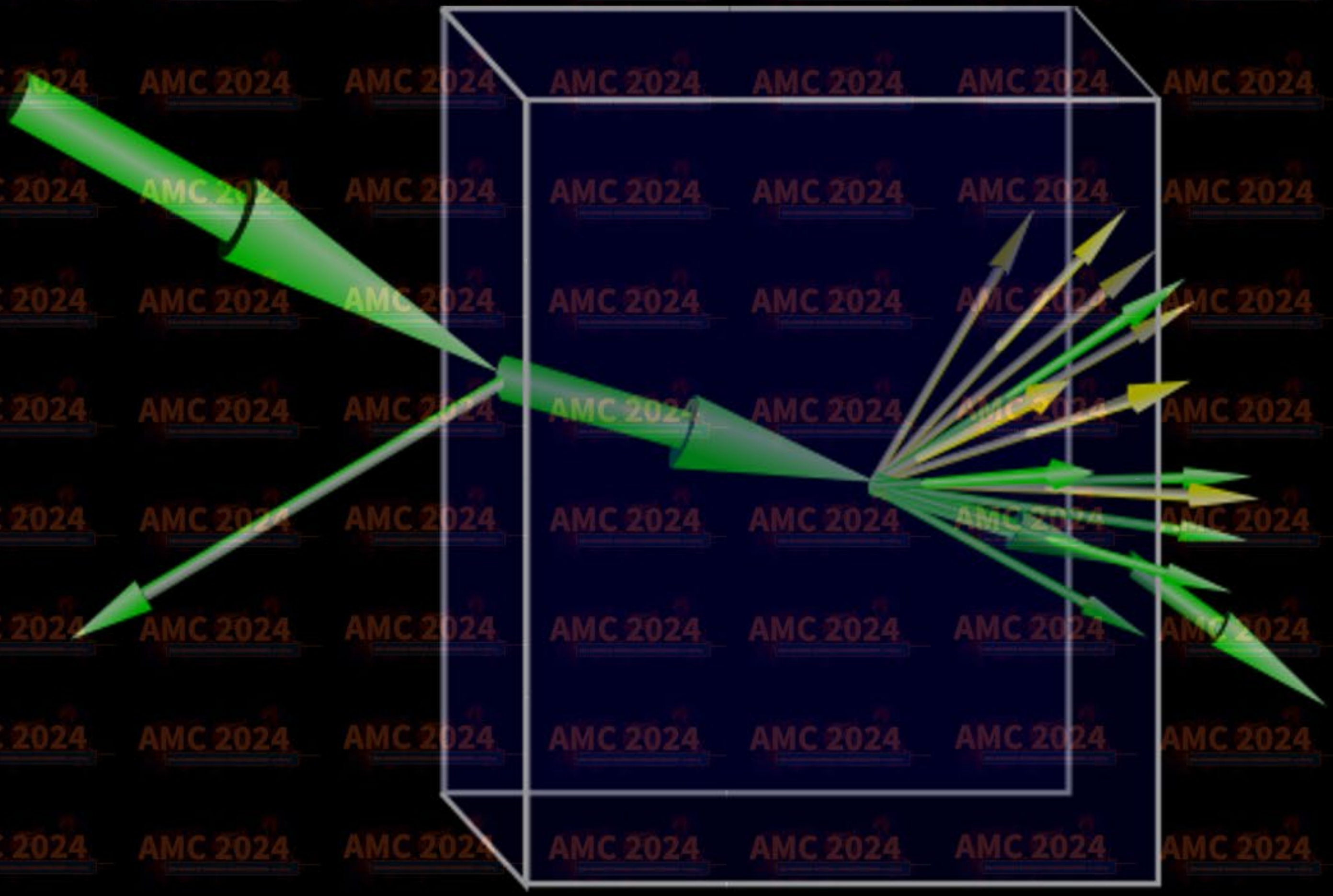
Light properties



- Direction of propagation
- Electric field direction or polarization
- Photon energy or wavelength
- Intensity

Light interactions

- Transmission
- Reflection
- Absorption
- Emission
- Scattering
- Refraction

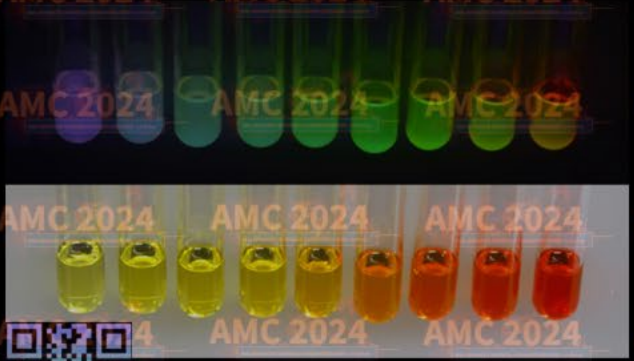


Non-linear effects

- SFG
- SHG
- DFG
- Multi-photon absorption

Light interactions with matter

Size



Lattice structure, dopants

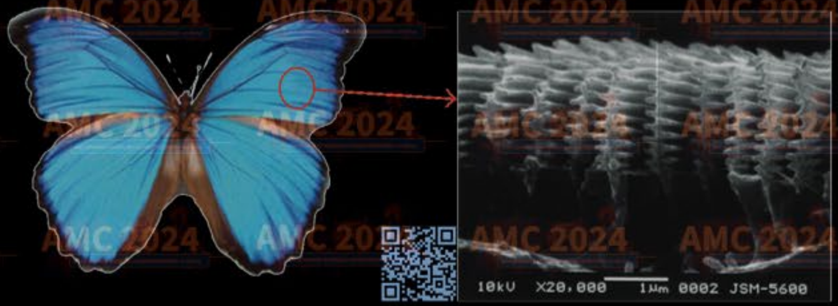
Temperature

Stress

Thickness

Concentration

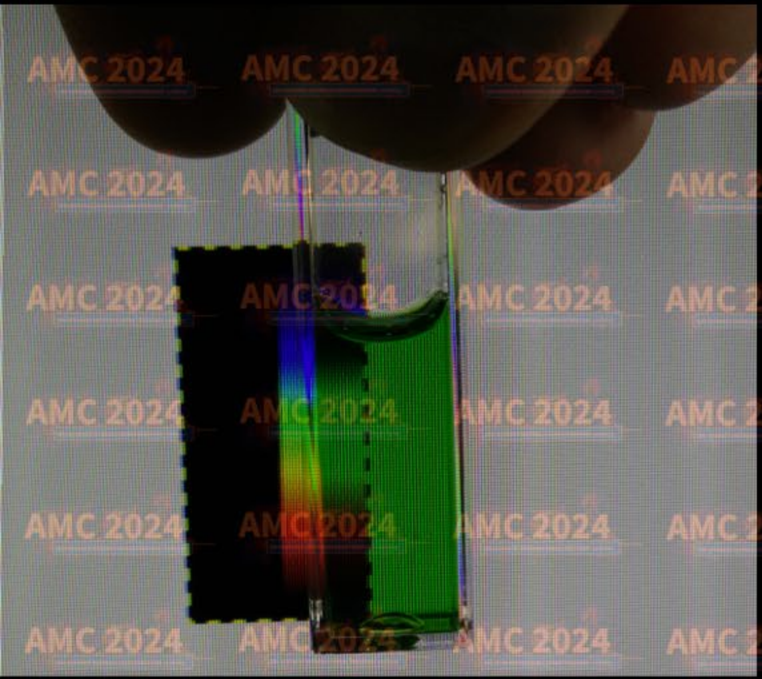
Microstructure

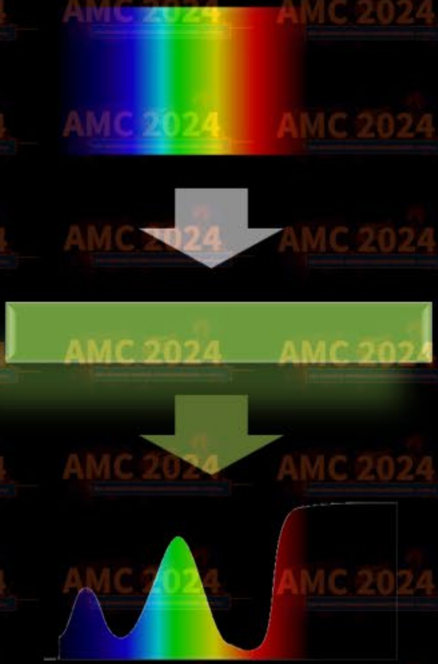


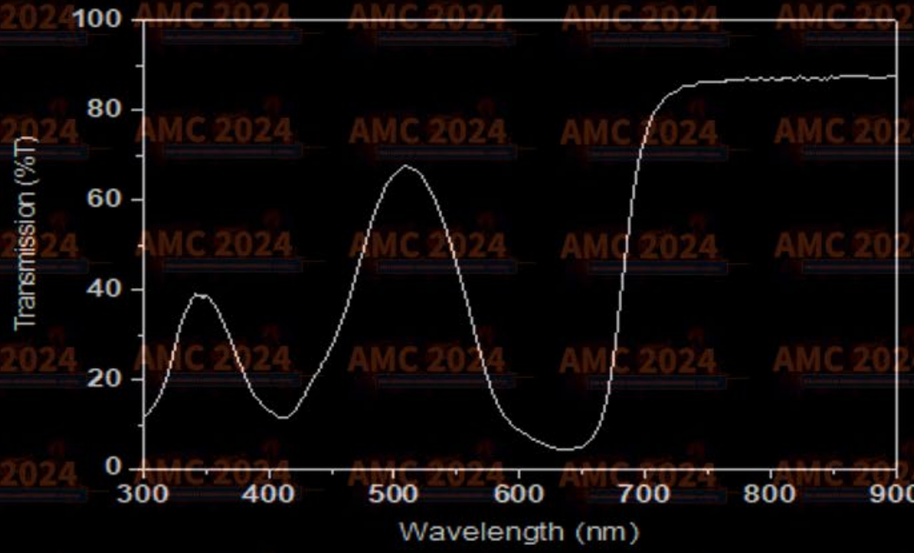
Composition

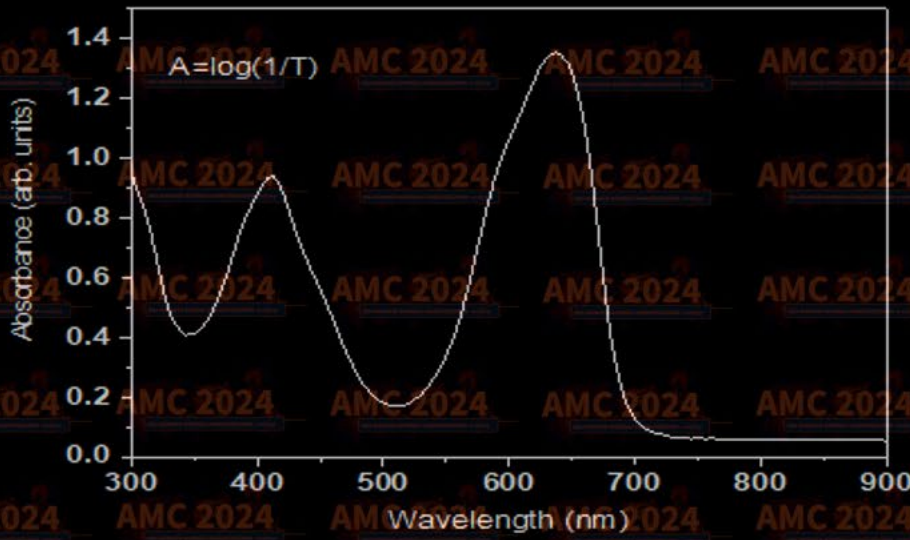
Light interactions with matter

Spectroscopy





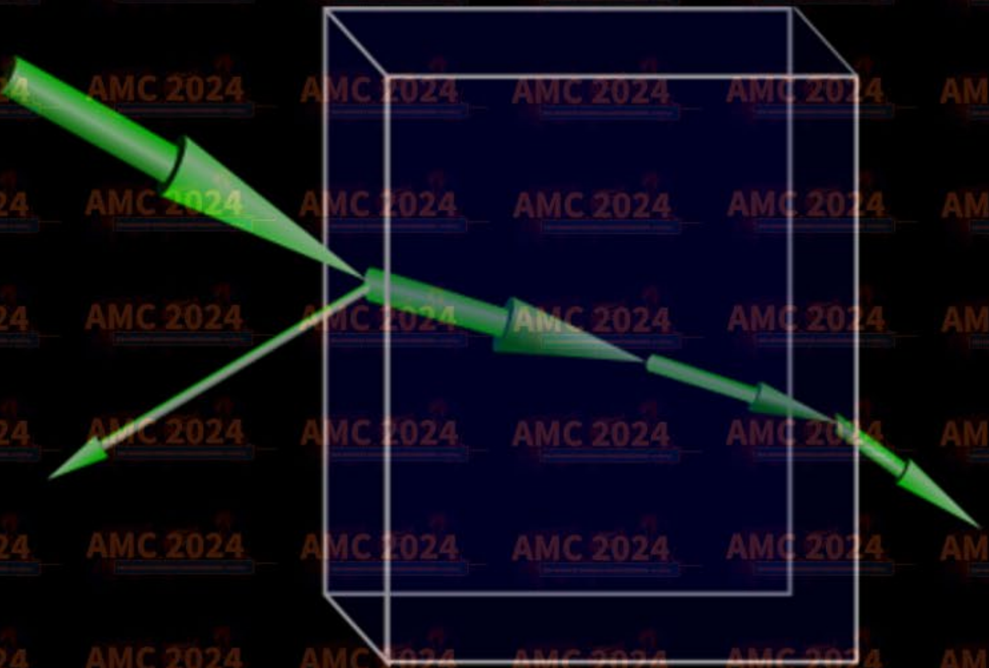


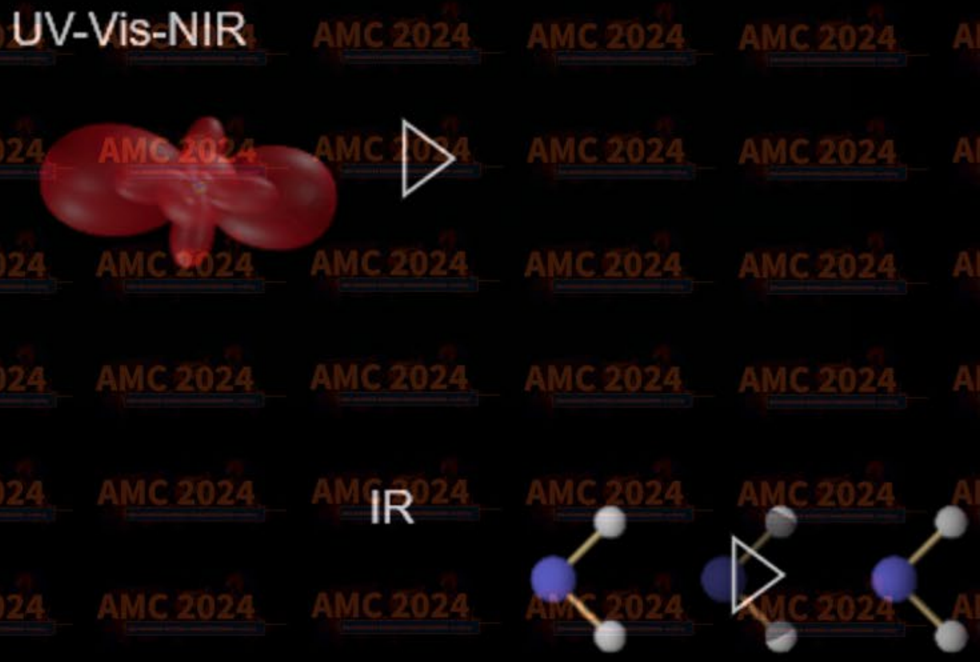


Transmission, Reflection, Absorption

What is measured:

The transmitted and reflected light intensity as a function of the incident photon energy, which depends on the material's electronic, atomic, chemical and morphological structure.





Spectrophotometry (UV-VIS-NIR)

Instrumentation:

Spectrophotometry (UV-VIS-NIR)

Instrumentation:

Spectrophotometry (UV-VIS-NIR)

Instrumentation:

Spectrophotometry (UV-VIS-NIR)

Instrumentation:

Spectrophotometry (UV-VIS-NIR)

Instrumentation:

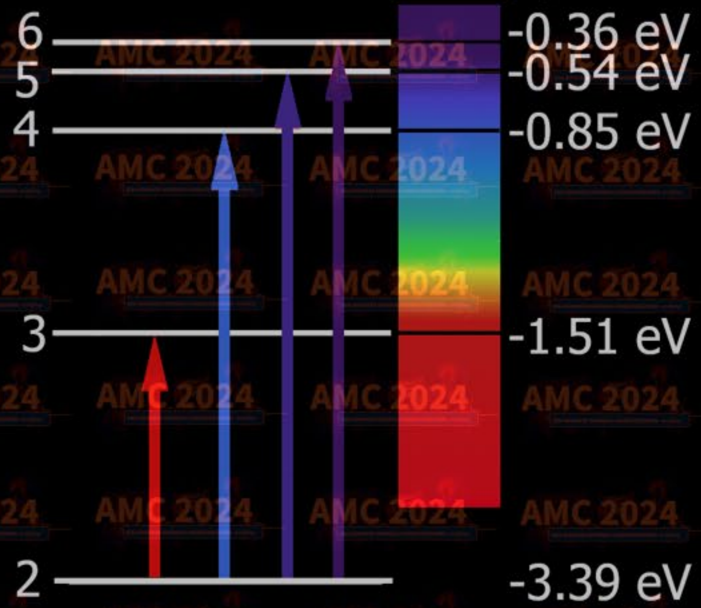
Spectrophotometry (UV-VIS-NIR)

Monoatomic gas (H_2)

Electronic levels

Electronic states of H

Absorption spectrum
(white light)

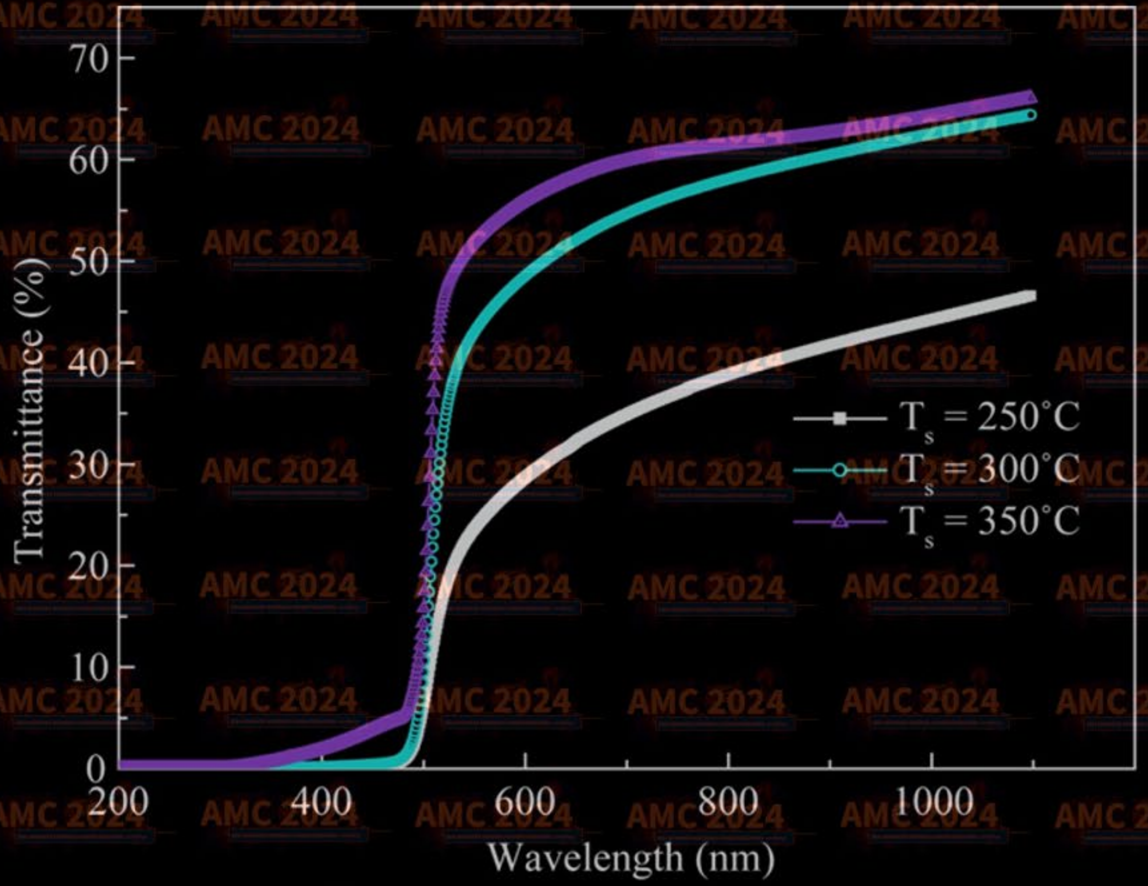


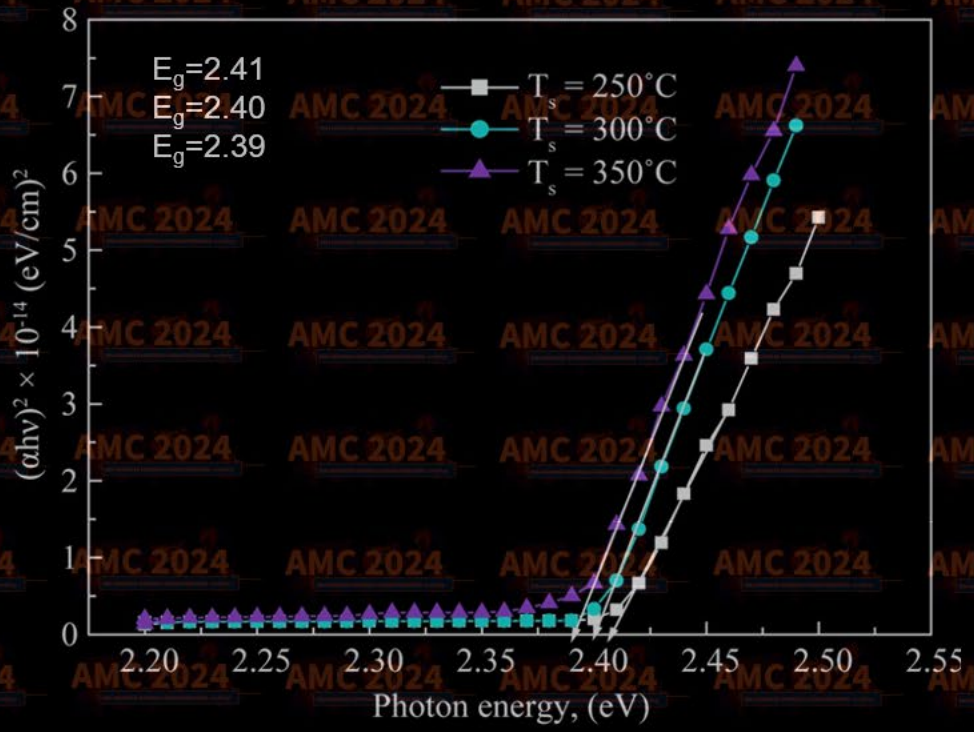
Solid material (CdS)

Electronic bands

Absorption spectrum
(white light)

Spectrophotometry (UV-VIS-NIR)





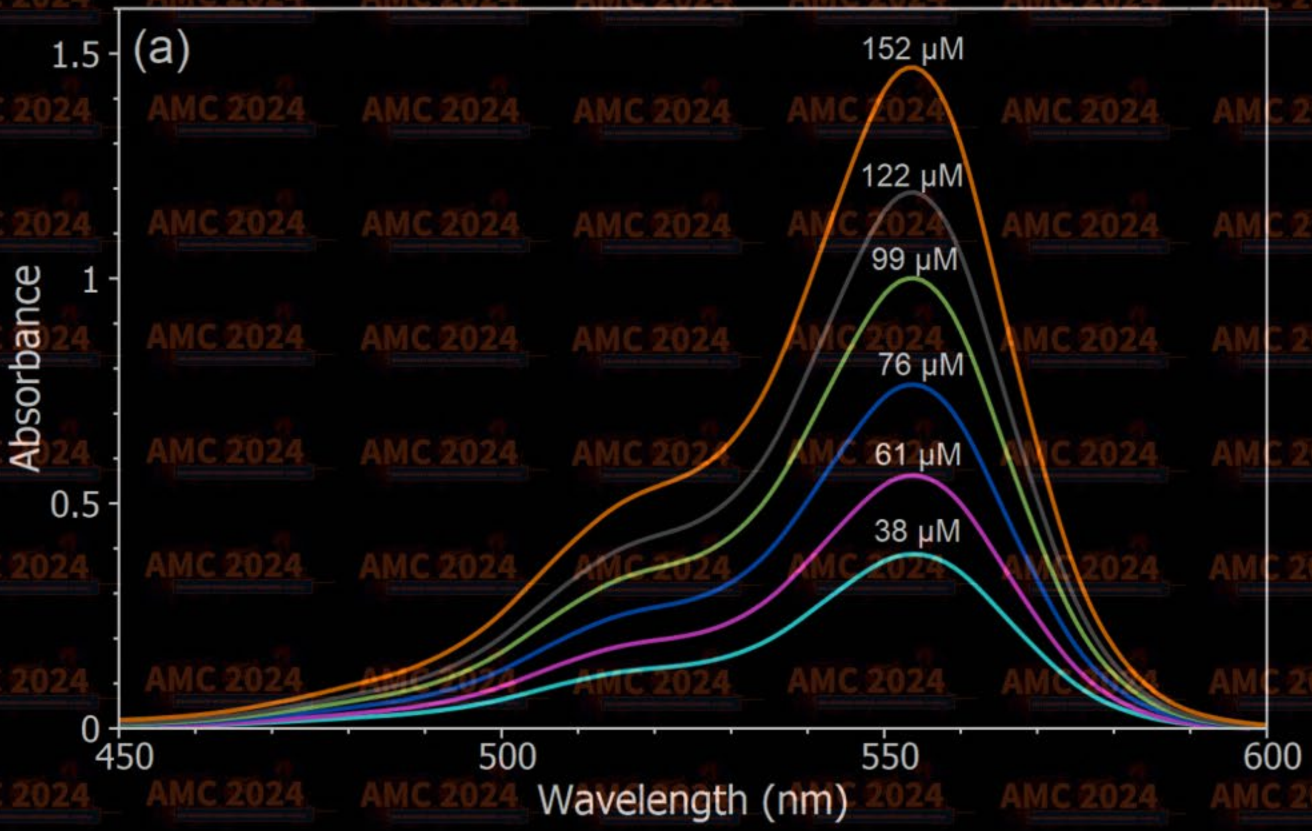
Optical band gap determination of CdS thin films as a function of growth substrate temperatures

Tauc's relation: $\alpha h\nu = A(h\nu - E_g)^m$

m = 0.5 for direct and 2 for indirect allowed transitions.

J. Surf. Eng. Mat. and Adv. Tech. **3**, 43 (2013)

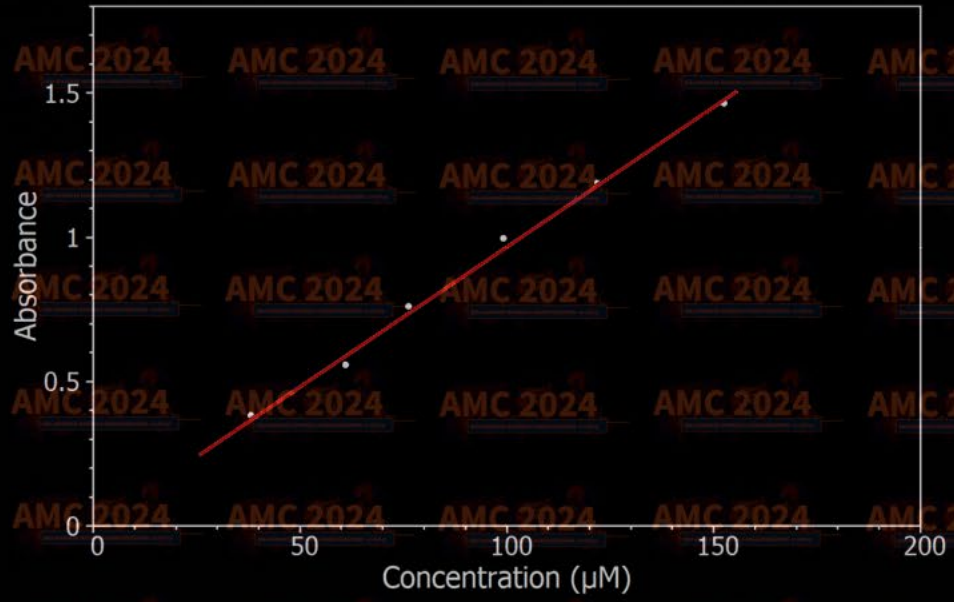
Spectrophotometry (UV-VIS-NIR)



Beer-Lambert Law

$Abs = K \ell c = a \ell$

$Abs = \log(1/T)$

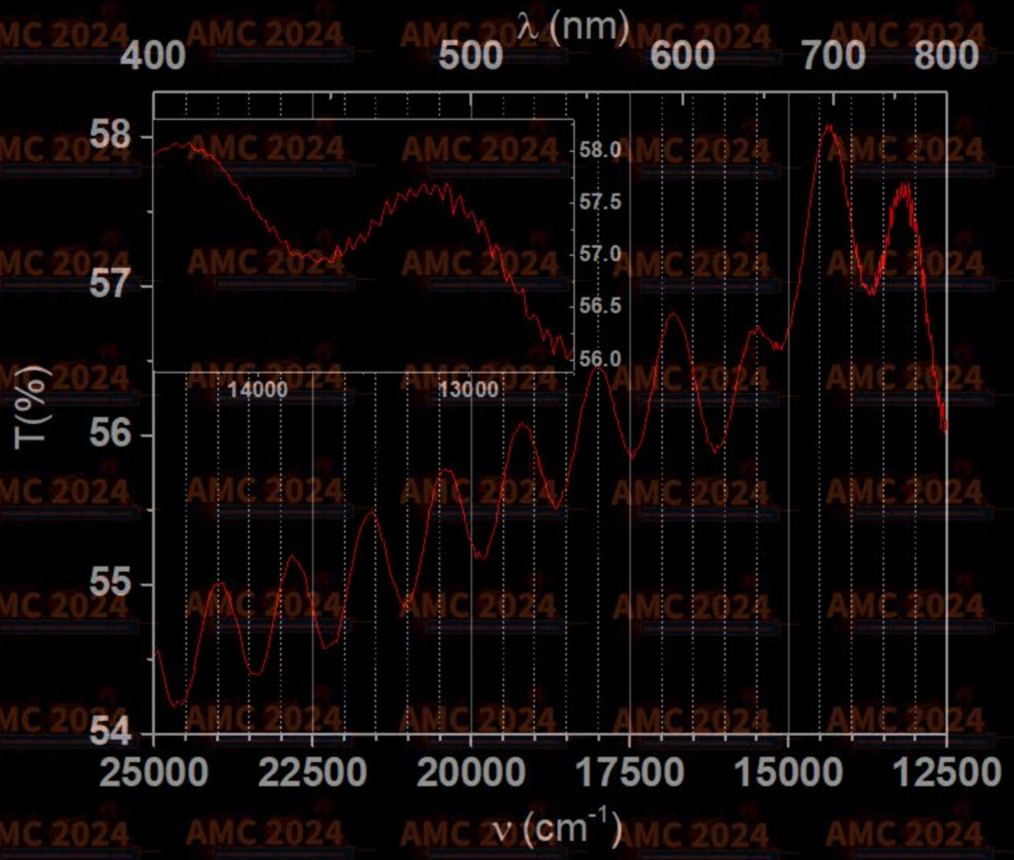


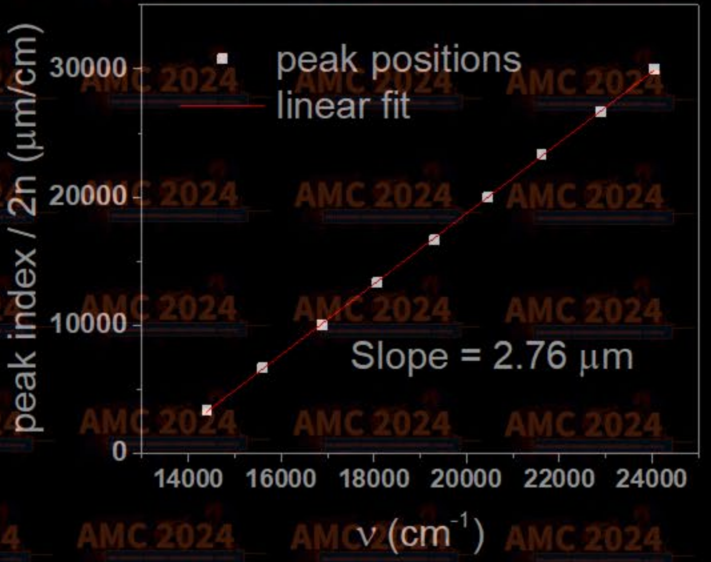
Using absorbance to determine Rhodamine B concentration in water solutions

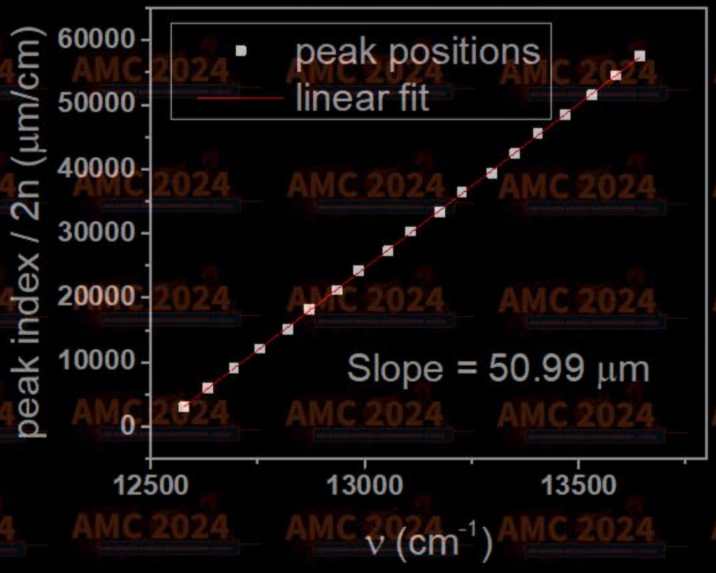
EDINBURGH INSTRUMENTS

Spectrophotometry (UV-VIS-NIR)

Spectrophotometry (UV-VIS-NIR)





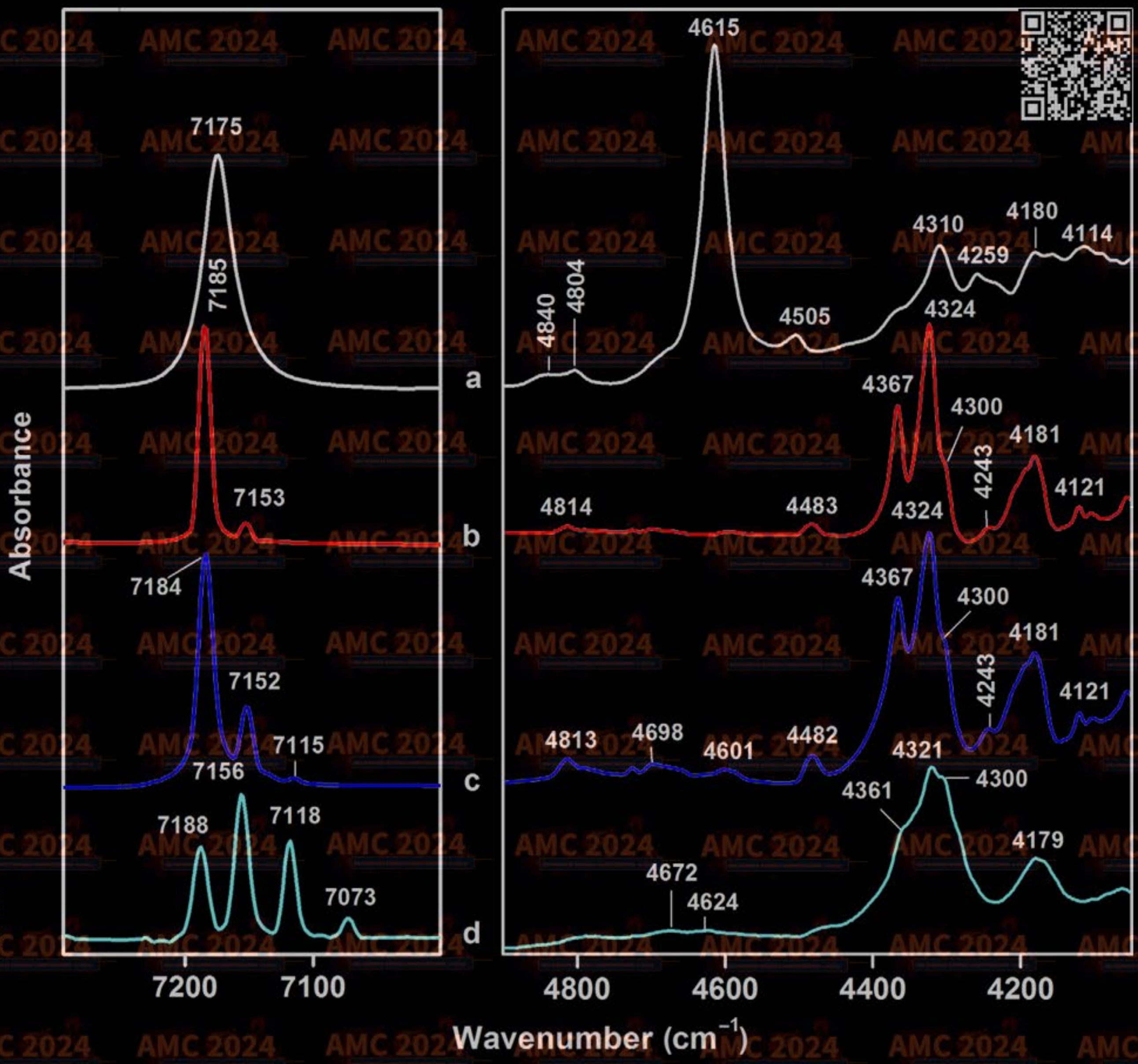


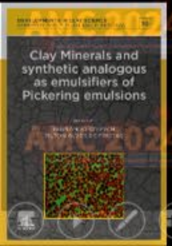
Using transmission interference fringes to determine thickness

Spectrophotometry (UV-VIS-NIR)

$Al_2Si_4O_{10}(OH)_2$

$Mg_3Si_4O_{10}(OH)_2$



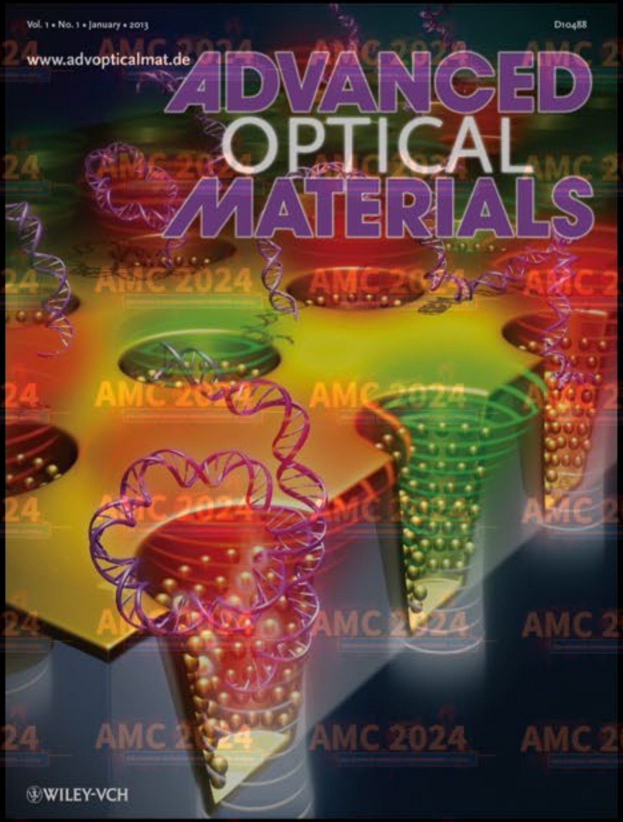


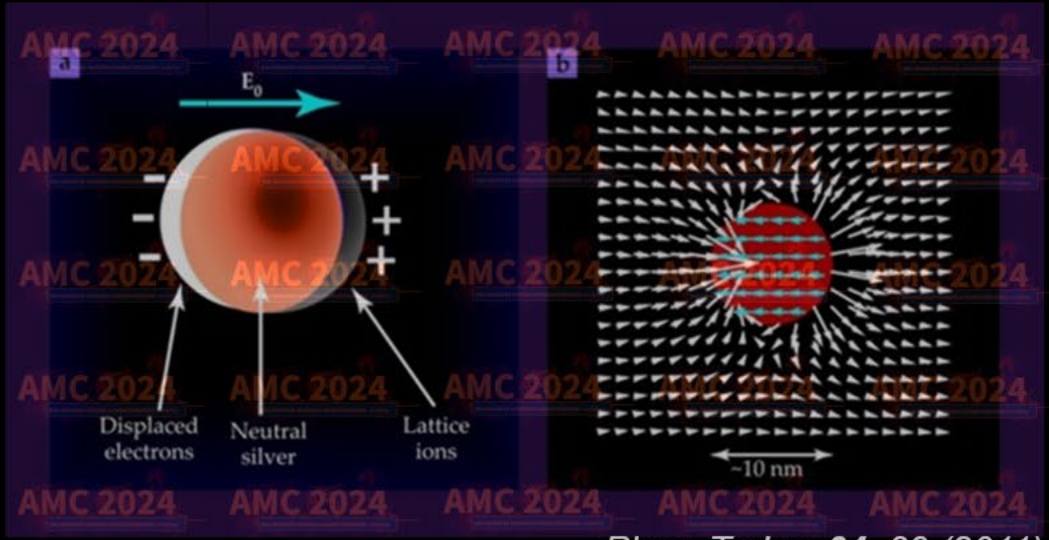
Spectra from *Developments in Clay Science*, Vol. 8. Ch. 5

Spectrophotometry (UV-VIS-NIR)

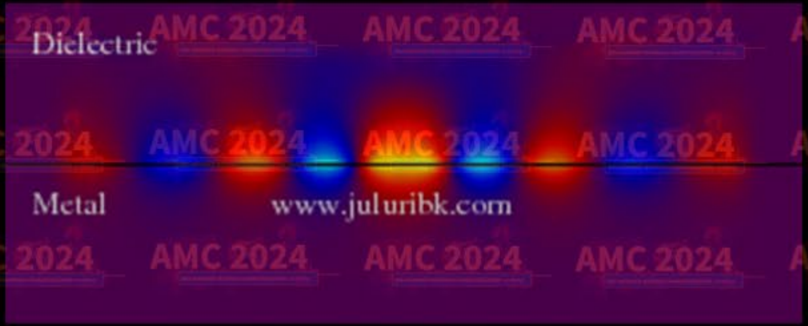
Excitations in materials

- Plasmons



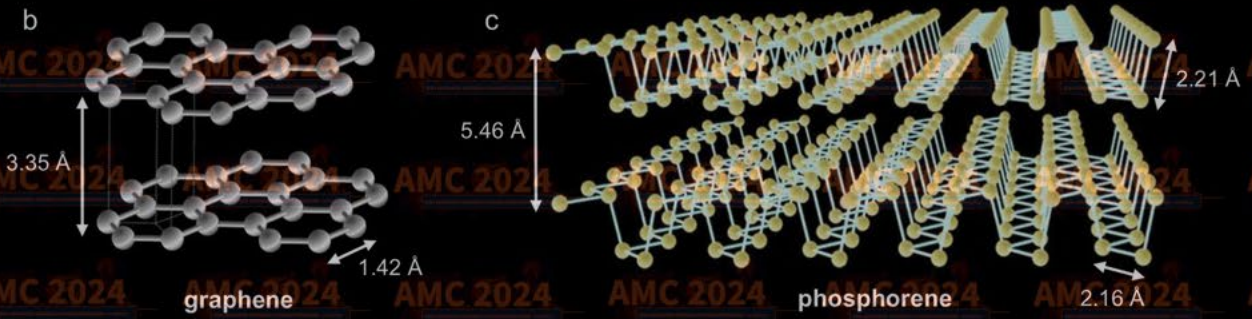


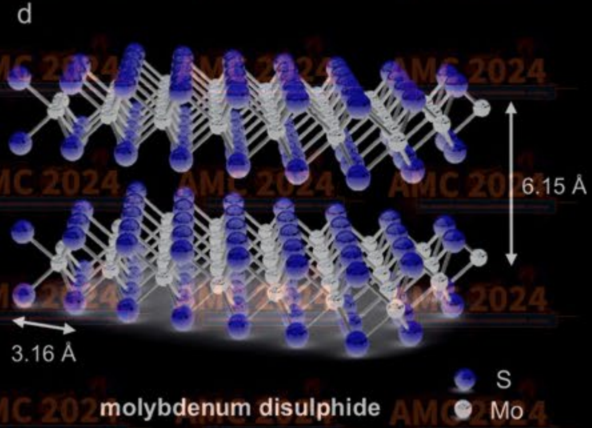
Phys. Today, ***64***, 39 (2011)



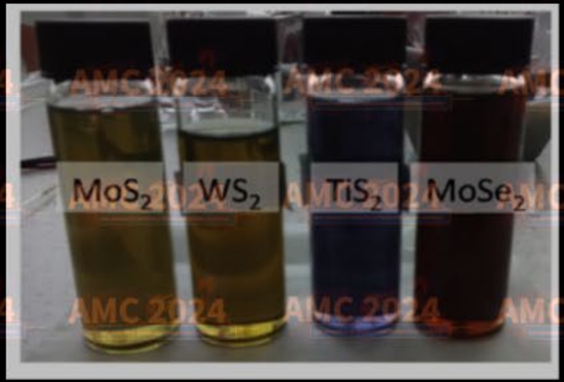
Plasmons are quanta of collective motion of charge-carriers in a gas with respect of an oppositely charged background. They play a significant role on transmission and reflection of light.

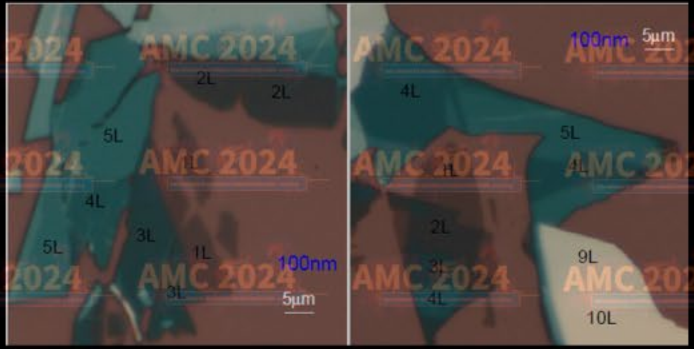
Spectrophotometry (UV-VIS-NIR)

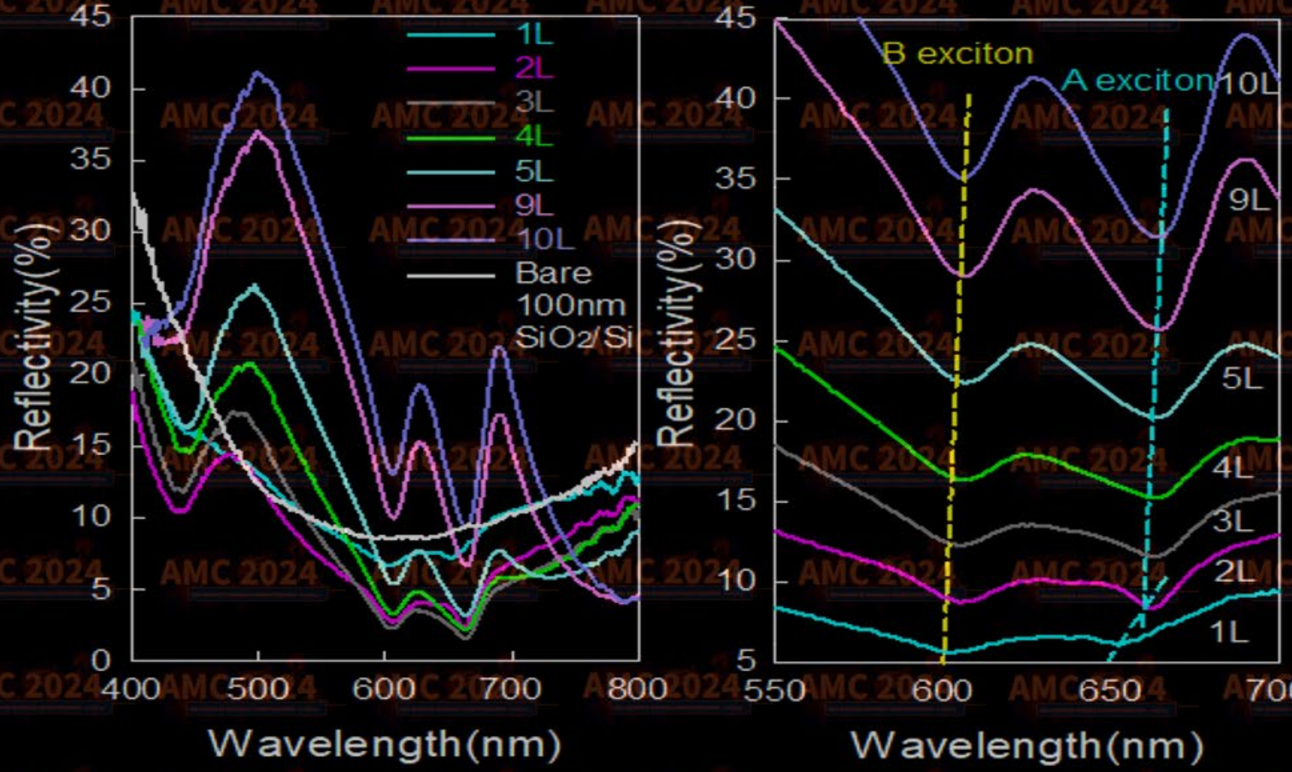




Applied Materials Today **8**, 68 (2017)







Optical Materials Express, 332858 (2018)

Vibrational spectroscopy

Normal vibrational modes in molecules:

CO_2 (4 modes)

$\nu_1 = 1388\ cm^{-1}$

$\nu_2 = 667\ cm^{-1}$

$\nu_3 = 2349\ cm^{-1}$

H_2O (3 modes)

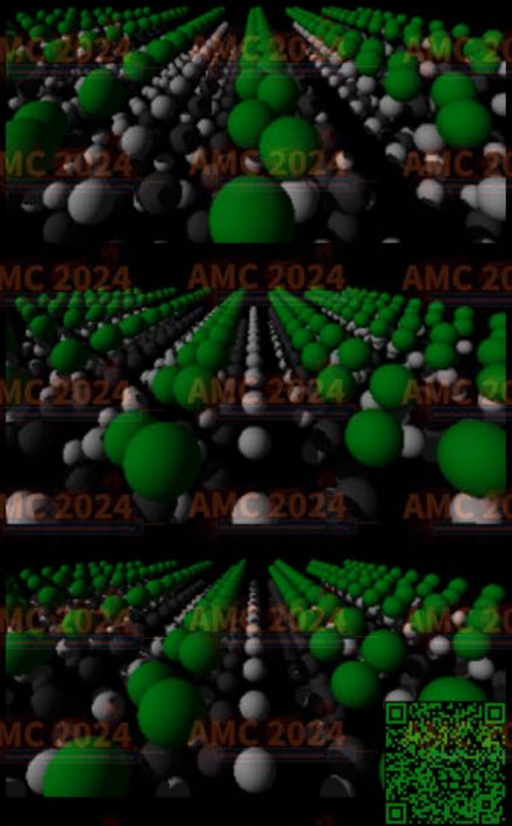
CH_4 (9 modes)

Number of modes:
3N-6 for non-linear molecules
3N-5 for linear molecules

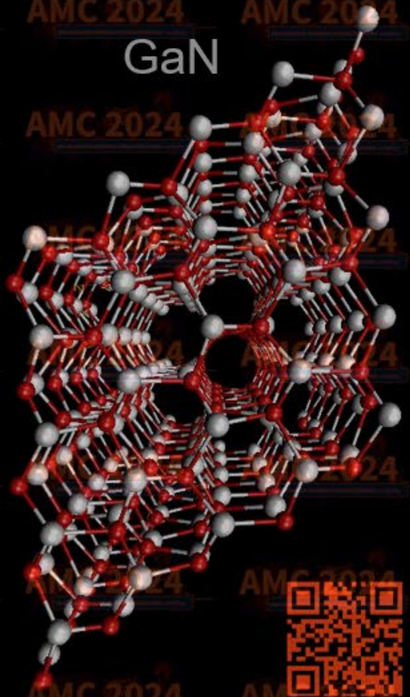
Vibrational spectroscopy

Normal vibrational modes in solids:

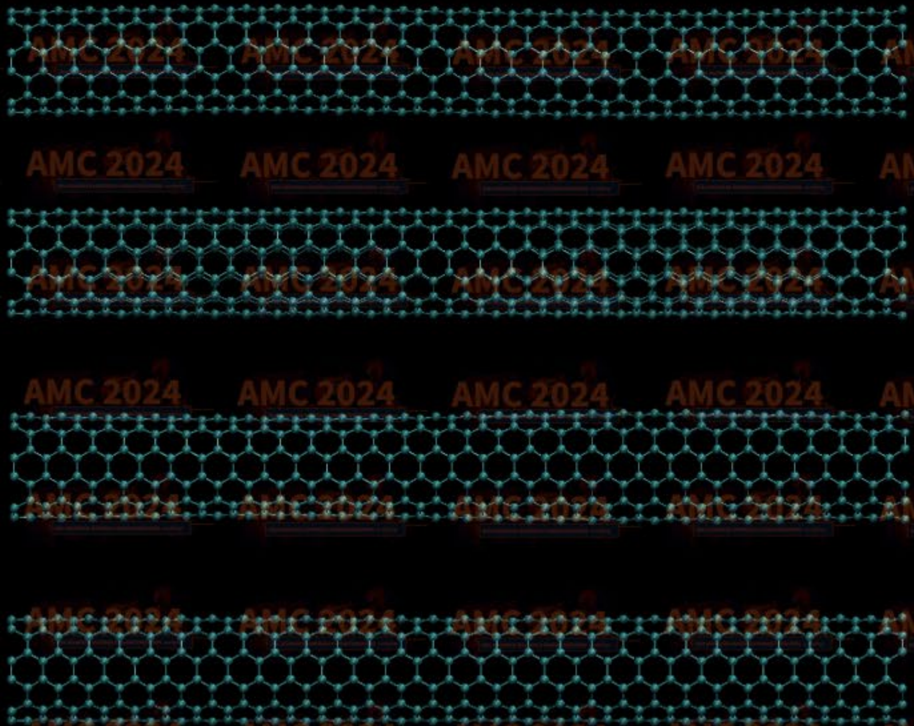
Sb/GaAs(110)



GaN



SWCNT



Fourier Transform IR spectroscopy (FTIR)

IR active vibrations

The intensity of a vibrational absorption depends on the change of the transition dipole momentum caused by that vibration, so a vibration mode j will be “IR active” only when the vibration causes a change in the dipole momentum of the molecule, i.e. $\Delta\mu \neq 0$

IR active

Fourier Transform IR spectroscopy (FTIR)

The Nobel Prize in Physics 1907
Albert A. Michelson

"for his optical precision instruments and the spectroscopic and metrological investigations carried out with their aid"

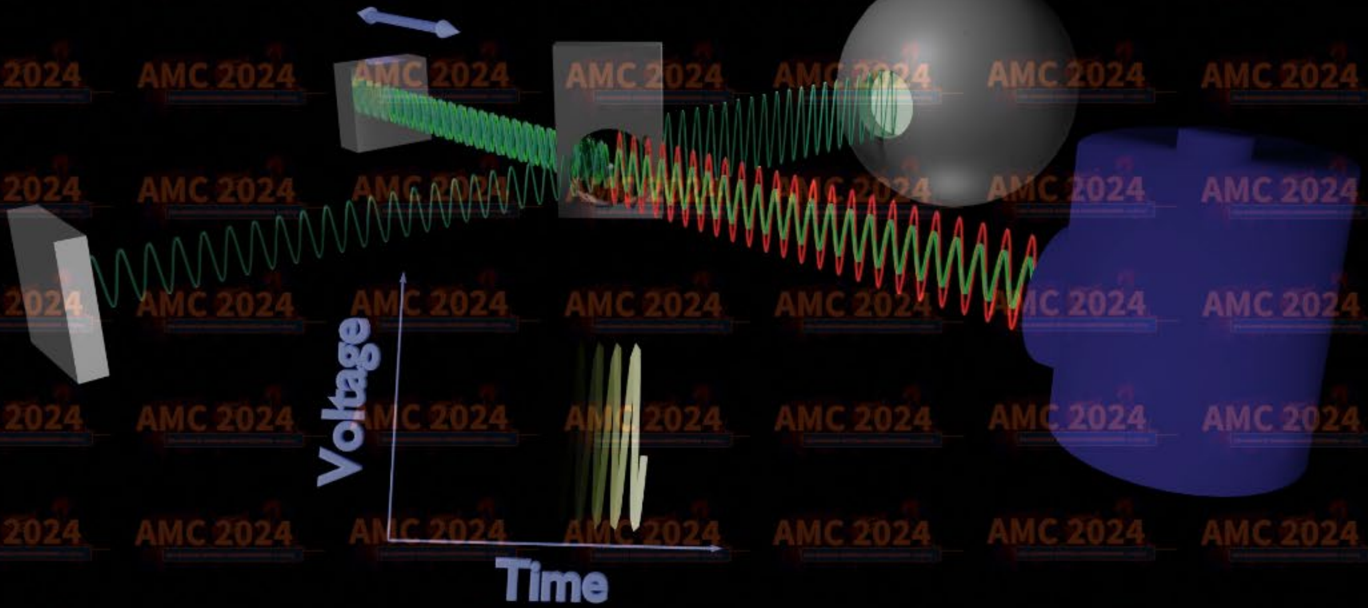
The Nobel Foundation

Instrumentation:

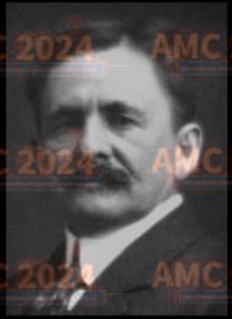
The FTIR uses a Michelson interferometer with a moving mirror, in place of a diffraction grating or prism.

$\Delta L = n\lambda$ => constructive interference

$\Delta L = (n+1/2)\,\lambda$ => destructive interference



Fourier Transform IR spectroscopy (FTIR)

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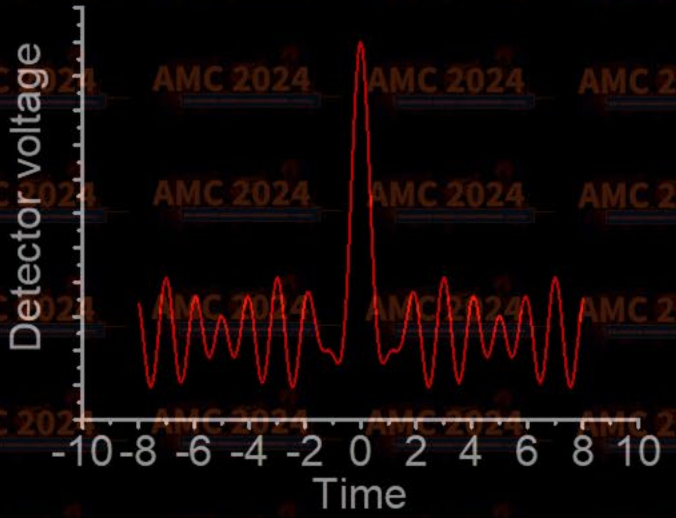
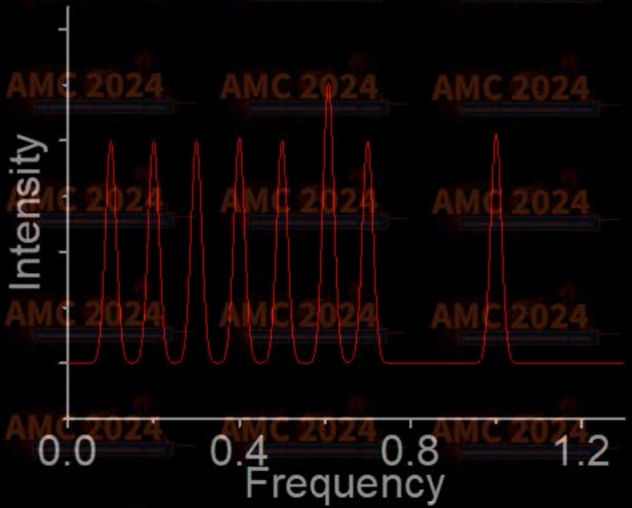
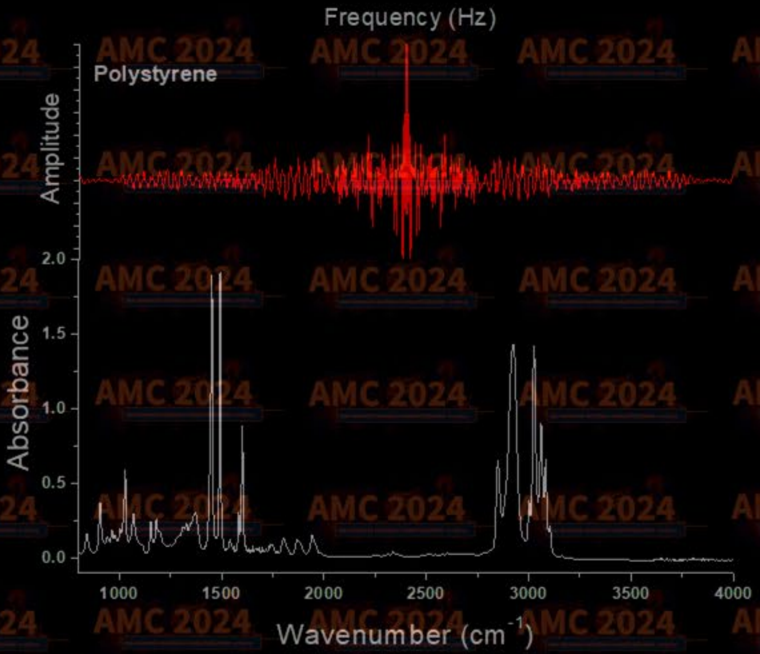
Fourier Transform IR spectroscopy (FTIR)



$$I(\nu) = \int_{-\infty}^{\infty} S(t) e^{2i\nu\pi t}\, dt$$

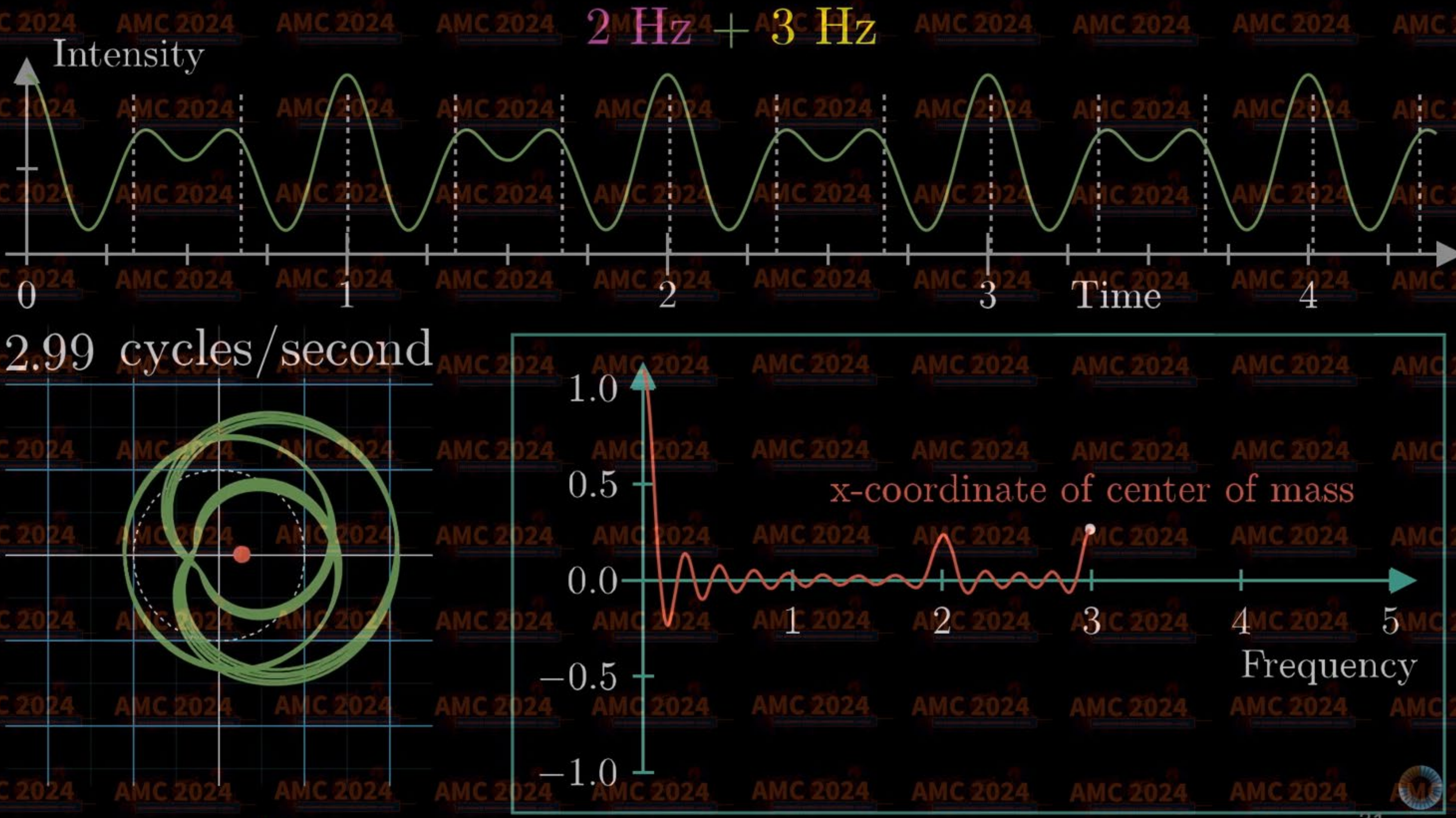




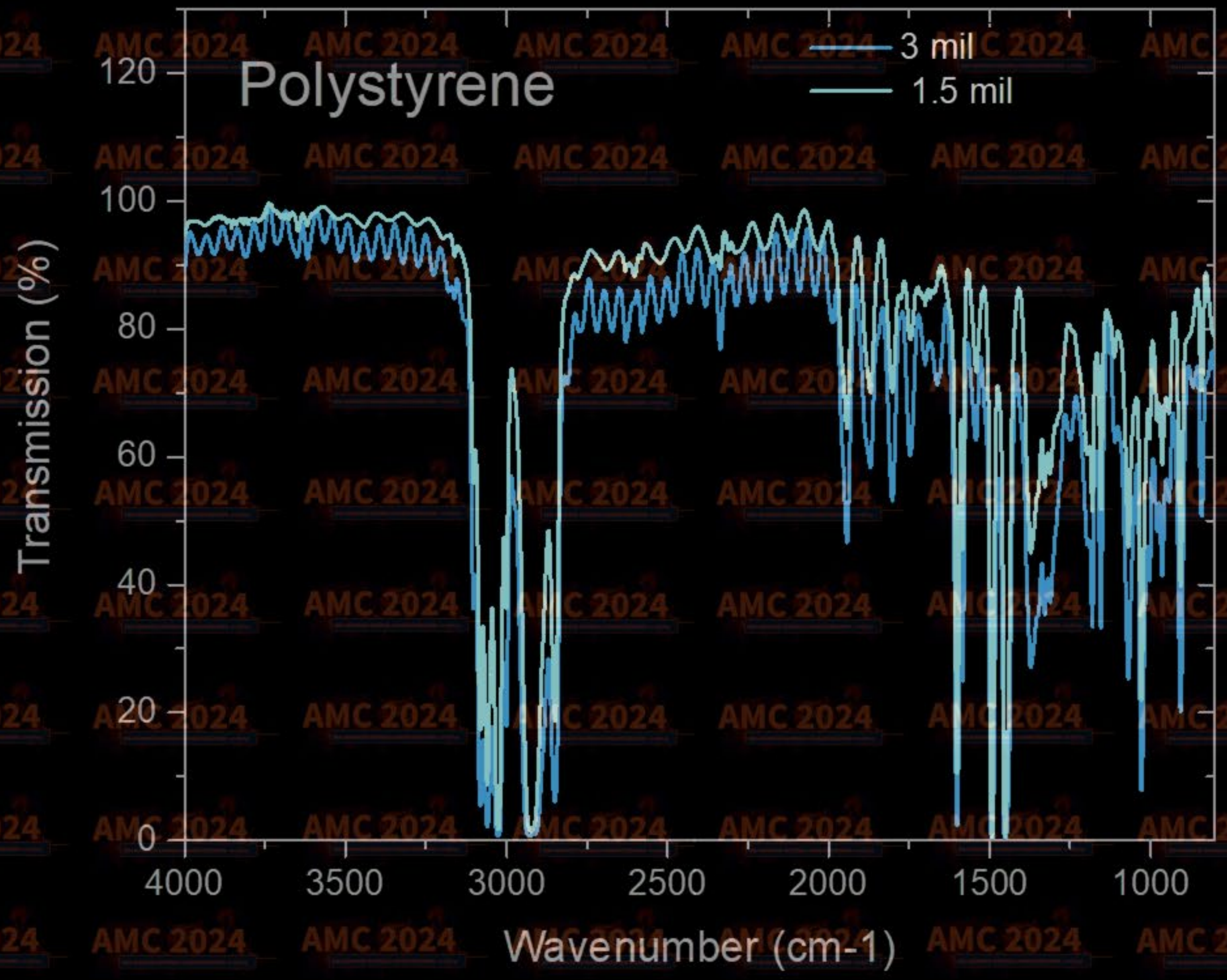
Fourier Transform IR spectroscopy (FTIR)

But what is the Fourier Transform? A visual introduction.

3Blue1Brown



Fourier Transform IR spectroscopy (FTIR)

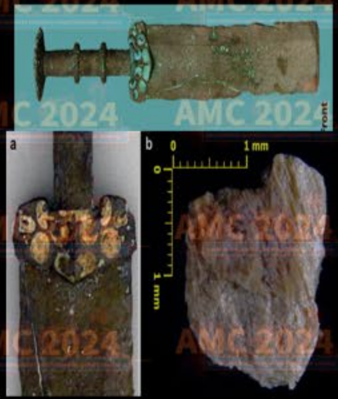


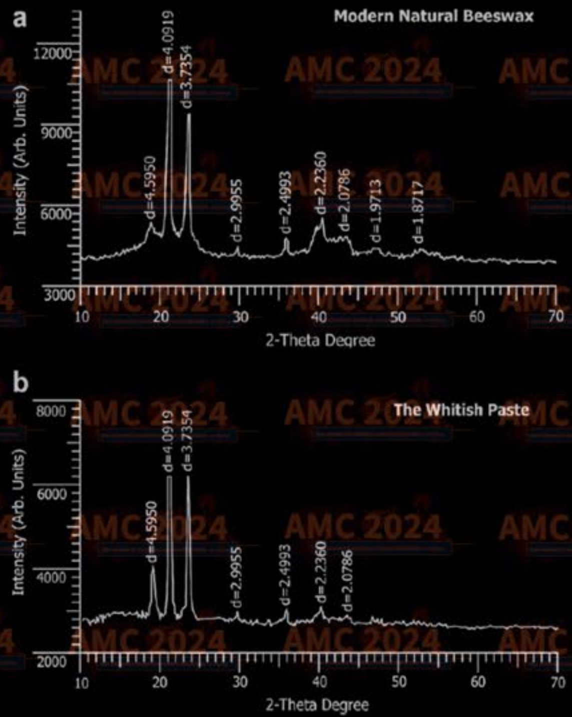
Fourier Transform IR spectroscopy (FTIR)

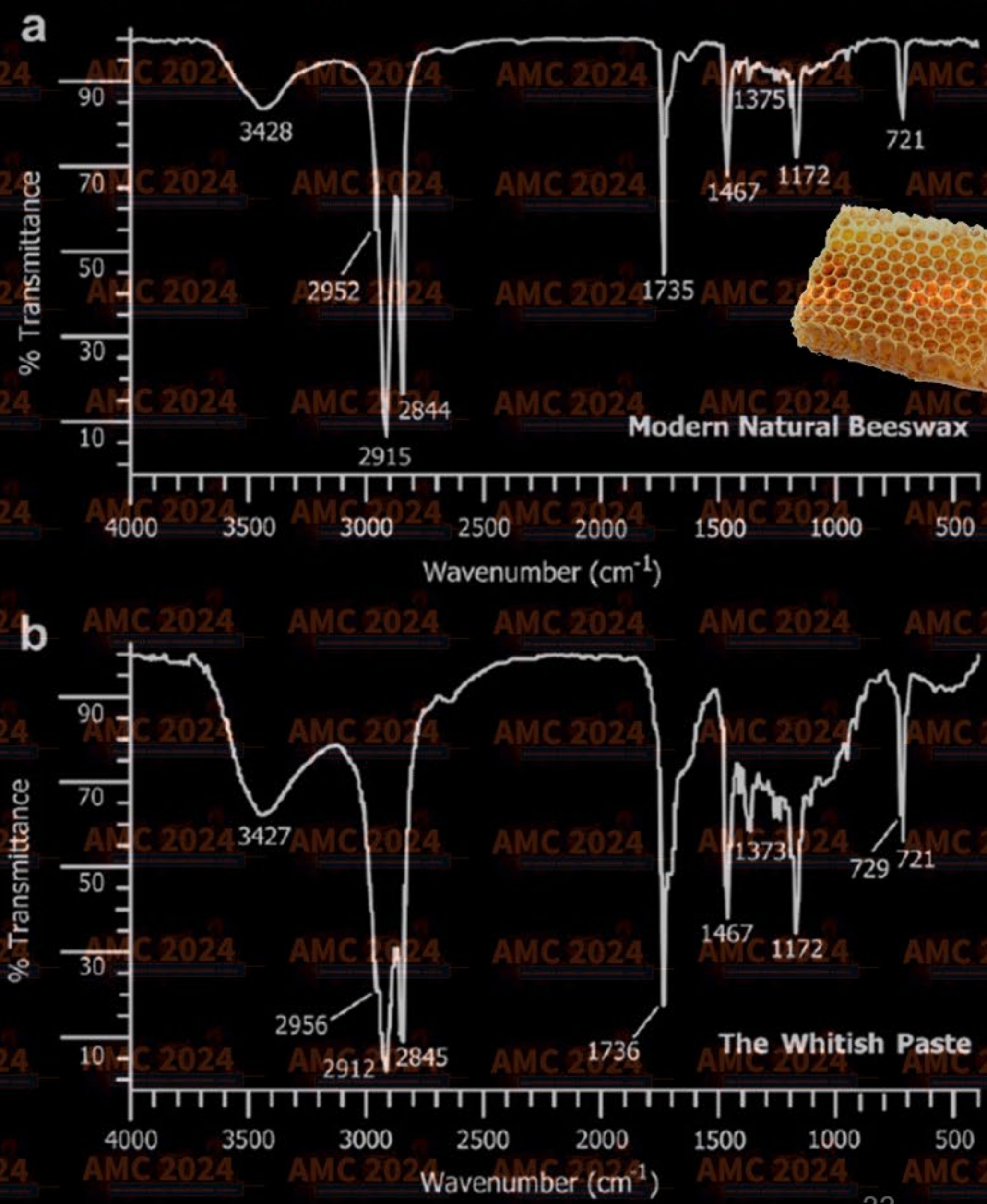
FTIR can be used to identify components in a mixture by comparison with reference spectra.

Discovery of beeswax as binding agent on a 6th-century BC Chinese turquoise-inlaid bronze sword

Wugan Luo, Tao Li, Changsui Wang, Fengchun Huang





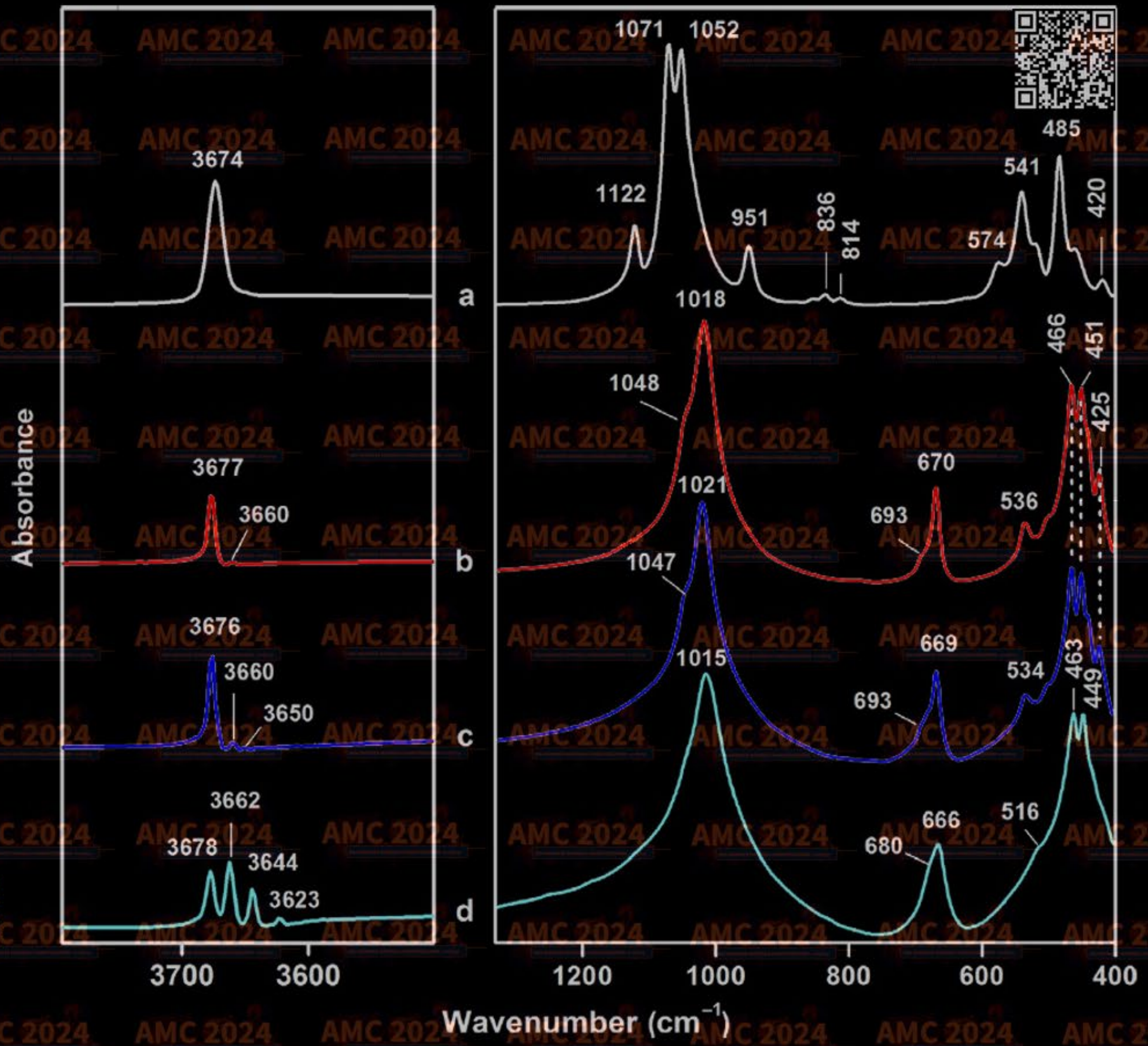


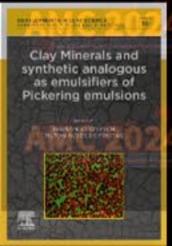
J. of Archaeological Sci. **39** (2012), 1227

Fourier Transform IR spectroscopy (FTIR)

$Al_2Si_4O_{10}(OH)_2$

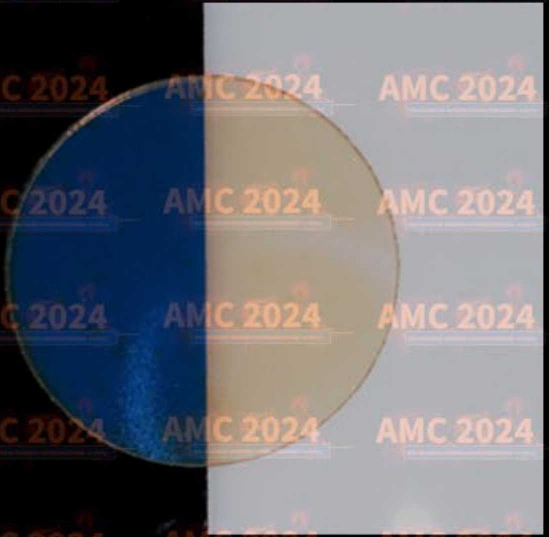
$Mg_3Si_4O_{10}(OH)_2$





Spectra from *Developments in Clay Science*, Vol. 8. Ch. 5

Spectrophotometry (UV-VIS-NIR) and FTIR

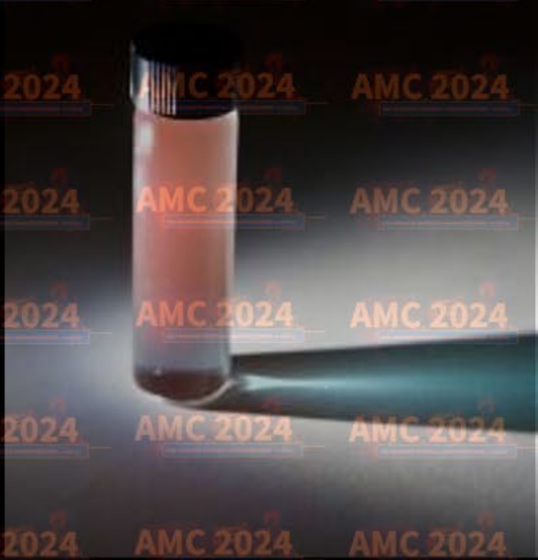


Limitations:

- Reference sample is often needed for quantitative analysis.
- Many contributions to the spectrum are small and can be buried in the background.
- Usually, unambiguous chemical identification requires the use of complementary techniques.
- Limited spatial resolution.

Strengths:

- Very little or simple sample preparation.
- Simplicity of use and data interpretation.
- Short acquisition time, for most cases.
- Non destructive.
- Broad range of photon energies.
- High sensitivity (~ 0.1 wt% typical for FTIR).

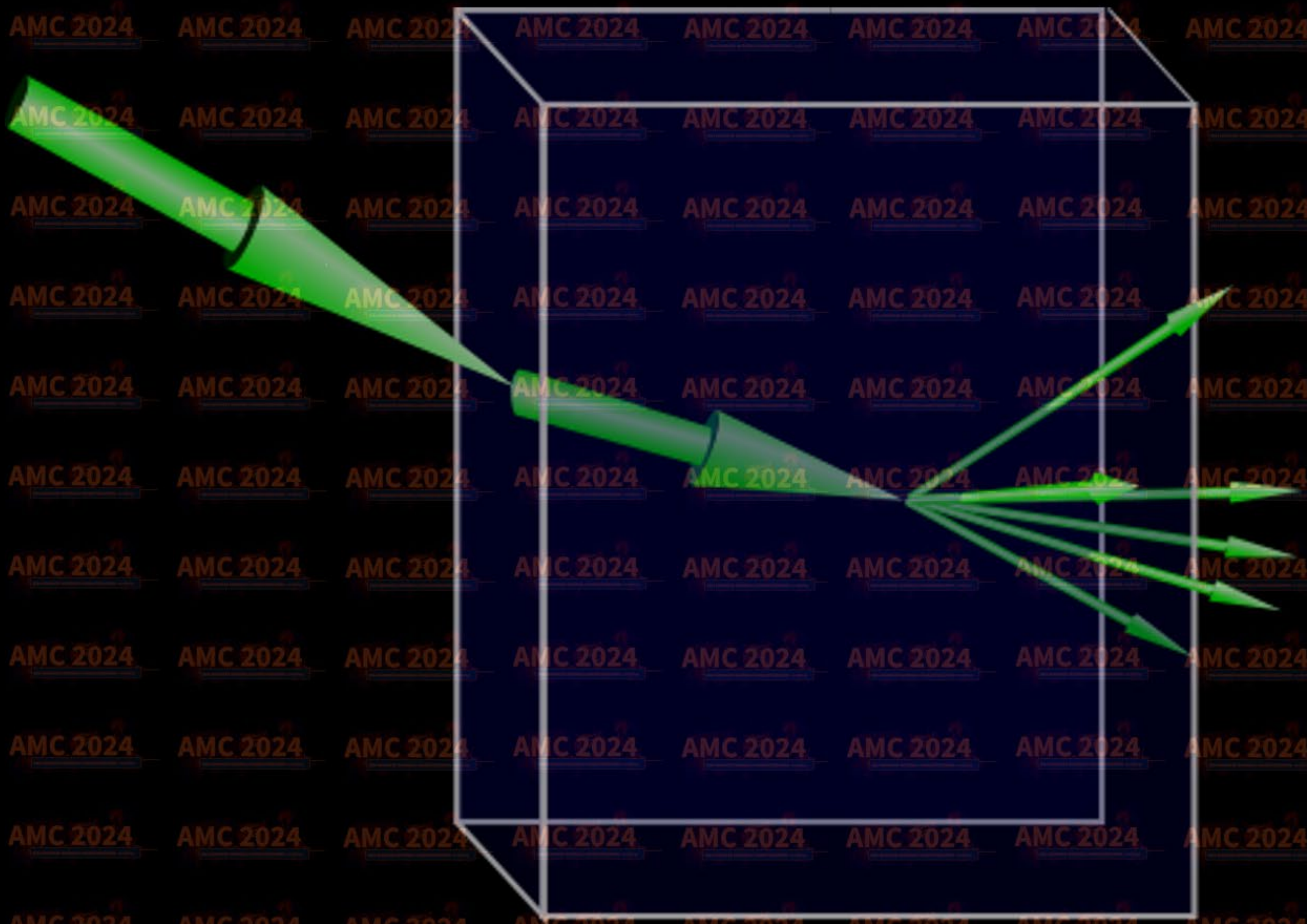


Complementary techniques:

Raman, Electron Energy Loss Spectroscopy (EELS), Extended X-ray Absorption Fine Structure (EXAFS), XPS, Auger, SIMS, XRD, SFG.

nanocomposix.com

Light scattering



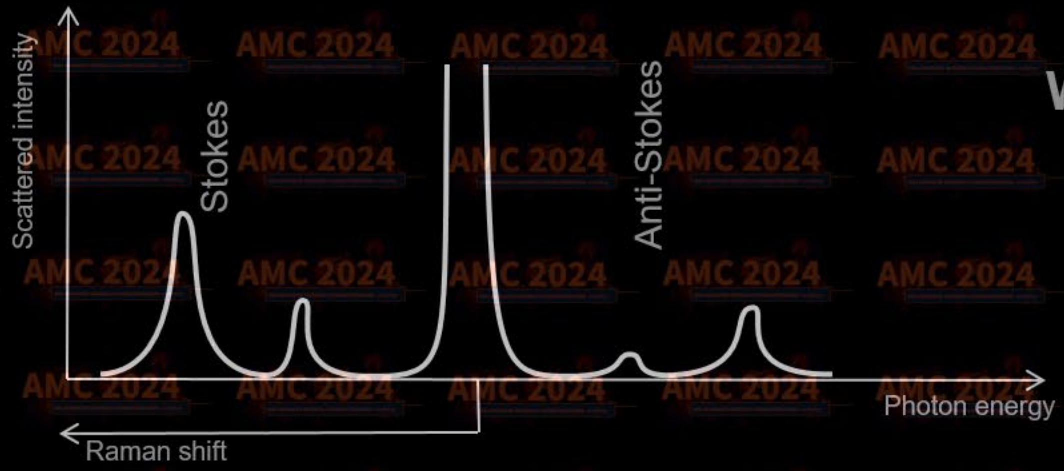
Sir Chandrasekhara Venkata Raman

The Nobel Prize in Physics 1930 was awarded to Sir Venkata Raman *"for his work on the scattering of light and for the discovery of the effect named after him"*.

Sir Kariamanikkam Srinivasa Krishnan

Co-discoverer of Raman scattering, for which his mentor C. V. Raman was awarded the 1930 Nobel Prize in Physics

Raman spectroscopy

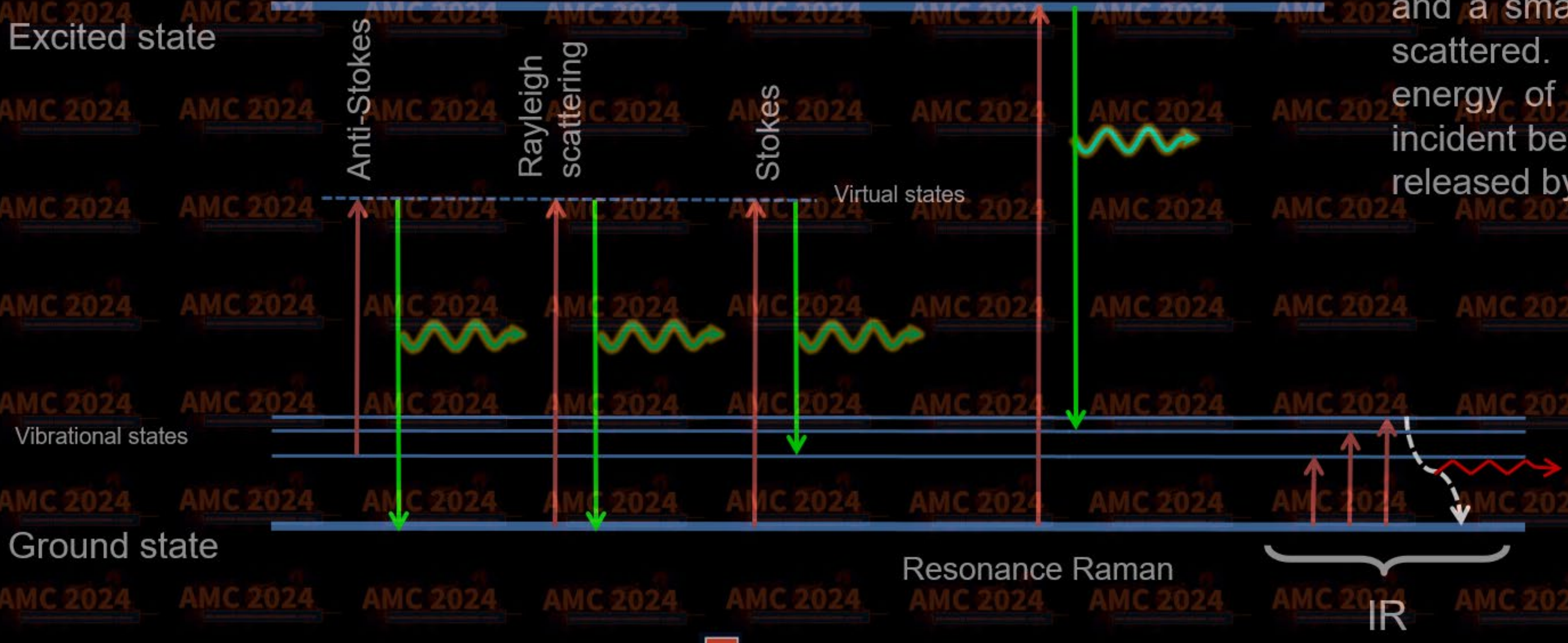


What is measured:

The light inelastically scattered by the material.

Basic principle:

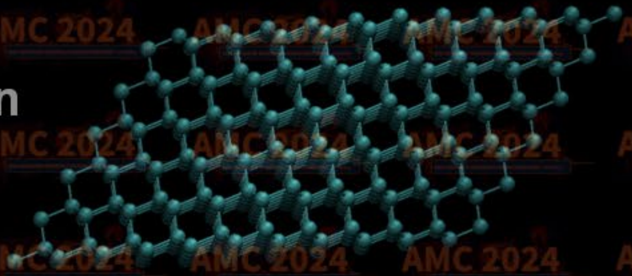
The impinging light couples with the lattice vibrations (phonons) of the material, and a small portion of it is inelastically scattered. The difference between the energy of the scattered light and the incident beam is the energy absorbed or released by the phonons.

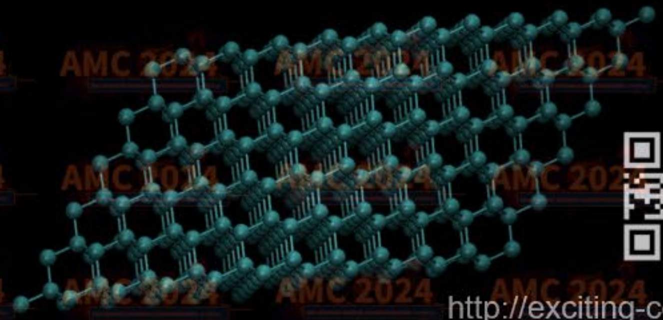


Raman spectroscopy

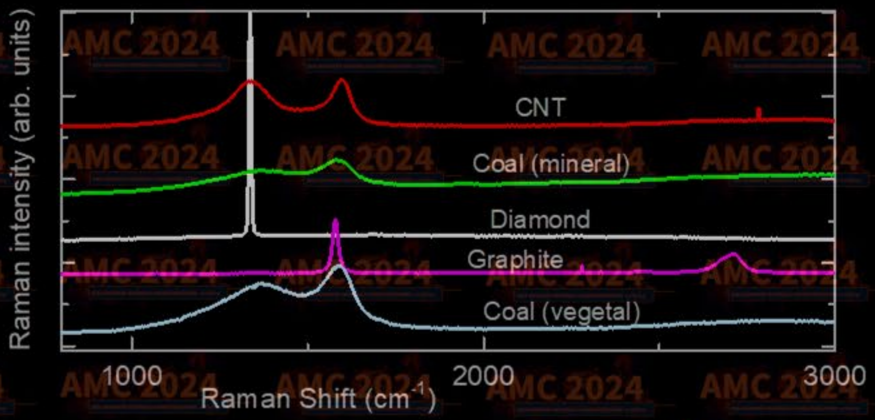
Impinging light couples with vibration modes of the material:

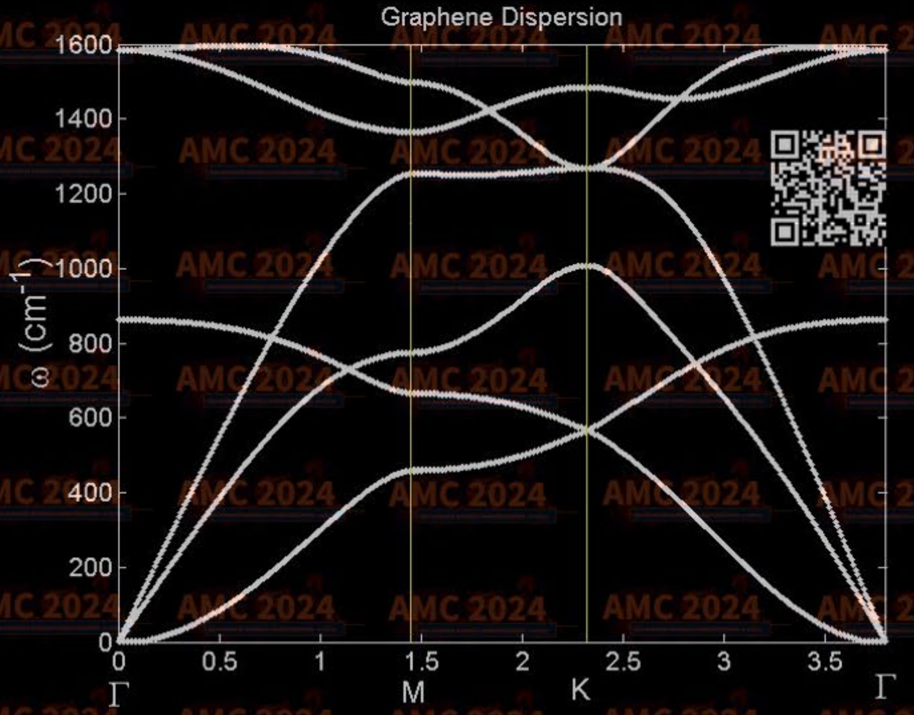
- Phonons
- Molecular vibrations





http://exciting-code.org

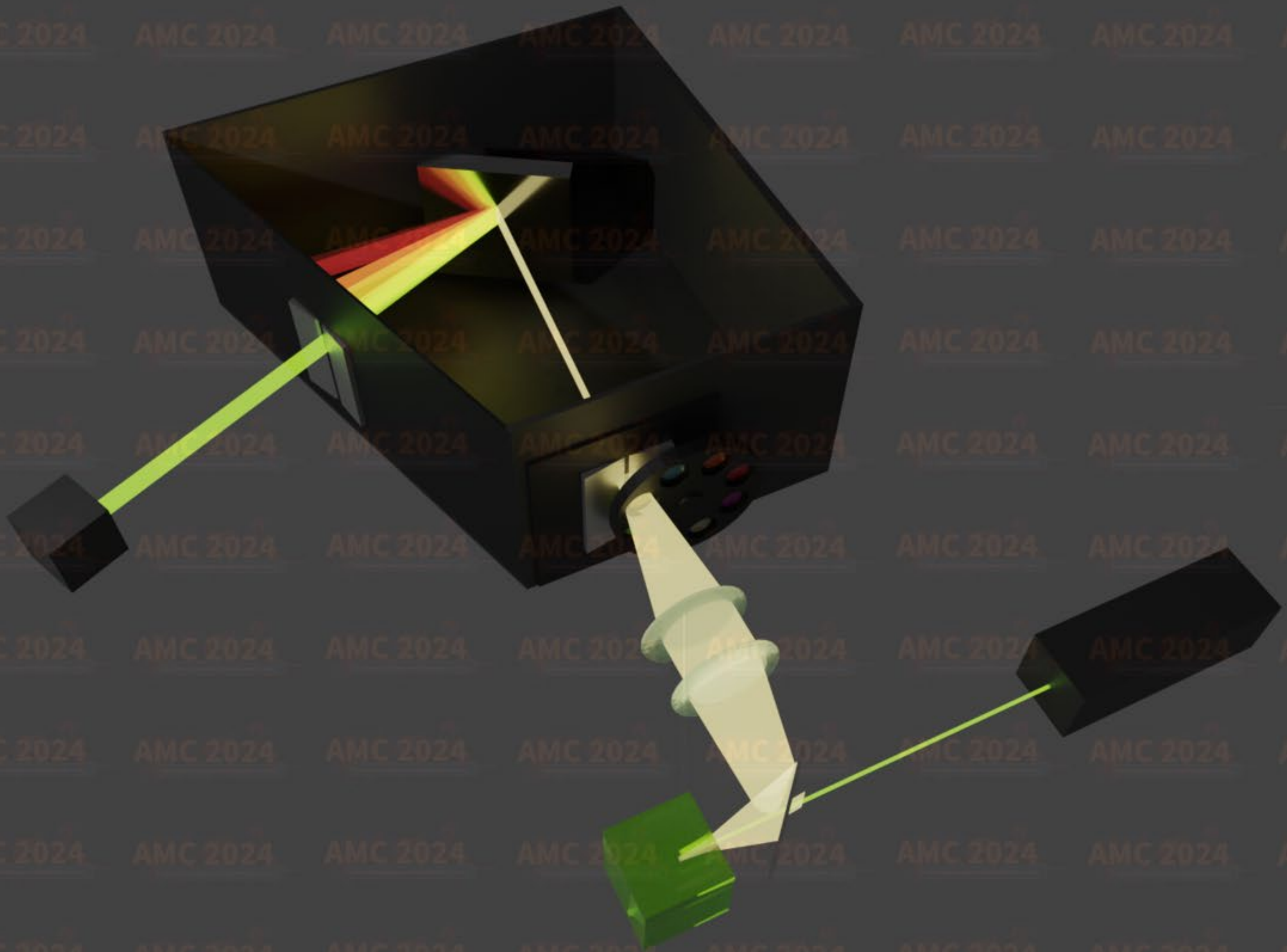




http://flex.phys.tohoku.ac.jp/~pourya

Raman spectroscopy

Instrumentation:



Raman spectroscopy

$$\mathbf{E} = \mathbf{E}_0 \cdot \cos\left(2\pi \cdot \nu_0 \cdot \mathrm{t}\right)$$

$$\mathbf{p} = \alpha \cdot \mathbf{E} + \frac{1}{2} \cdot \beta \cdot \mathbf{E}^2 + \frac{1}{6} \cdot \gamma \cdot \mathbf{E}^3 + \ldots$$

$$\alpha \sim 10^{10} \cdot \beta \sim 10^{20} \cdot \gamma$$

$$\mathbf{p} = \alpha \cdot \mathbf{E}_0 \cdot \cos\left(2\pi \cdot \nu_0 \cdot \mathrm{t}\right)$$

Raman spectroscopy

The α tensor is dependent on the shape, strength, and dimensions of the chemical bond. Since chemical bonds change during vibrations, α is dependent on the vibrations of the molecule:

$$Q_k = Q_{k0} \cdot \cos\left(2\pi \cdot \nu_k \cdot t + \varphi_k\right)$$

$$\alpha = \alpha_o + \sum_k \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \cdot Q_k$$

$$\alpha_k = \alpha_0 + \alpha'_k \cdot Q_k$$

$$\alpha_k = \alpha_0 + \alpha'_k \cdot Q_{k0} \cdot \cos\left(2\pi \cdot \nu_k \cdot t + \varphi_k\right)$$

$$\mathbf{p} = \alpha_0 \cdot \mathbf{E}_0 \cdot \cos\left(2\pi \cdot \nu_0 \cdot \mathrm{t}\right) +$$

$$+ \frac{1}{2} \cdot \alpha'_k \cdot Q_{k0} \cdot \mathbf{E}_0 \cdot [\cos\left(2\pi \cdot t \cdot (\nu_0 + \nu_k) + \varphi_k\right) +$$

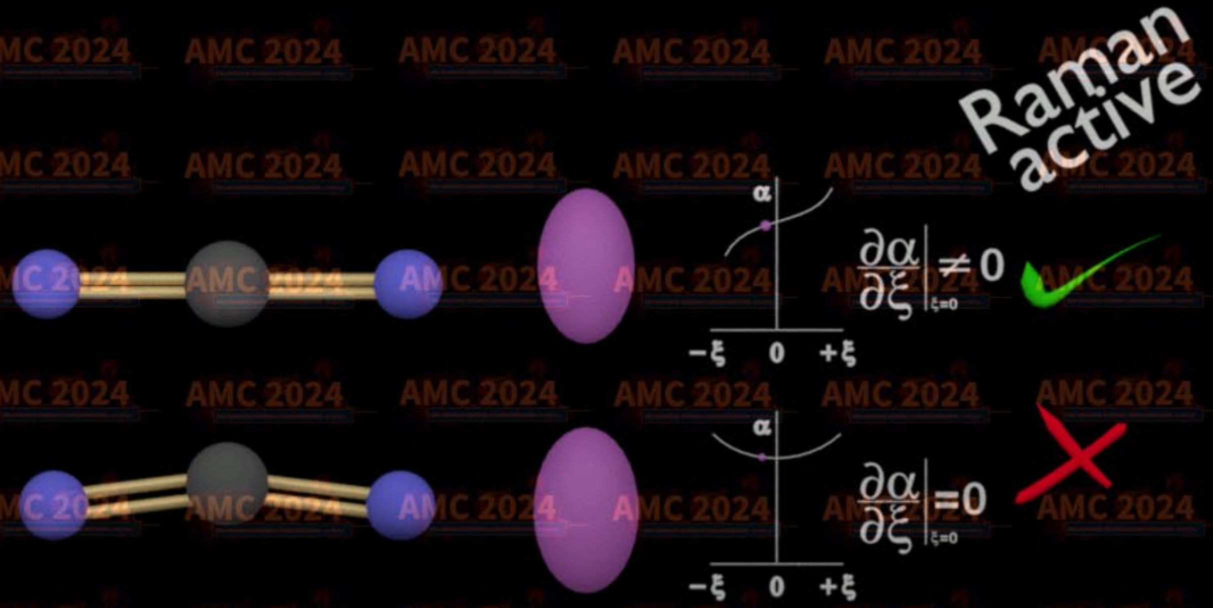
$$+ \cos\left(2\pi \cdot t \cdot (\nu_0 - \nu_k) - \varphi_k\right)]$$

$$\alpha'_k = \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \neq 0$$

the dipole oscillates with three frequencies simultaneously, corresponding to the three possible scattering modes (Rayleigh, Stokes Raman and anti-Stokes Raman)

Raman spectroscopy

$$\alpha'_k = \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \neq 0$$



Fourier Transform IR spectroscopy (FTIR)

IR active vibrations

Raman spectroscopy

Raman active vibrations

The intensity of the Raman scattering linked to a vibrational state depends on the change in the polarizability tensor

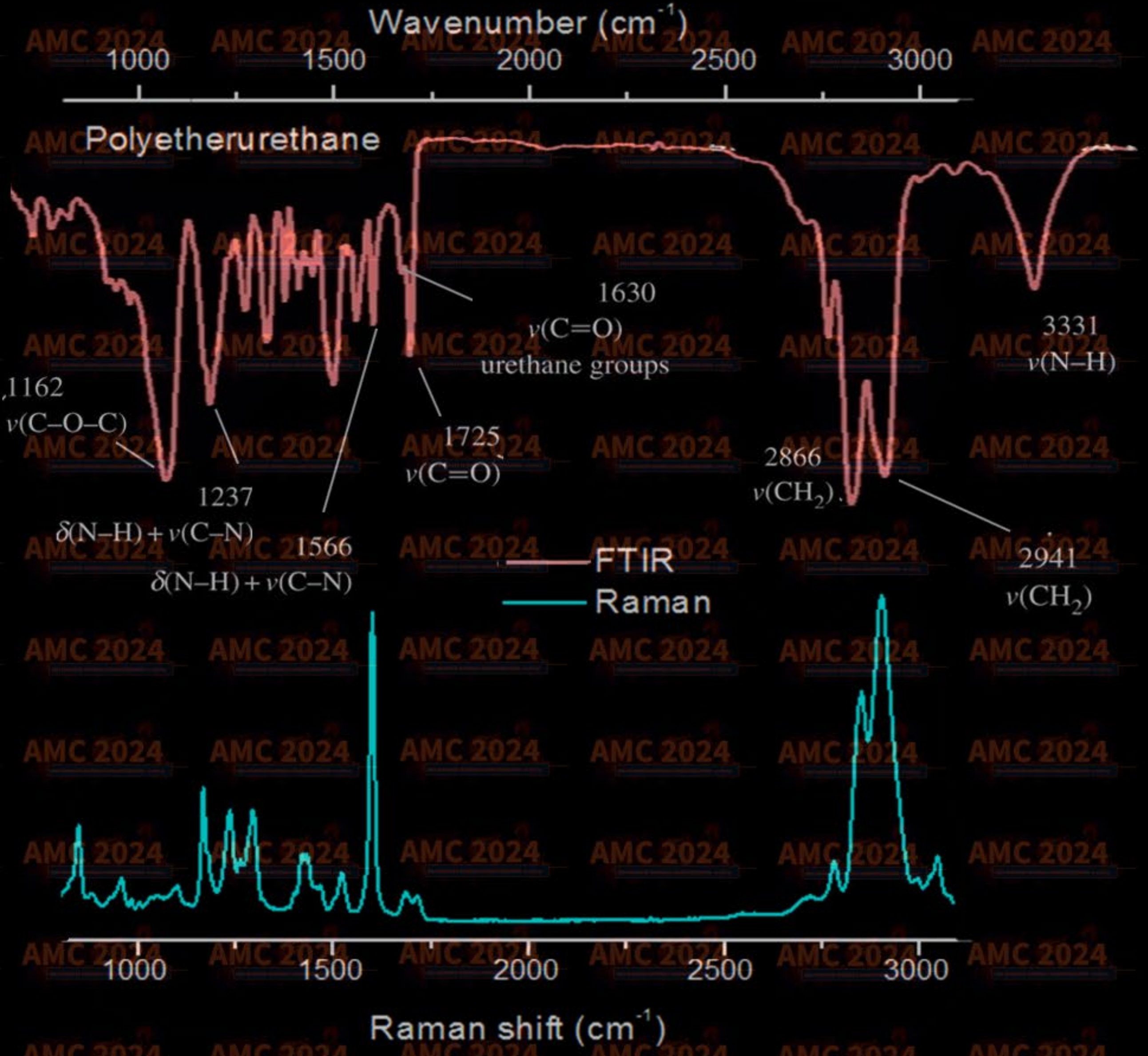
Raman spectroscopy

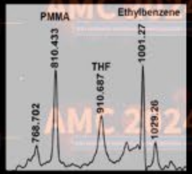
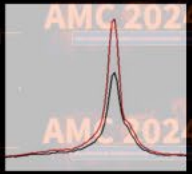
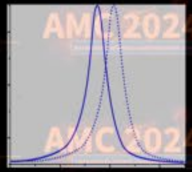
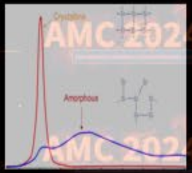
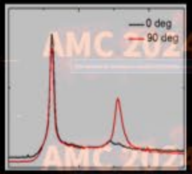
FTIR and Raman:

The two techniques are complementary (different selection rules).

$$\Delta\mu \neq 0$$

$$\alpha'_k = \left(\frac{\partial \alpha}{\partial Q_k}\right)_0 \neq 0$$



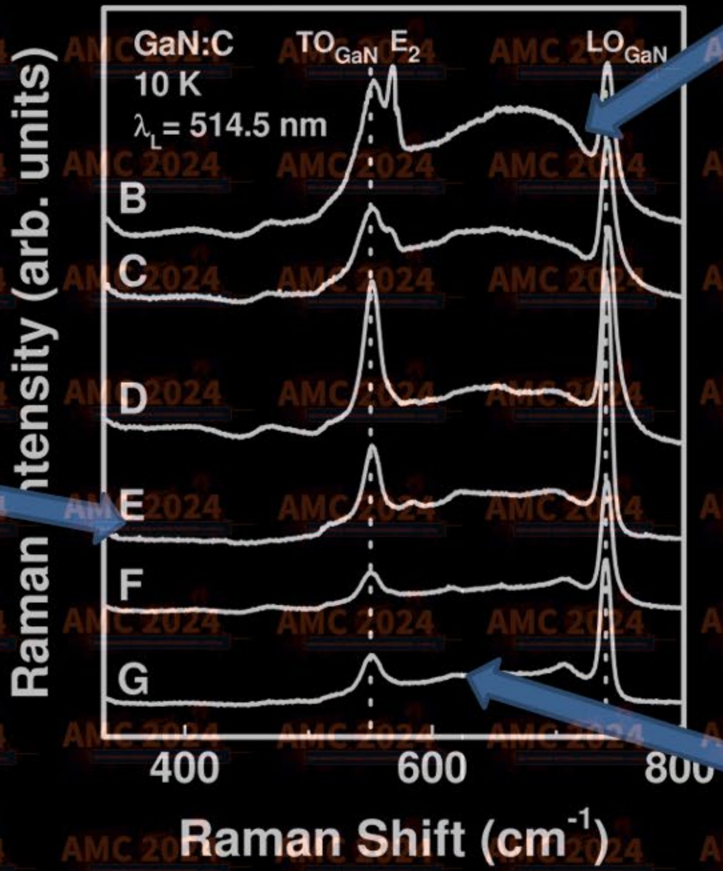
Studying the …		… we can estimate …
 Characteristic Raman frequencies	→	Identity and composition of materials
 Raman peak intensity	→	Volume of material probed
 Raman peak frequency shift	→	Strain, stress, crystal lattice distortion
 Raman peak width	→	Crystallinity of material
 Raman peak polarization dependency	→	Crystal orientation and symmetry

Raman spectroscopy

Molecular and crystalline structure characterization

Presence of N vacancies yields poor crystallinity

Substitutional C fills N vacancies improving the crystallinity



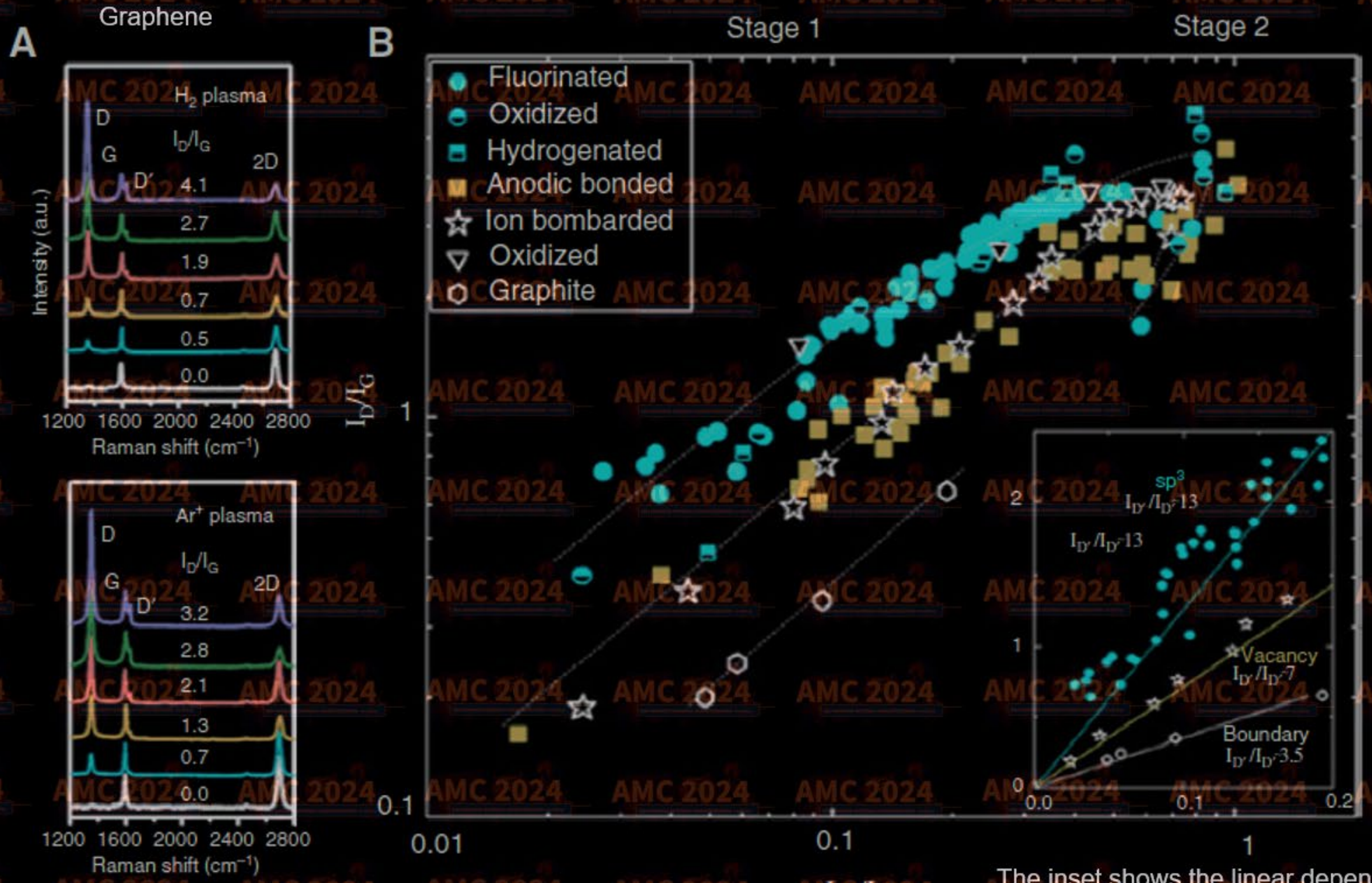
C content

C incorporates interstitially causing a degradation of the crystal lattice

PHYSICAL REVIEW B **68**, 155204 (2003)

Raman spectroscopy

Crystalline structure and defect characterization

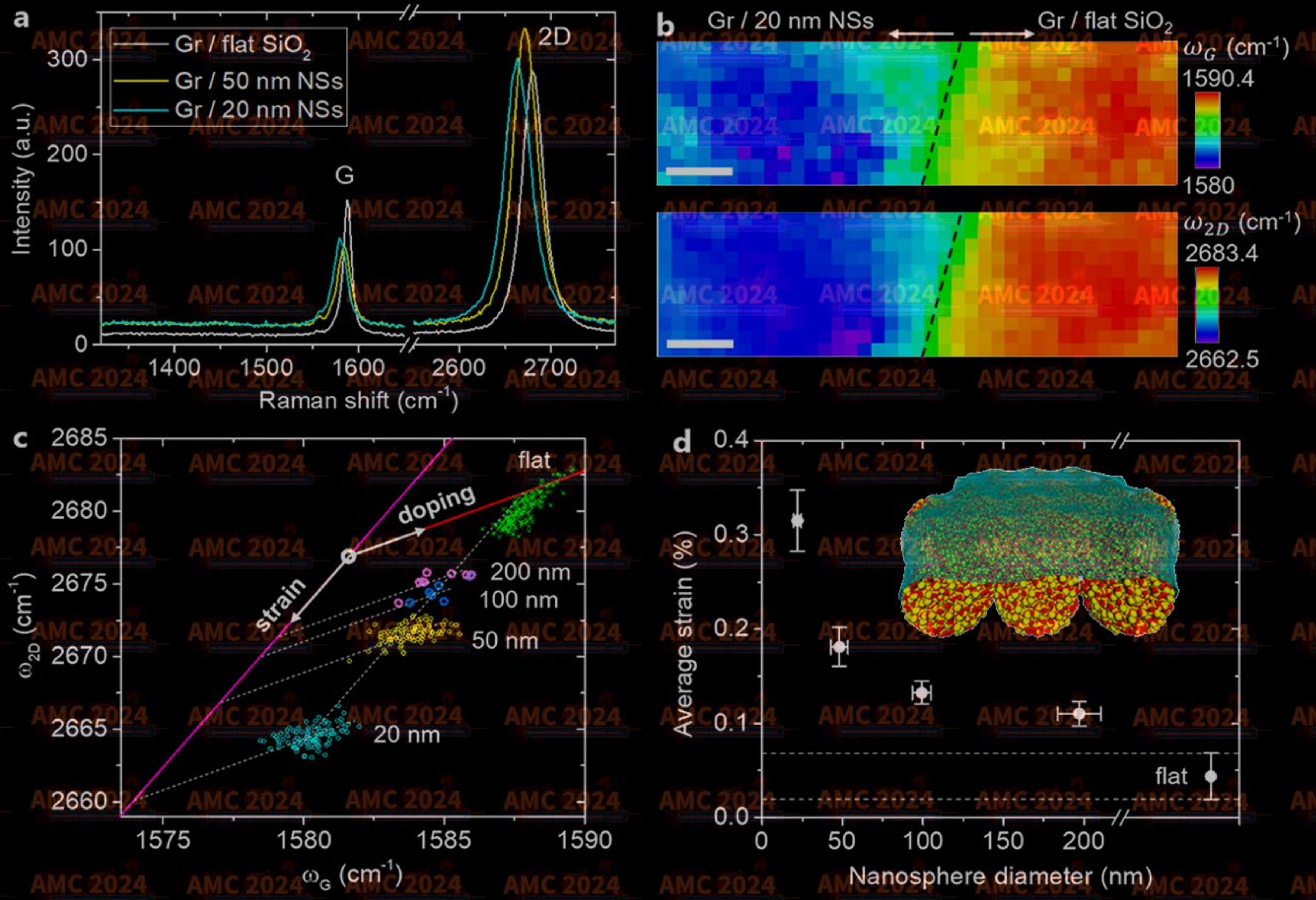


The inset shows the linear dependence between the two parameters at low defect concentration.

Nanophotonics **6,** 1219 (2017)

Raman spectroscopy

Strain/stress



Nano Lett. **18**, 2098 (2018)

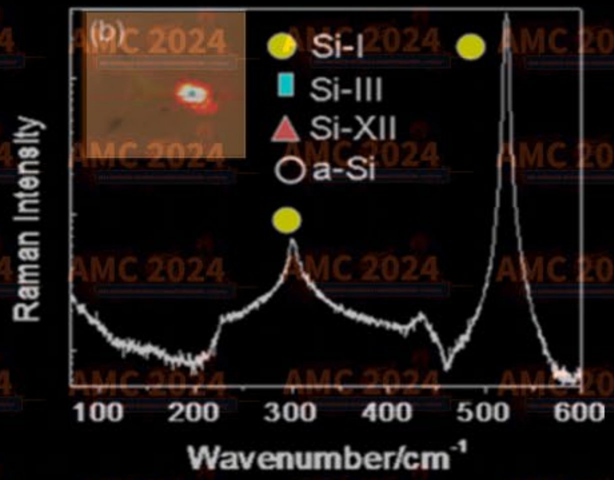
Raman spectroscopy

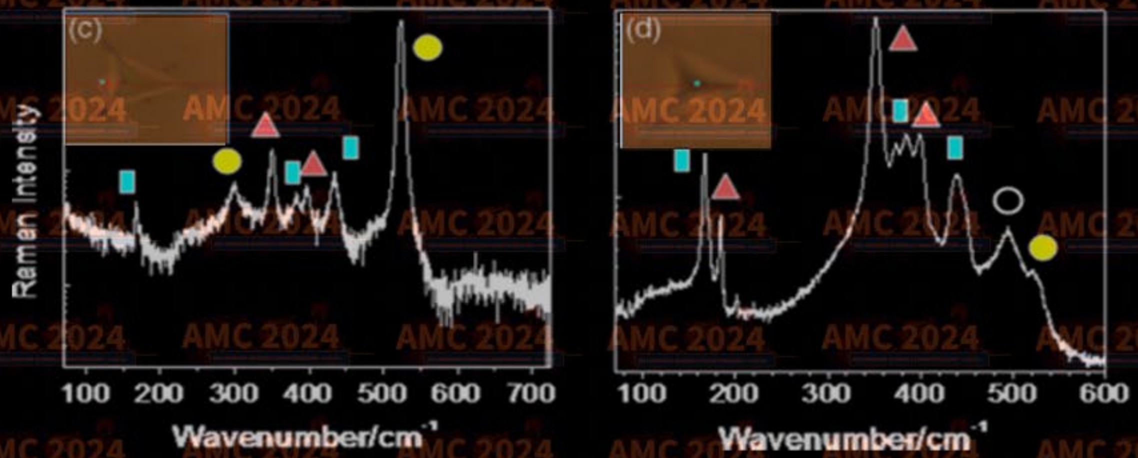
Phase transitions

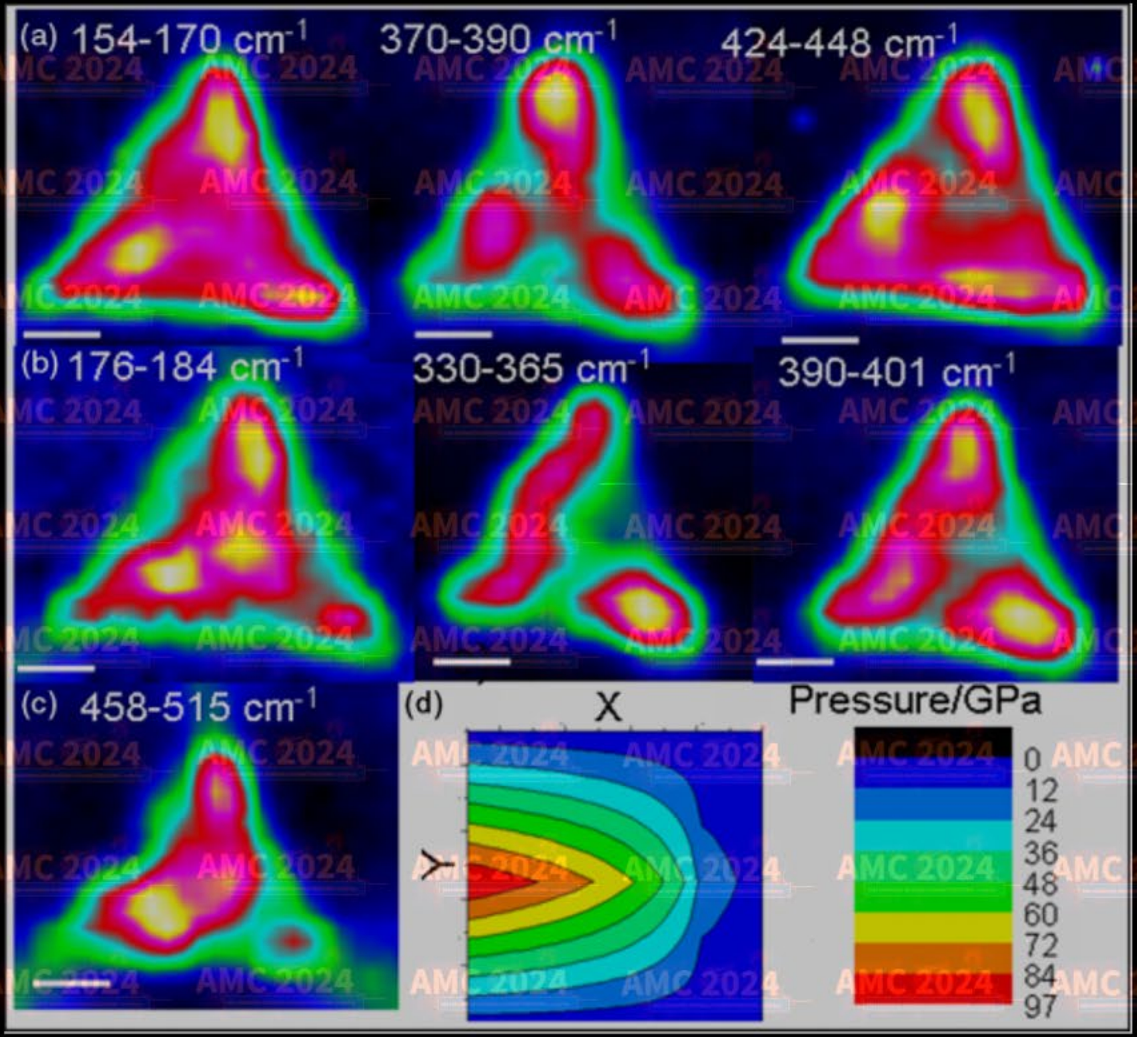
(a) Different Raman Modes

Si-I (cm^{-1})†	Si-III (cm^{-1})†	Si-XII (cm^{-1})†
300, 520	166, 171	182
a-Si (cm^{-1})†	384	352
475, 510	432, 463	397

† Ref 2,3





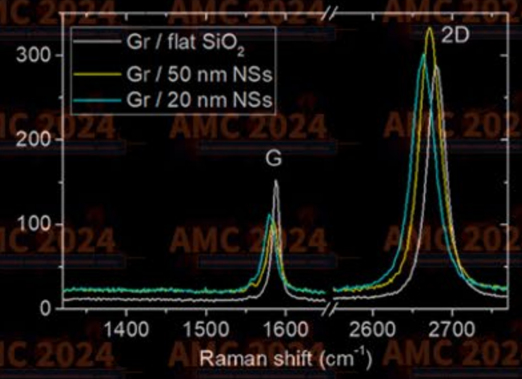


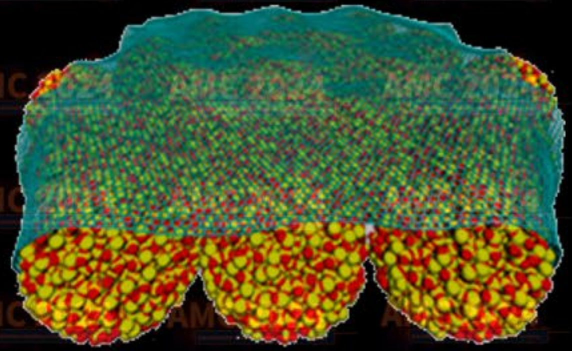
J. Raman Spectroscopy **41**, 334 (2010)

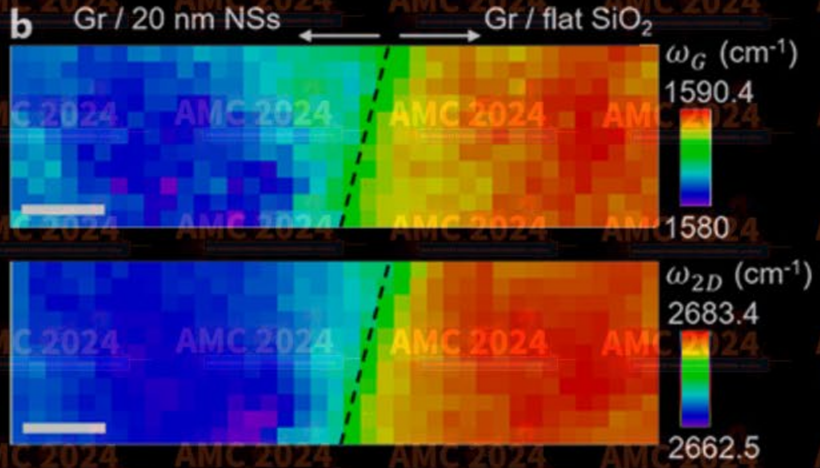
Raman spectroscopy

Primary Strengths:

- Very little sample preparation.
- Structural characterization.
- Non-destructive technique.
- Chemical information.
- Complementary to FTIR.







Primary Limitations:

- Expensive apparatus (for high spectral/spatial resolution and sensitivity).
- Weak signal, compared to fluorescence.
- Limited spatial resolution (diffraction limited).

Complementary techniques:

FTIR, EELS, Mass spectroscopy, EXAFS, XPS, AES, SIMS, XRD, SFG.

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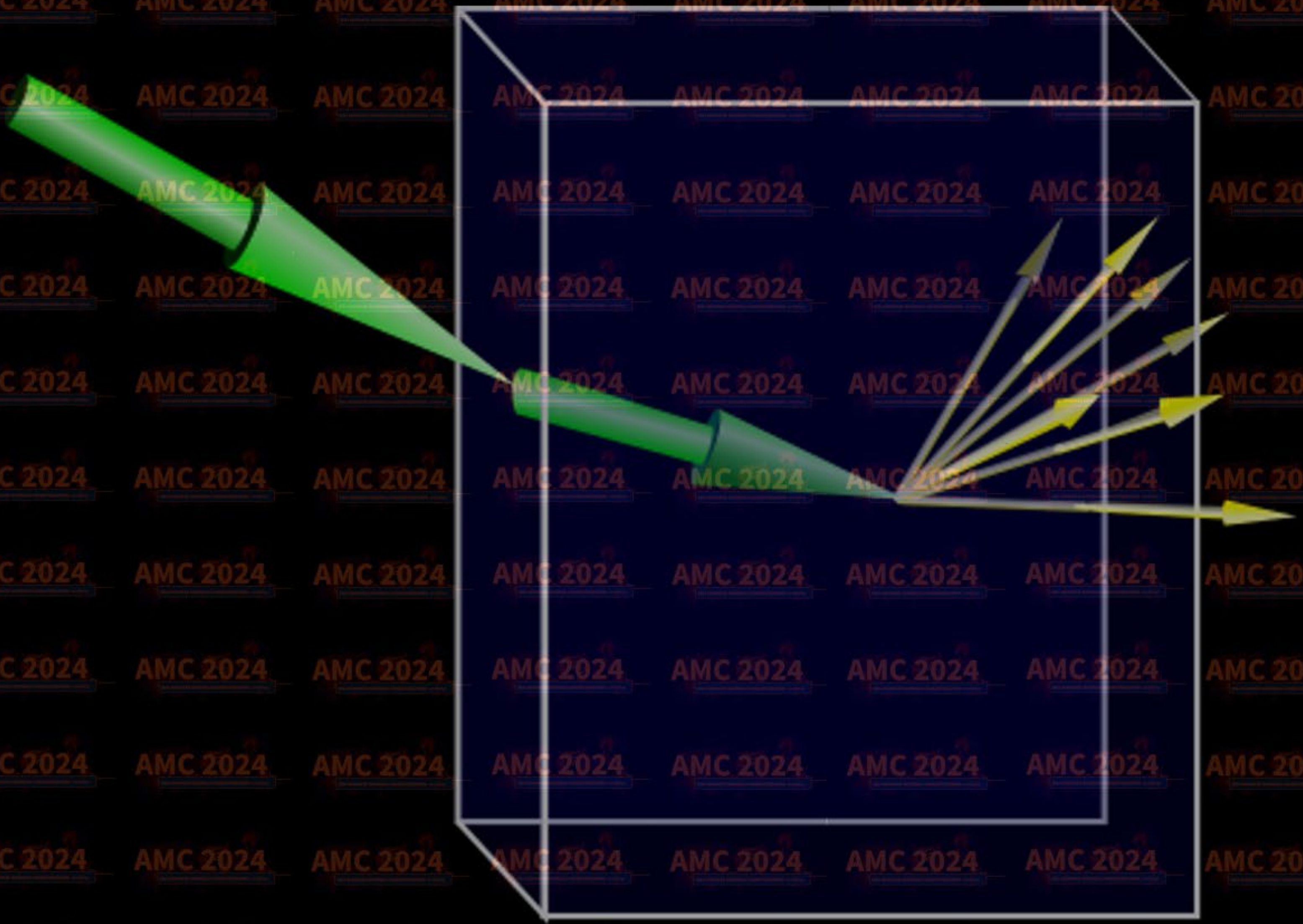
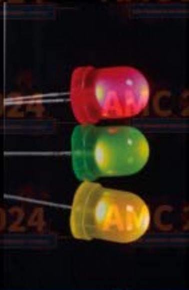
Luminescence



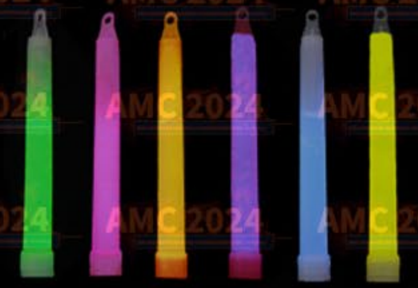
Luminescence



Lifetime: Phosphorescence, fluorescence

Mechanism: Photoluminescence, bioluminescence, chemoluminescence, thermoluminescence, piezoluminescence, etc.

Disney Pixar



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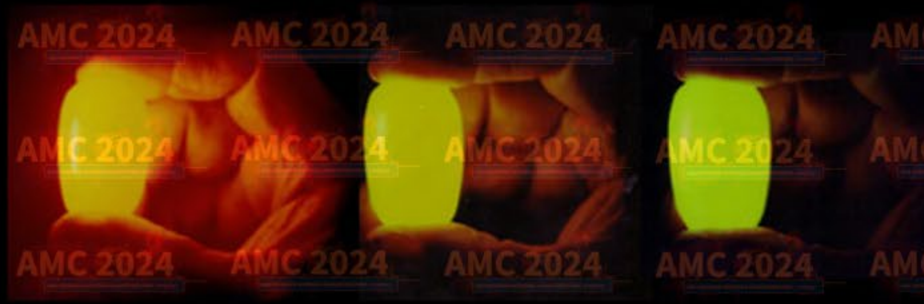
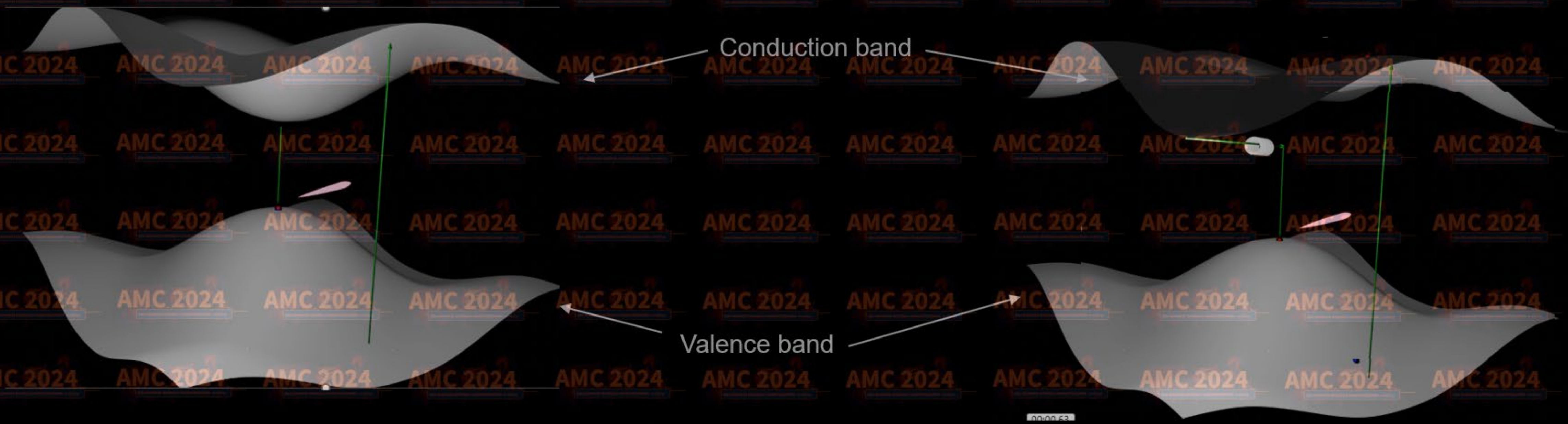


Photoluminescence

What is measured:

The emission spectra of materials due to radiative recombination following photo-excitation.

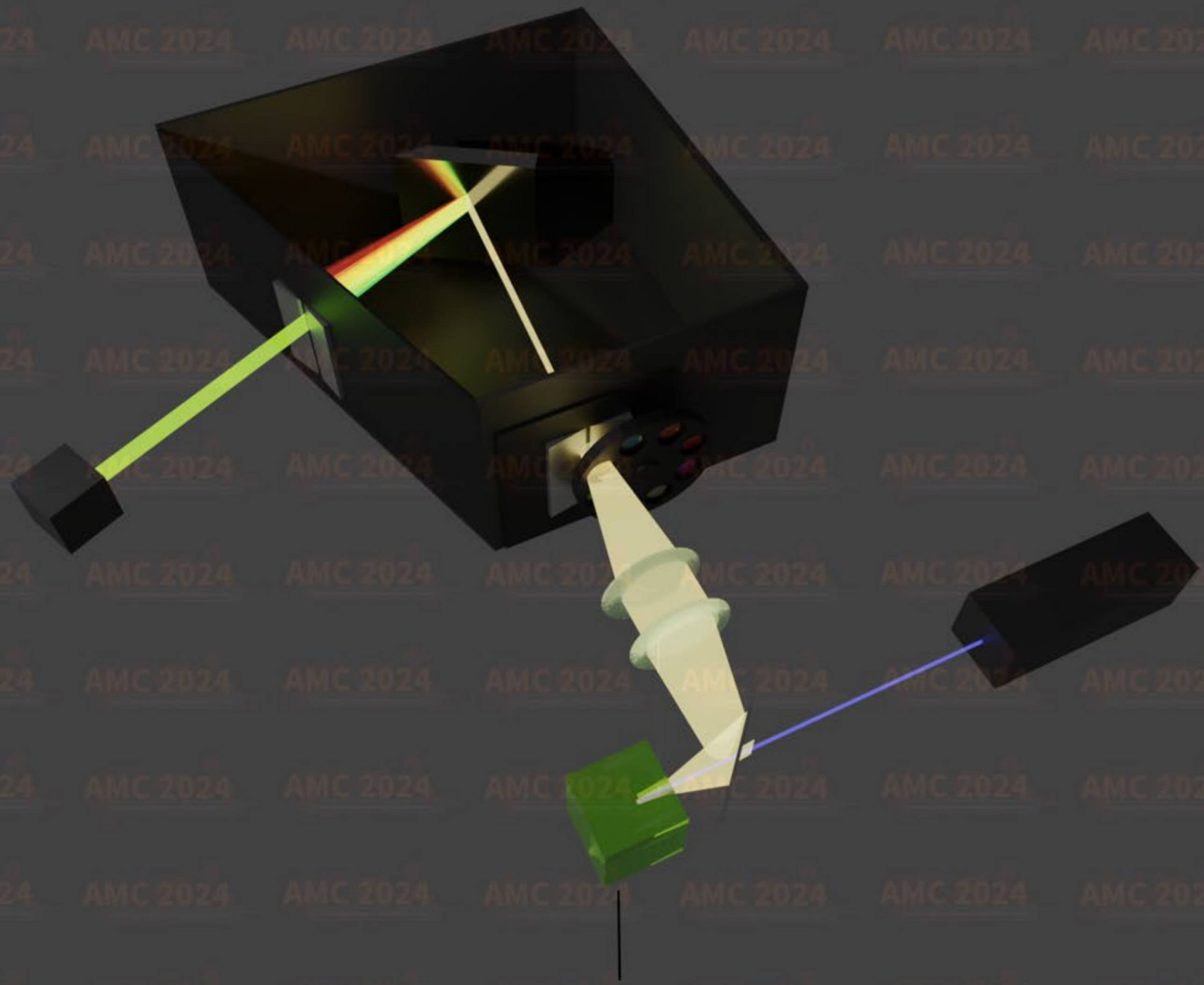
Basic principle:



direct band gap indirect band gap

Photoluminescence

Instrumentation:

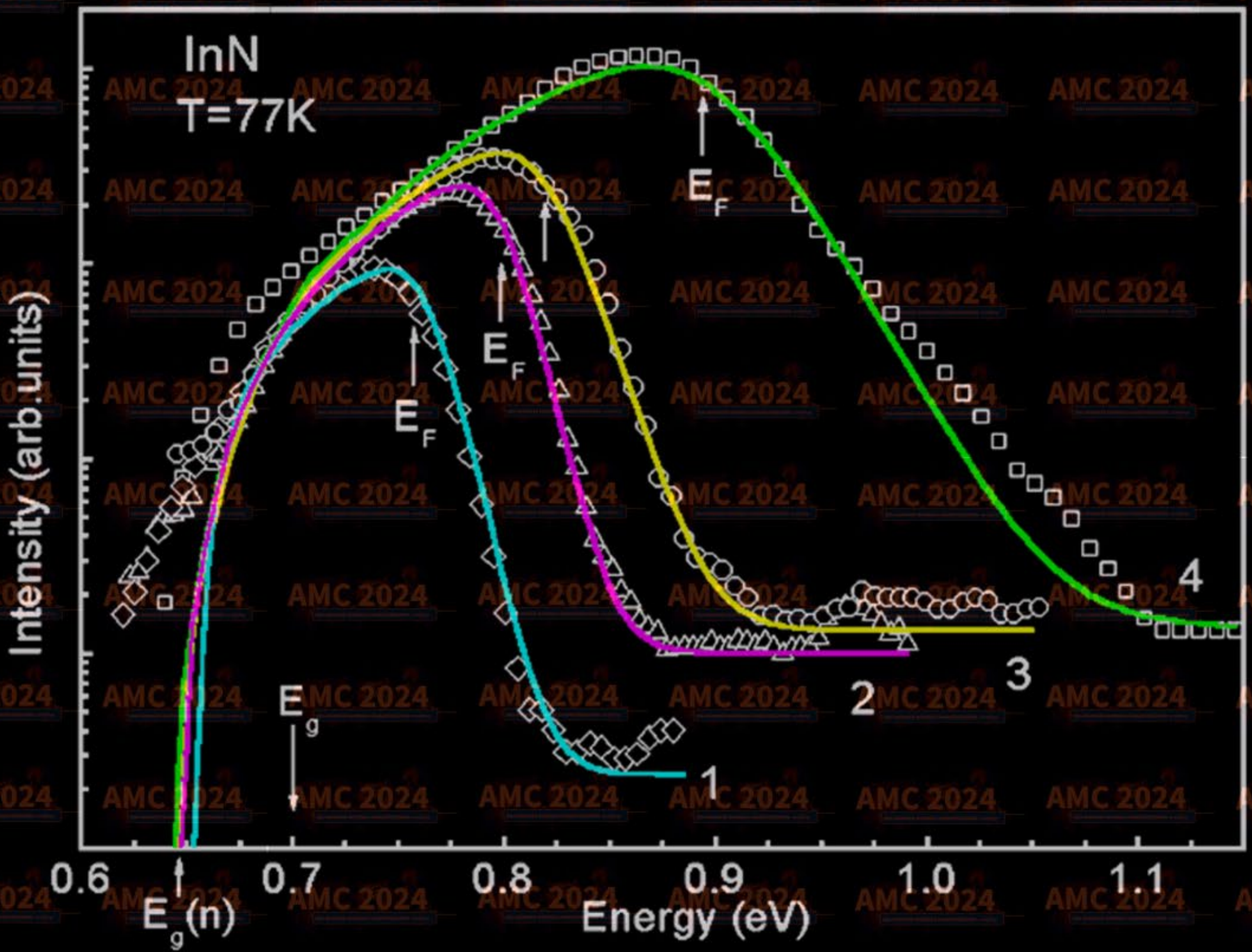


Photoluminescence

Carrier concentration

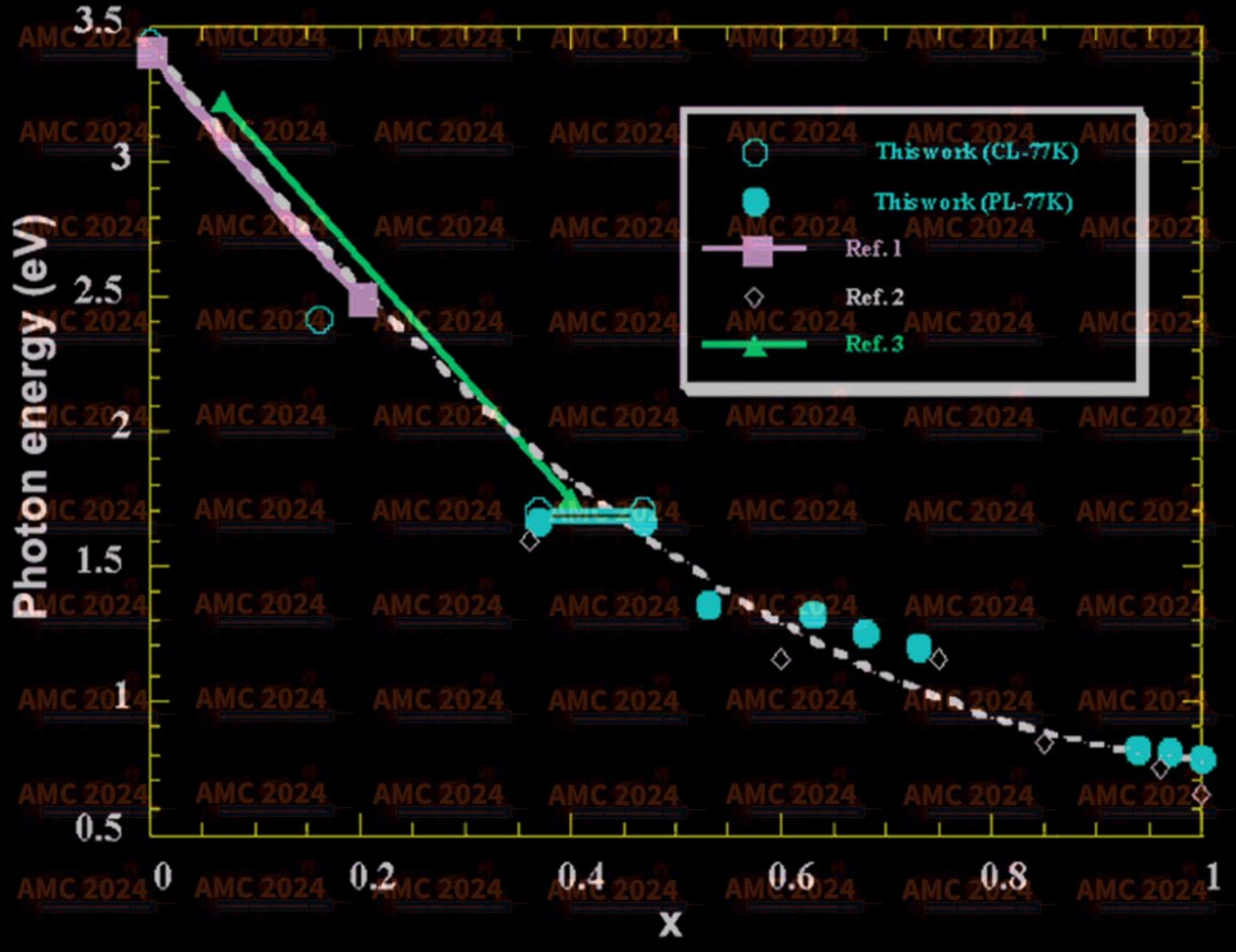
Photoluminescence spectra of InN layers with different carrier concentrations.

1 - n = 6×10^{18} cm^{-3} (MOCVD);
2 - n = 9×10^{18} cm^{-3} (MOMBE);
3 - n = 1.1×10^{19} cm^{-3} (MOMBE);
4 - n = 4.2×10^{19} cm^{-3} (PAMBE).



Phys. Stat. Solidi **(b)** **230** (2002**b**), R4

Photoluminescence



Alloy composition

$In_xGa_{1-x}N$ alloys. Luminescence peak positions of catodoluminescence and photoluminescence spectra vs. concentration x.

The plots of luminescence peak positions can be fitted to the curve

$$E_g(x)=3.48 - 2.70x - bx(1-x)$$

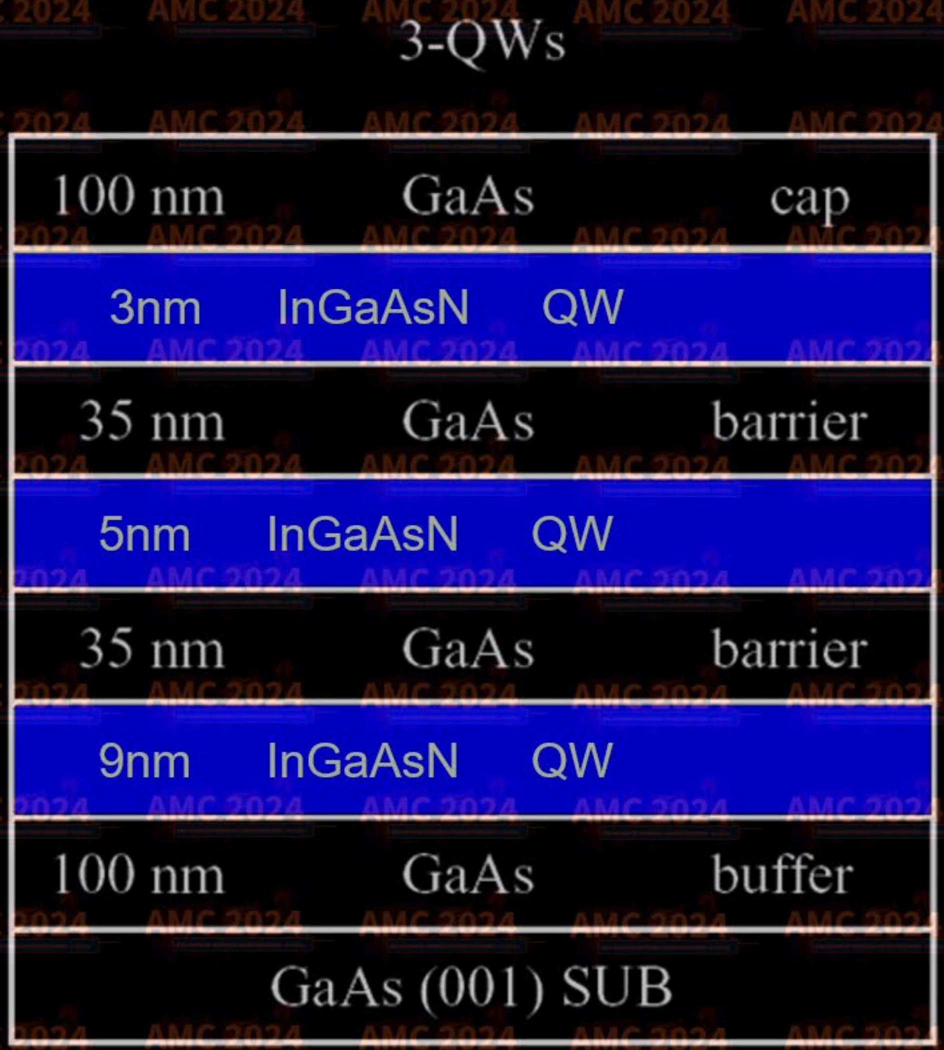
with a bowing parameter of **b=2.3 eV**

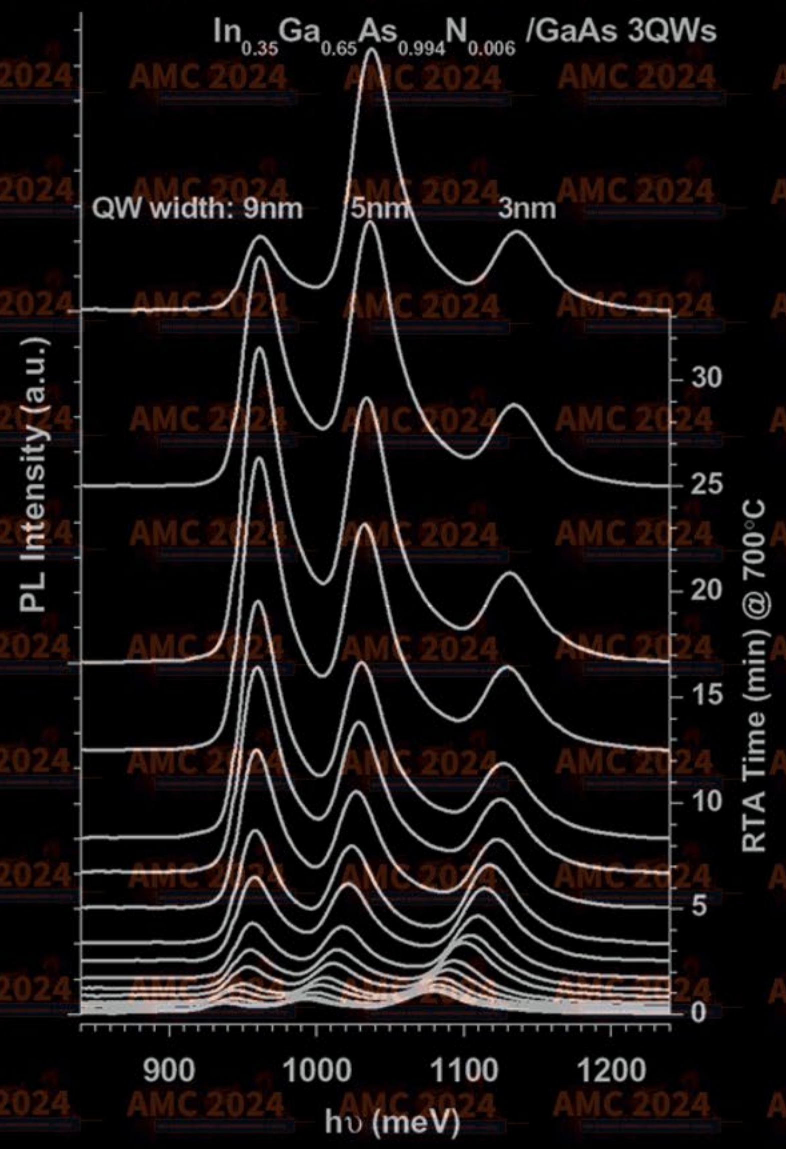
Ref.1 - Wetzel., *Appl. Phys. Lett.* **73,** 73 (1998).
Ref.2 - V. Yu. Davydov., *Phys. Stat. Sol.* **(b) 230,** R4 (2002).
Ref.3 - O'Donnel., *J. Phys .Condens. Matt.* **13,** 1994 (1998).

Extracted from *Phys. Stat. Sol.* **(b) 234** (2002) 750

Photoluminescence

Width and quality of semiconductor quantum wells.

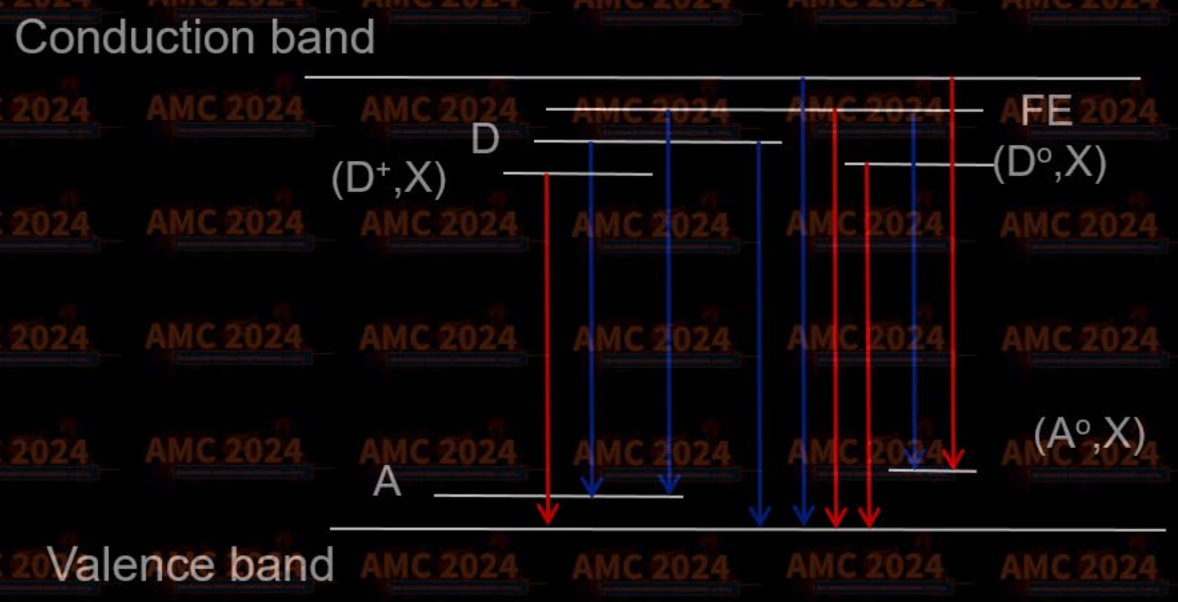


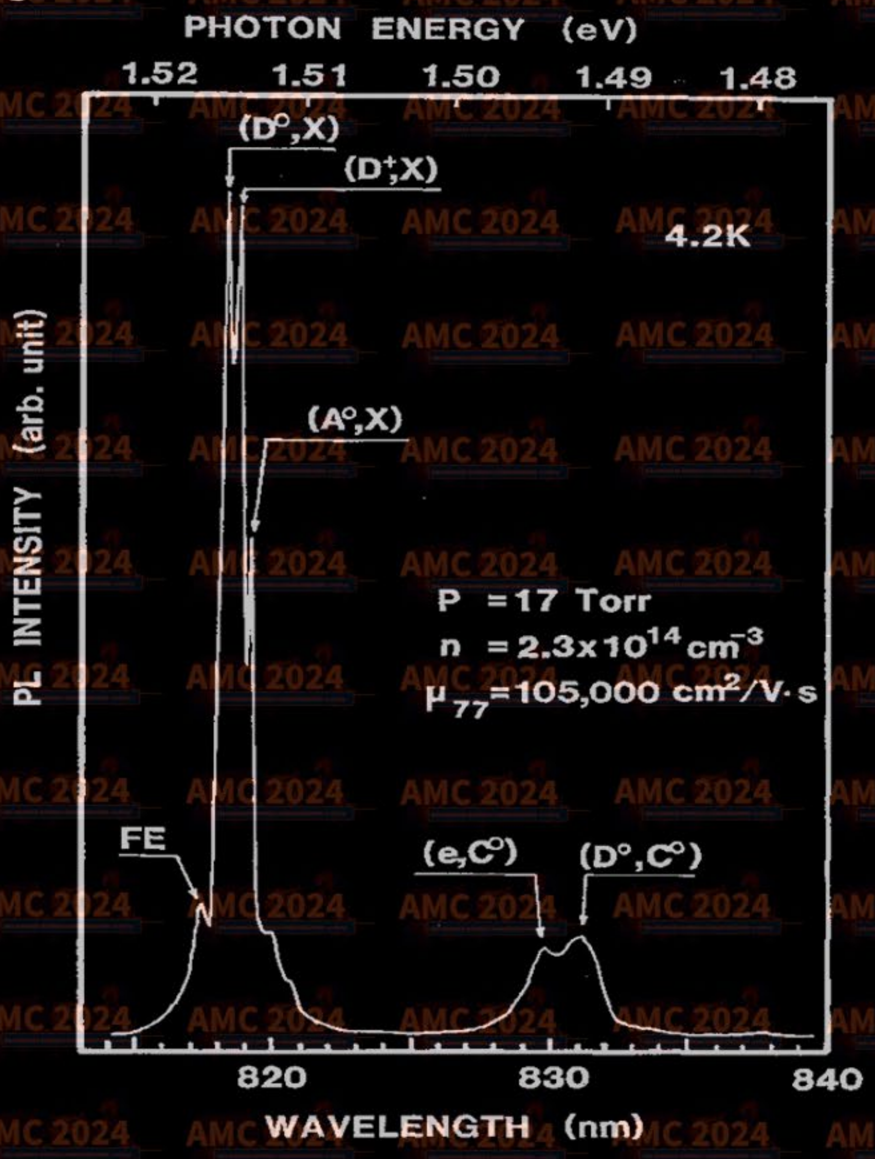


Journal of Crystal Growth 278 (2005) 259–263

Photoluminescence

Defect luminescence in GaAs



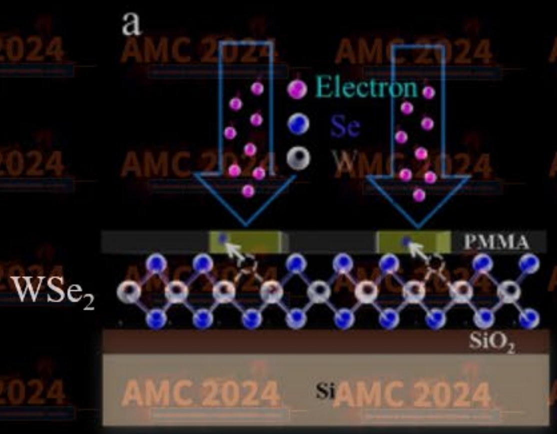


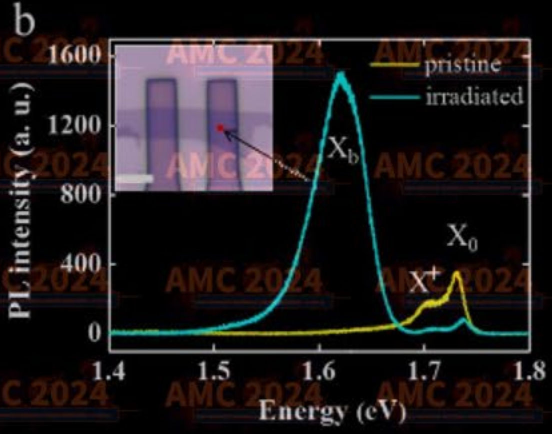
Jap. J. App. Phys. **23**, L100 (1984)

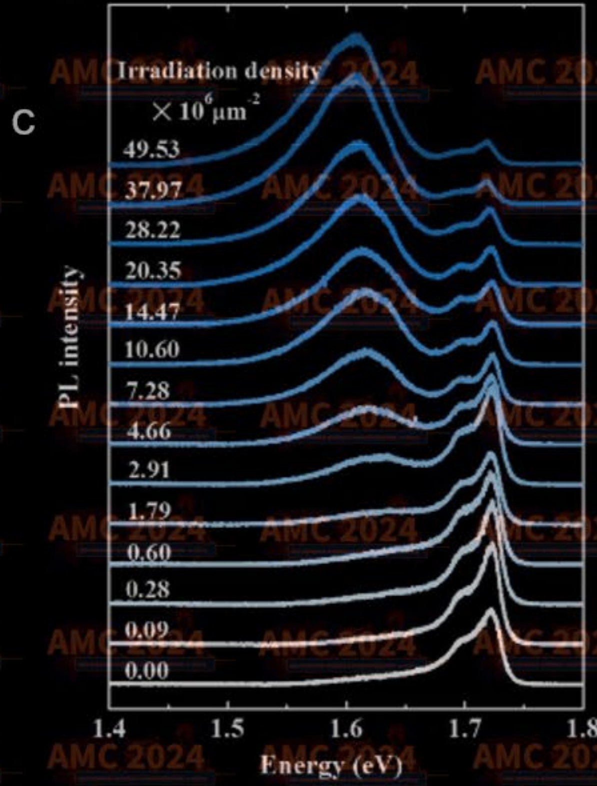
Defects in 2D materials

Defect induced PL emission.

a) Schematic diagram of electron beam irradiation on monolayer WSe_2 sample during the EBL process.
b) PL spectrum of pristine monolayer WSe_2 and monolayer WSe_2 after EBL.
The inset shows optical image of WSe_2 with PMMA patterned by EBL, scale bar is 5 μm
c) PL spectra of a pristine WSe_2 under different e^- beam irradiation density.







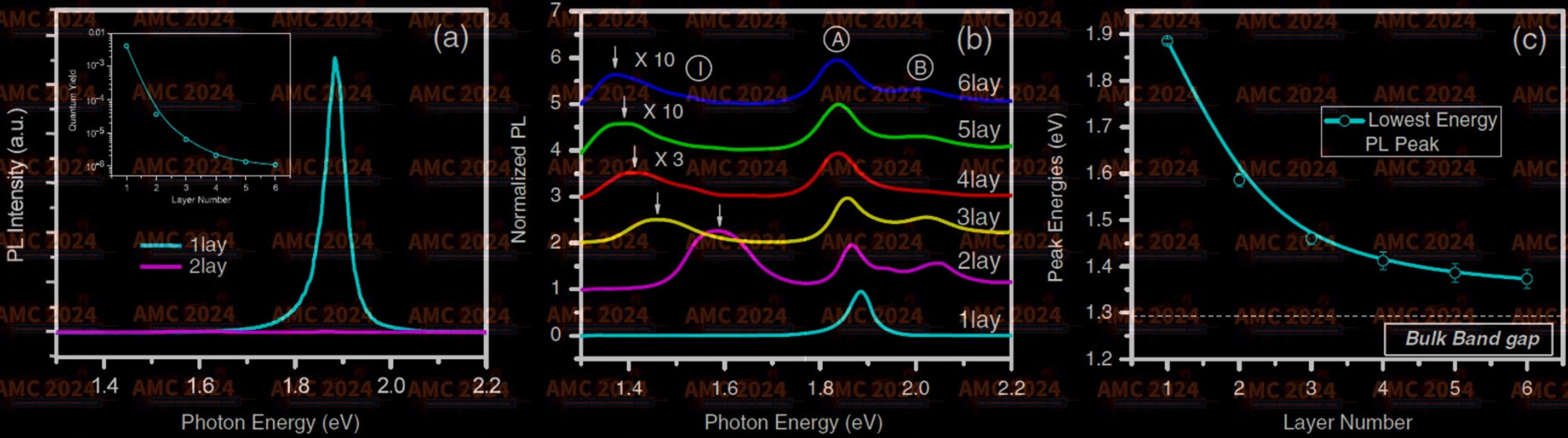
arXiv:1608.02043

Number of layers in 2D materials

a) PL spectra for mono- and bilayer MoS_2.
Inset: PL QY of thin layers for N = 1–6.

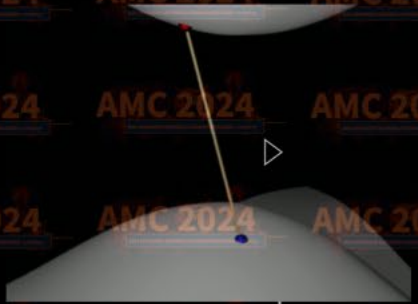
b) Normalized PL spectra by the intensity of peak A of thin layers of MoS_2 for N = 1–6. Feature I for N = 4–6 is magnified for clarity.

c) Band-gap energy of thin layers of MoS_2, inferred from the energy of the PL feature I for N = 2–6 and from the energy of the PL peak A for N = 1. The dashed line represents the (indirect) band-gap energy of bulk MoS_2.

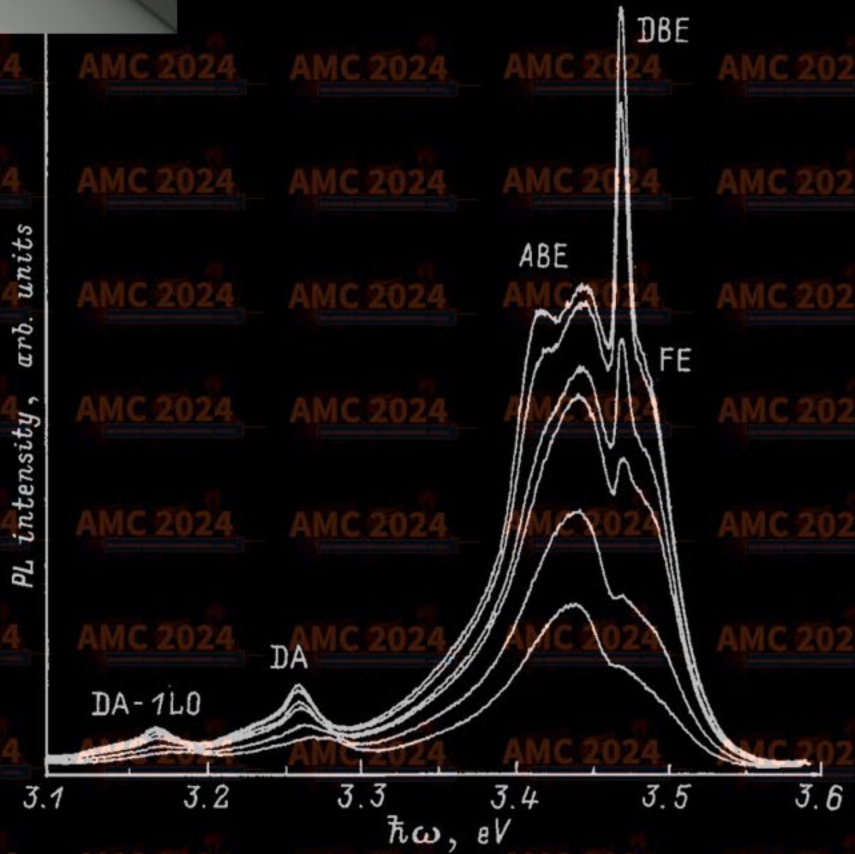


Phys. Rev. Lett. **105**, 136805 (2010)

Photoluminescence



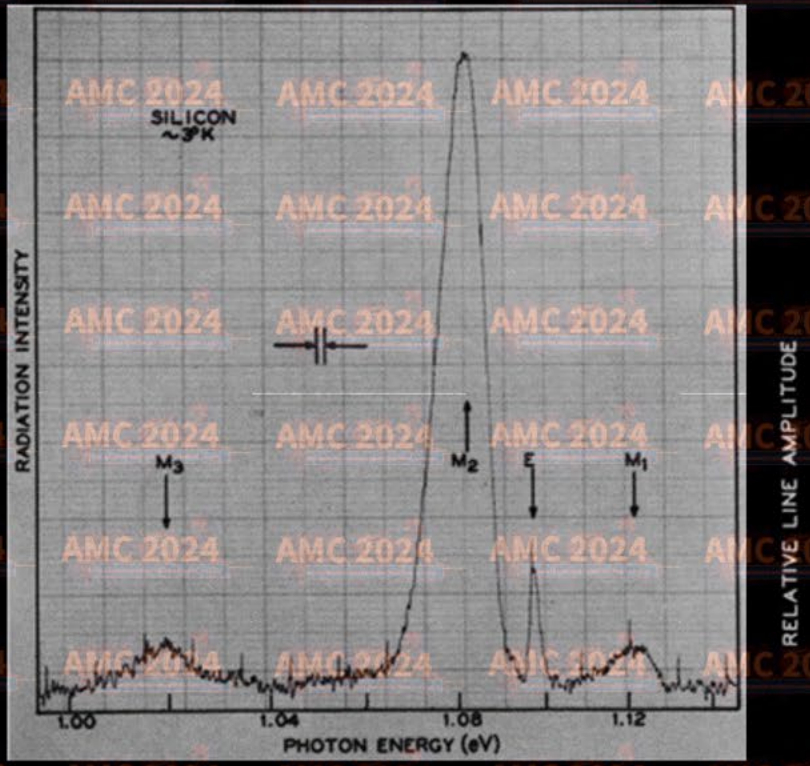
Free-exciton and bound-exciton luminescence in GaN



Low-temperature photoluminescence spectra of a sample of bulk GaN crystal at temperatures (from top to bottom) of 6, 10, 15, 20, 30, and 45 K. Excitation light comes from a DRSh- 250 lamp.

Semiconductors 33 (10), October 1999

Excitonic molecule luminescence in Si

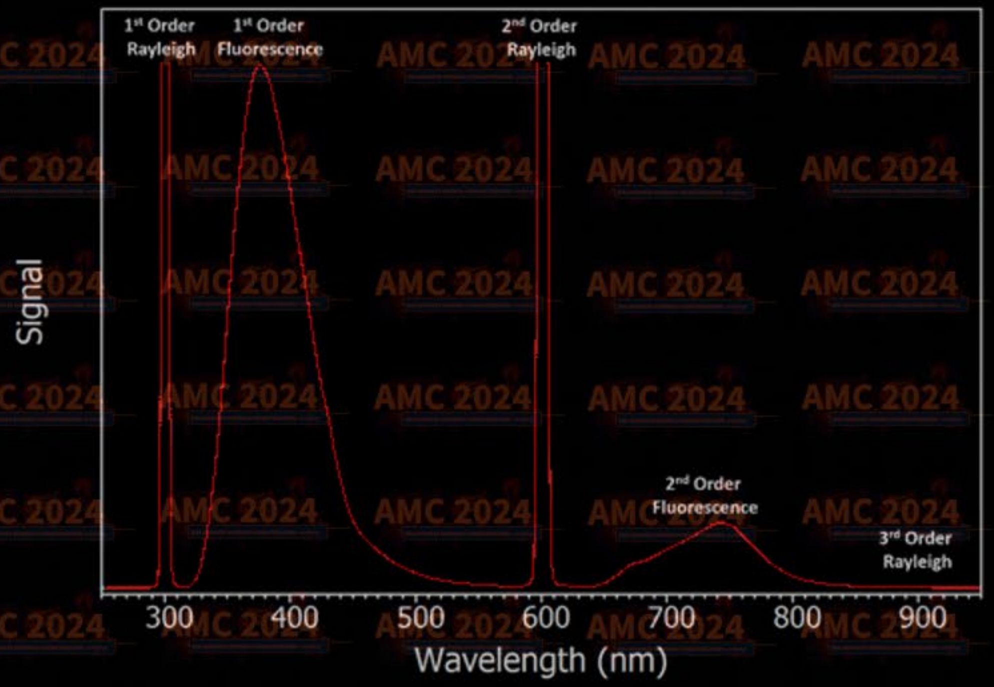


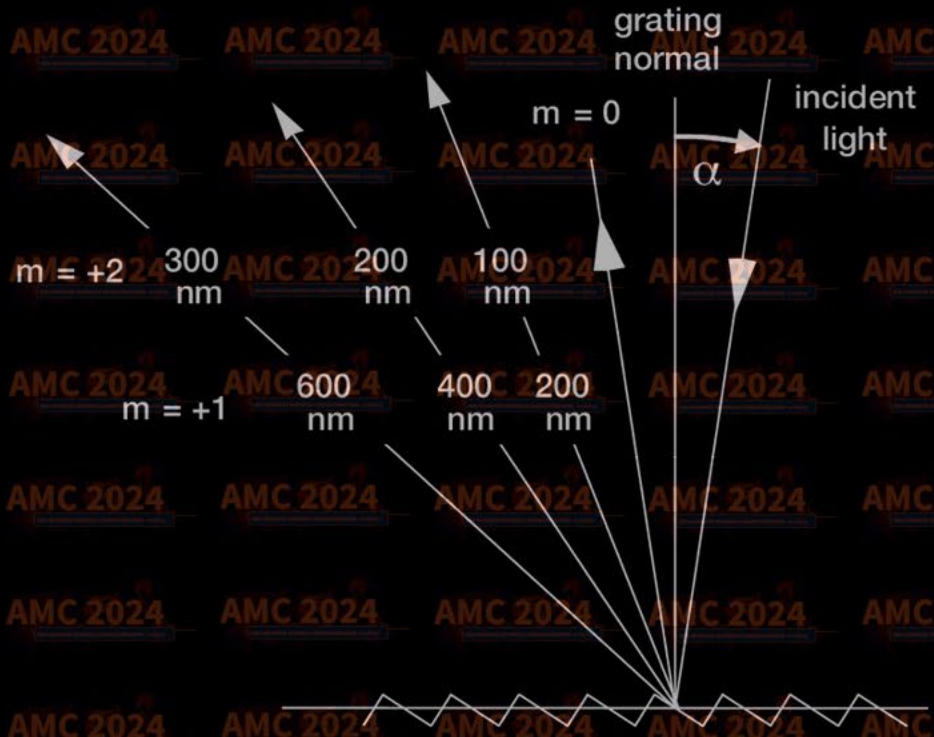
Spectrogram of a Si specimen at ~3 K. The horizontal axis is the energy of the emitted photons in eV. The vertical response is nearly proportional to the number of photons per unit energy interval. The specimen resistivity at room temperature was 9×10^3 Ω cm.

Phys. Rev. Lett. **17**, 860 (1966)

Photoluminescence

Pitfalls, artifacts, corrections …





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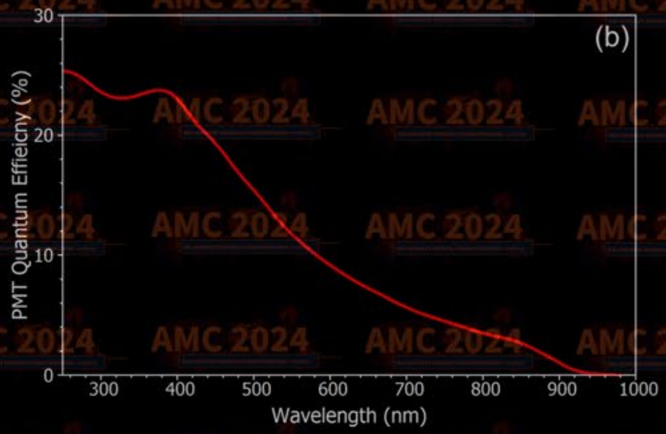
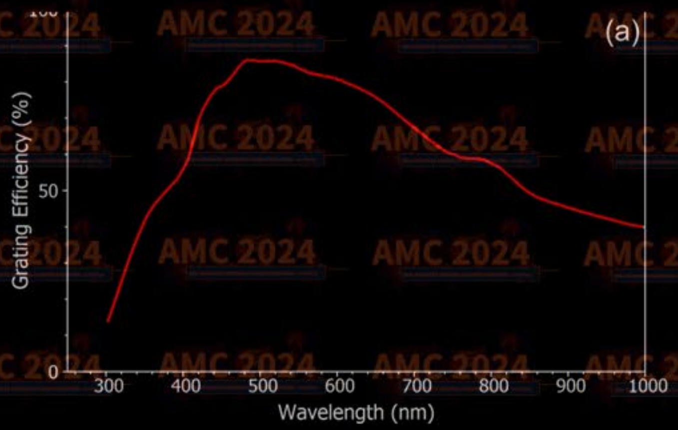
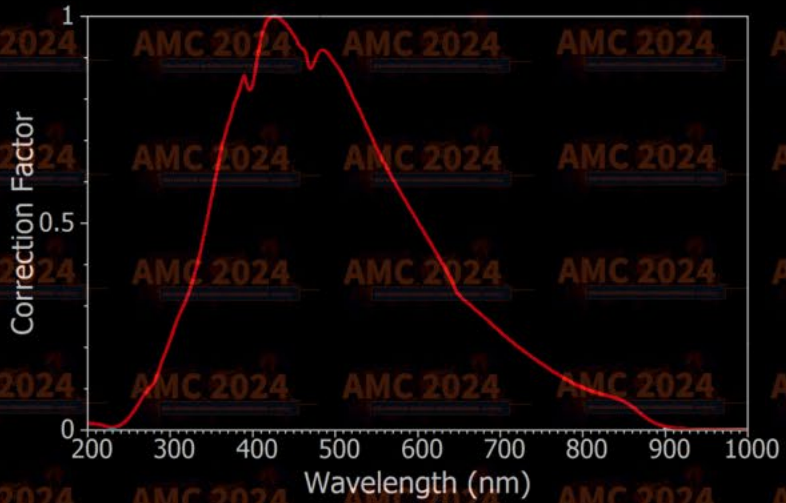
Photoluminescence

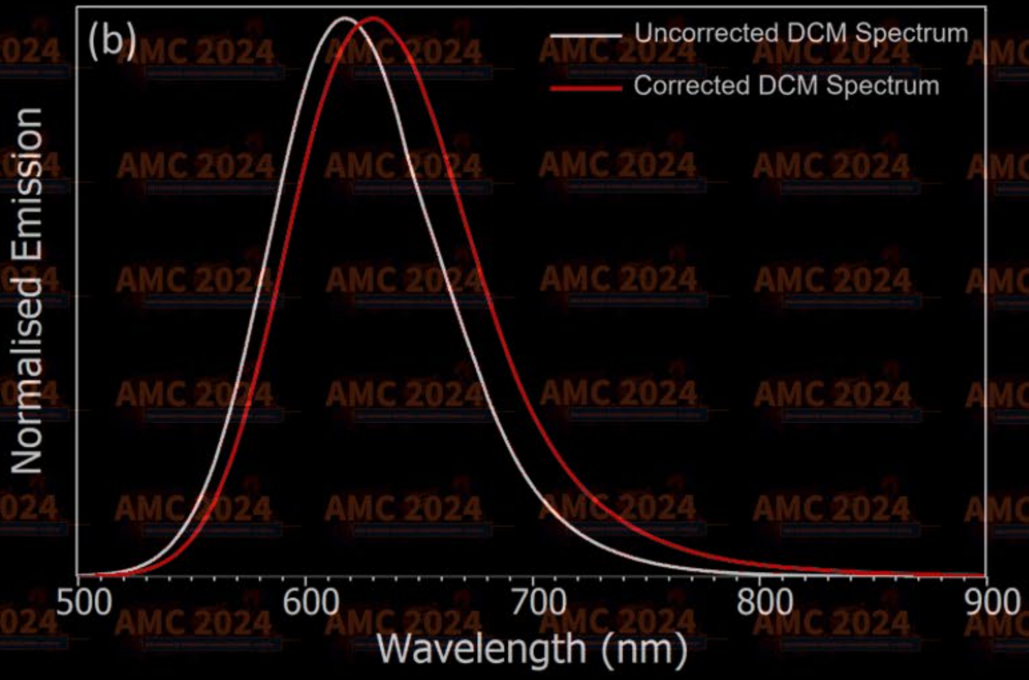
Pitfalls, artifacts, corrections …







Non-ideal components introduce spectral distortions



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Photoluminescence

Strengths:

- Very little to none sample preparation.
- Non destructive technique.
- Very informative spectrum.

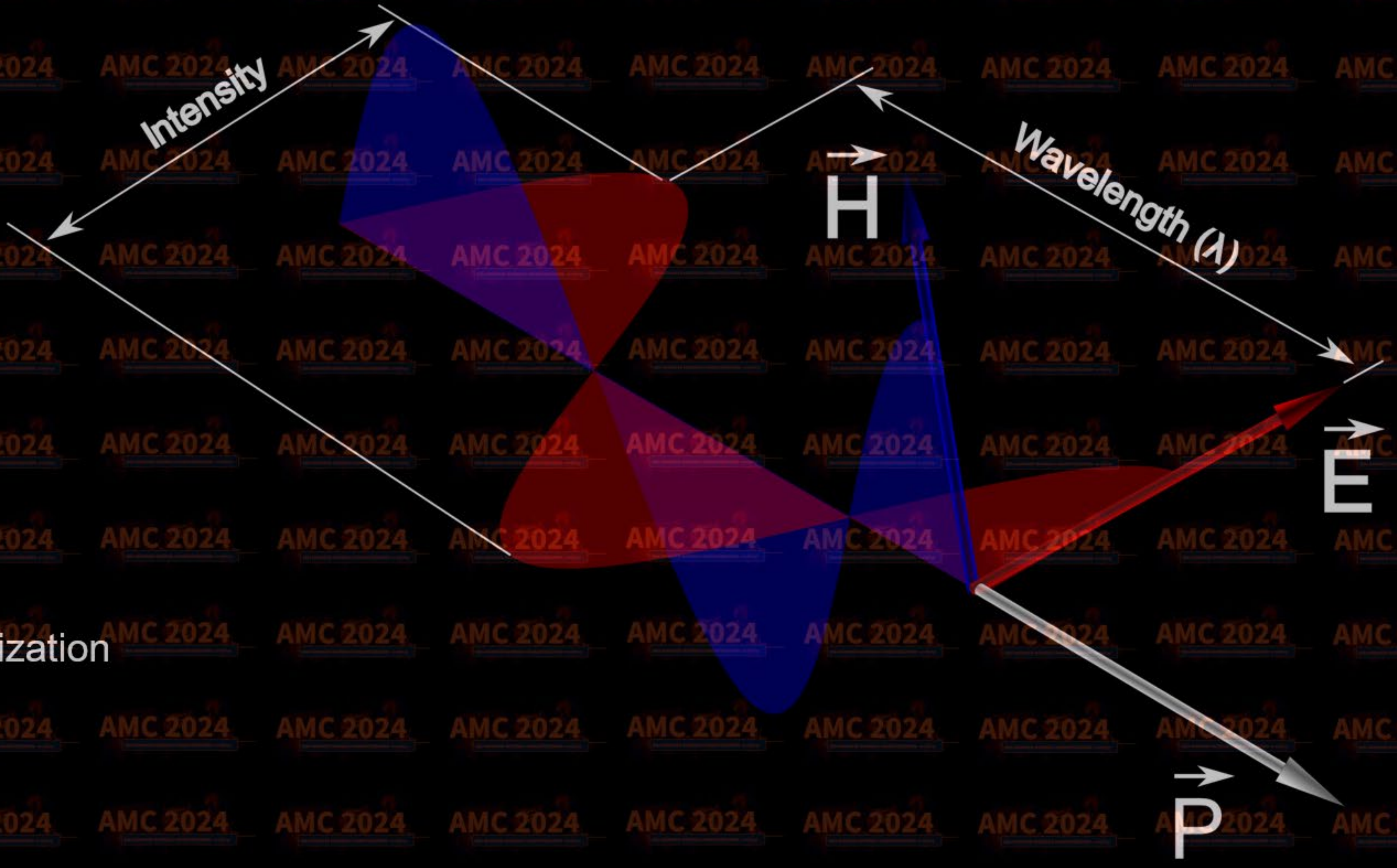
Limitations:

- Often requires low temperature.
- Data analysis may be complex.
- Many materials luminescence weakly.

Complementary techniques:

Ellipsometry, Modulation spectroscopies, Spectrophotometry, Raman.

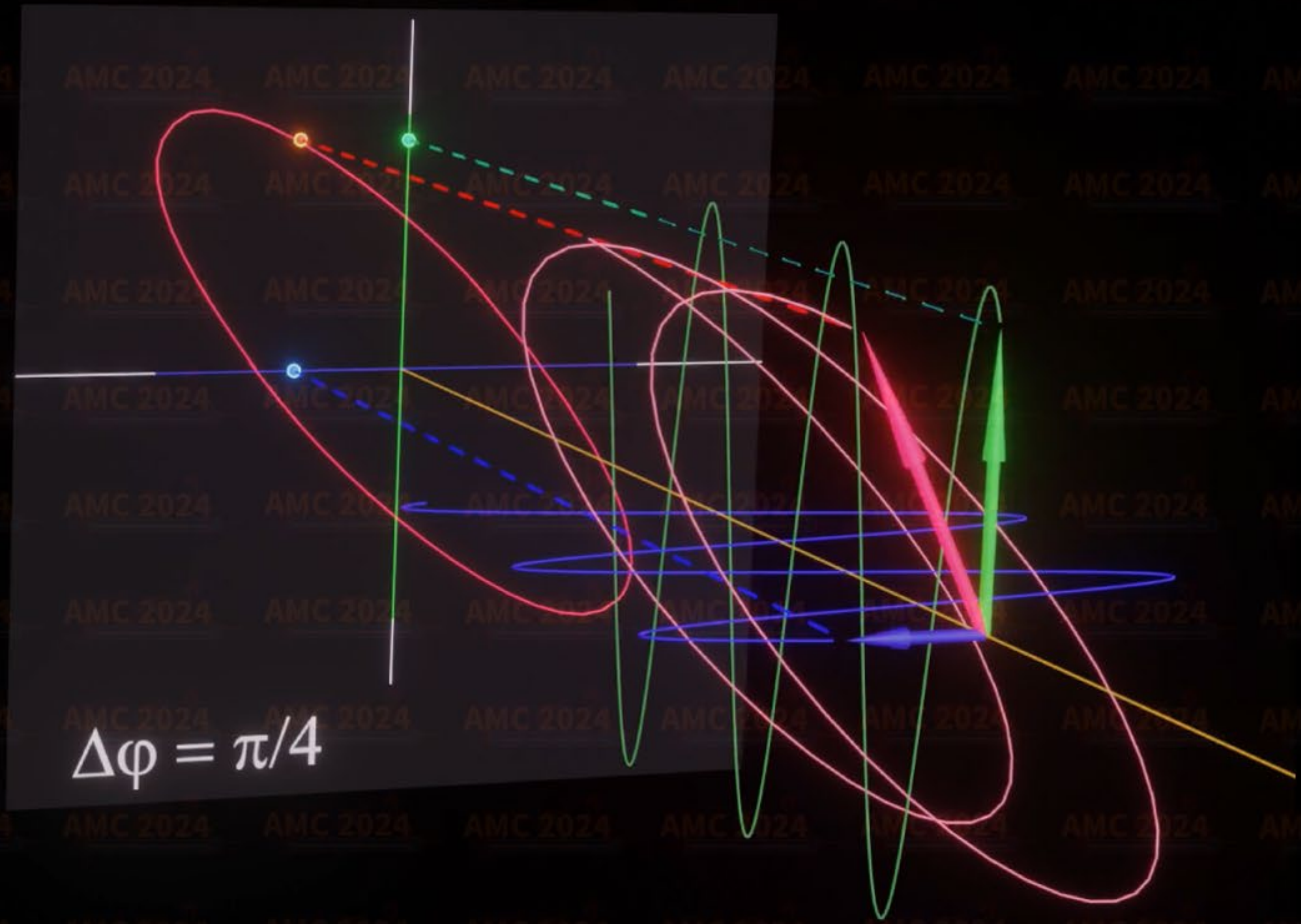
Light properties



- Direction of propagation
- Electric field direction or polarization
- Photon energy or wavelength
- Intensity

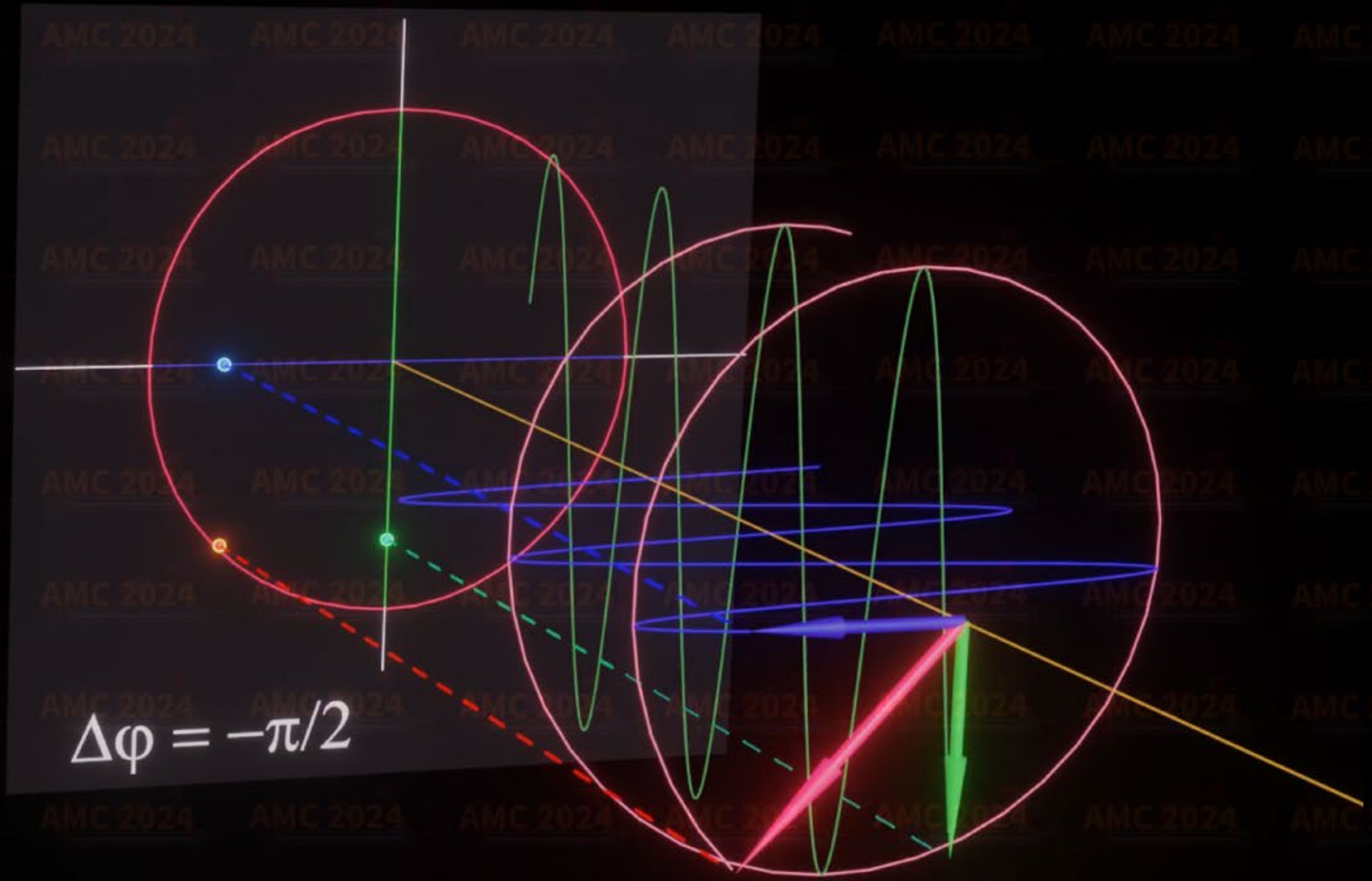
Polarization

Polarization

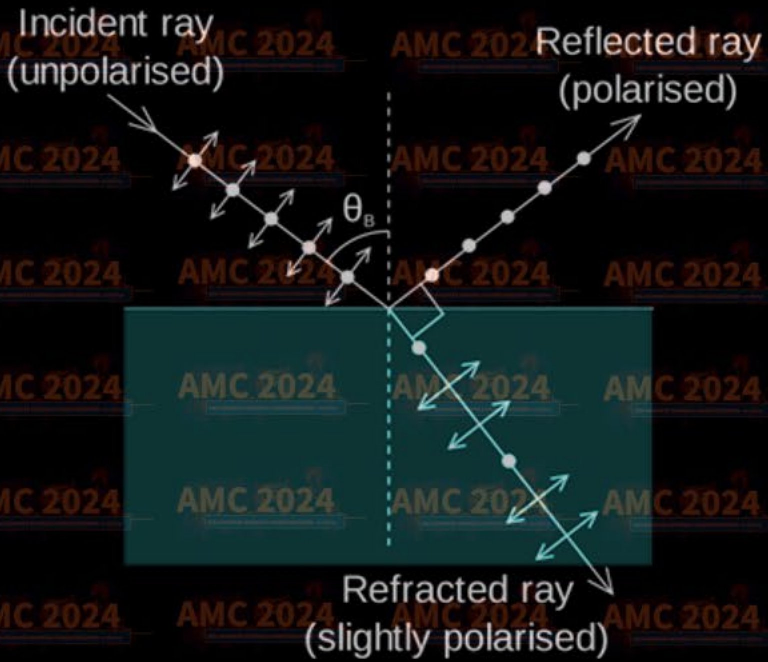


Polarization

Polarization



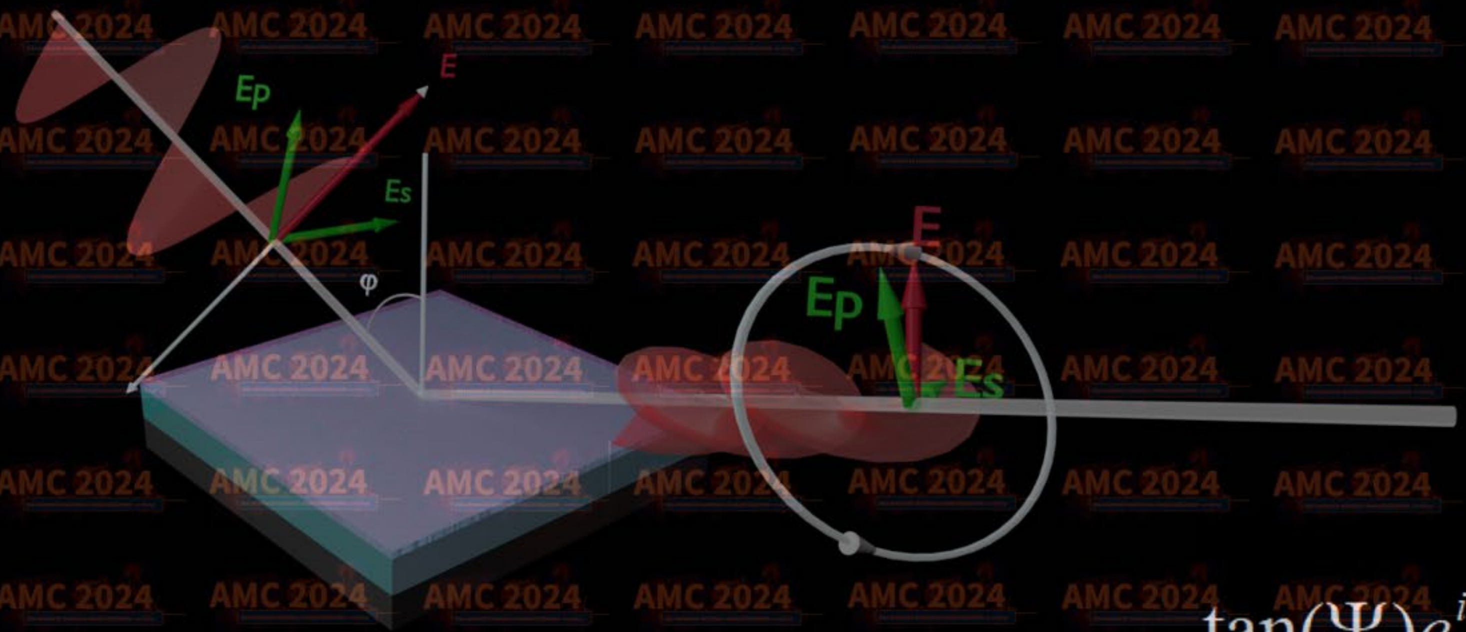
Polarization



Ellipsometry

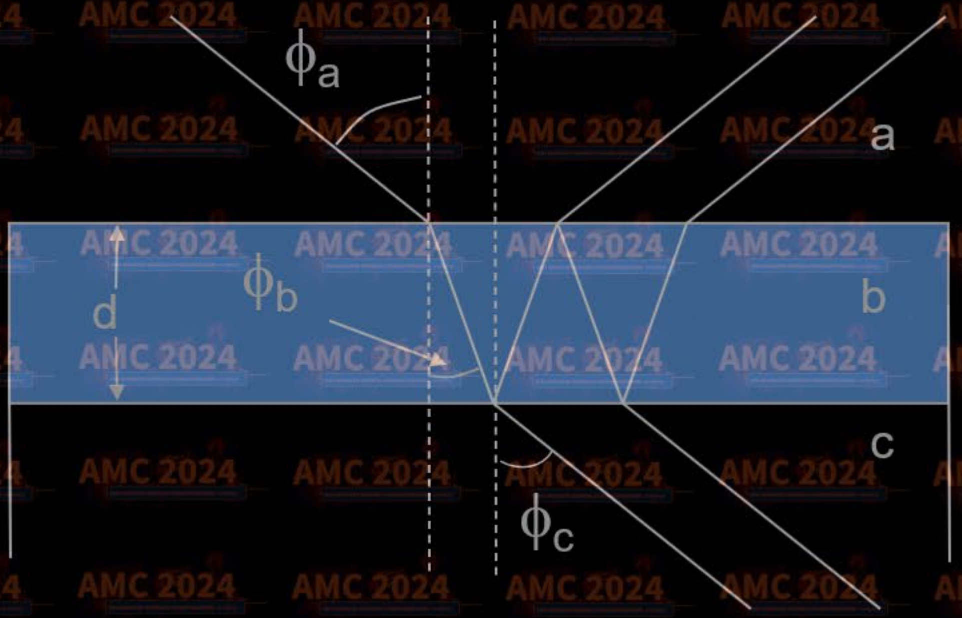
Basic principle:

The reflected light emerges from the surface elliptically polarized, i.e. its p and s polarization components are generally different in phase and amplitude.



$$\tan(\Psi)e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s}$$

Ellipsometry



$$\tilde{n} = n - ik \qquad \tilde{n}_1 \sin\phi_1 = \tilde{n}_2 \sin\phi_2$$

$$\tilde{r}_{12}^{p,s} = \frac{\tilde{n}_{2,1}\cos\phi_1 - \tilde{n}_{1,2}\cos\phi_2}{\tilde{n}_{2,1}\cos\phi_1 + \tilde{n}_{1,2}\cos\phi_2}$$

$$\tilde{R}_{p,s} = \frac{\tilde{r}_{ab}^{p,s} + \tilde{r}_{bc}^{p,s} e^{-2i\beta}}{1 + \tilde{r}_{ab}^{p,s}\tilde{r}_{bc}^{p,s} e^{-2i\beta}}$$

$$\beta = \frac{2\pi d}{\lambda}\tilde{n}_b \cos\phi_b$$

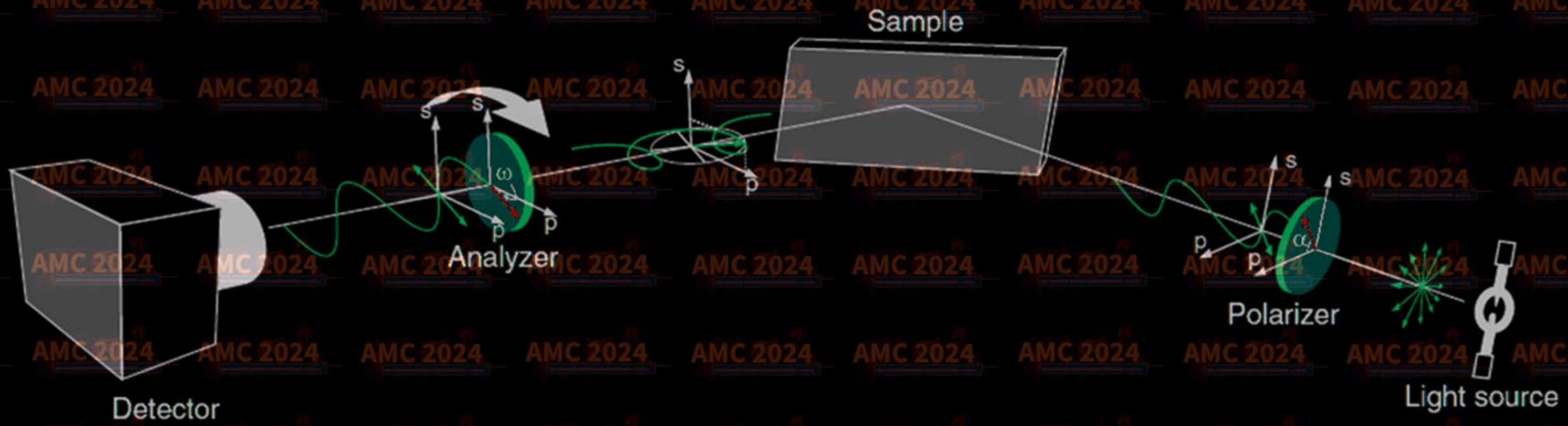
$$\tilde{R}_{p,s} = \frac{E_{p,s}^r}{E_{p,s}^i} e^{i(\delta_{p,s}^r - \delta_{p,s}^i)}$$

$$\tan(\Psi)e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} \Rightarrow \begin{cases} \tan(\Psi) = \dfrac{|\tilde{R}_p|}{|\tilde{R}_s|} \\ \Delta = \delta^r - \delta^i \end{cases}$$

Ellipsometry

What is measured:

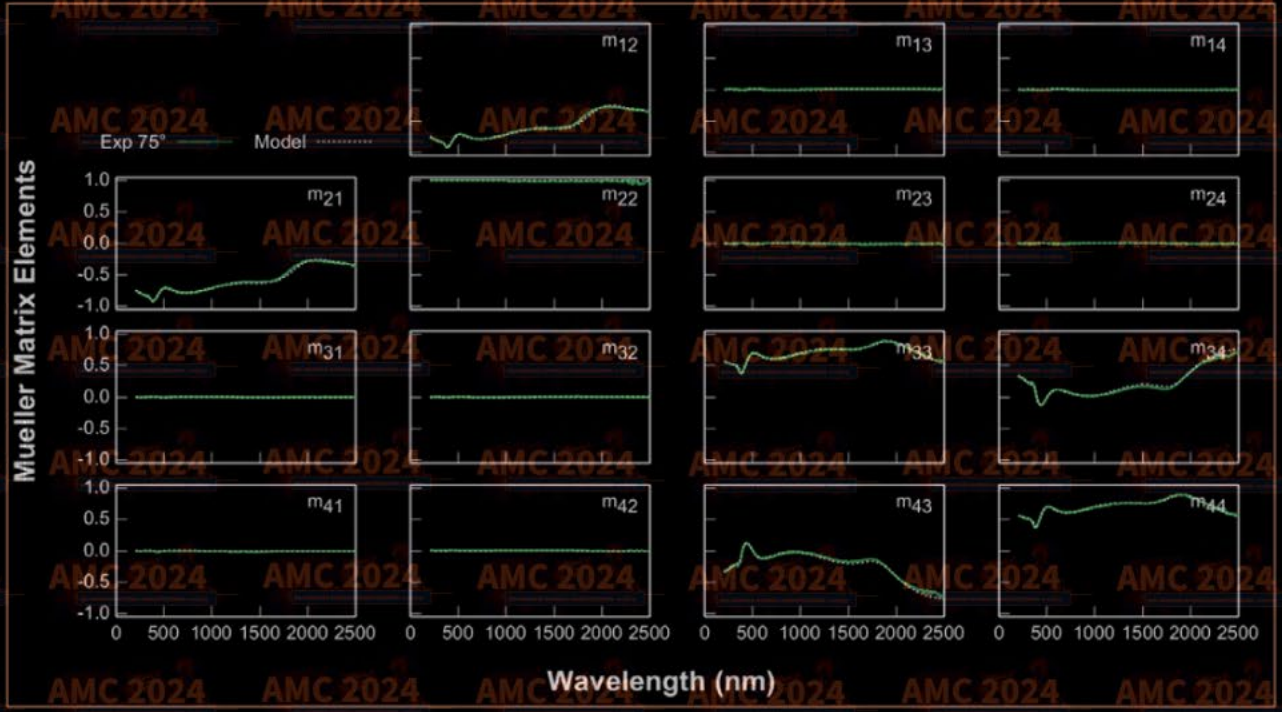
The changes in the polarization state of light upon reflection from a mirror like surface.



Ellipsometry

What is measured:

The changes in the polarization state of light upon reflection from a mirror like surface.



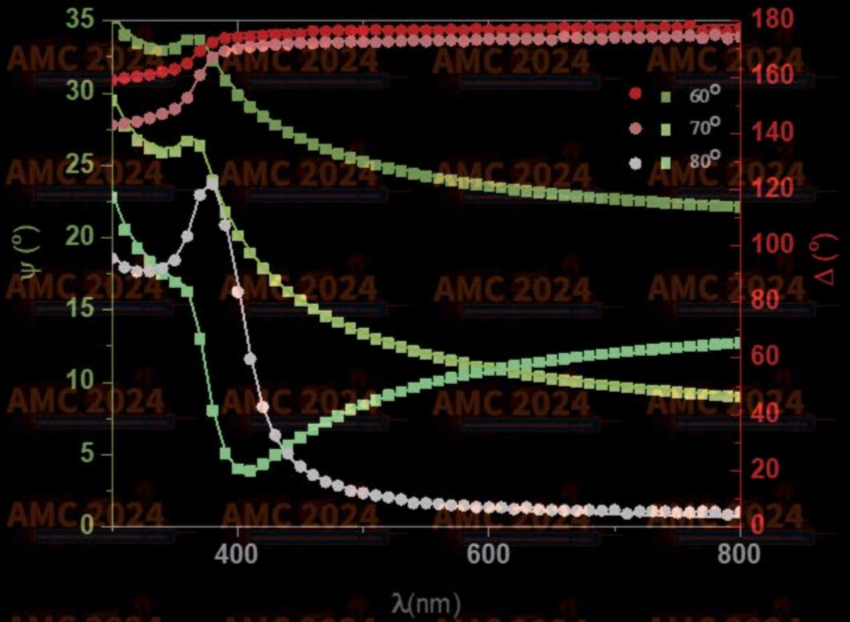
J.A. Woollam Co., Inc.

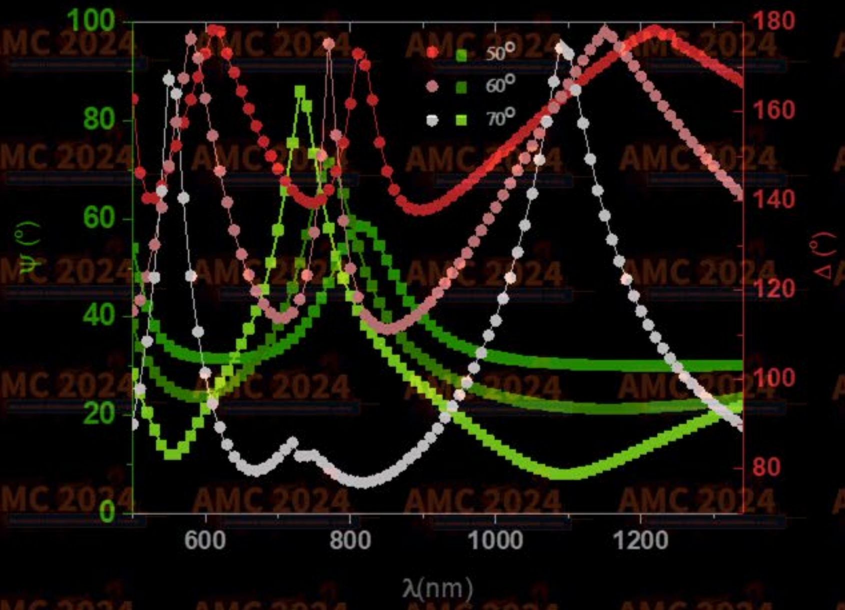
Ellipsometry

Applications

SiO_2	18.7 ± 0.2 Å
Si	

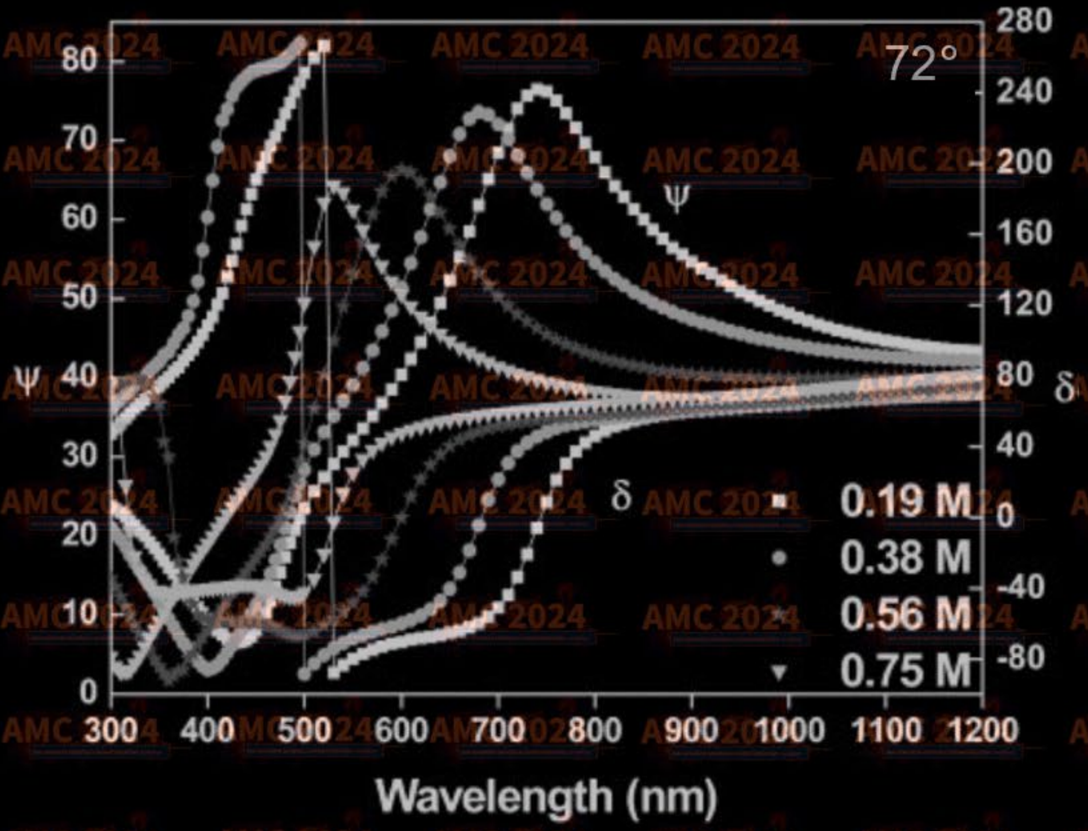
SiO_2	4923.1 ± 0.2 Å
Si	





Ellipsometry

Applications



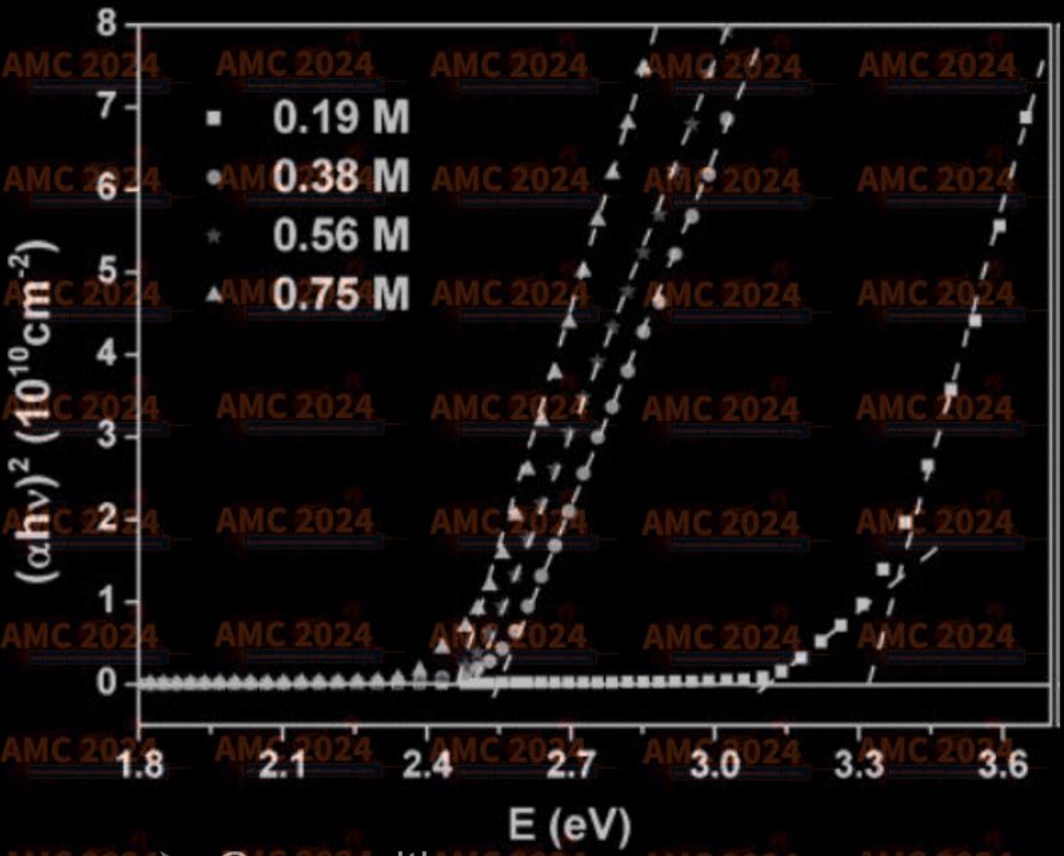
[NH4OH] (M)	Thickness (nm)	Roughness (nm)	ZnS (%)	Band-gap (eV)
0.19	42.12	23.77	99.7	3.49
0.38	73.79	7.15	45.5	2.52
0.56	50.89	5.94	32.3	2.45
0.75	18.59	4.54	5.2	2.43

Ellipsometric $\Psi(\lambda)$ and $\Delta(\lambda)$ spectra of $Cd_{1-x}Zn_xS$ thin films deposited under the different concentration of ammonia: 0.19, 0.38, 0.56, and 0.75 M

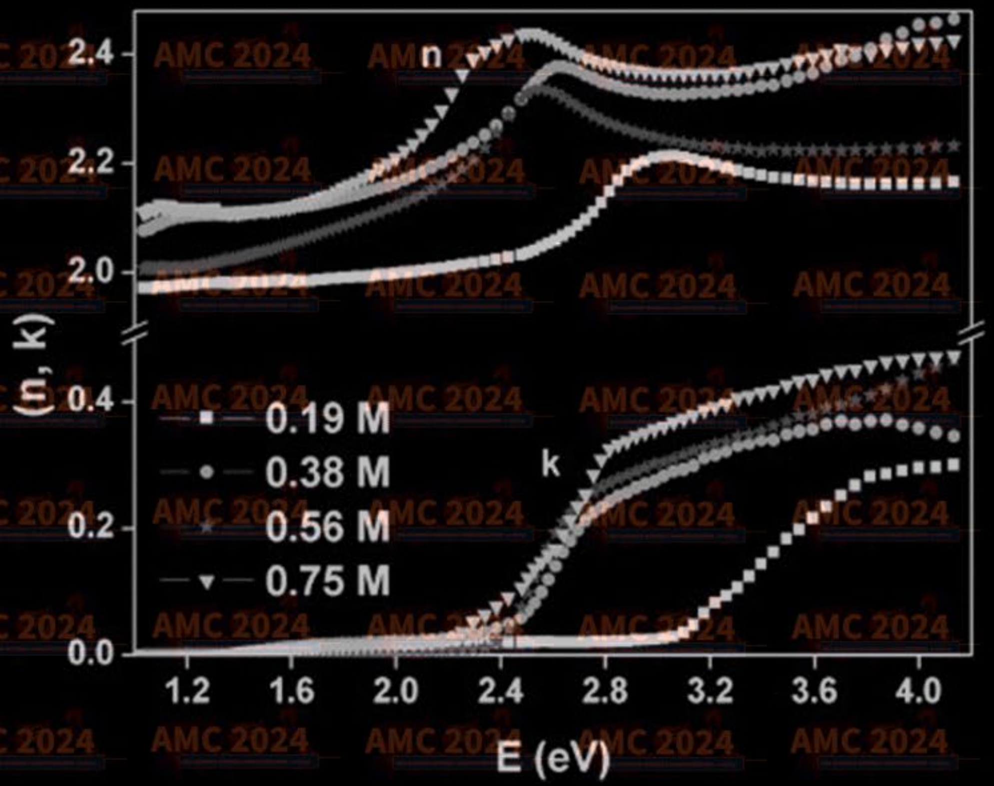
Jpn. J. Appl. Phys. 49 (2010) 081202

Ellipsometry

Applications



- Composition
- Surface roughness
- Film thickness
- Band gap energy
- Optical constants (dielectric function)



Jpn. J. Appl. Phys. 49 (2010) 081202

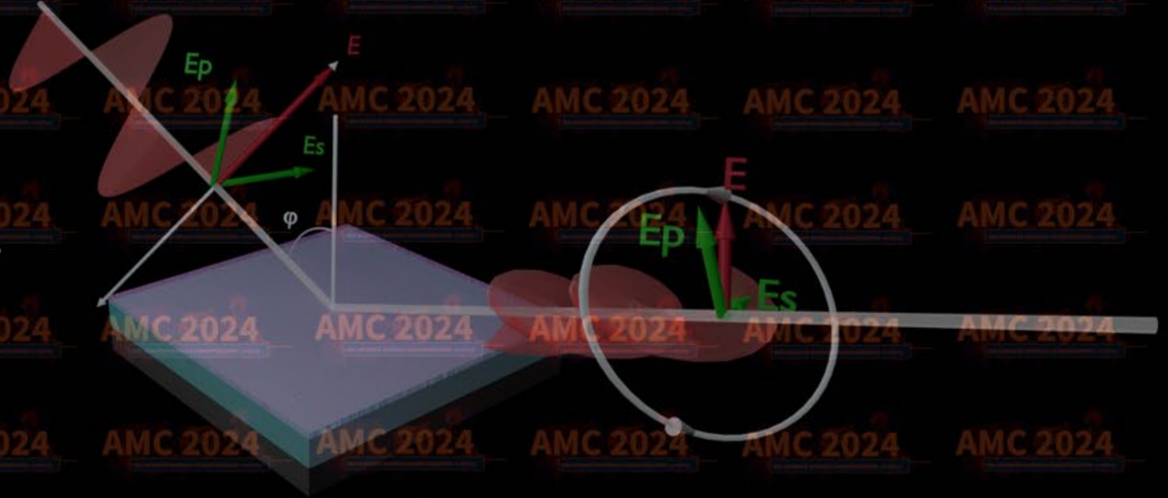
Ellipsometry

Limitations:

- Flat and parallel surface and interfaces with measurable reflectivity.
- A realistic physical model of the sample is required to obtain most useful information.

Strengths:

- Fast.
- Measures a ratio of two intensity values and a phase.
  - Highly accurate (even in low light levels).
  - No reference sample necessary.
  - Not susceptible to scatter, lamp or purge fluctuations.
  - Increased sensitivity, especially to ultrathin films (<10nm).
- Can be used in-situ.



Complementary techniques:

PL, Modulation spectroscopies, X-Ray Photoelectron Spectroscopy, Secondary Ion Mass Spectroscopy, XRD, Hall effect.

Optical microscopy

Von Leeuwenhoek microscope ca. late 1600's

Early microscope
"The Far Side" by Gary Larson.

Hooke microscope ca. 1670

Hand-held microscope ca. early 1700's

British microscope ca. 1850

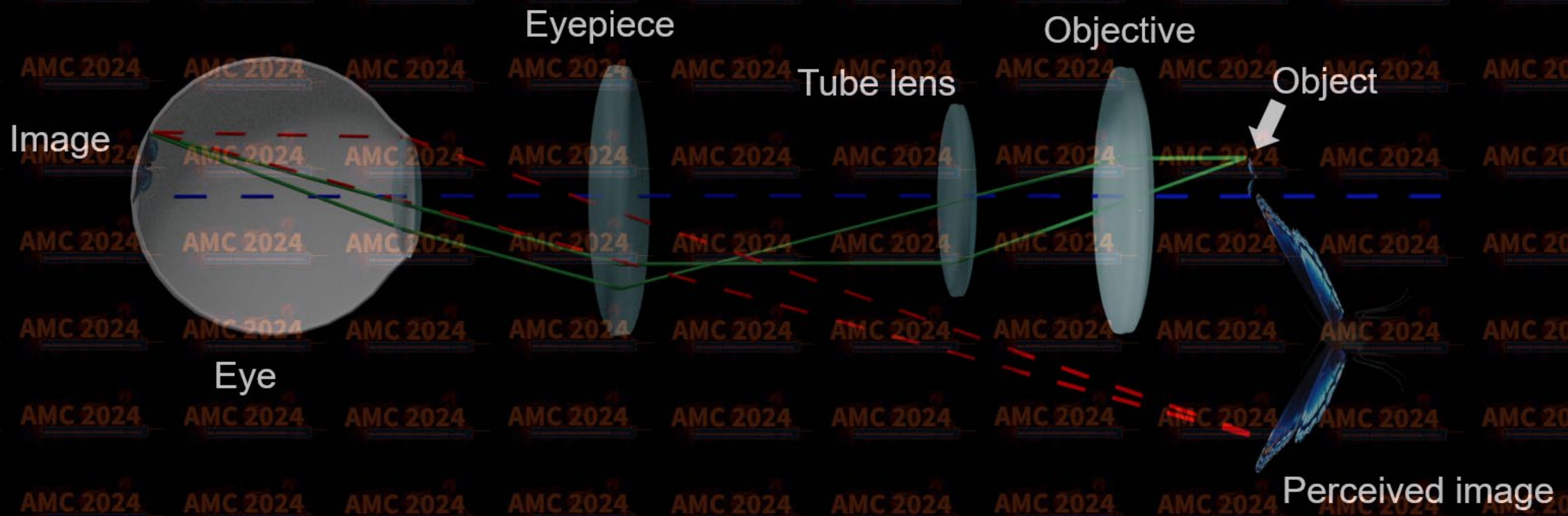
Zeiss microscope ca. 1930

Modern scientific microscope

ZEISS We make it visible.

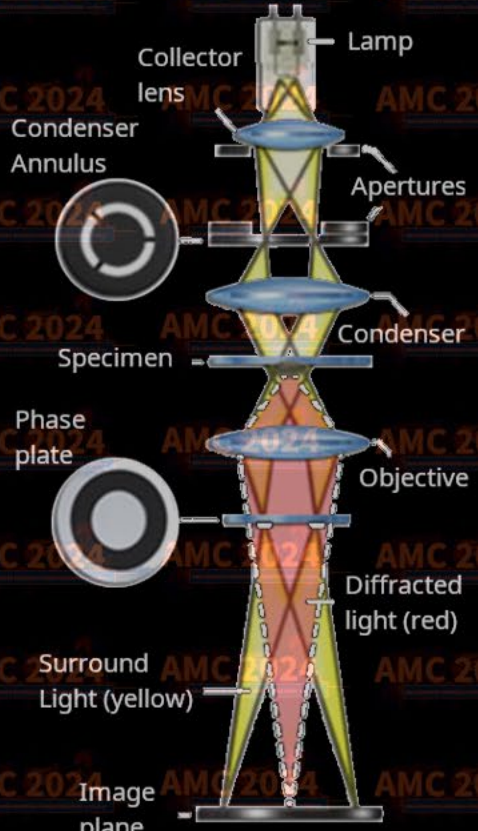
Optical microscopy

"Conventional" Optical Microscopy

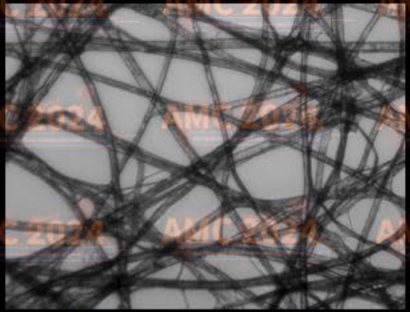


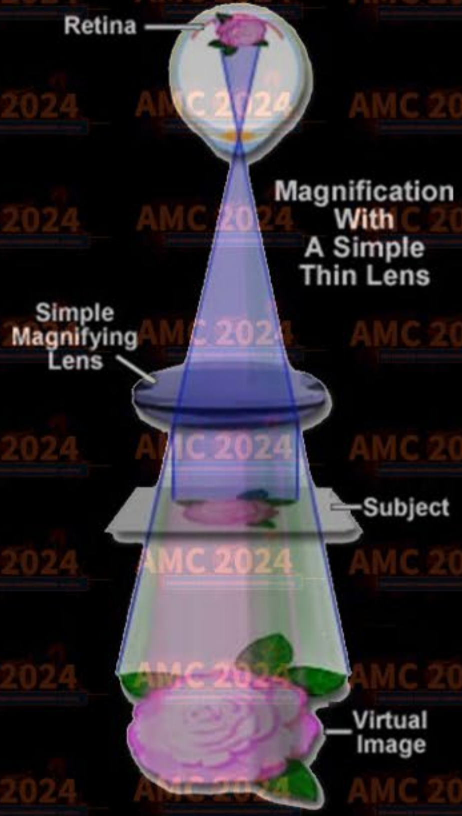
Optical microscopy

Phase contrast

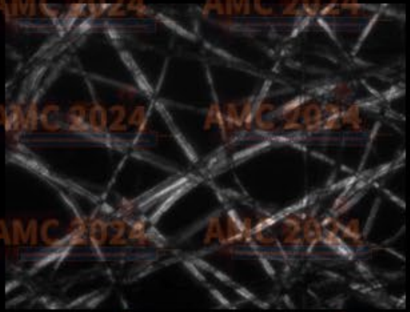


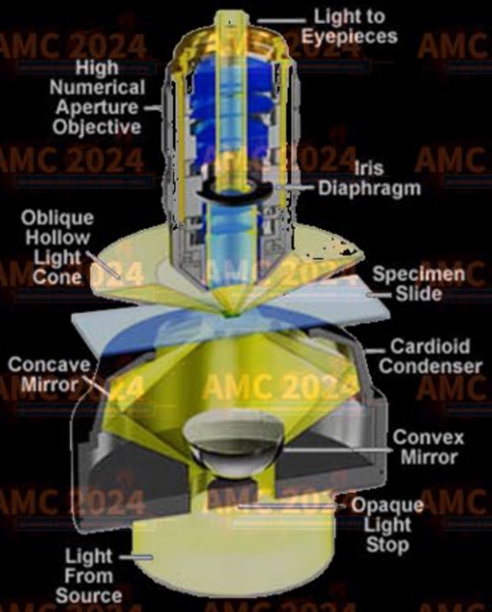
Bright field



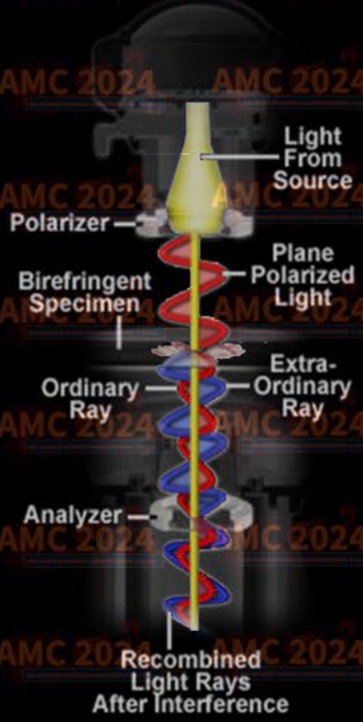


Dark field





Polarizing



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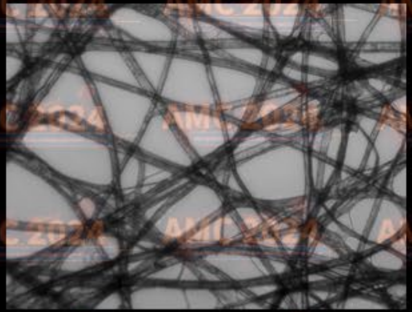
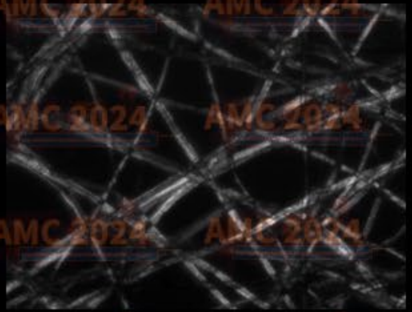
Optical microscopy

Phase contrast

Bright field

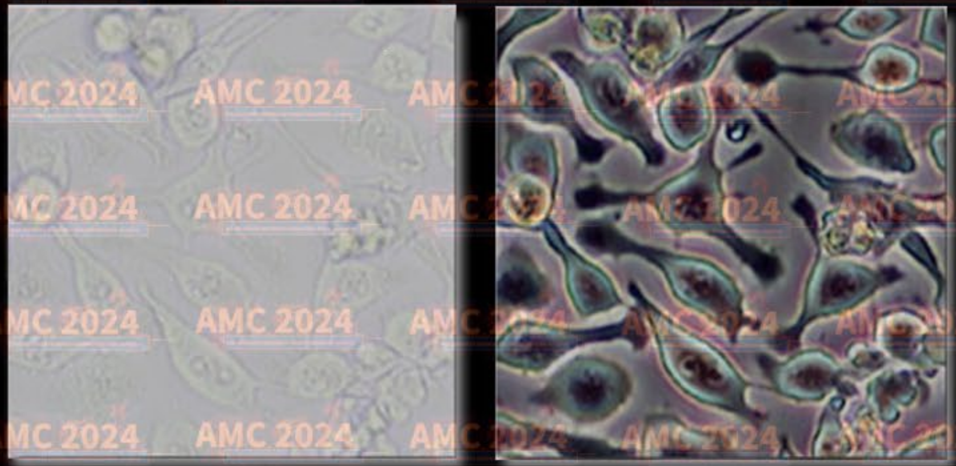


Dark field

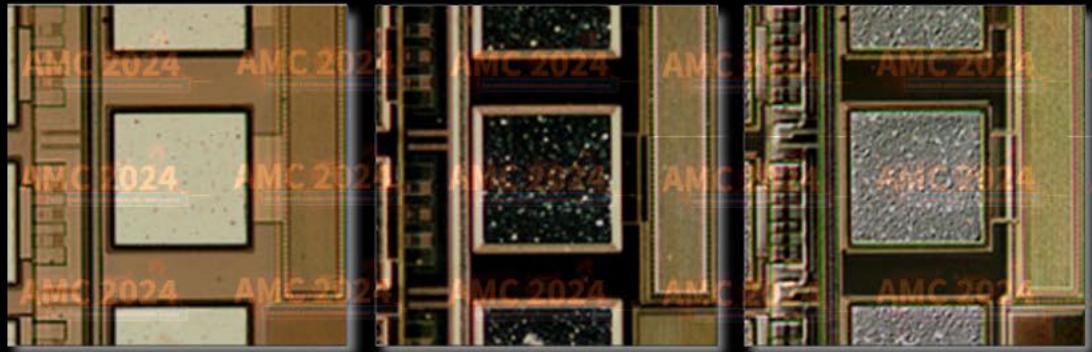


Polarizing

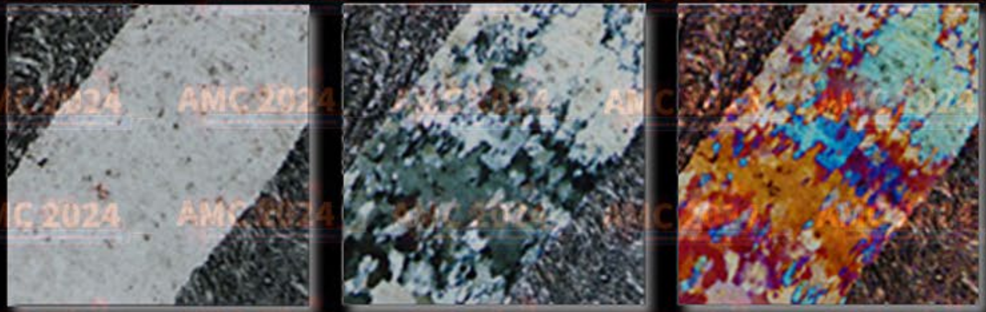
Living Cells in Brightfield and Phase Contrast



Integrated Circuit in Brightfield, Darkfield, and DIC with Reflected Light



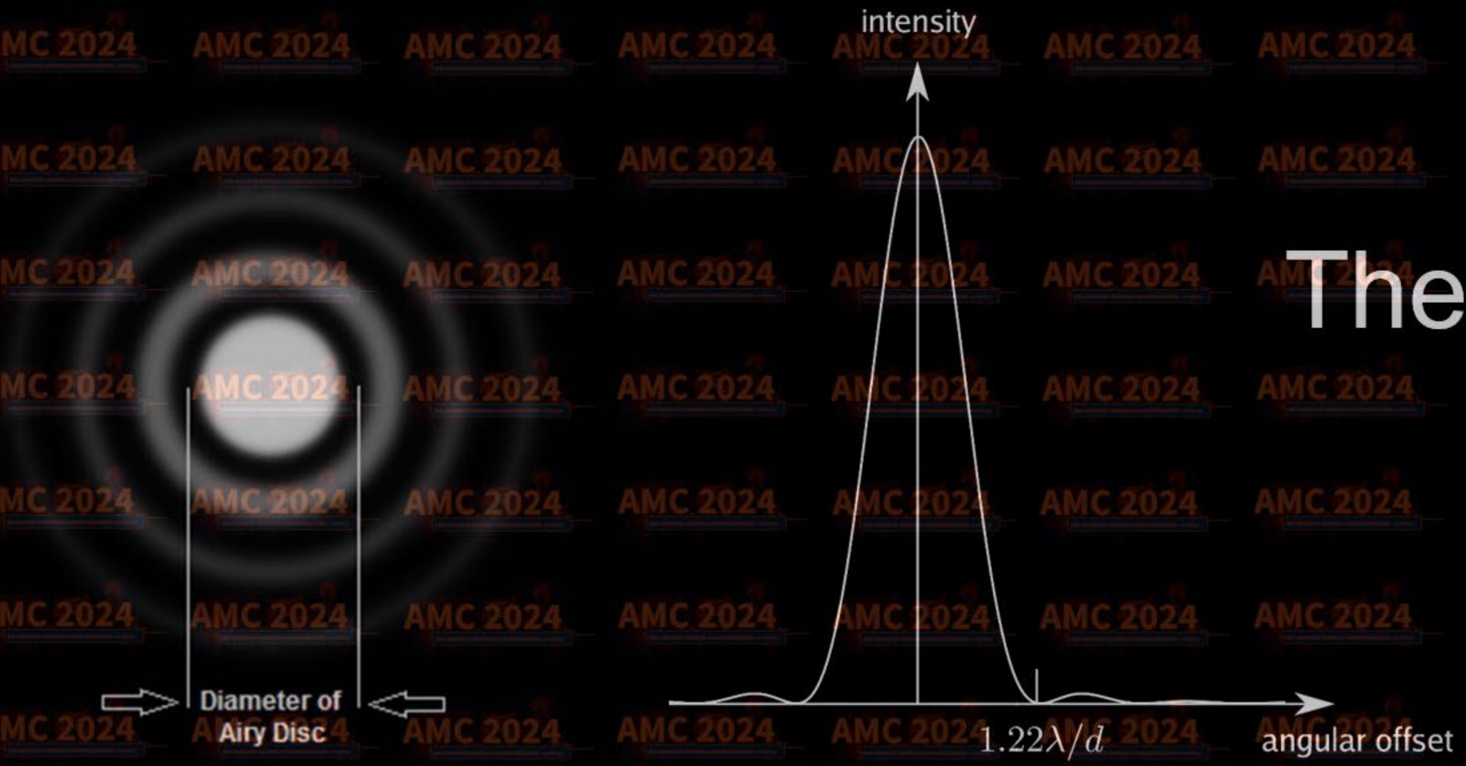
Phyllite Thin Section in Polarized Light



Resolution

- But how small a thing can we see?

Lateral resolution



The Airy pattern

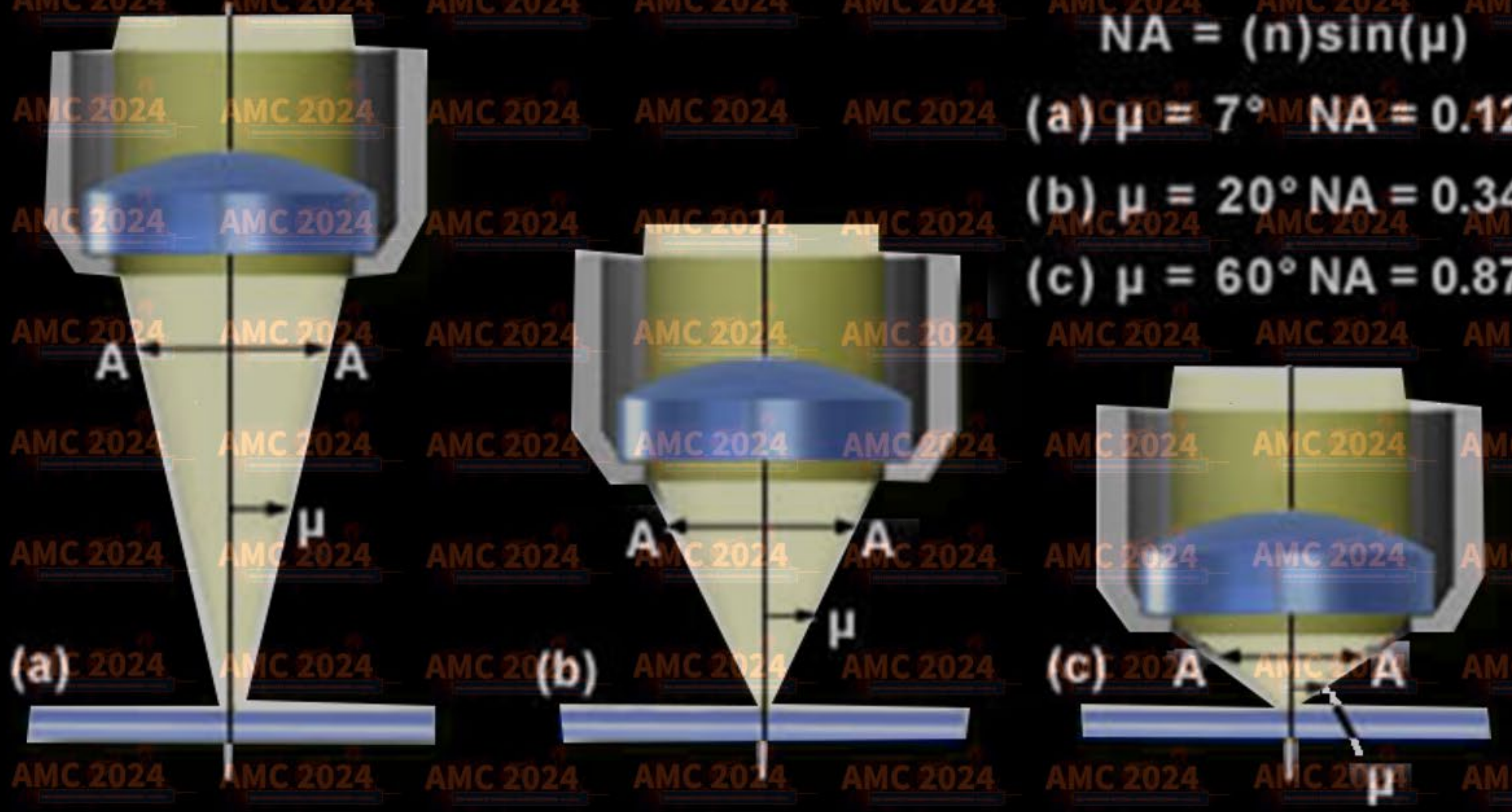
Lateral resolution

$NA = (n)\sin(\mu)$

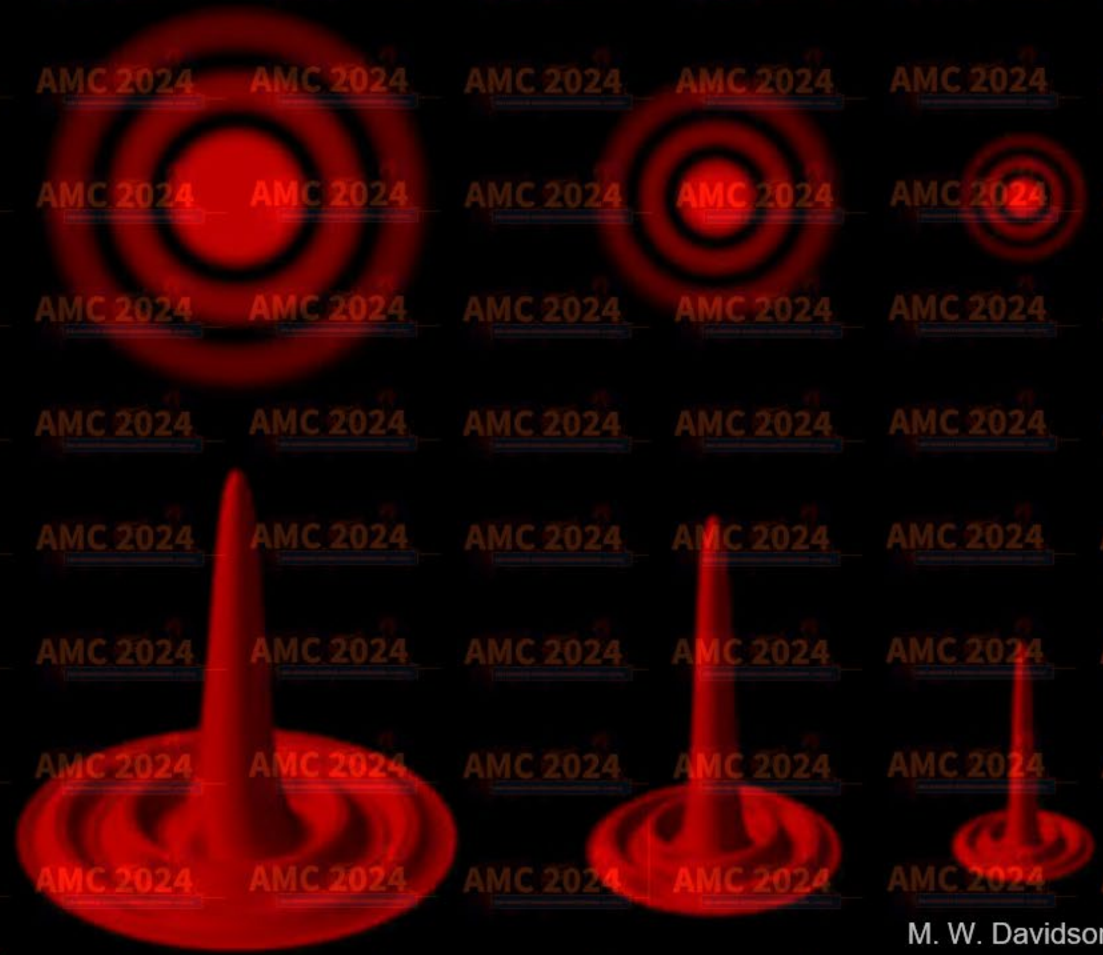
(a) $\mu = 7°$ NA = 0.12

(b) $\mu = 20°$ NA = 0.34

(c) $\mu = 60°$ NA = 0.87



Lateral resolution

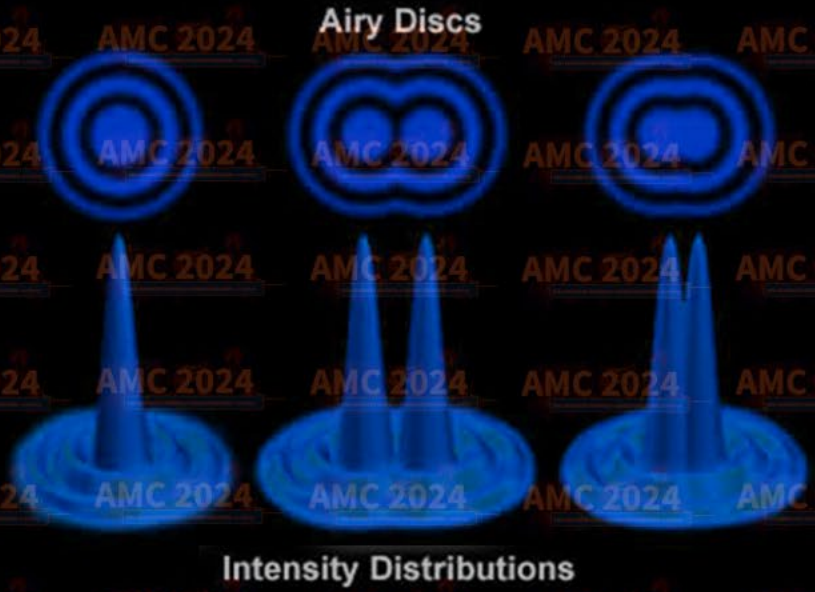


M. W. Davidson and M. Abramowitz

Numerical aperture →

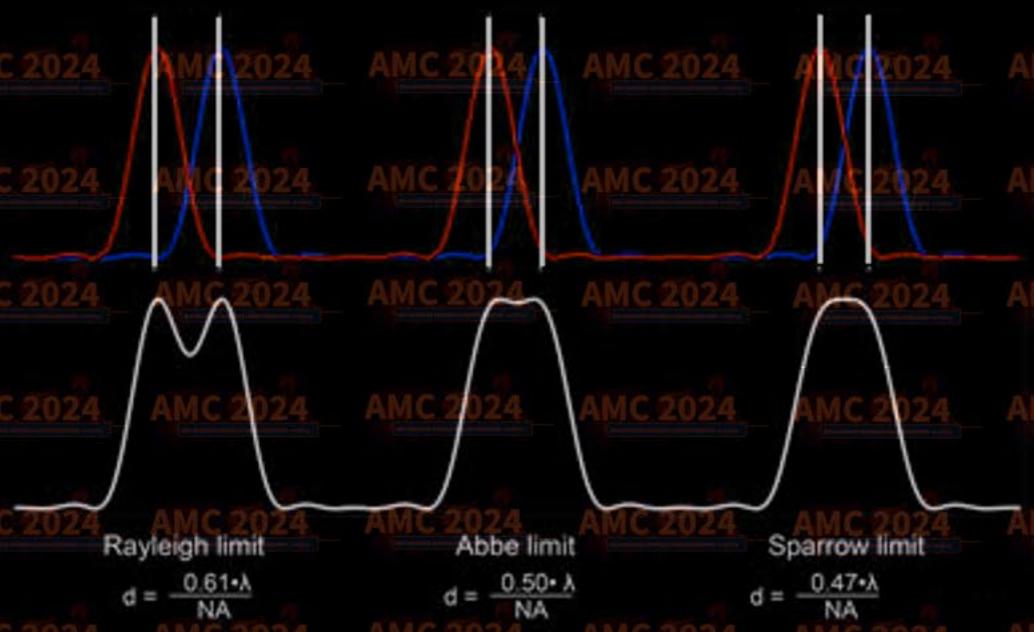
Lateral resolution

Resolution



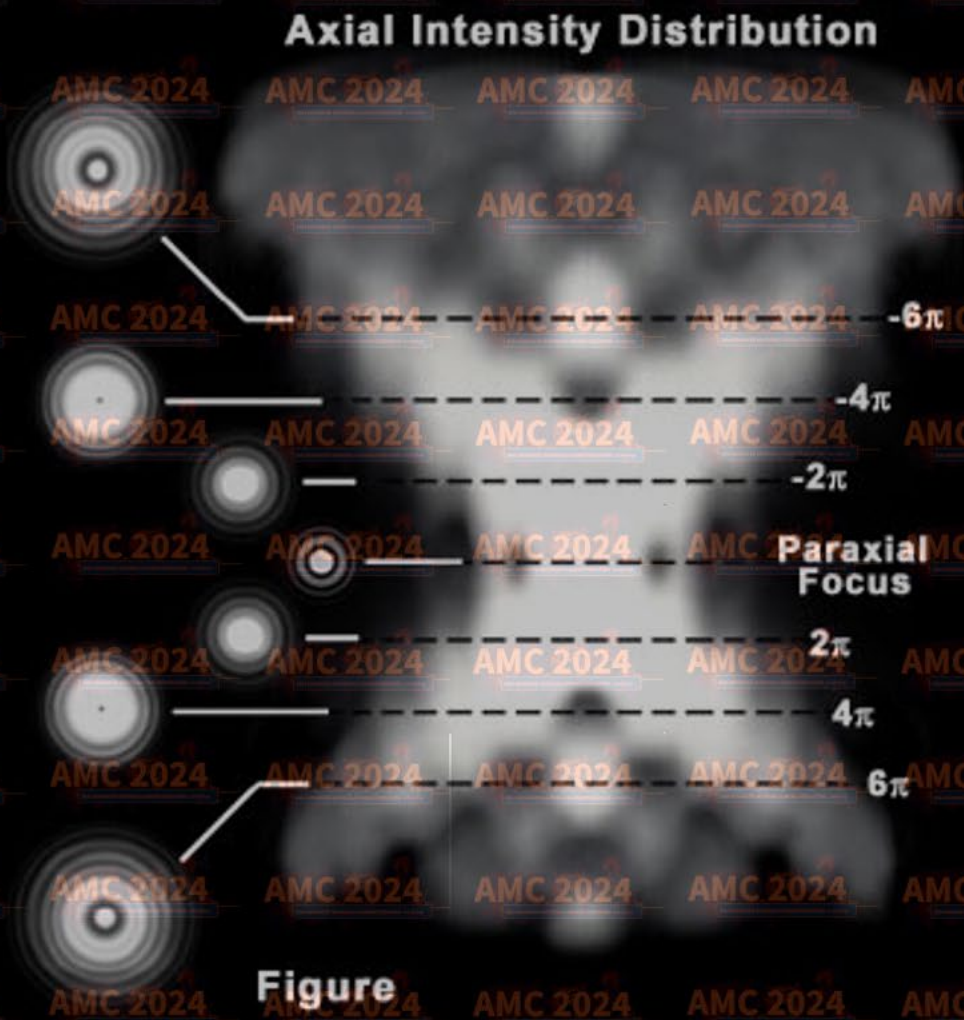
$$d \approx \frac{0.61\lambda}{NA}$$

Rayleigh criterion

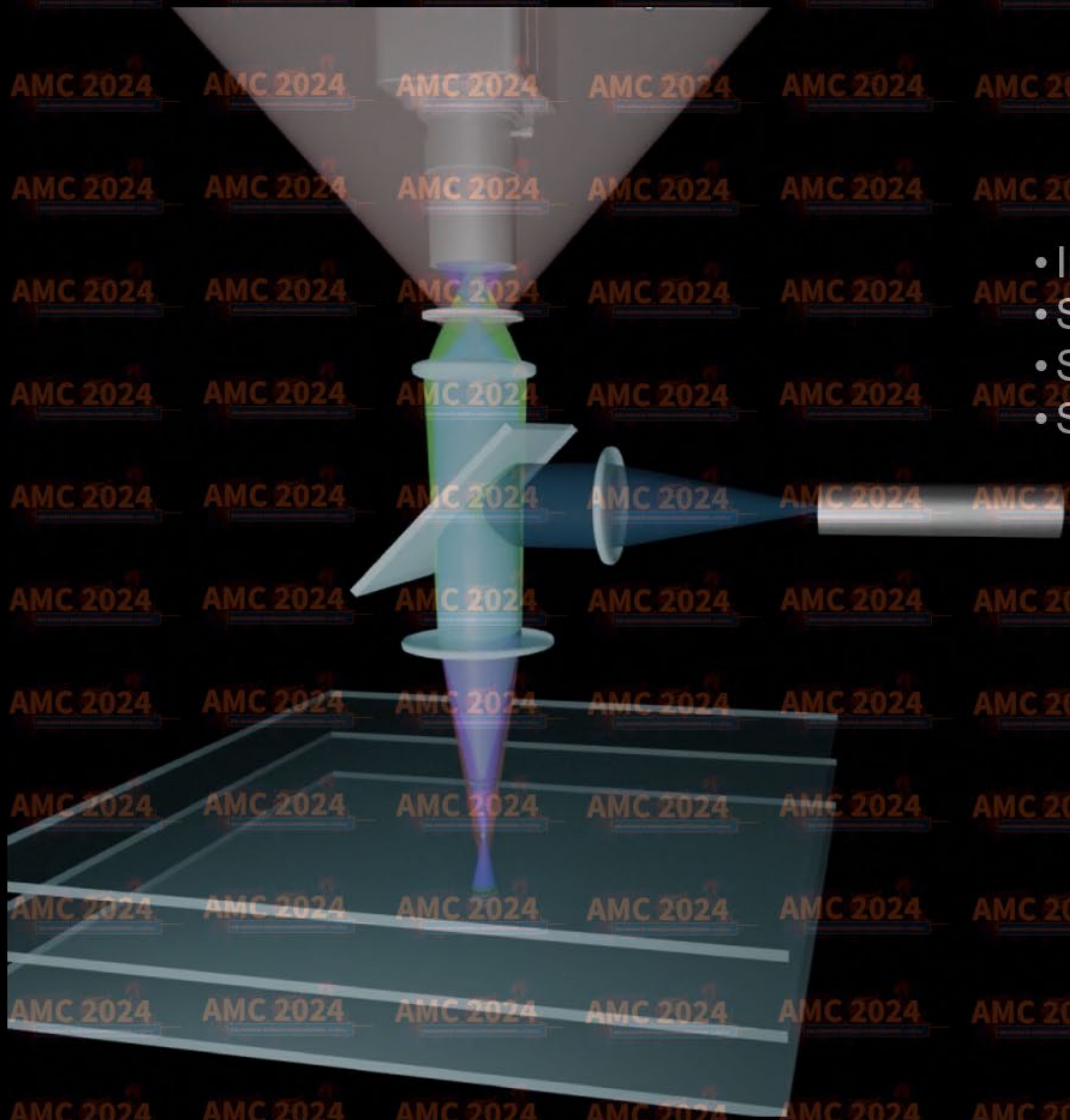


Abbé criterion

Depth resolution



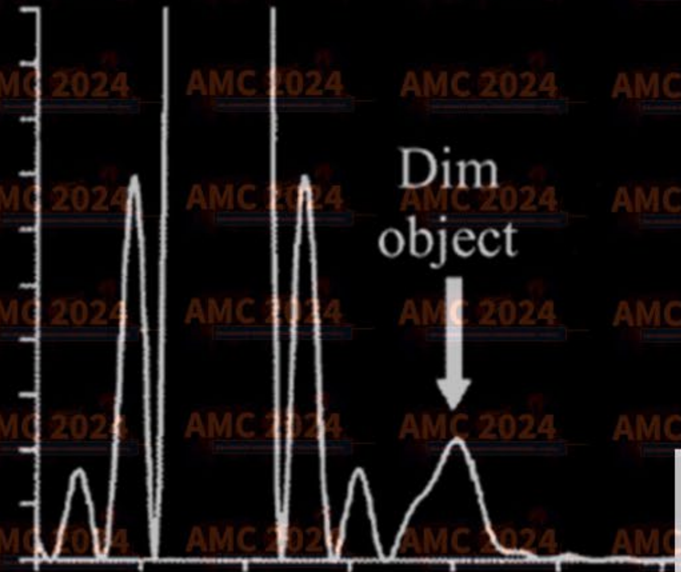
Confocal microscopy

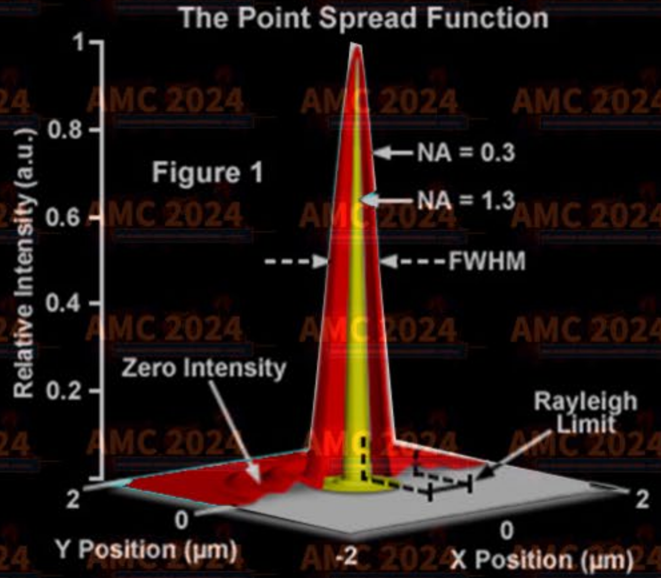


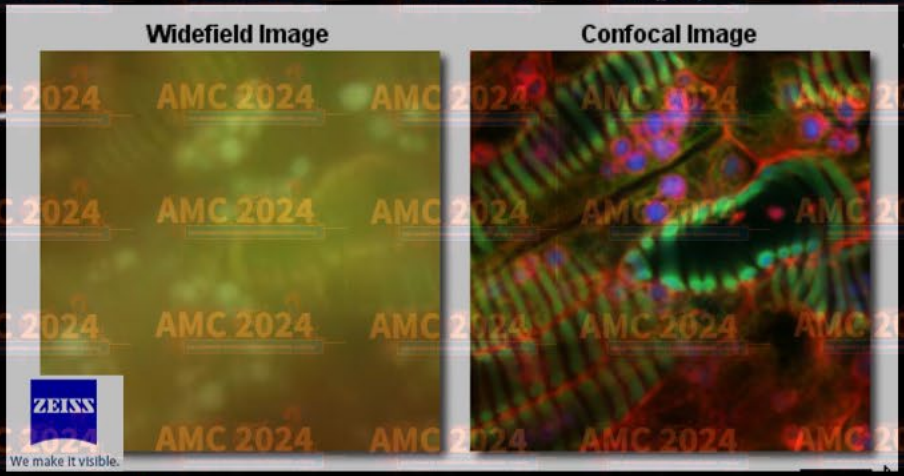
- Increased contrast => 200:1.
- Slightly increased in plane resolution (1.5 x)
- Significantly increased resolution along the optical axis.
- Scanning image formation.

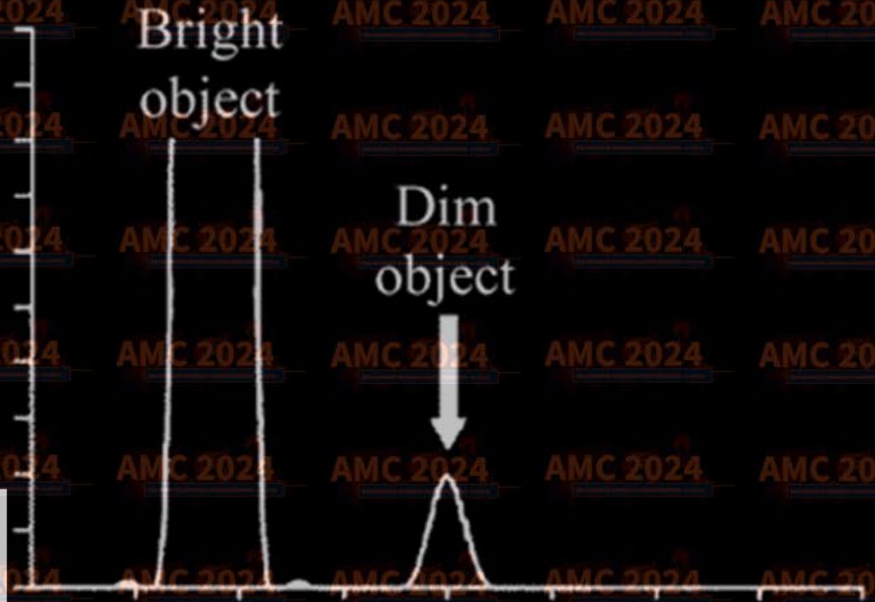
Confocal microscopy

The relation of the first ring maximum amplitude to the amplitude in the center is 2% in case of conventional point spreading function (PSF) in a focal plane, while in case of a confocal microscope this relation is 0.04%.





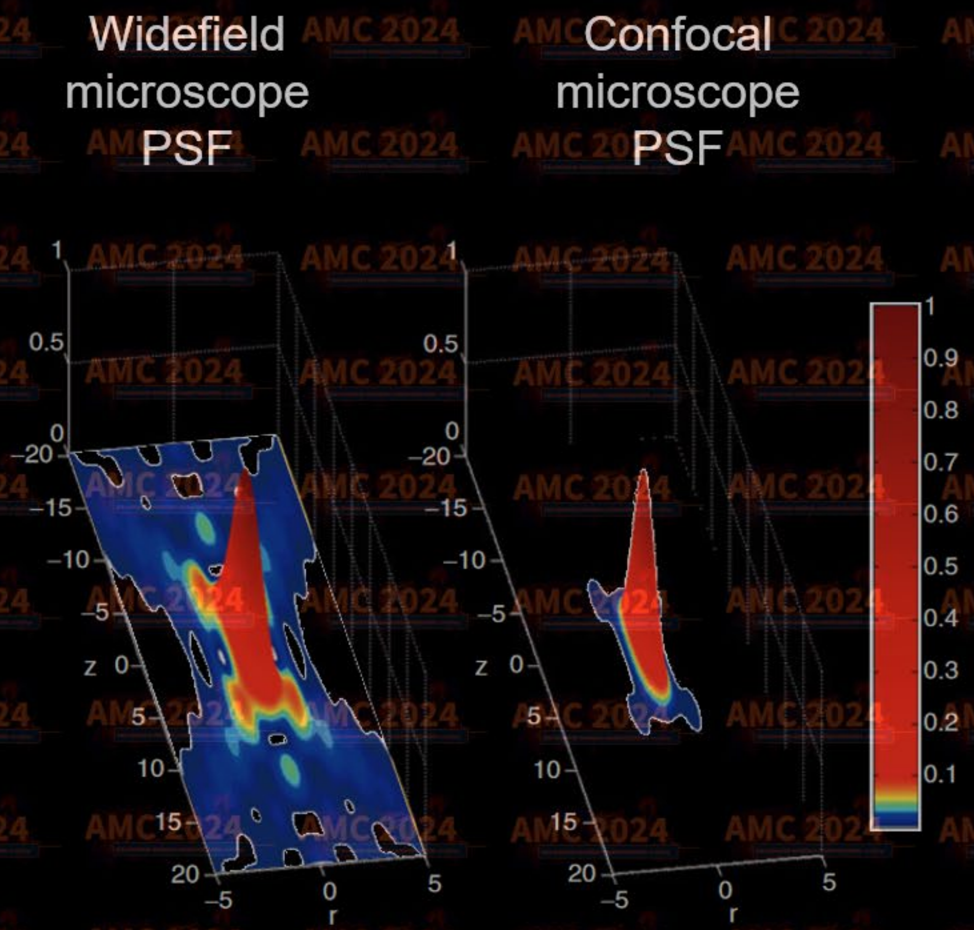


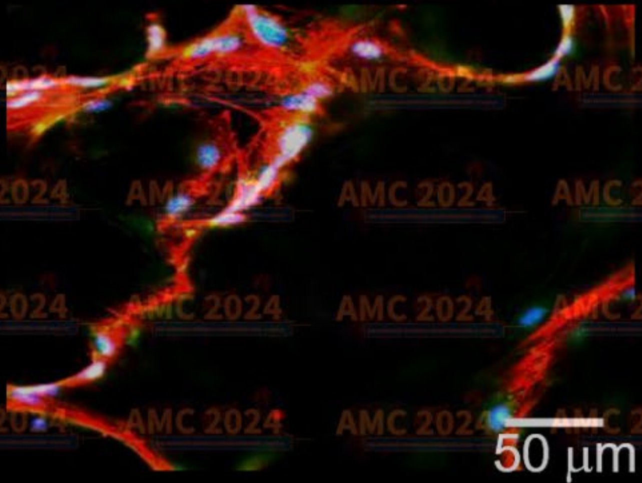


$$r_{resel} = 0.61\frac{\lambda}{n\sin\theta} = 1.22\frac{\lambda'}{D}F$$

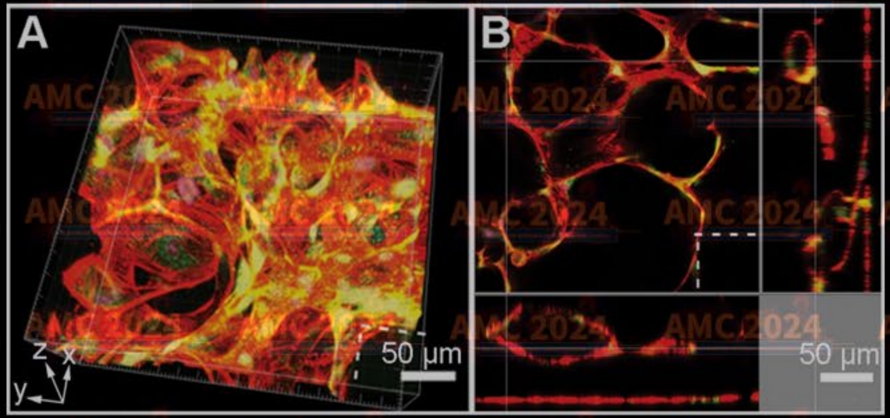
$$r_{conf} = 0.44\frac{\lambda}{n\sin\theta} = 0.88\frac{\lambda'}{D}F$$

Confocal microscopy combined with spectroscopy



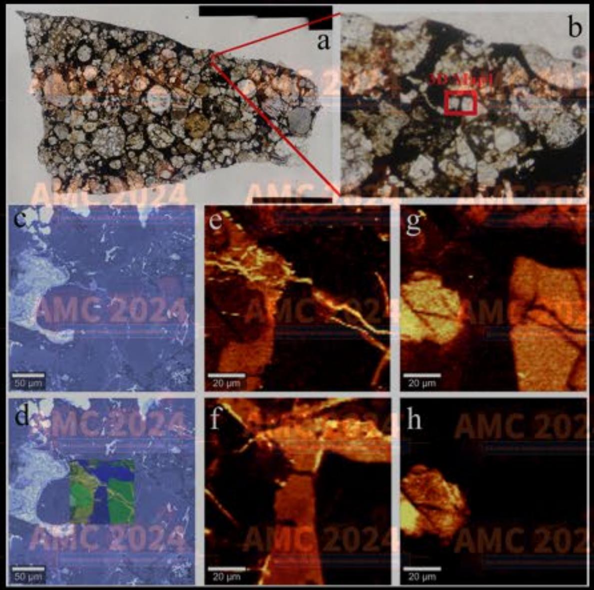


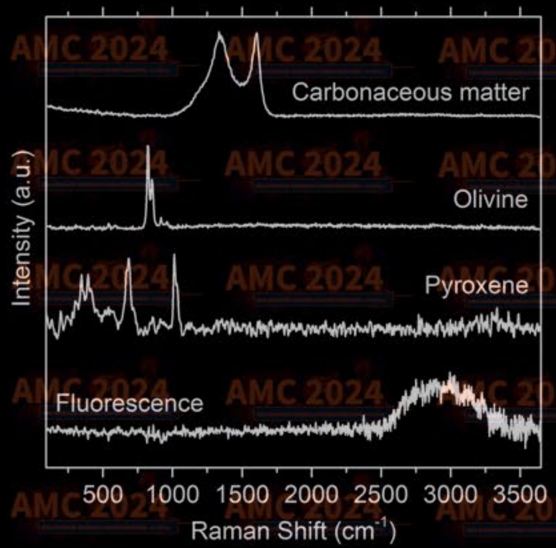
Confocal microscopy reconstruction of a 3D capillary bed



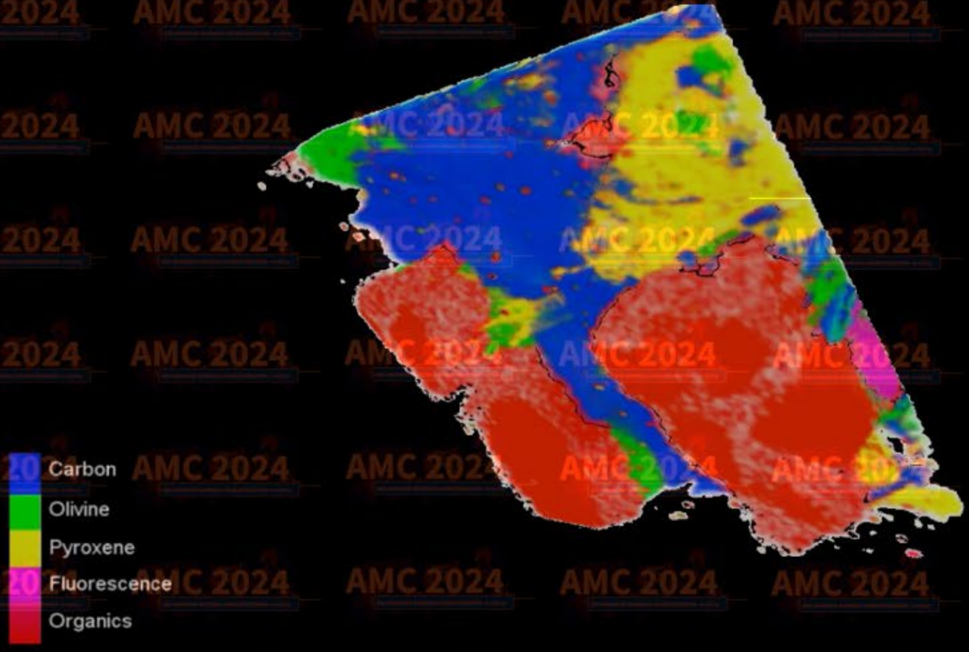
PLOS ONE 7(12): e50582 (2012)

Confocal microscopy combined with spectroscopy



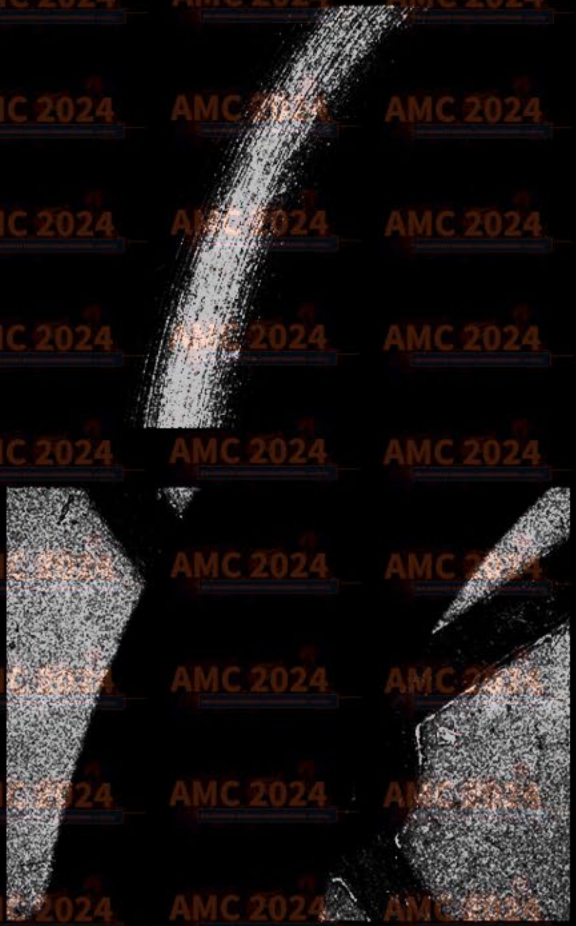


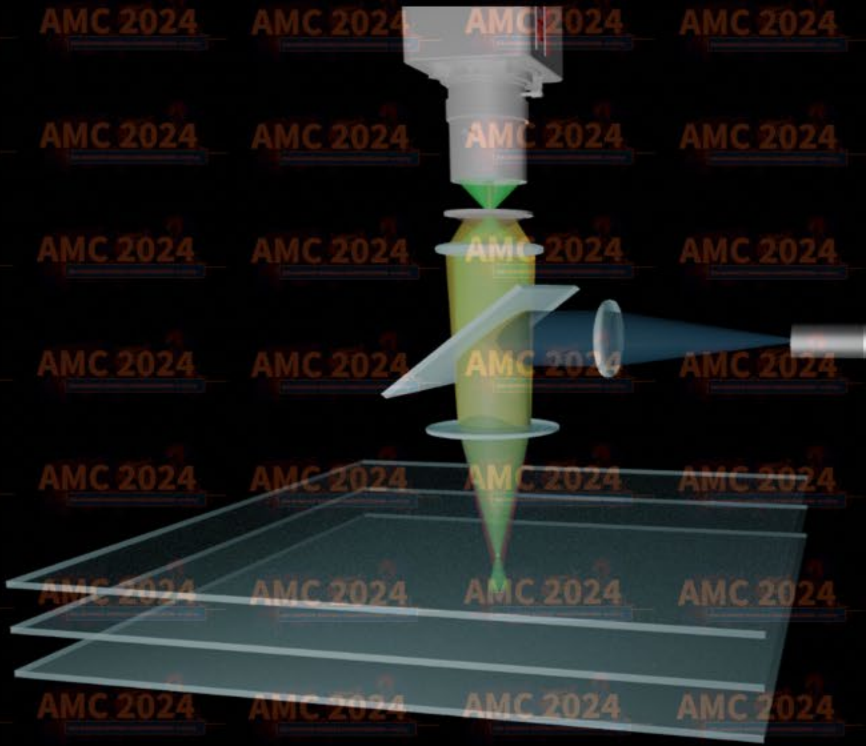
Chemical composition
Component identification
Components distribution



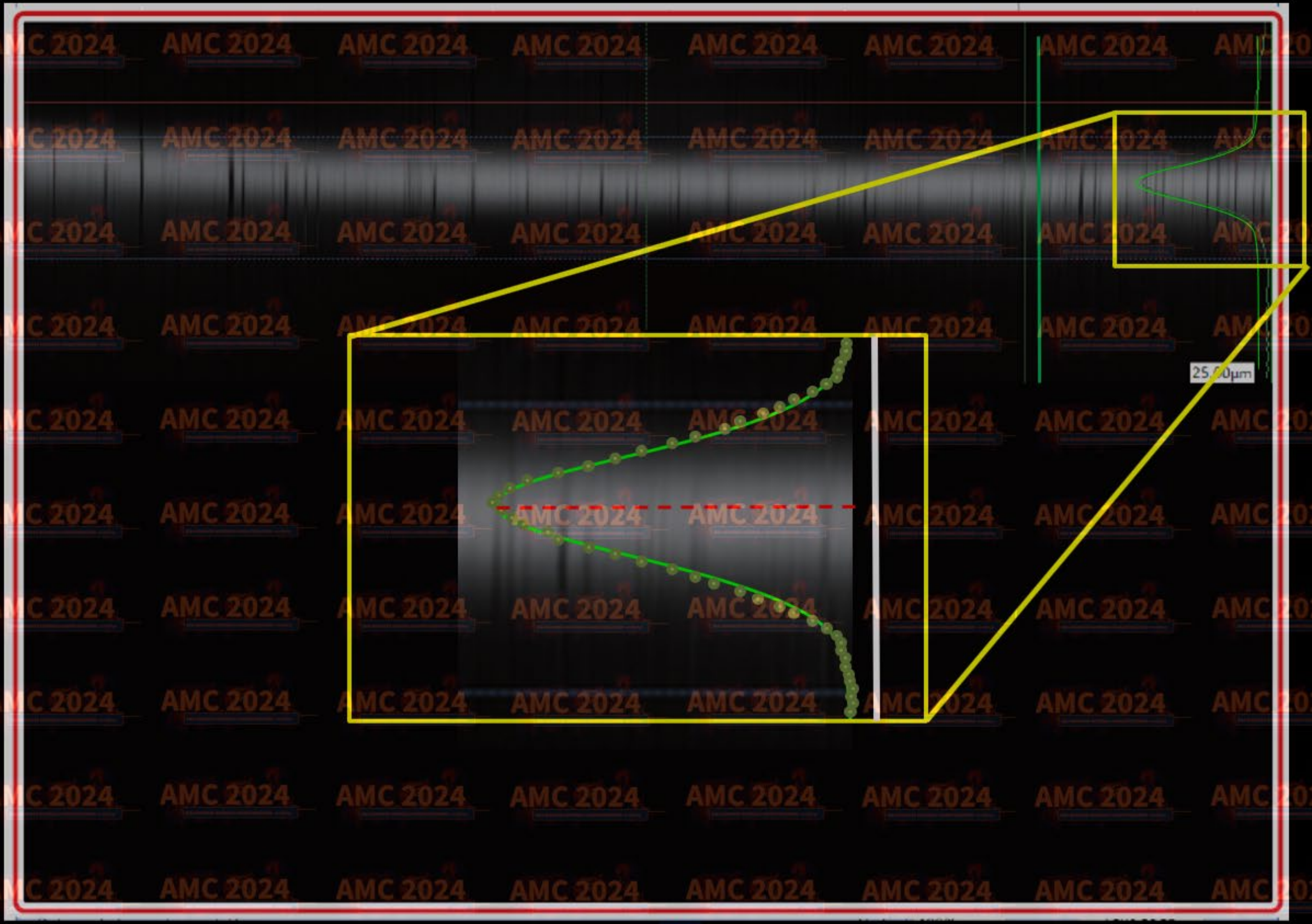
Earth and Space Science **5** (8), 380 (2018) DOI: (10.1029/2018EA000369)

Confocal microscopy z-stack



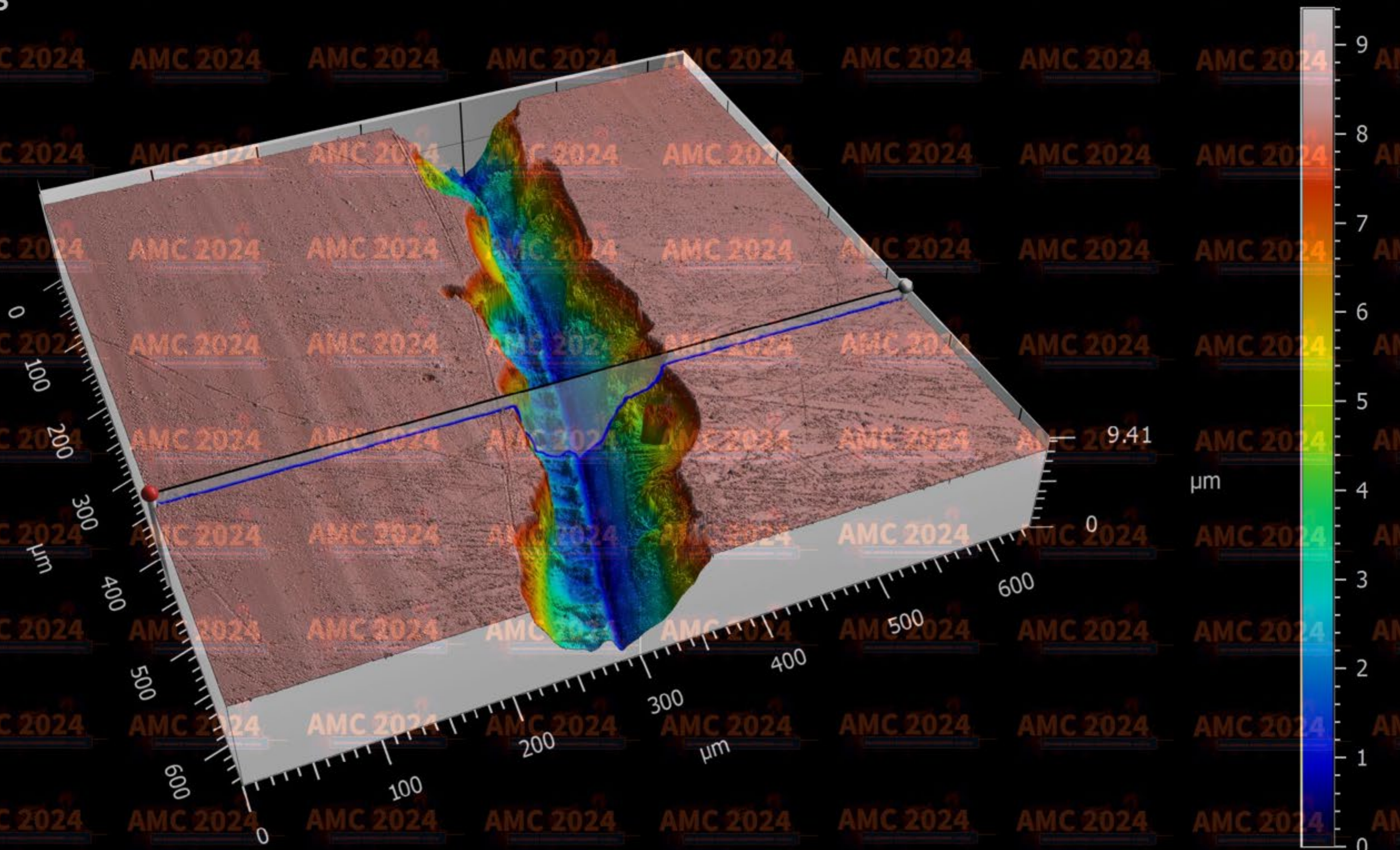


Confocal microscopy for measuring topography



Confocal microscopy

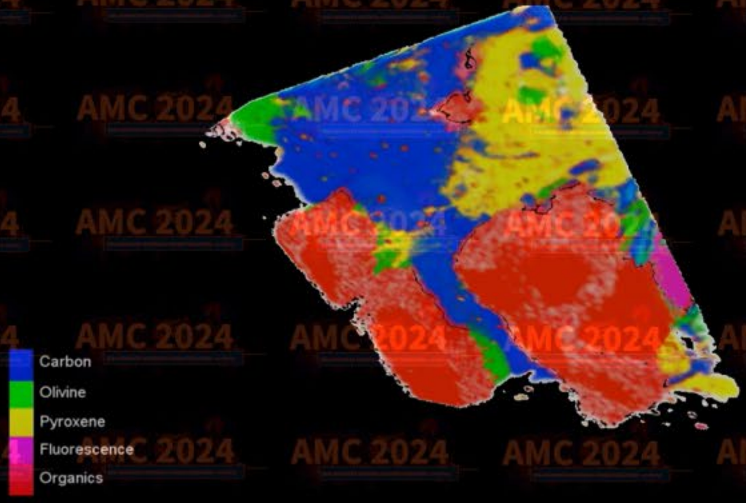
Scratch on glass

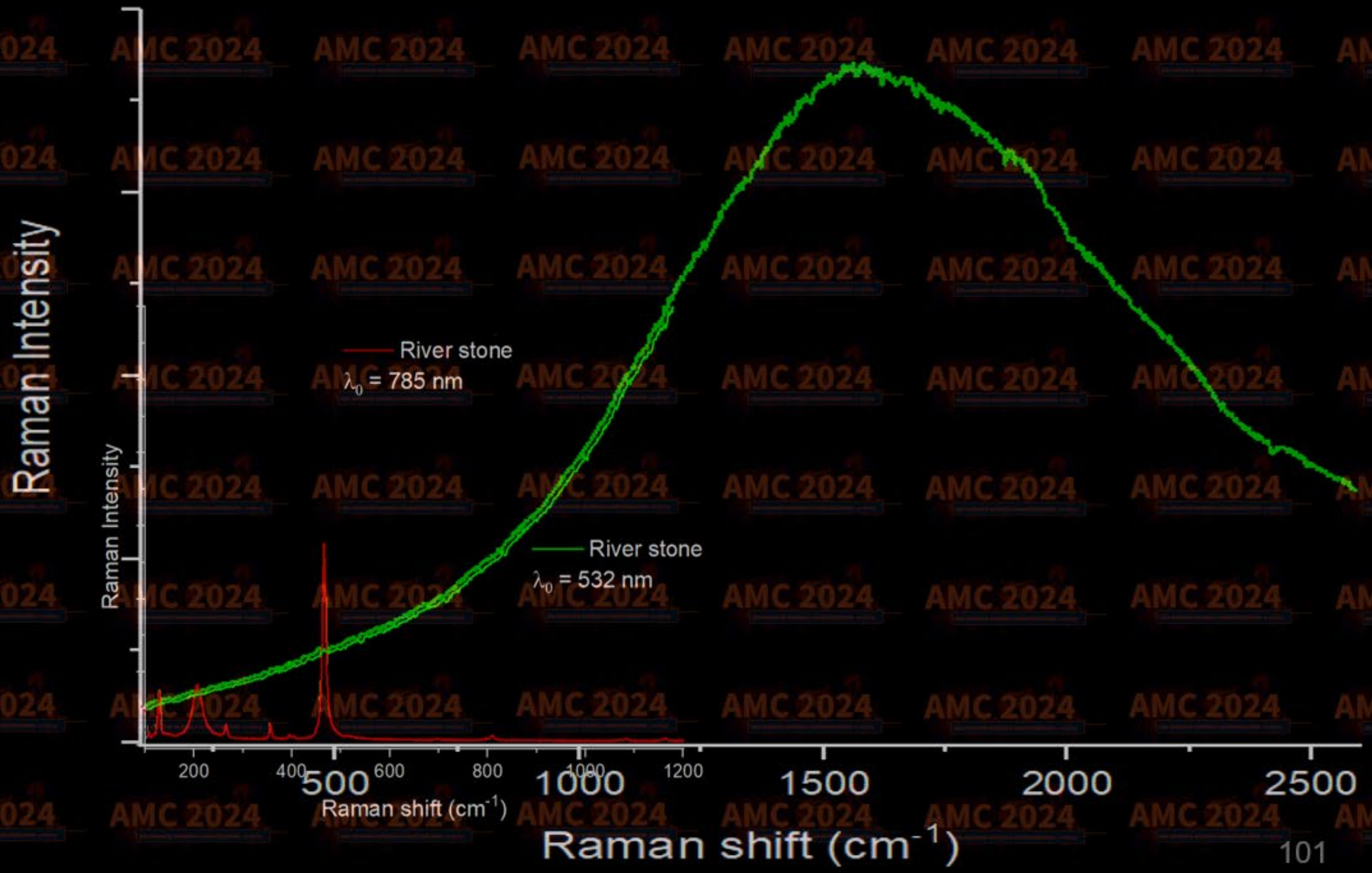


Raman spectroscopy

Primary Limitations:

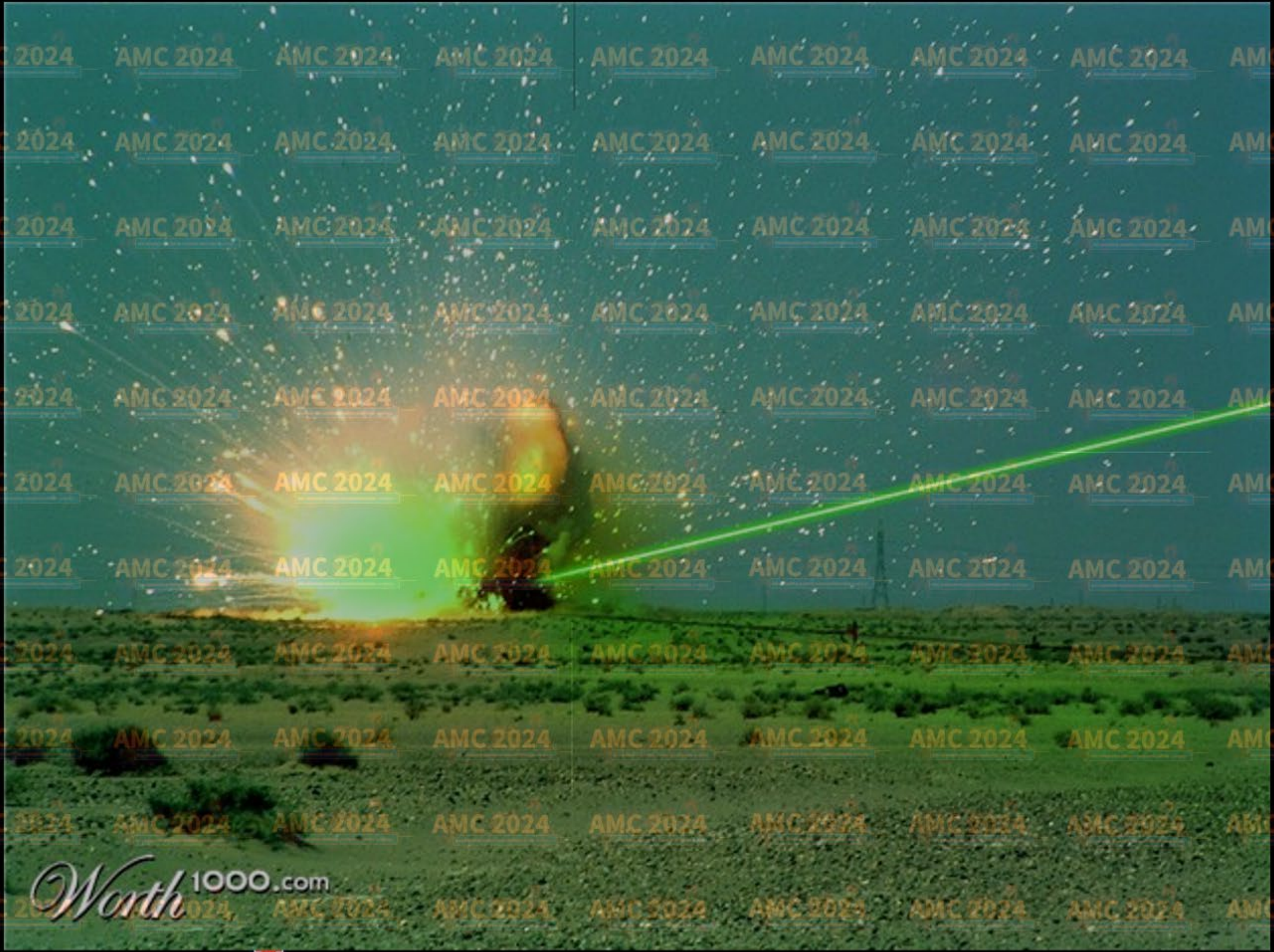
- Expensive apparatus (for high spectral/spatial resolution and sensitivity).
- Weak signal, compared to fluorescence.
- Limited spatial resolution (diffraction limited).





The More Time Approach

The More Power Approach



Surface Plasmons

Plasmons can be driven by photons at resonance to build large standing wave electric fields.

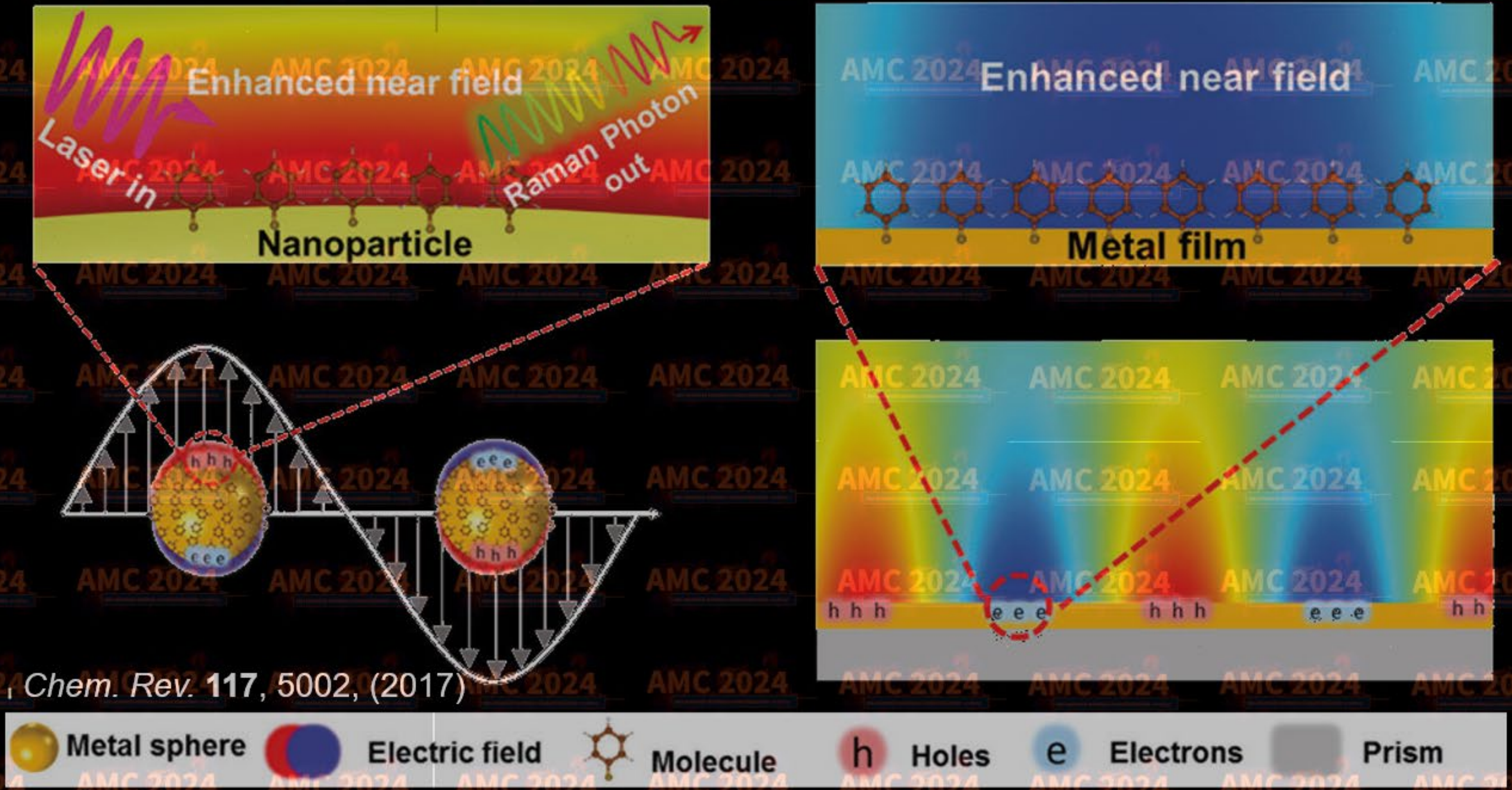
That leads to a strong enhancement of Raman scattering, proportional to the squared E field strength.

$$I = K\nu^4 p_0^2 \sin^2\theta$$

Surface Enhanced Raman Spectroscopy (SERS)

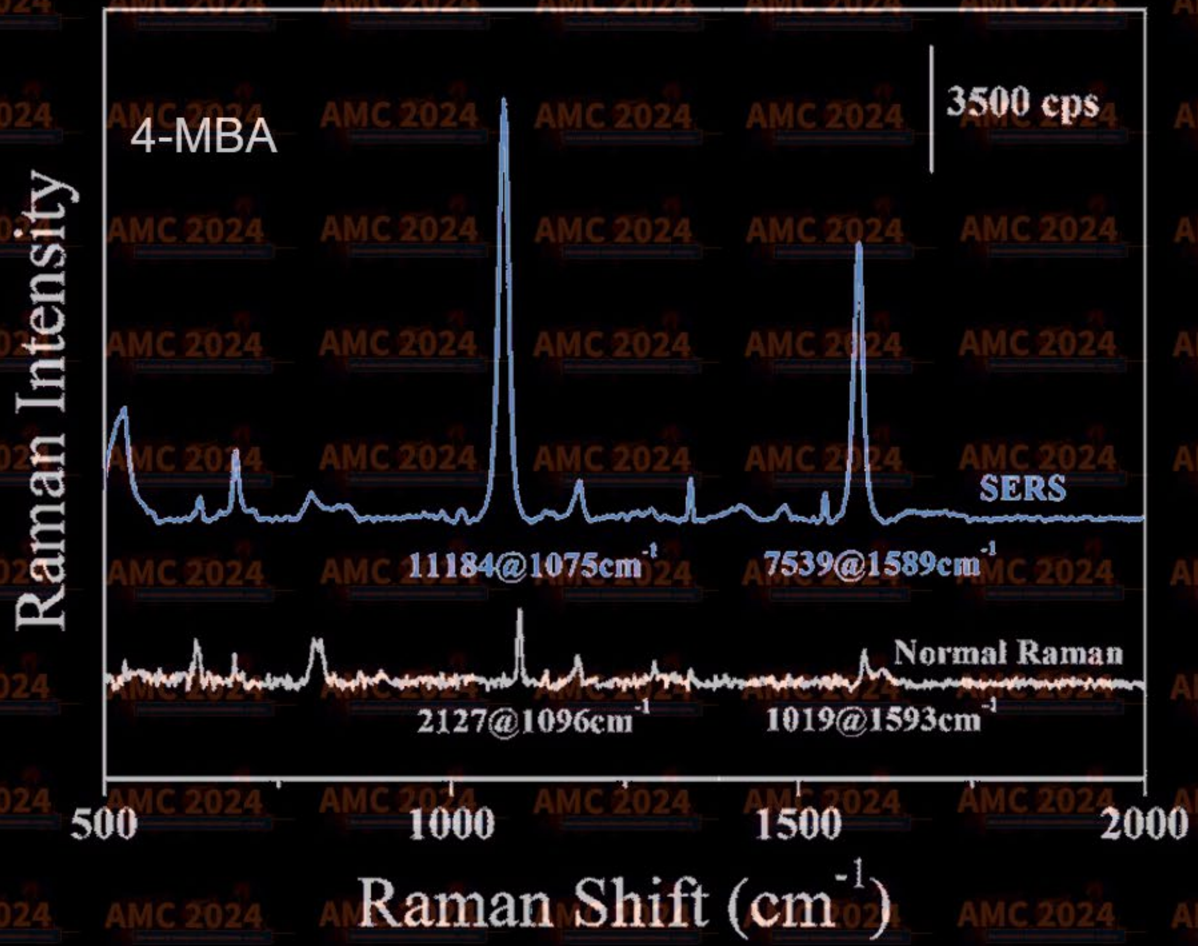
Typically achieved with corrugated gold/silver surface or gold/silver nanoparticles with molecules of interest attached.

Capable of boosting Raman signal up to **14 Orders of Magnitude** or more! *Science* **275**, 1102 (1997)



Chem. Rev. **117**, 5002, (2017)

Surface Enhanced Raman Spectroscopy (SERS)

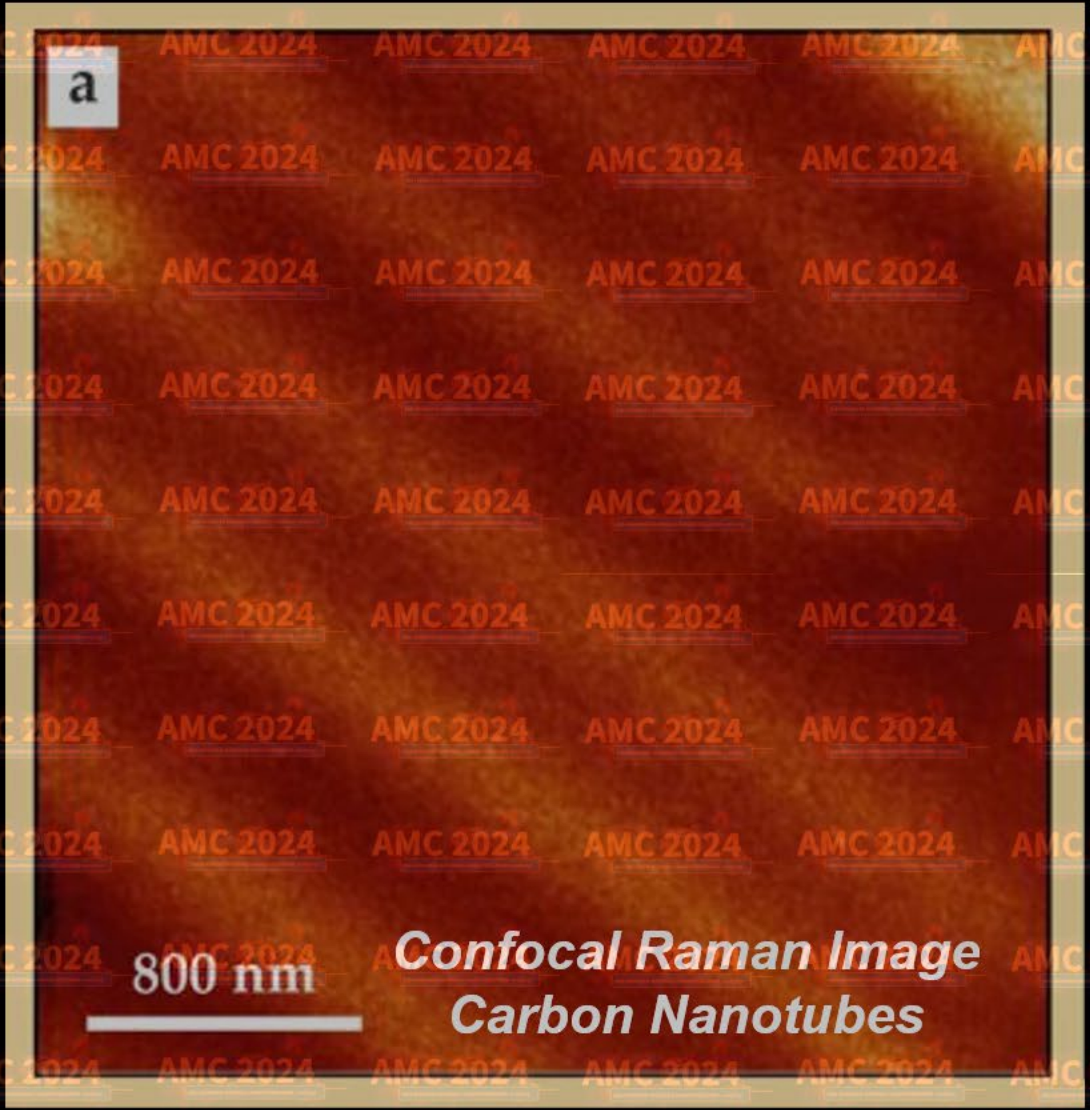


Anal. Methods, **6**, 9547 (2014)

Confocal Raman Microscopy

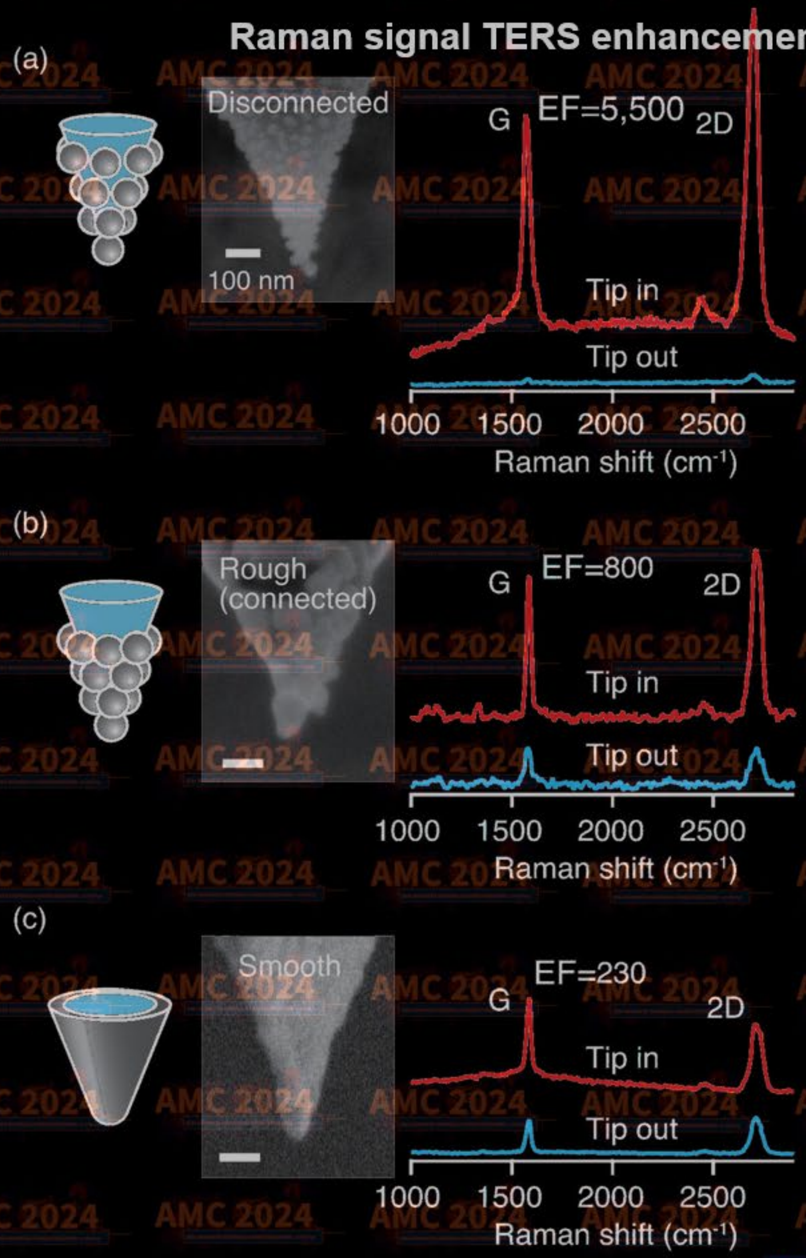
That's cool, but what about …

- Limited spatial resolution (diffraction limited).



Phys. Rev. Lett. **103**, 186101 (2009)

Tip Enhanced Raman Spectroscopy (TERS)

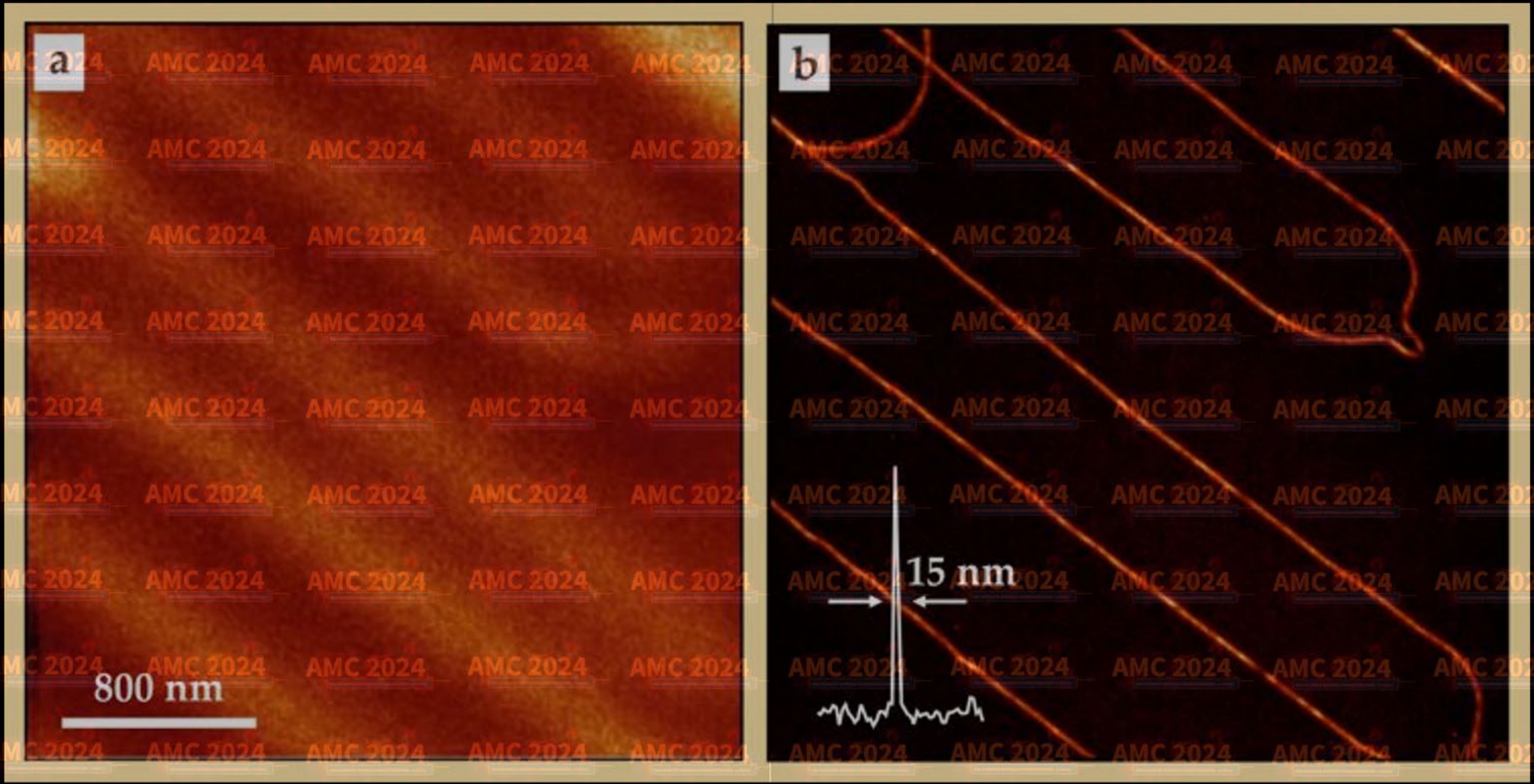


What is really cool is that this also works with a single metalized sharp tip, such as an STM or AFM tip!

Not only do you get the electric field enhancement, but now the source of the Raman signal is extremely localized.

Chem. Soc. Rev. **46**, 4077 (2017)

Tip Enhanced Raman Spectroscopy (TERS)



Confocal Raman Image

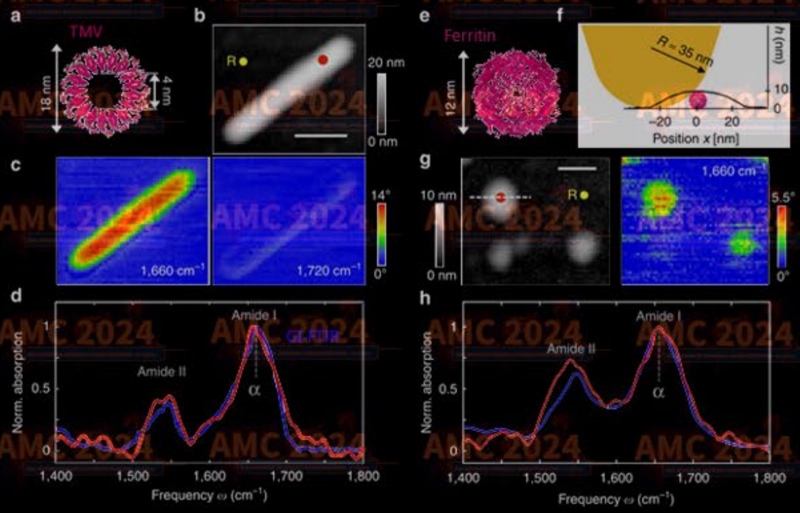
Tip Enhanced Raman Image

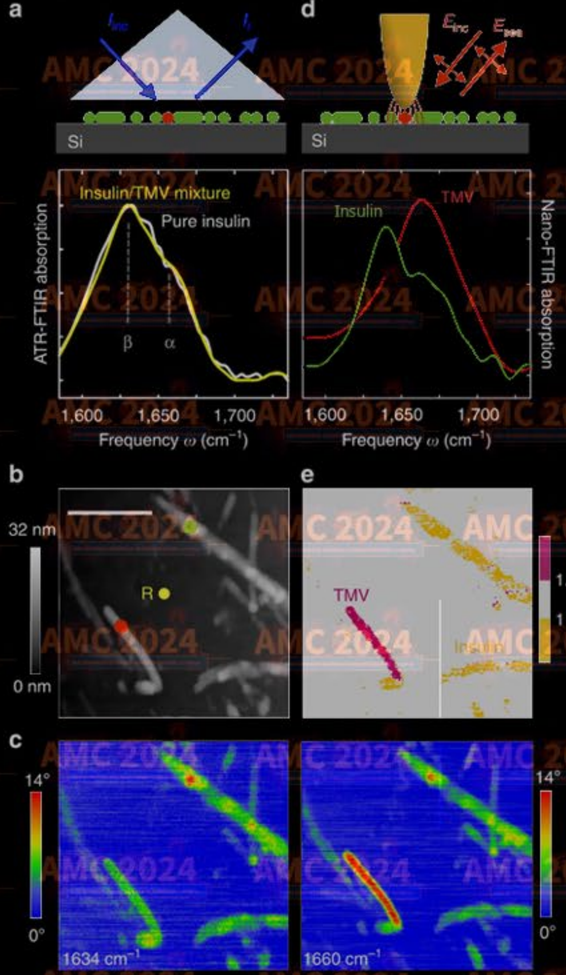
Carbon Nanotubes

Phys. Rev. Lett. **103**, 186101 (2009)

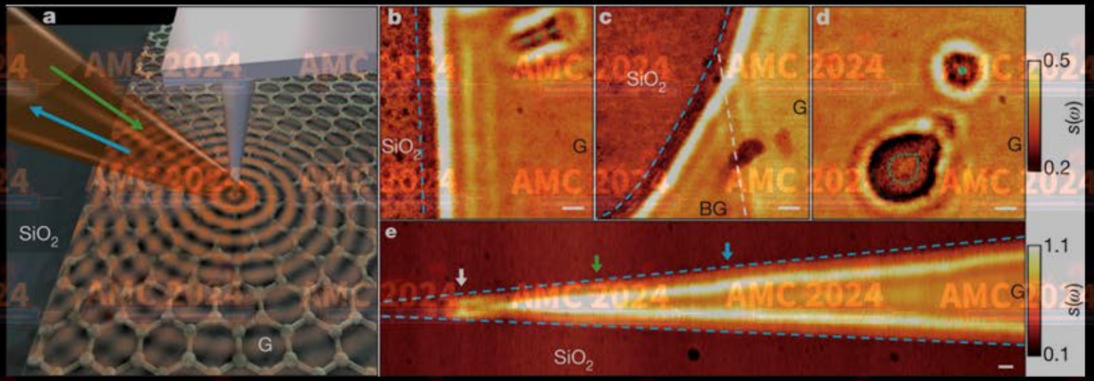
Near-field scanning optical nanospectroscopy

Nano-FTIR

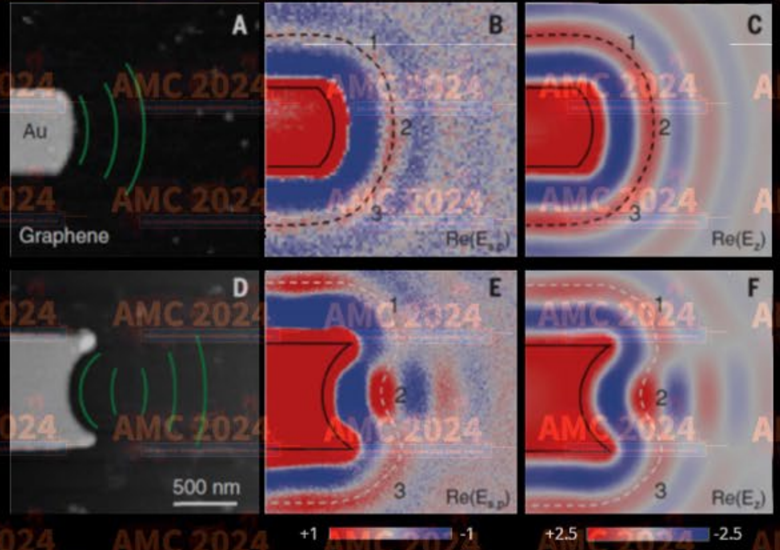




Nature Communications **4**, 2890



Nature 000, 1-4 (2012) doi:10.1038/nature11253



Science **344**, 1369

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