

Optical Characterization Methods

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Light properties

- Direction of propagation
- Electric field direction or polarization
- Photon energy or wavelength
- Intensity
- Speed (constant in vacuum = 299,792,458 m/s = 670,616,632 mph)





Light interactions

- Transmission \bullet
- Reflection •
- Absorption \bullet
- Emission \bullet
- Scattering \bullet
- Refraction \bullet

Non-linear effects

DFG

 \circ

0

SFG

SHG

Multi-photon absorption •

Light – matter interaction



Stress



Thickness



Lattice structure, dopants



Microstructure



Temperature



Concentration



Composition





Light interactions



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.





Instrumentation:





Instrumentation:





Instrumentation:





Instrumentation:













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

Tauc's relation:

$$\alpha h \nu = A \big(h \nu - E_g \big)^m$$

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

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





Using absorbance to determine Au/Hg concentration in water solutions





Excitations in materials •Plasmons





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.





Optics Express 13, 5669 (2005)

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





graphene







Ĵ2.21 Å

Applied Materials Today 8, 68 (2017)







Applied Materials Today 8, 68 (2017)



Optical Materials Express, 332858 (2018)





ACS Nano 12, 10880 (2018)



Normal vibrational modes in molecules:





Normal vibrational modes in solids:

Sb/GaAs(110)





http://www.phonon.fc.pl





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

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



IR active vibrations





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







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Instrumentation:

The **FTIR** Michelson uses а 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









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





Fingerprinting:

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

Complementary characterization techniques, like XRD can provide conclusive evidence for the identification.



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













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.



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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.



nanocomposix.com

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





What is measured:

The light inelastically scattered by the

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 absorbed energy or released by the phonons.



Inelastic scattering:

The dependence of the polarizability tensor $\vec{\alpha}$ on the normal coordinate Q associated with a normal vibrational mode of a material, for small amplitude oscillations near the equilibrium can be written:

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right)Q = \alpha_0 + \alpha' Q$$

For a harmonic oscillation ($Q = Q_0 \cos \omega t$) and $E = E_0 \cos \omega_0 t$, the time dependence of the induced dipole momentum μ ' will be:

$$\mu' = \alpha_0 E_0 \cos \omega_0 t + \frac{1}{2} \alpha' Q_0 E_0 [\cos(\omega_0 - \omega)t + \cos(\omega_0 + \omega)t]$$

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



Fourier Transform IR spectroscopy (FTIR)

IR active vibrations



Raman active vibrations

The intensity of the Raman scattering linked to a vibrational state depends on the change in the polarizability tensor $\left(\frac{\partial \vec{\alpha}}{\partial Q_j}\right)_0 \neq 0$





FTIR and Raman:

The two techniques are complementary (different selection rules).



Molecular and crystalline structure characterization





Molecular and crystalline structure characterization



Crystalline structure defect characterization

Graphene



Nature Nanotech. 5, 235 (2013)



Crystalline structure defect characterization

Graphene



Nature Nanotech. 5, 235 (2013)



Crystalline structure defect characterization



Type of single wall carbon nanotubes (SWNT)





Phase transitions



J. Raman Spectroscopy 41, 334 (2010)

Carbonaceous matter tensity (a.u.) Olivine Pyroxene munounnermannermanner Fluorescence 500 1000 1500 2000 2500 3000 3500 Raman Shift (cm⁻¹)

Raman spectroscopy

Chemical composition Component identification Components distribution



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



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.



Surface Plasmons

Excitations in materials •Plasmons



Plasmons are quanta of collective motion of charge-carriers in a gas with respect of an oppositely charged background.

They 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.

Phys. Today, 64, 39 (2011)





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)

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Anal. Methods, 6, 9547 (2014)

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Confocal Raman Microscopy



Confocal Raman Image Carbon Nanotubes

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



Tip Enhanced Raman Spectroscopy (TERS)



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



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



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Nano-FTIR

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Nano-FTIR



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Nano-FTIR

















Strengths:

- No sample preparation.
- Non destructive technique.
- Sub diffraction limit resolution (20 nm).

Requirements and limitations:

- Slow data acquisition.
- Limited to fairly flat samples (AFM-like).
- Interaction between tip and sample may make analysis difficult.

Complementary techniques: AFM, SEM,TEM, Confocal microscopy.

Luminescence





Luminescence



Lifetime: Phosphorescence, fluorescence Mechanism: Photoluminescence, bioluminescence, chemoluminescence, thermoluminescence, piezoluminescence, etc.





Disney Pixar



Radim Schreiber





Profilephotocovers.com



Trevor Morris

What is measured:

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



What is measured:

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



Number of layers in 2D materials

(a) PL spectra for mono- and bilayer MoS₂.

Inset: PL QY of thin layers for N = 1-6.

(b) Normalized PL spectra by the intensity of peak A of thin layers of MoS₂ 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)



Defects in 2D materials

- (a) 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.



Carrier concentration

Photoluminescence spectra of InN layers with different carrier concentrations.

1 - n = $6x10^{18}$ cm⁻³ (MOCVD); 2 - n = $9x10^{18}$ cm⁻³ (MOMBE); 3 - n = $1.1x10^{19}$ cm⁻³ (MOMBE); 4 - n = $4.2x10^{19}$ cm⁻³ (PAMBE).



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


 $In_xGa_{1-x}N$ 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). *Phys. Stat. Sol.* **(b) 234** (2002) 750





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



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.

www.glofish.com



Polarization



Guimond and Elmore - Oemagazine May 2004



) ©

http://www.photophysics.com/

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Polarization





www.bobatkins.com







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What is measured:

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





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.









Applications

Film thickness





Applications

Film thickness





Applications

- Composition
- Surface roughness
- Film thickness



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



Composition

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

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

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.







"Conventional" Optical Microscopy





























Phase contrast





Dark field

Polarizing



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



Phyllite Thin Section in Polarized Light









Living Cells in Brightfield and Phase Contrast





Contrast-Enhancing Techniques for Optical Microscopy

Specimen	Imaging		
Туре	Technique		
Transmitted Light			
Transparent Specimens Phase Objects Bacteria, Spermatozoa, Cells in Glass Containers, Protozoa, Mites, Fibers, etc.	Phase Contrast Differential Interference Contrast (DIC) Hoffman Modulation Contrast Oblique Illumination		
Light Scattering Objects Diatoms, Fibers, Hairs, Fresh Water Microorganisms, Radiolarians, etc.	Rheinberg Illumination Darkfield Illumination Phase Contrast and DIC		
Light Refracting Specimens Colloidal Suspensions powders and minerals Liquids	Phase Contrast Dispersion Staining DIC		
Amplitude Specimens Stained Tissue Naturally Colored Specimens Hair and Fibers Insects and Marine Algae	Brightfield Illumination		
Fluorescent Specimens Cells in Tissue Culture Fluorochrome-Stained Sections Smears and Spreads	Fluorescence Illumination		
Birefringent Specimens Mineral Thin Sections Liquid Crystals Melted and Recrystallized Chemicals Hairs and Fibers Bones and Feathers	Polarized Illumination		



http://micro.magnet.fsu.edu



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Contrast-Enhancing Techniques for Optical Microscopy

Specimen	Imaging	
Type	Technique	
Reflected Light		
Specular (Reflecting) Surface Thin Films, Mirrors Polished Metallurgical Samples Integrated Circuits	Brightfield Illumination Phase Contrast, DIC Darkfield Illumination	
Diffuse (Non-Reflecting) Surface Thin and Thick Films Rocks and Minerals Hairs, Fibers, and Bone Insects	Brightfield Illumination Phase Contrast, DIC Darkfield Illumination	
Amplitude Surface Features Dyed Fibers Diffuse Metallic Specimens Composite Materials Polymers	Brightfield Illumination Darkfield Illumination	
Birefringent Specimens Mineral Thin Sections Hairs and Fibers Bones and Feathers Single Crystals Oriented Films	Polarized Illumination	
Fluorescent Specimens Mounted Cells Fluorochrome-Stained Sections Smears and Spreads	Fluorescence Illumination	













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 $NA = (n)sin(\mu)$ (a) $\mu = 7^{\circ}$ NA = 0.12 (b) $\mu = 20^{\circ} \text{NA} = 0.34$



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





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%.





LASER SCANNING CONFOCAL MICROSCOPY

Nathan S. Claxton, Thomas J. Fellers, and Michael W. Davidson

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<fibroblasts network on epoxy> data/image courtesy of Joselle McCracken, Nuzzo Group



<cells bridge the gap> data/image courtesy of Joselle McCracken, Nuzzo Group









149.001µm





















Limitations:

- Image is scanned, resulting in slower data acquisition.
 - High intensity laser radiation can damage some samples.
- Cost (typically 5x more than a comparable wide-field system).

Strengths:

- Optical sectioning.
 - Three-dimensional images.
- Software localization of signal can bring z resolution to 20 nm.
 Improved contrast (200:1).
 Better resolution lateral (1.5x).
 Field of view defined by the scanning range.

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September 5th, 2019



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