

AMC2023

**Advanced Materials
Characterization
Workshop**



Optical Characterization Methods Part I

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University of Illinois at Urbana-Champaign

**The Grainger College
of Engineering**

UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

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PLEASE...



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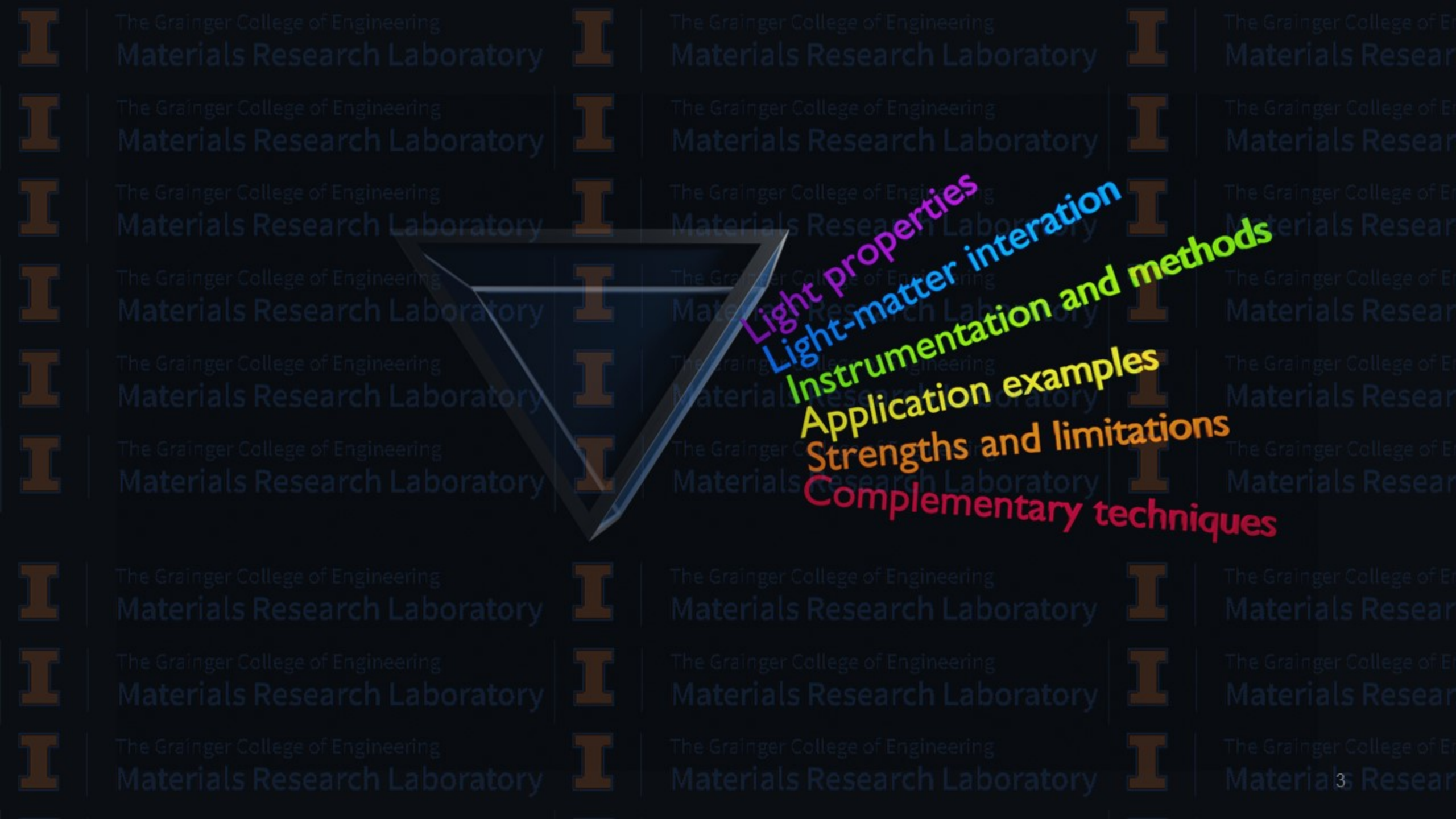
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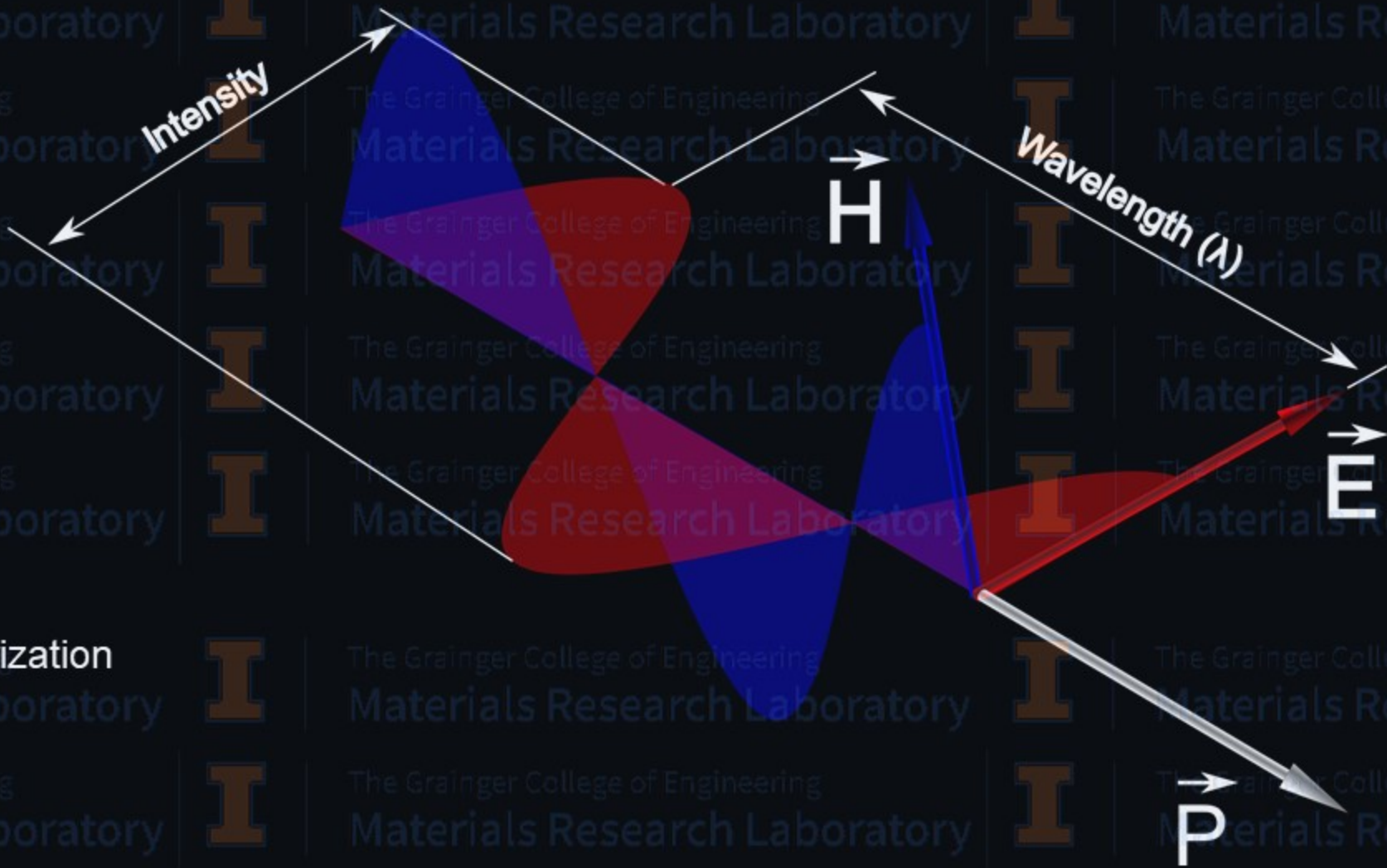
Optical Characterization





Light properties
Light-matter interaction
Instrumentation and methods
Application examples
Strengths and limitations
Complementary techniques

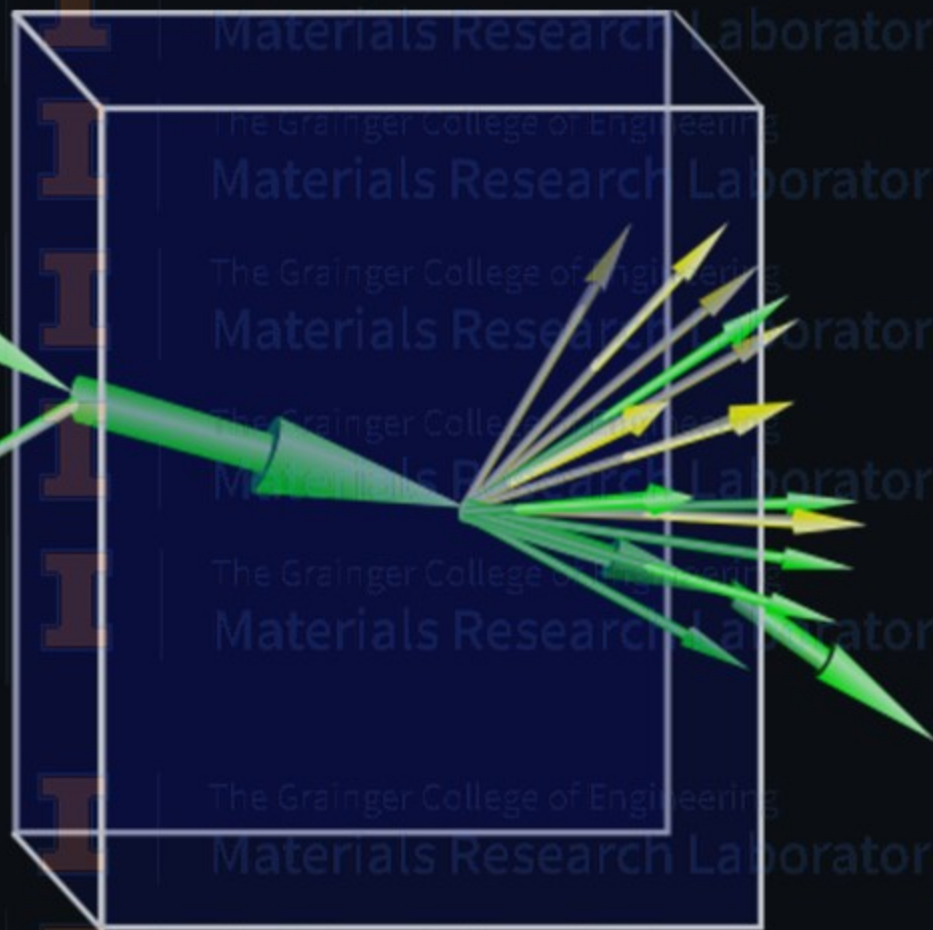
Light properties



- 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



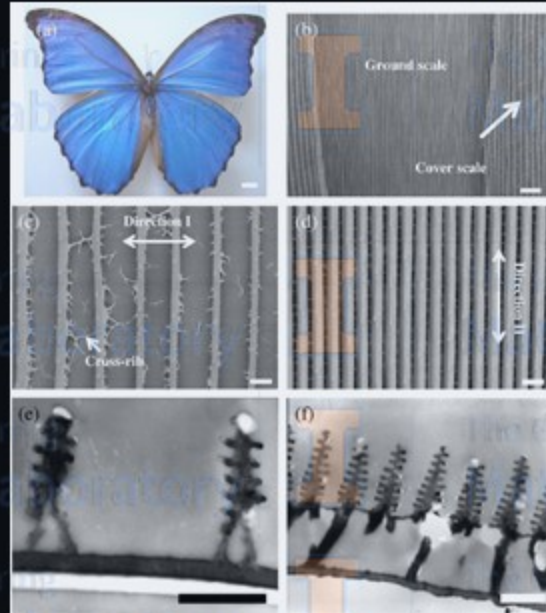
Stress



Thickness



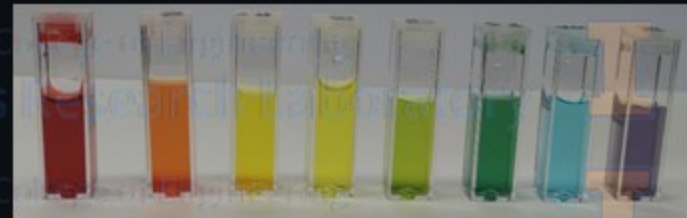
Microstructure



Concentration



Composition



Light interactions with matter

Photon energy

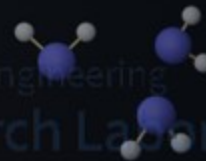
X-rays

Ultra-violet

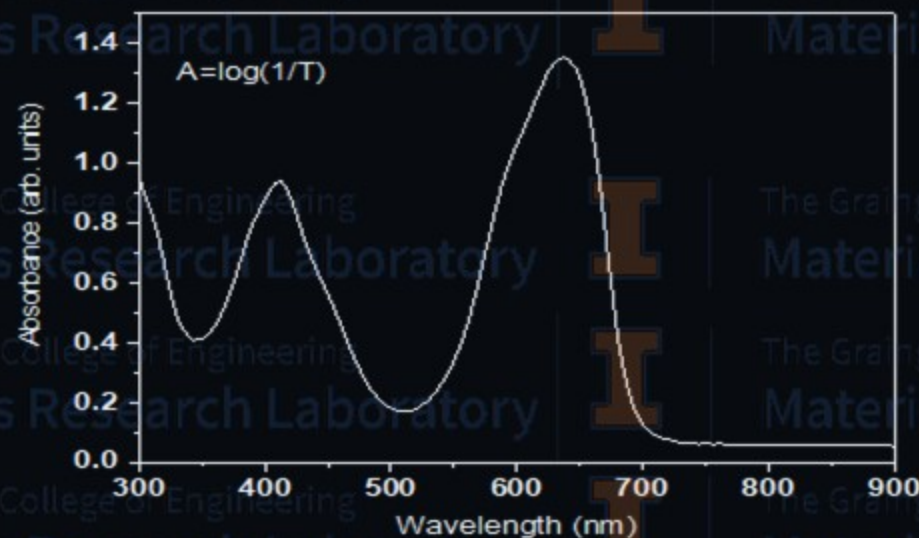
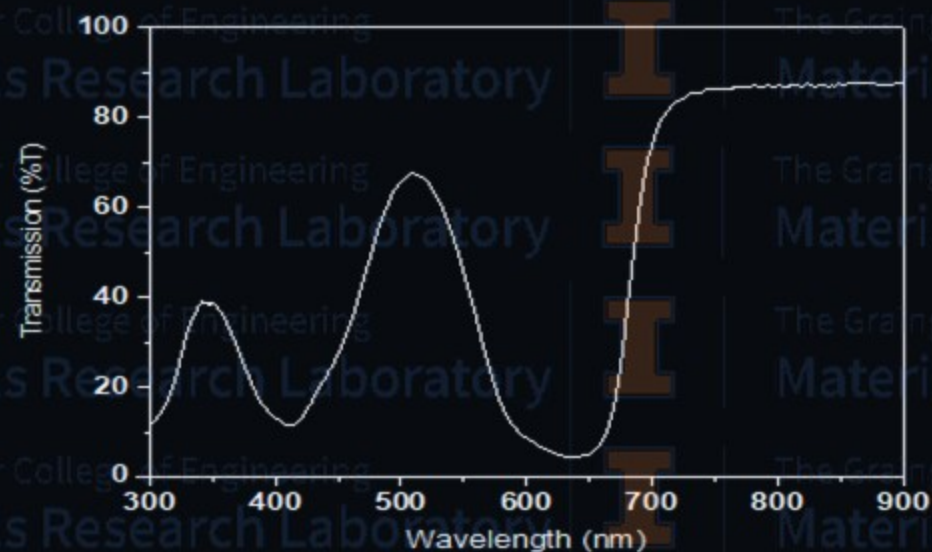
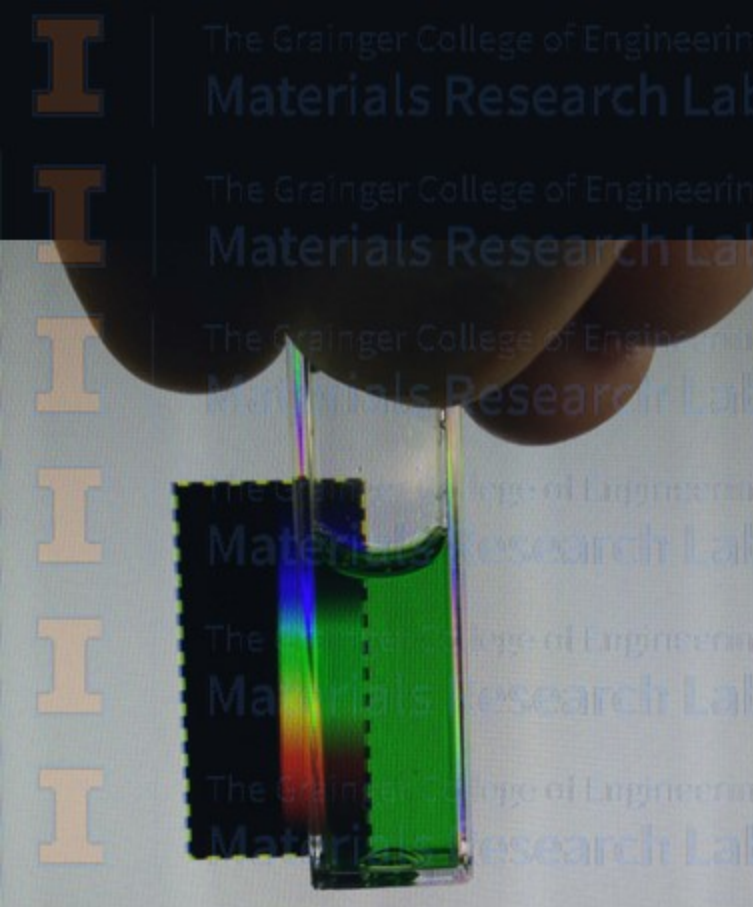
Visible

Infrared

Microwaves



Spectroscopy

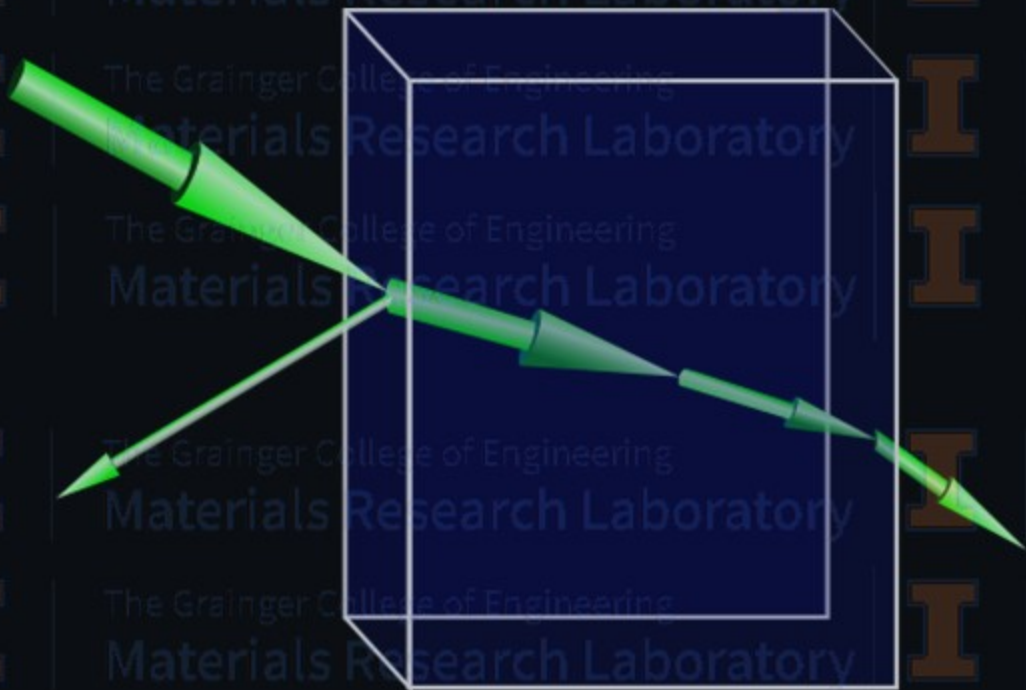


Transmission, Reflection, Absorption

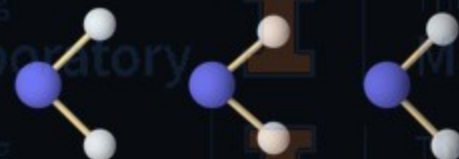
What is measured:

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.

UV-Vis-NIR

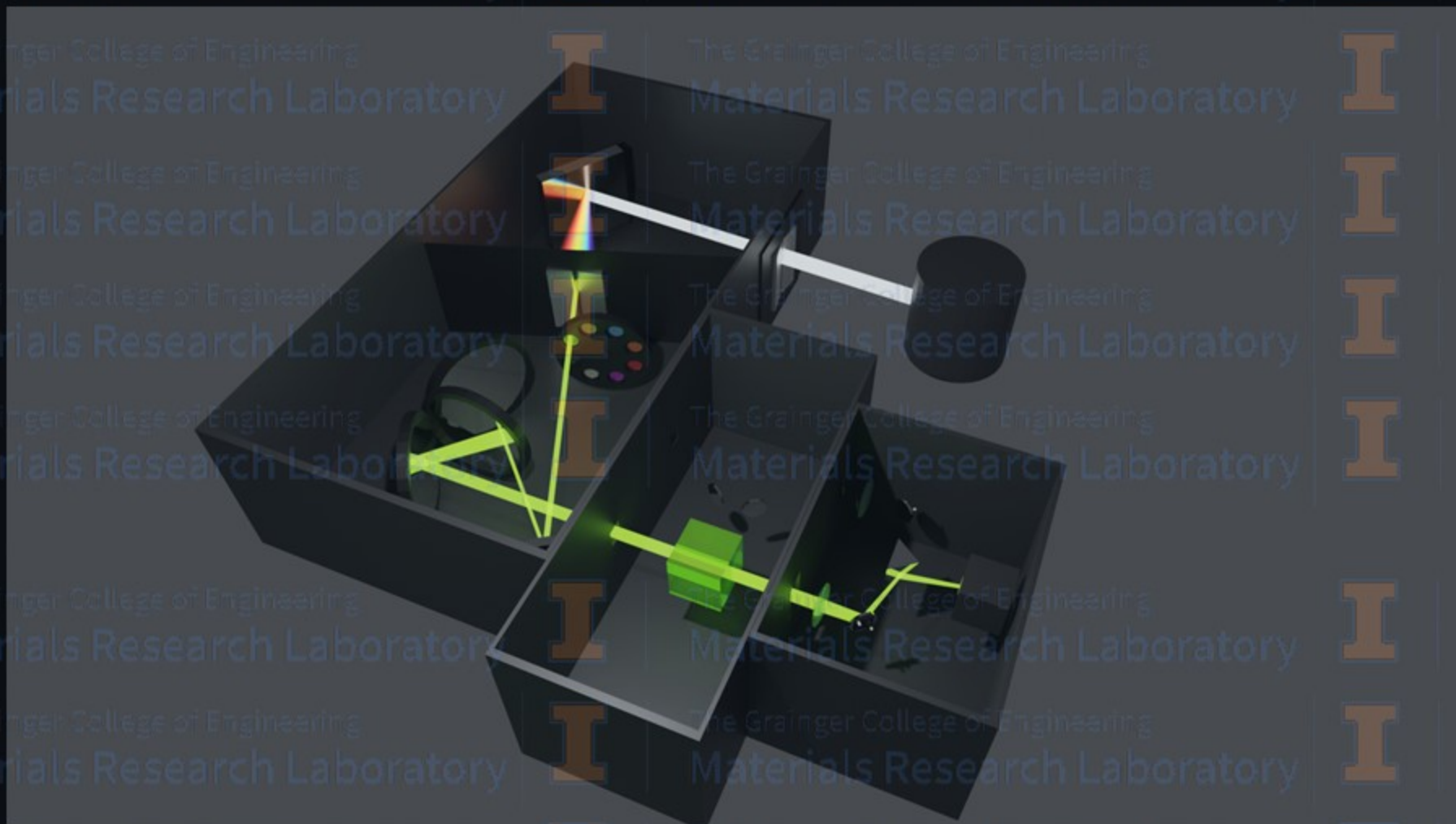


IR

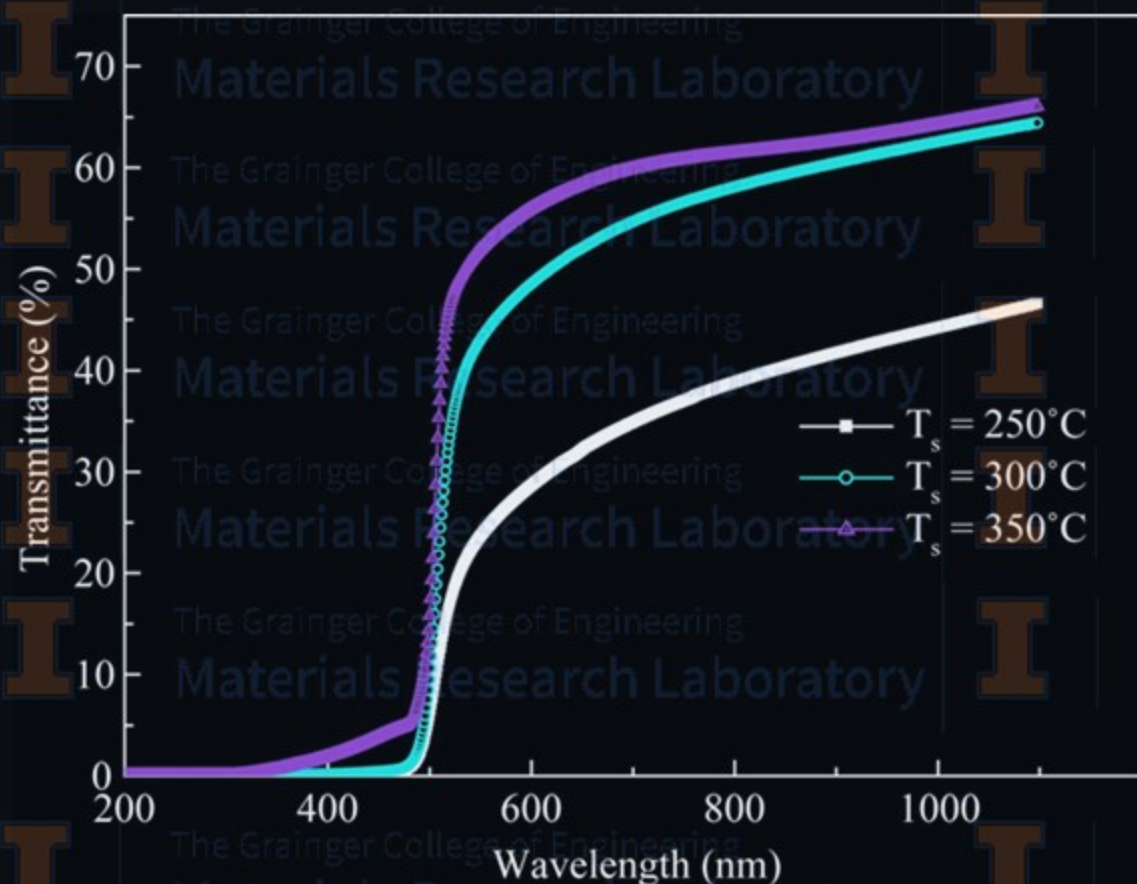


Spectrophotometry (UV-VIS-NIR)

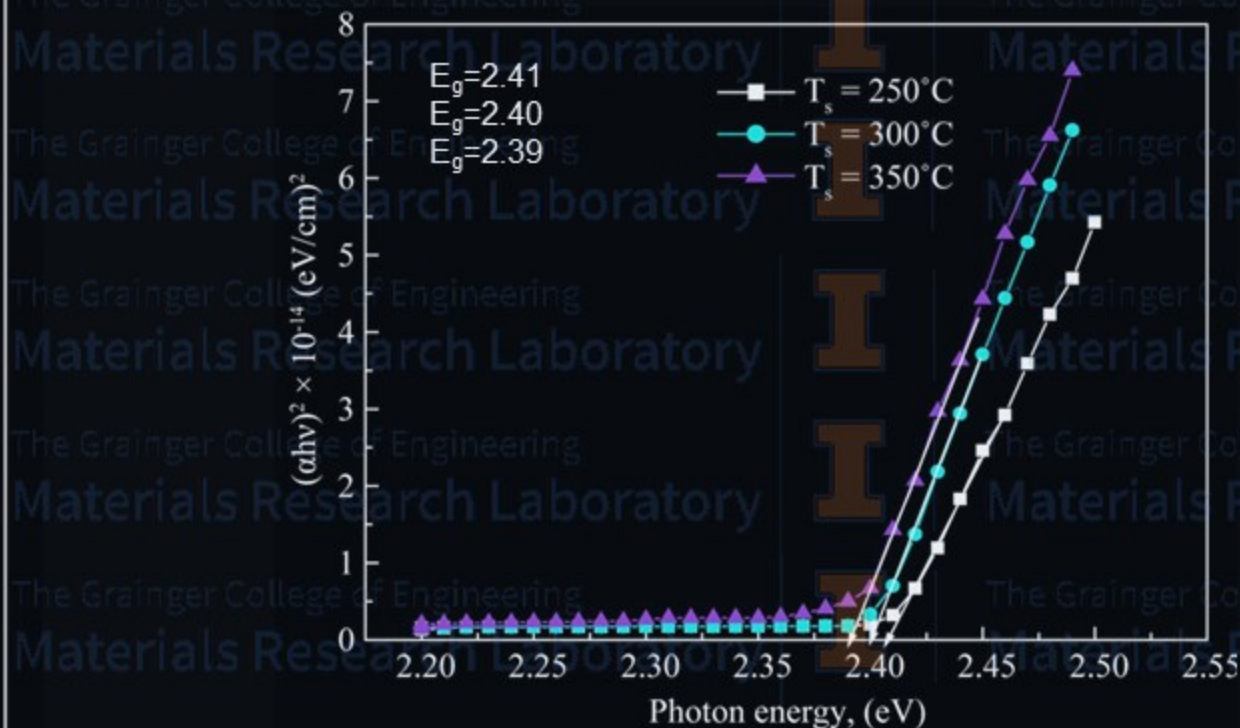
Instrumentation:



Spectrophotometry (UV-VIS-NIR)



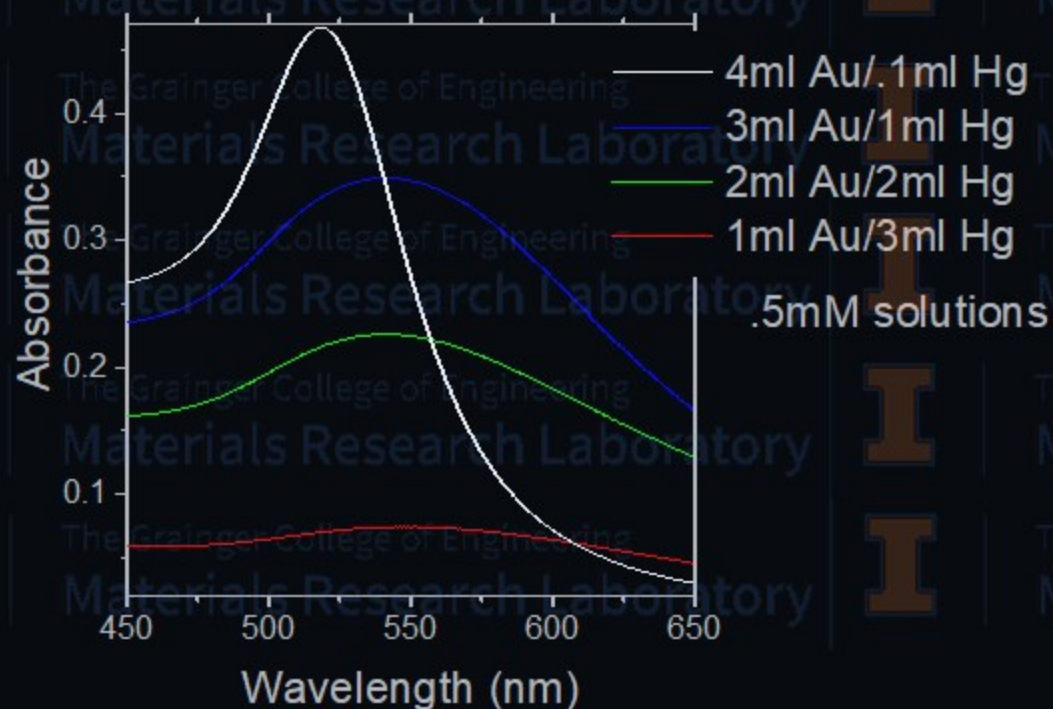
Optical band gap determination of CdS thin films as a function of growth substrate temperatures



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

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

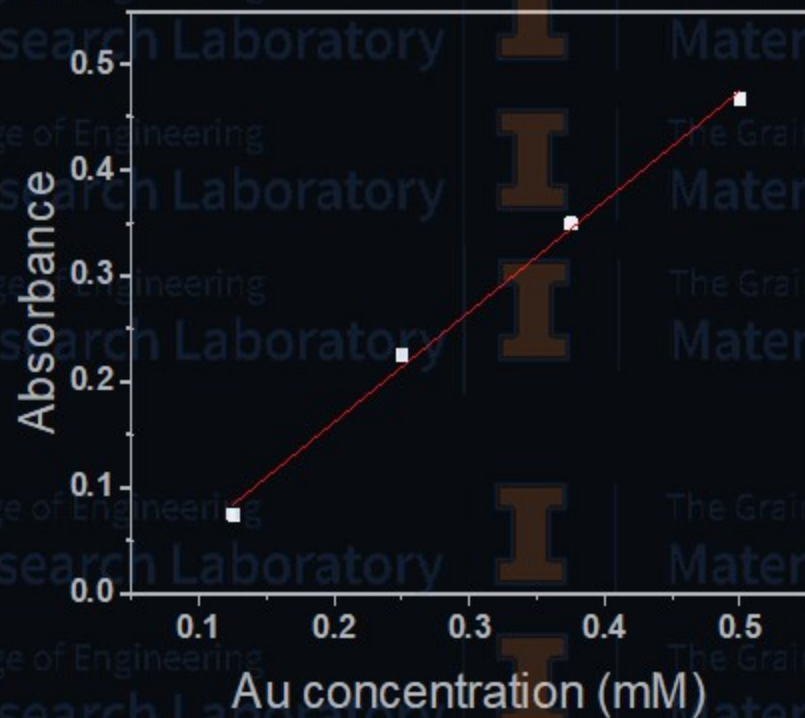
Spectrophotometry (UV-VIS-NIR)



Beer-Lambert Law

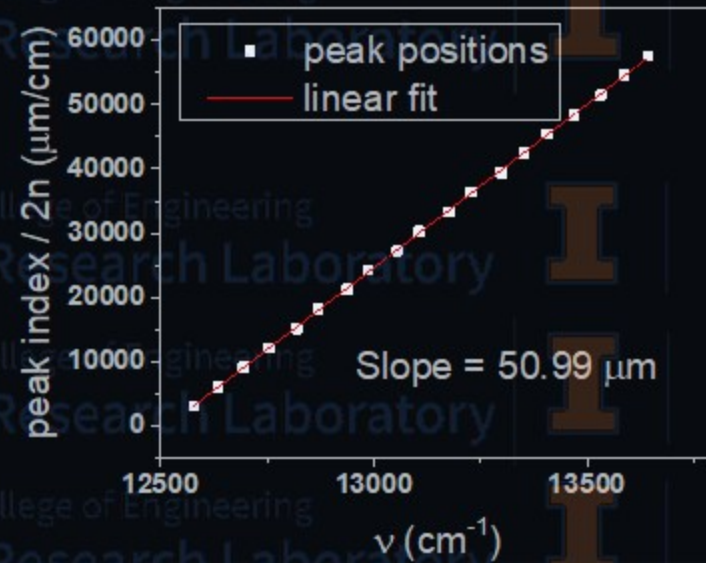
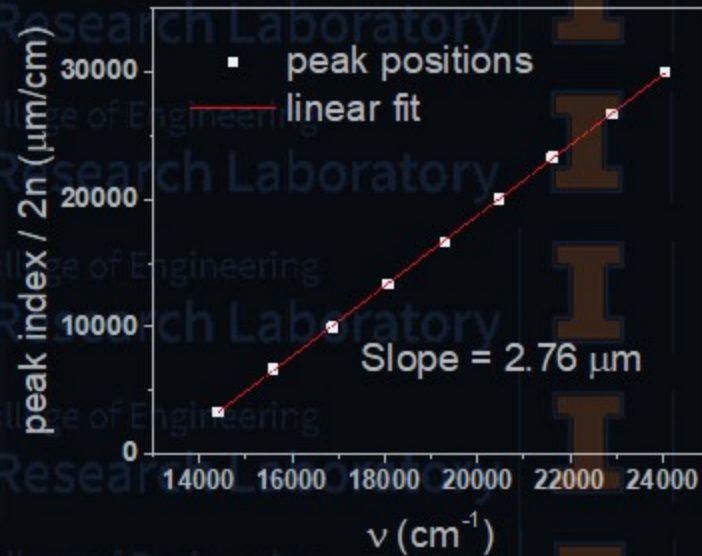
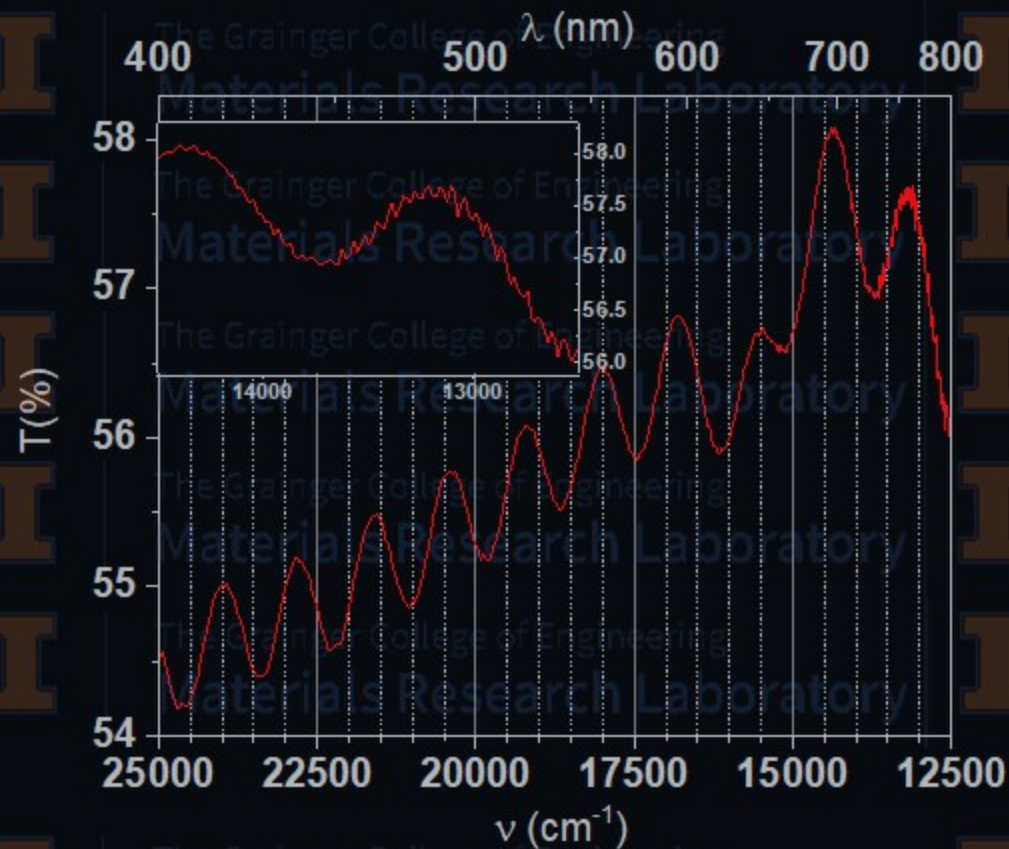
$$Abs = K \ell c = a \ell$$

$$Abs = \log (1/T)$$



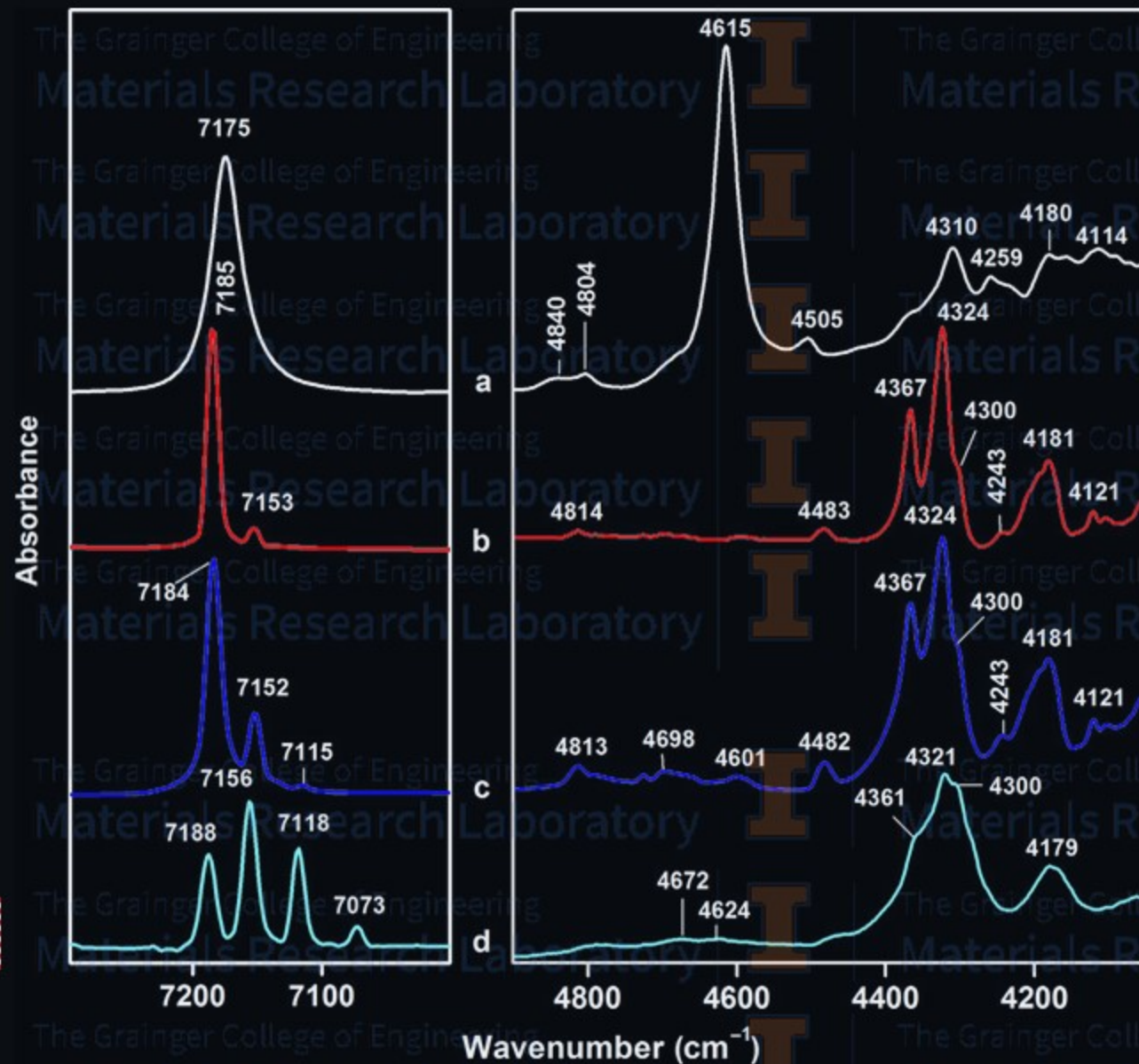
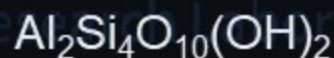
Using absorbance to determine Au/Hg concentration in water solutions

Spectrophotometry (UV-VIS-NIR)



Using transmission interference fringes to determine thickness

Spectrophotometry (UV-VIS-NIR)

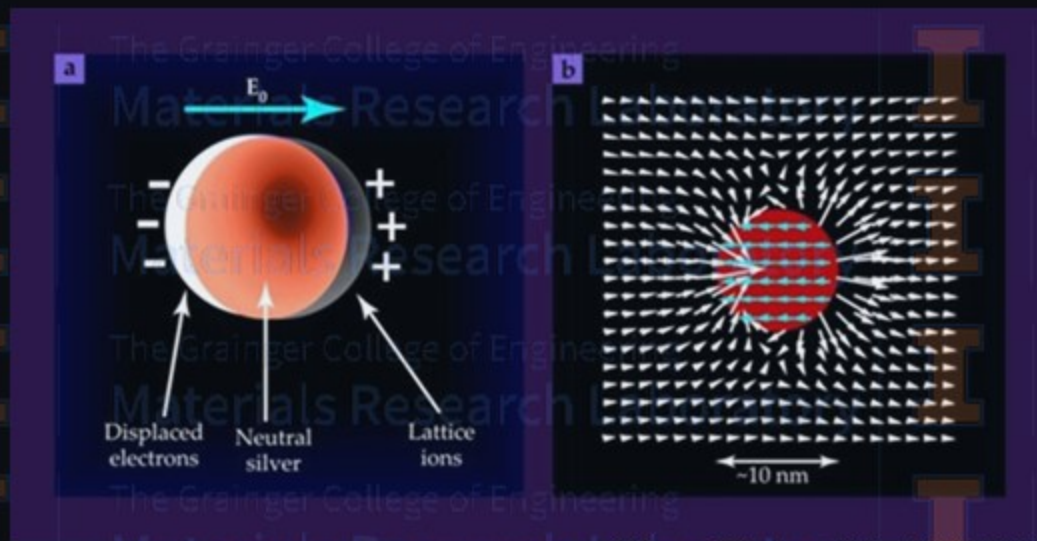
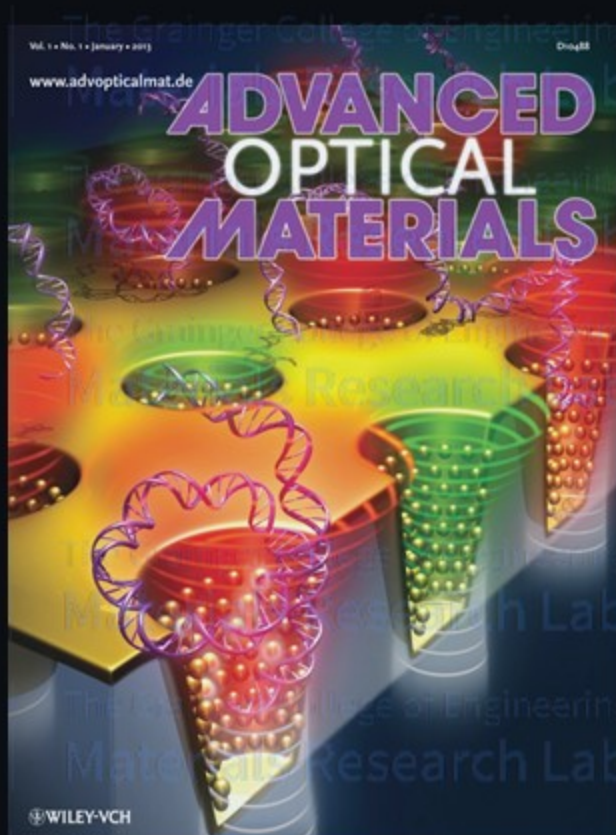


Images from Wikipedia and eurotalca.com
Spectra from *Developments in Clay Science*, Vol. 8, Ch. 5

Spectrophotometry (UV-VIS-NIR)

Excitations in materials

- Plasmons

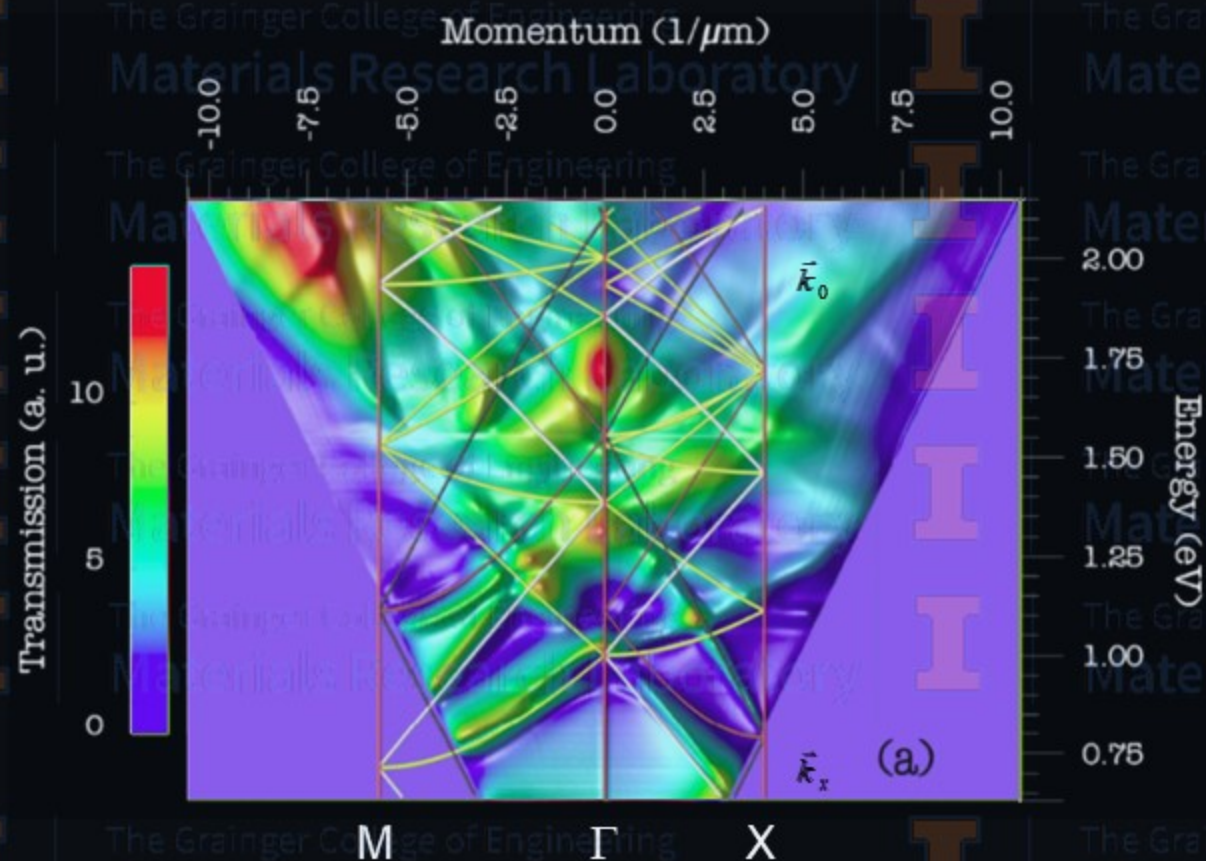
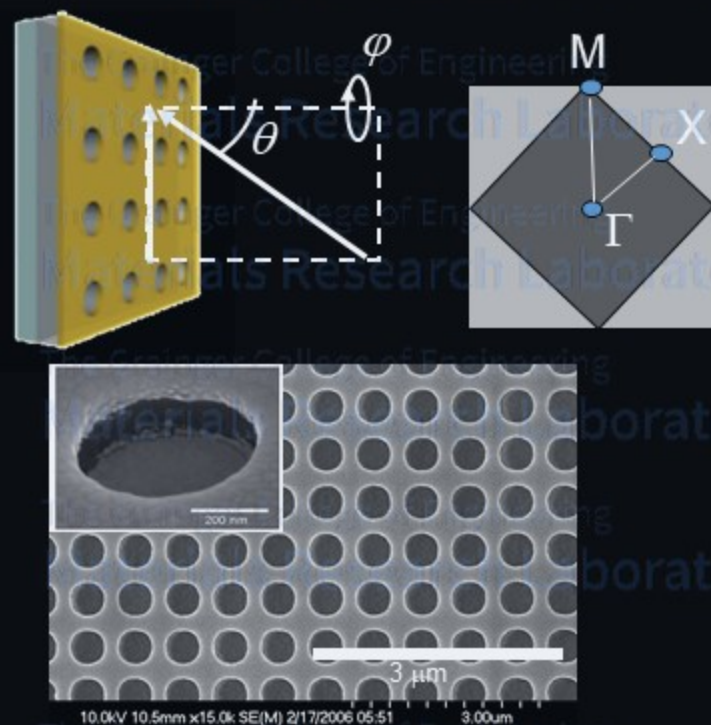


Phys. Today, 64, 39 (2011)



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.

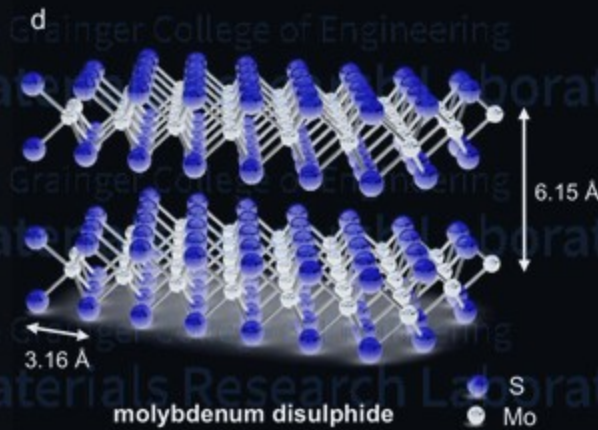
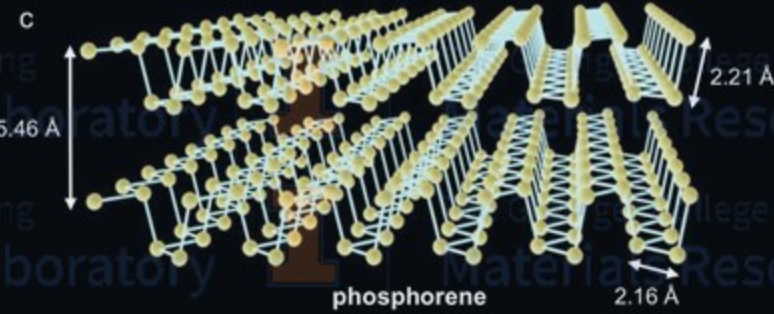
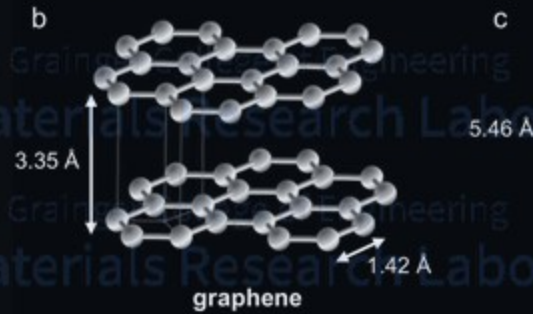
Spectrophotometry (UV-VIS-NIR)



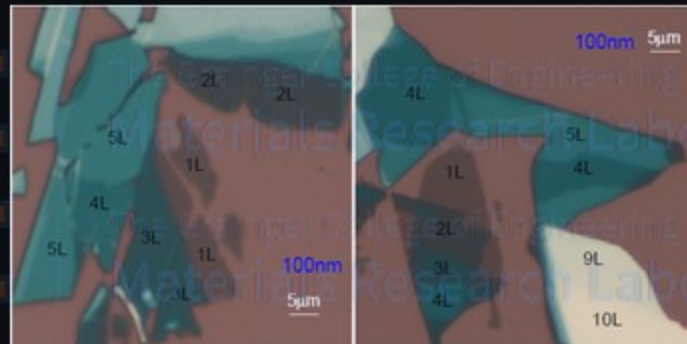
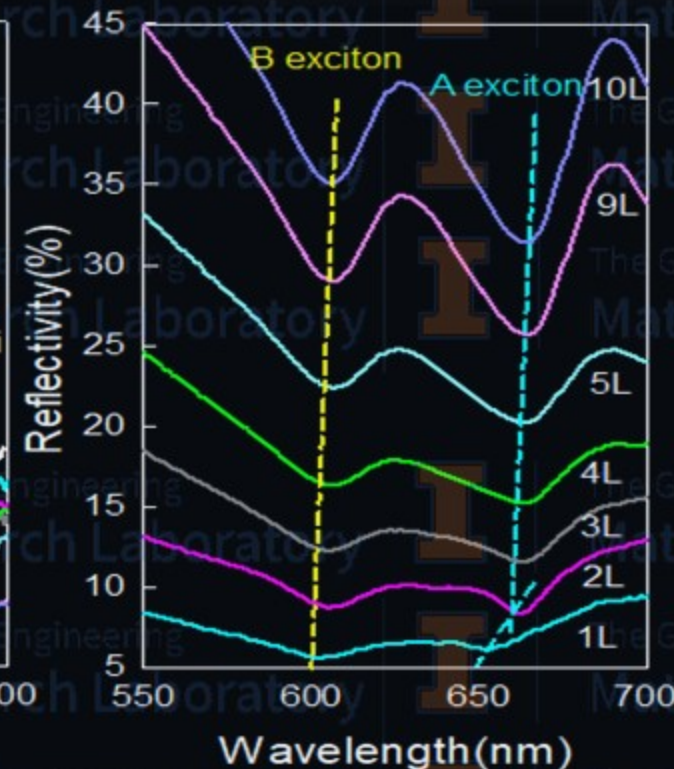
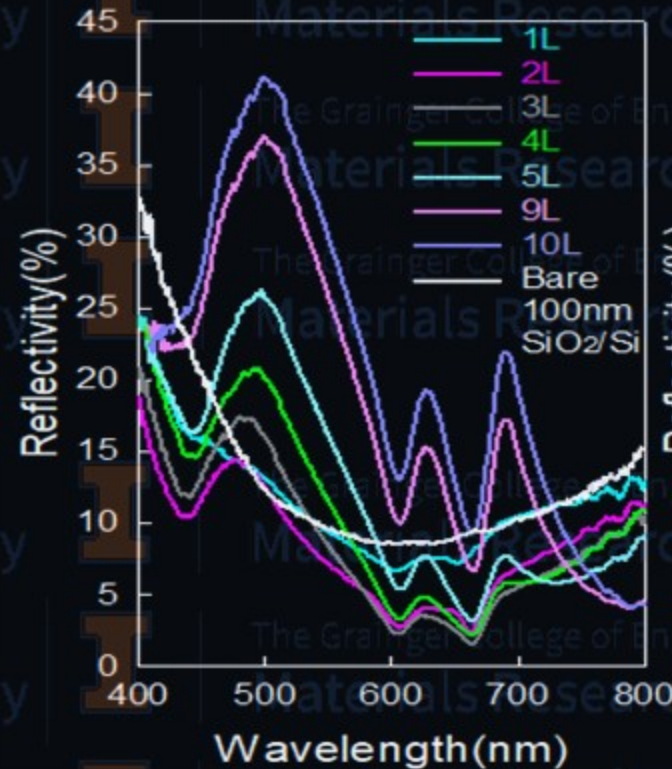
Optics Express 13, 5669 (2005)

Plasmonic crystal Brillouin zone from the transmission spectra measured for many different angles of incidence.

Spectrophotometry (UV-VIS-NIR)

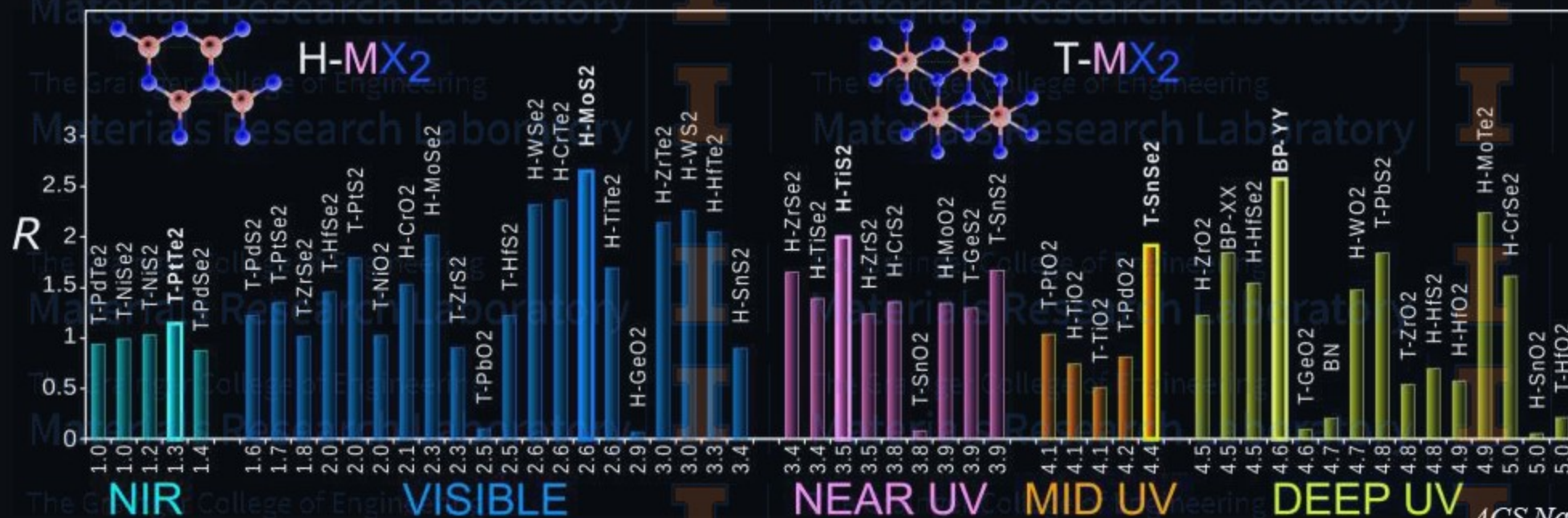
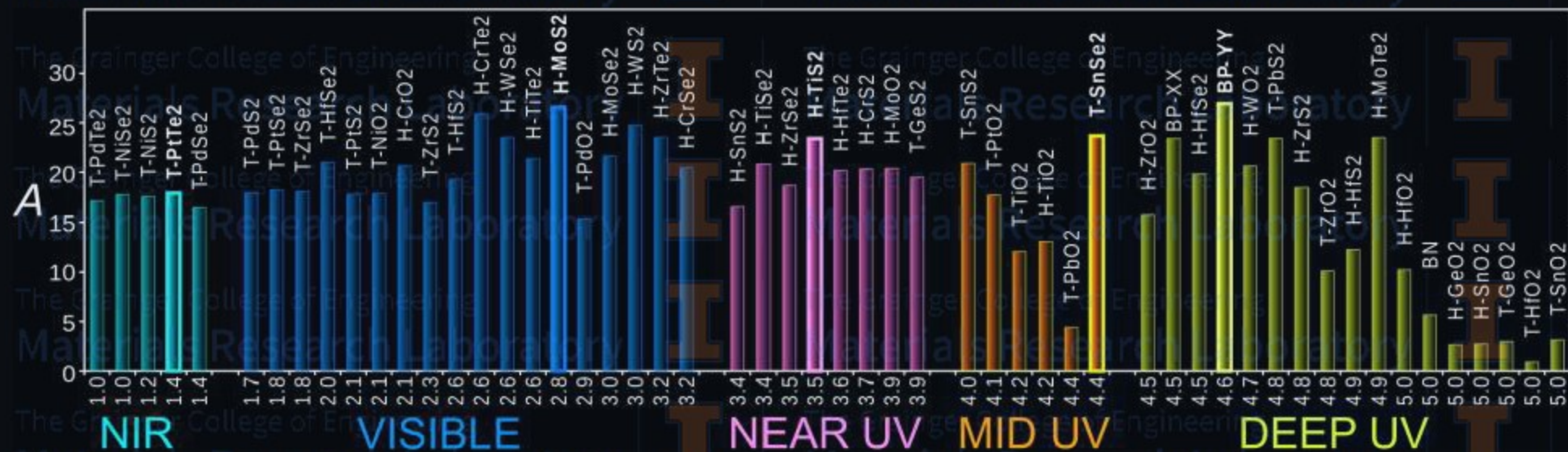


Applied Materials Today 8, 68 (2017)



Optical Materials Express, 332858 (2018)

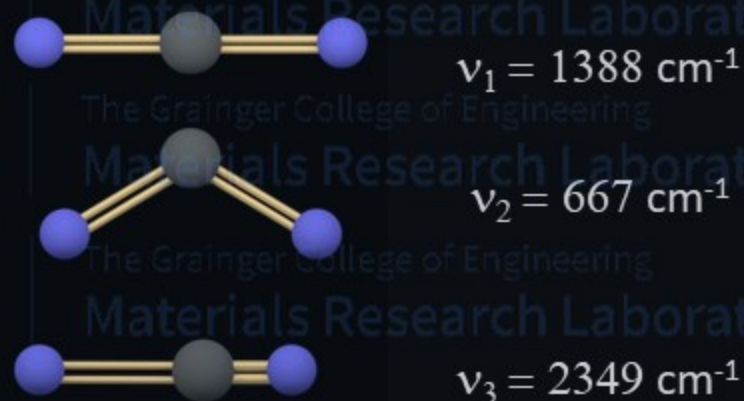
Spectrophotometry (UV-VIS-NIR)



Vibrational spectroscopy

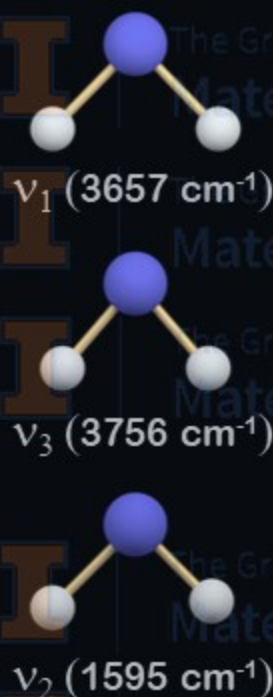
Normal vibrational modes in molecules:

CO₂ (4 modes)

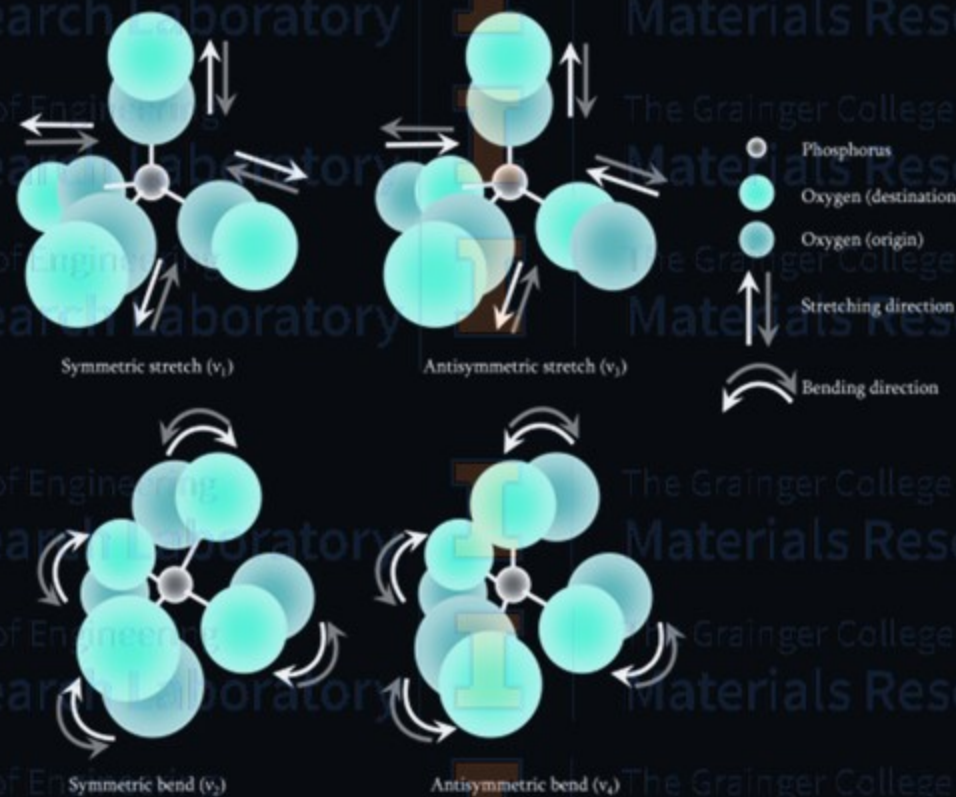


Number of modes:
3N-6 for non-linear molecules
3N-5 for linear molecules

H₂O (3 modes)



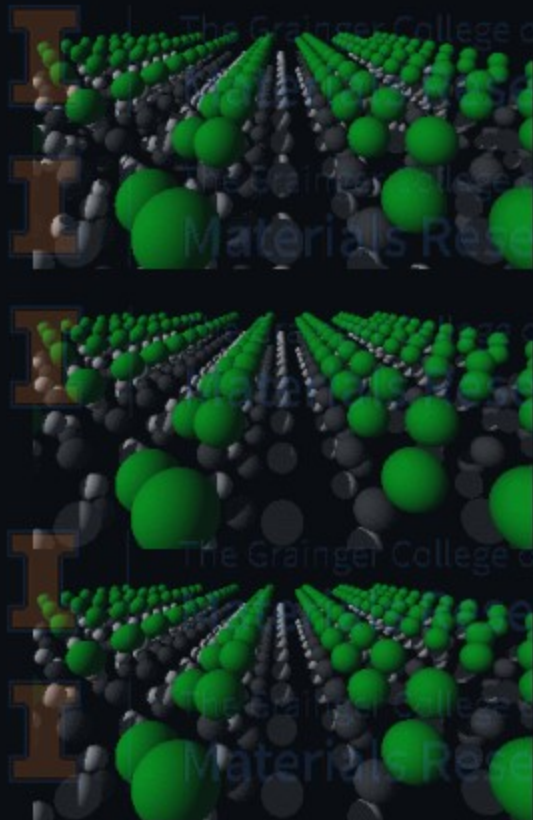
PO₄ (9 modes)



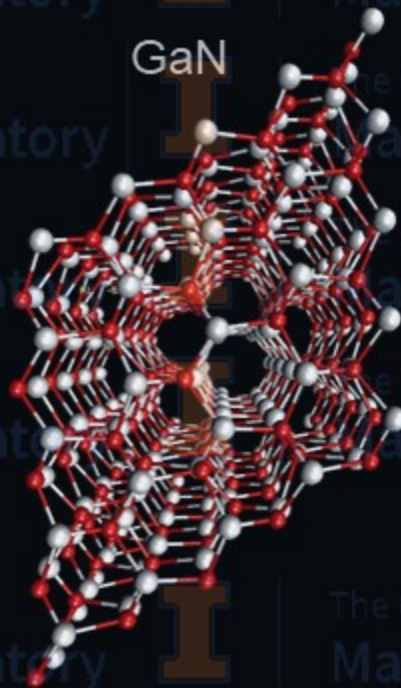
Vibrational spectroscopy

Normal vibrational modes in solids:

Sb/GaAs(110)



GaN



SWCNT



<http://www.phonon.fc.pl>

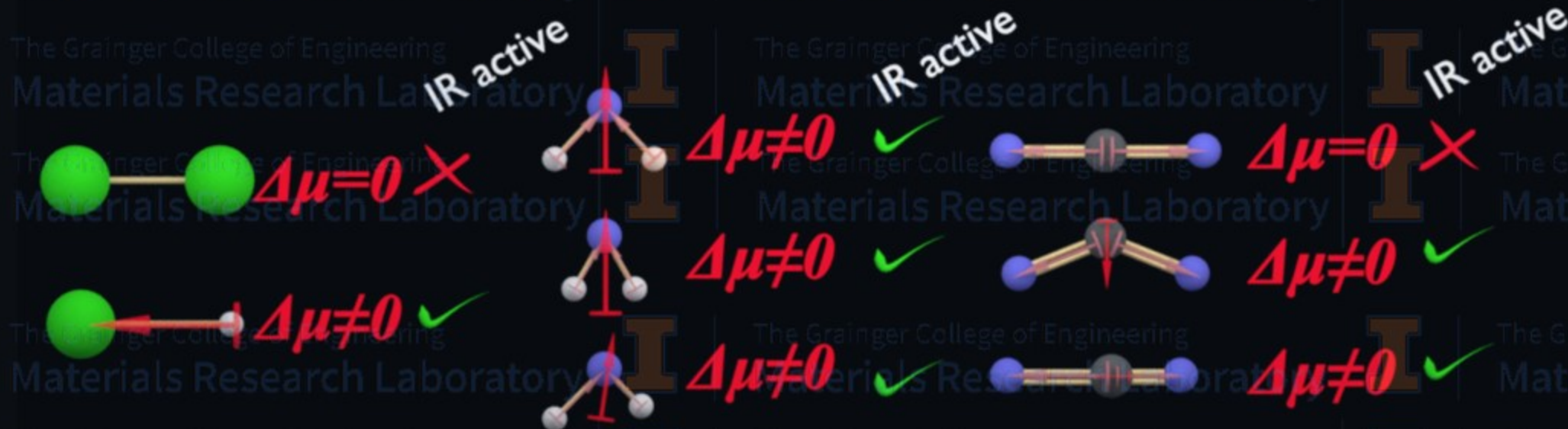
T. A. Beu and A. Farcas 2016 EPL 113 37004

<http://www.physik.tu-berlin.de/institute/IFFP/richter/new/research/surface-phonons.shtml>

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. $\Delta\mu \neq 0$



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"

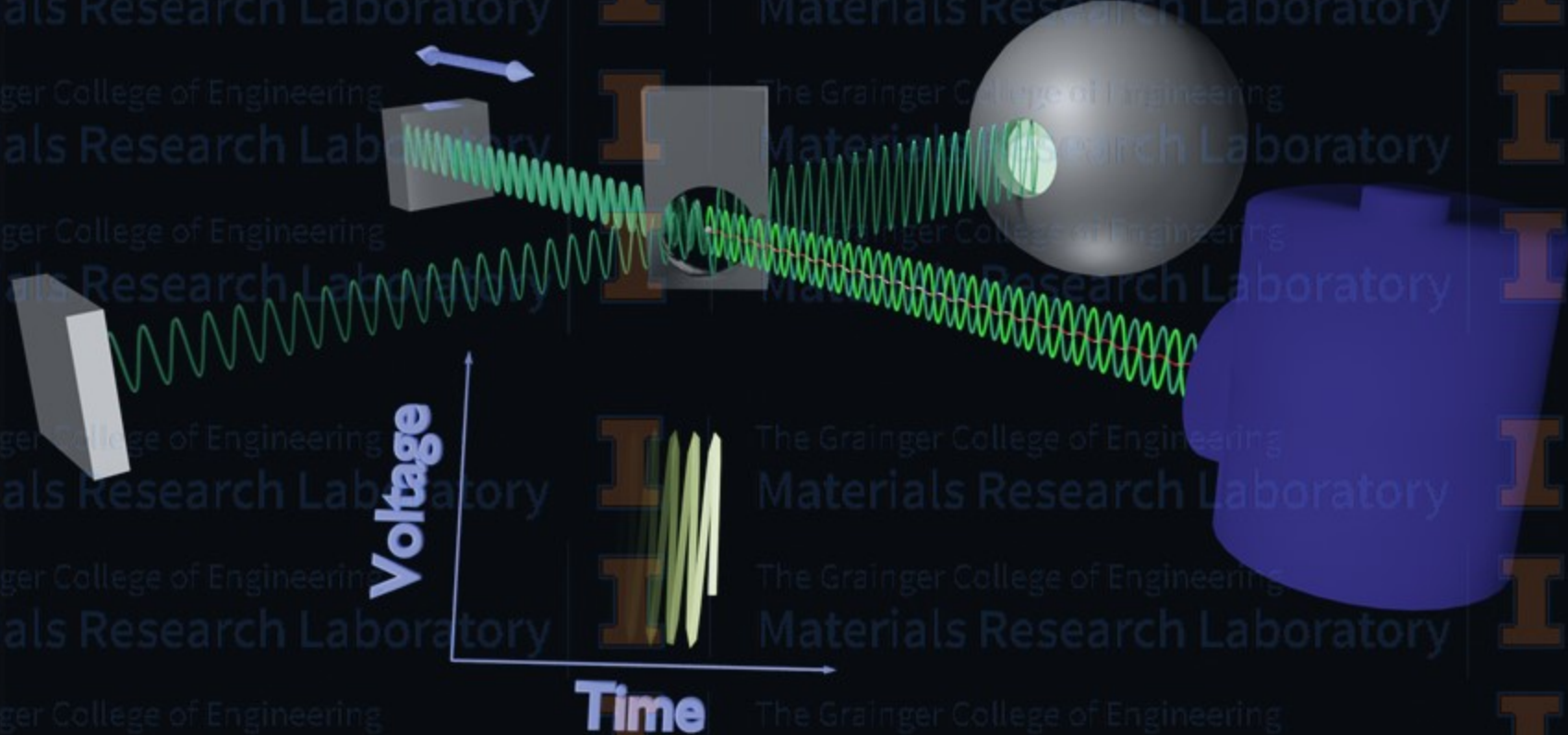
The Nobel Foundation

Instrumentation:

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

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

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



Fourier Transform IR spectroscopy (FTIR)



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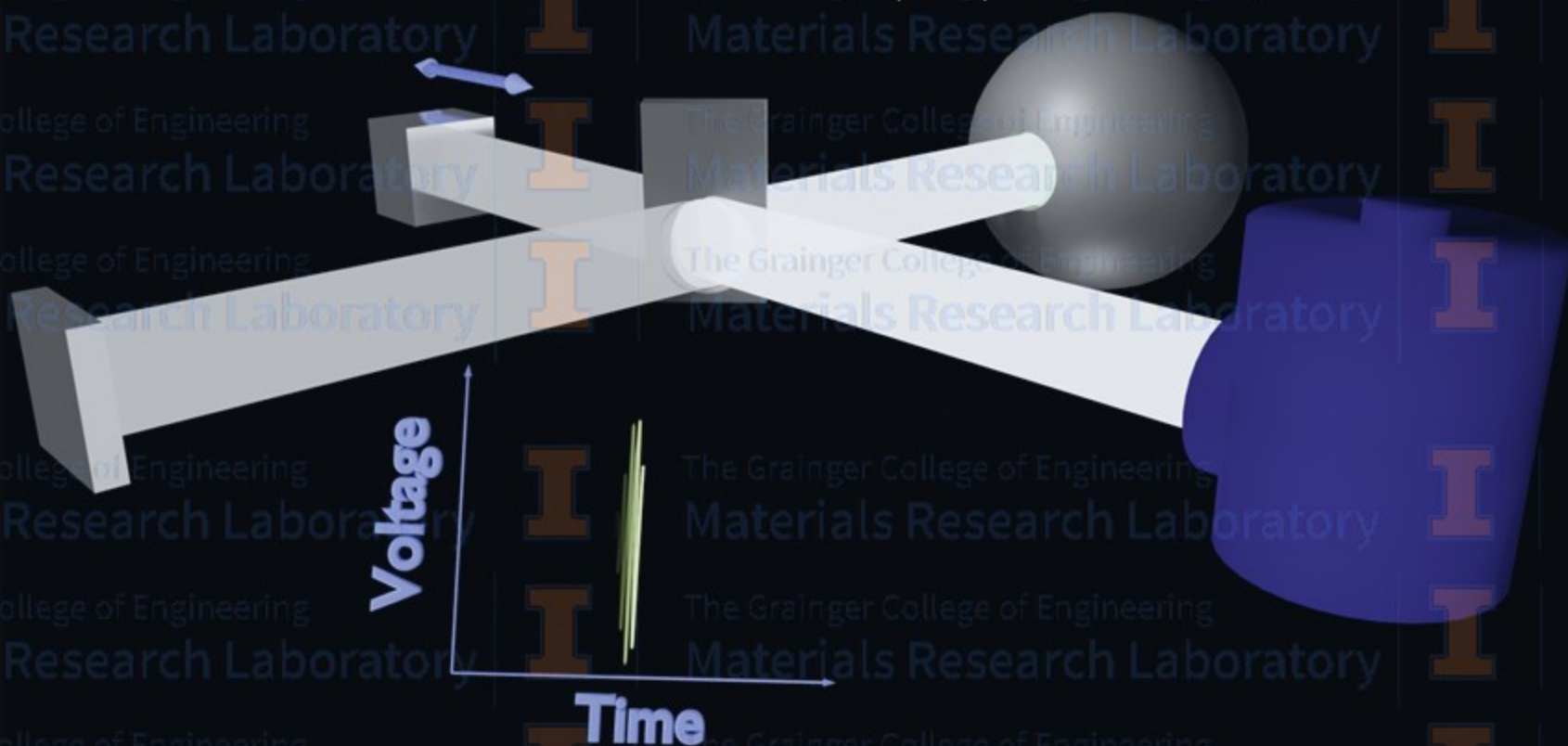
The Nobel Foundation

Instrumentation:

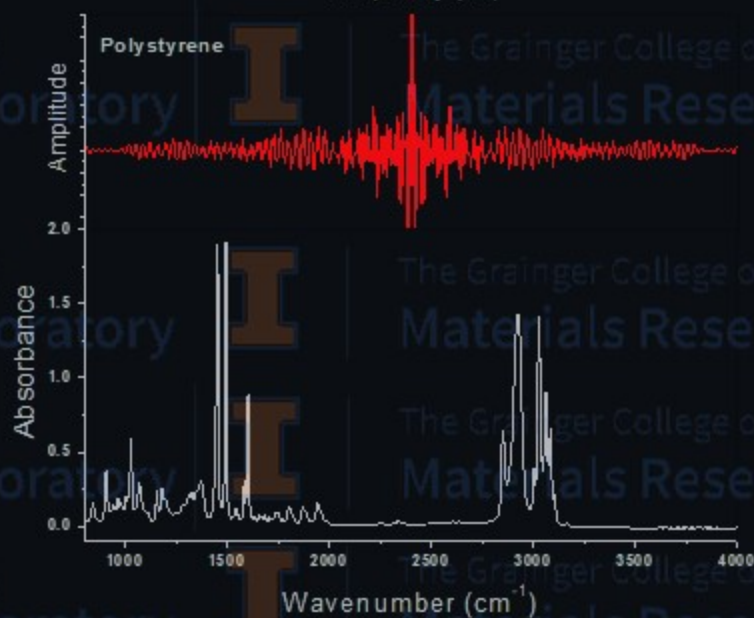
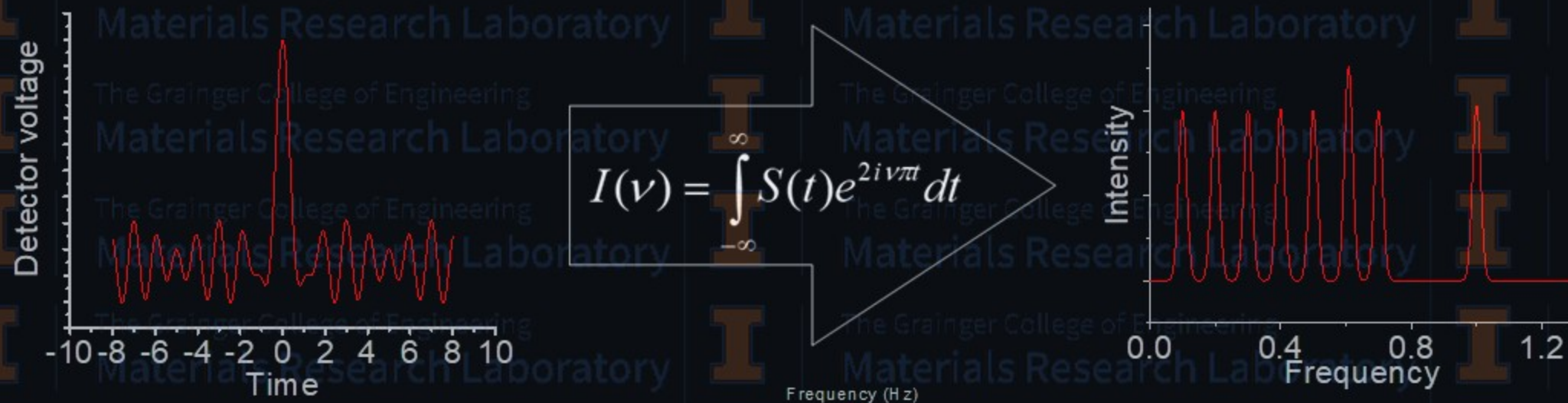
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Fourier Transform IR spectroscopy (FTIR)

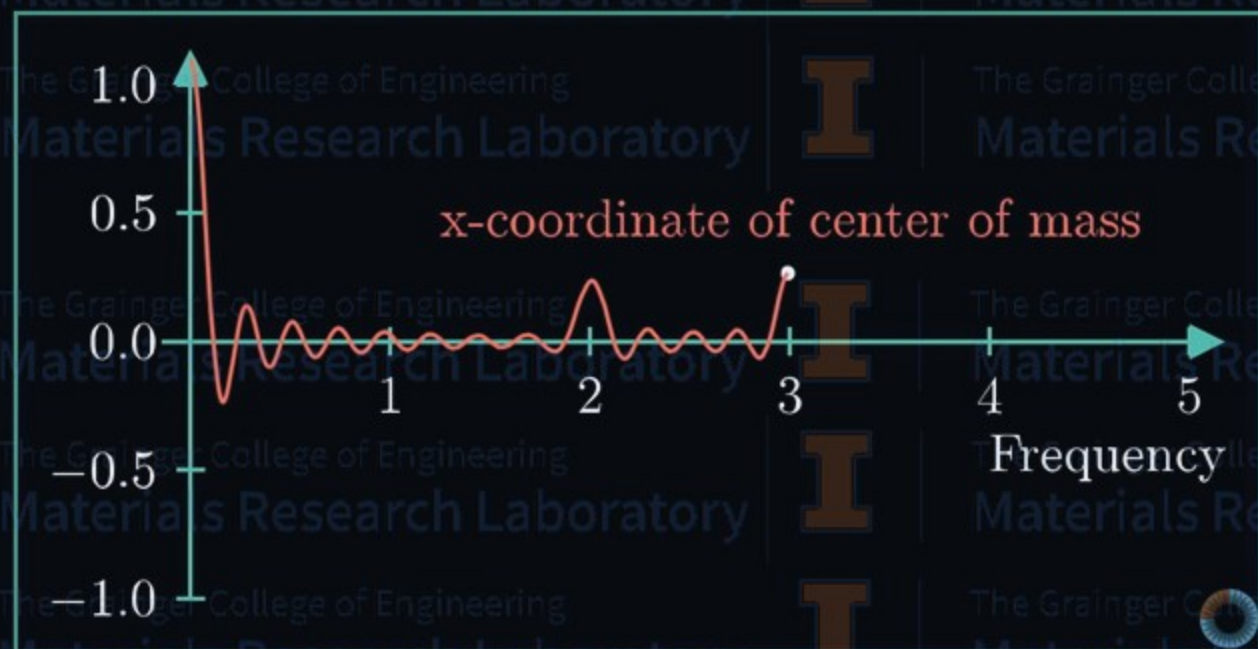
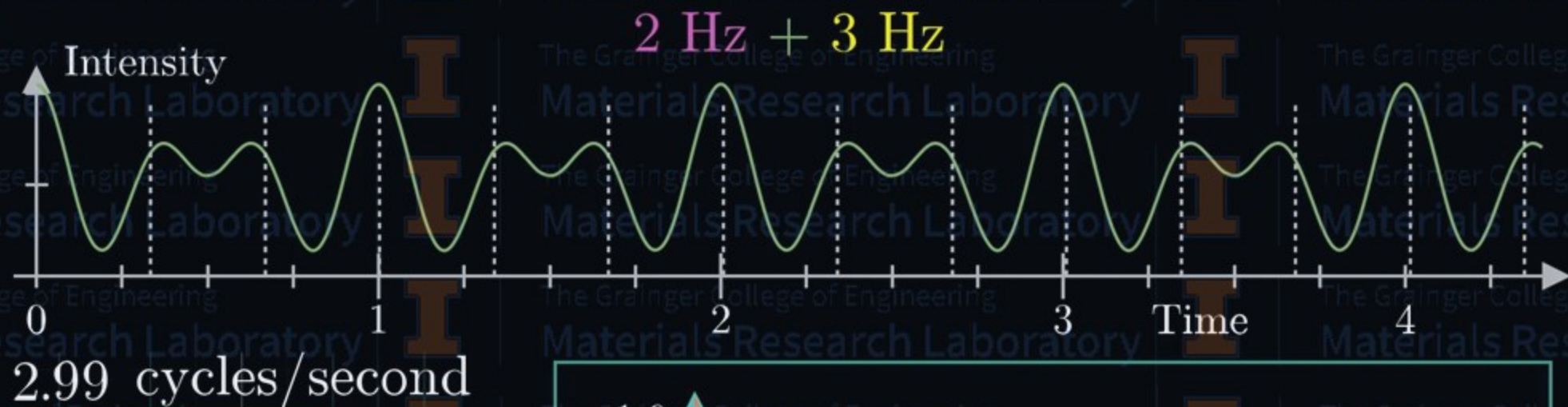


Fourier Transform IR spectroscopy (FTIR)

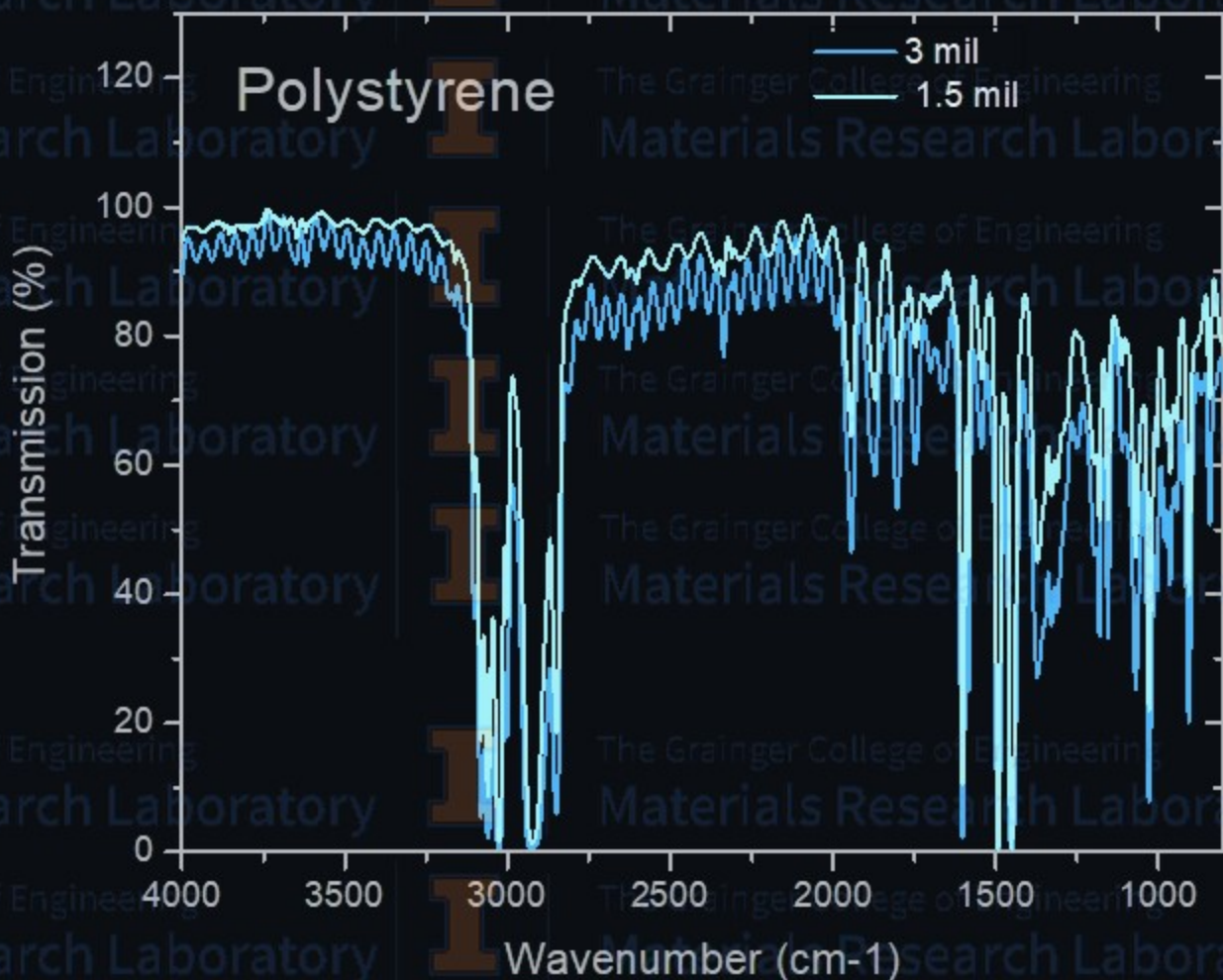
But what is the Fourier Transform? A visual introduction.



3Blue1Brown



Fourier Transform IR spectroscopy (FTIR)

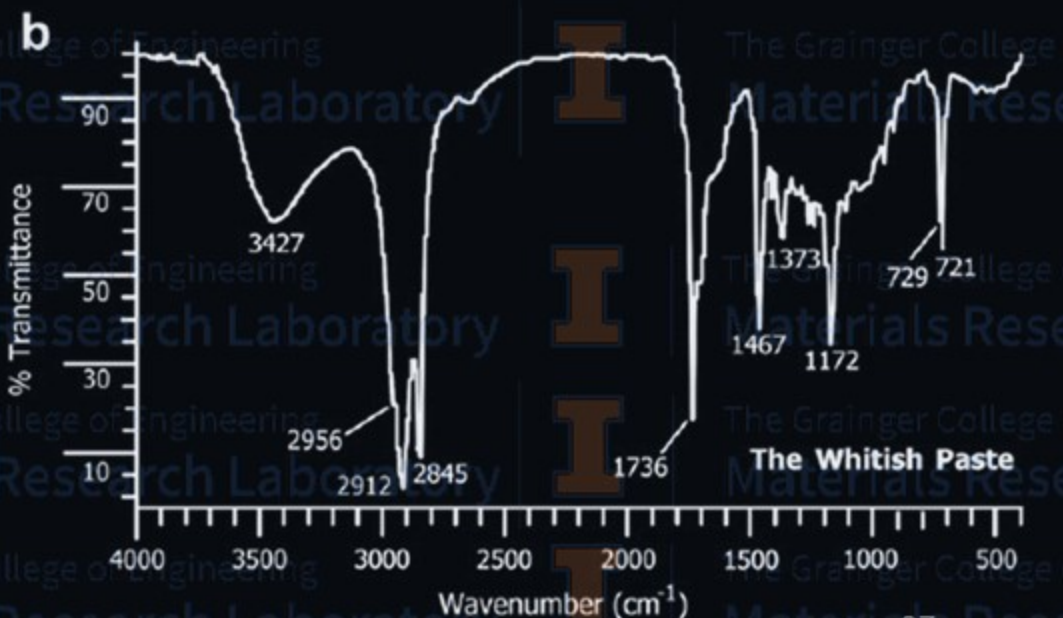
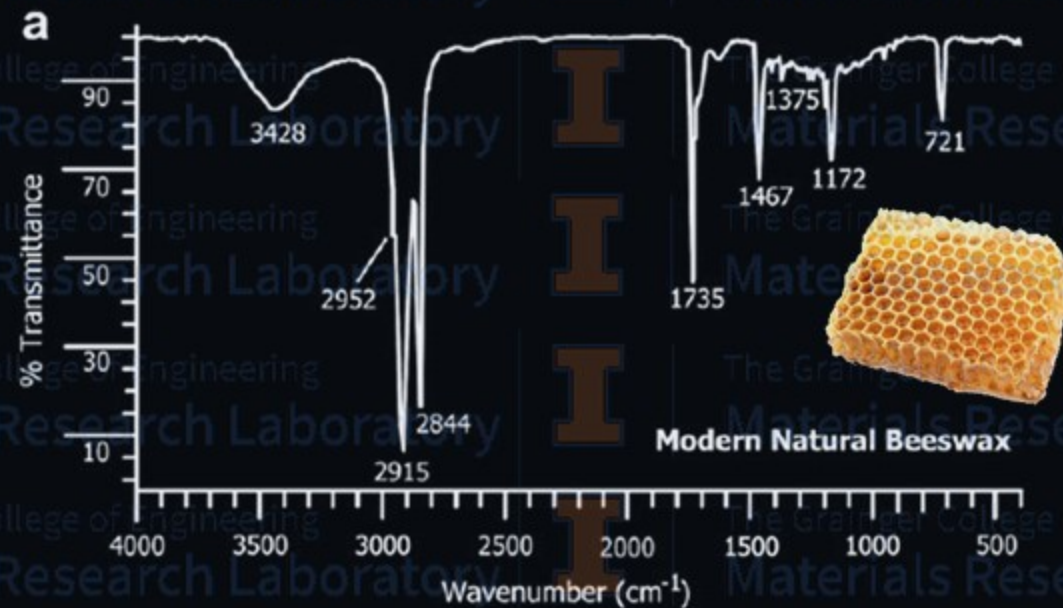
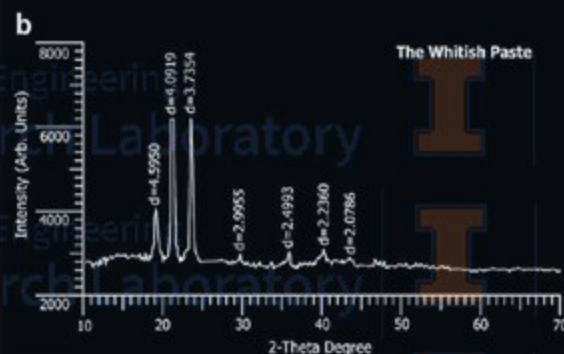
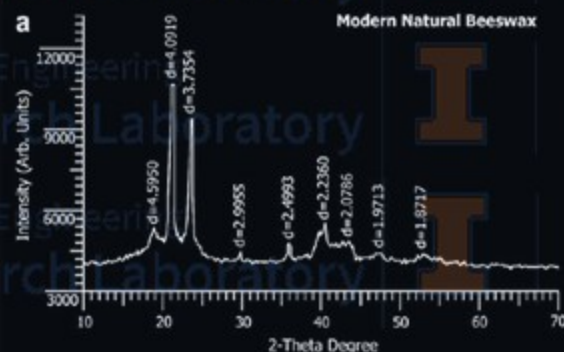


Fourier Transform IR spectroscopy (FTIR)

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

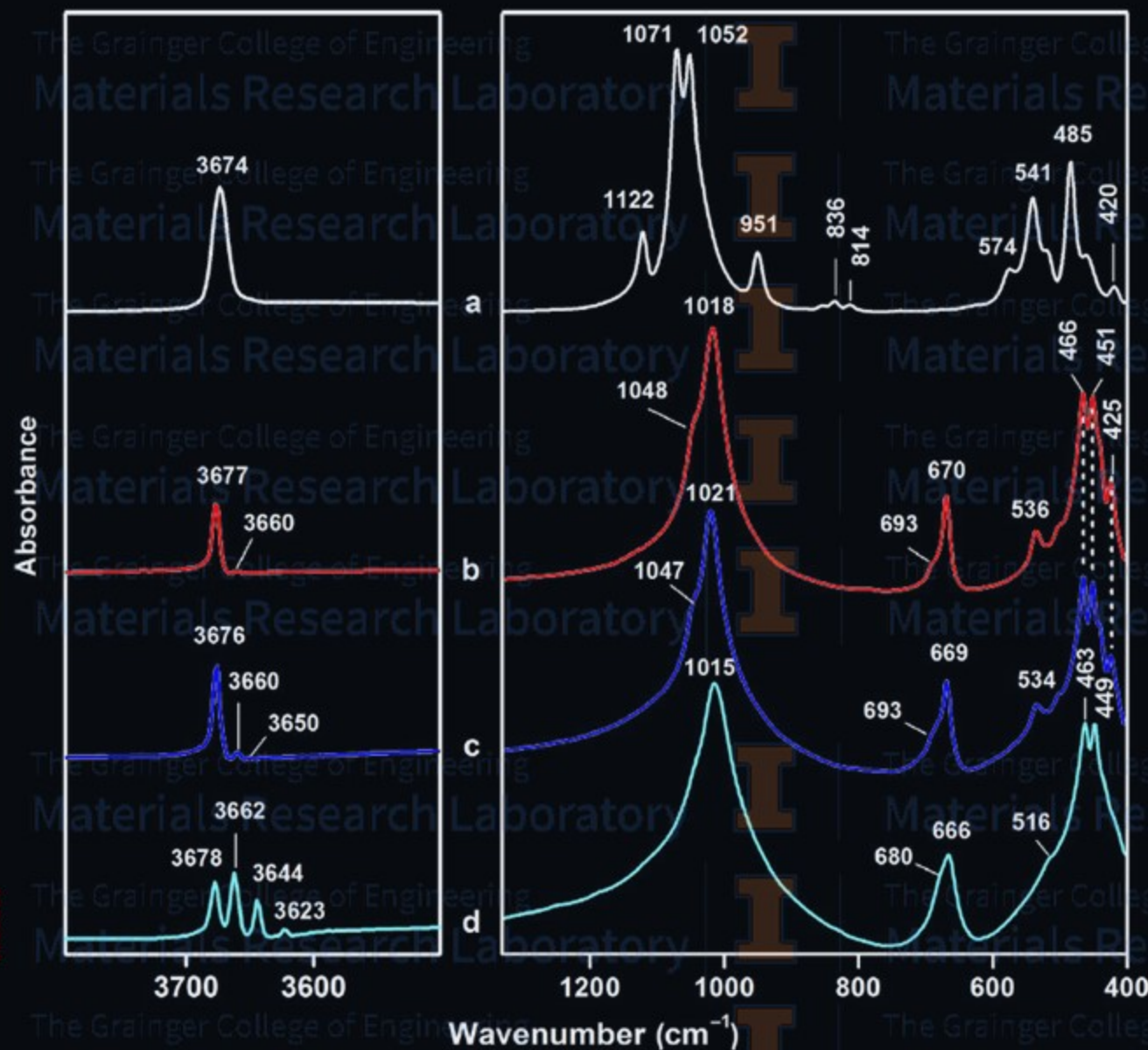
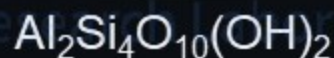
Discovery of beeswax as binding agent on a 6th-century BC Chinese turquoise-inlaid bronze sword

Wugan Luo, Tao Li, Changsui Wang, Fengchun Huang



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

Fourier Transform IR spectroscopy (FTIR)



Images from Wikipedia and eurocalc.com

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

Spectrophotometry (UV-VIS-NIR) and FTIR



Strengths:

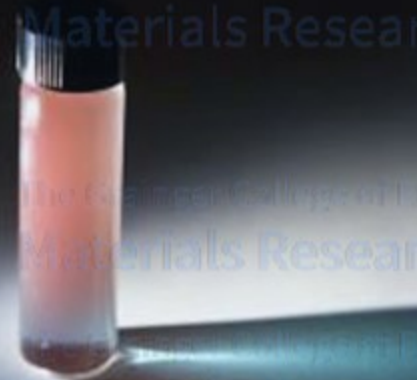
- Very little or simple sample preparation.
- Simplicity of use and data interpretation.
- Short acquisition time, for most cases.
- Non destructive.
- Broad range of photon energies.
- High sensitivity (~ 0.1 wt% typical for FTIR).

Complementary techniques:

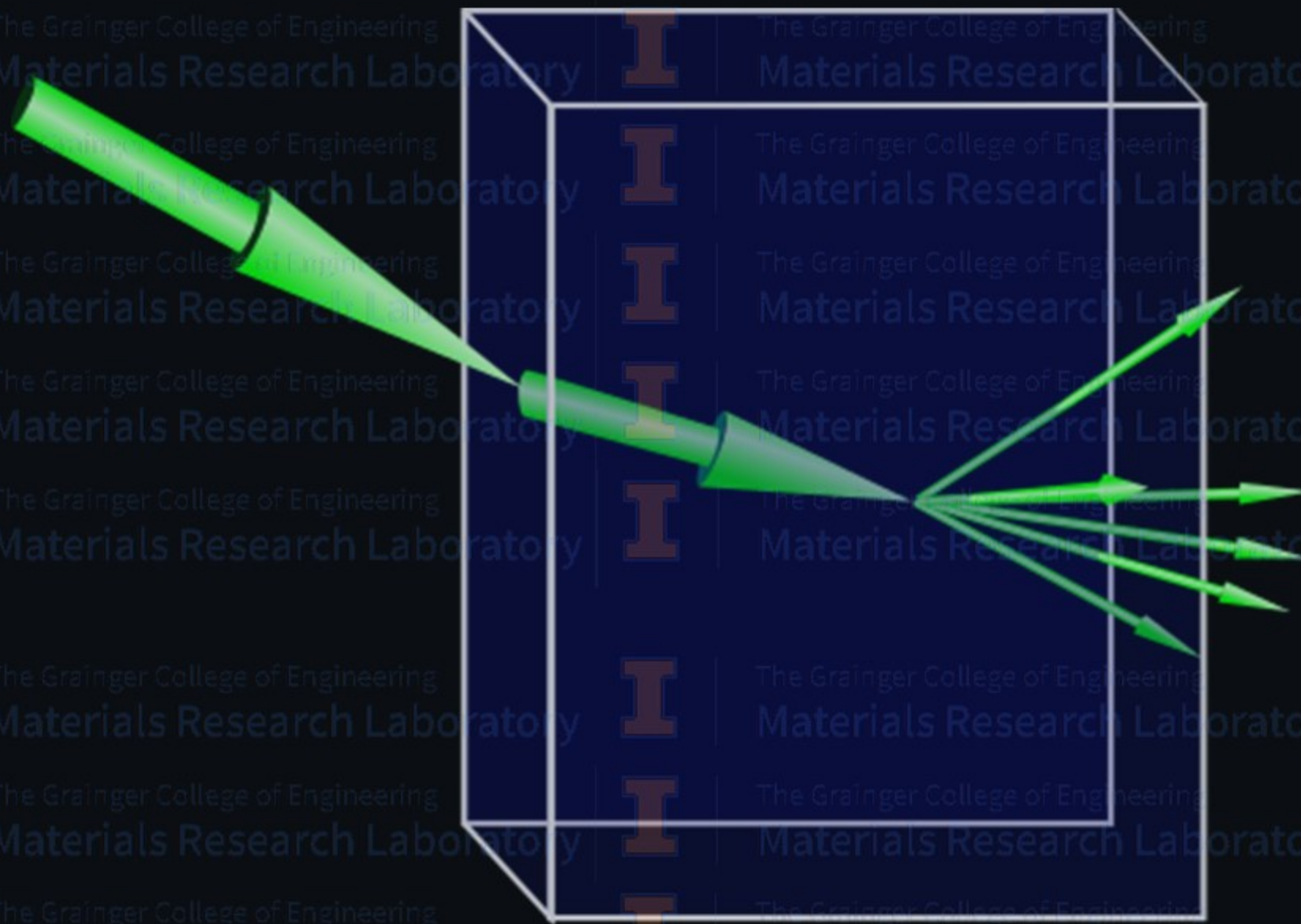
Raman, Electron Energy Loss Spectroscopy (EELS), Extended X-ray Absorption Fine Structure (EXAFS), XPS, Auger, SIMS, XRD, SFG.

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.



Light scattering



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"*.



The Nobel Foundation



Sir Kariamanikkam Srinivasa Krishnan

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

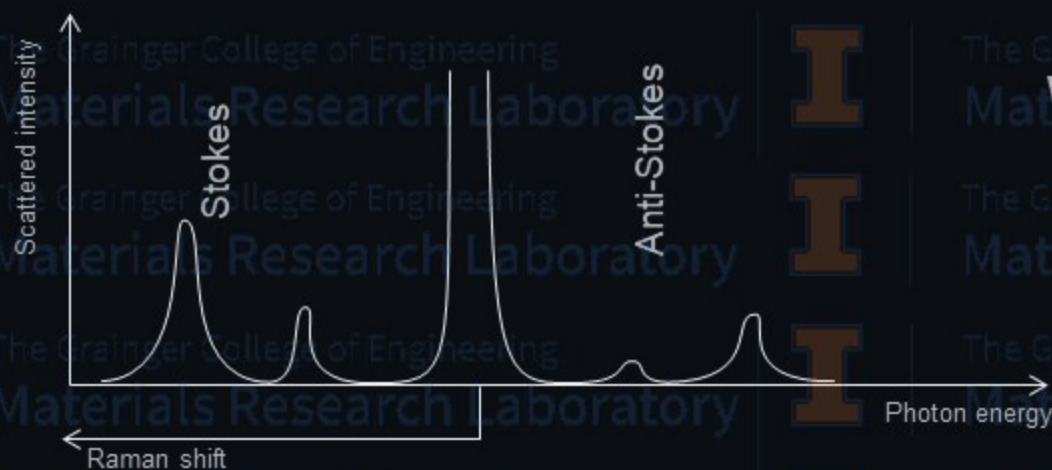
Raman spectroscopy

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.



Excited state

Anti-Stokes

Rayleigh scattering

Stokes

Virtual states

Vibrational states

Ground state

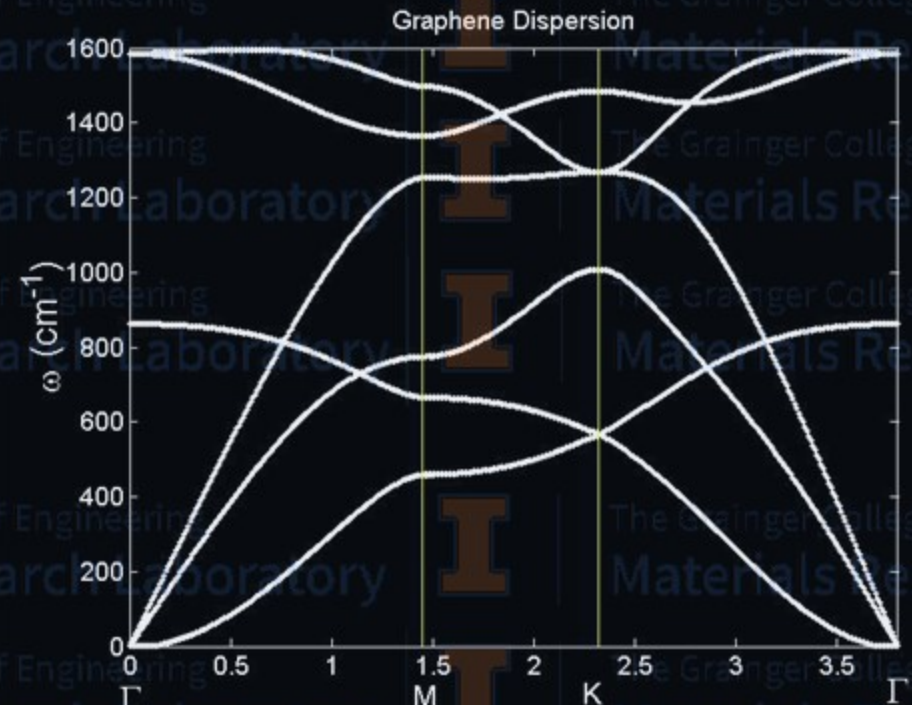
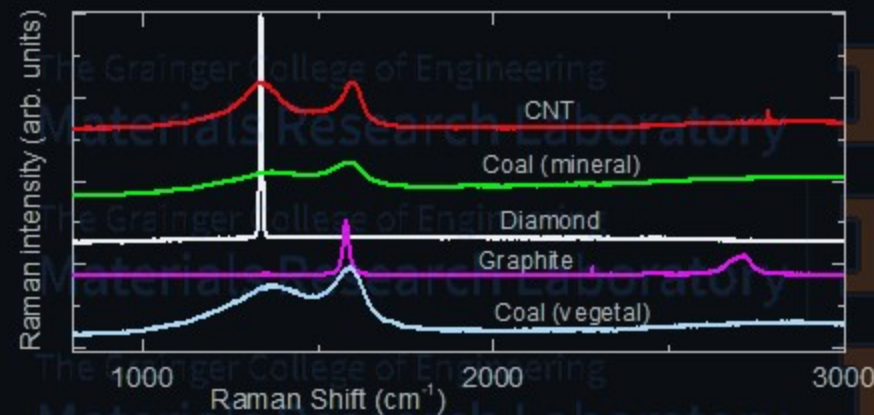
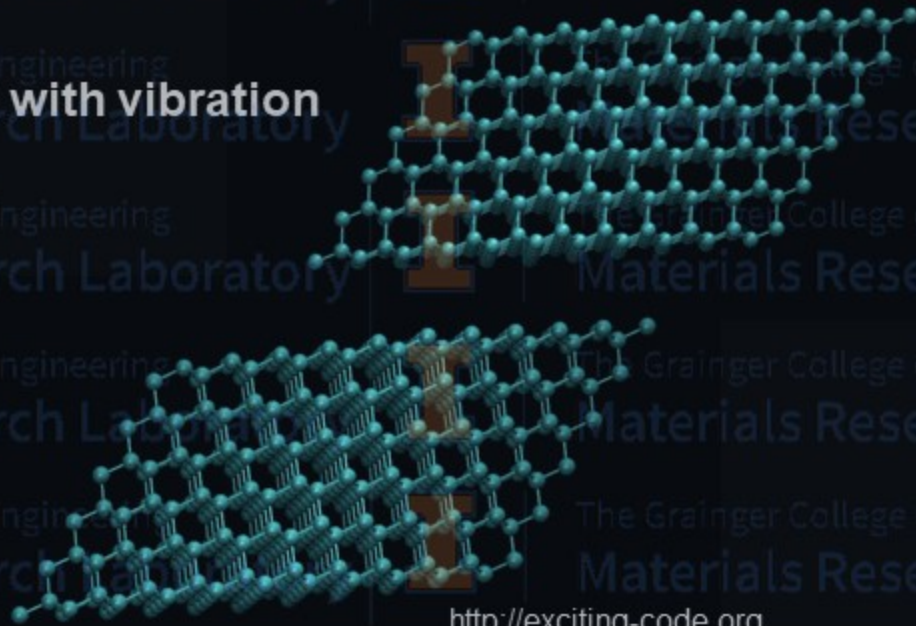
Resonance Raman

IR

Raman spectroscopy

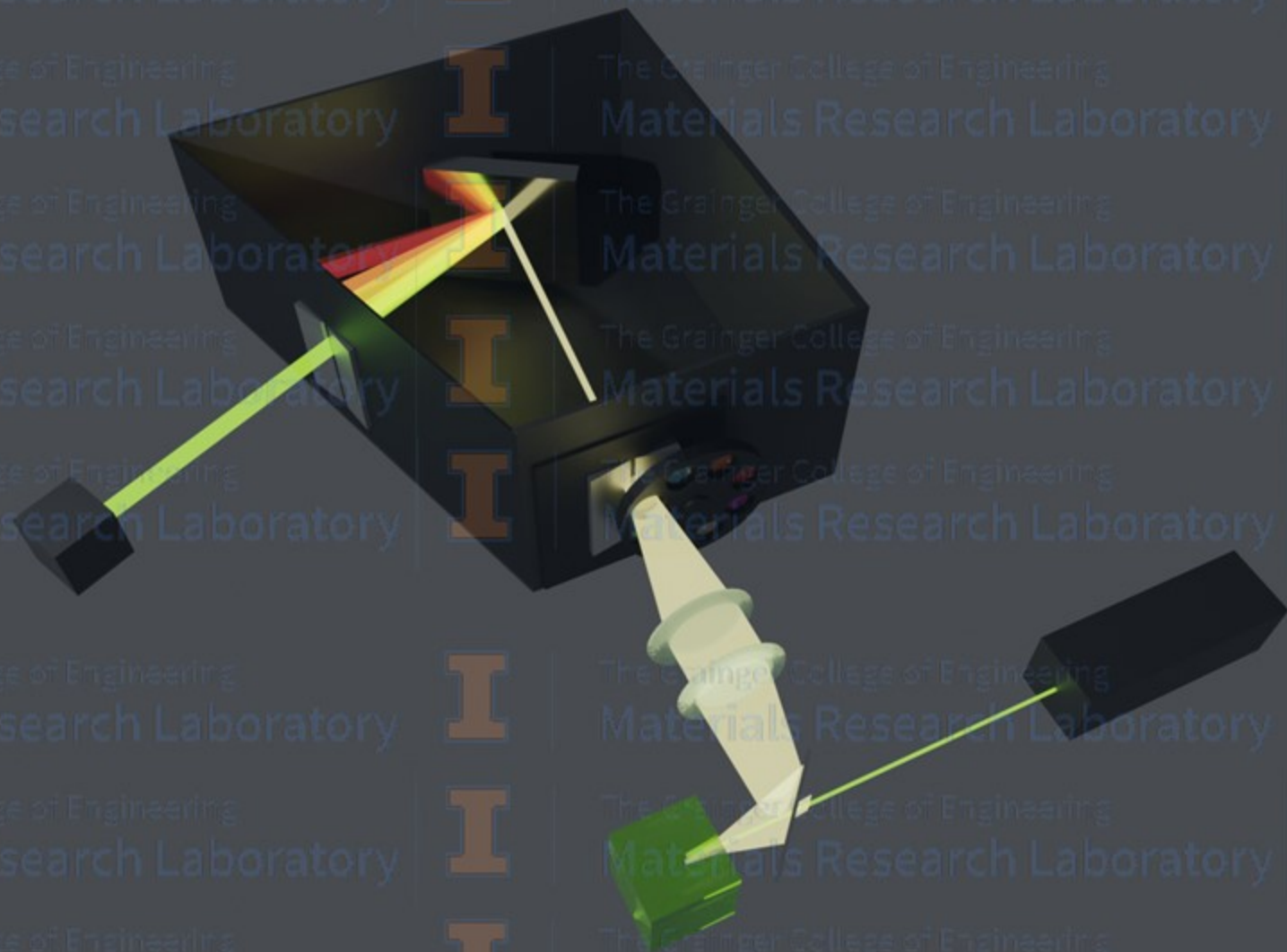
Impinging light couples with vibration modes of the material:

- Phonons
- Molecular vibrations



Raman spectroscopy

Instrumentation:

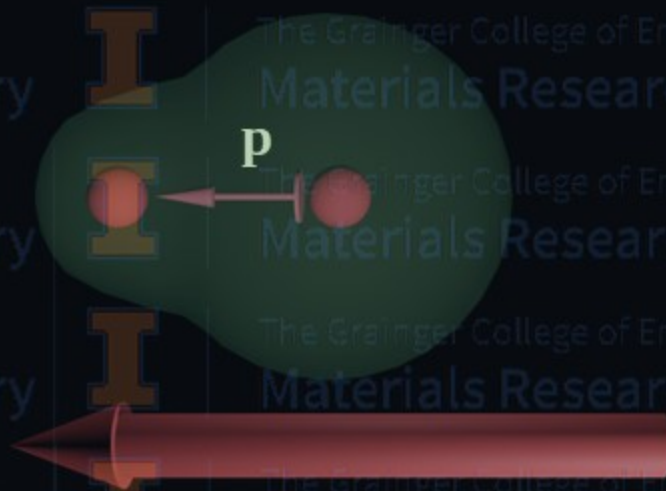


Raman spectroscopy



$$p = 0$$

Raman spectroscopy



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

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

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:

$$\alpha_k = \alpha_0 + \sum_k \left(\frac{\partial \alpha}{\partial Q_k} \right)_0 \cdot Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \alpha}{\partial Q_k \partial Q_l} \right)_0 \cdot Q_k \cdot Q_l + \dots$$

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

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

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:

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

$$\mathbf{p} = \alpha_0 \cdot \mathbf{E}_0 \cdot \cos(2\pi \cdot \nu_0 \cdot t) + \\ + \frac{1}{2} \cdot \alpha'_k \cdot Q_{k0} \cdot \mathbf{E}_0 \cdot [\cos(2\pi \cdot t \cdot (\nu_0 + \nu_k) + \varphi_k) + \\ + \cos(2\pi \cdot t \cdot (\nu_0 - \nu_k) - \varphi_k)]$$

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

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

Raman spectroscopy

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



Raman active

Fourier Transform IR spectroscopy (FTIR)

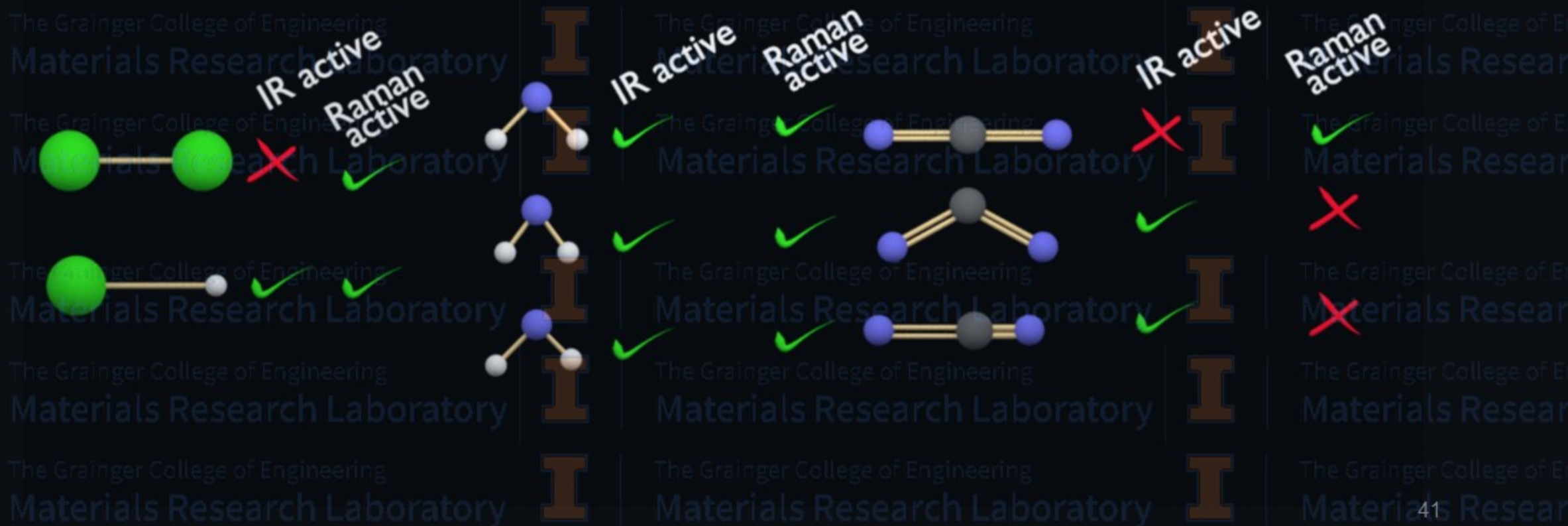
IR active vibrations



Raman spectroscopy

Raman active vibrations

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



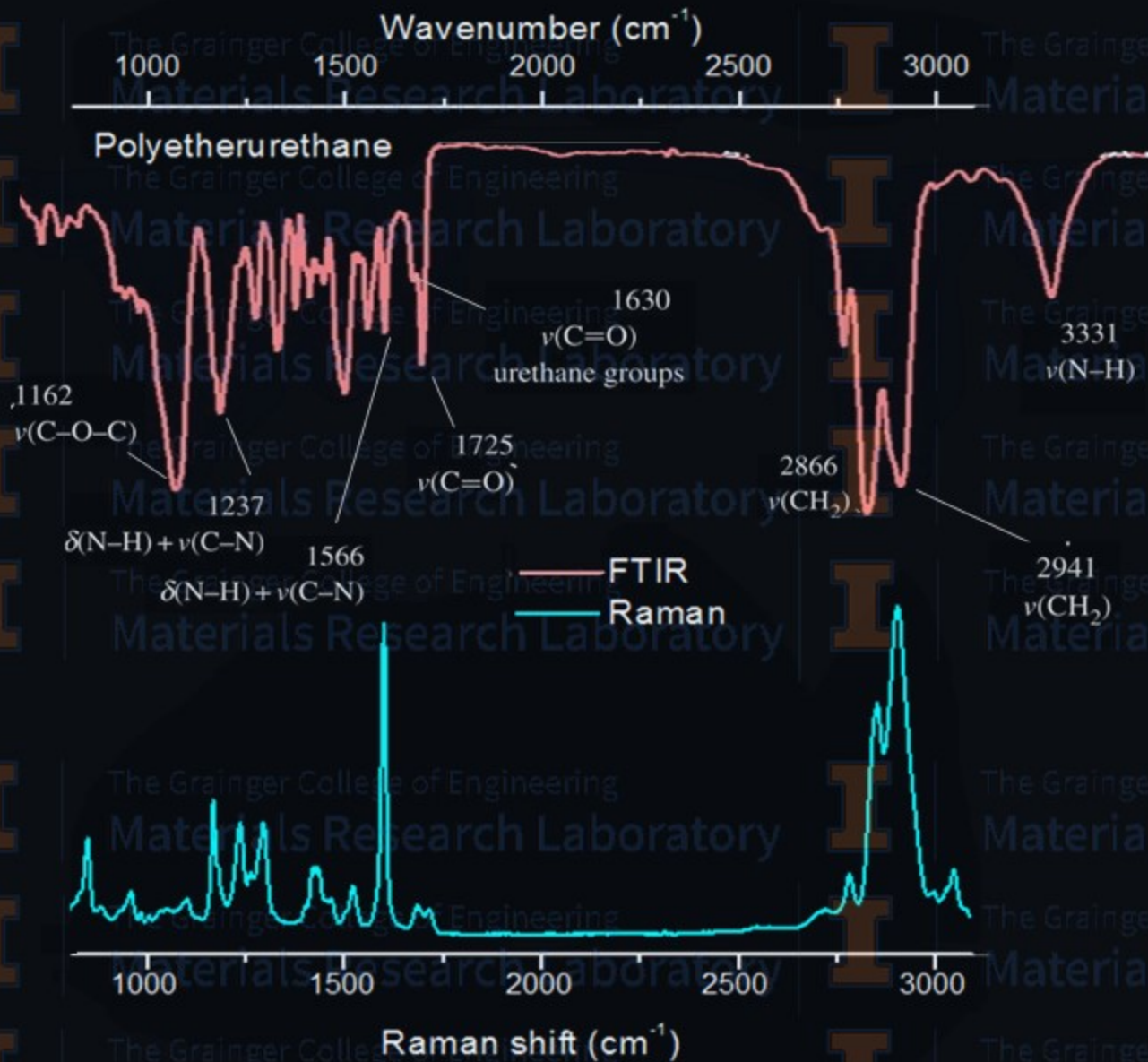
Raman spectroscopy

FTIR and Raman:

The two techniques are complementary
(different selection rules).

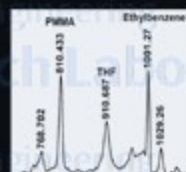
$$\Delta\mu \neq 0$$

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



Studying the ...

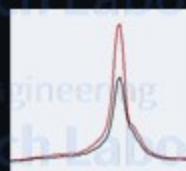
... we can estimate ...



Characteristic Raman frequencies



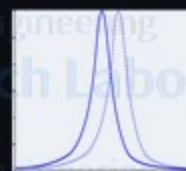
Identity and composition of materials



Raman peak intensity



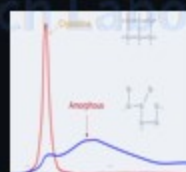
Volume of material probed



Raman peak frequency shift



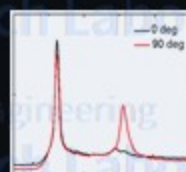
Strain, stress, crystal lattice distortion



Raman peak width



Crystallinity of material



Raman peak polarization dependency



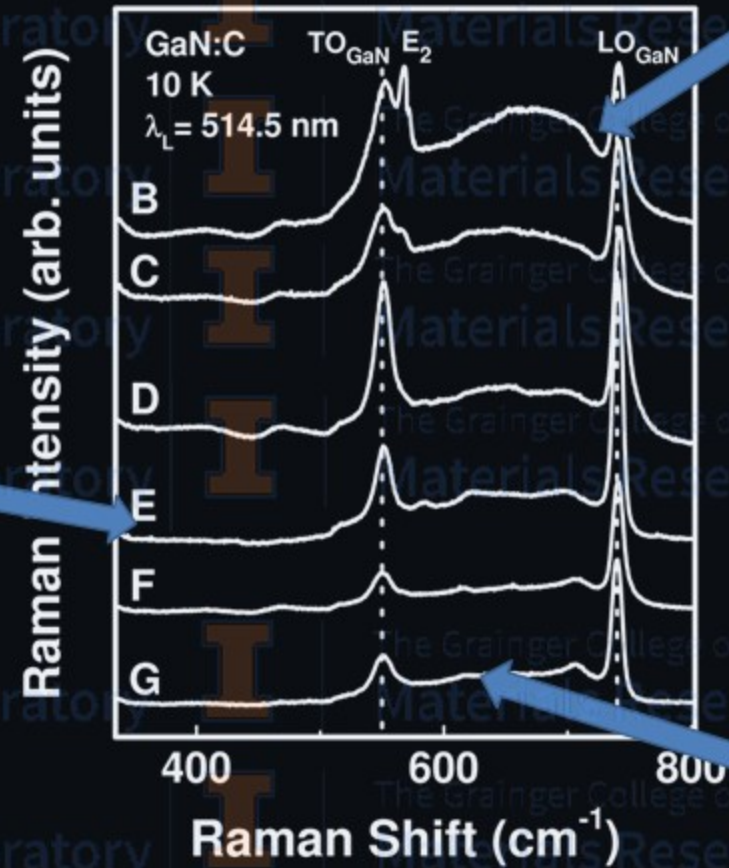
Crystal orientation and symmetry

Raman spectroscopy

Molecular and crystalline structure characterization

Presence of N vacancies yields poor crystallinity

Substitutional C fills N vacancies improving the crystallinity

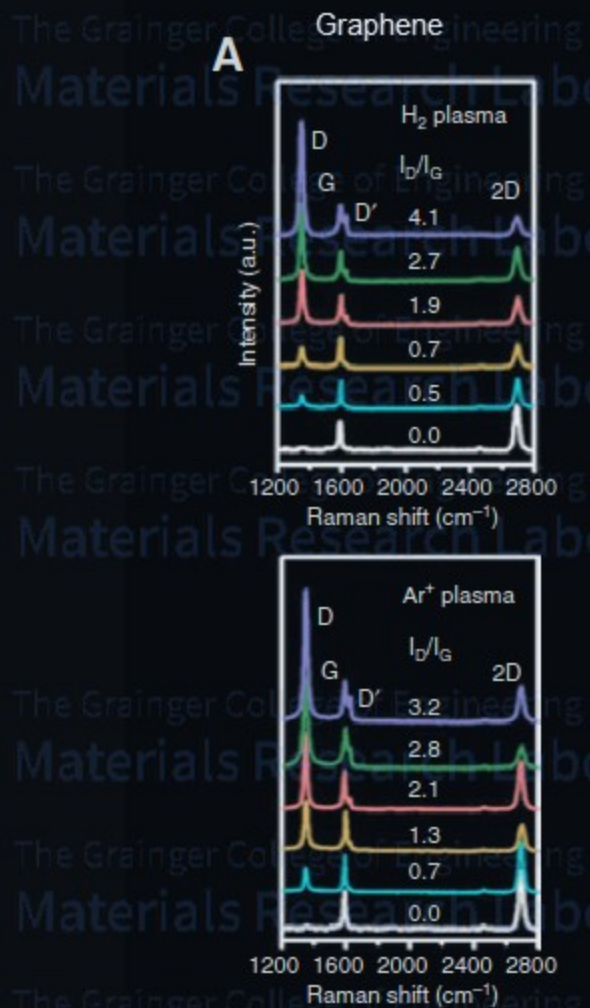


C content

C incorporates interstitially causing a degradation of the crystal lattice

PHYSICAL REVIEW B 68, 155204 (2003)

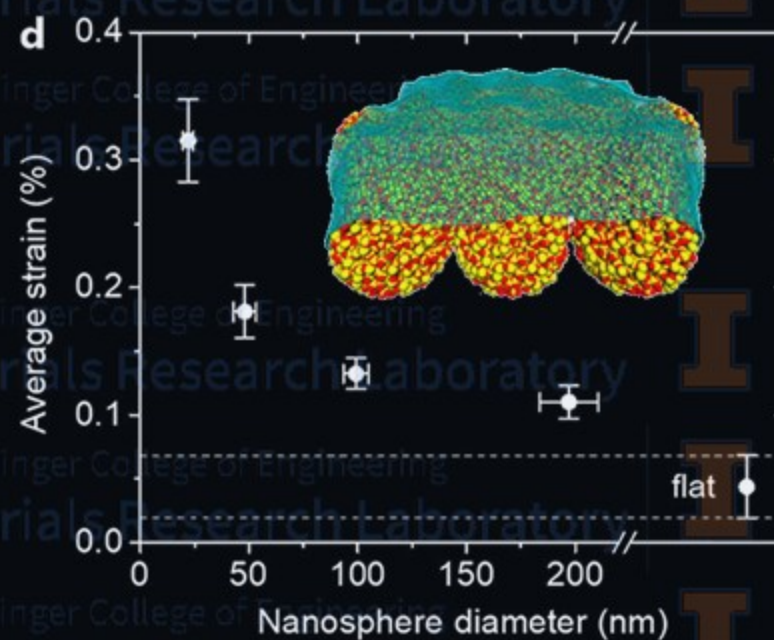
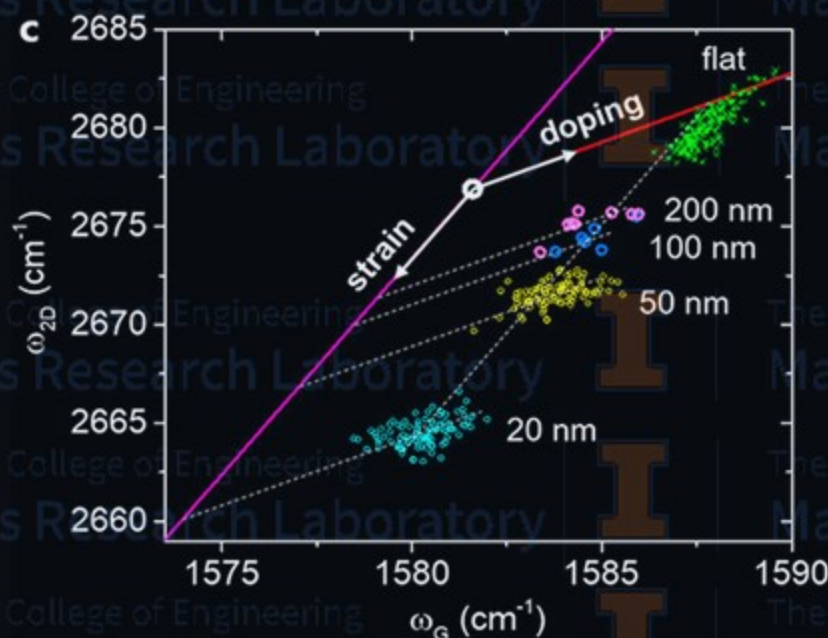
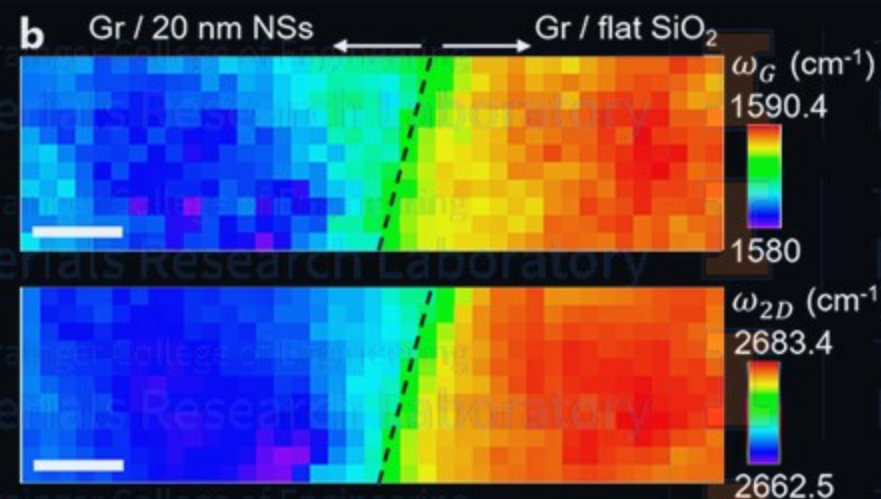
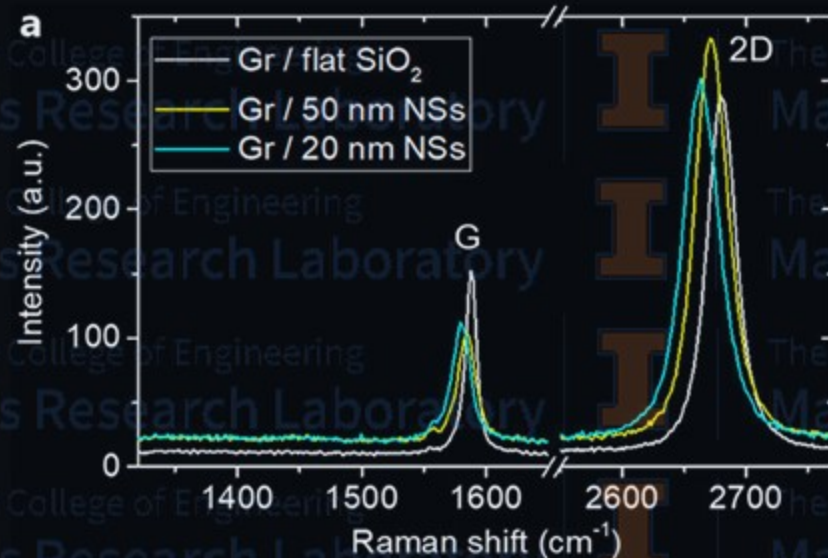
Characterization



The inset shows the linear dependence of I_D/I_G on the defect concentration parameters at low defect concentrations.

Raman spectroscopy

Strain/stress

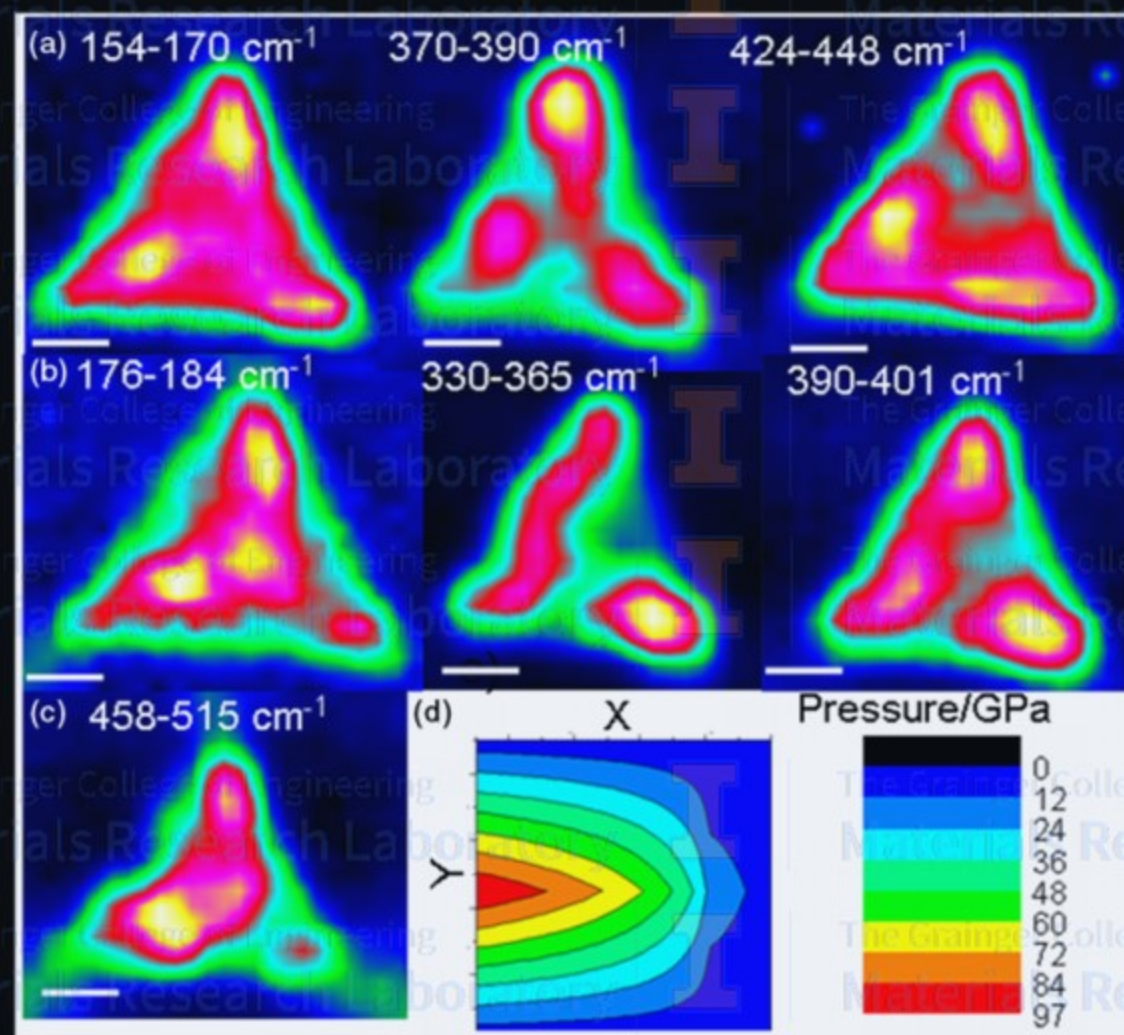
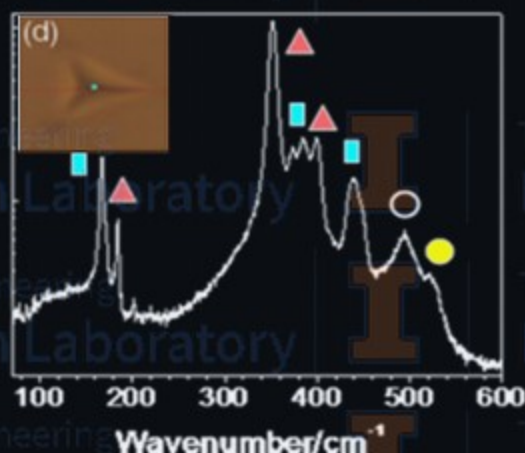
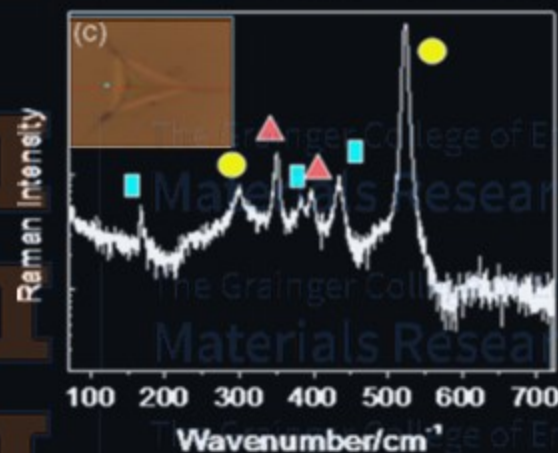
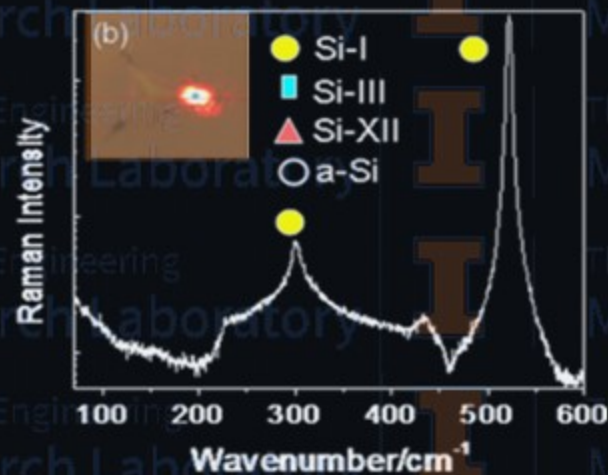


Phase transitions

(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

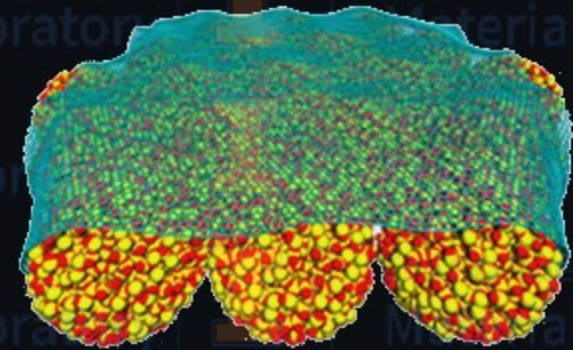
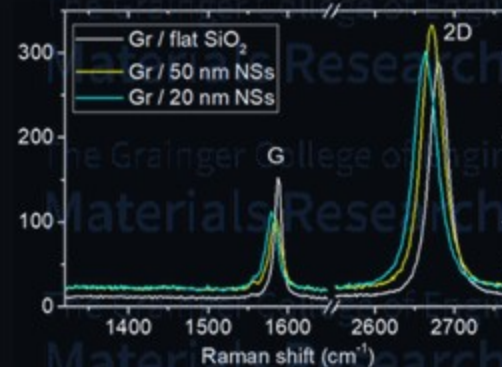
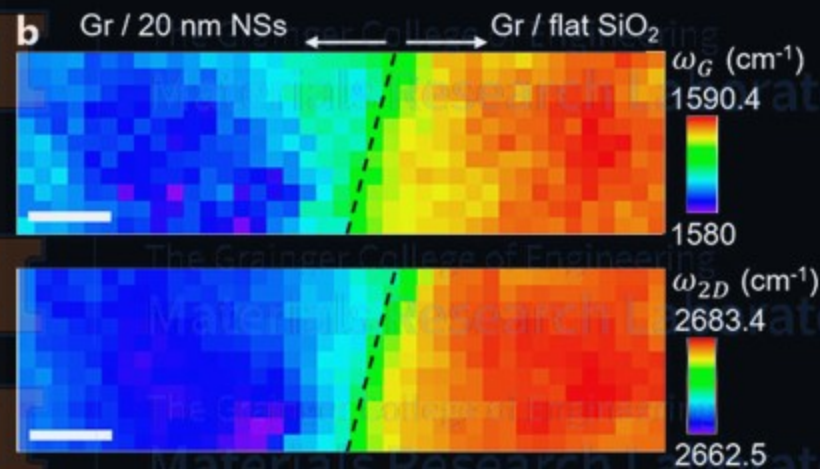
[†] Ref 2,3



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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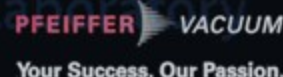


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**Advanced Materials
Characterization
Workshop**



Optical Characterization Methods Part II

Julio A. N. T. Soares

Materials Research Laboratory

University of Illinois at Urbana-Champaign



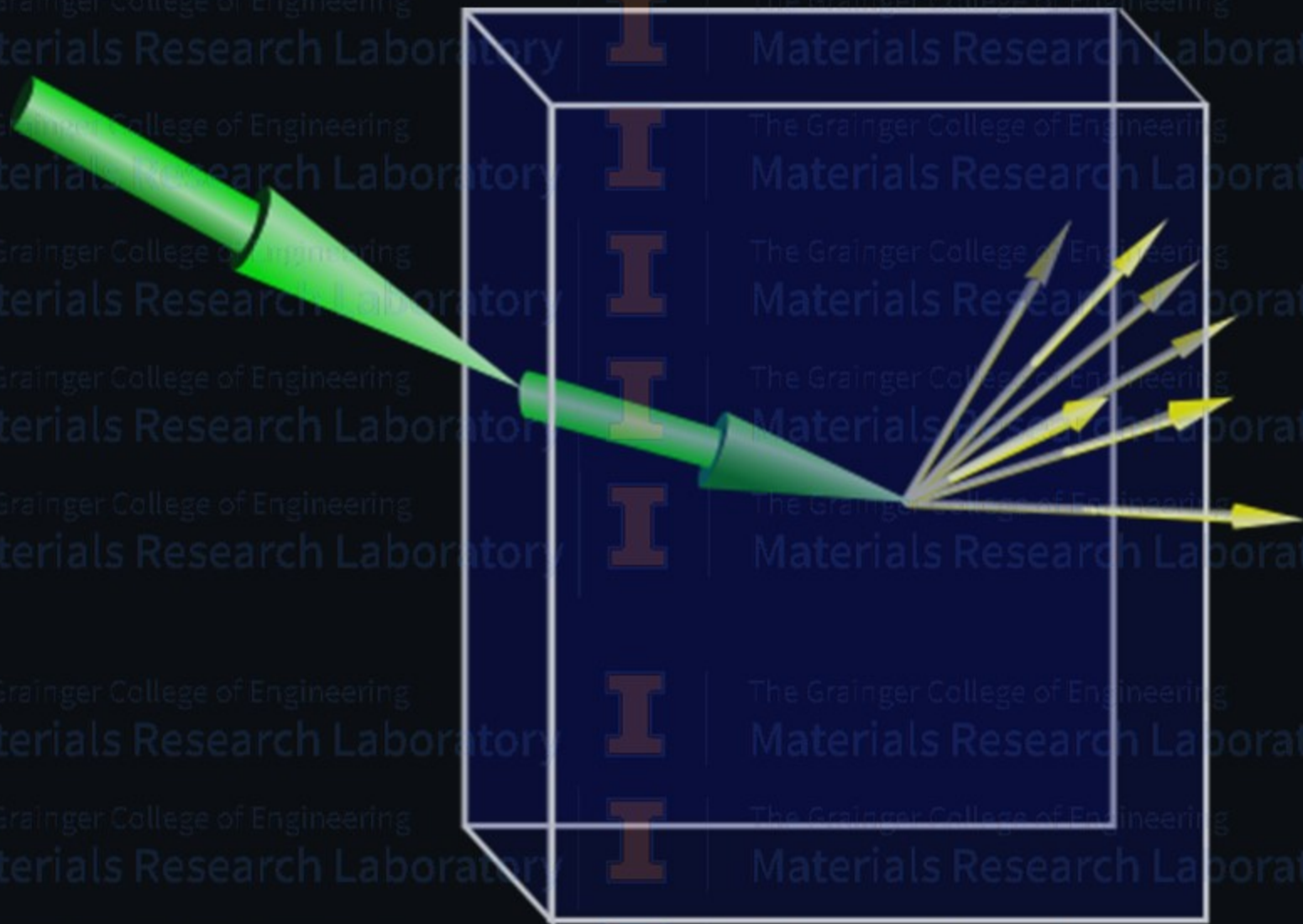
go.illinois.edu/AMC2023

**The Grainger College
of Engineering**

UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

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Luminescence



Luminescence

Lifetime: Phosphorescence, fluorescence

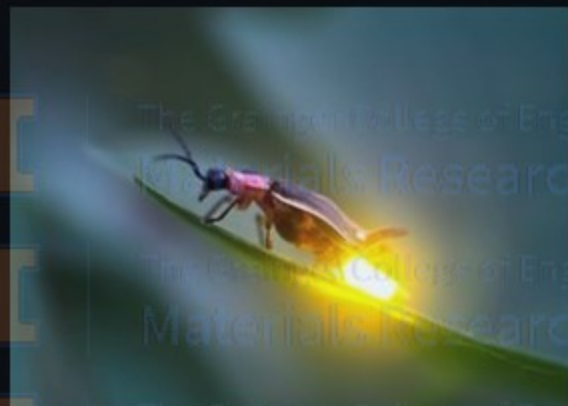
Mechanism: Photoluminescence, bioluminescence, chemoluminescence, thermoluminescence, piezoluminescence, etc.



Disney Pixar



Charles Hedcock ©



Radim Schreiber



Profilephotocovers.com



Profilephotocovers.com



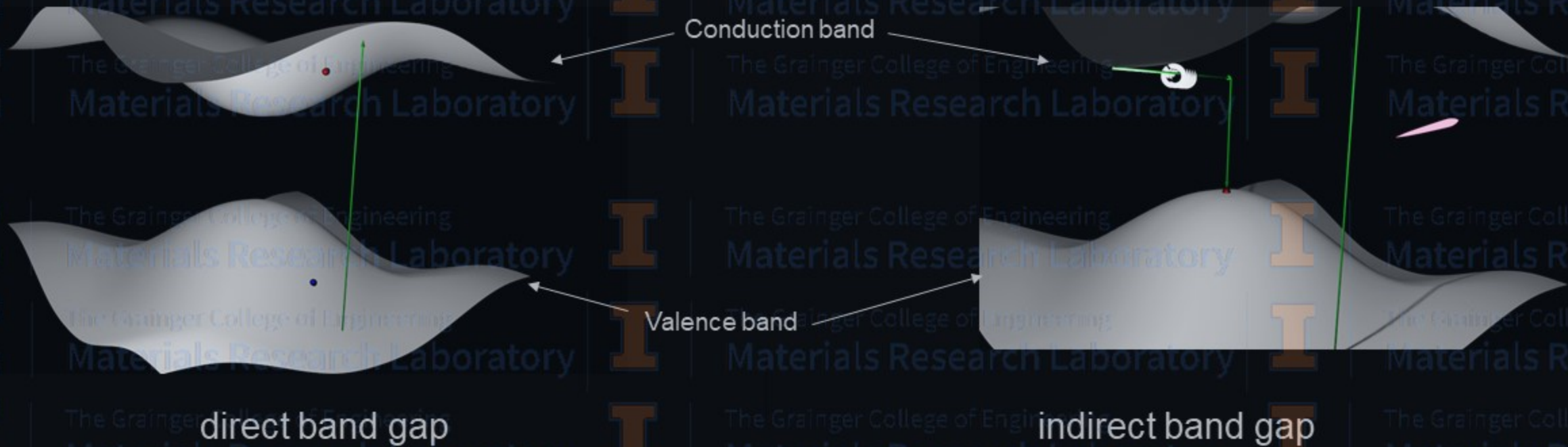
Trevor Morris

Photoluminescence

What is measured:

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

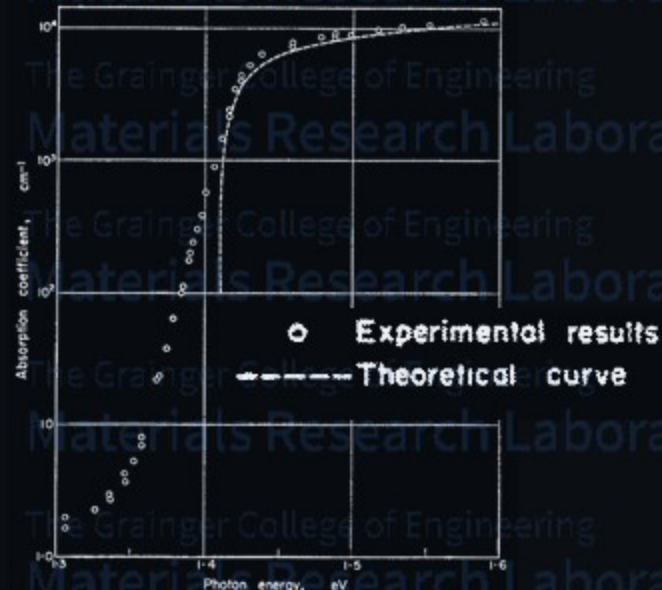
Basic principle:



Instrumentation:

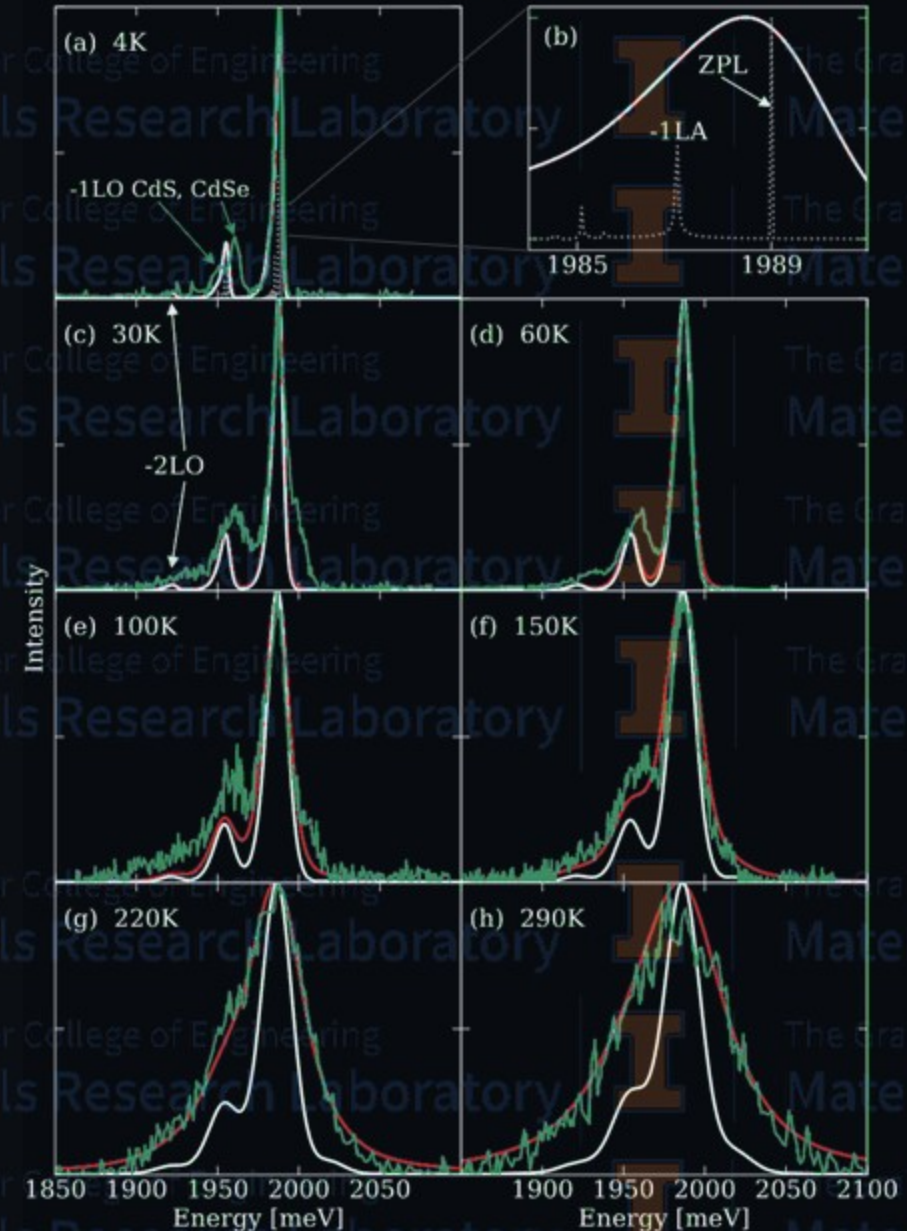


Photoluminescence



Room temperature absorption in GaAs

Infrared Physics, 1961, Vol. 1, pp. 111



Photoluminescence

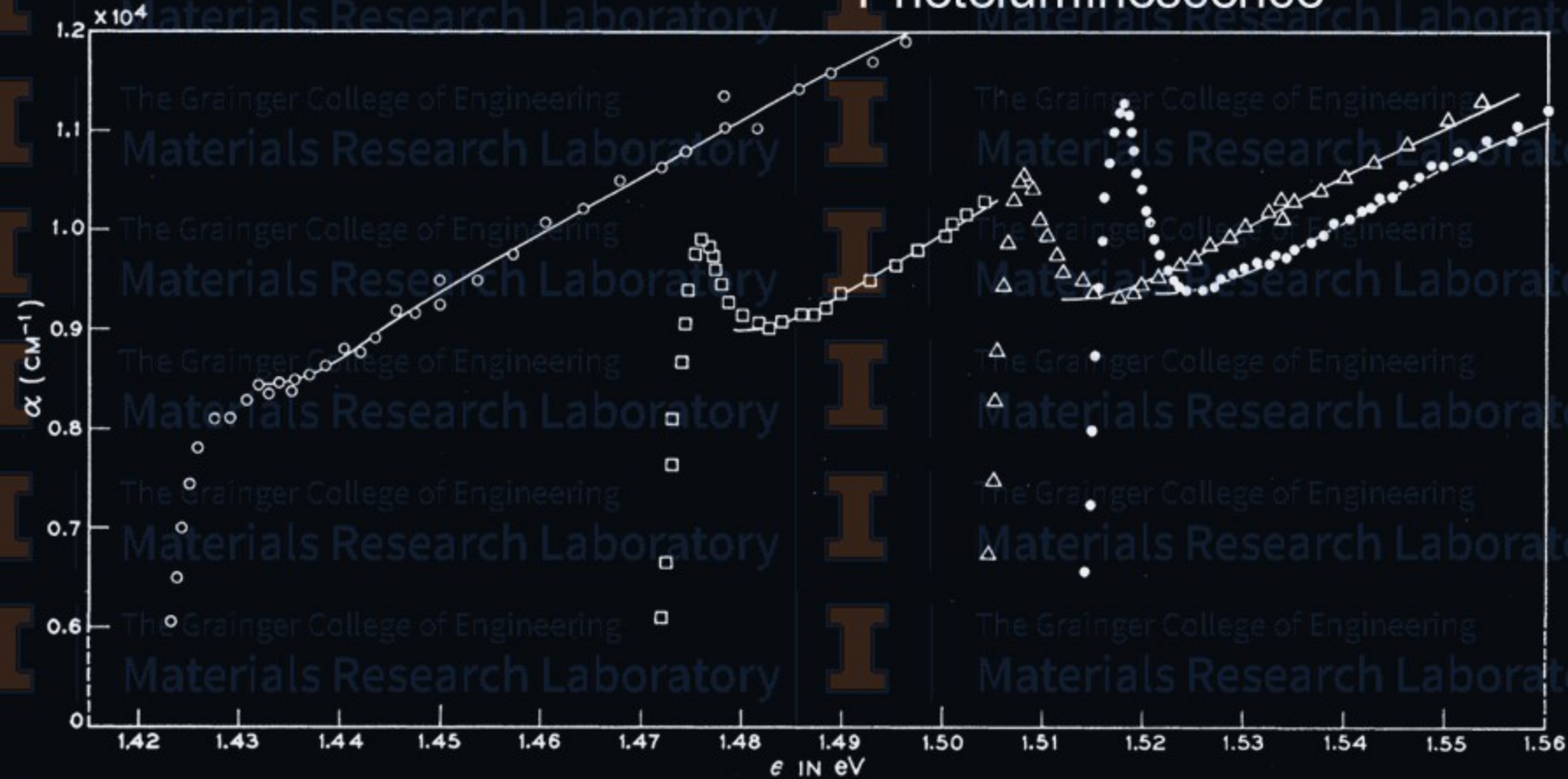


FIG. 3 Exciton absorption in GaAs; $\circ$ 294°K, $\square$ 186°K, Δ 90°K, $\bullet$ 21°K.

Photoluminescence

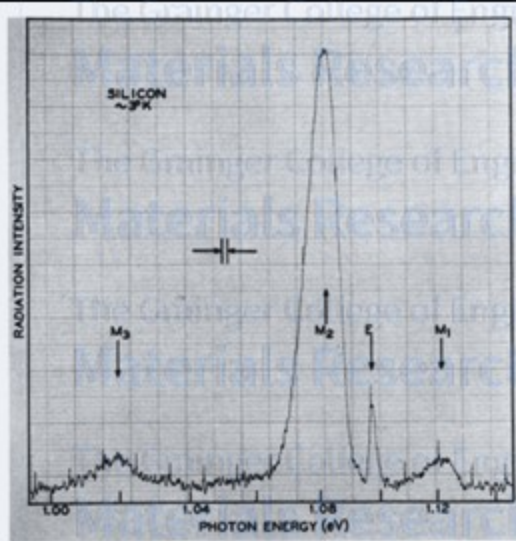
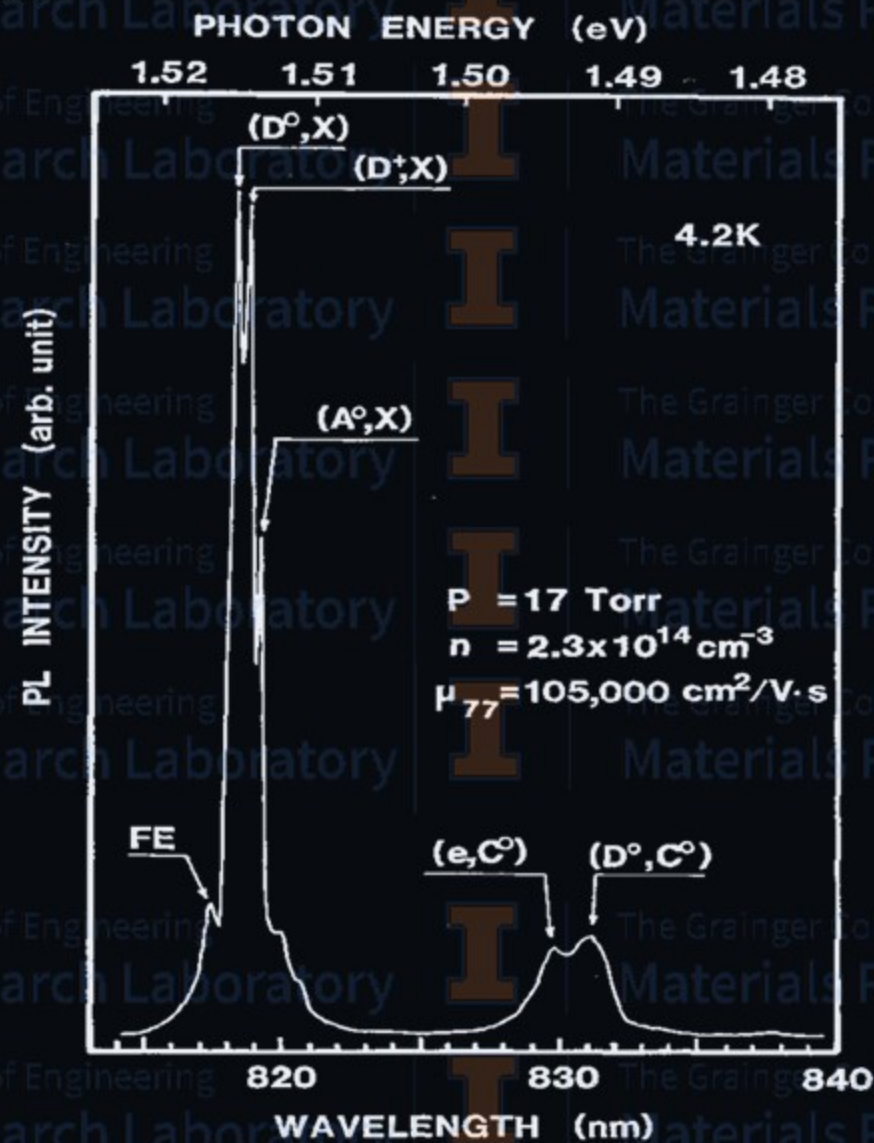


FIG. 1. Spectrogram of a Si specimen at $\sim 3^\circ\text{K}$. The horizontal axis is the energy of the emitted photons in eV. The vertical response is nearly proportional to the number of photons per unit energy interval. The specimen resistivity at room temperature was $9 \times 10^3 \Omega \text{ cm}$.

Excitonic molecule emission in Si

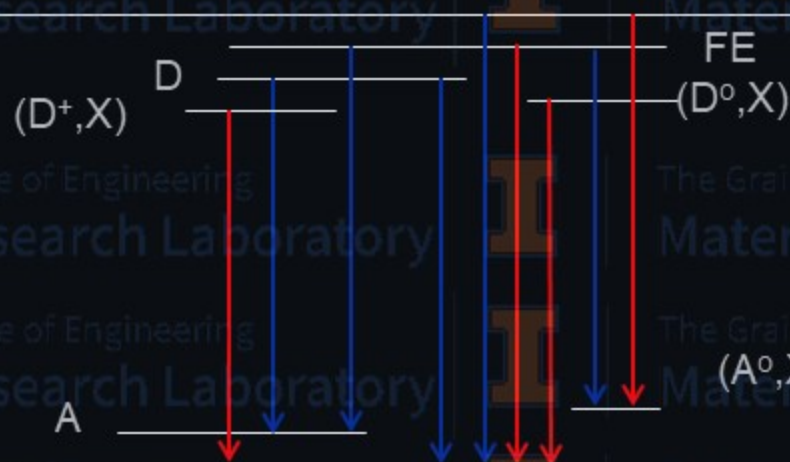
Phys. Rev. Lett. 17, 860 (1966)

Defect emission in GaAs



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

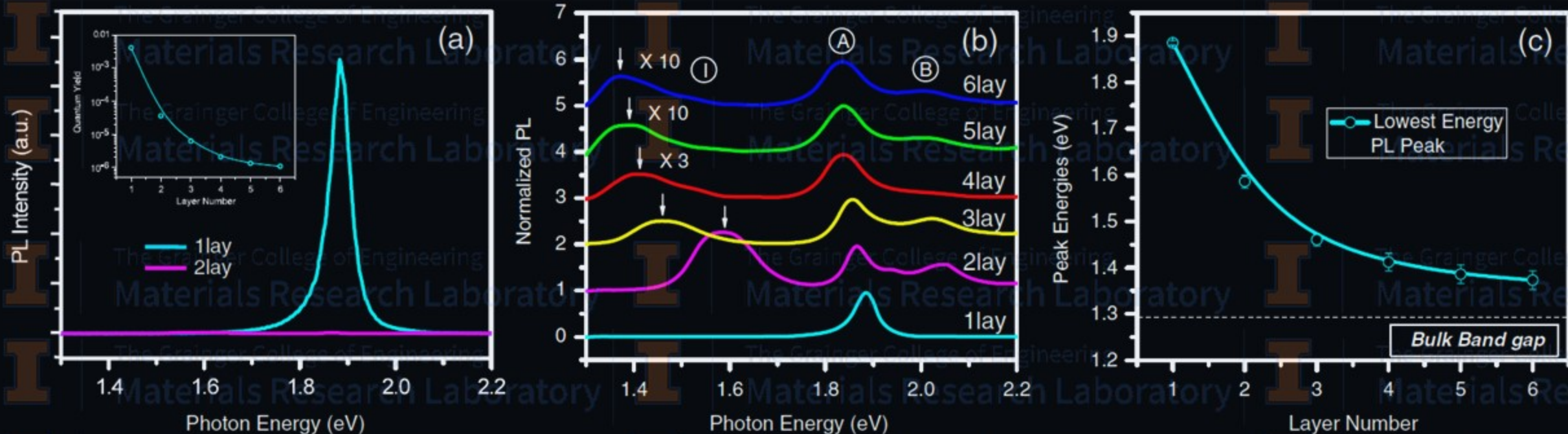
Conduction band



Valence band

Number of layers in 2D materials

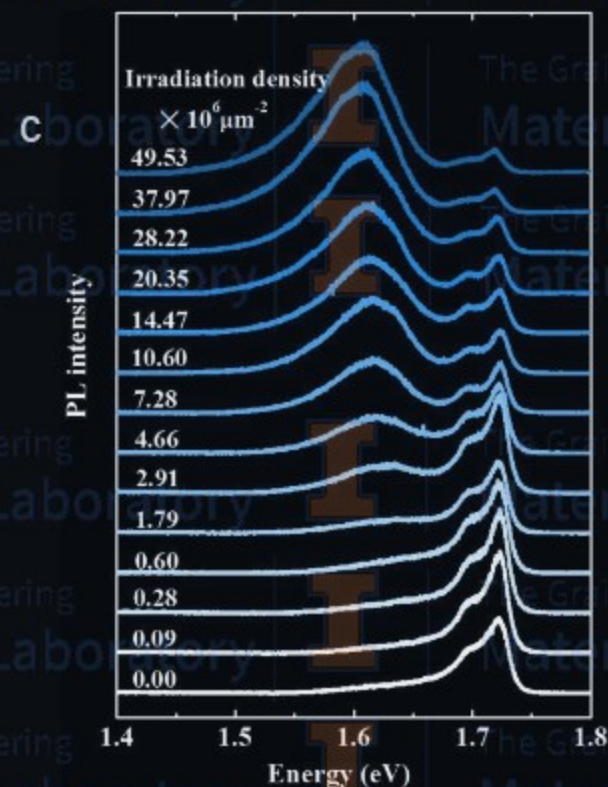
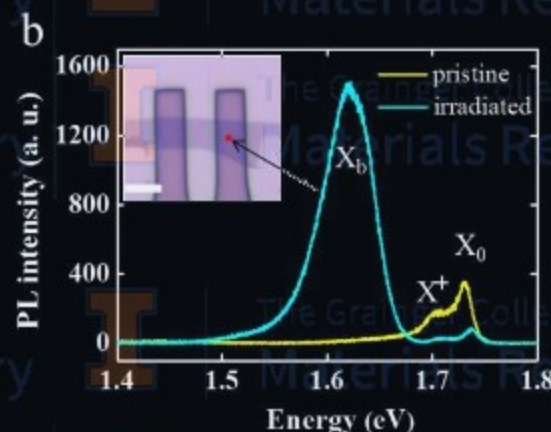
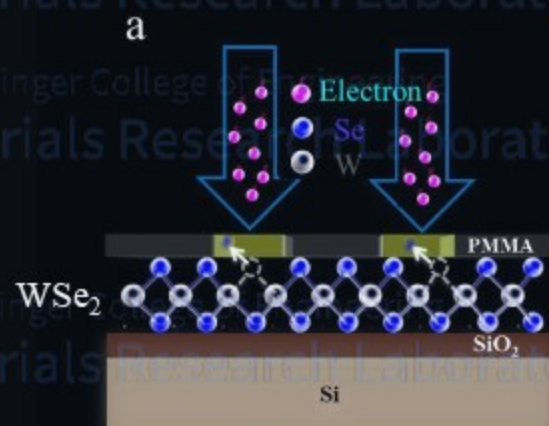
- a) PL spectra for mono- and bilayer MoS_2 .
Inset: PL QY of thin layers for $N = 1-6$.
- b) Normalized PL spectra by the intensity of peak A of thin layers of MoS_2 for $N = 1-6$. Feature I for $N = 4-6$ is magnified for clarity.
- c) Band-gap energy of thin layers of MoS_2 , inferred from the energy 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 .



Defects in 2D materials

Defect induced PL emission.

- a) Schematic diagram of electron beam irradiation on monolayer WSe₂ sample during the EBL process.
- b) PL spectrum of pristine monolayer WSe₂ and monolayer WSe₂ after EBL.
The inset shows optical image of WSe₂ with PMMA patterned by EBL, scale bar is 5 μm
- c) PL spectra of a pristine WSe₂ under different e⁻ beam irradiation density.

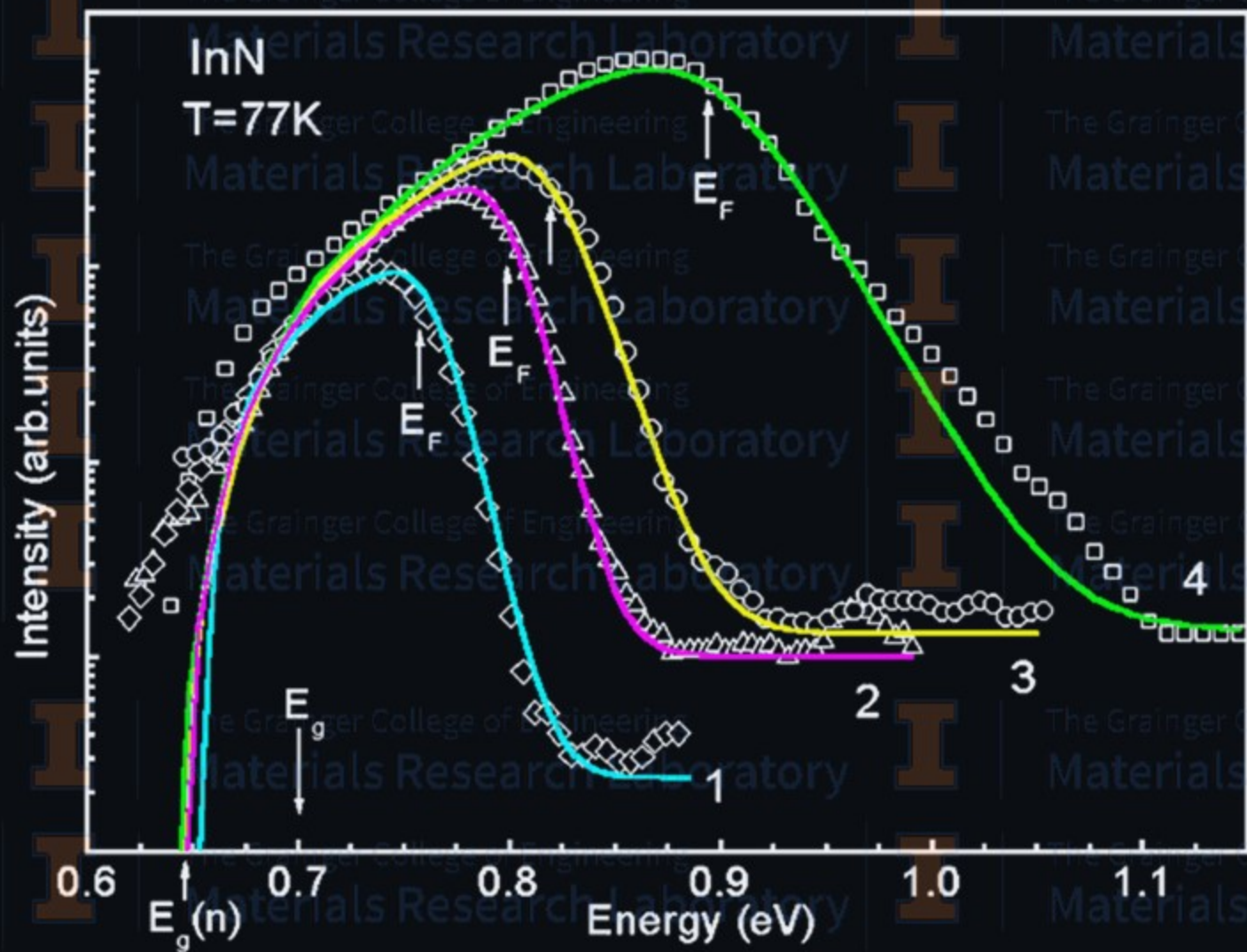


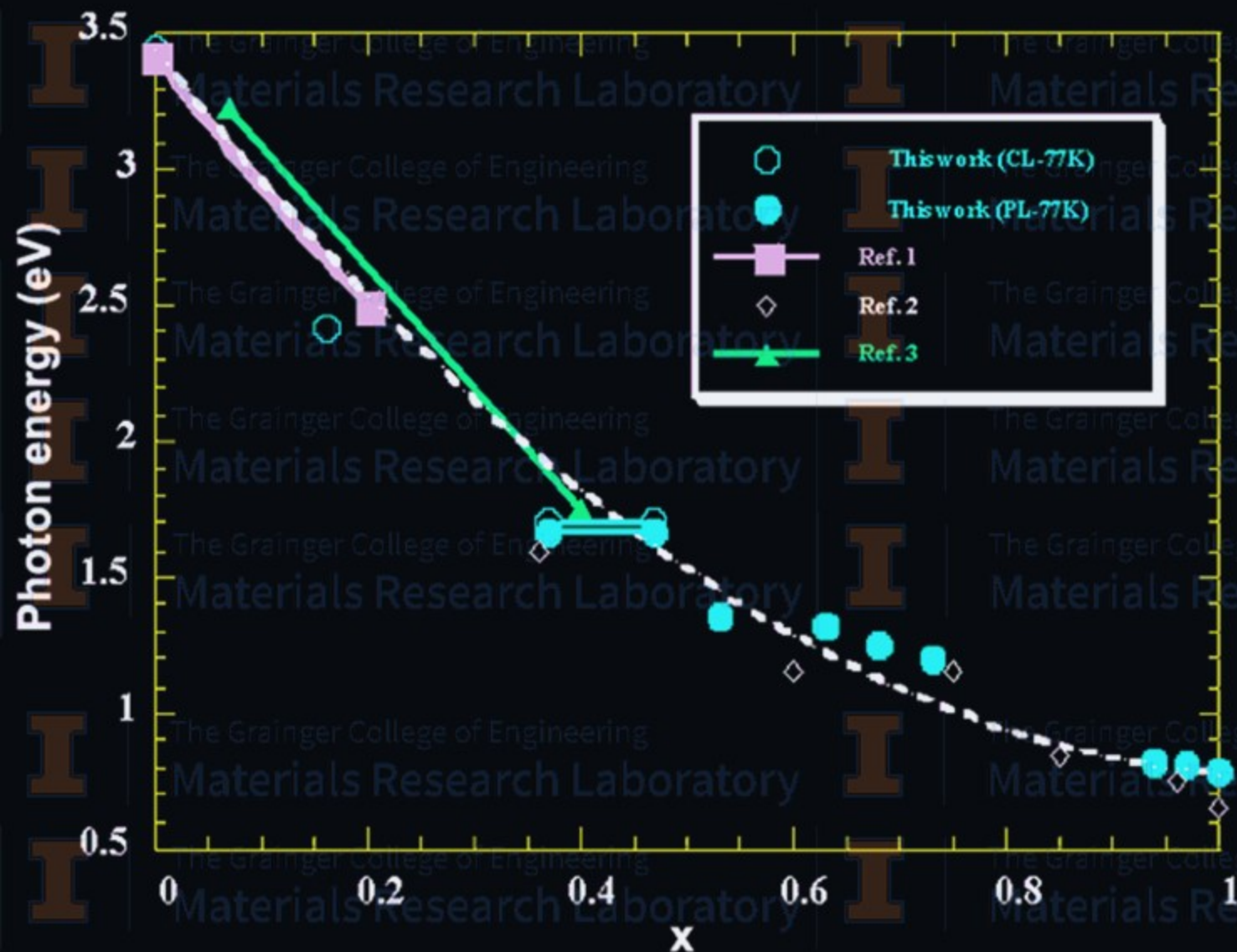
arXiv:1608.02043

Carrier concentration

Photoluminescence spectra of InN layers with different carrier concentrations.

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





$\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys. Luminescence peak positions of cathodoluminescence 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).

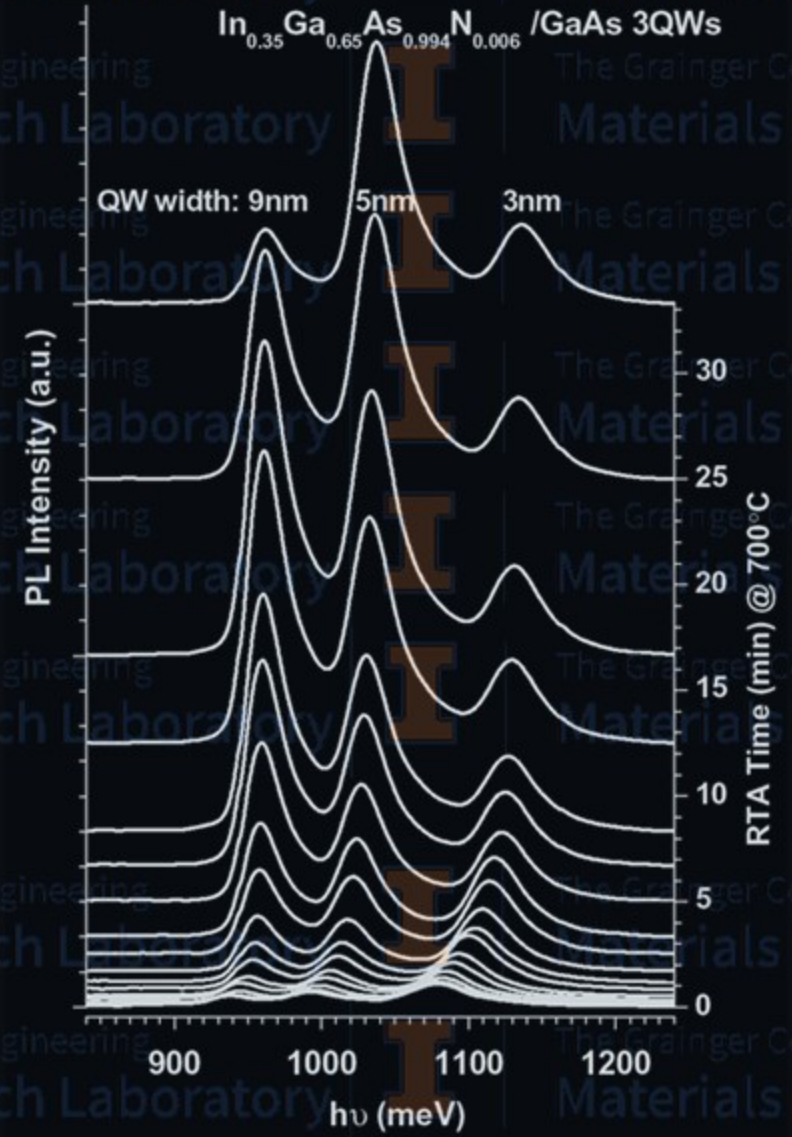
Extracted from *Phys. Stat. Sol. (b)* **234** (2002) 750.

Photoluminescence

Width and quality of semiconductor quantum wells.

3-QWs

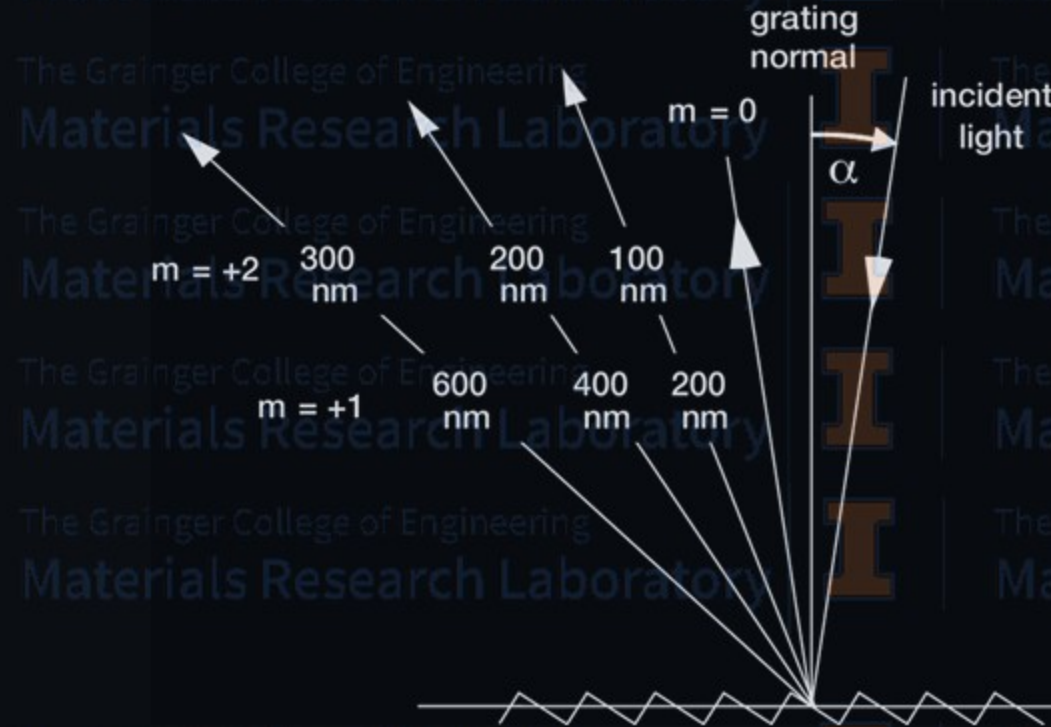
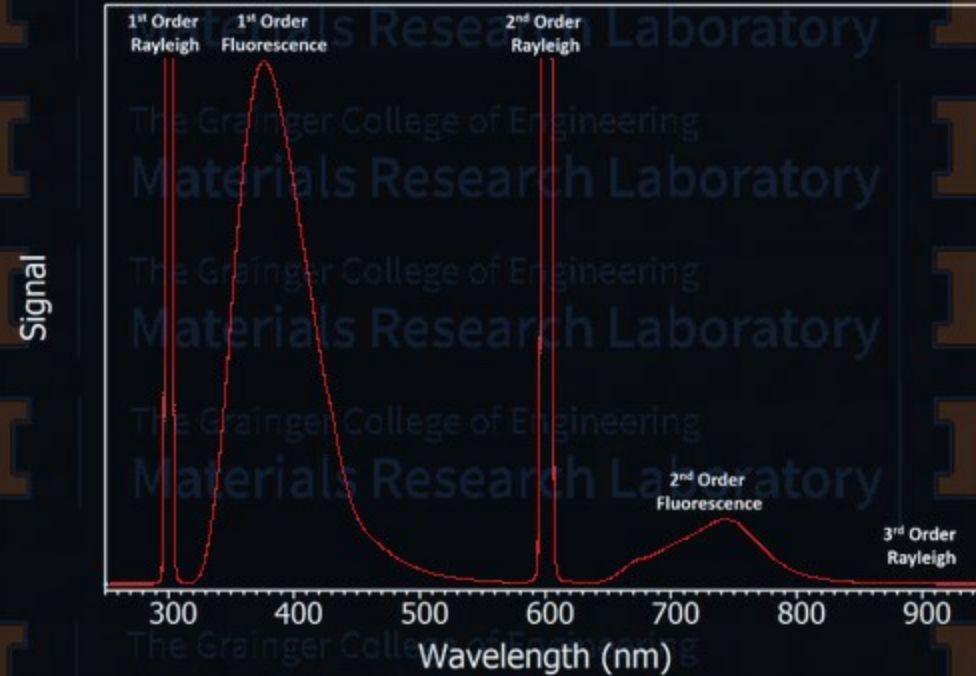
100 nm	GaAs	cap
3nm	InGaAsN	QW
35 nm	GaAs	barrier
5nm	InGaAsN	QW
35 nm	GaAs	barrier
9nm	InGaAsN	QW
100 nm	GaAs	buffer
GaAs (001) SUB		



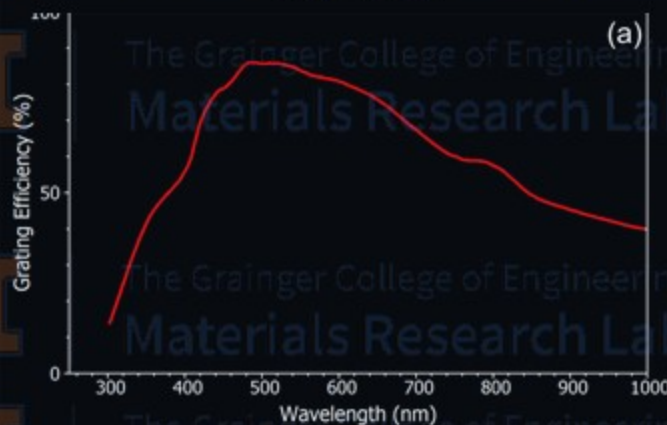
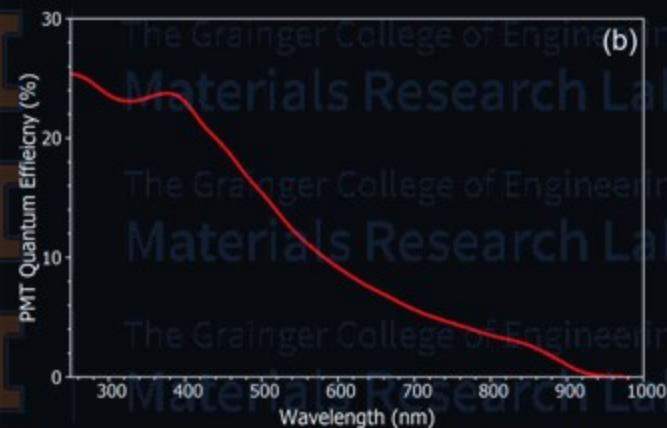
Journal of Crystal Growth 278 (2005) 259–263

Photoluminescence

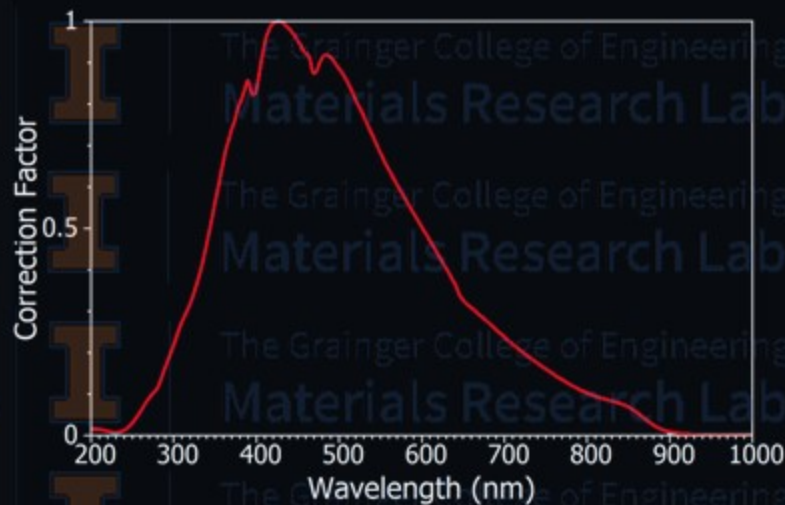
Pitfalls, artifacts, corrections ...



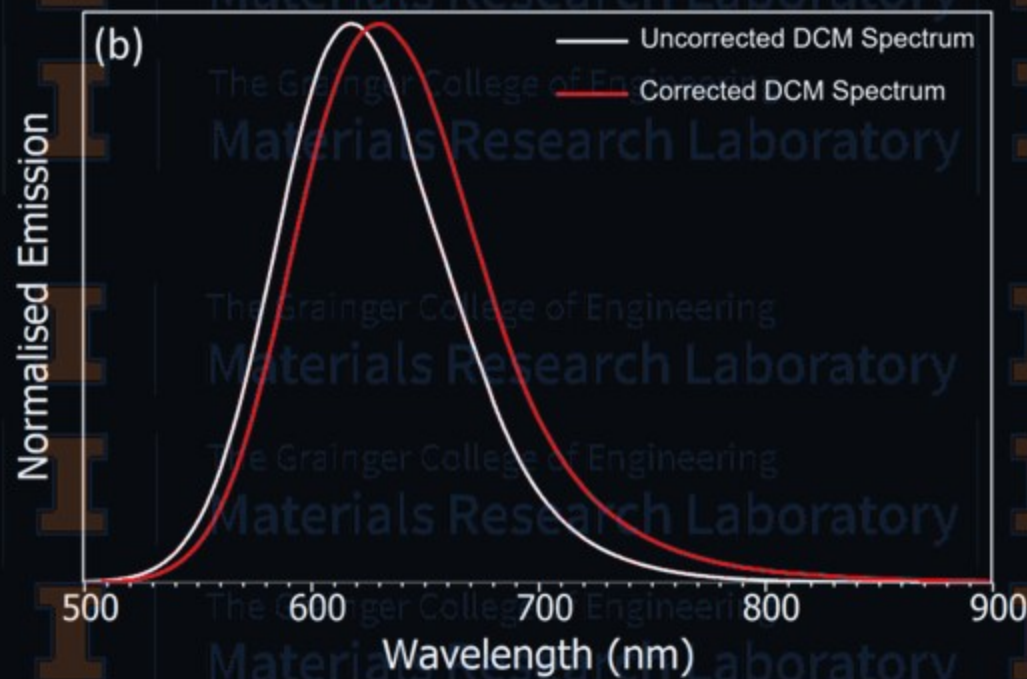
Pitfalls, artifacts, corrections ...



Photoluminescence



Non-ideal components
introduce spectral distortions



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.

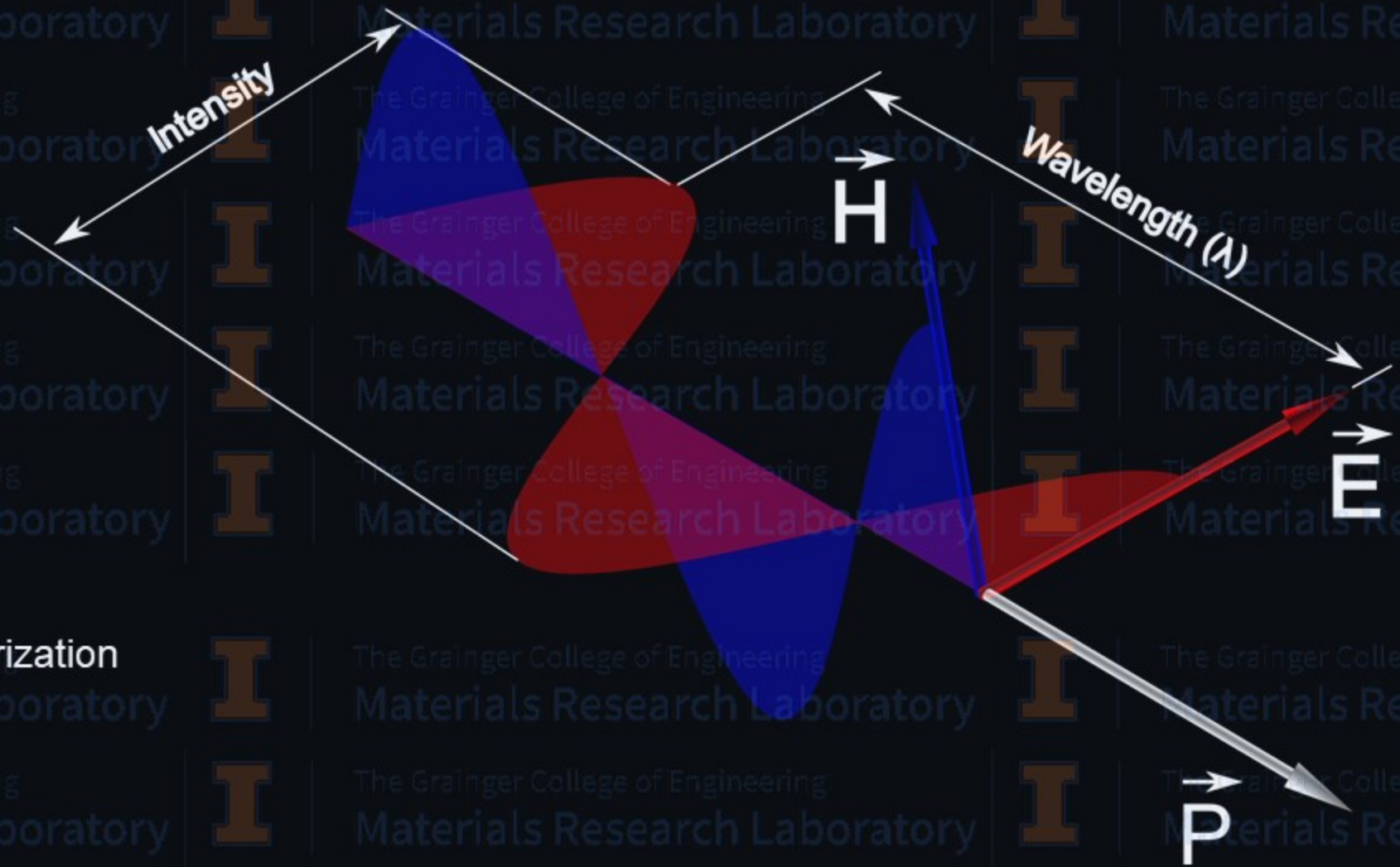
www.glofish.com

Complementary techniques:

Ellipsometry, Modulation spectroscopies,
Spectrophotometry, Raman.

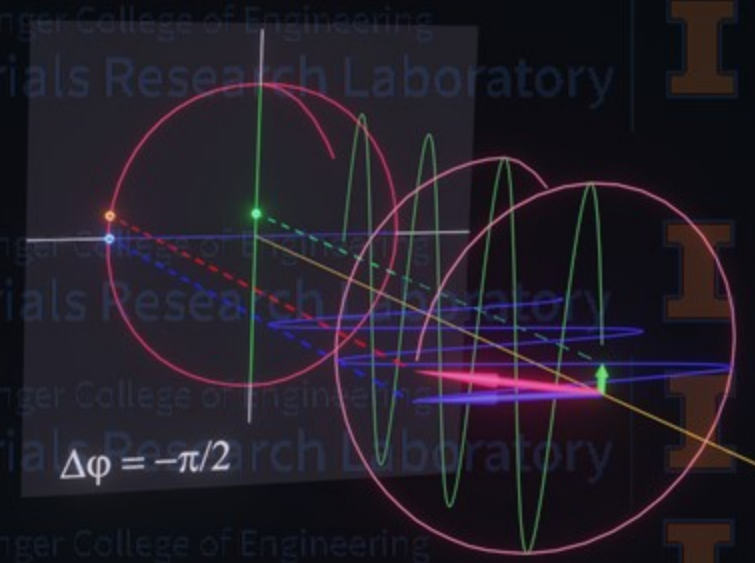
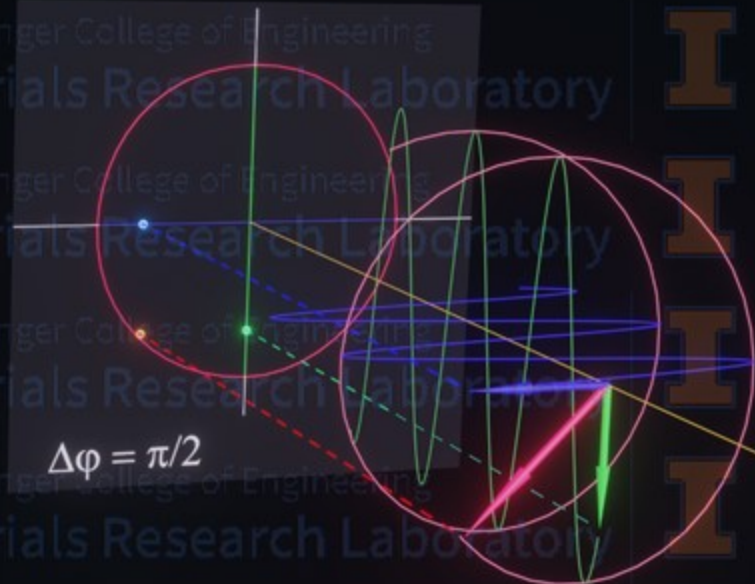
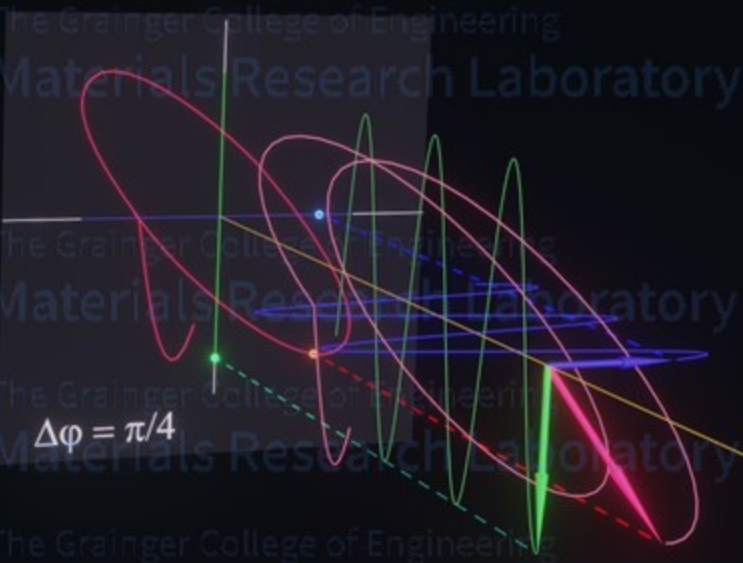
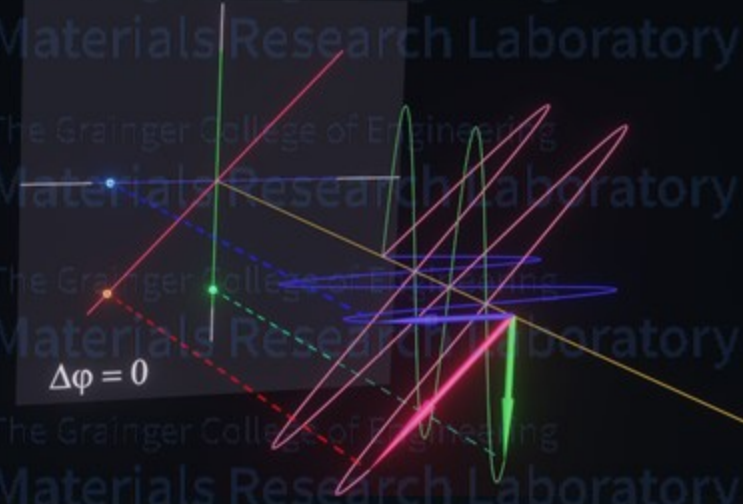


Light properties



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

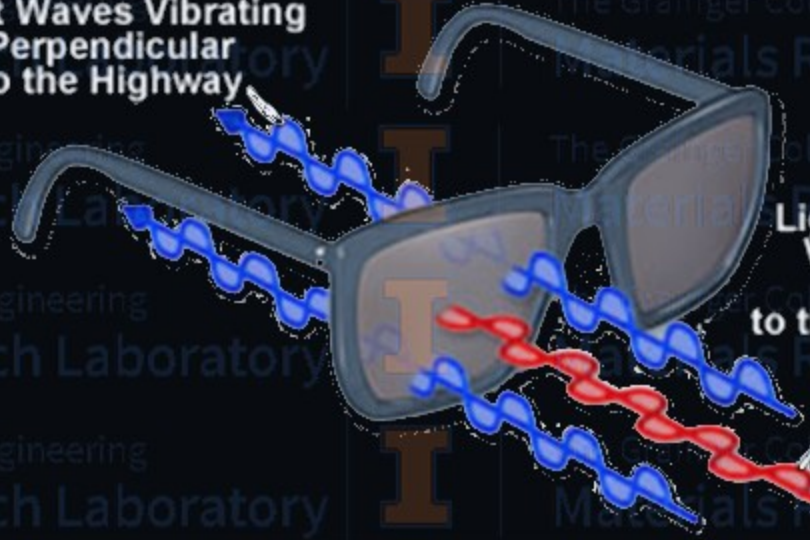
Polarization



Polarization

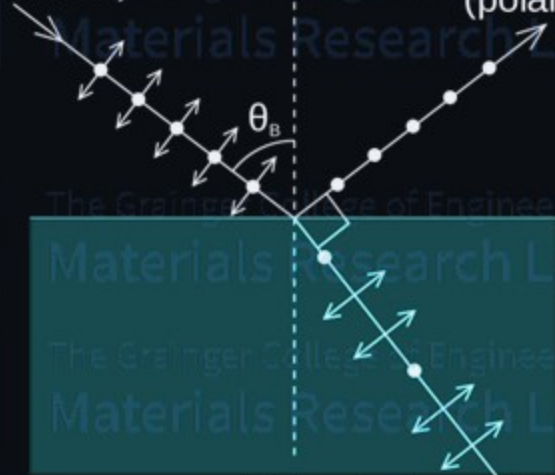
Light Waves Vibrating
Perpendicular
to the Highway

Light Waves
Vibrating
Parallel
to the Highway



Incident ray
(unpolarised)

Reflected ray
(polarised)



Refracted ray
(slightly polarised)

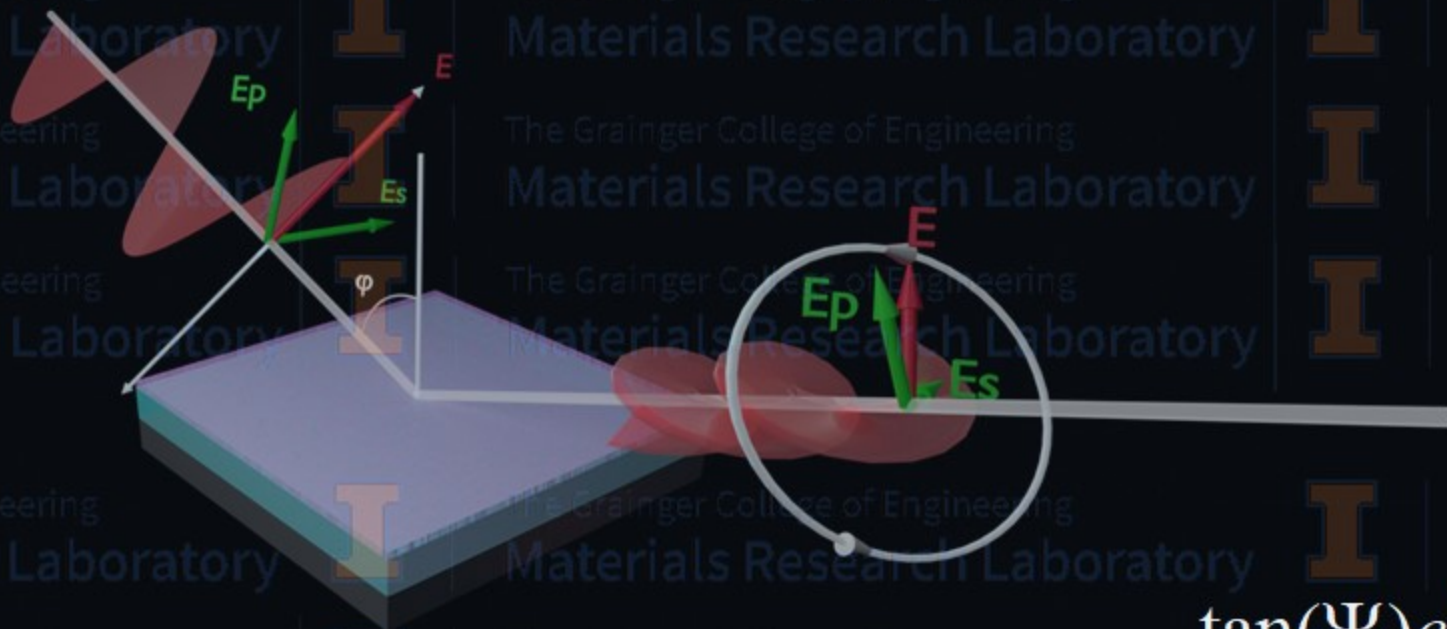


www.bobatkins.com

Ellipsometry

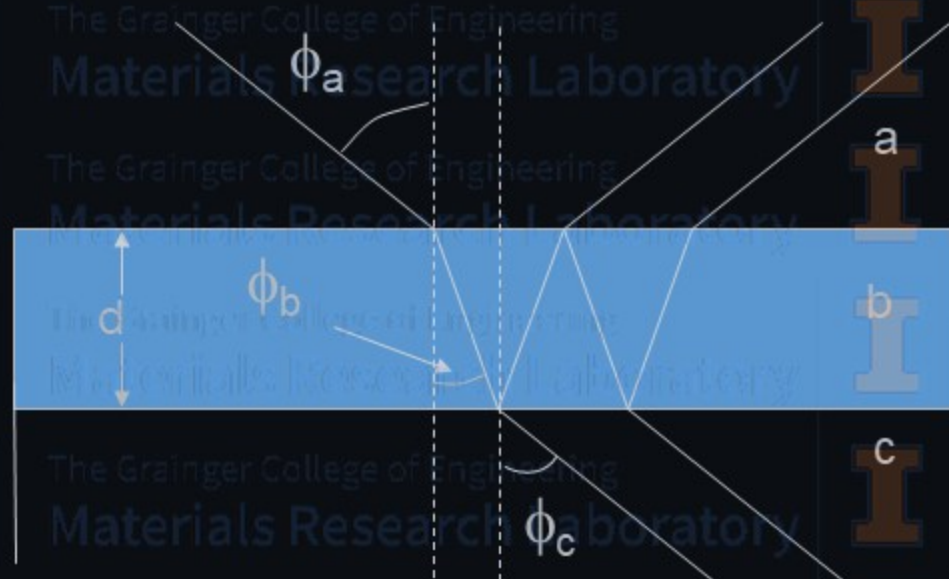
Basic principle:

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



$$\tilde{n} = n + ik \quad \tilde{n}_1 \sin \phi_1 = \tilde{n}_2 \sin \phi_2$$

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

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

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

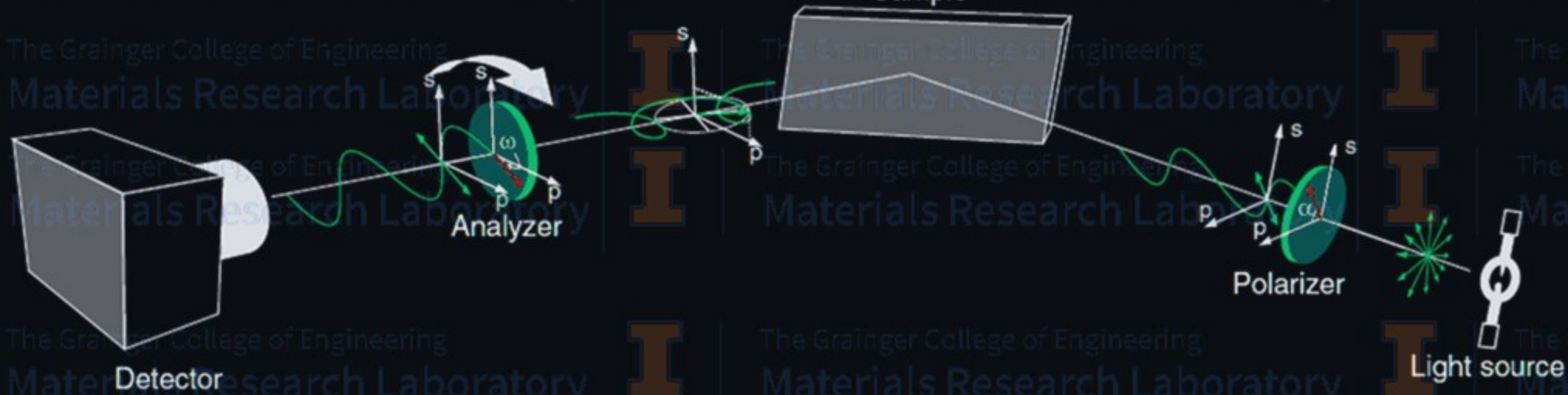
$$\tilde{R}_{p,s} = \frac{E_{p,s}^r}{E_{p,s}^i} e^{i(\delta_{p,s}^r - \delta_{p,s}^i)}$$

$$\tan(\Psi) e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} \Rightarrow \left\{ \begin{array}{l} \tan(\Psi) = \frac{|\tilde{R}_p|}{|\tilde{R}_s|} \\ \Delta = \delta^r - \delta^i \end{array} \right.$$

Ellipsometry

What is measured:

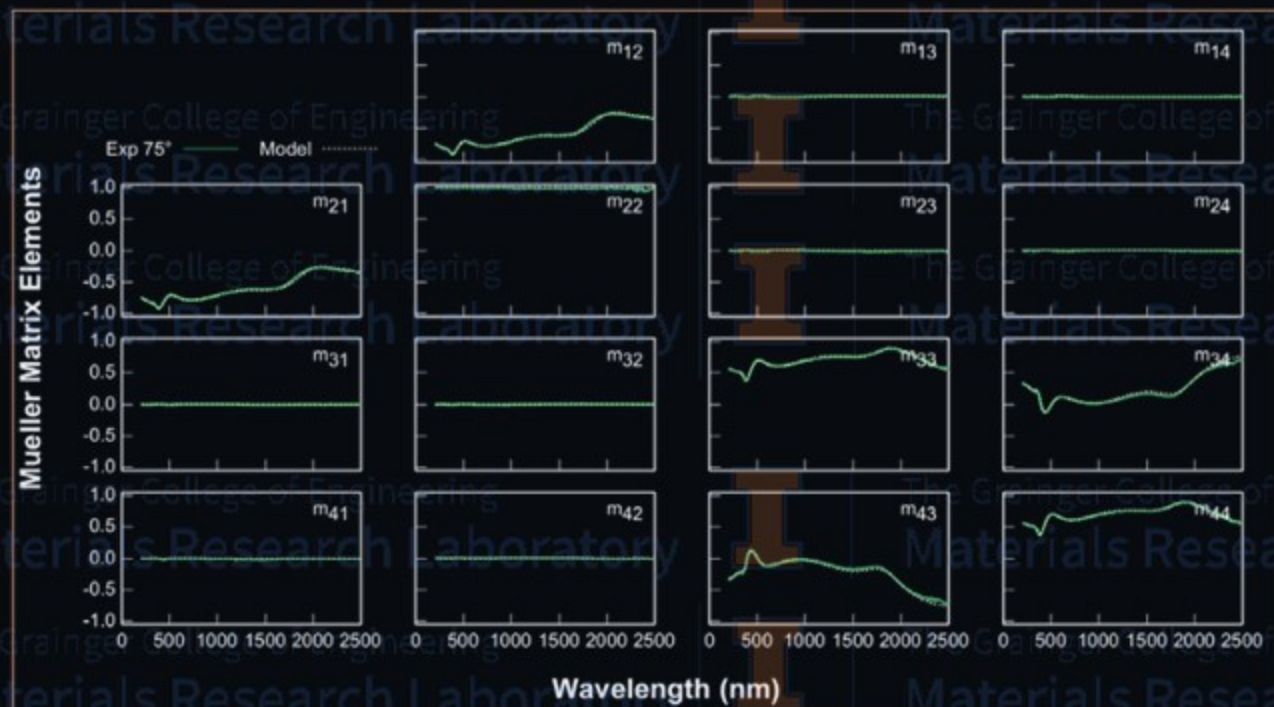
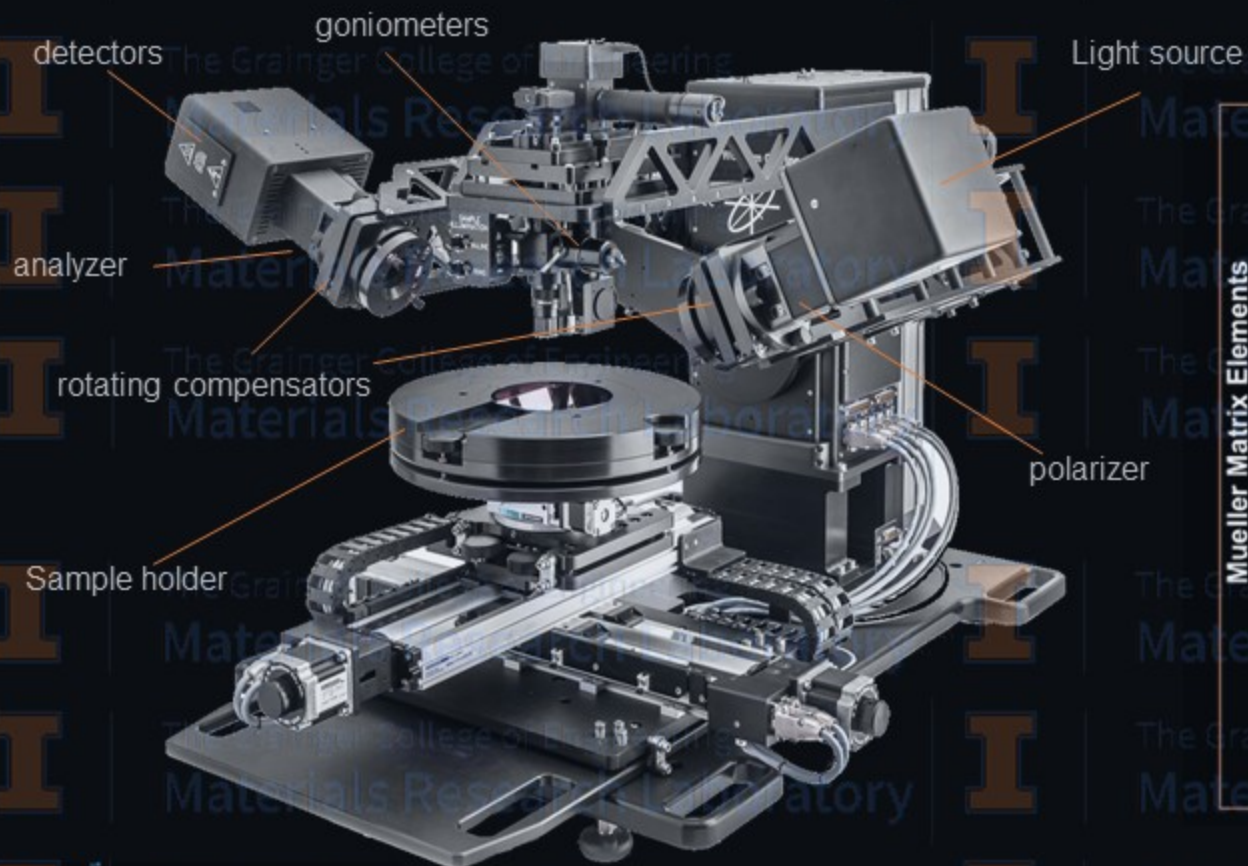
The changes in the polarization state of light upon reflection from a mirror like surface.



Ellipsometry

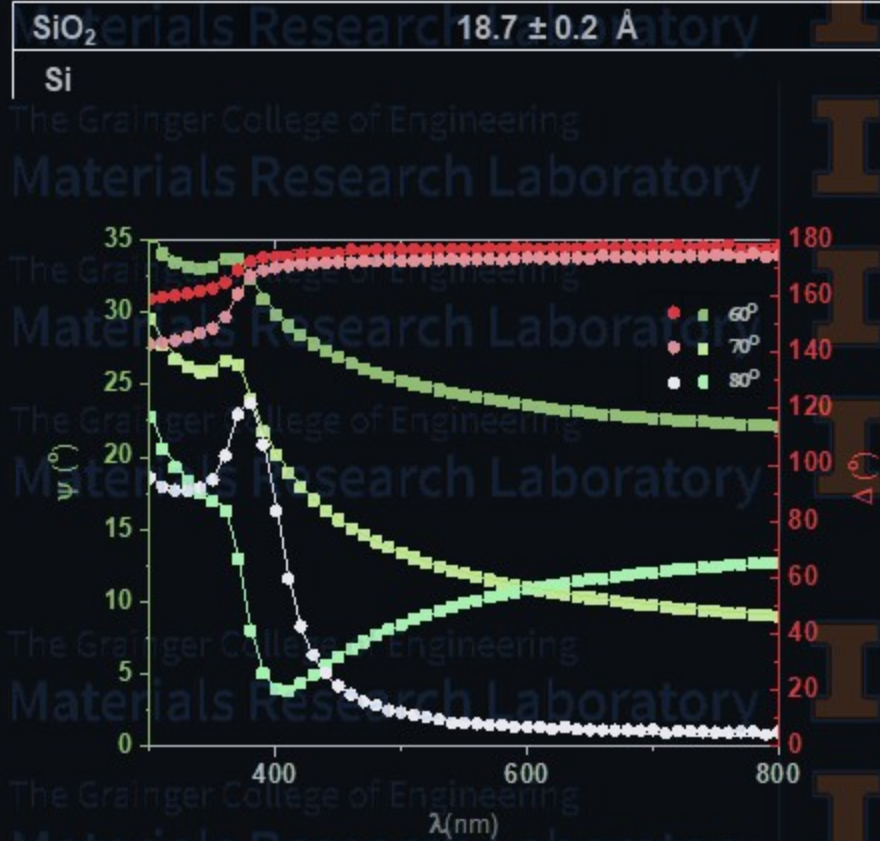
What is measured:

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



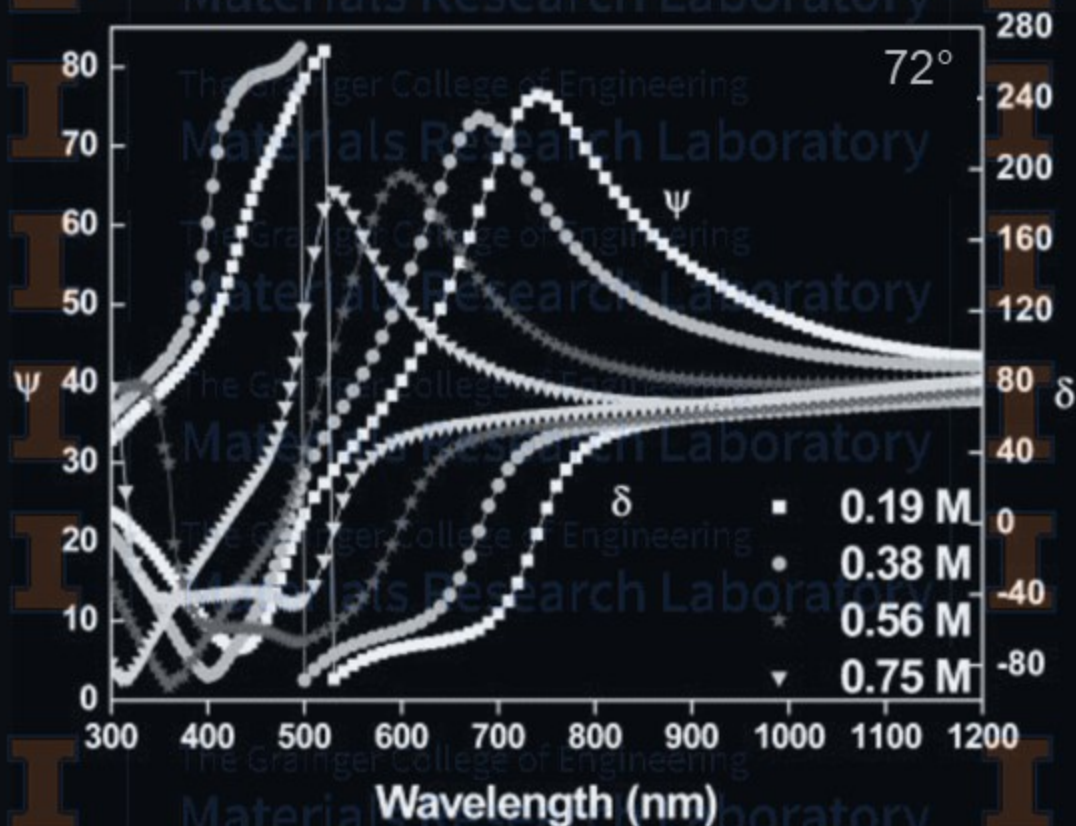
Ellipsometry

Applications



Ellipsometry

Applications

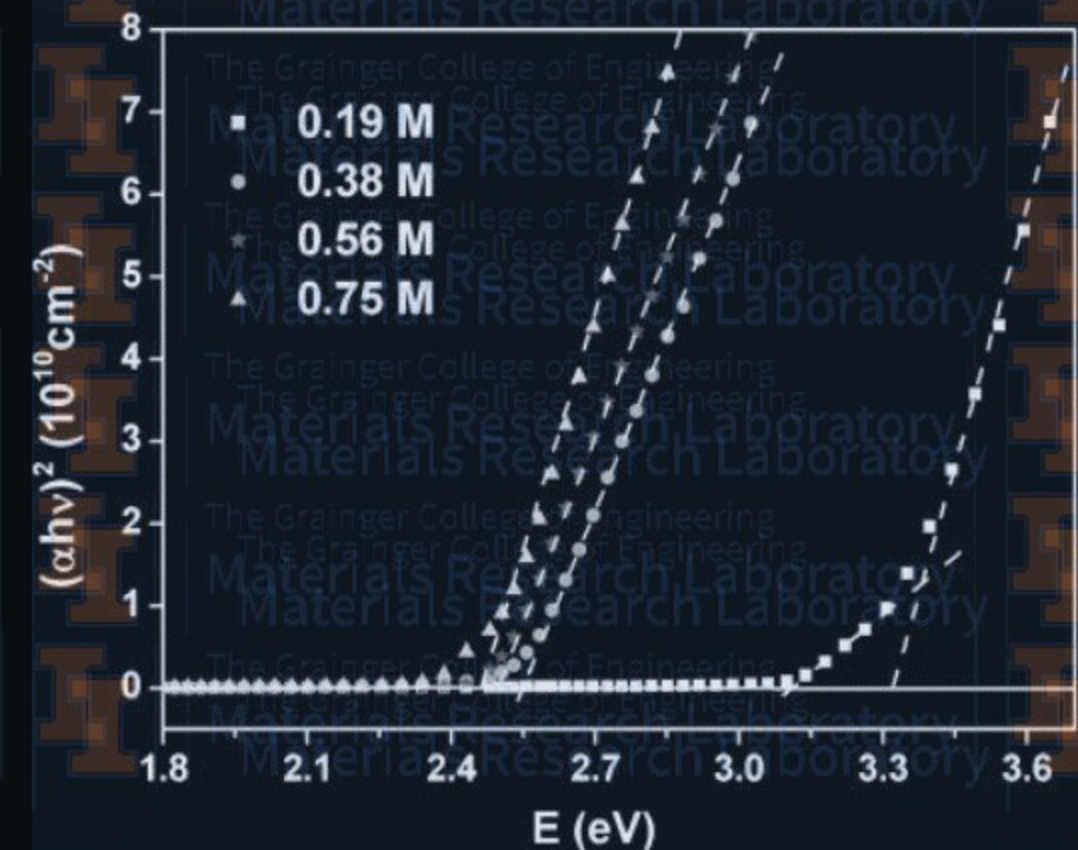


[NH ₄ OH] (M)	Thickness (nm)	Roughness (nm)	ZnS (%)	Band-gap (eV)
0.19	42.12	23.77	99.7	3.49
0.38	73.79	7.15	45.5	2.52
0.56	50.89	5.94	32.3	2.45
0.75	18.59	4.54	5.2	2.43

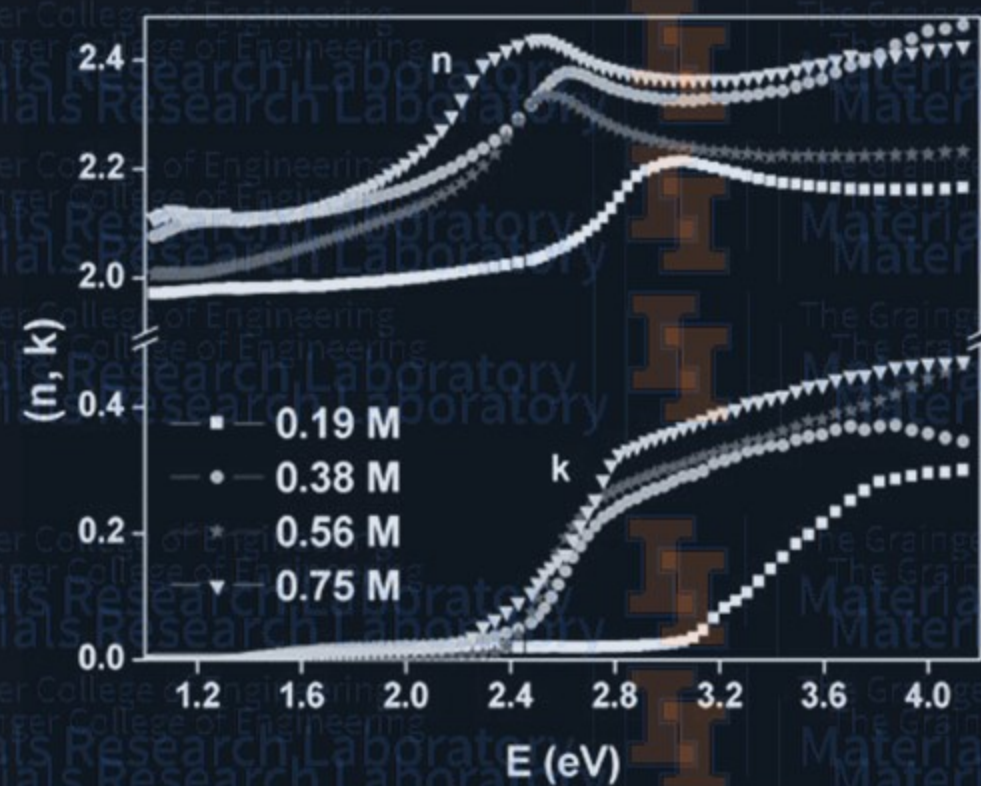
Ellipsometric $\Psi(\lambda)$ and $\Delta(\lambda)$ spectra of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films deposited under the different concentration of ammonia: 0.19, 0.38, 0.56, and 0.75 M

Ellipsometry

Applications



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



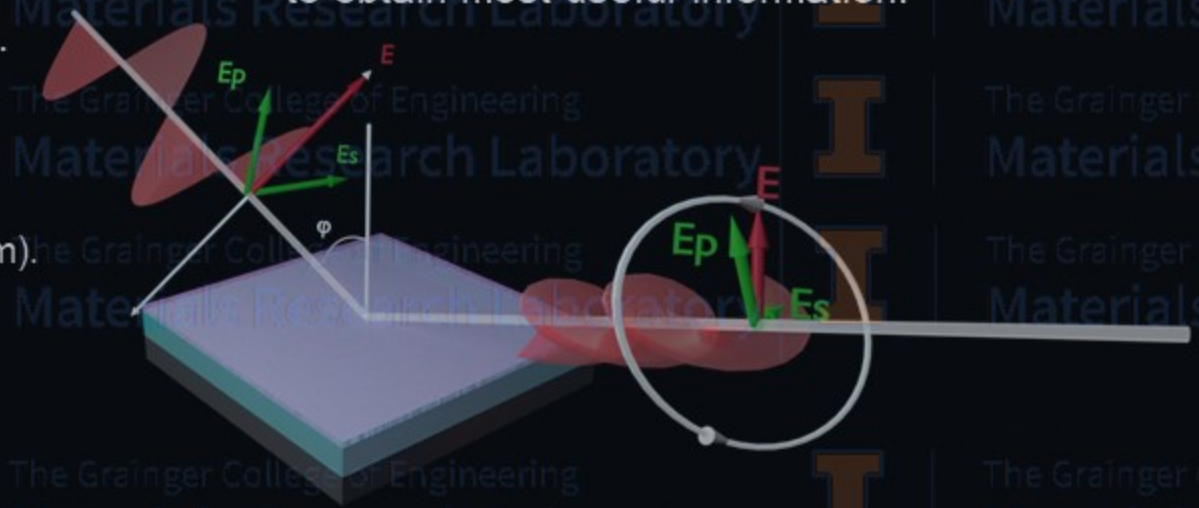
Ellipsometry

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.

Limitations:

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



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



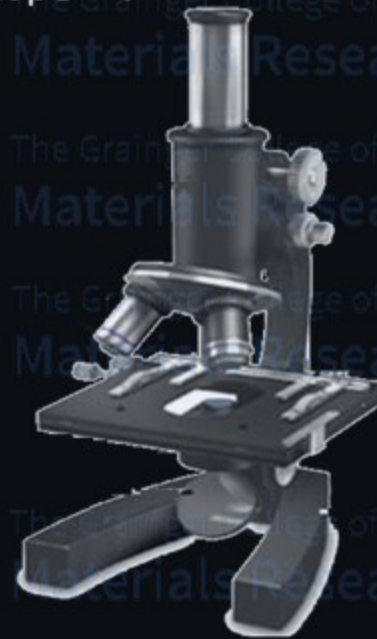
Hooke microscope
ca. 1670



British microscope
ca. 1850



Hand-held microscope ca. early 1700's



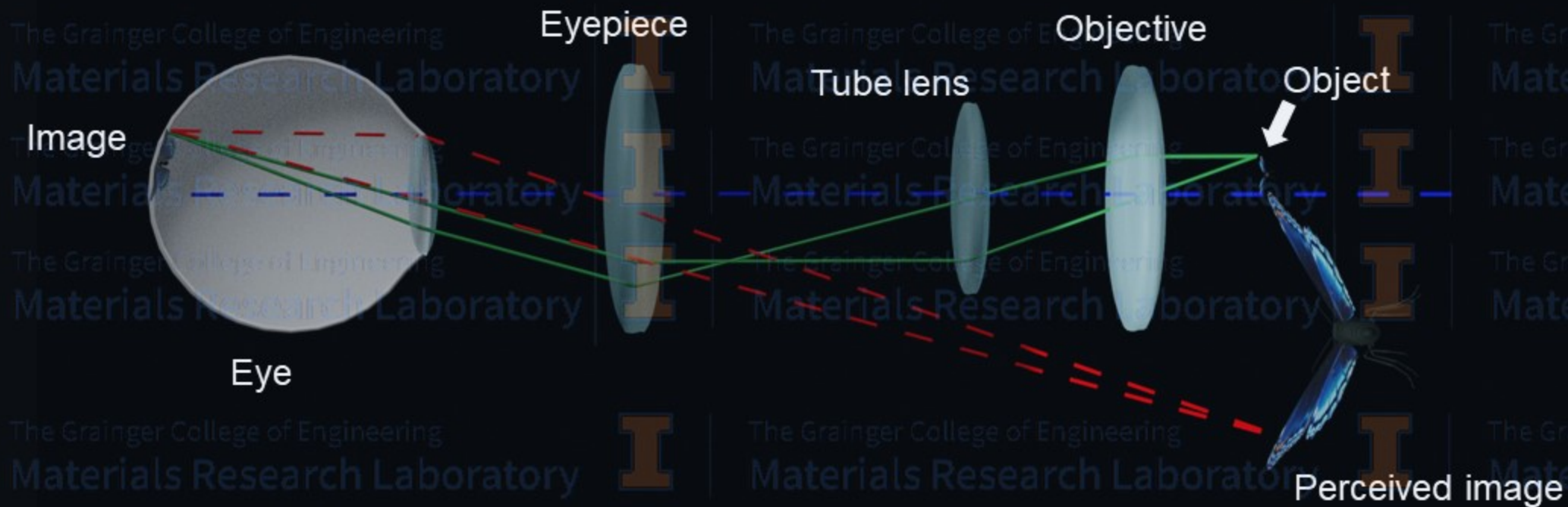
Zeiss microscope
ca. 1930



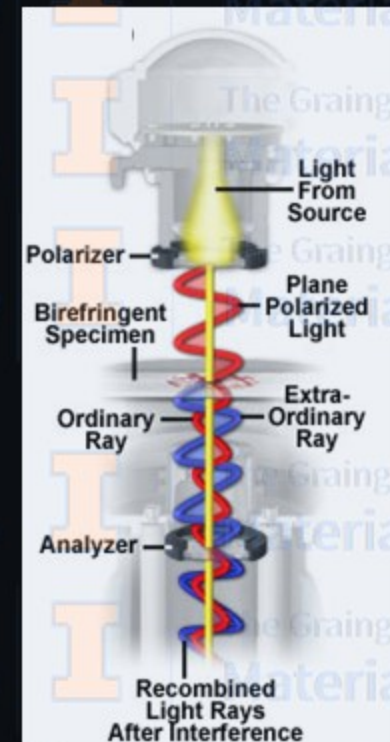
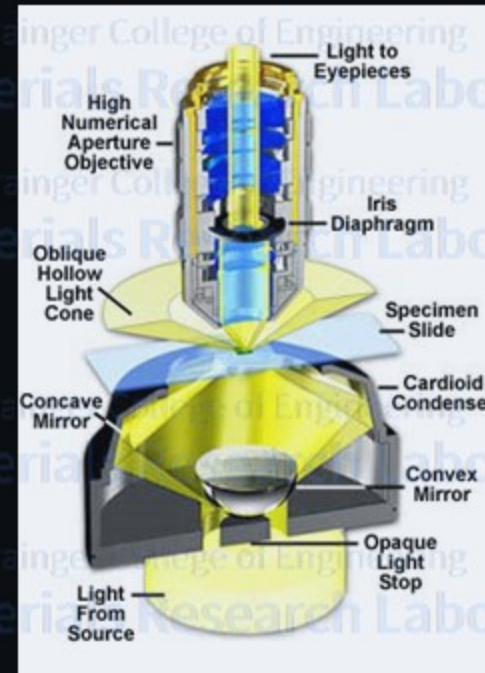
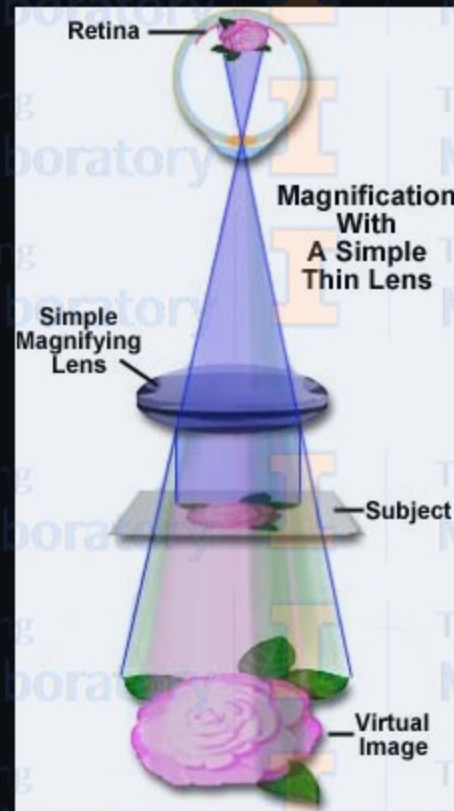
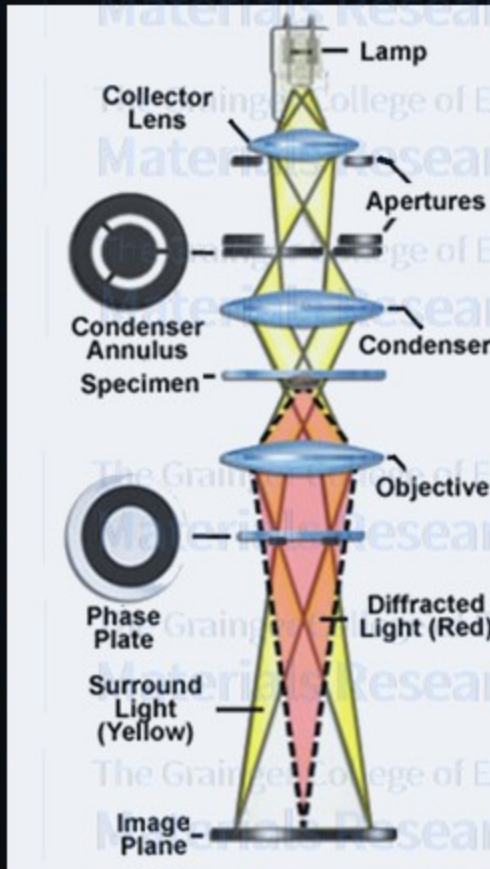
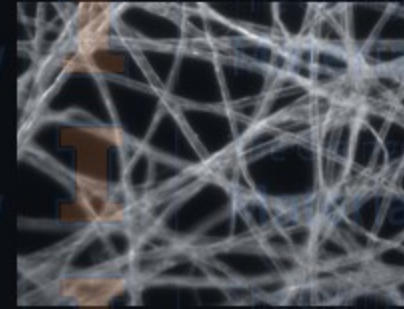
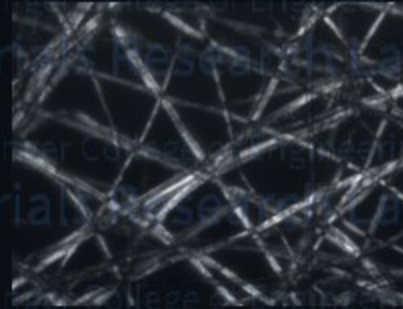
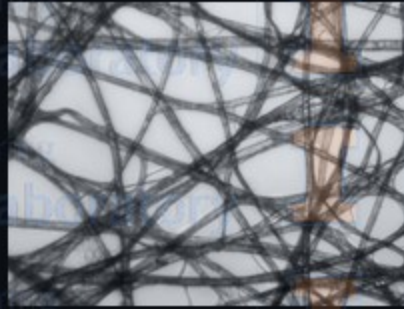
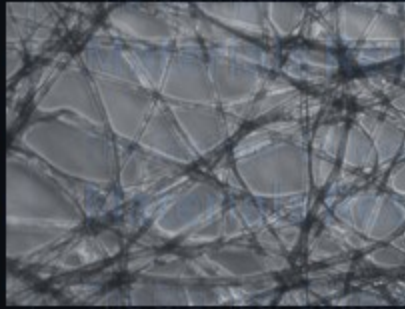
Modern scientific microscope

Optical microscopy

"Conventional" Optical Microscopy

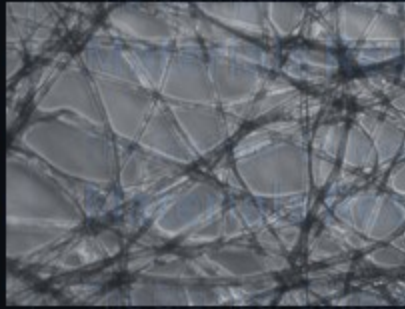


Optical microscopy

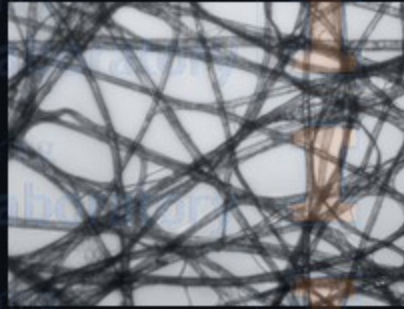


Optical microscopy

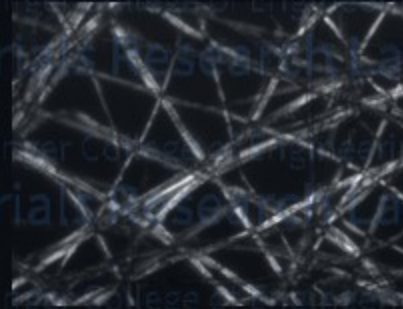
Phase contrast



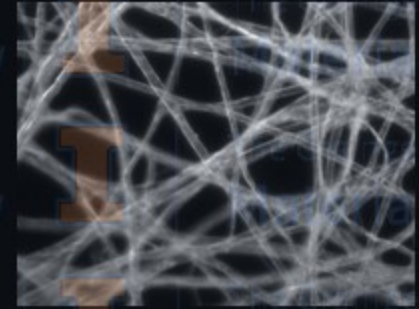
Bright field



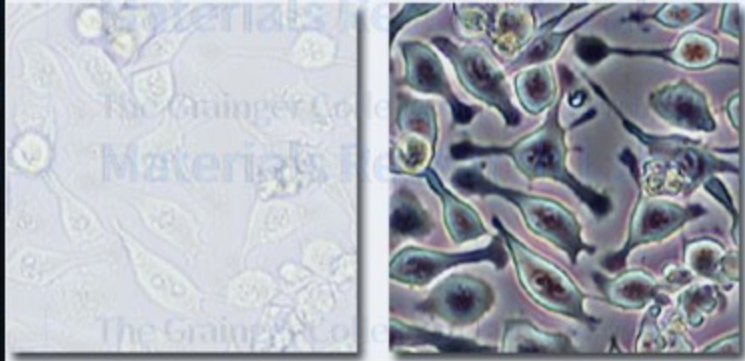
Dark field



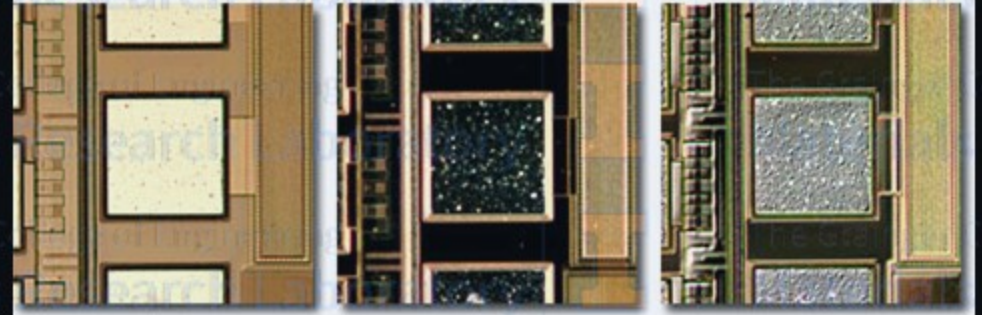
Polarizing



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?

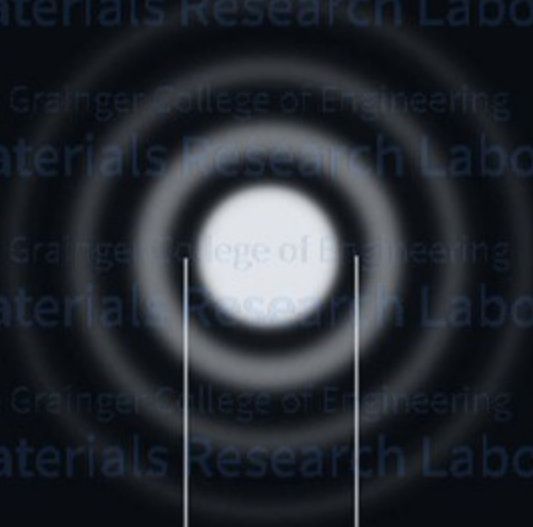


Resolution

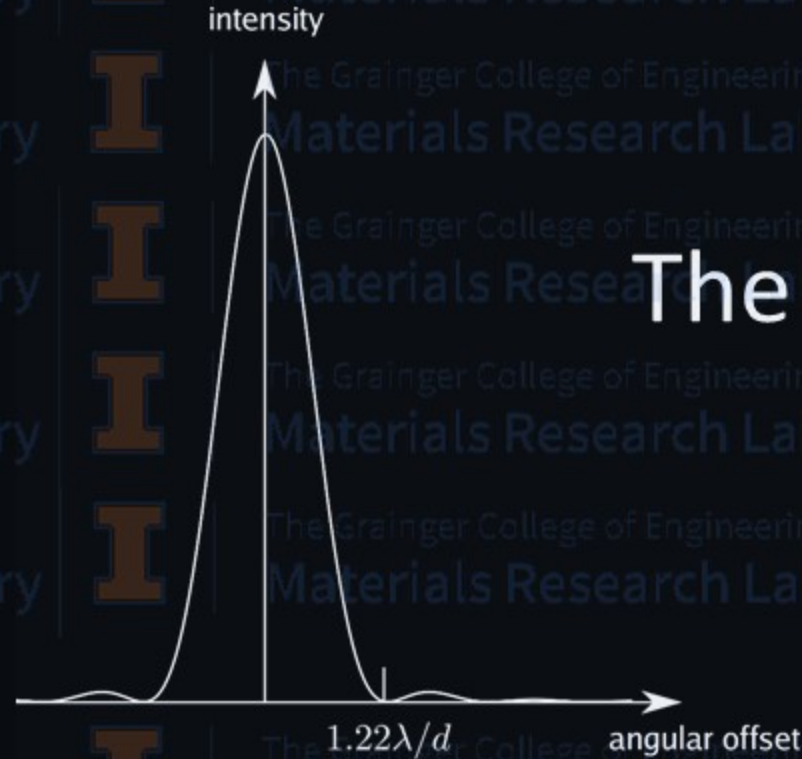
- But how small a thing can we see?



Lateral resolution

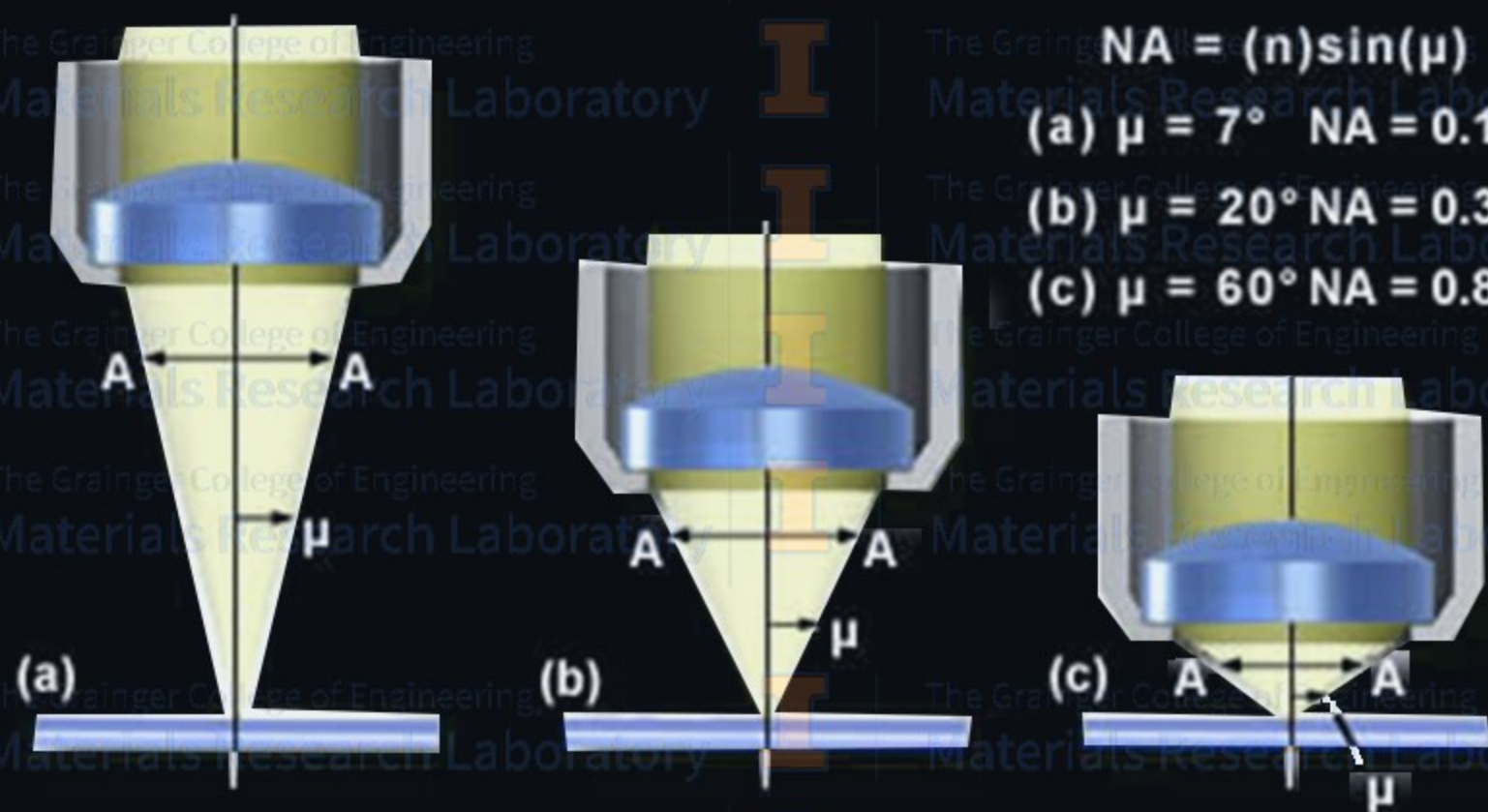


⇒ Diameter of
Airy Disc ⇐



The Airy pattern

Lateral resolution



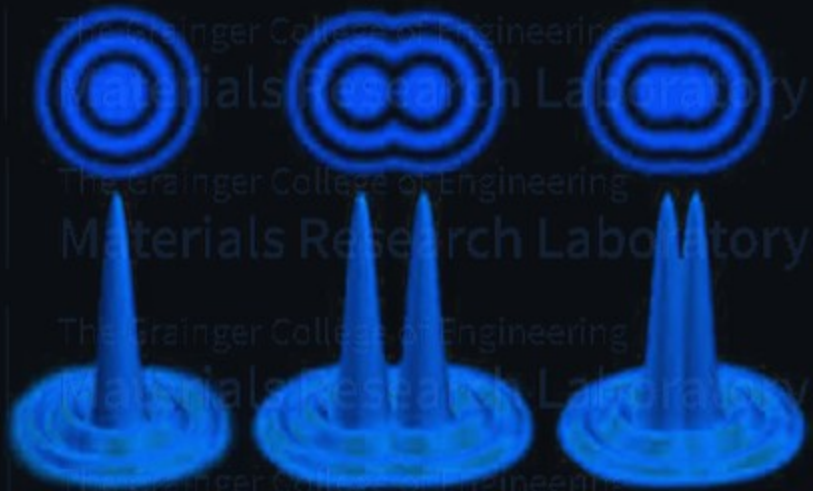
Lateral resolution

Numerical aperture

Lateral resolution

Resolution

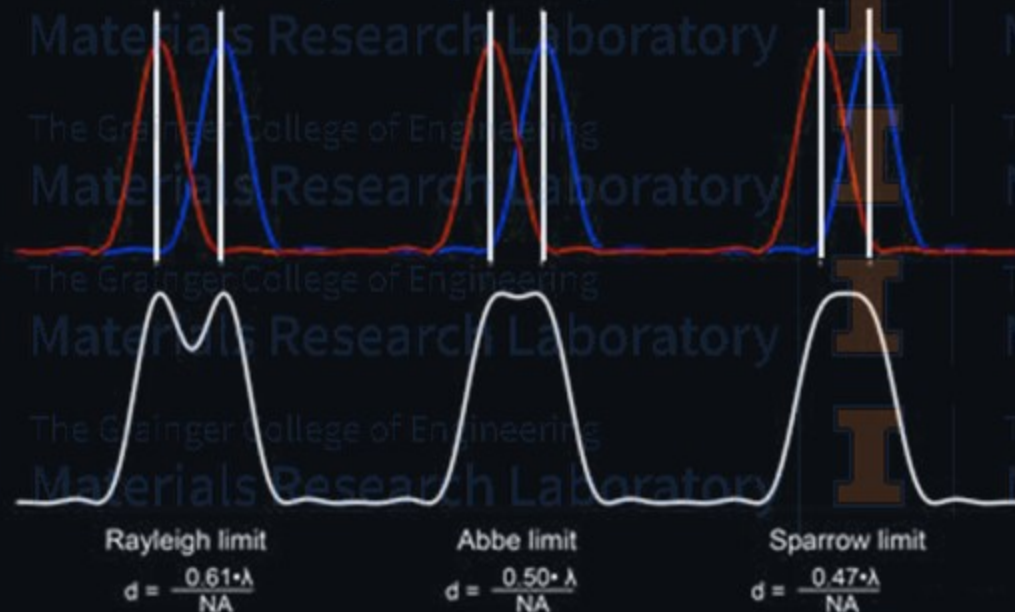
Airy Discs



Intensity Distributions

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

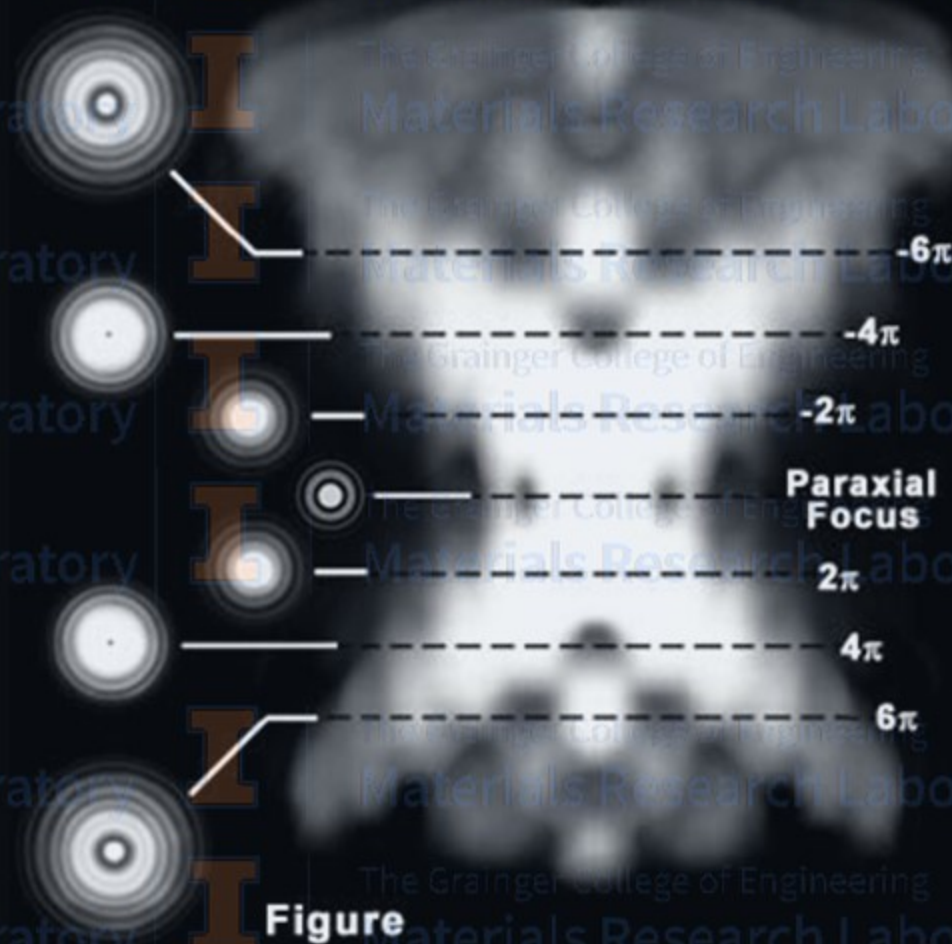
Rayleigh criterion



Abbé criterion

Depth resolution

Axial Intensity Distribution

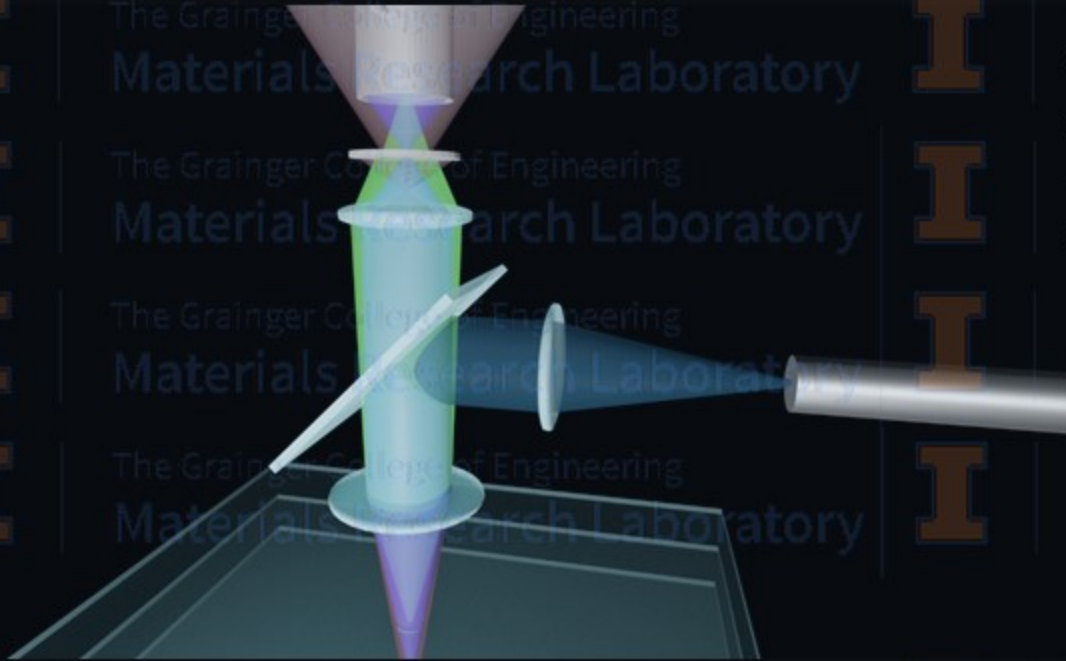


Confocal microscopy

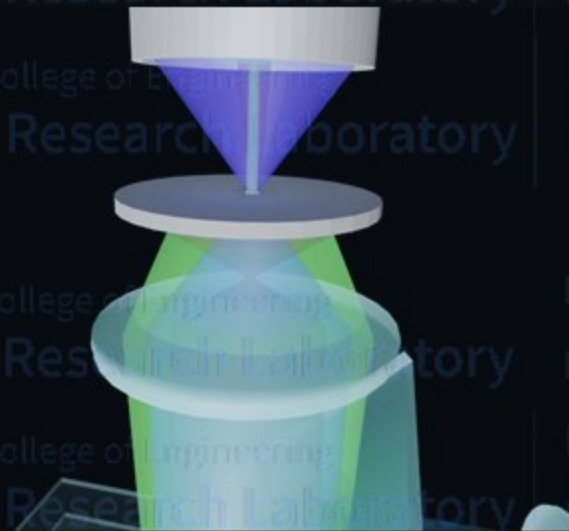


- Increased contrast $\Rightarrow$ 200:1.
- Slightly increased in plane resolution (1.5 x)
- Significantly increased resolution along the optical axis.
- Scanning image formation.

Confocal microscopy

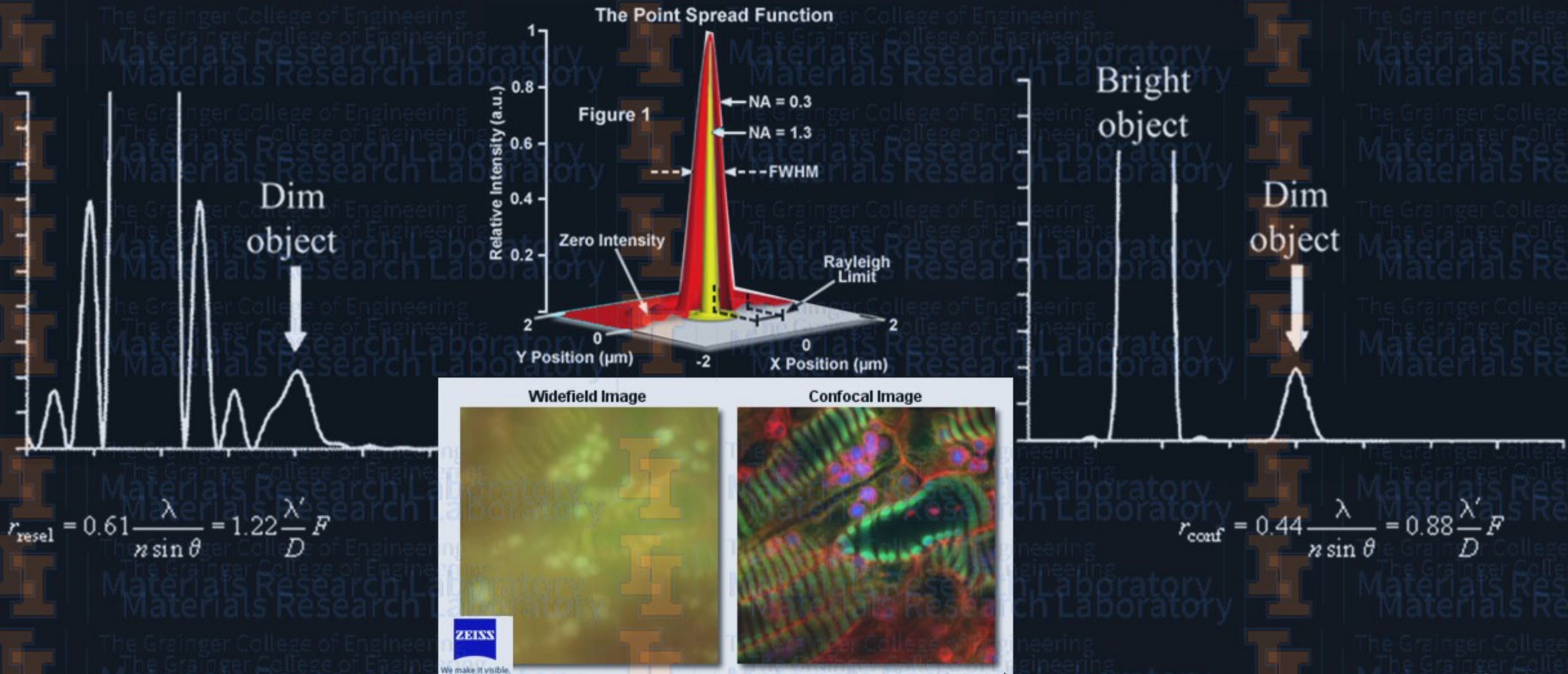


- Increased contrast $\Rightarrow$ 200:1.
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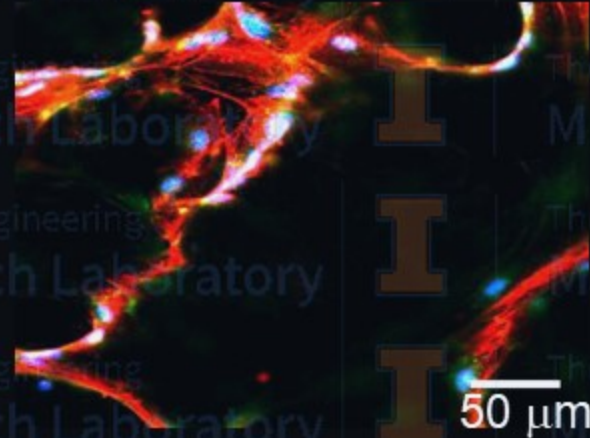
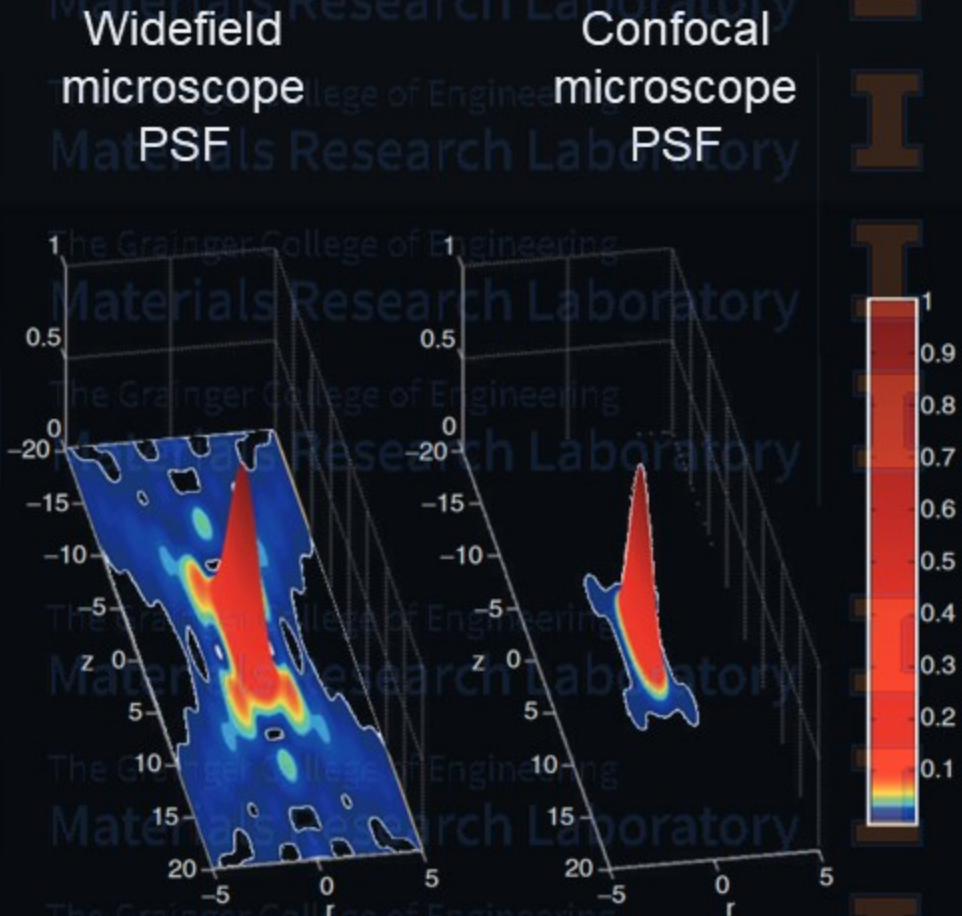


Confocal microscopy

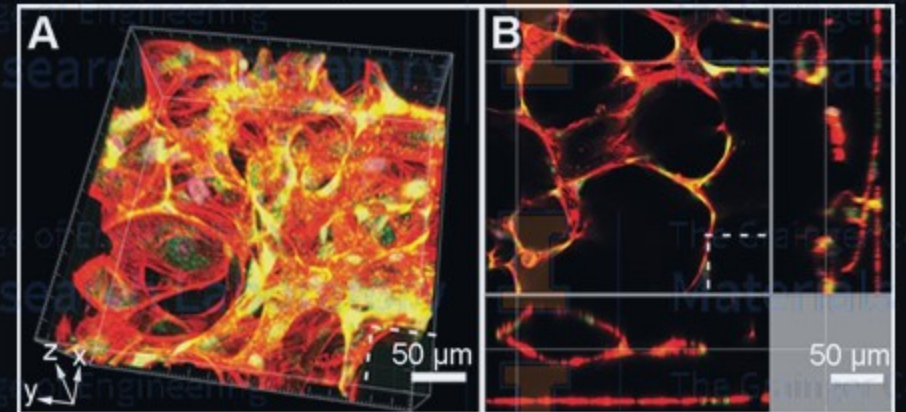
The relation of the first ring maximum amplitude to the amplitude in the center is 2% in case of conventional point spreading function (PSF) in a focal plane, while in case of a confocal microscope this relation is 0.04%.



Confocal microscopy combined with spectroscopy

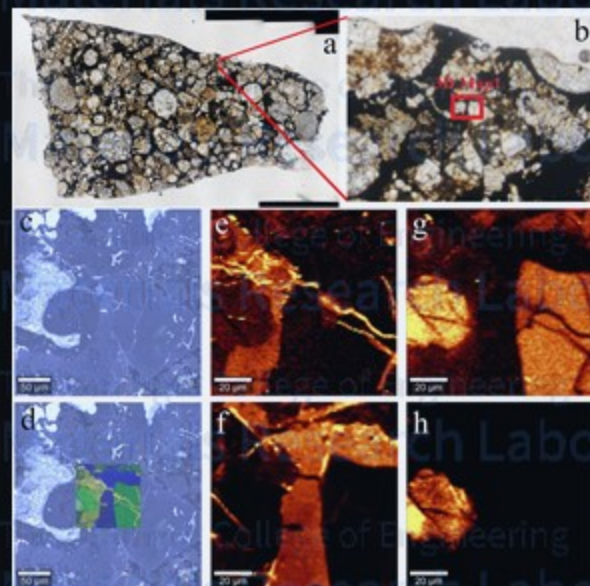


Confocal microscopy reconstruction of a 3D capillary bed

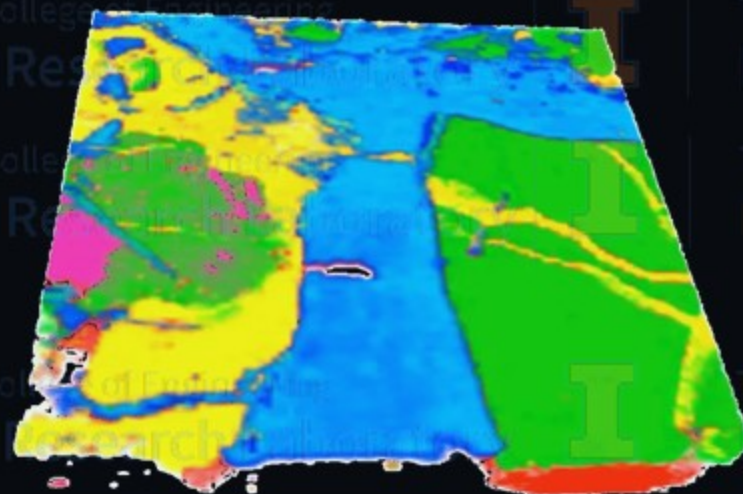
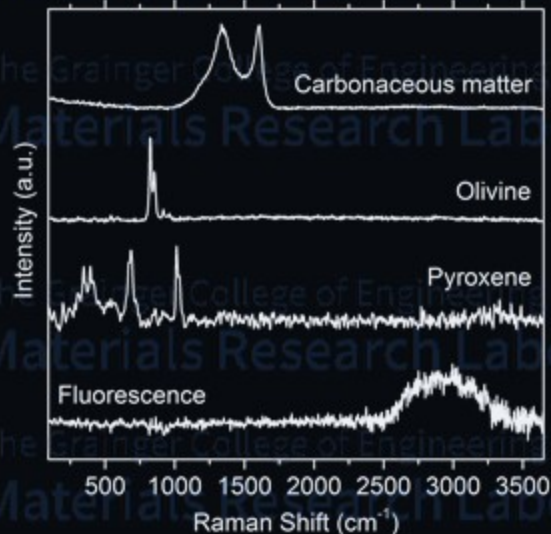


PLOS ONE 7(12): e50582 (2012)

Confocal microscopy combined with spectroscopy

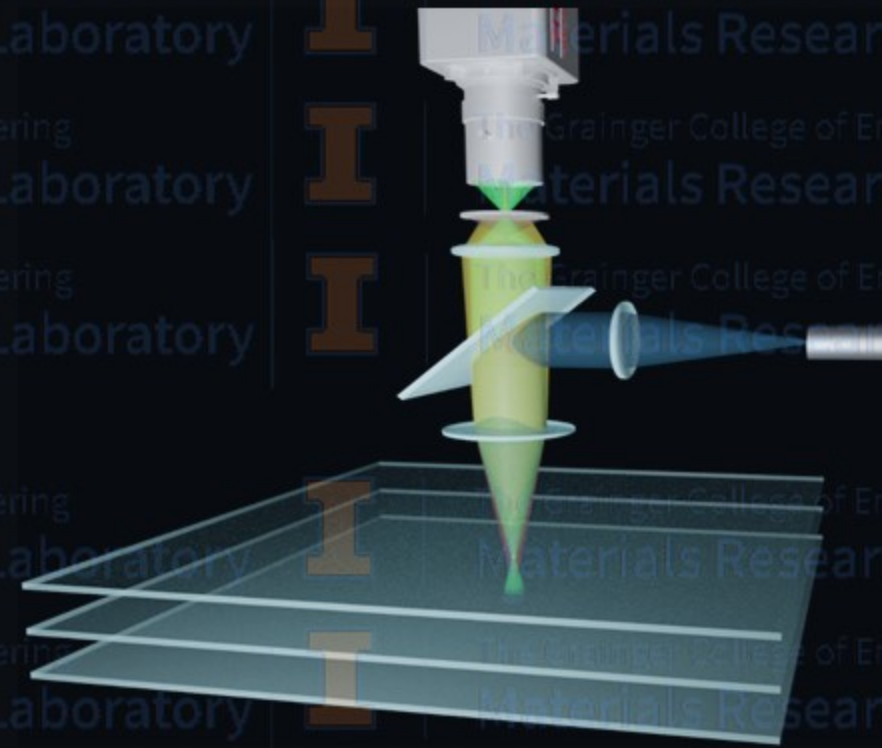


Chemical composition
Component identification
Components distribution

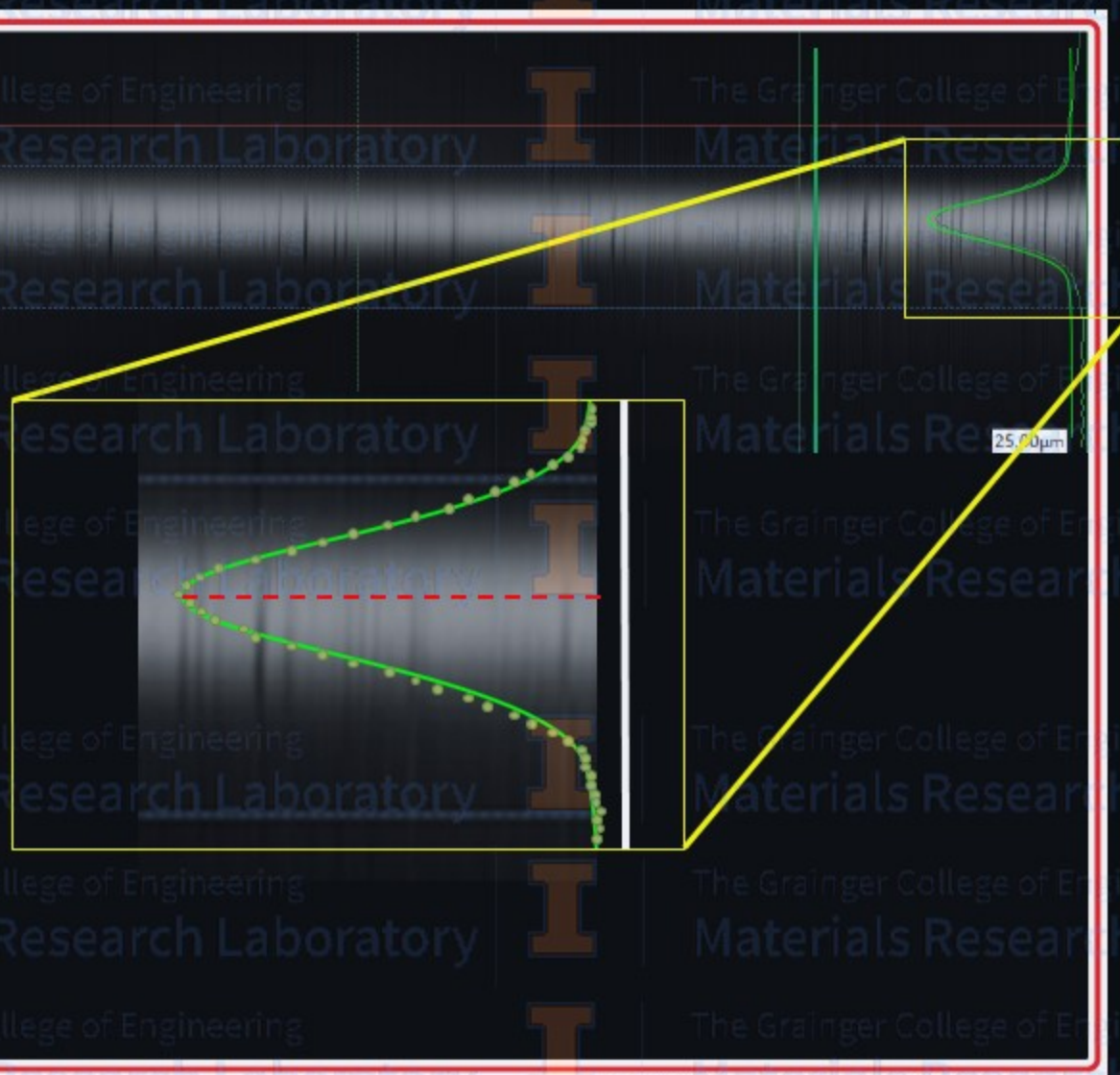


Confocal microscopy for measuring topography

Confocal microscopy z-stack

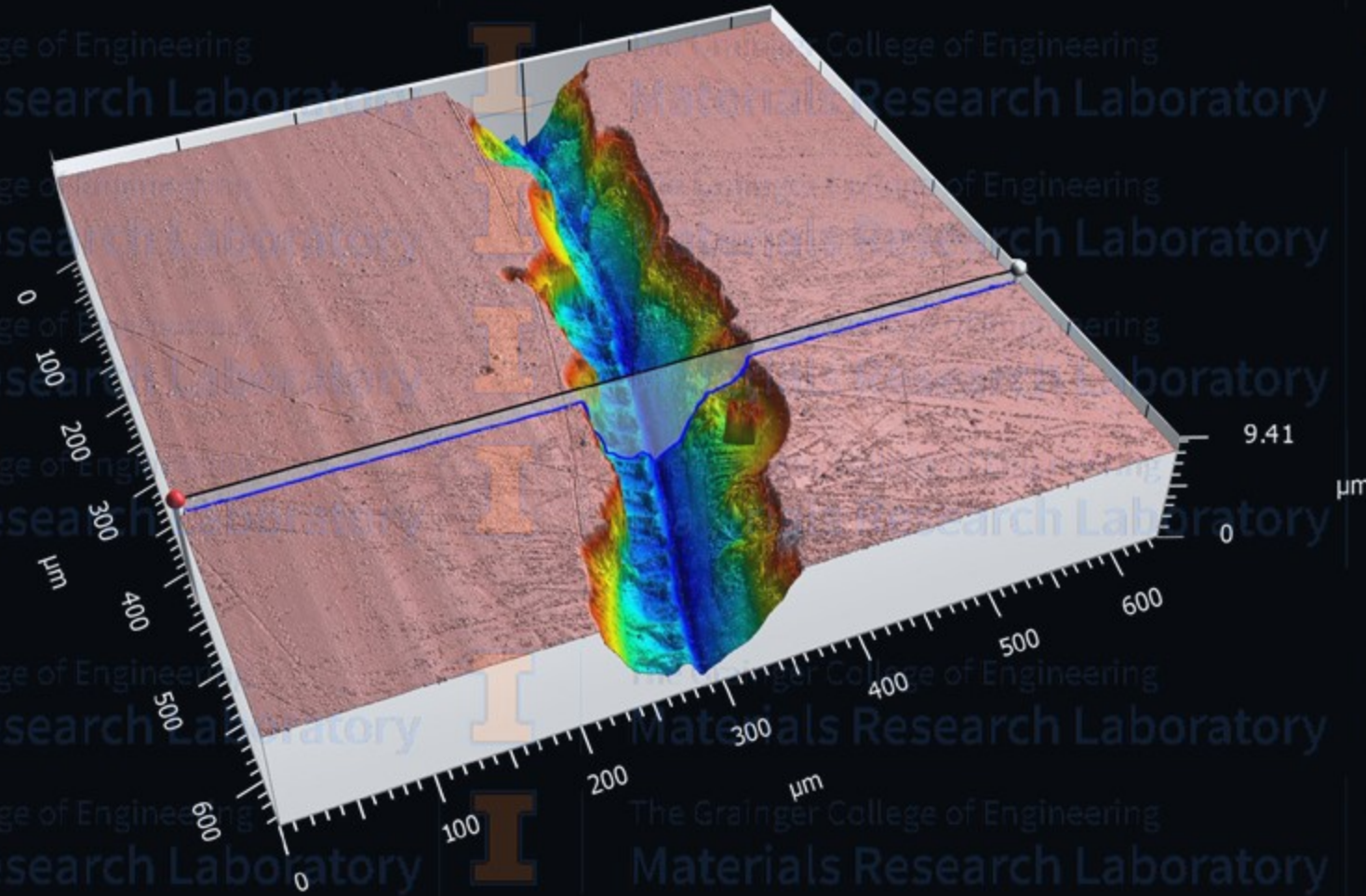


Confocal microscopy for measuring topography



Confocal microscopy

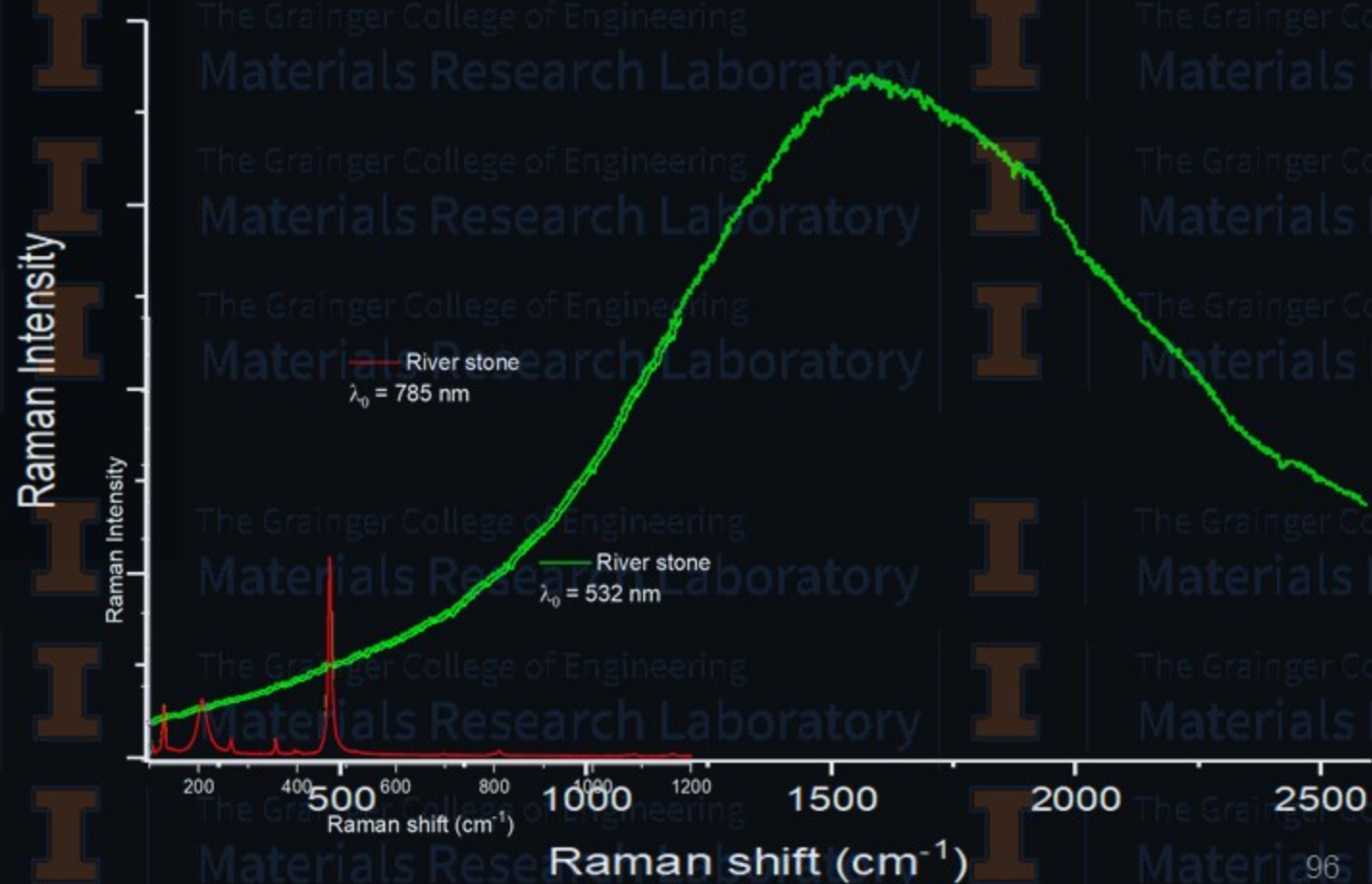
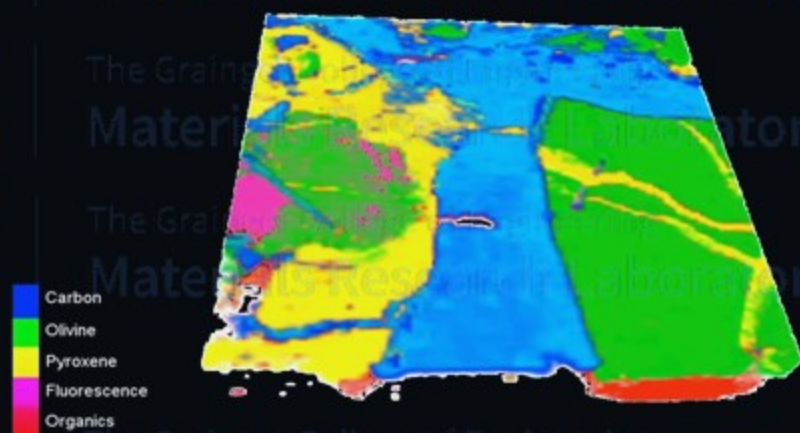
Scratch on glass



Raman spectroscopy

Primary Limitations:

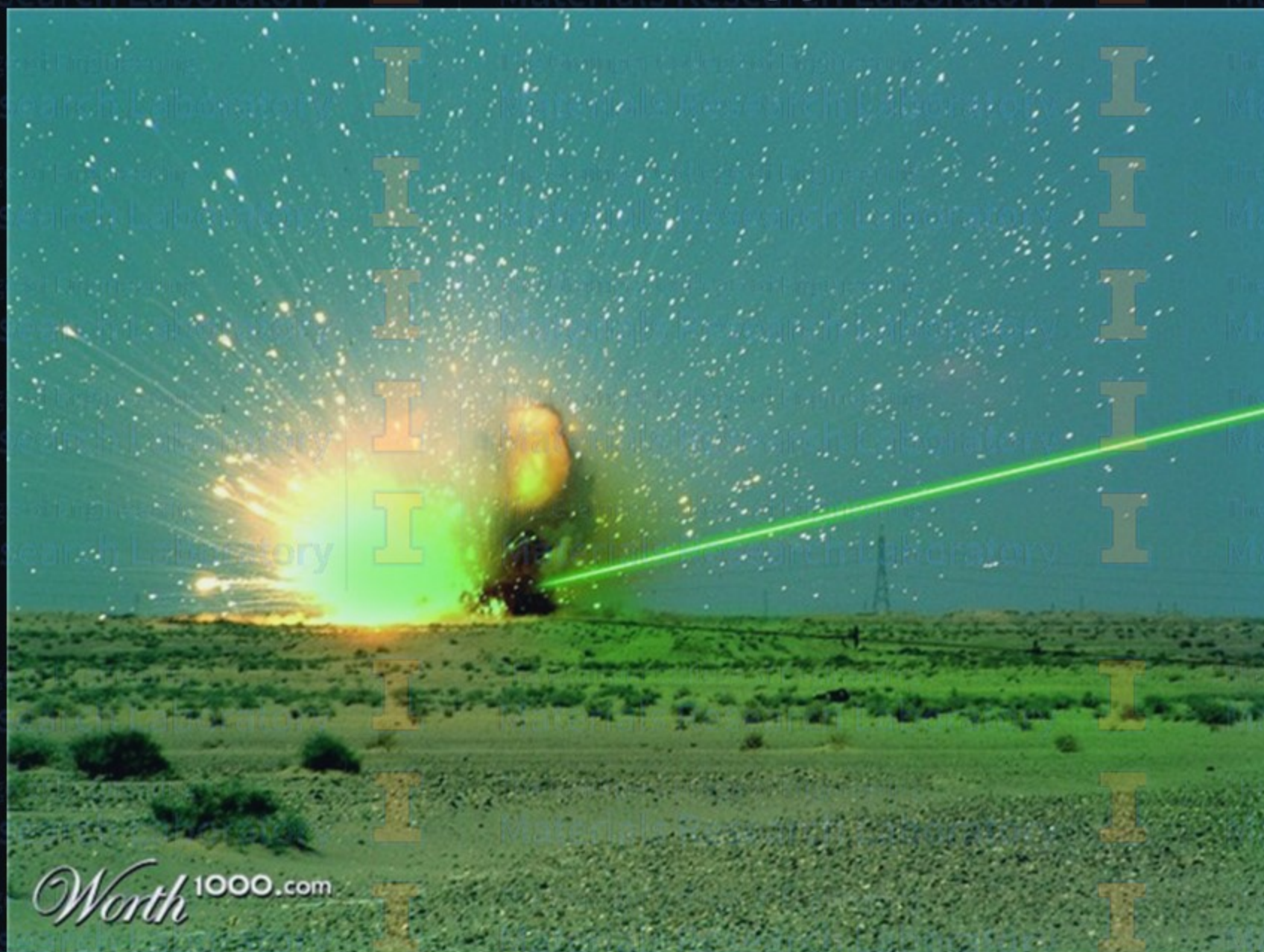
- Expensive apparatus (for high spectral/spatial resolution and sensitivity).
- Weak signal, compared to fluorescence.
- Limited spatial resolution (diffraction limited).



The More Time Approach



The More Power Approach



Surface Plasmons

Dielectric

Metal

www.juluribk.com

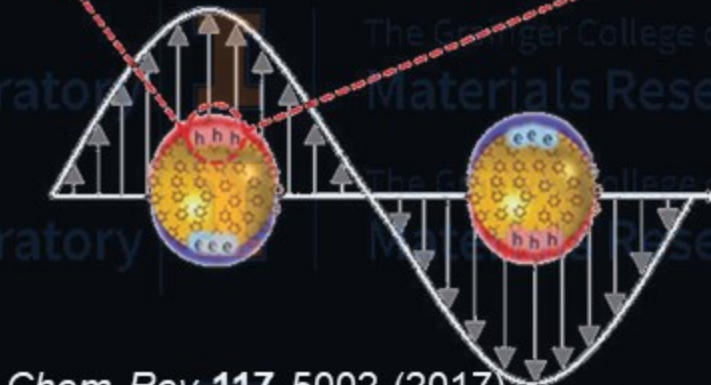
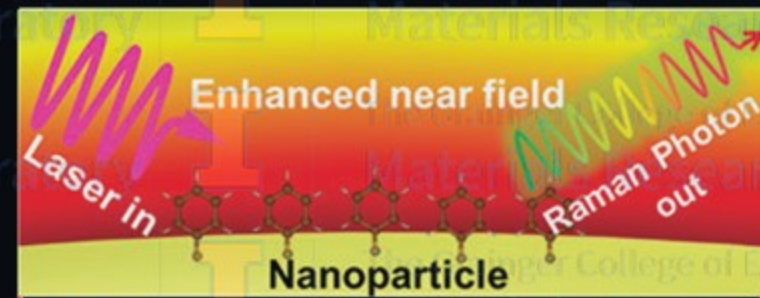
Plasmons can be driven by photons at resonance to build large standing wave electric fields.

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

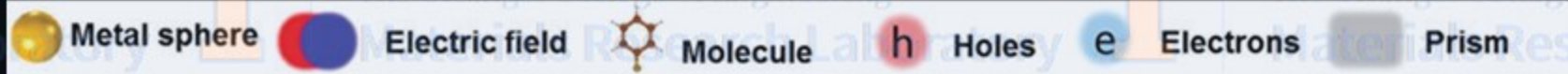
Surface Enhanced Raman Spectroscopy (SERS)

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

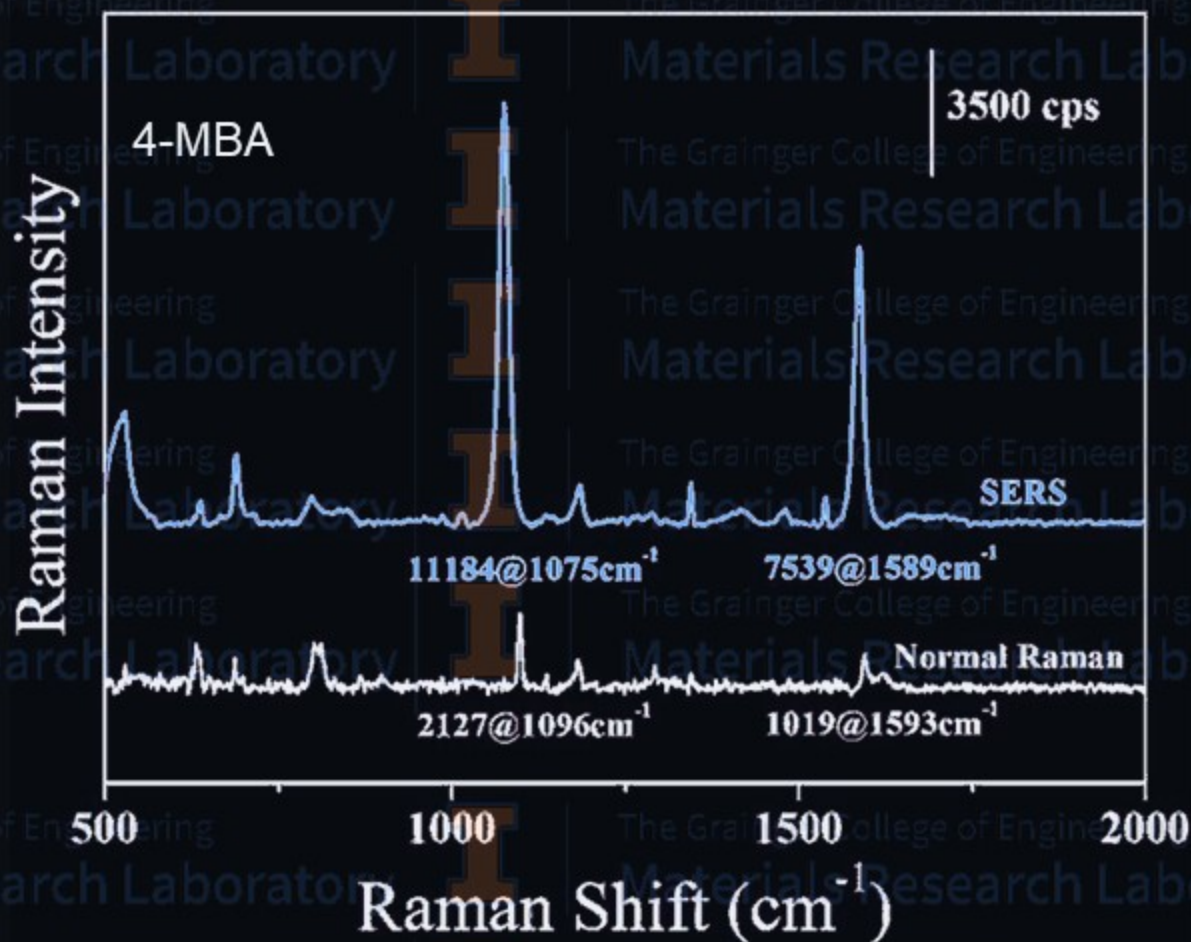
Capable of boosting Raman signal up to **14 Orders of Magnitude** or more! *Science* **275**, 1102 (1997)



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



Surface Enhanced Raman Spectroscopy (SERS)

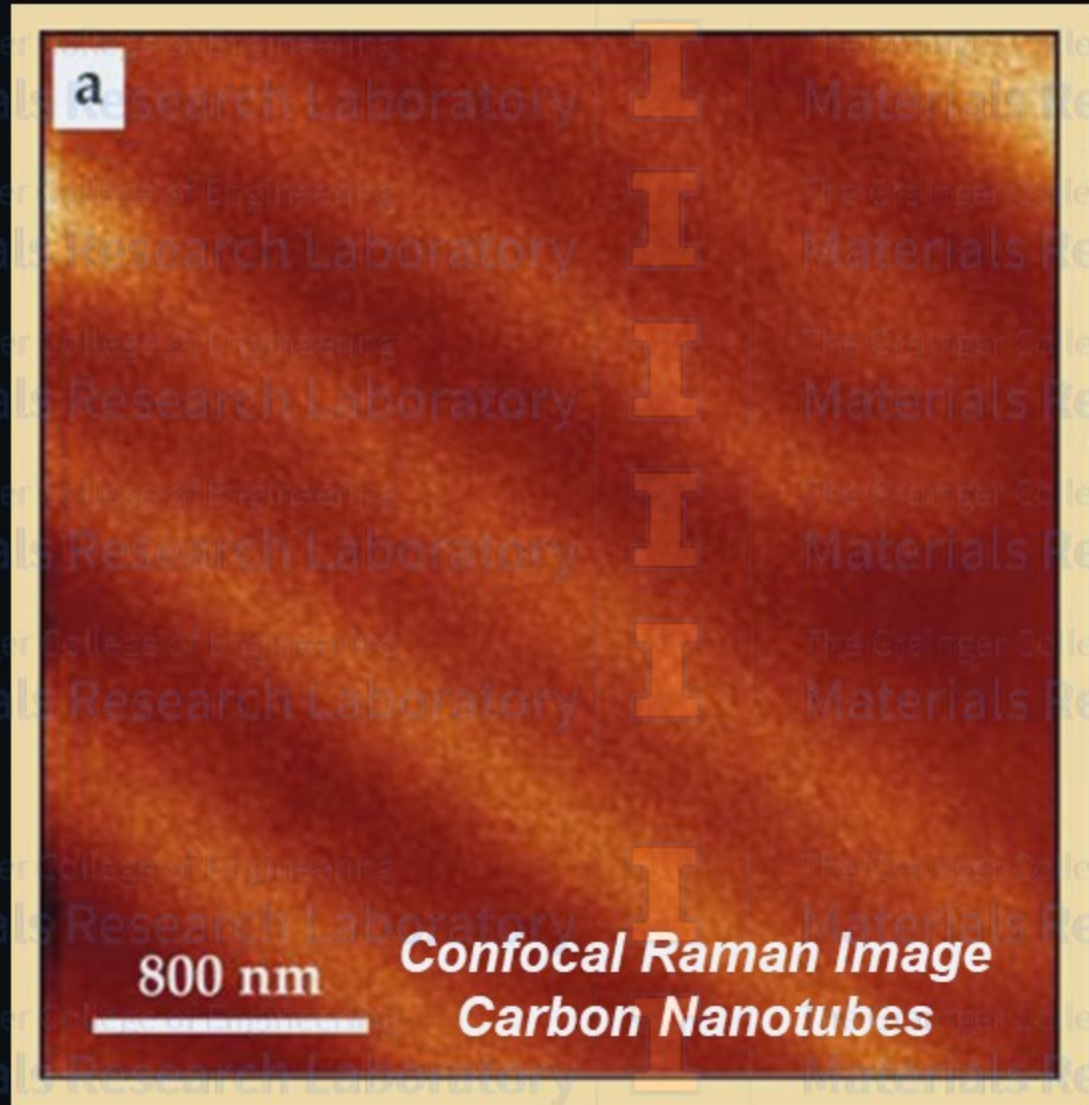


Anal. Methods, 6, 9547 (2014)

Confocal Raman Microscopy

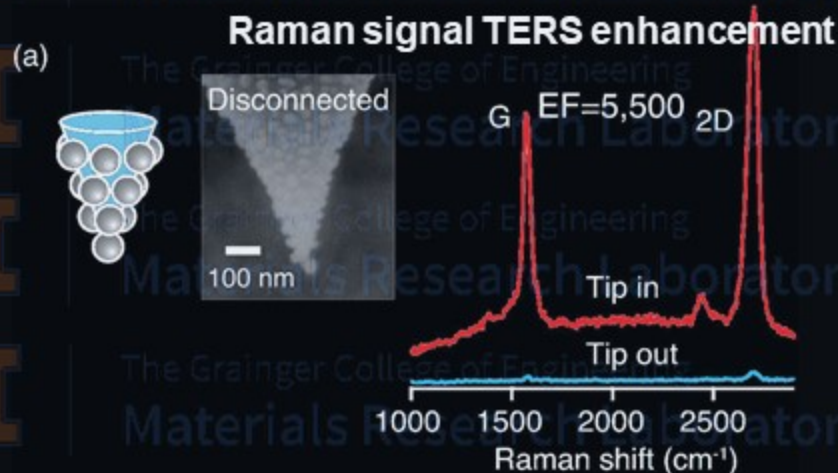
That's cool, but what about...

- Limited spatial resolution (diffraction limited).

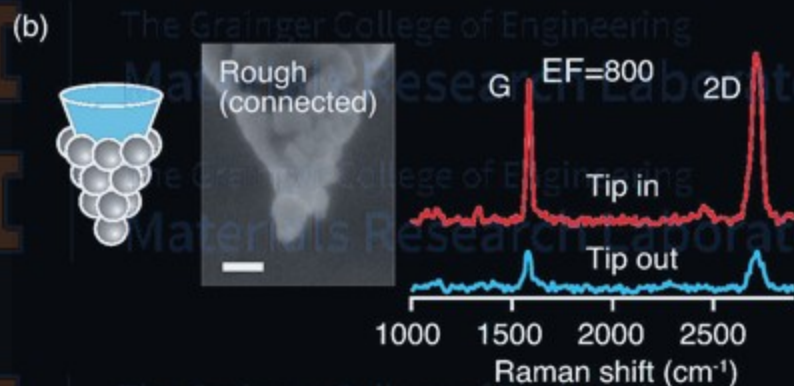


Phys. Rev. Lett. **103**, 186101 (2009)

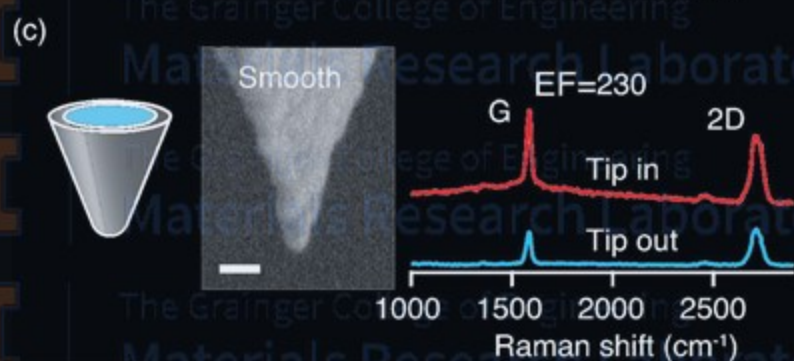
Tip Enhanced Raman Spectroscopy (TERS)



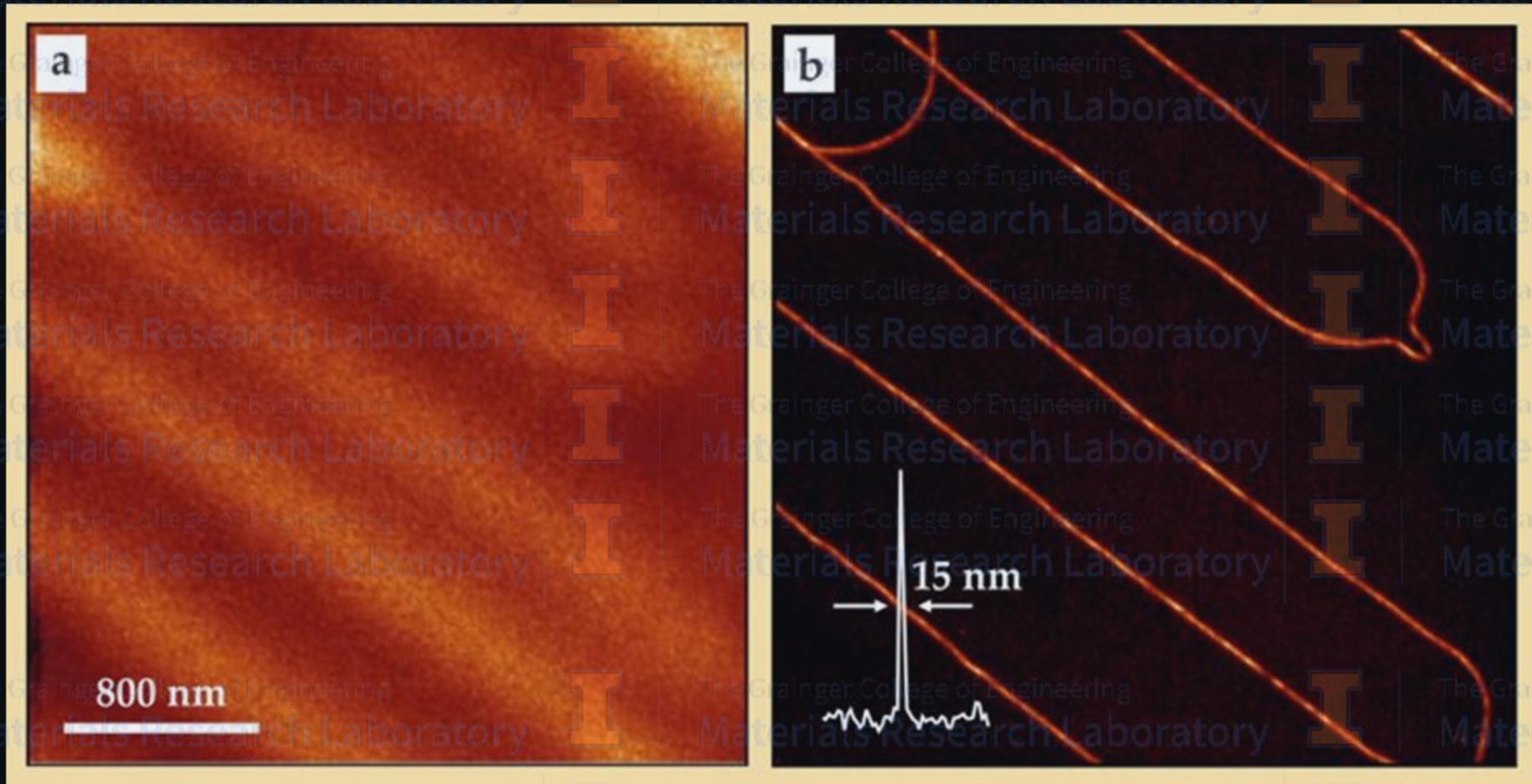
What is really cool is that this also works with a single metalized sharp tip, such as an STM or AFM tip!



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



Tip Enhanced Raman Spectroscopy (TERS)

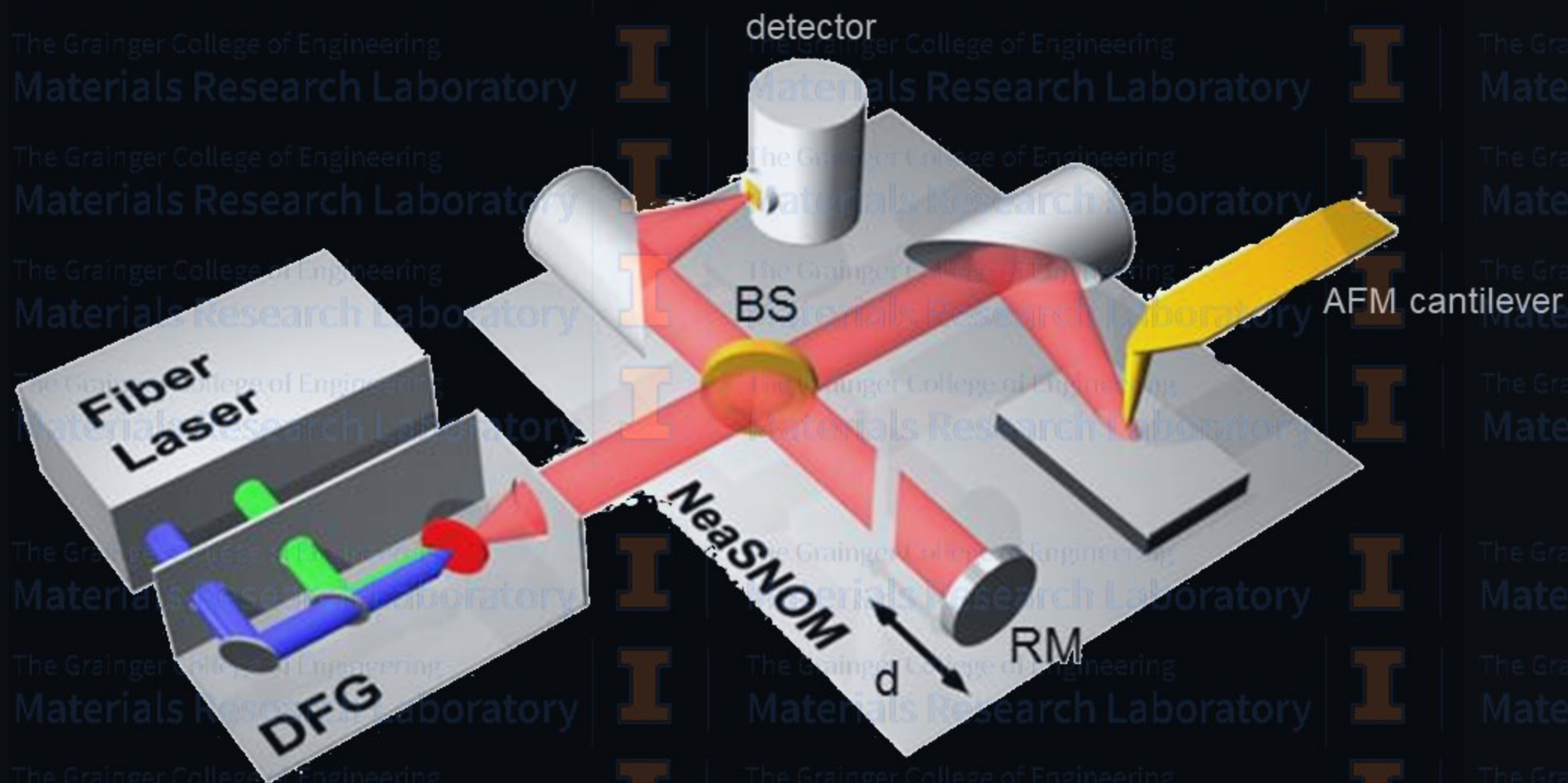


Confocal Raman Image

Tip Enhanced Raman Image

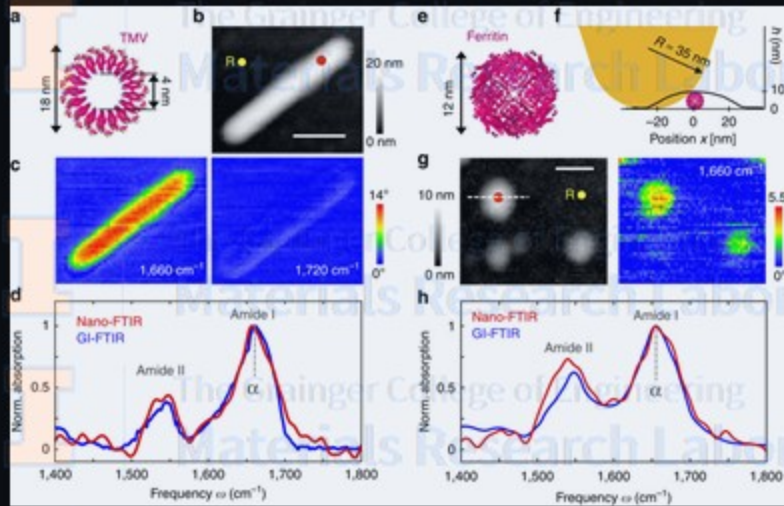
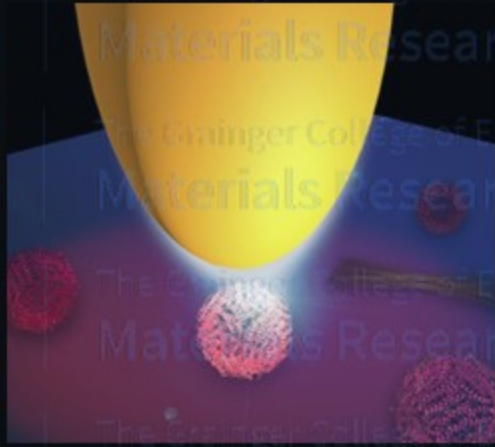
Carbon Nanotubes

Near-field scanning optical nanospectroscopy

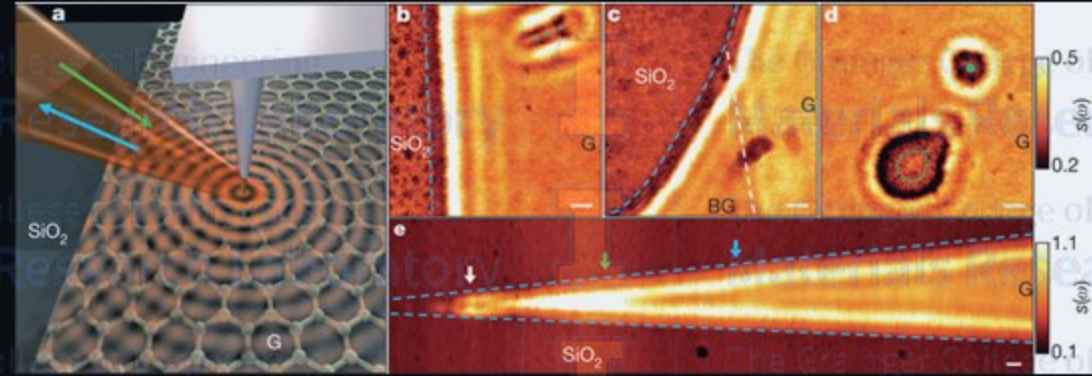
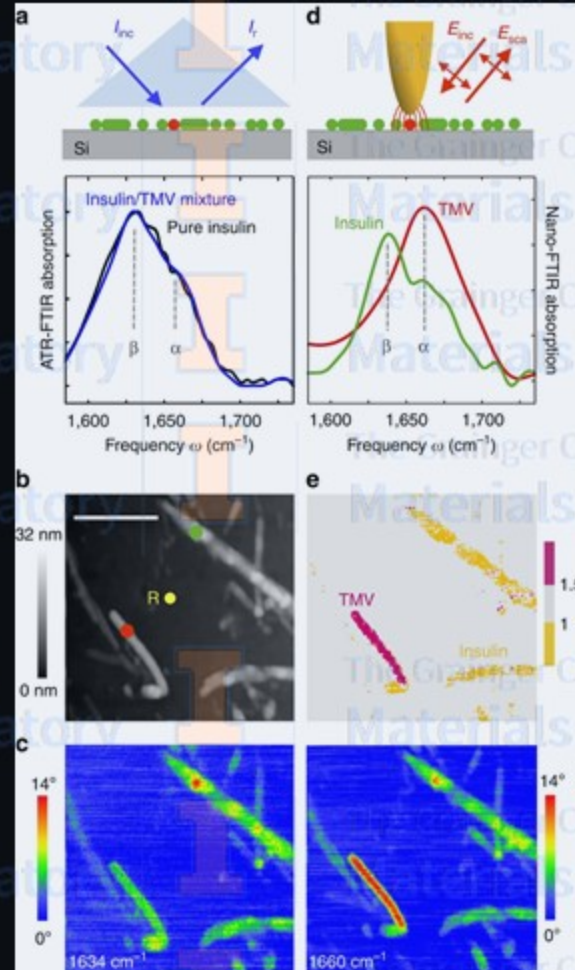


Near-field scanning optical nanospectroscopy

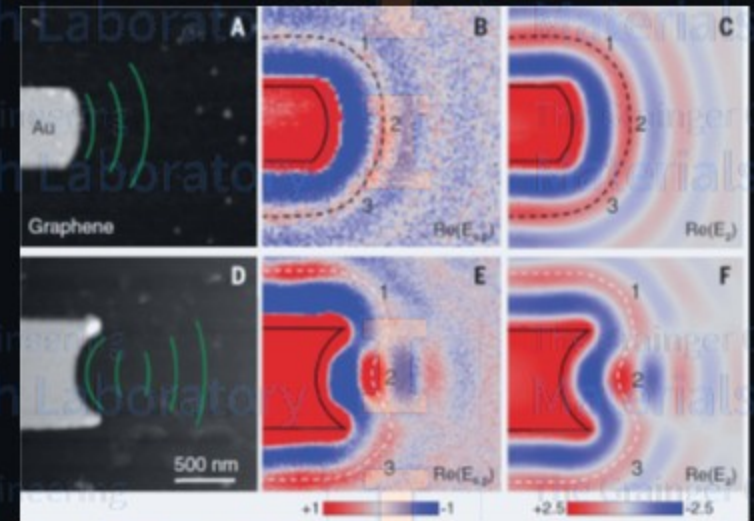
Nano-FTIR



Nature Communications 4, 2890



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



Science 344, 1369

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